QUANTUM MECHANICS

A Physical Approach

Solutions to Problems

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QUANTUM MECHANICS, A PHYSICAL APPROACH. SOLUTIONS TO PROBLEMS

Preface

This online book contains detailed solutions to all of the problems at the end of each chapter of the textbook *Quantum Mechanics. A Physical Approach*, by A. M. Cetto and L. de la Peña (Cambridge University Press, 2025).

The present volume is more than a compendium of solutions; it is a teaching and learning handbook. All along its preparation, we have kept in mind that the educational value of solving an exercise often outweighs the value of the solution itself. Solving exercises helps students acquire practical skills, but also, more importantly, consolidate and improve their understanding of a topic or problem. For this reason, the discussions are thorough. In some cases, alternative or complementary solutions are presented that focus more on the physics involved than on the method to be followed. These features make the book an effective teaching aid to be used alongside the corresponding textbook.

Like the textbook on which it is based, this volume is intended for university-level students, both undergraduate and graduate, who wish to acquire a solid understanding of the principles and methods of quantum mechanics. It is therefore useful for students of physics and related disciplines, as well as students of engineering and other scientific or technical fields.

In preparing this volume, we found the book entitled *Problemas y Ejercicios de Mecánica Cuántica*, by Luis de la Peña and Mirna Villavicencio (Mexico, FCE-UNAM, 2003) to be extremely valuable. In addition to detailed discussions of many of the problems in this volume, that book contains a long list of additional problems, some solved and others suggested as homework for students.

Over the course of our many years teaching this subject, two of us (AC and LP) have benefited from comments and suggestions from our colleagues, students, and teaching assistants. Special thanks go to our young colleague, José Francisco Pérez Barragán, who was, as always, ready to proofread much of this book's material.

Although we have tried to minimize both technical and typographical errors, it is very likely that the careful reader will still find some. We therefore invite you to send us your observations and comments, which we will gladly take into account for a future edition.

Mexico City, 2025

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CHAPTER 2

Matter and Field

P2.1 Obtain the limit expressions of the Planck distribution for small and large frequencies, at a fixed temperature. What is the form of the function $f(\omega/T)$ that appears in Wien's law, $\rho(\omega) = \omega^3 f\big(\omega/T\big)$, for high frequencies, and why is it not possible to determine it classically? Discuss your results.
Solution. Planck's formula for the spectral energy density of the field is

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\,\frac{1}{e^{\hbar\omega/kT} - 1}, \tag{2.1}$$

where $\omega = 2\pi\nu$ represents the angular frequency. Using the series expansion of the exponential function,

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}, \tag{2.2}$$

we get

$$e^{\hbar\omega/kT} - 1 = \sum_{n=1}^{\infty} \frac{1}{n!}\Big(\frac{\hbar\omega}{kT}\Big)^n. \tag{2.3}$$

In the limit $\omega/T \to 0$, only the lowest-order term contributes to the sum,

$$e^{\hbar\omega/kT} - 1 \simeq \frac{\hbar\omega}{kT}. \tag{2.4}$$

Hence,

$$\rho(\omega) \approx \frac{\hbar\omega^3}{\pi^2 c^3}\frac{kT}{\hbar\omega} = \frac{\omega^2}{\pi^2 c^3}\,kT, \tag{2.5}$$

which is exactly the Rayleigh–Jeans result. Comparing with Wien's law, $\rho(\omega) = \omega^3 f\big(\omega/T\big)$, we find for small frequencies (or high T)

$$f\big(\omega/T\big) = \frac{kT}{\pi^2 c^3\,\omega}. \tag{2.6}$$

At high frequencies (or low T), $e^{\hbar\omega/kT} \gg 1$, so the Planck distribution takes the Wien form

$$\rho(\omega) \simeq \frac{\hbar\omega^3}{\pi^2 c^3} e^{-\hbar\omega/kT}, \tag{2.7}$$

and thus

$$f\big(\omega/T\big) = \frac{\hbar}{\pi^2 c^3} e^{-\hbar\omega/kT}. \tag{2.8}$$

Because this exponential cutoff depends essentially on $\hbar$, it cannot be derived from classical principles alone; without quantization one obtains the ultraviolet catastrophe. In fact, Wien first proposed his heuristic distribution in 1896.

Finally, for any temperature one recovers

$$f\big(\omega/T\big) = \frac{\hbar}{\pi^2 c^3}\frac{1}{e^{\hbar\omega/kT}-1}. \tag{2.9}$$

It is clear that the two expressions obtained above are merely the limiting values of this function as $\omega/T \to 0$ or ∞. We also note here that dependence on Planck's constant explains why this function cannot be determined by purely classical methods. Indeed, we have taken the opposite approach to Planck: we obtained the two asymptotic values, for $T \to \infty$ (the classical high-temperature limit, applicable only at low frequencies to avoid the ultraviolet catastrophe and given by the Rayleigh–Jeans distribution) and for high frequencies (free from the catastrophe, but applicable only at low temperatures and given by the Wien distribution). In contrast, Planck heuristically interpolated between these two distributions to construct a new one, in the hope that it would correspond to reality, as it did.

P2.2 Show that Planck's law predicts that the spectral density of blackbody radiation has a maximum for each temperature, which occurs at the wavelength

$$\lambda_m = \frac{2\pi c\hbar}{4.965}\frac{1}{k_B T} \tag{2.10}$$

Calculate ν_m and explain why $\nu_m \neq c/\lambda_m$. This formula—known as *Wien's displacement law*— shows that as the temperature of the blackbody rises, the maximum intensity of the radiation shifts toward shorter wavelengths.

Solution. We rewrite the blackbody spectral radiance in the form $\rho_T(\nu)d\nu$, where the subscript T indicates that we are considering a constant temperature. It is convenient to first express this radiance in terms of wavelength, for which we must determine $\rho_T(\lambda)$. According the general theory of variable changes, we have $f(x)\,dx = f(x(y))\,|J|\,dy$, where $J = (\partial_x y)$ is the Jacobian of the transformation. From $\nu = c/\lambda$, it follows that

$$d\nu = -\frac{c}{\lambda^2}d\lambda \tag{2.11}$$

The minus sign indicates that an increase in frequency corresponds to a decrease in wavelength, as these variables are inversely proportional. The expression for the blackbody spectral radiance in terms of wavelength is therefore

$$\rho_T(\lambda) = \frac{c}{\lambda^2}\rho_T(c/\lambda) = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda k_B T}-1} \tag{2.12}$$

To find the maximum of this function, we must determine the value λ_m that satisfies the condition

$$\left.\frac{d\rho_T(\lambda)}{d\lambda}\right|_{\lambda_m} = 0, \tag{2.13}$$

or equivalently,

$$-5\lambda_m k_B T\left(e^{hc/\lambda_m k_B T}-1\right)+hce^{hc/\lambda_m k_B T}=0, \tag{2.14}$$

which can be rewritten as

$$e^{-x}+\frac{1}{5}x-1=0, \tag{2.15}$$

where $x=hc/\lambda_m k_B T$. This transcendental equation can be solved by successive approximations, yielding

$$x\sim 5(1-e^{-5})=4.965\ldots \tag{2.16}$$

Thus,

$$\lambda_m=\frac{2\pi hc}{4.965}\frac{1}{k_B T}. \tag{2.17}$$

In terms of the constant

$$b=\frac{hc}{4.965k_B}=2.8978\times 10^{-3}\,\mathrm{m}\cdot\mathrm{K}, \tag{2.18}$$

Wien's displacement law takes the form

$$\lambda_m T=b. \tag{2.19}$$

This law states that as the temperature of a blackbody increases, the peak of its energy distribution shifts towards shorter wavelengths. This is observed as a change in the body's color, which explains the name given to this result. Thus, the theory allows us to determine h in terms of the experimental value of Wien's constant b, which was the method used by Planck for the experimental determination of his constant. It is clear that b cannot be determined by classical methods.

The Jacobian factor (different from unity) in the transition from $\rho(\omega)$ to $\rho(\lambda)$ causes the equation determining the frequency at which the peak occurs to differ from $e^{-x}+\frac{1}{5}x-1=0$. Consequently, the relation $\nu_m=c/\lambda_m$ does not hold. This is confirmed by calculating the frequency ν_m for which the derivative of $\rho(\nu)$ given by $\rho_T(\nu)d\nu$ vanishes, leading to the equation

$$e^{-x}+\frac{1}{3}x-1=0,\quad x=h\nu_m/k_B T. \tag{2.20}$$

Wien's displacement law is widely used to investigate the temperature of hot bodies (with spectra similar to a blackbody), since it only requires knowing the wavelength at which the radiation intensity is maximal. For example, assuming the solar spectrum corresponds to that of a blackbody, the fact that the Sun's radiated energy peaks at $\lambda_m\sim 5\times 10^3$ Å implies that the solar surface temperature is

$$T=2.9\times 10^{-3}\times\frac{1}{5}\times 10^{-3}\times 10^{10}\approx 5800\,\mathrm{K}. \tag{2.21}$$

Another interesting application arises when considering the cosmic microwave background radiation, whose spectrum corresponds to a Planckian with a temperature of $T = 2.7\,\mathrm{K}$. At this temperature, the peak of the radiated energy density occurs at the wavelength $\lambda_m = 0.107\,\mathrm{cm}$, i.e., in the microwave band. This fact facilitated the detection of this radiation using microwave detectors.

P2.3 Construct a graph of the average energy of the Planck oscillators versus frequency and use it to show that Planck's postulate $E_n = n\hbar\omega$ introduces a cutoff in frequency space. Find this cutoff frequency. This result shows that the postulate prevents arbitrarily high frequency modes from being excited at a given temperature, in agreement with experimental observations.

Solution. It is convenient to start from the following observation. Let x be a random variable that can take on the values $x_1, x_2, \ldots, x_n$ with the associated probabilities $p_1, p_2, \ldots, p_n$ and

$$\sum_{i=1}^{n} p_i = 1, \tag{2.22}$$

such that $x_1 < x_2 < \cdots < x_n$. The mean value $\bar{x}$ of x then lies between the smallest and largest values the variable can take,

$$x_1 < \bar{x} < x_n. \tag{2.23}$$

Now consider the energy of the Planck oscillators as a random variable that can take the values

$$E_n(\omega) = n\hbar\omega, \quad n = 1, 2, 3, \ldots, \tag{2.24}$$

with probabilities

$$p_n = \frac{1}{Z}\, e^{-E_n/(kT)}. \tag{2.25}$$

The partition function $Z(T)$ is the normalization factor ensuring $\sum_{n=1}^{\infty} p_n = 1$. Since $E_1 < E_2 < \cdots$, from the above inequality we know that the average energy

$$\bar{E}(\omega) = \frac{\hbar\omega}{e^{\hbar\omega/(k_B T)} - 1} \tag{2.26}$$

must satisfy

$$\bar{E}(\omega) > E_1. \tag{2.27}$$

Figure 2.1 illustrates the quantities $E_1(\omega)$, $E_2(\omega)$, . . ., and $\bar{E}(\omega)$ as a function of frequency, as well as the frequency ω_c, defined as the intersection of the curves $E_1(\omega)$ and $\bar{E}(\omega)$. For $\omega > \omega_c$ one would have $\bar{E} < E_1$, which contradicts the previous inequality. Hence at temperature T oscillators with $\omega > \omega_c$ cannot be excited. Furthermore, since $E_1 = \hbar\omega$ represents the minimum possible energy of the Planck oscillators, and this cannot be exceeded by the average energy, the maximum frequency of excited oscillators does not exceed

$$\omega_c = \frac{\bar{E}(\omega)}{\hbar}. \tag{2.28}$$

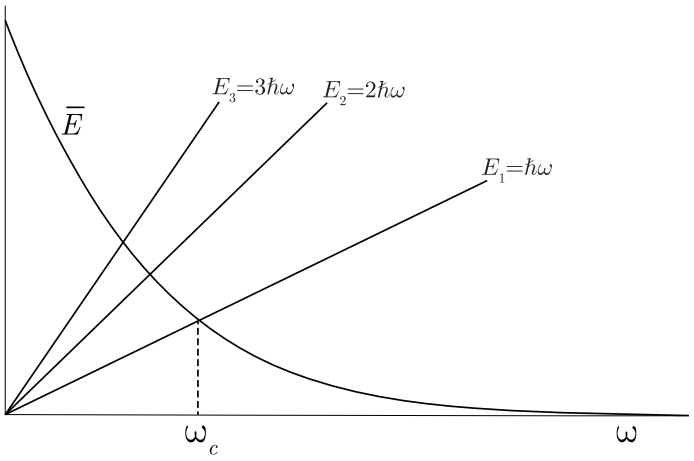

FIGURE 2.1. Average energy of Planck oscillators as a function of frequency, at a given temperature.

In short, ω_c is a cutoff frequency for the oscillators.

The cutoff frequency is determined by the condition $\bar{E}(\omega_c) = E_1(\omega_c)$; using the expression for $\bar{E}$, this becomes

$$\frac{\hbar\omega_c}{e^{\hbar\omega_c/(k_BT)} - 1} = \hbar\omega_c, \tag{2.29}$$

from which it follows that ω_c grows linearly with the absolute temperature T,

$$\omega_c = \frac{k_BT}{\hbar} \ln 2. \tag{2.30}$$

P2.4 Calculate the energy of a quantum of visible light of wavelength 6000Å. Calculate the number of quanta of this wavelength that are emitted per second by a 10-watt light source.

Solution. The energy of a light quantum is given by

$$E = h\nu = \frac{hc}{\lambda}. \tag{2.31}$$

Substituting the values $hc = 1.988 \times 10^{-25}$ J m and $\lambda = 6 \times 10^{-7}$ m, we obtain

$$E = 3.313 \times 10^{-19}\,\mathrm{J} = 2.07\,\mathrm{eV}. \tag{2.32}$$

A 10 watt lamp radiates 10 J per second (assuming all energy is converted into radiation of the same wavelength, which here represents an average wavelength). The number of quanta per second is then

$$N = \frac{\text{power}}{\text{energy per quantum}} = \frac{10\,\mathrm{J}\cdot\mathrm{s}^{-1}}{3.313 \times 10^{-19}\,\mathrm{J}}, \tag{2.33}$$

that is,

$$N = 3.018 \times 10^{19}\,\mathrm{s}^{-1}. \tag{2.34}$$

For light in this spectral region, the human eye's detection threshold is on the order of one hundred quanta per second, which according to the above calculation corresponds to a power of about 3.3×10^{-17} W.

P2.5 Taking the Sun as a blackbody at 5700 K, find the fraction of its mass that it emits as electromagnetic radiation per year.
Solution. The Stefan–Boltzmann law for the total power radiated per unit area from a blackbody surface is

$$M = \sigma T^4. \tag{2.35}$$

Assuming the Sun behaves as a perfect blackbody of temperature $T = 5700$ K, we calculate the energy it radiates in one year with: his radius $R_\odot = 6.96 \times 10^8$ m the Stefan–Boltzmann constant $\sigma = 5.6704 \times 10^{-8}\,\mathrm{W\ m^{-2}K^{-4}}$, and the duration of a sidereal year $\tau = 365.25\,\mathrm{d} = 3.1558 \times 10^7$ s, as

$$E_{\mathrm{yr}} \;=\; A\tau M = 4\pi R_\odot^2 \tau\ \sigma T^4 \;\approx\; 1.15 \times 10^{34}\ \mathrm{J}. \tag{2.36}$$

Given the solar mass $M_\odot = 1.989 \times 10^{30}\,\mathrm{kg}$ and using $E = mc^2$ with $c = 2.998 \times 10^8\,\mathrm{m\ s^{-1}}$, we calculate the energy equivalent of the total mass of the Sun

$$E_\odot = M_\odot c^2 = 1.787 \times 10^{47}\ \mathrm{J}. \tag{2.37}$$

Therefore the fraction of its total mass emitted as radiation per year is

$$\frac{E_{yr}}{E_\odot} = \frac{1.15 \times 10^{34}\ \mathrm{J}}{1.787 \times 10^{47}\ \mathrm{J}} \approx 6.4 \times 10^{-14} \tag{2.38}$$

Thus the Sun converts roughly 6×10^{-14} of its mass into electromagnetic radiation each year.

P2.6 Ultraviolet light of wavelength 3500Å is incident on a potassium surface. The maximum energy of the emitted photoelectrons is observed to be 1.6 eV. Calculate the work function of potassium, neglecting thermal corrections.
Solution. In a simplified version of the photoelectric effect, a photon is completely absorbed by an electron on the metal surface, so that when the electron is emitted, its kinetic energy is given by

$$K = h\nu - W, \tag{2.39}$$

where W is the work needed to remove the electron from the metal, i.e., the work required to overcome both the attractive forces of the surface atoms as well as the kinetic energy losses of the electron due to collisions with the plate's atoms during its journey to the surface.

When the electron receives all the energy absorbed by the atom and collision losses are negligible, the photoelectron emerges with the maximum kinetic energy $K_{\max} = h\nu - W_0$, where W_0 is the work function of the metal, that is the minimum energy required for a photoelectron to reach the metal surface and escape from

the forces that normally bind it to the metal. Thus, we can determine the work function as

$$W_0 = h\nu - K_{\max}. \tag{2.40}$$

For light of wavelength $\lambda = 3500\,\text{Å} = 3.5 \times 10^{-7}\,\text{m}$, the frequency is

$$\nu = c/\lambda = 8.571 \times 10^{14}\,\text{s}^{-1}. \tag{2.41}$$

and for the work function of potassium we get

$$W_0 = 6.626 \times 10^{-34} \times 8.571 \times 10^{14}\,\text{J} - 1.6 \times 1.602 \times 10^{-19}\,\text{J} \tag{2.42}$$

$$= 3.116 \times 10^{-19}\,\text{J} = 1.945\,\text{eV}. \tag{2.43}$$

This result implies that the threshold (or cutoff) wavelength for potassium is

$$\lambda_0 = \frac{hc}{W_0} = 6.379 \times 10^{-7}\,\text{m} = 637.9\,\text{nm} = 6379\text{Å}. \tag{2.44}$$

P2.7 A 100 MeV photon collides with an electron at rest and is scattered at 45° from the direction of incidence. Calculate the energy of each particle after the collision and determine the final direction of the electron.

Solution. Before the collision, the photon energy is $E_0 = 100\,\text{MeV}$, and the electron is at rest with energy $m_e c^2$. After the collision, the photon is scattered at an angle $\theta = 45°$ (shown schematically in Fig. 2.2) with energy E_1 and momentum p_1. The electron gains kinetic energy K and momentum p, being scattered at an angle φ.

From momentum conservation along the x- and y-axes:,

$$p_0 = p_1 \cos\theta + p\cos\varphi, \tag{2.45}$$

$$0 = p_1 \sin\theta - p\sin\varphi, \tag{2.46}$$

we get

$$p^2 = p_0^2 - 2p_0 p_1 \cos\theta + p_1^2. \tag{2.47}$$

Assuming that the electron is weakly bound, total energy conservation gives

$$E_0 + m_e c^2 = E_1 + K + m_e c^2, \tag{2.48}$$

$$E_0 = E_1 + K. \tag{2.49}$$

Using $E = pc$ for photons, we can write $E_0 = p_0 c$, $E_1 = p_1 c$, and $K = c(p_0 - p_1)$. The total energy of the electron after collision, $E = K + m_e c^2$, is expressed in terms of its momentum, $E^2 = m_e^2 c^4 + p^2 c^2$. Combining these expressions we get

$$K^2 + 2m_e c^2 K + m_e^2 c^4 = m_e^2 c^4 + p^2 c^2, \tag{2.50}$$

which gives

$$p^2 = \frac{K^2}{c^2} + 2m_e K, \tag{2.51}$$

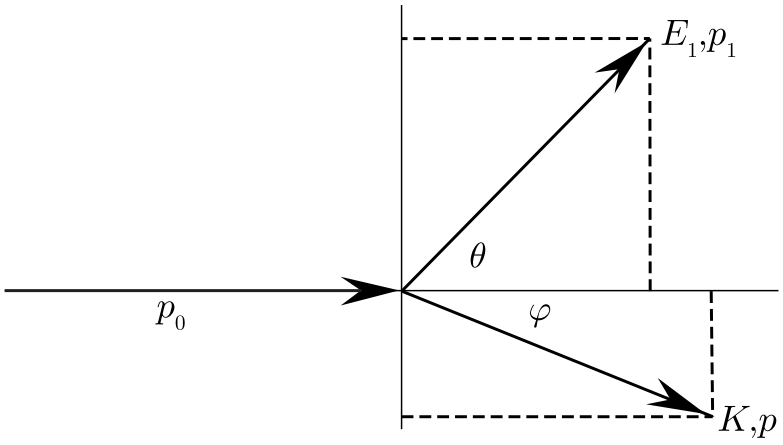

FIGURE 2.2. Compton scattering of a photon by an electron.

whence using Eq. (2.47) we get

$$\frac{K^2}{c^2} + 2m_e K = p_0^2 - 2p_0 p_1 \cos\theta + p_1^2, \tag{2.52}$$

or uing $K = c(p_0 - p_1)$,

$$2m_e c(p_0 - p_1) = 2p_1 p_0(1 - \cos\theta). \tag{2.53}$$

This leads to

$$\frac{1}{p_1} - \frac{1}{p_0} = \frac{1}{m_e c}(1 - \cos\theta), \tag{2.54}$$

which expressed in terms of de Broglie wavelength corresponds to the Compton wavelength shift

$$\Delta\lambda = \lambda_1 - \lambda_0 = \lambda_c(1 - \cos\theta), \tag{2.55}$$

where

$$\lambda_c = \frac{h}{m_e c} = 2.43 \times 10^{-12}\,\mathrm{m} = 0.0243\,\text{Å} \tag{2.56}$$

is Compton's wavelength.

Given $E_0 = 100\,\mathrm{MeV} = 1.602 \times 10^{-11}\,\mathrm{J}$,

$$p_0 = \frac{E_0}{c} = 5.344 \times 10^{-20}\,\mathrm{kg \cdot m/s} \tag{2.57}$$

$m_e = 9.109 \times 10^{-31}\,\mathrm{kg}$ and $\theta = 45°$, we get using Eq. (2.54),

$$p_1 = 9.164 \times 10^{-22}\,\mathrm{kg \cdot m/s}, \tag{2.58}$$

$$E_1 = cp_1 = 2.747 \times 10^{-13}\,\mathrm{J} = 1.715\,\mathrm{MeV}, \tag{2.59}$$

which barely exceeds 1% of E_0; in other words, the photon transfers more than 98% of its energy to the electron during this collision.

The kinetic energy gained by the electron is

$$K = E_0 - E_1 = 1.575 \times 10^{-11}\,\mathrm{J} = 98.29\,\mathrm{MeV}, \tag{2.60}$$

and the corresponding momentum is

$$p = \frac{K}{c}\left[1 + \frac{2m_e c^2}{K}\right]^{1/2} = \frac{1.575 \times 10^{-11}}{3 \times 10^8}(1 + 1.04 \times 10^{-2})^{1/2}, \tag{2.61}$$

$$p = 5.28 \times 10^{-20}\,\mathrm{kg \cdot m/s}. \tag{2.62}$$

From conservation of momentum in y we get

$$\sin\varphi = \frac{p_1}{p}\sin\theta, \tag{2.63}$$

so that

$$\varphi \approx \frac{\sin\theta}{100} = 0.70^\circ. \tag{2.64}$$

P2.8 Assuming that the relevant classical laws apply, calculate the power emitted by an electron moving in a circular Bohr orbit characterized by the quantum number n.

Solution. In classical physics, an external source would need to continuously compensate for the energy lost through radiation in order for an electron to describe a circular orbit. According to electromagnetic theory, accelerated charges radiate energy in the form of electromagnetic waves. Specifically, in the non-relativistic limit, the power radiated by an accelerating electric charge is given by the Larmor formula from electrodynamics,

$$P = \frac{2}{3}\frac{e^2 a^2}{4\pi\varepsilon_0 c^3}. \tag{2.65}$$

Temporarily disregarding the stability of Bohr orbits, let us calculate the power radiated by an electron moving in a Bohr circular orbit using classical methods. This orbit is characterized by the quantum number n. Consider an atom consisting of a nucleus with charge Ze and mass M, and a single electron with charge $-e$ and mass m. Since the electron's mass is very small compared to that of the nucleus, we can consider the latter as fixed in space. The stable orbits in Bohr's theory can be determined by equating the centrifugal inertial force and the Coulomb attraction exerted on the electron by the nucleus,

$$\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2} = \frac{mv^2}{r}. \tag{2.66}$$

For a circular orbit, the electron's angular momentum is $L = mvr$, and by applying Bohr's second postulate (or the Wilson-Sommerfeld rule to $J_p = L$) we obtain

$$mvr = n\hbar. \tag{2.67}$$

Substituting into Eq. (2.66) yields

$$r_n = \frac{4\pi\varepsilon_0\hbar^2}{mZe^2}n^2, \quad n = 1, 2, 3, \ldots \tag{2.68}$$

The angular momentum quantization condition restricts possible circular orbits to those with radii that satisfy this equation. Using the angular momentum relation, the electron's velocity becomes

$$v_n = \frac{Ze^2}{4\pi\varepsilon_0\hbar}\frac{1}{n} \tag{2.69}$$

while the acceleration, $a = v^2/r$, is given by

$$a_n = \frac{mZ^3e^6}{(4\pi\varepsilon_0)^3\hbar^4}\frac{1}{n^4}. \tag{2.70}$$

Substituting this expression into the Larmor formula gives the final result,

$$P = \frac{2}{3}\frac{Z^6e^{14}m^2}{(4\pi\varepsilon_0)^7c^3\hbar^5}\frac{1}{n^6}. \tag{2.71}$$

For example, for an electron in the first allowed orbit of a hydrogen atom ($Z = 1$, $n = 1$) we get

$$P = 2.9 \times 10^{10}\,\text{eV/s} = 2.9 \times 10^{4}\,\text{MeV/s}. \tag{2.72}$$

This energy loss rate is extremely high. For reference, recall that the electron's rest mass equals just over 0.5 MeV. Even worse, this is only the initial rate, since radiation would cause the orbit radius to decrease, thereby increasing P and making the electron lose energy increasingly faster and spiral into the nucleus. Without Bohr's stability postulate, which states that an electron in an allowed orbit does not radiate, an H atom would collapse in about 10^{-10} seconds. Obviously, this does not happen.

P2.9 Deuterium is an isotope of hydrogen whose nucleus consists of a tightly bound proton and neutron, with atomic weight 2 (the masses of the proton and neutron are nearly equal). Determine: a) the Rydberg constant for deuterium in terms of that for hydrogen; b) the ratio of the wavelengths of the deuterium spectrum to those of the corresponding hydrogen transitions.

Solution. The Rydberg constant R for a hydrogen-like atom is proportional to the reduced mass μ of the electron–nucleus system,

$$R = \mu\frac{e^4}{2c\hbar^3} \qquad \text{with} \qquad \mu = \frac{m_eM}{m_e + M}, \tag{2.73}$$

where M is the nuclear mass and m_e the electron mass. The reduced masses of hydrogen (μ_H) and deuterium (μ_D) are

$$\mu_\text{H} = \frac{m_eM_p}{m_e + M_p}, \qquad \mu_\text{D} = \frac{m_e(2M_p)}{m_e + 2M_p}, \tag{2.74}$$

where M_p is the proton mass (the neutron mass is essentially the same, so the deuterium nuclear mass is taken as $2M_p$).

With $r = m_e/M_p \approx 1/1836.15$, the ratio between Rydberg constants is then given by

$$\frac{R_{\rm D}}{R_{\rm H}} = \frac{\mu_{\rm D}}{\mu_{\rm H}} = \frac{2/(2+r)}{1/(1+r)} = \frac{2(1+r)}{2+r} \approx \frac{2(1+0.000544)}{2+0.000544} \approx 1.00027, \tag{2.75}$$

that is,

$$R_{\rm D} \;\simeq\; 1.00027\, R_{\rm H} \tag{2.76}$$

We have that

$$E_n = \frac{2\pi\hbar c}{n^2} R, \qquad E = h\nu, \qquad \nu = \frac{v}{\lambda}, \tag{2.77}$$

whence

$$\frac{\lambda_D}{\lambda_H} = \frac{E_H}{E_D} = \frac{R_H}{R_D} \approx 0.99973. \tag{2.78}$$

Thus the deuterium Rydberg constant is larger than that of hydrogen by about 0.027%, and all of its spectral lines are shorter in wavelength by the same fraction.

P2.10 Use the Wilson-Sommerfeld quantization rule to determine the emission spectrum of a particle moving in the potential

$$V(r) = V_0 \left(\frac{r}{a}\right)^k, \tag{2.79}$$

with $k \gg 1$, assuming that it is possible to restrict oneself to the study of circular orbits. Draw a representative graph of this potential, and compare your results with those of [**1**], Exercise E2.2.

Solution. The general form of $V(r)$ is illustrated in Figure 2.3 (for $k = 10$). The Hamiltonian in polar coordinates for a particle subject to this potential is

$$H = E = \frac{p_r^2}{2m} + \frac{p_\phi^2}{2mr^2} + V_0 \left(\frac{r}{a}\right)^k, \tag{2.80}$$

with

$$p_r = m\dot{r}, \quad p_\phi = mr^2\dot{\varphi} = L = \text{const} \tag{2.81}$$

and

$$\dot{p}_r = -\frac{\partial H}{\partial r} = \frac{p_\phi^2}{mr^3} - k\frac{V_0}{a}\left(\frac{r}{a}\right)^{k-1}. \tag{2.82}$$

We will consider only circular orbits, so we take $\dot{r} = 0$, $p_r = 0$, and $\dot{p}_r = 0$. This restriction is not entirely justified, since in the corresponding classical bound problem elliptical orbits are also possible for arbitrary k. With this selection, the problem therefore acquires an essentially academic character. We apply the Wilson-Sommerfeld quantization rules and substitute them into the previous Hamiltonian, which gives

$$E = \frac{(n_\phi h)^2}{2mr^2} + V_0 \left(\frac{r}{a}\right)^k. \tag{2.83}$$

From the equation with $\dot{p}_r = 0$ it follows that

$$L^2 = p_\phi^2 = n_\phi^2 h^2 = k\frac{mV_0}{a^k} r^{k+2}, \tag{2.84}$$

and thus the radius of the allowed orbits is given by

$$r_n = \left(\frac{n_\phi^2 h^2 a^k}{kmV_0}\right)^{1/(k+2)}, \quad n = n_\phi. \tag{2.85}$$

We have written $n \equiv n_\phi$ since there is no risk of confusion, as only one quantum number appears in this problem. The energy level quantization rule now becomes

$$E_n = V_0 \left(\frac{r_n}{a}\right)^k \left(\frac{k}{2} + 1\right) \tag{2.86}$$

or, explicitly

$$E_n = \left(\frac{k}{2} + 1\right) V_0 \left(\frac{n_\phi^2 h^2}{kmV_0 a^2}\right)^{\frac{k}{k+2}}, \quad k > 0. \tag{2.87}$$

From this result and Bohr's rule, the emission spectrum is given by

$$\omega_{nn'} = \frac{E_n - E_{n'}}{h} = \left(\frac{k}{2} + 1\right) \frac{V_0}{h} \left(\frac{h^2}{kmV_0 a^2}\right)^{\frac{k}{k+2}} \left(n^{\frac{2k}{k+2}} - n'^{\frac{2k}{k+2}}\right). \tag{2.88}$$

For $k \gg 1$, the previous expressions simplify considerably,

$$E_n = \frac{n^2 h^2}{2ma^2}, \quad \omega_{nn'} = \frac{h}{2ma^2}\left(n^2 - n'^2\right). \tag{2.89}$$

The student is invited to demonstrate that these results are similar to those for a rigid rotor with moment of inertia $I = ma^2$. This means that the potential $V = V_0(r/a)^k$ with $k \gg 1$ can be taken as a reasonable approximation to the constraint that maintains the rotor's rigidity. This is suggested by the behavior shown in Fig. 2.3 when considering the case $k \to \infty$. From the equation for r_n we see that

$$\frac{r}{a} \simeq \left(\frac{L^2}{kma^2 V_0}\right)^{1/k}, \tag{2.90}$$

which converges to 1 as $k \to \infty$. This confirms that for $k \gg 1$, we can take a as the system's radius when $L \neq 0$.

P2.11 Calculate the de Broglie wavelength of a point particle moving at speed $c/100$, in the following cases:

a) an electron ($m_e = 9.1 \times 10^{-28}\,\mathrm{g}$),
b) a proton ($m_p = 1\,836.1\, m_e$),
c) a pebble ($m = 10\,\mathrm{g}$),
d) the Earth ($M_T = 6 \times 10^{27}\,\mathrm{g}$).

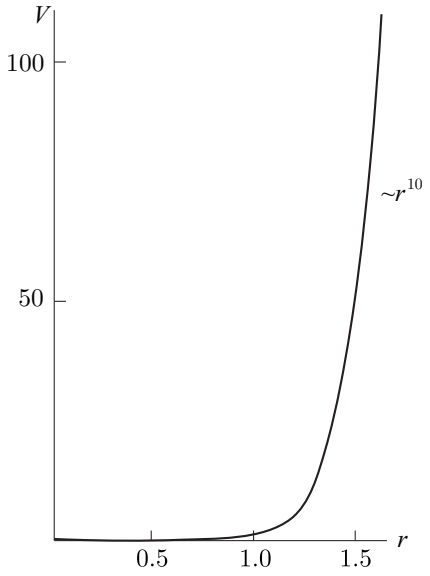

FIGURE 2.3. General form of the potential $V(r)$; the case $k = 10$ is illustrated.

Compare your results with the wavelength of yellow light and with the radius of the first Bohr orbit ($a = 0.529 \times 10^{-8}\,\text{cm}$).

Solution. The de Broglie wavelength is given by

$$\lambda = \frac{h}{p} = \frac{h}{mv}, \tag{2.91}$$

where the second equality holds in the non-relativistic regime. Substituting $v = c/100$, we get (with mass in kg and wavelength in m),

$$\lambda = \frac{100h}{mc} = \frac{2.21 \times 10^{-40}}{m}. \tag{2.92}$$

Using $\lambda_y = 580\,\text{Å} = 6 \times 10^{-7}\,\text{m}$ as a representative value for the wavelength of yellow light, we obtain

	m	λ	λ/λ_v	λ/a
(a)	9.1×10^{-31} kg	2.43×10^{-10} m	4.18×10^{-4}	4.59
(b)	$1836.1\, m_e$	1.32×10^{-13} m	2.28×10^{-7}	2.50×10^{-3}
(c)	10^{-2} kg	2.21×10^{-38} m	3.81×10^{-32}	4.18×10^{-28}
(d)	6×10^{24} kg	3.68×10^{-65} m	6.35×10^{-59}	6.96×10^{-55}

Note that the wavelengths of visible light are much greater than the de Broglie wavelengths of the studied objects, even for an electron moving at a speed of $c/100$

or higher. For more massive objects, the de Broglie wavelength is negligible even when compared to nuclear scales (of the order of $10^{-15}\,\mathrm{m} = 1\,\mathrm{fm}$); thus, no wave-like behavior associated with their motion can be observed. The same applies to small bodies as long as they are macroscopic. For instance, for a smoke particle with a diameter of one micron (i.e., $1\,\mu\mathrm{m}$) and a mass of about $10^{-15}\,\mathrm{kg}$ moving at a low speed of $1\,\mathrm{mm/s}$, $\lambda \sim 6 \times 10^{-6}\,\text{Å}$, which is about the size of an atomic nucleus. However, for particles with very small mass, such as electrons or nucleons, and speeds that are a fraction of the speed of light, the de Broglie wavelength can be comparable to interatomic distances. This makes them useful for determining crystal structures by diffraction, as observed when such particles pass through crystals.

P2.12 Find the expression for the orbital speed of the electron of a hydrogen atom that is in its lowest energy state using the Bohr model. Since this state is stationary, it can be described by an ensemble of H atoms in their ground state. Use this observation to determine the wavelength associated with the corresponding orbital velocity, and compare it with the circumference of the orbit. Discuss the result.

Solution. The electron is bound by the electrostatic attraction between the proton and electron, which provides the necessary centripetal force,

$$\frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2} = \frac{m_e v^2}{r}. \tag{2.93}$$

With the quantization condition for the angular momentum

$$L = n\hbar = m_e v r \quad (n = 1, 2, 3, ...) \tag{2.94}$$

we get for the velocity in the ground state ($n = 1$),

$$v = \frac{e^2}{4\pi\epsilon_0\hbar}. \tag{2.95}$$

The de Broglie wavelength λ is thus given by

$$\lambda = \frac{h}{p} = \frac{h}{m_e v} = \frac{8\pi^2\hbar^2\epsilon_0}{m_e e^2}. \tag{2.96}$$

On the other hand, the circumference of the orbit is given by $C = 2\pi r$, with r obtained by combining Eqs. (2.94) and (2.95),

$$r = \frac{4\pi\hbar^2\epsilon_0}{m_e e^2}.$$

Therefore, for the ground state $n = 1$, $\lambda = 2\pi r = C$, that is, the de Broglie wavelength associated with the orbital velocity is equal to the circumference of the orbit.

P2.13 In traditional optics, an optical instrument cannot resolve details of an object smaller than the wavelength used for observation. For example, a virus 200 Å in diameter cannot be studied with an instrument that uses visible light in the region of thousands of Å. An electron microscope, however, makes it possible.

Determine the acceleration potential required to produce a beam of electrons with a de Broglie wavelength $10^2 - 10^3$ times smaller than the dimensions of the virus.
Solution. We are asked to find the acceleration potential V required so that the beam of electrons has a de Broglie wavelength in the range

$$\lambda = \frac{d}{10^2} \quad \text{to} \quad \frac{d}{10^3}, \tag{2.97}$$

with $d = 10^{-8}\,\text{m}$. This gives

$$\lambda = 2 \times 10^{-10}\,\text{m} \quad \text{to} \quad 2 \times 10^{-11}\,\text{m} \tag{2.98}$$

For an electron accelerated through a potential V, its kinetic energy is $K = eV$. Using the non-relativistic relation $K = \frac{p^2}{2m_e}$, we have $p = \sqrt{2m_e eV}$, and thus

$$\lambda = \frac{h}{\sqrt{2m_e eV}} \quad \Rightarrow \quad V = \frac{h^2}{2m_e e\lambda^2}. \tag{2.99}$$

For the two limiting values λ we get
for $\lambda = 2 \times 10^{-10}\,\text{m}$,

$$V = \frac{(6.626 \times 10^{-34})^2}{2 \cdot 9.109 \times 10^{-31} \cdot 1.602 \times 10^{-19} \cdot (2 \times 10^{-10})^2} \approx 37.7\,\text{V} \tag{2.100}$$

and for $\lambda = 2 \times 10^{-11}\,\text{m}$,

$$V = \frac{(6.626 \times 10^{-34})^2}{2 \cdot 9.109 \times 10^{-31} \cdot 1.602 \times 10^{-19} \cdot (2 \times 10^{-11})^2} \approx 3770\,\text{V}. \tag{2.101}$$

Therefore, in order to resolve details that are $10^2 - 10^3$ times smaller than the virus, the required acceleration potential for the electrons must be approximately between 40 V and 4 kV.

P2.14 Determine the wavelength of a beam of neutrons which undergoes first-order diffraction by a crystal. The beam is incident at an angle of 40° with respect to the set of planes of the crystal lattice, whose spacing is 2.85Å. What is the kinetic energy of the incident neutrons?
Solution. First-order diffraction of neutrons by a crystal lattice is governed by Bragg's Law,

$$2\,d\,\sin\theta = n\lambda, \tag{2.102}$$

with $n = 1$. This gives, with $\theta = 40°$ and $d = 2.85\text{Å}$,

$$\lambda \approx 3.66\text{Å}. \tag{2.103}$$

The kinetic energy of the neutron is given by $K = \frac{p^2}{2m}$, so that with $\lambda = \frac{h}{p}$, we get

$$K = \frac{h^2}{2m\lambda^2} \approx 6.09\text{x}10^{-3}\text{eV}, \tag{2.104}$$

which is approximately 2,000 times smaller than that of electrons with the same wavelength.

P2.15 A technique for monochromatizing a beam of slow neutrons consists of directing the entire beam toward a crystal of known structure and positioning the collector to receive the monochromatic beam of diffracted neutrons. Suppose that a crystal is used whose distance between successive layers is 1.2 Å. Considering only Bragg diffraction of order 1, at what angle with respect to the initial direction of the beam should the collector be oriented to select the neutrons with $\lambda = 0.8$ Å?
Solution. Bragg's first–order condition for constructive interference is v. With $d = 1.2$ Å, $\lambda = 0.8$ Å, we get

$$\sin\theta = \frac{\lambda}{2d} = \frac{0.8}{2(1.2)} = \frac{1}{3}, \qquad \theta = \arcsin\left(\tfrac{1}{3}\right) \approx 19.5^\circ. \tag{2.105}$$

The diffracted (reflected) beam leaves the crystal symmetrically, so the angle between the incident beam and the diffracted beam is

$$2\theta \approx 39^\circ. \tag{2.106}$$

Hence the collector should be oriented about 39° with respect to the original neutron-beam direction to select the neutrons of wavelength 0.8 Å.

P2.16 Compare the zero-point energy of a radiation field mode of wavelength 6000Å, with the average thermal energy of the same field mode at room temperature.
Solution. The zero-point energy is given by

$$E_0 = \frac{1}{2}\hbar\omega. \tag{2.107}$$

For a field mode of wavelength 6000Å, using $\omega = 2\pi\nu$ and $\nu = c/\lambda$, we get

$$E_0 \approx 1.03\text{eV}. \tag{2.108}$$

The average thermal energy of a field mode of frequency ω is given by

$$E = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}, \tag{2.109}$$

where k is the Boltzmann constant and T is the temperature. At room temperature (300 K) we get

$$\frac{\hbar\omega}{kT} \approx \frac{2.07}{0.026} = 79.6 \tag{2.110}$$

$$E \approx \frac{2.07}{e^{79.6} - 1}\,\text{eV} \approx 2 \times \text{e}^{-79.6}\,\text{eV}. \tag{2.111}$$

Compared with the average thermal energy contribution at room temperature for a mode with a wavelength of 6000Å,the zero-point energy is significant.Thus, thermal effects do not appreciably excite this mode, and the zero-point energy

dominates.

P2.17 An electron in an antenna is subject to oscillations at a frequency $\nu = 10^{15}$ Hz. Calculate the mean amplitude Δx of the oscillations at zero temperature and at room temperature.

Solution. From Planck's complete (thermal + zero-point) law for the mean energy per mode

$$\langle E(T)\rangle = \tfrac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/kT}-1}, \tag{2.112}$$

and using the virial theorem for the harmonic oscillator potential, $\langle E(T)\rangle = 2\langle V\rangle$, whence

$$\langle V\rangle = \frac{m\omega^2\langle(\Delta x)^2\rangle}{2}, \tag{2.113}$$

we get

$$\langle(\Delta x)^2\rangle = \frac{E(T)}{m\omega^2}, \tag{2.114}$$

so that

$$\Delta x(T) = \sqrt{\frac{E(T)}{m\omega^2}}. \tag{2.115}$$

Setting $T = 0$ in Eq. 2.112 gives $E(0) = \frac{1}{2}\hbar\omega$. Then

$$\Delta x(0) = \sqrt{\frac{\hbar}{2m\omega}}, \tag{2.116}$$

or using $\nu = 10^{15}\,\mathrm{Hz}$ in$\omega = 2\pi\nu$ and $m = m_e$,

$$\Delta x(0) \approx\ 9.60\times10^{-11}\,\mathrm{m}\ \ =\ 0.96\ \text{Å}. \tag{2.117}$$

At $T = 300\,\mathrm{K}$, we have

$$\frac{\hbar\omega}{kT} \approx 1.60\times10^{2} \gg 1, \tag{2.118}$$

so the thermal term in Eq. 2.112 is exponentially suppressed and $E(T) \simeq \frac{1}{2}\hbar\omega$. Thus, at such high frequency, the mean amplitude of the oscillations is entirely determined by the zero-point motion at both $T = 0$ and room temperature.

CHAPTER 3

Quantum Mechanics in the Heisenberg (Matrix) Picture

P3.1 Demonstrate directly the following properties of the commutator:

$$[\widehat{u},\widehat{v}] = -\,[\widehat{v},\widehat{u}]\,, \tag{3.1}$$

$$[\widehat{u}+\widehat{v},\widehat{\omega}] = [\widehat{u},\widehat{\omega}] + [\widehat{v},\widehat{\omega}]\,, \tag{3.2}$$

$$[\widehat{u}\widehat{\omega},\widehat{v}] = \widehat{u}\,[\widehat{\omega},\widehat{v}] + [\widehat{u},\widehat{v}]\,\hat{\omega}, \tag{3.3}$$

$$[\widehat{u},[\widehat{v},\widehat{\omega}]] + [\widehat{v},[\widehat{\omega},\widehat{u}]] + [\widehat{\omega},[\widehat{u},\widehat{v}]] = 0 \tag{3.4}$$

The latter is the so-called Jacobi identity. Rewrite the last two results using the differential property of the commutator discussed in **[1]**, **Exercise E3.1**.

Solution. For property (3.1) we apply directly the formula for the commutator,

$$[\widehat{u},\widehat{v}] = \widehat{u}\widehat{v} - \widehat{v}\widehat{u} = -\widehat{v}\widehat{u} + \widehat{u}\widehat{v} = -(\widehat{v}\widehat{u} - \widehat{u}\widehat{v}) = -\,[\widehat{u},\widehat{v}]\,. \tag{3.5}$$

For the second property we write

$$[\widehat{u}+\widehat{v},\widehat{\omega}] = (\widehat{u}+\widehat{v})\widehat{\omega} - \widehat{\omega}(\widehat{u}+\widehat{v}) \tag{3.6}$$

$$= \widehat{u}\widehat{\omega} + \widehat{v}\widehat{\omega} - \widehat{\omega}\widehat{u} - \widehat{\omega}\widehat{v} \tag{3.7}$$

$$= (\widehat{u}\widehat{\omega} - \widehat{\omega}\widehat{u}) + (\widehat{v}\widehat{\omega} - \widehat{\omega}\widehat{v}) \tag{3.8}$$

$$= [\widehat{u},\widehat{\omega}] + [\widehat{v},\widehat{\omega}]\,. \tag{3.9}$$

The same procedure applies to the third property,

$$[\widehat{u}\widehat{\omega},\widehat{v}] = \widehat{u}\widehat{\omega}\widehat{v} - \widehat{v}\widehat{u}\widehat{\omega} \tag{3.10}$$

$$= \widehat{u}\widehat{\omega}\widehat{v} - \widehat{u}\widehat{v}\widehat{\omega} + \widehat{u}\widehat{v}\widehat{\omega} - \widehat{v}\widehat{u}\widehat{\omega} \tag{3.11}$$

$$= \widehat{u}\,(\widehat{\omega}\widehat{v} - \widehat{v}\widehat{\omega}) + (\widehat{u}\widehat{v} - \widehat{v}\widehat{u})\,\widehat{\omega} \tag{3.12}$$

$$= \widehat{u}\,[\widehat{\omega},\widehat{v}] + [\widehat{u},\widehat{v}]\,\widehat{\omega}. \tag{3.13}$$

To prove the Jacobi identity, we expand the commutators

$$[\widehat{u},[\widehat{v},\widehat{\omega}]] = \widehat{u}\,(\widehat{v}\widehat{\omega} - \widehat{\omega}\widehat{v}) - (\widehat{v}\widehat{\omega} - \widehat{\omega}\widehat{v})\,\widehat{u} \tag{3.14}$$

$$= \widehat{u}\widehat{v}\widehat{\omega} - \widehat{u}\widehat{\omega}\widehat{v} - \widehat{v}\widehat{\omega}\widehat{u} + \widehat{\omega}\widehat{v}\widehat{u}, \tag{3.15}$$

$$[\widehat{v},[\widehat{\omega},\widehat{u}]] = \widehat{v}\,(\widehat{\omega}\widehat{u} - \widehat{u}\widehat{\omega}) - (\widehat{\omega}\widehat{u} - \widehat{u}\widehat{\omega})\,\widehat{v} \tag{3.16}$$

$$= \widehat{v}\widehat{\omega}\widehat{u} - \widehat{v}\widehat{u}\widehat{\omega} - \widehat{\omega}\widehat{u}\widehat{v} + \widehat{u}\widehat{\omega}\widehat{v}, \tag{3.17}$$

$$[\widehat{\omega},[\widehat{u},\widehat{v}]] = \widehat{\omega}\,(\widehat{u}\widehat{v} - \widehat{v}\widehat{u}) - (\widehat{u}\widehat{v} - \widehat{v}\widehat{u})\,\widehat{\omega} \tag{3.18}$$

$$= \widehat{\omega}\widehat{u}\widehat{v} - \widehat{\omega}\widehat{v}\widehat{u} - \widehat{u}\widehat{v}\widehat{\omega} + \widehat{v}\widehat{u}\widehat{\omega}, \tag{3.19}$$

and add them up, to obtain

$$[\widehat{u},[\widehat{v},\widehat{\omega}]]+[\widehat{v},[\widehat{\omega},\widehat{u}]]+[\widehat{\omega},[\widehat{u},\widehat{v}]]=0.$$

P3.2 Show that if $[\hat{F},\hat{G}]=0$, then

$$\left[\hat{F}^{\,n},\,\hat{G}^{\,m}\right]=0,\qquad \left[f(\hat{F},\hat{G}),\,g(\hat{F},\hat{G})\right]=0 \tag{3.20}$$

for functions f,g that can be expanded in power series.

Solution. The requested results should be intuitive, since operators that commute can be treated as ordinary functions when operating with their relations. To provide a more formal demonstration, we begin with the premise that if two operators, $\hat{u}$ and $\hat{v}$ satisfy the relation

$$\left[\,[\hat{u},\hat{v}],\,\hat{u}\,\right]=0, \tag{3.21}$$

then it follows that

$$[\hat{u}^n,\hat{v}]=n\hat{u}^{n-1}[\hat{u},\hat{v}], \tag{3.22}$$

which is proved by an extension of the method used to solve the previous problem.

It is clear that if $[\hat{F},\hat{G}]=0$, we can write

$$[\hat{F}^m,\hat{G}]=m\hat{F}^{m-1}[\hat{F},\hat{G}]=0,\qquad [\hat{G}^m,\hat{F}]=m\hat{G}^{m-1}[\hat{G},\hat{F}]=0. \tag{3.23}$$

Using the third property from the previous problem and taking $\hat{u}=\hat{G}^{m-1}$, $\hat{v}=\hat{F}^n$, $\hat{w}=\hat{G}$, we can write

$$\left[\hat{F}^n,\hat{G}^m\right]=\hat{G}^{m-1}\left[\hat{F}^n,\hat{G}\right]+\left[\hat{F}^n,\hat{G}^{m-1}\right]\hat{G}=\left[\hat{F}^n,\hat{G}^{m-1}\right]\hat{G} \tag{3.24}$$

$$=\left[\hat{F}^n,\hat{G}^{m-2}\right]\hat{G}^2=\cdots=\left[\hat{F}^n,\hat{G}\right]\hat{G}^{m-1}=0 \tag{3.25}$$

which is one of the requested results.

Now consider two functions $f(\hat{F},\hat{G})$ and $g(\hat{F},\hat{G})$, which can be expanded into power series of $\hat{F}$ and $\hat{G}$ as

$$f(\hat{F},\hat{G})=\sum_{n,m}c_{nm}\hat{F}^n\hat{G}^m,\quad g(\hat{F},\hat{G})=\sum_{n,m}d_{nm}\hat{F}^n\hat{G}^m. \tag{3.26}$$

There is no ordering problem in this case because the operators commute. These expansions allow us to write

$$\left[f(\hat{F},\hat{G}),g(\hat{F},\hat{G})\right]=\sum_{n,m}\sum_{n',m'}c_{nm}d_{n'm'}\left[\hat{F}^n\hat{G}^m\hat{F}^{n'}\hat{G}^{m'}-\hat{F}^{n'}\hat{G}^{m'}\hat{F}^n\hat{G}^m\right]=0, \tag{3.27}$$

due once again to the fact that the operators involved and their powers commute. This concludes the solution.

P3.3 Show that if $\widehat{F}$, $\widehat{G}$ are two commuting operators, then

$$\left[\widehat{F}^{-1},\widehat{G}\right]=\left[\widehat{F},\widehat{G}^{-1}\right]=\left[\widehat{F}^{-1},\widehat{G}^{-1}\right]=0. \tag{3.28}$$

Solution. We start from the definition of the commutator,

$$\left[\widehat{F}^{-1},\widehat{G}\right]=\widehat{F}^{-1}\widehat{G}-\widehat{G}\widehat{F}^{-1} \tag{3.29}$$

and multiply both terms by F to the left and to the right, taking into account that F and G commute,

$$\widehat{F}\left(\widehat{F}^{-1}\widehat{G}-\widehat{G}\widehat{F}^{-1}\right)\widehat{F}=\left[\widehat{F},\widehat{G}\right]=0. \tag{3.30}$$

The remaining two equalities are proved analogously.

P3.4 Show that for two arbitrary operators $\hat{F},\hat{G}$, $\quad e^{\hat{F}\hat{G}}\hat{F}=\hat{F}e^{\hat{G}\hat{F}}$.
Solution. The exponential function of an operator is defined via its power series as

$$e^{\hat{A}}\equiv\sum_{n=0}^{\infty}\frac{1}{n!}\left(\hat{A}\right)^n. \tag{3.31}$$

Using this definition, we can write

$$e^{\hat{F}\hat{G}}\hat{F}=\sum_{n=0}^{\infty}\frac{1}{n!}(\hat{F}\hat{G})^n\hat{F}=\hat{F}+\hat{F}\hat{G}\hat{F}+\frac{1}{2!}\hat{F}\hat{G}\hat{F}\hat{G}\hat{F}+\frac{1}{3!}\hat{F}\hat{G}\hat{F}\hat{G}\hat{F}\hat{G}\hat{F}+\cdots \tag{3.32}$$

$$=\hat{F}\left[1+\hat{G}\hat{F}+\frac{1}{2!}\hat{G}\hat{F}\hat{G}\hat{F}+\frac{1}{3!}\hat{G}\hat{F}\hat{G}\hat{F}\hat{G}\hat{F}+\cdots\right] \tag{3.33}$$

$$=\hat{F}\sum_{n=0}^{\infty}\frac{1}{n!}(\hat{G}\hat{F})^n=\hat{F}e^{\hat{G}\hat{F}}, \tag{3.34}$$

which is the desired result.

P3.5 Show that

$$[\widehat{p},\sin\lambda x]=-i\lambda\cos\lambda x, \tag{3.35}$$

$$[\widehat{p},\cos\lambda x]=i\lambda\sin\lambda x, \tag{3.36}$$

and therefore,

$$\Delta\widehat{p}\Delta\sin\lambda x\geq\frac{\lambda\hbar}{2}\left|\langle\cos\lambda x\rangle\right|, \tag{3.37}$$

$$\Delta\widehat{p}\Delta\cos\lambda x\geq\frac{\lambda\hbar}{2}\left|\langle\sin\lambda x\rangle\,.\right| \tag{3.38}$$

Examine the limit $\lambda \to 0$ of this last equation.
Solution. For the first two equations the proof follows the same steps. We use the property of operators

$$\left[\widehat{p}, \widehat{G}(x)\right] = -i\hbar \frac{d\widehat{G}}{d\widehat{x}}, \tag{3.39}$$

substituting and taking $\hbar = 1$

$$\left[\widehat{p}, \widehat{G}(x)\right] = [\widehat{p}, \sin \lambda x] = -i\lambda \cos \lambda x. \tag{3.40}$$

Similarly,

$$\left[\widehat{p}, \widehat{G}(x)\right] = [\widehat{p}, \cos \lambda x] = i\lambda \sin \lambda x. \tag{3.41}$$

To prove the remaining equations we use the property

$$\Delta \widehat{F} \Delta \widehat{G} \geq \frac{1}{2} \left| \langle \widehat{C} \rangle \right|, \tag{3.42}$$

where

$$\left[\widehat{F}, \widehat{G}\right] = -i\widehat{C}. \tag{3.43}$$

This gives

$$\Delta \widehat{p} \Delta \sin(\lambda x) \geq \frac{1}{2} \left| \langle \widehat{C} \rangle \right|, \tag{3.44}$$

where $\widehat{C} = \hbar\lambda \cos \lambda x$, so that

$$\Delta \widehat{p} \Delta \sin(\lambda x) \geq \frac{\hbar\lambda}{2} \left| \langle \cos \lambda x \, \rangle \right|. \tag{3.45}$$

Similarly,

$$\Delta \widehat{p} \Delta \cos(\lambda x) \geq \frac{\hbar\lambda}{2} \left| \langle \sin \lambda x \, \rangle \right|. \tag{3.46}$$

In the limit $\lambda \to 0$, the inequality becomes trivial because

$$\cos \lambda x \to 1 \quad \text{(constant)} \tag{3.47}$$

and the commutator vanishes,

$$[\hat{p}, \cos \lambda x] \to [\hat{p}, 1] = 0. \tag{3.48}$$

P3.6 Let $\hat{A}$ be an operator satisfying the equation $\hat{A}^2 + 2a\hat{A} + 1 = 0$, with a a real constant. What values of a make the operator $\hat{A}$ Hermitian?
Solution. If $\hat{A}$ is Hermitian, it has a real spectrum and $\hat{A}^\dagger = \hat{A}$. Let $|\psi\rangle$ be an eigenvector of $\hat{A}$ with eigenvalue λ,

$$\hat{A}|\psi\rangle = \lambda|\psi\rangle. \tag{3.49}$$

Then acting on $|\psi\rangle$ with the operator equation, we get

$$\left(\hat{A}^2 + 2a\hat{A} + 1\right)|\psi\rangle = \left(\lambda^2 + 2a\lambda + 1\right)|\psi\rangle = 0 \Rightarrow \lambda^2 + 2a\lambda + 1 = 0. \tag{3.50}$$

Solving the quadratic equation we get

$$\lambda = -a \pm \sqrt{a^2 - 1}. \tag{3.51}$$

Since $\hat{A}$ is Hermitian, all of its eigenvalues must be real. Therefore, the discriminant must be nonnegative,

$$a^2 - 1 \geq 0 \Rightarrow |a| \geq 1, \tag{3.52}$$

and $\hat{A}$ can be Hermitian if and only if $|a| \geq 1$.

P3.7 Let $\widehat{B}$ be a Hermitian operator satisfying the equation $\widehat{B}^3 = 4\widehat{B}$. Which are its eigenvalues?

Solution. Given that $\hat{B}$ is Hermitian, its eigenvalues λ are real. If $|\lambda\rangle$ is an eigenvector associated with the eigenvalue λ, then

$$\hat{B}|\lambda\rangle = \lambda|\lambda\rangle. \tag{3.53}$$

Applying $\hat{B}^3$ to $|\lambda\rangle$ and using the given relation $\hat{B}^3 = 4\hat{B}$, we get

$$\hat{B}^3|\lambda\rangle = \lambda^3|\lambda\rangle = 4\hat{B}|\lambda\rangle = 4\lambda|\lambda\rangle, \tag{3.54}$$

which implies $\lambda^3 = 4\lambda$, that is, $\lambda(\lambda^2 - 4) = 0$. The solutions are

$$\lambda = 0, \quad \lambda^2 = 4 \quad \Rightarrow \quad \lambda = 0, \pm 2. \tag{3.55}$$

P3.8 Show that

$$\left[\hat{A}, \frac{1}{\hat{B}}\right] = -\frac{1}{\hat{B}}\left[\hat{A}, \hat{B}\right]\frac{1}{\hat{B}}. \tag{3.56}$$

Solution. We start by expanding the commutator

$$\left[\hat{A}, \frac{1}{\hat{B}}\right] = \hat{A}\frac{1}{\hat{B}} - \frac{1}{\hat{B}}\hat{A}. \tag{3.57}$$

Now factor out $\hat{B^{-1}}$ at both sides using the identity $\hat{B}\hat{B}^{-1} = \mathbb{I}$,

$$= -\frac{1}{\hat{B}}\left(-\hat{B}\hat{A}\frac{1}{\hat{B}} + \hat{A}\right) = -\frac{1}{\hat{B}}\left(-\hat{B}\hat{A} + \hat{A}\hat{B}\right)\frac{1}{\hat{B}} \tag{3.58}$$

$$= -\frac{1}{\hat{B}}[\hat{A}, \hat{B}]\frac{1}{\hat{B}}, \tag{3.59}$$

which is the desired result.

P3.9 Consider a classical dynamical system with initial conditions or other relevant parameters distributed in such a way that it is convenient to make a statistical description of it. Defining averages as usual, show that for two arbitrary real dynamical variables, the inequality

$$\overline{(\Delta A)^2(\Delta B)^2} \geq \left(\overline{AB} - \overline{AB}\right)^2 \tag{3.60}$$

holds.

Solution. The quantity $\overline{AB} - \overline{A}\,\overline{B}$ is the covariance of A and B, denoted as $\mathrm{Cov}(A,B)$. The inequality we want to prove is analogous to the classical Cauchy-Schwarz inequality in statistics.

For any pair of random variables A and B, the Cauchy-Schwarz inequality reads

$$(\overline{AB})^2 \leq \overline{A^2}\,\overline{B^2} \tag{3.61}$$

However, we need a version centered on the fluctuations, that is, on $\Delta A = A - \overline{A}$ and $\Delta B = B - \overline{B}$. We define

$$\delta A = A - \overline{A}, \quad \delta B = B - \overline{B}. \tag{3.62}$$

so that $\overline{\delta A} = 0, \quad \overline{\delta B} = 0$. The covariance can be written as

$$\mathrm{Cov}(A,B) = \overline{\delta A \delta B}, \tag{3.63}$$

and the variances are

$$(\Delta A)^2 = \overline{(\delta A)^2}, \quad (\Delta B)^2 = \overline{(\delta B)^2} \tag{3.64}$$

Applying the Cauchy-Schwarz inequality to the centered variables δA and δB

$$(\overline{\delta A \delta B})^2 \leq \overline{(\delta A)^2}\,\overline{(\delta B)^2} \tag{3.65}$$

and intorducing the definitions

$$(\mathrm{Cov}(A,B))^2 \leq (\Delta A)^2 (\Delta B)^2, \tag{3.66}$$

we get

$$\overline{(\Delta A)^2 (\Delta B)^2} \geq \left(\overline{AB} - \overline{AB}\right)^2. \tag{3.67}$$

P3.10 Using **Eqs. (3.60) and (3.61)** of Ref. [**1**] for the harmonic oscillator in an eigenstate n, calculate the square of $\hat{H}$ and show that the dispersion of $\hat{H}$ is zero. What is the physical meaning of this result?

Solution. For the 1D harmonic oscillator,

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2, \tag{3.68}$$

and the nonvanishing nearest-neighbor matrix elements of $\hat{x}$ and $\hat{p}$ in the energy basis $\{|n\rangle\}$ are (with x_{10} real without loss of generality),

$$x_{n,n-1} = \sqrt{n}\, x_{10}, \qquad x_{n,n+1} = \sqrt{n+1}\, x_{10}, \tag{3.69}$$

$$p_{n,n-1} = i\, m\omega \sqrt{n}\, x_{10}, \qquad p_{n,n+1} = -i\, m\omega \sqrt{n+1}\, x_{10}. \tag{3.70}$$

i) Off–diagonal elements of $\hat{H}$. Since $\hat{x}$ and $\hat{p}$ only connect n with $n \pm 1$, $\hat{H}$ can connect n with n and $n \pm 2$. For example,

$$H_{n,n+2} = \frac{1}{2m}\, p_{n,n+1} p_{n+1,n+2} + \frac{1}{2} m\omega^2\, x_{n,n+1} x_{n+1,n+2}. \tag{3.71}$$

Using (3.69)–(3.70),

$$\frac{1}{2m}\, p_{n,n+1}p_{n+1,n+2} = \frac{1}{2m}\,(-im\omega)^2\sqrt{(n+1)(n+2)}\, x_{10}^2 \tag{3.72}$$

$$= -\frac{1}{2}m\omega^2\sqrt{(n+1)(n+2)}\, x_{10}^2, \tag{3.73}$$

$$\frac{1}{2}m\omega^2\, x_{n,n+1}x_{n+1,n+2} = \frac{1}{2}m\omega^2\sqrt{(n+1)(n+2)}\, x_{10}^2. \tag{3.74}$$

Hence $H_{n,n+2} = 0$. The same calculation shows that $H_{n,n-2} = 0$. Therefore $\hat{H}$ is diagonal in the $\{|n\rangle\}$ basis.

ii) Diagonal elements of $\hat{H}$. Using (3.69)–(3.70),

$$H_{nn} = \frac{1}{2m}\Big(p_{n,n+1}p_{n+1,n} + p_{n,n-1}p_{n-1,n}\Big) + \frac{1}{2}m\omega^2\Big(x_{n,n+1}x_{n+1,n} + x_{n,n-1}x_{n-1,n}\Big), \tag{3.75}$$

$$= m\omega^2(2n+1)\, x_{10}^2. \tag{3.76}$$

From the commutator $[\hat{x},\hat{p}] = i\hbar$ calculated in the ground state, with $p_{10} = im\omega x_{10}$, we get

$$|x_{10}|^2 = \frac{\hbar}{2m\omega}, \tag{3.77}$$

which gives

$$H_{nn} = \hbar\omega\left(n + \tfrac{1}{2}\right) \equiv E_n, \tag{3.78}$$

as expected.

iii) Square of $\hat{H}$ and dispersion. Because $\hat{H}$ is diagonal,

$$\langle n|\hat{H}^2|n\rangle = \sum_{\ell} H_{n\ell}H_{\ell n} = H_{nn}^2 = E_n^2. \tag{3.79}$$

Therefore the variance of the energy in the eigenstate $|n\rangle$ is

$$(\Delta H)^2 = \langle n|\hat{H}^2|n\rangle - \langle n|\hat{H}|n\rangle^2 = E_n^2 - E_n^2 = 0. \tag{3.80}$$

This result indicates that, in an energy eigenstate, the energy is sharp, meaning there is no dispersion. This state is stationary, and time evolution only contributes a global phase.

P3.11 Calculate the commutator of two Pauli matrices, $[\hat{\sigma}_i, \hat{\sigma}_j]$, with $i \neq j = 1, 2, 3$, and express the result in terms of Pauli matrices.

Solution. The Pauli matrices $\hat{\sigma}_1$, $\hat{\sigma}_2$, and $\hat{\sigma}_3$ are

$$\hat{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{3.81}$$

The product $\hat{\sigma}_1\hat{\sigma}_2$ gives

$$\hat{\sigma}_1\hat{\sigma}_2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}, \tag{3.82}$$

and the product $\hat{\sigma_2}\hat{\sigma_1}$ gives

$$\hat{\sigma_2}\hat{\sigma_1} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}. \tag{3.83}$$

Therefore,

$$[\hat{\sigma_1}, \hat{\sigma_2}] = \hat{\sigma_1}\hat{\sigma_2} - \hat{\sigma_2}\hat{\sigma_1} = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = \begin{pmatrix} 2i & 0 \\ 0 & -2i \end{pmatrix}. \tag{3.84}$$

Therefore,

$$[\hat{\sigma_1}, \hat{\sigma_2}] = 2i\hat{\sigma_3}. \tag{3.85}$$

The remaining commutators are solved similarly and their results are analogous,

$$[\hat{\sigma_2}, \hat{\sigma_3}] = 2i\hat{\sigma_1}, \tag{3.86}$$

$$[\hat{\sigma_3}, \hat{\sigma_1}] = 2i\hat{\sigma_2}. \tag{3.87}$$

These results can be expressed in the compact form

$$[\hat{\sigma_i}, \hat{\sigma_j}] = 2i\epsilon_{ijk}\hat{\sigma_k}, \tag{3.88}$$

where ϵ_{ijk} is the Levi-Civita antisymmetric tensor.

P3.12 Use the Pauli matrices to calculate $(\mathbf{a}\cdot\hat{\boldsymbol{\sigma}})^2 \begin{pmatrix} b \\ c \end{pmatrix}$, where $\mathbf{a}$ is a unit vector with Cartesian components a_1, a_2, a_3 and $\begin{pmatrix} b \\ c \end{pmatrix}$ is an arbitrary state vector. Comment on the outcome.

Solution. With $\mathbf{a} = (a_1, a_2, a_3)$ the unit vector and $\hat{\boldsymbol{\sigma}} = (\hat{\sigma}_1, \hat{\sigma}_2, \hat{\sigma}_3)$ the Pauli matrices (3.81), we have

$$\mathbf{a}\cdot\hat{\boldsymbol{\sigma}} = a_1\hat{\sigma}_1 + a_2\hat{\sigma}_2 + a_3\hat{\sigma}_3 \tag{3.89}$$

$$= a_1 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + a_2 \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + a_3 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{3.90}$$

This gives

$$\mathbf{a}\cdot\hat{\boldsymbol{\sigma}} = \begin{pmatrix} a_3 & a_1 - ia_2 \\ a_1 + ia_2 & -a_3 \end{pmatrix}. \tag{3.91}$$

Now consider the square of this operator,

$$(\mathbf{a}\cdot\hat{\boldsymbol{\sigma}})^2 = \begin{pmatrix} a_3^2 + a_1^2 + a_2^2 & 0 \\ 0 & a_1^2 + a_2^2 + a_3^2 \end{pmatrix} = (a_1^2 + a_2^2 + a_3^2)\mathrm{I} = \mathrm{I}, \tag{3.92}$$

since $\mathbf{a}$ is a unit vector. Therefore,

$$(\mathbf{a}\cdot\hat{\boldsymbol{\sigma}})^2 \begin{pmatrix} b \\ c \end{pmatrix} = \begin{pmatrix} b \\ c \end{pmatrix}. \tag{3.93}$$

Applying the square of the operator $\mathbf{a}\cdot\hat{\boldsymbol{\sigma}}$ to any state vector yields the original vector. This tells us that the operator is *involutive* up to a sign, meaning its square

is the identity, and its eigenvalues are ± 1.

CHAPTER 4

Quantum Mechanics in the Schrödinger (Wave) Picture. Dirac's Notation

P4.1 Consider two functions ψ_1 and ψ_2 each corresponding to a Gaussian distribution of particles,

$$\psi_1 = A_1 e^{-(x-a_1)^2/4\sigma^2}, \qquad \psi_2 = A_2 e^{-(x-a_2)^2/4\sigma^2}, \qquad a_2 > a_1.$$

a) Determine the normalization coefficients A_1 and A_2. Calculate $\overline{x}$ and $\overline{x^2}$ when the particle density is $\rho_1 = |\psi_1|^2$. What is the meaning of the parameters a and σ that appear in the normal distributions?
b) Two new functions are constructed, ψ_+ and ψ_- defined as $\psi_\pm = A_\pm(\psi_1 \pm \psi_2)$. Determine the normalization constants A_+ and A_-. Construct and plot the particle densities $\rho_+ = |\psi_+|^2$, $\rho_- = |\psi_-|^2$. Discuss the two limiting cases $\sigma \to \infty$, $\sigma \to 0$.
Solution. a) The normalization condition for the probability amplitude is

$$1 = \int_{-\infty}^{\infty} \psi^*(x)\,\psi(x)\,dx. \tag{4.1}$$

Applying this condition to ψ_1, and setting $y = x - a_1$, yields

$$1 = |A_1|^2 \int_{-\infty}^{\infty} e^{-(x-a_1)^2/2\sigma^2} dx = |A_1|^2 \int_{-\infty}^{\infty} e^{-y^2/2\sigma^2} dy. \tag{4.2}$$

The required integral is listed in any table of integrals. For reference purposes, a more general formula is provided below. Using the definition of the gamma function and a simple change of variable, we have

$$\int_0^{\infty} e^{-\alpha y^2} y^n dy = \tfrac{1}{2}\alpha^{-(n+1)/2}\Gamma\left(\frac{n+1}{2}\right), \quad n \geq -1, \tag{4.3}$$

The cases $n = 0, 1, 2$ of this expression are especially important, and you should be familiar with them. The following properties of the gamma function are of interest:

$$\Gamma(n+1) = n!, \qquad n = 0, 1, 2, \ldots \tag{4.4}$$

$$\Gamma(n+1) = n\Gamma(n), \qquad \Gamma(0) = 1, \tag{4.5}$$

$$\Gamma\left(\tfrac{1}{2}\right) = \sqrt{\pi}. \tag{4.6}$$

In our case, $n = 0$, $\alpha = 1/2\sigma^2$. Taking A real and positive gives

$$A_1 = \sqrt{\frac{1}{\sqrt{2\pi\sigma}}}. \tag{4.7}$$

Since the result is independent of the displacement a_1, the same value is obtained for A_2, hence $A_2 = A_1 \equiv A$. With the above expressions the particle density in state ψ_1 is given by

$$\rho_1(x) = \psi_1^* \psi_1 = A^2 e^{-(x-a_1)^2/2\sigma^2} = \frac{1}{\sqrt{2\pi\sigma}} e^{-(x-a_1)^2/2\sigma^2}. \tag{4.8}$$

The following incidental observation is helpful. With the help of the formula 4.3 it is easy to verify that the mean value of x, obtained by averaging over the above distribution, is

$$\bar{x} \equiv \int_{-\infty}^{\infty} x\, \rho_1(x)\, dx = a_1, \tag{4.9}$$

so that

$$\rho_1(x) = \frac{1}{\sqrt{2\pi\sigma}} e^{-(x-\bar{x})^2/2\sigma^2}. \tag{4.10}$$

This is the standard form of a one-dimensional normal (Gaussian) distribution. Note that this distribution is characterized by two parameters, representing the mean value $\bar{x}$ and the width (or dispersion) σ.

b) We now construct the new functions

$$\psi_\pm = A_\pm(\psi_1 \pm \psi_2) = A_\pm A \left[e^{-(x-a_1)^2/4\sigma^2} \pm e^{-(x-a_2)^2/4\sigma^2} \right]. \tag{4.11}$$

The normalization condition is

$$1 = |A_\pm|^2 A^2 \int_{-\infty}^{\infty} \left[e^{-(x-a_1)^2/4\sigma^2} \pm e^{-(x-a_2)^2/4\sigma^2} \right]^2 dx. \tag{4.12}$$

This gives

$$1 = |A_\pm|^2 A^2 \left[2\sigma\sqrt{2\pi} \pm 2e^{-(a_1^2+a_2^2)/4\sigma^2} \int_{-\infty}^{\infty} e^{-[x^2-(a_1+a_2)x]/2\sigma^2} dx \right]. \tag{4.13}$$

Completing the square,

$$x^2 - (a_1+a_2)x = \left(x - \frac{a_1+a_2}{2} \right)^2 - \frac{1}{4}(a_1+a_2)^2 = y^2 - \frac{1}{4}(a_1+a_2)^2, \tag{4.14}$$

we get with the help of 4.3 and 4.7,

$$1 = |A_\pm|^2 A^2 \left[2\sigma\sqrt{2\pi} \pm 2e^{-(a_1^2+a_2^2)/4\sigma^2} e^{(a_1+a_2)^2/8\sigma^2} \int_{-\infty}^{\infty} e^{-y^2/2\sigma^2} dy \right], \tag{4.15}$$

which simplifies to

$$= 2|A_\pm|^2 \left[1 \pm e^{-(a_1-a_2)^2/8\sigma^2} \right]. \tag{4.16}$$

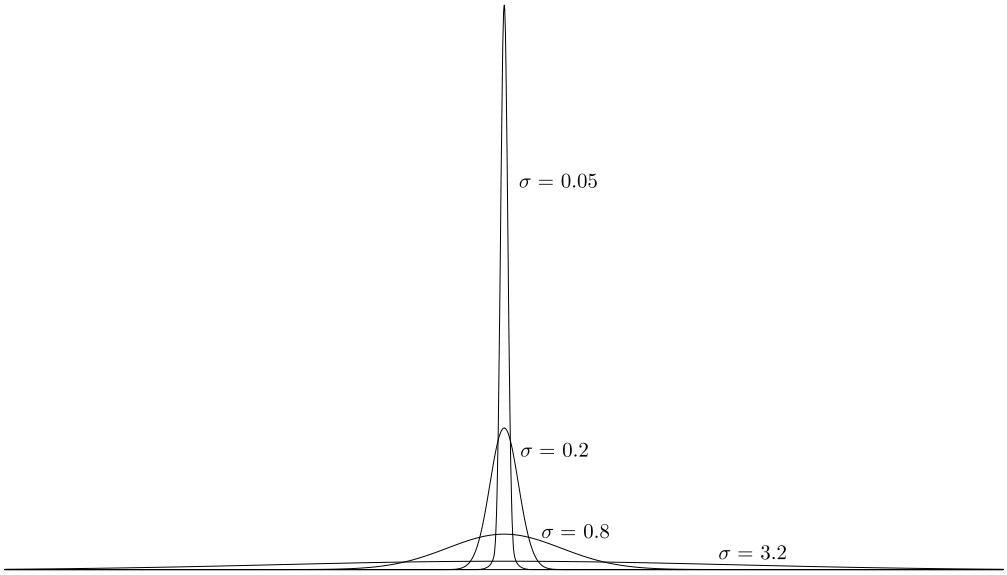

FIGURE 4.1. A comparison of several normal distributions with different variance values.

Solving gives

$$A_{\pm} = \frac{1}{\sqrt{2}} \left[1 \pm e^{-(a_1 - a_2)^2/8\sigma^2} \right]^{-1/2}, \tag{4.17}$$

and thus

$$\rho_{\pm} = \frac{1}{\sqrt{8\pi\sigma}} \left[1 \pm e^{-(a_1 - a_2)^2/8\sigma^2} \right]^{-1} \left[e^{-(x-a_1)^2/4\sigma^2} \pm e^{-(x-a_2)^2/4\sigma^2} \right]^2. \tag{4.18}$$

The two limiting cases, $\sigma \to 0$ and $x \neq a$, deserve special consideration. To analyze them we will study some properties of the normal or Gaussian distribution corresponding to each of the above wave functions ψ_1, ψ_2, and described by either equation 4.8 or 4.10. Since it is irrelevant, in what follows we will omit the index 1 or 2 with which these distributions were distinguished.

a) In the limit $\sigma \to 0$, for $x \neq a$ we get

$$\rho(x) = 0, \quad x \neq a. \tag{4.19}$$

However, at the point $x = a$ the exponent cancels out, the exponential is equal to unity, and

$$\rho(x) = \lim_{\sigma \to 0} \frac{1}{\sqrt{2\pi}\sigma} = \infty, \quad x = a. \tag{4.20}$$

These two results can be combined into one with the help of the Dirac δ distribution,

$$\rho(x) = \frac{1}{\sqrt{2\pi}\sigma} \lim_{\sigma \to 0} e^{-(x-a)^2/2\sigma^2} = \delta(x - a). \tag{4.21}$$

It can be verified that the integral properties of both members are equivalent. This result indicates that the function δ can be seen as the limit of a Gaussian distribution with a shrinking width. The normalization simultaneously increases the height until it finally becomes infinite at a single point and zero elsewhere. Figure 4.1 clearly shows this behavior.

b) In the limit $\sigma \to \infty$ the exponent cancels out for all x, so the distribution reduces to

$$\rho(x) = \lim_{\sigma\to\infty} \frac{1}{\sqrt{2\pi\sigma}} = \text{const.} \tag{4.22}$$

Therefore, it is a uniform distribution. Since it extends over the entire real line, the normalization constant becomes zero. However, it is sufficient to consider the distribution uniform within the finite interval $(-L, L)$ and zero outside of it, so that the normalization constant becomes finite (equal to $1/2L$). One can then take the limit $L \to \infty$ and see that a uniform distribution is the limit of a normal distribution whose width grows indefinitely. Figure 4.1 illustrates these properties.

The limiting behavior of the densities $\rho_\pm$ is easily derived from the previous results and does not require further discussion.

P4.2 Consider a system with spherical symmetry, described by the probability amplitude $\Psi(r) = N\exp(-r/a)$, where r is the radial coordinate, with $r = [0, \infty)$. Determine the value of the factor N so that Ψ is normalized to unity and find the mean value of r and of r^2 for this distribution. Relate the results to the parameters of the distribution.

Solution. For $\Psi(r)$ to be normalized to unity, the following condition must hold

$$\int_0^\infty |\Psi(r)|^2 dV = 1, \tag{4.23}$$

where dV is the volume element in spherical coordinates. For a spherically symmetric system, $dV = 4\pi r^2 dr$. Thus,

$$\int_0^\infty |Ne^{-r/a}|^2 \cdot 4\pi r^2 dr = 1, \tag{4.24}$$

or simplifying,

$$4\pi|N|^2 \int_0^\infty r^2 e^{-2r/a} dr = 1. \tag{4.25}$$

With

$$\int_0^\infty r^2 e^{-2r/a} dr = \frac{\Gamma(3)}{(2/a)^3} = \frac{2!}{(2/a)^3} = \frac{2a^3}{8} = \frac{a^3}{4}, \tag{4.26}$$

we get

$$4\pi|N|^2 \cdot \frac{a^3}{4} = 1 \quad \Rightarrow \quad \pi a^3 |N|^2 = 1. \tag{4.27}$$

The normalization factor is therefore

$$N = \frac{1}{\sqrt{\pi a^3}}. \tag{4.28}$$

The expectation value of r is given by

$$\langle r\rangle = \int_0^\infty r|\Psi(r)|^2 dV = 4\pi|N|^2 \int_0^\infty r^3 e^{-2r/a} dr. \tag{4.29}$$

With

$$\int_0^\infty r^3 e^{-2r/a} dr = \frac{\Gamma(4)}{(2/a)^4} = \frac{6a^4}{16} = \frac{3a^4}{8} \tag{4.30}$$

we get

$$\langle r\rangle = 4\pi \left(\frac{1}{\pi a^3}\right) \cdot \frac{3a^4}{8} = \frac{3a}{2}. \tag{4.31}$$

The expectation value of r^2 is:

$$\langle r^2\rangle = \int_0^\infty r^2|\Psi(r)|^2 dV = 4\pi|N|^2 \int_0^\infty r^4 e^{-2r/a} dr. \tag{4.32}$$

With

$$\int_0^\infty r^4 e^{-2r/a} dr = \frac{\Gamma(5)}{(2/a)^5} = \frac{24a^5}{32} = \frac{3a^5}{4} \tag{4.33}$$

we get

$$\langle r^2\rangle = 4\pi \left(\frac{1}{\pi a^3}\right) \cdot \frac{3a^5}{4} = 3a^2. \tag{4.34}$$

The parameter a represents the characteristic exponential decay scale of the distribution. the average displacement is proportional to a, $\langle r\rangle = \frac{3a}{2}$. The dispersion of the distribution scales with a^2, $\langle r^2\rangle = 3a^2$, and the variance of r is

$$\Delta r^2 = \langle r^2\rangle - \langle r\rangle^2 = 3a^2 - \left(\frac{3a}{2}\right)^2 = \frac{3a^2}{4}. \tag{4.35}$$

P4.3 A given function $\psi(x)$ is defined on the interval $(-\pi, \pi)$ in the form of a Fourier series

$$\psi(x) = \frac{A_0}{\sqrt{2\pi}} + \sum_{n=1}^{\infty} \left(\frac{A_n}{\sqrt{\pi}} \cos nx + \frac{B_n}{\sqrt{\pi}} \sin nx\right). \tag{4.36}$$

Using the orthogonality properties of the sine and cosine functions, obtain the coefficients A_0, A_n and B_n for this $\psi(x)$.

Solution. We will assume that the series defined in 4.36 converges uniformly on the interval $-\pi \le x \le \pi$; if this occurs, the series converges uniformly for all x. We multiply 4.36 by $\cos mx$, with m a positive integer, to obtain

$$\psi(x)\cos mx = \frac{A_0}{\sqrt{2\pi}} \cos mx + \sum_{n=1}^{\infty} \left(\frac{A_n}{\sqrt{\pi}} \cos nx \cos mx + \frac{B_n}{\sqrt{\pi}} \sin nx \cos mx\right). \tag{4.37}$$

This series is still convergent and can be integrated term by term, giving

$$\int_{-\pi}^{\pi} \psi(x) \cos mx \, dx = \frac{A_0}{\sqrt{2\pi}} \int_{-\pi}^{\pi} \cos mx \, dx + \sum_{n=1}^{\infty} \frac{A_n}{\sqrt{\pi}} \int_{-\pi}^{\pi} \cos nx \cos mx \, dx \quad (4.38)$$

$$+ \sum_{n=1}^{\infty} \frac{B_n}{\sqrt{\pi}} \int_{-\pi}^{\pi} \sin nx \cos mx \, dx. \quad (4.39)$$

Using the orthogonality properties of sine and cosine functions,

$$\int_{-\pi}^{\pi} \sin nx \cos mx \, dx = 0, \quad \forall \, n, m > 0 \quad (4.40)$$

$$\int_{-\pi}^{\pi} \cos nx \cos mx \, dx = \int_{-\pi}^{\pi} \sin nx \sin mx \, dx = \pi \delta_{nm}, \quad (4.41)$$

we obtain

$$\int_{-\pi}^{\pi} \psi(x) \cos mx \, dx = \sum_{n=1}^{\infty} \frac{A_n}{\sqrt{\pi}} \pi \delta_{nm} = A_m \sqrt{\pi}, \quad (4.42)$$

which leads to the well-known expression for the Fourier cosine coefficients,

$$A_n = \frac{1}{\sqrt{\pi}} \int_{-\pi}^{\pi} \psi(x) \cos nx \, dx. \quad (4.43)$$

The expression for the coefficients B_n is obtained analogously, by multiplying series 4.36 by $\sin mx$ and integrating,

$$\int_{-\pi}^{\pi} \psi(x) \sin mx \, dx = \frac{A_0}{\sqrt{2\pi}} \int_{-\pi}^{\pi} \sin mx \, dx + \sum_{n=1}^{\infty} \frac{A_n}{\sqrt{\pi}} \int_{-\pi}^{\pi} \cos nx \sin mx \, dx \quad (4.44)$$

$$+ \sum_{n=1}^{\infty} \frac{B_n}{\sqrt{\pi}} \int_{-\pi}^{\pi} \sin nx \sin mx \, dx. \quad (4.45)$$

Using the orthogonality properties, this expression reduces to

$$\int_{-\pi}^{\pi} \psi(x) \sin mx \, dx = \sum_{n=1}^{\infty} \frac{B_n}{\sqrt{\pi}} \pi \delta_{nm} = B_m \sqrt{\pi}, \quad (4.46)$$

or

$$B_n = \frac{1}{\sqrt{\pi}} \int_{-\pi}^{\pi} \psi(x) \sin nx \, dx. \quad (4.47)$$

Finally, the coefficient A_0 is determined by integrating the series 4.36 directly,

$$\int_{-\pi}^{\pi} \psi(x) \, dx = \int_{-\pi}^{\pi} \frac{A_0}{\sqrt{2\pi}} \, dx + \sum_{n=1}^{\infty} \frac{A_n}{\sqrt{\pi}} \int_{-\pi}^{\pi} \cos nx \, dx + \sum_{n=1}^{\infty} \frac{B_n}{\sqrt{\pi}} \int_{-\pi}^{\pi} \sin nx \, dx, \quad (4.48)$$

so that

$$A_0 = \frac{1}{\sqrt{2\pi}} \int_{-\pi}^{\pi} \psi(x) \, dx. \quad (4.49)$$

This result shows that the coefficient A_0 is proportional to the mean value of $\psi(x)$ in the interval $(-\pi, \pi)$. When $\psi(x)$ is an even function in $(-\pi, \pi)$, the coefficients B_n vanish and a cosine series is obtained. For odd functions, only the A_n coefficients vanish, and the series consists of sines.

P4.4 Determine the Fourier integral transform of the following functions:

a) The square function $F(x) = \begin{cases} a, & |x| \le d/2 \\ 0, & \text{otherwise.} \end{cases}$

b) The wave packet $F(x) = \begin{cases} ae^{-iqx}, & |x| \le d/2 \\ 0, & \text{otherwise.} \end{cases}$

c) The Lorentzian distribution $F(x) = \frac{\delta}{\pi}\frac{1}{\delta^2+x^2}$

d) The Gaussian distribution $F(x) = \frac{1}{\sqrt{2\pi\Delta^2}}e^{-x^2/2\Delta^2}$

Solution. The Fourier transform $\widetilde{F}(k)$ of a function $F(x)$ is defined in the standard form

$$\widetilde{F}(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} e^{ikx}F(x)\,dx. \tag{4.50}$$

We apply this definition to the previous cases as follows:
a) $\widetilde{F}(k) = \frac{a}{\sqrt{2\pi}}\int_{-d/2}^{d/2} e^{ikx}\,dx = \frac{a}{i\sqrt{2\pi}k}\left(e^{ikd/2} - e^{-ikd/2}\right)$, which reduces to

$$\widetilde{F}(k) = \sqrt{\frac{2}{\pi}}\frac{a}{k}\sin\frac{1}{2}kd. \tag{4.51}$$

b) $\widetilde{F}(k) = \frac{a}{\sqrt{2\pi}}\int_{-d/2}^{d/2} e^{i(k-q)x}\,dx = \frac{a}{i\sqrt{2\pi}(k-q)}\left[e^{i(k-q)d/2} - e^{-i(k-q)d/2}\right]$, or equivalently

$$\widetilde{F}(k) = \sqrt{\frac{2}{\pi}}\frac{a}{k-q}\sin\frac{1}{2}(k-q)d. \tag{4.52}$$

c) $\widetilde{F}(k) = \frac{1}{\sqrt{2\pi}}\delta\int_{-\infty}^{\infty}\frac{e^{ikx}}{\delta^2+x^2}dx$. We separate even and odd parts of the integrand to obtain

$$\int_{-\infty}^{\infty}\frac{e^{ikx}}{\delta^2+x^2}dx = \int_{-\infty}^{\infty}\frac{\cos kx}{\delta^2+x^2}dx + i\int_{-\infty}^{\infty}\frac{\sin kx}{\delta^2+x^2}dx = 2\int_0^{\infty}\frac{\cos kx}{\delta^2+x^2}dx.$$

Using tables of integrals we obtain

$$\widetilde{F}(k) = \frac{1}{\sqrt{2\pi}}e^{-\delta|k|}, \quad \text{Re } \delta > 0. \tag{4.53}$$

We can easily evaluate the integral by transforming the variable $x \to z$ in the complex plane and closing the integration contour with a circular arc of infinite radius in the upper half-plane ($z > 0$) if $k > 0$, or in the lower half-plane ($z < 0$) if $k < 0$.

For $k > 0$, the only pole enclosed by the integration contour C is at $z = i\delta$, with residue

$$\frac{e^{ikz}}{(z+i\delta)(z-i\delta)}(z-i\delta)\bigg|_{z=i\delta} = \frac{e^{-k\delta}}{2i\delta}, \tag{4.54}$$

so that

$$\widetilde{F}(k) = \frac{1}{\sqrt{2\pi}}\frac{\delta}{\pi}\int_{-\infty}^{\infty}\frac{e^{ikx}}{\delta^2+x^2}dx = \frac{1}{\sqrt{2\pi}}\frac{\delta}{\pi}\int_C \frac{e^{ikz}}{\delta^2+z^2}dz \tag{4.55}$$

$$0 = \frac{1}{\sqrt{2\pi}}\frac{\delta}{\pi}2\pi i\frac{e^{-k\delta}}{2i\delta} = \frac{1}{\sqrt{2\pi}}e^{-k\delta}, \quad \text{Re } \delta > 0. \tag{4.56}$$

The procedure is analogous for the case $k < 0$, and leads to the same result

$$\widetilde{F}(k) = \frac{1}{\sqrt{2\pi}}e^{-\delta|k|}. \tag{4.57}$$

d) $\widetilde{F}(k) = \frac{1}{2\pi\Delta}\int_{-\infty}^{\infty} e^{ikx}e^{-x^2/2\Delta^2}dx = \frac{1}{2\pi\Delta}e^{-\Delta^2k^2/2}\int_{-\infty}^{\infty} e^{-(x-i\Delta^2k)^2/2\Delta^2}dx$ gives

$$\widetilde{F}(k) = \frac{1}{\sqrt{2\pi}}e^{-k^2\Delta^2/2}. \tag{4.58}$$

Note that the Fourier transform of a Gaussian distribution with width Δ (as given in part (d)) is another Gaussian distribution, with width Δ^{-1}, so that

$$\sigma_x^2\sigma_k^2 = 1. \tag{4.59}$$

P4.5 Consider a function $f(x)$ that can be integrated twice, and $\tilde{f}(k)$ its Fourier transform. Express the Fourier transform of $\frac{df(x)}{dx}$ and of $xf(x)$ in terms of $\tilde{f}(k)$.

Solution. To compute the Fourier transform of $\dfrac{df}{dx}$ we define the Fourier transform $\tilde{f}(k)$ of a function $f(x)$ as[1]

$$\mathcal{F}\{f(x)\} = \tilde{f}(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} e^{ikx}f(x)\,dx. \tag{4.60}$$

Then

$$\mathcal{F}\left\{\frac{df}{dx}\right\} = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} e^{ikx}\frac{df}{dx}\,dx. \tag{4.61}$$

We apply integration by parts. Let

$$u = e^{ikx}, \qquad dv = \frac{df}{dx}\,dx, \tag{4.62}$$

[1]Details of the definition of the Fourier transform may vary from author to author. Common changes occur in the sign of the exponential and in the numerical factor, which here has been chosen (as is very usual) as $(2\pi)^{-1/2}$, but which may take other values, such as 1 or $(2\pi)^{-1}$. The inverse transform carries the coefficient $(2\pi)^{-1/2}$, $(2\pi)^{-1}$, or 1, respectively.

$$du = ik\, e^{ikx}\, dx, \qquad v = f(x). \tag{4.63}$$

Then

$$\int_{-\infty}^{\infty} e^{ikx} \frac{df}{dx}\, dx = e^{ikx} f(x)\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} ik\, e^{ikx} f(x)\, dx \tag{4.64}$$

$$= -ik \int_{-\infty}^{\infty} e^{ikx} f(x)\, dx. \tag{4.65}$$

Assuming that $f(x)\, e^{ikx} \to 0$ as $x \to \pm\infty$, the boundary term vanishes. Thus

$$\mathcal{F}\left\{\frac{df}{dx}\right\} = -ik \cdot \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{ikx} f(x)\, dx = -ik\, \tilde{f}(k), \tag{4.66}$$

and $\mathcal{F}\left\{\frac{df}{dx}\right\} = -ik\, \tilde{f}(k)$.

To compute the Fourier transform of $xf(x)$, we note that

$$xf(x)e^{ikx} = -i\frac{d}{dk}\left(f(x)e^{ikx}\right). \tag{4.67}$$

The Fourier transform becomes

$$\mathcal{F}\{xf(x)\} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} xf(x)\, e^{ikx} dx = -i\frac{d}{dk}\left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x)\, e^{ikx} dx\right] = -i\frac{d}{dk}\tilde{f}(k), \tag{4.68}$$

and $\mathcal{F}\{xf(x)\} = -i\frac{d}{dk}\tilde{f}(k)$.

P4.6 Solving an eigenvalue equation $\hat{L}\psi = \lambda\psi$ means determining the eigenfunctions ψ that satisfy it and fulfill certain requirements, and finding the corresponding eigenvalues λ. Solve the following eigenvalue problems.

a) $\hat{L} = id/dx$, with the requirement that $\psi(x) = \psi(x+a)$, i.e. that ψ is periodic with period a.

b) $\hat{L} = d/dx$, under the constraint that ψ is finite. What happens if we also claim that $\psi(x) = \psi(x+s)$?

c) $\hat{L}_c$ is such that $\hat{L}_c\psi(x) = \psi(-x)$.

d) Examine the orthogonality of the eigenfunctions in the three cases above.

Solution. a) The general solution to the differential equation

$$\hat{L}_a\psi = \psi, \quad \text{or} \quad i\frac{d\psi}{dx} = \lambda\psi \tag{4.69}$$

is $\psi(x) = Ae^{-i\lambda x}$, with A an arbitrary constant. If we restrict ourselves to periodic solutions with period a, $\psi(x) = \psi(x+a)$, we obtain

$$Ae^{-i\lambda x} = Ae^{-i\lambda(x+a)}, \tag{4.70}$$

which requires that $e^{i\lambda a} = 1$. This leads to the set of eigenvalues and eigenfunctions

$$\lambda_n = \frac{2\pi n}{a}, \quad \psi_n(x) = A_n e^{-i2\pi nx/a}, \quad n \in \mathbb{Z}. \tag{4.71}$$

These eigenfunctions are orthogonal in the interval $[-a/2, a/2]$ for different values of n, as can be verified from the orthogonality properties of the sine and cosine functions. Explicitly,

$$\int_{-a/2}^{a/2} \psi_n^*(x)\psi_{n'}(x)dx = A_n^* A_{n'} \int_{-a/2}^{a/2} e^{i\frac{2\pi x}{a}(n'-n)}dx = A_n^* A_{n'} a\delta_{nn'}. \tag{4.72}$$

If we further choose

$$A_n = \frac{e^{i\alpha}}{\sqrt{a}}, \quad \alpha \text{ real}, \tag{4.73}$$

the set becomes normalized to unity for $x \in [-a/2, a/2]$.

b) The general solution of the differential equation

$$\hat{L}_b\psi = \psi, \quad \text{or} \quad \frac{d}{dx}\psi(x) = \lambda\psi(x) \tag{4.74}$$

is $\psi(x) = Ae^{\lambda x}$, where A is an arbitrary constant. This function is unbounded, since $\psi(x) \to \infty$ when $|x| \to \infty$. Therefore, to impose the condition that $\psi(x)$ remains finite, we must restrict the domain of the variable x, excluding those values for which the function becomes infinite.

If we additionally require that the eigenfunctions be periodic with period s, we must have

$$Ae^{\lambda x} = Ae^{\lambda(x+s)}, \tag{4.75}$$

which implies (for $A \neq 0$) that $e^{\lambda s} = 1$. For real λ, the only allowed solution is $\lambda = 0$, corresponding to the eigenfunction $\psi(x) = A = \text{const}$. If we allow λ to be imaginary, the problem reduces to the previous case, and thus requires no further analysis. Since there is only one eigenfunction for real λ, there are no orthogonality properties to examine in this case.

c) For $\hat{L}_c$ an operator such that

$$\hat{L}_c\psi(x) = \psi(-x), \tag{4.76}$$

the corresponding eigenvalue equation is

$$\hat{L}_c\psi(x) = \lambda\psi(x) = \psi(-x). \tag{4.77}$$

Applying the operator $\hat{L}_c$ again yields

$$\lambda^2\psi(x) = \psi(x). \tag{4.78}$$

This means that the eigenvalues of $\hat{L}_c$ can only be $\lambda = \pm 1$, and the corresponding eigenfunctions satisfy

$$\psi_s(x) = \psi_s(-x) \qquad \text{for } \lambda = 1, \tag{4.79}$$

$$\psi_a(x) = -\psi_a(-x) \qquad \text{for } \lambda = -1. \tag{4.80}$$

In other words, the eigenfunctions of $\hat{L}_c$ are the set of even functions for the eigenvalue $+1$ and odd functions for the eigenvalue -1.

d) If we now introduce a new pair of functions without definite parity through the linear combinations

$$\psi_+ = \frac{1}{\sqrt{2}}(\psi_s + \psi_a), \quad \psi_- = \frac{1}{\sqrt{2}}(\psi_s - \psi_a), \tag{4.81}$$

we find that

$$\hat{L}_c\psi_+ = \frac{1}{\sqrt{2}}(\psi_s - \psi_a) = \psi_-, \tag{4.82}$$

$$\hat{L}_c\psi_- = \frac{1}{\sqrt{2}}(\psi_s + \psi_a) = \psi_+, \tag{4.83}$$

that is, the operator $\hat{L}_c$ exchanges the functions ψ_+ and ψ_-. Clearly, the functions $\psi_\pm$ are not eigenfunctions of $\hat{L}_c$. However, ψ_a and ψ_s are orthogonal to each other on the interval $(-\infty, \infty)$, as are ψ_+ and ψ_-. This gives us two equivalent orthonormal bases.

P4.7 An electron is enclosed in a 1D box with perfectly rigid walls, centered at the origin; the system is in a stationary state. Calculate the mean value of x and of x^2 as a function of energy.

Solution. For a one-dimensional infinite square well of width a, centered at the origin, the potential $V(x)$ is given by

$$V(x) = \begin{cases} 0, & -\frac{a}{2} < x < \frac{a}{2} \\ \infty, & \text{otherwise} \end{cases} \tag{4.84}$$

Inside the well, the time-independent Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x), \tag{4.85}$$

which simplifies into

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0, \quad \text{with } k = \frac{\sqrt{2mE}}{\hbar}. \tag{4.86}$$

The general solution of this differential equation is

$$\psi(x) = A\sin(kx) + B\cos(kx). \tag{4.87}$$

The wave function must vanish at the infinite walls of the well,

$$\psi\left(-\frac{a}{2}\right) = 0, \quad \psi\left(\frac{a}{2}\right) = 0. \tag{4.88}$$

Applying the boundary condition at $x = \pm\frac{a}{2}$, using the identities $\sin(-\theta) = -\sin(\theta)$ and $\cos(-\theta) = \cos(\theta)$, we get:

$$-A\sin\left(\frac{ka}{2}\right) + B\cos\left(\frac{ka}{2}\right) = 0, \tag{4.89}$$

$$A\sin\left(\frac{ka}{2}\right) + B\cos\left(\frac{ka}{2}\right) = 0. \tag{4.90}$$

Adding and subtracting these two equations, we get:

$$B\cos\left(\frac{ka}{2}\right) = 0, \quad A\sin\left(\frac{ka}{2}\right) = 0. \tag{4.91}$$

This means that either $B = 0$ with $\sin\left(\frac{ka}{2}\right) = 0$, or $A = 0$ with $\cos\left(\frac{ka}{2}\right) = 0$.

$B = 0 \Rightarrow \psi(x) = A\sin(kx)$, with

$$\sin\left(\frac{ka}{2}\right) = 0 \Rightarrow \frac{ka}{2} = n\pi \Rightarrow k = \frac{2n\pi}{a}, \quad n = 1, 2, 3, \ldots \tag{4.92}$$

$A = 0 \Rightarrow \psi(x) = B\cos(kx)$, with

$$\cos\left(\frac{ka}{2}\right) = 0 \Rightarrow \frac{ka}{2} = \left(n + \frac{1}{2}\right)\pi \Rightarrow k = \frac{(2n+1)\pi}{a}, \quad n = 0, 1, 2, \ldots \tag{4.93}$$

Combining the two cases, the normalized eigenfunctions are

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right), & n = 2, 4, 6, \ldots \\ \sqrt{\frac{2}{a}}\cos\left(\frac{n\pi x}{a}\right), & n = 1, 3, 5, \ldots \end{cases} \tag{4.94}$$

Using $k = \frac{\sqrt{2mE}}{\hbar}$, the quantized energy levels are

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{\pi^2\hbar^2}{2ma^2}n^2, \quad n = 1, 2, 3, \ldots \tag{4.95}$$

Note that the cosine solutions correspond to odd eigenfunctions (antisymmetric), and the sine ones to even eigenfunctions (symmetric), due to the symmetric placement of the well.

The mean value of the position of the particles inside the well in state n is then

$$\bar{x} = \frac{2}{a}\int_{-a/2}^{a/2} x\sin^2\left(\frac{n\pi}{a}x\right)dx \tag{4.96}$$

$$= \frac{2}{a}\left(\frac{x^2}{4} - \frac{ax}{4\pi n}\sin\left(\frac{2\pi nx}{a}\right) - \frac{a^2}{8\pi^2 n^2}\cos\left(\frac{2\pi nx}{a}\right)\right)\Bigg|_{-a/2}^{a/2} = 0 \tag{4.97}$$

for the even eigenfuctions, and

$$\bar{x} = \frac{2}{a}\int_{-a/2}^{a/2} x\cos^2\left(\frac{n\pi}{a}x\right)dx \tag{4.98}$$

$$= \frac{2}{a}\left(\frac{x^2}{4} + \frac{ax}{4\pi n}\sin\left(\frac{2\pi nx}{a}\right) + \frac{a^2}{8\pi^2n^2}\cos\left(\frac{2\pi nx}{a}\right)\right)\Bigg|_{-a/2}^{a/2} = 0 \tag{4.99}$$

for the odd eigenfuctions. Therefore,

$$\bar{x} = 0 \tag{4.100}$$

for all states, as a result of the symmetry of the problem. Furthermore,

$$\bar{x} = \frac{2}{a}\int_{-a/2}^{a/2} x\cos^2\left(\frac{n\pi}{a}x\right)dx \tag{4.101}$$

$$= \frac{2}{a}\left(\frac{a^3}{24\pi^3n^3}\left(\pi^3n^3 + (3\pi^2n^2 - 6)\sin(\pi n) + 6\pi n\cos(\pi n)\right)\right), \tag{4.102}$$

$$= \frac{a^2}{12}\left(1 - \frac{6}{\pi^2n^2}\right), \qquad n = 1, 3, 5, ... \tag{4.103}$$

for the odd eigenfunctions, and

$$\bar{x} = \frac{2}{a}\int_{0}^{a} x^2\sin^2\left(\frac{n\pi}{a}x\right)dx, \tag{4.104}$$

$$= \frac{2}{a}\left(\frac{a^3}{24\pi^3n^3}\left(\pi^3n^3 + (6 - 3\pi^2n^2)\sin(\pi n) - 6\pi n\cos(\pi n)\right)\right), \tag{4.105}$$

$$= \frac{a^2}{12}\left(1 - \frac{6}{\pi^2n^2}\right), \qquad n = 2, 4, 6, ... \tag{4.106}$$

for the even eigenfunctions. Substituting $n^2 = \frac{2ma^2E_n}{\hbar^2\pi^2}$, we get

$$\langle x^2\rangle = \frac{a^2}{12} - \frac{\hbar^2}{4mE_n}. \tag{4.107}$$

The variance of x is

$$\sigma_x^2 = \overline{(x-\bar{x})^2} = \overline{x^2} - \bar{x}^2 = \frac{a^2}{12}\left(1 - \frac{6}{\pi^2n^2}\right). \tag{4.108}$$

As n approaches infinity, the variance approaches $a^2/12$, which coincides with the value for uniformly distributed particles inside the box.

Based on previous results, we can obtain information about the momentum dispersion. Since the potential is zero throughout the interior, each eigenstate has

$$\overline{p^2} = 2mE_n, \tag{4.109}$$

and since symmetry considerations lead to $\bar{p} = 0$, it follows that

$$\sigma_p^2 = \overline{(p - \bar{p})^2} = \overline{p^2} - \bar{p}^2 = \overline{p^2} = \frac{\pi^2 \hbar^2}{a^2} n^2. \tag{4.110}$$

Note that the product $\sigma_x^2 \sigma_p^2$ is independent of the parameter a, so it is the same for all boxes of the same type,

$$\sigma_x^2 \sigma_p^2 = \frac{\pi^2 \hbar^2}{12} \left(n^2 - \frac{6}{\pi^2} \right). \tag{4.111}$$

It is interesting to compare the previous results with those corresponding to the classical problem. In the latter case, the distribution of particles inside the box is considered uniform and the magnitude of the momentum remains constant between elastic collisions. Thus, we have

$$\overline{x^2} = \frac{1}{a} \int_{-a/2}^{a/2} x^2 dx = \frac{a^2}{12}, \tag{4.112}$$

$$\overline{p^2} = 2mE. \tag{4.113}$$

Since $\bar{x} = 0$, it follows that

$$\sigma_x^2 \text{ (classical)} = \frac{a^2}{12}. \tag{4.114}$$

We see that $\sigma_x^2 < \sigma_x^2$ (classical) for all finite n states (this is because the dispersion is reduced by vanishing the wavefunctions at the walls). Only when $n \to \infty$ do the classical and quantum values coincide. On the other hand, the same relation, $\sigma_p^2 = 2mE$, holds for the classical case, only with arbitrary E.

P4.8 A 1D potential well of width a and infinite depth contains one electron; at a given moment, the electron probability density is triangular and symmetric, as in Fig. 4.2.

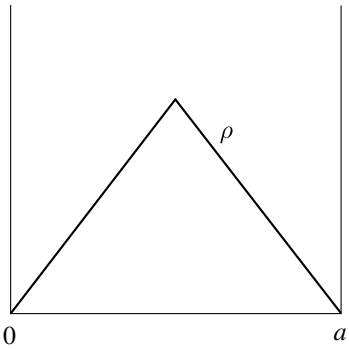

FIGURE 4.2. Initial electron probability density inside the well.

a) Determine the normalization constant and the maximum particle density.

b) Express the wave function in terms of the energy eigenfunctions for the infinite well. Would you expect this state to be stationary? Why (not)?

Solution. a) The density is given by the expression

$$\rho(x) = \begin{cases} bx, & \text{if } 0 \le x \le a/2, \\ b(a-x), & \text{if } a/2 \le x \le a, \end{cases} \tag{4.115}$$

where the constant b is determined from the normalization condition

$$\int_0^a \rho \, dx = \frac{1}{4} b a^2 = 1 \implies b = \frac{4}{a^2}. \tag{4.116}$$

The maximum particle density occurs at $x = a/2$ and is $2/a$, which is twice what would correspond to a uniform distribution.

Since $\sqrt{\rho}$ does not match any of the eigenfunctions of the stationary Schrödinger equation for the infinite square well, this is not a stationary state. In other words, taking the given distribution as the initial state, the corresponding wave function varies with time and can be expressed as a superposition of the eigenfunctions of the infinite well, with time-dependent coefficients. Solving the problem requires knowledge of methods that are introduced in connection with the time-dependent Schrödinger equation. For interested readers, we detail the solution as follows.

b) The wave function of the problem for an arbitrary time t can be expressed as a linear combination of the eigenfunctions of the infinite well, since they form a complete basis. This allows us to write

$$\psi(x,t) = \sum_{n=1}^{\infty} c_n \varphi_n(x) e^{-iE_n t/\hbar}, \tag{4.117}$$

where $\varphi_n(x)$ are the eigenfunctions for the infinite well, given by

$$\varphi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \tag{4.118}$$

and E_n the corresponding energy eigenvalues

$$E_n = \frac{\pi^2 \hbar^2}{2ma^2} n^2. \tag{4.119}$$

The constants c_n are determined from the initial wave function $\psi(x,0)$, as shown below.

At $t = 0$ the probability density is represented by Fig. 4.2. Taking $\psi(x,0)$ as a real function (which only affects an irrelevant global phase of the wave function), we can write

$$\psi(x,0) = \begin{cases} \frac{2}{a}\sqrt{x}, & 0 \le x \le \frac{a}{2}, \\ \frac{2}{a}\sqrt{a-x}, & \frac{a}{2} \le x \le a. \end{cases} \tag{4.120}$$

Substituting $t = 0$ in Eq. (4.117) we have

$$\psi(x,0) = \sum_{n=1}^{\infty} c_n \varphi_n(x). \tag{4.121}$$

Since the eigenfunctions are orthonormal and real, we get

$$c_n = \int_0^a \varphi_n(x)\psi(x,0)\,dx \tag{4.122}$$

$$= \left(\frac{2}{a}\right)^{\frac{3}{2}} \left[\int_0^{a/2} \sqrt{x}\sin\left(\frac{n\pi x}{a}\right)\,dx + \int_{a/2}^{a} \sqrt{a-x}\sin\left(\frac{n\pi x}{a}\right)\,dx\right], \tag{4.123}$$

$$= 2^{3/2}\left[\int_0^{1/2} \sqrt{u}\sin(\pi n u)\,du + \int_{1/2}^{1} \sqrt{1-u}\sin(\pi n u)\,du\right]. \tag{4.124}$$

In the last line, we introduced the dimensionless variable $u = x/a$. In the second integral, we make the change of variables $w = 1 - u$ and take into account that

$$\sin(\pi n - \pi n w) = (-1)^{n+1}\sin \pi n w, \tag{4.125}$$

thus obtaining

$$c_n = 2^{3/2}(1-(-1)^n)\int_0^{1/2} \sqrt{u}\sin \pi n u\,du. \tag{4.126}$$

Therefore, the coefficients c_n vanish for even n. For odd n, we introduce the new variable $s = n\pi u$ and integrate by parts, to find that

$$c_n = 4\sqrt{2}\int_0^{1/2} \sqrt{u}\sin \pi n u\,du = -\frac{4}{n\pi}\cos\left(\frac{1}{2}n\pi\right) + \left(\frac{2}{\pi n}\right)^{3/2}\int_0^{\pi n/2} \frac{\cos s}{\sqrt{s}}ds \tag{4.127}$$

$$= \left(\frac{2}{\pi n}\right)^{3/2}\sqrt{2\pi}C\left(\sqrt{\frac{1}{2}\pi n}\right), \tag{4.128}$$

where

$$C(x) = \frac{1}{\sqrt{2\pi}}\int_0^{x^2}\frac{\cos s}{\sqrt{s}}ds = \frac{2}{\sqrt{2\pi}}\sum_{k=0}^{\infty}\frac{(-1)^k x^{4k+1}}{(2k)!(4k+1)} \tag{4.129}$$

is the Fresnel cosine integral. To obtain the last equality, we considered that $\frac{1}{2}n\pi = 0$ for odd n. Substituting into the wave function expression we obtain

$$\psi(x,t) = \frac{4}{\pi}\sqrt{\frac{2}{a}}\sum_{n=1}^{\infty}\frac{C\left(\sqrt{\frac{1}{2}\pi n}\right)}{n^{3/2}}\sin\left(\frac{\pi n x}{a}\right)e^{-iE_n t/\hbar} \tag{4.130}$$

$$= \frac{4}{\pi}\sum_{n=1}^{\infty}\frac{C\left(\sqrt{\frac{1}{2}\pi n}\right)}{n^{3/2}}\varphi_n(x)e^{-iE_n t/\hbar}, \tag{4.131}$$

where the sum runs only over the odd values $n = 1, 3, 5, \ldots$

P4.9 Consider an electron in a square potential well of infinite depth and width a.

a) Calculate the expectation (average) values of $\hat{p}$ and $\hat{p}^2$ when the electrons are in an energy eigenstate n.

b) Calculate the matrix elements p_{nm} and $(p^2)_{nm}$.

Discuss the meaning of your results.

Solution. a) The normalized eigenfunctions for the infinite square well with perfectly rigid walls at $x = 0$ and $x = a$ are given by

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right). \tag{4.132}$$

The expectation value of an operator $\hat{O}$ in a normalized state $\psi_n(x)$ is defined by

$$\langle \hat{O} \rangle = \int_0^a \psi_n^*(x)\, \hat{O}\, \psi_n(x)\, dx. \tag{4.133}$$

In the case of the momentum operator $\hat{p} = -i\hbar \dfrac{d}{dx}$, the expectation value is

$$\langle \hat{p} \rangle = -i\hbar \int_0^a \psi_n(x) \frac{d}{dx} \psi_n(x)\, dx. \tag{4.134}$$

Computing the derivative $\frac{d}{dx}\psi_n(x) = \sqrt{\frac{2}{a}}\frac{n\pi}{a} \cos\left(\frac{n\pi x}{a}\right)$ and substituting into the integral we get

$$\langle \hat{p} \rangle = -i\hbar \frac{2n\pi}{a^2} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \cos\left(\frac{n\pi x}{a}\right) dx = -\frac{i\hbar}{a} \sin^2(\pi n). \tag{4.135}$$

Therefore,

$$\langle \hat{p} \rangle = 0 \tag{4.136}$$

To compute the expectation value of $\hat{p}^2$ we write

$$\hat{p}^2 = \left(-i\hbar \frac{d}{dx}\right)^2 = -\hbar^2 \frac{d^2}{dx^2} \tag{4.137}$$

and substituting in 4.133, to get

$$\langle \hat{p}^2 \rangle = \hbar^2 \frac{n^2\pi^2}{a^2} \cdot \frac{2}{a} \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{2\hbar^2 n^2 \pi^2}{a^3} \cdot \frac{a}{4} \left(2 - \frac{\sin(2\pi n)}{\pi n}\right) = \frac{\hbar^2 n^2 \pi^2}{a^2}. \tag{4.138}$$

Therefore,

$$\langle \hat{p}^2 \rangle = \frac{\hbar^2 n^2 \pi^2}{a^2}. \tag{4.139}$$

b) The matrix element of an operator $\hat{O}$ in the basis of eigenfunctions $\psi_n(x)$ is defined as

$$O_{nm} = \int_0^a \psi_n^*(x)\, \hat{O}\, \psi_m(x)\, dx, \tag{4.140}$$

so the matrix elements of the momentum operator are given by

$$p_{nm} = \int_0^a \psi_n^*(x) \left(-i\hbar \frac{d}{dx}\right) \psi_m(x)\, dx. \tag{4.141}$$

Therefore,

$$p_{nm} = -i\hbar \frac{2m\pi}{a^2} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \cos\left(\frac{m\pi x}{a}\right) dx \tag{4.142}$$

$$= -i\hbar \frac{2m\pi}{a^2} \cdot \frac{a}{\pi} \frac{(m \sin(\pi n)\sin(\pi m) + n\cos(\pi n)\cos(\pi m) - n)}{(m^2 - n^2)} \tag{4.143}$$

$$= -i\hbar \frac{2m}{a} \cdot \frac{n(\cos(\pi n)\cos(\pi m) - 1)}{m^2 - n^2}. \tag{4.144}$$

With $\cos(\pi n) = (-1)^n$ for n integer,

$$p_{nm} = -i\hbar \frac{2nm}{a} \cdot \frac{(-1)^{n+m} - 1}{m^2 - n^2}. \tag{4.145}$$

The above expression $\frac{(-1)^{n+m}-1}{m^2-n^2}$ is 0 if $n+m$ is even and $-\frac{2}{m^2-n^2}$ if $n+m$ is odd, except when $n = m$, which results in $0/0$. To calculate the limit we apply L'Hôpital's rule

$$\lim_{m\to n} \frac{nm(\cos(\pi n)\cos(\pi m) - 1)}{m^2 - n^2} = \lim_{m\to n} \frac{n(\cos(\pi n)\cos(\pi m) - m\cos(\pi n)\sin(\pi m) - 1)}{2m} \tag{4.146}$$

$$= \frac{n(1-1)}{2n} = 0 \tag{4.147}$$

Therefore,

$$p_{nm} = \begin{cases} 0 & \text{if } \; n+m \; \text{ is even} \\ -\frac{4i\hbar}{a}\frac{nm}{(n^2-m^2)} & \text{if } \; n+m \; \text{ is odd} \end{cases} \tag{4.148}$$

Writing the matrix explicitly,

$$\hat{p} = -\frac{4i\hbar}{a} \begin{pmatrix} 0 & -\frac{2}{3} & 0 & -\frac{4}{15} & \cdots \\ \frac{2}{3} & 0 & -\frac{6}{5} & 0 & \cdots \\ 0 & \frac{6}{5} & 0 & -\frac{12}{7} & \cdots \\ \frac{4}{15} & 0 & \frac{12}{7} & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \tag{4.149}$$

To compute the matrix elements of $\hat{p}^2$ we write

$$p_{nm}^2 = \int_0^a \psi_n^*(x) \left(-\hbar^2 \frac{d^2}{dx^2}\right) \psi_m(x)\, dx. \tag{4.150}$$

Explicitly, this reads

$$p_{nm}^2 = \frac{2\hbar^2 m^2\pi^2}{a^3}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right)dx \tag{4.151}$$

$$= \frac{2\hbar^2 m^2\pi^2}{a^3}\cdot\frac{a}{\pi}\frac{n\sin(\pi m)\cos(\pi n) - m\cos(\pi m)\sin(\pi n)}{m^2-n^2}, \tag{4.152}$$

which is 0 for any $n \neq m$. For $n = m$ we again apply L'Hôpital's rule

$$\lim_{m\to n}\frac{n\sin(\pi m)\cos(\pi n) - m\cos(\pi m)\sin(\pi n)}{m^2-n^2} \tag{4.153}$$

$$= \lim_{m\to n}\frac{\pi n\cos(\pi m)\cos(\pi n) + m\sin(\pi m)\sin(\pi n) - \cos(\pi m)\sin(\pi n)}{2m} \tag{4.154}$$

$$= \frac{\pi n}{2n} = \frac{\pi}{2}. \tag{4.155}$$

Therefore,

$$p_{nm}^2 = \begin{cases} 0 & \text{if } n \neq m \\ \frac{\hbar^2 n^2\pi^2}{a^2} & \text{if } n = m \end{cases} = \frac{\hbar^2 n^2\pi^2}{a^2}\delta_{nm} \tag{4.156}$$

Writing the matrix explicitly,

$$\hat{p}^2 = \frac{\hbar^2\pi^2}{a^2}\begin{pmatrix} 1 & 0 & 0 & \cdots \\ 0 & 4 & 0 & \cdots \\ 0 & 0 & 9 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \tag{4.157}$$

P4.10 Three eigenfunctions ψ_1, ψ_2 and ψ_3 of some operator are linearly independent and degenerate, but not necessarily orthogonal. Construct three linear, orthogonal and normalized combinations from them. Are the new functions eigenfunctions? Are they degenerate?

Solution. The Gram-Schmidt orthogonalization method allows constructing, from a set of non-orthogonal and linearly independent functions, a set of orthogonal functions over an arbitrary interval with respect to an arbitrary weight or density factor. In other words, this process is equivalent to a matrix transformation that relates an orthogonal basis with a non-orthogonal set of vectors. As an illustration, we apply this method to the present problem.

Let:

- $\{\psi_n(x)\}$ be the linearly independent, non-orthogonal, and not necessarily normalized system,
- $\{u_n(x)\}$ be the linearly independent, orthogonal, but not normalized system,
- $\{\phi_n(x)\}$ be the linearly independent, orthogonal, and normalized system.

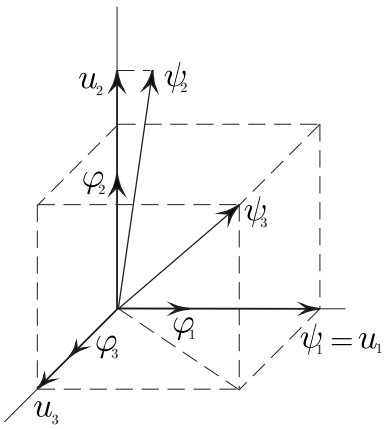

FIGURE 4.3. Construction of an orthonormal basis from a set of arbitrary vectors using the Gram-Schmidt method, for $n = 3$.

The idea of the procedure is illustrated in Fig. 4.3 for the case of three vectors.

We start with $n = 1$, set

$$u_1(x) = \psi_1(x) \tag{4.158}$$

and obtain after normalization

$$\phi_1(x) = \frac{u_1(x)}{\int_{-\infty}^{\infty} u_1^*(x)u_1(x)dx} = \frac{\psi_1(x)}{\int_{-\infty}^{\infty} \psi_1^*(x)\psi_1(x)dx}. \tag{4.159}$$

For $n = 2$ we take

$$u_2(x) = \psi_2(x) + \alpha_2\phi_1(x). \tag{4.160}$$

The following condition must be satisfied since $u_2(x)$ must be orthogonal to $\phi_1(x)$,

$$\int_{-\infty}^{\infty} \phi_1^*(x)u_2(x)dx = 0, \tag{4.161}$$

which leads to

$$\int_{-\infty}^{\infty} \phi_1^*(x)\psi_2(x)dx + \alpha_2 \int_{-\infty}^{\infty} \phi_1^*(x)\phi_1(x)dx = 0. \tag{4.162}$$

This means that we must take

$$\alpha_2 = -\int_{-\infty}^{\infty} \phi_1^*(x)\psi_2(x)dx. \tag{4.163}$$

The normalized vector is

$$\phi_2(x) = \frac{u_2(x)}{\sqrt{\int_{-\infty}^{\infty} u_2^*(x)u_2(x)\,dx}}. \tag{4.164}$$

We use the same procedure for $n = 3$, taking

$$u_3(x) = \psi_3(x) + a_{31}\phi_1(x) + a_{32}\phi_2(x) \tag{4.165}$$

and applying the orthogonality condition between $u_3(x)$ and $\phi_1(x)$,

$$\int_{-\infty}^{\infty} u_3^*(x)\phi_1(x)\,dx = \int_{-\infty}^{\infty} \psi_3^*(x)\phi_1(x)\,dx + a_{31}^* \int_{-\infty}^{\infty} \phi_1^*(x)\phi_1(x)\,dx + a_{32}^* \int_{-\infty}^{\infty} \phi_2^*(x)\phi_1(x)\,dx = 0. \tag{4.166}$$

Since $\phi_1(x)$ is normalized and $\phi_2(x)$ and $\phi_1(x)$ are orthogonal,

$$a_{31} = -\int_{-\infty}^{\infty} \psi_3(x)\phi_1^*(x)\,dx. \tag{4.167}$$

Similarly, the orthogonality condition between $u_3(x)$ and $\phi_2(x)$ leads to

$$\int_{-\infty}^{\infty} u_3^*(x)\phi_2(x)\,dx = \int_{-\infty}^{\infty} \psi_3^*(x)\phi_2(x)\,dx + a_{31}^* \int_{-\infty}^{\infty} \phi_1^*(x)\phi_2(x)\,dx + a_{32}^* \int_{-\infty}^{\infty} \phi_2^*(x)\varphi_2(x)\,dx = 0. \tag{4.168}$$

which leads to

$$a_{32} = -\int_{-\infty}^{\infty} \psi_3(x)\phi_2^*(x)\,dx. \tag{4.169}$$

The normalized vector is

$$\phi_3(x) = \frac{u_3(x)}{\sqrt{\int_{-\infty}^{\infty} u_3^*(x)u_3(x)\,dx}}. \tag{4.170}$$

The previous results can be expressed in terms of the original functions if desired, though we will not do so here as it does not provide new insights.

Now suppose that the original functions $\psi_n(x)$ are degenerate eigenfunctions of an operator $\hat{L}$, such that

$$\hat{L}\psi_n(x) = \lambda_n \psi_n(x). \tag{4.171}$$

It follows that any linear combination of the $\psi_n(x)$ is an eigenfunction of $\hat{L}$ with the same eigenvalue. With $\phi_n = \sum_k a_{nk}\psi_k(x)$ and $\lambda_k = \lambda$, we have

$$\hat{L}\phi_n = \hat{L}\sum_k a_{nk}\psi_k = \sum_k a_{nk}\lambda_k\psi_k = \lambda\sum_k a_{nk}\psi_k = \lambda\phi_n \tag{4.172}$$

Since the functions ψ_1, ψ_2, and ψ_3 are degenerate by hypothesis, both the $u_n(x)$ and $\phi_n(x)$ functions will be degenerate eigenfunctions of $\hat{L}$. These are merely linear transformations from one basis to an equivalent one.

P4.11 An important problem in quantum mechanics is that of a particle subjected to a linear restoring force, e.g. the harmonic oscillator. The 1D stationary Schrödinger equation for this system is

$$-\frac{\hbar^2}{2m}\varphi'' + \frac{1}{2}kx^2\varphi = E\varphi, \tag{4.173}$$

where k is the oscillator constant. Solutions of the following types are proposed:

a) $\varphi = A_1 \exp(ax^2) + A_2 \exp(-ax^2)$, with real and positive a,
b) $\varphi = (B_1 + B_2 x) \exp(-bx^2)$, with real and positive b.

Find the values that the constants $A_i,\ B_i,\ a$ and b must have for these functions to be physically acceptable and normalized to unity. Determine the corresponding energy E in each case, expressed in terms of the system parameters.

Solution. a) We start from the trial function

$$\varphi(x) = A_1\, e^{ax^2} + A_2\, e^{-ax^2}, \qquad a > 0. \tag{4.174}$$

For a wave function to be physically acceptable it must be square–integrable, $\int_{-\infty}^{\infty} |\varphi(x)|^2\, dx < \infty$. The term e^{ax^2} diverges super-exponentially as $|x| \to \infty$; the only way to keep the integral finite is to set its coefficient to zero. Hence,

$$A_1 = 0, \qquad \Longrightarrow \qquad \varphi(x) = A_2\, e^{-ax^2}$$

is the only physically admissible form of the ansatz. From the normalization condition

$$1 = \int_{-\infty}^{\infty} |\varphi(x)|^2\, dx = A_2^2 \int_{-\infty}^{\infty} e^{-2ax^2} dx = A_2^2 \sqrt{\frac{\pi}{2a}} \tag{4.175}$$

we get

$$A_2 = \left(\frac{2a}{\pi}\right)^{1/4}. \tag{4.176}$$

Taking derivatives of φ,

$$\varphi' = -2ax\varphi, \qquad \varphi'' = (4a^2x^2 - 2a)\varphi, \tag{4.177}$$

and substituting in the stationary Schrödinger equation,

$$-\frac{\hbar^2}{2m}\,\varphi'' + \frac{1}{2}kx^2\varphi = -\frac{\hbar^2}{2m}\big(4a^2x^2 - 2a\big)\varphi + \frac{1}{2}kx^2\varphi = E\varphi \tag{4.178}$$

gives (after canceling the common factor φ)

$$\left(-\frac{2\hbar^2a^2}{m} + \frac{1}{2}k\right)x^2 + \frac{\hbar^2 a}{m} = E. \tag{4.179}$$

Grouping together the coefficients of equal powers of x we get from the coefficient of x^2

$$-\frac{2\hbar^2a^2}{m} + \frac{1}{2}k = 0 \quad \Longrightarrow \quad a = \frac{\sqrt{mk}}{2\hbar}, \tag{4.180}$$

and from the constant terms

$$\frac{\hbar^2 a}{m} = E \quad \Longrightarrow \quad E = \frac{\hbar^2 a}{m} = \frac{1}{2}\,\hbar\sqrt{\frac{k}{m}} \equiv \frac{1}{2}\hbar\omega, \tag{4.181}$$

where $\omega = \sqrt{\frac{k}{m}}$.

From Eqs. (4.176) and (4.180) we obtain the normalized ground-state wave function for the quantum harmonic oscillator

$$\varphi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\!\left(-\tfrac{m\omega}{2\hbar}\, x^2\right) . \tag{4.182}$$

The energy is given by Eq. (4.181), namely the zero-point energy $E = \frac{1}{2}\hbar\omega$.

b) Starting with

$$\varphi(x) = \big(B_1 + B_2 x\big)\, e^{-bx^2}, \qquad b > 0 \tag{4.183}$$

we calculate the derivatives

$$\varphi'(x) = \big(B_2 - 2bx(B_1 + B_2 x)\big)\, e^{-bx^2}, \tag{4.184}$$

$$\varphi''(x) = \Big[4b^2x^2 - 2b\Big]\varphi(x) \;-\; 4bB_2 x\, e^{-bx^2}. \tag{4.185}$$

and substitute into the Schrödinger equation,

$$-\,\frac{\hbar^2}{2m}\Big[(4b^2x^2 - 2b)\varphi - 4bB_2 x\, e^{-bx^2}\Big] \;+\; \frac{1}{2}kx^2\varphi = E\varphi. \tag{4.186}$$

Using the explicit form $\varphi(x) = \big(B_1 + B_2 x\big)e^{-bx^2}$ and canceling the common factor e^{-bx^2} gives a polynomial equation in x,

$$-\,\frac{\hbar^2}{2m}\big[4b^2B_2\, x^3 + 4b^2B_1\, x^2 - 6bB_2\, x - 2bB_1\big] + \frac{k}{2}\big[B_2\, x^3 + B_1\, x^2\big] = E\big(B_2\, x + B_1\big). \tag{4.187}$$

By grouping together equal powers of x, we obtain

$$B_2\left(\frac{k}{2} - \frac{2\hbar^2b^2}{m}\right)x^3 + B_1\left(\frac{k}{2} - \frac{2\hbar^2b^2}{m}\right)x^2 + B_2\left(\frac{3\hbar^2b}{m} - E\right)x + B_1\left(\frac{\hbar^2b}{m} - E\right) = 0, \tag{4.188}$$

that is,

$$B_2\left(\frac{k}{2} - \frac{2\hbar^2b^2}{m}\right) = 0, \quad B_2\left(\frac{k}{2} - \frac{2\hbar^2b^2}{m}\right) = 0, \tag{4.189}$$

$$B_2\left(\frac{3\hbar^2b}{m} - E\right) = 0, \quad B_1\left(\frac{\hbar^2b}{m} - E\right) = 0. \tag{4.190}$$

These four algebraic conditions determine the admissible values of B_1, B_2, b and the corresponding energy E. There are two mutually exclusive possibilities.

Case I: $\dfrac{k}{2} - \dfrac{2\hbar^2b^2}{m} = 0$. This eliminates the prefactor in (4.189) without forcing B_1 or B_2 to vanish. Solving for b gives

$$b = \frac{m\omega}{2\hbar}, \qquad \omega \equiv \sqrt{\frac{k}{m}}. \tag{4.191}$$

If $B_2 \neq 0$, from (4.190) we get

$$E = \frac{3}{2}\,\hbar\omega, \tag{4.192}$$

and $B_1 = 0$. This produces the odd (first excited) state, $\varphi(x) = B_2\, x\, e^{-bx^2}$.

If $B_1 \neq 0$, we get from (4.190)

$$E = \frac{1}{2}\,\hbar\omega, \tag{4.193}$$

and $B_2 = 0$. The result is the even (ground) state, $\varphi(x) = B_1\, e^{-bx^2}$.

Case II: $\dfrac{k}{2} - \dfrac{2\hbar^2 b^2}{m} \neq 0$. Now Eqs. (4.189) enforce $B_1 = B_2 = 0$, resulting in only the trivial (non-physical) solution.

We now determine the respective normalization constants. For the ground state $\varphi_0(x) = B_1 e^{-bx^2}$, the integral obtained from the normalization condition gives

$$B_1 = \left(\frac{2b}{\pi}\right)^{1/4}. \tag{4.194}$$

For the first excited state $\varphi_1(x) = B_2 x e^{-bx^2}$, we normalize by imposing

$$\int_{-\infty}^{\infty} |\varphi_1(x)|^2 dx = 1 \implies B_2^2 \int_{-\infty}^{\infty} x^2 e^{-2bx^2} dx = 1. \tag{4.195}$$

This integral can be calculated using 4.3, and evaluates to

$$\int_{-\infty}^{\infty} x^2 e^{-2bx^2} dx = \frac{\sqrt{\pi}}{4b^{3/2}}, \tag{4.196}$$

so that

$$B_2^2 \cdot \frac{\sqrt{\pi}}{4b^{3/2}} = 1 \implies B_2 = \left(\frac{4b^{3/2}}{\sqrt{\pi}}\right)^{1/2}. \tag{4.197}$$

Thus, the normalized eigenfunctions are

$$\varphi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}, \qquad \varphi_1(x) = \left(\frac{4m^3\omega^3}{\pi\hbar^3}\right)^{1/4} x\, e^{-\frac{m\omega}{2\hbar}x^2}. \tag{4.198}$$

P4.12 Using the Schrödinger equation, show that a wave function with more nodes has higher energy, and vice versa. Consider two wave functions ψ_1, ψ_2, that intersect at a point P.

Solution. To prove that wave functions with more nodes have higher energy, consider two wavefunctions ψ_1 and ψ_2 that are solutions of the 1D Schrödinger equation,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x), \tag{4.199}$$

where ψ_1 has n_1 nodes and energy E_1, and ψ_2 has n_2 nodes and energy E_2, with $n_2 > n_1$.

Assume that ψ_1 and ψ_2 intersect at a point P,

$$\psi_1(P) = \psi_2(P). \tag{4.200}$$

Define the function

$$\phi(x) = \psi_2(x) - \psi_1(x), \tag{4.201}$$

such that at P,

$$\phi(P) = \psi_2(P) - \psi_1(P) = 0. \tag{4.202}$$

Differentiating $\phi(x)$, we get

$$\phi'(x) = \psi_2'(x) - \psi_1'(x). \tag{4.203}$$

At P, if ψ_1 and ψ_2 are tangent (i.e., $\psi_1'(P) = \psi_2'(P)$), then $\phi'(P) = 0$, indicating a critical point for $\phi(x)$ at P.

The Schrödinger equation for ψ_1 and ψ_2 at P is

$$-\frac{\hbar^2}{2m}\psi_1''(P) + V(P)\psi_1(P) = E_1\psi_1(P) \tag{4.204}$$

and

$$-\frac{\hbar^2}{2m}\psi_2''(P) + V(P)\psi_2(P) = E_2\psi_2(P). \tag{4.205}$$

Subtracting these equations and using $\psi_1(P) = \psi_2(P)$, we get

$$-\frac{\hbar^2}{2m}(\psi_2''(P) - \psi_1''(P)) = (E_2 - E_1)\psi_1(P). \tag{4.206}$$

If $\psi_1(P) \neq 0$,

$$E_2 - E_1 = -\frac{\hbar^2}{2m}\frac{\phi''(P)}{\psi_1(P)}. \tag{4.207}$$

Since ψ_2 has more nodes than ψ_1, its second derivative ψ_2'' is more negative (or less positive) than ψ_1'' at P. Therefore,

$$\phi''(P) = \psi_2''(P) - \psi_1''(P) < 0 \quad \Rightarrow \quad E_2 - E_1 > 0 \tag{4.208}$$

P4.13 Find an expression for the expectation value $\langle \hat{p}^2 \rangle$, in terms of the velocities v, u introduced in **[1]**, Section 4.4. Discuss your result.

Solution. We begin by writing the expression (in 1D, for simplicity)

$$v - iu = \frac{\hbar}{2m}\left[i\left(\frac{1}{\psi^*}\frac{\partial\psi^*}{\partial x} - \frac{1}{\psi}\frac{\partial\psi}{\partial x}\right) - i\left(\frac{1}{\psi^*}\frac{\partial\psi^*}{\partial x} + \frac{1}{\psi}\frac{\partial\psi}{\partial x}\right)\right], \tag{4.209}$$

and simplify the terms inside the brackets,

$$m(v - iu) = \frac{\hbar}{2}\left[i\left(-\frac{2}{\psi}\frac{\partial\psi}{\partial x}\right)\right] = -i\hbar\frac{1}{\psi}\frac{\partial\psi}{\partial x}. \tag{4.210}$$

This expression multiplied by ψ is precisely the action of the momentum operator on ψ,

$$\hat{p}\psi = -i\hbar\frac{\partial\psi}{\partial x} = m(v - iu)\psi, \tag{4.211}$$

which suggests introducing the complex variable π

$$\hat{p} \to \pi \equiv m(v - iu) \tag{4.212}$$

as a means to calculate the quantum average of a function of the *operator* $\hat{p}$ by averaging over a complex variable (a *c-number*). The second moment $\langle p^2\rangle$ would thus be reproduced according to the usual rule for calculating the second moments of a complex variable (see, e.g., **[2]**, Sect. 8.1). A direct calculation yields

$$\left\langle \pi^2 \right\rangle = m^2 \left\langle v^2 + u^2 \right\rangle = \left\langle \hat{p}^2 \right\rangle. \tag{4.213}$$

The need to resort to a complex variable to reproduce the quantum expectation values is linked to the fact that, as we have seen, $\hat{p}$ extracts from the (complex) wave function information regarding *two* velocities, namely v and u.

P4.14 Given two operators $\hat{A}, \hat{B}$, express the matrix element C_{mn} of the product $\hat{C} = \hat{A}\hat{B}$ in terms of the matrix elements of $\hat{A}$ and $\hat{B}$. Now express the matrix element D_{mn} of the product $\hat{D} = \hat{B}\hat{A}$. How are the elements of matrices $\hat{C}$ and $\hat{D}$ related?

Solution. The matrix element C_{mn} is given by

$$C_{mn} = \int \varphi_m^* \hat{C} \varphi_n dx. \tag{4.214}$$

Substituting,

$$C_{mn} = \int \varphi_m^* \hat{C} \varphi_n dx = \int \varphi_m^* (\hat{A}\hat{B}) \varphi_n dx. \tag{4.215}$$

Expanding and reorganizing we have the matrix elements of $\hat{A}$ and $\hat{B}$:

$$A_{mn} = \int \varphi_m^* \hat{A} \varphi_n dx \tag{4.216}$$

and

$$\int \varphi_m^* \hat{B} \varphi_n dx. \tag{4.217}$$

Let us write the matrix representation of $\hat{A}$ and $\hat{B}$ in an orthonormal basis $\{|m\rangle\}$,

$$A_{mn} = \langle m|\hat{A}|n\rangle, \quad B_{mn} = \langle m|\hat{B}|n\rangle. \tag{4.218}$$

The matrix element of $\hat{C} = \hat{A}\hat{B}$ is

$$C_{mn} = \langle m|\hat{C}|n\rangle = \langle m|\hat{A}\hat{B}|n\rangle \tag{4.219}$$

We insert a complete set of states $\sum_k |k\rangle\langle k| = I$ between $\hat{A}$ and $\hat{B}$, to get

$$C_{mn} = \sum_k \langle m|\hat{A}|k\rangle\langle k|\hat{B}|n\rangle = \sum_k A_{mk} B_{kn}. \tag{4.220}$$

An analogous procedure leads to

$$\hat{D} = \hat{B}\hat{A} = \sum_k B_{mk}A_{kn}. \tag{4.221}$$

In general, $\hat{C} \neq \hat{D}$ because matrix (or operator) multiplication is not commutative. The difference between $\hat{C}$ and $\hat{D}$ is given by the commutator

$$\hat{C} - \hat{D} = \hat{AB} - \hat{BA} = [\hat{A}, \hat{B}]. \tag{4.222}$$

P4.15 Show that the expressions

$$\sum_n |n\rangle\langle n| = 1, \quad \sum_n \varphi_n^*(x)\varphi_n(x') = \delta(x - x') \tag{4.223}$$

are equivalent.

Solution. We start from the orthonormality condition applied to the continuous variable x —which could be, but is not necessarily, the position—

$$\langle x|x'\rangle = \delta(x - x'), \tag{4.224}$$

to write, inserting the identity expansion in terms of the discrete representation $|\, n\rangle$, $\sum_n |n\rangle\langle n| = 1$,

$$\delta(x - x') = \langle x|x'\rangle = \sum_n \langle x|n\rangle\langle n|x'\rangle = \sum_n \varphi_n^*(x')\varphi_n(x), \tag{4.225}$$

where the following identification was made

$$\langle x|n\rangle = \varphi_n(x), \quad \langle n|x\rangle = \varphi_n^*(x). \tag{4.226}$$

This shows the equivalence of both expressions. In fact, they represent the same, but $\sum_n \langle x|n\rangle\langle n|x'\rangle$ expresses it in abstract form, whereas $\sum_n \varphi_n^*(x')\varphi_n(x) = \delta(x - x')$ states it in terms of a specific representation.

As an additional illustration, it is useful to present the following variant of the previous calculation, which simultaneously uses the completeness (or closure) properties for a discrete variable, $\sum_n |n\rangle\langle n| = 1$, and for continuous variables, which is expressed in the form

$$\int dx\, |x\rangle\langle x| = 1. \tag{4.227}$$

We write successively, combining these properties,

$$\sum_n |n\rangle\langle n| = 1 = \sum_n \int dx \int dx'\, |x\rangle\langle x|n\rangle\langle n|x'\rangle\langle x'| \tag{4.228}$$

$$= \int dx \int dx'\, |x\rangle \left(\sum_n \langle x|n\rangle\langle n|x'\rangle \right) \langle x'| \tag{4.229}$$

$$= \int dx\, |x\rangle\langle x| = \int dx \int dx'\, |x\rangle\delta(x-x')\langle x'|, \tag{4.230}$$

from which it follows that

$$\sum_n \langle x|n\rangle\langle n|x'\rangle = \delta(x-x'), \tag{4.231}$$

which is Eq. 4.225.

P4.16 a) Calculate the average values of the Pauli matrices $\hat{\sigma}_i$ $(i = 1, 2, 3)$ in the states $|+\rangle$ and $|-\rangle$.

b) Calculate the average values of $\hat{\sigma}_i\hat{\sigma}_j$ $(i, j = 1, 2, 3)$ in the states $|+\rangle$ and $|-\rangle$.

Solution. See Problem P3.11 for the Pauli matrices. The states $|+\rangle$ and $|-\rangle$ are defined as the eigenstates of $\hat{\sigma}_3$,

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{4.232}$$

a) Appying the three Pauli matrices to these vectors gives the respective average values,

$$\langle +|\hat{\sigma}_1|+\rangle = \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0, \tag{4.233}$$

$$\langle +|\hat{\sigma}_2|+\rangle = \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0, \tag{4.234}$$

$$\langle +|\hat{\sigma}_3|+\rangle = \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 1. \tag{4.235}$$

$$\langle -|\hat{\sigma}_1|-\rangle = \begin{pmatrix} 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0, \tag{4.236}$$

$$\langle -|\hat{\sigma}_2|-\rangle = \begin{pmatrix} 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0, \tag{4.237}$$

$$\langle -|\hat{\sigma}_3|-\rangle = \begin{pmatrix} 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -1. \tag{4.238}$$

b) Using the Pauli matrix relations

$$\hat{\sigma}_i\hat{\sigma}_j = \delta_{ij}I + i\epsilon_{ijk}\hat{\sigma}_k, \tag{4.239}$$

where δ_{ij} is the Kronecker delta, I is the identity matrix, and ϵ_{ijk} is the Levi-Civita symbol, we get when $i = j$, $\langle \pm|\hat{\sigma}_i\hat{\sigma}_j|\pm\rangle = 1$,that is,

$$\langle \pm|\hat{\sigma}_i^2|\pm\rangle = 1, \quad i = 1, 2, 3. \tag{4.240}$$

When $i \neq j$, $\hat{\sigma}_i\hat{\sigma}_j = i\epsilon_{ijk}\hat{\sigma}_k$and the expectation values are given by $\langle\pm|\hat{\sigma}_i\hat{\sigma}_j|\pm\rangle = i\epsilon_{ijk}\langle\pm|\hat{\sigma}_k|\pm\rangle$, or explicitly,

$$\hat{\sigma}_1\hat{\sigma}_2 = i\hat{\sigma}_3: \quad \langle+|\hat{\sigma}_1\hat{\sigma}_2|+\rangle = i, \qquad \langle-|\hat{\sigma}_1\hat{\sigma}_2|-\rangle = -i, \tag{4.241}$$

$$\hat{\sigma}_2\hat{\sigma}_3 = i\hat{\sigma}_1: \quad \langle+|\hat{\sigma}_2\hat{\sigma}_3|+\rangle = 0, \qquad \langle-|\hat{\sigma}_2\hat{\sigma}_3|-\rangle = 0, \tag{4.242}$$

$$\hat{\sigma}_3\hat{\sigma}_1 = i\hat{\sigma}_2: \quad \langle+|\hat{\sigma}_3\hat{\sigma}_1|+\rangle = 0, \qquad \langle-|\hat{\sigma}_3\hat{\sigma}_1|-\rangle = 0. \tag{4.243}$$

P4.17 Show that for any Hermitian operator $\hat{A}$,

$$\langle n|(\Delta\hat{A})^2|n\rangle = \sum_{n'\neq n}\left|\langle n|\hat{A}|n'\rangle\right|^2, \tag{4.244}$$

where the deviation $\Delta\hat{A}$ is defined as

$$\Delta\hat{A} = \hat{A} - \langle n|\hat{A}|n\rangle. \tag{4.245}$$

Solution. The dispersion (in the state $|n\rangle$) of an arbitrary Hermitian operator $\hat{A}$ is given by

$$\langle n|(\Delta\hat{A})^2|n\rangle = \langle n|\hat{A}^2|n\rangle - \langle n|\hat{A}|n\rangle^2. \tag{4.246}$$

Inserting the resolution of the identity in the basis $|n\rangle$ and using the property of Hermitian operators

$$\langle n|\hat{A}|n'\rangle = \Big(\langle n'|\hat{A}|n\rangle\Big)^*,$$

we can write

$$\langle n|\hat{A}^2|n\rangle = \sum_{n'}\langle n|\hat{A}|n'\rangle\langle n'|\hat{A}|n\rangle = \sum_{n'}\langle n|\hat{A}|n'\rangle\langle n|\hat{A}|n'\rangle^* = \sum_{n'}\left|\langle n|\hat{A}|n'\rangle\right|^2. \tag{4.247}$$

Separating the term corresponding to $n' = n$, it follows that

$$\langle n|\hat{A}^2|n\rangle - \langle n|\hat{A}|n\rangle^2 = \sum_{n'}\left|\langle n|\hat{A}|n'\rangle\right|^2 - \left|\langle n|\hat{A}|n\rangle\right|^2 = \sum_{n'\neq n}\left|\langle n|\hat{A}|n'\rangle\right|^2. \tag{4.248}$$

From 4.246 and 4.248 we get the requested result,

$$\langle n|(\Delta\hat{A})^2|n\rangle = \sum_{n'\neq n}\left|\langle n|\hat{A}|n'\rangle\right|^2. \tag{4.249}$$

CHAPTER 5

One-Dimensional Potential Steps, Barriers, and Wells.

P5.1 A particle moves in a symmetric potential $V(x) = V(-x)$, such that the spectrum is discrete for $E < 0$ and continuous for $E > 0$. Draw a graph showing the general form of this potential if it is known that

a) there are an infinite number of bound states,

b) there are a small number of bound states.

Explain your argument. What would happen if the potential were not symmetric?

Finales/Fig $5.1_n ueva.eps Finales/Fig 5.1_n ueva.eps$

FIGURE 5.1. Symmetric potential wells that produce a discrete spectrum for $E < 0$ and a continuous spectrum for $E > 0$. (a) A potential of this form admits an infinite number of bound states. (b) A potential of this shape admits a finite number of bound states.

Solution. For a symmetric potential satisfying $V(x) \leq 0$ for all x, the spectrum will be continuous for $E > 0$. The states corresponding to these energies will be doubly degenerate, since particles can move either to the right or to the left.

To have bound states for $E < 0$, the potential must possess two classical turning points. These bound states are non-degenerate.

For an infinite number of bound states, it suffices to have either infinite depth with finite width or finite depth with infinite width, as illustrated in **Fig.** 5.1(a)**.** Conversely, for a finite number of bound states, both the potential depth and width must be finite, as in Fig. 5.1(b). The narrower and shallower the well, the fewer bound states it can contain. However, it will always admit at least one bound state, as illustrated in problem P5.4 below.

When the potential is not symmetric, the previous analysis remains valid, though no conclusions can be drawn about eigenfunction symmetry. The potential may even satisfy $V(x) \geq 0$, with the sole requirement that for $E > 0$ there exists only one classical turning point.

P5.2 Show that the principle of invariance against time reversal implies that, for a given energy, the coefficients of transmission and reflection by a potential step are the same, whether the particles are incident from the right or from the left.

Solution. Time reversal changes the sign of momentum, so to implement it, the

substitution of momenta by their negatives must be made. Since the formulas for the reflection coefficient R and the transmission coefficient T

$$R = \left(\frac{k-k_1}{k+k_1}\right)^2, \quad T = \frac{4kk_1}{(k+k_1)^2}, \tag{5.1}$$

are invariant under the transformation $k \to -k,\ k_1 \to -k_1$, they are also invariant under time reversal. If we now consider that particles are incident from the left instead of from the right, we must perform the substitution $k \to k_1,\ k_1 \to k$, an operation that also leaves invariant the results concerning the one-dimensional potential step.

From the physical point of view, it can be said that the wave function describing the motion of the particles—and therefore the probability flux—is partially reflected because there is a change in the potential. This applies regardless of whether the potential increases or decreases in the direction in which the particle is incident.

The behavior of the coefficients R and T under the interchange $k \leftrightarrow k_1$ expresses a property that is characteristic of all waves, known in optics as the principle of *reciprocity*. When light passes perpendicularly through the interface between two media with different refractive indices, a fraction of the light is reflected due to the abrupt change in its wavelength. The same fraction is reflected regardless of whether the wave is incident on one side of the interface or the other. We could say that the same happens when particles undergo a change in their de Broglie wavelength. That is, de Broglie waves satisfy the principle of reciprocity.

P5.3 Calculate the reflection coefficient for particles of mass m and energy $E > 0$, incident from the left on the complex potential step

$$V(x) = \begin{cases} 0, & x \le 0, \\ (1+ia)V_0, & x > 0, \end{cases} \tag{5.2}$$

where a is real and $V_0 > E$.

Solution. The general form of the (time-independent) Schrödinger equation is $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi$. For $x \le 0$, the solution is of the form

$$\psi_1(x) = Ae^{ikx} + Be^{-ikx}, \quad k = \sqrt{\frac{2mE}{\hbar^2}}. \tag{5.3}$$

For $x > 0$, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + (1+ia)V_0\psi = E\psi. \tag{5.4}$$

With q given by

$$q = \sqrt{\frac{2m}{\hbar^2}\left((1+ia)V_0 - E\right)}, \tag{5.5}$$

the general solution is

$$\psi_2(x) = Ce^{qx} + De^{-qx}. \tag{5.6}$$

For $x \to \infty$, the solution must be finite. If we take $\mathrm{Re}q > 0$, e^{-qx} decreases while e^{qx} grows with x. Therefore $C = 0$, and we are left with

$$\psi_2(x) = De^{-qx}, \quad \mathrm{Re}(q) > 0. \tag{5.7}$$

From the continuity conditions at $x = 0$ we get

$$\psi_1(0) = \psi_2(0) \implies A + B = D, \quad \psi_1'(0) = \psi_2'(0) \implies ik(A - B) = -qD, \tag{5.8}$$

whence

$$A = \frac{k + iq}{2k} D, \quad B = \frac{k - iq}{2k} D, \tag{5.9}$$

and

$$\frac{|B|^2}{|A|^2} = \frac{k^2 + |q|^2 + 2k\mathrm{Im}q}{k^2 + |q|^2 - 2k\mathrm{Im}q}. \tag{5.10}$$

The reflection coefficient R is the ratio of the reflected to the incident probability density currents for $x \leq 0$. Since the incident and reflected particles move at the same speed, R is precisely given by

$$R = \frac{k^2 + |q|^2 + 2k\mathrm{Im}q}{k^2 + |q|^2 - 2k\mathrm{Im}q},$$

where k and q are given by Eqs. (5.3) and (5.5), respectively. From Eq. (5.5), the sign of $\mathrm{Im}q$ is equal to the sign of $aV_0/(V_0 - E)$. Therefore, when $a > 0$, $R > 1$, meaning particles are created by the potential V. By contrast, negative values of a mean the potential is absorptive.

P5.4 Show that a 1D square well has exactly $n + 1$ even bounded states if

$$\frac{2\pi^2\hbar^2}{ma^2} n^2 \leq V_0 < \frac{2\pi^2\hbar^2}{ma^2}(n + 1)^2 \tag{5.11}$$

and $n + 1$ odd bound states if

$$\frac{2\pi^2\hbar^2}{ma^2} \left(n + \frac{1}{2}\right)^2 \leq V_0 < \frac{2\pi^2\hbar^2}{ma^2} \left(n + \frac{3}{2}\right)^2. \tag{5.12}$$

Solution. The even bound states of the well are given by the solutions of equation

$$\tan y = \frac{\sqrt{y_0^2 - y^2}}{y}, \tag{5.13}$$

where

$$y_0 = \frac{a}{2\hbar}\sqrt{2mV_0}, \qquad y = \frac{a}{2\hbar}\sqrt{2m\,(V_0 - |E|)}. \tag{5.14}$$

The position of the zeros is determined by the intersections of the curves $\sqrt{y_0^2 - y^2}/y$ and $\tan y$, as illustrated in Fig. 5.2a. The number of intersections $n+1$ equals the largest integer contained in y_0/π, so we can write

$$n\pi \leq y_0 < (n + 1)\pi. \tag{5.15}$$

For example, for $n = 0$, $0 \leq y_0 < \pi$, and from Fig. 5.2 it follows that there is exactly one solution. Since $V_0 = 2y_0^2\hbar^2/ma^2$, squaring and multiplying by $2\hbar^2/ma^2$ we obtain

$$\frac{2\pi^2\hbar^2}{ma^2}n^2 \leq V_0 < \frac{2\pi^2\hbar^2}{ma^2}(n+1)^2, \tag{5.16}$$

which is the desired condition.

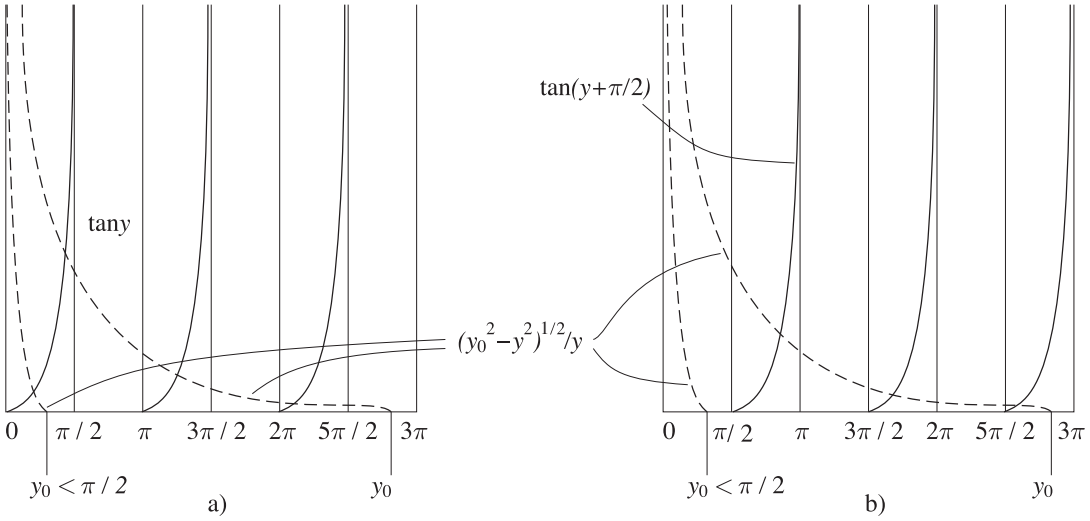

FIGURE 5.2. Location of the eigenvalues of the energy for the finite square well. The even solutions are shown in (a), and the odd ones are shown in (b).

The odd case is very similar; the most important difference lies in the need to add an additional interval of $\pi/2$ to the parameter y_0 in the previous conditions, as clearly seen in Fig. 5.2b. Therefore, when

$$\left(n + \frac{1}{2}\right)\pi \leq y_0 < \left(n + \frac{3}{2}\right)\pi, \tag{5.17}$$

there are exactly $n + 1$ solutions. This condition is equivalent to

$$\frac{2\pi^2\hbar^2}{ma^2}\left(n + \frac{1}{2}\right)^2 \leq V_0 < \frac{2\pi^2\hbar^2}{ma^2}\left(n + \frac{3}{2}\right)^2. \tag{5.18}$$

The result reveals a fundamental characteristic of quantum systems: a finite attractive well typically possesses a limited number of bound states. In the following problem it is shown that it is not enough for the depth to be infinite for an infinite number of stationary states to exist, since the well must also be sufficiently wide. This is seen in the previous results by observing that, for example, in 5.15 the parameter that characterizes the well is the product a^2V_0, and not each factor separately.

An alternative way to carry out the analysis is to note that Eq. 5.13 is equivalent to

$$\cos^2 y = \frac{1}{1+\tan^2 y} = \frac{y^2}{y_0^2}, \tag{5.19}$$

or $\cos y = y/y_0$, which is easier to analyze than 5.13.

P5.5 Show that an extremely narrow and deep attractive potential that can be represented as a Dirac delta, $V(x) = -\delta(x)/a$, contains a single bound state, and find the corresponding energy eigenvalue. Hint: solve the Schrödinger equation for $x \neq 0$ and note that ψ' is not continuous at $x = 0$.

Solution. The time-independent Schrödinger equation for this problem is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) - a\delta(x)\psi(x) = E\psi(x). \tag{5.20}$$

We are interested in solutions with $E < 0$, as these correspond to possible bound states. For $x \neq 0$, this equation reduces to

$$\frac{d^2}{dx^2}\psi(x) - k^2\psi(x) = 0, \tag{5.21}$$

where

$$k = \sqrt{\frac{2m|E|}{\hbar^2}}. \tag{5.22}$$

The solution to this equation is:

$$\psi(x) = \begin{cases} A_1 e^{-kx}, & x > 0, \\ A_2 e^{kx}, & x < 0. \end{cases} \tag{5.23}$$

We have considered that the wavefunction must be square-integrable, which excludes exponentially growing solutions. The continuity condition at $x = 0$ implies $A_1 = A_2 \equiv A$. Note that there is no continuity of $\psi'(x)$ at $x = 0$. Direct integration of the Schrödinger equation around the origin gives, with ϵ arbitrarily small and positive,

$$\left.\frac{d\psi}{dx}\right|_{+\epsilon} - \left.\frac{d\psi}{dx}\right|_{-\epsilon} = \frac{2m}{\hbar^2}\left[\int_{-\epsilon}^{\epsilon} V(x)\psi(x)dx - E\int_{-\epsilon}^{\epsilon}\psi(x)dx\right]. \tag{5.24}$$

Since $\psi(x)$ is continuous, the last integral vanishes as $\epsilon \to 0$. For the remaining term we get

$$\frac{2m}{\hbar^2}\int_{-\epsilon}^{\epsilon} V(x)\psi(x)dx = -\frac{2ma}{\hbar^2}\int_{-\epsilon}^{\epsilon}\delta(x)\psi(x)dx = -\frac{2ma}{\hbar^2}\psi(0), \tag{5.25}$$

which gives

$$\left.\frac{d\psi}{dx}\right|_{x=0^+} - \left.\frac{d\psi}{dx}\right|_{x=0^-} = -\frac{2ma}{\hbar^2}\psi(0) = -\frac{2maA}{\hbar^2}. \tag{5.26}$$

This result shows that the derivative of the wave function is discontinuous at the point where the Dirac delta argument is zero, and that the magnitude of

this discontinuity is proportional to the value of the wave function at that point. Evaluating the derivatives yields

$$-k-k=-\frac{2ma}{\hbar^2} \quad \Rightarrow \quad k=\frac{ma}{\hbar^2}, \tag{5.27}$$

which demonstrates that the continuity requirement fixes the value of k, and consequently, the energy,

$$E=-\frac{ma^2}{2\hbar^2}. \tag{5.28}$$

It is clear that there exists only one bound state and one energy eigenvalue.

The mathematical simplicity of modeling narrow potentials with delta functions, as exemplified here, has been successfully employed in various applications to obtain basic semi-quantitative information about the system's behavior.

P5.6 Extend the study of the finite rectangular well to the 3D case using Cartesian coordinates. Show that if the well is very deep, the results of Exercise **E5.2** are recovered.

Solution. In order to make a formal generalization of the rectangular well problem in the Cartesian coordinate system from one to three dimensions, we write the potential in the following form

$$V(\boldsymbol{r})=V(x_1)+V(x_2)+V(x_3)=\sum_{i=1}^{3}V_i, \tag{5.29}$$

where

$$V(x_i)=\begin{cases}-V_0, & \text{if } 0<x_i<a_i,\\ 0, & \text{otherwise.}\end{cases} \tag{5.30}$$

It must be made clear that this is not a 3D square well with spherical symmetry (which is defined as $V(r)=V_0$ for $r\le a$, $V(r)=0$ for $r>a$), but rather a square potential in each of the three orthogonal Cartesian directions.

Introducing $\psi(\boldsymbol{r})=\psi_1(x_1)\psi_2(x_2)\psi_3(x_3)$ into the time-independent Schrödinger equation and dividing by $\psi(\boldsymbol{r})$, we obtain

$$\sum_{i=1}^{3}\left(\frac{1}{\psi_i}\frac{d^2\psi_i}{dx_i^2}-\frac{2m}{\hbar^2}V_i\right)=-\frac{2m}{\hbar^2}E. \tag{5.31}$$

Since the parentheses in the sum contains independent variables, the equality can only be valid for each triad (x_1,x_2,x_3) if each term is a constant, that is, if

$$\frac{1}{\psi_i}\frac{d^2\psi_i}{dx_i^2}-\frac{2m}{\hbar^2}V_i=-\frac{2m}{\hbar^2}E_i, \quad i=1,2,3, \tag{5.32}$$

such that $E = E_1 + E_2 + E_3$. In this way, the Schrödinger equation separates into three one-dimensional equations, whose solutions are those of the 1D finite well,

$$\psi_1(x) = A_{2x} \sin q_1 x + B_{2x} \cos q_1 x, \qquad 0 \le x \le a; \tag{5.33}$$

$$\psi_2(y) = A_{2y} \sin q_2 y + B_{2y} \cos q_2 y, \qquad 0 \le y \le b; \tag{5.34}$$

$$\psi_3(z) = A_{2z} \sin q_3 z + B_{2z} \cos q_3 z, \qquad 0 \le z \le c; \tag{5.35}$$

$$\psi_1(x) = B_{3x} e^{-\kappa_1 x}, \qquad x \ge a; \tag{5.36}$$

$$\psi_2(y) = B_{3y} e^{-\kappa_2 y}, \qquad y \ge b; \tag{5.37}$$

$$\psi_3(z) = B_{3z} e^{-\kappa_3 z}, \qquad z \ge c; \tag{5.38}$$

where we have written $x_1, x_2, x_3 = x, y, z,\ a_1 = a,\ a_2 = b,\ a_3 = c$, and

$$\kappa_i^2 = \frac{2m|E_i|}{\hbar^2}, \qquad q_i^2 = \frac{2m(V_0 - |E_i|)}{\hbar^2}, \tag{5.39}$$

$$\kappa_1^2 + \kappa_2^2 + \kappa_3^2 = \frac{2m}{\hbar^2}|E|, \qquad q_1^2 + q_2^2 + q_3^2 = \frac{2m}{\hbar^2}(3V_0 - |E|). \tag{5.40}$$

The final solution is obtained separately for each ψ_i as shown in Problem 5.4; this process leads to the expected quantization of energy.

In the limit $V_0 \to \infty$, the particles are all trapped by the potential and the wave function vanishes outside the well, which reduces it to

$$\psi_{n_1 n_2 n_3}(x, y, z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{\pi n_1}{a} x\right) \sin\left(\frac{\pi n_2}{b} y\right) \sin\left(\frac{\pi n_3}{c} z\right). \tag{5.41}$$

The energy is then

$$E_{n_1 n_2 n_3} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right), \quad n_1, n_2, n_3 = 1, 2, 3, \ldots \tag{5.42}$$

If the ratio of any pair of sides is an irrational number, all energy levels are non-degenerate. For rational ratios, the energy spectrum is generally degenerate. For example, if $a = b = c$, the level corresponding to $n_1^2 + n_2^2 + n_3^2 = 6$ is triply degenerate, since three linearly independent eigenfunctions correspond to the same eigenvalue: $E_{121} = E_{112} = E_{211} = 6\pi^2\hbar^2/2ma^2$. The ground state E_{111} is non-degenerate.

P5.7 Study the energy degeneracy as a function of the quantum numbers for a cubic potential well with impenetrable walls.

Solution. Mathematically, the potential of a 3D infinite square well of side length a is written as

$$V(x, y, z) = \begin{cases} 0, & \text{if } 0 < x < a,\ 0 < y < a,\ 0 < z < a, \\ \infty, & \text{otherwise.} \end{cases} \tag{5.43}$$

This potential ensures that the particle is strictly confined within the cube, and its wave function must vanish at the boundaries.

The 3D Schrödinger equation is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z)+V(x,y,z)\psi(x,y,z)=E\psi(x,y,z), \tag{5.44}$$

with the Laplacian operator in Cartesian coordinates given by

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}.$$

In the present case the potential is zero in all three directions within the well. We therefore propose a factorizable solution in the three spatial variables,

$$\psi(x,y,z)=X(x)Y(y)Z(z). \tag{5.45}$$

Substituting this ansatz into the Schrödinger equation and applying the Laplacian operator to $\psi(x,y,z)=X(x)Y(y)Z(z)$,

$$\nabla^2\psi=Y(y)Z(z)\frac{d^2X(x)}{dx^2}+X(x)Z(z)\frac{d^2Y(y)}{dy^2}+X(x)Y(y)\frac{d^2Z(z)}{dz^2} \tag{5.46}$$

we get

$$-\frac{\hbar^2}{2m}\left[YZ\frac{d^2X}{dx^2}+XZ\frac{d^2Y}{dy^2}+XY\frac{d^2Z}{dz^2}\right]+V(x,y,z)XYZ=EXYZ. \tag{5.47}$$

Inside the cube, $V(x,y,z)=0$, so that, upon dividing by XYZ, we get

$$\frac{1}{X}\frac{d^2X}{dx^2}+\frac{1}{Y}\frac{d^2Y}{dy^2}+\frac{1}{Z}\frac{d^2Z}{dz^2}=-\frac{2mE}{\hbar^2}. \tag{5.48}$$

We now separate the variable x by moving the y and z-dependent terms to the right-hand side

$$\frac{1}{X}\frac{d^2X}{dx^2}=-\frac{1}{Y}\frac{d^2Y}{dy^2}-\frac{1}{Z}\frac{d^2Z}{dz^2}-\frac{2mE}{\hbar^2}. \tag{5.49}$$

The two sides depend on different variables, so they must be equal to a constant, which we call $-K_1^2$,

$$\frac{1}{X}\frac{d^2X}{dx^2}=-K_1^2 \tag{5.50}$$

and

$$\frac{1}{Y}\frac{d^2Y}{dy^2}+\frac{1}{Z}\frac{d^2Z}{dz^2}+\frac{2mE}{\hbar^2}=K_1^2. \tag{5.51}$$

We now isolate the y-dependent term,

$$\frac{1}{Y}\frac{d^2Y}{dy^2}=-\frac{1}{Z}\frac{d^2Z}{dz^2}-\frac{2mE}{\hbar^2}+K_1^2 \tag{5.52}$$

and define the new separation constant $-K_2^2$,

$$\frac{1}{Y}\frac{d^2Y}{dy^2}=-K_2^2 \tag{5.53}$$

so that the rest of the equation becomes

$$\frac{1}{Z}\frac{d^2Z}{dz^2} + \frac{2mE}{\hbar^2} = K_1^2 + K_2^2. \tag{5.54}$$

We rewrite each of the three separate equations in the standard form,

$$\frac{d^2X}{dx^2} + K_1^2 X = 0, \tag{5.55}$$

$$\frac{d^2Y}{dy^2} + K_2^2 Y = 0, \tag{5.56}$$

$$\frac{d^2Z}{dz^2} + \left(\frac{2mE}{\hbar^2} - K_1^2 - K_2^2\right) Z = 0. \tag{5.57}$$

The general solutions are

$$X(x) = C_x \sin(K_1 x) + C'_x \cos(K_1 x), \tag{5.58}$$

$$Y(y) = C_y \sin(K_2 y) + C'_y \cos(K_2 y), \tag{5.59}$$

$$Z(z) = C_z \sin\left(\sqrt{\frac{2mE}{\hbar^2} - K_1^2 - K_2^2}\, z\right) + C'_z \cos\left(\sqrt{\frac{2mE}{\hbar^2} - K_1^2 - K_2^2}\, z\right). \tag{5.60}$$

We now apply the boundary conditions, which require the wave function to vanish at the walls,

$$X(0) = X(a) = Y(0) = Y(a) = Z(0) = Z(a) = 0. \tag{5.61}$$

From $X(0) = 0$, we get

$$X(0) = C_x \sin(0) + C'_x \cos(0) = C'_x \Rightarrow C'_x = 0. \tag{5.62}$$

The same argument applies to $Y(0)$ and $Z(0)$, so all cosine terms vanish and we are left with

$$X(x) = C_x \sin(K_1 x), \quad Y(y) = C_y \sin(K_2 y), \quad Z(z) = C_z \sin(K_3 z). \tag{5.63}$$

Now we impose $X(a) = Y(a) = 0$. For example,

$$X(a) = C_x \sin(K_1 a) = 0 \Rightarrow \sin(K_1 a) = 0 \Rightarrow K_1 a = n_x \pi \Rightarrow K_1 = \frac{n_x \pi}{a}, \tag{5.64}$$

and similarly,

$$K_2 = \frac{n_y \pi}{a}. \tag{5.65}$$

To determine the allowed values for the energy, we focus on the function $Z(z)$. Applying $Z(a) = 0$, we get

$$Z(a) = C_z \sin\left(\sqrt{\frac{2mE}{\hbar^2} - K_1^2 - K_2^2}\, a\right) = 0 \Rightarrow \sqrt{\frac{2mE}{\hbar^2} - K_1^2 - K_2^2}\, a = n_z \pi. \tag{5.66}$$

Solving for the energy E, we obtain

$$\frac{2mE}{\hbar^2} = K_1^2 + K_2^2 + \left(\frac{n_z\pi}{a}\right)^2 \tag{5.67}$$

and substituting $K_1 = \frac{n_x\pi}{a}$, $K_2 = \frac{n_y\pi}{a}$, we find

$$E = \frac{\hbar^2\pi^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right), \qquad n_x, n_y, n_z = 1, 2, 3, \ldots \tag{5.68}$$

The solutions for each component then become

$$X(x) = C_x \sin\left(\frac{n_x\pi}{a}x\right), \tag{5.69}$$

$$Y(y) = C_y \sin\left(\frac{n_y\pi}{a}y\right), \tag{5.70}$$

$$Y(y) = C_z \sin\left(\frac{n_z\pi}{a}z\right). \tag{5.71}$$

The normalized eigenfunctions must satisfy the condition

$$\iiint_{\text{box}} |\psi_{n_x,n_y,n_z}(x,y,z)|^2\, dx\, dy\, dz = 1. \tag{5.72}$$

From 5.69,5.70,5.71, we can write the eigenfunctions as

$$\psi_{n_x,n_y,n_z}(x,y,z) = A \sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{a}\right)\sin\left(\frac{n_z\pi z}{a}\right), \tag{5.73}$$

where $A = C_xC_yC_z$. We substitute into the normalization condition,

$$|A|^2 \int_0^a \sin^2\left(\frac{n_x\pi x}{a}\right)dx \int_0^a \sin^2\left(\frac{n_y\pi y}{a}\right)dy \int_0^a \sin^2\left(\frac{n_z\pi z}{a}\right)dz = 1. \tag{5.74}$$

Each integral evaluates to

$$\int_0^a \sin^2\left(\frac{n\pi u}{a}\right)du = \frac{a}{2}, \tag{5.75}$$

so that

$$|A|^2\left(\frac{a}{2}\right)^3 = 1. \tag{5.76}$$

The final form of the eigenfuntions is then

$$\psi_{n_x,n_y,n_z}(x,y,z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{a}\right)\sin\left(\frac{n_z\pi z}{a}\right). \tag{5.77}$$

We now proceed to analyze the degeneracy of the energy levels. From Eq. (5.68) and defining n such that

$$n^2 \equiv n_x^2 + n_y^2 + n_z^2, \tag{5.78}$$

we write for the total energy

$$E_n = \frac{\hbar^2\pi^2 n^2}{2ma^2}. \tag{5.79}$$

Different combinations of the quantum numbers (n_x, n_y, n_z) can result in the same value of n^2, and therefore the same energy eigenvalue; this leads to degeneracy of the energy levels. The different permutations correspond to physically distinct (orthogonal) eigenfunctions, so the degeneracy is a result of the symmetry of the potential (a cube, in this case) under permutation of coordinates. Degeneracy increases with energy because there are more combinations of integers that can sum to a given higher value of n^2. This is sometimes called *accidental degeneracy*, though it arises from the geometric symmetry of the system in this case. Table 1 lists some values of n_x, n_y, n_z, the corresponding n^2, and the degeneracy associated with each energy level.

n_x	n_y	n_z	n^2	Energy	Degeneracy
1	1	1	3	$\frac{3\hbar^2\pi^2}{2ma^2}$	1
2	1	1	6	$\frac{6\hbar^2\pi^2}{2ma^2}$	3
1	2	1	6		
1	1	2	6		
2	2	1	9	$\frac{9\hbar^2\pi^2}{2ma^2}$	3
2	1	2	9		
1	2	2	9		
3	1	1	11	$\frac{11\hbar^2\pi^2}{2ma^2}$	3
1	3	1	11		
1	1	3	11		
2	2	2	12	$\frac{12\hbar^2\pi^2}{2ma^2}$	1
3	2	1	14	$\frac{14\hbar^2\pi^2}{2ma^2}$	6
3	1	2	14		
1	2	3	14		
1	3	2	14		
2	1	3	14		
2	3	1	14		
3	2	2	17	$\frac{17\hbar^2\pi^2}{2ma^2}$	3
2	3	2	17		
2	2	3	17		

TABLE 1. Degeneracy of energy levels in a 3D cubic infinite potential well.

Figure 5.3 shows a histogram of the degeneracy of the energy levels as a function of the value n^2. Gaps in the plot appear because not all integers can be expressed as the sum of three perfect squares. As the energy increases (i.e., as n^2 becomes larger), the number of contributing combinations increases as well, causing the degeneracy to grow, on average.

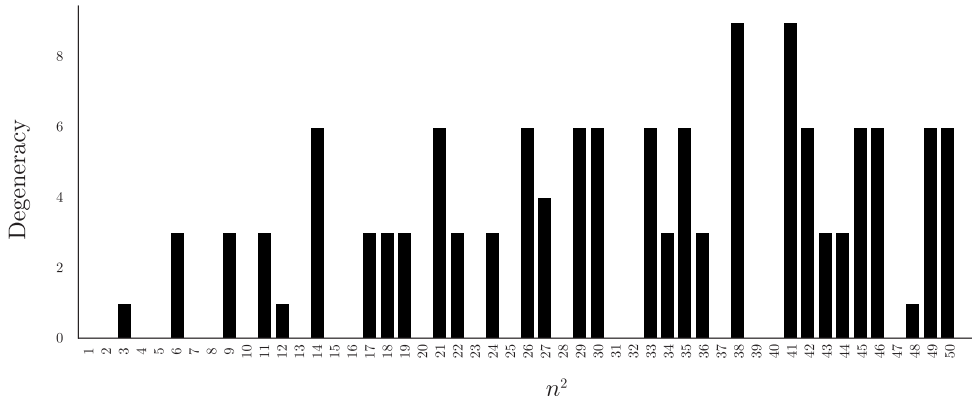

FIGURE 5.3. Histogram of the degeneracy of energy levels in a 3D infinite cubic potential well as a function of $n^2 = n_x^2 + n_y^2 + n_z^2$. Notice that some values of n^2 do not appear due to number-theoretic constraints; not all integers can be expressed as a sum of three squares.

P5.8 Show that the S-matrix for particles through a 1D potential is unitary. Use the result to prove the following relations,

$$|S_{11}|^2 + |S_{12}|^2 = 1, \tag{5.80}$$

$$|S_{21}|^2 + |S_{22}|^2 = 1, \tag{5.81}$$

$$S_{11}S_{12}^* + S_{21}S_{22}^* = 0. \tag{5.82}$$

Solution. The matrix S is defined by the expression

$$\psi_{\text{out}} = S\psi_{\text{in}}. \tag{5.83}$$

Consider the expression

$$\psi_{\text{out}}^\dagger \psi_{\text{out}} = \psi_{\text{in}}^\dagger S^\dagger S \psi_{\text{in}}. \tag{5.84}$$

From the above, it follows that

$$\psi_{\text{out}}^\dagger = \psi_{\text{in}}^\dagger S^\dagger, \tag{5.85}$$

and thus

$$\psi_{\text{out}}^\dagger \psi_{\text{out}} = \psi_{\text{in}}^\dagger S^\dagger S \psi_{\text{in}}. \tag{5.86}$$

Now, we impose the condition of flux conservation, which can be written as

$$\psi_{\text{out}}^\dagger \psi_{\text{out}} = \psi_{\text{in}}^\dagger \psi_{\text{in}}, \tag{5.87}$$

that is, as a condition for the conservation of normalization. Note that instead of quantities like $\psi^*\psi = |\psi|^2$, we are considering the product $\psi^\dagger\psi$, since we are dealing with matrices and the result must be a scalar. As explained in [**1**], **Section 6.2**, ψ is represented by a column matrix, so its adjoint (equal to the conjugate transpose) is a row matrix, and the product $\psi^\dagger\psi$ yields a number, as desired. From the last two equations we get $S^\dagger S = 1$. We use this result to write $S = S(S^\dagger S) = (SS^\dagger)S$,

from which it follows that $SS^\dagger = 1$ must also hold. Combining the two expressions, we conclude that

$$S^\dagger = S^{-1}, \tag{5.88}$$

which is the defining property of a unitary matrix. For a two-dimensional problem the matrix S takes the form

$$S = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \tag{5.89}$$

and its adjoint is

$$S^\dagger = S^{T*} = \begin{pmatrix} S_{11}^* & S_{21}^* \\ S_{12}^* & S_{22}^* \end{pmatrix}. \tag{5.90}$$

We introduce these expressions into $S^\dagger S = 1$, to get

$$1 = \begin{pmatrix} S_{11}^* & S_{21}^* \\ S_{12}^* & S_{22}^* \end{pmatrix} \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} = \begin{pmatrix} S_{11}^* S_{11} + S_{21}^* S_{21} & S_{11}^* S_{12} + S_{21}^* S_{22} \\ S_{12}^* S_{11} + S_{22}^* S_{21} & S_{12}^* S_{12} + S_{22}^* S_{22} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{5.91}$$

From this it follows that

$$|S_{11}|^2 + |S_{21}|^2 = 1, \tag{5.92}$$

$$|S_{12}|^2 + |S_{22}|^2 = 1, \tag{5.93}$$

$$S_{12}^* S_{11} + S_{22}^* S_{21} = 0. \tag{5.94}$$

plus the complex conjugate of the last expression. Similarly, from $SS^\dagger = 1$ we obtain

$$|S_{11}|^2 + |S_{12}|^2 = 1, \tag{5.95}$$

$$|S_{21}|^2 + |S_{22}|^2 = 1, \tag{5.96}$$

$$S_{11} S_{21}^* + S_{12} S_{22}^* = 0. \tag{5.97}$$

All these relations are characteristic of a unitary matrix and can be written in condensed form as

$$S^\dagger S = 1 \Longrightarrow \sum_j S_{ij}^* S_{jk} = \delta_{ik}; \tag{5.98}$$

$$SS^\dagger = 1 \Longrightarrow \sum_j S_{ij} S_{jk}^* = \delta_{ik}. \tag{5.99}$$

The second expression is simply the complex conjugate of the first one.

P5.9 Determine the general form of the elements S_{ij} of the S-matrix describing the dispersion of particles through a 1D square well with $E > 0$.

From Fig. 5.4 we see that the incoming and outgoing wave functions can be written in the form

$$\psi_{\text{in}} = \begin{pmatrix} A_1 \\ B_3 \end{pmatrix}, \quad \psi_{\text{out}} = \begin{pmatrix} A_3 \\ B_1 \end{pmatrix}. \tag{5.100}$$

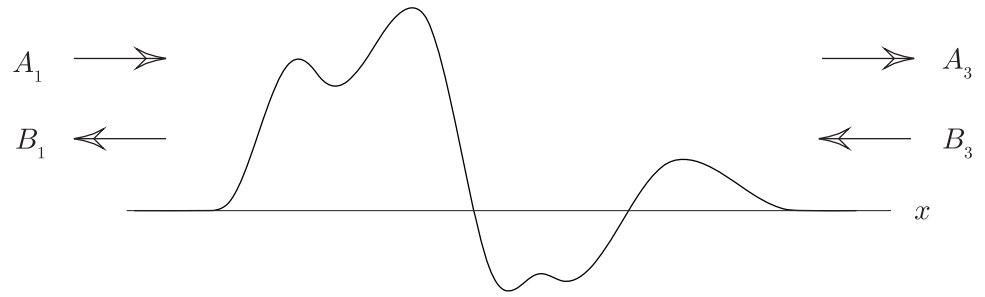

FIGURE 5.4. Incoming and outgoing wave functions.

In terms of these expressions and 5.89, Eq. 5.83 takes the form [1]

$$\begin{pmatrix} A_3 \\ B_1 \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} A_1 \\ B_3 \end{pmatrix}. \tag{5.104}$$

To simplify the calculation, we assume that particles are incident from the left, such that in region III there is only flow to the right, and $B_3 = 0$; this gives

$$A_3 = S_{11}A_1, \qquad B_1 = S_{21}A_1. \tag{5.105}$$

The transmission and reflection coefficients are then given by

$$T = \frac{|A_3|^2}{|A_1|^2} = |S_{11}|^2, \quad R = \frac{|B_1|^2}{|A_1|^2} = |S_{21}|^2. \tag{5.106}$$

From

$$T + R = 1 = |S_{11}|^2 + |S_{21}|^2, \tag{5.107}$$

[1]Note that similar treatments in terms of matrices (which could generally be called *transfer* matrices) are common in theories dealing with linear systems. For example, consider an electrical circuit that linearly transforms the input signal (voltage and current v_1, i_1) into an output signal with voltage and current v_2, i_2. Given the linearity of the system, one can write in the most general form:

$$v_2 = S_{11}v_1 + S_{12}i_1, \tag{5.101}$$

$$i_2 = S_{21}v_1 + S_{22}i_1. \tag{5.102}$$

Note that while the coefficients S_{11} and S_{22} are dimensionless, S_{12} has dimensions of impedance and S_{21} of conductance. To give a matrix form to this expression, we can define an input vector $V_{\text{in}} = \begin{pmatrix} v_1 \\ i_1 \end{pmatrix}$ and an output vector $V_{\text{out}} = \begin{pmatrix} v_2 \\ i_2 \end{pmatrix}$, and obtain $V_{\text{out}} = SV_{\text{in}}$. For example, the impedance z_2 that the output presents is

$$z_2 = \frac{v_2}{i_2} = \frac{S_{11}z_1 + S_{12}}{S_{21}z_1 + S_{22}}, \tag{5.103}$$

where $z_1 = v_1/i_1$ is the input impedance. Similar descriptions are used in mechanical, acoustic, optical studies, etc.

combined with equation 5.95, we get

$$|S_{21}|^2 = |S_{12}|^2 = R, \tag{5.108}$$

and from 5.96 and 5.106 we get

$$|S_{22}|^2 = |S_{11}|^2 = T. \tag{5.109}$$

To find the solution of these equations, subject to the condition expressed in 5.94, we write the matrix elements in the form

$$S_{11} = \sqrt{T}e^{i\alpha}, \quad S_{12} = \sqrt{R}e^{i\beta}, \quad S_{21} = \sqrt{R}e^{i\gamma}, \quad S_{22} = \sqrt{T}e^{i\delta}. \tag{5.110}$$

This gives

$$e^{i(\alpha-\beta)} = -e^{i(\gamma-\delta)} \tag{5.111}$$

or, explicitly,

$$\cos(\alpha-\beta) + i\sin(\alpha-\beta) = -\cos(\gamma-\delta) - i\sin(\gamma-\delta), \tag{5.112}$$

which implies

$$\alpha - \beta = \gamma - \delta + \pi, \quad \alpha - \beta = \delta - \gamma, \tag{5.113}$$

and therefore

$$\delta = \gamma + \frac{\pi}{2}, \quad \alpha = \beta + \frac{\pi}{2}. \tag{5.114}$$

Therefore, the solutions become

$$S_{11} = \sqrt{T}e^{i\alpha}, \quad S_{12} = \sqrt{R}e^{i(\alpha-\frac{\pi}{2})}, \tag{5.115}$$

$$S_{21} = \sqrt{R}e^{i(\delta-\frac{\pi}{2})}, \quad S_{22} = \sqrt{T}e^{i\delta}. \tag{5.116}$$

We now introduce the following symmetry consideration. We perform a spatial inversion and denote the elements describing the transformed system with a bar,

$$\bar{\psi}_{\text{sal}} = \begin{pmatrix} A_1 \\ B_3 \end{pmatrix}, \quad \bar{\psi}_{\text{ent}} = \begin{pmatrix} A_3 \\ B_1 \end{pmatrix}, \tag{5.117}$$

$$\begin{pmatrix} A_1 \\ B_3 \end{pmatrix} = \bar{S} \begin{pmatrix} A_3 \\ B_1 \end{pmatrix}. \tag{5.118}$$

Since $\bar{S} = S^{-1} = S^\dagger$, in the case of a symmetric well we must have $\bar{S} = S$. Combining the above, it follows that

$$S = S^\dagger, \tag{5.119}$$

which means that under these conditions the matrix S is also self-adjoint (Hermitian). Therefore,

$$S_{11} = S_{11}^*, \quad S_{12} = S_{21}^*, \quad S_{22} = S_{22}^*, \tag{5.120}$$

and it follows that

$$\alpha = 0 \qquad \text{and} \qquad \delta = \pi - \alpha = \pi. \tag{5.121}$$

The matrix then takes the form

$$S = \begin{pmatrix} \sqrt{T} & -i\sqrt{R} \\ i\sqrt{R} & -\sqrt{T} \end{pmatrix}. \tag{5.122}$$

The expressions for T and R for a specific problem are given by

$$R = \left|\frac{B_1}{A_1}\right|^2 = 1 - T, \tag{5.123}$$

$$T = \left|\frac{A_3}{A_1}\right|^2 = \left[1 + \frac{1}{4}\left(\frac{q_1}{k} - \frac{k}{q_1}\right)^2 \sin^2(q_1 a)\right]^{-1}, \tag{5.124}$$

where $k^2 = \frac{2mE}{\hbar^2}, q_1^2 = \frac{2m}{\hbar^2}(E + V_0)$.

P5.10 Determine the scattering matrix for the potential

$$V(x) = -a\delta(x - b). \tag{5.125}$$

Solution. The time-independent Schrödinger equation for the problem is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - a\delta(x - b)\psi(x) = E\psi(x) \tag{5.126}$$

For $x \neq b$, the potential is zero, and the general solution is a combination of plane waves,

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x < b, \\ Ce^{ikx} + De^{-ikx}, & x > b. \end{cases} \tag{5.127}$$

From the continuity of the wave function we get

$$\psi(b^-) = \psi(b^+) \implies Ae^{ikb} + Be^{-ikb} = Ce^{ikb} + De^{-ikb} \tag{5.128}$$

and integrating the Schrödinger equation around $x = b$, we obtain

$$-\frac{\hbar^2}{2m}[\psi'(b^+) - \psi'(b^-)] - a\psi(b) = 0 \tag{5.129}$$

We then substitute the derivatives

$$-\frac{\hbar^2}{2m}[ikCe^{ikb} - ikDe^{-ikb} - ikAe^{ikb} + ikBe^{-ikb}] - a(Ae^{ikb} + Be^{-ikb}) = 0 \tag{5.130}$$

and simplify,

$$-\frac{i\hbar^2 k}{2m}[(C - A)e^{ikb} - (D - B)e^{-ikb}] - a(Ae^{ikb} + Be^{-ikb}) = 0 \tag{5.131}$$

Grouping the exponential terms, we get

$$-\frac{i\hbar^2 k}{2m}(C - A) - aA = 0 \quad \text{and} \quad \frac{i\hbar^2 k}{2m}(D - B) - aB = 0, \tag{5.132}$$

or in terms of the dimensionless parameter $\beta = \frac{2ma}{\hbar^2 k}$,

$$C = A(1 - i\beta), \quad D = B(1 + i\beta). \tag{5.133}$$

The scattering matrix S relates the outgoing wave amplitudes (C and B) to the incoming amplitudes (A and D),

$$\begin{pmatrix} B \\ C \end{pmatrix} = S \begin{pmatrix} A \\ D \end{pmatrix}. \tag{5.134}$$

From $C = A(1 - i\beta)$, we see that C depends only on A, and from the continuity at $x = b$,

$$Ae^{ikb} + Be^{-ikb} = (1 - i\beta)Ae^{ikb} + De^{-ikb}, \tag{5.135}$$

or rearranging terms and multiplying by e^{ikb},

$$B = -i\beta Ae^{2ikb} + D. \tag{5.136}$$

Therefore, the S-matrix is:

$$S = \begin{pmatrix} -i\beta e^{2ikb} & 1 \\ 1 - i\beta & 0 \end{pmatrix}. \tag{5.137}$$

P5.11 Derive in detail the formula

$$T = \frac{1}{1 + \left[\frac{1}{4}\left(\frac{q}{k} + \frac{k}{q}\right)^2 - 1\right] \sin^2(qa)} \tag{5.138}$$

for the transmission coefficient of particles through a rectangular barrier when $E > V_0$.

Solution. Consider a rectangular potential barrier of height V_0 and width a, defined by

$$V(x) = \begin{cases} 0, & x < 0, \\ V_0, & 0 \le x \le a, \\ 0, & x > a. \end{cases} \tag{5.139}$$

For the region $x < 0$, the incident and reflected waves are

$$\psi_1(x) = e^{ikx} + re^{-ikx}. \tag{5.140}$$

For $0 \le x \le a$, the transmitted and reflected waves within the barrier are

$$\psi_2(x) = Ae^{iqx} + Be^{-iqx}. \tag{5.141}$$

For $x > a$, the transmitted wave is

$$\psi_3(x) = te^{ikx}. \tag{5.142}$$

At $x = 0$, the condition of continuity of ψ gives

$$1 + r = A + B, \tag{5.143}$$

and that of ψ' gives

$$ik(1 - r) = iq(A - B) \tag{5.144}$$

Likewise, at $x = a$, we have

$$Ae^{iqa} + Be^{-iqa} = te^{ika}, \tag{5.145}$$

and

$$iq(Ae^{iqa} - Be^{-iqa}) = ikte^{ika} \tag{5.146}$$

From the conditions at $x = 0$, we express A and B in terms of r,

$$A = \frac{1}{2}\left(1 + r + \frac{k}{q}(1 - r)\right), \quad B = \frac{1}{2}\left(1 + r - \frac{k}{q}(1 - r)\right), \tag{5.147}$$

which introduced into into the conditions at $x = a$gives

$$te^{ika} = Ae^{iqa} + Be^{-iqa}, \quad \frac{q}{k}te^{ika} = Ae^{iqa} - Be^{-iqa}. \tag{5.148}$$

Solving for t and r yields

$$t = \frac{4kqe^{-ika}}{(k+q)^2e^{-iqa} - (k-q)^2e^{iqa}}, \quad r = \frac{(k^2 - q^2)\sin(qa)}{2ikq\cos(qa) + (k^2 + q^2)\sin(qa)}. \tag{5.149}$$

This gives for the transmission coefficient $T = |t|^2$

$$|t|^2 = \frac{16k^2q^2}{(k+q)^4 + (k-q)^4 - 2(k^2 - q^2)^2\cos(2qa)}. \tag{5.150}$$

Using trigonometric identities and simplifying, we obtain the final result,

$$T = \frac{1}{1 + \left[\frac{1}{4}\left(\frac{q}{k} + \frac{k}{q}\right)^2 - 1\right]\sin^2(qa)}. \tag{5.151}$$

CHAPTER 6

The WKB Approximation: Electronic Properties of Solids

P6.1 Derive **Eq. (6.56)** for the transmission coefficient T from the expression of the wave function for a rectangular barrier obtained in **[1], Chapter 5**, considering the barrier of arbitrary profile as built up by a succession of rectangular barriers that become infinitely narrow in the limit.

Solution. We will consider that the barrier extends from x_1 to x_2, and that $V(x) \geq E$, $x \in (x_1, x_2)$. We divide the barrier arbitrarily into rectangular segments; the rectangles have a width given by $\Delta x_i = x_i - x_{i-1}$, and a height $V(x_i)$. For a square barrier of width Δx_i, the transmission coefficient is given by

$$T_i = \exp\left[-\frac{2\Delta x_i}{\hbar}\sqrt{2m\left(V(x_i) - E\right)}\right]. \tag{6.1}$$

The transmission coefficient across the entire barrier is obtained by multiplying the transmission coefficients T_i of each elemental column into which the potential has been decomposed,

$$T = \prod_{i=1}^{n} \exp\left[-\frac{2\Delta x_i}{\hbar}\sqrt{2m\left(V(x_i) - E\right)}\right] \tag{6.2}$$

$$= \exp\left[-\frac{2}{\hbar}\sum_{i=1}^{n}\sqrt{2m\left(V(x_i) - E\right)}\Delta x_i\right]. \tag{6.3}$$

In the limit $\Delta x_i \to 0$ one obtains

$$T = \lim_{\Delta x_i \to 0} \exp\left[-\frac{2}{\hbar}\sum_{i=1}^{n}\sqrt{2m\left(V(x_i) - E\right)}\Delta x_i\right] \tag{6.4}$$

$$= \exp\left[-\frac{2}{\hbar}\int_{x_1}^{x_2}\sqrt{2m\left(V(x) - E\right)}\,dx\right], \tag{6.5}$$

which is the requested result.

P6.2 A particle moves in a conical potential that vanishes for $|x| > a$, has the value $-V_0$ at $x = 0$, and grows linearly from $-V_0$ to 0 in the intervals $|x| \leq a$. Study the bound states of the system using the WKB method.

Solution. The potential can be expressed as

$$V(x) = \begin{cases} 0, & x < -a; \\ -V_0\left(\frac{x}{a}+1\right) - V_1(x), & -a < x < 0; \\ V_0\left(\frac{x}{a}-1\right) - V_2(x), & 0 < x < a; \\ 0, & x > a. \end{cases} \tag{6.6}$$

Bound states are obtained when $-V_0 < E < 0$. There are two classical turning points given by

$$-V_0\left(\frac{x_1}{a}+1\right) = -E \quad \Rightarrow \quad x_1 = -\left(1 - \frac{|E|}{V_0}\right)a, \tag{6.7}$$

$$V_0\left(\frac{x_2}{a}-1\right) = -E \quad \Rightarrow \quad x_2 = \left(1 - \frac{|E|}{V_0}\right)a. \tag{6.8}$$

The WKB quantization condition gives in this case

$$J_n = \oint p\,dx = 2\pi\hbar\left(n + \frac{1}{2}\right), \tag{6.9}$$

or explicitly,

$$J_n = \int_{x_1}^{0} \sqrt{2m(E_n - V_1(x))}dx + \int_{0}^{x_2} \sqrt{2m(E_n - V_2(x))}dx \tag{6.10}$$

$$= \frac{4a}{3V_0}\sqrt{2m(E_n + V_0)^{3/2}} = \pi\hbar\left(n + \frac{1}{2}\right). \tag{6.11}$$

The allowed energy values are therefore

$$E_n = -V_0 + \left(\frac{3\pi\hbar V_0}{4a\sqrt{2m}}\right)^{2/3}\left(n + \frac{1}{2}\right)^{2/3} \tag{6.12}$$

$$= -V_0 + V_0\left(\frac{3J_n}{8a\sqrt{2mV_0}}\right)^{2/3} \tag{6.13}$$

From this expression it follows that the total number of discrete levels the well can contain is equal to $n' + 1$, where n' is the largest integer for which E_n has a negative value.

The wave function for the interval $x_1 < x < 0$ is given by

$$\psi(x) = \frac{A}{\sqrt{p}}\sin\left(\frac{1}{\hbar}\int_{x_1}^{x} p\,dx + \frac{\pi}{4}\right) \tag{6.14}$$

$$= \frac{A}{[2m(E - V_1(x))]^{1/4}}\sin\left[\frac{1}{\hbar}\int_{x_1}^{x}\sqrt{2m\left(E + V_0 + \frac{V_0}{a}x\right)}\,dx + \frac{\pi}{4}\right]. \tag{6.15}$$

For $x_1 < x < 0$, the wave function is

$$\psi(x) = \frac{A}{[2m(E - V_1(x))]^{1/4}} \sin\left[\frac{2\sqrt{2ma}}{3\hbar V_0}\left(E + V_0 + \frac{V_0}{a}x\right)^{3/2} + \frac{\pi}{4}\right]. \tag{6.16}$$

For $0 < x < x_2$, the wave function is

$$\psi(x) = \frac{A}{[2m(E - V_2)]^{1/4}} \sin\left[\frac{1}{\hbar}\int_{x_1}^{0}\sqrt{2m\left(E + V_0 + \frac{V_0}{a}x\right)}dx + \frac{1}{\hbar}\int_{0}^{x}\sqrt{2m\left(E + V_0 - \frac{V_0}{a}x\right)}dx + \frac{\pi}{4}\right], \tag{6.17}$$

which can be expressed as

$$\psi(x) = \frac{A}{[2m(E - V_2)]^{1/4}} \sin\left[\frac{4\sqrt{2ma}}{3\hbar V_0}(E + V_0)^{3/2} - \frac{2\sqrt{2ma}}{3\hbar V_0}\left(E + V_0 - \frac{V_0}{a}x\right)^{3/2} + \frac{\pi}{4}\right], \quad 0 < x < x_2. \tag{6.18}$$

Outside the well, in the regions $x < -a$ and $x > a$, $|p| = \sqrt{-2mE}$ is real and the wave functions cease to be oscillatory. For $x < -a$, we obtain

$$\psi(x) = \frac{A}{2(2m|E|)^{1/4}} \exp\left[-\frac{1}{\hbar}\int_{x}^{-a}\sqrt{2m|E|}\,dx\right] = \frac{A}{2(2m|E|)^{1/4}}\exp\left[\frac{\sqrt{2m|E|}}{\hbar}(a + x)\right], \quad x < -a. \tag{6.19}$$

Similarly, for $x > a$

$$\psi(x) = \frac{A}{2(2m|E|)^{1/4}} \exp\left[-\frac{1}{\hbar}\int_{a}^{x}\sqrt{2m|E|}\,dx\right] = \frac{A}{2(2m|E|)^{1/4}}\exp\left[-\frac{\sqrt{2m|E|}}{\hbar}(x - a)\right], \quad x > a. \tag{6.20}$$

In the region $-a < x < x_1$, which is also classically forbidden, we have $E < V_1(x) = -V_0\left(\frac{x}{a} + 1\right)$, whence $|p| = \sqrt{-2m(E - V_1)}$, and the wave function becomes

$$\psi(x) = \frac{A}{2\sqrt{|p|}}\exp\left[-\frac{1}{\hbar}\int_{x}^{x_1}|p|\,dx\right] \tag{6.21}$$

$$= \frac{A}{2\left[-2m(E-V_1)\right]^{1/4}} \exp\left[-\frac{\sqrt{2m}}{\hbar}\int_x^{x_1}\sqrt{-(E+V_0+V_0x/a)}\,dx\right], \qquad (6.22)$$

that is,

$$\psi(x) = \frac{A}{2\left[-2m\left(E-V_1\right)\right]^{1/4}} \exp\left[-\frac{2a\sqrt{2m}}{3\hbar V_0}\left(|E|-V_0-\frac{V_0}{a}x\right)^{3/2}\right] \qquad (6.23)$$

For the region $x_2 < x < a$, where $E < V_2(x) = V_0(x/a-1)$, we have $|p| = \sqrt{2m|E-V_2|}$, and the wave function becomes

$$\psi(x) = \frac{A}{2\sqrt{|p|}} \exp\left[-\frac{1}{\hbar}\int_{x_2}^{x}|p|\,dx\right] \qquad (6.24)$$

$$= \frac{A}{2\left[2m|E-V_2|\right]^{1/4}} \exp\left[-\frac{\sqrt{2m}}{\hbar}\int_{x_2}^{x}\sqrt{-\left(E+V_0-V_0\frac{x}{a}\right)}\,dx\right], \qquad (6.25)$$

that is,

$$\psi(x) = \frac{A}{2\left[2m|E-V_2|\right]^{1/4}} \exp\left[-\frac{2a\sqrt{2m}}{3\hbar V_0}\left(|E|-V_0+V_0\frac{x}{a}\right)^{3/2}\right]. \qquad (6.26)$$

P6.3 An electron with energy $E > V_0$ moves in the potential

$$V(x) = V_0\cosh^{-2}(x/a), \qquad V_0 > 0. \qquad (6.27)$$

Determine the conditions under which the WKB method is applicable and obtain the transmission coefficient through the barrier.

Solution. In order for the WKB method to be applicable, the following condition must be satisfied,

$$\frac{1}{p^2}\left|\frac{dp}{dx}\right| \ll \hbar^{-1}. \qquad (6.28)$$

For the potential $V(x) = V_0\cosh^{-2}(x/a)$, with $V_0 > 0$, the particle momentum is

$$p = \sqrt{2m\left(E - \frac{V_0}{\cosh^2(x/a)}\right)} \qquad (6.29)$$

and its derivative is

$$\frac{dp}{dx} = \frac{2mV_0\sinh(x/a)}{ap(x)\cosh^3(x/a)}. \qquad (6.30)$$

From 6.28 it follows that the WKB method is applicable to this problem if

$$\frac{\hbar}{(2mE)^{1/2}a}\cdot\frac{V_0}{E}\cdot\frac{|\sinh(x/a)|}{\left(\cosh^2(x/a)-V_0/E\right)^{3/2}} \ll 1. \qquad (6.31)$$

This condition can be easily satisfied in regions far from the barrier, characterized by $|x/a| \gg 1$, where one can approximate $\sinh(x/a) \simeq \cosh(x/a) \simeq e^{x/a}/2$. For

the region where the barrier is located, which is of interest in the present case, and assuming the ratio V_0/E does not differ much from unity, the condition demands that

$$\left(\frac{E}{V_0}\right)^3 \gg \frac{\hbar^2}{2ma^2V_0}. \tag{6.32}$$

The transmission coefficient through the barrier can be written in the form $T = e^{i\delta(E)}$, where

$$\delta(E) = \frac{\sqrt{2m}}{\hbar}\int_{-\infty}^{\infty}\left(\sqrt{E-V}-\sqrt{E}\right)dx. \tag{6.33}$$

For the present case, the integral becomes complicated,

$$\delta(E) = \frac{\sqrt{2mE}}{\hbar}\int_{-\infty}^{\infty}\left(\sqrt{1-\frac{V_0}{E\cosh^2(x/a)}}-1\right)dx. \tag{6.34}$$

We can estimate the value of this integral for V_0/E sufficiently small by noting that as $\cosh^2(x/a) \geq 1$, a first approximation gives

$$\delta(E) \simeq -\frac{V_0\sqrt{2mE}}{E\hbar}\int_0^{\infty}\frac{dx}{\cosh^2(x/a)} = -\frac{aV_0}{2\hbar}\sqrt{\frac{2m}{E}}B\left(\frac{1}{2},1\right), \tag{6.35}$$

where $B(x,y)$ is a beta function. Now using the formula relating the beta function with gamma functions,

$$B(x,y) = \int_0^1 t^{x-1}(1-t)^{y-1}dt = \frac{\Gamma(x)\Gamma(y)}{\Gamma(x+y)}, \qquad x,y>0, \tag{6.36}$$

we obtain

$$\delta(E) \simeq -\frac{aV_0}{2\hbar}\sqrt{\frac{2m}{E}}\frac{\Gamma\left(\frac{1}{2}\right)\Gamma(1)}{\Gamma\left(\frac{3}{2}\right)} = -\frac{aV_0}{\hbar}\sqrt{\frac{2m}{E}}. \tag{6.37}$$

Hence, the transmission coefficient for $E > V_0$ is

$$T \simeq \exp\left(-i\frac{aV_0}{\hbar}\sqrt{\frac{2m}{E}}\right). \tag{6.38}$$

We see that $|T|^2 \simeq 1$. This means that, although the barrier can significantly affect the phase of the wave function that crosses it, it does not affect its amplitude.

P6.4 Use the WKB method to find the quantization conditions for particles moving in a well, one of the walls of which is impenetrable.

Solution. Consider a potential well with turning points at $x_1 = 0$ (where we place the impenetrable wall) and $x_2 > 0$. The wave function inside the well can be written in the form

$$\psi(x) = \frac{A}{\sqrt{p}}\sin\left[\frac{1}{\hbar}\int_x^{x_2} p\,dx + \frac{\pi}{4}\right]. \tag{6.39}$$

Since the potential is infinite at $x = 0$, we can write

$$\psi(0) = \frac{A}{\sqrt{p}} \sin\left[\frac{1}{\hbar}\int_0^{x_2} p\,dx + \frac{\pi}{4}\right] = 0. \tag{6.40}$$

This condition can only be satisfied if

$$\frac{1}{\hbar}\int_0^{x_2} p\,dx + \frac{\pi}{4} = (n+1)\pi, \quad n = 0, 1, 2, \ldots, \tag{6.41}$$

which can be rewritten as

$$\int_0^{x_2} p\,dx = \pi\hbar\left(n + \frac{3}{4}\right). \tag{6.42}$$

Recognizing that 0 and x_2 are the classical turning points, this result can be expressed in the more conventional form

$$J_n = \oint p\,dx = 2\pi\hbar\left(n + \frac{3}{4}\right), \quad n = 0, 1, 2, \ldots. \tag{6.43}$$

P6.5 Use the WKB method to find the energy of the stationary states of particles moving inside a box with impenetrable walls. Analyze the results and compare them with the exact ones.

Solution. The quantization rule for the one-dimensional case is

$$\oint p\,dx = 2\pi\hbar\left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, \ldots \tag{6.44}$$

Applied to the infinite square well of width a and constant p, one obtains $\oint p\,dx = 2ap$, that is,

$$E_n^{\text{WKB}} = \frac{\langle p^2\rangle}{2m} = \frac{\pi^2\hbar^2}{2ma^2}\left(n + \frac{1}{2}\right)^2. \tag{6.45}$$

The exact solution is given by

$$E_n = \frac{\pi^2\hbar^2}{2ma^2}n^2. \quad n = 1, 2, 3\ldots \tag{6.46}$$

and differs from the previous expression in that one must substitute $n + \frac{1}{2} \to n + 1$, so the error introduced by the WKB approximation is

$$\frac{\Delta E_n}{E_n} = \frac{(n+1)^2 - (n+\frac{1}{2})^2}{(n+1)^2} = \frac{n+\frac{3}{4}}{(n+1)^2} \longrightarrow_{n\to\infty} \frac{1}{n}. \tag{6.47}$$

The 3D problem is equally simple to treat since the quantization rule is given by

$$\oint p_i dx_i = 2\pi\hbar\left(n + \frac{c}{4} + \frac{r}{2}\right), \quad n = 0, 1, 2, \ldots, \tag{6.48}$$

where c is the number of times the integration contour crosses the caustic surface[1] and r is the number of times this contour touches the wall. Taking the x-direction and denoting with C the integration contour one obtains

$$\oint_C p_x dx = 2\int_0^{a_1} p_x dx = 2\sqrt{2mE}a_1.$$

Since $c = 0$ and $r = 2$ in this case, it follows that

$$\sqrt{2mEa_1} = \pi\hbar(n_1 + 1). \tag{6.49}$$

P6.6 Determine the transmission coefficient for a monochromatic electron beam of energy 1000 eV and intensity 1 mA incident on a rectangular barrier of width 10Å and height of 200 eV. The barrier height is now increased to 2000 eV; determine the new transmission coefficient and compare the results.

Solution. Case 1. $V_0 = 200$ eV ($E > V_0$),

$$E = 1000\,\text{eV} = 1.602 \times 10^{-16}\ \text{J} \tag{6.50}$$

$$V_0 = 200\,\text{eV} = 3.204 \times 10^{-17}\ \text{J}. \tag{6.51}$$

The wave numbers $k = (2mE/\hbar^2)^{1/2}$ and $k = (2m(E-V)/\hbar^2)^{1/2}$ are then given by

$$k = \frac{\sqrt{2 \times 9.109 \times 10^{-31} \times 1.602 \times 10^{-16}}}{1.055 \times 10^{-34}} = 1.622 \times 10^{10}\ \text{m}^{-1} \tag{6.52}$$

$$q = \frac{\sqrt{2 \times 9.109 \times 10^{-31} \times (1.602 \times 10^{-16} - 3.204 \times 10^{-17})}}{1.055 \times 10^{-34}} \tag{6.53}$$

$$= 1.451 \times 10^{10}\ \text{m}^{-1} \tag{6.54}$$

This gives

$$qa = (1.451 \times 10^{10}) \times (10 \times 10^{-10}) = 14.51, \tag{6.55}$$

therefore, $\sin^2(14.51) \approx 0.991$. Furthermore,

$$\frac{q}{k} + \frac{k}{q} = \frac{1.451}{1.622} + \frac{1.622}{1.451} \approx 2.013. \tag{6.56}$$

Consequently,

$$T = \frac{1}{1 + \left[\frac{1}{4}(2.013)^2 - 1\right] \times 0.991} \approx 0.987 \tag{6.57}$$

Case 2. $E < V_0$. In this case the electrons tunnel across the potential barrier, and the transmission coefficient is given by

$$T = \frac{1}{1 + \left(\frac{k^2+\kappa^2}{2k\kappa}\right)^2 \sinh^2(\kappa a)}, \tag{6.58}$$

[1]A caustic surface is the envelope surface of rays reflected or refracted by a curved surface.

where

$$\kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \tag{6.59}$$

For $V_0 = 2000$ eV,

$$V_0 = 2000 \times 1.602 \times 10^{-19} = 3.204 \times 10^{-16} \text{ J}, \tag{6.60}$$

and the values of the poarameters are

$$k = 1.622 \times 10^{10} \text{ m}^{-1}, \tag{6.61}$$

$$\kappa = \frac{\sqrt{2 \times 9.109 \times 10^{-31} \times (3.204 \times 10^{-16} - 1.602 \times 10^{-16})}}{1.055 \times 10^{-34}} \tag{6.62}$$

$$= 1.622 \times 10^{10} \text{ m}^{-1}, \tag{6.63}$$

which gives

$$\kappa a = 16.22, \tag{6.64}$$

and

$$\sinh^2(16.22) \approx 3.0 \times 10^{13}. \tag{6.65}$$

Furthermore,

$$\frac{k^2 + \kappa^2}{2k\kappa} = 1. \tag{6.66}$$

Consequently,

$$T \approx 3.3 \times 10^{-14}. \tag{6.67}$$

When $V_0 = 200$ eV, there is high transmission ($T \approx 98.7\%$) of electrons with an energy of 1000 eV, meaning the barrier is "transparent". However, for $V_0 = 2000$ eV, transmission is negligible ($T \approx 3.3 \times 10^{-12}\%$), meaning the barrier is effectively opaque due to minimal tunneling of electrons with the same energy.

P6.7 Use the WKB method to determine the energy levels of a one-dimensional harmonic oscillator. Discuss your result.

Solution. We begin by applying the quantization rule

$$\oint p(x)\, dx = 2\pi\hbar \left(n + \frac{1}{2} \right) \qquad n = 0, 1, 2, ..., \tag{6.68}$$

where the integral is taken over the entire classical period of motion between the turning points. The classical momentum $p(x)$ is given by

$$p(x) = \sqrt{2m\,(E - V(x))}. \tag{6.69}$$

In the case of the harmonic oscillator, the potential energy is $V(x) = \frac{1}{2}m\omega^2 x^2$, so the classical momentum becomes

$$p(x) = \sqrt{2m\left(E - \frac{1}{2}m\omega^2 x^2 \right)} = m\omega\sqrt{\frac{2E}{m\omega^2} - x^2} = m\omega\sqrt{a^2 - x^2}, \tag{6.70}$$

where $a^2 \equiv 2E/m\omega^2$. The classical turning points correspond to the positions where the total energy equals the potential energy (Fig. 6.1),

$$E = \frac{1}{2}m\omega^2 x^2 \quad \Rightarrow \quad x = \pm\sqrt{\frac{2E}{m\omega^2}}. = \pm a. \tag{6.71}$$

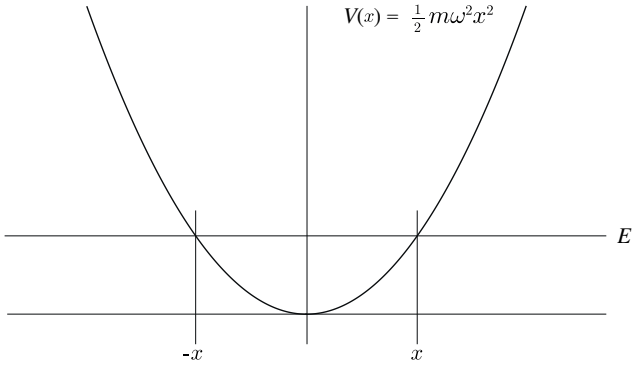

FIGURE 6.1. Turning points of the harmonic oscillator potential.

Inserting this into the quantization condition:

$$\oint p\,dx = 2\int_{-a}^{a} m\omega\sqrt{a^2 - x^2}\,dx = 2m\omega \cdot \frac{\pi a^2}{2} = \pi m\omega a^2, \tag{6.72}$$

and substituting the result of the integral into the quantization rule

$$\pi m\omega a^2 = 2\pi\hbar\left(n + \frac{1}{2}\right), \tag{6.73}$$

and solving for E, we obtain the energy levels,

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \qquad n = 0, 1, 2, ... \tag{6.74}$$

This result coincides with the known energy spectrum of the quantum harmonic oscillator, showing that the WKB approximation yields an exact result in this case.

P6.8 Use the WKB method to find the ratio between the width and depth of a one-dimensional square well that is required for no bound state to exist.

Solution. Consider a 1D square potential well of width a (extending from $x = -a/2$ to $x = a/2$) and depth V_0 ($V(x) = -V_0$ inside the well and $V(x) = 0$ outside).

The WKB method gives for a potential well

$$\int_{x_1}^{x_2} \sqrt{\frac{2m}{\hbar^2}(E - V(x))}\,dx = \left(n + \frac{1}{2}\right)\pi, \tag{6.75}$$

where x_1 and x_2 are classical turning points (where $E = V(x)$), and n is a non-negative integer quantum number ($n = 0, 1, 2, \ldots$). For a square well with $V(x) = -V_0$ inside the well, the energies of the bound states are negative. The turning points are situated at $x = \pm a/2$. Therefore, for the ground state ($n = 0$), the WKB condition reduces to

$$\int_{-a/2}^{a/2} \sqrt{\frac{2m}{\hbar^2}(E + V_0)}\, dx = \frac{\pi}{2} \tag{6.76}$$

Since the integrand is constant inside the well, this gives

$$\sqrt{\frac{2m}{\hbar^2}(V_0 - |E|)} \cdot a = \frac{\pi}{2}. \tag{6.77}$$

In the limit where the ground state disappears ($E \to 0$), this becomes

$$\sqrt{\frac{2mV_0}{\hbar^2}} \cdot a = \frac{\pi}{2} \tag{6.78}$$

Therefore, for no bound states to exist (not even the ground state), the condition

$$\sqrt{\frac{2mV_0}{\hbar^2}} \cdot a < \frac{\pi}{2} \tag{6.79}$$

must hold, which expressed in terms of a and V_0 becomes

$$a\sqrt{V_0} < \frac{\pi\hbar}{2\sqrt{2m}}. \tag{6.80}$$

P6.9 Use the semiclassical approximation to determine the average value of the kinetic energy of a stationary state.

Solution. In the semiclassical (WKB) approximation, the wave function has the general form

$$\psi(x) = \frac{C}{\sqrt{|p(x)|}} \exp\left[\pm\frac{i}{\hbar}\int^x p(x')\, dx'\right], \tag{6.81}$$

where C is a normalization constant. Taking the squared modulus, we find

$$|\psi(x)|^2 = \psi^*\psi = \frac{C^2}{p(x)}, \tag{6.82}$$

where we have used that $p(x) > 0$ in the classically allowed region. To determine the constant C, we assume that the total probability is normalized to one within the classically allowed region, so the normalization condition becomes

$$\int_{x_1}^{x_2} \frac{|C|^2}{p(x)} dx = 1, \tag{6.83}$$

which gives

$$|C|^2 = \left(\int_{x_1}^{x_2} \frac{1}{p(x)} dx \right)^{-1}. \tag{6.84}$$

To evaluate this integral semiclassically, we recall that the classical period of oscillation T_{osc} is given by:

$$T_{\text{osc}} = \oint \frac{dx}{v(x)} = 2 \int_{x_1}^{x_2} \frac{dx}{v(x)} = 2m \int_{x_1}^{x_2} \frac{dx}{p(x)}, \tag{6.85}$$

so that

$$\int_{x_1}^{x_2} \frac{dx}{p(x)} = \frac{T_{\text{osc}}}{2m}. \tag{6.86}$$

For the harmonic oscillator, the period is known to be $T_{\text{osc}} = 2\pi/\omega$, hence

$$\int_{x_1}^{x_2} \frac{dx}{p(x)} = \frac{\pi}{m\omega}, \tag{6.87}$$

and therefore the normalization constant is

$$|C|^2 = \frac{m\omega}{\pi}. \tag{6.88}$$

The classical expression for the kinetic energy is

$$T(x) = \frac{p(x)^2}{2m}. \tag{6.89}$$

Therefore, the semiclassical approximation for the expectation value of the kinetic energy is

$$\langle T \rangle = \int \psi^*(x) \frac{p(x)^2}{2m} \psi(x)\, dx \tag{6.90}$$

$$= \frac{|C|^2}{2m} \int \frac{p(x)^2}{p(x)}\, dx = \frac{|C|^2}{2m} \int p(x)\, dx. \tag{6.91}$$

Again, the classically allowed region is bounded by the turning points x_1 and x_2, which satisfy the condition $E = V(x)$. Therefore, the expectation value of the kinetic energy becomes

$$\langle T \rangle = \frac{|C|^2}{2m} \int_{x_1}^{x_2} p(x)\, dx. \tag{6.92}$$

Using the semiclassical quantization rule,

$$\oint p(x)\, dx = 2\pi\hbar \left(n + \frac{1}{2} \right), \tag{6.93}$$

we have that

$$\int_{x_1}^{x_2} p(x)\, dx = \frac{1}{2} \oint p(x)\, dx = \pi\hbar \left(n + \frac{1}{2} \right). \tag{6.94}$$

Thus, using (6.88) we get for the average value of the kinetic energy in the semi-classical approximation

$$\langle T\rangle = \frac{\hbar\omega}{2}\left(n+\frac{1}{2}\right) \tag{6.95}$$

for any (1D) stationary state.

P6.10 Apply the reasoning used to arrive at **Eq. (6.91)** in [**1**], to obtain the formulae for the density of states as a function of the maximum energy level:

a) for a 2D layer,

b) for a 1D wire.

Solution. a) We assume that electrons can move freely within a two-dimensional, square, metallic sheet with a surface area L^2. Following the reasoning used to arrive at Eq. (6.91), the momentum states in 2D ($i = x, y$) are

$$p_i = \frac{2\pi\hbar}{L}n_i, \quad \Delta n_i \to \frac{L}{2\pi\hbar}dp_i, \tag{6.96}$$

$$\Delta^2 n = \frac{L^2}{(2\pi\hbar)^2}d^2p. \tag{6.97}$$

In polar coordinates ($d^2p = 2\pi p\, dp$) and taking into account the two spin states,

$$dN = 2\cdot\frac{L^2}{(2\pi\hbar)^2}2\pi p\, dp = \frac{L^2 p}{\pi\hbar^2}dp, \tag{6.98}$$

or using $E = \frac{p^2}{2m}$,

$$dN = \frac{L^2 m}{\pi\hbar^2}dE. \tag{6.99}$$

The density of states per unit area is therefore determined by the maximum energy level E_F according to

$$\rho_{2D} = \frac{mE_F}{\pi\hbar^2}. \tag{6.100}$$

b) Now, let us consider a one-dimensional wire of length L. Following the same reasoning, with $p = \frac{2\pi\hbar}{L}n$ and taking into account the two spin states,

$$dN = 2\cdot\frac{L}{2\pi\hbar}dp = \frac{L}{\pi\hbar}dp, \tag{6.101}$$

therefore,

$$\rho_{1D} = \frac{N}{L} = \frac{p_F}{\pi\hbar} \tag{6.102}$$

where p_F is the maximum value of the momentum. In terms of $E_F = p_F^2/2m$,

$$\rho_{1D} = \frac{\sqrt{2mE_F}}{\pi\hbar}. \tag{6.103}$$

Note that, in general, the density of states is proportional to E_F^s, where s equals the number of dimensions of the system divided by 2.

P6.11 Consider an infinite 1D periodic potential $V(x) = V(x + a)$. Starting from the Schrödinger equation for ψ_k as an eigenfunction corresponding to the energy E_k, obtain the Schrödinger equation for $u_k(x)$.

Solution. For any 1D periodic potential, the wave function can be written using the Bloch formula

$$\psi_n(x) = Ae^{i\varkappa x}u_n(x), \tag{6.104}$$

We substitute this expression into the Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} + V(x)\psi_n = E_n\psi_n. \tag{6.105}$$

First, we compute the derivatives:

$$\frac{d\psi_n}{dx} = A\left(i\varkappa e^{i\varkappa x}u_n(x) + e^{i\varkappa x}\frac{du_n}{dx}\right), \tag{6.106}$$

$$\frac{d^2\psi_n}{dx^2} = A\left(-\varkappa^2 e^{i\varkappa x}u_n(x) + 2i\varkappa e^{i\varkappa x}\frac{du_n}{dx} + e^{i\varkappa x}\frac{d^2u_n}{dx^2}\right). \tag{6.107}$$

and introduce them into the Schrödinger equation,

$$-\frac{\hbar^2}{2m}A\left(-\varkappa^2 e^{i\varkappa x}u_n + 2i\varkappa e^{i\varkappa x}\frac{du_n}{dx} + e^{i\varkappa x}\frac{d^2u_n}{dx^2}\right) + V(x)Ae^{i\varkappa x}u_n = E_nAe^{i\varkappa x}u_n. \tag{6.108}$$

By dividing both sides by $Ae^{i\varkappa x}$ we get

$$-\frac{\hbar^2}{2m}\left(-\varkappa^2 u_n + 2i\varkappa\frac{du_n}{dx} + \frac{d^2u_n}{dx^2}\right) + V(x)u_n = E_nu_n. \tag{6.109}$$

This yields the effective Schrödinger equation for $u_n(x)$:

$$-\frac{\hbar^2}{2m}\left(\frac{d}{dx} + i\varkappa\right)^2 u_n + V(x)u_n = E_nu_n. \tag{6.110}$$

Equation (6.104) is a special instance of Floquet's theorem. This theorem is used to find solutions to linear, second-order, homogeneous differential equations with periodic coefficients, writing them as the product of a periodic function and an exponential function with a constant coefficient. Therefore, it can also be used to analyze systems with time-periodic potentials.

P6.12 Find the energy bands for the periodic potential

$$V(x) = g\sum_{n=-\infty}^{\infty}\delta(x - na),g, a > 0. \tag{6.111}$$

Solution. Our task is to find the energy ranges $E(k)$ that can be occupied by a particle of mass m in this potential, where k is the wave vector.

Between two delta potentials ($na < x < (n+1)a$), $V(x) = 0$ and the general solution of the Schrödinger equation is

$$\psi(x) = A_n e^{iqx} + B_n e^{-iqx}, \quad \text{where} \quad q = \sqrt{\frac{2mE}{\hbar^2}}. \tag{6.112}$$

At $x = na$, $\psi(x)$ must satisfy continuity

$$\psi(na^+) = \psi(na^-), \tag{6.113}$$

and derivative discontinuity due to the delta potential

$$\psi'(na^+) - \psi'(na^-) = \frac{2mg}{\hbar^2}\psi(na). \tag{6.114}$$

Due to periodicity, $\psi(x)$ satisfies Bloch's theorem

$$\psi(x + a) = e^{ika}\psi(x). \tag{6.115}$$

This implies

$$\begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix} = e^{ika} \begin{pmatrix} A_n \\ B_n \end{pmatrix}. \tag{6.116}$$

Applying the matching conditions at $x = 0$ and $x = a$ yields a system of equations for A_0 and B_0. The condition for non-trivial solutions requires the determinant of the coefficient matrix to vanish,

$$\cos(ka) = \cos(qa) + \frac{mg}{\hbar^2 q}\sin(qa). \tag{6.117}$$

This is the dispersion relation that determines the energy bands $E(k)$. The equation can be rewritten as

$$\cos(ka) = \cos(qa) + \lambda\frac{\sin(qa)}{qa}, \quad \text{where} \quad \lambda = \frac{mga}{\hbar^2}. \tag{6.118}$$

In the allowed bands, k must be real,

$$\left|\cos(qa) + \lambda\frac{\sin(qa)}{qa}\right| \leq 1. \tag{6.119}$$

The energy bands correspond to values of E (or q) that satisfy the inequality. In the gaps, that is, for values of q that satisfy the condition

$$\left|\cos(qa) + \lambda\frac{\sin(qa)}{qa}\right| > 1, \tag{6.120}$$

no electronic states exist.

In the case of a weak potential ($\lambda \ll 1$), the bands are nearly those of a free particle ($E \approx \frac{\hbar^2 k^2}{2m}$), with small gaps at $k = \pm\pi/a$. In strong potentials ($\lambda \gg 1$) the bands narrow around the energy levels of an isolated well ($E_n \approx -\frac{mg^2}{2\hbar^2 n^2}$), with large gaps.

Inserting the values for q and λ given above, the energy bands $E(k)$ for the periodic Dirac delta potential become determined by the dispersion relation

$$\cos(ka) = \cos\left(\sqrt{\frac{2mE}{\hbar^2}}a\right) + \frac{mg}{\hbar^2\sqrt{2mE/\hbar^2}}\sin\left(\sqrt{\frac{2mE}{\hbar^2}}a\right). \tag{6.121}$$

P6.13 Estimate the minimum energy of the first allowed band for the previous problem, when $\lambda = 8$ and $g/a = 1\,\text{eV}$.

Solution. We use Eq. (6.118) derived in the previous problem and define the variable $x \equiv qa$, so that the equation becomes:

$$\cos(x) + \frac{\lambda}{x}\sin(x) = \cos(ka). \tag{6.122}$$

The minimum energy of the first allowed band corresponds to the lowest possible energy for which a solution exists. This occurs when the right-hand side is maximal, that is, when $\cos(ka) = 1$. Substituting the given value $\lambda = 8$ yields the transcendental equation

$$\cos(x) + \frac{8}{x}\sin(x) = 1. \tag{6.123}$$

Solving this numerically gives

$$x \approx 2.53. \tag{6.124}$$

With $x = qa = a\sqrt{2mE/\hbar^2}$, we get for the energy

$$\sqrt{\frac{2mE_{\text{min}}}{\hbar^2}} = \frac{x}{a} \quad \Rightarrow \quad E_{\text{min}} = \frac{x^2\hbar^2}{2ma^2}. \tag{6.125}$$

From the definition of the dimensionless parameter $\lambda = \frac{gma}{\hbar^2}$, we can isolate $\frac{1}{a^2}$ as follows

$$\frac{1}{a^2} = \left(\frac{g}{a}\right)\left(\frac{m}{\hbar^2\lambda}\right). \tag{6.126}$$

Substituting this into the expression for E_{min} gives

$$E_{\text{min}} = \frac{x^2\hbar^2}{2m}\cdot\left(\frac{g}{a}\cdot\frac{m}{\hbar^2\lambda}\right) = \frac{x^2}{2\lambda}\cdot\frac{g}{a}, \tag{6.127}$$

Using the given values $\lambda = 8$, $\frac{g}{a} = 1\,\text{eV}$, and $x \approx 2.53$, we obtain

$$E_{\text{min}} = \frac{1}{8}\cdot\frac{(2.53)^2}{2} \approx 0.4\,\text{eV}. \tag{6.128}$$

The same procedure can be used to obtain the maximum energy of the first band by taking $\cos(ka) = -1$. At very low temperatures the electrons cannot travel freely the crystal is an insulator. At room temperature, $kT \simeq 10^{-2}\,\text{eV}$, some electrons acquire enough energy to move and contribute to the electric current; for this reason, the material is called a semiconductor.

CHAPTER 7

The Free Particle. The Time-Dependent Schrödinger Equation

P7.1 Prove in detail the following properties of the Dirac delta function:

a) $\delta(x) = \delta(-x)$,

b) $a\delta(ax) = \delta(x)$, $a > 0$,

c) $\delta\left(x^2 - a^2\right) = \frac{1}{2a}\left[\delta(x-a) + \delta(x+a)\right]$,

d) $\delta\left[f(x)\right] = \sum_i \frac{\delta(x-x_i)}{|f'(x_i)|}$, where x_i are the roots of $f(x_i) = 0$.

Solution. In one dimension, the Dirac delta function is defined as a generalized function with the following properties,

$$\delta(x) = 0, \quad \forall\, x \neq 0, \tag{7.1}$$

$$\int_{-\infty}^{\infty} \delta(x)\, dx = 1, \tag{7.2}$$

$$\int_{-\infty}^{\infty} f(x)\delta(x)\, dx = f(0). \tag{7.3}$$

Recall that the Dirac delta is not a regular function but rather a distribution, whose properties are well-defined when appearing under an integral sign, as in the cases above.

a) Symmetry property. Consider an integrable function $f(x)$ that is otherwise arbitrary. Using a change of variables and repeatedly applying this property, we get

$$\int_{-\infty}^{\infty} f(x)\delta(-x)\, dx = \int_{-\infty}^{\infty} f(-x')\delta(x')\, dx' = f(0) = \int_{-\infty}^{\infty} f(x)\delta(x)\, dx. \tag{7.4}$$

Since $f(x)$ is arbitrary, it follows that

$$\delta(x) = \delta(-x). \tag{7.5}$$

b) Scaling property. For $a > 0$, we perform the substitution $y = ax$ to obtain

$$\int_{-\infty}^{\infty} f(x)\, \delta(ax)\, dx = \frac{1}{a}\int_{-\infty}^{\infty} f\left(\frac{y}{a}\right)\, \delta(y)\, dy = \frac{1}{a} f(0) = \frac{1}{a}\int_{-\infty}^{\infty} f(x)\, \delta(x)\, dx, \tag{7.6}$$

which implies the scaling property

$$\delta(ax) = \frac{1}{a}\delta(x). \tag{7.7}$$

For the case $a < 0$, the same substitution $y = ax$ reverses the integration limits

$$\int_{-\infty}^{\infty} \delta(ax) f(x)\, dx = \frac{1}{a} \int_{-\infty}^{\infty} \delta(y) f\left(\frac{y}{a}\right)\, dy = -\frac{1}{a} f(0). \tag{7.8}$$

Therefore, the general scaling property for any non-zero a is

$$\delta(ax) = \frac{1}{|a|}\delta(x), \quad a \neq 0. \tag{7.9}$$

c) Delta function of quadratic arguments. We write

$$\delta(x^2 - a^2) = \delta[(x + a)(x - a)] \tag{7.10}$$

and observe that $\delta(x^2 - a^2)$ is non-zero only at the points $x = \pm a$. Therefore,

$$\int_{-\infty}^{\infty} \delta(x^2-a^2) f(x)\, dx = \int_{-a-\epsilon}^{-a+\epsilon} \delta[(x+a)(x-a)] f(x)\, dx + \int_{a-\epsilon}^{a+\epsilon} \delta[(x+a)(x-a)] f(x)\, dx, \tag{7.11}$$

where $0 < \epsilon < 2a$ and ϵ can be arbitrarily small.

Near $x = -a$, the factor $(x - a)$ can be replaced by $-2a$ in the first integral, allowing us to write

$$\int_{-a-\epsilon}^{-a+\epsilon} \delta[(x + a)(x - a)] f(x)\, dx = \int_{-a-\epsilon}^{-a+\epsilon} \delta[-2a(x + a)] f(x)\, dx \tag{7.12}$$

$$= \int_{-a-\epsilon}^{-a+\epsilon} \delta[2a(x + a)] f(x)\, dx = \frac{1}{2a} \int_{-\infty}^{\infty} \delta(x + a) f(x)\, dx, \tag{7.13}$$

where we have extended the integration limits. Similarly, we can show that

$$\int_{a-\epsilon}^{a+\epsilon} \delta[(x + a)(x - a)] f(x)\, dx = \frac{1}{2a} \int_{-\infty}^{\infty} \delta(x - a) f(x)\, dx. \tag{7.14}$$

Combining the two results gives

$$\int_{-\infty}^{\infty} \delta(x^2 - a^2) f(x)\, dx = \frac{1}{2a} \left[\int_{-\infty}^{\infty} \delta(x + a) f(x)\, dx + \int_{-\infty}^{\infty} \delta(x - a) f(x)\, dx \right] \tag{7.15}$$

and therefore,

$$\delta(x^2 - a^2) = \frac{1}{2a} \left[\delta(x + a) + \delta(x - a)\right]. \tag{7.16}$$

d) Delta function of general functions. Consider an arbitrary integrable function $g(x)$ and the integral

$$\int_{-\infty}^{\infty} g(x)\delta(f(x))\, dx. \tag{7.17}$$

Using the change of variables $y = f(x)$ with $dy = f'(x)dx$, we obtain

$$\int_{-\infty}^{\infty} g(x)\delta(f(x))\, dx = \int_{y=f(-\infty)}^{y=f(\infty)} \frac{h(y)}{f'(x(y))}\delta(y)\, dy = \sum_i \left.\frac{h(y)}{f'(x)}\right|_{x_i}, \tag{7.18}$$

where $h(y) = g(x(y))$ and x_i are the points satisfying $f(x_i) = 0$. Therefore,

$$\int_{-\infty}^{\infty} g(x)\delta(f(x))\,dx = \sum_i \left.\frac{g(x)}{|f'(x)|}\right|_{x_i}. \tag{7.19}$$

Using the properties of the Dirac delta, we can write

$$\sum_i \left.\frac{g(x)}{|f'(x)|}\right|_{x_i} = \sum_i \int_{-\infty}^{\infty} \frac{g(x)}{|f'(x)|}\delta(x - x_i)\,dx = \int_{-\infty}^{\infty} g(x)\delta[f(x)]\,dx. \tag{7.20}$$

Since $g(x)$ is arbitrary, this implies

$$\delta[f(x)] = \sum_i \frac{\delta(x - x_i)}{|f'(x_i)|}, \quad \text{where } f(x_i) = 0. \tag{7.21}$$

An important property of the Dirac delta relates to its derivatives,

$$\int_{-\infty}^{\infty} f(x)\delta^{(n)}(x)\,dx = (-1)^n f^{(n)}(0), \tag{7.22}$$

where $\delta^{(n)}$ and $f^{(n)}$ denote the n-th derivatives. This expression can be demonstrated through integration by parts (treating $\delta^{(n)}(x)$ under the integral sign as an ordinary function),

$$\int_{-\infty}^{\infty} f(x)\delta'(x)dx = f(x)\delta(x)|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} f'(x)\delta(x)dx = -f'(0). \tag{7.23}$$

By repeating this process n times, we obtain the general result for the n-th derivative.

The Dirac delta function is commonly considered as the derivative of the Heaviside step function $H(x)$, defined as:

$$H(x) = \begin{cases} 1, & \text{if } x > 0; \\ 0, & \text{if } x < 0. \end{cases} \tag{7.24}$$

To understand this relationship, consider the following Stieltjes integral for an integrable function $f(x)$,

$$\int_{-\infty}^{\infty} f(x)\,dH(x) = f(0). \tag{7.25}$$

Comparing this with the fundamental property of the Dirac delta, we establish the equivalence $dH(x) \to \delta(x)dx$. This reveals that the Dirac delta is more properly understood not as a function, but as a Stieltjes measure. Its widespread use in physics provides a practical way to evaluate Stieltjes-type integrals.

P7.2 Show that the normal distribution

$$\rho(x, \sigma) = \frac{1}{\sqrt{2\pi\sigma}} e^{-(x-a)^2/2\sigma^2} \tag{7.26}$$

has the property $\lim_{\sigma\to 0}\rho(x,\sigma)=\delta(x-a)$.

Solution. This property was qualitatively observed in problem P4.1, where it was shown that in the limit $\sigma\to 0$, $\rho(x)=0$ if $x\neq a$, but $\rho(x)=\infty$ if $x=a$. To complete the proof, it is enough to take an arbitrary integrable function $f(x)$ and consider the integral

$$\lim_{\sigma\to 0^+}\frac{1}{\sqrt{2\pi\sigma}}\int_{-\infty}^{\infty}f(x)e^{-(x-a)^2/2\sigma^2}dx=f(a). \tag{7.27}$$

To arrive at this result, it was noted that with $\sigma>0$ but arbitrarily small, the exponential is negligible for all $x\neq a$, so the only contribution to the integral comes from a small neighborhood of $x=a$. We can therefore approximate $f(x)$ by the constant $f(a)$, which leads to 7.27 because $\rho(x,\sigma)$ is normalized to unity.

P7.3 When the Jacobian of a transformation from x_i to ξ_i vanishes, the transformation is no longer one-to-one. For example, at the origin of a polar system, $x=y=0$ and $r=0$, but θ has an arbitrary value. A coordinate that has no determinate value at a singular point of a transformation (where the Jacobian vanishes), is called an ignorable variable. Show that if there are ignorable variables, the transformation equation should be changed to

$$\delta(x_1-\alpha_1)...\delta(x_n-\alpha_n)=\frac{\delta(\xi_1-\beta_1)...\delta(\xi_n-\beta_n)}{|J_k|}, \tag{7.28}$$

where ξ_i, $i=1,2,...k$ are the non-ignorable variables, and $J_k=\int...\int Jd\xi_{k+1}...d\xi_n$, where J is the Jacobian of the transformation and the integral is performed over the ignorable variables.

Solution. In three-dimensional Cartesian space, the Dirac delta function can be written as

$$\delta(\boldsymbol{x}-\boldsymbol{x}_0)=\delta(x_1-x_{01})\delta(x_2-x_{02})\delta(x_3-x_{03}), \tag{7.29}$$

with the normalization condition

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\delta(x_1-x_{01})\delta(x_2-x_{02})\delta(x_3-x_{03})\,dx_1dx_2dx_3=1. \tag{7.30}$$

In n-dimensional space, we have

$$\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\delta(x_1-x_{01})\cdots\delta(x_n-x_{0n})\,dx_1\cdots dx_n=1. \tag{7.31}$$

Under the coordinate transformation $\{x_i\}\to\{\xi_i\}$, the volume element becomes

$$dx_1\cdots dx_n=|J|\,d\xi_1\cdots d\xi_n, \tag{7.32}$$

where J is the transformation Jacobian. Thus,

$$\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\delta(x_1-x_{01})\cdots\delta(x_n-x_{0n})|J|\,d\xi_1\cdots d\xi_n=1. \tag{7.33}$$

In any coordinate space, the following normalization must hold,

$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \delta(\xi_1 - \beta_1) \cdots \delta(\xi_n - \beta_n)\, d\xi_1 \cdots d\xi_n = 1. \tag{7.34}$$

From this and previous expressions, we derive the transformation rule

$$\delta(x_1 - x_{01}) \cdots \delta(x_n - x_{0n}) = \frac{\delta(\xi_1 - \beta_1) \cdots \delta(\xi_n - \beta_n)}{|J|}, \tag{7.35}$$

where β_i corresponds to x_{0i} in the transformed coordinate system.

Consider $(x_{01}, \ldots, x_{0n})$ as a singular point where $|J| = 0$, such that $x_{0i} \to \beta_i$ is well-defined for $i = 1, \ldots, k$ and the remaining $\xi_{k+1}, \ldots, \xi_n$ are ignorable coordinates. The fundamental relation

$$\int \cdots \int \delta(\boldsymbol{x} - \boldsymbol{x}_0)|J|\, d\xi_1 \cdots d\xi_n = 1 \tag{7.36}$$

remains valid, but $\delta(\boldsymbol{x} - \boldsymbol{x}_0) = \varphi(\xi_1, \ldots, \xi_k)$ depends only on the first k variables. Therefore

$$1 = \int \cdots \int \varphi(\xi_1, \ldots, \xi_k)|J|\, d\xi_1 \cdots d\xi_n \tag{7.37}$$

$$= \int \cdots \int \varphi(\xi_1, \ldots, \xi_k)\, d\xi_1 \cdots d\xi_k \int \cdots \int |J|\, d\xi_{k+1} \cdots d\xi_n \tag{7.38}$$

$$= \int \cdots \int \varphi(\xi_1, \ldots, \xi_k)|J_k|\, d\xi_1 \cdots d\xi_k \tag{7.39}$$

$$= \int \cdots \int \delta(\mathbf{x} - \mathbf{x}_0)|J_k|\, d\xi_1 \cdots d\xi_k, \tag{7.40}$$

where the reduced Jacobian is given by

$$|J_k| = \int \cdots \int |J|\, d\xi_{k+1} \cdots d\xi_n. \tag{7.41}$$

Since the k-dimensional delta function satisfies

$$\int \cdots \int \delta(\xi_1 - \beta_1) \cdots \delta(\xi_k - \beta_k)\, d\xi_1 \cdots d\xi_k = 1, \tag{7.42}$$

we obtain the generalized transformation formula for singular points,

$$\delta(x_1 - x_{01}) \cdots \delta(x_n - x_{0n}) = \frac{\delta(\xi_1 - \beta_1) \cdots \delta(\xi_k - \beta_k)}{|J_k|}. \tag{7.43}$$

This completes the proof for coordinate transformations involving ignorable variables at singular points.

P7.4 Show that in the plane we can write

$$\delta(x - x_0)\delta(y - y_0) = \frac{\delta(r - r_0)\delta(\theta - \theta_0)}{r} \quad (r_0 \neq 0) \tag{}$$

where r and θ are the polar variables. At the origin θ is ignorable. Show that at this point we must write

$$\delta(x)\delta(y) = \frac{\delta(r)}{2\pi r}. \tag{7.44}$$

Solution. The polar coordinates are defined by $x = r\cos\theta, \qquad y = r\sin\theta$, which gives

$$|J| = r. \tag{7.45}$$

From the results of the previous exercise it follows that

$$\delta(x - x_0)\delta(y - y_0) = \frac{\delta(r - r_0)\delta(\theta - \theta_0)}{r}, \qquad r_0 \neq 0. \tag{7.46}$$

Now, at the origin the variable θ is ignorable, but the results from the previous problem allow us to write

$$\delta(x)\delta(y) = \frac{\delta(r)}{|J_r|}, \tag{7.47}$$

with

$$|J_r| = \int_0^{2\pi} |J|\, d\theta = 2\pi r. \tag{7.48}$$

Therefore,

$$\delta(x)\delta(y) = \frac{\delta(r)}{2\pi r}. \tag{7.49}$$

P7.5 Consider a free-particle wave function that at $t = 0$ has the form $\varphi(x)e^{ip_0x/\hbar}$, where $\varphi(x)$ is real and differs from 0 only for values of x in the interval $(-\delta, \delta)$. Find the interval of x in which the wave function is significantly different from zero at time t.

Solution. We express the initial wave function in terms of its Fourier transform

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \tilde{\Psi}(p, 0)e^{ipx/\hbar}dp, \tag{7.50}$$

where $\tilde{\Psi}(p, 0)$ is the Fourier transform of $\Psi(x, 0)$,

$$\tilde{\Psi}(p, 0) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \varphi(x)e^{i(p_0-p)x/\hbar}dx. \tag{7.51}$$

Since $\varphi(x)$ is localized in $(-\delta, \delta)$, the integral reduces to

$$\tilde{\Psi}(p, 0) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\delta}^{\delta} \varphi(x)e^{i(p_0-p)x/\hbar}dx. \tag{7.52}$$

This transform $\tilde{\Psi}(p, 0)$ is significant for values of p close to p_0, since $\varphi(x)$ acts as an envelope function that limits the contribution of the momenta.

For a free particle, the wave function at $t > 0$ is obtained through the time evolution of each momentum component

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \tilde{\Psi}(p,0) e^{i(px - E_p t)/\hbar} dp, \tag{7.53}$$

where $E_p = p^2/2m$. Substituting $\tilde{\Psi}(p,0)$,

$$\Psi(x,t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \left(\int_{-\delta}^{\delta} \varphi(x') e^{i(p_0 - p)x'/\hbar} dx' \right) e^{i(px - \frac{p^2 t}{2m})/\hbar} dp. \tag{7.54}$$

Interchanging the order of integration,

$$\Psi(x,t) = \frac{1}{2\pi\hbar} \int_{-\delta}^{\delta} \varphi(x') e^{ip_0 x'/\hbar} \left(\int_{-\infty}^{\infty} e^{ip(x-x')/\hbar - \frac{ip^2 t}{2m\hbar}} dp \right) dx'. \tag{7.55}$$

The integral over p is a Gaussian that can be evaluated by completing the square

$$\int_{-\infty}^{\infty} e^{ip(x-x')/\hbar - \frac{ip^2 t}{2m\hbar}} dp = \sqrt{\frac{2\pi m\hbar}{it}} e^{im(x-x')^2/(2\hbar t)}. \tag{7.56}$$

Thus,

$$\Psi(x,t) = \sqrt{\frac{m}{2\pi\hbar i t}} \int_{-\delta}^{\delta} \varphi(x') e^{ip_0 x'/\hbar} e^{im(x-x')^2/(2\hbar t)} dx'. \tag{7.57}$$

The term $e^{im(x-x')^2/(2\hbar t)}$ oscillates rapidly unless $x - x' \approx \frac{p_0}{m} t$. Therefore, the integral is significant when

$$x \approx \frac{p_0}{m} t + x', \tag{7.58}$$

where $x' \in (-\delta, \delta)$. This implies that the wave packet moves with velocity $v_g = p_0/m$ and spreads due to the dispersion of momenta. The center of the packet moves as

$$x_{\text{center}}(t) = \frac{p_0}{m} t. \tag{7.59}$$

The width of the packet grows with time due to the initial spread δ and the momentum dispersion $\Delta p \approx \hbar/\delta$. The width at $t > 0$ is

$$\Delta x(t) \approx \delta + \frac{\hbar t}{m\delta}. \tag{7.60}$$

Therefore, the wave function is significantly different from zero in the interval

$$x \in \left(\frac{p_0 t}{m} - \delta - \frac{\hbar t}{m\delta}, \frac{p_0 t}{m} + \delta + \frac{\hbar t}{m\delta} \right). \tag{7.61}$$

P7.6 Find the wave function at time t for free particles whose amplitude at $t = 0$ is

$$\psi(\boldsymbol{r}, 0) = \frac{1}{(\pi\sigma^2)^{3/4}} \exp\left(-\frac{r^2}{2\sigma^2} + \frac{i\boldsymbol{p}_0 \cdot \boldsymbol{r}}{\hbar} \right). \tag{7.62}$$

Solution. The time evolution of the single-particle wave function for $t > 0$ is obtained by convolution with the propagator, namely

$$\psi(\boldsymbol{r}, t) = \int_{\mathbb{R}^3} K(\boldsymbol{r}, t|\boldsymbol{r}', 0)\psi(\boldsymbol{r}', 0)\, dr', \qquad t > 0, \tag{7.63}$$

and for a free particle the propagator has the well-known form

$$K(\boldsymbol{r}, t|\boldsymbol{r}', 0) = \left(\frac{m}{2\pi i\hbar t}\right)^{3/2} \exp\left[\frac{im|\boldsymbol{r} - \boldsymbol{r}'|^2}{2\hbar t}\right], \qquad t > 0. \tag{7.64}$$

Substituting this propagator together with the Gaussian initial state into (7.63) yields

$$\psi(\boldsymbol{r}, t) = \left(\frac{m}{2\pi i\hbar t}\right)^{3/2} \frac{1}{\left(\pi\sigma^2\right)^{3/4}} \int_{\mathbb{R}^3} \exp\left[\frac{im}{2\hbar t}|\boldsymbol{r} - \boldsymbol{r}'|^2 - \frac{\boldsymbol{r}'^2}{2\sigma^2} + \frac{i}{\hbar}\boldsymbol{p}_0 \cdot \boldsymbol{r}'\right] d^3r'. \tag{7.65}$$

After expanding $|\boldsymbol{r} - \boldsymbol{r}'|^2$ and collecting powers of $\boldsymbol{r}'$, the exponent can be arranged so that

$$\psi(\boldsymbol{r}, t) = \left(\frac{m}{2\pi i\hbar t}\right)^{3/2} \frac{1}{\left(\pi\sigma^2\right)^{3/4}} \int_{\mathbb{R}^3} \exp\left[\left(\frac{im}{2\hbar t} - \frac{1}{2\sigma^2}\right)\boldsymbol{r}'^2 + \frac{i}{\hbar}\left(\boldsymbol{p}_0 - \frac{m}{t}\boldsymbol{r}\right) \cdot \boldsymbol{r}' + \frac{im}{2\hbar t}\boldsymbol{r}^2\right] d^3r'. \tag{7.66}$$

It is convenient to introduce the quadratic and linear coefficients in the integrand by defining

$$-\alpha = \frac{im}{2\hbar t} - \frac{1}{2\sigma^2} = \frac{im\sigma^2 - \hbar t}{2\hbar t\sigma^2}, \qquad -\boldsymbol{\beta} = \frac{i}{\hbar}\left(\boldsymbol{p}_0 - \frac{m}{t}\boldsymbol{r}\right) = \frac{i(t\boldsymbol{p}_0 - m\boldsymbol{r})}{\hbar t}, \tag{7.67}$$

so that the wavefunction may be written as the product of the prefactor, an $\boldsymbol{r}$-dependent phase factor taken outside the integral, and the remaining Gaussian integral,

$$\psi(\boldsymbol{r}, t) = \left(\frac{m}{2\pi i\hbar t}\right)^{3/2} \frac{1}{\left(\pi\sigma^2\right)^{3/4}} \exp\left(\frac{im}{2\hbar t}\boldsymbol{r}^2\right) \int_{\mathbb{R}^3} \exp\left(-\alpha\, \boldsymbol{r}'^2 - \boldsymbol{\beta} \cdot \boldsymbol{r}'\right) d^3r'. \tag{7.68}$$

This is a standard three-dimensional Gaussian and, for $\mathrm{Re}(\alpha) > 0$, it satisfies

$$\int_{\mathbb{R}^3} \exp\left(-\alpha\, \boldsymbol{r}'^2 - \boldsymbol{\beta} \cdot \boldsymbol{r}'\right) d^3r' = \left(\frac{\pi}{\alpha}\right)^{3/2} \exp\left(\frac{\boldsymbol{\beta}^2}{4\alpha}\right). \tag{7.69}$$

Using this identity and inserting the definitions (7.67) into (7.68) leads to

$$\psi(\boldsymbol{r}, t) = \left(\frac{m}{2i\hbar t\,\alpha}\right)^{3/2} \frac{1}{\left(\pi\sigma^2\right)^{3/4}} \exp\left(\frac{im}{2\hbar t}\boldsymbol{r}^2 + \frac{\boldsymbol{\beta}^2}{4\alpha}\right), \tag{7.70}$$

which, after straightforward algebraic simplifications of the prefactor and the exponent, can be cast in the form

$$\psi(\boldsymbol{r},t)=\frac{1}{(\pi\sigma^2)^{3/4}}\left(\frac{m\sigma^2}{i\hbar t+m\sigma^2}\right)^{3/2}\exp\left(\frac{im}{2\hbar t}\boldsymbol{r}^2-\frac{\sigma^2\left(m\boldsymbol{r}-\boldsymbol{p}_0t\right)^2}{2\hbar t\left(\hbar t-im\sigma^2\right)}\right). \tag{7.71}$$

The overall multiplicative factor outside the exponential may be written in a more compact, dimensionless form as

$$\frac{1}{(\pi\sigma^2)^{3/4}}\left(\frac{m\sigma^2}{i\hbar t+m\sigma^2}\right)^{3/2}=\frac{1}{(\pi\sigma^2)^{3/4}\left(1+\frac{i\hbar t}{m\sigma^2}\right)^{3/2}}, \tag{7.72}$$

while the exponent combines the free-particle phase with the Gaussian spreading and center-of-mass motion. A compact form of the combined exponent is

$$\frac{im}{2\hbar t}\boldsymbol{r}^2-\frac{\sigma^2\left(m\boldsymbol{r}-\boldsymbol{p}_0t\right)^2}{2\hbar t\left(\hbar t-im\sigma^2\right)}=\frac{im\boldsymbol{r}^2(\hbar t-im\sigma^2)-\sigma^2(m\boldsymbol{r}-\boldsymbol{p}_0t)^2}{2\hbar t(\hbar t-im\sigma^2)} \tag{7.73}$$

$$=\frac{1}{1+\dfrac{i\hbar t}{m\sigma^2}}\left(-\frac{\boldsymbol{r}^2}{2\sigma^2}+i\,\frac{\boldsymbol{r}\cdot\boldsymbol{p}_0}{\hbar}-i\,\frac{t\,\boldsymbol{p}_0^2}{2m\hbar}\right). \tag{7.74}$$

Collecting these results yields the closed-form expression for the time-evolved Gaussian wave packet

$$\psi(\boldsymbol{r},t)=\frac{1}{(\pi\sigma^2)^{3/4}\left(1+\frac{i\hbar t}{m\sigma^2}\right)^{3/2}}\exp\left(\frac{1}{1+\dfrac{i\hbar t}{m\sigma^2}}\left(-\frac{\boldsymbol{r}^2}{2\sigma^2}+i\,\frac{\boldsymbol{r}\cdot\boldsymbol{p}_0}{\hbar}-i\,\frac{t\,\boldsymbol{p}_0^2}{2m\hbar}\right)\right). \tag{7.75}$$

This expression exhibits the familiar features of free evolution: a global dispersive amplitude factor that depends on the dimensionless parameter $\hbar/m\sigma^2$, a quadratic phase proportional to $\boldsymbol{r}^2$ coming from free propagation, and terms that describe the drift of the packet with initial momentum $\boldsymbol{p}_0$ as well as the temporal increase of its spatial width.

P7.7 Using the general solution of the Schrödinger equation for a free particle

$$\psi(x,t)=Ae^{-iEt/\hbar+ipx/\hbar}+Be^{-iEt/\hbar-ipx/\hbar}, \tag{7.76}$$

show that the initial conditions can be chosen such that:

a) $\psi(x,t)$ is an eigenfunction of the operator $\hat{p}=-i\hbar\partial/\partial x$,

b) the probability density is independent of time, i.e. it represents a standing wave.

Solution. a) We compute the derivative of $\psi(x,t)$ with respect to x,

$$\hat{p}\psi(x,t)=-i\hbar\frac{\partial}{\partial x}\left(Ae^{i(px-Et)/\hbar}+Be^{-i(px+Et)/\hbar}\right). \tag{7.77}$$

Differentiating each term,

$$\hat{p}\psi(x,t) = -i\hbar\left(A\cdot\frac{ip}{\hbar}e^{i(px-Et)/\hbar} + B\cdot\frac{-ip}{\hbar}e^{-i(px+Et)/\hbar}\right). \tag{7.78}$$

Simplifying,

$$\hat{p}\psi(x,t) = pAe^{i(px-Et)/\hbar} - pBe^{-i(px+Et)/\hbar}. \tag{7.79}$$

For $\psi(x,t)$ to be an eigenfunction of $\hat{p}$, it must satisfy

$$\hat{p}\psi(x,t) = \lambda\psi(x,t), \tag{7.80}$$

where λ is the eigenvalue. Equating the expressions,

$$pAe^{i(px-Et)/\hbar} - pBe^{-i(px+Et)/\hbar} = \lambda\left(Ae^{i(px-Et)/\hbar} + Be^{-i(px+Et)/\hbar}\right). \tag{7.81}$$

For this to hold for all x and t, the coefficients of the exponential terms must be equal,

$$pA = \lambda A \quad \text{and} \quad -pB = \lambda B. \tag{7.82}$$

This implies:

- If $A \neq 0$, then $\lambda = p$, and $B = 0$.
- If $B \neq 0$, then $\lambda = -p$, and $A = 0$.

In conclusion:

- For $\lambda = p$, we choose $B = 0$,

$$\psi(x,t) = Ae^{i(px-Et)/\hbar}. \tag{7.83}$$

- For $\lambda = -p$, we choose $A = 0$,

$$\psi(x,t) = Be^{-i(px+Et)/\hbar}. \tag{7.84}$$

The initial conditions are chosen such that either $B = 0$ (eigenfunction with eigenvalue $+p$) or $A = 0$ (eigenfunction with eigenvalue $-p$).

b) Using the general solution

$$\psi(x,t) = Ae^{i(px-Et)/\hbar} + Be^{-i(px+Et)/\hbar}. \tag{7.85}$$

The probability density is

$$|\psi(x,t)|^2 = \left|Ae^{ipx/\hbar}e^{-iEt/\hbar} + Be^{-ipx/\hbar}e^{-iEt/\hbar}\right|^2. \tag{7.86}$$

Factoring out $e^{-iEt/\hbar}$,

$$|\psi(x,t)|^2 = \left|e^{-iEt/\hbar}\left(Ae^{ipx/\hbar} + Be^{-ipx/\hbar}\right)\right|^2 = \left|Ae^{ipx/\hbar} + Be^{-ipx/\hbar}\right|^2, \tag{7.87}$$

since $|e^{-iEt/\hbar}| = 1$.

For $|\psi(x,t)|^2$ to be independent of t, the above expression already satisfies this condition because there are no remaining time-dependent terms. However, to obtain a standing wave, we require $\psi(x,t)$ to be a combination of counter-propagating waves with related amplitudes.

A typical standing wave has the form

$$\psi(x,t) = C\cos\left(\frac{px}{\hbar}\right)e^{-iEt/\hbar} + D\sin\left(\frac{px}{\hbar}\right)e^{-iEt/\hbar}. \tag{7.88}$$

Compared with the general solution, this is achieved if $A = B$ (for the cosine term) or $A = -B$ (for the sine term).

P7.8 Solve the free-particle problem in cylindrical polar coordinates.
Solution. For a free particle ($V = 0$) the stationary Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\rho,\varphi,z) = E\,\psi(\rho,\varphi,z), \tag{7.89}$$

where in cylindrical polar coordinates (ρ,φ,z),

$$\nabla^2 = \frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial z^2}. \tag{7.90}$$

We look for separable eigenstates

$$\psi(\rho,\varphi,z) = R(\rho)\,\Phi(\varphi)\,Z(z). \tag{7.91}$$

Inserting (7.91) into (7.89) and dividing by $R\Phi Z$ gives

$$\frac{1}{R}\left(\frac{\mathrm{d}^2R}{\mathrm{d}\rho^2} + \frac{1}{\rho}\frac{\mathrm{d}R}{\mathrm{d}\rho}\right) + \frac{1}{\rho^2\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\varphi^2} + \frac{1}{Z}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2} = -k^2, \qquad k^2 \equiv \frac{2mE}{\hbar^2}. \tag{7.92}$$

Because the three coordinate variables are independent, each term must equal a constant. We write

$$\frac{1}{Z}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2} = -k_z^2, \qquad \frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\varphi^2} = -m^2, \qquad k_\perp^2 \equiv k^2 - k_z^2, \tag{7.93}$$

so that $m \in \mathbb{Z}$ and $k_\perp \geq 0$. The z– and φ–equations are solved immediately,

$$Z(z) = e^{\pm ik_z z}, \qquad \Phi(\varphi) = e^{im\varphi}\ (m = 0, \pm1, \pm2, \dots). \tag{7.94}$$

Because φ and $\varphi + 2\pi$ denote the same physical direction, the angular factor must satisfy

$$\Phi(\varphi + 2\pi) = \Phi(\varphi). \tag{7.95}$$

For the separated solution $\Phi(\varphi) = A\,e^{im\varphi}$ this gives $A\,e^{im(\varphi+2\pi)} = A\,e^{im\varphi} \Rightarrow e^{i2\pi m} = 1$, which holds only when $m \in \mathbb{Z}$. Hence the azimuthal quantum number is necessarily an integer.

The remaining radial equation is

$$\frac{\mathrm{d}^2R}{\mathrm{d}\rho^2} + \frac{1}{\rho}\frac{\mathrm{d}R}{\mathrm{d}\rho} + \left(k_\perp^2 - \frac{m^2}{\rho^2}\right)R = 0, \tag{7.96}$$

whose regular solutions at the origin are the Bessel functions $J_m(k_\perp\rho)$. The irregular Y_m are discarded because they blow up at $r = 0$. Hence

$$R_{mk_\perp}(\rho) = J_m(k_\perp\rho). \tag{7.97}$$

Collecting all factors, an eigenstate is

$$\psi_{k_\perp m k_z}(\rho,\varphi,z) = A\cdot J_m(k_\perp\rho)\, e^{im\varphi}\, e^{ik_z z}, \tag{7.98}$$

with eigenenergy

$$E = \frac{\hbar^2}{2m}\big(k_\perp^2 + k_z^2\big). \tag{7.99}$$

The constant A depends on the normalization method.

The integer m is the (azimuthal) angular-momentum quantum number around the z-axis, k_z is the longitudinal wave number and $k_\perp$ plays the role of a radial wave number in the transverse plane. The degeneracy of the free particle is reflected in the continuous labels $k_\perp$ and k_z together with the discrete m. Any physically acceptable free-particle state in cylindrical geometry can be expanded as a superposition of these eigenfunctions.

P7.9 Consider a packet of free particles with a Gaussian momentum distribution, $A(k) = A_0 e^{-(k-k_0)^2/q^2}$.

a) Find $\psi(x,t)$ for this packet at time t.

b) At what speed does the center of mass of the packet move?

c) What is the rate at which the spatial dispersion of the particle increases? Can this speed be greater than the speed of light? Explain your answer.

Solution. a) The wave function at $t = 0$ is obtained via the Fourier transform of $\phi(k)$,

$$\psi(x,0) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)e^{ikx}dk. \tag{7.100}$$

Substituting the normalized Gaussian amplitude $\phi(k) = (\pi q^2)^{-1/4}\, e^{-(k-k_0)^2/2q^2}$,

$$\psi(x,0) = \frac{(\pi q^2)^{-1/4}}{\sqrt{2\pi}}\int_{-\infty}^{\infty} e^{-(k-k_0)^2/2q^2}e^{ikx}dk. \tag{7.101}$$

To evaluate the integral we complete the square in the exponent,

$$-\frac{k^2}{2q^2} + \left(\frac{k_0}{q} + iqx\right)\frac{k}{q} - \frac{k_0^2}{2q^2} = -\frac{1}{2}\left(\frac{k-k_0}{q} - iqx\right)^2 + ik_0x - \frac{q^2x^2}{2}. \tag{7.102}$$

The integral evaluates to a Gaussian centered at $k = k_0 + iq^2x$,

$$\psi(x,0) = \left(\frac{q^2}{\pi}\right)^{1/4} e^{ik_0x}e^{-q^2x^2/2}. \tag{7.103}$$

The evolution of the wave packet is obtained from

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)e^{i(kx-\omega_k t)}dk, \quad \omega_k = \frac{\hbar k^2}{2m}. \tag{7.104}$$

Substituting $A(k)$ and simplifying gives, after integration,

$$\psi(x,t)=\left(\frac{q^2}{\pi}\right)^{1/4}\left(1+\frac{i\hbar q^2 t}{m}\right)e^{ik_0\left(x-\frac{\hbar k_0 t}{2m}\right)}e^{-\frac{\left(x-\frac{\hbar k_0 t}{m}\right)^2 q^2}{2\left(1+\frac{i\hbar q^2 t}{m}\right)}}. \tag{7.105}$$

b) The Gaussian peak follows

$$x_{\rm c}(t)=\frac{\hbar k_0}{m}t, \tag{7.106}$$

which gives for the velocity of the center of mass of the packet

$$v_{\rm c}=\frac{\hbar k_0}{m}. \tag{7.107}$$

Therefore, the packet travels with a group velocity that satisfies de Broglie's relation $\lambda=h/mv_c$, with $\lambda=2\pi/k_0$.

c) The Gaussian width spreads as

$$\Delta x(t)=\Delta x(0)\sqrt{1+\left(\frac{\hbar t}{2m\Delta x(0)^2}\right)^2};\;\; \Delta x(0)=\frac{1}{\sqrt{2}q}, \tag{7.108}$$

so that the spreading rate is

$$v_{\rm disp}=\frac{d\Delta x(t)}{dt}=\frac{\hbar^2 t}{4m^2\Delta x(0)^3}\left(1+\left(\frac{\hbar t}{2m\Delta x(0)^2}\right)^2\right)^{-1/2}. \tag{7.109}$$

At $t\to\infty$, it asymptotically approaches

$$\frac{d\Delta x(t)}{dt}\approx\frac{\hbar}{2m\Delta x(0)}, \tag{7.110}$$

thus, in terms of the dispersion of the wave number, given by $\Delta k=q/\sqrt{2}$,

$$v_{\rm disp}=\frac{\hbar q}{\sqrt{2}m}=\frac{\hbar\Delta k}{m}. \tag{7.111}$$

For massive particles ($m\neq 0$), $v_{\rm disp}\ll c$ unless q is extremely large. Relativistic effects become significant for ultra-high q or $m\to 0$, but non-relativistic quantum mechanics ensures $v_{\rm disp}<c$.

Note that, using $\Delta p=\hbar\Delta k$, we may combine the above results to obtain, for $t\geq 0$,

$$\Delta x(t)\Delta p\geq\Delta x(0)\Delta p=\frac{\hbar}{2}. \tag{7.112}$$

P7.10 Show that if the coherent superposition **(7.109)** in [**1**] involves a finite number $N>2$ of energy eigenstates n,m, the oscillations of ψ are not periodic unless the frequencies $\omega_{nm}=|E_n-E_m|/\hbar$ are all related by rational numbers.

Solution. We begin by considering the coherent superposition of a finite number N of energy eigenstates,

$$\psi(x,t) = \sum_{n=1}^{N} c_n \, \varphi_n(x) \, e^{-iE_n t/\hbar}. \tag{7.113}$$

To analyze the periodicity of the quantum state, we consider the probability density function $\rho(x,t) = |\psi(x,t)|^2$.

Case $N = 1$: The wave function consists of a single energy eigenstate,

$$\psi(t) = c_1 \, \varphi_1(x) \, e^{-iE_1 t/\hbar} \tag{7.114}$$

and the probability density becomes

$$\rho(x,t) = |\psi(t)|^2 = |c_1|^2 |\phi_1(x)|^2, \tag{7.115}$$

which is independent of time. Therefore, $\rho(x,t)$ is constant and hence trivially periodic.

Case $N = 2$: We consider a superposition of two energy eigenstates,

$$\psi(t) = c_1 \, \varphi_1(x) \, e^{-i\omega_1 t} + c_2 \, \varphi_2(x) \, e^{-i\omega_2 t}, \tag{7.116}$$

where $\omega_n = \frac{E_n}{\hbar}$. The probability density becomes

$$\rho(x,t) = |c_1|^2 |\varphi_1(x)|^2 + |c_2|^2 |\varphi_2(x)|^2 + 2\,\mathrm{Re}\left[c_1^* c_2 \, \varphi_1^*(x) \varphi_2(x) \, e^{-i(\omega_2 - \omega_1)t}\right]. \tag{7.117}$$

This contains a term oscillating in time as a cosine,

$$\cos\left((\omega_2 - \omega_1)t\right), \tag{7.118}$$

which is periodic. Hence, $\rho(x,t)$ is periodic in time.

General case $N > 2$: The probability density is given by

$$\rho(x,t) = |\psi(x,t)|^2 = \left| \sum_{n=1}^{N} c_n \, \varphi_n(x) \, e^{-i\omega_n t} \right|^2. \tag{7.119}$$

Expanding the square modulus, we obtain

$$\rho(x,t) = \sum_{n=1}^{N} |c_n|^2 |\varphi_n(x)|^2 + 2 \sum_{n \neq m}^{N} \mathrm{Re}\left(c_n c_m^* \, \varphi_n(x) \varphi_m^*(x) \, e^{-i\omega_{mn} t}\right), \tag{7.120}$$

where $\omega_{mn} = \omega_n - \omega_m$.We focus on the oscillatory part, i.e. the time dependent one. A function $f(t)$ is said to be *periodic* if there exists a period T such that $f(t) = f(t+T)$ for all t. So we must have

$$\sum_{n \neq m}^{N} c_n c_m^* \, \varphi_n(x) \varphi_m^*(x) \, e^{-i\omega_{mn} t} e^{-i\omega_{mn} T} = \sum_{n \neq m}^{N} c_n c_m^* \, \varphi_n(x) \varphi_m^*(x) \, e^{-i\omega_{mn} t}, \tag{7.121}$$

that is,

$$e^{-i\omega_{mn} t} e^{-i\omega_{mn} T} = e^{-i\omega_{nm} t} \quad \Rightarrow \quad e^{-i\omega_{nm} T} = 1. \tag{7.122}$$

This implies that each $\omega_{nm}T$ must be an integer multiple of 2π,

$$\omega_{nm}T = 2\pi k_{nm}, \quad \Rightarrow \quad T = \frac{2\pi k_{nm}}{\omega_{nm}} \quad k_{nm} \in \mathbb{Z}. \tag{7.123}$$

This relation must hold for all ω_{nm}, so in general we have

$$\frac{2\pi k_{ij}}{\omega_{ij}} = \frac{2\pi k_{kl}}{\omega_{kl}} \quad \Rightarrow \quad \frac{\omega_{ij}}{\omega_{kl}} = \frac{k_{ij}}{k_{kl}} = r \quad , \quad r \in \mathbb{Q}. \tag{7.124}$$

Therefore, the periodicity of $\rho(x,t)$ requires that all the relative frequencies ω_{nm} be commensurable, that is, their ratios must be rational.

P7.11 Show that if ψ_1 and ψ_2 are solutions of the time-dependent Schrödinger equation, the equation

$$\frac{\partial}{\partial t}\psi_1^*\psi_2 + \frac{i\hbar}{2m}\nabla\cdot(\psi_2\nabla\psi_1^* - \psi_1^*\nabla\psi_2) = 0 \tag{7.125}$$

generalizes the continuity equation.

Solution. The solutions satisfy

$$i\hbar\frac{\partial\psi_1}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi_1 + V\psi_1, \quad i\hbar\frac{\partial\psi_2}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi_2 + V\psi_2. \tag{7.126}$$

We take the complex conjugate of the equation for ψ_1,

$$-i\hbar\frac{\partial\psi_1^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi_1^* + V\psi_1^*. \tag{7.127}$$

The time derivative of the product is

$$\frac{\partial}{\partial t}(\psi_1^*\psi_2) = \psi_2\frac{\partial\psi_1^*}{\partial t} + \psi_1^*\frac{\partial\psi_2}{\partial t}. \tag{7.128}$$

Substituting the Schrödinger equations,

$$\frac{\partial}{\partial t}(\psi_1^*\psi_2) = \psi_2\left(\frac{i\hbar}{2m}\nabla^2\psi_1^* - \frac{i}{\hbar}V\psi_1^*\right) + \psi_1^*\left(-\frac{i\hbar}{2m}\nabla^2\psi_2 + \frac{i}{\hbar}V\psi_2\right). \tag{7.129}$$

the potential terms V cancel and we are left with

$$\frac{\partial}{\partial t}(\psi_1^*\psi_2) = \frac{i\hbar}{2m}(\psi_2\nabla^2\psi_1^* - \psi_1^*\nabla^2\psi_2). \tag{7.130}$$

We express the right-hand side as a divergence,

$$\psi_2\nabla^2\psi_1^* - \psi_1^*\nabla^2\psi_2 = \nabla\cdot(\psi_2\nabla\psi_1^* - \psi_1^*\nabla\psi_2), \tag{7.131}$$

using the identities

$$\nabla\cdot(\psi_2\nabla\psi_1^*) = \nabla\psi_2\cdot\nabla\psi_1^* + \psi_2\nabla^2\psi_1^*, \tag{7.132}$$

$$\nabla\cdot(\psi_1^*\nabla\psi_2) = \nabla\psi_1^*\cdot\nabla\psi_2 + \psi_1^*\nabla^2\psi_2. \tag{7.133}$$

Subtracting these yields

$$\nabla\cdot(\psi_2\nabla\psi_1^* - \psi_1^*\nabla\psi_2) = \psi_2\nabla^2\psi_1^* - \psi_1^*\nabla^2\psi_2. \tag{7.134}$$

Substituting back,

$$\frac{\partial}{\partial t}(\psi_1^*\psi_2) = \frac{i\hbar}{2m}\nabla\cdot(\psi_2\nabla\psi_1^* - \psi_1^*\nabla\psi_2). \tag{7.135}$$

Rearranging gives the generalized continuity equation

$$\frac{\partial}{\partial t}(\psi_1^*\psi_2) + \frac{i\hbar}{2m}\nabla\cdot(\psi_2\nabla\psi_1^* - \psi_1^*\nabla\psi_2) = 0. \tag{7.136}$$

When $\psi_1 = \psi_2 = \psi$, this reduces to the standard probability continuity equation

$$\frac{\partial}{\partial t}|\psi|^2 + \nabla\cdot\boldsymbol{j} = 0, \tag{7.137}$$

where $\boldsymbol{j} = \frac{\hbar}{2mi}(\psi^*\nabla\psi - \psi\nabla\psi^*)$ is the probability current density.

P7.12 A physical system is initially (at $t = 0$) in a state which is a coherent superposition of the eigenfunctions φ_1 and φ_2 of a Hamiltonian with eigenenergies E_1 and E_2, respectively. The φ_1 state is three times more probable than the φ_2 state. Write the most general possible initial wave function $\psi_0(x)$ consistent with the above data and determine $\psi(x,t)$ for all $t > 0$. Is the system in a stationary state? Does this state possess any time-invariant properties?

Solution. A coherent superposition of two eigenfunctions at $t = 0$ is of the form

$$\psi(x,0) = c_1\varphi_1(x) + c_2\varphi_2(x), \tag{7.138}$$

where the squared moduli $|c_1|^2$ and $|c_2|^2$ represent the probabilities of the system being in the states φ_1 and φ_2, respectively. We are told that the probability of being in the state φ_1 is three times greater than that of φ_2, so

$$|c_1|^2 = 3|c_2|^2. \tag{7.139}$$

The normalization condition imposes that

$$|c_1|^2 + |c_2|^2 = 1. \tag{7.140}$$

Substituting the relation above, we get

$$3|c_2|^2 + |c_2|^2 = 4|c_2|^2 = 1 \quad \Rightarrow \quad |c_2|^2 = \frac{1}{4}, \quad |c_1|^2 = \frac{3}{4}. \tag{7.141}$$

Therefore, we can write (up to arbitrary phases)

$$c_1 = \frac{\sqrt{3}}{2}e^{i\theta_1}, \quad c_2 = \frac{1}{2}e^{i\theta_2}. \tag{7.142}$$

The most general initial wave function is then

$$\psi(x,0) = \frac{\sqrt{3}}{2}e^{i\theta_1}\varphi_1(x) + \frac{1}{2}e^{i\theta_2}\varphi_2(x). \tag{7.143}$$

Factoring out the global phase $e^{i\theta_1}$, which is physically unobservable, and defining $\theta = \theta_2 - \theta_1$, we obtain

$$\psi(x,0) = \frac{\sqrt{3}}{2}\varphi_1(x) + \frac{1}{2}e^{i\theta}\varphi_2(x). \tag{7.144}$$

To construct the time-dependent wave function $\psi(x,t)$, we multiply each term by the corresponding time evolution factor $e^{-iE_nt/\hbar}$,

$$\psi(x,t) = \frac{\sqrt{3}}{2}\varphi_1(x)e^{-iE_1t/\hbar} + \frac{1}{2}e^{i\theta}\varphi_2(x)e^{-iE_2t/\hbar}. \tag{7.145}$$

A stationary state is one in which the probability density $\rho(x,t) = |\psi(x,t)|^2$ is independent of time. In our case, since the wave function is a coherent superposition of two energy eigenstates with different energies, the cross terms in $|\psi(x,t)|^2$ will contain oscillatory factors of the form $e^{\pm i(E_2-E_1)t/\hbar}$. Therefore, the probability density is time-dependent, and the system is not in a stationary state. Nevertheless, the state does possess some time-invariant properties. Specifically:

The probability of each eigenstate $|c_i|^2$ is time independent, therefore the total probability is conserved,

$$\int |\psi(x,t)|^2\,dx = |c_1|^2 + |c_2|^2 = \frac{3}{4} + \frac{1}{4} = 1, \quad \text{for all } t. \tag{7.146}$$

The expectation value of the Hamiltonian is constant in time,

$$\langle H\rangle = |c_1|^2E_1 + |c_2|^2E_2 = \frac{3}{4}E_1 + \frac{1}{4}E_2. \tag{7.147}$$

This is because the Hamiltonian is time-independent, and its expectation value in any normalized state remains constant under unitary time evolution. In summary, the system is not in a stationary state, but it retains some time-invariant physical quantities, such as total probability and average energy.

P7.13 Show that a non-stationary state cannot have a separable wave function of the form $\psi(x,t) = \chi(t)\varphi(x)$.

Solution. The time-dependent Schrödinger equation is

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi. \tag{7.148}$$

Let us assume that the wave function can be written in the separable form $\psi(x,t) = \chi(t)\varphi(x)$,

$$i\hbar\varphi(x)\frac{d\chi}{dt} = -\frac{\hbar^2}{2m}\chi(t)\frac{d^2\varphi}{dx^2} + V(x)\chi(t)\varphi(x). \tag{7.149}$$

Dividing both sides by $\chi(t)\varphi(x)$ we get

$$i\hbar\frac{1}{\chi}\frac{d\chi}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\varphi}\frac{d^2\varphi}{dx^2} + V(x). \tag{7.150}$$

The left side depends only on t and the right side only on x. For equality to hold for all x and t, both sides must equal at constant E,

$$i\hbar\frac{1}{\chi}\frac{d\chi}{dt} = E, \quad -\frac{\hbar^2}{2m}\frac{1}{\varphi}\frac{d^2\varphi}{dx^2} + V(x) = E. \tag{7.151}$$

From the first equation we get

$$\frac{d\chi}{dt} = -\frac{iE}{\hbar}\chi \implies \chi(t) = Ce^{-iEt/\hbar} \tag{7.152}$$

and from the second one,

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi}{dx^2} + V(x)\varphi = E\varphi, \tag{7.153}$$

which is the time-independent Schrödinger equation for $\varphi(x)$.

Substituting $\chi(t)$ back,

$$\psi(x,t) = Ce^{-iEt/\hbar}\varphi(x). \tag{7.154}$$

This is identical to a stationary state, where $\varphi(x)$ is the spatial part and $e^{-iEt/\hbar}$ gives the temporal phase evolution.

We thus conclude that any separable solution $\psi(x,t) = \chi(t)\varphi(x)$ must be a stationary state. Non-stationary states (which don't have the form $\varphi(x)e^{-iEt/\hbar}$) cannot be written as separable products.

P7.14 Consider the relativistic Klein–Gordon equation for the free particle **([1], Section 19.1)**

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\psi(x,t) = \frac{m^2c^2}{\hbar^2}\psi(x,t). \tag{7.155}$$

Show that a conservation law similar to Eq. **(7.118)** is satisfied, with

$$\boldsymbol{j}(x,t) = \frac{i\hbar}{2m}\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right). \tag{7.156}$$

What is now the value of $\rho(x,t)$? From this result discuss why the Klein–Gordon equation is not a good candidate to replace the Schrödinger equation for electrons in the relativistic case.

Solution. We calculate $\nabla\cdot\boldsymbol{j}$ using the given definition of $\boldsymbol{j}$,

$$\nabla\cdot\boldsymbol{j}(x,t) = \frac{i\hbar}{2m}\left[\nabla\psi\cdot\nabla\psi^* + \psi\nabla^2\psi^* - \nabla\psi^*\cdot\nabla\psi - \psi^*\nabla^2\psi\right]. \tag{7.157}$$

The first and third terms cancel out, therefore

$$\nabla\cdot\boldsymbol{j}(x,t) = \frac{i\hbar}{2m}\left(\psi\nabla^2\psi^* - \psi^*\nabla^2\psi\right). \tag{7.158}$$

Using the Klein-Gordon equation to substitute $\nabla^2\psi$ and $\nabla^2\psi^*$ gives

$$\nabla^2\psi = \frac{m^2c^2}{\hbar^2}\psi + \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2} \quad \text{and} \quad \nabla^2\psi^* = \frac{m^2c^2}{\hbar^2}\psi^* + \frac{1}{c^2}\frac{\partial^2\psi^*}{\partial t^2}, \tag{7.159}$$

$$\nabla \cdot \boldsymbol{j}(x,t) = \left[\psi\left(\frac{m^2c^2}{\hbar^2}\psi^* + \frac{1}{c^2}\frac{\partial^2\psi^*}{\partial t^2}\right) - \psi^*\left(\frac{m^2c^2}{\hbar^2}\psi + \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}\right)\right] \tag{7.160}$$

$$= \frac{i\hbar}{2mc^2}\left[\psi\frac{\partial^2\psi^*}{\partial t^2} - \psi^*\frac{\partial^2\psi}{\partial t^2}\right] = \frac{i\hbar}{2mc^2}\frac{\partial}{\partial t}\left[\psi\frac{\partial\psi^*}{\partial t} - \psi^*\frac{\partial\psi}{\partial t}\right], \tag{7.161}$$

so that we have

$$\nabla \cdot \boldsymbol{j}(x,t) + \frac{\partial}{\partial t}\frac{i\hbar}{2mc^2}\left(\psi^*\frac{\partial\psi}{\partial t} - \psi\frac{\partial\psi^*}{\partial t}\right) = 0. \tag{7.162}$$

We define

$$\rho(x,t) \equiv \frac{i\hbar}{2mc^2}\left(\psi^*\frac{\partial\psi}{\partial t} - \psi\frac{\partial\psi^*}{\partial t}\right), \tag{7.163}$$

therefore,

$$\nabla \cdot \boldsymbol{j} + \frac{\partial\rho}{\partial t} = 0. \tag{7.164}$$

This expression poses a fundamental problem: unlike the Schrödinger probability density $|\psi(x,t)|^2$, the Klein-Gordon density $\rho(x,t)$ is not guaranteed to be positive definite. That is, $\rho(x,t)$ can take negative values depending on the time derivative of the wave function. Since a probability density must always be non-negative to be physically meaningful, $\rho(x,t)$ cannot be consistently interpreted as a probability density.

This issue undermines the probabilistic interpretation of quantum mechanics when applied to the Klein-Gordon equation. Consequently, the Klein-Gordon equation is not suitable to describe electrons, which are spin-$\frac{1}{2}$ particles requiring a probability interpretation and proper normalization. Instead, electrons are more accurately described by the Dirac equation, which ensures a positive-definite probability density and accounts for spin in a relativistically consistent framework.

P7.15 A particle is in its ground state in a 1D infinite square well of width L. Suddenly, at $t = 0$, the right wall of the well moves from $x = L$ to $x = 2L$. Is the particle still in a stationary state? Determine the probability of the new ground state.

Solution. We have an infinite square well of width L (from $x = 0$ to $x = L$), with ground state ($n = 1$)

$$\psi_{\text{ini}}(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right), \quad 0 \le x \le L \tag{7.165}$$

and energy

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2} \tag{7.166}$$

For the infinite square well of width $2L$ (from $x = 0$ to $x = 2L$), the new stationary state is

$$\phi_n(x) = \sqrt{\frac{1}{L}} \sin\left(\frac{n\pi x}{2L}\right), \quad E'_n = \frac{n^2\pi^2\hbar^2}{8mL^2}, \quad n = 1, 2, 3, \ldots \tag{7.167}$$

The sudden potential change means that $\psi_{\text{in}}(x)$ is no longer an eigenfunction of the new Hamiltonian. The particle is now in a superposition of the new stationary states $\phi_n(x)$, which is not a stationary state.

The probability for the particle to be in the new ground state $\phi_1(x)$ is

$$P_1 = |\langle \phi_1 | \psi_{\text{in}} \rangle^2| \tag{7.168}$$

To calculate the overlap integral

$$\langle \phi_1 | \psi_{\text{in}} \rangle = \int_0^L \sqrt{\frac{1}{L}} \sin\left(\frac{\pi x}{2L}\right) \cdot \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \tag{7.169}$$

we use the trigonometric identity

$$\sin A \sin B = \frac{1}{2}[\cos(A - B) - \cos(A + B)]. \tag{7.170}$$

With $A = \frac{\pi x}{2L}$, $B = \frac{\pi x}{L}$, the integral becomes

$$\langle \phi_1 | \psi_{\text{in}} \rangle = \frac{\sqrt{2}}{L} \int_0^L \left[\cos\left(-\frac{\pi x}{2L}\right) - \cos\left(\frac{3\pi x}{2L}\right)\right] dx \tag{7.171}$$

Solving the integrals

$$\int_0^L \cos\left(\frac{\pi x}{2L}\right) dx = \frac{2L}{\pi} \sin\left(\frac{\pi}{2}\right) = \frac{2L}{\pi} \tag{7.172}$$

$$\int_0^L \cos\left(\frac{3\pi x}{2L}\right) dx = \frac{2L}{3\pi} \sin\left(\frac{3\pi}{2}\right) = -\frac{2L}{3\pi} \tag{7.173}$$

we get

$$\langle \phi_1 | \psi_{\text{in}} \rangle = \frac{\sqrt{2}}{L} \left(\frac{2L}{\pi} + \frac{2L}{3\pi}\right) = \frac{8\sqrt{2}}{3\pi}. \tag{7.174}$$

The probability is therefore

$$P_1 = \left(\frac{8\sqrt{2}}{3\pi}\right)^2 = \frac{128}{9\pi^2} \approx 0.360. \tag{7.175}$$

P7.16 Show that the propagator given by

$$K(x, t | x', t') = \sum_n e^{-i\omega_n(t-t')} \varphi_n^*(x') \varphi_n(x) = \sum_n \psi_n^*(x', t') \psi_n(x, t), \tag{7.176}$$

has the following integral property:

$$K(x_1, t_1 \mid x_2, t_2) = \int K(x_1, t_1 \mid x, t)\, K(x, t \mid x_2, t_2)\, dx, \qquad t_1 < t < t_2. \tag{7.177}$$

Solution. From Eq. 7.176, we have

$$K(x,t \mid x_2,t_2) = \sum_n e^{-i\omega_n(t-t_2)}\varphi_n^*(x_2)\varphi_n(x), \tag{7.178}$$

$$K(x_1,t_1 \mid x) = \sum_{n'} e^{-i\omega_{n'}(t_1-t)}\varphi_{n'}^*(x)\varphi_{n'}(x_1). \tag{7.179}$$

Multiplying the two expressions and integrating over x, we obtain

$$\int K(x_1,t_1 \mid x,t)\, K(x,t \mid x_2,t_2)\, dx$$

$$= \sum_{nn'} e^{-i(\omega_n-\omega_{n'})t} e^{i(\omega_n t_2-\omega_{n'}t_1)} \varphi_n^*(x_2)\varphi_{n'}(x_1) \int \varphi_{n'}^*(x)\varphi_n(x)\, dx. \tag{7.180}$$

Taking into account the orthonormality of the eigenfunctions $\varphi_n(x)$

$$\int \varphi_{n'}^*(x)\varphi_n(x)\, dx = \delta_{nn'}, \tag{7.181}$$

and performing the sum over n', we get

$$\int K(x_1,t_1 \mid x,t)\, K(x,t \mid x_2,t_2)\, dx = \sum_n e^{-i\omega_n(t_2-t_1)}\varphi_n^*(x_2)\varphi_n(x_1) \tag{7.182}$$

$$= K(x_1,t_1 \mid x_2,t_2). \tag{7.183}$$

This is the desired result. Note that in the integral expression, x takes all possible values, while t must be a fixed time strictly between t_1 and t_2. It is easy to show that this integral property of the propagator extends to an arbitrary number of integrations, chronologically ordered.

From a physical point of view, the previous result is natural for the description of a linear system. Starting from the general expression

$$\psi(x,t) = \int K(x,t \mid x_1,t_1)\, \psi(x_1,t_1)\, dx_1, \qquad t > t_1, \tag{7.184}$$

it follows by iteration, with $t > t_1 > t_0$, that

$$\psi(x,t) = \iint K(x,t \mid x_1,t_1)\, K(x_1,t_1 \mid x_0,t_0)\, \psi(x_0,t_0)\, dx_1 dx_0. \tag{7.185}$$

In turn, Eq. 7.184 can be rewritten as

$$\psi(x,t) = \int K(x,t \mid x_0,t_0)\, \psi(x_0,t_0)\, dx_0, \qquad t > t_0, \tag{7.186}$$

from which Eq. 7.183 follows immediately (with an appropriate change of variable names). This derivation is possible because the effects of the source at x_0 are propagated by $K(x_1,t_1 \mid x_0,t_0)$ and become a new source $\psi(x_1,t_1)$, which is in turn propagated by $K(x,t \mid x_1,t_1)$. For this latter propagator, whether $\psi(x_1,t_1)$

is directly a source, or the result of previous propagation from an earlier source, is indistinguishable.

CHAPTER 8

Dynamics of Quantum Systems

P8.1 Show that the commutator of two variables that are conserved is also a conserved quantity.

Solution. A quantity (not explicitly dependent on time) is said to be conserved if the time derivative of its expectation value vanishes. This condition is expressed as

$$i\hbar\frac{d\langle\hat{F}\rangle}{dt} = \langle[\hat{F},\hat{H}]\rangle, = 0, \tag{8.1}$$

so a quantity is conserved if and only if its commutator with the Hamiltonian vanishes.

Let $\hat{F}$ and $\hat{G}$ be two conserved quantities. This means that they commute with the Hamiltonian $\hat{H}$,

$$[\hat{F},\hat{H}] = 0, \qquad [\hat{G},\hat{H}] = 0. \tag{8.2}$$

We want to show that $[\hat{F},\hat{G}]$ is also conserved. To do so, consider the commutator of $[\hat{F},\hat{G}]$ with $\hat{H}$,

$$[[\hat{F},\hat{G}],\hat{H}] = [\hat{F},\hat{G}]\hat{H} - \hat{H}[\hat{F},\hat{G}] = (\hat{F}\hat{G} - \hat{G}\hat{F})\hat{H} - \hat{H}(\hat{F}\hat{G} - \hat{G}\hat{F}) \tag{8.3}$$

$$= \hat{F}\hat{G}\hat{H} - \hat{G}\hat{F}\hat{H} - \hat{H}\hat{F}\hat{G} + \hat{H}\hat{G}\hat{F} = \hat{F}\hat{G}\hat{H} - \hat{G}\hat{F}\hat{H} - \hat{F}\hat{H}\hat{G} + \hat{G}\hat{H}\hat{F} \tag{8.4}$$

$$= \hat{F}(\hat{G}\hat{H} - \hat{H}\hat{G}) - \hat{G}(\hat{F}\hat{H} - \hat{H}\hat{F}) = \hat{F}[\hat{G},\hat{H}] - \hat{G}[\hat{F},\hat{H}] = 0, \tag{8.5}$$

where the fact that because of $\hat{F},\hat{G}$ commuting with $\hat{H}$ implies $\hat{F}\hat{H} = \hat{H}\hat{F}, \hat{G}\hat{H} = \hat{H}\hat{G}$ was used. Therefore,

$$[[\hat{F},\hat{G}],\hat{H}] = 0. \tag{8.6}$$

This shows that $[\hat{F},\hat{G}]$ also commutes with the Hamiltonian and is thus a conserved quantity.

P8.2 Prove the validity of the following expression of the virial theorem for a system of several particles, where α denotes the particles and i,j are their Cartesian coordinates,

$$\sum_\alpha \left\langle -\frac{1}{m^\alpha}\hat{p}_i^\alpha\hat{p}_j^\alpha + x_i^\alpha\frac{\partial V}{\partial x_j^\alpha}\right\rangle = 0. \tag{8.7}$$

Solution. The Hamiltonian of a quantum many-particle system is constructed

analogously to the corresponding classical case, and can be written in the following form for the three-dimensional case

$$\hat{H} = \sum_{i=1}^{3} \sum_{\alpha=1}^{N} \frac{(p_i^\alpha)^2}{2m^\alpha} + V\left(\boldsymbol{r}^\alpha\right), \tag{8.8}$$

where the index α labels the individual particles or their coordinates. For a bounded system (with motion restricted to a finite region of space) that has reached a stationary state, the following condition must hold,

$$\frac{d}{dt}\left\langle \sum_{\alpha=1}^{N} \sum_{i=1}^{3} x_i^\alpha p_i^\alpha \right\rangle = 0. \tag{8.9}$$

This requirement is a natural generalization of the condition

$$\frac{d}{dt}\left\langle \boldsymbol{r} \cdot \hat{\boldsymbol{p}} \right\rangle = 0. \tag{8.10}$$

However, we can be more general. Observing that once a stationary state has been reached, the expectation value of any time-independent variable becomes time-independent, we obtain the following more informative condition that is more general,

$$\frac{d}{dt}\left\langle \sum_{\alpha=1}^{N} x_i^\alpha p_j^\alpha \right\rangle = 0. \tag{8.11}$$

This requirement is a particular case of the general condition

$$\left\langle \left[\hat{A}, \hat{H}\right] \right\rangle = 0, \tag{8.12}$$

where $\hat{A}$ is an arbitrary time-independent dynamical variable, and the average is taken over a stationary state (this generalization follows directly from the condition $\left\langle d\hat{A}/dt \right\rangle = 0$).

Using the Heisenberg equation of motion, we rewrite the previous expression as

$$\sum_{\alpha=1}^{N} \left\langle \left[x_i^\alpha p_j^\alpha, \hat{H}\right] \right\rangle = 0. \tag{8.13}$$

We will compute the two required commutators separately. First, we have

$$\sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} \sum_{k=1}^{3} \left[x_i^\alpha p_j^\alpha, \frac{1}{2m_\beta} p_k^\beta p_k^\beta\right] = \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} \sum_{k=1}^{3} \frac{1}{2m_\beta} \left[x_i^\alpha, p_k^\beta p_k^\beta\right] p_j^\alpha \tag{8.14}$$

$$= i\hbar \sum_{\alpha=1}^{N} \frac{1}{m^\alpha} p_i^\alpha p_j^\alpha. \tag{8.15}$$

The remaining commutator is

$$\sum_{\alpha=1}^{N}\left[x_i^\alpha p_j^\alpha, V\right] = \sum_{\alpha=1}^{N} x_i^\alpha \left(-i\hbar\frac{\partial V}{\partial x_j^\alpha}\right). \tag{8.16}$$

Adding the two results and using the previous equation, we obtain

$$\sum_{\alpha=1}^{N}\left(\frac{1}{m^\alpha}\left\langle p_i^\alpha p_j^\alpha\right\rangle - \left\langle x_i^\alpha \frac{\partial V}{\partial x_j^\alpha}\right\rangle\right) = 0. \tag{8.17}$$

This is the desired (tensorial) generalization of the quantum virial theorem.

P8.3 Show that an attractive potential of the type $V \sim r^n$ only produces stable orbits if $n > -2$.
Solution. From the virial theorem we have that in this case,

$$\langle E\rangle = \frac{n+2}{2}\langle V\rangle. \tag{8.18}$$

With the usual convention $V(r \to \infty) \to 0$, in order for the system to be in a bound state it is required that $\langle V\rangle < 0$ (attractive potential) and $E < 0$, which implies that $n + 2 > 0$, that is, $n > -2$.

This result shows that both the Coulomb potential and the harmonic oscillator potential can produce bound states. But, for example, the interaction between two magnetic dipoles with interaction potential $V \sim r^{-3}$, cannot produce stable orbits. The reason for this behavior is that the effective radial potential (which is obtained by adding to V the potential associated with the centrifugal repulsion) has a minimum around which stationary states can be produced only if $n > -2$, since the centrifugal potential grows as r^{-2}.

P8.4 Show that for an electron subject to the 1D potential $V = -Cx$ with $C > 0$, the momentum dispersion Δp is constant.
Solution. The momentum dispersion Δp is defined as

$$\Delta p = \sqrt{\langle p^2\rangle - \langle p\rangle^2}. \tag{8.19}$$

We use Ehrenfest's theorem to connect quantum expectation values with classical equations. For $\langle x\rangle$ we get

$$\frac{d}{dt}\langle x\rangle = \frac{\langle p\rangle}{m}, \tag{8.20}$$

for $\langle p\rangle$ we get

$$\frac{d}{dt}\langle p\rangle = -\langle \nabla V\rangle = C, \tag{8.21}$$

and finally, for $\langle p^2\rangle$,

$$\frac{d}{dt}\langle p^2\rangle = \frac{1}{i\hbar}\langle [p^2, H]\rangle. \tag{8.22}$$

The commutator gives

$$[p^2, V] = p^2V - Vp^2 \tag{8.23}$$
$$= -i\hbar(2p\nabla V + \nabla V \cdot p) \tag{8.24}$$
$$= -i\hbar(-2Cp - Cp) \tag{8.25}$$
$$= 3i\hbar Cp. \tag{8.26}$$

Therefore,

$$\frac{d}{dt}\langle p^2\rangle = \frac{1}{i\hbar}\langle 3i\hbar Cp\rangle = 3C\langle p\rangle. \tag{8.27}$$

The time derivative of $(\Delta p)^2$ is

$$\frac{d}{dt}(\Delta p)^2 = \frac{d}{dt}\langle p^2\rangle - 2\langle p\rangle\frac{d}{dt}\langle p\rangle = 3C\langle p\rangle - 2\langle p\rangle(C) = C\langle p\rangle. \tag{8.28}$$

For Δp to remain constant, we require that

$$C\langle p\rangle = 0. \tag{8.29}$$

This condition is satisfied when either $\langle p\rangle = 0$ (stationary states or states with even symmetry), or $C = 0$ (trivial case of null potential).

P8.5 Show that

$$\frac{d}{dt}\langle(\Delta x)^2\rangle = \frac{1}{m}\langle\hat{x}\hat{p} + \hat{p}\hat{x}\rangle - \frac{2}{m}\bar{x}\bar{p}. \tag{}$$

Solution. By definition, we have

$$(\Delta\hat{x})^2 = \hat{x}^2 - \langle\hat{x}\rangle^2. \tag{8.30}$$

Since the $\langle\hat{x}\rangle^2$ is, in general, a function of time, to study the time evolution of $(\Delta\hat{x})^2$ we must use the full Heisenberg equation of motion, which gives

$$i\hbar\frac{d}{dt}(\Delta\hat{x})^2 = \left[\hat{x}^2, \hat{H}\right] - 2i\hbar\langle\hat{x}\rangle\frac{d\langle\hat{x}\rangle}{dt}. \tag{8.31}$$

From

$$\left[\hat{x}, \hat{H}\right] = \frac{i\hbar}{m}\hat{p} \tag{8.32}$$

it follows that

$$\left[\hat{x}^2, \hat{H}\right] = \hat{x}\left[\hat{x}, \hat{H}\right] + \left[\hat{x}, \hat{H}\right]\hat{x} = \frac{i\hbar}{m}(\hat{x}\hat{p} + \hat{p}\hat{x}), \tag{8.33}$$

which substituted into 8.31 gives

$$\frac{d}{dt}(\Delta\hat{x})^2 = \frac{1}{m}\langle\hat{x}\hat{p} + \hat{p}\hat{x}\rangle - \frac{2}{m}\langle\hat{x}\rangle\langle\hat{p}\rangle. \tag{8.34}$$

Taking expectation values we obtain

$$\frac{d}{dt}\left\langle(\Delta\hat{x})^2\right\rangle = \frac{1}{m}\left\langle\hat{x}\hat{p} + \hat{p}\hat{x} - 2\overline{xp}\right\rangle, \tag{8.35}$$

as was to be demonstrated.

It is common (though not universally practiced) to take the quantity

$$\Gamma_{xp} = \frac{1}{2}\langle \hat{x}\hat{p} + \hat{p}\hat{x}\rangle - \overline{xp}$$

as the correlation between the variables x and p. Accepting this definition, Eq. 8.35 establishes that it is the correlation Γ_{xp} that determines the evolution of σ_x^2,

$$\frac{d\sigma_x^2}{dt} = \frac{2}{m}\Gamma_{xp}. \tag{8.36}$$

With appropriate definitions, the same occurs in classical systems, since Eq. 8.35 follows directly from the general definition 8.30 (note that Heisenberg's equations are formally identical to the corresponding classical equations).

P8.6 In [**1**], **Section 8.4,** we proved that if two dynamical variables F, G have simultaneous well-defined values, their respective operators must commute. Show that this condition is also sufficient, i.e. if $\widehat{F}$ and $\widehat{G}$ commute, they have simultaneous well-defined values.

Solution. We assume

$$[\hat{F}, \hat{G}] = \hat{F}\hat{G} - \hat{G}\hat{F} = 0. \tag{8.37}$$

Since $\hat{F}$ and $\hat{G}$ commute, it can be shown that they share a complete set of eigenvectors. To demonstrate this we assume $\hat{F}$ that has a discrete non-degenerate spectrum (for simplicity; the argument generalizes to degenerate cases).

Let $\{|\psi_n\rangle\}$ be an orthonormal eigenbasis of $\hat{F}$, such that

$$\hat{F}|\psi_n\rangle = f_n|\psi_n\rangle. \tag{8.38}$$

Applying $\hat{G}$ to both sides and using the commutation relation we get

$$\hat{F}(\hat{G}|\psi_n\rangle) = \hat{G}(\hat{F}|\psi_n\rangle) = f_n(\hat{G}|\psi_n\rangle). \tag{8.39}$$

This shows that $\hat{G}|\psi_n\rangle$ is also an eigenvector of $\hat{F}$ with eigenvalue f_n.

If the spectrum of $\hat{F}$ is non-degenerate, $\hat{G}|\psi_n\rangle$ must be proportional to $|\psi_n\rangle$, i.e.:

$$\hat{G}|\psi_n\rangle = g_n|\psi_n\rangle. \tag{8.40}$$

Therefore, $|\psi_n\rangle$ is also an eigenvector of $\hat{G}$.

If $\hat{F}$ has degeneracy, the eigenvectors corresponding to an eigenvalue f_n form a subspace $\mathcal{H}_n$. The operator $\hat{G}$ acts within $\mathcal{H}_n$ (since $[\hat{F}, \hat{G}] = 0$) and can be diagonalized in this subspace, yielding a common eigenbasis for both operators. So any common eigenvector $|\psi\rangle$ of $\hat{F}$ and $\hat{G}$ satisfies

$$\hat{F}|\psi\rangle = f|\psi\rangle, \quad \hat{G}|\psi\rangle = g|\psi\rangle. \tag{8.41}$$

In the state $|\psi\rangle$, a measurement of F will yield f with certainty, and a measurement of G will yield g with certainty. Thus, both observables have well-defined values simultaneously.

The commutation relation $[\hat{F}, \hat{G}] = 0$ guarantees the existence of a simultaneous eigenbasis, which is a sufficient condition for F and G to have well-defined values in the same states.

P8.7 Study the motion of a packet of free particles in the Heisenberg description. *Hint:* Calculate the dispersions of $\hat{x}$ and $\hat{p}$ as functions of time.
Solution. The Heisenberg equations of motion are

$$\dot{\hat{q}} = \frac{\partial \hat{H}}{\partial \hat{p}}, \qquad \dot{\hat{p}} = -\frac{\partial \hat{H}}{\partial \hat{q}}. \tag{8.42}$$

The Hamiltonian of the free particle is $\hat{H} = \hat{p}^2/2m$. By substituting, we obtain

$$\frac{d\hat{q}}{dt} = \frac{\hat{p}}{m}; \qquad \frac{d\hat{p}}{dt} = 0, \tag{8.43}$$

whose general solution is

$$\hat{p} = \hat{p}_0; \qquad \hat{q} = \hat{q}_0 + \frac{\hat{p}_0}{m}t, \tag{8.44}$$

where $\hat{q}_0$ and $\hat{p}_0$ are the operators representing the initial conditions. The expectation values, both for position and momentum, follow the classical laws

$$\langle \hat{p} \rangle = \langle \hat{p}_0 \rangle, \tag{8.45}$$

$$\langle \hat{q} \rangle = \langle \hat{q}_0 \rangle + \frac{\langle \hat{p}_0 \rangle}{m}t. \tag{8.46}$$

For the quadratic deviations of these quantities we obtain

$$\langle (\Delta p)^2 \rangle = \langle (\Delta p_0)^2 \rangle = \text{const.}, \tag{8.47}$$

$$\langle (\Delta q)^2 \rangle = \langle (\Delta q_0)^2 \rangle + \left(\langle \hat{p}_0 \hat{q}_0 \rangle + \langle \hat{q}_0 \hat{p}_0 \rangle - 2\bar{q}_0 \bar{p}_0 \right) \frac{t}{m} + \langle (\Delta p_0)^2 \rangle \frac{t^2}{m^2}. \tag{8.48}$$

While the momentum dispersion remains constant (since no effective force acts on the ensemble), the spatial width of the packet grows indefinitely over time. This is a consequence of the fact that the slower particles near the rear edge lag behind, while the faster ones, near the front, move ahead — and this happens continuously. Eventually, it is the initial momentum dispersion that determines the value of $\langle (\Delta q)^2 \rangle$. In the case where positions and momenta are initially uncorrelated, so that

$$\langle \hat{q}_0 \hat{p}_0 \rangle + \langle \hat{p}_0 \hat{q}_0 \rangle = 2\bar{q}_0 \bar{p}_0, \tag{8.49}$$

one obtains

$$\langle (\Delta q)^2 \rangle = \langle (\Delta q_0)^2 \rangle + \langle (\Delta p_0)^2 \rangle \frac{t^2}{m^2}. \tag{8.50}$$

From equation 8.44, we obtain that the fundamental commutator is

$$[\hat{q}, \hat{p}] = \left[\hat{q}_0 + \frac{\hat{p}_0}{m}t, \hat{p}_0 \right] = [\hat{q}_0, \hat{p}_0] = i\hbar. \tag{8.51}$$

We see that the matrices corresponding to the initial conditions, although arbitrary in principle, must satisfy the quantum laws. This means that the quantum properties of the packet are encoded from the beginning. In particular, the initial commutator $[\hat{q}_0, \hat{p}_0] = i\hbar$ leads to the Heisenberg inequality

$$\langle(\Delta q_0)^2\rangle\langle(\Delta p_0)^2\rangle \geq \hbar^2/4, \tag{8.52}$$

and thus to a limitation on the possible minimal values of the initial dispersions.

P8.8 Show that the transformation $\widehat{U}$ given by Eqs. **(8.114)-(8.119)** in [**1**], is unitary.

Solution. According to **(8.116)** and **(8.117)**, the operator $\hat{U}$ transforms the basis $\{u_\mu\}$ (eigenfunctions of $\hat{Q}$) into the basis $\{\varphi_m\}$ (eigenfunctions of $\hat{R}$) via

$$\varphi_m = \sum_\lambda U_{\lambda m} u_\lambda, \quad \text{with} \quad U_{\mu m} = \int u_\mu^* \varphi_m \, dx. \tag{8.53}$$

The matrix elements of $\hat{U}$ on the basis of $\{u_\mu\}$ are $U_{\mu m}$. The adjoint matrix $\hat{U}^\dagger$ has elements

$$(\hat{U}^\dagger)_{m\mu} = U_{\mu m}^* = \int \varphi_m^* u_\mu \, dx. \tag{8.54}$$

We now compute the matrix elements of $\hat{U}^\dagger\hat{U}$,

$$(\hat{U}^\dagger\hat{U})_{mn} = \sum_\lambda (\hat{U}^\dagger)_{m\lambda} U_{\lambda n} = \sum_\lambda \left(\int \varphi_m^* u_\lambda \, dx\right)\left(\int u_\lambda^* \varphi_n \, dx\right). \tag{8.55}$$

Using the completeness relation of the basis $\{u_\lambda\}$ ($\sum_\lambda u_\lambda(x) u_\lambda^*(x') = \delta(x - x')$) we get

$$(\hat{U}^\dagger\hat{U})_{mn} = \int \varphi_m^* \varphi_n \, dx = \delta_{mn}, \tag{8.56}$$

where the last equality follows because $\{\varphi_m\}$ is an orthonormal basis. Similarly, the matrix elements of $\hat{U}\hat{U}^\dagger$ are

$$(\hat{U}\hat{U}^\dagger)_{\mu\nu} = \sum_m U_{\mu m} (\hat{U}^\dagger)_{m\nu} = \sum_m \left(\int u_\mu^* \varphi_m \, dx\right)\left(\int \varphi_m^* u_\nu \, dx\right). \tag{8.57}$$

Using the completeness relation of $\{\varphi_m\}$, we get

$$(\hat{U}\hat{U}^\dagger)_{\mu\nu} = \int u_\mu^* u_\nu \, dx = \delta_{\mu\nu}, \tag{8.58}$$

since $\{u_\mu\}$ is also orthonormal. Therefore, $\hat{U}$ is unitary.

P8.9 Use the projection operators to construct an expression for the function $f(\hat{A})$, where $\hat{A}$ is an operator with eigenvectors $|n\rangle$ and eigenvalues a_n.

Solution. Let $|n\rangle$ be the eigenvectors of the operator A and a_n its eigenvalues,

$$\hat{A}|n\rangle = a_n|n\rangle. \tag{8.59}$$

We construct the projection operators $\hat{P}_n$ associated with the basis $|n\rangle$,

$$\hat{P}_n = |n\rangle\langle n|. \tag{8.60}$$

Now let $f(x)$ be a function of x that can be developed as a Taylor series around the origin

$$f(x) = \sum_s \frac{1}{s!} f^{(s)}(0) x^s. \tag{8.61}$$

We wish to find a suitable definition of the function $f(\hat{A})$. We expand the operator $\hat{A}$ in its own representation, that is,

$$\hat{A} = \sum_k a_k \hat{P}_k = \sum_k a_k |k\rangle\langle k|. \tag{8.62}$$

It follows that

$$\hat{A}^2 = \sum_{k,k'} a_k a_{k'} |k\rangle\langle k||k'\rangle\langle k'| = \sum_k a_k^2 |k\rangle\langle k| = \sum_n a_n^2 \hat{P}_n, \tag{8.63}$$

and more generally,

$$\hat{A}^s = \sum_n a_n^s \hat{P}_n. \tag{8.64}$$

Substituting into the series expansion of the function f, we obtain

$$f(\hat{A}) = \sum_{s,n} \frac{1}{s!} f^{(s)}(0) a_n^s \hat{P}_n = \sum_n \hat{P}_n \sum_s \frac{1}{s!} f^{(s)}(0) a_n^s = \sum_n \hat{P}_n f(a_n). \tag{8.65}$$

Therefore, the desired expression is

$$f(\hat{A}) = \sum_n f(a_n) \hat{P}_n. \tag{8.66}$$

P8.10 Consider the two-dimensional problem of a particle of mass m moving on the xy plane under the action of a radial force $f(r)$. Analyze the symmetries of the Hamiltonian and find the associated constants of motion.

Solution. The radial force is

$$\boldsymbol{f}(r) = f(r)\hat{r}, \quad \text{where} \quad r = \sqrt{x^2 + y^2}. \tag{8.67}$$

The associated potential $V(r)$ satisfies

$$f(r) = -\frac{dV(r)}{dr}. \tag{8.68}$$

The Hamiltonian in Cartesian coordinates is

$$H = \frac{p_x^2 + p_y^2}{2m} + V(r), \quad \text{with} \quad r = \sqrt{x^2 + y^2}. \tag{8.69}$$

H is invariant under rotations about the z-axis. This implies that the angular momentum L_z is conserved. In polar coordinates (r, ϕ),

$$L_z = xp_y - yp_x = -i\hbar\frac{\partial}{\partial\phi} \tag{8.70}$$

Now, since $[H, L_z] = 0$, L_z is a constant of motion, H has no explicit time dependence, so the total energy E is conserved and H is invariant under $x \to -x$ and $y \to -y$; but this doesn't generate new constants of motion.

Since H is rotationally invariant, L_z is conserved,

$$\frac{dL_z}{dt} = \frac{i}{\hbar}[H, L_z] = 0. \tag{8.71}$$

Energy conservation follows from the time-independence of H,

$$\frac{dE}{dt} = \frac{\partial H}{\partial t} = 0. \tag{8.72}$$

In polar coordinates (r, ϕ),

$$H = -\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\right) + V(r). \tag{8.73}$$

Given that $[H, L_z] = 0$, the eigenfunctions of H can be written as

$$\psi(r, \phi) = R(r)e^{i\ell\phi}, \tag{8.74}$$

where ℓ is the quantum number associated with L_z (with $L_z\psi = \hbar\ell\psi$).

CHAPTER 9

The One-Dimensional Harmonic Oscillator

P9.1 Derive explicitly Eqs. **(9.15) and (9.16)** of Ref. [**1**] for the minimum-dispersion packet.

Solution. The goal is to calculate the dispersion of $\hat{x}$ and $\hat{p}$ for the coherent packet described by the wave function $\Psi(x,t)$ for the harmonic oscillator (HO). We start from

$$\langle \hat{x} \rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \int_{-\infty}^{\infty} x \exp\left[-\frac{m\omega}{\hbar}\left(x - x_0\cos\omega t\right)^2\right] dx. \tag{9.1}$$

and carry out the change of variable $y = x - x_0\cos\omega t$, to get

$$\langle \hat{x} \rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \int_{-\infty}^{\infty} (y + x_0\cos\omega t) \exp\left[-\frac{m\omega}{\hbar}y^2\right] dy \tag{9.2}$$

$$= \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} x_0\cos\omega t \int_{-\infty}^{\infty} \exp\left[-\frac{m\omega}{\hbar}y^2\right] dy = x_0\cos\omega t. \tag{9.3}$$

Similarly, we have

$$\langle \hat{x}^2 \rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \int_{-\infty}^{\infty} (y + x_0\cos\omega t)^2 \exp\left[-\frac{m\omega}{\hbar}y^2\right] dy \tag{9.4}$$

$$= \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \int_{-\infty}^{\infty} \left(y^2 + x_0^2\cos^2\omega t\right) \exp\left[-\frac{m\omega}{\hbar}y^2\right] dy \tag{9.5}$$

$$= \frac{\hbar}{\sqrt{\pi}m\omega} \int_{-\infty}^{\infty} z^2 e^{-z^2} dz + \frac{1}{\sqrt{\pi}} x_0^2\cos^2\omega t \int_{-\infty}^{\infty} e^{-z^2} dz, \tag{9.6}$$

where we made the change of variable $z = (m\omega/\hbar)^{1/2}y$. Evaluating the integrals yields

$$\left\langle \hat{x}^2 \right\rangle = \frac{\hbar}{2m\omega} + x_0^2\cos^2\omega t = \frac{\hbar}{2m\omega} + \langle \hat{x} \rangle^2 . \tag{9.7}$$

From this it follows that the dispersion of $\hat{x}$ for this state is

$$\left\langle (\Delta\hat{x})^2 \right\rangle = \left\langle \hat{x}^2 \right\rangle - \langle \hat{x} \rangle^2 = \frac{1}{4a} = \frac{\hbar}{2m\omega} \tag{9.8}$$

For the calculation of $\bar{p}$ we start from

$$\langle \hat{p} \rangle = -i\hbar \int_{-\infty}^{\infty} \Psi^*(x,t) \frac{\partial}{\partial x} \Psi(x,t)\, dx \tag{9.9}$$

$$= -i\hbar \int \Psi^*(x,t) \left(-\frac{m\omega}{\hbar}(x - x_0 \cos\omega t) - i\frac{m\omega}{\hbar} x_0 \sin\omega t \right) \Psi(x,t)\, dx. \tag{9.10}$$

By Eq. (9.3), the integral of the first term gives $im\omega \langle x - x_0 \cos\omega t \rangle = 0$. Thus, we are left with

$$\langle \hat{p} \rangle = -i\hbar \left(-i\frac{m\omega}{\hbar} x_0 \sin\omega t \right) \int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\, dx = -m\omega x_0 \sin\omega t. \tag{9.11}$$

Following a procedure similar to that used to calculate $\langle \hat{x}^2 \rangle$, we arrive at

$$\left\langle \hat{p}^2 \right\rangle = m\hbar\omega - m^2\omega^2 x_0^2 e^{-2i\omega t} - m^2\omega^2 \left\langle \hat{x}^2 \right\rangle + 2m^2\omega^2 x_0 e^{-i\omega t} \left\langle \hat{x} \right\rangle, \tag{9.12}$$

that is,

$$\left\langle \hat{p}^2 \right\rangle = \tfrac{1}{2} m\hbar\omega + m^2\omega^2 x_0^2 \sin^2\omega t = \tfrac{1}{2} m\hbar\omega + \left\langle \hat{p} \right\rangle^2. \tag{9.13}$$

Therefore,

$$\left\langle (\Delta\hat{p})^2 \right\rangle = \left\langle \hat{p}^2 \right\rangle - \left\langle \hat{p} \right\rangle^2 = \tfrac{1}{2} m\hbar\omega = \hbar^2 a. \tag{9.14}$$

From (9.8) and (9.14), it follows that the product of the dispersions is

$$\left\langle (\Delta\hat{x})^2 \right\rangle \left\langle (\Delta\hat{p})^2 \right\rangle = \tfrac{1}{4}\hbar^2. \tag{9.15}$$

This is the minimum value that the product can take, showing that the coherent oscillator packet has the minimal dispersion compatible with quantum laws; hence we call it minimal. From the previous relations it also follows that this minimal packet satisfies the condition.

$$\left\langle (\Delta\hat{p})^2 \right\rangle = m^2\omega^2 \left\langle (\Delta\hat{x})^2 \right\rangle. \tag{9.16}$$

P9.2 Show that the stationary states of the harmonic oscillator satisfy the following relations:

$$E_n = m\omega^2 \langle n|x^2|n\rangle; \quad \langle n|\hat{T}|n\rangle = \langle n|\hat{V}|n\rangle = \frac{1}{2} E_n. \tag{9.17}$$

Discuss these results from the point of view of the virial theorem.

Solution. We will calculate the values $\langle n|\hat{x}^2|n\rangle$ and $\langle n|\hat{p}^2|n\rangle$ directly. The nonzero matrix elements of $\hat{x}$ for the harmonic oscillator are

$$x_{n,n-1} = x_{n-1,n} = \sqrt{\frac{\hbar}{2m\omega}}\, n, \quad x_{n,n+1} = x_{n+1,n} = \sqrt{\frac{\hbar}{2m\omega}(n+1)}. \tag{9.18}$$

Using the rules for matrix multiplication, we can write:

$$\langle n|\hat{x}^2|m\rangle = \sum_k \langle n|\hat{x}|k\rangle\langle k|\hat{x}|m\rangle \tag{9.19}$$

$$= \langle n|\hat{x}|n+1\rangle\langle n+1|\hat{x}|m\rangle + \langle n|\hat{x}|n-1\rangle\langle n-1|\hat{x}|m\rangle \tag{9.20}$$

$$= \langle n|\hat{x}|n+1\rangle\langle n+1|\hat{x}|n\rangle\delta_{nm} + \langle n|\hat{x}|n+1\rangle\langle n+1|\hat{x}|n+2\rangle\delta_{n+2,m} \tag{9.21}$$

$$+ \langle n|\hat{x}|n-1\rangle\langle n-1|\hat{x}|n\rangle\delta_{nm} + \langle n|\hat{x}|n-1\rangle\langle n-1|\hat{x}|n-2\rangle\delta_{n-2,m}. \tag{9.22}$$

Therefore, the only non-zero matrix elements of $\hat{x}^2$ involving the state n of the harmonic oscillator are

$$x_{nn}^2 = \langle n|\hat{x}^2|n\rangle = \langle n|\hat{x}|n+1\rangle\langle n+1|\hat{x}|n\rangle + \langle n|\hat{x}|n-1\rangle\langle n-1|\hat{x}|n\rangle, \tag{9.23}$$

$$x_{nn}^2 = \frac{\hbar}{2m\omega}(2n+1). \tag{9.24}$$

$$x_{n,n+2}^2 = \langle n|\hat{x}^2|n+2\rangle = \langle n|\hat{x}|n+1\rangle\langle n+1|\hat{x}|n+2\rangle \tag{9.25}$$

$$= \frac{\hbar}{2m\omega}\sqrt{(n+1)(n+2)}, \tag{9.26}$$

$$x_{n,n-2}^2 = \langle n|\hat{x}^2|n-2\rangle = \langle n|\hat{x}|n-1\rangle\langle n-1|\hat{x}|n-2\rangle \tag{9.27}$$

$$= \frac{\hbar}{2m\omega}\sqrt{(n-1)n}. \tag{9.28}$$

The matrix elements of $\hat{p}^2$ are similar, but multiplied by $m^2\omega^2$; in particular,

$$p_{nn}^2 = \langle n|\hat{p}^2|n\rangle = m^2\omega^2\langle n|\hat{x}^2|n\rangle = \frac{1}{2}m\hbar\omega(2n+1). \tag{9.29}$$

With the previous results, we can calculate the expectation values of the kinetic and potential energy in state n, which are

$$\langle n|\hat{T}|n\rangle = \frac{1}{2m}\langle n|\hat{p}^2|n\rangle = \frac{1}{2}m\omega^2\langle\hat{x}^2\rangle, \tag{9.30}$$

$$\langle n|\hat{V}|n\rangle = \frac{1}{2}m\omega^2\langle n|\hat{x}^2|n\rangle = \frac{1}{2}m\omega^2\langle\hat{x}^2\rangle = \frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right), \tag{9.31}$$

from which it follows that

$$E_n = \langle n|\hat{T}+\hat{V}|n\rangle = m\omega^2\langle\hat{x}^2\rangle, \tag{9.32}$$

and

$$\langle n|\hat{T}|n\rangle = \langle n|\hat{V}|n\rangle = \frac{1}{2}E_n. \tag{9.33}$$

The quantum virial theorem states that for a potential of the form $V = ar^s$, the stationary states must satisfy the condition given by

$$\langle\hat{T}\rangle = \frac{s}{2}\langle\hat{V}\rangle = \frac{s}{s+2}E. \tag{9.34}$$

For the harmonic oscillator, $s = 2$, and this condition reduces to

$$\langle\hat{T}\rangle = \langle\hat{V}\rangle = \frac{1}{2}E, \tag{9.35}$$

which coincides with 9.33. Thus, the stationary states of the harmonic oscillator satisfy the virial theorem, as expected.

P9.3 Determine the energy eigenvalues for the 1D Schrödinger equation with the potential

$$V(x) = \begin{cases} \frac{1}{2}m\omega^2 x^2, & x > 0 \\ +\infty & x < 0. \end{cases} \tag{9.36}$$

Solution. The time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi(x) = E\psi(x). \tag{9.37}$$

This is the harmonic oscillator equation with the additional boundary condition $\psi(0) = 0$. The general solutions for the harmonic oscillator are the eigenfunctions of the Hamiltonian,

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-\frac{m\omega x^2}{2\hbar}}, \tag{9.38}$$

where H_n are the Hermite polynomials. The corresponding energy levels are

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \ldots \tag{9.39}$$

From the parity of the Hermite polynomials, if n is even, $\psi_n(0) \neq 0$ (it does not satisfy $\psi(0) = 0$) and if n is odd, $\psi_n(0) = 0$ (it satisfies the boundary condition). Therefore only eigenfunctions with odd n are physically acceptable,

$$n = 1, 3, 5, \ldots \tag{9.40}$$

The corresponding energy levels are

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 1, 3, 5, \ldots \tag{9.41}$$

To express the energy levels more compactly, we make the substitution $n = 2k + 1$ where $k = 0, 1, 2, \ldots$,

$$E_k = \left((2k + 1) + \frac{1}{2}\right)\hbar\omega = \left(2k + \frac{3}{2}\right)\hbar\omega. \tag{9.42}$$

The wave function for the ground state ($k = 0$, $n = 1$) is

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{2m\omega}{\hbar}} x e^{-\frac{m\omega x^2}{2\hbar}}, \tag{9.43}$$

and the corresponding energy is

$$E_0 = \frac{3}{2}\hbar\omega. \tag{9.44}$$

The energy eigenvalues for this system are therefore

$$E_k = \left(2k + \frac{3}{2}\right)\hbar\omega, \quad k = 0, 1, 2, \ldots \tag{9.45}$$

P9.4 Find the probability that the particles lie within the classically allowed range for the eigenstates of the HO, and determine the value of this probability for the ground state. *Note:* $(erf)(1) = 0.8427\ldots$

Solution. We begin by recalling the eigenfunctions of the quantum harmonic oscillator in terms of the dimensionless variable $\xi = \frac{x}{\alpha_0}$, where $\alpha_0 = \sqrt{\hbar/m\omega}$. These are given by

$$\psi_n(\xi) = C_n e^{-\frac{1}{2}\xi^2} H_n(\xi), \tag{9.46}$$

where $H_n(\xi)$ are the Hermite polynomials and C_n is the normalization constant

$$C_n = \left(\sqrt{\pi}\alpha_0 2^n n!\right)^{-1/2}. \tag{9.47}$$

To compute the probability that the particle lies within a specific region $x \in [a, b]$, we evaluate the following integral

$$P = \int_a^b |\psi_n(x)|^2 dx. \tag{9.48}$$

Changing variables to $\xi = \frac{x}{\alpha_0}$, this becomes

$$P = \int_{\frac{a}{\alpha_0}}^{\frac{b}{\alpha_0}} |\psi_n(\xi)|^2 \alpha_0 d\xi. \tag{9.49}$$

The limits $x_\pm$ are the classical turning points, determined by equating the total energy with the potential energy,

$$\frac{1}{2}m\omega^2 x_\pm^2 = \hbar\omega\left(n + \frac{1}{2}\right), \tag{9.50}$$

which gives

$$x_\pm = \pm\sqrt{\frac{2\hbar}{m\omega}\left(n + \frac{1}{2}\right)} = \pm\alpha_0\sqrt{2n+1}. \tag{9.51}$$

Outside of this region, the classical particles would not have enough energy to pass through. Thus, the probability that the particle lies within the classically allowed region $[x_-, x_+]$ is

$$P_n = \alpha_0 C_n^2 \int_{-\sqrt{2n+1}}^{\sqrt{2n+1}} e^{-\xi^2} |H_n(\xi)|^2 d\xi = 2\alpha_0 C_n^2 \int_0^{\sqrt{2n+1}} e^{-\xi^2} |H_n(\xi)|^2 d\xi \tag{9.52}$$

$$= \left(\sqrt{\pi} 2^{n-1} n!\right)^{-1} \int_0^{\sqrt{2n+1}} e^{-\xi^2} |H_n(\xi)|^2 d\xi. \tag{9.53}$$

For the ground state $n = 0$, we have

$$H_0(\xi) = 1, \quad C_0 = \left(\sqrt{\pi}\alpha_0\right)^{-1/2} \tag{9.54}$$

and the probability becomes

$$P_0 = \frac{2}{\sqrt{\pi}} \int_0^1 e^{-\xi^2}\, d\xi = \frac{2}{\sqrt{\pi}} \cdot \frac{\sqrt{\pi}}{2} \mathrm{erf}(1). \tag{9.55}$$

Using $\mathrm{erf}(1) = 0.8427$, the probability that the particle in the ground state lies within the classically allowed region is approximately

$$P_0 \approx 84.3\%. \tag{9.56}$$

As n increases, the classical turning points are farther apart, and the probability that a particle lies within the classically allowed region increases because of the dominance of the exponentially decreasing factor.

P9.6 Solve the 3D harmonic oscillator problem in Cartesian coordinates. Discuss the degeneracy for the isotropic case.

Solution. The potential in this problem is a separable function in each of the Cartesian coordinates, so we can write

$$V(x,y,z) = \frac{1}{2} m \left(\omega_1^2 x^2 + \omega_2^2 y^2 + \omega_3^2 z^2\right) = V(x) + V(y) + V(z). \tag{9.57}$$

This allows us to reduce the problem to the case of three independent one-dimensional harmonic oscillators, with frequencies ω_1, ω_2, and ω_3, oscillating along the axes Ox, Oy, and Oz, respectively. The wave function is the product of the three corresponding eigenfunctions

$$\psi_{n_1,n_2,n_3}(x,y,z) = \psi_{n_1}(x)\psi_{n_2}(y)\psi_{n_3}(z) = \prod_{i=1}^{3} \left(\frac{1}{2^{n_i} n_i!}\right)^{1/2} \left(\frac{m\omega_i}{\pi\hbar}\right)^{1/4} e^{-\xi_i^2/2} H_{n_i}(\xi_i), \tag{9.58}$$

where

$$\xi_i = \sqrt{\frac{m\omega_i}{\hbar}} x_i, \quad i = 1,2,3, \quad n_i = 0,1,2,3,\ldots \tag{9.59}$$

The energy of the 3D harmonic oscillator is the sum of the energies of the three independent oscillators,

$$E_{n_1,n_2,n_3} = \sum_{i=1}^{3} E_{n_i} = \hbar\omega_1 \left(n_1 + \frac{1}{2}\right) + \hbar\omega_2 \left(n_2 + \frac{1}{2}\right) + \hbar\omega_3 \left(n_3 + \frac{1}{2}\right). \tag{9.60}$$

From this expression we see that if the ratio between the frequencies ω_i is irrational, the energy levels are non-degenerate. However, the ground state is always non-degenerate.

In the particular isotropic case $\omega_1 = \omega_2 = \omega_3 = \omega$, the total energy can be written as

$$E_n = \hbar\omega \left(n + \frac{3}{2}\right), \tag{9.61}$$

with

$$n = n_1 + n_2 + n_3. \tag{9.62}$$

In this case, all energy levels, except for the ground state, are degenerate. Indeed, if we fix n_1, then n_2 can take values from 0 to $n-n_1$, so that the sum $n = n_1+n_2+n_3$ for given n_1 and n can be found in $n - n_1 + 1$ different ways. The degeneracy of the n-th state is therefore given by

$$\sum_{n_1=0}^{n}(n - n_1 + 1) = \frac{1}{2}(n + 1)(n + 2). \tag{9.63}$$

P9.5 Small-amplitude vibrations in diatomic molecules can be studied using as a model for molecular vibrational potential the potential of the HO, $V(x) = \frac{1}{2}k_f x^2$, with k_f the force constant. For a typical diatomic molecule, $k_f \simeq 1 \times 10^3 \mathrm{J} \cdot \mathrm{m}^{-2}$.

a) Use this data to estimate the value of the zero-point vibrational energy.

b) Estimate the spacing, in energy, between two successive states.

Solution. The potential is modeled as a harmonic oscillator

$$V(x) = \frac{1}{2}k_f x^2, \tag{9.64}$$

where k_f is the force constant and x is the displacement from the equilibrium. The angular frequency ω of the oscillator is given by

$$\omega = \sqrt{\frac{k_f}{\mu}}, \tag{9.65}$$

where μ is the reduced mass of the molecule. For a diatomic molecule with masses m_1 and m_2,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}. \tag{9.66}$$

The zero-point energy ($n = 0$) for a quantum harmonic oscillator is $E_0 = \frac{1}{2}\hbar\omega$. Substituting ω we get

$$E_0 = \frac{\hbar}{2}\sqrt{\frac{k_f}{\mu}}, \tag{9.67}$$

and fthe spacing between successive levels of a harmonic oscillator is given by

$$\Delta E = \hbar\sqrt{\frac{k_f}{\mu}}. \tag{9.68}$$

For the particular case of the H_2 molecule, we get, with $\mu \simeq 0.8 \times 10^{-27}\mathrm{kg}$, $\omega \simeq 10^{15}\mathrm{s}^{-1}$.Therefore, with $\hbar \simeq 10^{-34}\mathrm{J} \cdot \mathrm{s}$, we have

$$E_0 = \frac{\hbar\omega}{2} \simeq 0.5 \times 10^{-19}\mathrm{J}, \quad \Delta\mathrm{E} = \hbar\omega \simeq 10^{-19}\mathrm{J} = 10^{-12}\mathrm{erg}. \tag{9.69}$$

The energy between two successive vibrational energy states is therefore larger than the energy between the molecule's rotational states, which is of the order of 10^{-21}J.

P9.7 A one-dimensional oscillator moves in the external electric field generated by the potential $-e\boldsymbol{\mathcal{E}}x(t)$.

a) State the equations of motion for $\hat{x}(t)$ and $\hat{p}(t)$ and show that they have precisely the form of the corresponding classical equations.

b) Solve for $\hat{x}(t)$ and $\hat{p}(t)$ as a function of $\hat{x}(0)$ and $\hat{p}(0)$.

c) Determine the commutation relations $[x(t_1), x(t_2)]$ for arbitrary $t_1 - t_2$.

Solution. a) The Hamiltonian for this problem is

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 - e\mathcal{E}\hat{x} \tag{9.70}$$

From the Heisnberg equation for $\hat{x}(t)$ we get

$$\frac{d\hat{x}}{dt} = \frac{i}{\hbar}[\hat{H}, \hat{x}] = \frac{i}{\hbar}\left[\frac{\hat{p}^2}{2m}, \hat{x}\right]. \tag{9.71}$$

or using $[\hat{p}^2, \hat{x}] = \hat{p}[\hat{p}, \hat{x}] + [\hat{p}, \hat{x}]\hat{p} = -2i\hbar\hat{p}$,

$$\left[\frac{\hat{p}^2}{2m}, \hat{x}\right] = \frac{1}{2m}(-2i\hbar\hat{p}) = -\frac{i\hbar}{m}\hat{p}, \tag{9.72}$$

whence

$$\frac{d\hat{x}}{dt} = \frac{i}{\hbar}\left(-\frac{i\hbar}{m}\hat{p}\right) = \frac{\hat{p}}{m}. \tag{9.73}$$

Similarly, for $\hat{p}(t)$ we get

$$\frac{d\hat{p}}{dt} = \frac{i}{\hbar}[\hat{H}, \hat{p}] = \frac{i}{\hbar}\left(\left[\frac{1}{2}m\omega^2\hat{x}^2, \hat{p}\right] + [-e\mathcal{E}\hat{x}, \hat{p}]\right). \tag{9.74}$$

Calculating each commutator,

$$[\hat{x}^2, \hat{p}] = \hat{x}[\hat{x}, \hat{p}] + [\hat{x}, \hat{p}]\hat{x} = 2i\hbar\hat{x}, \quad [\hat{x}, \hat{p}] = i\hbar \tag{9.75}$$

$$\left[\frac{1}{2}m\omega^2\hat{x}^2, \hat{p}\right] = \frac{1}{2}m\omega^2(2i\hbar\hat{x}) = i\hbar m\omega^2\hat{x} \tag{9.76}$$

$$[-e\mathcal{E}\hat{x}, \hat{p}] = -e\mathcal{E}(i\hbar) \tag{9.77}$$

and combining, we obtain

$$\frac{d\hat{p}}{dt} = \frac{i}{\hbar}(i\hbar m\omega^2\hat{x} - i\hbar e\mathcal{E}) = -m\omega^2\hat{x} + e\mathcal{E}. \tag{9.78}$$

The classical equations for a particle under force $F = -m\omega^2 x + e\mathcal{E}$ are

$$\frac{dx}{dt} = \frac{p}{m}, \quad \frac{dp}{dt} = -m\omega^2 x + e\mathcal{E}, \tag{9.79}$$

therefore the quantum equations have identical form to the classical ones.

b) The differential equation for $\hat{x}(t)$,

$$\frac{d^2\hat{x}}{dt^2} + \omega^2\hat{x} = \frac{e\mathcal{E}}{m}, \tag{9.80}$$

has the homogeneous solution: $\hat{x}_h(t) = A\cos(\omega t) + B\sin(\omega t)$ and the particular solution $\hat{x}_p = eE/m\omega^2$. Therefore the general solution is

$$\hat{x}(t) = A\cos(\omega t) + B\sin(\omega t) + \frac{e\mathcal{E}}{m\omega^2}. \tag{9.81}$$

The constants A and B are determined by the initial conditions,

$$\hat{x}(0) = A + \frac{e\mathcal{E}}{m\omega^2} \implies A = \hat{x}(0) - \frac{e\mathcal{E}}{m\omega^2} \tag{9.82}$$

$$\frac{d\hat{x}}{dt}(0) = \frac{\hat{p}(0)}{m} = \omega B \implies B = \frac{\hat{p}(0)}{m\omega}. \tag{9.83}$$

Substituting

$$\hat{x}(t) = \left(\hat{x}(0) - \frac{e\mathcal{E}}{m\omega^2}\right)\cos(\omega t) + \frac{\hat{p}(0)}{m\omega}\sin(\omega t) + \frac{e\mathcal{E}}{m\omega^2} \tag{9.84}$$

and rearranging we get for $\hat{x}(t)$,

$$\hat{x}(t) = \hat{x}(0)\cos(\omega t) + \frac{\hat{p}(0)}{m\omega}\sin(\omega t) + \frac{e\mathcal{E}}{m\omega^2}(1 - \cos(\omega t)). \tag{9.85}$$

For $\hat{p}(t)$, using $\hat{p} = m\frac{d\hat{x}}{dt}$, we obtain

$$\frac{d\hat{x}}{dt} = -\omega\left(\hat{x}(0) - \frac{e\mathcal{E}}{m\omega^2}\right)\sin(\omega t) + \frac{\hat{p}(0)}{m}\cos(\omega t), \tag{9.86}$$

$$\hat{p}(t) = \hat{p}(0)\cos(\omega t) - m\omega\hat{x}(0)\sin(\omega t) + \frac{e\mathcal{E}}{\omega}\sin(\omega t). \tag{9.87}$$

c) The third term in the expression for $\hat{x}(t)$ does not contribute to the commutator, so that

$$[\hat{x}(t_1), \hat{x}(t_2)] = \left[\hat{x}(0)c_1 + \frac{\hat{p}(0)}{m\omega}s_1, \hat{x}(0)c_2 + \frac{\hat{p}(0)}{m\omega}s_2\right], \tag{9.88}$$

where $c_i = \cos(\omega t_i)$, $s_i = \sin(\omega t_i)$. Expanding the right hand side gives

$$c_1c_2[\hat{x}(0), \hat{x}(0)] + \frac{c_1s_2}{m\omega}[\hat{x}(0), \hat{p}(0)] + \frac{s_1c_2}{m\omega}[\hat{p}(0), \hat{x}(0)] + \frac{s_1s_2}{m^2\omega^2}[\hat{p}(0), \hat{p}(0)]. \tag{9.89}$$

Using $[\hat{x}(0), \hat{p}(0)] = i\hbar$ and $[\hat{p}(0), \hat{x}(0)] = -i\hbar$, we thus get

$$[\hat{x}(t_1), \hat{x}(t_2)] = \frac{i\hbar}{m\omega}\sin(\omega(t_2 - t_1)). \tag{9.90}$$

The different-time commutator oscillates with a frequency equal to its natural frequency, regardless of the applied electric field.

P9.8 Consider a harmonic oscillator of frequency ω in its ground state. At time $t = 0$, the oscillation frequency is abruptly reduced to the value $\omega' = \omega/k$, with $1 < k < \infty$. Calculate $\psi(x, t)$ for $t > 0$. Determine:
a) the probability that the system is in the eigenstate with energy E_n at time t;
b) the value of n for which this probability reaches its maximum.

Discuss the results.

Solution. Until $t = 0$, the system is in its ground state with wave function

$$\psi_0(x,0) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar}x^2\right). \tag{9.91}$$

From $t > 0$, the frequency is ω', so the propagator is

$$K(x,t,x',0) = \sqrt{\frac{-im\omega'}{2\pi\hbar\sin\omega' t}} \exp\left[\frac{im\omega'}{\hbar}\frac{(x^2+x'^2)\cos\omega' t - 2xx'}{2\sin\omega' t}\right]. \tag{9.92}$$

The wave function for $t > 0$ determined by this propagator is

$$\psi(x,t) = \int_{-\infty}^{\infty} K(x,t,x',0)\psi(x',0)\,dx' \tag{9.93}$$

$$= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{-im\omega'}{2\pi\hbar\sin\omega' t}} \int_{-\infty}^{\infty} \exp\left[\frac{im\omega'}{\hbar}\frac{(x^2+x'^2)\cos\omega' t - 2xx'}{2\sin\omega' t} - \frac{m\omega}{2\hbar}x'^2\right] dx'. \tag{9.94}$$

This expression can be rewritten as

$$\begin{aligned}\psi(x,t) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} &\sqrt{\frac{-im\omega'}{2\pi\hbar\sin\omega' t}} \exp\left(\frac{im\omega'}{2\hbar}x^2\cot\omega' t\right) \\ &\times \int_{-\infty}^{\infty} \exp\left[-\frac{m}{2\hbar}\left(\omega - i\omega'\cot\omega' t\right)x'^2 - i\frac{m\omega'}{\hbar}xx'\csc\omega' t\right] dx'.\end{aligned} \tag{9.95}$$

Using the formula

$$\int_{-\infty}^{\infty} \exp(-\alpha x^2 - \beta x)\,dx = \sqrt{\frac{\pi}{\alpha}} \exp\left(\frac{\beta^2}{4\alpha}\right), \tag{9.96}$$

we write 9.95 in the form

$$\psi(x,t) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{-i}{2\pi\hbar\sin\omega' t}} \sqrt{\frac{2\pi\hbar}{k - i\cot\omega' t}} \exp\left(\frac{im\omega' x^2\cos\omega' t}{2\hbar\sin\omega' t}\right)$$

$$\times \exp\left[-\frac{\hbar}{2m}\left(\frac{im\omega' x}{\hbar \sin\omega' t}\right)^2 \frac{1}{i\omega' \cot\omega' t - \omega}\right] \tag{9.97}$$

$$= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{\cos\omega' t + ik\sin\omega' t}} \times \exp\left(-\frac{m\omega x^2}{2\hbar} \cdot \frac{k\cos\omega' t + i\sin\omega' t}{\cos\omega' t + ik\sin\omega' t}\right) \tag{9.98}$$

$$= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{\cos\frac{\omega t}{k} + ik\sin\frac{\omega t}{k}}} \times \exp\left[-\frac{m\omega}{2\hbar} \cdot \frac{\cos\frac{\omega t}{k} + \frac{i}{k}\sin\frac{\omega t}{k}}{\cos\frac{\omega t}{k} + ik\sin\frac{\omega t}{k}} x^2\right]. \tag{9.99}$$

This function appropriately reduces to $\psi(x,0)$ when $t = 0$, and to the ground-state wave function $\psi_0(x,t)$ for $k = 1$.

The probability that at time t the system is in the eigenstate ψ_n is

$$P_n = |\langle\psi(x,t) \mid \psi_n\rangle|^2, \tag{9.100}$$

with

$$\langle\psi(x,t) \mid \psi_n\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{\alpha_0' C_n}{\sqrt{\cos\omega' t - ik\sin\omega' t}} \times \int_{-\infty}^{\infty} \exp\left[-\frac{1}{2}\left(\frac{k\cos\omega' t - i\sin\omega' t}{\cos\omega' t - ik\sin\omega' t} + 1\right)\xi^2\right] H_n(\xi)\, d\xi, \tag{9.101}$$

$x = \alpha_0'\xi, \quad \alpha_0' = \left(\frac{\hbar}{m\omega'}\right)^{1/2}$. Setting

$$\frac{1}{2}\left(\frac{k\cos\omega' t - i\sin\omega' t}{\cos\omega' t - ik\sin\omega' t} + 1\right)\xi^2 = \gamma\xi^2 \equiv \xi'^2, \tag{9.102}$$

we can rewrite the transition amplitude in the form

$$\langle\psi(x,t) \mid \psi_n\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{\alpha_0' C_n}{\sqrt{\cos\omega' t - ik\sin\omega' t}} \cdot \frac{1}{\sqrt{\gamma}} \int_{-\infty}^{\infty} e^{-\xi'^2} H_n\left(\frac{1}{\sqrt{\gamma}}\xi'\right) d\xi'. \tag{9.103}$$

Since the parity of the Hermite polynomials H_n is given by their index n, the amplitude $\langle\psi(x,t) \mid \psi_n\rangle$ is non-zero only if n is even; this means that the states with odd n do not contribute to the wavefunction for $t > 0$. This is due to the fact that the initial state is even. Making the substitution $n \to 2n$, with n an integer, we find that the non-zero amplitudes are

$$\langle\psi(x,t) \mid \psi_{2n}\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{\alpha_0' C_{2n}}{\sqrt{\cos\omega' t - ik\sin\omega' t}} \cdot \frac{1}{\sqrt{\gamma}} \int_{-\infty}^{\infty} e^{-\xi'^2} H_{2n}\left(\frac{1}{\sqrt{\gamma}}\xi'\right) d\xi'. \tag{9.104}$$

Using the formula ([**3**], 7.373,2)

$$\int_{-\infty}^{\infty} e^{-x^2} H_{2m}(xy)\,dx = \sqrt{\pi}\cdot\frac{(2m)!}{m!}(y^2-1)^m \tag{9.105}$$

and the definitions for α_0' and C_{2n}, we get

$$\langle\psi(x,t)\mid\psi_{2n}\rangle = \frac{(2n)!}{2^{2n}}\frac{(\omega'\omega)^{1/4}}{n!}\cdot\frac{1}{\sqrt{\omega'\cos\omega' t - i\omega\sin\omega' t}}\cdot\frac{1}{\sqrt{\gamma}}\left(\frac{1-\gamma}{\gamma}\right)^n. \tag{9.106}$$

From this and 9.100, we obtain the probability that the system is in the eigenstate with energy E_{2n} at time t,

$$P_{2n} = \frac{(2n)!}{2^{2n}(n!)^2}\cdot\frac{\sqrt{k}}{\sqrt{\cos^2\omega' t + k^2\sin^2\omega' t}}\left|\frac{1}{\sqrt{\gamma}}\left(\frac{1-\gamma}{\gamma}\right)^n\right|^2. \tag{9.107}$$

With

$$\gamma = \frac{k+1}{2}\cdot\frac{\cos\omega' t - i\sin\omega' t}{\cos\omega' t - ik\sin\omega' t}, \tag{9.108}$$

and

$$\frac{1-\gamma}{\gamma} = \frac{\omega-\omega'}{\omega+\omega'} = \frac{k-1}{k+1}, \tag{9.109}$$

we get

$$\left|\frac{1}{\sqrt{\gamma}}\left(\frac{1-\gamma}{\gamma}\right)^n\right|^2 = \frac{2}{k+1}\left(\frac{k-1}{k+1}\right)^{2n}\cdot\sqrt{\cos^2\omega' t + k^2\sin^2\omega' t}, \tag{9.110}$$

which gives

$$P_{2n} = \frac{(2n)!}{2^{2n}(n!)^2}\cdot\frac{2\sqrt{\omega\omega'}}{\omega+\omega'}\left(\frac{\omega'-\omega}{\omega'+\omega}\right)^{2n}. \tag{9.111}$$

The probability that the system is in the eigenstate with energy E_{2n+1} is zero,

$$P_{2n+1} = 0. \tag{9.112}$$

As n increases, the value of P_{2n} decreases; the value for which the maximum probability occurs is the ground state, $n = 0$. The maximum probability P_0 is given by the ratio of the geometric mean to the arithmetic mean of the two frequencies,

$$P_0 = \frac{2\sqrt{\omega\omega'}}{\omega+\omega'} = \frac{2\sqrt{k}}{1+k}. \tag{9.113}$$

P9.9 Derive the evolution equations for $\langle\hat{x}\rangle$ and $\langle\hat{p}\rangle$ for systems with Hamiltonians

$$\widehat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\left(\omega^2x^2 + \beta x + \mathcal{E}\right), \tag{9.114}$$

$$\widehat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2x^2 - \frac{A}{x^2}. \tag{9.115}$$

Solve the equations for the first case.

Solution. With the first Hamiltonian given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \frac{1}{2}m\beta\hat{x} + \frac{1}{2}m\mathcal{E}, \tag{9.116}$$

we get for the evolution of $\langle\hat{x}\rangle$, from

$$\frac{d}{dt}\langle\hat{x}\rangle = \frac{i}{\hbar}\langle[\hat{H},\hat{x}]\rangle \tag{9.117}$$

and

$$[\hat{H},\hat{x}] = \left[\frac{\hat{p}^2}{2m},\hat{x}\right] = \left\langle -\frac{i\hbar}{m}\hat{p}\right\rangle, \tag{9.118}$$

the result

$$\frac{d}{dt}\langle\hat{x}\rangle = \frac{i}{\hbar}\left\langle -\frac{i\hbar}{m}\hat{p}\right\rangle = \frac{\langle\hat{p}\rangle}{m}. \tag{9.119}$$

For the evolution of $\langle\hat{p}\rangle$ we use

$$\frac{d}{dt}\langle\hat{p}\rangle = \frac{i}{\hbar}\langle[\hat{H},\hat{p}]\rangle, \tag{9.120}$$

with

$$[\hat{H},\hat{p}] = \left[\frac{1}{2}m\omega^2\hat{x}^2,\hat{p}\right] + \left[\frac{1}{2}m\beta\hat{x},\hat{p}\right] \tag{9.121}$$

$$= i\hbar m\omega^2\hat{x} + i\hbar\frac{m\beta}{2}. \tag{9.122}$$

The result is therefore

$$\frac{d}{dt}\langle\hat{p}\rangle = -m\omega^2\langle\hat{x}\rangle - \frac{m\beta}{2}. \tag{9.123}$$

Differentiating the first result and substituting the second gives

$$\frac{d^2}{dt^2}\langle\hat{x}\rangle = \frac{1}{m}\frac{d}{dt}\langle\hat{p}\rangle = \frac{1}{m}\left(-m\omega^2\langle\hat{x}\rangle - \frac{m\beta}{2}\right), \tag{9.124}$$

that is,

$$\frac{d^2}{dt^2}\langle\hat{x}\rangle + \omega^2\langle\hat{x}\rangle = -\frac{\beta}{2}. \tag{9.125}$$

The homogeneous solution of this equation is

$$\langle\hat{x}\rangle_h = C_1\cos(\omega t) + C_2\sin(\omega t), \tag{9.126}$$

and the particular solution, assuming $\langle\hat{x}\rangle_p = K$ (constant), is

$$\omega^2 K = -\frac{\beta}{2} \implies K = -\frac{\beta}{2\omega^2}. \tag{9.127}$$

The general solution is thus

$$\langle\hat{x}\rangle(t) = C_1\cos(\omega t) + C_2\sin(\omega t) - \frac{\beta}{2\omega^2}, \tag{9.128}$$

and its time derivative is

$$\frac{d}{dt}\langle\hat{x}\rangle = -\omega C_1 \sin(\omega t) + \omega C_2 \cos(\omega t). \tag{9.129}$$

or in terms of the initial conditions: $\langle\hat{x}\rangle(0) = x_0$, $\langle\hat{p}\rangle(0) = p_0$, the integration constants are given by

$$\langle\hat{x}\rangle(0) = C_1 - \frac{\beta}{2\omega^2} = x_0 \implies C_1 = x_0 + \frac{\beta}{2\omega^2}, \tag{9.130}$$

$$\frac{d}{dt}\langle\hat{x}\rangle\bigg|_{t=0} = \omega C_2 = \frac{p_0}{m} \implies C_2 = \frac{p_0}{m\omega}. \tag{9.131}$$

Therefore,

$$\langle\hat{x}\rangle(t) = \left(x_0 + \frac{\beta}{2\omega^2}\right)\cos(\omega t) + \frac{p_0}{m\omega}\sin(\omega t) - \frac{\beta}{2\omega^2}, \tag{9.132}$$

and

$$\langle\hat{p}\rangle(t) = p_0\cos(\omega t) - m\omega\left(x_0 + \frac{\beta}{2\omega^2}\right)\sin(\omega t). \tag{9.133}$$

With the second Hamiltonian given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 - \frac{A}{\hat{x}^2}, \tag{9.134}$$

we get the following, using the Heisenberg equations again,

$$\frac{d}{dt}\langle\hat{x}\rangle = \frac{\langle\hat{p}\rangle}{m} \quad \text{(same as before)}, \tag{9.135}$$

and

$$\frac{d}{dt}\langle\hat{p}\rangle = -m\omega^2\langle\hat{x}\rangle - 2A\langle\hat{x}^{-3}\rangle. \tag{9.136}$$

P9.10 Derive the creation and annihilation operators for the harmonic oscillator, based on the description of the system in momentum space.

Solution. In the momentum representation, the operator $\hat{x}$ is given by

$$\hat{x} = i\hbar\frac{\partial}{\partial p}, \tag{9.137}$$

so the Hamiltonian of the 1D harmonic oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \tag{9.138}$$

takes the form

$$\hat{H} = \frac{p^2}{2m} - \frac{1}{2}m\omega^2\hbar^2\frac{\partial^2}{\partial p^2}. \tag{9.139}$$

The Schrödinger equation in this representation is

$$i\hbar\frac{\partial\phi(p,t)}{\partial t} = \left(\frac{p^2}{2m} - \frac{1}{2}m\omega^2\hbar^2\frac{\partial^2}{\partial p^2}\right)\phi(p,t). \tag{9.140}$$

Comparing 9.140 with the corresponding Schrödinger equation in the coordinate representation,

$$i\hbar\frac{\partial\psi(x,t)}{\partial t}=\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\frac{1}{2}m\omega^2x^2\right)\psi(x,t), \tag{9.141}$$

we see that one transforms into the other under the substitution

$$p\leftrightarrow m\omega x=m\omega\alpha_0\xi=\sqrt{m\hbar\omega}\,\xi. \tag{9.142}$$

Therefore, in terms of the dimensionless variable

$$\eta=\frac{p}{p_0},\qquad p_0=\sqrt{m\hbar\omega}, \tag{9.143}$$

The correspondence is reduced to $\eta\leftrightarrow\xi$. Using this correspondence, we can write the eigenfunctions of 9.140 directly from the eigenfunctions in the coordinate representation

$$\psi_n=\left(2^n n!\alpha_0\sqrt{\pi}\right)^{-1/2}e^{-\xi^2/2}H_n(\xi), \tag{9.144}$$

thus obtaining

$$\phi_n(p)=\left(2^n n!p_0\sqrt{\pi}\right)^{-1/2}e^{-\eta^2/2}H_n(\eta). \tag{9.145}$$

The procedure followed is legitimate because, since the system has finite energy, $\phi_n(p)$ must vanish as $|p|\to\infty$, which is a boundary condition analogous to that satisfied by the solution in coordinate space.

The expression of the eigenfunctions is the same, so again we have

$$\frac{1}{\sqrt{2}}\left(\eta+\frac{\partial}{\partial\eta}\right)\phi_n=\sqrt{n}\phi_{n-1}, \tag{9.146}$$

$$\frac{1}{\sqrt{2}}\left(\eta-\frac{\partial}{\partial\eta}\right)\phi_n=\sqrt{n+1}\phi_{n+1}. \tag{9.147}$$

In this case , the dimensionless operator is given by

$$\frac{\partial}{\partial\eta}=\hbar\sqrt{\frac{m\omega}{\hbar}}\frac{\partial}{\partial p}=-i\sqrt{\frac{m\omega}{\hbar}}\hat{x}. \tag{9.148}$$

It is clear from Eqs. (9.146), (9.147) that the effect of the operators

$$\hat{a}=\frac{1}{\sqrt{2}}\left(\eta+\frac{\partial}{\partial\eta}\right)=\frac{1}{\sqrt{2}}\left(\frac{p}{\sqrt{m\omega\hbar}}-i\sqrt{\frac{m\omega}{\hbar}}\hat{x}\right)=\sqrt{\frac{m\omega}{2\hbar}}\left(\frac{p}{m\omega}-i\hat{x}\right), \tag{9.149}$$

$$\hat{a}^\dagger=\frac{1}{\sqrt{2}}\left(\eta-\frac{\partial}{\partial\eta}\right)=\frac{1}{\sqrt{2}}\left(\frac{p}{\sqrt{m\omega\hbar}}+i\sqrt{\frac{m\omega}{\hbar}}\hat{x}\right)=\sqrt{\frac{m\omega}{2\hbar}}\left(\frac{p}{m\omega}+i\hat{x}\right), \tag{9.150}$$

is to lower and raise by 1 the index n, respectively. The annihilation and creation operators expressed in momentum space are therefore

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\left(\frac{p}{m\omega} + \hbar\frac{\partial}{\partial p}\right), \tag{9.151}$$

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\frac{p}{m\omega} - \hbar\frac{\partial}{\partial p}\right), \tag{9.152}$$

and it is easy to confirm that

$$[\hat{a}, \hat{a}^\dagger] = 1. \tag{9.153}$$

P9.11 Calculate the matrix elements x_{nm} and x^2_{nm} for the harmonic oscillator, using $x = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a} + \hat{a}^\dagger)$ and

$$\hat{a}\psi_n = \sqrt{n}\psi_{n-1} \tag{9.154}$$

$$\hat{a}^\dagger\psi_n = \sqrt{n+1}\psi_{n+1} \tag{9.155}$$

Solution. In Dirac notation, we write

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle, \quad \hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle, \tag{9.156}$$

and write the matrix elements of the position operator $\hat{x}$ as:

$$x_{nm} = \langle n|\hat{x}|m\rangle = \sqrt{\frac{\hbar}{2m_0\omega}}\langle n|(\hat{a} + \hat{a}^\dagger)|m\rangle \tag{9.157}$$

$$= \sqrt{\frac{\hbar}{2m_0\omega}}\left(\sqrt{m}\langle n|m-1\rangle + \sqrt{m+1}\langle n|m+1\rangle\right). \tag{9.158}$$

$$= \sqrt{\frac{\hbar}{2m_0\omega}}\left(\sqrt{n+1}\delta_{n,m-1} + \sqrt{n}\delta_{n,m+1}\right). \tag{9.159}$$

Similarly, with $\alpha_0^2 = \hbar/m_0\omega$,

$$\hat{x}^2|m\rangle = \sqrt{\frac{\hbar}{2m_0\omega}}\left(\hat{x}\hat{a}|m\rangle + \hat{x}\hat{a}^\dagger|m\rangle\right) \tag{9.160}$$

$$= \frac{\alpha_0^2}{2}\Big(\sqrt{m}\hat{a}|m-1\rangle + \sqrt{m}\hat{a}^\dagger|m-1\rangle$$
$$+ \sqrt{m+1}\hat{a}|m+1\rangle + \sqrt{m+1}\hat{a}^\dagger|m+1\rangle\Big) \tag{9.161}$$

$$= \frac{\alpha_0^2}{2}\Big(\sqrt{m(m-1)}|m-2\rangle + (2m+1)|m\rangle$$
$$+ \sqrt{(m+1)(m+2)}|m+2\rangle\Big), \tag{9.162}$$

from which it follows that

$$x^2_{nm} = \frac{\hbar}{2m_0\omega}\Big(\sqrt{m(m-1)}\delta_{n,m-2} + (2m+1)\delta_{n,m}$$

$$+\sqrt{(m+1)(m+2)}\delta_{n,m+2}\Big). \tag{9.163}$$

P9.12 Show that

$$e^{\lambda\hat{a}}\hat{a}^\dagger e^{-\lambda\hat{a}} = \hat{a}^\dagger + \lambda, \tag{9.164}$$

$$e^{\lambda\hat{a}^\dagger}\hat{a}e^{-\lambda\hat{a}^\dagger} = \hat{a} - \lambda, \tag{9.165}$$

$$e^{\lambda\hat{a}}f(\hat{a},\hat{a}^\dagger)e^{-\lambda\hat{a}} = f(\hat{a},\hat{a}^\dagger+\lambda), \quad \text{etc.}, \tag{9.166}$$

where f represents a function admitting a power series expansion of $\hat{a}$ and $\hat{a}^\dagger$.
Solution. It can be shown that for a pair of operators $\hat{A}$ and $\hat{B}$, the identity

$$e^{\hat{B}}\hat{A}e^{-\hat{B}} = \hat{A} + [\hat{B},\hat{A}] + \frac{1}{2!}[\hat{B},[\hat{B},\hat{A}]] + \frac{1}{3!}[\hat{B},[\hat{B},[\hat{B},\hat{A}]]] + \cdots \tag{9.167}$$

holds, which follows from expanding the exponentials and regrouping terms.

Taking $\hat{B} = \lambda\hat{a}$ and $\hat{A} = \hat{a}^\dagger$, the above expression gives

$$e^{\lambda\hat{a}}\hat{a}^\dagger e^{-\lambda\hat{a}} = \hat{a}^\dagger + [\lambda\hat{a},\hat{a}^\dagger] + \frac{1}{2!}[\lambda\hat{a},[\lambda\hat{a},\hat{a}^\dagger]] + \cdots \tag{9.168}$$

$$= \hat{a}^\dagger + \lambda[\hat{a},\hat{a}^\dagger] + \frac{\lambda^2}{2!}[\hat{a},[\hat{a},\hat{a}^\dagger]] + \cdots . \tag{9.169}$$

Since

$$[\hat{a},\hat{a}^\dagger] = 1, \quad [\hat{a},[\hat{a},\hat{a}^\dagger]] = 0, \tag{9.170}$$

all higher-order nested commutators vanish and we find

$$e^{\lambda\hat{a}}\hat{a}^\dagger e^{-\lambda\hat{a}} = \hat{a}^\dagger + \lambda. \tag{9.171}$$

Similarly, it can be verified that

$$e^{\lambda\hat{a}^\dagger}\hat{a}e^{-\lambda\hat{a}^\dagger} = \hat{a} - \lambda. \tag{9.172}$$

Equation 9.172 can alternatively be obtained by taking the Hermitian adjoint of Eq. 9.171 and making the change $\lambda \to -\lambda$.

Using again the expansion 9.167 we now write

$$e^{\lambda\hat{a}}\hat{a}^{\dagger m}e^{-\lambda\hat{a}} = \hat{a}^{\dagger m} + \lambda[\hat{a},\hat{a}^{\dagger m}] + \frac{\lambda^2}{2!}[\hat{a},[\hat{a},\hat{a}^{\dagger m}]] + \cdots . \tag{9.173}$$

Using the identity

$$[\hat{A},\hat{B}^n] = n\hat{B}^{n-1}[\hat{A},\hat{B}], \tag{9.174}$$

which holds when $\hat{A}$ and $\hat{B}$ commute with $[\hat{A},\hat{B}]$, we find

$$[\hat{a},\hat{a}^{\dagger m}] = m\hat{a}^{\dagger(m-1)}[\hat{a},\hat{a}^\dagger] = m\hat{a}^{\dagger(m-1)}, \tag{9.175}$$

$$] = m(m-1)\hat{a}^{\dagger(m-2)}, \quad \ldots \tag{9.176}$$

Substituting into 9.173, we obtain

$$e^{\lambda\hat{a}}\hat{a}^{\dagger m}e^{-\lambda\hat{a}} = \hat{a}^{\dagger m} + m\lambda\hat{a}^{\dagger(m-1)} + \frac{1}{2!}m(m-1)\lambda^2\hat{a}^{\dagger(m-2)} + \cdots = (\hat{a}^\dagger+\lambda)^m. \tag{9.177}$$

This result is a generalization of Eq. 9.171 to arbitrary powers m, and shows that the operator $\hat{a}$ acts as a displacement operator. Similarly, applying the same reasoning to Eq. 9.172, we obtain

$$e^{-\lambda\hat{a}^\dagger}\hat{a}^m e^{\lambda\hat{a}^\dagger} = (\hat{a}-\lambda)^m. \tag{9.178}$$

An alternative form of 9.177, which is sometimes useful, can be written as

$$\begin{aligned}&\hat{a}^{\dagger m} + m\lambda\hat{a}^{\dagger(m-1)} + \frac{1}{2!}m(m-1)\lambda^2\hat{a}^{\dagger(m-2)} + \cdots \\ &= \left(1 + \lambda\frac{d}{d\hat{a}^\dagger} + \frac{\lambda^2}{2!}\frac{d^2}{d\hat{a}^{\dagger 2}} + \cdots\right)\hat{a}^{\dagger m} = e^{\lambda\, d/d\hat{a}^\dagger}\hat{a}^{\dagger m}.\end{aligned} \tag{9.179}$$

Substituting this result into 9.177 yields

$$e^{\lambda\hat{a}}\hat{a}^{\dagger m}e^{-\lambda\hat{a}} = e^{\lambda\partial/\partial\hat{a}^\dagger}\hat{a}^{\dagger m}. \tag{9.180}$$

Now, let $f(\hat{a},\hat{a}^\dagger)$ be a function of the annihilation and creation operators which can be expressed as a power series:

$$f(\hat{a},\hat{a}^\dagger) = \sum_{n,m} c_{nm}\hat{a}^n\hat{a}^{\dagger m}. \tag{9.181}$$

Using 9.177, we find

$$e^{\lambda\hat{a}}f(\hat{a},\hat{a}^\dagger)e^{-\lambda\hat{a}} = \sum_{n,m} c_{nm}e^{\lambda\hat{a}}\hat{a}^n\hat{a}^{\dagger m}e^{-\lambda\hat{a}} \tag{9.182}$$

$$= \sum_{n,m} c_{nm}\hat{a}^n\left(e^{\lambda\hat{a}}\hat{a}^{\dagger m}e^{-\lambda\hat{a}}\right) \tag{9.183}$$

$$= \sum_{n,m} c_{nm}\hat{a}^n(\hat{a}^\dagger+\lambda)^m, \tag{9.184}$$

that is,

$$e^{\lambda\hat{a}}f(\hat{a},\hat{a}^\dagger)e^{-\lambda\hat{a}} = f(\hat{a},\hat{a}^\dagger+\lambda). \tag{9.185}$$

P9.13 Determine the eigenvalues of the Hamiltonian

$$\hat{H} = h_0\hat{a}^\dagger\hat{a} + h_1(\hat{a}+\hat{a}^\dagger). \tag{9.186}$$

Hint: Introduce a new pair of creation and annihilation operators that diagonalize $\hat{H}$.

Solution. Consider a new pair of mutually adjoint operators,

$$\hat{A} = \hat{a} - \beta, \quad \hat{A}^\dagger = \hat{a}^\dagger - \beta^*, \tag{9.187}$$

where β is a parameter to be determined. The goal is to find a value of β that diagonalizes the given Hamiltonian; once achieved, the problem can be solved using standard methods.

Substituting into the proposed Hamiltonian yields

$$\tilde{H} = h_0(\hat{A}^\dagger + \beta^*)(\hat{A} + \beta) + h_1(\hat{A}^\dagger + \beta^* + \hat{A} + \beta) \tag{9.188}$$

$$= h_0\hat{A}^\dagger\hat{A} + (h_0\beta + h_1)\hat{A}^\dagger + (h_0\beta^* + h_1)\hat{A} \tag{9.189}$$

$$+ h_0\beta^*\beta + h_1(\beta^* + \beta). \tag{9.190}$$

To diagonalize this expression, it suffices to require that the coefficients of $\hat{A}^\dagger$ and $\hat{A}$ vanish. This is accomplished by choosing

$$\beta^* = \beta = -h_1/h_0. \tag{9.191}$$

With this selection, the Hamiltonian reduces to the standard form

$$H = h_0\hat{A}^\dagger\hat{A} - \frac{h_1^2}{h_0}, \tag{9.192}$$

and the new creation and annihilation operators become

$$\hat{A} = \hat{a} + h_1/h_0, \quad \hat{A}^\dagger = \hat{a}^\dagger + h_1/h_0. \tag{9.193}$$

The commutation relations remain unchanged,

$$[\hat{A}, \hat{A}^\dagger] = [\hat{a}, \hat{a}^\dagger]. \tag{9.194}$$

The Schrödinger equation to solve is now

$$E\psi = \left(h_0\hat{A}^\dagger\hat{A} - \frac{h_1^2}{h_0}\right)\psi. \tag{9.195}$$

We set

$$E = E' - \tfrac{1}{2}h_0 - \frac{h_1^2}{h_0}, \tag{9.196}$$

which yields

$$E'\psi = \left(h_0\hat{A}^\dagger\hat{A} + \tfrac{1}{2}h_0\right)\psi. \tag{9.197}$$

Defining a frequency ω through the relation $h_0 = \hbar\omega$, this equation represents a harmonic oscillator with energy eigenvalues

$$E' = \hbar\omega\left(n + \tfrac{1}{2}\right) = h_0\left(n + \tfrac{1}{2}\right). \tag{9.198}$$

The energy eigenvalues of the original Hamiltonian are given by

$$E_n = h_0 n - \frac{h_1^2}{h_0}, \quad n = 1, 2, 3, \ldots \tag{9.199}$$

This diagonalization method has proven to be extremely useful in various applications, exactly in linear situations (as in the present case), or as an approximate method for nonlinear and more complex problems.

P9.14 Show that if $\hat{A} = \hat{A}(t = 0)$ is an operator at time $t = 0$, then $\hat{A}(-t)\psi(x, t) = A\psi(x, t)$, where $\psi(x, 0)$ is the eigenstate of $\hat{A}$. Use this result to build the Feynman propagator of the harmonic oscillator. Verify that it approaches the free-particle

propagator as $\omega \to 0$. Why does the same happen for ω fixed ($< \infty$) when $t - t' \to 0$?

Solution. Let us consider an eigenstate of the operator $\hat{A}$ at time $t = 0$, such that

$$\hat{A}\psi(x,0) = A\psi(x,0). \tag{9.200}$$

Assuming the Hamiltonian is time-independent, the wave function at time t can be written as $\psi(x,t) = e^{-i\hat{H}t/\hbar}\psi(x,0)$, which allows us to rewrite the previous equation as

$$\hat{A}e^{i\hat{H}t/\hbar}\psi(x,t) = Ae^{i\hat{H}t/\hbar}\psi(x,t), \tag{9.201}$$

that is,

$$e^{-i\hat{H}t/\hbar}\hat{A}e^{i\hat{H}t/\hbar}\psi(x,t) = A\psi(x,t). \tag{9.202}$$

But since $e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}$ is the Heisenberg-picture operator $\hat{A}(t)$, this is equivalent to

$$\hat{A}(-t)\psi(x,t) = A\psi(x,t). \tag{9.203}$$

This result shows that if $\psi(x,0)$ is an eigenfunction of an operator $\hat{A}$ at time $t = 0$, then $\psi(x,t)$ is an eigenfunction of the time-evolved operator $\hat{A}(-t)$ with the same eigenvalue A.

To build the Green function (or Feynman propagator) of the harmonic oscillator based on this result, we recall that the Green function is the solution of Schrödinger's equation with a delta source $\delta(x - x_0)$, that is, it is an eigenfunction of $\hat{x}$ with eigenvalue x_0 at $t = 0$,

$$\hat{x}G(t=0) = x_0 G(t=0). \tag{9.204}$$

From 9.203, it follows that at time t we have

$$\hat{x}(-t)G = x_0 G. \tag{9.205}$$

From $\hat{x}(t) = \hat{x}_0 \cos\omega t + \frac{\hat{p}_0}{m\omega}\sin\omega t$, we have for the harmonic oscillator that

$$\hat{x}(-t) = \hat{x}\cos\omega t - \frac{\hat{p}}{m\omega}\sin\omega t. \tag{9.206}$$

Then the equation becomes

$$\left(x\cos\omega t + \frac{i\hbar}{m\omega}\sin\omega t\,\frac{\partial}{\partial x}\right)G = x_0 G. \tag{9.207}$$

The solution to this equation is

$$G(x,x_0,t) = G_0(t)\exp\left(\frac{im\omega}{2\hbar}\cdot\frac{x^2\cos\omega t - 2x_0 x}{\sin\omega t}\right). \tag{9.208}$$

To determine $G_0(t)$, we require that $G(x,x_0,t)$ be a solution to the Schrödinger equation for $t > 0$. When 9.208 is substituted into the Schrödinger equation, all

x-dependence cancels out, and a differential equation for $G_0(t)$ remains, whose solution is

$$G_0(t) = \frac{C}{\sqrt{\sin \omega t}} \exp\left(\frac{im\omega}{2\hbar} \cdot \frac{x_0^2 \cos \omega t}{\sin \omega t}\right). \tag{9.209}$$

By inserting this result and performing the variable change $t \to t - t'$, $x_0 \to x'$, we obtain for $t - t' \geq 0$

$$\begin{aligned} K(x, t \mid x', t') &\equiv G(x, x', t - t') \\ &= \frac{C}{\sqrt{\sin \omega(t - t')}} \exp\left[\frac{im\omega}{2\hbar} \cdot \frac{(x^2 + x'^2)\cos \omega(t - t') - 2xx'}{\sin \omega(t - t')}\right]. \end{aligned} \tag{9.210}$$

Since $G(x, x_0, 0) = \delta(x - x_0)$, the normalization condition $\int G(x, x_0, 0)\, dx = 1$ determines the constant C, yielding

$$C = \sqrt{\frac{-im\omega}{2\pi\hbar}}. \tag{9.211}$$

The final result is precisely the Feynman propagator

We now verify that the propagator of the harmonic oscillator reduces to that of the free particle in the appropriate limits. In the limit $\theta \approx 0$ we have that

$$\sin \theta \approx \theta, \quad \cos \theta \approx 1.$$

This holds for both $\omega \to 0$ and $t \to t'$ Substituting into 9.210 we have immediately that

$$K(x, t \mid x', t') \approx \sqrt{\frac{m\omega}{2\pi i\hbar}} \frac{1}{\sqrt{\omega(t - t')}} \exp\left[\frac{im\omega}{2\hbar} \cdot \frac{x^2 + x'^2 - 2xx'}{\omega(t - t')}\right] \tag{9.212}$$

$$= \sqrt{\frac{m}{2\pi i\hbar(t - t')}} \exp\left[\frac{im(x - x')^2}{2\hbar(t - t')}\right]. \tag{9.213}$$

Thus, we recover the free-particle propagator. For $\omega = 0$, the Schrodinger equation becomes the free particle equation. The fact that the same behavior holds for $t \to t'$ tells us that for very short time intervals, the potential has a negligible effect, and the particle behaves as if it were free. In other words, motion is dominated by inertia rather than potential for very short times.

P9.15 Prove that if $f(\hat{a}^\dagger)$ is a polynomial in $\hat{a}^\dagger$, then

$$\hat{a} f(\hat{a}^\dagger)|0\rangle = \frac{df(\hat{a}^\dagger)}{d\hat{a}^\dagger}|0\rangle, \tag{9.214}$$

$$e^{\lambda \hat{a}} f(\hat{a}^\dagger)|0\rangle = f(\hat{a}^\dagger + \lambda)|0\rangle. \tag{9.215}$$

Solution. To prove (9.214), let $f(\hat{a}^\dagger) = \sum_{k=0}^{n} c_k (\hat{a}^\dagger)^k$ be a finite polynomial. The

state is

$$f(\hat{a}^\dagger)|0\rangle = \sum_{k=0}^{n} c_k (\hat{a}^\dagger)^k |0\rangle. \tag{9.216}$$

Applying $\hat{a}$,

$$\hat{a} f(\hat{a}^\dagger)|0\rangle = \sum_{k=0}^{n} c_k \hat{a} (\hat{a}^\dagger)^k |0\rangle. \tag{9.217}$$

For each term, using the commutator and $\hat{a}|0\rangle = 0$,

$$\hat{a}(\hat{a}^\dagger)^k|0\rangle = [\hat{a}, (\hat{a}^\dagger)^k]|0\rangle. \tag{9.218}$$

Calculating the commutator recursively for $k \geq 1$ we get

$$[\hat{a}, (\hat{a}^\dagger)^k] = \sum_{j=0}^{k-1} (\hat{a}^\dagger)^{k-1-j} [\hat{a}, \hat{a}^\dagger] (\hat{a}^\dagger)^j = k(\hat{a}^\dagger)^{k-1}, \tag{9.219}$$

since there are k identical terms. For $k = 0$, the term vanishes. Thus,

$$\hat{a}(\hat{a}^\dagger)^k|0\rangle = \begin{cases} k(\hat{a}^\dagger)^{k-1}|0\rangle & \text{if } k \geq 1, \\ 0 & \text{if } k = 0. \end{cases} \tag{9.220}$$

Substituting,

$$\hat{a} f(\hat{a}^\dagger)|0\rangle = \sum_{k=1}^{n} c_k k (\hat{a}^\dagger)^{k-1} |0\rangle. \tag{9.221}$$

The formal derivative of f with respect to $\hat{a}^\dagger$ is

$$\frac{df(\hat{a}^\dagger)}{d\hat{a}^\dagger} = \sum_{k=1}^{n} c_k k (\hat{a}^\dagger)^{k-1}. \tag{9.222}$$

Therefore,

$$\frac{df(\hat{a}^\dagger)}{d\hat{a}^\dagger}|0\rangle = \sum_{k=1}^{n} c_k k (\hat{a}^\dagger)^{k-1} |0\rangle = \hat{a} f(\hat{a}^\dagger)|0\rangle. \tag{9.223}$$

To prove (9.215), we use the displacement operator property obtained in Problem P9.12. For operators satisfying $[\hat{a}, \hat{a}^\dagger] = 1$,

$$e^{\lambda \hat{a}} \hat{a}^\dagger e^{-\lambda \hat{a}} = \hat{a}^\dagger + \lambda, \tag{9.224}$$

which implies

$$e^{\lambda \hat{a}} \hat{a}^\dagger = (\hat{a}^\dagger + \lambda) e^{\lambda \hat{a}}. \tag{9.225}$$

Extending to a polynomial $f(\hat{a}^\dagger)$,

$$e^{\lambda \hat{a}} f(\hat{a}^\dagger) e^{-\lambda \hat{a}} = f(e^{\lambda \hat{a}} \hat{a}^\dagger e^{-\lambda \hat{a}}) = f(\hat{a}^\dagger + \lambda), \tag{9.226}$$

rearranging terms

$$e^{\lambda \hat{a}} f(\hat{a}^\dagger) = f(\hat{a}^\dagger + \lambda) e^{\lambda \hat{a}} \tag{9.227}$$

and applying to $|0\rangle$, we get

$$e^{\lambda\hat{a}} f(\hat{a}^\dagger)|0\rangle = f(\hat{a}^\dagger + \lambda) e^{\lambda\hat{a}}|0\rangle. \tag{9.228}$$

Since $\hat{a}|0\rangle = 0$, the exponential acts as

$$e^{\lambda\hat{a}}|0\rangle = \sum_{n=0}^{\infty} \frac{(\lambda\hat{a})^n}{n!}|0\rangle = |0\rangle, \tag{9.229}$$

because $\hat{a}^n|0\rangle = 0$ for $n \geq 1$. Substituting, we finally obtain

$$e^{\lambda\hat{a}} f(\hat{a}^\dagger)|0\rangle = f(\hat{a}^\dagger + \lambda)|0\rangle. \tag{9.230}$$

P9.16 Prove that

$$e^{\alpha\hat{a}+\beta\hat{a}^\dagger} = e^{\alpha\hat{a}} e^{\beta\hat{a}^\dagger} e^{\alpha\beta/2}. \tag{9.231}$$

Solution. The problem can be most easily approached using the Baker-Campbell-Hausdorff formula, which is given up to third-order commutators in [**1**], **Appendix A.3**,

$$\begin{aligned}\ln(\mathrm{e}^P \mathrm{e}^Q) = P + Q + \frac{1}{2}[P,Q] + \frac{1}{12}([P,[P,Q]] \\ + [Q,[Q,P]]) - \frac{1}{24}[Q,[P,[P,Q]]],\end{aligned} \tag{9.232}$$

where P, Q are two noncommuting operators. In the present case, with $P = \alpha\hat{a}$, $Q = \beta\hat{a}^\dagger$, we have, up to third order,

$$\begin{aligned}\ln(\mathrm{e}^{\alpha\hat{a}}\mathrm{e}^{\beta\hat{a}^\dagger}) = \alpha\hat{a} + \beta\hat{a}^\dagger + \frac{\alpha\beta}{2}[\hat{a},\hat{a}^\dagger] + \frac{\alpha\beta}{12}(\alpha[\hat{a},[\hat{a},\hat{a}^\dagger]] \\ + \beta[\hat{a}^\dagger,[\hat{a}^\dagger,\hat{a}]]) - \frac{\alpha^2\beta^2}{24}[\hat{a}^\dagger,[\hat{a},[\hat{a},\hat{a}^\dagger]]].\end{aligned} \tag{9.233}$$

Using the basic commutator $[\hat{a},\hat{a}^\dagger] = 1$, this reduces to

$$\ln(\mathrm{e}^{\alpha\hat{a}}\mathrm{e}^{\beta\hat{a}^\dagger}) = \alpha\hat{a} + \beta\hat{a}^\dagger + \frac{\alpha\beta}{2}. \tag{9.234}$$

As can be seen, the higher-order terms will not contribute to this equation. Therefore, we get

$$e^{\alpha\hat{a}+\beta\hat{a}^\dagger} = e^{\alpha\hat{a}} e^{\beta\hat{a}^\dagger} e^{\alpha\beta/2}, \tag{9.235}$$

which is the desired result.

P9.17 Calculate the normal frequencies Ω_1 and Ω_2 of the Hamiltonian given by

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right) + \tfrac{1}{2}m\omega_1^2 x_1^2 + \tfrac{1}{2}m\omega_2^2 x_2^2 - m\omega_{12}^2 x_1 x_2. \tag{9.236}$$

Solution. The system consists of two 1D oscillators with equal mass but different

frequencies, linearly coupled. To obtain the normal coordinates of the problem (where the oscillators decouple), we introduce new variables X and x through a linear transformation from x_1, x_2 with coefficients a_{ij},

$$X = a_{11}x_1 + a_{12}x_2, \quad x = a_{21}x_1 + a_{22}x_2. \tag{9.237}$$

The problem is solved using an orthogonal transformation. With the transformation determinant equal to 1,

$$a_{11}a_{22} - a_{12}a_{21} = 1, \tag{9.238}$$

the inverse transformation is:

$$x_1 = a_{22}X - a_{12}x, \quad x_2 = -a_{21}X + a_{11}x. \tag{9.239}$$

For the transformation to be orthogonal ($\hat{a}^T = \hat{a}^{-1}$), a comparison of (9.237) and (9.239) shows that

$$a_{11} = a_{22}; \quad a_{12} = -a_{21}. \tag{9.240}$$

Conditions (9.238) and (9.240) leave only one free parameter, which we will choose to diagonalize the frequency matrix. Thus we set

$$a_1 \equiv a_{11} = a_{22}, \quad a_0 \equiv a_{12} = -a_{21}, \quad a_0^2 + a_1^2 = 1. \tag{9.241}$$

It is straightforward to verify that the transformation preserves the diagonality of the kinetic energy,

$$\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} = \left(a_1\frac{\partial}{\partial X} - a_0\frac{\partial}{\partial x}\right)^2 + \left(a_0\frac{\partial}{\partial X} + a_1\frac{\partial}{\partial x}\right)^2 \tag{9.242}$$

$$= (a_0^2 + a_1^2)\frac{\partial^2}{\partial X^2} + (a_0^2 + a_1^2)\frac{\partial^2}{\partial x^2} \tag{9.243}$$

$$+ 2(-a_0a_1 + a_0a_1)\frac{\partial}{\partial x}\frac{\partial}{\partial X} \tag{9.244}$$

$$= \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial x^2}. \tag{9.245}$$

The potential energy now takes the form

$$V = \frac{m}{2}\omega_1^2(a_1X - a_0x)^2 + \frac{m}{2}\omega_2^2(a_0X + a_1x)^2 \tag{9.246}$$

$$- m\omega_{12}^2(a_1X - a_0x)(a_0X + a_1x) \tag{9.247}$$

$$= \frac{m}{2}\Big[(\omega_1^2a_0^2 + \omega_2^2a_1^2 + 2\omega_{12}^2a_0a_1)x^2 \tag{9.248}$$

$$+ (\omega_1^2a_1^2 + \omega_2^2a_0^2 - 2\omega_{12}^2a_0a_1)X^2\Big] \tag{9.249}$$

$$+ m\Big[(\omega_2^2 - \omega_1^2)a_0a_1 + \omega_{12}^2(a_0^2 - a_1^2)\Big]Xx. \tag{9.250}$$

To decouple the oscillators, we choose the free parameter to eliminate the cross term, requiring

$$(\omega_2^2 - \omega_1^2)a_0a_1 + \omega_{12}^2(a_0^2 - a_1^2) = 0. \tag{9.251}$$

This condition determines a value for the ratio $\beta \equiv a_1/a_0$ as a function of the system frequencies. With this value known, the solution can be written as

$$a_0 = \frac{1}{\sqrt{1+\beta^2}}, \quad a_1 = \frac{\beta}{\sqrt{1+\beta^2}}. \tag{9.252}$$

The frequencies of the normal modes are given by

$$\Omega_1^2 \equiv \omega_x^2 = \omega_1^2 a_0^2 + \omega_2^2 a_1^2 + 2\omega_{12}^2 a_0 a_1 \tag{9.253}$$

$$= a_0^2 \left(\omega_1^2 + \omega_2^2\beta^2 + 2\omega_{12}^2\beta\right), \tag{9.254}$$

$$\Omega_2^2 \equiv \omega_X^2 = \omega_1^2 a_1^2 + \omega_2^2 a_0^2 - 2\omega_{12}^2 a_0 a_1 \tag{9.255}$$

$$= a_0^2 \left(\omega_1^2\beta^2 + \omega_2^2 - 2\omega_{12}^2\beta\right). \tag{9.256}$$

The new Hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial x^2}\right) + \frac{m}{2}\omega_X^2 X^2 + \frac{m}{2}\omega_x^2 x^2, \tag{9.257}$$

and the energy eigenvalues are

$$E_{Nn} = \hbar\omega_X\left(N + \frac{1}{2}\right) + \hbar\omega_x\left(n + \frac{1}{2}\right). \tag{9.258}$$

The corresponding wavefunction is

$$\Psi_{Nn}(X, x) = \Phi_N(X)\psi_n(x), \tag{9.259}$$

where each factor is a harmonic oscillator wave function.

For the particular case where both oscillators have the same frequency, $\omega_1 = \omega_2 \equiv \omega$, (9.251) yields $a_0^2 = a_1^2$. We can therefore take $\beta = 1$, and from (9.237) we obtain

$$X = \frac{1}{\sqrt{2}}(x_2 + x_1), \quad x = \frac{1}{\sqrt{2}}(x_2 - x_1). \tag{9.260}$$

In this case, the normal modes describe the center-of-mass oscillations (X coordinate) and the relative motion oscillations (x coordinate).

Note that the solution obtained for the normal coordinates and their corresponding frequencies in the general case is the same as that of the classical problem of two coupled harmonic oscillators..

P9.18 Two particles with masses m_1 and m_2 moving along a straight line interact through the potential

$$V(x_1, x_2) = a(x_1 - x_2) + b(x_1 - x_2)^2, \quad b > 0. \tag{9.261}$$

Determine the eigenenergies and the corresponding wave functions.

Solution. The total Hamiltonian of the system is given by

$$\hat{H} = -\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} + V(x_1, x_2), \tag{9.262}$$

and the time-independent Schrödinger equation reads

$$\left[-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2}-\frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2}+a(x_1-x_2)+b(x_1-x_2)^2\right]\Psi(x_1,x_2)=E\Psi(x_1,x_2). \tag{9.263}$$

We now introduce the change of variables to center-of-mass and relative coordinates:

$$x=x_1-x_2, \qquad X=\frac{m_1x_1+m_2x_2}{m_1+m_2}. \tag{9.264}$$

We define $M=m_1+m_2$.

Next, we express the derivatives with respect to x_1 and x_2 in terms of derivatives with respect to x and X. Using the chain rule,

$$\frac{\partial}{\partial x_1}=\frac{\partial X}{\partial x_1}\frac{\partial}{\partial X}+\frac{\partial x}{\partial x_1}\frac{\partial}{\partial x}=\frac{m_1}{M}\frac{\partial}{\partial X}+\frac{\partial}{\partial x}, \tag{9.265}$$

$$\frac{\partial}{\partial x_2}=\frac{\partial X}{\partial x_2}\frac{\partial}{\partial X}+\frac{\partial x}{\partial x_2}\frac{\partial}{\partial x}=\frac{m_2}{M}\frac{\partial}{\partial X}-\frac{\partial}{\partial x}. \tag{9.266}$$

Now we compute the second derivatives using the expressions obtained above,

$$\frac{\partial^2}{\partial x_1^2}=\left(\frac{m_1}{M}\frac{\partial}{\partial X}+\frac{\partial}{\partial x}\right)^2 \tag{9.267}$$

$$=\left(\frac{m_1}{M}\right)^2\frac{\partial^2}{\partial X^2}+2\frac{m_1}{M}\frac{\partial^2}{\partial X\partial x}+\frac{\partial^2}{\partial x^2}, \tag{9.268}$$

$$\frac{\partial^2}{\partial x_2^2}=\left(\frac{m_2}{M}\frac{\partial}{\partial X}-\frac{\partial}{\partial x}\right)^2 \tag{9.269}$$

$$=\left(\frac{m_2}{M}\right)^2\frac{\partial^2}{\partial X^2}-2\frac{m_2}{M}\frac{\partial^2}{\partial X\partial x}+\frac{\partial^2}{\partial x^2}. \tag{9.270}$$

We compute:

$$\frac{1}{m_1}\frac{\partial^2}{\partial x_1^2}+\frac{1}{m_2}\frac{\partial^2}{\partial x_2^2}=\left(\frac{m_1+m_2}{M^2}\right)\frac{\partial^2}{\partial X^2}+\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\frac{\partial^2}{\partial x^2} \tag{9.271}$$

$$=\frac{1}{M}\frac{\partial^2}{\partial X^2}+\frac{1}{m}\frac{\partial^2}{\partial x^2}, \tag{9.272}$$

where m is the reduced mass defined by

$$\frac{1}{m}=\frac{1}{m_1}+\frac{1}{m_2}. \tag{9.273}$$

Therefore, the Schrödinger equation becomes:

$$-\frac{\hbar^2}{2M}\frac{\partial^2\Psi}{\partial X^2}-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}+V(x)\Psi=E\Psi. \tag{9.274}$$

We now perform a separation of variables by proposing

$$\Psi(x,X)=\varphi(x)\phi(X), \tag{9.275}$$

and substituting into the Schrödinger equation

$$-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2}\left[\varphi(x)\phi(X)\right]-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left[\varphi(x)\phi(X)\right]+V(x)\varphi(x)\phi(X)=E\varphi(x)\phi(X). \tag{9.276}$$

Applying the derivatives,

$$-\frac{\hbar^2}{2M}\varphi(x)\frac{d^2\phi(X)}{dX^2}-\frac{\hbar^2}{2m}\phi(X)\frac{d^2\varphi(x)}{dx^2}+V(x)\varphi(x)\phi(X)=E\varphi(x)\phi(X) \tag{9.277}$$

and dividing both sides by $\varphi(x)\phi(X)$, we obtain

$$-\frac{\hbar^2}{2M}\frac{1}{\phi(X)}\frac{d^2\phi(X)}{dX^2}-\frac{\hbar^2}{2m}\frac{1}{\varphi(x)}\frac{d^2\varphi(x)}{dx^2}+V(x)=E. \tag{9.278}$$

Since the left-hand side is the sum of a function of X and a function of x, and the right-hand side is a constant, each term must independently be equal to a constant. We thus define

$$E=E_{\rm cm}+E_{\rm rel}, \tag{9.279}$$

and write the resulting equations for the center-of-mass motion

$$-\frac{\hbar^2}{2M}\frac{d^2\phi(X)}{dX^2}=E_{\rm cm}\phi(X), \tag{9.280}$$

and the relative motion,

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi(x)}{dx^2}+V(x)\varphi(x)=E_{\rm rel}\varphi(x). \tag{9.281}$$

The former is the eqution for a free particle,

$$\frac{d^2\phi(X)}{dX^2}+K^2\phi(X)=0, \tag{9.282}$$

with $K^2=\frac{2ME_{\rm cm}}{\hbar^2}$, and general solution

$$\phi(X)\sim e^{\pm iKX}. \tag{9.283}$$

The corresponding energy of the center-of-mass motion is

$$E_{\rm cm}=\frac{\hbar^2K^2}{2M},\qquad K\in\mathbb{R}. \tag{9.284}$$

To solve the equation for the relative motion, we start from

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi(x)}{dx^2}+(bx^2+ax)\varphi(x)=E_{rel}\varphi(x). \tag{9.285}$$

We now complete the square in the potential

$$bx^2+ax=b\left(x+\frac{a}{2b}\right)^2-\frac{a^2}{4b}. \tag{9.286}$$

define a new variable

$$\chi=x+\frac{a}{2b}\quad\Rightarrow\frac{\partial\psi}{\partial x}=\frac{\partial\psi}{\partial\chi}\frac{\partial\chi}{\partial x}=\frac{\partial\psi}{\partial\chi}, \tag{9.287}$$

and redefine the energy as

$$E' = \frac{a^2}{4b} + E_{\text{rel}}. \tag{9.288}$$

where $b = \frac{1}{2}m\omega^2$, so that $\omega = \sqrt{\frac{2b}{m}}$. Substituting into the Schrödinger equation, we obtain

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi(\chi)}{d\chi^2} + \frac{1}{2}m\omega^2\chi^2\varphi(\chi) = E'\varphi(\chi), \tag{9.289}$$

which is now the Schrödinger equation for a harmonic oscillator centered at $\chi = 0$, with frequency

$$\omega = \sqrt{\frac{2b}{m}}. \tag{9.290}$$

We now define a dimensionless variable

$$\chi = \alpha\xi, \qquad \text{with} \quad \alpha^2 = \frac{\hbar}{m\omega}, \tag{9.291}$$

and introduce the dimensionless energy

$$\varepsilon = \frac{2E'}{\hbar\omega}. \tag{9.292}$$

Using the chain rule, we have

$$\frac{d}{d\chi} = \frac{1}{\alpha}\frac{d}{d\xi}, \qquad \frac{d^2}{d\chi^2} = \frac{1}{\alpha^2}\frac{d^2}{d\xi^2}. \tag{9.293}$$

Substituting into the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi(\chi)}{d\chi^2} + b\chi^2\varphi(\chi) = E'\varphi(\chi), \tag{9.294}$$

we obtain

$$-\frac{\hbar^2}{2m}\cdot\frac{1}{\alpha^2}\frac{d^2\varphi(\xi)}{d\xi^2} + b\alpha^2\xi^2\varphi(\xi) = E'\varphi(\xi). \tag{9.295}$$

Therefore, since $\alpha^2 = \frac{\hbar}{m\omega}$ and $b = \frac{1}{2}m\omega^2$,

$$\frac{\hbar^2}{2m\alpha^2} = \frac{\hbar^2}{2m}\cdot\frac{m\omega}{\hbar} = \frac{\hbar\omega}{2}, \qquad b\alpha^2 = \frac{1}{2}m\omega^2\cdot\frac{\hbar}{m\omega} = \frac{\hbar\omega}{2}, \tag{9.296}$$

the equation becomes

$$-\frac{\hbar\omega}{2}\frac{d^2\varphi(\xi)}{d\xi^2} + \frac{\hbar\omega}{2}\xi^2\varphi(\xi) = E'\varphi(\xi). \tag{9.297}$$

Dividing through by $\frac{\hbar\omega}{2}$, we obtain the dimensionless form

$$-\varphi'' + \xi^2\varphi = \varepsilon\psi \tag{9.298}$$

which is the standard form of the harmonic oscillator Schrödinger equation in dimensionless variables. The solutions to the dimensionless harmonic oscillator equation are known and given by

$$\varphi_n(\xi) = C_n\, e^{-\xi^2/2} H_n(\xi), \tag{9.299}$$

where $H_n(\xi)$ are the Hermite polynomials, and the normalization constant is

$$C_n = \left(\sqrt{\pi}\,\alpha\, 2^n\, n!\right)^{-1/2}. \tag{9.300}$$

The corresponding energy eigenvalues are

$$E' = \hbar\omega\left(n + \frac{1}{2}\right). \tag{9.301}$$

Recalling the shift applied to complete the square, we obtain for the energy of the relative motion

$$E_{\text{rel}} = \hbar\sqrt{\frac{2b}{m}}\left(n + \frac{1}{2}\right) - \frac{a^2}{4b}. \tag{9.302}$$

The total wave function is given by the product of the center-of-mass and relative motion solutions

$$\Psi(x, X) = \phi(X)\,\varphi_n(x). \tag{9.303}$$

Substituting everything, we obtain the full wave function

$$\Psi_n^K(x, X) = C_n\, e^{\pm iKX}\, \exp\left[-\frac{1}{2}\left(\frac{x + \frac{a}{2b}}{\alpha}\right)^2\right] H_n\left(\frac{x + \frac{a}{2b}}{\alpha}\right), \tag{9.304}$$

or in terms of the particle variables,

$$\Psi_n^K(x_1, x_2) = C_n\, \exp\left[\pm iK\left(\frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}\right) - \frac{1}{2}\left(\frac{x_1 - x_2 + \frac{a}{2b}}{\alpha}\right)^2\right] H_n\left(\frac{x_1 - x_2 + \frac{a}{2b}}{\alpha}\right), \tag{9.305}$$

where $\alpha = \sqrt{\frac{\hbar}{m\omega}} = (\frac{\hbar^2}{2mb})^{1/4}$.

Finally, the total energy of the system is given by

$$E_n^K = \frac{\hbar^2 K^2}{2M} + \hbar\sqrt{\frac{2b}{m}}\left(n + \frac{1}{2}\right) - \frac{a^2}{4b}, \qquad n \in \mathbb{N},\ K \in \mathbb{R}. \tag{9.306}$$

CHAPTER 10

The Physics Underlying Quantum Phenomena

P10.1 Two very thin metal plates, 10 Å on each side and initially neutral, are 20 Å apart. Calculate the number of electrons that need to be added to each plate for the Coulomb repulsion to counteract the Casimir attraction.

Solution. The electric field produced by a single infinite thin plate with surface charge density σ is given by

$$E = \frac{\sigma}{2\varepsilon_0}. \tag{10.1}$$

Since the system consists of two plates with equal and opposite charges, the field created by one plate at the location of the other is still $\frac{\sigma}{2\varepsilon_0}$. The total electrostatic force F_E acting on one plate due to the other is then

$$F_E = QE = Q \cdot \frac{\sigma}{2\varepsilon_0} = \frac{Q^2}{2\varepsilon_0 A}, \tag{10.2}$$

where $A = R^2$ is the area of the plate such that $\sigma = Q/A$. The total charge on the plates is given by the number N of electrons added to each plate, which is equal to N times the elementary charge e. Therefore,

$$F_E = \frac{N^2 e^2}{2\varepsilon_0 A}. \tag{10.3}$$

The Casimir attractive force is given by (see [**1**], **Section 10.2.1**)

$$F_c = -\frac{\pi^2 \hbar c A}{240 R^4}. \tag{10.4}$$

To counteract the Casimir attraction, we impose the condition

$$F_E + F_C = 0. \tag{10.5}$$

Substituting the expressions for each force,

$$\frac{N^2 e^2}{2\varepsilon_0 A} - \frac{\pi^2 \hbar c A}{240 R^4} = 0. \tag{10.6}$$

Solving for N, we find

$$N = \sqrt{\frac{\varepsilon_0 A^2 \pi^2 \hbar c}{120 e^2 R^4}} \approx 0.237. \tag{10.7}$$

This result implies that less than one electron is required to completely cancel the Casimir force. Therefore, even the addition of a single electron would overcompensate the attraction, highlighting the extreme weakness of the Casimir force compared to electrostatic interactions at these scales.

P10.2 Construct the general solution $x(t)$ for the harmonic oscillator immersed in the zero-point field with arbitrary initial conditions, and show that the stationary solution satisfies

$$\lim_{t\to\infty} x(t) \approx E_C(R;k_c) = \frac{\hbar c L^2 k_c^3}{2\pi}\left(-1-6x+2\Delta+\frac{2\zeta\Delta^2}{x}-\frac{\zeta\Delta^2}{x^2}+\frac{2\zeta\Delta^3}{x^2}\right), \tag{10.8}$$

where $\zeta = \exp(-1/x)$ and $\Delta = (1-\zeta)^{-1}$.

Solution. The approximate equation of motion for a 1D oscillator with frequency ω_0 moving in the zero-point field with spectral density $\rho(\omega)$ given by equation $\rho_0(\omega) = \hbar\omega^3/2\pi^2c^3$ is

$$\ddot{x} + \omega_0^2 x - \tau\dddot{x} = \frac{e}{m}E(x,t), \tag{10.9}$$

where $E(x,t)$ represents the x-component of the zero-point field. We will solve this equation in the *long-wavelength approximation*, meaning we assume the field $E(x,t)$ is essentially uniform across all positions $x(t)$ occupied by the oscillator. Thus we can approximate $E(x,t) \approx E(x_C,t) = E(t)$, where x_C is a fixed coordinate associated with the particle (such as the mean position $\overline{x(t)}$).

This approximation is valid when the amplitude of relevant motions is much smaller than the shortest wavelength of the involved field. In studying the interaction between a mechanical system (oscillator, atom, etc.) and the radiation field, this simplification typically corresponds to considering only the dipole coupling between the system and the field. Hence the frequent identification of the dipole approximation with the long-wavelength approximation.

The term $-m\tau\dddot{x}$ in (10.9) is the radiation reaction force, accounting for the particle's recoil due to Larmor radiation. The parameter τ is determined by classical electrodynamics,

$$\tau = \frac{2e^2}{3mc^3}. \tag{10.10}$$

For an electron, $\tau \simeq 10^{-23}$ s. This small value ensures $\tau\omega \ll 1$ for all frequencies of practical interest. In classical electrodynamics, an equation like (10.9) that includes radiation reaction is called the *Abraham-Lorentz equation*. However, since (10.9) also contains a stochastic force, it resembles what in stochastic process theory is known as a *Langevin equation*. In the specific form of stochastic electrodynamics, corresponding to a stochastic equation for colored noise with radiation reaction, it is called the *Braffort-Marshall equation*.

The radiation reaction provides an approximate description of the effect of radiation emission on the emitting particle itself. This approximation is generally acceptable, though it can lead to difficulties such as divergent solutions. These

divergent solutions can be eliminated through the following procedure, presented here for completeness.

We rewrite equation (10.9) as

$$\ddot{x} - \tau \dddot{x} = \frac{1}{m} f(t) + \frac{e}{m} E(t), \tag{10.11}$$

where, to make the derivation more general, we write $f(t)$ (equivalent to $f(x(t))$) instead of $-m\omega_0^2 x$. We introduce an integration factor $\mu(t)$ that allows us to associate the radiation reaction with the acceleration,

$$\frac{d}{dt}[\dot{x}\mu(t)] = \mu\ddot{x} + \dot{\mu}\dot{x} = (\ddot{x} - \tau\dddot{x})\mu(t), \tag{10.12}$$

from which it follows that we must take $\mu = \exp(-t/\tau)$. Combining this expression with (10.11) we obtain

$$\frac{d}{dt}[\dot{x}\mu(t)] = \mu(t)\left(\frac{1}{m}f + \frac{e}{m}E\right) = -\frac{1}{m\tau}\mu(t)(f + eE), \tag{10.13}$$

yielding after integration

$$x = -e^{t/\tau}\int_{-\infty}^{t} e^{t'/\tau}[f(x(t')) + eE(t')]dt' + A. \tag{10.14}$$

If we assign a finite value to the bracketed factor in (10.14), the acceleration $\ddot{x}$ becomes infinite as $t \to \infty$; this acceleration runaway demonstrates that the approximation described by the Abraham-Lorentz equation is indeed unsatisfactory and must be handled with care. A partial remedy to this problem is obtained by requiring that the final acceleration be a specified constant (which we'll take, as is customary, to be zero). This condition fixes the integration constant A in (10.14) as

$$A = \frac{1}{m\tau}\int^{\infty} e^{-(t'-t)/\tau}\left[f(x(t')) + eE(t')\right]dt', \tag{10.15}$$

which when reinserted into the previous equation reduces it to

$$m\ddot{x} = \frac{1}{\tau}\int_{t}^{\infty} e^{-(t'-t)/\tau}\left[f\left(x\left(t'\right)\right) + eE(t')\right]dt', \tag{10.16}$$

or alternatively, with the variable change $s = (t' - t)/\tau$

$$m\ddot{x} = \int_{0}^{\infty} e^{-s}\left[f\left(x\left(t + \tau s\right)\right) + eE(t + \tau s)\right]ds. \tag{10.17}$$

The acceleration issue has been resolved, but at the cost of introducing a new problem: now the acceleration at time t is determined by external forces at *all future times* $t + \tau s$, $s \in (0, \infty)$. This is the *preacceleration* phenomenon, which is clearly unphysical.

From a pragmatic standpoint, this phenomenon is often considered unimportant because the exponential in the integrand of (10.10) ensures significant contributions only for $s \lesssim 10$, for such s values, the time shifts τs are negligible and

the quantum fluctuations dominate at these timescales, masking the difference $f(t+\tau s)-f(t)$

However, no such considerations can change the fundamental acausality of the equation. Another manifestation of this difficulty appears in the derivation itself, where we had to impose a final condition on the acceleration - conceptually unsatisfactory since instantaneous motion shouldn't depend on future states. Since the integro-differential equation (10.17) is too complex for applications, we simplify it by expanding $f(x(t'))$ around $x(t)$ and truncating at order τ due to its smallness ($\tau \sim 10^{-23}$ s for electrons)

$$f\left(x\left(t+\tau s\right)\right)=f\left(x\left(t\right)\right)+\tau s\frac{df\left(x\left(t\right)\right)}{dt}+\cdots \tag{10.18}$$

Substituting into (10.17) and using $\int_0^\infty s^n e^{-s}ds = n!$, we obtain

$$m\ddot{x}=f\left(x\right)+\tau\dot{x}\frac{df\left(x\right)}{dx}+e\int_0^\infty E(t+\tau s)e^{-s}ds. \tag{10.19}$$

The net effect of all these transformations is twofold. The radiation reaction with its peculiar (and acausal) dependence on $\dddot{x}$ has been replaced by a friction force $\tau\dot{x}f'$ (generally position-dependent). The electric force $eE(t)$ has been replaced by the integral expression that represents a convolution with the weight factor e^{-s} and is equivalent to a weighted average over future times. Despite causality issues, keeping this form is advantageous because it helps reduce divergence problems in certain integrals we'll encounter later. The simple substitution $\dddot{x}\to\tau\dot{x}f'$ would worsen these divergences.

For the specific oscillator case (10.9), the above equation becomes

$$\ddot{x}+\omega_0^2x+\tau\omega_0^2\dot{x}=\frac{e}{m}\int_0^\infty E(t+\tau s)e^{-s}ds. \tag{10.20}$$

The stationary part of the solution to this integro-differential equation can be found by transforming to Fourier space. We write

$$x(t)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\tilde{x}(\omega)e^{i\omega t}d\omega, \tag{10.21}$$

$$E(t)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\tilde{E}(\omega)e^{i\omega t}d\omega. \tag{10.22}$$

Substituting these expressions into (10.20) yields

$$\begin{aligned}&\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\left(-\omega^2+\omega_0^2+i\tau\omega_0^2\omega\right)\tilde{x}(\omega)e^{i\omega t}d\omega\\&=\frac{e}{m\sqrt{2\pi}}\int_{-\infty}^{\infty}\int_0^\infty\tilde{E}(\omega)e^{-s}e^{i\omega(t+\tau s)}d\omega ds\\&=\frac{e}{m\sqrt{2\pi}}\int_{-\infty}^{\infty}\frac{\tilde{E}(\omega)}{1-i\tau\omega}e^{i\omega t}d\omega.\end{aligned} \tag{10.23}$$

Since this expression must hold for all t, we obtain the solution in frequency space

$$\tilde{x}(\omega) = \frac{e}{m\,(1 - i\tau\omega)} \frac{\tilde{E}(\omega)}{(-\omega^2 + \omega_0^2 + i\tau\omega_0^2\omega)}. \tag{10.24}$$

Substituting this result into (10.21) gives

$$x(t) = \frac{e}{m\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\tilde{E}(\omega) e^{i\omega t}}{(1 - i\tau\omega)(-\omega^2 + \omega_0^2 + i\tau\omega_0^2\omega)} d\omega, \tag{10.25}$$

apart from changes in notation and denominator representation (valid up to order τ terms).

The complete solution is obtained by adding to the stationary solution the general solution of the homogeneous equation associated with (10.20),

$$\ddot{x} + \omega_0^2 x + \tau\omega_0^2 \dot{x} = 0. \tag{10.26}$$

This transient solution is

$$x_{\text{trans}} = (x_1 e^{i\omega_1 t} + x_2 e^{-i\omega_1 t}) e^{-\gamma t}, \quad \omega_1 = \omega_0 \sqrt{1 - \tau^2\omega_0^2/4} \approx \omega_0, \quad \gamma = \frac{\tau\omega_0^2}{2}. \tag{10.27}$$

The exponential factor $e^{-\gamma t}$ ensures that the field-independent contribution x_{trans} vanishes over time. Therefore, for sufficiently long times (specifically, $t \gg \gamma^{-1} = 2/(\tau\omega_0^2)$), the complete solution is given by (10.25) and becomes determined solely by the zero-point field, regardless of initial conditions.

P10.3 Use the previous results to derive in detail the autocorrelation function and the variance of $p(t)$ for the stationary harmonic oscillator.
Solution. From the given expression for the position $x(t)$,

$$x(t) = \frac{e}{m} \int_{-\infty}^{\infty} d\omega\, \frac{E(\omega) e^{i\omega t}}{\omega_0^2 - \omega^2 + i\tau\omega^3} + \text{c.c.}, \tag{10.28}$$

we compute the momentum $p(t)$ by differentiating with respect to time and multiplying by m,

$$p(t) = m\frac{dx(t)}{dt} \tag{10.29}$$

$$= e \int_{-\infty}^{\infty} d\omega\, \frac{i\omega E(\omega) e^{i\omega t}}{\omega_0^2 - \omega^2 + i\tau\omega^3} + \text{c.c.} \tag{10.30}$$

The autocorrelation function is then given by

$$\langle p(t)p(t')\rangle = e^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\omega\, d\omega'\, \omega\omega' \frac{\langle E(\omega)E^*(\omega')\rangle e^{i\omega t - i\omega' t'}}{(\omega_0^2 - \omega^2 + i\tau\omega^3)(\omega_0^2 - \omega'^2 - i\tau\omega'^3)}. \tag{10.31}$$

Substituting

$$\langle E(\omega)E^*(\omega')\rangle = \frac{2\pi}{3}\rho_0(\omega)\delta(\omega - \omega'), \tag{10.32}$$

we obtain:

$$\langle p(t)p(t')\rangle = e^2 \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} d\omega\, d\omega'\, \omega\omega' \,\frac{2\pi}{3}\rho_0(\omega)\frac{\delta(\omega-\omega')e^{i\omega t - i\omega' t'}}{(\omega_0^2-\omega^2+i\tau\omega^3)(\omega_0^2-\omega'^2-i\tau\omega'^3)} \tag{10.33}$$

$$= \frac{2\pi e^2}{3}\int_{-\infty}^{\infty} d\omega\, \frac{\omega^2\rho_0(\omega)e^{i\omega(t-t')}}{|\omega_0^2-\omega^2+i\tau\omega^3|^2} = \frac{2\pi e^2}{3}\int_{-\infty}^{\infty} d\omega\, \frac{\omega^2\rho_0(\omega)e^{i\omega(t-t')}}{(\omega_0^2-\omega^2)^2+\tau^2\omega^6}. \tag{10.34}$$

The variance of the momentum is obtained by setting $t = t'$ in the autocorrelation function,

$$\langle p^2(t)\rangle = \frac{2\pi e^2}{3}\int_{-\infty}^{\infty} d\omega\, \frac{\omega^2\rho_0(\omega)}{(\omega_0^2-\omega^2)^2+\tau^2\omega^6}. \tag{10.35}$$

Using the relation $\tau = \frac{2e^2}{3mc^3}$, we can express the prefactor in terms of τ,

$$\frac{2\pi e^2}{3} = \pi mc^3\tau. \tag{10.36}$$

Thus, the variance of the momentum becomes

$$\langle p^2(t)\rangle = 2\pi mc^3\int_0^{\infty} d\omega\, \rho_0(\omega)\omega^2\frac{\tau}{(\omega_0^2-\omega^2)^2+\tau^2\omega^6}. \tag{10.37}$$

The dominant contribution to the integral comes from frequencies near $\omega \approx \omega_0$. Let us define

$$y = \omega - \omega_0, \tag{10.38}$$

so that

$$(\omega_0^2-\omega^2)^2 = (\omega_0+\omega)^2(\omega_0-\omega)^2 = (\omega_0+\omega)^2y^2 \approx 4\omega_0^2y^2, \tag{10.39}$$

and the denominator becomes

$$(\omega_0^2-\omega^2)^2+\tau^2\omega^6 \approx 4\omega_0^2y^2+\tau^2\omega_0^6 = 4\omega_0^2\left(y^2+\frac{\tau^2\omega_0^4}{4}\right). \tag{10.40}$$

Thus,

$$\frac{\tau}{(\omega_0^2-\omega^2)^2+\tau^2\omega^6} \approx \frac{\tau}{4\omega_0^2\left(y^2+\frac{\tau^2\omega_0^4}{4}\right)} = \frac{1}{2\omega_0^4}\frac{\frac{\tau\omega_0^2}{2}}{y^2+\frac{\tau^2\omega_0^4}{4}} = \frac{1}{2\omega_0^4}\frac{\gamma}{y^2+\gamma^2} \tag{10.41}$$

were we defined

$$\gamma = \frac{\tau\omega_0^2}{2} \ll 1. \tag{10.42}$$

Using the identity

$$\lim_{\gamma\to 0}\frac{\gamma}{y^2+\gamma^2} = \pi\delta(y), \tag{10.43}$$

equation 10.37 becomes

$$\langle p^2(t)\rangle = 2\pi mc^3 \int_0^\infty d\omega\ \frac{\rho_0(\omega)\omega^2}{2\omega_0^4}\pi\delta(\omega-\omega_0) \simeq 2\pi^2 mc^3 \int_{-\infty}^\infty d\omega\ \frac{\rho_0(\omega)\omega^2}{2\omega_0^4}\delta(\omega-\omega_0) \tag{10.44}$$

$$= \pi^2 mc^3 \cdot \frac{\rho_0(\omega_0)}{\omega_0^2}. \tag{10.45}$$

Using the spectral density of the zero-point field

$$\rho_0(\omega) = \frac{\hbar\omega^3}{2\pi^2c^3}, \tag{10.46}$$

we obtain the final result,

$$\langle p^2(t)\rangle = \frac{m\hbar\omega_0}{2}. \tag{10.47}$$

Therefore, the average kinetic energy accounts for half of the total energy, in agreement with the virial theorem (see problem **P9.2**).

P10.4 Show that the definitions used in early SED give for the dispersion of the ground state energy $\sigma_H^2 = \langle E_0^2\rangle$.

Solution. Stochastic methods demonstrate that the spatial density for the harmonic oscillator corresponds to a normal distribution with zero mean and variance $\sigma_x^2 = \hbar/2m\omega_0$,

$$\rho(x) = \frac{1}{\sqrt{2\pi\sigma_x^2}}\exp\left(-\frac{x^2}{2\sigma_x^2}\right) = \sqrt{\frac{m\omega_0}{\pi\hbar}}\exp\left(-\frac{m\omega_0 x^2}{\hbar}\right), \tag{10.48}$$

in agreement with the quantum result for the ground state. Similarly, the momentum space density is also Gaussian with zero mean and variance $\sigma_p^2 = \frac{1}{2}m\hbar\omega_0$,

$$\rho_p(p) = \frac{1}{\sqrt{2\pi\sigma_p^2}}\exp\left(-\frac{p^2}{2\sigma_p^2}\right) = \sqrt{\frac{1}{\pi m\hbar\omega_0}}\exp\left(-\frac{p^2}{m\hbar\omega_0}\right), \tag{10.49}$$

again coinciding with quantum solution for the ground state. From these distributions follow immediately

$$\langle x^4(t)\rangle = \int_{-\infty}^\infty x^4\rho(x)dx = 3\sigma_x^4 = \frac{3}{4}\frac{\hbar^2}{m^2\omega_0^2}, \tag{10.50}$$

$$\langle p^4(t)\rangle = \int_{-\infty}^\infty p^4\rho_p(p)dp = 3\sigma_p^4 = \frac{3}{4}m^2\hbar^2\omega_0^2. \tag{10.51}$$

The mean energy of the stationary (ground) state is:

$$\langle H\rangle = \left\langle \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2x^2\right\rangle = \frac{\sigma_p^2}{2m} + \frac{1}{2}m\omega_0^2\sigma_x^2$$

$$= \frac{1}{4}\hbar\omega_0 + \frac{1}{4}\hbar\omega_0 = \frac{1}{2}\hbar\omega_0, \tag{10.52}$$

in agreement with quantum mechanics. However, for real stochastic variables in this theory (with x and p uncorrelated):

$$\langle H^2\rangle = \left\langle \frac{p^4}{4m^2} + \frac{1}{2}\omega_0^2 x^2 p^2 + \frac{1}{4}m^2\omega_0^4 x^4 \right\rangle$$
$$= \frac{3}{16}\hbar^2\omega_0^2 + \frac{1}{8}\hbar^2\omega_0^2 + \frac{3}{16}\hbar^2\omega_0^2 = \frac{1}{2}\hbar^2\omega_0^2 = 2\langle H\rangle^2, \tag{10.53}$$

the energy dispersion is

$$\sigma_E^2 = \langle H^2\rangle - \langle H\rangle^2 = \langle H\rangle^2, \tag{10.54}$$

that is,

$$\sigma_E^2 = E_0^2, \tag{10.55}$$

whereas the corresponding quantum value is $\sigma_E^2 = 0$, since the ground stste is an eigenstate of the Hamiltonian. However, note that σ_E^2 and $\langle(\Delta\hat{H})^2\rangle_{\text{quantum}} \equiv \langle\psi_0|\hat{H}^2 - E^2|\psi_0\rangle$ are conceptually different quantities; their different values are therefore not surprising. Care must be taken to avoid confusing these concepts.

To clarify this point, σ_E^2 is calculated using phase space distributions, whereas the quantum result involves operator expectations in Hilbert space.

P10.5 Stationary white noise is so named because its spectral energy density is a constant, the same for all frequencies. Show that the autocorrelation function of a white noise is

$$\langle E(t')E(t)\rangle = A\delta(t'-t) \tag{10.56}$$

and express the value of the constant A in terms of the power density.
Solution. The autocorrelation function of the field is given by

$$\langle E_i(t')E_j(t)\rangle_0 = \frac{2\pi}{3}\int \rho_0(\omega)e^{i\omega(t'-t)}d\omega. \tag{10.57}$$

Since $\rho_0(\omega) = A'$ is constant for white noise, the autocorrelation becomes

$$\langle E(t')E(t)\rangle = \frac{2\pi}{3}\int_{-\infty}^{\infty} A'\, e^{i\omega(t'-t)}\, d\omega = \frac{4\pi^2}{3}A'\,\delta(t'-t). \tag{10.58}$$

Therefore,

$$\langle E(t')E(t)\rangle_0 = A\delta(t'-t), \tag{10.59}$$

with $A = \frac{4\pi^2}{3}A'$. The total energy density is given by

$$u = \int_0^{\infty} \rho_0(\omega)\, d\omega. \tag{10.60}$$

For white noise $\rho_0(\omega)$ is a constant for all frequencies. To avoid divergence, we introduce a frequency cutoff and consider a finite frequency band. That is, instead of integrating over all frequencies, we define the energy density as

$$u = A'\int_{\omega_{\min}}^{\omega_{\max}} d\omega = A'\,(\omega_{\max} - \omega_{\min}) = A'R_\omega, \tag{10.61}$$

where R_ω is the frequency range. Solving for A', we get

$$A' = \frac{3}{4\pi^2}A = \frac{u}{R_\omega} \quad \Rightarrow \quad A = \frac{4\pi^2 u}{3R_\omega}. \tag{10.62}$$

A dimensional analysis shows that the units for A are those of power density,

$$[A] = [\frac{J \cdot s}{m^3}] = [\frac{W}{m^3}]. \tag{10.63}$$

P10.6 Consider the 1D infinite square well of width a. a) Using the eigenfunctions obtained in [**1**], **Exercise E4.4**, determine the transition frequencies ω_{nk} and the corresponding response coefficients (matrix elements) x_{kn} for $n = 1$. b) Carry out the same calculations for $n = 2$. c) Make a drawing of the spectral absorption bands obtained for the two cases.

Solution. a) For the one-dimensional infinite potential well of width a, the eigenfunctions and eigenenergies are

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \quad E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}, \quad n = 1, 2, 3, \dots \tag{10.64}$$

For $n = 1$, allowed transitions are to even states k ($k = 2, 4, 6, \dots$) due to the selection rules, with the transition frequencies given by

$$\omega_{k1} = \frac{E_k - E_1}{\hbar} = \frac{\pi^2\hbar}{2ma^2}(k^2 - 1). \tag{10.65}$$

For $k = 2$,4,6 we get

$$\omega_{21} = \frac{3\pi^2\hbar}{2ma^2}, \quad \omega_{41} = \frac{15\pi^2\hbar}{2ma^2}, \quad \omega_{61} = \frac{35\pi^2\hbar}{2ma^2}. \tag{10.66}$$

The response coefficients are the matrix elements $|\langle k|x|1\rangle|$,

$$|\langle k|x|1\rangle| = \frac{8ak}{\pi^2(k^2 - 1)^2}. \tag{10.67}$$

For $k = 2$,4,6 we get

$$|\langle 2|x|1\rangle| = \frac{16a}{9\pi^2} \quad |\langle 4|x|1\rangle| = \frac{32a}{225\pi^2}, \quad |\langle 6|x|1\rangle| = \frac{48a}{1225\pi^2}. \tag{10.68}$$

b) Transitions from the state $n = 2$

Allowed transitions are to odd states k greater than 2 ($k = 3, 5, 7, \dots$), or to the ground state $k = 1$. For the latter case, the solutions are the ω_{21} and $|\langle 2|x|1\rangle|$ given above. The transition frequency to k greater than 2 is given by the general formula

$$\omega_{k2} = \frac{E_k - E_2}{\hbar} = \frac{\pi^2\hbar}{2ma^2}(k^2 - 4). \tag{10.69}$$

For $k = 3, 5, 7$ we get

$$\omega_{32} = \frac{5\pi^2\hbar}{2ma^2}, \quad \omega_{52} = \frac{21\pi^2\hbar}{2ma^2}, \quad \omega_{72} = \frac{45\pi^2\hbar}{2ma^2}. \tag{10.70}$$

The response coefficients are the matrix elements $|\langle k|x|2\rangle|$, given in general by

$$|\langle k|x|2\rangle| = \frac{16ak}{\pi^2(k^2-4)^2}, \quad k \text{ odd}, \, k > 2. \tag{10.71}$$

For $k = 3, 5, 7$ we get

$$|\langle 3|x|2\rangle| = \frac{48a}{25\pi^2}, \quad \langle 5|x|2\rangle| = \frac{80a}{441\pi^2}, \quad |\langle 7|x|2\rangle| = \frac{112a}{2025\pi^2}. \tag{10.72}$$

The intensity of a spectral line is proportional to the squared modulus of the respective matrix element $|\langle k|x|n\rangle|$. Note that in both cases a) and b), the absorption lines to the nearest upper state are the most intense ones, as shown in Fig. 12.

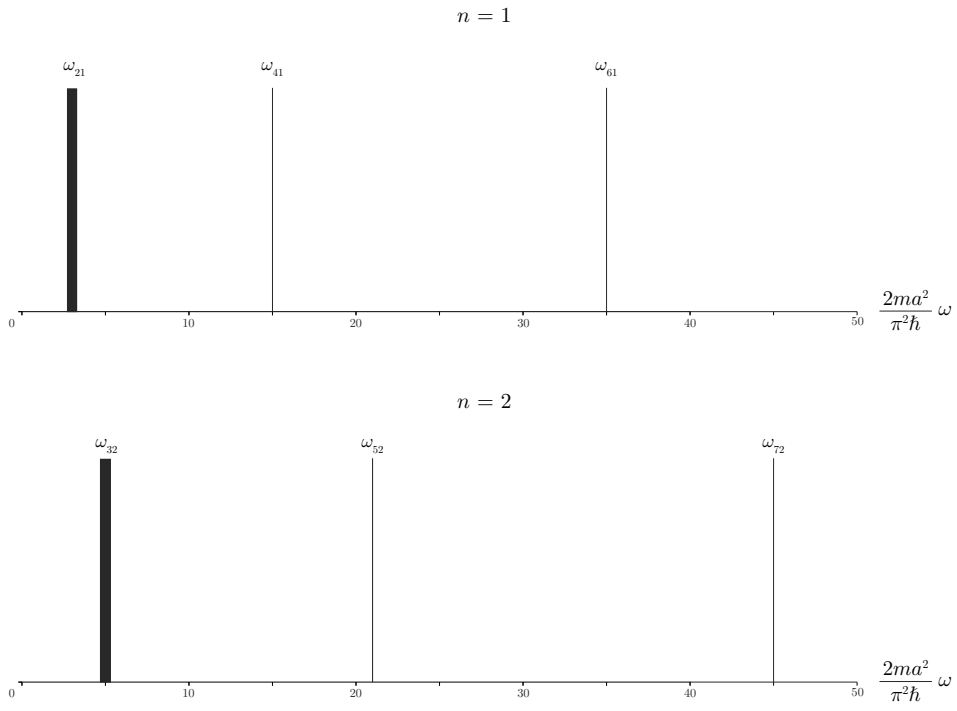

FIGURE 10.1. The three lowest-frequency absorption lines (n, k) for a) $n = 1$, and b) $n = 2$.

CHAPTER 11

Angular Momentum Theory

P11.1 Determine the relationship between the angular momentum defined in two different inertial reference systems when: a) the systems are at relative rest, with origins separated by a distance a; b) the systems move with constant relative velocity $\boldsymbol{v}$.

Solution. The angular momentum of a particle with mass m is defined as $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$, where $\boldsymbol{r}$ is the position vector and $\boldsymbol{p} = m\boldsymbol{v}$ is the linear momentum. We consider two inertial systems S and S'.

a) Position relation:

$$\boldsymbol{r} = \boldsymbol{r}' + \boldsymbol{a}. \tag{11.1}$$

Velocity and momentum: Since there is no relative motion between the systems, $\boldsymbol{v} = \boldsymbol{v}'$ and $\boldsymbol{p} = \boldsymbol{p}'$.

Angular momentum in S:

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} = (\boldsymbol{r}' + \boldsymbol{a}) \times \boldsymbol{p}' = \boldsymbol{r}' \times \boldsymbol{p}' + \boldsymbol{a} \times \boldsymbol{p}'. \tag{11.2}$$

With

$$\boldsymbol{r}' \times \boldsymbol{p}' = \boldsymbol{L}', \tag{11.3}$$

The final result is

$$\boldsymbol{L} = \boldsymbol{L}' + \boldsymbol{a} \times \boldsymbol{p}. \tag{11.4}$$

The angular momentum in S differs from that in S' by a term $\vec{\boldsymbol{a}} \times \vec{\boldsymbol{p}}$, which depends on the separation between origins and the linear momentum.

b) Position and velocity relations (Galilean transformations):

$$\boldsymbol{r} = \boldsymbol{r}' + \boldsymbol{v}_{S'}t, \quad \boldsymbol{v} = \boldsymbol{v}' + \boldsymbol{v}_{S'}, \quad \boldsymbol{p} = m(\boldsymbol{v}' + \boldsymbol{v}_{S'}) = \boldsymbol{p}' + m\boldsymbol{v}_{S'}. \tag{11.5}$$

Angular momentum in S:

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} = (\boldsymbol{r}' + \boldsymbol{v}_{S'}t) \times (\boldsymbol{p}' + m\boldsymbol{v}_{S'}). \tag{11.6}$$

Expanding the cross product one obtains the final relation

$$\boldsymbol{L} = \boldsymbol{L}' + m(\boldsymbol{r}' \times \boldsymbol{v}_{S'}) + t(\boldsymbol{v}_{S'} \times \boldsymbol{p}'), \tag{11.7}$$

where $m(\boldsymbol{r}' \times \boldsymbol{v}_{S'})$ is the angular momentum associated with the relative motion of S' and $t(\boldsymbol{v}_{S'} \times \boldsymbol{p}')$ depends on time and the relative velocity between systems.

P11.2 Prove that

$$[\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{L}}, \boldsymbol{r}] = -i\hbar(\hat{\boldsymbol{n}} \times \boldsymbol{r}), \tag{11.8}$$

$$[\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{L}}, \hat{\boldsymbol{p}}] = -i\hbar(\hat{\boldsymbol{n}} \times \hat{\boldsymbol{p}}), \tag{11.9}$$

$$[\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{L}}, \hat{\boldsymbol{L}}] = -i\hbar(\hat{\boldsymbol{n}} \times \hat{\boldsymbol{L}}). \tag{11.10}$$

In the above expressions, $\hat{\boldsymbol{n}}$ is a constant unit vector in any direction.
Solution. We represent the unit vector $\hat{\boldsymbol{n}}$ in the form $\hat{\boldsymbol{n}} = \sum_i \alpha_i \hat{\boldsymbol{e}}_i$, where $\{\hat{\boldsymbol{e}}_i\}$ is a Cartesian basis in three dimensions. Using the components $\hat{L}_i$ of the orbital angular momentum, given by

$$\hat{L}_i = \varepsilon_{ijk}\hat{x}_j\hat{p}_k = -i\hbar\varepsilon_{ijk}x_j\frac{\partial}{\partial x_k}, \tag{11.11}$$

we can write

$$[\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{L}}, \hat{x}_j] = [\alpha_i\hat{L}_i, \hat{x}_j] = -i\hbar\alpha_i\varepsilon_{ilm}x_l\left(\frac{\partial}{\partial x_m}x_j - x_j\frac{\partial}{\partial x_m}\right) \tag{11.12}$$

$$= -i\hbar\varepsilon_{ilj}\alpha_i x_l = -i\hbar(\hat{\boldsymbol{n}} \times \hat{\boldsymbol{r}})_j. \tag{11.13}$$

From this it follows that

$$[\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{L}}, \hat{\boldsymbol{r}}] = -i\hbar(\hat{\boldsymbol{n}} \times \hat{\boldsymbol{r}}). \tag{11.14}$$

In an analogous manner, we obtain

$$[\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{L}}, \hat{p}_j] = [\alpha_i\hat{L}_i, \hat{p}_j] = -i\hbar\alpha_i\left(\hat{L}_i\frac{\partial}{\partial x_j} - \frac{\partial}{\partial x_j}\hat{L}_i\right) \tag{11.15}$$

$$= -\hbar^2\varepsilon_{jim}\alpha_i\frac{\partial}{\partial x_m} = -i\hbar\varepsilon_{jim}\alpha_i\hat{p}_m = -i\hbar(\hat{\boldsymbol{n}} \times \hat{\boldsymbol{p}})_j, \tag{11.16}$$

whose vectorial version is

$$[\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{L}}, \hat{\boldsymbol{p}}] = -i\hbar(\hat{\boldsymbol{n}} \times \hat{\boldsymbol{p}}). \tag{11.17}$$

Finally, we have

$$[\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{L}}, \hat{L}_j] = \alpha_i[\hat{L}_i, \hat{L}_j] = -i\hbar\varepsilon_{jil}\alpha_i\hat{L}_l = -i\hbar(\hat{\boldsymbol{n}} \times \hat{\boldsymbol{L}})_j, \tag{11.18}$$

that is,

$$[\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{L}}, \hat{\boldsymbol{L}}] = -i\hbar(\hat{\boldsymbol{n}} \times \hat{\boldsymbol{L}}). \tag{11.19}$$

These results confirm the role of the angular momentum operator as the generator of rotations.

P11.3 Show that the total orbital momentum of a two-particle system can be expressed in terms of the center-of-mass and relative coordinates in the form

$$\hat{L} = \boldsymbol{R} \times \hat{\boldsymbol{P}} + \boldsymbol{r} \times \hat{\boldsymbol{p}}, \tag{11.20}$$

where

$$\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2, \quad \hat{\boldsymbol{p}} = m\left(\frac{\hat{\boldsymbol{p}}_1}{m_1} - \frac{\hat{\boldsymbol{p}}_2}{m_2}\right), \quad m = \frac{m_1 m_2}{m_1 + m_2}, \tag{11.21}$$

$$\boldsymbol{R} = \frac{m_1\boldsymbol{r}_1 + m_2\boldsymbol{r}_2}{M}, \quad \hat{\boldsymbol{P}} = \hat{\boldsymbol{p}}_1 + \hat{\boldsymbol{p}}_2, \quad M = m_1 + m_2. \tag{11.22}$$

Solution. The total angular momentum of a two-particle system is

$$\boldsymbol{L} = \boldsymbol{L}_1 + \boldsymbol{L}_2, \tag{11.23}$$

therefore the corresponding angular momentum operator is written in the form

$$\hat{\boldsymbol{L}} = \hat{\boldsymbol{L}}_1 + \hat{\boldsymbol{L}}_2. \tag{11.24}$$

The relative and center-of-mass variables are defined similarly to the classical case, that is,

$$\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2, \quad \boldsymbol{R} = \frac{m_1\boldsymbol{r}_1 + m_2\boldsymbol{r}_2}{m_1 + m_2}, \tag{11.25}$$

where $M = m_1 + m_2$ is the total mass of the system. By inverting these expressions we obtain

$$\boldsymbol{r}_1 = \boldsymbol{R} + \frac{m_2}{M}\boldsymbol{r}, \quad \boldsymbol{r}_2 = \boldsymbol{R} - \frac{m_1}{M}\boldsymbol{r}. \tag{11.26}$$

Substituting the previous results into (11.24) we obtain the final result

$$\hat{L} = \boldsymbol{R} \times \hat{\boldsymbol{P}} + \boldsymbol{r} \times \hat{\boldsymbol{p}}, \tag{11.27}$$

where the *total* momentum operator (associated with the center-of-mass coordinate $\vec{R}$ and total mass M) and the *relative* momentum operator (associated with the relative velocity $\boldsymbol{v}_1 - \boldsymbol{v}_2$ and reduced mass $m = m_1m_2/M$) are given respectively by

$$\hat{\boldsymbol{P}} = \hat{\boldsymbol{p}}_1 + \hat{\boldsymbol{p}}_2 = -i\hbar(\nabla_1 + \nabla_2) = -i\hbar\nabla_R, \tag{11.28}$$

$$\boldsymbol{p} = m\left(\frac{\hat{\boldsymbol{p}}_1}{m_1} - \frac{\hat{\boldsymbol{p}}_2}{m_2}\right) = -i\hbar\left(\frac{m_2}{M}\nabla_1 - \frac{m_1}{M}\nabla_2\right) = -i\hbar\nabla_r. \tag{11.29}$$

P11.4 Show that any function that depends only on r is an eigenfunction of $\hat{L}_z$ and $\hat{\boldsymbol{L}}^2$, with both eigenvalues equal to zero, and that any function $g(z, r)$ is an eigenfunction of the z component with zero eigenvalue. Determine the eigenfunction of $\hat{L}_x$ corresponding to zero eigenvalue and angular momentum 1.

Solution. The expressions for the operators $\hat{L}_z$ and $\hat{\boldsymbol{L}}^2$ in spherical coordinates are

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}, \tag{11.30}$$

$$\hat{\boldsymbol{L}}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]. \tag{11.31}$$

If we apply these operators to a function that depends only on the radial coordinate, $f(r)$, the derivatives with respect to θ and φ vanish. Therefore,

$$\hat{L}_z f(r) = -i\hbar \frac{\partial}{\partial \varphi} f(r) = 0, \tag{11.32}$$

and

$$\hat{\boldsymbol{L}}^2 f(r) = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial f(r)}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2 f(r)}{\partial \varphi^2} \right] = 0. \tag{11.33}$$

Now consider a function $g(r, z)$. Recall that in spherical coordinates,

$$z = r\cos\theta. \tag{11.34}$$

Then

$$\hat{L}_z g(r,z) = -i\hbar \frac{\partial}{\partial \varphi} g(r,z) = -i\hbar \frac{\partial g}{\partial z} \frac{\partial z}{\partial \varphi} = 0. \tag{11.35}$$

We seek a function ψ such that

$$\hat{L}_x \psi = 0. \tag{11.36}$$

The simultaneous eigenfunctions of $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$ are the spherical harmonics $Y_\ell^m(\theta, \varphi)$. Since we are interested in the case of angular momentum $\ell = 1$, the allowed magnetic quantum numbers are $m = -1, 0, 1$. Therefore, any state with $\ell = 1$ can be expressed as a linear combination of these eigenfunctions,

$$\psi = aY_1^{-1} + bY_1^0 + cY_1^1. \tag{11.37}$$

Since we are not considering spin, we have $j = \ell = 1$. The operator $\hat{L}_x$ can be written in terms of the ladder operators as:

$$\hat{L}_x = \frac{1}{\sqrt{2}} \left(\hat{L}_+ + \hat{L}_- \right), \tag{11.38}$$

where the ladder operators act on the eigenstates $|\ell, m\rangle$ as follows:

$$\hat{L}_+ |\ell, m\rangle = \hbar C_{\ell,m} |\ell, m+1\rangle, \tag{11.39}$$

$$\hat{L}_- |\ell, m\rangle = \hbar C_{\ell,m-1} |\ell, m-1\rangle, \tag{11.40}$$

with

$$C_{\ell,m} = \sqrt{\frac{1}{2}(\ell - m)(\ell + m + 1)}. \tag{11.41}$$

For $\ell = 1$, these become

$$C_{1,m} = \sqrt{\frac{1}{2}(1 - m)(1 + m + 1)} = \sqrt{\frac{1}{2}(2 - m)(1 + m)}. \tag{11.42}$$

We now operate with $\hat{L}_x$ on the state ψ,

$$\begin{aligned}\hat{L}_x\psi &= \frac{1}{\sqrt{2}}\left(\hat{L}_+ + \hat{L}_-\right)\left(a|1,-1\rangle + b|1,0\rangle + c|1,1\rangle\right)\\ &= \frac{1}{\sqrt{2}}\Big[a\hat{L}_+|1,-1\rangle + b\hat{L}_+|1,0\rangle + c\hat{L}_+|1,1\rangle\\ &\qquad + a\hat{L}_-|1,-1\rangle + b\hat{L}_-|1,0\rangle + c\hat{L}_-|1,1\rangle\Big]\\ &= \frac{\hbar}{\sqrt{2}}\Big[aC_{1,-1}|1,0\rangle + bC_{1,0}|1,1\rangle\\ &\qquad + bC_{1,0}|1,-1\rangle + cC_{1,1}|1,0\rangle\Big].\end{aligned}$$

The states $|1,-2\rangle$ and $|1,2\rangle$ lie outside the allowed space for $\ell = 1$, their coefficients are equal to 0. We are left with

$$\hat{L}_x\psi = \frac{\hbar}{\sqrt{2}}\left[(a+c)|1,0\rangle + b(|1,1\rangle + |1,-1\rangle)\right] = 0. \tag{11.43}$$

This equation implies

$$a + c = 0, \tag{11.44}$$

$$b = 0. \tag{11.45}$$

Therefore, the solution must be of the form

$$\psi = c\left(|1,1\rangle - |1,-1\rangle\right) = c\left(Y_1^1 - Y_1^{-1}\right). \tag{11.46}$$

We now normalize the function,

$$\begin{aligned}\int \psi^*\psi\, d\Omega &= |c|^2 \int \left(Y_1^1 - Y_1^{-1}\right)^*\left(Y_1^1 - Y_1^{-1}\right) d\Omega\\ &= |c|^2 \int \left(|Y_1^1|^2 + |Y_1^{-1}|^2 - Y_1^{-1*}Y_1^1 - Y_1^{1*}Y_1^{-1}\right) d\Omega\\ &= |c|^2(1+1) = 2|c|^2 = 1,\end{aligned}$$

hence

$$c = \frac{1}{\sqrt{2}}. \tag{11.47}$$

The eigenfunction is therefore given by

$$\begin{aligned}\psi &= \frac{1}{\sqrt{2}}\left(Y_1^1 - Y_1^{-1}\right)\\ &= \frac{1}{\sqrt{2}}\left[\left(-\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\varphi}\right) - \left(\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\varphi}\right)\right]\\ &= -\sqrt{\frac{3}{4\pi}}\sin\theta\cos\varphi.\end{aligned} \tag{11.48}$$

P11.5 Calculate the expectation value of the operator $\frac{1}{2}(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x)$ and its square, in an eigenstate of $\hat{L}^2$ and $\hat{L}_z$.
Solution. We write the operator

$$A \equiv \frac{1}{2}(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x) \tag{11.49}$$

in terms of ladder operators,

$$\hat{L}_x = \frac{\hat{L}_+ + \hat{L}_-}{2}, \quad \hat{L}_y = \frac{\hat{L}_+ - \hat{L}_-}{2i}, \tag{11.50}$$

$$\hat{L}_x\hat{L}_y = \frac{1}{4i}(\hat{L}_+ + \hat{L}_-)(\hat{L}_+ - \hat{L}_-) \tag{11.51}$$

$$= \frac{1}{4i}(\hat{L}_+^2 - \hat{L}_+\hat{L}_- + \hat{L}_-\hat{L}_+ - \hat{L}_-^2), \tag{11.52}$$

$$\hat{L}_y\hat{L}_x = \frac{1}{4i}(\hat{L}_+ - \hat{L}_-)(\hat{L}_+ + \hat{L}_-) \tag{11.53}$$

$$= \frac{1}{4i}(\hat{L}_+^2 + \hat{L}_+\hat{L}_- - \hat{L}_-\hat{L}_+ - \hat{L}_-^2). \tag{11.54}$$

Adding the two expressions we get

$$\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x = \frac{1}{4i}\left[2\hat{L}_+^2 - 2\hat{L}_-^2\right] = \frac{1}{2i}(\hat{L}_+^2 - \hat{L}_-^2), \tag{11.55}$$

therefore

$$\hat{A} = \frac{1}{4i}(\hat{L}_+^2 - \hat{L}_-^2). \tag{11.56}$$

The expectation value in $|l, m\rangle$ is

$$\left\langle \hat{A} \right\rangle = \left\langle l, m \left| \frac{1}{4i}(\hat{L}_+^2 - \hat{L}_-^2) \right| l, m \right\rangle = \frac{1}{4i}\left[\left\langle l, m \left| \hat{L}_+^2 l, m-l, m\hat{L}_-^2 \right| l, m \right\rangle \right], \tag{11.57}$$

where $\hat{L}_+^2|l, m\rangle$ is proportional to $|l, m+2\rangle$ for $m+2 \leq l$, and $\hat{L}_-^2|l, m\rangle$ is proportional to $|l, m-2\rangle$ for $m-2 \geq -l$. Since both $|l, m+2\rangle$ and $|l, m-2\rangle$ are orthogonal to $|l, m\rangle$, the matrix elements vanish,

$$\left\langle l, m \left| \hat{L}_+^2 \right| l, m \right\rangle = 0, \quad \left\langle l, m \left| \hat{L}_-^2 \right| l, m \right\rangle = 0. \tag{11.58}$$

Thus, $\left\langle \hat{A} \right\rangle = 0$.

The square of $\hat{A}$ is

$$\hat{A}^2 = \left[\frac{1}{4i}(\hat{L}_+^2 - \hat{L}_-^2)\right]^2 = -\frac{1}{16}(\hat{L}_+^4 - \hat{L}_+^2\hat{L}_-^2 - \hat{L}_-^2\hat{L}_+^2 + \hat{L}_-^4) \tag{11.59}$$

and its expectation value is

$$\left\langle \hat{A}^2 \right\rangle = -\frac{1}{16} \left\langle l,m \left| \hat{L}_+^4 - \hat{L}_+^2 \hat{L}_-^2 - \hat{L}_-^2 \hat{L}_+^2 + \hat{L}_-^4 \right| l,m \right\rangle . \tag{11.60}$$

Since both $\hat{L}_+^4 |l,m\rangle \propto |l,m+4\rangle$ and $\hat{L}_-^4 |l,m\rangle \propto |l,m-4\rangle$ are orthogonal to $|l,m\rangle$, we are left with

$$\left\langle \hat{A}^2 \right\rangle = \frac{1}{16} \left\langle l,m \left| \hat{L}_+^2 \hat{L}_-^2 + \hat{L}_-^2 \hat{L}_+^2 \right| l,m \right\rangle . \tag{11.61}$$

The matrix elements can be calculated with the help of the ladder operators,

$$\hat{L}_+ |l,m\rangle = \hbar\sqrt{(l-m)(l+m+1)}|l,m+1\rangle, \;\; \hat{L}_- |l,m\rangle = \hbar\sqrt{(l+m)(l-m+1)}|l,m-1\rangle. \tag{11.62}$$

Thus, for $\left\langle l,m \left| \hat{L}_+^2 \hat{L}_-^2 \right| l,m \right\rangle$ we have

$$\hat{L}_-^2 |l,m\rangle = \hbar^2\sqrt{(l+m)(l-m+1)(l+m-1)(l-m+2)}|l,m-2\rangle, \tag{11.63}$$

$$\hat{L}_+^2 |l,m-2\rangle = \hbar^2\sqrt{(l-m+2)(l+m-1)(l-m+1)(l+m)}|l,m\rangle, \tag{11.64}$$

so that

$$\left\langle l,m \left| \hat{L}_+^2 \hat{L}_-^2 \right| l,m \right\rangle = \hbar^4 (l+m)(l+m-1)(l-m+1)(l-m+2). \tag{11.65}$$

For $\left\langle l,m \left| \hat{L}_-^2 \hat{L}_+^2 \right| l,m \right\rangle$ we have

$$\hat{L}_+^2 |l,m\rangle = \hbar^2\sqrt{(l-m)(l+m+1)(l-m-1)(l+m+2)}|l,m+2\rangle, \tag{11.66}$$

$$\hat{L}_-^2 |l,m+2\rangle = \hbar^2\sqrt{(l+m+2)(l-m-1)(l+m+1)(l-m)}|l,m\rangle, \tag{11.67}$$

so that

$$\left\langle l,m \left| \hat{L}_-^2 \hat{L}_+^2 \right| l,m \right\rangle = \hbar^4 (l-m)(l-m-1)(l+m+1)(l+m+2). \tag{11.68}$$

Adding the two terms

$$\left\langle \hat{A}^2 \right\rangle = \frac{\hbar^4}{16} \left[2l^4 + 4l^3 - 4l^2m^2 - 2l^2 - 4lm^2 - 4l + 2m^4 + 10m^2 \right] \tag{11.69}$$

and simplifying in terms of $l(l+1)$, we obtain finally

$$\left\langle \hat{A}^2 \right\rangle = \frac{\hbar^4}{8} \left[(l(l+1) - m^2)^2 - 2l(l+1) + 5m^2 \right] . \tag{11.70}$$

P11.6 Determine the expression for the eigenfunctions of $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$ in momentum space.

Solution. To find the angular momentum eigenfunctions in momentum space, we begin by recalling that in this representation the position operator is given by

$$\hat{\boldsymbol{r}} = i\hbar\nabla_{\boldsymbol{p}}, \quad \hat{\boldsymbol{p}} = \boldsymbol{p}.$$

Therefore the orbital angular momentum operator takes the form

$$\hat{\boldsymbol{L}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}} = -\hat{\boldsymbol{p}} \times \hat{\boldsymbol{r}} = -i\hbar\,(\boldsymbol{p} \times \nabla_{\boldsymbol{p}}),$$

which is the same as in x-space with $\nabla \to \nabla_{\boldsymbol{p}}$. We thus have

$$\hat{\boldsymbol{L}} = -i\hbar \left(\hat{a}_\varphi \frac{\partial}{\partial \theta_p} - \hat{a}_\theta \frac{1}{\sin\theta_p} \frac{\partial}{\partial \varphi_p} \right), \tag{11.71}$$

where

$$\mathbf{p} = (p_x, p_y, p_z), \quad p^2 = p_x^2 + p_y^2 + p_z^2,$$
$$p_x = p \sin\theta_p \cos\varphi_p, \quad p_y = p \sin\theta_p \sin\varphi_p, \quad p_z = p\cos\theta_p.$$

The operators $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$ take therefore the standard form

$$\hat{\boldsymbol{L}}^2 = -\hbar^2 \left[\frac{1}{\sin\theta_p} \frac{\partial}{\partial \theta_p} \left(\sin\theta_p \frac{\partial}{\partial \theta_p} \right) + \frac{1}{\sin^2\theta_p} \frac{\partial^2}{\partial \varphi_p^2} \right], \tag{11.72}$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi_p}, \tag{11.73}$$

and the eigenfunctions of these operators in momentum space must satisfy

$$\hat{\boldsymbol{L}}^2 Y(\theta_p, \varphi_p) = \hbar^2 \ell(\ell+1) Y(\theta_p, \varphi_p), \quad \hat{L}_z Y(\theta_p, \varphi_p) = \hbar m Y(\theta_p, \varphi_p),$$

which are exactly the spherical harmonics $Y_\ell^m(\theta_p, \varphi_p)$. Thus, the eigenfunctions of $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$ in momentum space are also the spherical harmonics $Y_\ell^m(\theta_p, \varphi_p)$.

P11.7 Prove that there is no solution to the eigenvalue problem $\hat{p}_r R(r) = \alpha R(r)$ that satisfies the condition $\lim rR(r) = 0$. What can be concluded from here?
Solution. Using

$$\hat{p}_r = \frac{1}{r}\,(\hat{\boldsymbol{r}} \cdot \hat{\boldsymbol{p}} - i\hbar) = -i\hbar \left(\frac{\partial}{\partial r} + \frac{1}{r} \right), \tag{11.74}$$

the eigenvalue equation $\hat{p}_r R(r) = \alpha R(r)$becomes

$$\frac{\partial R}{\partial r} + \frac{R}{r} = \frac{i\alpha}{\hbar} R. \tag{11.75}$$

The general solution to this equation is

$$R(r) = \frac{C}{r} \exp\left(\frac{i\alpha}{\hbar} r \right), \tag{11.76}$$

where C is the normalization constant. From (11.76) it follows that

$$\lim_{r\to 0} rR(r) = C, \tag{11.77}$$

which is non-zero for $R \neq 0$. Therefore, there exists no eigenfunction of $\hat{p}_r$ that satisfies the condition $\lim_{r\to 0} rR(r) = 0$. Moreover, since $\lim_{r\to 0} R(r) = \infty$, the function R given by (11.76) does not qualify as a physically acceptable wave function for $C \neq 0$.

An immediate consequence of this result is that there are no physically acceptable eigenstates of the operator $\hat{p}_r$, meaning that the radial momentum (canonically conjugate to r) cannot be fixed. It is interesting to compare this with the classical case, where it is possible to construct circular orbits for the Kepler problem for which p_r vanishes (and is therefore fixed). Thus, strictly speaking, there are no quantum solutions corresponding to classical circular orbits. This is important to keep in mind, as in atomic physics one often speaks of "circular orbits"; the conventional meaning of this terminology should be clearly understood.

P11.8 Consider an eigenfunction $\psi_{nlm}(\boldsymbol{r})$ of a radial Hamiltonian and show that

$$\psi' = e^{i\alpha\,\hat{\mathbf{n}}\cdot\hat{\boldsymbol{L}}/\hbar}\,\psi_{nlm}(\boldsymbol{r}) \tag{11.78}$$

is an eigenfunction of the Hamiltonian with the same angular momentum l, independent of the value of α and the orientation of the $\hat{\boldsymbol{n}}$ axis. Is it also an eigenstate of $\hat{L}_z$?

Solution. Let $\psi_{nlm}(\boldsymbol{r})$ be an eigenfunction of a radial Hamiltonian, that is

$$\hat{H}\psi_{nlm} = E_{nl}\psi_{nlm}, \tag{11.79}$$

where the Hamiltonian has the form

$$\hat{H} = \frac{\hat{p}_r^2}{2m} + \frac{\hat{L}^2}{2mr^2} + V(r). \tag{11.80}$$

Now consider a rotated function defined by:

$$\psi' = e^{i\alpha\,\hat{\mathbf{n}}\cdot\hat{\mathbf{L}}/\hbar}\psi_{nlm} = \hat{U}(\hat{\boldsymbol{L}})\,\psi. \tag{11.81}$$

Since the system is radially symmetric, the Hamiltonian commutes with the total angular momentum operator,

$$[\hat{H}, \hat{\boldsymbol{L}}] = 0. \tag{11.82}$$

Furthermore, from Problem P3.2, we know that if an operator $\hat{A}$ commutes with $\hat{H}$, then any function $f(\hat{A})$ that can be expanded in a power series also commutes with $\hat{H}$, that is,

$$[\hat{H}, f(\hat{A})] = 0. \tag{11.83}$$

Therefore, since $\hat{U} = e^{i\alpha\hat{\mathbf{n}}\cdot\hat{\mathbf{L}}/\hbar}$ is a function of $\hat{\boldsymbol{L}}$, we conclude that

$$\hat{H}\psi' = \hat{H}\hat{U}\psi = \hat{U}\hat{H}\psi = E_{nl}\hat{U}\psi = E_{nl}\psi', \tag{11.84}$$

which means that ψ' is also an eigenfunction of $\hat{H}$ with the same eigenvalue E_{nl}.

Now, since ψ_{nlm} has angular momentum l, it satisfies

$$\hat{L}^2\psi_{nlm} = \hbar^2 l(l+1)\psi_{nlm}. \tag{11.85}$$

Again, since $[\hat{L}^2, \hat{\boldsymbol{L}}] = 0$, we have

$$[\hat{L}^2, f(\hat{\mathbf{L}})] = 0 \quad \Rightarrow \quad \hat{L}^2\psi' = \hat{L}^2\hat{U}\psi = \hat{U}\hat{L}^2\psi = \hbar^2 l(l+1)\psi', \tag{11.86}$$

which means that ψ' also has the same total angular momentum l.

Concerning $\hat{L}_z$, we know that in general, $[\hat{\boldsymbol{L}}, \hat{L}_z] \neq 0$, and in particular

$$[\hat{L}_z, \hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{L}}] = i\hbar\,(\hat{\boldsymbol{n}} \times \hat{\boldsymbol{e}}_z) \cdot \hat{\boldsymbol{L}} \neq 0, \tag{11.87}$$

which implies that

$$\hat{L}_z \hat{U} \neq \hat{U} \hat{L}_z. \tag{11.88}$$

Therefore, ψ' is generally *not* an eigenfunction of $\hat{L}_z$, unless $\hat{\boldsymbol{n}}$ is parallel to the z-axis.

P11.9 Construct the matrices representing the angular-momentum operators for $j = 1$ and $j = 3/2$.

Solution. For $j = 1$, the quantum number m can take the values $-1, 0, 1$. From

$$\langle j, m \pm 1 \,|J_x|\, j, m\rangle = \frac{\hbar}{2}\sqrt{(j \pm m + 1)(j \mp m)} \tag{11.89}$$

and

$$\langle j, m \pm 1 \,|J_y|\, j, m\rangle = \mp\frac{i\hbar}{2}\sqrt{(j \pm m + 1)(j \mp m)} \tag{11.90}$$

we obtain the matrix elements of J_x,

$$\begin{aligned} \langle 1, 1 \,|J_x|\, 1, 1\rangle &= 0, \\ \langle 1, 1 \,|J_x|\, 1, 0\rangle &= \frac{\hbar}{\sqrt{2}}, \\ \langle 1, 1 \,|J_x|\, 1, -1\rangle &= 0. \end{aligned} \tag{11.91}$$

The matrix elements of $\hat{J}_x$ for $j = 1$ are

$$\langle 1, 0 \,|J_x|\, 1, 1\rangle = \frac{\hbar}{\sqrt{2}}, \quad \langle 1, 0 \,|J_x|\, 1, 0\rangle = 0, \quad \langle 1, 0 \,|J_x|\, 1, -1\rangle = \frac{\hbar}{\sqrt{2}}; \tag{11.92}$$

$$\langle 1, -1 \,|J_x|\, 1, 1\rangle = 0, \quad \langle 1, -1 \,|J_x|\, 1, 0\rangle = \frac{\hbar}{\sqrt{2}}, \quad \langle 1, -1 \,|J_x|\, 1, -1\rangle = 0. \tag{11.93}$$

The corresponding matrix representation is

$$J_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}. \tag{11.94}$$

Similarly, the matrix elements of $\hat{J}_y$ are

$$\langle 1, 1 \,|J_y|\, 1, 1\rangle = 0, \quad \langle 1, 1 \,|J_y|\, 1, 0\rangle = -i\frac{\hbar}{\sqrt{2}}, \quad \langle 1, 1 \,|J_y|\, 1, -1\rangle = 0; \tag{11.95}$$

$$\langle 1, 0 \,|J_y|\, 1, 1\rangle = i\frac{\hbar}{\sqrt{2}}, \quad \langle 1, 0 \,|J_y|\, 1, 0\rangle = 0, \quad \langle 1, 0 \,|J_y|\, 1, -1\rangle = -i\frac{\hbar}{\sqrt{2}}; \tag{11.96}$$

$$\langle 1, -1 \,|J_y|\, 1, 1\rangle = 0, \quad \langle 1, -1 \,|J_y|\, 1, 0\rangle = i\frac{\hbar}{\sqrt{2}}, \quad \langle 1, -1 \,|J_y|\, 1, -1\rangle = 0, \tag{11.97}$$

and the matrix representation is

$$J_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}. \tag{11.98}$$

Finally, according to

$$\left\langle \frac{1}{2} m' | \hat{J}_z | \frac{1}{2} m \right\rangle = \hbar m \delta_{mm'}, \tag{11.99}$$

the matrix $\hat{J}_z$ is diagonal, with eigenvalues $m\hbar$,

$$\left\langle 1,1 \left| \hat{J}_z \right| 1,1 \right\rangle = \hbar, \quad \left\langle 1,1 \left| \hat{J}_z \right| 1,0 \right\rangle = 0, \quad \left\langle 1,1 \left| \hat{J}_z \right| 1,-1 \right\rangle = 0; \tag{11.100}$$

$$\left\langle 1,0 \left| \hat{J}_z \right| 1,1 \right\rangle = 0, \quad \left\langle 1,0 \left| \hat{J}_z \right| 1,0 \right\rangle = 0, \quad \left\langle 1,0 \left| \hat{J}_z \right| 1,-1 \right\rangle = 0; \tag{11.101}$$

$$\left\langle 1,-1 \left| \hat{J}_z \right| 1,1 \right\rangle = 0, \quad \left\langle 1,-1 \left| \hat{J}_z \right| 1,0 \right\rangle = 0, \quad \left\langle 1,-1 \left| \hat{J}_z \right| 1,-1 \right\rangle = -\hbar, \tag{11.102}$$

so that

$$\hat{J}_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{11.103}$$

Using the previous results, we can write the matrix $\hat{J}_{\hat{\boldsymbol{n}}} = \hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{J}}$, which represents the component of angular momentum (or spin) 1 in the direction $\hat{\boldsymbol{n}} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$, as

$$\hat{J}_{\hat{\boldsymbol{n}}} = \hbar \begin{pmatrix} \cos\theta & \frac{1}{\sqrt{2}}\sin\theta e^{-i\varphi} & 0 \\ \frac{1}{\sqrt{2}}\sin\theta e^{i\varphi} & 0 & \frac{1}{\sqrt{2}}\sin\theta e^{-i\varphi} \\ 0 & \frac{1}{\sqrt{2}}\sin\theta e^{i\varphi} & -\cos\theta \end{pmatrix}. \tag{11.104}$$

The corresponding eigenvectors with eigenvalues $\hbar, 0, -\hbar$, respectively, are

$$\begin{pmatrix} \frac{1}{2}(1+\cos\theta)e^{-i\varphi} \\ \frac{1}{\sqrt{2}}\sin\theta \\ \frac{1}{2}(1-\cos\theta)e^{i\varphi} \end{pmatrix}, \quad \begin{pmatrix} -\frac{1}{\sqrt{2}}\sin\theta e^{-i\varphi} \\ \cos\theta \\ \frac{1}{\sqrt{2}}\sin\theta e^{i\varphi} \end{pmatrix}, \quad \begin{pmatrix} \frac{1}{2}(1-\cos\theta)e^{-i\varphi} \\ -\frac{1}{\sqrt{2}}\sin\theta \\ \frac{1}{2}(1+\cos\theta)e^{i\varphi} \end{pmatrix}. \tag{11.105}$$

We take advantage of the explicit form of the vectors (11.105) to add some comments. For $\theta = 0$, $\varphi = 0$ these eigenvectors reduce to

$$\boldsymbol{e}'_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \boldsymbol{e}'_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \boldsymbol{e}'_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \tag{11.106}$$

These vectors represent a possible Cartesian basis for describing angular momentum 1 states; in this basis, the general vector has the form

$$\boldsymbol{\psi} = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} = \sum_i \boldsymbol{e}'_i \psi_i. \tag{11.107}$$

In many applications it is more convenient to use a spherical basis for describing angular momentum states (in which $\hat{L}_z$ is diagonal). This spherical basis consists of the triad of orthonormal vectors,

$$\begin{aligned} \boldsymbol{e}_1 &= -\frac{1}{\sqrt{2}}(\boldsymbol{e}'_1 + i\boldsymbol{e}'_2) = -\frac{1}{\sqrt{2}}\begin{pmatrix}1\\ i\\ 0\end{pmatrix}, \\ \boldsymbol{e}_0 &= \boldsymbol{e}'_3 = \begin{pmatrix}0\\ 0\\ 1\end{pmatrix}, \\ \boldsymbol{e}_{-1} &= \frac{1}{\sqrt{2}}(\boldsymbol{e}'_1 - i\boldsymbol{e}'_2) = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ -i\\ 0\end{pmatrix}. \end{aligned} \tag{11.108}$$

The spherical vectors $\boldsymbol{e}_\alpha$ ($\alpha = 1, 0, -1$) are eigenvectors of $\hat{\boldsymbol{L}}^2$ (with eigenvalue 2) and of $\hat{L}_0 = \hat{L}_3$. This is clearly seen by comparing them with the spherical harmonics $Y_1^m(\theta, \varphi)$ for $m = 1, 0, -1$, which we can write as

$$Y_1^m(\theta,\varphi) = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \frac{1}{r} \times \begin{cases} -\frac{1}{\sqrt{2}}(x+iy), & m = 1, \\ z, & m = 0, \\ \frac{1}{\sqrt{2}}(x-iy), & m = -1. \end{cases} \tag{11.109}$$

We see that these spherical harmonics correspond (up to the factor $\sqrt{3/4\pi}\, r^{-1}$) to the spherical representation of the vector $\boldsymbol{r} = \{x, y, z\} = \{x_1, x_0, x_{-1}\}$. The transition between the Cartesian representation $\boldsymbol{\psi} = \{\psi'_1, \psi'_2, \psi'_3\}$ and the spherical one $\{\psi_1, \psi_0, \psi_{-1}\}$ is performed by a unitary matrix,

$$\boldsymbol{\psi}' = \hat{U}\boldsymbol{\psi}, \quad \hat{U} = \begin{pmatrix} -1/\sqrt{2} & -i/\sqrt{2} & 0 \\ 0 & 0 & 1 \\ 1/\sqrt{2} & -i/\sqrt{2} & 0 \end{pmatrix}. \tag{11.110}$$

In the case $j = 3/2$, m takes the values $-3/2$, $-1/2$, $1/2$, $3/2$. As we know, the diagonal elements of $\hat{J}_x$ are all zero; for the off-diagonal elements we obtain

$$\left\langle \frac{3}{2}, \frac{1}{2} | J_x | \frac{3}{2}, -\frac{1}{2} \right\rangle = \left\langle \frac{3}{2}, -\frac{1}{2} | J_x | \frac{3}{2}, \frac{1}{2} \right\rangle = \hbar,$$
$$\left\langle \frac{3}{2}, \frac{1}{2} | J_x | \frac{3}{2}, -\frac{3}{2} \right\rangle = \left\langle \frac{3}{2}, -\frac{3}{2} | J_x | \frac{3}{2}, \frac{1}{2} \right\rangle = 0,$$
$$\left\langle \frac{3}{2}, -\frac{1}{2} | J_x | \frac{3}{2}, \frac{3}{2} \right\rangle = \left\langle \frac{3}{2}, \frac{3}{2} | J_x | \frac{3}{2}, -\frac{1}{2} \right\rangle = 0,$$
$$\left\langle \frac{3}{2}, -\frac{1}{2} | J_x | \frac{3}{2}, -\frac{3}{2} \right\rangle = \left\langle \frac{3}{2}, -\frac{3}{2} | J_x | \frac{3}{2}, -\frac{1}{2} \right\rangle = \frac{\sqrt{3}}{2}\hbar,$$
$$\left\langle \frac{3}{2}, -\frac{3}{2} | J_x | \frac{3}{2}, \frac{3}{2} \right\rangle = \left\langle \frac{3}{2}, \frac{3}{2} | J_x | \frac{3}{2}, -\frac{3}{2} \right\rangle = 0.$$

Therefore, the matrix representation is

$$J_x = \frac{\hbar}{2} \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}. \tag{11.111}$$

Similarly, the non-zero matrix elements of J_y are

$$\left\langle \frac{3}{2}, \frac{3}{2} | J_y | \frac{3}{2}, \frac{1}{2} \right\rangle = -\left\langle \frac{3}{2}, \frac{1}{2} | J_y | \frac{3}{2}, \frac{3}{2} \right\rangle = -i\frac{\sqrt{3}}{2}\hbar,$$
$$\left\langle \frac{3}{2}, \frac{1}{2} | J_y | \frac{3}{2}, -\frac{1}{2} \right\rangle = -\left\langle \frac{3}{2}, -\frac{1}{2} | J_y | \frac{3}{2}, \frac{1}{2} \right\rangle = -i\hbar,$$
$$\left\langle \frac{3}{2}, -\frac{1}{2} | J_y | \frac{3}{2}, -\frac{3}{2} \right\rangle = -\left\langle \frac{3}{2}, -\frac{3}{2} | J_y | \frac{3}{2}, -\frac{1}{2} \right\rangle = -i\frac{\sqrt{3}}{2}\hbar.$$

Thus, the matrix representation is

$$J_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i\sqrt{3} & 0 & 0 \\ i\sqrt{3} & 0 & -i2 & 0 \\ 0 & i2 & 0 & -i\sqrt{3} \\ 0 & 0 & i\sqrt{3} & 0 \end{pmatrix}. \tag{11.112}$$

Finally, J_z is diagonal with the m values on the main diagonal,

$$J_z = \frac{\hbar}{2} \begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix}. \tag{11.113}$$

P11.10 Since $\hat{S}_i$ are the components of a vector, they are transformed under rotation according to the laws of vectors. For example, under rotation around of the z-axis by an angle θ, which performs the transformation $\hat{S} \to \hat{S}'$,

$$\hat{S}'_x = \hat{S}_x \cos\theta + \hat{S}_y \sin\theta, \quad \hat{S}'_y = -\hat{S}_x \sin\theta + \hat{S}_y \cos\theta, \quad \hat{S}'_z = \hat{S}_z. \tag{11.114}$$

Use the commutation rules for $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ to show that the transformed components $\hat{S}'_x$, $\hat{S}'_y$ and $\hat{S}'_z$ satisfy exactly the same rules.

Solution. To verify that the transformed components $\hat{S}'_x$, $\hat{S}'_y$, and $\hat{S}'_z$ obey the same commutation relations as the original components $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$, we start with the known commutation relation for Pauli matrices

$$[\hat{\sigma}_i, \hat{\sigma}_j] = 2i\epsilon_{ijk}\hat{\sigma}_k. \tag{11.115}$$

Thus, for $\hat{S}_i = \frac{\hbar}{2}\hat{\sigma}_i$, we have

$$[\hat{S}_i, \hat{S}_j] = i\hbar\epsilon_{ijk}\hat{S}_k. \tag{11.116}$$

We now verify that the transformed components satisfy the same algebra. Let us compute

$$\begin{aligned}
[\hat{S}'_x, \hat{S}'_y] &= [\hat{S}_x \cos\theta + \hat{S}_y \sin\theta, -\hat{S}_x \sin\theta + \hat{S}_y \cos\theta] \\
&= -\cos\theta \sin\theta [\hat{S}_x, \hat{S}_x] + \cos^2\theta [\hat{S}_x, \hat{S}_y] - \sin^2\theta [\hat{S}_y, \hat{S}_x] + \sin\theta\cos\theta [\hat{S}_y, \hat{S}_y] \\
&= \cos^2\theta [\hat{S}_x, \hat{S}_y] + \sin^2\theta [\hat{S}_x, \hat{S}_y] \\
&= [\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z = i\hbar\hat{S}'_z.
\end{aligned} \tag{11.117}$$

Next,

$$\begin{aligned}
[\hat{S}'_x, \hat{S}'_z] &= [\hat{S}_x \cos\theta + \hat{S}_y \sin\theta, \hat{S}_z] \\
&= \cos\theta [\hat{S}_x, \hat{S}_z] + \sin\theta [\hat{S}_y, \hat{S}_z] \\
&= i\hbar\cos\theta \hat{S}_y - i\hbar\sin\theta \hat{S}_x \\
&= i\hbar(-\hat{S}_x \sin\theta + \hat{S}_y \cos\theta) = i\hbar\hat{S}'_y,
\end{aligned} \tag{11.118}$$

$$\begin{aligned}
[\hat{S}'_y, \hat{S}'_z] &= [-\hat{S}_x \sin\theta + \hat{S}_y \cos\theta, \hat{S}_z] \\
&= -\sin\theta [\hat{S}_x, \hat{S}_z] + \cos\theta [\hat{S}_y, \hat{S}_z] \\
&= -i\hbar\sin\theta \hat{S}_y - i\hbar\cos\theta \hat{S}_x \\
&= -i\hbar(\hat{S}_x \cos\theta + \hat{S}_y \sin\theta) = -i\hbar\hat{S}'_x.
\end{aligned} \tag{11.119}$$

Therefore, the transformed components obey the same commutation relations,

$$[\hat{S}'_i, \hat{S}'_j] = i\hbar\epsilon_{ijk}\hat{S}'_k. \tag{11.120}$$

P11.11 If $\hat{\boldsymbol{n}}$ is a constant unit vector with direction cosines l, m, n with respect to the x-, y- and z-axes, respectively, show that

$$\hat{\sigma}_{\boldsymbol{n}} = \hat{\boldsymbol{n}} \cdot \hat{\sigma} = \begin{pmatrix} n & l - im \\ l + im & -n \end{pmatrix}, \quad (\hat{\boldsymbol{n}} \cdot \hat{\sigma})^2 = I. \tag{11.121}$$

Confirm that the eigenvalues of $\hat{\sigma}_{\boldsymbol{n}}$ are ± 1. What does this mean?

Solution. If $\hat{\boldsymbol{n}} = l\boldsymbol{i} + m\boldsymbol{j} + n\boldsymbol{k}$ is a unit vector, it satisfies $l^2 + m^2 + n^2 = 1$. Since

$$\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{\sigma}} = l\hat{\sigma}_1 + m\hat{\sigma}_2 + n\hat{\sigma}_3, \tag{11.122}$$

using the explicit form of the Pauli matrices, we obtain

$$\hat{\sigma}_{\boldsymbol{n}} = \hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{\sigma}} = \begin{pmatrix} n & l - im \\ l + im & -n \end{pmatrix}. \tag{11.123}$$

The rest of the problem follows immediately from here, since squaring gives

$$(\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{\sigma}})^2 = \begin{pmatrix} l^2 + m^2 + n^2 & 0 \\ 0 & l^2 + m^2 + n^2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{11.124}$$

This result can be obtained directly using equation

$$\hat{\sigma}_i \hat{\sigma}_j = I\delta_{ij} + i\epsilon_{ijk}\hat{\sigma}_k$$

to calculate

$$(\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{\sigma}})^2 = \sum_{i,j} n_i n_j \hat{\sigma}_i \hat{\sigma}_j = \sum_{i,j} n_i n_j (\delta_{ij} + i\epsilon_{ijk}\hat{\sigma}_k) = \sum_i n_i^2 = 1. \tag{11.125}$$

If the system's state is described by the spinor

$$|\Psi\rangle = \psi_+(x)|+\rangle + \psi_-(x)|-\rangle = \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}, \tag{11.126}$$

the expectation value of σ_n becomes

$$\langle\Psi|\hat{\sigma}_n|\Psi\rangle = \begin{pmatrix} \psi_+^* & \psi_-^* \end{pmatrix} \begin{pmatrix} n & l - im \\ l + im & -n \end{pmatrix} \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}$$

$$= n|\psi_+|^2 - n|\psi_-|^2 + (l - im)\psi_+^*\psi_- + (l + im)\psi_-^*\psi_+. \tag{11.127}$$

We see that if either of the two wavefunctions ψ_- or ψ_+ vanishes, which would correspond to a spin-up or spin-down state respectively, the expectation value of $\hat{\sigma}_n$ is $\pm n$.The eigenvalues and eigenvectors of the operator $\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{\sigma}}$ are obtained by diagonalizing it. For this purpose, we use (11.123) and write the eigenvalue equation

$$\begin{pmatrix} n & l - im \\ l + im & -n \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \lambda \begin{pmatrix} a \\ b \end{pmatrix}, \tag{11.128}$$

from which we obtain the pair of homogeneous equations

$$\begin{aligned} (n - \lambda)\, a + (l - im)\, b &= 0, \\ (l + im)\, a - (n + \lambda)\, b &= 0. \end{aligned} \tag{11.129}$$

A non-trivial solution to this system exists only if its determinant vanishes

$$\begin{vmatrix} n-\lambda & l-im \\ l+im & -n-\lambda \end{vmatrix} = 0 \Rightarrow \lambda^2 - 1 = 0. \tag{11.130}$$

Thus the eigenvalues of the operator $\hat{\sigma}_n$ are $\lambda = \pm 1$. The eigenvectors are determined by substituting the corresponding eigenvalue into (11.129) and normalizing, which gives for $\lambda = 1$

$$|\varphi_1\rangle = \sqrt{\frac{n+1}{2}} \begin{pmatrix} 1 \\ \frac{l+im}{n+1} \end{pmatrix}; \tag{11.131}$$

and for $\lambda = -1$

$$|\varphi_2\rangle = \sqrt{\frac{n+1}{2}} \begin{pmatrix} -\frac{l-im}{n+1} \\ 1 \end{pmatrix}. \tag{11.132}$$

In the usual representation in terms of the angles θ and φ of a spherical coordinate system, we have $l = \sin\theta\cos\varphi$, $m = \sin\theta\sin\varphi$, $n = \cos\theta$, and Eq. (11.127) becomes

$$\langle\Psi|\hat{\sigma}_n|\Psi\rangle = \left(|\psi_+|^2 - |\psi_-|^2\right)\cos\theta + \left(\psi_+^*\psi_- e^{-i\varphi} + \psi_-^*\psi_+ e^{i\varphi}\right)\sin\theta. \tag{11.133}$$

In turn, (11.131)-(11.132) take the form

$$|\varphi_1\rangle = \sqrt{\frac{1+\cos\theta}{2}} \begin{pmatrix} 1 \\ \frac{\sin\theta}{1+\cos\theta} e^{i\varphi} \end{pmatrix} = \begin{pmatrix} \cos(\theta/2) \\ e^{i\varphi}\sin(\theta/2) \end{pmatrix}, \tag{11.134}$$

$$|\varphi_2\rangle = \sqrt{\frac{1+\cos\theta}{2}} \begin{pmatrix} -\frac{\sin\theta}{1+\cos\theta} e^{-i\varphi} \\ 1 \end{pmatrix} = \begin{pmatrix} -e^{-i\varphi}\sin(\theta/2) \\ \cos(\theta/2) \end{pmatrix}. \tag{11.135}$$

P11.12 The spin projection of an electron on a certain z-axis is $\hbar/2$. Determine the probability that the projection of this spin on a certain z'-axis has the value $\hbar/2$ or $-\hbar/2$, as well as the average value of this projection.

Solution. If the spin projection along the z-axis is $+\hbar/2$, the system is in a state $|\psi\rangle$ such that

$$\hat{S}_z|\psi\rangle = \frac{\hbar}{2}|\psi\rangle, \tag{11.136}$$

that is,

$$|\psi\rangle = |+\rangle_z = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \tag{11.137}$$

where the basis vectors are

$$|+\rangle_z = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |-\rangle_z = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{11.138}$$

Now, let us consider a rotated axis z' that forms an angle θ with the original z-axis. We set the axes such that the z'-axis lies in the x-z plane. The basis vectors corresponding to this rotated axis are obtained by applying a rotation around the

y-axis to the original basis vectors.The rotation operator around an arbitrary axis $\hat{\boldsymbol{n}}$ by an angle θ is given by

$$\hat{T}_{\hat{\boldsymbol{n}}}(\theta) = e^{-\frac{i}{\hbar}\theta\,\hat{\mathbf{n}}\cdot\hat{\mathbf{J}}}, \tag{11.139}$$

for $\hat{\boldsymbol{J}} = \hat{\boldsymbol{S}}$, spin $s = \frac{1}{2}$, and rotation around the y-axis ($\hat{\boldsymbol{n}} = \hat{\boldsymbol{y}}$), we have

$$\hat{T} = e^{-\frac{i}{\hbar}\theta\hat{S}_y} = e^{-i\frac{\theta}{2}\hat{\sigma}_y}. \tag{11.140}$$

Expanding in a power series,

$$\hat{T} = \sum_{n=0}^{\infty}\frac{1}{n!}\left(-i\frac{\theta}{2}\hat{\sigma}_y\right)^n = \sum_{\text{even } n}\left(-i\frac{\theta}{2}\right)^n\mathbb{I} + \sum_{\text{odd } n}\left(-i\frac{\theta}{2}\right)^n\hat{\sigma}_y \tag{11.141}$$

because $\hat{\sigma}_i^2 = \mathbb{I}$. We then have

$$\hat{T} = \sum_{n=0}^{\infty}\frac{(-1)^n}{(2n)!}\left(\frac{\theta}{2}\right)^{2n}\mathbb{I} - i\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)!}\left(\frac{\theta}{2}\right)^{2n+1}\hat{\sigma}_y = \cos\left\{\frac{\theta}{2}\right\}\mathbb{I} - i\sin\left\{\frac{\theta}{2}\right\}\hat{\sigma}_y, \tag{11.142}$$

which corresponds to the matrix

$$\hat{T} = \begin{pmatrix}\cos\frac{\theta}{2} & -\sin\frac{\theta}{2}\\ \sin\frac{\theta}{2} & \cos\frac{\theta}{2}\end{pmatrix}. \tag{11.143}$$

The vectors of the rotated basis are then

$$|+\rangle_{z'} = \hat{T}|+\rangle_z = \begin{pmatrix}\cos\frac{\theta}{2}\\ \sin\frac{\theta}{2}\end{pmatrix} = \cos\frac{\theta}{2}|+\rangle_z + \sin\frac{\theta}{2}|-\rangle_z, \tag{11.144}$$

$$|-\rangle_{z'} = \hat{T}|-\rangle_z = \begin{pmatrix}-\sin\frac{\theta}{2}\\ \cos\frac{\theta}{2}\end{pmatrix} = -\sin\frac{\theta}{2}|+\rangle_z + \cos\frac{\theta}{2}|-\rangle_z. \tag{11.145}$$

These new vectors satisfy

$$\hat{S}_{z'}|+\rangle_{z'} = \frac{\hbar}{2}|+\rangle_{z'}, \tag{11.146}$$

$$\hat{S}_{z'}|+\rangle_{z'} = -\frac{\hbar}{2}|-\rangle_{z'}. \tag{11.147}$$

Thus, the projection of the state $|\psi\rangle = |+\rangle_z$ onto the rotated basis $\{|+\rangle_{z'}, |-\rangle_{z'}\}$ (i.e., the probabilities of obtaining $\pm\hbar/2$ along z') is

$$\langle\psi|+\rangle_{z'} = \left\langle +_z\right|\left(\cos\frac{\theta}{2}|+\rangle_z + \sin\frac{\theta}{2}|-\rangle_z\right)\Big\rangle = \cos\frac{\theta}{2}, \tag{11.148}$$

$$\langle\psi|-\rangle_{z'} = \left\langle +_z\right|\left(-\sin\frac{\theta}{2}|+\rangle_z + \cos\frac{\theta}{2}|-\rangle\right)\Big\rangle = -\sin\frac{\theta}{2}. \tag{11.149}$$

The probabilities of obtaining the values $+\hbar/2$ and $-\hbar/2$ along the rotated axis z' are:

$$P_{z'}(+) = |\langle\psi|+\rangle_{z'}|^2 = \cos^2\frac{\theta}{2}, \tag{11.150}$$

$$P_{z'}(-) = |\langle\psi|-\rangle_{z'}|^2 = \sin^2\frac{\theta}{2}. \tag{11.151}$$

Now, we calculate the expectation value of the spin projection $\hat{S}_{z'}$ in the state $|\psi\rangle$,

$$\langle\psi|\hat{S}_{z'}|\psi\rangle. \tag{11.152}$$

To do this, we express $|\psi\rangle = |+\rangle_z$ in the rotated basis; from (11.146) and (11.147) we have

$$|+\rangle_z = \cos\frac{\theta}{2}|+\rangle_{z'} - \sin\frac{\theta}{2}|-\rangle_{z'}. \tag{11.153}$$

Thus,

$$\begin{aligned}\langle\psi|\hat{S}_{z'}|\psi\rangle &= \left(\cos\frac{\theta}{2}\langle+|_{z'} - \sin\frac{\theta}{2}\langle-|_{z'}\right)\hat{S}_{z'}\left(\cos\frac{\theta}{2}|+\rangle_{z'} - \sin\frac{\theta}{2}|-\rangle_{z'}\right)\\ &= \frac{\hbar}{2}\cos^2\frac{\theta}{2} - \frac{\hbar}{2}\sin^2\frac{\theta}{2} = \frac{\hbar}{2}\left(\cos^2\frac{\theta}{2} - \sin^2\frac{\theta}{2}\right)\\ &= \frac{\hbar}{2}\cos\theta. \end{aligned}\tag{11.154}$$

Therefore, the probabilities of obtaining $\pm\hbar/2$ when measuring the spin along the rotated axis z' are $\cos^2(\theta/2)$ and $\sin^2(\theta/2)$ respectively. The average value of the projection is

$$\langle\hat{S}_{z'}\rangle = \frac{\hbar}{2}\cos\theta. \tag{11.155}$$

P11.13 Consider an ion with spin 1, characterized by the Hamiltonian

$$\hat{H} = D\hat{S}_z^2 + E\left(\hat{S}_x^2 + \hat{S}_y^2\right), \tag{11.156}$$

with D and E constant, $D \gg E$. Determine the energy levels.

Solution. We use the matrix representation of the spin operators in the basis of eigenstates of $\hat{S}_z$, denoted as $|m\rangle$ with $m = -1, 0, 1$. The matrices of the operators are

$$\hat{S}_x = \frac{\hbar}{\sqrt{2}}\begin{pmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{pmatrix}, \quad \hat{S}_y = \frac{\hbar}{\sqrt{2}}\begin{pmatrix}0 & -i & 0\\ i & 0 & -i\\ 0 & i & 0\end{pmatrix}. \tag{11.157}$$

Calculating $\hat{S}_x^2$ and $\hat{S}_y^2$

$$\hat{S}_x^2 = \left(\frac{\hbar}{\sqrt{2}}\right)^2\begin{pmatrix}1 & 0 & 1\\ 0 & 2 & 0\\ 1 & 0 & 1\end{pmatrix} = \frac{\hbar^2}{2}\begin{pmatrix}1 & 0 & 1\\ 0 & 2 & 0\\ 1 & 0 & 1\end{pmatrix}, \tag{11.158}$$

$$\hat{S}_y^2 = \left(\frac{\hbar}{\sqrt{2}}\right)^2 \begin{pmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & 1 \end{pmatrix} = \frac{\hbar^2}{2} \begin{pmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & 1 \end{pmatrix}. \tag{11.159}$$

and adding $\hat{S}_x^2 + \hat{S}_y^2$, we get

$$\hat{S}_x^2 + \hat{S}_y^2 = \frac{\hbar^2}{2} \begin{pmatrix} 2 & 0 & 0 \\ 0 & 4 & 0 \\ 0 & 0 & 2 \end{pmatrix} = \hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{11.160}$$

which substituted into the Hamiltonian gives

$$\hat{H} = D \cdot \frac{\hbar^2}{2} \begin{pmatrix} 1 & 0 & 1 \\ 0 & 2 & 0 \\ 1 & 0 & 1 \end{pmatrix} + E \cdot \hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \hbar^2 \begin{pmatrix} \frac{D}{2} + E & 0 & \frac{D}{2} \\ 0 & D + 2E & 0 \\ \frac{D}{2} & 0 & \frac{D}{2} + E \end{pmatrix}. \tag{11.161}$$

The Hamiltonian matrix

$$\hat{H} = \hbar^2 \begin{pmatrix} \frac{D}{2} + E & 0 & \frac{D}{2} \\ 0 & D + 2E & 0 \\ \frac{D}{2} & 0 & \frac{D}{2} + E \end{pmatrix} \tag{11.162}$$

is block-diagonal. The eigenstate $|m = 0\rangle$ (second row/column) is decoupled and has energy

$$E_{m=0} = \hbar^2(D + 2E). \tag{11.163}$$

The eigenstates $|m = 1\rangle$ and $|m = -1\rangle$ are coupled and form a 2×2 submatrix:

$$\begin{pmatrix} \frac{D}{2} + E & \frac{D}{2} \\ \frac{D}{2} & \frac{D}{2} + E \end{pmatrix}. \tag{11.164}$$

The eigenvalues of this submatrix are obtained by solving $\det \begin{pmatrix} a - \lambda & b \\ b & a - \lambda \end{pmatrix} = 0$ with $a = \frac{D}{2} + E$ and $b = \frac{D}{2}$,

$$(a - \lambda)^2 - b^2 = 0 \implies \lambda = a \pm b. \tag{11.165}$$

Substituting,

$$\lambda_1 = a + b = \left(\frac{D}{2} + E\right) + \frac{D}{2} = D + E, \tag{11.166}$$

$$\lambda_2 = a - b = \left(\frac{D}{2} + E\right) - \frac{D}{2} = E. \tag{11.167}$$

Thus, the energies for this subspace are $\hbar^2(D + E)$ and $\hbar^2 E$.The three energy levels are $\hbar^2 E$, $\hbar^2(D + E)$ and $\hbar^2(D + 2E)$. These levels are non-degenerate in general, since D and E are arbitrary constants with $D \gg E$, but their signs are not specified. The corresponding eigenstates are

$$\hbar^2 E : \frac{1}{\sqrt{2}}(|m = 1\rangle - |m = -1\rangle), \tag{11.168}$$

$$\hbar^2(D+E) : \frac{1}{\sqrt{2}}(|m=1\rangle + |m=-1\rangle), \tag{11.169}$$

$$\hbar^2(D+2E) : |m=0\rangle. \tag{11.170}$$

P11.14 Consider a system of angular momentum 1 represented by the state vector

$$\psi = \frac{1}{\sqrt{26}} \begin{pmatrix} 1 \\ 4 \\ -3 \end{pmatrix}. \tag{11.171}$$

What is the probability that a measurement of $\hat{L}_x$ returns the value zero?
Solution. We are given the state

$$\psi = \frac{1}{\sqrt{26}} \left(|1,1\rangle + 4|1,0\rangle - 3|1,-1\rangle \right), \tag{11.172}$$

where the kets $|l,m\rangle$ correspond to the eigenstates of total angular momentum with $l=1$ and $m=-1,0,1$. These three states form a complete basis for the $l=1$ subspace,

$$|1,1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \qquad |1,0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \qquad |1,-1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \tag{11.173}$$

The eigenfunction of $\hat{L}_x$ for $l=1$ with eigenvalue $m_x=0$ was obtained in Problem P11.4, and it is given by

$$\psi_0 = \frac{1}{\sqrt{2}} \left(|1,1\rangle - |1,-1\rangle \right) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}. \tag{11.174}$$

To find the probability that the system is in the state ψ_0, we compute the projection of ψ onto ψ_0,

$$\langle \psi_0 | \psi \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & -1 \end{pmatrix} \cdot \frac{1}{\sqrt{26}} \begin{pmatrix} 1 \\ 4 \\ -3 \end{pmatrix} = \frac{1}{\sqrt{2 \cdot 26}} (1 \cdot 1 + 0 \cdot 4 + (-1) \cdot (-3)) \tag{11.175}$$

$$= \frac{1+3}{\sqrt{52}} = \frac{4}{\sqrt{52}} = \frac{2}{\sqrt{13}}. \tag{11.176}$$

Therefore, the probability is the squared modulus

$$P = |\langle \psi_0 | \psi \rangle|^2 = \left(\frac{2}{\sqrt{13}} \right)^2 = \frac{4}{13} \approx 0.3. \tag{11.177}$$

P11.15 Calculate directly the Clebsch-Gordan coefficients for the coupling of angular momenta 1/2 and 1. Compare your results with those in **Table 11.1** of Ref. **[1]**.

Solution. The total angular momentum can be $j = 3/2$, with possible projections $3/2$, $1/2$, $-1/2$, $-3/2$, or $j = 1/2$, with possible projections $1/2$, $-1/2$. In the first case we speak of a quadruplet ($2 \times 3/2 + 1$ components), and in the second case of a doublet ($2 \times 1/2 + 1$ components). The state $\left|\frac{3}{2}\ \frac{3}{2}\right\rangle$ can only be constructed with $m_1 = 1$, $m_2 = 1/2$, and the only possibility is (with $\left|\frac{1}{2} \pm \frac{1}{2}\right\rangle$) for the spin-1/2 subsystem,

$$\left|\frac{3}{2}\ \frac{3}{2}\right\rangle = |1\ 1\,|+\rangle\,. \tag{11.178}$$

The state $\left|\frac{3}{2}\ \frac{1}{2}\right\rangle$ can be obtained from $\left|\frac{3}{2}\ \frac{3}{2}\right\rangle$ by applying once the lowering operator $J_- = J_{1-} + J_{2-}$. This gives

$$J_- \left|\frac{3}{2}\ \frac{3}{2}\right\rangle = \hbar C_{\frac{3}{2}\frac{1}{2}} \left|\frac{3}{2}\ \frac{1}{2}\right\rangle = (J_{1-}\,|1\ 1\rangle)\,|+\rangle + |1\ 1\,(J_{2-}\,|+\rangle) \tag{11.179}$$

$$= \hbar\,(C_{10}\,|1\ 0\rangle)\,|+\rangle + C_{\frac{1}{2}-\frac{1}{2}}\,|1\ 1\,|-\rangle\,, \tag{11.180}$$

that is,

$$\left|\frac{3}{2}\ \frac{1}{2}\right\rangle = \frac{C_{10}}{C_{\frac{3}{2}\frac{1}{2}}}\,|1\ 0\,|+\rangle + \frac{C_{\frac{1}{2}-\frac{1}{2}}}{C_{\frac{3}{2}\frac{1}{2}}}\,|1\ 1\,|-\rangle = \sqrt{\frac{2}{3}}\,|1\ 0\,|+\rangle + \sqrt{\frac{1}{3}}\,|1\ 1\,|-\rangle\,. \tag{11.181}$$

We apply the same procedure to obtain the state $\left|\frac{3}{2}\ -\frac{1}{2}\right\rangle$,

$$J_- \left|\frac{3}{2}\ \frac{1}{2}\right\rangle = \hbar C_{\frac{3}{2}-\frac{1}{2}} \left|\frac{3}{2}\ -\frac{1}{2}\right\rangle = \hbar\sqrt{2}\left|\frac{3}{2}\ -\frac{1}{2}\right\rangle \tag{11.182}$$

$$= \hbar\sqrt{\frac{2}{3}}\,(C_{1-1}\,|1\ -1\rangle\,|+\rangle + C_{\frac{1}{2}-\frac{1}{2}}\,|1\ 0\,|-\rangle) \tag{11.183}$$

$$+ \hbar\sqrt{\frac{1}{3}}\,(C_{10}\,|1\ 0\rangle)\,|-\rangle + 0 \tag{11.184}$$

$$= \hbar\sqrt{\frac{2}{3}}\,|1\ -1\rangle\,|+\rangle + 2\hbar\sqrt{\frac{1}{3}}\,|1\ 0\,|-\rangle\,, \tag{11.185}$$

that is,

$$\left|\frac{3}{2}\ -\frac{1}{2}\right\rangle = \sqrt{\frac{1}{3}}\,|1\ -1\rangle\,|+\rangle + \sqrt{\frac{2}{3}}\,|1\ 0\,|-\rangle\,. \tag{11.186}$$

Finally, the state $\left|\frac{3}{2}\ -\frac{3}{2}\right\rangle$ can only be:

$$\left|\frac{3}{2}\ -\frac{3}{2}\right\rangle = |1\ -1\,|-\rangle\,. \tag{11.187}$$

With this we have determined the four states belonging to the quadruplet. We can verify the previous results with the following consistency test,

$$\hat{J}_- \left|\frac{3}{2}\ -\ \frac{1}{2}\right\rangle = \hbar C_{\frac{3}{2}-\frac{3}{2}} \left|\frac{3}{2}\ -\ \frac{3}{2}\right\rangle = \hbar\sqrt{\frac{3}{2}}\left|\frac{3}{2}\ -\ \frac{3}{2}\right\rangle \tag{11.188}$$

$$= \hbar\sqrt{\frac{1}{3}}\left(0 + C_{\frac{1}{2}-\frac{1}{2}}\,|1\ -\ 1\rangle\,|-\rangle\right) \tag{11.189}$$

$$+ \hbar\sqrt{\frac{2}{3}}\left(C_{1-1}\,|1\ -\ 1\rangle\,|-\rangle + 0\right) \tag{11.190}$$

$$= \hbar\left(\sqrt{\frac{1}{3}}\cdot\frac{1}{2} + \sqrt{\frac{2}{3}}\right)|1\ -\ 1\rangle\,|-\rangle\,, \tag{11.191}$$

that is

$$\left|\frac{3}{2}\ -\frac{3}{2}\right\rangle = \sqrt{\frac{2}{3}}\left(\sqrt{\frac{1}{6}} + \sqrt{\frac{2}{3}}\right)|1\ {-1}\rangle\,|-\rangle = \left(\sqrt{\frac{1}{9}} + \sqrt{\frac{4}{9}}\right)|1\ {-1}\rangle\,|-\rangle\,, \tag{11.192}$$

which coincides with (11.187).To construct the states corresponding to the doublet with $j = 1/2$ we start from the fact that they must be of the form

$$\left|\frac{1}{2}\ \frac{1}{2}\right\rangle = a\,|1\ 1\rangle\ |-\rangle + b\,|1\ 0\rangle\ |+\rangle\,, \tag{11.193}$$

$$\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle = c\,|1\ 0\rangle\ |-\rangle + d\,|1\ -1\rangle\ |+\rangle\,. \tag{11.194}$$

Furthermore, the vectors $\left|\frac{1}{2}\ \frac{1}{2}\right\rangle$ and $\left|\frac{3}{2}\ \frac{1}{2}\right\rangle$ must be mutually orthogonal, a condition that requires

$$\sqrt{\frac{2}{3}}b + \sqrt{\frac{1}{3}}a = 0. \tag{11.195}$$

From this condition and the normalization condition it follows that $a = \sqrt{2/3}$, $b = -\sqrt{1/3}$, that is,

$$\left|\frac{1}{2}\ \frac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}\,|1\ 1\rangle\ |-\rangle - \sqrt{\frac{1}{3}}\,|1\ 0\rangle\ |+\rangle\,. \tag{11.196}$$

Finally, the remaining vector $\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$ is obtained from the previous one by applying the lowering operator, as done above. This gives

$$\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle = \sqrt{\frac{1}{3}}\,|1\ 0\rangle\ |-\rangle - \sqrt{\frac{2}{3}}\,|1\ -1\rangle\ |+\rangle\,. \tag{11.197}$$

P11.16 An orbital angular momentum $\hat{\boldsymbol{L}}$ couples with a spin $\hat{\boldsymbol{S}}$ to produce a state of total angular momentum $\hat{\boldsymbol{J}}$. Find out what angles between the vectors $\hat{\boldsymbol{L}}$ and

$\hat{\boldsymbol{S}}$ are allowed by quantum rules.

Solution. Let us consider the total angular momentum operator defined as

$$\hat{\boldsymbol{J}} = \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}}, \tag{11.198}$$

so that

$$\hat{\boldsymbol{J}}^2 = \hat{\boldsymbol{L}}^2 + \hat{\boldsymbol{S}}^2 + 2\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}. \tag{11.199}$$

From this, we can express the scalar product between $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$ as

$$\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} = \frac{1}{2}\left(\hat{\boldsymbol{J}}^2 - \hat{\boldsymbol{L}}^2 - \hat{\boldsymbol{S}}^2\right). \tag{11.200}$$

Now, the scalar product can also be written in terms of the angle θ between $\boldsymbol{L}$ and $\boldsymbol{S}$,

$$\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} = |\hat{\boldsymbol{L}}||\hat{\boldsymbol{S}}| \cos\theta, \tag{11.201}$$

where

$$|\hat{\boldsymbol{L}}| = \sqrt{\hat{\boldsymbol{L}}^2}, \quad |\hat{\boldsymbol{S}}| = \sqrt{\hat{\boldsymbol{S}}^2}.$$

To compute the allowed angles, we consider an eigenstate of total angular momentum $|jm\rangle$, where the quantum numbers satisfy

$$|l - s| \leq j \leq l + s, \quad m = m_l + m_s.$$

Taking expectation values in the state $|jm\rangle$, we find

$$\langle jm||\hat{\mathbf{L}}||\hat{\mathbf{S}}| \cos\theta |jm\rangle = \langle jm| \frac{1}{2}\left(\hat{\boldsymbol{J}}^2 - \hat{\boldsymbol{L}}^2 - \hat{\boldsymbol{S}}^2\right) |jm\rangle \tag{11.202}$$

$$\Rightarrow \hbar^2 \sqrt{l(l+1)s(s+1)} \cos\theta = \frac{1}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]\hbar^2, \tag{11.203}$$

therefore

$$\cos\theta = \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)s(s+1)}}. \tag{11.204}$$

The angles allowed by quantum rules between $\boldsymbol{L}$ and $\boldsymbol{S}$ are given by

$$\theta_{lsj} = \arccos\left(\frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)s(s+1)}}\right). \tag{11.205}$$

P11.17 Is it possible for one photon to spontaneously decay into two photons? And into three photons? Explain your answers.

Solution. We make the analysis for two photons first. A photon has spin $s = 1$ (intrinsic angular momentum $\hbar$), and its state is described with total angular momentum quantum numbers $j = 1$ and negative parity.The final state of two photons must conserve total angular momentum $j = 1$. However, because photons are identical bosons, their wave function must be symmetric under exchange. For two photons, the possible combinations of total angular momentum and parity that satisfy this symmetry are restricted. In particular, a state with $j = 1$ for two photons would have positive parity (given that the parity of a two-photon

system is $(-1)^j = (-1)^1 = -1$ if j is odd, but the intrinsic parity of each photon is -1, resulting in total parity $(-1) \times (-1) \times (-1)^j = +1$ for odd j, whichleads to a contradiction). This inconsistency in parity and symmetry implies that two-photon decay violates conservation of angular momentum and parity, and is therefore forbidden.

Now, we analyze the three-photon case. The total angular momentum can couple to $j = 1$ (for example, through combinations of states with $m = 0, \pm 1$). The total parity of the system would be $(-1)^3 \times (-1)^j = -1 \times (-1)^1 = +1$ for $j = 1$, but the initial photon has negative parity. Nevertheless, combinations of angular momenta for three particles allow adjustments that could reconcile the total parity with that of the initial state. However, one must additionally consider conservation of energy and linear momentum. In vacuum, an isolated photon has energy $E = \hbar\omega$ and linear momentum $\vec{p} = \hbar\vec{k}$. For it to decay into three photons, the sums of energies and linear momenta of the resulting photons would have to equal those of the initial photon. Since all these particles are massless, the dispersion relations ($E = |\vec{p}|c$) impose strict constraints. In conclusion a photon cannot spontaneously decay into two photons due to violations of angular momentum and parity, nor into three photons due to the impossibility of conserving energy and linear momentum in vacuum.

P11.18 The deuteron has spin 1. What are the possible states of spin and total angular momentum of a system of two deuterons when their total orbital angular momentum is L?

To determine the possible values of the total spin and total angular momentum of a system composed of two deuterons (each with spin $s = 1$), we proceed by coupling angular momenta.The total spin $\hat{\mathbf{S}}$ results from coupling the individual spins of the two deuterons,

$$\hat{\boldsymbol{S}} = \hat{\boldsymbol{s}}_1 + \hat{\boldsymbol{s}}_2. \tag{11.206}$$

The possible values of the total spin quantum number S are given by the standard angular momentum addition rule

$$|s_1 - s_2| \leq S \leq s_1 + s_2. \tag{11.207}$$

Since each deuteron has spin $s_1 = s_2 = 1$, we obtain

$$0 \leq S \leq 2 \quad \Rightarrow \quad S = 0,\ 1,\ 2. \tag{11.208}$$

Next, we consider the coupling of the total spin $\boldsymbol{S}$ with the total orbital angular momentum $L = l_1 + l_2$ to obtain the total angular momentum $\boldsymbol{J}$,

$$\hat{\boldsymbol{J}} = \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}}. \tag{11.209}$$

The allowed values of the total angular momentum quantum number j are then given by

$$|L - S| \leq j \leq L + S. \tag{11.210}$$

Let us now enumerate the possible values of the total angular momentum j for each allowed value of total spin S.

- For $S = 0$, the allowed values of j are given by

$$|L| \leq j \leq L \quad \Rightarrow \quad j = L \tag{11.211}$$

- For $S = 1$, the allowed values are

$$|L - 1| \leq j \leq L + 1 \tag{11.212}$$

  - If $L = 0$, then $j = 1$,
  - If $L \geq 1$, then $j = L - 1,\ L,\ L + 1$.
- For $S = 2$, the allowed values are

$$|L - 2| \leq j \leq L + 2 \tag{11.213}$$

  - If $L = 0$, then $j = 2$,
  - If $L = 1$, then $j = 1,\ 2,\ 3$,
  - If $L \geq 2$, then $j = L - 2,\ L - 1,\ L,\ L + 1,\ L + 2$.

Therefore, for each fixed value of L, the allowed total spin values are $S = 0, 1, 2$, and for each such S, the allowed total angular momentum j values follow from the rule $|L - S| \leq j \leq L + S$.

P11.19 Consider a spin $1/2$ particle confined by a central potential. a) Determine the wave functions that are simultaneously eigenfunctions of the operators $\hat{L}^2$, $\hat{J}^2$ and $\hat{J}_z = \hat{L}_z + \hat{S}_z$;

b) If an interaction term of the form $\gamma \hat{L} \cdot \hat{S}$ with γ small is added to the Hamiltonian, what are the eigenfunctions of the system?

Solution. a) For a spin-$1/2$ particle in a central potential, the simultaneous eigenfunctions of the operators $\hat{L}^2$, $\hat{J}^2$, and $\hat{J}_z$ are constructed by coupling the orbital angular momentum ($\hat{L}$) and spin ($\hat{S}$) on the basis of the total angular momentum. The wave function has the form

$$\psi_{n,l,j,m_j}(r, \theta, \phi, \sigma) = R_{nl}(r) Y^{l,s=1/2}_{j,m_j}(\theta, \phi, \sigma), \tag{11.214}$$

where $R_{nl}(r)$ is the radial part, which depends on the central potential and is common to all spin states, since the potential is central and initially spin-independent, $Y^{l,s=1/2}_{j,m_j}$ is the spin spherical harmonic, which couples the angular and spin degrees of freedom, and m_j is the total magnetic quantum number, with values $m_j = -j, -j + 1, \ldots, j$.

For orbital angular momentum l and spin $s = 1/2$, the total angular momentum j can take two values if $l > 0$,

$$j = l \pm \frac{1}{2}. \tag{11.215}$$

When $l = 0$, only $j = \frac{1}{2}$ is possible.

Spin spherical harmonics are expressed as linear combinations of uncoupled states $|l, m_l\rangle \otimes |s, m_s\rangle$. For $j = l + \frac{1}{2}$,

$$Y^{l,\frac{1}{2}}_{l+\frac{1}{2},m_j} = \sqrt{\frac{l+m_j+\frac{1}{2}}{2l+1}} Y_l^{m_j-\frac{1}{2}}(\theta,\phi)\chi_+ + \sqrt{\frac{l-m_j+\frac{1}{2}}{2l+1}} Y_l^{m_j+\frac{1}{2}}(\theta,\phi)\chi_-. \quad (11.216)$$

For $j = l - \frac{1}{2}$ $(l > 0)$,

$$Y^{l,\frac{1}{2}}_{l-\frac{1}{2},m_j} = -\sqrt{\frac{l-m_j+\frac{1}{2}}{2l+1}} Y_l^{m_j-\frac{1}{2}}(\theta,\phi)\chi_+ + \sqrt{\frac{l+m_j+\frac{1}{2}}{2l+1}} Y_l^{m_j+\frac{1}{2}}(\theta,\phi)\chi_-, \quad (11.217)$$

where $\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ are the Pauli spinors.The corresponding eigenvalues are given by

$$\hat{L}^2\psi = \hbar^2 l(l+1)\psi, \quad (11.218)$$

$$\hat{J}^2\psi = \hbar^2 j(j+1)\psi, \quad (11.219)$$

$$\hat{J}_z\psi = \hbar m_j \psi. \quad (11.220)$$

The radial part $R_{nl}(r)$ is not fixed by these operators (it depends on the specific central potential), but it is the same for all spin states in this basis.

b) When adding a spin-orbit interaction term (with γ a small constant), the total Hamiltonian becomes

$$\hat{H} = \hat{H}_0 + \gamma \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \quad (11.221)$$

where $\hat{H}_0$ is the Hamiltonian without spin-orbit interaction. Using

$$\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} = \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2). \quad (11.222)$$

and remembering that $\hat{H}$ commutes with $\hat{L}^2$, $\hat{S}^2$, $\hat{J}^2$, and $\hat{J}_z$, and that the spin-orbit interaction is diagonal in the coupled basis of part a), we conclude that the eigenfunctions remain the same as in part a),

$$\psi_{n,l,j,m_j}(r,\theta,\phi,\sigma) = R_{nl}(r) Y^{l,s=1/2}_{j,m_j}(\theta,\phi,\sigma). \quad (11.223)$$

Also $\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}$ is diagonal in this basis, with eigenvalue

$$\frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]. \quad (11.224)$$

The radial part $R_{nl}(r)$ does not depend on j because it does not act on r (it is constant in the subspace of fixed l and j). The radial equation remains the same as without interaction, except for a constant energy shift. The modified energies are given by

$$E_{nlj} = E^{(0)}_{nl} + \frac{\gamma\hbar^2}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right], \quad (11.225)$$

where $E^{(0)}_{nl}$ is the energy without spin-orbit interaction.

CHAPTER 12

Central Potentials. The Hydrogen Atom

P12.1 Consider a diatomic molecule made up of ions with charge $\pm q$ and masses m_1 and m_2, respectively. Show that:
a) The external gravitational field (near the earth's surface) produces an effect on the movement of the CM of the molecule, but not on its internal (relative) motion;
b) An external uniform electric field $\mathcal{E}$ along the z-axis does not affect the CM motion, but it does affect the internal one, since it induces a dipole electric moment given by

$$\frac{\partial}{\partial \mathcal{E}} \left(q\mathcal{E} \cdot \vec{r} \right) = qz.$$

Hint: study the general case corresponding to the potential

$$V(r) = f_1 z_1 + f_2 z_2$$

and take the particular case.
Solution. Let us consider a system of two particles that interact through a potential $V(\boldsymbol{r}_1 - \boldsymbol{r}_2)$, and that are also subjected to a common external potential of the form

$$V_a(\boldsymbol{r}) = f_1 z_1 + f_2 z_2, \tag{12.1}$$

where f_1 and f_2 are constants. The stationary Schrödinger equation for this system is

$$E\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \left[-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + f_1 z_1 + f_2 z_2 + V(\mathbf{r}_1 - \mathbf{r}_2) \right] \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2). \tag{12.2}$$

In terms of relative and center-of-mass coordinates (with $Z = R_z$, $z = r_z$), one has

$$f_1 z_1 + f_2 z_2 = (f_1 + f_2) Z + \frac{f_1 m_2 - f_2 m_1}{M} z, \tag{12.3}$$

where $M = m_1 + m_2$. Therefore, equation (12.2) can be rewritten in the form

$$E\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \left[-\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + (f_1 + f_2) Z + f_r z + V(\mathbf{r}) \right] \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2), \tag{12.4}$$

where, to simplify the notation, we have introduced the quantity

$$f_r = \frac{f_1 m_2 - f_2 m_1}{M}. \tag{12.5}$$

This equation is solved using the method of separation of variables, by writing the wave function in the form $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \Phi(\boldsymbol{R})\,\psi(\boldsymbol{r})$, which leads to the following pair of Schrödinger equations,

$$E_R\Phi(\boldsymbol{R}) = -\frac{\hbar^2}{2M}\nabla^2_{\boldsymbol{R}}\Phi(\boldsymbol{R}) + (f_1+f_2)Z\,\Phi(\boldsymbol{R}), \tag{12.6}$$

$$E_r\psi(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\nabla^2_{\boldsymbol{r}}\psi(\boldsymbol{r}) + f_r z\,\psi(\boldsymbol{r}) + V(\boldsymbol{r})\,\psi(\boldsymbol{r}). \tag{12.7}$$

We will now study various particular cases. a) When the ions are in a uniform gravitational field acting in the $\hat{\mathbf{z}}$ direction, the external potential is

$$V_a = -m_1 g z_1 - m_2 g z_2. \tag{12.8}$$

Comparing this expression with (12.1) we find $f_1 = -m_1 g$, $f_2 = -m_2 g$, hence $f_1 + f_2 = -Mg$ and $f_1 m_2 - f_2 m_1 = 0$, so that $f_r = 0$. Therefore, equations (12.6) and (12.7) reduce to

$$E_R\Phi(\boldsymbol{R}) = -\frac{\hbar^2}{2M}\nabla^2_{\boldsymbol{R}}\Phi(\boldsymbol{R}) - MgZ\Phi(\boldsymbol{R}), \tag{12.9}$$

$$E_r\psi(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\nabla^2_{\boldsymbol{r}}\psi(\boldsymbol{r}) + V(\boldsymbol{r})\psi(\boldsymbol{r}). \tag{12.10}$$

These equations show that the gravitational field affects the motion of the center of mass, but not the relative motion. b) When the ions are in an external electric field $\mathcal{E}$, constant in the $\hat{\mathbf{z}}$ direction, the potential becomes

$$V_a = q\mathcal{E}z_1 - q\mathcal{E}z_2, \tag{12.11}$$

which corresponds to $f_1 = -f_2 = q\mathcal{E}$; in this case, $f_1 + f_2 = 0$, and $f_1 m_2 - f_2 m_1 = f_1 M = f_r M = Mq\mathcal{E}$, so that Eqs. (12.6) and (12.7) reduce to

$$E_R\Phi(\boldsymbol{R}) = -\frac{\hbar^2}{2M}\nabla^2_{\boldsymbol{R}}\Phi(\boldsymbol{R}), \tag{12.12}$$

$$E_r\psi(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\nabla^2_{\boldsymbol{r}}\psi(\boldsymbol{r}) + q\mathcal{E}z\psi(\boldsymbol{r}) + V(\boldsymbol{r})\psi(\boldsymbol{r}). \tag{12.13}$$

We see that the electric field does not affect the motion of the center of mass, but it does affect the relative motion. This example illustrates the importance of how the external field couples to the system.

P12.2 Two oscillators interact linearly with each other, in such a way that the Hamiltonian of the system is

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{1}{2}m_1\omega^2 x_1^2 + \frac{1}{2}m_2\omega^2 x_2^2 + \frac{1}{2}m\omega^2\beta(x_1 - x_2)^2. \tag{12.14}$$

Show that the relative and CM coordinates coincide with the normal coordinates, separate these variables, and determine the eigenvalues of the energy. Study the energy spectrum for the attractive ($\beta > 0$) and repulsive ($\beta < 0$) cases, in the

limits $|\beta| \ll 1$ and $|\beta| \gg 1$.

Solution. In the proposed Hamiltonian (12.14) the sign of the coupling constant β determines whether the interaction between the oscillators is attractive or repulsive, that is, whether the interaction increases or decreases the system's potential energy. In terms of the relative and center-of-mass coordinates

$$y_1 = x_1 - x_2, \quad y_2 = \frac{m_1}{M}x_1 + \frac{m_2}{M}x_2, \tag{12.15}$$

where $M = m_1 + m_2$ is the total mass of the system, we have

$$x_1 = y_2 + \frac{m_2}{M}y_1, \quad x_2 = y_2 - \frac{m_1}{M}y_1, \tag{12.16}$$

$$\frac{\partial^2}{\partial x_1^2} = \frac{m_1^2}{M^2}\frac{\partial^2}{\partial y_2^2} + 2\frac{m_1}{M}\frac{\partial^2}{\partial y_1 \partial y_2} + \frac{\partial^2}{\partial y_1^2}, \tag{12.17}$$

$$\frac{\partial^2}{\partial x_2^2} = \frac{m_2^2}{M^2}\frac{\partial^2}{\partial y_2^2} - 2\frac{m_2}{M}\frac{\partial^2}{\partial y_1 \partial y_2} + \frac{\partial^2}{\partial y_1^2}. \tag{12.18}$$

The kinetic energy operator is now expressed as

$$\frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial y_1^2} - \frac{\hbar^2}{2M}\frac{\partial^2}{\partial y_2^2}, \tag{12.19}$$

where $\mu = \frac{m_1 m_2}{M}$ is the reduced mass, while the potential energy is

$$\frac{1}{2}m_1\omega^2 x_1^2 + \frac{1}{2}m_2\omega^2 x_2^2 + \frac{1}{2}m\omega^2\beta\,(x_1 - x_2)^2 = \frac{1}{2}\mu\omega^2(1+\beta)y_1^2 + \frac{1}{2}M\omega^2 y_2^2. \tag{12.20}$$

The particular case $\beta = -1$ is exceptional, as the relative motion disappears, neutralized by the interaction effect. In this case, the two oscillators move in phase, forming a "rigid" system that oscillates around the center of mass. In terms of the new variables, the Schrödinger equation is

$$E\psi(y_1, y_2) = \left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial y_1^2} - \frac{\hbar^2}{2M}\frac{\partial^2}{\partial y_2^2} + \frac{1}{2}M\omega^2 y_2^2 + \frac{1}{2}\mu\omega^2(1+\beta)y_1^2\right]\psi(y_1, y_2). \tag{12.21}$$

To separate variables, we write

$$\psi(y_1, y_2) = \phi_1(y_1)\phi_2(y_2). \tag{12.22}$$

We decompose the energy into the sum,

$$E = E_1 + E_2. \tag{12.23}$$

This leads to the system of Schrödinger equations

$$E_1\varphi_1 = -\frac{\hbar^2}{2\mu}\frac{\partial^2\varphi_1}{\partial y_1^2} + \frac{1}{2}\mu\omega^2(1+\beta)y_1^2\varphi_1, \tag{12.24}$$

$$E_2\varphi_2 = -\frac{\hbar^2}{2M}\frac{\partial^2\varphi_2}{\partial y_2^2} + \frac{1}{2}M\omega^2 y_2^2\varphi_2, \tag{12.25}$$

which describes two independent harmonic oscillators provided that $\beta > -1$ (the case $\beta < -1$ will not be analyzed here). Since this is precisely what happens when transforming to a system of normal coordinates, the pair of relative and center-of-mass coordinates coincides with the normal coordinates of the problem. This coincidence is due to the equality of the frequencies of the two original oscillators. The frequency of the oscillator associated with the relative motion y_1 is affected by the interaction, and becomes

$$\omega_r \equiv \omega_1 = \omega\sqrt{1+\beta}. \tag{12.26}$$

The system's energy is the sum of the energies associated with each of the two quasiparticles, and is obtained using the equation

$$E = \hbar\omega\left(n + \frac{1}{2}\right)$$

for the eigenvalues of a harmonic oscillator's energy. For the relative motion we have

$$E_{n1} = \hbar\omega\sqrt{\beta+1}\left(n_1 + \frac{1}{2}\right), \quad n_1 = 0, 1, 2, \ldots, \tag{12.27}$$

while the center-of-mass energy is

$$E_{n2} = \hbar\omega\left(n_2 + \frac{1}{2}\right), \quad n_2 = 0, 1, 2, \ldots \tag{12.28}$$

The total energy of the system becomes

$$E_{n_1 n_2} = \hbar\omega\left[n_1\sqrt{1+\beta} + n_2 + \frac{1}{2}\left(1 + \sqrt{1+\beta}\right)\right]. \tag{12.29}$$

This result shows that the mutual interaction modifies not only the energy of excited states but also the zero-point energy, since the oscillation frequency has been affected. For values of β such that $\sqrt{\beta+1}$ is a rational number, the excited levels become degenerate; if, on the contrary, $\sqrt{\beta+1}$ is irrational, there is no degeneracy.When $|\beta| \ll 1$, the mutual interaction of the oscillators can be treated as a small correction to the energy values corresponding to the system of two independent oscillators:

$$E_{n_1 n_2} = \hbar\omega\left(n_1 + n_2 + 1\right) + \frac{1}{2}\beta\hbar\omega\left(\frac{1}{2} + n_1\right) + \cdots. \tag{12.30}$$

This energy will be slightly higher or lower than that of the uncoupled oscillators, depending on the sign of β. In the opposite limit, $\beta \gg 1$, the energy eigenvalues can be approximated as

$$E = \hbar\omega\left[\sqrt{\beta}n_1 + n_2 + \frac{1}{2}\sqrt{\beta} + \frac{1}{2} + \cdots\right]. \tag{12.31}$$

P12.3 Determine the normalization coefficient of the radial wave function of the hydrogen-like atom.

Solution. The radial function is given, using the notation $\rho = 2\alpha r$, with $\alpha = \sqrt{-2mE/\hbar^2}$, by

$$R_{nl}(\rho) = C_{nl}\rho^l e^{-\rho/2} Q^{2l+1}_{n-l-1}(\rho), \tag{12.32}$$

where $Q^k_n(\rho)$ are the associated Laguerre polynomials, which can be defined via Rodrigues' formula

$$\begin{aligned} Q^k_n(\rho) =& \frac{1}{n!} e^{\rho}\rho^{-k}\frac{d^n}{d\rho^n}\left(e^{-\rho}\rho^{n+k}\right) \\ =& \sum_{s=0}^{n}(-1)^s \frac{(n+m)!}{s!(n-s)!(m+s)!}\rho^s. \end{aligned} \tag{12.33}$$

In terms of the (generalized) Laguerre polynomials $L_n(x)$, defined by

$$L_n(x) = \frac{1}{n!}e^x\frac{d^n}{dx^n}\left(x^n e^{-x}\right), \qquad n = 0, 1, 2, \ldots, \tag{12.34}$$

the associated Laguerre polynomials can be written as

$$Q^k_n(x) = (-1)^k \frac{d^k}{dx^k} L_{n+k}(x), \qquad k = 0, 1, 2, \ldots \tag{12.35}$$

These polynomials satisfy the orthonormality condition

$$\int_0^\infty e^{-\rho}\rho^k Q^k_n(\rho) Q^k_m(\rho)\, d\rho = \frac{(n+k)!}{n!}\delta_{nm}, \tag{12.36}$$

and also the integral identity

$$\int_0^\infty e^{-\rho}\rho^{k+1} Q^k_n(\rho) Q^k_n(\rho)\, d\rho = \frac{(n+k)!}{n!}(2n+k+1). \tag{12.37}$$

Now, using the normalization condition for the radial wave function,

$$\int_0^\infty r^2 R^2_{nl}(r)\, dr = 1,$$

and the change of variable $\rho = 2\alpha r$, we can write

$$\frac{1}{8\alpha^3}\int_0^\infty \rho^2 R^2_{nl}(\rho)\, d\rho = \frac{C^2_{nl}}{8\alpha^3}\int_0^\infty e^{-\rho}\rho^{2l+2} Q^{2l+1}_{n-l-1}(\rho)^2\, d\rho = 1. \tag{12.38}$$

Using the identity (12.37), we obtain

$$\frac{C^2_{nl}}{8\alpha^3}\cdot\frac{2n(n+l)!}{(n-l-1)!} = 1. \tag{12.39}$$

Finally, using the expression $\alpha = \frac{Z}{a_0 n}$ and

$$\frac{Z}{\beta a_0} = k + l + 1 \equiv n, \tag{12.40}$$

we find the normalization constant,

$$C_{nl} = \frac{2}{n^2}\sqrt{\left(\frac{Z}{a_0}\right)^3 \frac{(n-l-1)!}{(n+l)!}}. \tag{12.41}$$

P12.4 By comparing the corresponding differential equations, show that the Laguerre polynomials can be written as confluent hypergeometric functions in the form

$$Q_k^{2l+1}(\rho) = {}_1F_1(-k, 2(l+1); \rho). \tag{12.42}$$

Use this result to obtain the physically acceptable values of the quantum number k.

Solution. The confluent hypergeometric differential equation (sometimes called Kummer's equation)

$$xy''(x) + (c-x)\,y'(x) - ay(x) = 0 \tag{12.43}$$

has as its solution the confluent hypergeometric function, commonly denoted as ${}_1F_1(a, c; x)$ or $M(a, c; x)$. Specifically,

$$y(x) = {}_1F_1(a, c; x) \equiv M(a, c; x) \tag{12.44}$$

$$= 1 + \frac{a}{c}\frac{x}{1!} + \frac{a(a+1)}{c(c+1)}\frac{x^2}{2!} + \frac{a(a+1)(a+2)}{c(c+1)(c+2)}\frac{x^3}{3!} + \cdots, \tag{12.45}$$

with $c \neq 0, -1, -2, \ldots$. This function converges for all finite x, and in terms of the *Pochhammer symbols*

$$(a)_n = \frac{(a+n-1)!}{(a-1)!}, \quad (a)_0 = 1 \tag{12.46}$$

it can be written as

$$M(a, c; x) = \sum_{n=0}^{\infty} \frac{(a)_n x^n}{(c)_n n!}. \tag{12.47}$$

In turn, the associated Laguerre polynomials $y \equiv Q_k^{2l+1}(x)$ are solutions of the Laguerre equation,

$$xy''(x) + [2(l+1) - x]y'(x) + \left(\frac{Z}{a_0} - l - 1\right) y(x) = 0. \tag{12.48}$$

Comparing this equation with (12.43) we see that they coincide if we take

$$c = 2(l+1), \quad a = l + 1 - \frac{Z}{a_0}. \tag{12.49}$$

With this correspondence, the associated Laguerre polynomial can be written as the confluent hypergeometric function

$$Q_k^{2l+1}(\rho) = {}_1F_1(-k, 2(l+1); \rho), \tag{12.50}$$

under the condition that

$$2(l+1) \neq 0, -1, -2, \ldots \tag{12.51}$$

To determine the physically acceptable values of k we observe from (12.44) that $M(a, c; x)$ reduces to a polynomial if and only if the parameter a is a negative integer, that is, if

$$a = -k, \quad \text{with } k = 0, 1, 2, 3, \ldots \tag{12.52}$$

Since this choice reduces $Q_k^{2l+1}(\rho)$ to a polynomial, it guarantees the exponential decay of the hydrogenic wave function at infinity. Under these conditions, it is natural that the equality (12.52) is equivalent to the quantization condition for the hydrogenic atom, that is,

$$\frac{Z\alpha}{a_0} = k + l + 1 = n. \tag{12.53}$$

P12.5 Show that the eccentricity of the hydrogen-like orbits can be taken as

$$\epsilon = \sqrt{1 - \frac{l(l+1)}{n^2}}.$$

Note from here that the minimum eccentricity (closest to circular orbits) corresponds to $l = n - 1$ and is $\epsilon_{\min} = \frac{1}{\sqrt{n}}$, which tends to zero as $n \to \infty$.

Solution. The turning points (which correspond to the maximum and minimum values of the radial distance vector) in the classical Kepler problem are given by the values of r that solve the equation

$$\frac{p_r^2}{2m_0} = E + \frac{Ze^2}{r} - \frac{\boldsymbol{L}^2}{2m_0 r^2} \tag{12.54}$$

when $p_r = 0$. These solutions are

$$r_{\max/\min} = \frac{Ze^2}{2|E|}\left(1 \pm \sqrt{1 - \frac{2|E|}{Z^2 e^4 m_0}\boldsymbol{L}^2}\right). \tag{12.55}$$

If in this expression we introduce the eigenvalues of the energy of the hydrogen-like atom,

$$E_n = -\frac{Z^2 e^4 m_0}{2\hbar^2 n^2}, \tag{12.56}$$

and of the angular momentum,

$$\langle \hat{\boldsymbol{L}}^2 \rangle = \hbar^2 \ell(\ell+1), \tag{12.57}$$

we obtain

$$r_{\max/\min} = \frac{n^2 a_0}{Z}\left(1 \pm \sqrt{1 - \frac{\ell(\ell+1)}{n^2}}\right). \tag{12.58}$$

The eccentricity of an elliptical orbit is defined in terms of the major semi-axis a and the minor semi-axis b as

$$\epsilon = \sqrt{1 - \frac{b^2}{a^2}}, \tag{12.59}$$

and in terms of it, one can write

$$r_{\max/\min} = a(1 \pm \epsilon). \tag{12.60}$$

Comparing this equation with (12.58), we obtain the pair of identifications

$$a = \frac{n^2 a_0}{Z}, \qquad \epsilon = \sqrt{1 - \frac{\ell(\ell+1)}{n^2}}. \tag{12.61}$$

The first of these results shows that the quantum analog of the major semi-axis of the elliptical orbits is the quantity $(a_0/Z)\, n^2$. The second result gives a possible definition for the eccentricity, and coincides with the expression proposed in the problem. Since $\ell \leq n-1$, the eccentricity defined in this way (which in classical theory corresponds to circular orbits) can never vanish; the minimum value it can attain occurs precisely for $\ell = n-1$, and is $\epsilon_{\min} = 1/\sqrt{n}$. With this definition, quantum "circular" orbits correspond to those with the smallest eccentricity for a given energy (that is, a given n). For finite ℓ, the eccentricity defined by Eq. (12.61) approaches unity in the limit $n \to \infty$, which corresponds to infinitely elongated orbits; however, $\epsilon_{\min} \to 0$ when $n \to \infty$, as corresponds to circular orbits.

It is interesting to re-express the above result in terms of the quantum number $k = n - \ell - 1$,

$$\epsilon = \frac{\sqrt{k^2 + (2k+1)(\ell+1)}}{k + \ell + 1}. \tag{12.62}$$

For the minimum value $k = 0$, the minimum eccentricity $1/\sqrt{\ell+1} = 1/\sqrt{n}$ is obtained. For the maximum value $k = n-1$ and $\ell = 0$, the maximum $\epsilon = 1$ (infinitely elongated ellipses) is reached. These results suggest interpreting the number k as a measure of the eccentricity of the orbits. Thus, the principal quantum number is expressed as a contribution of the angular momentum plus a contribution from the eccentricity—this combination defines the energy of the state.[1]

[1]The interpretation suggested here is consistent with the ensemble interpretation of quantum mechanics, according to which the particle always retains its corpuscular (localized) nature, regardless of whether wave-like effects take place. In the orthodox interpretation, the notion of trajectory for quantum particles is completely discarded, so within that framework only the formal aspects of the previous calculation are meaningful.

An alternate way of viewing this problem is through the so-called *eccentricity vector* or *Laplace–Runge–Lenz vector*, defined as[2]

$$\boldsymbol{A} = \frac{\boldsymbol{r}}{r} + \frac{1}{2Ze^2 m_0}\left(\boldsymbol{L}\times\boldsymbol{p} - \boldsymbol{p}\times\boldsymbol{L}\right). \tag{12.63}$$

In the classical Kepler problem, it is shown that, due to $\boldsymbol{A}\cdot\boldsymbol{L} = 0$, the vector $\boldsymbol{A}$ is fixed in space and points in the direction of the perihelion of the orbit, with a magnitude equal to the eccentricity, $A = \epsilon$. These properties can be transferred to the quantum case and lead to a (formal, if preferred) definition of the eccentricity, very close (although not identical) to Eq. (12.61).

P12.6 Derive the following results for the expectation value of r^n for the H atom, where $\rho_{at} = r/a_0$ is measured in atomic units ($m = \hbar = e = 1$), i. e., $\rho_{at} = (2n/Z)\rho$:

$$\langle\rho_{at}\rangle = \frac{1}{2Z}\left[3n^2 - l(l+1)\right]; \quad \langle\rho_{at}^2\rangle = \frac{n^2}{2Z^2}\left[5n^2 + 1 - 3l(l+1)\right], \tag{12.64}$$

$$\left\langle\frac{1}{\rho_{at}}\right\rangle = \frac{Z}{n^2}; \quad \left\langle\frac{1}{\rho_{at}^2}\right\rangle = \frac{Z^2}{n^3(l+\frac{1}{2})}; \quad \left\langle\frac{1}{\rho_{at}^3}\right\rangle = \frac{Z^3}{n^3(l+1)(l+\frac{1}{2})}. \tag{12.65}$$

Solution. The expectation value of r^k for the hydrogen-like atom is

$$\langle r^k\rangle = \int_0^\infty dr\; r^{2+k} R_{nl}^2(r), \tag{12.66}$$

with $R_{nl}(\rho)$ given in [**1**], **Eq. (12.91)**. Using $\rho = 2\alpha r$ we obtain directly, in the current notation,

$$\langle r\rangle = \frac{C_{nl}^2}{16\alpha^4}\int_0^\infty \rho^{2l+3} e^{-\rho}\left(Q_{n-l-1}^{2l+1}(\rho)\right)^2 d\rho. \tag{12.67}$$

This integral can be evaluated using the recurrence relation for Laguerre polynomials

$$\rho Q_n^k = (2n+k+1)Q_n^k - (n+k)Q_{n-1}^k - (n+1)Q_{n+1}^k, \tag{12.68}$$

and their properties of orthogonality. Combining them appropriately we arrive at

$$\langle r\rangle = \frac{C_{nl}^2}{16\alpha^4}\left(6n^2 - 2l^2 - 2l\right)\int_0^\infty \rho^{2l+1} e^{-\rho} Q_{n-l-1}^{2l+1}(\rho) Q_{n-l-1}^{2l+1}(\rho) d\rho, \tag{12.69}$$

$$\langle r\rangle = \frac{C_{nl}^2}{16\alpha^4}\left(6n^2 - 2l^2 - 2l\right)\frac{(n+l)!}{(n-l-1)!}. \tag{12.70}$$

Introducing the value of the normalization constant (see [**1**], **Section 12.5.1**) and $\alpha = Z/na_0$, we obtain

$$\langle r\rangle = \frac{a_0}{2Z}\left[3n^2 - l(l+1)\right], \tag{12.71}$$

[2] In the literature, it is more commonly known as the Runge–Lenz vector, but it was already discussed in the work of Laplace. An introduction to the topic can be found in [**Gold80**], Section 3–9.

which, when re-expressed in atomic units $\rho_{\rm at} = r/a_0$, leads to the requested result,

$$\langle \rho_{\rm at} \rangle = \frac{1}{2Z}\left[3n^2 - l(l+1)\right]. \tag{12.72}$$

To calculate $\langle r^2 \rangle$ we proceed analogously,

$$\langle r^2 \rangle = \frac{C_{nl}^2}{32\alpha^5}\int_0^\infty \rho^{2l+4} e^{-\rho}\left(Q_{n-l-1}^{2l+1}(\rho)\right)^2 d\rho. \tag{12.73}$$

$$= \frac{C_{nl}^2}{32\alpha^5} 4n\left[5n^2 + 1 - 3l(l+1)\right] \tag{12.74}$$

$$\times \int_0^\infty \rho^{2l+1} e^{-\rho} Q_{n-l-1}^{2l+1}(\rho) Q_{n-l-1}^{2l+1}(\rho) d\rho \tag{12.75}$$

$$= \frac{C_{nl}^2}{32\alpha^5} 4n\left[5n^2 + 1 - 3l(l+1)\right]\frac{(n+l)!}{(n-l-1)!}. \tag{12.76}$$

and use $\alpha = Z/na_0$ to arrive at

$$\langle r^2 \rangle = \left(\frac{Z}{a_0}\right)^3 \frac{1}{2n^3\alpha^5}\left[5n^2 + 1 - 3l(l+1)\right] \tag{12.77}$$

$$= \frac{n^2 a_0^2}{2Z^2}\left[5n^2 + 1 - 3l(l+1)\right], \tag{12.78}$$

or, in atomic units,

$$\langle \rho_{\rm at}^2 \rangle = \frac{n^2}{2Z^2}\left[5n^2 + 1 - 3l(l+1)\right]. \tag{12.79}$$

To proceed, we write

$$\left\langle \frac{1}{\rho_{\rm at}} \right\rangle = a_0 \left\langle \frac{1}{r} \right\rangle = \frac{a_0 C_{nl}^2}{4\alpha^2}\int_0^\infty \rho^{2l+1} e^{-\rho} Q_{n-l-1}^{2l+1}(\rho) Q_{n-l-1}^{2l+1}(\rho) d\rho \tag{12.80}$$

$$= \frac{a_0 C_{nl}^2}{4\alpha^2}\frac{(n+l)!}{(n-l-1)!}, \tag{12.81}$$

which leads to

$$\left\langle \frac{1}{\rho_{\rm at}} \right\rangle = \frac{Z}{n^2}. \tag{12.82}$$

To calculate $\langle r^{-s} \rangle$, $s = 1, 2, 3, \ldots$ in a more direct but systematic way, we can proceed as follows. The expression

$$\left\langle \frac{1}{r^s} \right\rangle = \int_0^\infty r^{2-s} R_{nl}^2 dr = \frac{1}{(2\alpha)^{3-s}}\int_0^\infty \rho^{2-s} R_{nl}^2(\rho) d\rho \tag{12.83}$$

is rewritten as

$$\left\langle \frac{1}{r^s} \right\rangle = \frac{C_{nl}^2}{(2\alpha)^{3-s}}\int_0^\infty \rho^{2-s+2l} e^{-\rho}\left[Q_{n-l-1}^{2l+1}(\rho)\right]^2 d\rho \tag{12.84}$$

$$= \frac{C_{nl}^2}{(2\alpha)^{3-s}}\int_0^\infty \rho^{m+1-s} e^{-\rho}\left[Q_k^m(\rho)\right]^2 d\rho, \tag{12.85}$$

where we set $k = n - l - 1$, $m = 2l + 1$. If we now express one of the polynomials $Q_k^m(\rho)$ explicitly as a power series,

$$Q_k^m(\rho) = \sum_{j=0}^{k} \frac{(-1)^j (k+m)!}{j!(k-j)!(m+j)!} \rho^j, \tag{12.86}$$

and write the other using the corresponding Rodrigues formula as

$$Q_k^m(\rho) = \frac{1}{k!} e^{\rho} \rho^{-m} \frac{d^k}{d\rho^k} \left(e^{-\rho} \rho^{k+m} \right), \tag{12.87}$$

we obtain

$$\left\langle \frac{1}{r^s} \right\rangle = \frac{C_{nl}^2}{(2\alpha)^{3-s}} \frac{1}{k!} \sum_{j=0}^{k} \frac{(-1)^j (k+m)!}{j!(k-j)!(m+j)!} \int_0^\infty \rho^{1-s+j} \frac{d^k}{d\rho^k} \left(e^{-\rho} \rho^{k+m} \right) d\rho. \tag{12.88}$$

This integral can be solved by parts without difficulty, but we must distinguish the following possibilities:

a) If $1 - s + j < 0$, the integral is non-zero for all values of k.

b) If $1 - s + j > 0$, the integral is non-zero only when $1 - s + j \geq k$. For $s = 2$, $1 - s + j = j - 1$, and if $j - 1 > 0$, the integral only contributes when $j - 1 \geq k$, a condition that cannot be satisfied since the maximum value j can take is precisely k. Therefore, the only term that contributes in (12.88) for $s = 2$ is the one corresponding to $j - 1 < 0$, that is, $j = 0$. We thus obtain

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{C_{nl}^2}{2\alpha} \frac{1}{(k!)^2} \frac{(k+m)!}{m!} \int_0^\infty \rho^{-1} \frac{d^k}{d\rho^k} \left(e^{-\rho} \rho^{k+m} \right) d\rho. \tag{12.89}$$

Integrating by parts k times,

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{C_{nl}^2}{2\alpha} \frac{1}{(k!)^2} \frac{(k+m)!}{m!} k! \int_0^\infty \rho^{m-1} e^{-\rho} \, d\rho \tag{12.90}$$

$$= \frac{C_{nl}^2}{2\alpha} \frac{(k+m)!}{k!} \frac{(m-1)!}{m!} = \frac{C_{nl}^2}{2\alpha} \frac{(n+l)!}{(n-l-1)!(2l+1)}. \tag{12.91}$$

Substituting the normalization coefficient value we finally arrive at

$$\left\langle \frac{1}{\rho_{\text{at}}^2} \right\rangle = \left\langle \frac{a_0^2}{r^2} \right\rangle = \frac{Z^2}{n^3} \frac{1}{l + \frac{1}{2}}. \tag{12.92}$$

In the case $s = 3$, we have $1 - s + j = j - 2$, and again, if $j - 2 > 0$, it must satisfy $j - 2 \geq k$, a condition that is not met since the maximum possible value of j is precisely k. Therefore, possible contributions occur when $j - 2 < 0$, meaning that in expression (12.88) only the terms corresponding to $j = 0$ and $j = 1$ contribute. Hence,

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{C_{nl}^2}{k!} \left[\frac{(k+m)!}{k!m!} \int_0^\infty \rho^{-2} \frac{d^k}{d\rho^k} \left(e^{-\rho} \rho^{k+m} \right) d\rho \right. \tag{12.93}$$

$$-\frac{(k+m)!}{(k-1)!(m+1)!}\int_0^\infty \rho^{-1}\frac{d^k}{d\rho^k}\left(e^{-\rho}\rho^{k+m}\right)\,d\rho\Bigg]. \tag{12.94}$$

Integrating by parts k times,

$$\left\langle\frac{1}{r^3}\right\rangle = \frac{C_{nl}^2}{k!}\left[\frac{(k+m)!(k+1)!}{k!m!}\int_0^\infty \rho^{m-2}e^{-\rho}\,d\rho\right. \tag{12.95}$$

$$\left.-\frac{(k+m)!k!}{(k-1)!(m+1)!}\int_0^\infty \rho^{m-1}e^{-\rho}\,d\rho\right] \tag{12.96}$$

$$=\frac{C_{nl}^2}{k!}\left[\frac{(k+m)!(m-2)!}{m!}(k+1)-\frac{(k+m)!(m-1)!}{(m+1)!}k\right] \tag{12.97}$$

$$=C_{nl}^2\frac{(k+m)!}{k!m}\left[\frac{2k+m+1}{(m+1)(m-1)}\right]=C_{nl}^2\frac{(n+l)!n}{(n-l-1)!2l(l+1)(2l+1)}. \tag{12.98}$$

Substituting the expression for C_{nl}^2 we finally obtain

$$\left\langle\frac{1}{\rho_{\rm at}^3}\right\rangle=\left\langle\frac{a_0^3}{r^3}\right\rangle=\frac{Z^3}{n^3}\frac{1}{l(l+1)\left(l+\frac{1}{2}\right)}. \tag{12.99}$$

An alternative way to derive $\langle r^{-2}\rangle$ uses the Feynman-Hellmann theorem. This theorem is given by equation

$$\frac{\partial f_n}{\partial\lambda}=\langle\psi_n(\lambda)|\,\frac{\partial\tilde{F}}{\partial\lambda}\,|\psi_n(\lambda)\rangle\,, \tag{12.100}$$

where $\tilde{F}$ is an operator that depends on a parameter λ, and f_n is its expectation value in state n. To use the theorem we consider a generalized central Hamiltonian of the form

$$\hat{h}(\lambda)=\frac{1}{2m_0}\hat{p}_r^2+V(r)+\frac{\hbar^2\lambda(\lambda+1)}{2m_0r^2}. \tag{12.101}$$

The eigenvalues $E_n(\lambda)$ of this Hamiltonian correspond to the physical energy values for $\lambda=l=$ integer. Applying the Feynman-Hellmann theorem we obtain

$$\langle n\lambda|\frac{\partial\tilde{h}}{\partial\lambda}|n\lambda\rangle=\frac{\hbar^2(2\lambda+1)}{2m_0}\langle n\lambda|\frac{1}{r^2}|n\lambda\rangle=\frac{\partial E_n(\lambda)}{\partial\lambda}, \tag{12.102}$$

that is,

$$\left\langle\frac{1}{r^2}\right\rangle=\frac{2m_0}{\hbar^2}\left[\frac{1}{(2\lambda+1)}\frac{\partial E_n(\lambda)}{\partial\lambda}\right]_{\lambda=l}. \tag{12.103}$$

When applied to the hydrogen-like atom with $E_{kl}=-(m_0Z^2e^4/2\hbar^2)(k+l+1)^{-2}$, this formula reproduces Eq. (12.92). For the isotropic harmonic oscillator the energy levels are $E_{kl}=\hbar\omega\left(2k+l+\frac{3}{2}\right)$, and (12.103) yields the interesting result

$$\left\langle\frac{1}{r^2}\right\rangle=\frac{2m_0\omega}{\hbar(2l+1)}. \tag{12.104}$$

Since $\langle r^2\rangle = E_{kl}/m_0\omega^2$, the result can be written in a form similar to (12.92):

$$\left\langle \frac{1}{r^2} \right\rangle \langle r^2\rangle = \frac{2k + l + \frac{3}{2}}{l + \frac{1}{2}} = \frac{n}{l + \frac{1}{2}}. \tag{12.105}$$

P12.7 Derive the recurrence relation for $\langle r^s\rangle$ for the potential $V = qr^n$. Verify that the results of **Exercise E12.2** [**1**] are particular cases of this expression.
Solution. We start from the following result, derived in [**1**] for a general potential $V = V(r)$,

$$\left\langle \hat{\hat{p}}_r\, r^{s+1} \right\rangle + \frac{s+1}{m} \left\langle \hat{p}_r^2\, r^s \right\rangle + \frac{\hbar^2}{4m} s(s^2-1) \left\langle r^{s-2} \right\rangle = 0. \tag{12.106}$$

We now compute $\hat{p}_r$ and $\hat{p}_r^2$ for the potential $V(r) = qr^n$. The Hamiltonian is

$$\hat{H} = \frac{\hat{p}_r^2}{2m} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} + qr^n. \tag{12.107}$$

Therefore,

$$\dot{p}_r = \frac{i}{\hbar}\left[\hat{H}, \hat{p}_r\right] = -\frac{i}{\hbar}\left(\frac{\hbar^2\ell(\ell+1)}{2m} \left[\hat{p}_r, \frac{1}{r^2}\right] + q\left[\hat{p}_r, r^n\right] \right), \tag{12.108}$$

since $[\hat{p}_r, \hat{p}_r^2] = 0$. We apply the known identity $[\hat{p}_r, r^n] = -i\hbar n r^{n-1}$, and compute,

$$\begin{aligned} \dot{p}_r &= -\frac{i}{\hbar}\left(\frac{\hbar^2\ell(\ell+1)}{2m}\left(-\frac{2\hbar}{i} r^{-3}\right) + q\left(\frac{\hbar n r^{n-1}}{i}\right)\right) \\ &= \frac{\hbar^2\ell(\ell+1)}{mr^3} - qnr^{n-1}. \end{aligned} \tag{12.109}$$

On the other hand, equating $\hat{H} = E$ and using the radial Hamiltonian, we have

$$\frac{\hat{p}_r^2}{2m} + \frac{\hbar^2\ell(\ell+1)}{2mr^2} + qr^n = E, \tag{12.110}$$

which implies

$$\hat{p}_r^2 = 2m\left(E - \frac{\hbar^2\ell(\ell+1)}{2mr^2} - qr^n\right). \tag{12.111}$$

Substituting this expression into Eq. (12.106), we obtain

$$\begin{aligned} \frac{\hbar^2\ell(\ell+1)}{m}\left\langle r^{s-2}\right\rangle - qn\left\langle r^{s+1+n-1}\right\rangle + 2(s+1)E\left\langle r^s\right\rangle - \frac{\hbar^2\ell(\ell+1)}{m}(s+1)\left\langle r^{s-2}\right\rangle \\ -2(s+1)q\left\langle r^{s+n}\right\rangle + \frac{\hbar^2}{4m}s(s^2-1)\left\langle r^{s-2}\right\rangle = 0. \end{aligned}$$

We observe that the two terms involving q can be rewritten as

$$-qn\left\langle r^{s+1+n-1}\right\rangle = -\left\langle nqr^{n-1}r^{s+1}\right\rangle = -\left\langle V' r^{s+1}\right\rangle, \tag{12.112}$$

$$-2(s+1)q\left\langle r^{s+n}\right\rangle = -2(s+1)\left\langle qr^n r^s\right\rangle = -2(s+1)\left\langle Vr^s\right\rangle. \tag{12.113}$$

Therefore, the recurrence relation becomes

$$2(s+1)E\left\langle r^s\right\rangle - 2(s+1)\left\langle Vr^s\right\rangle - \left\langle V'r^{s+1}\right\rangle + \frac{\hbar^2}{m}s\left(\frac{s^2-1}{4} - \ell(\ell+1)\right)\left\langle r^{s-2}\right\rangle = 0. \tag{12.114}$$

Let us now verify that the results from **Exercise E12.2** are particular cases of this general expression. For the hydrogen-like atom potential

$$V(r) = -\frac{C}{r}, \quad \Rightarrow \quad V'(r) = \frac{C}{r^2}, \tag{12.115}$$

$$-2(s+1)\left\langle Vr^s\right\rangle = 2(s+1)C\left\langle \frac{r^s}{r}\right\rangle, \tag{12.116}$$

$$-\left\langle V'r^{s+1}\right\rangle = -C\left\langle \frac{r^{s+1}}{r^2}\right\rangle, \tag{12.117}$$

which yields the recurrence relation

$$2(s+1)E\left\langle r^s\right\rangle + C(2s+1)\left\langle r^{s-1}\right\rangle + \frac{\hbar^2}{m}s\left(\frac{s^2-1}{4} - \ell(\ell+1)\right)\left\langle r^{s-2}\right\rangle = 0. \tag{12.118}$$

We now consider the harmonic oscillator potential

$$V(r) = \frac{1}{2}m\omega^2 r^2 \quad \Rightarrow \quad V'(r) = m\omega^2 r. \tag{12.119}$$

Then we have

$$2(s+1)\left\langle r^s V\right\rangle = m\omega^2(s+1)\left\langle r^{s+2}\right\rangle, \tag{12.120}$$

$$\left\langle r^{s+1}V'\right\rangle = m\omega^2\left\langle r^{s+2}\right\rangle. \tag{12.121}$$

Substituting into the general recurrence relation, we obtain

$$2E(s+1)\left\langle r^s\right\rangle - \frac{1}{2}m\omega^2(2s+4)\left\langle r^{s+2}\right\rangle + \frac{\hbar^2}{m}s\left(\frac{s^2-1}{4} - \ell(\ell+1)\right)\left\langle r^{s-2}\right\rangle = 0. \tag{12.122}$$

P12.8 Show that in the ground state of the H atom the expectation value of r^n is

$$\langle 100|r^n|100\rangle = \frac{1}{2}\left(\frac{a_0}{Z}\right)^n (n+2)!.$$

Solution. The radial wavefunction for the hydrogenic ground state is

$$R_{10}(\rho) = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\rho/2}Q_0^1(\rho) = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\rho/2}. \tag{12.123}$$

With $\rho = 2\alpha r$ we obtain

$$\langle 100 \mid r^n \mid 100\rangle = 4\left(\frac{Z}{a_0}\right)^3 \frac{1}{(2\alpha)^{n+3}}\int_0^\infty \rho^{2+n}e^{-\rho}\,d\rho \tag{12.124}$$

$$= 4\left(\frac{Z}{a_0}\right)^3 \frac{1}{(2\alpha)^{n+3}}\,(n+2)!. \tag{12.125}$$

Introducing the relation $\alpha = Z/a_0$ (valid for the ground state) we arrive at the requested result,

$$\langle 100 \mid r^n \mid 100\rangle = \frac{1}{2}\left(\frac{a_0}{2Z}\right)^n (n+2)!. \tag{12.126}$$

P12.9 Solve the H atom problem with an additional potential γ/r^2 and show that for any value of the parameter $\gamma \neq 0$, the degeneracy with respect to l is broken.
Solution. It is possible to draw some general conclusions for arbitrary γ without the need to previously solve the problem. Proceeding exactly as with the hydrogen-like atom problem, one recovers the same result but with an additional term

$$Q'' + \left(\frac{2l+1}{\rho} - 1\right)Q' + \left(\frac{n-l-1}{\rho} + \frac{4\alpha^2\gamma}{\rho^2}\right)Q = 0. \tag{12.127}$$

The appearance of this term is essential, since the energy levels now depend explicitly on the pair of parameters γ and $n-l-1$, which breaks the degeneracy in l. In other words, this degeneracy can be understood as a consequence of the fact that, when transforming the differential equation for the radial function u,

$$u'' + \left(-\frac{1}{4} + \frac{Z}{\alpha a_0 \rho} - \frac{l(l+1)}{\rho^2}\right)u = 0, \tag{12.128}$$

into Eq. (12.127) with $\gamma = 0$, for $u(\rho) = \rho^{l+1}e^{-\rho/2}Q(\rho)$, the coefficient of the last term $\sim 1/\rho^2$ vanishes identically. As this is no longer true when $\gamma \neq 0$, as follows from (12.127), the degeneracy is broken.The explicit solution can be obtained by noting that the effective potential to which the electron is subject is, with $\beta = 2m_0\gamma/\hbar^2$,

$$V(r) = -\frac{Ze^2}{r} + \frac{\hbar^2}{2m_0}\frac{l(l+1)+\beta}{r^2} = -\frac{Ze^2}{r} + \frac{\hbar^2}{2m_0}\frac{\lambda(\lambda+1)}{r^2}, \tag{12.129}$$

where the new constant λ is determined (for $\beta > 0$) by the equation

$$\lambda(\lambda+1) = l(l+1) + \beta \quad \Rightarrow \quad \lambda = -\frac{1}{2} + \sqrt{\left(l+\frac{1}{2}\right)^2 + \beta}. \tag{12.130}$$

From this identification, the problem is solved in the usual way, but with λ playing the role previously played by l[3].A simple way to deal with this problem is to use perturbation theory, treating the γ/r^2 potential as a perturbation applied to the hydrogen-like atom. It can be shown that the presence of this perturbation breaks the degeneracy in l, no matter how small the value of the parameter γ, as discussed above.

[3]The explicit solution of this problem can be found in **[LL65]**, §35.

P12.10 Find the probability that in a hydrogen atom in its ground state, the electron and the proton separate beyond the value allowed by classical mechanics at the same energy.

Solution. Given the ground state wavefunction of hydrogen

$$\psi_{100}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}, \tag{12.131}$$

where a_0 is the Bohr radius. The ground state energy is

$$E_1 = -\frac{ke^2}{2a_0}, \quad \text{with } k = \frac{1}{4\pi\epsilon_0}. \tag{12.132}$$

For energy E_1, the classical turning point occurs when $E_1 = V(r)$

$$-\frac{ke^2}{2a_0} = -\frac{ke^2}{r_{\text{class}}}. \tag{12.133}$$

Solving for r_{class},

$$\frac{1}{2a_0} = \frac{1}{r_{\text{class}}} \implies r_{\text{class}} = 2a_0. \tag{12.134}$$

The radial probability density for the ground state is

$$p(r)dr = |\psi_{100}|^2 \cdot 4\pi r^2 dr = \frac{4r^2}{a_0^3} e^{-2r/a_0} dr. \tag{12.135}$$

and the probability for $r > 2a_0$ is given by

$$P(r > 2a_0) = \int_{2a_0}^{\infty} \frac{4r^2}{a_0^3} e^{-2r/a_0} dr. \tag{12.136}$$

Introducing $u = \frac{2r}{a_0}$

$$P(r > 2a_0) = \frac{1}{2} \int_4^{\infty} u^2 e^{-u} du, \tag{12.137}$$

solving by parts

$$\int u^2 e^{-u} du = -e^{-u}(u^2 + 2u + 2) + C \tag{12.138}$$

and evaluating from 4 to ∞

$$\int_4^{\infty} u^2 e^{-u} du = 26e^{-4}, \tag{12.139}$$

we get

$$P(r > 2a_0) = \frac{1}{2} \times 26e^{-4} = 13e^{-4}. \tag{12.140}$$

This small value indicates that the electron is tightly bound to the nucleus.

P12.11 An H atom is in the state $n = 2, \ell = 1, m = 0$. Express the corresponding electronic wave function in momentum space.

Solution. We start by writing the position-space wavefunction

$$\psi_{210}(r, \theta, \varphi) = R_{21}(r) Y_1^0(\theta, \varphi), \tag{12.141}$$

with

$$\beta = \frac{1}{2a_0}. \tag{12.142}$$

The radial wavefunction for this state is

$$R_{21}(r) = \beta \sqrt{\frac{1}{6a_0^3}}\, r\, e^{-\beta r}, \tag{12.143}$$

so the complete wave function becomes

$$\psi_{210}(r, \theta, \varphi) = \beta (6a_0^3)^{-1/2}\, r\, e^{-\beta r}\, Y_1^0(\theta, \varphi). \tag{12.144}$$

The wave function in momentum space is given by the Fourier transform of the wave function in position space,

$$\widetilde{\psi}(\boldsymbol{p}) = \frac{1}{(2\pi\hbar)^{3/2}} \int \psi(\boldsymbol{r}) e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\, d^3 r. \tag{12.145}$$

The exponential can be expanded in spherical harmonics using the plane wave expansion,

$$e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} = 4\pi \sum_{\ell m} (-i)^\ell j_\ell(kr) Y_\ell^{m*}(\theta, \varphi) Y_\ell^m(\theta_k, \varphi_k). \tag{12.146}$$

We then can rewrite the Fourier transform in spherical coordinates of the wave function as

$$\widetilde{\psi}(\boldsymbol{p}) = \frac{4\pi}{(2\pi\hbar)^{3/2}} \sum_{\ell', m'} Y_{\ell'}^{m'}(\theta_k, \varphi_k)(-i)^{\ell'} \int_0^\infty R_{n\ell}(r) j_{\ell'}(kr) r^2 dr \int Y_\ell^m(\theta, \varphi) Y_{\ell'}^{m'*}(\theta, \varphi)\, \sin\theta\, d\theta\, d\varphi. \tag{12.147}$$

Due to the orthonormality relation

$$\int_0^{2\pi} \int_0^\pi Y_\ell^m(\theta, \varphi) Y_{\ell'}^{m'*}(\theta, \varphi) \sin\theta\, d\theta\, d\varphi = \delta_{\ell\ell'} \delta_{mm'}, \tag{12.148}$$

and with $k = \frac{p}{\hbar}$, the expression simplifies to

$$\widetilde{\psi}(\boldsymbol{p}) = \frac{4\pi}{(2\pi\hbar)^{3/2}} Y_\ell^m(\theta_p, \varphi_p)(-i)^\ell \int_0^\infty R_{n\ell}(r) j_\ell\left(\frac{pr}{\hbar}\right) r^2 dr, \tag{12.149}$$

where θ_p and φ_p are the spherical angles of the momentum vector $\boldsymbol{p}$. In our particular case, $n = 2$, $\ell = 1$, $m = 0$, so we obtain

$$\widetilde{\psi}(\boldsymbol{p}) = \frac{4\pi}{(2\pi\hbar)^{3/2}} Y_1^0(\theta_p, \varphi_p)(-i) \int_0^\infty R_{21}(r) j_1\left(\frac{pr}{\hbar}\right) r^2 dr. \tag{12.150}$$

We now compute the radial integral explicitly. The spherical Bessel function of order 1 is

$$j_1\left(\frac{pr}{\hbar}\right) = \frac{\sin\left(\frac{pr}{\hbar}\right)}{\left(\frac{pr}{\hbar}\right)^2} - \frac{\cos\left(\frac{pr}{\hbar}\right)}{\left(\frac{pr}{\hbar}\right)}. \tag{12.151}$$

The radial integral becomes

$$\mathcal{I} = \beta\sqrt{\frac{1}{6a_0^3}}\int_0^\infty r^3 e^{-\beta r}\left(\frac{\sin\left(\frac{pr}{\hbar}\right)}{\left(\frac{pr}{\hbar}\right)^2} - \frac{\cos\left(\frac{pr}{\hbar}\right)}{\left(\frac{pr}{\hbar}\right)}\right)dr, \tag{12.152}$$

which gives

$$\mathcal{I} = \beta\sqrt{\frac{1}{6a_0^3}}\,\frac{8\beta p}{\hbar\left(\frac{p^2}{\hbar^2}+\beta^2\right)^3} = \sqrt{\frac{1}{6a_0^3}}\,\frac{8\beta^2\hbar^5 p}{\left(p^2+\hbar^2\beta^2\right)^3}. \tag{12.153}$$

Thus, the Fourier transform of the hydrogen-like $2p$ state with $m=0$ is

$$\widetilde{\psi}_{210}(\boldsymbol{p}) = -\frac{4\pi i}{(2\pi\hbar)^{3/2}}\sqrt{\frac{3}{4\pi}}\sqrt{\frac{1}{6a_0^3}}\,\frac{8\beta^2\hbar^5 p}{\left(p^2+\hbar^2\beta^2\right)^3}\cos\theta_p. \tag{12.154}$$

Combining all constants and recalling that $\beta = 1/(2a_0)$, we get the final simplified expression

$$\widetilde{\psi}_{210}(\boldsymbol{p}) = -\frac{i}{\pi}\left(\frac{\hbar}{a_0}\right)^{7/2}\frac{p\cos\theta_p}{\left(p^2+\frac{\hbar^2}{4a_0^2}\right)^3}. \tag{12.155}$$

P12.12 In classical electrodynamics the magnetic moment μ_z produced by an electric current density $\boldsymbol{J}_{e1}$ is given by

$$\mu_z = \frac{1}{2c}\int(\boldsymbol{r}\times\boldsymbol{J}_{e1})_z d^3x. \tag{12.156}$$

Show that for discrete charges q this expression reduces to $\mu_z = \frac{q}{2m_0c}L_z$ and, transferring this result to the quantum case, show that

$$\langle\hat{\mu}_z\rangle = e\frac{\langle\hat{L}_z\rangle}{2m_ec} = \frac{e\hbar}{2m_ec}m \tag{12.157}$$

for a wave function of the form $\psi = \Phi(r,\theta)e^{im\varphi}$, with Φ a real function.
Solution. For a continuous charge distribution, the current density is

$$\boldsymbol{j}_{\rm el} = \int \rho_{\rm el}(\boldsymbol{x})\boldsymbol{v}(\boldsymbol{x})d^3x. \tag{12.158}$$

When the current is generated by a set of discrete point charges, this expression takes the form

$$\boldsymbol{j}_{\rm el} = \sum_n q_n\boldsymbol{v}_n = \sum_n \frac{q_n}{m_n}\boldsymbol{p}_n. \tag{12.159}$$

For identical particles, from this expression it follows that

$$\mu_z = \frac{1}{2c}\int (\boldsymbol{r}\times\boldsymbol{j}_{\rm el})_z\, d^3x \tag{12.160}$$

$$= \frac{q}{2m_0c}\int \sum_n (\boldsymbol{r}\times\boldsymbol{p}_n)_z\, d^3x = \frac{q}{2m_0c}\int \sum_n (\boldsymbol{L}_n)_z\, d^3x, \tag{12.161}$$

where $\boldsymbol{L}_n = \boldsymbol{r}\times\boldsymbol{p}_n$ is the angular momentum of particle n. In terms of the total angular momentum, $\boldsymbol{L} = \sum_n \boldsymbol{L}_n$, we obtain

$$\mu_z = \frac{q}{2m_0c}L_z. \tag{12.162}$$

Due to the linearity of this expression, it can be directly transcribed into quantum terms, with $m_0 \to m_e$, $q \to e = -e_0$ for the electron mass and charge, respectively. This yields

$$\hat{\mu}_z = \frac{e}{2m_ec}\hat{L}_z = -\mu_0\frac{\hat{L}_z}{\hbar}, \tag{12.163}$$

where

$$\mu_0 = e_0\hbar/2m_ec \tag{12.164}$$

is the *Bohr magneton*. This is precisely the result obtained from a direct application of the Schrödinger equation to a particle in a magnetic field, as seen in [**1**], **Section 13.5**. This agreement can be considered as verification of the validity of the transition from Eq. (12.162) to Eq. (12.163). The same result is rederived in the following problem using a systematic quantum procedure.

Note that Eq. (12.163) predicts for the orbital gyromagnetic ratio of the electron the value $e/2m_ec = -\mu_0/\hbar$, which coincides with the corresponding classical ratio.

Now consider the expectation value of $\hat{\mu}_z$ calculated for a state of the form $\Phi(r,\theta)e^{im\varphi}$. It is immediately verified that this is an eigenstate of the orbital angular momentum projection along the Oz axis,

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}, \tag{12.165}$$

which applied to $\psi = \Phi(r,\theta)e^{im\varphi}$ gives $\hat{L}_z\psi = m\hbar\psi$. Therefore, for these states we have

$$\mu_z \equiv \langle\hat{\mu}_z\rangle = \frac{e\hbar}{2m_ec}m = -\mu_0 m. \tag{12.166}$$

P12.13 Show that when the quadratic effects of the magnetic field are taken into account, the magnetic moment of an atom is

$$\mu = -\mu_0 m - \frac{e^2B}{6m_ec^2}\langle r^2\rangle. \tag{12.167}$$

Notes: The first term represents a permanent magnetic moment (independent of the external field) and can have any sign; this is the *paramagnetic component* of the magnetic moment. The second term (which, because it comes from a quadratic effect, is generally very small for weak fields) represents an induced magnetic moment (it vanishes when $B = 0$). It is always negative and exists for all atoms; this is the *diamagnetic moment*.

Solution. The Hamiltonian of the atom in the presence of an electromagnetic field is obtained by applying the *principle of minimal coupling*[4] to the corresponding Hamiltonian in the absence of the field, as discussed in [**1**], **Section 12.7.1**. Using this rule, one gets

$$\hat{H} = \frac{1}{2m_e}\left(\hat{\boldsymbol{p}} - \frac{e}{c}\boldsymbol{A}\right)^2 + e\Phi = \hat{H}_0 - \frac{e}{2m_e c}\left(\boldsymbol{A}\cdot\hat{\boldsymbol{p}} + \hat{\boldsymbol{p}}\cdot\boldsymbol{A}\right) + \frac{e^2}{2m_e c^2}\boldsymbol{A}^2, \quad (12.168)$$

where

$$\hat{H}_0 = \frac{\hat{\boldsymbol{p}}^2}{2m_e} + e\Phi \quad (12.169)$$

is the Hamiltonian in the absence of a magnetic field (but in the presence of the scalar potential Φ). Let us consider the case of a constant and uniform magnetic field of intensity $\boldsymbol{B}$; in this case, one can write the vector potential in the particular form given by

$$\boldsymbol{A} = \frac{1}{2}\boldsymbol{B}\times\boldsymbol{r}, \quad (12.170)$$

since it identically satisfies the relation

$$\boldsymbol{B} = \nabla\times\boldsymbol{A}. \quad (12.171)$$

Since $\nabla\cdot\boldsymbol{A} = 0$, it follows that with this choice $\hat{\boldsymbol{p}}$ and $\boldsymbol{A}$ commute,

$$\hat{\boldsymbol{p}}\cdot\boldsymbol{A} = -i\hbar(\nabla\cdot\boldsymbol{A}) + \boldsymbol{A}\cdot\hat{\boldsymbol{p}} = \boldsymbol{A}\cdot\hat{\boldsymbol{p}}, \quad (12.172)$$

and the Hamiltonian simplifies to

$$\hat{H} = \hat{H}_0 - \frac{e}{m_e c}\boldsymbol{A}\cdot\hat{\boldsymbol{p}} + \frac{e^2}{2m_e c^2}\boldsymbol{A}^2. \quad (12.173)$$

We choose a coordinate system with the Oz axis aligned along the magnetic field direction, which gives

$$\boldsymbol{A} = \frac{B}{2}\left(-\hat{y}x + \hat{x}y\right), \quad (12.174)$$

and

$$\boldsymbol{A}^2 = \frac{B^2}{4}\left(x^2 + y^2\right). \quad (12.175)$$

[4]The neologism *minimal* refers (analogously to how it is used in the text) to a theory constructed with a minimal set of elements, that is, *structurally minimal*; it does not qualify in any way the value yielded by the theory, as the term *minimum* would.

Another important advantage of writing $\boldsymbol{A}$ this way is that it leads to the following very useful result,

$$\boldsymbol{A}\cdot\hat{\boldsymbol{p}}=\frac{1}{2}\left(\boldsymbol{B}\times\boldsymbol{r}\right)\cdot\hat{\boldsymbol{p}}=\frac{1}{2}\boldsymbol{B}\cdot\left(\boldsymbol{r}\times\hat{\boldsymbol{p}}\right)=\frac{1}{2}\boldsymbol{B}\cdot\hat{\boldsymbol{L}}. \tag{12.176}$$

With these expressions, the Hamiltonian (12.173) becomes

$$\hat{H}=\hat{H}_0-\frac{e}{2m_ec}\boldsymbol{B}\cdot\hat{\boldsymbol{L}}+\frac{e^2B^2}{8m_ec^2}\left(x^2+y^2\right). \tag{12.177}$$

We now consider the case in which, in the absence of $\boldsymbol{A}$, the system possesses spherical symmetry, so that $\langle x^2\rangle=\langle y^2\rangle=\langle z^2\rangle$, which implies

$$\langle x^2+y^2\rangle=\frac{2}{3}\langle r^2\rangle. \tag{12.178}$$

From Eq. (12.177) it follows that

$$E=\left\langle\hat{H}_0\right\rangle-\frac{e}{2m_ec}\left\langle\boldsymbol{B}\cdot\hat{\boldsymbol{L}}\right\rangle+\frac{e^2B^2}{12m_ec^2}\left\langle r^2\right\rangle. \tag{12.179}$$

The magnetic moment is generally defined as

$$\boldsymbol{\mu}=-\frac{\partial E}{\partial\boldsymbol{B}}. \tag{12.180}$$

Applying this definition to the energy (12.179) we obtain

$$\boldsymbol{\mu}=\frac{e}{2m_ec}\left\langle\hat{\boldsymbol{L}}\right\rangle-\frac{e^2}{6m_ec^2}\boldsymbol{B}\left\langle r^2\right\rangle, \tag{12.181}$$

a result which suggests defining the corresponding operator as

$$\hat{\boldsymbol{\mu}}=\frac{e}{2m_ec}\hat{\boldsymbol{L}}-\frac{e^2}{6m_ec^2}\boldsymbol{B}r^2. \tag{12.182}$$

For eigenstates of $\hat{L}_z$ with eigenvalue $\hbar m$, one can write in particular

$$\mu_z=-\mu_0m-\frac{e^2}{6m_ec^2}B\left\langle r^2\right\rangle, \tag{12.183}$$

where the definition of the Bohr magneton was introduced.From the last expression it follows that the diamagnetic susceptibility (per atom) is given by

$$\chi_z^{\text{diamag}}=N\frac{\partial\mu_z^{\text{diamag}}}{\partial B}=-\frac{e^2N}{6m_ec^2}\left\langle r^2\right\rangle, \tag{12.184}$$

where N is Avogadro's number. This value is always nonzero (and negative); however, the diamagnetic properties of materials described by this expression are often masked by paramagnetism, when present, which tends to dominate.

P12.14 Using

$$W_{nk}^{\text{em}}(N=0)\equiv A_{nk}=\frac{4e^2\omega^3}{3\hbar c^3}|\langle n|\mathbf{r}|k\rangle|^2=\frac{\hbar\omega^3}{\pi^2c^3}B_{nk} \tag{12.185}$$

for the Einstein A coefficient, derive in detail

$$A_{nlm\to n',l+1,\text{all } m'} = \frac{4e^2\omega_{nn'}^3}{3\hbar c^3}\,\frac{l+1}{2l+1}|\langle n'l+1|r|nl\rangle|^2 \tag{12.186}$$

and

$$A_{nlm\to n',l-1,\text{all } m'} = \frac{4e^2\omega_{nn'}^3}{3\hbar c^3}\,\frac{l}{2l-1}|\langle n'l-1|r|nl\rangle|^2. \tag{12.187}$$

Solution. The Einstein coefficients for allowed spontaneous transitions in the hydrogen atom must be determined, taking into the previously obtained selection rule $\Delta l = \pm 1$ into account. The relevant matrix elements are

$$\langle n'l'm'|\boldsymbol{r}|nlm\rangle = \langle n'l'|r|nl\rangle\langle l'm'|\hat{\boldsymbol{a}}_r|lm\rangle, \tag{12.188}$$

where the angular factor was obtained previously,

$$\langle l'm'|\hat{\boldsymbol{a}}_r|lm\rangle = \hat{\boldsymbol{a}}_+\left(A_{lm}^+\delta_{l',l+1} + B_{lm}^+\delta_{l',l-1}\right)\delta_{m',m+1} \tag{12.189}$$

$$+\,\hat{\boldsymbol{a}}_-\left(A_{lm}^-\delta_{l',l+1} + B_{lm}^-\delta_{l',l-1}\right)\delta_{m',m-1} \tag{12.190}$$

$$+\,\hat{\boldsymbol{a}}_z\left(A_{lm}\delta_{l',l+1} + B_{lm}\delta_{l',l-1}\right)\delta_{m',m}. \tag{12.191}$$

Let us first consider transitions from l to $l' = l+1$, for which

$$\langle l+1,m'|\hat{\boldsymbol{a}}_r|lm\rangle = \hat{\boldsymbol{a}}_+A_{lm}^+\delta_{m',m+1} + \hat{\boldsymbol{a}}_-A_{lm}^-\delta_{m',m-1} + \hat{\boldsymbol{a}}_zA_{lm}\delta_{m',m}. \tag{12.192}$$

Each of the three components of this result contributes to transitions with different m'; summing the contributions, we obtain

$$|\langle l+1,m+1|\hat{\boldsymbol{a}}_r|lm\rangle + \langle l+1,m-1|\hat{\boldsymbol{a}}_r|lm\rangle + \langle l+1,m|\hat{\boldsymbol{a}}_r|lm\rangle|^2 \tag{12.193}$$

$$= \frac{1}{2}(A_{lm}^+)^2 + \frac{1}{2}(A_{lm}^-)^2 + (A_{lm})^2, \tag{12.194}$$

where we have taken into account that

$$\hat{\boldsymbol{a}}_\pm^2 = \frac{1}{2}, \quad \hat{\boldsymbol{a}}_z^2 = 1. \tag{12.195}$$

This result, combined with the appropriate ones, gives for the decay probability from state (n,l,m) to state $(n,l+1,m')$, for all allowed m',

$$A_{nlm\to n',l+1,m'} = \frac{4e^2\omega_{nn'}^3}{3\hbar c^3}\,|\langle n',l+1|r|nl\rangle|^2\left[\frac{1}{2}(A_{lm}^+)^2 + \frac{1}{2}(A_{lm}^-)^2 + (A_{lm})^2\right] \tag{12.196}$$

$$= \frac{4e^2\omega_{nn'}^3}{3\hbar c^3}\,\frac{l+1}{2l+1}\,|\langle n',l+1|r|nl\rangle|^2\,. \tag{12.197}$$

This is the equation that was requested. Now consider the transitions $(nlm)\to(n',l-1,m')$, for which we have

$$\langle l-1,m'|\hat{\boldsymbol{a}}_r|lm\rangle = \hat{\boldsymbol{a}}_+B_{lm}^+\delta_{m',m+1} + \hat{\boldsymbol{a}}_-B_{lm}^-\delta_{m',m-1} + \hat{\boldsymbol{a}}_zB_{lm}\delta_{m',m}. \tag{12.198}$$

The transition probability becomes

$$|\langle l-1,m+1|\hat{\boldsymbol{a}}_r|lm\rangle + \langle l-1,m-1|\hat{\boldsymbol{a}}_r|lm\rangle + \langle l-1,m|\hat{\boldsymbol{a}}_r|lm\rangle|^2 \tag{12.199}$$

$$= \frac{1}{2}(B^+_{lm})^2 + \frac{1}{2}(B^-_{lm})^2 + (B_{lm})^2 = \frac{l}{2l-1}. \tag{12.200}$$

Thus,

$$A_{nlm\to n',l-1,\text{all } m'} = \frac{4e^2\omega^3_{nn'}}{3\hbar c^3}\frac{l}{2l-1}\left|\langle n', l-1|r|nl\rangle\right|^2. \tag{12.201}$$

P12.15 Calculate the mean lifetime of the hydrogen-like $3s$ state.
Solution. The hydrogen-like $3s$ state can spontaneously decay only to the $2p$ state, since the transition to the ground state $1s$ is forbidden. Since this is a transition $l \to l+1$ (with $l = 0$), we must apply equation

$$A_{nl\to n',l+1} = \frac{4e^2\omega^3_{nn'}}{3\hbar c^3}\frac{l+1}{2l+1}\left|\langle n', l+1 \mid r \mid nl\rangle\right|^2. \tag{12.202}$$

to determine the transition probability, which gives

$$A_{3s\to 2p} = \frac{4e^2\omega^3_{32}}{3\hbar c^3}\left|\langle 2\ 1 \mid r \mid 3\ 0\rangle\right|^2. \tag{12.203}$$

The radial wave functions for the hydrogen states $|2\ 1\rangle$ and $|3\ 0\rangle$ are:

$$R_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{1}{2a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}, \tag{12.204}$$

$$R_{30}(r) = 2\left(\frac{1}{3a_0}\right)^{3/2}\left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right)e^{-r/3a_0}, \tag{12.205}$$

which gives

$$\langle 2\ 1 \mid r \mid 3\ 0\rangle = \int_0^\infty r^3 R_{21}(r)R_{30}(r)\,dr \tag{12.206}$$

$$= \frac{1}{9\sqrt{2}a_0^4}\left(\int_0^\infty r^4 e^{-5r/6a_0}\,dr - \frac{2}{3a_0}\int_0^\infty r^5 e^{-5r/6a_0}\,dr + \frac{2}{27a_0^2}\int_0^\infty r^6 e^{-5r/6a_0}\,dr\right).$$

Using

$$\int_0^\infty x^n e^{-x}\,dx = n!, \tag{12.207}$$

we find

$$\langle 2\ 1 \mid r \mid 3\ 0\rangle = \frac{4}{9\sqrt{2}}\left(\frac{6}{5}\right)^6 a_0. \tag{12.208}$$

On the other hand, since

$$\omega_{32} = \frac{E_3 - E_2}{\hbar} = \frac{me^4}{2\hbar^3 c}\left(\frac{1}{4} - \frac{1}{9}\right) = \frac{5}{36}Rc, \tag{12.209}$$

$$R = \frac{\alpha}{2a_0}, \quad \alpha = \frac{e^2}{\hbar c}, \tag{12.210}$$

we obtain

$$A_{3s\to 2p} = 3\left(\frac{2}{5}\right)^9 \alpha^3 Rc. \tag{12.211}$$

Using the approximate values

$$Rc \simeq 2\times 10^6\,\mathrm{s}^{-1}, \quad \alpha \simeq \frac{1}{137},$$

we get

$$A_{3s\to 2p} = 6.12\times 10^6\,\mathrm{s}^{-1}.$$

Therefore, the mean lifetime of the hydrogen 3s state is

$$T_{3s} = \frac{1}{A_{3s\to 2p}} \simeq 1.63\times 10^{-7}\,\mathrm{s}. \tag{12.212}$$

P12.16 Show that when a quantum system has two or more operators that commute with the Hamiltonian but not with each other, in general the states of the system are degenerate. What general property of the system does this fact reflect?
Solution. Let F and G be the two non-commuting operators and

$$F|n\rangle = f_n|n\rangle, \quad G|n\rangle = g_n|n\rangle \tag{12.213}$$

their eigenvalue equations. Since F and G do not commute, in general we will have $\varphi_n \neq \psi_n$. However, since both operators commute with the Hamiltonian, it must have both φ_n and ψ_n as eigenfunctions, so

$$\hat{H}\varphi_n = E_n\varphi_n, \quad \hat{H}\psi_n = E_n\psi_n. \tag{12.214}$$

The way to satisfy both Eqs. (12.214) simultaneously is by writing, for example,

$$\psi_n = \sum_i c_{n_i}\varphi_{n_i}, \quad \text{with } \hat{H}\varphi_{n_i} = E_n\varphi_{n_i}, \tag{12.215}$$

where each of the functions φ_{n_i} corresponds to the same eigenvalue E_n of $\hat{H}$, but may correspond to different eigenvalues of $\hat{F}$. That the expansion (12.215) can be made follows from this fact, since the eigenfunctions of the Hamiltonian form a basis of the corresponding Hilbert space, which is contained in that of the operators $\hat{F}$ and $\hat{G}$, given that these commute with the Hamiltonian. Since in general the functions φ_n and ψ_n are different, we should expect that more than one coefficient c_{n_i} will be non-zero. This expansion means that the eigenfunctions φ_{n_i} of $\hat{H}$ require an additional index i for their characterization, and that the energy does not depend on this index. In other words, in general, the eigenstates of $\hat{H}$ are degenerate in this case.

A simple yet illustrative example of such a situation is provided by the angular momentum in a central potential problem. Since it is a conserved quantity (as $\hat{\boldsymbol{L}} = \boldsymbol{r}\times\boldsymbol{F} = 0$), each of its Cartesian components commutes with the Hamiltonian, although they themselves do not commute with each other. If there were only

one angular momentum component, which we could denote as $\hat{l}$, the eigenstates of the system would be characterized by the quantum numbers n for energy and l for angular momentum, giving the basis $|nl\rangle$. But the existence of the operator $\hat{L}_x$, for example, which also commutes with the Hamiltonian and corresponds to the same angular momentum l, but does not commute with the other angular momentum projections, has its specific eigenfunctions of the form $\sum_m c_{lm} Y_l^m(\Omega)$, which demands the existence of the quantum number m and gives rise to the states $|nlm\rangle$. The system is degenerate with respect to this quantum number, precisely due to the central symmetry of the problem, which makes the Hamiltonian independent of any preferred direction and therefore independent of the arbitrary orientation of the z- axis.As a specific example, consider the rigid rotor, whose general wave function we write in the form

$$\psi(t) = \sum_{l,m} c_{lm} Y_l^m e^{-iEt/\hbar}. \tag{12.216}$$

The expectation values of H, $\hat{L}_z$, and $\hat{L}_\pm$ in this state are

$$\left\langle \hat{H} \right\rangle = \sum_{l,m} E_l \left| c_{lm} \right|^2, \tag{12.217}$$

$$\left\langle \hat{L}_z \right\rangle = \hbar \sum_{l,m} m \left| c_{lm} \right|^2, \tag{12.218}$$

$$\left\langle \hat{L}_\pm \right\rangle = -\hbar \sum_{l,m} \sqrt{(l \pm m - 1)(l \mp m)}\, c^*_{lm\pm1} c_{lm}. \tag{12.219}$$

In general, one might expect that the expectation value of operators for which Y_l^m is not an eigenfunction would depend on time. However, we see that this is not the case for $\hat{L}_\pm$, since this operator commutes with the Hamiltonian, and its average value is given by combinations of amplitudes $c^*_{lm\pm1}$, c_{lm} that refer to different states (different m's) but with the same l, that is, the same energy E_l. Therefore, the eigenvalue E_l generally corresponds to multiple wave functions. It is clear, however, that the expectation value of an operator that commutes with $\hat{L}_z$ but not with H depends explicitly on time. For example, we have

$$\langle z \rangle = \sum_{l,m} \sqrt{\frac{(l-m+1)(l+m+1)}{(2l+1)(2l+3)}} c^*_{l+1,m} c_{lm} e^{i\omega_{l+1,l}t}$$

$$+ \sum_{l,m} \sqrt{\frac{(l-m)(l+m)}{(2l+1)(2l-1)}} c^*_{l-1,m} c_{lm} e^{-i\omega_{l,l-1}t}$$

P12.17 Prove that in the presence of a magnetic field, $m\hat{v}_i = \hat{p}_i - \frac{e}{c}A_i$, and the velocities $\hat{v}_i$ satisfy the commutation relations

$$[\hat{v}_i, \hat{v}_j] = \frac{ie\hbar}{m^2 c}\varepsilon_{ijk}B_k. \tag{12.220}$$

Solution. The canonical momentum of quantum particles in the presence of a magnetic field is given by

$$\hat{\boldsymbol{p}} = m\hat{\boldsymbol{v}} + \frac{e}{c}\boldsymbol{A}. \tag{12.221}$$

Thus, we can solve for the velocity operator $m\hat{\boldsymbol{v}} = \hat{\boldsymbol{p}} - \frac{e}{c}\boldsymbol{A}$. To derive the commutation relation between velocity components, we write

$$[\hat{v}_i, \hat{v}_j] = \left[\frac{\hat{p}_i}{m} - \frac{e}{mc}A_i, \frac{\hat{p}_j}{m} - \frac{e}{mc}A_j\right]. \tag{12.222}$$

Expanding this expression yields

$$\begin{aligned}[\hat{v}_i, \hat{v}_j] &= \frac{1}{m^2}[\hat{p}_i, \hat{p}_j] - \frac{e}{mc}\left([\hat{p}_i, A_j] + [A_i, \hat{p}_j]\right) + \frac{e^2}{m^2c^2}[A_i, A_j] \\ &= -\frac{e}{m^2 c}\left([\hat{p}_i, A_j] + [A_i, \hat{p}_j]\right),\end{aligned} \tag{12.223}$$

where we used $[\hat{p}_i, \hat{p}_j] = 0$ and $[A_i, A_j] = 0$. Since $\boldsymbol{A} = \boldsymbol{A}(x, y, z)$ and

$$\left[\hat{p}, \hat{G}(\hat{x})\right] = -i\hbar\frac{d\hat{G}}{d\hat{x}}, \tag{12.224}$$

the commutators are

$$[\hat{p}_i, A_j] = -i\hbar\partial_i A_j \qquad\qquad [A_i, \hat{p}_j] = i\hbar\partial_j A_i. \tag{12.225}$$

Substituting these results into (12.223), we obtain

$$\begin{aligned}[\hat{v}_i, \hat{v}_j] &= -\frac{e}{m^2 c}\left([\hat{p}_i, A_j] + [A_i, \hat{p}_j]\right) \\ &= -\frac{e}{m^2 c}\left(-i\hbar\partial_i A_j + i\hbar\partial_j A_i\right) \\ &= \frac{ie\hbar}{m^2 c}\left(\partial_i A_j - \partial_j A_i\right).\end{aligned} \tag{12.226}$$

From $\boldsymbol{\nabla} \times \boldsymbol{A} = \boldsymbol{B}$, we have

$$(\boldsymbol{\nabla} \times \boldsymbol{A})_k = \varepsilon_{kmn}\partial_m A_n = B_k. \tag{12.227}$$

Inserting ε_{ijk} in both sides, we obtain

$$\varepsilon_{ijk}\varepsilon_{kmn}\partial_m A_n = \varepsilon_{ijk}B_k. \tag{12.228}$$

Using the Levi-Civita symbol identity

$$\varepsilon_{ijk}\varepsilon_{kmn} = \delta_{im}\delta_{jn} - \delta_{in}\delta_{jm}, \tag{12.229}$$

we find

$$\partial_i A_j - \partial_j A_i = \varepsilon_{ijk}B_k. \tag{12.230}$$

Substituting into Eq. (12.226), we finally get

$$[\hat{v}_i, \hat{v}_j] = \frac{ie\hbar}{m^2 c}\varepsilon_{ijk}B_k. \tag{12.231}$$

P12.18 Determine the wavelength of the three Zeeman lines produced at the $3d \to 2p$ transition of an H atom placed in a 10^4 Gauss magnetic field.
Solution. The transition $n = 3 \to n = 2$ corresponds to the Hα line of the Balmer series.The wavelength without a magnetic field for Hα is $\lambda_0 = 656.3$ nm (standard value).The photon energy without a field is, with $hc \approx 1240$ eV $\cdot$ nm,

$$E_0 = \frac{hc}{\lambda_0}E_0 = \frac{1240}{656.3} \approx 1.8890 \text{ eV}. \tag{12.232}$$

In the normal Zeeman effect (ignoring spin contributions), the magnetic field splits each level into $2l+1$ sublevels according to the orbital magnetic quantum number m_l,

- 3d level: $l = 2$, $m_l = -2, -1, 0, 1, 2$.
- 2p level: $l = 1$, $m_l = -1, 0, 1$.

The energy shift for each level is

$$\Delta E = m_l \mu_B B, \tag{12.233}$$

where $\mu_B = 5.788 \times 10^{-5}$ eV/T is the Bohr magneton and $B = 1$ T. For a transition with $\Delta m_l = m_{l,\text{upper}} - m_{l,\text{lower}} = 0, \pm 1$, the photon energy change is

$$\delta E = \mu_B B \Delta m_l. \tag{12.234}$$

The three Zeeman lines correspond to: π component $\Delta m_l = 0$, $\delta E = 0$. σ^+ component $\Delta m_l = +1$, $\delta E = +\mu_B B$ (positive energy shift). and σ^- component $\Delta m_l = -1$, $\delta E = -\mu_B B$ (negative energy shift). For $B = 1$ T,

$$\mu_B B = (5.788 \times 10^{-5} \text{ eV/T}) \times (1 \text{ T}) = 5.788 \times 10^{-5} \text{ eV}. \tag{12.235}$$

The wavelength shift is calculated using

$$|\delta\lambda| = \frac{\lambda_0^2}{hc}|\delta E|, \tag{12.236}$$

where $\lambda_0 = 656.3$ nm, $hc = 1240$ eV $\cdot$ nm, $\lambda_0^2 = (656.3)^2 = 430705.69$ nm^2 and $\lambda_0^2/hc = 430705.69/1240 \approx 347.342$ nm/eV. For $\delta E = \mu_B B = 5.788 \times 10^{-5}$ eV,

$$|\delta\lambda| = 347.342 \times 5.788 \times 10^{-5} \approx 0.0201 \text{ nm}. \tag{12.237}$$

The wavelengths of the three lines are:
σ^+ component ($\Delta m_l = +1$, shorter wavelength)

$$\lambda_{\sigma^+} = \lambda_0 - |\delta\lambda| = 656.3 - 0.0201 = 656.2799 \text{ nm} \approx 656.280 \text{ nm}, \tag{12.238}$$

π component ($\Delta m_l = 0$, no shift)

$$\lambda_\pi = \lambda_0 = 656.300 \text{ nm}. \tag{12.239}$$

σ^- component ($\Delta m_l = -1$, longer wavelength)

$$\lambda_{\sigma^-} = \lambda_0 + |\delta\lambda| = 656.3 + 0.0201 = 656.3201 \text{ nm} \approx 656.320 \text{ nm}. \tag{12.240}$$

CHAPTER 13

Stationary Perturbation Theory and the Variational Method

P13.1 Show that if $\hat{f}$ is a dynamical variable of a perturbed system, its first-order perturbed matrix elements are

$$f_{nm} = f_{nm}^{(0)} + \sum_{k\neq n} \frac{V_{nk} f_{km}^{(0)}}{E_n^{(0)} - E_k^{(0)}} + \sum_{k\neq m} \frac{V_{km} f_{nk}^{(0)}}{E_m^{(0)} - E_k^{(0)}}. \tag{13.1}$$

Solution. To first order in perturbation theory, the wave function is given by Eq. (13.3), [**1**]. Therefore, the matrix element f_{nm} of a generic dynamical variable $\hat{f}$ of the system is, to first order,

$$f_{nm} = \left\langle \Psi_n | \hat{f} | \Psi_m \right\rangle = \left\langle \psi_n^{(0)} + \sum_l C_{nl}^{(1)} \psi_l^{(0)} \middle| \hat{f} \middle| \psi_m^{(0)} + \sum_k C_{mk}^{(1)} \psi_k^{(0)} \right\rangle$$

$$= \left\langle \psi_n^{(0)} \middle| \hat{f} \middle| \psi_m^{(0)} \right\rangle + \sum_k C_{mk}^{(1)} \left\langle \psi_n^{(0)} \middle| \hat{f} \middle| \psi_k^{(0)} \right\rangle + \sum_l C_{nl}^{(1)} \left\langle \psi_l^{(0)} \middle| \hat{f} \middle| \psi_m^{(0)} \right\rangle, \tag{13.2}$$

that is,

$$f_{nm} = f_{nm}^{(0)} + \sum_k C_{mk}^{(1)} f_{nk}^{(0)} + \sum_l C_{nl}^{(1)} f_{lm}^{(0)}. \tag{13.3}$$

Recalling that $C_{nn}^{(1)} = 0$, we have

$$f_{nm} = f_{nm}^{(0)} + \sum_{k\neq m} C_{mk}^{(1)} f_{nk}^{(0)} + \sum_{k\neq n} C_{nk}^{(1)} f_{km}^{(0)}. \tag{13.4}$$

Using the formula

$$C_{nl}^{(1)} = \frac{V_{ln}}{E_n^{(0)} - E_l^{(0)}}, \tag{13.5}$$

we find that, to first order in perturbation theory, the matrix elements of a generic dynamical variable can be written as

$$f_{nm} = f_{nm}^{(0)} + \sum_{k\neq n} \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} f_{km}^{(0)} + \sum_{k\neq m} \frac{V_{km}}{E_m^{(0)} - E_k^{(0)}} f_{nk}^{(0)}. \tag{13.6}$$

It is clear that this result can only be applied when the levels n, m are non-degenerate, and their energies are sufficiently separated from those of any possible intermediate state k, such that none of the denominators

$$E_n^{(0)} - E_k^{(0)} \text{ or } E_m^{(0)} - E_k^{(0)}$$

becomes so small that the correction terms cease to be small compared to $f^{(0)}_{nm}$. In particular, for the expectation value in the state n we obtain (taking into account that $f_{nk} = f^*_{kn}$)

$$f_{nn} = f^{(0)}_{nn} + \sum_{k\neq n} \frac{V_{kn}}{E^{(0)}_n - E^{(0)}_k} \left(f^{(0)}_{nk} + f^{(0)*}_{nk} \right), \tag{13.7}$$

while for dynamical variables with diagonal matrices (the constants of motion) it follows from (13.6) that

$$f_{nm} = f^{(0)}_{nm} + \frac{f^{(0)}_{mm} V_{mn} - f^{(0)}_{nn} V_{nm}}{E^{(0)}_n - E^{(0)}_m}. \tag{13.8}$$

We note that, to first order, all constants of motion remain unchanged,

$$f_{nn} = f^{(0)}_{nn}. \tag{13.9}$$

P13.2 The potential of a one-dimensional anharmonic oscillator can be approximated by the expression

$$V = \frac{1}{2} m\omega^2 x^2 \left[1 + \alpha \frac{x}{x_0} + \beta \left(\frac{x}{x_0} \right)^2 \right], \tag{13.10}$$

where $x_0 = \sqrt{\hbar/m\omega}$. Use perturbation theory to determine the corrections to the energy up to second order and the first-order wave functions. Use your results to calculate $\langle x \rangle, \langle \hat{p} \rangle, \langle (\Delta x)^2 \rangle, \langle (\Delta p)^2 \rangle$.

Solution. The Hamiltonian of the problem can be written as

$$\hat{H} = \hat{H}_0 + \hat{H}', \tag{13.11}$$

where

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 x^2 \tag{13.12}$$

is the Hamiltonian of the one-dimensional harmonic oscillator, and

$$\hat{H}' \equiv V(x) = \frac{1}{2} m\omega^2 \alpha \frac{x^3}{x_0} + \frac{1}{2} m\omega^2 \beta \frac{x^4}{x_0^2} \tag{13.13}$$

is the remaining part of the Hamiltonian, which will be treated as a perturbation, assuming that α and β are sufficiently small parameters. Since this is a one-dimensional problem, all states are non-degenerate and it is possible to apply perturbation theory for non-degenerate systems. The eigenfunctions of $\hat{H}_0$ are

$$\psi^{(0)}_n = \psi_n = \left(\sqrt{\pi}\, 2^n n!\, x_0 \right)^{-1/2} e^{-x^2/2x_0^2} H_n \left(\frac{x}{x_0} \right), \tag{13.14}$$

corresponding to the eigenvalues

$$E_n^{(0)} = \hbar\omega\left(n + \frac{1}{2}\right). \tag{13.15}$$

To obtain the energy corrections to different orders of approximation, we require the matrix elements of the perturbation Hamiltonian

$$V_{nn'} \equiv \langle n|\hat{H}'|n'\rangle = \frac{1}{2}m\omega^2\left(\frac{\alpha}{x_0}\langle n|x^3|n'\rangle + \frac{\beta}{x_0^2}\langle n|x^4|n'\rangle\right). \tag{13.16}$$

To calculate these elements we will use the methods of [**1**], **Chapter 9**, which involve the creation and annihilation operators. From

$$x = \frac{x_0}{\sqrt{2}}\left(\hat{a} + \hat{a}^\dagger\right), \tag{13.17}$$

we obtain, using

$$\hat{a}\psi_n = \sqrt{n}\psi_{n-1},\ \hat{a}^\dagger\psi_n = \sqrt{n+1}\psi_{n+1}$$

repeatedly.

$$x|n\rangle = \frac{x_0}{\sqrt{2}}\left(\sqrt{n+1}\,|n+1\rangle + \sqrt{n}\,|n-1\rangle\right), \tag{13.18}$$

$$x^2|n\rangle = \frac{x_0^2}{2}\left(\sqrt{(n+1)(n+2)}\,|n+2\rangle + (2n+1)|n\rangle + \sqrt{n(n-1)}\,|n-2\rangle\right), \tag{13.19}$$

$$\begin{aligned} x^3|n\rangle = \frac{x_0^3}{2\sqrt{2}}\Big[&\sqrt{(n+1)(n+2)(n+3)}\,|n+3\rangle + 3(n+1)\sqrt{n+1}\,|n+1\rangle \\ &+ 3n\sqrt{n}\,|n-1\rangle + \sqrt{n(n-1)(n-2)}\,|n-3\rangle\Big], \end{aligned} \tag{13.20}$$

$$\begin{aligned} x^4|n\rangle = \frac{x_0^4}{4}\Big[&\sqrt{(n+1)(n+2)(n+3)(n+4)}\,|n+4\rangle \\ &+ (4n+6)\sqrt{(n+1)(n+2)}\,|n+2\rangle + \left(3n^2 + 3(n+1)^2\right)|n\rangle \\ &+ (4n-2)\sqrt{n(n-1)}\,|n-2\rangle + \sqrt{n(n-1)(n-2)(n-3)}\,|n-4\rangle\Big]. \end{aligned} \tag{13.21}$$

Thus, we have

$$
\begin{aligned}
V_{nn'} = \frac{\alpha\hbar\omega}{4\sqrt{2}}\Big\{ & \sqrt{(n'+1)(n'+2)(n'+3)}\,\delta_{n,n'+3} + 3(n'+1)^{3/2}\,\delta_{n,n'+1} + 3(n')^{3/2}\,\delta_{n,n'-1} \\
& + \sqrt{n'(n'-1)(n'-2)}\,\delta_{n,n'-3}\Big\} \\
& + \frac{\beta}{8}\hbar\omega\Big\{ \sqrt{(n'+1)(n'+2)(n'+3)(n'+4)}\,\delta_{n,n'+4} \\
& \quad + (4n'+6)\sqrt{(n'+1)(n'+2)}\,\delta_{n,n'+2} + \left(3n'^2 + 3(n'+1)^2\right)\delta_{n,n'} \\
& \quad + (4n'-2)\sqrt{n'(n'-1)}\,\delta_{n,n'-2} + \sqrt{n'(n'-1)(n'-2)(n'-3)}\,\delta_{n,n'-4}\Big\}.
\end{aligned}
\tag{13.22}
$$

To first order in perturbation theory, the energy correction is given by

$$
\delta E_n^{(1)} = \langle n|\hat{H}'|n\rangle = V_{nn}. \tag{13.23}
$$

From (13.22) we see that $\langle n|\hat{H}'|n\rangle$ contains only one term, coming from the part of the perturbative potential proportional to x^4; specifically,

$$
\delta E_n^{(1)} = \frac{3}{4}\beta\hbar\omega\left(n^2 + n + \frac{1}{2}\right). \tag{13.24}
$$

This is the entire first-order energy correction from perturbation theory. Later, after calculating the first corrections to the wave functions, the second-order corrections to the energy will be determined. The above result can be regarded as a perturbation if (among other conditions)

$$
\frac{\delta E_n^{(1)}}{E_n^{(0)}} = \frac{3}{4}\beta\left(\frac{n^2}{n+\frac{1}{2}} + 1\right) \ll 1. \tag{13.25}
$$

For the ground state it suffices that $\frac{3}{4}\beta \ll 1$; but for highly excited states the condition becomes much more restrictive, $\frac{3}{4}\beta n \ll 1$.We write the first-order wave functions (from perturbation theory) in the form

$$
\Psi_n = \psi_n + \sum_l C_{nl}^{(1)}\,\psi_l, \tag{13.26}
$$

with the coefficients given by

$$
C_{nl}^{(1)} = \frac{V_{ln}}{E_n^{(0)} - E_l^{(0)}}. \tag{13.27}
$$

From (13.22) we see that the only non-zero matrix elements of the perturbative potential involving the state n, and the corresponding corrections to the wave function, are the following:

a) Generated by the perturbation $\sim x^3$:

$$C_{n,n+3} = \frac{V_{n+3,n}}{-3\hbar\omega} = -\frac{\alpha}{12\sqrt{2}}\sqrt{(n+1)(n+2)(n+3)}; \tag{13.28}$$

$$C_{n,n+1} = \frac{V_{n+1,n}}{-\hbar\omega} = -\frac{\alpha}{4\sqrt{2}}\,3(n+1)\sqrt{n+1}; \tag{13.29}$$

$$C_{n,n-1} = \frac{V_{n-1,n}}{\hbar\omega} = \frac{\alpha}{4\sqrt{2}}\,3n\sqrt{n}; \tag{13.30}$$

$$C_{n,n-3} = \frac{V_{n-3,n}}{3\hbar\omega} = \frac{\alpha}{12\sqrt{2}}\sqrt{n(n-1)(n-2)}. \tag{13.31}$$

b) Generated by the perturbation $\sim x^4$:

$$C_{n,n+4} = \frac{V_{n+4,n}}{-4\hbar\omega} = -\frac{\beta}{32}\sqrt{(n+1)(n+2)(n+3)(n+4)}; \tag{13.32}$$

$$C_{n,n+2} = \frac{V_{n+2,n}}{-2\hbar\omega} = -\frac{\beta}{16}(4n+6)\sqrt{(n+1)(n+2)}; \tag{13.33}$$

$$V_{n,n} = \frac{\beta}{8}\hbar\omega\left[3n^2 + 3(n+1)^2\right]; \tag{13.34}$$

$$C_{n,n-2} = \frac{V_{n-2,n}}{2\hbar\omega} = \frac{\beta}{16}(4n-2)\sqrt{n(n-1)}; \tag{13.35}$$

$$C_{n,n-4} = \frac{V_{n-4,n}}{4\hbar\omega} = \frac{\beta}{32}\sqrt{n(n-1)(n-2)(n-3)}. \tag{13.36}$$

The first-order wave function of state n in perturbation theory is given by

$$\begin{aligned}\Psi_n = \psi_n &+ \frac{\alpha}{4\sqrt{2}}\left\{-\sqrt{n+1}\left[\frac{1}{3}\sqrt{(n+2)(n+3)}\,\psi_{n+3} + 3(n+1)\,\psi_{n+1}\right]\right.\\ &\left.+\sqrt{n}\left[3n\,\psi_{n-1} + \frac{1}{3}\sqrt{(n-1)(n-2)}\,\psi_{n-3}\right]\right\}\\ &+\frac{\beta}{8}\left\{\sqrt{n(n-1)}\left[\frac{1}{4}\sqrt{(n-2)(n-3)}\,\psi_{n-4} + (2n-1)\,\psi_{n-2}\right]\right.\\ &\left.-\sqrt{(n+1)(n+2)}\left[(2n+3)\,\psi_{n+2} + \frac{1}{4}\sqrt{(n+3)(n+4)}\,\psi_{n+4}\right]\right\}.\end{aligned} \tag{13.37}$$

With the above results we can now compute the second-order correction to the energy. Using the formula

$$\delta E_n^{(2)} = \sum_{n'\neq n}\frac{|V_{nn'}|^2}{E_n^{(0)} - E_{n'}^{(0)}}. \tag{13.38}$$

Substituting the non-zero matrix elements and simplifying, we find

$$\begin{aligned}\delta E_n^{(2)} = \frac{\alpha^2\hbar\omega}{32}\Bigg[&-\frac{1}{3}(n+1)(n+2)(n+3) - 9(n+1)^3 \\ &+ 9n^3 + \frac{1}{3}n(n-1)(n-2)\Bigg] \\ &+ \frac{\beta^2\hbar\omega}{64}\Bigg[\frac{1}{4}n(n-1)(n-2)(n-3) + \frac{1}{2}(4n-2)^2 n(n-1) \\ &- \frac{1}{2}(4n+6)^2(n+1)(n+2) - \frac{1}{4}(n+1)(n+2)(n+3)(n+4)\Bigg] \end{aligned} \tag{13.39}$$

$$= -\frac{15}{16}\alpha^2\hbar\omega\left(n^2+n+\frac{11}{30}\right) - \frac{1}{32}\beta^2\hbar\omega\left(34n^3+51n^2+59n+21\right).$$

As expected, this correction is negative for all levels. We now calculate the requested expectation values using the wave function corrected to first order. Using Eqs. (13.18) and (13.19), we obtain, to this order,

$$\begin{aligned} x\Psi_n = \frac{x_0}{\sqrt{2}}\Big\{&\sqrt{n+1}\,\psi_{n+1} + \sqrt{n}\,\psi_{n-1} \\ &+ \frac{\alpha}{12\sqrt{2}}\Big[-\sqrt{(n+1)(n+2)} \\ &\times\left(\sqrt{(n+3)(n+4)}\,\psi_{n+4} + (10n+12)\,\psi_{n+2}\right) \\ &- 9(2n+1)\,\psi_n + \sqrt{n(n-1)} \\ &\times\left((10n+12)\,\psi_{n-2} + \sqrt{(n-2)(n-3)}\,\psi_{n-4}\right)\Big] \\ &+ \frac{\beta}{32}\Big[-\sqrt{(n+1)(n+2)(n+3)(n+4)(n+5)}\,\psi_{n+5} \\ &- (9n+16)\sqrt{(n+1)(n+2)(n+3)}\,\psi_{n+3} \\ &- 4(2n+3)(n+2)\sqrt{n+1}\,\psi_{n+1} \\ &+ 4(2n-1)(n-1)\sqrt{n}\,\psi_{n-1} \\ &+ (9n-7)\sqrt{n(n-1)(n-2)}\,\psi_{n-3} \\ &+\sqrt{n(n-1)(n-2)(n-3)(n-4)}\,\psi_{n-5}\Big]\Big\}, \end{aligned} \tag{13.40}$$

$$
\begin{aligned}
x^2\Psi_n = \frac{x_0^2}{2}\Bigg\{ & \sqrt{(n+1)(n+2)}\,\psi_{n+2} + (2n+1)\,\psi_n + \sqrt{n(n-1)}\,\psi_{n-2} \\
& + \frac{\alpha}{12\sqrt{2}}\Big[- \sqrt{(n+1)(n+2)(n+3)(n+4)(n+5)}\,\psi_{n+5} \\
& - (11n+16)\sqrt{(n+1)(n+2)(n+3)}\,\psi_{n+3} \\
& - (10n^2+50n+33)\sqrt{n+1}\,\psi_{n+1} \\
& + (10n^2-30n-7)\sqrt{n}\,\psi_{n-1} + (11n-5)\sqrt{n(n-1)(n-2)}\,\psi_{n-3} \\
& + \sqrt{n(n-1)(n-2)(n-3)(n-4)}\,\psi_{n-5}\Big] \\
& + \frac{\beta}{32}\Big[- \sqrt{(n+1)(n+2)(n+3)(n+4)(n+5)(n+6)}\,\psi_{n+6} \\
& - (10n+21)\sqrt{(n+1)(n+2)(n+3)(n+4)}\,\psi_{n+4} \\
& - (17n^2+71n+72)\sqrt{(n+1)(n+2)}\,\psi_{n+2} \\
& - 4(12n^2+12n+6)\,\psi_n + (17n^2-37n+18)\sqrt{n(n-1)}\,\psi_{n-2} \\
& + (10n-11)\sqrt{n(n-1)(n-2)(n-3)}\,\psi_{n-4} \\
& + \sqrt{(n-1)(n-2)(n-3)(n-4)(n-5)}\,\psi_{n-6}\Big]\Bigg\}. \qquad (13.41)
\end{aligned}
$$

From these expressions we get for the expectation value of x

$$\langle\Psi_n|x|\Psi_n\rangle = \frac{3}{8}x_0\left[\alpha\left(n^2-3n-2\right) + \frac{1}{8}\alpha\beta\left(9n^4+18n^3+59n^2+50n+\frac{52}{3}\right)\right]. \qquad (13.42)$$

However, the contribution proportional to $\alpha\beta$ is not reliable, since the second-order wave functions may contain terms that generate additional contributions of this nature. The firm conclusion we can draw is that the expectation value of x, calculated to first order in perturbation theory, is

$$\langle\Psi_n|x|\Psi_n\rangle = \frac{3}{8}x_0\alpha\left(n^2-3n-2\right). \qquad (13.43)$$

Similarly, we obtain for the expectation value of x^2 calculated to first order, that is, omitting all non-linear terms in α and β,

$$\langle\Psi_n|x^2|\Psi_n\rangle = x_0^2\left[\left(n+\frac{1}{2}\right) + \frac{3}{4}\beta\left(n^2+n+\frac{1}{2}\right)\right]. \qquad (13.44)$$

The variance or spread of the position variable to this order of approximation is

$$\langle(\Delta x)^2\rangle = \langle x^2\rangle - \langle x\rangle^2 = x_0^2\left[\left(n+\frac{1}{2}\right) + \frac{3}{4}\beta\left(n^2+n+\frac{1}{2}\right)\right]. \qquad (13.45)$$

The analogous calculation for the momentum can be done starting from the expression $\hat{p} = \frac{i\hbar}{x_0\sqrt{2}}\left(\hat{a}^\dagger - \hat{a}\right)$, which leads to

$$\begin{aligned}
\hat{p}\Psi_n = &\frac{i\hbar}{x_0\sqrt{2}}\left(\sqrt{n+1}\,\psi_{n+1} - \sqrt{n}\,\psi_{n-1}\right) \\
&+ \frac{i\hbar}{x_0\sqrt{2}}\Bigg\{\frac{\alpha}{12\sqrt{2}}\Big[-\sqrt{(n+1)(n+2)(n+3)(n+4)}\,\psi_{n+4} \\
&- (8n+6)\sqrt{(n+1)(n+2)}\,\psi_{n+2} + 9\left(2n^2+2n+1\right)\psi_n \\
&- (8n+2)\sqrt{n(n-1)}\,\psi_{n-2} - \sqrt{n(n-1)(n-2)(n-3)}\,\psi_{n-4}\Big] \\
&+ \frac{\beta}{32}\Big[-\sqrt{(n+1)(n+2)(n+3)(n+4)(n+5)}\,\psi_{n+5} \\
&- (7n+8)\sqrt{(n+1)(n+2)(n+3)}\,\psi_{n+3} + 4(2n+3)(n+2)\sqrt{n+1}\,\psi_{n+1} \\
&+ 4(2n-1)(n-1)\sqrt{n}\,\psi_{n-1} + (1-7n)\sqrt{n(n-1)(n-2)}\,\psi_{n-3} \\
&- \sqrt{n(n-1)(n-2)(n-3)(n-4)}\,\psi_{n-5}\Big]\Bigg\},
\end{aligned} \tag{13.46}$$

$$\begin{aligned}
\hat{p}^2\Psi_n = &-\frac{\hbar^2}{2x_0^2}\Bigg\{\sqrt{(n+1)(n+2)}\,\psi_{n+2} - (2n+1)\,\psi_n + \sqrt{n(n-2)}\,\psi_{n-2} \\
&+ \frac{\alpha}{12\sqrt{2}}\Big[-\sqrt{(n+1)(n+2)(n+3)(n+4)(n+5)}\,\psi_{n+5} \\
&- (7n+2)\sqrt{(n+1)(n+2)(n+3)}\,\psi_{n+3} + (26n^2+40n+21)\sqrt{n+1}\,\psi_{n+1} \\
&- (26n^2+12n+7)\sqrt{n}\,\psi_{n-1} + (7n+5)\sqrt{n(n-1)(n-2)}\,\psi_{n-3} \\
&+ \sqrt{n(n-1)(n-2)(n-3)(n-4)}\,\psi_{n-5}\Big] \\
&+ \frac{\beta}{32}\Big[-\sqrt{(n+1)(n+2)(n+3)(n+4)(n+5)(n+6)}\,\psi_{n+6} \\
&- (6n+3)\sqrt{(n+1)(n+2)(n+3)(n+4)}\,\psi_{n+4} + (15n^2+57n+48)\sqrt{(n+1)(n+2)}\,\psi_{n+2} \\
&- 24(2n^2+2n+1)\,\psi_n - (15n^2-27n+6)\sqrt{n(n-1)}\,\psi_{n-2} \\
&+ (6n+3)\sqrt{n(n-1)(n-2)(n-3)}\,\psi_{n-4} \\
&+ \sqrt{(n-1)(n-2)(n-3)(n-4)(n-5)}\,\psi_{n-6}\Big]\Bigg\}.
\end{aligned} \tag{13.47}$$

The corresponding first-order expectation values are

$$\langle\Psi_n|\hat{p}|\Psi_n\rangle = -\frac{i\hbar}{x_0}\frac{3}{4}\alpha\left(n^2+n+\frac{1}{2}\right), \tag{13.48}$$

$$\langle\Psi_n|\hat{p}^2|\Psi_n\rangle = \frac{\hbar^2}{x_0^2}\left[\left(n+\frac{1}{2}\right)+\frac{3}{4}\beta\left(n^2+n+\frac{1}{2}\right)\right]. \tag{13.49}$$

Finally, for the variance of the momentum operator we obtain

$$\left\langle(\Delta\hat{p})^2\right\rangle = \langle\hat{p}^2\rangle - \langle\hat{p}\rangle^2 = \frac{\hbar^2}{x_0^2}\left[\left(n+\frac{1}{2}\right)+\frac{3}{4}\beta\left(n^2+n+\frac{1}{2}\right)\right] = \frac{\hbar^2}{x_0^4}\left\langle(\Delta\hat{x})^2\right\rangle. \tag{13.50}$$

In the above calculation we have considered the wave function corrected to first order and have explicitly kept all the terms that appear in various calculations, which makes the calculation straightforward but laborious.

P13.3 A particle moves on a vertical circle of radius R; neglecting the effects of friction, but taking into account the force of gravity, the Hamiltonian of the system is

$$\hat{H} = \frac{\hat{L}_z^2}{2mR^2} + mgR\sin\varphi. \tag{13.51}$$

Determine the unperturbed solutions, as well as the first- and second- order corrections to the energy, treating the gravitational term as a perturbation. Under what conditions is this solution valid?

Solution. The Hamiltonian of the problem can be written as

$$\hat{H} = \hat{H}_0 + \hat{V}, \tag{13.52}$$

where

$$\hat{H}_0 = \frac{\hat{L}_z^2}{2m_0R^2}, \quad \hat{V} = m_0gR\sin\varphi. \tag{13.53}$$

Assuming the gravitational term $\hat{V}$ is small compared to the Hamiltonian's kinetic energy part associated with rotation, it can be treated as a perturbation, and the problem with Hamiltonian $\hat{H}_0$ becomes the unperturbed system. Since

$$\hat{L}_z^2 = -\hbar^2\frac{\partial^2}{\partial\varphi^2}, \tag{13.54}$$

the eigenvalue equation for this unperturbed problem takes the form

$$-\frac{\hbar^2}{2m_0R^2}\frac{\partial^2\psi_m^{(0)}}{\partial\varphi^2} = E_m^{(0)}\psi_m^{(0)}. \tag{13.55}$$

The eigenfunctions are

$$\psi_m^{(0)} = \frac{1}{\sqrt{2\pi}}e^{im\varphi}, \quad m = 0, \pm1, \pm2, \ldots \tag{13.56}$$

with the corresponding eigenvalues

$$E_m^{(0)} = \frac{\hbar^2 m^2}{2m_0 R^2}. \tag{13.57}$$

Note that only the ground state, corresponding to $m = 0$, is non-degenerate; all other states exhibit double degeneracy. Therefore, to determine the effects of the gravitational term, it will be necessary to use perturbation theory for degenerate systems.The matrix elements of the perturbation are given by

$$V_{mm'} = m_0 gR \int_0^{2\pi} \psi_m^{*(0)} \sin\varphi \, \psi_{m'}^{(0)} d\varphi = \frac{m_0 gR}{2\pi} \int_0^{2\pi} e^{i(m'-m)\varphi} \sin\varphi \, d\varphi, \tag{13.58}$$

$$= \frac{m_0 gR}{2\pi} \frac{1}{2i} \int_0^{2\pi} \left(e^{i(m'-m+1)\varphi} - e^{i(m'-m-1)\varphi} \right) d\varphi \tag{13.59}$$

$$= i \frac{m_0 gR}{2} \left(\delta_{m',m+1} - \delta_{m',m-1} \right), \tag{13.60}$$

therefore, the non-zero matrix elements are

$$V_{m,m+1} = i\tfrac{1}{2} m_0 gR, \quad V_{m,m-1} = -i\tfrac{1}{2} m_0 gR. \tag{13.61}$$

The presence of degeneracy for $m \neq 0$ requires, in principle, the use of degenerate perturbation theory; however, a fortunate circumstance somewhat simplifies matters. It happens that up to second order in perturbation theory (the approximation used here), the degeneracy is preserved (except for $m = \pm 1$, where the levels split), allowing the application of non-degenerate perturbation theory up to and including this order, as done below. This means, in particular, that the functions $\psi_m^{(0)}$ given in (13.56) constitute the correct zeroth-order basis functions.Since $\delta E_m^{(1)} = V_{mm} = 0$, there are no first-order corrections. To second order we obtain

$$\delta E_m^{(2)} = \sum_{m' \neq m} \frac{|V_{mm'}|^2}{E_m^{(0)} - E_{m'}^{(0)}} = \frac{m_0^3 g^2 R^4}{2\hbar^2} \left[\frac{1}{m^2 - (m-1)^2} + \frac{1}{m^2 - (m+1)^2} \right]. \tag{13.62}$$

Introducing the rotor's moment of inertia $I = m_0 R^2$, we have up to second order in perturbation theory

$$E_m = \frac{\hbar^2}{2I} m^2 + \frac{m_0 I^2 g^2}{\hbar^2} \frac{1}{4m^2 - 1}. \tag{13.63}$$

The result shows that for $m \neq 0$, $\delta E_m^{(2)} > 0$, but for $m = 0$, $\delta E_m^{(2)} < 0$. In other words, the external field's effects on the energy of a particle at rest (or, in the classical limit, rotating very slowly) have the opposite sign to those obtained when there is rotation. However, the relative importance of these corrections diminishes as the quantum number m increases.

P13.4 Study the normal Zeeman effect of spinless particles using the methods of perturbation theory.

Solution. The normal Zeeman effect (that is, for spinless particles) occurs in

atoms immersed in a uniform and constant magnetic field. In the linear approximation, the Hamiltonian of the system is given by

$$\hat{H} = \hat{H}_0 - \frac{e}{2m_0c}\boldsymbol{B}\cdot\hat{\boldsymbol{L}}, \tag{13.64}$$

with $\hat{H}_0$ being the atomic Hamiltonian in the absence of the magnetic field. If we take the z-direction along the field, the last term simplifies and we obtain

$$\hat{H} = \hat{H}_0 - \frac{e}{2m_0c}B\hat{L}_z. \tag{13.65}$$

We will consider the interaction with the magnetic field as a perturbation. The unperturbed atomic states are eigenstates of the operator $\hat{L}_z$, so we can write $\hat{L}_z\,|nlm\rangle = \hbar m\,|nlm\rangle$; in general, these are degenerate states, since the unperturbed energy levels do not depend on the quantum number m. The matrix elements of the perturbation between these degenerate states are

$$\langle nlm|\hat{H}'|nlm'\rangle = -\frac{em'}{2m_0c}B\hbar\langle nlm|nlm'\rangle = -\frac{e\hbar B}{2m_0c}m\delta_{m,m'} = \mu_0 Bm\delta_{m,m'}, \tag{13.66}$$

where μ_0 is the Bohr magneton. To apply perturbation theory, we must first solve the corresponding secular equation (see [1], Section 13.3). However, since the only surviving terms are those found along the main diagonal, the determinant reduces to a product of factors of the form $H'_{mm} - \delta E^{(1)} = 0$, so for each level at first order we obtain

$$\Delta E_{nlm} = \mu_0 Bm. \tag{13.67}$$

This result coincides with that given in the textbook [1].

P13.5 Show that the matrix $\widehat{A}$ defined by $\varphi = \hat{A}\psi$, also satisfies the condition $\widehat{A}\widehat{A}^\dagger = 1$, which, taken together with $\widehat{A}^\dagger\widehat{A} = 1$, guarantees that $\widehat{A}$ is unitary.
Solution. The matrix $\hat{A}$ transforms the zeroth-order state vectors corresponding to a degenerate level into the correct set of state vectors, i.e., those appropriate for initiating the perturbative calculation. To perform the requested demonstration, we can start from condition $\hat{A}^\dagger\hat{A} = 1$. Then from $\varphi = \hat{A}\psi$, it follows that

$$\hat{A}^\dagger\varphi = \hat{A}^\dagger\hat{A}\psi = \psi, \tag{13.68}$$

and, using the orthonormality property of the $|\psi\rangle$ states,

$$\langle\psi|\psi\rangle = \langle\hat{A}^\dagger\varphi|\hat{A}^\dagger\varphi\rangle = \langle\varphi|\hat{A}\hat{A}^\dagger|\varphi\rangle = 1. \tag{13.69}$$

From this, we must take

$$\hat{A}\hat{A}^\dagger = 1 \tag{13.70}$$

to guarantee that the new basis is orthonormal.

P13.6 Explain why the linear Stark effect increases with the principal quantum number n.

Solution. The perturbation potential in the Stark effect is usually written as

$$\hat{V} = -e\mathcal{E} \cdot \hat{\boldsymbol{r}}, \tag{13.71}$$

where $\mathcal{E}$ represents the intensity of the uniform and constant electric field to which the atom is subjected. According to perturbation theory, the linear Stark effect occurs only for the excited states of the hydrogen atom, since these are the ones that exhibit degeneracy. The increase with the principal quantum number of the separation between the energy levels due to the Stark effect can be understood by considering that for larger n the mean diameter of the electron's orbit is greater, and therefore, the difference in potential energy between diametrically opposite points in that orbit is also greater.

P13.7 Calculate the Stark effect on the H atom for the levels with $n = 3$. Make maximum use of the symmetry properties of the system, using spherical coordinates.

Solution. The H atom has 9 degenerate states with $n = 3$; these correspond to $(l, m) = (0, 0), (1, -1), (1, 0), (1, 1), (2, -2), (2, -1), (2, 0), (2, 1), (2, 2)$, which we will label from 1 to 9 in this order; therefore, the secular determinant has dimension 9×9. The matrix elements of the perturbation potential,

$$\hat{V} = -eEz = -eEr\cos\theta, \tag{13.72}$$

are given by

$$\langle nlm|\hat{V}|n'l'm'\rangle = -eE \int R^*_{nl}(r) R_{n'l'}(r) r^3 dr \int Y_l^{m*}(\theta,\varphi)\cos\theta\, Y_{l'}^{m'}(\theta,\varphi) d\Omega. \tag{13.73}$$

It is possible to determine which of these matrix elements vanish by considering that the parity of $Y_l^m(\theta,\varphi)$ is $(-1)^l$, $\cos\theta$ is odd under coordinate reflection and the recurrence relation holds,

$$\cos\theta Y_l^{m'} = \sqrt{\frac{(l'+m'+1)(l'-m'+1)}{(2l'+1)(2l'+3)}} Y_{l'+1}^{m'} + \sqrt{\frac{(l'+m')(l'-m')}{(2l'-1)(2l'+1)}} Y_{l'-1}^{m'}, \tag{13.74}$$

and taking into account the orthogonality condition of spherical harmonics,

$$\int Y_l^{m*}(\theta,\varphi) Y_{l'}^{m'}(\theta,\varphi) d\Omega = \delta_{l,l'}\delta_{m,m'}. \tag{13.75}$$

From these considerations, it follows that only matrix elements of the form $\langle n, l, m|\tilde{V}|n, l\pm 1, m\rangle$ can be non-zero. These elements are easily determined by first computing

the angular integral

$$\langle nlm|\tilde{V}|nl'm'\rangle = -e\mathcal{E}\int R^*_{nl}(r)R_{nl'}(r)r^3dr \times\left[\sqrt{\frac{(l'+m'+1)(l'-m'+1)}{(2l'+1)(2l'+3)}}\delta_{l,l'+1} + \sqrt{\frac{(l'+m')(l'-m')}{(2l'-1)(2l'+1)}}\delta_{l,l'-1}\right]\delta_{m,m'}. \quad (13.76)$$

The only non-zero matrix elements are

$$\langle 300|\tilde{V}|310\rangle = \langle 310|\tilde{V}|300\rangle \equiv A, \quad (13.77)$$

$$\langle 31-1|\tilde{V}|32-1\rangle = \langle 32-1|\tilde{V}|31-1\rangle \equiv B, \quad (13.78)$$

$$\langle 310|\tilde{V}|320\rangle = \langle 320|\tilde{V}|310\rangle \equiv C, \quad (13.79)$$

$$\langle 311|\tilde{V}|321\rangle = \langle 321|\tilde{V}|311\rangle \equiv D. \quad (13.80)$$

Since the result in (13.76) is invariant under the substitution $m' \leftrightarrow -m'$, it additionally holds that

$$D = B.$$

Using (13.76) and the radial functions given by

$$\psi_n(x) = C_n e^{-x^2/2\alpha_0^2}H_n(x/\alpha_0), \quad (13.81)$$

we obtain for the coefficient A

$$A = -\frac{e\mathcal{E}}{\sqrt{3}}\int R^*_{30}(r)R_{31}(r)r^3\,dr = -\frac{8\sqrt{2}e\mathcal{E}}{3\sqrt{3}}\left(\frac{1}{3a_0}\right)^4\int_0^\infty\left(1-\frac{2r}{3a_0}+\frac{2r^2}{27a_0^2}\right)\left(1-\frac{r}{6a_0}\right)r^4e^{-2r/3a_0}\,dr. \quad (13.82)$$

With the change of variable $x = 2r/3a_0$ and using the formula

$$\int_0^\infty e^{-x}x^n dx = n!, \quad (13.83)$$

we arrive at

$$A = -\frac{1}{2\sqrt{6}}e\mathcal{E}a_0\int_0^\infty\left(x^4-\tfrac{5}{4}x^5+\tfrac{5}{12}x^6-\tfrac{1}{24}x^7\right)e^{-x}dx = 6\sqrt{\tfrac{3}{2}}V_0, \quad (13.84)$$

where we set $V_0 = e\mathcal{E}a_0$. Similarly, we obtain

$$B = D = -\frac{e\mathcal{E}}{\sqrt{5}} \int R^*_{31}(r) R_{32}(r) r^3 \, dr \tag{13.85}$$

$$= -\frac{16}{45} e\mathcal{E} \left(\frac{1}{3a_0}\right)^6 \int_0^\infty r^6 \left(1 - \frac{r}{6a_0}\right) e^{-2r/3a_0} \, dr \tag{13.86}$$

$$= -\frac{e\mathcal{E}a_0}{120} \int_0^\infty \left(x^6 - \tfrac{1}{4}x^7\right) e^{-x} \, dx = \tfrac{9}{2} V_0, \tag{13.87}$$

$$C = -\frac{2e\mathcal{E}}{\sqrt{15}} \int R^*_{31}(r) R_{32}(r) r^3 dr = \frac{2}{\sqrt{3}} B = 3\sqrt{3} V_0. \tag{13.88}$$

The secular equation takes the form, with $\delta E \equiv \delta E_3^{(1)}$,

$$\begin{vmatrix}
-\delta E & 0 & A & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -\delta E & 0 & 0 & 0 & B & 0 & 0 & 0 \\
A & 0 & -\delta E & 0 & 0 & 0 & C & 0 & 0 \\
0 & 0 & 0 & -\delta E & 0 & 0 & 0 & D & 0 \\
0 & 0 & 0 & 0 & -\delta E & 0 & 0 & 0 & 0 \\
0 & B & 0 & 0 & 0 & -\delta E & 0 & 0 & 0 \\
0 & 0 & C & 0 & 0 & 0 & -\delta E & 0 & 0 \\
0 & 0 & 0 & D & 0 & 0 & 0 & -\delta E & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\delta E
\end{vmatrix} = 0. \tag{13.89}$$

Expanding the determinant yields

$$\left(\delta E_3^{(1)}\right)^3 \left[\left(\delta E_3^{(1)}\right)^2 - D^2\right] \left[\left(\delta E_3^{(1)}\right)^2 - B^2\right] \left[\left(\delta E_3^{(1)}\right)^2 - \left(A^2 + C^2\right)\right] = 0. \tag{13.90}$$

From this it follows that the first-order energy corrections for the nine degenerate states corresponding to the $n = 3$ level due to the electric field are 0 for three states, $\pm B = \pm\frac{9}{2}V_0$ for two states, $\pm D = \pm\frac{9}{2}V_0$ for another two states, and $\pm\sqrt{A^2 + C^2} = \pm 9V_0$ for the remaining two states. In total, the level splits into five components, symmetrically arranged around the original energy and separated by $\pm\frac{9}{2}V_0$. The initial degeneracy persists at this order for three states whose energy remains unchanged; degeneracy also continues for the two pairs of states whose corrections coincide due to the equality of B and D, a consequence of the symmetry with respect to inversion of the z-axis. As this example clearly shows, the method used is not only excessively cumbersome but also makes it difficult to draw systematic conclusions.

It is preferable to use other approaches, such as employing a system of parabolic coordinates where the perturbed problem has an exact solution. As noted in the textbook [**1**], these more powerful methods yield for the first-order corrections

$$E_n^{(1)} = \frac{3}{2} k n V_0, \quad k = 0, \pm 1, \pm 2, \ldots, \pm(n-1). \tag{13.91}$$

P13.8 Calculate the intensities of the components of the H_α line of hydrogen, split by the linear Stark effect.

Solution. The H_α line is generated by the transition $n = 3 \to n = 2$; in the previous problem we saw that, due to the linear Stark effect, the $n = 3$ level splits into five levels (to first order in the external electric field). Since the $n = 2$ level in turn splits into three components (as follows from (13.91)), the H_α line splits into 15 closely spaced lines, as detailed below. The external field decomposes the $n = 2$ level to first order into the following three energy levels ($a_0 = \hbar^2/m_0e^2$), as follows from (13.91),

$$E_2 = E_2^{(0)} + \begin{cases} 3V_0 \\ 0 \\ -3V_0 \end{cases}, \quad V_0 = e\mathcal{E}a_0, \quad E_2^{(0)} = -\frac{me^4}{8\hbar^2}. \tag{13.92}$$

In turn, for $n = 3$, the degeneracy (of degree 9) is partially lifted to give rise to the following five energy levels (as also follows from (13.91)),

$$E_3 = E_3^{(0)} + \begin{cases} 9V_0 \\ \frac{9}{2}V_0 \\ 0 \\ -\frac{9}{2}V_0 \\ -9V_0 \end{cases}, \quad E_3^{(0)} = -\frac{me^4}{18\hbar^2}. \tag{13.93}$$

With the notation[1]

$$\omega_0 = \frac{\left(E_3^{(0)} - E_2^{(0)}\right)}{\hbar} = \frac{5}{72}\,\text{ua}, \quad \omega' = \frac{V_0}{\hbar} = e\mathcal{E}\,\text{ua}, \tag{13.94}$$

with $1\,\text{ua} = m_0e^4/\hbar^3$, the 15 components generated by these splittings result in (see Fig. 13.1)

$$\omega_0, \quad \omega_0 \pm \frac{3}{2}\omega', \quad \omega_0 \pm 3\omega', \quad \omega_0 \pm \frac{9}{2}\omega', \quad \omega_0 \pm 6\omega', \quad \omega_0 \pm \frac{15}{2}\omega', \quad \omega_0 + 9\omega', \quad \omega_0 + 12\omega'.$$

To calculate the intensities of the new lines we require the first-order corrected wave functions; their determination is greatly simplified by working with a system of parabolic coordinates, since, as already noted, the Stark effect problem in these coordinates is separable, and the calculation of the expressions for the wave functions corresponding to $n = 2$ and $n = 3$ is relatively straightforward. In terms of

[1]The unit of electric field intensity in atomic units is the field produced by a proton at a distance $a_0 = \hbar^2/(m_0e^2)$ (Bohr radius), which is equal to 5.142×10^9 V/cm.

the parabolic coordinates ξ, η, φ, defined by the relations

$$x = \sqrt{\xi\eta}\cos\varphi, \quad y = \sqrt{\xi\eta}\sin\varphi, \quad z = \frac{1}{2}(\xi - \eta), \tag{13.95}$$

and in atomic units ($m_0 = \hbar = e = 1$), the eigenfunctions of the hydrogen atom in the presence of the Stark effect are (see, e.g., [**6**], p. 315)

$$\psi = u_1(\xi)\, u_2(\eta)\, e^{im\varphi}, \tag{13.96}$$

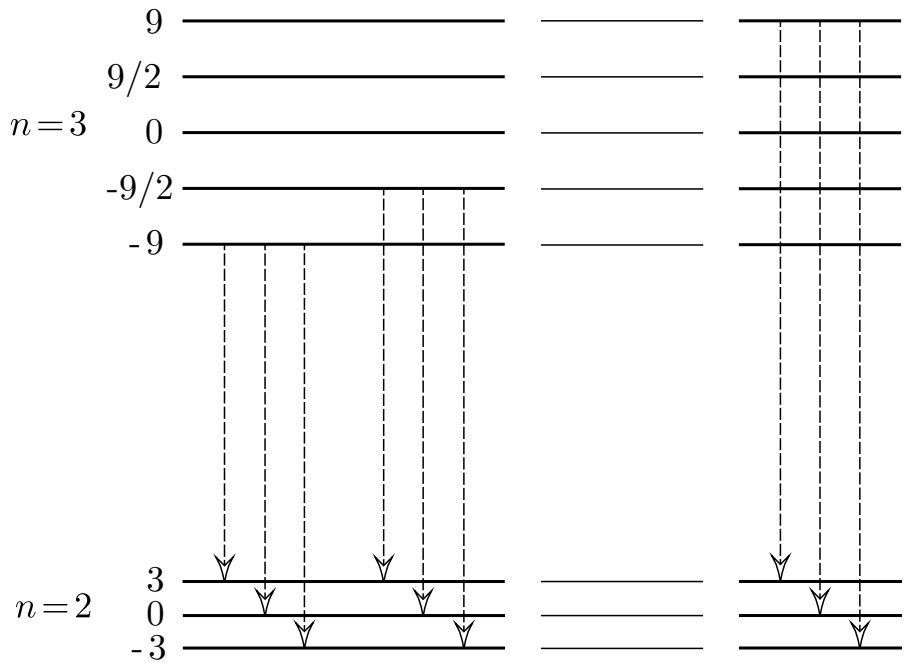

FIGURE 13.1. Splitting of the $n = 2$ and $n = 3$ levels of the H_α line, due to the linear Stark effect .

where

$$u_1(\xi) = \frac{\sqrt{n_1!}}{[(n_1+m)!]^{3/2}} e^{-\varepsilon\xi/2} \xi^{m/2} \varepsilon^{(m+1)/2} L^m_{n_1+m}(\varepsilon\xi) \tag{13.97}$$

and an analogous expression for $u_2(\eta)$; furthermore,

$$\varepsilon = \sqrt{-2E}, \quad n_1, n_2, m = 1, 2, 3, \ldots \tag{13.98}$$

The first-order energy in $\mathcal{E}$ is

$$E = -\frac{Z^2}{2n^2} + \frac{3\mathcal{E}}{2Z} n\,(n_1 - n_2)\,, \quad n = n_1 + n_2 + m. \tag{13.99}$$

For the calculation of the Einstein A coefficients that determine the probabilities of spontaneous emission, and hence the line intensities, we need to know the selection rules that apply in the present case. In the presence of an electric field there is only one selection rule, which applies to the magnetic quantum number m, which in this case determines the component of the orbital angular momentum with respect to the direction of the electric field. This rule establishes that the allowed transitions correspond to:

- $\Delta m = 0$ for radiation polarized in the direction parallel to the field;
- $\Delta m = \pm 1$ for radiation polarized in a direction perpendicular to the field.

There is no selection rule for the parabolic quantum numbers n_1 and n_2. However, there exists a quasi-selection rule, which states that the most widely separated components, which one would expect to appear in the line pattern, generally have unobservable intensities. This happens, for example, for the $\pi 8$ component of the H_α line, which is shifted by $8\mathcal{E}/15620$ cm^{-1} with respect to the unperturbed line and corresponds to the transition from the state $n = 3$, $n_1 = 2$, $n_2 = m = 0$ to the state $n = 2$, $n_1 = 0$, $n_2 = 1$, $m = 0$.

The intensities of the Stark components of the Balmer series were first calculated by Schrödinger in 1926, and since then the predictions have been compared in detail with experimental data. To determine these intensities, we consider that, in general, various situations can occur. A simple case occurs when the electrons remain distributed with equal probability among the states corresponding to a degenerate level (of the unperturbed system); in this case, the intensity of the line due to the $nl \to n'l'$ transition is

$$J_{nl}^{n'l'} = (2l+1)\,\hbar\omega_{nn'}A_{nn'}. \tag{13.100}$$

This expression is called *statistical intensity*. On the other hand, under natural conditions, the intensity of the radiation emitted by a given transition is obtained by multiplying the previous statistical intensity by the lifetime of the state from which the transition originates. The latter is $\tau_{nl} = (\sum_{n'} A_{nn'})^{-1}$, and the emitted intensity is then given by

$$\left[J_{nl}^{n'l'}\right] = J_{nl}^{n'l'}\tau_{nl} = (2l+1)\,\hbar\omega_{nn'}\,\frac{A_{nn'}}{\sum_{n'} A_{nn'}}. \tag{13.101}$$

This is called the *dynamic intensity*. At the end of the problem, this topic is expanded further. The determination of the Einstein coefficients $A_{nn'}$ requires the matrix elements of the coordinates x and z. These were obtained by Gordon for a parabolic coordinate system[2] and are given by the following expressions: a) For

[2]W. Gordon, *Ann. d. Phys.* **2** (1929) 1031.

radiation polarized parallel to the field,

$$z_{n_1 n_2 m}^{n_1' n_2' m} = (-1)^{n_1'+n_2'} \frac{a_0}{4\,(m!)^2} \sqrt{\frac{(n_1+m)!\,(n_2+m)!\,(n_1'+m)!\,(n_2'+m)!}{n_1!\,n_2!\,n_1'!\,n_2'!}}$$
$$\times \left(\frac{4nn'}{(n-n')^2}\right)^{m+2} \left(\frac{n-n'}{n+n'}\right)^{n+n'}$$
$$\times \left\{ \left[2\,(n_1'-n_2') \frac{n^2+n'^2}{(n+n')^2} - (n_1-n_2) \frac{4nn'}{(n+n')^2} \right] \Psi_m(n_1 n_1')\, \Psi_m(n_2 n_2') \right.$$
$$\left. - 2\,[n_1'\, \Psi_m(n_1, n_1'-1)\, \Psi_m(n_2 n_2') - n_2'\, \Psi_m(n_1, n_1')\, \Psi_m(n_2, n_2'-1)] \right\}. \tag{13.102}$$

b) For radiation with polarization perpendicular to the field,

$$x_{n_1 n_2 m}^{n_1' n_2' m'} = \frac{(-1)^{n_1'+n_2'} a_0}{4\,[(m')!]^2}$$
$$\times \sqrt{\frac{(n_1+m)!\,(n_2+m)!\,(n_1'+m')!\,(n_2'+m')!}{n_1!\,n_2!\,n_1'!\,n_2'!}}$$
$$\times \left(\frac{4nn'}{(n-n')^2}\right)^{m+1} \left(\frac{n-n'}{n+n'}\right)^{n+n'}$$
$$\times \left\{ \Psi_{m'}(n_1 n_1')\, \Psi_{m'}(n_2 n_2') - \left(\frac{n-n'}{n+n'}\right)^2 \Psi_{m'}(n_1+1, n_1')\, \Psi_{m'}(n_2+1, n_2') \right\}. \tag{13.103}$$

In these expressions, $m' = m-1$ and Ψ_m is the confluent hypergeometric function

$$\Psi_m(n_i, n_i') = F\left(-n_i,\, -n_i',\, m+1,\, -\frac{4nn'}{(n-n')^2}\right). \tag{13.104}$$

We now tabulate the transition probabilities originating in the levels (with Stark effect) for $n = 3$. In them[3], the triplet $n_1 n_2 m$ denotes the quantum numbers of the initial state, A_{rel} is the transition probability in arbitrary units, A_{abs} is in units of 10^8 s^{-1}, and τ is the mean lifetime $\times 10^{-8}$ s.

The intensities of the components of the Stark effect for the H_α lines are as follows.

$\Delta\nu$ denotes the displacement of the line with respect to its position in the absence of a field, in units of $\mathcal{E}/15620$ cm^{-1}; J_S and J_D express the statistical and dynamical intensities, respectively, in units such that the most intense component has a value of 100. The subscripts T and E denote the theoretical and experimental results, respectively. The first tables allow one to determine the mean lifetime

[3]These tables are found in the work by Schrödinger and in [**6**].

a) For π polarization:

n_1n_2m	Final state	A_{rel}
002	–	0
110	100	729
110	101	729
101	001	1152
200	100	1681
200	010	1

b) For σ polarization:

n_1n_2m	Final state	A_{rel}
002	001	2304
110	001	882
101	100	968
101	010	8
200	010	18

c) For $\sigma + 2\pi$:

n_1n_2m	A_{rel}	A_{abs}	τ
002	4608	0.64	1.56
110	3222	0.45	2.22
101	3104	0.43	0.80
200	1718	0.24	0.94

TABLE 1. *

a) With polarization parallel to the electric field:

Initial state	Statistical weight	Final state	$\Delta\nu$	J_{ST}	J_{DT}	J_{SE}	J_{DE}
110	1	010	2	32	89	31	79
101	2	001	3	100	100	100	100
200	1	100	4	73	86	76	92
200	1	010	8	0	0	0	0

with Stark effect of the terms with principal quantum number $n = 3$. The last two tables are used in the calculation of the intensities of the H_α components; for this purpose, it is customary to consider one of the following situations:

- The *occupation* of each level is proportional to its statistical weight (that is, on average each level is occupied by the same number of atoms).
- The *production* of each level is proportional to its statistical weight (that is, the same number of atoms per unit time arrives at each level).

Under the first of these assumptions, the emission intensities are statistical, and are calculated by multiplying the transition probabilities from the tables by the

TABLE 2. *

b) With polarization perpendicular to the field:

Initial state	Statistical weight	Final state	$\Delta\nu$	J_{ST}	J_{DT}	J_{SE}	J_{DE}
002	2	001	0	100	100	100	100
110	1	001	0	100	100	100	100
101	2	100	1	35	17	38	38
101	2	010	5	0	0	0	0
200	1	001	6	0	0	0	0

statistical weight of the initial state. The results correspond, in this case, to those of Schrödinger.

The experimental results tabulated above were obtained using two different procedures. In the first, a mixture of hydrogen and nitrogen was maintained at a (relatively) high pressure (0.02 to 0.03 mm Hg) to increase the probability of continuous excitation of hydrogen atoms by collision. In the second case, the emission was carried out essentially in vacuum (10^{-14} mm Hg), so that only atoms that entered already excited into the region under observation contributed. The data obtained with the first type of experiment agree satisfactorily with the statistical intensities of Schrödinger, whereas those obtained with the second method agree satisfactorily with the dynamical intensities. This is to be expected, since in the experiments carried out under pressure the continuous collisions ensured a uniform distribution of the atoms among the different Stark levels, whereas in the experiments in vacuum it would not be correct to assume a uniform distribution among levels.

P13.9 Two coupled oscillators have the Hamiltonian

$$\hat{H} = \frac{1}{2m}(\hat{p}_1^2 + \hat{p}_2^2) + \frac{1}{2}m\omega_1^2 x_1^2 + \frac{1}{2}m\omega_2^2 x_2^2 + m\omega^2\beta x_1 x_2,$$

where $\omega^2 = \omega_1\omega_2$ and β is arbitrary. Study this problem with perturbative methods when: a) ω_1/ω_2 is an irrational number; b) ω_1/ω_2 is a rational number. Solve the problem exactly and compare results.

Solution. We write the Hamiltonian in the standard form of perturbation theory,

$$\hat{H} = \hat{H}_0 + \hat{H}', \quad \hat{H}' = m\omega^2\beta x_1 x_2. \tag{13.105}$$

$$\hat{H}_0 = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} + \tfrac{1}{2}m\omega_1^2 x_1^2 + \tfrac{1}{2}m\omega_2^2 x_2^2 \tag{13.106}$$

is the unperturbed system Hamiltonian, describing two independent harmonic oscillators. The unperturbed wave functions are

$$\psi_{n_1 n_2}(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2), \tag{13.107}$$

with $\psi_{n_i}(x_i)$ and energy eigenvalues

$$E^{(0)}_{n_1 n_2} = \hbar\omega_1\left(n_1 + \tfrac{1}{2}\right) + \hbar\omega_2\left(n_2 + \tfrac{1}{2}\right), \quad n_1, n_2 = 0, 1, 2, \ldots \tag{13.108}$$

When the frequency ratio $\zeta = \omega_2/\omega_1$ is an irrational number, these energy levels are non-degenerate; but when ζ is rational we can write, setting $\zeta = N_2/N_1$ with N_1, N_2 integers,

$$E^{(0)}_{n_1 n_2} = \frac{\hbar\omega_1}{N_1}\left(N_1 n_1 + N_2 n_2\right) + \frac{\hbar\omega_1}{2N_1}\left(N_1 + N_2\right), \tag{13.109}$$

This expression shows that (apart from parameters) $E^{(0)}_{n_1 n_2}$ actually depends on a single integer $N_1 n_1 + N_2 n_2$, which can be constructed through various combinations of n_1 and n_2, making the energy level degenerate.We will first focus on the non-degenerate case with irrational frequency ratio. Denoting by $|n_1 n_2\rangle = |n_1\rangle|n_2\rangle$ the eigenstates, the perturbation matrix elements are

$$\langle n_1 n_2|\hat{H}'|n_1' n_2'\rangle = m\omega^2\beta\langle n_1 n_2|x_1 x_2|n_1' n_2'\rangle \tag{13.110}$$

$$= m\omega^2\beta\langle n_1|x_1|n_1'\rangle\langle n_2|x_2|n_2'\rangle. \tag{13.111}$$

We determine the non-zero matrix elements

$$\langle n_1 n_2|\hat{H}'|n_1+1, n_2+1\rangle = \tfrac{1}{2}\beta\hbar\omega\sqrt{(n_1+1)(n_2+1)}, \tag{13.112}$$

$$\langle n_1 n_2|\hat{H}'|n_1-1, n_2+1\rangle = \tfrac{1}{2}\beta\hbar\omega\sqrt{n_1(n_2+1)}, \tag{13.113}$$

$$\langle n_1 n_2|\hat{H}'|n_1+1, n_2-1\rangle = \tfrac{1}{2}\beta\hbar\omega\sqrt{(n_1+1)n_2}, \tag{13.114}$$

$$\langle n_1 n_2|\hat{H}'|n_1-1, n_2-1\rangle = \tfrac{1}{2}\beta\hbar\omega\sqrt{n_1 n_2}, \tag{13.115}$$

plus the corresponding elements of the transposed matrix. At first order of perturbation theory there is no energy correction, since the diagonal matrix elements vanish, $\langle n_1 n_2|\hat{H}'|n_1 n_2\rangle = 0$, so we must proceed to second order,

$$\delta E^{(2)}_{n_1 n_2} = \sum{}' \frac{|\langle n_1 n_2|\hat{H}'|n_1' n_2'\rangle|^2}{E^{(0)}_{n_1 n_2} - E^{(0)}_{n_1' n_2'}} \tag{13.116}$$

$$= \tfrac{1}{4}\beta^2\hbar\omega^2\left[-\frac{(n_1+1)(n_2+1)}{\omega_1+\omega_2} + \frac{n_1(n_2+1)}{\omega_1-\omega_2}\right. \tag{13.117}$$

$$\left. -\frac{(n_1+1)n_2}{\omega_1-\omega_2} + \frac{n_1 n_2}{\omega_1+\omega_2}\right], \tag{13.118}$$

or, simplified,

$$\delta E^{(2)}_{n_1 n_2} = \tfrac{1}{4}\beta^2\hbar\omega^2\left(\frac{n_1-n_2}{\omega_1-\omega_2} - \frac{1+n_1+n_2}{\omega_1+\omega_2}\right). \tag{13.119}$$

To find the first-order wave functions, we determine the first-order superposition coefficients

$$C_{nn'} = \frac{\langle n_1' n_2'|\hat{H}'|n_1 n_2\rangle}{E^{(0)}_{n_1 n_2} - E^{(0)}_{n_1' n_2'}}, \tag{13.120}$$

to obtain

$$\Psi_{n_1n_2} = \psi^{(0)}_{n_1n_2} + \tfrac{1}{2}\beta\omega\Bigg[- \frac{\sqrt{(n_1+1)(n_2+1)}}{\omega_1+\omega_2}\psi^{(0)}_{n_1+1,n_2+1} + \frac{\sqrt{n_1(n_2+1)}}{\omega_1-\omega_2}\psi^{(0)}_{n_1-1,n_2+1} - \frac{\sqrt{(n_1+1)n_2}}{\omega_1-\omega_2}\psi^{(0)}_{n_1+1,n_2-1} + \frac{\sqrt{n_1n_2}}{\omega_1+\omega_2}\psi^{(0)}_{n_1-1,n_2-1}\Bigg]. \quad (13.121)$$

This solution is obtained by using as variables x and X the pair corresponding to the system's normal modes, which are found through an orthogonal transformation with a matrix $\hat{a}$ of elements a_{ij}, such that we can write

$$X = a_{11}x_1 + a_{12}x_2, \quad x = a_{21}x_1 + a_{22}x_2, \quad (13.122)$$

$$a_1 = a_{11} = a_{22}, \quad a_0 = a_{12} = -a_{21}, \quad a_0^2 + a_1^2 = 1. \quad (13.123)$$

We see that there remains one free real parameter, which is precisely determined by the requirement of normal mode independence. In these coordinates, the potential energy takes the form

$$V = \frac{m}{2}\Big[(\omega_1^2a_0^2 + \omega_2^2a_1^2 - 2\omega^2\beta a_0a_1)x^2 + (\omega_1^2a_1^2 + \omega_2^2a_0^2 + 2\omega^2\beta a_0a_1)X^2\Big] + m\Big[(\omega_2^2-\omega_1^2)a_0a_1 + \omega^2\beta(a_1^2-a_0^2)\Big]xX. \quad (13.124)$$

To decouple the oscillators, it suffices to require that the coefficient of the cross term vanishes, i.e., that the following condition is satisfied,

$$(\omega_2^2-\omega_1^2)a_0a_1 + \omega^2\beta(a_1^2-a_0^2) = 0. \quad (13.125)$$

This condition determines the following value for the coefficient $\gamma = a_1/a_0$, as a function of the system frequencies and the coupling coefficient β (it's sufficient to use one of the signs; the other simply exchanges the solutions),

$$\gamma = \frac{\omega_2^2-\omega_1^2 \pm \sqrt{(\omega_2^2-\omega_1^2)^2 + 4\omega^4\beta^2}}{2\beta\omega^2}. \quad (13.126)$$

We can then take the values

$$a_0 = \frac{1}{\sqrt{1+\gamma^2}}, \quad a_1 = \frac{\gamma}{\sqrt{1+\gamma^2}}. \quad (13.127)$$

The solution also determines the normal mode frequencies, which from the expression for V are given by

$$\Omega_1^2 = \omega_x^2 = \omega_1^2 a_0^2 + \omega_2^2 a_1^2 - 2\omega^2 \beta a_0 a_1 \tag{13.128}$$

$$= a_0^2(\omega_1^2 + \omega_2^2\gamma^2 - 2\omega^2\beta\gamma), \tag{13.129}$$

$$\Omega_2^2 = \omega_X^2 = \omega_1^2 a_1^2 + \omega_2^2 a_0^2 + 2\omega^2 \beta a_0 a_1 \tag{13.130}$$

$$= a_0^2(\omega_1^2\gamma^2 + \omega_2^2 + 2\omega^2\beta\gamma). \tag{13.131}$$

The new Hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial x^2}\right) + \frac{m}{2}\omega_X^2 X^2 + \frac{m}{2}\omega_x^2 x^2, \tag{13.132}$$

with corresponding wave function

$$\psi_{Nn} = \phi_N(X)\phi_n(x), \tag{13.133}$$

where each factor is a harmonic oscillator wave function. The energy eigenvalues are, with $N = n_1$, $n = n_2$,

$$E_{Nn} = \hbar\omega_X\left(n_1 + \tfrac{1}{2}\right) + \hbar\omega_x\left(n_2 + \tfrac{1}{2}\right). \tag{13.134}$$

To compare with the results from perturbation theory, we will study the case where ω_1/ω_2 is a rational number (leading to the degenerate case) and, in particular, take $\omega_1 = \omega_2$. For this case we obtain

$$\gamma = 1, \quad a_0 = a_1 = \tfrac{1}{\sqrt{2}}, \tag{13.135}$$

$$\omega_x^2 = \omega_1^2(1-\beta), \quad \omega_X^2 = \omega_1^2(1+\beta), \tag{13.136}$$

$$E_{n_1 n_2} = \hbar\omega_1\left[\sqrt{1+\beta}\left(n_1 + \tfrac{1}{2}\right) + \sqrt{1-\beta}\left(n_2 + \tfrac{1}{2}\right)\right]. \tag{13.137}$$

Defining $n_1 = i - 1$ and $n_2 = n - i + 1$, this expression can be rewritten as

$$E_n = \hbar\omega_1\left[\sqrt{1+\beta}\left(i - \tfrac{1}{2}\right) + \sqrt{1-\beta}\left(n - i + \tfrac{3}{2}\right)\right], \tag{13.138}$$

Expanding this expression in a Taylor series around $\beta = 0$, for small values of β we obtain

$$E_n = \hbar\omega_1\left[n + 1 - \tfrac{1}{2}\beta(n + 2 - 2i) - \tfrac{1}{2}\beta^2(n+1) + \cdots\right] \tag{13.139}$$

or, rearranged,

$$E_n^{(i)} = E_n^{(0)}\left(1 - \tfrac{1}{2}\beta^2 + \cdots\right) - \tfrac{1}{2}\beta\hbar\omega_1(n+2-2i) + \cdots, \quad i = 1, 2, \ldots, n+1. \tag{13.140}$$

The first-order corrections (linear in β) range from $(-\frac{1}{2})\beta\hbar\omega_1$ (for $i = 1$) to $(\frac{1}{2})\beta\hbar\omega_1 n$ (for $i = n+1$), in equal steps of $\beta\hbar\omega_1$, and completely break the original degeneracy. In contrast, the second-order corrections (proportional to β^2) are independent of i, i.e., equal for all degenerate states. For the case $n = 1$ we obtain

$$\delta E_{1,2}^{(1)} = \pm\tfrac{1}{2}\beta\hbar\omega_1, \tag{13.141}$$

while the case $n = 2$ gives

$$\delta E^{(1)}_{1,2,3} = -\beta\hbar\omega_1, 0, \beta\hbar\omega_1. \tag{13.142}$$

P13.10 Determine the emission spectrum of the coupled oscillators of the previous problem, and compare it with the corresponding spectrum of two independent oscillators.

Solution. We will consider the non-degenerate case, that is, when the ratio of the frequencies is an irrational number. Since there are no first-order corrections, the transition frequencies between the states $n_1n_2, n_1'n_2'$ are

$$\omega' \equiv \omega_{n_1n_2,n_1'n_2'} = \frac{1}{\hbar}\left(E_{n_1n_2} - E_{n_1'n_2'}\right), \tag{13.143}$$

$$\omega' = \frac{1}{\hbar}\left(E^{(0)}_{n_1n_2} - E^{(0)}_{n_1'n_2'}\right) + \frac{1}{\hbar}\left(\delta E^{(2)}_{n_1n_2} - \delta E^{(2)}_{n_1'n_2'}\right). \tag{13.144}$$

It follows from here that the coupling produces the frequency shift

$$\delta^{(2)}\omega' = \frac{1}{\hbar}\left(\delta E^{(2)}_{n_1n_2} - \delta E^{(2)}_{n_1'n_2'}\right) \tag{13.145}$$

$$= \frac{1}{4}\beta^2\omega^2\left[\frac{(n_1 - n_1') - (n_2 - n_2')}{\omega_1 - \omega_2} - \frac{(n_1 - n_1') + (n_2 - n_2')}{\omega_1 + \omega_2}\right] \tag{13.146}$$

$$= \frac{1}{2}\beta^2\frac{\omega^2}{\omega_1^2 - \omega_2^2}\left[\omega_2(n_1 - n_1') - \omega_1(n_2 - n_2')\right]. \tag{13.147}$$

In the absence of perturbation, the absorption spectrum would contain only the lines that correspond to the selection rule $n_i' - n_i = 1$ ($n_i' - n_i = 0$ corresponds to the case in which the oscillator makes no transition). However, in the general case the coupling between oscillators slightly affects the selection rules (because it affects the matrix elements and the frequencies), so the spectrum is considerably enriched, although the additional lines would normally be of very low intensity. It is clear that from the study of the new frequencies (which are shifted with respect to the unperturbed ones) one can obtain information about the parameters that characterize the perturbation potential, that is, about the form of the interaction. In the present case, however, with the bilinear coupling considered in the previous problems, the usual selection rules of the harmonic oscillator remain valid for the normal modes.

P13.11 Consider a particle inside a 3D square well of side L. Find the corrections to the energy levels and wave functions when perturbed by gravity.

Solution. For a particle of mass m confined in a 3D infinite square well with side length L, the potential is

$$V(x,y,z) = \begin{cases} 0 & \text{if } 0 < x, y, z < L \\ \infty & \text{otherwise} \end{cases} \tag{13.148}$$

The gravitational perturbation is

$$H' = mgz, \tag{13.149}$$

where g is the acceleration due to gravity.The unperturbed Hamiltonian is

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z). \tag{13.150}$$

The eigenfunctions and eigenvalues are

$$\psi^{(0)}_{n_x n_y n_z}(x,y,z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right), \tag{13.151}$$

$$E^{(0)}_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2), \quad n_x, n_y, n_z = 1, 2, 3, \ldots \tag{13.152}$$

The first-order energy correction is

$$E^{(1)} = \langle \psi^{(0)}_{n_x n_y n_z} | H' | \psi^{(0)}_{n_x n_y n_z} \rangle = mg\langle z \rangle. \tag{13.153}$$

For the calculation of $\langle z \rangle$

$$\langle z \rangle = \frac{8}{L^3} \int_0^L \int_0^L \int_0^L z \sin^2\left(\frac{n_x \pi x}{L}\right) \sin^2\left(\frac{n_y \pi y}{L}\right) \sin^2\left(\frac{n_z \pi z}{L}\right) dx\, dy\, dz \tag{13.154}$$

we use

$$\int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{L}{2} \tag{13.155}$$

and

$$\int_0^L z \sin^2\left(\frac{n_z \pi z}{L}\right) dz = \frac{L^2}{4}. \tag{13.156}$$

Thus,

$$\langle z \rangle = \frac{8}{L^3} \cdot \frac{L}{2} \cdot \frac{L}{2} \cdot \frac{L^2}{4} = \frac{L}{2}. \tag{13.157}$$

The first-order energy correction is state-independent,

$$E^{(1)} = \frac{1}{2} mgL. \tag{13.158}$$

The first-order correction to the wave function is

$$|\psi^{(1)}_{n_x n_y n_z}\rangle = \sum_{k \neq n} \frac{\langle \psi^{(0)}_k | H' | \psi^{(0)}_{n_x n_y n_z} \rangle}{E^{(0)}_n - E^{(0)}_k} |\psi^{(0)}_k\rangle. \tag{13.159}$$

Since $H' = mgz$ only depends on z, it only connects states with the same n_x, n_y but different n_z,

$$\langle \psi^{(0)}_{n'_x n'_y n'_z} | H' | \psi^{(0)}_{n_x n_y n_z} \rangle = mg\delta_{n_x n'_x} \delta_{n_y n'_y} \langle n'_z | z | n_z \rangle. \tag{13.160}$$

The matrix element gives

$$\langle n'_z | z | n_z \rangle = \frac{2}{L} \int_0^L z \sin\left(\frac{n'_z \pi z}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) dz. \tag{13.161}$$

This is non-zero only when n_z and n'_z have opposite parity. The integral evaluates to

$$\langle n'_z|z|n_z\rangle = -\frac{8Ln_zn'_z}{\pi^2(n_z^2-n'_z{}^2)^2} \quad \text{(for } n'_z \neq n_z \text{ and opposite parity)}. \tag{13.162}$$

The energy difference is

$$E^{(0)}_{n_xn_yn_z} - E^{(0)}_{n_xn_yn'_z} = \frac{\pi^2\hbar^2}{2mL^2}(n_z^2 - n'_z{}^2). \tag{13.163}$$

The coefficients for the wave function correction are

$$c_{n'_z} = \frac{mg\langle n'_z|z|n_z\rangle}{E^{(0)}_n - E^{(0)}_k} = -\frac{16m^2gL^3n_zn'_z}{\pi^4\hbar^2(n_z^2-n'_z{}^2)^3}, \tag{13.164}$$

and the corrected wave function is therefore

$$\psi_{n_xn_yn_z} = \psi^{(0)}_{n_xn_yn_z} + \sum_{\substack{n'_z\neq n_z \\ \text{opposite parity}}} c_{n'_z}\psi^{(0)}_{n_xn_yn'_z} \tag{13.165}$$

P13.13 Consider the Hamiltonian

$$\hat{H} = \hat{a}^\dagger\hat{a} + \frac{1}{2} + \eta(\hat{a}^\dagger\hat{a}^\dagger + \hat{a}\hat{a}), \quad |\eta| < \frac{1}{2}, \tag{13.166}$$

representing an oscillator perturbed by an interaction with coupling constant η. Consider the linear transformation

$$\hat{a} = \alpha\hat{\lambda} + \beta\hat{\lambda}^\dagger, \quad \hat{a}^\dagger = \alpha\hat{\lambda}^\dagger + \beta\hat{\lambda}, \tag{13.167}$$

with real α, β, and $\alpha^2 - \beta^2 = 1$, where $\hat{\lambda}, \hat{\lambda}^\dagger$ are two new operators that comply with the usual commutation rule (which allows us to equate them with creation and annihilation operators), $[\hat{\lambda}, \hat{\lambda}^\dagger] = I$. This leads to a Hamiltonian without interaction

$$\hat{H} = \sqrt{1-4\eta^2}\left(\hat{\lambda}^\dagger\hat{\lambda} + \frac{1}{2}\right), \tag{13.168}$$

if

$$\alpha^2 + \beta^2 + 4\eta\alpha\beta = \sqrt{1-4\eta^2}, \tag{13.169}$$

$$\frac{1}{2} + 2\eta\alpha\beta + \beta^2 = \frac{1}{2}\sqrt{1-4\eta^2}. \tag{13.170}$$

This is the so-called *canonical Bogolyubov transformation*. Determine the operator that performs this transformation.

Solution. Substituting these results into the Hamiltonian, it transforms into

$$\hat{H} = \sqrt{1-4\eta^2}\left(\hat{\lambda}^\dagger\hat{\lambda} + \tfrac{1}{2}\right). \tag{13.171}$$

Thus the problem has been reduced to that of a harmonic oscillator in the $\hat{\lambda}$ representation. The eigenstates and corresponding eigenenergies are

$$|n\rangle = \frac{1}{\sqrt{n!}}\left(\hat{\lambda}^\dagger\right)^n |0\rangle, \quad \hat{\lambda}|0\rangle = 0, \tag{13.172}$$

$$E_n = \sqrt{1-4\eta^2}\left(n+\tfrac{1}{2}\right). \tag{13.173}$$

It can be shown that this transformation is unitary, which justifies its name.

P13.14 To solve the harmonic oscillator problem with the variational method, the following test functions are proposed: i) $A_0 e^{-\alpha x^2}$ for the ground state; ii) $A_1 x e^{-\alpha x^2}$ for the first excited state; iii) $A_2(1+bx^2)e^{-\alpha x^2}$ for the second excited state. Justify this selection and determine the wave functions and the energy eigenvalues for the first three states.

Solution. The basic characteristics of the ground state wave function of the harmonic oscillator are: it vanishes exponentially as $|x| \to \infty$, it is even, and it has no nodes. The proposed trial function,

$$\psi(x) = A_0 e^{-\alpha x^2}, \tag{13.174}$$

has these properties. The proposed functions for the excited states vanish at infinity, each of them has one additional node compared to the previous state, they alternate their parity, and their coefficients can be chosen to ensure that each is orthogonal to the other two functions. In addition to this, one can note the simplicity of the three proposed functions. For all these reasons, they are excellent trial functions to investigate the first three states of the oscillator. In each case the constants A_i (which we will take to be real and positive) are determined from the normalization condition.

i) For the ground state we have

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)\,dx = A_0^2 \int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = A_0^2 \sqrt{\frac{\pi}{2\alpha}} = 1, \tag{13.175}$$

which gives

$$\psi(x) = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2}. \tag{13.176}$$

The constant α is fixed using the variational procedure so that the trial function minimizes the energy. The expectation value of $\hat{H}$ for the ground state, calculated with this trial function, is

$$\begin{aligned}\left\langle \hat{H} \right\rangle &= A_0^2 \int_{-\infty}^{\infty} e^{-\alpha x^2} \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2\right) e^{-\alpha x^2} dx \\ &= A_0^2 \left[\frac{\alpha\hbar^2}{m}\int_{-\infty}^{\infty} e^{-2\alpha x^2} dx + \left(\frac{1}{2}m\omega^2 - \frac{2\alpha^2\hbar^2}{m}\right)\int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx\right], \end{aligned} \tag{13.177}$$

$$\left\langle \hat{H} \right\rangle = \frac{\alpha\hbar^2}{2m} + \frac{m\omega^2}{8\alpha}. \tag{13.178}$$

To minimize this value with respect to the parameter α, we impose the condition

$$\frac{d\langle \hat{H} \rangle}{d\alpha} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0, \tag{13.179}$$

from which we obtain

$$\alpha = \frac{m\omega}{2\hbar}. \tag{13.180}$$

Since

$$\left.\frac{d^2\langle \hat{H} \rangle}{d\alpha^2}\right|_{\alpha=m\omega/2\hbar} = \left.\frac{m\omega^2}{4\alpha^3}\right|_{\alpha=m\omega/2\hbar} = \frac{2\hbar^3}{m^2\omega} > 0, \tag{13.181}$$

this is indeed a minimum, whose value is

$$\left\langle \hat{H} \right\rangle_{\min} = \left\langle \hat{H}\left(\alpha = \frac{m\omega}{2\hbar}\right) \right\rangle = \frac{1}{2}\hbar\omega. \tag{13.182}$$

It follows that for the ground state energy of the harmonic oscillator

$$E_0 \leq \left\langle \hat{H} \right\rangle_{\min} = \frac{1}{2}\hbar\omega. \tag{13.183}$$

The bound obtained by taking the equality sign coincides with the exact value of the ground state energy; this is because the trial function with α given by (13.180) coincides with the exact solution of the problem,

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar}x^2\right). \tag{13.184}$$

ii) For the first excited state, the proposed trial function is

$$\psi_1(x) = A_1 x e^{-\alpha x^2}. \tag{13.185}$$

This function is orthogonal to $\psi_0(x)$, since

$$\int_{-\infty}^{\infty} \psi_1^*(x)\,\psi_0(x)\,dx \propto \int_{-\infty}^{\infty} x e^{-2\alpha x^2} dx = 0. \tag{13.186}$$

From the normalization condition

$$\int_{-\infty}^{\infty} \psi_1^*(x)\,\psi_1(x)\,dx = A_1^2 \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx = A_1^2 \frac{1}{4}\sqrt{\frac{\pi}{2\alpha^3}} = 1 \tag{13.187}$$

it follows that

$$A_1 = 2\left(\frac{2\alpha^3}{\pi}\right)^{1/4}. \tag{13.188}$$

The expectation value of $\hat{H}$ calculated with the trial function $\psi_1(x)$ is

$$\begin{aligned}\left\langle \hat{H} \right\rangle &= A_1^2 \int_{-\infty}^{\infty} x e^{-\alpha x^2} \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \right) x e^{-\alpha x^2} dx \\ &= A_1^2 \left[\frac{3\alpha\hbar^2}{m} \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx + \left(\frac{1}{2}m\omega^2 - \frac{2\alpha^2\hbar^2}{m} \right) \int_{-\infty}^{\infty} x^4 e^{-2\alpha x^2} dx \right],\end{aligned} \tag{13.189}$$

$$\left\langle \hat{H} \right\rangle = \frac{3\alpha\hbar^2}{2m} + \frac{3m\omega^2}{8\alpha}. \tag{13.190}$$

This energy is minimized if

$$\frac{d\langle \hat{H} \rangle}{d\alpha} = \frac{3\hbar^2}{2m} - \frac{3m\omega^2}{8\alpha^2} = 0, \tag{13.191}$$

which gives

$$\alpha = \frac{m\omega}{2\hbar}. \tag{13.192}$$

Note that this value coincides with that obtained previously, Eq. (13.180), which suggests a common exponential for the wave functions (as is indeed the case). Once again,

$$\left. \frac{d^2\langle \hat{H} \rangle}{d\alpha^2} \right|_{\alpha = m\omega/2\hbar} = \left. \frac{3m\omega^2}{4\alpha^3} \right|_{\alpha = m\omega/2\hbar} = \frac{6\hbar^3}{m^2\omega} > 0 \tag{13.193}$$

so this is indeed a minimum; its value is

$$\hat{H}_{1\min} = \left\langle \hat{H} \left(\alpha = \frac{m\omega}{2\hbar} \right) \right\rangle = \frac{3}{2}\hbar\omega, \tag{13.194}$$

which yields an upper bound for the energy of the first excited state of the harmonic oscillator,

$$E_1 \leq \frac{3}{2}\hbar\omega. \tag{13.195}$$

The trial function (13.185) coincides with the eigenfunction of the first excited state when the value of the parameters determined by the above procedure is inserted, which gives

$$\psi_1(x) = 2 \left(\frac{m^3\omega^3}{4\pi\hbar^3} \right)^{1/4} x \exp\left(-\frac{m\omega}{2\hbar} x^2 \right). \tag{13.196}$$

It follows that, also in this case, the bound given by the equality in (13.195) coincides with the exact eigenvalue.

iii) The proposed trial function for the second excited state of the 1D harmonic oscillator is

$$\psi_2(x) = A_2 \left(1 + bx^2 \right) e^{-\alpha x^2}. \tag{13.197}$$

This function is orthogonal to the wave function of the first excited state for any selection of parameters b and α, since they are functions of different parity.

However, since it must also be orthogonal to the ground state function, we must have

$$\int_{-\infty}^{\infty} \left(1 + bx^2\right) e^{-2\alpha x^2} dx = \sqrt{\pi}(2\alpha)^{-1/2} + \frac{1}{2}\sqrt{\pi} b (2\alpha)^{-3/2} = 0, \tag{13.198}$$

which gives

$$b = -4\alpha. \tag{13.199}$$

As in the previous cases, A_2 is fixed by normalization. We obtain

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} \psi_2^*(x)\psi_2(x)\, dx = A_2^2 \int_{-\infty}^{\infty} \left(1 - 4\alpha x^2\right)^2 e^{-2\alpha x^2} dx \\ &= A_2^2 \left(\int_{-\infty}^{\infty} e^{-2\alpha x^2} dx - 8\alpha \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx + 16\alpha^2 \int_{-\infty}^{\infty} x^4 e^{-2\alpha x^2} dx \right) \\ &= A_2^2 \sqrt{\frac{2\pi}{\alpha}}, \end{aligned} \tag{13.200}$$

so that

$$A_2 = \left(\frac{\alpha}{2\pi}\right)^{1/4}. \tag{13.201}$$

The expectation value of the Hamiltonian with this trial function is

$$\begin{aligned} \left\langle \hat{H} \right\rangle &= A_2^2 \int_{-\infty}^{\infty} \left(1 - 4\alpha x^2\right) e^{-\alpha x^2} \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2 \right) \left(1 - 4\alpha x^2\right) e^{-\alpha x^2} dx \\ &= A_2^2 \left\{ \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left(10\alpha - 84\alpha^2 x^2 + 192\alpha^3 x^4 - 64\alpha^4 x^6\right) e^{-2\alpha x^2} dx \right. \\ &\quad \left. + \frac{1}{2} m\omega^2 \int_{-\infty}^{\infty} \left(x^2 - 8\alpha x^4 + 16\alpha^2 x^6\right) e^{-2\alpha x^2} dx \right\}, \end{aligned} \tag{13.202}$$

$$\left\langle \hat{H} \right\rangle = \frac{5\alpha\hbar^2}{2m} + \frac{5m\omega^2}{8\alpha}. \tag{13.203}$$

Minimizing $\langle \hat{H} \rangle$ as a function of α,

$$\frac{d\langle \hat{H} \rangle}{d\alpha} = \frac{5\hbar^2}{2m} - \frac{5m\omega^2}{8\alpha^2} = 0, \tag{13.204}$$

we again obtain

$$\alpha = \frac{m\omega}{2\hbar}. \tag{13.205}$$

It is easy to verify that this is a minimum, with value

$$\left\langle \hat{H} \left(\alpha = \frac{m\omega}{2\hbar}\right) \right\rangle = \frac{5}{2}\hbar\omega. \tag{13.206}$$

For the second excited state of the harmonic oscillator, the upper bound is thus obtained as

$$E_2 \leq \frac{5}{2}\hbar\omega. \tag{13.207}$$

With the value of α from (13.205), the optimal proposal for the wave function of the second excited state of the 1D harmonic oscillator is

$$\psi_2(x) = \left(\frac{m\omega}{4\pi\hbar}\right)^{1/4} \left(1 - \frac{2m\omega}{\hbar}x^2\right) \exp\left(-\frac{m\omega}{2\hbar}x^2\right). \tag{13.208}$$

This is the exact eigenfunction; for the same reason, $E_2 = \frac{5}{2}\hbar\omega$ coincides with the maximum value allowed by the bound (13.207).The excellent quality of the above results should not be misleading. The relative simplicity of the example has allowed us to propose trial functions that reproduce the exact results. Clearly, this cannot be expected in more complex situations. Nevertheless, the example clearly shows that the judicious selection of trial functions is essential for the success of the variational procedure.

P13.15 Study the problem of a particle bound by the Yukawa potential,

$$V(r) = -g^2\frac{e^{-\alpha r}}{r}, \tag{13.209}$$

using the variational method. Find the maximum value of α for which there is at least one bound state. Go to the limit of the Coulomb potential and show that for this potential there is always a discrete spectrum. Find the optimal ground-state energy and wave function in the Coulomb limit.

Hint: For Coulomb solutions to be exact, it is convenient to use $\psi(r) = Ae^{-\beta r}$ as a test function.

Solution. The trial wave function suggested is

$$\psi(r) = Ae^{-\beta r}, \tag{13.210}$$

where β is the variational parameter. This function satisfies all requirements for a good trial wave function to study the ground state of the given system (it is square-integrable, decays exponentially at infinity, has no nodes, approaches the Coulomb solution as a limit, is simple to handle, and contains only one parameter). The normalization constant A is determined by

$$4\pi A^2 \int_0^\infty r^2 e^{-2\beta r} dr = \frac{\pi A^2}{\beta^3} = 1, \tag{13.211}$$

$$A = \sqrt{\frac{\beta^3}{\pi}}. \tag{13.212}$$

The expectation value of the energy calculated with this trial function is

$$\langle\hat{H}\rangle = 4\beta^3 \int_0^\infty r^2 e^{-\beta r}\left(-\frac{\hbar^2}{2m}\nabla^2 - g^2\frac{e^{-\alpha r}}{r}\right)e^{-\beta r} dr \tag{13.213}$$

$$= 4\beta^3\left[-\frac{\hbar^2\beta}{2m}\int_0^\infty e^{-2\beta r} r^2\left(\beta - \frac{2}{r}\right)dr - g^2\int_0^\infty r e^{-(2\beta+\alpha)r} dr\right] \tag{13.214}$$

$$= 4\beta^3\left[\frac{\hbar^2}{4m\beta} - \frac{\hbar^2}{8m\beta} - \frac{g^2}{(2\beta+\alpha)^2}\right], \tag{13.215}$$

which simplifies to

$$\langle \hat{H} \rangle = \frac{\hbar^2}{2m}\beta^2 - \frac{4g^2\beta^3}{(2\beta+\alpha)^2} = \frac{\hbar^2\alpha^2}{8m}\lambda^2 - \frac{g^2\alpha\lambda^3}{2(1+\lambda)^2}. \tag{13.216}$$

We introduce the dimensionless parameter

$$\lambda = \frac{2\beta}{\alpha}. \tag{13.217}$$

Defining

$$K = \frac{2mg^2}{\hbar^2\alpha}, \tag{13.218}$$

we can express (13.216) in dimensionless form,

$$\frac{\langle \hat{H} \rangle}{\alpha g^2} = \frac{\lambda^2}{4K} - \frac{\lambda^3}{2(1+\lambda)^2}. \tag{13.219}$$

Taking λ as the variational parameter, the optimal value λ_0 that minimizes the energy is obtained from

$$\frac{d}{d\lambda}\left(\frac{\langle \hat{H} \rangle}{\alpha g^2}\right)\bigg|_{\lambda=\lambda_0} = 0, \tag{13.220}$$

which yields

$$\frac{\lambda_0}{2K} - \frac{3\lambda_0^2}{2(1+\lambda_0)^2} + \frac{\lambda_0^3}{(1+\lambda_0)^3} = 0, \tag{13.221}$$

or, equivalently,

$$K = \frac{(1+\lambda_0)^3}{\lambda_0(\lambda_0+3)}. \tag{13.222}$$

Substituting into (13.219) and solving, we obtain the minimized energy $E = \langle \hat{H}(\lambda_0) \rangle$,

$$E = -\alpha g^2 \frac{\lambda_0^3(\lambda_0-1)}{4(1+\lambda_0)^3}. \tag{13.223}$$

From (13.217), since $\lambda_0 > 0$, we see that at least one bound state exists, provided

$$\lambda_0 \geq 1, \tag{13.224}$$

which in turn requires that

$$K = \frac{2mg^2}{\hbar^2\alpha} = \frac{(1+\lambda_0)^3}{\lambda_0(\lambda_0+3)} \geq 2, \tag{13.225}$$

or, equivalently,

$$\alpha \leq \frac{mg^2}{\hbar^2}. \tag{13.226}$$

Therefore, the maximum value that α can take for at least one bound state to exist, is given by

$$\alpha_{\max} = \frac{mg^2}{\hbar^2}. \tag{13.227}$$

If α exceeds this limit, the binding potential differs from zero in a spatial region insufficient to keep the particle bound. From the potential expression

$$V = -g^2 \frac{e^{-\alpha r}}{r}, \tag{13.228}$$

we observe that the spatial extent of the potential becomes too narrow when $\alpha > \alpha_{\max}$, preventing the formation of bound states. The effective range of the potential is of order $R_{\text{ef}} = \alpha^{-1}$, so the previous condition requires $R_{\text{ef}} \geq \hbar^2/mg^2$. When written in the form

$$V = -g^2 \frac{e^{-\alpha r}}{r} = -\alpha g^2 \frac{e^{-\alpha r}}{\alpha r} \equiv -V_0 \frac{e^{-\alpha r}}{\alpha r}, \quad V_0 = \frac{g^2}{R_{\text{ef}}}, \tag{13.229}$$

the condition becomes $V_0 R_{\text{ef}}^2 \geq \hbar^2/m$. Comparing with result for delta-potential bound particles, we see that in this limit the Yukawa potential can be considered essentially equivalent to a Dirac delta function, with the same constraints.The Coulomb limit is obtained by taking $\alpha \to 0$ and $g^2 \to e^2$. In this limit $\lambda_0 = 2\beta_0/\alpha \gg 1$, so we can approximate

$$E = -e^2 \alpha \frac{\lambda_0^3(\lambda_0 - 1)}{4(1+\lambda_0)^3} \approx -e^2 \alpha \frac{\lambda_0}{4} = -\frac{1}{2} e^2 \beta_0. \tag{13.230}$$

Since this value is negative, there is always a discrete spectrum in this case, independent of α. Furthermore, in this limit

$$K = \frac{2me^2}{\hbar^2 \alpha} = \frac{(\alpha + 2\beta_0)^3}{2\alpha\beta_0(3\alpha + 2\beta_0)} \simeq \frac{2\beta_0}{\alpha}, \tag{13.231}$$

from which we find the β that minimizes the energy expectation value,

$$\beta_0 = \frac{me^2}{\hbar^2} = \frac{1}{a_0}, \tag{13.232}$$

where a_0 is the Bohr radius. The ground state energy in the Coulomb limit becomes

$$E = \lim_{\alpha \to 0} \left[-e^2 \frac{(2\beta_0)^3 (2\beta_0 - \alpha)}{4(\alpha + 2\beta_0)^3} \right] = -\frac{e^2}{2} \beta_0 = -\frac{e^2}{2a_0}. \tag{13.233}$$

This result exactly reproduces the H atom ground state energy. The best wave function approximation is obtained by substituting (13.232) into (13.210),

$$\psi_0(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}, \tag{13.234}$$

which matches the exact solution for this case.

P13.16 In nuclear physics, a truncated harmonic-oscillator potential

$$V = \frac{1}{2} m\omega^2 \left(x^2 - a^2 \right)$$

for $|x| \leq a$ and $V = 0$ for $|x| > a$, is often used as a model for an attractive well.

a) Use the variational method to estimate the energy of the ground state and the first excited state.

b) Estimate the above eigenvalues using the WKB method. Under what conditions can the well contain only one bound state? Compare the results and determine which are more reliable.

Solution. a) The potential

$$V(x) = \begin{cases} \frac{1}{2}m\omega^2\left(x^2 - a^2\right), & |x| \leq a, \\ 0, & |x| \geq a, \end{cases} \tag{13.235}$$

is attractive in the interval $|x| \leq a$ and has a minimum value $V_{\min} = -\frac{1}{2}m\omega^2 a^2$ at the point $x = 0$, so that stationary solutions with $V_{\min} < E < 0$ correspond to bound states. Since the trial function to study the ground state must be even, with no nodes, and decay sufficiently fast outside the well, a reasonable approximation is given by the function

$$\psi(x) = \begin{cases} \left(b^2 - x^2\right)^2, & |x| \leq b, \\ 0, & |x| \geq b, \end{cases} \tag{13.236}$$

which decreases smoothly in the "inner" region $|x| \leq b$; b^2 will be taken as the variational parameter. The expectation value of the energy is

$$\langle \hat{H} \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}, \tag{13.237}$$

with

$$\langle \psi | \psi \rangle = \int_{-b}^{b} \left(b^2 - x^2\right)^4 dx = \frac{2^8}{5 \cdot 7 \cdot 9} b^9. \tag{13.238}$$

We shall assume that $b < a$ when performing the integrals, which yields

$$\begin{aligned} \langle \psi | \hat{H} | \psi \rangle &= \int_{-b}^{b} \left(b^2 - x^2\right)^2 \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2\left(x^2 - a^2\right) \right] \left(b^2 - x^2\right)^2 dx \\ &= \frac{2^7}{5 \cdot 7 \cdot 9} \left(\frac{3\hbar^2}{mb^2} + \frac{1}{11}m\omega^2 b^2 - m\omega^2 a^2 \right) b^9. \end{aligned} \tag{13.239}$$

Therefore, the expectation value of the energy is

$$\langle \hat{H} \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{3}{2}\frac{\hbar^2}{mb^2} + \frac{1}{22}m\omega^2 b^2 - \frac{1}{2}m\omega^2 a^2. \tag{13.240}$$

The legitimacy of the hypothesis $b < a$ can be verified at the end, noting that (13.240) must be consistent with the condition $\langle \hat{H} \rangle < 0$, which determines a maximum acceptable value for the quantity $\hbar/(m\omega a^2)$. Differentiating with respect to the variational parameter b^2 and setting the derivative to zero, one finds that

the expectation value of the energy is minimized when

$$b^2 = \sqrt{33}\,\frac{\hbar}{m\omega}. \tag{13.241}$$

In this approximation, the estimated value (taken as the upper bound) of the ground-state energy is, using (13.240),

$$E_0 = \frac{1}{2}\sqrt{\frac{12}{11}}\hbar\omega - \frac{1}{2}m\omega^2 a^2 = 0.522\,\hbar\omega - \frac{1}{2}m\omega^2 a^2. \tag{13.242}$$

For the first excited state, we propose the trial function

$$\psi(x) = \begin{cases} x\left(b^2 - x^2\right)^2, & |x| \le b, \\ 0, & |x| \ge b, \end{cases} \tag{13.243}$$

which is odd (and therefore orthogonal to the trial function for the ground state), decreases smoothly at the ends of the region $|x| \le b$ and has a node inside the well. In this case

$$\langle\psi|\psi\rangle = \int_{-b}^{b} x^2\left(b^2 - x^2\right)^4 dx = \frac{2^8}{5\cdot 7\cdot 9\cdot 11}b^{11}. \tag{13.244}$$

Again assuming $b < a$,

$$\begin{aligned}\langle\psi|\hat{H}|\psi\rangle &= \int_{-b}^{b} x\left(b^2 - x^2\right)^2\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2\left(x^2 - a^2\right)\right]x\left(b^2 - x^2\right)^2 dx \\ &= \frac{2^7}{5\cdot 7\cdot 9\cdot 11}\left(\frac{11\hbar^2}{mb^2} + \frac{3}{13}m\omega^2 b^2 - m\omega^2 a^2\right)b^{11}.\end{aligned} \tag{13.245}$$

From this, the expectation value of the energy calculated with this trial function is

$$\langle\hat{H}\rangle = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{11}{2}\frac{\hbar^2}{mb^2} + \frac{3}{26}m\omega^2 b^2 - \frac{1}{2}m\omega^2 a^2. \tag{13.246}$$

This $\langle\hat{H}\rangle$ takes a minimum value for

$$b^2 = \sqrt{\frac{11\cdot 13}{3}}\,\frac{\hbar}{m\omega}, \tag{13.247}$$

which gives for the first excited-state energy (equal to the upper bound)

$$E_1 = \sqrt{\frac{33}{13}}\hbar\omega - \frac{1}{2}m\omega^2 a^2 \simeq 1.593\,\hbar\omega - \frac{1}{2}m\omega^2 a^2. \tag{13.248}$$

b) Let us now analyze this problem with the WKB method. The quantization condition is

$$\int_{x_1}^{x_2} p(x)\,dx = \pi\hbar\left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, \ldots \tag{13.249}$$

where x_1 and $x_2 > x_1$ are the turning points determined by the condition $V(x_1) = V(x_2) = E$. For $V(x) = \frac{1}{2}m\omega^2\left(x^2 - a^2\right)$ these points are

$$x_2 = -x_1 = \sqrt{a^2 + \frac{2E}{m\omega^2}}. \tag{13.250}$$

In the semiclassical approximation, the momentum is

$$p = \sqrt{2mE + m^2\omega^2a^2 - m^2\omega^2x^2}, \tag{13.251}$$

and the energy levels are given by the condition

$$\begin{aligned}\int_{x_1}^{x_2} p\,dx &= \sqrt{2mE + m^2\omega^2a^2}\int_{x_1}^{x_2}\sqrt{1 - \frac{m^2\omega^2}{2mE + m^2\omega^2a^2}x^2}\,dx \\ &= \frac{2E + m\omega^2a^2}{\omega}\int_{-1}^{1}\sqrt{1-t^2}\,dt = \pi\hbar\left(n + \frac{1}{2}\right),\end{aligned} \tag{13.252}$$

where we set

$$t = \sqrt{\frac{m^2\omega^2}{2mE + m^2\omega^2a^2}}\,x. \tag{13.253}$$

Considering that

$$\int_{-1}^{1}\sqrt{1-t^2}\,dt = \frac{\pi}{2}, \tag{13.254}$$

we obtain

$$\frac{2E + m\omega^2a^2}{2\omega} = \hbar\left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, \ldots \tag{13.255}$$

and the discrete energy levels result in

$$E_n^{\mathrm{WKB}} = \hbar\omega\left(n + \frac{1}{2}\right) - \frac{1}{2}m\omega^2a^2. \tag{13.256}$$

The condition $E < 0$ implies that there cannot be an infinite number of bound states. The maximum possible value of n, $N_{\max}$, is given by the largest integer n satisfying

$$\hbar\omega\left(N_{\max} + \frac{1}{2}\right) - \frac{1}{2}m\omega^2a^2 \leq 0, \tag{13.257}$$

that is,

$$N_{\max} = \sup(n \in \mathbb{Z}) \leq \frac{m\omega a^2}{2\hbar} - \frac{1}{2}. \tag{13.258}$$

In the present approximation, the energies of the ground state and first excited state are

$$\begin{aligned}E_0^{\mathrm{WKB}} &= \frac{1}{2}\hbar\omega - \frac{1}{2}m\omega^2a^2, \\ E_1^{\mathrm{WKB}} &= \frac{3}{2}\hbar\omega - \frac{1}{2}m\omega^2a^2.\end{aligned}$$

For a bound state to exist (compare with the turning points) we must have

$$\frac{1}{2}m\omega^2 a^2 > \frac{1}{2}\hbar\omega,$$

that is, $a^2 > \frac{\hbar}{m\omega}$, and for it to be unique, we must also have $a^2 < \frac{3\hbar}{m\omega}$ so that the first excited state cannot occur. Therefore, the condition for having a single bound state is

$$\frac{\hbar}{m\omega} < a^2 < \frac{3\hbar}{m\omega}. \tag{13.259}$$

It is straightforward to verify that these values for a^2 are consistent with the condition $b < a$ assumed when employing the variational method.

The results obtained with the WKB method are more reliable than those obtained with the variational method, since the latter depend largely on the quality of the proposed trial function, which is essentially arbitrary. Moreover, the variational method provides upper bounds for the energy, not its exact values. In the present case, one may also add the consideration that the harmonic oscillator potential is truncated in a region where the wave function is small (due to the exponential decay outside the turning points), so it is to be expected that the WKB calculation, which gives exact results for the harmonic oscillator, is very reliable, even though we are dealing with low-lying excited states.

P13.17 Use the variational method to show that every purely attractive 1D potential has at least one bound state, regardless of its depth.

Hint: A Gaussian test function works well for this purpose.

Solution. For a system with at least one bound state (which will be an s-state with no nodes), a Gaussian trial function centered at the origin is sufficiently general due to its rapid decay. Using

$$\psi(x) = Ae^{-\alpha x^2}, \quad \alpha > 0, \tag{13.260}$$

the normalization condition

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)\,dx = A^2 \int_{-\infty}^{\infty} e^{-2\alpha x^2}\,dx = A^2\sqrt{\frac{\pi}{2\alpha}} = 1 \tag{13.261}$$

yields the normalized trial function

$$\psi(x) = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2}. \tag{13.262}$$

Let E_0 be the ground state energy. From the Rayleigh-Ritz variational method, we know that

$$E_0 \leq E' \equiv \int_{-\infty}^{\infty} \psi^*(x)\hat{H}\psi(x)\,dx. \tag{13.263}$$

For our case,

$$E' = \int_{-\infty}^{\infty} \psi^*(x) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x)\, dx \tag{13.264}$$

$$= \frac{\hbar^2 \alpha}{m} \sqrt{\frac{2\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-2\alpha x^2} (1 - 2\alpha x^2)\, dx \tag{13.265}$$

$$+ \sqrt{\frac{2\alpha}{\pi}} \int_{-\infty}^{\infty} V(x) e^{-2\alpha x^2}\, dx \tag{13.266}$$

$$= \frac{\hbar^2 \alpha}{2m} + \sqrt{\frac{2\alpha}{\pi}} \int_{-\infty}^{\infty} V(x) e^{-2\alpha x^2}\, dx. \tag{13.267}$$

The minimum value of E' is obtained for $\alpha_{\min}$ satisfying

$$\left. \frac{dE'}{d\alpha} \right|_{\alpha_{\min}} = 0. \tag{13.268}$$

Explicitly, this condition becomes

$$\frac{\hbar^2}{2m} + \sqrt{\frac{1}{2\pi\alpha}} \int_{-\infty}^{\infty} (1 - 4\alpha x^2) V(x) e^{-2\alpha x^2}\, dx = 0. \tag{13.269}$$

From the minimization condition, $\alpha_{\min}$ must satisfy

$$\frac{\hbar^2 \alpha}{2m} = -\sqrt{\frac{\alpha}{2\pi}} \int_{-\infty}^{\infty} (1 - 4\alpha x^2) V(x) e^{-2\alpha x^2}\, dx. \tag{13.270}$$

Substituting this result into (13.267) yields

$$E' = \left[\sqrt{\frac{2\alpha}{\pi}} - \sqrt{\frac{\alpha}{2\pi}} \right] \int_{-\infty}^{\infty} V(x) e^{-2\alpha x^2}\, dx \tag{13.271}$$

$$+ 4\alpha \sqrt{\frac{\alpha}{2\pi}} \int_{-\infty}^{\infty} x^2 V(x) e^{-2\alpha x^2}\, dx \tag{13.272}$$

$$= \sqrt{\frac{\alpha}{2\pi}} \int_{-\infty}^{\infty} V(x) e^{-2\alpha x^2}\, dx \tag{13.273}$$

$$+ 4\alpha \sqrt{\frac{\alpha}{2\pi}} \int_{-\infty}^{\infty} x^2 V(x) e^{-2\alpha x^2}\, dx, \tag{13.274}$$

which simplifies to

$$E' = \sqrt{\frac{\alpha}{2\pi}} \int_{-\infty}^{\infty} (1 + 4\alpha x^2) V(x) e^{-2\alpha x^2}\, dx. \tag{13.275}$$

We conclude that the ground-state energy must satisfy

$$E_0 \leq E' = \sqrt{\frac{\alpha}{2\pi}} \int_{-\infty}^{\infty} (1 + 4\alpha x^2) V(x) e^{-2\alpha x^2}\, dx, \quad \alpha > 0. \tag{13.276}$$

For purely attractive potentials (negative for all x), the integrand is negative and

$$E_0 \leq E' < 0. \tag{13.277}$$

These results demonstrate that for purely attractive potentials ($V(x) < 0$ for all x), there always exists an $\alpha > 0$ for which the integral in (13.276) is negative. This proves that at least one bound state exists, regardless of the potential's depth.

CHAPTER 14

The Electron Spin. Entangled States

P14.1 Show that

$$[\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{J}_i] = 0, \tag{14.1}$$

Solution. The components of the spin operator $\hat{\boldsymbol{S}}$ commute with the components of the orbital angular momentum operator $\hat{\boldsymbol{L}}$, since they act in different spaces. Moreover, because $\hat{\boldsymbol{L}}$, $\hat{\boldsymbol{S}}$, and $\hat{\boldsymbol{J}}$ are all angular-momentum operators, they satisfy the standard commutation relations:

$$[\hat{L}^2, \hat{L}_i] = 0, \qquad [\hat{L}_i, \hat{L}_j] = i\hbar\, \epsilon_{ijk} \hat{L}_k. \tag{14.2}$$

$$[\hat{S}^2, \hat{S}_i] = 0, \qquad [\hat{S}_i, \hat{S}_j] = i\hbar\, \epsilon_{ijk} \hat{S}_k. \tag{14.3}$$

$$[\hat{J}^2, \hat{J}_i] = 0, \qquad [\hat{J}_i, \hat{J}_j] = i\hbar\, \epsilon_{ijk} \hat{J}_k. \tag{14.4}$$

From these relations and $\hat{\boldsymbol{J}} = \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}}$, it follows that [1]

$$\begin{aligned}[\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{J}_i] &= [\hat{L}_j \hat{S}_j,\ \hat{L}_i + \hat{S}_i] = -[\hat{L}_i, \hat{L}_j]\hat{S}_j - \hat{L}_j[\hat{S}_i, \hat{S}_j] \\ &= -i\hbar\big(\epsilon_{ijk} \hat{L}_k \hat{S}_j + \epsilon_{ijk} \hat{L}_j \hat{S}_k\big).\end{aligned} \tag{14.5}$$

If we interchange the dummy indices in the first term on the right-hand side and reverse their order in the second, the expression cancels, giving

$$[\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{J}_i] = -i\hbar\big(\epsilon_{ikj} \hat{L}_j \hat{S}_k - \epsilon_{ikj} \hat{L}_j \hat{S}_k\big) = 0, \tag{14.6}$$

and by extension,

$$[\hat{\boldsymbol{L}} \cdot \hat{S}, \hat{J}^2] = [\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}},\ \hat{J}_i \hat{J}_i] = \hat{J}_i[\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{J}_i] + [\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{J}_i]\hat{J}_i = 0. \tag{14.7}$$

On the other hand, a direct use of (14.2) yields

$$[\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{L}^2] = [\hat{L}_i \hat{S}_i,\ \hat{L}^2] = [\hat{L}_i, \hat{L}^2]\, \hat{S}_i = 0, \tag{14.8}$$

and from (14.3) it follows that

$$[\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{S}^2] = [\hat{L}_i \hat{S}_i,\ \hat{S}^2] = \hat{L}_i[\hat{S}_i, \hat{S}^2] = 0. \tag{14.9}$$

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[1] For simplicity, throughout this chapter we also omit the summation signs over repeated indices.

P14.2 Any analytic function of the Pauli matrices can be written as a linear expression of these matrices plus the unit 2×2 matrix. Give the following expressions this form,

$$(1+\sigma_x)^n, \quad (1+\sigma_x)^{1/2}, \quad (a\sigma_x+b\sigma_y)^2, \tag{14.10}$$

$$\sigma_x^{-k}, \quad (a+\sigma_x)^{-1} \quad (a\neq\pm1). \tag{14.11}$$

Note: For the last term the correct condition is $a\neq\pm1$ (rather than $a\neq1$), since σ_x has eigenvalues ±1.

Solution. We begin by recalling the fundamental properties of Pauli matrices

$$[\hat\sigma_i,\hat\sigma_j]=2i\varepsilon_{ijk}\hat\sigma_k, \tag{14.12}$$

$$\hat\sigma_i\hat\sigma_j+\hat\sigma_j\hat\sigma_i=2\delta_{ij}, \tag{14.13}$$

$$\hat\sigma_i\hat\sigma_j=\mathbb{I}\delta_{ij}+i\varepsilon_{ijk}\hat\sigma_k. \tag{14.14}$$

In particular, for $i=j$,

$$\hat\sigma_x^2=\hat\sigma_y^2=\hat\sigma_z^2=\mathbb{I}. \tag{14.15}$$

From this last equality it immediately follows that:

$$(\mathbb{I}+\hat\sigma_x)^2=\mathbb{I}+2\hat\sigma_x+\hat\sigma_x^2=2(\mathbb{I}+\hat\sigma_x), \tag{14.16}$$

$$(\mathbb{I}+\hat\sigma_x)^3=2(\mathbb{I}+\hat\sigma_x)^2=2^2(\mathbb{I}+\hat\sigma_x). \tag{14.17}$$

After $n-1$ similar successive steps, we obtain:

$$(\mathbb{I}+\hat\sigma_x)^n=2^{n-1}(\mathbb{I}+\hat\sigma_x), \tag{14.18}$$

which is indeed a linear expression in $\mathbb{I}$ and $\hat\sigma_x$. Hereafter, for simplicity, we will write simply 1 to denote the identity matrix when no confusion arises. Taking the square root of (14.16) and solving gives:

$$(1+\hat\sigma_x)^{1/2}=\tfrac{1}{\sqrt2}(1+\hat\sigma_x). \tag{14.19}$$

This result shows that (14.18) applies to non-integer values of n. Now let a and b be two real numbers. Using (14.14) we can write

$$(a\hat\sigma_x+b\hat\sigma_y)^2=a^2\hat\sigma_x^2+ab(\hat\sigma_x\hat\sigma_y+\hat\sigma_y\hat\sigma_x)+b^2\hat\sigma_y^2=a^2+b^2. \tag{14.20}$$

Incidentally, note that with c constant this implies

$$(a\hat\sigma_x+b\hat\sigma_y+c\hat\sigma_z)^2=a^2+b^2+c^2. \tag{14.21}$$

Defining the vector $\boldsymbol{q}=(a,b,c)$, (14.21) establishes a very useful result in electron spin theory:

$$(\boldsymbol{q}\cdot\hat{\boldsymbol{\sigma}})^2=\boldsymbol{q}^2, \tag{14.22}$$

Observing that $\hat\sigma_x^k=\hat\sigma_x^{k-2}\hat\sigma_x^2=\hat\sigma_x^{k-2}=\hat\sigma_x^{k-4}=\ldots$, we obtain the important results:

$$\begin{aligned}\hat\sigma_x^k &= \hat\sigma_x, \text{ if } k \text{ is an odd integer,}\\ \hat\sigma_x^k &= \mathbb{I}, \text{ if } k \text{ is an even integer.}\end{aligned} \tag{14.23}$$

Since the eigenvalues of $\hat{\sigma}_x$ are ± 1, the inverse $\hat{\sigma}_x^{-1}$ exists. In fact, from $\hat{\sigma}_x^2 = 1$ it follows that $\hat{\sigma}_x^{-1} = \hat{\sigma}_x$, and more generally, combining with the previous equalities:

$$\begin{array}{rcl} \hat{\sigma}_x^{-k} & = & \hat{\sigma}_x, \text{ for } k \text{ odd;} \\ \hat{\sigma}_x^{-k} & = & 1, \text{ for } k \text{ even.} \end{array} \tag{14.24}$$

Finally, from the identity valid for $|a| \neq 1$,

$$\left(\frac{\hat{\sigma}_x}{1-a^2} - \frac{a}{1-a^2} \right) (\hat{\sigma}_x + a) = 1 \tag{14.25}$$

it immediately follows that

$$(a + \hat{\sigma}_x)^{-1} = \frac{\hat{\sigma}_x - a}{1-a^2}, \quad |a| \neq 1. \tag{14.26}$$

P14.3 Show in detail that

$$e^{\,i\hat{\boldsymbol{\sigma}}\cdot\hat{\boldsymbol{n}}\,\theta} = \cos\theta + i\,\hat{\boldsymbol{\sigma}}\cdot\hat{\boldsymbol{n}}\,\sin\theta, \tag{14.27}$$

Solution. We place the z-axis of the reference system along the $\hat{\boldsymbol{n}}$ axis, so that the directions $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{a}}_z$ coincide, so that

$$\hat{\sigma}_{\mathbf{n}} = \hat{\boldsymbol{\sigma}}\cdot\hat{\boldsymbol{n}} \quad \longrightarrow \quad \hat{\boldsymbol{\sigma}}_z.$$

With this choice, the problem reduces to proving (without loss of generality) that

$$e^{\,i\hat{\sigma}_z\theta} = \cos\theta + i\hat{\sigma}_z \sin\theta. \tag{14.28}$$

Since any analytic function of $\hat{\sigma}_z$ can be reduced to a linear function of $\hat{\sigma}_z$, it is possible to write

$$e^{\,i\hat{\sigma}_z\theta} = f(\theta) + i\hat{\sigma}_z g(\theta), \tag{14.29}$$

where f and g are two functions to be determined, which must satisfy the initial conditions $f(0) = 1$, $g(0) = 0$. Differentiating (14.29) with respect to θ and taking into account (14.15), we obtain

$$i\hat{\sigma}_z\big(f(\theta) + i\hat{\sigma}_z g(\theta)\big) = -g(\theta) + i\hat{\sigma}_z f(\theta) = f'(\theta) + i\hat{\sigma}_z g'(\theta), \tag{14.30}$$

that is,

$$f' = -g, \qquad g' = f, \qquad f'(0) = 0, \quad g'(0) = 1. \tag{14.31}$$

Differentiating a second time, we obtain

$$f'' = -g' = -f, \qquad g'' = f' = -g. \tag{14.32}$$

We see that both functions satisfy the differential equation $f'' + f = 0$. The solutions that satisfy the given initial conditions are $f(\theta) = \cos\theta$, $g(\theta) = \sin\theta$. Substituting into (14.29), we obtain the expected result,

$$e^{\,i\hat{\boldsymbol{\sigma}}\cdot\hat{\boldsymbol{n}}\,\theta} = \cos\theta + i\,\hat{\boldsymbol{\sigma}}\cdot\hat{\boldsymbol{n}}\,\sin\theta. \tag{14.33}$$

P14.4 Construct the spinors that are eigenfunctions of the operator

$$\widehat{S} = \widehat{S}_x \cos\theta + \widehat{S}_y \sin\theta \tag{14.34}$$

and show that their eigenvalues are $\lambda = \pm\frac{\hbar}{2}$. Apply your result to the particular cases $\theta = 0, \frac{\pi}{2}, \pi, 2\pi$.

Solution. The explicit matrix form of the required spin operator is obtained by introducing the Pauli matrices,

$$\hat{S}_\theta = \frac{\hbar}{2}(\hat{\sigma}_x \cos\theta + \hat{\sigma}_y \sin\theta) = \frac{\hbar}{2}\begin{pmatrix} 0 & e^{-i\theta} \\ e^{i\theta} & 0 \end{pmatrix}. \tag{14.35}$$

To find the eigenvectors and eigenvalues of this operator, we must determine values a, b, and λ that satisfy the eigenvalue equation

$$\hat{S}_\theta \begin{pmatrix} a \\ b \end{pmatrix} = \lambda \frac{\hbar}{2} \begin{pmatrix} a \\ b \end{pmatrix}, \tag{14.36}$$

which explicitly becomes

$$\begin{pmatrix} 0 & e^{-i\theta} \\ e^{i\theta} & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \lambda \begin{pmatrix} a \\ b \end{pmatrix}. \tag{14.37}$$

Expanding this yields the homogeneous system

$$e^{-i\theta} b - \lambda a = 0, \tag{14.38}$$

$$e^{i\theta} a - \lambda b = 0. \tag{14.39}$$

For non-trivial solutions to exist, the determinant must vanish,

$$\begin{vmatrix} -\lambda & e^{-i\theta} \\ e^{i\theta} & -\lambda \end{vmatrix} = 0. \tag{14.40}$$

An alternative, faster and more direct (though somewhat more formal) approach consists in diagonalizing the matrix $\hat{S}_\theta$ from the outset. Starting from (14.35), we write:

$$\begin{vmatrix} \mu & e^{-i\theta} \\ e^{i\theta} & \mu \end{vmatrix} = 0, \tag{14.41}$$

to determine the eigenvalues μ. With $\mu = -\lambda$, this equation coincides with (14.40). Solving yields $\lambda = \pm 1$, showing that the eigenvalues of $\hat{S}_\theta$ are $\pm\frac{\hbar}{2}$ (as expected for spin operators). For $\lambda = +1$, we substitute into (14.38) and (14.39),

$$e^{-i\theta} b = a, \tag{14.42}$$

$$e^{i\theta} a = b. \tag{14.43}$$

We express a in the convenient form $a = \gamma e^{-i\theta/2}$ (with γ and θ real), obtaining $b = \gamma e^{i\theta/2}$ and

$$\varphi_+ \equiv \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} a \\ e^{i\theta} a \end{pmatrix} = a e^{i\theta/2} \begin{pmatrix} e^{-i\theta/2} \\ e^{i\theta/2} \end{pmatrix} = \gamma \begin{pmatrix} e^{-i\theta/2} \\ e^{i\theta/2} \end{pmatrix}. \tag{14.44}$$

After normalization to unity, this eigenvector becomes

$$\varphi_+ = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\theta/2} \\ e^{i\theta/2} \end{pmatrix}. \tag{14.45}$$

For $\lambda = -1$, we proceed analogously to obtain

$$\varphi_- = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\theta/2} \\ -e^{i\theta/2} \end{pmatrix}. \tag{14.46}$$

For the requested particular cases:

$$\theta = 0: \quad \varphi_+ = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad \varphi_- = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}; \tag{14.47}$$

$$\theta = \frac{\pi}{2}: \quad \varphi_+ = \frac{1}{2} \begin{pmatrix} 1-i \\ -1-i \end{pmatrix}, \quad \varphi_- = \frac{1}{2} \begin{pmatrix} 1-i \\ 1+i \end{pmatrix}; \tag{14.48}$$

$$\theta = \pi: \quad \varphi_+ = \frac{i}{\sqrt{2}} \begin{pmatrix} -1 \\ 1 \end{pmatrix}, \quad \varphi_- = \frac{-i}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}; \tag{14.49}$$

$$\theta = 2\pi: \quad \varphi_+ = \frac{-1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad \varphi_- = \frac{-1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}. \tag{14.50}$$

Comparing the last result (14.50) with (14.47), we see that –as expected– the transformation $\theta \to \theta + 2\pi$ changes the sign of these spinors. The spinors (14.45)-(14.46) remain invariant only under $\theta \to \theta' = \theta + 4\pi$ (two complete rotations of the reference system).

P14.5 Solve the Pauli equation for a free particle. Which are the conserved quantities?

Solution. The Pauli equation for a free electron can be written as

$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{1}{2m} (\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{p}})^2 \Psi, \tag{14.51}$$

where $\hat{\boldsymbol{\sigma}}$ are the Pauli matrices. We look for a solution of the form $\Psi = T(t)\psi$, where $T(t)$ is a function that only depends on time, and

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

is a two-component spinor that only depends on position. With this, Eq. (14.51) is separated in the form

$$\left(i\hbar \frac{1}{T} \frac{\partial T}{\partial t} \right) \psi = \frac{1}{2m} (\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{p}})^2 \psi = \text{const}\, \psi \equiv E\psi. \tag{14.52}$$

The time dependence of the wave function is then given by the equation $i\hbar \dot{T} = ET$, with solution

$$T(t) = e^{-iEt/\hbar}. \tag{14.53}$$

In turn, the spinorial wavefunction is the solution of the equation

$$E\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \frac{1}{2m}(\hat{\boldsymbol{\sigma}}\cdot\hat{\boldsymbol{p}})^2\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}. \tag{14.54}$$

It is convenient to symmetrize the operator $(\hat{\boldsymbol{\sigma}}\cdot\hat{\boldsymbol{p}})^2$ to obtain (see (14.22))

$$(\hat{\boldsymbol{\sigma}}\cdot\hat{\boldsymbol{p}})^2 = \hat{\sigma}_i\hat{\sigma}_j\hat{p}_i\hat{p}_j = \tfrac{1}{2}\left(\hat{\sigma}_i\hat{\sigma}_j + \hat{\sigma}_j\hat{\sigma}_i\right)\hat{p}_i\hat{p}_j = \delta_{ij}\hat{p}_i\hat{p}_j = \hat{\boldsymbol{p}}^2. \tag{14.55}$$

which leads to two Schrödinger equations for a free particle,

$$E\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \frac{1}{2m}\hat{\boldsymbol{p}}^2\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}, \tag{14.56}$$

or, separating components,

$$E\psi_1 = \frac{1}{2m}\hat{\boldsymbol{p}}^2\psi_1, \tag{14.57}$$

$$E\psi_2 = \frac{1}{2m}\hat{\boldsymbol{p}}^2\psi_2. \tag{14.58}$$

The most general explicit solution is

$$\Psi = e^{i(-Et+\mathbf{p}\cdot\mathbf{x})/\hbar}\begin{pmatrix}C_1\\ C_2\end{pmatrix}, \qquad |C_1|^2 + |C_2|^2 = 1. \tag{14.59}$$

It is clear that this is an eigenfunction of $\hat{\boldsymbol{p}}$ (and consequently of $\hat{H}$), since it is a solution of the Schrödinger equation for a free particle. However, it is not necessarily an eigenfunction of, say, $\hat{\sigma}_z$, since we have

$$\hat{\sigma}_z\Psi = e^{i(-Et+\mathbf{p}\cdot\mathbf{x})/\hbar}\begin{pmatrix}C_1\\ -C_2\end{pmatrix} \neq \text{const.}\cdot\Psi \quad \text{if } C_1 \neq 0 \text{ or } C_2 \neq 0. \tag{14.60}$$

Furthermore, the eigenvalue of $\hat{\sigma}_z$ is

$$\langle\Psi|\hat{\sigma}_z|\Psi\rangle = |C_1|^2 - |C_2|^2. \tag{14.61}$$

This result shows that $|\psi_1|^2$ gives the probability that the electron has its spin pointing upwards (at point $\boldsymbol{r}$ and time t), and $|\psi_2|^2$ gives the probability that the spin is pointing downwards. With the polarization (along the z-axis) defined as

$$P = \langle\hat{\sigma}_z\rangle, \tag{14.62}$$

the solution corresponds in general to states of partial polarization along the z-axis (that is, $-1 \leq P \leq 1$). This solution will be an eigenfunction of $\hat{\sigma}_z$ (with total polarization along the z-axis, i.e., $P = \pm 1$) when one of the coefficients C_1, C_2 vanishes (and the other reduces to unity in absolute value). It is clear that by choosing adequately the coefficients C_1, C_2, one can construct solutions that correspond to the same linear momentum and energy as the previous solution, but that are eigenstates of other spin operators, which would represent the integral of the corresponding motion. The reduction that led to (14.56) can be carried out without difficulty even in the presence of an external potential $V(\boldsymbol{r})$, as long as no (or negligible) magnetic effects exist. This means that it is possible to interpret the Schrödinger equation as the one governing the behavior of each one of the two

spinor components (including all factors), in the absence of forces that affect the spin.

P14.6 Show that if the magnetic field varies only with time, the Pauli wave function can be factored into a spatial part that satisfies the Schrödinger equation with no magnetic field and a spinorial part $|\chi(t)\rangle$, solution of the equation

$$i\hbar\frac{\partial|\chi(t)\rangle}{\partial t} = \mu_0(\hat{\sigma}\cdot\boldsymbol{B})|\chi(t)\rangle. \tag{14.63}$$

Solution. The Pauli equation for a spin-1/2 particle in a magnetic field is

$$i\hbar\frac{\partial\,|\chi(t)\rangle}{\partial t} = \mu_0\hat{\sigma}\cdot\boldsymbol{B}\,|\chi(t)\rangle\,. \tag{14.64}$$

When $\boldsymbol{B}$ depends only on time, it is convenient to write the Pauli equation as:

$$i\hbar\frac{\partial\,|\Psi\rangle}{\partial t} + \frac{\hbar e}{2mc}\boldsymbol{B}(t)\cdot\hat{\sigma}\,|\Psi\rangle = \left[\frac{1}{2m}\left(\hat{\boldsymbol{p}} - \frac{e}{c}\boldsymbol{A}\right)^2 + V\right]|\Psi\rangle\,. \tag{14.65}$$

We propose a solution of the form

$$|\Psi\rangle = \varphi(\boldsymbol{r})e^{-iEt/\hbar}\,|\chi(t)\rangle\,, \tag{14.66}$$

where $|\chi(t)\rangle$ is a normalized spinor ($\langle\chi|\chi\rangle = 1$) with time-dependent components, and $\varphi(\boldsymbol{r})$ is a scalar position-dependent function. Substituting into the equation and multiplying from the left by $\langle\chi|$ yields

$$i\hbar\langle\chi|\frac{\partial\,|\chi\rangle}{\partial t} + \frac{\hbar e}{2mc}\boldsymbol{B}(t)\cdot\langle\chi|\hat{\sigma}\,|\chi\rangle = \frac{1}{\varphi}\left[\frac{1}{2m}\left(\hat{\boldsymbol{p}} - \frac{e}{c}\boldsymbol{A}\right)^2 + V - E\right]\varphi. \tag{14.67}$$

Applying the method of separation of variables, we consider each side of the equation equal to a constant $E'\langle\chi|\chi\rangle = E'$. The spinor part satisfies (for an electron with $e = -e_0$)

$$i\hbar\frac{\partial\,|\chi(t)\rangle}{\partial t} - \mu_0\boldsymbol{B}(t)\cdot\hat{\sigma}\,|\chi(t)\rangle = E'\,|\chi(t)\rangle\,, \tag{14.68}$$

where $\mu_0 = \hbar e_0/2m_0c$ is the Bohr magneton. The spatial part satisfies the Schrödinger equation without magnetic field,

$$(E + E')\varphi = \left[\frac{1}{2m}\left(\hat{\boldsymbol{p}} - \frac{e}{c}\boldsymbol{A}\right)^2 + V\right]\varphi. \tag{14.69}$$

The proposed solution in the statement corresponds to taking the separation constant $E' = 0$, effectively absorbing it into the constant E.

P14.7 Show that

$$\langle JJ|\hat{S}_z|JJ\rangle = \frac{J(J+1) + S(S+1) - L(L+1)}{2(J+1)}. \tag{14.70}$$

Hint: First prove that

$$\hat{\boldsymbol{J}}\cdot\hat{\boldsymbol{S}} = (\hat{J}_z + 1)\hat{S}_z + \hat{S}_-\hat{J}_+ + \hat{J}_-\hat{S}_+,$$

in units $\hbar = 1$.

Solution. We start from

$$\hat{\boldsymbol{J}} \cdot \hat{\boldsymbol{S}} = \hat{J}_z \hat{S}_z + \hat{J}_+ \hat{S}_- + \hat{J}_- \hat{S}_+. \tag{14.71}$$

We use the commutation rule between components $\hat{J}_+$ and $\hat{J}_-$, but applied to the spin, that is,

$$[\hat{S}_+, \hat{S}_-] = \hbar \hat{S}_z, \tag{14.72}$$

so that we can write (we will take $\hbar = 1$ in what follows)

$$\hat{J}_+ \hat{S}_- = (\hat{L}_+ + \hat{S}_+)\hat{S}_- = \hat{S}_- \hat{L}_+ + \hat{S}_+ \hat{S}_- = \hat{S}_- \hat{J}_+ + \hat{S}_z. \tag{14.73}$$

Substituting into (14.71) we obtain

$$\hat{\boldsymbol{J}} \cdot \hat{\boldsymbol{S}} = (\hat{J}_z + 1)\hat{S}_z + \hat{S}_- \hat{J}_+ + \hat{J}_- \hat{S}_+. \tag{14.74}$$

With the help of this expression we calculate the expectation value of the operator $\hat{\boldsymbol{J}} \cdot \hat{\boldsymbol{S}}$ in the eigenstate $|jm_j\rangle$ which corresponds to the maximum possible value of m_j, $|jj\rangle$. We have

$$\langle jj|\hat{\mathbf{J}} \cdot \hat{\mathbf{S}}|jj\rangle = \langle jj|(\hat{J}_z + 1)\hat{S}_z|jj\rangle = j\langle jj|\hat{S}_z|jj\rangle + \langle jj|\hat{S}_z|jj\rangle = (j+1)\langle jj|\hat{S}_z|jj\rangle, \tag{14.75}$$

since the last two terms of (14.74) do not contribute because $\hat{J}_+|jj\rangle = 0$, $\langle jj|\hat{J}_- = 0$. On the other hand, we can also write, by squaring the expression $\hat{\boldsymbol{L}} = \hat{\boldsymbol{J}} - \hat{\boldsymbol{S}}$ and solving,

$$\hat{\boldsymbol{J}} \cdot \hat{\boldsymbol{S}} = \tfrac{1}{2}\left(\hat{\boldsymbol{J}}^2 + \hat{\boldsymbol{S}}^2 - \hat{\boldsymbol{L}}^2\right). \tag{14.76}$$

Taking the expectation value in the same state $|jj\rangle$ and combining with (14.75), we obtain

$$\langle jj|\hat{\boldsymbol{J}} \cdot \hat{\boldsymbol{S}}|jj\rangle = \tfrac{1}{2}\left(j(j+1) + s(s+1) - l(l+1)\right) = (j+1)\langle jj|\hat{S}_z|jj\rangle, \tag{14.77}$$

that is,

$$\langle jj|\hat{S}_z|jj\rangle = \frac{j(j+1) + s(s+1) - l(l+1)}{2(j+1)}, \tag{14.78}$$

which is the desired result.

P14.8 Show that the mass appearing in the relativistic correction to the kinetic energy of the electron of a hydrogen-like atom, $-\frac{p^4}{8m^3c^2}$, is the mass of the electron and not the reduced mass.

Solution. In the non-relativistic treatment of the H atom, the kinetic energy of the electron-proton system in the center-of-mass frame is

$$K = \frac{P_e^2}{2m_e} + \frac{P_p^2}{2m_p} = P^2\left(\frac{1}{2m_e} + \frac{1}{2m_p}\right) = \frac{P^2}{2m}, \tag{14.79}$$

where $m = m_e m_p/(m_e + m_p)$ represents the reduced mass. In the relativistic case, the kinetic energy must be written as

$$K = \left(P_e^2 c^2 + m_e^2 c^4\right)^{\frac{1}{2}} + \left(P_p^2 c^2 + m_p^2 c^4\right)^{\frac{1}{2}} \tag{14.80}$$

$$= m_e c^2 \left(1 + \frac{P_e^2}{m_e^2 c^2}\right)^{\frac{1}{2}} + m_p c^2 \left(1 + \frac{P_p^2}{m_p^2 c^2}\right)^{\frac{1}{2}}. \tag{14.81}$$

To determine the relativistic correction predicted by (14.81), we perform a series expansion keeping terms to the desired order. Given the small ratio m_e/m_p, proton motion corrections are negligible, so we approximate,

$$K \simeq m_e c^2 \left[1 + \frac{1}{2}\frac{P_e^2}{m_e^2 c^2} - \frac{1}{8}\left(\frac{P_e^2}{m_e^2 c^2}\right)^2 + \cdots\right] \tag{14.82}$$

$$+ m_p c^2 \left(1 + \frac{1}{2}\frac{P_p^2}{m_p^2 c^2} + \cdots\right), \tag{14.83}$$

$$= m_e c^2 + m_p c^2 + \frac{P^2}{2m_e} + \frac{P^2}{2m_p} - \frac{P^4}{8m_e^3 c^2} + \cdots, \tag{14.84}$$

$$K \simeq m_e c^2 + m_p c^2 + \frac{P^2}{2m} - \frac{P^4}{8m_e^3 c^2} + \cdots, \tag{14.85}$$

where we took $P_e^2 = P_p^2 = P^2$ in the center-of-mass frame. The $(m_e + m_p)c^2$ term represents the rest mass energy and is dynamically irrelevant in non-relativistic treatments (serving only as an energy reference). The result shows that the relativistic correction to the kinetic energy depends on the electron mass but not on the nuclear mass.

P14.9 Show that the correction to the energy of a hydrogen-like atom whose nucleus is modeled as a sphere of radius R_N with uniform charge distribution is given by

$$\delta E = \frac{2}{5}\frac{Z^4 e^2 R_N^2}{a_0^3 n^3}\,\delta_{l0}. \tag{14.86}$$

Note: in the nuclear region we can make the approximation $|\psi(r)|^2 \simeq |\psi(0)|^2$.
Solution. The potential energy of the electron immersed in the field generated by the extended nucleus, taken as a uniformly charged sphere of radius R_N, is

$$V(r) = \begin{cases} -\dfrac{Ze^2}{R_N}\left(\dfrac{3}{2} - \dfrac{1}{2}\dfrac{r^2}{R_N^2}\right), & 0 \le r \le R_N, \\ -\dfrac{Ze^2}{r}, & r \ge R_N. \end{cases} \tag{14.87}$$

This potential can be taken as the sum of the Coulomb potential due to a point nucleus, plus a perturbation $\hat{H}'$ given by

$$\hat{H}'(r) = \begin{cases} -\dfrac{Ze^2}{R_N}\left(\dfrac{3}{2} - \dfrac{1}{2}\dfrac{r^2}{R_N^2}\right) + \dfrac{Ze^2}{r}, & 0 \leq r \leq R_N, \\ 0, & r \geq R_N. \end{cases} \tag{14.88}$$

We see that the perturbation is nonzero only in the region occupied by the nucleus, so it should be expected that only s electrons are affected by it, since these are the only ones that have a nonzero probability of visiting the nuclear region, due to the centrifugal barrier vanishing for them. To first order in perturbation theory, the energy correction is

$$\delta E = \langle n| \left[\frac{Ze^2}{r} - \frac{3Ze^2}{2R_N} + \frac{Ze^2 r^2}{2R_N^3}\right] |n\rangle, \tag{14.89}$$

where the integrals must be taken only within a sphere of radius R_N. Because of the smallness of the nucleus, we can approximate the wave function in the nuclear region by its value at the origin and write $|\psi_{nl}(r)|^2 \simeq |\psi_{nl}(0)|^2$. Since the radial wave function is proportional to r^l, $\psi_{nl}(0)$ is different from zero only for $l = 0$; furthermore, at the origin the associated Legendre polynomials equal 1, so that finally we obtain that the electron density at the origin is

$$|\psi_{nl}(0)|^2 = \frac{1}{4\pi}\frac{4}{n^3}\left(\frac{Z}{a_0}\right)^3 \delta_{l0}. \tag{14.90}$$

With all this taken into account, we obtain

$$\begin{aligned} \delta E =& \frac{1}{4\pi}\frac{4}{n^3}\left(\frac{Z}{a_0}\right)^3 \delta_{l0} \\ \delta E =& \frac{1}{4\pi}\frac{4}{n^3}\left(\frac{Z}{a_0}\right)^3 \delta_{l0} \cdot 4\pi Ze^2 \int_0^{R_N} \left(\frac{1}{r} - \frac{3}{2R_N} + \frac{1}{2R_N^3} r^2\right) r^2 dr, \end{aligned}$$

that is,

$$\delta E = \frac{2}{5}\frac{Z^4 e^2 R_N^2}{a_0^3 n^3}\delta_{l0} = \frac{2}{5}\frac{Z^4}{n^3} R_N^2 \delta_{l0} \text{ a.u.} \tag{14.91}$$

The factor δ_{l0} shows that, as expected, only the s states are perturbed. For hydrogen ($Z = 1$) in its ground state ($n = 1$) one obtains $\delta E = \frac{2}{5} R_N^2$ in atomic units, a result that is similar in structure and order of magnitude to that obtained with an exponential distribution.

P14.10 Calculate the relativistic and spin-orbit coupling effects on the energy of an isotropic 3D harmonic oscillator of mass m and frequency ω.

Solution. These effects can be summarized in three corrections for central systems:

a) The relativistic correction to kinetic energy

$$\hat{H}_1 = -\frac{\hat{p}^4}{8m_0^3c^2}, \tag{14.92}$$

where $\hat{p}$ is the momentum operator, m_0 is the electron rest mass and c is the speed of light. This term represents the first-order relativistic correction to the kinetic energy operator, arising from the expansion of the relativistic energy-momentum relation.

b) The Darwin term, arising from quantum fluctuations around the orbit

$$\hat{H}_2 = \frac{\hbar^2}{8m_0^2c^2}\nabla^2 V. \tag{14.93}$$

c) The direct spin-orbit coupling between orbital and spin angular momenta

$$\hat{H}_3 = \frac{1}{2m_0^2c^2}\left(\frac{1}{r}\frac{dV}{dr}\right)\hat{\mathbf{S}}\cdot\hat{\mathbf{L}}. \tag{14.94}$$

When using the $|jlsm_j\rangle$ eigenstates as a basis, $\hat{H}_3$ can be replaced by the effective Hamiltonian

$$\hat{H}_3 = \frac{\hbar^2}{4m_0^2c^2}q\left(\frac{1}{r}\frac{dV}{dr}\right), \tag{14.95}$$

where q is

$$q = j(j+1) - l(l+1) - s(s+1). \tag{14.96}$$

These expressions apply to an isotropic harmonic oscillator when treated as time-independent perturbations. For the relativistic correction from $\hat{H}_1$, using $|n\rangle \equiv |nlm\rangle$ and the approximation $\hat{p}^2 \simeq 2m(E_n - V)$,

$$\delta E_1 = \langle n|\hat{H}_1|n\rangle = -\frac{1}{2m_0c^2}\langle n|(E_n - V)^2|n\rangle \tag{14.97}$$

$$= -\frac{1}{2m_0c^2}\left(E_n^2 - 2E_n\langle n|V|n\rangle + \tfrac{1}{4}m_0^2\omega^4\langle n|r^4|n\rangle\right). \tag{14.98}$$

Since for a harmonic oscillator in a stationary state the quantum virial theorem gives $\left\langle \hat{T}\right\rangle = \langle V\rangle = \frac{1}{2}\langle E\rangle$, it follows that the first two terms of the last equality cancel each other out, so the correction δE_1 reduces to

$$\delta E_1 = -\frac{m_0\omega^4}{8c^2}\left\langle n \mid r^4 \mid n\right\rangle, \tag{14.99}$$

a result that can be obtained directly from (14.92) with the substitution $\left\langle \hat{B}^4\right\rangle \to \langle (m_0\omega r)^4\rangle$. To evaluate δE_1 we use the recurrence relation derived in Problem P12.7 for stationary states and central potential $V(r)$, which we write in the form

$$2(k+1)E\left\langle r^k\right\rangle - 2(k+1)\left\langle r^k V\right\rangle - \left\langle r^{k+1}V'\right\rangle + \frac{\hbar^2}{m_0}k\left(\frac{k^2-1}{4} - l(l+1)\right)\left\langle r^{k-2}\right\rangle = 0. \tag{14.100}$$

For the harmonic oscillator we must take $k = 2$ and $E_n = \hbar\omega(n + \frac{3}{2})$; solving we obtain

$$\left\langle n \mid r^4 \mid n \right\rangle = \frac{3E_n}{2m_0\omega^2} \left\langle n \mid r^2 \mid n \right\rangle + \frac{\hbar^2}{2m_0^2\omega^2} \left[\frac{3}{4} - l(l+1)\right] \tag{14.101}$$

$$= \frac{3}{2}\left(\frac{E_n}{m_0\omega^2}\right)^2 + \frac{1}{2}\left(\frac{\hbar}{m_0\omega}\right)^2 \left[\frac{3}{4} - l(l+1)\right]. \tag{14.102}$$

$$= \frac{3}{2}\left(\frac{\hbar}{m_0\omega}\right)^2 \left(n(n+3) + \frac{5}{2} - \frac{1}{3}l(l+1)\right). \tag{14.103}$$

The relativistic correction to the kinetic energy then results, from (14.98),

$$\delta E_1 = -\frac{3}{16}\frac{\hbar^2\omega^2}{m_0c^2}\left(n(n+3) + \frac{5}{2} - \frac{1}{3}l\,(l+1)\right). \tag{14.104}$$

The Darwin term reduces for the isotropic oscillator to

$$\delta E_2 = \left\langle n \mid \hat{H}_2 \mid n \right\rangle = \frac{\hbar^2}{8m_0^2c^2} \left\langle n \mid \nabla \cdot (\nabla V) \mid n \right\rangle = \frac{3}{8}\frac{\hbar^2\omega^2}{m_0c^2}, \tag{14.105}$$

and affects all levels equally, so it does not modify the emission spectrum of the oscillator. The energy correction due to spin-orbit coupling, if dealing with states with well-defined j and l, is

$$\delta E_3 = \left\langle n \mid \hat{H}_3 \mid n \right\rangle = \frac{\hbar^2}{4m_0^2c^2} q \left\langle n \right| \left(\frac{1}{r}\frac{dV}{dr}\right) \left| n \right\rangle = \frac{\hbar^2\omega^2}{4m_0c^2} q. \tag{14.106}$$

If the oscillator is an electron, we can take $s = 1/2$ and write

$$\delta E_3 = \frac{\hbar^2\omega^2}{4m_0c^2}\left(j(j+1) - l\,(l+1) - \frac{3}{4}\right). \tag{14.107}$$

The simultaneous effect of the three corrections, that is, the sum of terms (14.104)-(14.106), depends in a complicated way on the set of quantum numbers n, j, l, s, generally breaking the original degeneracy of the oscillator.

P14.11 Determine the energy eigenvalues and eigenfunctions for a charged particle (without spin) moving in a space occupied by an electric field and a magnetic field, both uniform and constant, whose directions are perpendicular to each other.
Solution. The Schrödinger equation for a charged particle in the presence of an electromagnetic field, described by the scalar potential Φ and the vector potential $\boldsymbol{A}$, is given by

$$\hat{H}\psi = E\psi, \qquad \hat{H} = \frac{1}{2m}\left(\hat{\boldsymbol{p}} - \frac{e}{c}\boldsymbol{A}\right)^2 + e\Phi. \tag{14.108}$$

We set the electric field along the $\hat{x}$ direction and the magnetic field along the $\hat{z}$ direction. For this, we choose the following gauge for the potentials. Scalar potential (electric field):

$$\Phi = \mathcal{E}x \qquad \Rightarrow \qquad -\nabla\Phi = (\mathcal{E}, 0, 0) = \boldsymbol{E}. \tag{14.109}$$

Vector potential (magnetic field):

$$\boldsymbol{A} = (0, Bx, 0) \qquad \Rightarrow \qquad \nabla \times \boldsymbol{A} = (0, 0, B) = \boldsymbol{B}. \tag{14.110}$$

Therefore $\boldsymbol{E} \perp \boldsymbol{B}$. The Hamiltonian takes the form

$$\hat{H} = \frac{1}{2m}\left(\hat{p}_x,\ \hat{p}_y - \frac{eB}{c}x,\ \hat{p}_z\right)^2 - e\mathcal{E}x, \tag{14.111}$$

which expands to

$$\hat{H} = \frac{1}{2m}\left[\hat{p}_x^2 + \left(\hat{p}_y - \frac{eB}{c}x\right)^2 + \hat{p}_z^2\right] - e\mathcal{E}x. \tag{14.112}$$

We note that the Hamiltonian has the form

$$\hat{H} = H(\hat{p}_x, \hat{p}_y, \hat{p}_z, x). \tag{14.113}$$

From the commutation relations we know that $[\hat{p}_i, \hat{p}_j] = 0$, $[x_i, \hat{p}_j] = i\hbar\delta_{ij}$. Therefore, $\hat{H}$ commutes with $\hat{p}_y$ and $\hat{p}_z$. This implies that the eigenfunctions of the system can be taken as simultaneous eigenfunctions of $\hat{H}$, $\hat{p}_y$, and $\hat{p}_z$. The eigenvalue equation for the momentum operators $\hat{p}_i$ is

$$\hat{p}_i\psi_i = \hbar k_i \psi_i, \qquad k_i = \frac{\sqrt{2mE_i}}{\hbar} \in \mathbb{R} \quad \Rightarrow \quad E_i = \frac{\hbar^2 k_i^2}{2m}, \tag{14.114}$$

with eigenfunctions of the form

$$\psi_i = e^{ik_i x_i}. \tag{14.115}$$

Thus, the wave function of the full Hamiltonian can be written as

$$\Psi(x, y, z) = \phi(x)\, e^{i(k_y y + k_z z)}, \tag{14.116}$$

where k_y and k_z are the eigenvalues associated with $\hat{p}_y$ and $\hat{p}_z$. Substituting this ansatz into the Hamiltonian, we obtain

$$\begin{aligned}
\hat{H} =& \frac{\hat{p}_x^2}{2m} + \frac{1}{2m}\left(\hbar k_y - \frac{eB}{c}x\right)^2 + \frac{\hbar^2 k_z^2}{2m} - e\mathcal{E}x \\
=& \frac{\hat{p}_x^2}{2m} + \frac{1}{2m}\left(\hbar^2 k_y^2 - 2\hbar k_y \frac{eB}{c}x + \frac{e^2B^2}{c^2}x^2\right) + E_z - e\mathcal{E}x \\
=& \frac{\hat{p}_x^2}{2m} + E_y - \frac{e\hbar}{mc}k_y B\, x + \frac{e^2B^2}{2mc^2}x^2 + E_z - e\mathcal{E}x.
\end{aligned} \tag{14.117}$$

Grouping terms, this becomes

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{e^2B^2}{2mc^2}x^2 - \left(\frac{e\hbar}{mc}k_y B + e\mathcal{E}\right)x + E_y + E_z. \tag{14.118}$$

To simplify notation, let us define

$$a = \frac{e^2B^2}{2mc^2}, \qquad b = \frac{e\hbar}{mc}k_y B + e\mathcal{E}. \tag{14.119}$$

We now complete the square,

$$ax^2 - bx = a\left(x - \frac{b}{2a}\right)^2 - \frac{b^2}{4a}. \tag{14.120}$$

Substituting back into (14.118), the Hamiltonian becomes

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + a\left(x - \frac{b}{2a}\right)^2 - \frac{b^2}{4a} + E_y + E_z, \tag{14.121}$$

which corresponds to a displaced harmonic oscillator. To identify the frequency, we recall that

$$\frac{1}{2}m\omega^2 = a, \tag{14.122}$$

which gives

$$\omega = \sqrt{\frac{2a}{m}} = \frac{eB}{mc}. \tag{14.123}$$

This is precisely the Larmor frequency. The displacement of the oscillator is given by

$$x_0 = \frac{b}{2a} = \frac{\hbar k_y c}{eB} + \frac{mc^2\mathcal{E}}{eB^2}. \tag{14.124}$$

We now evaluate the constant term

$$\frac{b^2}{4a} = \frac{mc^2}{2e^2B^2}\left(\frac{e\hbar}{mc}k_yB + e\mathcal{E}\right)^2 = \frac{\hbar^2k_y^2}{2m} + \frac{\hbar k_y\mathcal{E}c}{B} + \frac{mc^2}{2}\frac{\mathcal{E}^2}{B^2}. \tag{14.125}$$

Therefore, the Hamiltonian takes the form

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2(x - x_0)^2 + E_z - \frac{\hbar k_y\mathcal{E}c}{B} - \frac{mc^2}{2}\frac{\mathcal{E}^2}{B^2}, \tag{14.126}$$

The Schrödinger equation now reads

$$\left[\frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2(x - x_0)^2\right]\Psi = E'\Psi, \tag{14.127}$$

with

$$E' = E - E_z + \frac{\hbar k_y\mathcal{E}c}{B} + \frac{mc^2}{2}\frac{\mathcal{E}^2}{B^2}. \tag{14.128}$$

This is the equation of a shifted harmonic oscillator, whose eigenvalues are

$$E' = \hbar\omega\left(n + \tfrac{1}{2}\right), \qquad n = 0, 1, 2, \ldots \tag{14.129}$$

Thus, the total energy spectrum is

$$E = \hbar\omega\left(n + \tfrac{1}{2}\right) + \frac{\hbar^2k_z^2}{2m} - \frac{\hbar k_yc\mathcal{E}}{B} - \frac{mc^2}{2}\frac{\mathcal{E}^2}{B^2}. \tag{14.130}$$

Finally, the eigenfunctions are given by

$$\Psi(x, y, z) = \phi_n(x - x_0)\, e^{i(k_yy + k_zz)}, \tag{14.131}$$

where $\phi_n(x)$ are the normalized eigenfunctions of the 1D harmonic oscillator.

P14.12 Determine exactly the energy spectrum of a charged (spinless) isotropic oscillator immersed in a constant, uniform magnetic field.

Solution. For a particle of mass m and charge q (without spin), subject to 3D isotropic harmonic oscillator potential

$$V(r) = \frac{1}{2}m\omega_0^2(x^2 + y^2 + z^2) \tag{14.132}$$

and a uniform magnetic field $\boldsymbol{B} = B\hat{z}$ (aligned along the z-axis), the total Hamiltonian is given by

$$\hat{H} = \frac{1}{2m}(\hat{\boldsymbol{p}} - q\boldsymbol{A})^2 + \frac{1}{2}m\omega_0^2(\hat{x}^2 + \hat{y}^2 + \hat{z}^2), \tag{14.133}$$

where the symmetric gauge is used, $\boldsymbol{A} = \frac{B}{2}(-y\hat{x} + x\hat{y})$. The motion decouples into parallel (z) and perpendicular (xy) components relative to $\boldsymbol{B}$,

$$\hat{H} = \hat{H}_{xy} + \hat{H}_z. \tag{14.134}$$

The oscillating motion in the$z$-direction (unaffected by $\boldsymbol{B}$)

$$\hat{H}_z = \frac{\hat{p}_z^2}{2m} + \frac{1}{2}m\omega_0^2\hat{z}^2 \tag{14.135}$$

has an associated energy

$$E_z = \hbar\omega_0\left(n_z + \frac{1}{2}\right), \quad n_z = 0, 1, 2, \ldots \tag{14.136}$$

The motion on the xy-plane is governed by the Hamiltonian

$$\hat{H}_{xy} = \frac{1}{2m}\left[\left(\hat{p}_x + \frac{qB}{2}y\right)^2 + \left(\hat{p}_y - \frac{qB}{2}x\right)^2\right] + \frac{1}{2}m\omega_0^2(\hat{x}^2 + \hat{y}^2), \tag{14.137}$$

which simplifies into

$$\hat{H}_{xy} = \frac{\hat{p}_x^2 + \hat{p}_y^2}{2m} + \frac{1}{2}m\omega_{\text{eff}}^2(\hat{x}^2 + \hat{y}^2) - \frac{qB}{2m}\hat{L}_z, \tag{14.138}$$

where

$$\omega_{\text{eff}} = \sqrt{\omega_0^2 + \left(\frac{|q|B}{2m}\right)^2} \tag{14.139}$$

is the effective frequency and the angular momentum operator is $\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$.

The Hamiltonian $\hat{H}_{xy}$ is diagonalized using the radial quantum number n_r: $n_r = 0, 1, 2, \ldots$ and magnetic quantum number m_l: $m_l = 0, \pm1, \pm2, \ldots$ (eigenvalues of $\hat{L}_z$: $m_l\hbar$). This gives for the energy in the xy-plane

$$E_{xy} = \hbar\omega_{\text{eff}}(2n_r + |m_l| + 1) - \frac{qB\hbar}{2m}m_l. \tag{14.140}$$

Combining the contributions from z and xy, we get

$$E = \hbar\omega_0\left(n_z + \frac{1}{2}\right) + \hbar\omega_{\text{eff}}(2n_r + |m_l| + 1) - \frac{qB\hbar}{2m}m_l, \tag{14.141}$$

with $\omega_0 = \sqrt{\frac{k}{m}}$, the natural oscillator frequency, $\omega_{\text{eff}} = \sqrt{\omega_0^2 + \left(\frac{|q|B}{2m}\right)^2}$ the effective frequency in the xy-plane, and $\omega_c = \frac{|q|B}{m}$ the cyclotron frequency. The quantum number $n_z = 0, 1, 2, \ldots$ is the oscillator quantum number in z. $n_r = 0, 1, 2, \ldots$ is the radial quantum number in xy (analogous to n in 1D), and $m_l = 0, \pm1, \pm2, \ldots$ is the magnetic quantum number. In the limit $B \to 0$ $\omega_{\text{eff}} \to \omega_0$, and the Zeeman term vanishes. Total energy is given by

$$E = \hbar\omega_0\left(n_z + 2n_r + |m_l| + \frac{3}{2}\right) = \hbar\omega_0\left(N + \frac{3}{2}\right), \tag{14.142}$$

where $N = n_z + 2n_r + |m_l|$ is the total quantum number of the 3D isotropic oscillator.

P14.13 An electron is in a magnetic field that varies with time according to the law

$$B_x = B\sin\theta\cos\omega t, \quad B_y = B\cos\theta\sin\omega t, \quad B_z = B\cos\theta. \tag{14.143}$$

At time $t = 0$ the projection of the spin in the direction of the field is $+1/2$. Find the probability as a function of time that the particle is in the $-1/2$ spin state in the direction of the field, for $t > 0$.

Solution. The magnetic field is given by

$$\vec{B} = B\left(\sin\theta\cos\omega t,\ \cos\theta\sin\omega t,\ \cos\theta\right). \tag{14.144}$$

The Hamiltonian for a spin immersed in a magnetic field is

$$\hat{H} = \mu_0\vec{B}\cdot\hat{\vec{\sigma}}, \tag{14.145}$$

where $\hat{\vec{\sigma}} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$. Therefore, the Hamiltonian becomes

$$H = \mu_0 B\sin\theta\cos\omega t\,\hat{\sigma}_x + \mu_0 B\cos\theta\sin\omega t\,\hat{\sigma}_y + \mu_0 B\cos\theta\,\hat{\sigma}_z. \tag{14.146}$$

We define

$$\alpha = \cos\theta, \qquad \beta = \sin\theta, \qquad \omega_L = \frac{\mu_0 B}{\hbar}, \tag{14.147}$$

and wwrite the Hamiltonian as

$$\hat{H} = \hbar\omega_L\alpha\hat{\sigma}_z + \hbar\omega_L\beta\cos(\omega t)\hat{\sigma}_x + \hbar\omega_L\alpha\sin(\omega t)\hat{\sigma}_y. \tag{14.148}$$

Thus we separate

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \tag{14.149}$$

with $\hat{H}_0 = \hbar\omega_L\alpha\,\hat{\sigma}_z$ and the perturbation $\hat{H}_1$ given by the oscillating terms. We now write $\hat{H}_1$ in the interaction representation

$$\hat{H}_I = e^{i\hat{H}_0 t/\hbar}\,\hat{H}_1\,e^{-i\hat{H}_0 t/\hbar}. \tag{14.150}$$

Explicitly,

$$\hat{H}_I = \hbar\omega_L\beta\cos(\omega t)\left(e^{i\omega_L\alpha t\hat{\sigma}_z}\hat{\sigma}_x e^{-i\omega_L\alpha t\hat{\sigma}_z}\right) + \hbar\omega_L\beta\sin(\omega t)\left(e^{i\omega_L\alpha t\hat{\sigma}_z}\hat{\sigma}_y e^{-i\omega_L\alpha t\hat{\sigma}_z}\right). \tag{14.151}$$

We compute

$$e^{i\omega_L\alpha t\hat{\sigma}_z}\hat{\sigma}_x e^{-i\omega_L\alpha t\hat{\sigma}_z} = \begin{pmatrix} 0 & e^{2i\alpha\omega_L t} \\ e^{-2i\alpha\omega_L t} & 0 \end{pmatrix}, \tag{14.152}$$

$$e^{i\omega_L\alpha t\hat{\sigma}_z}\hat{\sigma}_y e^{-i\omega_L\alpha t\hat{\sigma}_z} = \begin{pmatrix} 0 & -ie^{2i\alpha\omega_L t} \\ ie^{-2i\alpha\omega_L t} & 0 \end{pmatrix}. \tag{14.153}$$

Using the identities

$$\cos(\omega t) = \tfrac{1}{2}\left(e^{-i\omega t} + e^{i\omega t}\right), \qquad \sin(\omega t) = \tfrac{i}{2}\left(-e^{-i\omega t} + e^{i\omega t}\right), \tag{14.154}$$

and defining

$$\Omega_\beta = \omega_L\beta, \qquad \Omega_\alpha = \omega_L\alpha, \tag{14.155}$$

the interaction Hamiltonian can be simplified using the rotating-wave approximation, for this we neglect the rapidly oscillating terms ($e^{\pm i(\omega+2\Omega_\alpha)t}$), and thus obtain

$$H_I \simeq \frac{\hbar\Omega_\beta}{2}\begin{pmatrix} 0 & e^{-i(\omega-2\Omega_\alpha)t} \\ e^{i(\omega-2\Omega_\alpha)t} & 0 \end{pmatrix} + \frac{\hbar\Omega_\alpha}{2}\begin{pmatrix} 0 & e^{-i(\omega-2\Omega_\alpha)t} \\ ie^{i(\omega-2\Omega_\alpha)t} & 0 \end{pmatrix}. \tag{14.156}$$

Collecting terms, this can be written as

$$H_I = \frac{\hbar\Omega}{2}\begin{pmatrix} 0 & e^{i\Delta\omega t} \\ e^{-i\Delta\omega t} & 0 \end{pmatrix}, \tag{14.157}$$

where we defined

$$\Omega = \Omega_\beta + \Omega_\alpha, \qquad \Delta\omega = 2\Omega_\alpha - \omega. \tag{14.158}$$

The spinor evolves according to (see Problem P14.6)

$$i\hbar\frac{\partial}{\partial t}\chi(t) = H_I\chi(t), \tag{14.159}$$

with

$$\chi(t) = \begin{pmatrix} a(t) \\ b(t) \end{pmatrix}. \tag{14.160}$$

From the interaction Hamiltonian we obtain

$$i\hbar\frac{d}{dt}\begin{pmatrix} a(t) \\ b(t) \end{pmatrix} = \frac{\hbar\Omega}{2}\begin{pmatrix} 0 & e^{i\Delta\omega t} \\ e^{-i\Delta\omega t} & 0 \end{pmatrix}\begin{pmatrix} a(t) \\ b(t) \end{pmatrix}. \tag{14.161}$$

This gives the system of coupled differential equations

$$i\dot{a}(t) = \frac{\Omega}{2}b(t)e^{i\Delta\omega t}, \tag{14.162}$$

$$i\dot{b}(t) = \frac{\Omega}{2}a(t)e^{-i\Delta\omega t}. \tag{14.163}$$

Given that at $t = 0$, χ is in the $+1/2$ state in the field direction, the initial condition is $\chi(0) = \chi_+ = \begin{pmatrix}1\\0\end{pmatrix}$, i.e.

$$a(0) = 1, \qquad b(0) = 0, \tag{14.164}$$

Differentiating Eq. (14.162)

$$i\ddot{a}(t) = \frac{\Omega}{2}\left(\dot{b}(t)e^{i\Delta\omega t} + i\Delta\omega b(t)e^{i\Delta\omega t}\right) \tag{14.165}$$

and using Eqs. (14.163) and (14.162)

$$i\ddot{a}(t) = -\frac{\Omega^2}{4}a(t) + i\Delta\omega\dot{a}(t), \tag{14.166}$$

we obtain the second-order differential equation

$$\ddot{a}(t) - i\Delta\omega\dot{a}(t) + \frac{\Omega^2}{4}a(t) = 0. \tag{14.167}$$

To solve this equation we introduce the ansatz $a(t) = e^{i\tilde{\omega}t}$, for which

$$\dot{a}(t) = i\tilde{\omega}a(t), \qquad \ddot{a}(t) = -\tilde{\omega}^2 a(t).$$

Substituting into (14.167) gives the characteristic equation

$$\tilde{\omega}^2 - \Delta\omega\,\tilde{\omega} - \frac{\Omega^2}{4} = 0. \tag{14.168}$$

which has solutions

$$\tilde{\omega}_\pm = \frac{1}{2}\left(\Delta\omega \pm \sqrt{(\Delta\omega)^2 + \Omega^2}\right). \tag{14.169}$$

We define

$$\Delta = \frac{\Delta\omega}{2}, \qquad \delta = \tfrac{1}{2}\sqrt{(\Delta\omega)^2 + \Omega^2}.$$

Thus the general solution for $a(t)$ is

$$\begin{aligned} a(t) &= a_1 e^{i\tilde{\omega}_+ t} + a_2 e^{-i\tilde{\omega}_- t} \\ &= a_1 e^{i(\Delta+\delta)t} + a_2 e^{-i(\delta-\Delta)t}. \end{aligned} \tag{14.170}$$

The initial condition $a(0) = 1$ imposes

$$a_1 + a_2 = 1. \tag{14.171}$$

To determine $b(t)$ we differentiate (14.170)

$$\dot{a}(t) = ia_1(\Delta+\delta)e^{i(\Delta+\delta)t} + ia_2(\Delta-\delta)e^{-i(\delta-\Delta)t}$$

and substitute in (14.162), hence

$$b(t) = -\frac{2}{\Omega}e^{-i\Delta\omega t}\left[a_1(\Delta+\delta)e^{i\delta t} + a_2(\Delta-\delta)e^{-i\delta t}\right]. \tag{14.172}$$

Imposing the initial condition $b(0) = 0$ determines the relation between a_1 and a_2,

$$a_1(\Delta+\delta) + a_2(\Delta-\delta) = 0, \qquad a_1 + a_2 = 1, \tag{14.173}$$

which gives

$$a_1 = \tfrac{1}{2}\left(1 - \frac{\Delta}{\delta}\right), \qquad a_2 = \tfrac{1}{2}\left(1 + \frac{\Delta}{\delta}\right). \tag{14.174}$$

Finally, for the amplitudes $a(t)$ and $b(t)$ we obtain

$$\begin{aligned} a(t) &= \tfrac{1}{2}\left(1 - \tfrac{\Delta}{\delta}\right) e^{i(\delta+\Delta)t} + \tfrac{1}{2}\left(1 + \tfrac{\Delta}{\delta}\right) e^{-i(\delta-\Delta)t} \\ &= \left[\tfrac{1}{2}\left(e^{i\delta t} + e^{-i\delta t}\right) + \tfrac{\Delta}{\delta}\,\tfrac{1}{2}\left(e^{-i\delta t} - e^{i\delta t}\right)\right] e^{i\Delta t}, \end{aligned}$$

that is,

$$a(t) = \Big[\cos(\delta t) - i\tfrac{\Delta}{\delta}\sin(\delta t)\Big] e^{i\Delta t}. \tag{14.175}$$

For $b(t)$,

$$\begin{aligned} b(t) &= -\tfrac{2}{\Omega}\left(\tfrac{1}{2}\left(1 - \tfrac{\Delta}{\delta}\right)(\Delta+\delta)e^{i\delta t} + \tfrac{1}{2}\left(1 + \tfrac{\Delta}{\delta}\right)(\Delta-\delta)e^{-i\delta t}\right) e^{-i\Delta t} \\ &= -\frac{\Omega}{2\delta}\left[(\delta-\Delta)(\Delta+\delta)e^{i\delta t} - (\delta+\Delta)(\delta-\Delta)e^{-i\delta t}\right] e^{-i\Delta t} \\ &= -\frac{\delta^2-\Delta^2}{\Omega\delta}\left(e^{i\delta t} - e^{-i\delta t}\right) e^{-i\Delta t} = -\frac{\delta^2-\Delta^2}{\Omega\delta} 2i\sin(\omega t) e^{-i\Delta t}. \end{aligned}$$

Recall that

$$\delta^2 - \Delta^2 = \tfrac{1}{4}\big(\Delta\omega^2 + \Omega^2\big) - \Delta^2 = \Delta^2 + \tfrac{\Omega^2}{4} - \Delta^2 = \tfrac{\Omega^2}{4}.$$

Therefore,

$$b(t) = -i\,\frac{\Omega}{2\delta}\,\sin(\delta t)\, e^{-i\Delta t}. \tag{14.176}$$

The probability that the spin is in the state χ_- ($-\frac{1}{2}$ along the field direction) is

$$|b(t)|^2 = \frac{\Omega^2}{4\delta^2}\,\sin^2(\delta t).$$

Substituting the definitions of the parameters Ω, and δ we obtain

$$\begin{aligned} |b(t)|^2 &= \frac{1+\sin(2\theta)}{(2\cos\theta - \frac{\omega}{\omega_L})^2 + \sin(2\theta) + 1}\ \sin^2\Big(\tfrac{\omega_L}{2}\sqrt{(2\cos\theta - \tfrac{\omega}{\omega_L})^2 + \sin(2\theta) + 1}\ t\Big). \\ &= \left[\frac{(2\cos\theta - \frac{\omega}{\omega_L})^2}{\sin(2\theta)+1} + 1\right]^{-1} \sin^2\Big(\tfrac{\omega_L}{2}\sqrt{(2\cos\theta - \tfrac{\omega}{\omega_L})^2 + \sin(2\theta) + 1}\ t\Big). \end{aligned} \tag{14.177}$$

P14.14 Three particles with spin 1/2, placed at the corners of an equilateral triangle, are described by the interaction Hamiltonian

$$\hat{H} = \frac{1}{3}\lambda(\hat{\sigma}_1\cdot\hat{\sigma}_2 + \hat{\sigma}_1\cdot\hat{\sigma}_3 + \hat{\sigma}_2\cdot\hat{\sigma}_3). \tag{14.178}$$

List the energy levels and their degeneracy.
Solution. The Hamiltonian can be written as

$$\hat{H} = \frac{\lambda}{3} \sum_{i<j} \hat{\boldsymbol{\sigma}}_i \cdot \hat{\boldsymbol{\sigma}}_j. \tag{14.179}$$

However, it is more useful to express $\hat{H}$ in terms of $\boldsymbol{\Sigma}^2$, defined as

$$\boldsymbol{\Sigma}^2 = \sum_{i=1}^{3} \hat{\boldsymbol{\sigma}}_i^2 + 2 \sum_{i<j} \hat{\boldsymbol{\sigma}}_i \cdot \hat{\boldsymbol{\sigma}}_j. \tag{14.180}$$

Since $\hat{\boldsymbol{\sigma}}_i^2 = 3I$ (for spin 1/2),

$$\boldsymbol{\Sigma}^2 = 9I + 2 \sum_{i<j} \hat{\boldsymbol{\sigma}}_i \cdot \hat{\boldsymbol{\sigma}}_j \implies \sum_{i<j} \hat{\boldsymbol{\sigma}}_i \cdot \hat{\boldsymbol{\sigma}}_j = \frac{1}{2}(\boldsymbol{\Sigma}^2 - 9I). \tag{14.181}$$

so that

$$\hat{H} = \frac{\lambda}{6}(\boldsymbol{\Sigma}^2 - 9I). \tag{14.182}$$

The eigenvalues of $\boldsymbol{\Sigma}^2$ are $4s(s+1)$, where s is the total spin. The symmetric quartet ($s = 3/2$) has an eigenvalue $4 \cdot \frac{3}{2} \cdot \frac{5}{2} = 15$ and a degeneracy 4 ($m_s = -3/2, -1/2, 1/2, 3/2$). There are two independent doublets ($s = 1/2$, total dimension 4) having an eigenvalue $4 \cdot \frac{1}{2} \cdot \frac{3}{2} = 3$. These eigenvalues of $\boldsymbol{\Sigma}^2$ introduced into $\hat{H}$ give, for $s = 3/2$,

$$E = \frac{\lambda}{6}(15 - 9) = \lambda, \tag{14.183}$$

and for $s = 1/2$,

$$E = \frac{\lambda}{6}(3 - 9) = -\lambda. \tag{14.184}$$

The energy level $E = \lambda$ corresponds to the symmetric quartet ($s = 3/2$), and the energy level $E = -\lambda$ corresponds to the two doublets ($s = 1/2$).

P14.15 Consider a neutron interference experiment in which the two beams have opposite polarizations on the z-axis, so that the superposition of the beams at the output of the instrument has the spin in the xy-plane. Under these conditions, if the spin of one of the two branches is inverted by means of a magnetic field, the final spin will be completely polarised on the z-axis. Show that this is so.
Solution. In a neutron interference experiment, the incoming beam is divided into two beams. In the present case, the two beams have originally opposite spin polarizations, with total spin projection $S_z = 0$. We call 1 the beam with positive spin along the z axis and 2 the beam with negative spin along the z axis. The initial state is therefore

$$|0\rangle = |+\rangle_1 |-\rangle_2 . \tag{14.185}$$

The general formula for the spin projetion operator is $\hat{T}_{\mathbf{n}}(\theta) = \exp(-i\mathbf{n} \cdot \hat{\boldsymbol{\sigma}}\theta/2)$, where $\mathbf{n}$ is the axis of rotation and θ is the rotation angle. To invert the spin

polarization of beam 2 we apply a rotation of $\theta = \pi$ around an axis on the xy plane, say the x-axis,

$$\hat{T}_x(\theta = \pi) = \exp(-i\hat{\sigma}_x \pi/2) \tag{14.186}$$

to the state vector $|-\rangle_2$. Taking into account that $\hat{\sigma}_x^{2k} = 1$ and $\hat{\sigma}_x^{2k+1} = \hat{\sigma}_x$, a Taylor series expansion of (14.186) gives $\hat{T}_x(\pi) = -\hat{\sigma}_x$, so that

$$\hat{T}_x(\pi)\,|0\rangle = -\,|+\rangle_1\,\hat{\sigma}_x\,|-\rangle_2 = -\,|+\rangle_1\,|+\rangle_2 = -\,|1\rangle\,.$$

This confirms that the final spin is polarized on the z-axis.

CHAPTER 15

Identical-Particle Systems. Quantum Statistics. The Density Matrix

P15.1 Show that the particle exchange operator $\widehat{P}_{ij}$ is Hermitian and that it commutes with $\widehat{P}_{nm}$ only when (i, j) and (n, m) refer to different pairs of particles (there is no common particle).

Solution. A projector $\hat{P}$ is a Hermitian idempotent operator, $\hat{P} = \hat{P}^\dagger$, $\hat{P}^2 = \hat{P}$. If $\hat{P}_i$ and $\hat{P}_j$ are two projectors onto their respective subspaces $\mathcal{H}_i$ and $\mathcal{H}_j$ of the corresponding Hilbert space, their product is a projector (if the subspaces coincide) or null (if the subspaces are disjoint),

$$\hat{P}_i \hat{P}_j = \hat{P}_j \hat{P}_i = \hat{P}_i \delta_{ij}. \tag{15.1}$$

In short, if $i \neq j$, then $\hat{P}_i$ and $\hat{P}_j$ are orthogonal and $\hat{P}_i \hat{P}_j = 0$; but if $i = j$, (15.15) is simply the idempotency property. From this latter property it follows that the eigenvalues of a projector are 0 or 1. A set of projectors is complete if $\sum_i \hat{P}_i = 1$, where the sum extends over the entire Hilbert space of the problem.Now consider the operators

$$\hat{P}_{ij}^{\pm} \equiv \frac{1}{2}\left(1 \pm \hat{P}_{ij}\right). \tag{15.2}$$

Since $\hat{P}_{ij}$ is Hermitian, it is clear that these operators are also Hermitian. Moreover, each of them is idempotent,

$$\left(\hat{P}_{ij}^{\pm}\right)^2 = \tfrac{1}{4}\left(1 \pm 2\hat{P}_{ij} + \hat{P}_{ij}^2\right) = \tfrac{1}{2}\left(1 \pm \hat{P}_{ij}\right) = \hat{P}_{ij}^{\pm}, \tag{15.3}$$

and $\hat{P}_{ij}^{+}$ and $\hat{P}_{ij}^{-}$ are mutually orthogonal,

$$\hat{P}_{ij}^{+} \hat{P}_{ij}^{-} = \tfrac{1}{4}\left(1 + \hat{P}_{ij}\right)\left(1 - \hat{P}_{ij}\right) = \tfrac{1}{4}\left(1 - \hat{P}_{ij}^2\right) = 0. \tag{15.4}$$

These properties show that $\hat{P}_{ij}^{\pm}$ are projection operators, mutually orthogonal. We will now determine the subspace onto which they project.Let $\Psi^S(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N)$ be a wave function symmetric under the exchange of any pair of indices (in short: totally symmetric). This means that for any pair i, j,

$$\Psi^S(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N) = \Psi^S(\xi_1, \ldots, \xi_j, \xi_i, \ldots, \xi_N). \tag{15.5}$$

It immediately follows that in this case we can write the equalities

$$\begin{aligned}\Psi^S(\xi_1,\ldots,\xi_j,\xi_i,\ldots,\xi_N) &= \hat{P}_{ij}\Psi^S(\xi_1,\ldots,\xi_i,\xi_j,\ldots,\xi_N)\\ &= \Psi^S(\xi_1,\ldots,\xi_i,\xi_j,\ldots,\xi_N),\end{aligned} \tag{15.6}$$

from which it follows that

$$\hat{P}^+_{ij}\Psi^S(\xi_1,\ldots,\xi_i,\xi_j,\ldots,\xi_N) = \tfrac{1}{2}(1+\hat{P}_{ij})\Psi^S(\xi_1,\ldots,\xi_i,\xi_j,\ldots,\xi_N) \tag{15.7}$$

$$= \Psi^S(\xi_1,\ldots,\xi_i,\xi_j,\ldots,\xi_N). \tag{15.8}$$

Similarly, it can be shown that

$$\hat{P}^-_{ij}\Psi^S(\xi_1,\ldots,\xi_i,\xi_j,\ldots,\xi_N) = 0. \tag{15.9}$$

These results show that $\hat{P}^+_{ij}$ projects totally symmetric wave functions onto themselves, while $\hat{P}^-_{ij}$ cancels the totally symmetric component of the function it operates on. Now let $\Psi^A(\xi_1,\ldots,\xi_i,\xi_j,\ldots,\xi_N)$ be totally antisymmetric functions, characterized by the fact that for any pair i, j,

$$\Psi^A(\xi_1,\ldots,\xi_j,\xi_i,\ldots,\xi_N) = -\Psi^A(\xi_1,\ldots,\xi_i,\xi_j,\ldots,\xi_N). \tag{15.10}$$

It immediately follows that

$$\hat{P}_{ij}\Psi^A(\xi_1,\ldots,\xi_i,\xi_j,\ldots,\xi_N) = -\Psi^A(\xi_1,\ldots,\xi_i,\xi_j,\ldots,\xi_N), \tag{15.11}$$

$$\hat{P}^+_{ij}\Psi^A(\xi_1,\ldots,\xi_i,\xi_j,\ldots,\xi_N) = \tfrac{1}{2}(1+\hat{P}_{ij})\Psi^A(\xi_1,\ldots,\xi_i,\xi_j,\ldots,\xi_N) = 0, \tag{15.12}$$

$$\hat{P}^-_{ij}\Psi^A(\xi_1,\ldots,\xi_i,\xi_j,\ldots,\xi_N) = \Psi^A(\xi_1,\ldots,\xi_i,\xi_j,\ldots,\xi_N). \tag{15.13}$$

These results show that $\hat{P}^-_{ij}$ projects totally antisymmetric wave functions onto themselves, while $\hat{P}^+_{ij}$ cancels these components. In short, $\hat{P}^+_{ij}$ is the projector for symmetric states and eliminates the antisymmetric component, while $\hat{P}^-_{ij}$ is the projector for antisymmetric states and eliminates the symmetric component.

P15.2 Show that the operators

$$\widehat{P}^{\pm}_{ij} \equiv \tfrac{1}{2}\left(1 \pm \widehat{P}_{ij}\right) \tag{15.14}$$

are projectors. What is the effect of these operators on a fully symmetric state function $\Psi(\xi_1,\ldots,\xi_i,\xi_j\ldots,\xi_N)$?

A projector $\hat{P}$ is a Hermitian idempotent operator, satisfying $\hat{P} = \hat{P}^\dagger$ and $\hat{P}^2 = \hat{P}$. If $\hat{P}_i$ and $\hat{P}_j$ are two projectors onto the respective subspaces H_i and H_j of the corresponding Hilbert space, their product is a projector (if the subspaces coincide), or vanishes (if the subspaces are disjoint):

$$\hat{P}_i\hat{P}_j = \hat{P}_j\hat{P}_i = \hat{P}_i\,\delta_{ij}. \tag{15.15}$$

In short, if $i \neq j$ then $\hat{P}_i$ and $\hat{P}_j$ are orthogonal and $\hat{P}_i\hat{P}_j = 0$; if $i = j$, (15.15) is simply the idempotency property. From this last property it follows that the

eigenvalues of a projector are 0 or 1. A set of projectors is complete if $\sum_i \hat{P}_i = 1$, where the sum extends over the entire Hilbert space of the problem. Let us now consider the operators

$$\hat{P}_{ij}^{\pm} \equiv \tfrac{1}{2}\left(1 \pm \hat{P}_{ij}\right). \tag{15.16}$$

Since $\hat{P}_{ij}$ is Hermitian, it is clear that these operators are as well. Moreover, each one of them is idempotent:

$$\left(\hat{P}_{ij}^{\pm}\right)^2 = \frac{1}{4}\left(1 \pm 2\hat{P}_{ij} + \hat{P}_{ij}^2\right) = \frac{1}{2}\left(1 \pm \hat{P}_{ij}\right) = \hat{P}_{ij}^{\pm}, \tag{15.17}$$

and $\hat{P}_{ij}^{+}$ and $\hat{P}_{ij}^{-}$ are mutually orthogonal:

$$\hat{P}_{ij}^{+}\hat{P}_{ij}^{-} = \frac{1}{4}\left(1 + \hat{P}_{ij}\right)\left(1 - \hat{P}_{ij}\right) = \frac{1}{4}\left(1 - \hat{P}_{ij}^2\right) = 0. \tag{15.18}$$

These properties show that $\hat{P}_{ij}^{\pm}$ are projection operators, mutually orthogonal. We will now find out what subspace they project onto. Let $\Psi^S(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N)$ be a symmetric wave function under the exchange of any pair of indices (in short: totally symmetric). This means that for any pair i, j one has

$$\Psi^S(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N) = \Psi^S(\xi_1, \ldots, \xi_j, \xi_i, \ldots, \xi_N). \tag{15.19}$$

It follows immediately that in this case we can write the equalities

$$\Psi^S(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N) = \hat{P}_{ij}\Psi^S(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N) = \Psi^S(\xi_1, \ldots, \xi_j, \xi_i, \ldots, \xi_N), \tag{15.20}$$

from which it follows that

$$\hat{P}_{ij}^{+}\Psi^S(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N)$$

$$= \frac{1}{2}\left(1 + \hat{P}_{ij}\right)\Psi^S(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N) = \Psi^S(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N), \tag{15.21}$$

and similarly one proves that

$$\hat{P}_{ij}^{-}\Psi^S(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N) = 0. \tag{15.22}$$

In words: $\hat{P}_{ij}^{+}$ projects totally symmetric wave functions onto themselves, while $\hat{P}_{ij}^{-}$ cancels the totally symmetric component of the function upon which it acts.Now let $\Psi^A(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N)$ be totally antisymmetric functions, characterized by the fact that for any pair i, j one has

$$\Psi^A(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N) = -\Psi^A(\xi_1, \ldots, \xi_j, \xi_i, \ldots, \xi_N). \tag{15.23}$$

It follows immediately that

$$\hat{P}_{ij}\Psi^A(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N) = -\Psi^A(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N), \tag{15.24}$$

$$\hat{P}_{ij}^{+}\Psi^A(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N) = \frac{1}{2}(1 + \hat{P}_{ij})\Psi^A(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N) = 0, \tag{15.25}$$

$$\hat{P}_{ij}^{-}\Psi^A(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N) = \Psi^A(\xi_1, \ldots, \xi_i, \xi_j, \ldots, \xi_N). \tag{15.26}$$

These results show that $\hat{P}_{ij}^{-}$ projects totally antisymmetric wave functions onto themselves, while $\hat{P}_{ij}^{+}$ cancels these components.In short, $\hat{P}_{ij}^{+}$ is the projector of symmetric states and eliminates the antisymmetric component, while $\hat{P}_{ij}^{-}$ is the projector of antisymmetric states and eliminates the symmetric component.

P15.3 Obtain the solution [**1**] **Eq. (15.49)** using perturbation theory for degenerate systems. The degenerate wave functions are considered to be $\psi_{\pm}$.
Solution. In [**1**], **Section 15.3**, it is shown that the perturbation of a two-electron system by a symmetric potential $V(\boldsymbol{r}_1, \boldsymbol{r}_2) = V(\boldsymbol{r}_2, \boldsymbol{r}_1)$ shifts the initial energy eigenvalue $E^{(0)}$ to the value $E^{(0)} + J \pm K$, where the sign of the last term depends on the symmetry or antisymmetry of the wave function with respect to particle exchange. The quantities J and K are given by

$$J = \langle mn|V(\boldsymbol{r}_1, \boldsymbol{r}_2)|mn\rangle = \int |\psi_n(2)|^2 |\psi_m(1)|^2 V(\boldsymbol{r}_1, \boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2, \tag{15.27}$$

$$K = \int \psi_n^*(1)\psi_m^*(2) V(\boldsymbol{r}_1, \boldsymbol{r}_2) \psi_n(2)\psi_m(1) d\boldsymbol{r}_1 d\boldsymbol{r}_2. \tag{15.28}$$

Since the potential is symmetric, exchanging $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ in (15.27) does not affect the value of J, and we can write this quantity in the form:

$$J = \frac{1}{2} \int |\psi_n(2)|^2 |\psi_m(1)|^2 V(\boldsymbol{r}_1, \boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2 \tag{15.29}$$

$$+ \frac{1}{2} \int |\psi_n(2)|^2 |\psi_m(1)|^2 V(\boldsymbol{r}_2, \boldsymbol{r}_1) d\boldsymbol{r}_1 d\boldsymbol{r}_2 \tag{15.30}$$

$$= \frac{1}{2} \int |\psi_n(2)|^2 |\psi_m(1)|^2 V(\boldsymbol{r}_1, \boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2 \tag{15.31}$$

$$+ \frac{1}{2} \int |\psi_m(2)|^2 |\psi_n(1)|^2 V(\boldsymbol{r}_1, \boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2. \tag{15.32}$$

This expression suggests interpreting J as the contribution to the energy due to the fact that in half of the cases electron 1 is in state m and electron 2 in state n, and in the remaining half of cases the roles of the two electrons are exchanged: electron 1 ends up in state n and electron 2 in state m. Then in the classical analogue, J would equate to the entire first-order energy correction, assuming both configurations are equally probable. However, the term K also appears, the so-called exchange energy, which has no classical analogue, as it is generated by the superposition of amplitudes for the statistical description; in this term, the electron with label 1 appears simultaneously partly in state m and partly in state n, and something similar occurs with electron 2, which also appears as if it were simultaneously in both states. As we already know, these quantum interference phenomena characteristically appear when the wave functions are not factorizable.

Considering the potential $V(|\mathbf{r}_1 - \mathbf{r}_2|)$ as a perturbation, we will treat the problem with the perturbation theory of degenerate systems. Being symmetric,

the potential commutes with the exchange operator $\hat{P}_{12}$, which means that the perturbation does not mix states of different permutational symmetry. The unperturbed system has as symmetric eigenstates the non-factorizable orbital wave functions

$$\psi_\pm = \frac{1}{\sqrt{2}}\left[\psi_n(2)\psi_m(1) \pm \psi_n(1)\psi_m(2)\right]. \tag{15.33}$$

Since we are dealing with electrons, the total wave function is obtained by multiplying $\psi_\pm$ by the corresponding spinor, such that the resulting wave function is antisymmetric. The + sign therefore corresponds to the spin-0 state (antisymmetric spinor), while the − sign is associated with the spin-1 state (symmetric spinor). The states $\psi_\pm$ are degenerate, since

$$\hat{H}_0\psi_\pm = E^{(0)}\psi_\pm. \tag{15.34}$$

We obtain the first-order energy corrections from perturbation theory by solving the secular equation

$$\begin{vmatrix} V_{++} - \delta E^{(1)} & V_{+-} \\ V_{-+} & V_{--} - \delta E^{(1)} \end{vmatrix} = 0, \tag{15.35}$$

where we have set $V_{++} = \langle\psi_+|V|\psi_+\rangle$, etc. Explicitly, for V_{++} or V_{--} we obtain

$$\begin{aligned} V_{\pm\pm} = \frac{1}{2}\int &\left[\psi_n^*(2)\psi_m^*(1) \pm \psi_n^*(1)\psi_m^*(2)\right] V \left[\psi_n(2)\psi_m(1)\right. && (15.36)\\ &\left.\pm\psi_n(1)\psi_m(2)\right] d\mathbf{r}_1 d\mathbf{r}_2 && (15.37)\\ = \frac{1}{2}\Bigg\{&\int |\psi_n(2)|^2|\psi_m(1)|^2 V d\mathbf{r}_1 d\mathbf{r}_2 + \int |\psi_n(1)|^2|\psi_m(2)|^2 V d\mathbf{r}_1 d\mathbf{r}_2 && (15.38)\\ &\pm \int \psi_n^*(1)\psi_m^*(2) V \psi_n(2)\psi_m(1) d\mathbf{r}_1 d\mathbf{r}_2 && (15.39)\\ &+ \int \psi_n^*(2)\psi_m^*(1) V \psi_n(1)\psi_m(2) d\mathbf{r}_1 d\mathbf{r}_2\Bigg\}. && (15.40) \end{aligned}$$

Exchanging indices $1 \leftrightarrow 2$ does not affect the value of these integrals (it is merely a renaming of the integration variables), so we can write

$$V_{\pm\pm} = \frac{1}{2}(2J \pm 2K) = J \pm K. \tag{15.41}$$

Similarly, we obtain

$$V_{+-} = \int \psi_+^* V \psi_- d\mathbf{r}_1 d\mathbf{r}_2 = 0, \tag{15.42}$$

$$V_{-+} = 0. \tag{15.43}$$

This confirms the observation that the symmetric perturbation does not mix states of different symmetry. Consequently, the determinant of the secular equation turns

out to be diagonal and the problem can be treated as non-degenerate,

$$\begin{vmatrix} J+K-\delta E^{(1)} & 0 \\ 0 & J-K-\delta E^{(1)} \end{vmatrix} = 0, \tag{15.44}$$

that is,

$$(J+K-\delta E^{(1)})(J-K-\delta E^{(1)}) = 0. \tag{15.45}$$

Hence, the first-order energy corrections are

$$\delta E_{\pm}^{(1)} = J \pm K, \tag{15.46}$$

an consequently, the energy is given to the first order by

$$E_{\pm} = E^{(0)} + J \pm K, \tag{15.47}$$

which is the requested result. This result shows that the presence of an interaction that explicitly involves the electron spin is not necessary for it to manifest: the antisymmetrization of the wave function naturally leads to an energy difference of value $2K$ between the spin states $S = 0$ and $S = 1$, known as exchange splitting.

P15.4 Show that if $\psi_{Nn}(x_1, x_2)$ is the wave function of the two linearly coupled oscillators (see problem **P12.2**), then

$$\hat{P}_{12}\psi_{Nn} = (-1)^n \psi_{Nn}, \tag{15.48}$$

where N, n represent the excitation quantum number of the center of mass and relative motion, respectively.

Solution. Problem P12.2 was solved using the relative and center-of-mass coordinates,

$$y \equiv y_1 = x_1 - x_2, \tag{15.49}$$

$$Y \equiv y_2 = \frac{1}{M}(m_1 x_1 + m_2 x_2), \tag{15.50}$$

where $M = m_1 + m_2$ is the total mass of the system. In terms of these coordinates, the Hamiltonian reduces to that of two decoupled oscillators, and the wave function of the system factorizes as

$$\psi_{Nn}(Y, y) = \psi_N(Y)\, \psi_n(y), \tag{15.51}$$

where each factor is a harmonic oscillator wave function. In particular,

$$\psi_n(y) = \left(\sqrt{\frac{\pi\hbar}{m\omega_1}}\, 2^n n!\right)^{-\frac{1}{2}} \exp\left(-\frac{m\omega_1}{2\hbar} y^2\right) H_n\left(\sqrt{\frac{M\omega_1}{\hbar}}\, y\right), \tag{15.52}$$

where $\omega_1^2 = \omega^2(1+\beta)$ (β measures the coupling strength). Upon an exchange of particles 1 and 2, the relative coordinate changes its sign, while the center-of-mass coordinate remains invariant. Therefore,

$$\hat{P}_{12}\psi_{Nn}(y_2, y_1) = \psi_N(y_2)\, \psi_n(-y_1). \tag{15.53}$$

The parity of $\psi_n(y)$ given by (15.52) corresponds to that of the Hermite polynomial H_n, and it is $(-1)^n$ (since it is an even or odd polynomial depending on whether n is even or odd, respectively). Hence,

$$\hat{P}_{12}\psi_n(y_1) = \psi_n(-y_1) = (-1)^n\psi_n(y_1). \tag{15.54}$$

Substituting into equation (15.53), the desired result is obtained,

$$\hat{P}_{12}\psi_{Nn} = (-1)^n\psi_{Nn}. \tag{15.55}$$

P15.5 The Hamiltonian of a system of three linearly coupled identical spin-zero bosons is

$$\hat{H} = \sum_{i=1}^{3}\frac{\hat{p}_i^2}{2m} + \sum_{i=1}^{3}\frac{1}{2}m\omega^2 x_i^2 + \sum_{j>i}\sum_{i=1}^{3}\frac{1}{2}m\omega^2\beta(x_i - x_j)^2.$$

In terms of the normal coordinates

$$Z = \frac{1}{3}(x_1 + x_2 + x_3); \quad z_1 = x_1 - x_2; \quad z_2 = x_3 - \frac{1}{2}(x_1 + x_2),$$

the Hamiltonian takes the form

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{1}{2}M\omega^2 Z^2 + \frac{\hat{p}_{z_1}^2}{2m_1} + \frac{1}{2}m_1\omega_1^2 z_1^2 + \frac{\hat{p}_{z_2}^2}{2m_2} + \frac{1}{2}m_2\omega_2^2 z_2^2,$$

where

$$\hat{P} = \hat{p}_1 + \hat{p}_2 + \hat{p}_3; \quad \hat{p}_{z_1} = \frac{1}{2}(\hat{p}_1 - \hat{p}_2); \quad \hat{p}_{z_2} = \frac{2}{3}\left(\hat{p}_3 - \frac{\hat{p}_1 + \hat{p}_2}{2}\right);$$

$$\omega_1^2 = \omega_2^2 = \omega^2(1 + 3\beta);$$

$$M = 3m; \quad m_1 = \frac{m}{2}; \quad m_2 = \frac{2m}{3}.$$

a) Find the solutions of the Schrödinger equation;
b) determine the eigenvalues of the Hamiltonian;
c) indicate which states are physically realizable;
d) show that solutions with exchange degeneracy are not necessarily orthogonal.

Solution. This Hamiltonian describes three coupled identical linear harmonic oscillators, but they can be decoupled by expressing it in terms of normal modes. We aim to show that these are given by the transformation

$$Z = \frac{1}{3}\left(x_1 + x_2 + x_3\right), \quad z_1 = x_1 - x_2, \quad z_2 = x_3 - \frac{1}{2}\left(x_1 + x_2\right); \tag{15.56}$$

$$\hat{P} = \hat{p}_1 + \hat{p}_2 + \hat{p}_3, \quad \hat{p}_{z_1} = \frac{1}{2}\left(\hat{p}_1 - \hat{p}_2\right), \quad \hat{p}_{z_2} = \frac{2}{3}\left(\hat{p}_3 - \frac{1}{2}\left(\hat{p}_1 + \hat{p}_2\right)\right). \tag{15.57}$$

The inverse transformation yields

$$x_1 = Z + \tfrac{1}{2}z_1 - \tfrac{1}{3}z_2, \quad x_2 = Z - \tfrac{1}{2}z_1 - \tfrac{1}{3}z_2, \quad x_3 = Z + \tfrac{2}{3}z_2. \tag{15.58}$$

$$\hat{p}_1 = \tfrac{1}{3}\hat{P} + \hat{p}_{z_1} - \tfrac{1}{2}\hat{p}_{z_2}, \quad \hat{p}_2 = \tfrac{1}{3}\hat{P} - \hat{p}_{z_1} - \tfrac{1}{2}\hat{p}_{z_2}, \quad \hat{p}_3 = \tfrac{1}{3}\hat{P} + \hat{p}_{z_2} \tag{15.59}$$

The Hamiltonian expressed in terms of these variables becomes

$$\hat{H} = \frac{1}{2m}\left(\tfrac{1}{3}\hat{P}^2 + 2\hat{p}_{z_1}^2 + \tfrac{3}{2}\hat{p}_{z_2}^2\right) \tag{15.60}$$

$$+ \tfrac{1}{2}m\omega^2\left(3Z^2 + \tfrac{1}{2}z_1^2 + \tfrac{2}{3}z_2^2\right) + \tfrac{1}{2}m\omega^2\beta\left(\tfrac{3}{2}z_1^2 + 2z_2^2\right). \tag{15.61}$$

If we introduce here the masses

$$M = 3m, \quad m_1 = \frac{1}{2}m, \quad m_2 = \frac{2}{3}m, \tag{15.62}$$

we obtain

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{\hat{p}_{z_1}^2}{2m_1} + \frac{\hat{p}_{z_2}^2}{2m_2} + \frac{1}{2}M\omega^2 Z^2 + \frac{1}{2}m_1\omega^2 z_1^2 + \frac{1}{2}m_2\omega^2 z_2^2 \tag{15.63}$$

$$+ \frac{3}{2}m_1\omega^2\beta z_1^2 + \frac{3}{2}m_2\omega^2\beta z_2^2, \tag{15.64}$$

which can be identified as the Hamiltonian of three independent oscillators with frequencies ω^2, $\omega_1^2 = \omega_2^2 = \omega^2(1+3\beta)$. Thus, the new coordinates indeed correspond to the normal modes of the system. The coordinate Z directly describes the CM (center of mass) of the system; z_1 describes the relative position of particles 1 and 2, and z_2 corresponds to the relative position of particle 3 with respect to the CM of the 1-2 system. It is clear that an arbitrary permutation of these labels can be made without changing the result.

P15.6 Consider a system of four uncoupled, equal and collinear harmonic oscillators. Construct the wave functions and specify the energy eigenvalues of the physically realizable steady states when:**(a)** All four particles are bosons with spin zero.**(b)** All four particles are fermions with spin 1/2.

Solution. The stationary Schrödinger equation for the problem is

$$\left(\sum_{i=1}^{4}\frac{\hat{p}_i^2}{2m} + \sum_{i=1}^{4}\frac{1}{2}m\omega^2 x_i^2\right)\Psi\left(x_1, x_2, x_3, x_4\right) = E\Psi\left(x_1, x_2, x_3, x_4\right). \tag{15.65}$$

The orbital wave functions that are solutions of this equation are the product of four harmonic oscillator wave functions,

$$\Psi_{klmn}\left(x_1, x_2, x_3, x_4\right) = \psi_k\left(x_1\right)\psi_l\left(x_2\right)\psi_m\left(x_3\right)\psi_n\left(x_4\right), \tag{15.66}$$

with the $\psi_n(x_i)$ harmonic oscillator eigenfunctions of the form

$$\psi_n(y) = \left(\sqrt{\frac{\pi\hbar}{m\omega_1}}2^n n!\right)^{-\frac{1}{2}}\exp\left(-\frac{m\omega_1}{2\hbar}y^2\right)H_n\left(\sqrt{\frac{m\omega_1}{\hbar}}y\right),$$

with total energies given by

$$E_{klmn} = \hbar\omega\left(k+l+m+n+2\right), \quad k,l,m,n = 0,1,2,\ldots \tag{15.67}$$

From these solutions, those describing bosons or fermions are constructed as follows.

a) For four spin-0 bosons, the wave function is totally symmetric, and the following cases can occur:

i) $k = l = m = n$. The function (15.66) is already symmetric, so we simply have

$$\Psi^S\left(x_1,x_2,x_3,x_4\right) = \psi_n\left(x_1\right)\psi_n\left(x_2\right)\psi_n\left(x_3\right)\psi_n\left(x_4\right), \tag{15.68}$$

corresponding to the energy

$$E = 2\hbar\omega\left(2n+1\right), \quad n = 0,1,2,\ldots \tag{15.69}$$

These states are non-degenerate, regardless of the value of n; among them is the ground state of the system (with $n = 0$).

ii) $k = l$, but $n \neq l$ and $m \neq l$. The only totally symmetric wave function is

$$\Psi^S = \frac{1}{\sqrt{12}}(\Psi_{kknm} + \Psi_{kknm} + \Psi_{kmkn} + \Psi_{kmnk}$$
$$+ \Psi_{kmnk} + \Psi_{knkm} + \Psi_{nkkm} + \Psi_{nkmk} + \Psi_{mnkk} + \Psi_{mnkk}), \tag{15.70}$$

corresponding to the energy

$$E = \hbar\omega(2k+m+n+2), \quad k,m,n = 0,1,2,\ldots \tag{15.71}$$

iii) $k = l = m \neq n$. The only realizable state is

$$\Psi^S = \frac{1}{\sqrt{4}}(\Psi_{kkkn} + \Psi_{kknk} + \Psi_{knkk} + \Psi_{knnk}) \tag{15.72}$$

corresponding to the energy

$$E = \hbar\omega(3k+n+2), \quad k,n = 0,1,2,\ldots \tag{15.73}$$

iv) $k = l$ and $m = n$. The only realizable state is

$$\Psi^S = \frac{1}{\sqrt{6}}\left(\Psi_{nkkn} + \Psi_{nknk} + \Psi_{nnkk} + \Psi_{kknn} + \Psi_{knkn} + \Psi_{nkkk}\right) \tag{15.74}$$

corresponding to the energy

$$E = 2\hbar\omega\left(k+n+1\right), \quad k,n = 0,1,2,\ldots \tag{15.75}$$

v) k,l,m,n all different. The only realizable state is

$$\Psi^S = \frac{1}{\sqrt{24}}(\Psi_{klmn} + \Psi_{klnm} + \Psi_{kmln} + \Psi_{kmnl} + \Psi_{kmnl} + \Psi_{knlm} \tag{15.76}$$
$$+ \Psi_{lkmn} + \Psi_{lknm} + \Psi_{lmkn} + \Psi_{lmnk} + \Psi_{lnkm} + \Psi_{lnmk} \tag{15.77}$$
$$+ \Psi_{nklm} + \Psi_{nkml} + \Psi_{nlkm} + \Psi_{nlmk} + \Psi_{nmlk} + \Psi_{nmkl} \tag{15.78}$$
$$+ \Psi_{mkln} + \Psi_{mknl} + \Psi_{mlkn} + \Psi_{mlnk} + \Psi_{mnkl} + \Psi_{mnlk}) \tag{15.79}$$

corresponding to the energy

$$E = \hbar\omega(k + l + m + n + 2). \tag{15.80}$$

b) When dealing with four spin 1/2 fermions, one must choose the totally antisymmetric solutions, including, besides the spatial coordinates x_i, the spin coordinate, a set of variables that we denote with ξ_i. Since for Hamiltonians that do not depend on spin, as is the present case, the wave functions of a single particle reduce to the product of the spin function $\chi_\pm$ by the orbital function $\psi_n(x_i)$, one can alternatively write

$$\psi_n^\pm(x_i) \equiv \psi_n(\xi_i) = \psi_n(x_i)\,\chi_\pm. \tag{15.81}$$

The spin orientation $\pm$ of each of the four particles will be denoted by a, b, c, d, so the unsymmetrized wave function that replaces (15.66) can be written in the synthetic form

$$\Psi_{klmn}^{abcd} = \psi_k^a(x_1)\,\psi_l^b(x_2)\,\psi_m^c(x_3)\,\psi_n^d(x_4)\,. \tag{15.82}$$

The totally antisymmetric wave function constructed from this basis is given by the Slater determinant

$$\left(\Psi_{klmn}^{abcd}\right)^A = \frac{1}{\sqrt{24}}\begin{vmatrix} \psi_k^a(x_1) & \psi_k^a(x_2) & \psi_k^a(x_3) & \psi_k^a(x_4) \\ \psi_l^b(x_1) & \psi_l^b(x_2) & \psi_l^b(x_3) & \psi_l^b(x_4) \\ \psi_m^c(x_1) & \psi_m^c(x_2) & \psi_m^c(x_3) & \psi_m^c(x_4) \\ \psi_n^d(x_1) & \psi_n^d(x_2) & \psi_n^d(x_3) & \psi_n^d(x_4) \end{vmatrix}, \tag{15.83}$$

or explicitly,

$$\left(\Psi_{klmn}^{abcd}\right)^A = \frac{1}{\sqrt{24}}\Big(\Psi_{klmn}^{abcd} - \Psi_{kl\,nm}^{abdc} - \Psi_{kml\,n}^{acbd} + \Psi_{knlm}^{adbc} + \Psi_{kmnl}^{acdb} - \Psi_{kmnl}^{adcb} \tag{15.84}$$

$$-\Psi_{lkmn}^{bacd} + \Psi_{lkmn}^{bade} + \Psi_{mkl\,n}^{cabd} - \Psi_{nklm}^{adbc} - \Psi_{mknl}^{cadb} + \Psi_{nkml}^{dacb} \tag{15.85}$$

$$+\Psi_{lmkn}^{bead} - \Psi_{lnkm}^{bdec} - \Psi_{mlkn}^{cbad} + \Psi_{nlkm}^{dbac} + \Psi_{mmkl}^{cdab} - \Psi_{mmkl}^{dcab} \tag{15.86}$$

$$-\Psi_{lmnk}^{bcda} + \Psi_{l\,nmk}^{bdea} + \Psi_{ml\,nk}^{cbda} - \Psi_{nlmk}^{dbca} - \Psi_{mmlk}^{cdba} + \Psi_{mmlk}^{dcba}\Big). \tag{15.87}$$

However, while the quantum numbers k, l, m, n may be equal or different, the spin quantum numbers, a, b, c, d, cannot all be different, since they can only take one of the values + or -. This reduces the possibilities to the following cases:
i) $l = n = m = k$. As there will necessarily be equal spin indices, the Slater determinant has at least two equal rows and vanishes. This means that this state is not realized.
ii) $k = l = m \neq n$. The same consideration as the previous case applies, since here too at least two of the indices a, b, c, d have to be equal.
iii) $k = l \neq m = n$. The conditions for the Slater determinant to be different from zero are $a \neq b$, $c \neq d$. It follows that the following four states are realizable,

$$(abcd) = (+\,-\;\;-+), (-\,+\,+-), (+\,-\;\;+-), (-\,+\,-\,+). \tag{15.88}$$

The energy corresponding to these states is

$$E = 2\hbar\omega\,(n+k+1)\,, \quad k,n = 0,1,2,\ldots, n \neq k. \tag{15.89}$$

Among these states are those of minimum energy, with $k=0$, $n=1$, or $k=1$, $n=0$. Therefore, in this case the ground state is degenerate and its energy is higher than that of the corresponding ground state of four similar bosons. As an example, one of these four realizable states is

$$\begin{aligned}(\Psi^{+-\ -+}_{kknn})^A = \frac{1}{\sqrt{24}}\big(&\Psi^{+-\ -+}_{kknn} - \Psi^{+-\ +-}_{kknn} + \Psi^{++-+}_{knkn} + \Psi^{+-\ -+}_{knkn} + \Psi^{++-+}_{knnk} && (15.90)\\ &-\Psi^{+-\ -+}_{knnk} - \Psi^{-++-}_{kknn} + \Psi^{-+-\ +}_{kknn} + \Psi^{-++-}_{nkkn} - \Psi^{-+-\ +}_{nkkn} && (15.91)\\ &-\Psi^{-++-}_{nknk} + \Psi^{-+-\ +}_{nknk} + \Psi^{-++-}_{knkn} - \Psi^{-+-\ +}_{knkn} - \Psi^{+-\ -+}_{nkkn} && (15.92)\\ &+\Psi^{+-\ +-}_{nkkn} + \Psi^{+-\ -+}_{nnkk} - \Psi^{+-\ +-}_{nnkk} - \Psi^{-++-}_{knnk} + \Psi^{-+-\ +}_{knnk} && (15.93)\\ &+\Psi^{+-\ -+}_{nknk} - \Psi^{+-\ +-}_{nknk} - \Psi^{-++-}_{nnkk} + \Psi^{-+-\ +}_{nnkk}\Big). && (15.94)\end{aligned}$$

iv) $k=l$, but $m,n \neq l, m \neq n$. In this case a and b must be different, but c and d can take any value. There are 8 realizable states, characterized by

$$\begin{aligned}(abcd) = (+-++),(+--&-),(+-+-),(+--+), && (15.95)\\ (-+++),(-+--&),(-++-),(-+-+) && (15.96)\end{aligned}$$

and their energy is

$$E = \hbar\omega(2k+m+n+2), \quad k,m,n = 0,1,2,\ldots \tag{15.97}$$

An example of these states is

$$\begin{aligned}(\Psi^{+--+}_{kknm})^A = \frac{1}{\sqrt{24}}\Big(&\Psi^{+--+}_{kknm} - \Psi^{+--+}_{kknm} - \Psi^{++-+}_{kmkn} + \Psi^{++-+}_{knkm} + \Psi^{++-+}_{kmnk} && (15.98)\\ &- \Psi^{++-+}_{kmnk} - \Psi^{-+++}_{kkmn} + \Psi^{-+++}_{kkmn} + \Psi^{++-+}_{mkkn} - \Psi^{++-+}_{nkkm} && (15.99)\\ &- \Psi^{++-+}_{mknk} + \Psi^{++-+}_{nkmk} + \Psi^{-+++}_{kmkn} - \Psi^{-+++}_{knkm} - \Psi^{+-++}_{mkkn} && (15.100)\\ &+ \Psi^{+-++}_{nkkm} + \Psi^{++-+}_{mnkk} - \Psi^{++-+}_{nmkk} - \Psi^{-+++}_{kmnk} + \Psi^{-+++}_{kmnk} && (15.101)\\ &+ \Psi^{+-++}_{mknk} - \Psi^{+-++}_{nkmk} - \Psi^{++-+}_{mnkk} + \Psi^{++-+}_{mnkk}\Big). && (15.102)\end{aligned}$$

v) k, l, m, n different. All possible combinations of the spin indices are acceptable, so there are 2^4 realizable spin states. Among these states there are those with defined symmetry with respect to the exchange of spatial or spin coordinates separately. The energy of these states is

$$E = \hbar\omega\,(k+l+m+n+2)\,. \tag{15.103}$$

These 16 realizable states correspond to

$$(abcd) = (++++), (-+++), (+-++), (++-+), (+++-), \tag{15.104}$$
$$(+--+), (-+--), (--+-), (---+), (++--), \tag{15.105}$$
$$(--++), (-++-), (+--+), (-+-+), (+-+-), \tag{15.106}$$
$$(----). \tag{15.107}$$

For example, one of these states is

$$(\Psi^{++++}_{klmn})^A = \frac{1}{\sqrt{24}}\Big(\Psi^{++++}_{klnm} - \Psi^{++++}_{klnm} - \Psi^{++++}_{knlm} + \Psi^{++++}_{knlm} + \Psi^{++++}_{kmnl} \tag{15.108}$$
$$-\Psi^{++++}_{kmnl} - \Psi^{++++}_{lkmn} + \Psi^{++++}_{lkmn} + \Psi^{++++}_{mkln} - \Psi^{++++}_{nklm} \tag{15.109}$$
$$-\Psi^{++++}_{mknl} + \Psi^{++++}_{nkml} + \Psi^{++++}_{lmkn} - \Psi^{++++}_{lnkm} - \Psi^{++++}_{mlkn} \tag{15.110}$$
$$+\Psi^{++++}_{nlkm} + \Psi^{++++}_{mnkl} - \Psi^{++++}_{nmkl} - \Psi^{++++}_{lmnk} + \Psi^{++++}_{lnmk} \tag{15.111}$$
$$+\Psi^{++++}_{mlnk} - \Psi^{++++}_{nlmk} - \Psi^{++++}_{mnlk} + \Psi^{++++}_{nmlk} \Big). \tag{15.112}$$

The states of maximum spin belong to this category, whose minimum energy is very high ($E_{\text{mín}} = 8\hbar\omega$), and from which a large number of possible orbital states are excluded due to the restriction that the four quantum numbers k, l, m, n have to be different. The example shows once again the impact of the presence of electron spin on the energy spectrum, even in the absence of any direct coupling of the spin to the rest of the system.

P15.7 The deuteron (consisting of a proton and a neutron) has spin 1. List the possible states of spin and total angular momentum of a system of two deuterons in a state of angular momentum L.

Solution. The deuteron is a spin–1 composite particle, hence two deuterons are *identical bosons*. Therefore the total two–particle state must be symmetric under particle exchange,

$$\hat{P}_{12}\,\Psi = +\,\Psi. \tag{15.113}$$

We write the total state as (orbital)×(spin), $\Psi = \Psi^{(L)}_{\text{orb}}\,\chi^{(S)}$. Under exchange, the relative coordinate changes as $\boldsymbol{r} \to -\boldsymbol{r}$, so the orbital factor acquires the phase

$$\hat{P}_{12}\,\Psi^{(L)}_{\text{orb}} = (-1)^L\,\Psi^{(L)}_{\text{orb}}. \tag{15.114}$$

For two spin–1 particles the addition $1\otimes 1 = 2\oplus 1\oplus 0$ splits into exchange–symmetry sectors,

$$\eta_{\text{spin}}(S) = \begin{cases} +1, & S = 0, 2 \quad \text{(symmetric)}, \\ -1, & S = 1 \quad \text{(antisymmetric)}. \end{cases} \tag{15.115}$$

Bosonic symmetry requires the product of orbital and spin parities to be $+1$,

$$(-1)^L\,\eta_{\text{spin}}(S) = +1. \tag{15.116}$$

Hence the allowed spin values are

$$L \text{ even } \Rightarrow \; S = 0, 2; \qquad L \text{ odd } \Rightarrow \; S = 1. \tag{15.117}$$

For each allowed S, the possible total angular momenta follow from vector addition,

$$J = |L - S|, \, |L - S| + 1, \, \ldots, \, L + S. \tag{15.118}$$

The explicit possible values are already given in P11.18.

P15.8 Three particles of spin zero are rigidly joined to form an equilateral triangle that rotates on a circle of radius r. Determine the rotational levels of this system.
Solution. The system rotates in a plane around an axis perpendicular to it and passing through its center of mass (CM), with each particle at a fixed distance r from the CM. The moment of inertia I of the system with respect to the axis of rotation (z-axis) is

$$I = \sum_{i=1}^{3} m r_i^2 = 3mr^2, \tag{15.119}$$

since each particle contributes mr^2 and there are three particles. The Hamiltonian for a rigid rotor in 2D (rotation in the xy-plane) is

$$\hat{H} = \frac{\hat{L}_z^2}{2I}, \tag{15.120}$$

where $\hat{L}_z$ is the angular momentum operator along the z-axis. The eigenfunctions of the operator $\hat{L}_z$ are plane waves:

$$\psi_K(\phi) = \frac{1}{\sqrt{2\pi}} e^{iK\phi}, \tag{15.121}$$

where ϕ is the azimuthal angle and K is an integer quantum number (positive or negative) representing the angular momentum in units of $\hbar$. The corresponding eigenvalues are

$$\hat{L}_z \psi_K(\phi) = K\hbar \psi_K(\phi). \tag{15.122}$$

By applying the Hamiltonian operator to the eigenfunctions,

$$\hat{H}\psi_K(\phi) = \frac{\hat{L}_z^2}{2I}\psi_K(\phi) = \frac{K^2\hbar^2}{2I}\psi_K(\phi), \tag{15.123}$$

we obtain for the rotational energies

$$E_K = \frac{K^2\hbar^2}{6mr^2}, \quad (\text{using } I = 3mr^2). \tag{15.124}$$

The allowed energies are

$$E_n = \frac{(3n)^2\hbar^2}{6mr^2} = \frac{3n^2\hbar^2}{2mr^2}, \quad n = 0, 1, 2, \ldots \tag{15.125}$$

For $n = 0$ there is only one possible state ($K = 0$), with a constant wave function $\psi_0 = \frac{1}{\sqrt{2\pi}}$.

For $n \geq 1$ there are two independent states: $K = +3n$ and $K = -3n$, corresponding to $e^{i3n\phi}$ and $e^{-i3n\phi}$, as shown in the table below.

Quantum number n	Angular momentum K	Energy E_n	Degeneracy
0	0	0	1
1	± 3	$\frac{3\hbar^2}{2mr^2}$	2
2	± 6	$\frac{12\hbar^2}{2mr^2} = \frac{6\hbar^2}{mr^2}$	2
3	± 9	$\frac{27\hbar^2}{2mr^2}$	2

P15.9 Let $\widehat{F}$ be an operator of the form

$$\widehat{F}(1, 2, \ldots, N) = \hat{f}(1) + \hat{f}(2) + \cdots + \hat{f}(N) = \sum_{i=1}^{N} \hat{f}(i), \tag{15.126}$$

where $\hat{f}(i)$ operates only on the coordinates of particle i in a system of N identical particles. Show that

$$\left\langle \Psi^A \mid \widehat{F} \mid \Psi^A \right\rangle = \sum_{i=1}^{N} \left\langle \psi_i \mid \hat{f}(i) \mid \psi_i \right\rangle, \tag{15.127}$$

where Ψ^A is the antisymmetric wave function and the one-particle wave functions ψ_i are orthonormal.

Solution. The antisymmetric wave function for N particles can be written as

$$\psi_A = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P[\psi_1(\xi_1)\psi_2(\xi_2)\cdots\psi_N(\xi_N)], \tag{15.128}$$

where P runs over all permutations of the particles and $(-1)^P$ is the parity of the permutation. The operator $\hat{F}$ is a sum of single-particle operators,

$$\hat{F} = \sum_{i=1}^{N} \hat{f}^{(i)}, \tag{15.129}$$

where $\hat{f}^{(i)}$ acts only on particle i. The expectation value is

$$\langle \psi_A | \hat{F} | \psi_A \rangle = \sum_{i=1}^{N} \langle \psi_A | \hat{f}^{(i)} | \psi_A \rangle. \tag{15.130}$$

Due to the symmetry of ψ_A under a permutation of identical particles, each term $\langle \psi_A | \hat{f}^{(i)} | \psi_A \rangle$ is independent of i. Therefore, it is sufficient to compute the term for $i = 1$ and multiply by N. Substituting ψ_A:

$$\langle \psi_A | \hat{f}^{(1)} | \psi_A \rangle = \frac{1}{N!} \sum_P \sum_Q (-1)^{P+Q} \int d\xi_1 \cdots d\xi_N \, (Q\Phi^*) \, \hat{f}^{(1)} \, (P\Phi), \tag{15.131}$$

where $\Phi = \psi_1(\xi_1)\psi_2(\xi_2)\cdots\psi_N(\xi_N)$ and Φ^* is its complex conjugate. The integral is factored as follows,

$$\int d\xi_1\, \psi^*_{q_1}(\xi_1)\hat{f}^{(1)}\psi_{p_1}(\xi_1)\prod_{j=2}^{N}\int d\xi_j\, \psi^*_{q_j}(\xi_j)\psi_{p_j}(\xi_j), \tag{15.132}$$

where p_j and q_j are the indices determined by the permutations P and Q. Due to the orthonormality of the functions ψ_i, the integrals for $j = 2$ to N satisfy

$$\int d\xi_j\, \psi^*_{q_j}(\xi_j)\psi_{p_j}(\xi_j) = \delta_{q_j p_j}. \tag{15.133}$$

Therefore, the total integral is nonzero only if $p_j = q_j$ for all $j = 2, \ldots, N$, which implies that $P = Q$. Thus, the sum reduces to

$$\langle\psi_A|\hat{f}^{(1)}|\psi_A\rangle = \frac{1}{N!}\sum_P \int d\xi_1\, \psi^*_{P(1)}(\xi_1)\hat{f}^{(1)}\psi_{P(1)}(\xi_1), \tag{15.134}$$

since $(-1)^{P+Q} = 1$ when $P = Q$, and the integrals for $j \geq 2$ are 1. For each permutation P, the term $\int d\xi_1\, \psi^*_{P(1)}\hat{f}\psi_{P(1)}$ depends on the index $k = P(1)$. There are $(N-1)!$ permutations that fix $P(1) = k$ for each $k = 1, \ldots, N$. Therefore,

$$\sum_P \int d\xi_1\, \psi^*_{P(1)}\hat{f}\psi_{P(1)} = \sum_{k=1}^{N}(N-1)!\,\langle\psi_k|\hat{f}|\psi_k\rangle, \tag{15.135}$$

and

$$\langle\psi_A|\hat{f}^{(1)}|\psi_A\rangle = \frac{1}{N!}\sum_{k=1}^{N}(N-1)!\,\langle\psi_k|\hat{f}|\psi_k\rangle = \frac{1}{N}\sum_{k=1}^{N}\langle\psi_k|\hat{f}|\psi_k\rangle. \tag{15.136}$$

For $\hat{F}$, we have

$$\begin{aligned}&\langle\psi_A|\hat{F}|\psi_A\rangle\\ &= \sum_{i=1}^{N}\langle\psi_A|\hat{f}^{(i)}|\psi_A\rangle = N\cdot\langle\psi_A|\hat{f}^{(1)}|\psi_A\rangle = N\cdot\frac{1}{N}\sum_{k=1}^{N}\langle\psi_k|\hat{f}|\psi_k\rangle = \sum_{k=1}^{N}\langle\psi_k|\hat{f}|\psi_k\rangle,\end{aligned} \tag{15.137}$$

since $\hat{f}^{(i)}$ is the same operator for each particle. Thus, it is shown that the expectation value of $\hat{F}$ in the antisymmetric state ψ_A is the sum of the expectation values of $\hat{f}$ in the individual states ψ_i.

P15.10 Prove that the lattice Hamiltonian introduced in [1], Section 5.4.1, namely Eq. (15.76), transforms into (15.80) in the reciprocal space.
Solution. We are asked to prove that the lattice Hamiltonian

$$H = \frac{1}{2m}\sum_{i=1}^{N}p_i^2 + \frac{1}{2}m\omega^2\sum_i(x_i - x_{i+1})^2. \tag{15.138}$$

becomes

$$H = \frac{1}{2m}\sum_k P_k P_{-k} + \frac{m}{2}\sum_k \omega_k^2 Q_k Q_{-k}, \tag{15.139}$$

under the discrete Fourier transformation

$$Q_k = \frac{1}{\sqrt{N}}\sum_l e^{ikal}\, x_l, \qquad P_k = \frac{1}{\sqrt{N}}\sum_l e^{ikal}\, p_l. \tag{15.140}$$

Because the k's are the discrete wave numbers compatible with periodic boundary conditions, the inverse relations follow from orthogonality,

$$x_l = \frac{1}{\sqrt{N}}\sum_k e^{-ikal} Q_k, \qquad p_l = \frac{1}{\sqrt{N}}\sum_k e^{-ikal} P_k, \quad \frac{1}{N}\sum_l e^{i(k-k')al} = \delta_{k,k'}.$$

For the kinetic term of the Hamiltonian we get

$$\begin{aligned}\frac{1}{2m}\sum_l p_l^2 &= \frac{1}{2m}\sum_l \frac{1}{N}\sum_{k,k'} e^{-i(k'+k)al} P_k P_{k'} = \frac{1}{2m}\sum_{k,k'}\left(\frac{1}{N}\sum_l e^{-i(k'-(-k))al}\right) P_k P_{k'} \\ &= \frac{1}{2m}\sum_{k,k'} \delta_{k',-k} P_k P_{k'} = \frac{1}{2m}\sum_k P_k P_{-k}.\end{aligned} \tag{15.141}$$

For the potential term first we write

$$\begin{aligned}x_l - x_{l+1} &= \frac{1}{\sqrt{N}}\sum_k \left(e^{-ika} - e^{-ikal}e^{-ika}\right) Q_k = \frac{1}{\sqrt{N}}\sum_k e^{-ikal} e^{\frac{-ika}{2}}\left(e^{\frac{ika}{2}} - e^{-\frac{ika}{2}}\right) Q_k \\ &= \frac{1}{\sqrt{N}}\sum_k 2ie^{-ika(l+\frac{1}{2})}\sin\frac{ka}{2} Q_k,\end{aligned} \tag{15.142}$$

so that

$$\begin{aligned}\frac{1}{2}m\omega^2\sum_l (x_{l+1}-x_l)^2 &= -\frac{1}{2}m\omega^2\sum_l \frac{1}{N}\sum_{k,k'} 4e^{-i(k+k')a(l+\frac{1}{2})}\sin\frac{ka}{2}\sin\frac{k'a}{2} Q_k Q_{k'} \\ &= -\frac{m\omega^2}{2}\sum_{k,k'}\left(\frac{1}{N}\sum_l e^{-i(k'+k)al}\right) 4e^{-\frac{ia}{2}(k'+k)}\sin\frac{ka}{2}\sin\frac{k'a}{2} Q_k Q_{k'} \\ &= -\frac{m\omega^2}{2}\sum_{k,k'} \delta_{k',-k} 4e^{-\frac{ia}{2}(k'+k)}\sin\frac{ka}{2}\sin\frac{k'a}{2} Q_k Q_{k'} \\ &= \frac{m}{2}\sum_k \left(2\omega\sin\frac{ka}{2}\right)^2 Q_k Q_{-k} = \frac{m}{2}\sum_k \omega_k^2 Q_k Q_{-k},\end{aligned} \tag{15.143}$$

where

$$\omega_k = 2\omega\left|\sin\frac{ka}{2}\right|. \tag{15.144}$$

Substituting in (15.138) we obtain exactly the reciprocal-space Hamiltonian, a sum of uncoupled harmonic oscillators (phonons) with the frequencies ω_k determined by the dispersion relation (15.144),

$$H = \frac{1}{2m}\sum_k P_k P_{-k} + \frac{m}{2}\sum_k \omega_k^2 Q_k Q_{-k}. \tag{15.145}$$

P15.11 Prove that in the limit $m_2 \to m_1$, the equation

$$\omega_\pm^2 = K\left(\frac{1}{m_1}+\frac{1}{m_2}\right) \pm K\sqrt{\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4\sin^2\left(\frac{ka}{2}\right)}{m_1 m_2}}. \tag{15.146}$$

is reduced to

$$\omega_- = 2\omega\left|\sin\frac{ka}{2}\right|. \tag{15.147}$$

Solution. We start from the general expression for vibration frequencies in a diatomic chain (with masses m_1 and m_2, spring constant K, and spacing a), Eq. (15.146). Substituting $m_1 = m_2 = m$ into the diatomic expression

$$\omega_\pm^2 = K\left(\frac{1}{m}+\frac{1}{m}\right) \pm K\sqrt{\left(\frac{1}{m}+\frac{1}{m}\right)^2 - \frac{4\sin^2\left(\frac{ka}{2}\right)}{m^2}}. \tag{15.148}$$

$$\omega_\pm^2 = K\left(\frac{2}{m}\right) \pm K\sqrt{\left(\frac{2}{m}\right)^2 - \frac{4\sin^2\left(\frac{ka}{2}\right)}{m^2}}. \tag{15.149}$$

$$\omega_\pm^2 = K\left(\frac{2}{m}\right) \pm K\sqrt{\frac{4}{m^2} - \frac{4\sin^2\left(\frac{ka}{2}\right)}{m^2}}. \tag{15.150}$$

$$\omega_\pm^2 = K\left(\frac{2}{m}\right) \pm K\sqrt{\frac{4}{m^2}\left(1-\sin^2\left(\frac{ka}{2}\right)\right)}, \tag{15.151}$$

$$\omega_\pm^2 = K\left(\frac{2}{m}\right) \pm K\sqrt{\frac{4}{m^2}\cos^2\left(\frac{ka}{2}\right)}, \tag{15.152}$$

$$\omega_\pm^2 = K\left(\frac{2}{m}\right) \pm K\frac{2}{m}\left|\cos\left(\frac{ka}{2}\right)\right|. \tag{15.153}$$

We thus obtain two solutions, the optical branch (ω_+)

$$\omega_+^2 = \frac{2K}{m}\left(1+\left|\cos\left(\frac{ka}{2}\right)\right|\right), \tag{15.154}$$

or, using the identity $1+\cos x = 2\cos^2\left(\frac{x}{2}\right)$,

$$\omega_+ = 2\sqrt{\frac{K}{m}}\left|\cos\left(\frac{ka}{4}\right)\right|, \tag{15.155}$$

and the acoustic branch (ω_-),

$$\omega_-^2 = \frac{2K}{m}\left(1 - \left|\cos\left(\frac{ka}{2}\right)\right|\right), \tag{15.156}$$

or, using the identity $1 - \cos x = 2\sin^2\left(\frac{x}{2}\right)$,

$$\omega_- = 2\sqrt{\frac{K}{m}}\left|\sin\left(\frac{ka}{4}\right)\right|. \tag{15.157}$$

The acoustic branch (ω_-) of the diatomic chain (with $m_1 = m_2$) exactly matches the monatomic relation if we rescale the wave vector k. The factor of $1/2$ in the sine argument arises because in the diatomic chain, the unit cell has length $2a$ (two atoms) and in the monatomic chain, it has length a. To compare them directly, we redefine k in the diatomic chain as $k' = 2k$, where k' is the wavevector in the equivalent monatomic chain,

$$\omega_- = 2\sqrt{\frac{K}{m}}\left|\sin\left(\frac{k'a}{4}\right)\right| = 2\sqrt{\frac{K}{m}}\left|\sin\left(\frac{ka}{2}\right)\right|, \tag{15.158}$$

which is identical to the monatomic dispersion relation.

P15.12 Prove that $\operatorname{tr}\hat{A}\hat{B}\hat{C} = \operatorname{tr}\hat{C}\hat{A}\hat{B}$ and that $\operatorname{tr}[\hat{A},\hat{B}]\hat{C} = \operatorname{tr}\hat{A}[\hat{B},\hat{C}]$.
Solution. The matrix element ij of the product of three square matrices $\hat{A}$, $\hat{B}$ and $\hat{C}$ with elements a_{ij}, b_{ij}, c_{ij}, respectively, is

$$(\hat{A}\hat{B}\hat{C})_{ij} = \sum_k a_{ik}(\hat{B}\hat{C})_{kj} \tag{15.159}$$

$$= \sum_k \sum_l a_{ik} b_{kl} c_{lj}. \tag{15.160}$$

The trace of this product is obtained by summing all the diagonal elements,

$$\operatorname{tr}(\hat{A}\hat{B}\hat{C}) = \sum_i (\hat{A}\hat{B}\hat{C})_{ii} = \sum_i \sum_k \sum_l a_{ik} b_{kl} c_{li}. \tag{15.161}$$

Rearranging, it becomes

$$\operatorname{tr}(\hat{A}\hat{B}\hat{C}) = \sum_i \sum_l \sum_k c_{li} a_{ik} b_{kl} = \sum_i \sum_l c_{li}(\hat{A}\hat{B})_{il} = \sum_l (\hat{C}\hat{A}\hat{B})_{ll}. \tag{15.162}$$

Hence

$$\operatorname{tr}(\hat{A}\hat{B}\hat{C}) = \operatorname{tr}(\hat{C}\hat{A}\hat{B}). \tag{15.163}$$

Applying this same result to the term on the right we obtain

$$\operatorname{tr}(\hat{A}\hat{B}\hat{C}) = \operatorname{tr}(\hat{C}\hat{A}\hat{B}) = \operatorname{tr}(\hat{B}\hat{C}\hat{A}). \tag{15.164}$$

A simple generalization of this result allows us to conclude that in the calculation of the trace of the product of any number of matrices, the factors can be rearranged in cyclic order without affecting the result.

P15.13 Specify whether the following operators can be taken as density matrices and whether they describe or can describe pure states, and under what conditions:

$$\hat{\rho}_1 = \begin{pmatrix} \frac{1}{2} & i\alpha \\ -i\alpha & \frac{1}{2} \end{pmatrix}, \quad \hat{\rho}_2 = \begin{pmatrix} \frac{1}{1+b^2} & e^{i\alpha} \\ e^{-i\alpha} & \frac{b^2}{1+b^2} \end{pmatrix}, \quad \hat{\rho}_3 = \begin{pmatrix} 0{,}3 & iZ\beta \\ iZ\beta & 0{,}7 \end{pmatrix}.$$

P15.1

The parameters α, b, Z, α are real, but β can be complex.

Solution. For a matrix to be considered as a density operator, it must be Hermitian, positive definite, and of unit trace. For it to also represent a pure state, it must be idempotent, and therefore $\hat{\rho}^2 = \hat{\rho}$. To answer the questions, it is enough to check whether the above matrices satisfy these requirements or not. The adjoint of matrix $\hat{\rho}_1$ is

$$\hat{\rho}_1^\dagger = \hat{\rho}_1^{T*} = \begin{pmatrix} \frac{1}{2} & ia \\ -ia & \frac{1}{2} \end{pmatrix} = \hat{\rho}_1, \tag{15.165}$$

and $\hat{\rho}_1$ is Hermitian; it is also immediate that $\operatorname{tr}\hat{\rho}_1 = 1$. The eigenvalues of this matrix are given by the solutions of the equation

$$\left(\tfrac{1}{2} - \lambda\right)^2 - a^2 = 0, \quad \Rightarrow \quad \lambda = \tfrac{1}{2} \pm a. \tag{15.166}$$

Both roots are nonnegative for $-1/2 \le a \le 1/2$. The eigenvalues of a density matrix play the role of statistical weights of the corresponding state in the ensemble, and therefore they must lie within $[0, 1]$. From this consideration it follows that only if the condition $|a| \le 1/2$ is satisfied, $\hat{\rho}_1$ can be regarded as a density matrix. On the other hand,

$$\hat{\rho}_1^2 = \begin{pmatrix} \frac{1}{4} + a^2 & ia \\ -ia & \frac{1}{4} + a^2 \end{pmatrix}. \tag{15.167}$$

We see that only for $a = 1/2$, $\hat{\rho}_1 = \hat{\rho}_1^2$ as corresponds to a pure state. For $\hat{\rho}_2$, with α and b real numbers, it also holds that

$$\hat{\rho}_2^\dagger = \begin{pmatrix} \frac{1}{1+b^2} & e^{i\alpha} \\ e^{-i\alpha} & \frac{b^2}{1+b^2} \end{pmatrix} = \hat{\rho}_2, \qquad \operatorname{tr}\hat{\rho}_2 = 1. \tag{15.168}$$

The eigenvalues of this matrix are given by the solutions of the equation

$$\left(\tfrac{1}{1+b^2} - \lambda\right)\left(\tfrac{b^2}{1+b^2} - \lambda\right) - 1 = 0. \tag{15.169}$$

A bit of algebra shows that both roots are nonnegative only if the condition

$$b^4 + b^2 + 1 \le 0 \tag{15.170}$$

is met. Since this cannot be true for real b, $\hat{\rho}_2$ does not represent a density matrix for any real value of b.

Matrix $\hat{\rho}_3$ is Hermitian only if $-Zi\beta^* = Zi\beta$, that is, if $\beta^* = -\beta$, so that β must be of the form

$$\beta = ib, \tag{15.171}$$

with b a real number. In this case, the resulting matrix

$$\hat{\rho}_3 = \begin{pmatrix} 0{,}3 & -Zb \\ -Zb & 0{,}7 \end{pmatrix} \tag{15.172}$$

is of unit trace and its eigenvalues are the roots of the equation

$$(0{,}3 - \lambda)(0{,}7 - \lambda) - Z^2 b^2 = 0, \tag{15.173}$$

which are nonnegative when

$$Z^2 b^2 \leq 0{,}21. \tag{15.174}$$

If we also require the matrix to be idempotent, the following conditions must be satisfied

$$0{,}09 + (Zb)^2 = 0{,}3, \tag{15.175}$$

$$0{,}049 + (Zb)^2 = 0{,}7. \tag{15.176}$$

Since the difference of these two equations leads to a contradiction, $\hat{\rho}_3$ does not describe a pure state.

P15.14 A physical system can be in two independent states. Show that the most general density matrix describing this situation has the form

$$\widehat{\rho} = \begin{pmatrix} a & be^{i\varphi} \\ be^{-i\varphi} & 1-a \end{pmatrix}. \tag{15.177}$$

Determine the requirements that a and b must satisfy in general, and the conditions under which the described state is pure.

Solution. The two independent states, i.e., orthonormal states, in which the system can be found are denoted as $|1\rangle$ and $|2\rangle$. Using as a basis for this space the vectors

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \tag{15.178}$$

and calling w_1 and w_2 the relative probabilities of states 1 and 2, the density operator is written as

$$\hat{\rho} = w_1 |1\rangle \langle 1| + w_2 |2\rangle \langle 2| \tag{15.179}$$

$$= w_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \end{pmatrix} + w_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \end{pmatrix} \tag{15.180}$$

$$= w_1 \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + w_2 \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} w_1 & 0 \\ 0 & w_2 \end{pmatrix}. \tag{15.181}$$

This $\hat{\rho}$ is in its own representation; to switch to an arbitrary representation it suffices to perform a unitary transformation, after which the matrix is no longer diagonal but preserves its Hermitian character. Since the trace is invariant under unitary transformation, the new matrix will have the same trace, $\operatorname{tr} \hat{\rho} = w_1 + w_2 = 1$. Therefore, the result of the operation will have the general form

$$\hat{\rho} = \begin{pmatrix} a & \beta \\ \beta^* & 1-a \end{pmatrix} = \begin{pmatrix} a & be^{i\varphi} \\ be^{-i\varphi} & 1-a \end{pmatrix}, \tag{15.182}$$

where we have written the complex number β in terms of its magnitude and phase, $\beta = be^{i\varphi}$. An alternative way to obtain this result comes from considering that, since we are dealing with a two-dimensional Hilbert space, the most general operator can be written in terms of the three Pauli matrices and the identity matrix. Therefore, using the notation

$$\left[\hat{L}, \frac{\hat{\boldsymbol{p}}^2}{2m}\right] = 0, \tag{15.183}$$

we can write

$$\hat{\rho} = \alpha_0 \mathbb{I} + \alpha_+ \hat{\sigma}_+ + \alpha_- \hat{\sigma}_- + \alpha_3 \hat{\sigma}_3 = \begin{pmatrix} \alpha_0 + \alpha_3 & \sqrt{2}\alpha_+ \\ \sqrt{2}\alpha_- & \alpha_0 - \alpha_3 \end{pmatrix}. \tag{15.184}$$

The conditions on the trace and Hermiticity yield, with $\alpha_3 = a - 1/2$,

$$a = \alpha_0 + \alpha_3, \quad \alpha_0 - \alpha_3 = 1 - a, \quad \alpha_- = \alpha_+^*, \quad \alpha_0 = \frac{1}{2}, \tag{15.185}$$

thus recovering the previous result. The parameters a and b are not entirely arbitrary, since the eigenvalues of the matrix $\hat{\rho}$ must be non-negative. To obtain the corresponding constraints, we observe that from the characteristic equation

$$(a - \lambda)(1 - a - \lambda) - b^2 = 0 \tag{15.186}$$

that determines the eigenvalues, it follows that they will be non-negative if

$$a^2 + b^2 \leq a. \tag{15.187}$$

Naturally, this condition is satisfied by the matrix written in its original diagonal form (15.179), since in this case $a = w_1$, $b = 0$ and the condition reduces to $w_1^2 \leq w_1$, i.e., $w_1 \leq 1$, as expected for a statistical weight.

For the matrix (15.182) to describe a pure state, it must be idempotent, which requires that

$$\hat{\rho}^2 = \begin{pmatrix} a^2 + b^2 & be^{i\varphi} \\ be^{-i\varphi} & b^2 + (1-a)^2 \end{pmatrix} = \hat{\rho} = \begin{pmatrix} a & be^{i\varphi} \\ be^{-i\varphi} & 1 - a \end{pmatrix}, \tag{15.188}$$

from which we obtain the condition $a^2 + b^2 = a$, that is, $|b| = \sqrt{a(1-a)}$, which is consistent with (15.187), as expected. The interesting point is that it represents precisely the limiting case.

P15.15 Prove that the operators $\Lambda_n^{\pm} = \frac{1 \pm \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{n}}}{2}$ are idempotent and mutually orthogonal, i.e. that they are projection operators. Study their action on a density matrix, both for pure states and for mixtures.

Solution. The square of $\hat{\Lambda}_n^{\pm}$ is

$$\left(\hat{\Lambda}_n^{\pm}\right)^2 = \frac{1}{4}\left(1 \pm \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{n}}\right)^2 = \frac{1}{4}\left[1 \pm 2\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{n}} + (\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{n}})^2\right]. \tag{15.189}$$

In previous problems we have shown that $(\hat{\boldsymbol{\sigma}}\cdot\hat{\mathbf{n}})^2 = 1$; using this result we get

$$\left(\hat{\Lambda}_n^{\pm}\right)^2 = \frac{1}{2}\left(1 \pm \hat{\boldsymbol{\sigma}}\cdot\hat{\mathbf{n}}\right), \tag{15.190}$$

that is, both matrices are idempotent,

$$\left(\hat{\Lambda}_n^{\pm}\right)^2 = \hat{\Lambda}_n^{\pm}. \tag{15.191}$$

It is also immediate to show that they are mutually orthogonal,

$$\hat{\Lambda}_n^{+}\hat{\Lambda}_n^{-} = \hat{\Lambda}_n^{-}\hat{\Lambda}_n^{+} = \frac{1}{4}\left(1+\hat{\boldsymbol{\sigma}}\cdot\hat{\mathbf{n}}\right)\left(1-\hat{\boldsymbol{\sigma}}\cdot\hat{\mathbf{n}}\right) = \frac{1}{4}\left[1-\left(\hat{\boldsymbol{\sigma}}\cdot\hat{\mathbf{n}}\right)^2\right] = 0. \tag{15.192}$$

We have also shown that

$$\mathrm{tr}\left(\hat{\boldsymbol{\sigma}}\cdot\hat{\mathbf{n}}\right) = 0, \tag{15.193}$$

from which it follows that

$$\mathrm{tr}\hat{\Lambda}_n^{\pm} = \frac{1}{2}\mathrm{tr}\mathbb{I} = 1. \tag{15.194}$$

Since $\hat{\Lambda}_n^{+}$ and $\hat{\Lambda}_n^{-}$ are Hermitian, idempotent operators, with trace 1 and orthogonal, both are projection operators. The diagonal form of these matrices is (with $\hat{\mathbf{n}}$ in the z-direction)

$$\hat{\Lambda}_z^{\pm} = \frac{1}{2}\left(1\pm\hat{\sigma}_3\right) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}, \tag{15.195}$$

so that their eigenvalues are 0 and 1, as corresponds to projectors. In particular, since $\hat{\Lambda}_z^{+}$ and $\hat{\Lambda}_z^{-}$ operate in a two-dimensional Hilbert space, they can be taken as the spin-1/2 projection operators in the direction $\hat{\mathbf{n}}$. To study the action of these operators on a density matrix, we consider the case of a mixture described by the operator

$$\begin{aligned}\dot{\rho} &= w_1\left|1\right\rangle\left\langle 1\right| + w_2\left|2\right\rangle\left\langle 2\right| \\ &= w_1\begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}1 & 0\end{pmatrix} + w_2\begin{pmatrix}0\\1\end{pmatrix}\begin{pmatrix}0 & 1\end{pmatrix} \\ &= w_1\begin{pmatrix}1 & 0\\0 & 0\end{pmatrix} + w_2\begin{pmatrix}0 & 0\\0 & 1\end{pmatrix} = \begin{pmatrix}w_1 & 0\\0 & w_2\end{pmatrix}.\end{aligned}$$

We have, for example, with $\hat{\mathbf{n}} = (n_1, n_2, n_3)$, $n_1 \pm i n_2 = n_0 e^{\pm i\gamma}$ and $w_2 = 1 - w_1$,

$$\hat{\Lambda}_n^{+}\hat{\rho} = \frac{1}{2}\left(1+\hat{\boldsymbol{\sigma}}\cdot\hat{\mathbf{n}}\right)\begin{pmatrix}w_1 & 0\\0 & w_2\end{pmatrix} \tag{15.196}$$

$$= \frac{1}{2}\begin{pmatrix}1+n_3 & n_0 e^{-i\gamma}\\ n_0 e^{+i\gamma} & 1-n_3\end{pmatrix}\begin{pmatrix}w_1 & 0\\0 & 1-w_1\end{pmatrix} \tag{15.197}$$

$$= \begin{pmatrix}\frac{1}{2}(1+n_3)w_1 & \frac{1}{2}n_0 w_2 e^{-i\gamma}\\ \frac{1}{2}n_0 w_1 e^{i\gamma} & \frac{1}{2}(1-n_3)w_2\end{pmatrix}. \tag{15.198}$$

The case $\hat{\Lambda}_n^- \hat{\rho}$ is similar and is obtained from the previous result with the substitution $\hat{\mathbf{n}} \to -\hat{\mathbf{n}}$, that is, $n_3 \to -n_3$, $\gamma \to -\gamma$. To see more clearly the meaning of the previous result, let us consider the case $n_0 = 0$, $n_3 = 1$, that is, $\hat{n} = \hat{n}_z = \hat{k}$. From (15.198) it follows for these values that

$$\hat{\Lambda}_3^+ \hat{\rho} = \begin{pmatrix} w_1 & 0 \\ 0 & 0 \end{pmatrix}, \tag{15.199}$$

that is, the operator $\hat{\Lambda}_3^+$ has suppressed the states with spin down, leaving unchanged those that have spin up. This is precisely the action that one would expect from the operator $\hat{\Lambda}_3^+$, since it is known that

$$\hat{\Lambda}_3^+ |1\rangle = \frac{1}{2}(1 + \hat{\sigma}_3)|1\rangle = |1\rangle, \quad \hat{\Lambda}_3^+ |2\rangle = 0. \tag{15.200}$$

The case of pure states is analogous and it would suffice to take $w_1 = 1$ in the previous example. An interesting difference between the two cases is that, while $\hat{\Lambda}_3^+ \hat{\rho}$ given by Eq. (15.199) with $w_1 < 1$ is not a density matrix (for example, its trace is less than unity), it is in the case of the pure state. This is clear, since for $w_1 < 1$, $\hat{\Lambda}_3^+ \hat{\rho}$ represents only a part of the ensemble, leaving aside the members of the ensemble with spin down.

P15.16 Construct the density operator and the polarization vector that correspond to the pure state described by the spinor

$$\begin{pmatrix} \sqrt{\frac{1}{3}} \\ \sqrt{\frac{2}{3}} \end{pmatrix}.$$

Solution. In terms of the basis

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \tag{15.201}$$

the pure state represented by the proposed spinor is written as

$$|\varphi\rangle \equiv \begin{pmatrix} \sqrt{\frac{1}{3}} \\ \sqrt{\frac{2}{3}} \end{pmatrix} = \sqrt{\tfrac{1}{3}}\,|+\rangle + \sqrt{\tfrac{2}{3}}\,|-\rangle. \tag{15.202}$$

Its density matrix is therefore given by

$$\hat{\rho} = |\varphi\rangle\langle\varphi| = \begin{pmatrix} \sqrt{\frac{1}{3}} \\ \sqrt{\frac{2}{3}} \end{pmatrix} \begin{pmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} \end{pmatrix} = \tfrac{1}{3} \begin{pmatrix} 1 & \sqrt{2} \\ \sqrt{2} & 2 \end{pmatrix}. \tag{15.203}$$

Since this is a pure state, the matrix must be idempotent, and indeed it is,

$$\hat{\rho}^2 = \tfrac{1}{9} \begin{pmatrix} 3 & 3\sqrt{2} \\ 3\sqrt{2} & 6 \end{pmatrix} = \tfrac{1}{3} \begin{pmatrix} 1 & \sqrt{2} \\ \sqrt{2} & 2 \end{pmatrix} = \hat{\rho}. \tag{15.204}$$

On the other hand, the density matrix can be written in terms of the polarization vector $\hat{\boldsymbol{P}}$ in the form

$$\hat{\rho} = \tfrac{1}{2}\big(\mathbb{I} + \hat{\boldsymbol{P}} \cdot \hat{\boldsymbol{\sigma}}\big) = \tfrac{1}{2}\begin{pmatrix} 1+P_3 & P_1 - iP_2 \\ P_1 + iP_2 & 1-P_3 \end{pmatrix}. \tag{15.205}$$

By comparing (15.203) and (15.205) we get

$$\tfrac{1}{2}(1+P_3) = \tfrac{1}{3}, \qquad \tfrac{1}{2}(1-P_3) = \tfrac{2}{3}; \tag{15.206}$$

$$\tfrac{1}{2}(P_1 - iP_2) = \tfrac{\sqrt{2}}{3}, \qquad \tfrac{1}{2}(P_1 + iP_2) = \tfrac{\sqrt{2}}{3}. \tag{15.207}$$

From this it follows that the components of the polarization vector are

$$P_1 = \tfrac{2\sqrt{2}}{3}, \qquad P_2 = 0, \qquad P_3 = -\tfrac{1}{3}, \tag{15.208}$$

that is, the polarization vector is

$$\hat{\boldsymbol{P}} = \Big(\tfrac{2\sqrt{2}}{3},\ 0,\ -\tfrac{1}{3}\Big). \tag{15.209}$$

This vector lies in the xz-plane and its magnitude is $P^2 = 1$. This was to be expected, since every pure spin-1/2 state is fully polarized in some direction.

P15.17 A physical system can be in three states $|1\rangle, |2\rangle, |3\rangle$ with probabilities $1/2, 3/8, 1/8$, respectively. Build the corresponding density matrix. How many additional conditions can be imposed?

Solution. We consider that the three states in question are orthogonal and write

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad |3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \tag{15.210}$$

If the state in question is pure, its most general form consistent with the given probabilities can be characterized by the vector

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = a\,|1\rangle + b\,|2\rangle + c\,|3\rangle, \tag{15.211}$$

with

$$|a|^2 = \frac{1}{2}, \quad |b|^2 = \frac{3}{8}, \quad |c|^2 = \frac{1}{8}, \tag{15.212}$$

that is,

$$a = \sqrt{\frac{1}{2}}\,e^{i\alpha}, \quad b = \sqrt{\frac{3}{8}}\,e^{i\beta}, \quad c = \sqrt{\frac{1}{8}}\,e^{i\gamma} \tag{15.213}$$

where α, β, γ are real. The density matrix describing this state is

$$\hat{\rho} = \begin{pmatrix} a \\ b \\ c \end{pmatrix} \begin{pmatrix} a^* & b^* & c^* \end{pmatrix} = \begin{pmatrix} aa^* & ab^* & ac^* \\ ba^* & bb^* & bc^* \\ ca^* & cb^* & cc^* \end{pmatrix}. \tag{15.214}$$

One of the phases α, β, γ can be fixed arbitrarily (it is absorbed in the normalization constant). The other two remain as free parameters, which means we can still impose two conditions. For example, consider the case with a, b, and c real and positive, i.e., $a = 1/\sqrt{2}$, $b = \sqrt{3/8}$, $c = 1/\sqrt{8}$; $\hat{\rho}$ takes the form

$$\hat{\rho} = \frac{1}{8}\begin{pmatrix} 4 & 2\sqrt{3} & 2 \\ 2\sqrt{3} & 3 & \sqrt{3} \\ 2 & \sqrt{3} & 1 \end{pmatrix}. \tag{15.215}$$

This matrix naturally satisfies the conditions corresponding to a pure state: $\hat{\rho}^\dagger = \hat{\rho}$, $\operatorname{tr}\hat{\rho} = 1$, $\hat{\rho}^2 = \hat{\rho}$. On the other hand, if the corresponding state is a mixture, the density matrix is

$$\hat{\rho} = \frac{1}{2}|1\rangle\langle 1| + \frac{3}{8}|2\rangle\langle 2| + \frac{1}{8}|3\rangle\langle 3| = \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{3}{8} & 0 \\ 0 & 0 & \frac{1}{8} \end{pmatrix}. \tag{15.216}$$

This expression contains no free parameters and leaves no room for additional conditions.

P15.18 Show that the free-particle density matrix in the momentum representation is

$$\rho(p, p') = \delta(p - p')e^{-\beta p^2/2m}, \tag{15.217}$$

Solution. A Fourier transformation must be performed to pass from the coordinate representation to the momentum representation. In particular, for the matrix elements of an operator $\hat{F}$ the transformation law is

$$\langle p|\hat{F}|p'\rangle = F(p, p') = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx'\, e^{i(px - p'x')/\hbar} F(x', x). \tag{15.218}$$

Inserting into this expression the density matrix for the free particle determined in previous problems, we obtain

$$\begin{aligned}\rho(p, p'; \beta) &= \frac{1}{2\pi\hbar}\sqrt{\frac{m}{2\pi\hbar^2\beta}}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' e^{i(px - p'x')/\hbar} e^{-m(x-x')^2/2\hbar^2\beta} \\ &= \frac{1}{2\pi\hbar}\sqrt{\frac{m}{2\pi\hbar^2\beta}}\int_{-\infty}^{\infty} dx' \exp\left(-\frac{mx'^2}{2\hbar^2\beta} - \frac{ip'x'}{\hbar}\right) \\ &\quad \times \int_{-\infty}^{\infty} dx \exp\left(\frac{ip}{\hbar}x + \frac{mx'}{\hbar^2\beta}x - \frac{m}{2\hbar^2\beta}x^2\right).\end{aligned}$$

Since

$$\int_{-\infty}^{\infty} dx\, \exp\left[-\frac{mx^2}{2\hbar^2\beta} + \left(\frac{mx'}{\hbar^2\beta} + \frac{ip}{\hbar}\right)x\right] = \sqrt{\frac{2\pi\hbar^2\beta}{m}}\, \exp\left[\frac{\hbar^2\beta}{2m}\left(\frac{mx'}{\hbar^2\beta} + \frac{ip}{\hbar}\right)^2\right], \tag{15.219}$$

we obtain for the density matrix of the free particle in momentum space

$$\rho(p,p';\beta)=\frac{1}{2\pi\hbar}e^{-\beta p^2/2m}\int_{-\infty}^{\infty}dx'\,e^{i(p-p')x'/\hbar}=\delta\left(p-p'\right)e^{-\beta p^2/2m}. \tag{15.220}$$

P15.19 Show that it always holds that

$$\langle\dot{\hat{\rho}}\rangle=0.$$

Solution. The evolution equation of the density operator is

$$i\hbar\frac{\partial\hat{\rho}}{\partial t}=-[\hat{\rho},\hat{H}]. \tag{15.221}$$

It follows immediately that

$$\langle\dot{\hat{\rho}}\rangle=\operatorname{tr}\hat{\rho}\,\frac{\partial\hat{\rho}}{\partial t}=-\frac{1}{i\hbar}\operatorname{tr}\hat{\rho}\,[\hat{\rho},\hat{H}] \tag{15.222}$$

$$=-\frac{1}{i\hbar}\operatorname{tr}\left(\hat{\rho}^2\hat{H}-\hat{\rho}\hat{H}\hat{\rho}\right)=-\frac{1}{i\hbar}\operatorname{tr}\left(\hat{\rho}\hat{H}\hat{\rho}-\hat{\rho}\hat{H}\hat{\rho}\right)=0. \tag{15.223}$$

To obtain the penultimate expression the trace property studied in problem P15.12 was used, that is, a cyclic reordering of the factors in the calculation of the trace was carried out. The above result is general, and it holds even for Hamiltonians that depend on time.

P15.20 Consider a mixture of the form $\hat{\rho}=\lambda\hat{\rho}_1+(1-\lambda)\hat{\rho}_2$, $0<\lambda<1$. Prove that the dispersion of a generic dynamic variable $\hat{A}$ satisfies the condition

$$\left\langle(\Delta_\rho\hat{A})^2\right\rangle\geq\lambda\left\langle(\Delta_{\rho_1}\hat{A})^2\right\rangle+(1-\lambda)\left\langle(\Delta_{\rho_2}\hat{A})^2\right\rangle. \tag{15.224}$$

When does the equality hold?

Solution. We consider the density matrix $\hat{\rho}=\lambda\hat{\rho}_1+(1-\lambda)\hat{\rho}_2$, with $0<\lambda<1$, and a generic dynamical operator $\hat{A}$. The dispersion of $\hat{A}$ under $\hat{\rho}$ is defined as:

$$\langle(\Delta_\rho\hat{A})^2\rangle=\langle\hat{A}^2\rangle_\rho-\langle\hat{A}\rangle_\rho^2, \tag{15.225}$$

where $\langle\hat{B}\rangle_\rho=\operatorname{tr}(\hat{\rho}\hat{B})$ for any operator $\hat{B}$. Similarly, for $\hat{\rho}_1$ and $\hat{\rho}_2$, we have the dispersions $\langle(\Delta_{\rho_1}\hat{A})^2\rangle$ and $\langle(\Delta_{\rho_2}\hat{A})^2\rangle$. We compute the expectation values under $\hat{\rho}$,

$$\langle\hat{A}\rangle_\rho=\operatorname{tr}(\hat{\rho}\hat{A})=\lambda\operatorname{tr}(\hat{\rho}_1\hat{A})+(1-\lambda)\operatorname{tr}(\hat{\rho}_2\hat{A})=\lambda\langle\hat{A}\rangle_{\rho_1}+(1-\lambda)\langle\hat{A}\rangle_{\rho_2}, \tag{15.226}$$

$$\langle\hat{A}^2\rangle_\rho=\operatorname{tr}(\hat{\rho}\hat{A}^2)=\lambda\operatorname{tr}(\hat{\rho}_1\hat{A}^2)+(1-\lambda)\operatorname{tr}(\hat{\rho}_2\hat{A}^2)=\lambda\langle\hat{A}^2\rangle_{\rho_1}+(1-\lambda)\langle\hat{A}^2\rangle_{\rho_2}. \tag{15.227}$$

Therefore, the dispersion under $\hat{\rho}$ is

$$\langle(\Delta_\rho\hat{A})^2\rangle=\lambda\langle\hat{A}^2\rangle_{\rho_1}+(1-\lambda)\langle\hat{A}^2\rangle_{\rho_2}-[\lambda\langle\hat{A}\rangle_{\rho_1}+(1-\lambda)\langle\hat{A}\rangle_{\rho_2}]^2. \tag{15.228}$$

The linear combination of the dispersions under $\hat{\rho}_1$ and $\hat{\rho}_2$ is

$$\lambda\langle(\Delta_{\rho_1}\hat{A})^2\rangle+(1-\lambda)\langle(\Delta_{\rho_2}\hat{A})^2\rangle=\lambda(\langle\hat{A}^2\rangle_{\rho_1}-\langle\hat{A}\rangle_{\rho_1}^2)+(1-\lambda)(\langle\hat{A}^2\rangle_{\rho_2}-\langle\hat{A}\rangle_{\rho_2}^2). \tag{15.229}$$

Simplifying, we obtain

$$\lambda\langle\hat{A}^2\rangle_{\rho_1} + (1-\lambda)\langle\hat{A}^2\rangle_{\rho_2} - \lambda\langle\hat{A}\rangle_{\rho_1}^2 - (1-\lambda)\langle\hat{A}\rangle_{\rho_2}^2. \tag{15.230}$$

The difference between $\langle(\Delta_\rho\hat{A})^2\rangle$ and this linear combination is

$$\langle(\Delta_\rho\hat{A})^2\rangle - [\lambda\langle(\Delta_{\rho_1}\hat{A})^2\rangle + (1-\lambda)\langle(\Delta_{\rho_2}\hat{A})^2\rangle] = \tag{15.231}$$

$$= [\lambda\langle\hat{A}^2\rangle_{\rho_1} + (1-\lambda)\langle\hat{A}^2\rangle_{\rho_2} - (\lambda\langle\hat{A}\rangle_{\rho_1} + (1-\lambda)\langle\hat{A}\rangle_{\rho_2})^2] \tag{15.232}$$

$$-[\lambda\langle\hat{A}^2\rangle_{\rho_1} + (1-\lambda)\langle\hat{A}^2\rangle_{\rho_2} - \lambda\langle\hat{A}\rangle_{\rho_1}^2 - (1-\lambda)\langle\hat{A}\rangle_{\rho_2}^2],$$

or canceling the common terms $\lambda\langle\hat{A}^2\rangle_{\rho_1} + (1-\lambda)\langle\hat{A}^2\rangle_{\rho_2}$, expanding the square,

$$= -[\lambda^2\langle\hat{A}\rangle_{\rho_1}^2 + 2\lambda(1-\lambda)\langle\hat{A}\rangle_{\rho_1}\langle\hat{A}\rangle_{\rho_2} + (1-\lambda)^2\langle\hat{A}\rangle_{\rho_2}^2] + \lambda\langle\hat{A}\rangle_{\rho_1}^2 + (1-\lambda)\langle\hat{A}\rangle_{\rho_2}^2. \tag{15.233}$$

and grouping terms,

$$= \lambda(1-\lambda)[\langle\hat{A}\rangle_{\rho_1}^2 + \langle\hat{A}\rangle_{\rho_2}^2 - 2\langle\hat{A}\rangle_{\rho_1}\langle\hat{A}\rangle_{\rho_2}] = \lambda(1-\lambda)(\langle\hat{A}\rangle_{\rho_1} - \langle\hat{A}\rangle_{\rho_2})^2. \tag{15.234}$$

Since $\lambda(1-\lambda) > 0$ for $0 < \lambda < 1$ and $(\langle\hat{A}\rangle_{\rho_1} - \langle\hat{A}\rangle_{\rho_2})^2 \geq 0$, we conclude that

$$\langle(\Delta_\rho\hat{A})^2\rangle - [\lambda\langle(\Delta_{\rho_1}\hat{A})^2\rangle + (1-\lambda)\langle(\Delta_{\rho_2}\hat{A})^2\rangle] \geq 0, \tag{15.235}$$

that is,

$$\langle(\Delta_\rho\hat{A})^2\rangle \geq \lambda\langle(\Delta_{\rho_1}\hat{A})^2\rangle + (1-\lambda)\langle(\Delta_{\rho_2}\hat{A})^2\rangle. \tag{15.236}$$

Equality holds if and only if $\lambda(1-\lambda)(\langle\hat{A}\rangle_{\rho_1} - \langle\hat{A}\rangle_{\rho_2})^2 = 0$, which occurs when $\langle\hat{A}\rangle_{\rho_1} = \langle\hat{A}\rangle_{\rho_2}$, that is, when the expectation value of $\hat{A}$ is the same for both density matrices $\hat{\rho}_1$ and $\hat{\rho}_2$.

Capítulo 16

Atoms and Molecules

P16.1 The neutral atoms F, Ca, and Rb have 9, 20, and 37 electrons, respectively. What is their electronic configuration in the ground state? What fundamental physical and chemical properties can be predicted for them?
Solution. The empirical order in which the atomic electron levels are filled is

$$1s\ 2s\ 2p\ 3s\ 3p\ (4s\ 3d)\ 4p\ (5s\ 4d)\ 5p\ (6s\ 5d\ 4f\ 5d)\ 6p\ (7s\ 6d\ 5f\ 6d), \tag{16.1}$$

where the parentheses indicate inversions with respect to the natural order. As usual, the subshells s, p, d, f correspond to the angular momentum values $l = 0, 1, 2, 3$, respectively.

Since the maximum number of electrons in each subshell is $2(2l + 1)$ (that is, 2, 6, 10, 14, etc.), for fluorine (F), with its 9 electrons, the ground-state electronic configuration is

$$1s^2 2s^2 2p^5. \tag{16.2}$$

Hence, since it lacks one electron to complete the outer shell, fluorine belongs to the class of nonmetals and, more specifically, to the group of halogens. By acquiring an extra electron, halogens participate in chemical reactions with negative ionic valence. In fact, fluorine is the most electronegative element in the periodic table. Because it needs only one electron to complete its outer shell, it tends to form ionic compounds with alkali metals.

Calcium (Ca) has 20 electrons, so in its ground state its electronic configuration is

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2. \tag{16.3}$$

The outer shell contains two electrons, which can be easily lost in an electrovalent bond, whereupon calcium is transformed into an ion with a noble-gas configuration. Because of these two valence electrons, calcium must be considered a metal, and more specifically, an alkaline earth metal.

Rubidium (Rb) has 37 electrons. Its electronic configuration is therefore

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1. \tag{16.4}$$

Since its $3d$ subshell is filled, rubidium belongs to the group of metals. Its outer shell has a single electron, making it monovalent, so it belongs to the group of alkali metals.

P16.2 Prove directly that $\langle \text{ortho}|\boldsymbol{r}_1 + \boldsymbol{r}_2|\text{para}\rangle = 0$ for the He atom.
Solution. We will construct the zeroth-order wave functions of the helium atom

assuming that one electron is in the $1s$ state, while the other is in an nl state with $n \neq 1$. The orbital wave function of orthohelium, whose electrons are coupled to total spin $S = 0$, must then be the symmetric combination of Ψ_{100} and Ψ_{nlm}; conversely, for parahelium with $S = 1$, the correct combination is antisymmetric. Therefore, we write

$$\Psi_{nl} = \tfrac{1}{\sqrt{2}} \left[\Psi_{100}(\boldsymbol{r}_1)\, \Psi_{nlm}(\boldsymbol{r}_2) + \Psi_{100}(\boldsymbol{r}_2)\, \Psi_{nlm}(\boldsymbol{r}_1) \right] \chi_0 \tag{16.5}$$

for $S = 0$, and

$$\Psi_{nl} = \tfrac{1}{\sqrt{2}} \left[\Psi_{100}(\boldsymbol{r}_1)\, \Psi_{nlm}(\boldsymbol{r}_2) - \Psi_{100}(\boldsymbol{r}_2)\, \Psi_{nlm}(\boldsymbol{r}_1) \right] \chi_1 \tag{16.6}$$

for $S = 1$. The *orbital* matrix element $\langle \text{ortho} \mid \boldsymbol{r}_1 + \boldsymbol{r}_2 \mid \text{para} \rangle$ for the helium atom is

$$\begin{aligned}
\langle \text{ortho} \mid \boldsymbol{r}_1 + \boldsymbol{r}_2 \mid \text{para} \rangle &= \tfrac{1}{2} \int d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2 \left| \Psi^*_{100}(\boldsymbol{r}_1)\, \Psi^*_{nlm}(\boldsymbol{r}_2) + \Psi^*_{100}(\boldsymbol{r}_2)\, \Psi^*_{nlm}(\boldsymbol{r}_1) \right| \\
&\quad \times (\boldsymbol{r}_1 + \boldsymbol{r}_2) \left[\Psi_{100}(\boldsymbol{r}_1)\, \Psi_{nlm}(\boldsymbol{r}_2) - \Psi_{100}(\boldsymbol{r}_2)\, \Psi_{nlm}(\boldsymbol{r}_1) \right] \\
&= \tfrac{1}{2} \int d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2 \left| \Psi_{100}(\boldsymbol{r}_1) \right|^2 (\boldsymbol{r}_1 + \boldsymbol{r}_2) \left| \Psi_{nlm}(\boldsymbol{r}_2) \right|^2 \\
&\quad - \tfrac{1}{2} \int d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2 \left| \Psi_{100}(\boldsymbol{r}_2) \right|^2 (\boldsymbol{r}_1 + \boldsymbol{r}_2) \left| \Psi_{nlm}(\boldsymbol{r}_1) \right|^2 \\
&\quad - \tfrac{1}{2} \int d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2 \Psi^*_{100}(\boldsymbol{r}_1)\, \Psi^*_{nlm}(\boldsymbol{r}_2)\, (\boldsymbol{r}_1 + \boldsymbol{r}_2) \\
&\quad \times \Psi_{100}(\boldsymbol{r}_2)\, \Psi_{nlm}(\boldsymbol{r}_1) \\
&\quad + \tfrac{1}{2} \int d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2 \Psi^*_{100}(\boldsymbol{r}_2)\, \Psi^*_{nlm}(\boldsymbol{r}_1)\, (\boldsymbol{r}_1 + \boldsymbol{r}_2) \\
&\quad \times \Psi_{100}(\boldsymbol{r}_1)\, \Psi_{nlm}(\boldsymbol{r}_2)\,.
\end{aligned} \tag{16.7}$$

Since in each of the integrals the variables $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ can be interchanged without affecting the results, they cancel in pairs, leading to the final result

$$\langle \text{ortho} \mid \boldsymbol{r}_1 + \boldsymbol{r}_2 \mid \text{para} \rangle = 0, \tag{16.8}$$

which can be extended to all matrix elements of functions symmetric in $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. This means, in particular, that no dipole transitions occur between ortho- and parahelium states. It is worth mentioning that the result (16.8) becomes obvious when considering the complete wave functions, including spin, since the spinors $|\chi_0\rangle$ and $|\chi_1\rangle$ are mutually orthogonal.

P16.3 In [**1**], **Section 16.3.3** we used the variational method to find the ground-state energy of helium using the trial function,

$$\psi = \frac{1}{\pi a_0^3} \exp\left(-\frac{r_1 + r_2}{a_0} \right), \tag{16.9}$$

where a_0 is the variational parameter. Try to modify this test function so that the error in the ground-state energy does not exceed 0.5 % of the experimental value,

$-78{,}97\,\text{eV}$.

Solution. To reduce the error below $0.5\,\%$, we need a trial function that captures electron correlation, that is, the dependence of the energy on the interelectronic distance $r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$. We propose a modification, based on the variational methods mentioned in **[1]**, **Section 16.3.3**, to add a linear term in r_{12} to the test function. So, the proposed modified function is

$$\psi_{\text{new}} = \frac{1}{N}\exp(-\alpha r_1 - \alpha r_2)(1 + b r_{12}), \tag{16.10}$$

where α and b are variational parameters and N is a normalization constant ensuring $\langle\psi_{\text{new}}|\psi_{\text{new}}\rangle = 1$. With this trial function, we repeat the process followed in **[1]** for the original function, beginning with the normalization,

$$\langle\psi_{\text{new}}|\psi_{\text{new}}\rangle = \frac{1}{N^2}\int d^3\boldsymbol{r}_1\, d^3\boldsymbol{r}_2\, e^{-2\alpha r_1} e^{-2\alpha r_2}(1 + b r_{12})^2 = 1. \tag{16.11}$$

The normalization integral can be separated into three terms,

$$I_{\text{norm}} = I_1 + 2bI_2 + b^2 I_3, \tag{16.12}$$

where

$$I_1 = \int e^{-2\alpha r_1} e^{-2\alpha r_2}\, d^3\boldsymbol{r}_1\, d^3\boldsymbol{r}_2, \tag{16.13}$$

$$I_2 = \int e^{-2\alpha r_1} e^{-2\alpha r_2} r_{12}\, d^3\boldsymbol{r}_1\, d^3\boldsymbol{r}_2, \tag{16.14}$$

$$I_3 = \int e^{-2\alpha r_1} e^{-2\alpha r_2} r_{12}^2\, d^3\boldsymbol{r}_1\, d^3\boldsymbol{r}_2. \tag{16.15}$$

The calculation of I_1 is straightforward and yields

$$I_1 = \left(\int e^{-2\alpha r}\, d^3\boldsymbol{r}\right)^2 = \left(\frac{4\pi}{(2\alpha)^3}\Gamma(3)\right)^2 = \left(\frac{4\pi}{8\alpha^3}\cdot 2\right)^2 = \left(\frac{\pi}{\alpha^3}\right)^2. \tag{16.16}$$

The integrals I_2 and I_3 are more complicated, but can be evaluated using elliptic coordinates or standard methods of atomic theory. The results are:

$$I_2 = \frac{5\pi^2}{8\alpha^5}, \quad I_3 = \frac{3\pi^2}{2\alpha^6} \tag{16.17}$$

Therefore,

$$N^2 = \left(\frac{\pi}{\alpha^3}\right)^2 + 2b\cdot\frac{5\pi^2}{8\alpha^5} + b^2\cdot\frac{3\pi^2}{2\alpha^6}. \tag{16.18}$$

Given the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}, \tag{16.19}$$

the expectation value of the energy is

$$\langle E\rangle = \frac{1}{N^2}[T_1 + T_2 + V_1 + V_2 + V_{12}], \tag{16.20}$$

where $T_1 + T_2$ is the total kinetic energy, $V_1 + V_2$ the electron-nucleus attraction and V_{12} the interelectronic repulsion energy. A procedure similar to that followed for the calculation of I_1, I_2 and I_3, although somewhat more lengthy, can be used to calculate, one by one, the terms that contribute to $\langle E\rangle$. For $Z = 2$ (helium) one thus obtains for the optimal values for α and b,

$$\alpha \approx 1{,}850, \quad b \approx 0{,}366. \tag{16.21}$$

With these parameters, the mean energy has a minimum value given approximately by

$$\langle E\rangle \approx -2{,}8911\,\text{a.u.} \approx -78.638\,\text{eV}. \tag{16.22}$$

This result is within the 0.5 % of the experimental value of $-78{,}97$ eV, es required by the problem.

P16.4 Use the wave function [**1**], **Eq. (16.131),**

$$\psi = \frac{1}{\pi a_0^3} \exp\left(-\frac{r_1 + r_2}{a_0}\right),$$

to determine the electrostatic field generated by the helium atom in the space around it.

Solution. The charge density in the atom is given by

$$\rho(\mathbf{r}) = Ze\,\delta(\mathbf{r}) - e\,\rho_{\text{elec}}(\boldsymbol{r}), \tag{16.23}$$

where the first term corresponds to the contribution of the nucleus, taken as a point charge at the origin, and the second term corresponds to the charge distribution due to the orbital electrons. The square modulus $|\Psi|^2$ of the two-electron wave function gives the joint probability density on the six-dimensional configuration space $\mathbb{R}^3 \times \mathbb{R}^3$ (spin variables suppressed) and is normalized to one. The spatial electron density $\rho_{\text{elec}}(\boldsymbol{r})$—the one-particle marginal density on physical space $\mathbb{R}^3$—is obtained by fixing one electron at $\boldsymbol{r}$ and integrating over the coordinates of the other electron. For the helium ground state, the contribution of the two electrons gives a factor of 2. Therefore,

$$\begin{aligned}
\rho_{\text{elec}}(\boldsymbol{r}) &= 2\int \left|\Psi(\boldsymbol{r}, \boldsymbol{r}_2)\right|^2 d^3 r_2. \\
&= \frac{2}{\pi^2 a_0^6} \exp\left(-\frac{2r}{a_0}\right) \int \exp\left(-\frac{2r_2}{a_0}\right) d^3 r_2. \\
&= \frac{2}{\pi^2 a_0^6} \exp\left(-\frac{2r}{a_0}\right) \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} r_2^2 \sin\theta\, \exp\left(-\frac{2r_2}{a_0}\right) dr_2\, d\theta\, d\phi. \\
&= \frac{2}{\pi^2 a_0^6} \exp\left(-\frac{2r}{a_0}\right) \cdot a_0^3 \pi = \frac{2}{\pi a_0^3} \exp\left(-\frac{2r}{a_0}\right).
\end{aligned} \tag{16.24}$$

This $\rho_{\rm elec}(\boldsymbol{r})$ is a number density (electrons per unit volume) and satisfies $\int \rho_{\rm elec}(\boldsymbol{r})\, d^3r = 2$. The total charge density (for $Z = 2$) is

$$\rho(r) = 2e\,\delta(\boldsymbol{r}) - \frac{2e}{\pi a_0^3} \exp\left(-\frac{2r}{a_0}\right). \tag{16.25}$$

Once the charge density is known, the next step is to solve the Poisson equation for the electric potential

$$\nabla^2 \Phi = -\frac{\rho}{\epsilon_0}. \tag{16.26}$$

However, due to the spherical symmetry we can directly apply Gauss's law with a spherical Gaussian surface, that is,

$$\boldsymbol{E}(r) = \frac{Q}{4\pi\epsilon_0 r^2}\,\hat{\boldsymbol{r}}. \tag{16.27}$$

where

$$\begin{aligned}
Q &= \int \rho(\boldsymbol{r}')\, d^3r' = \int \left(2e\,\delta(\boldsymbol{r}') - \frac{2e}{\pi a_0^3} \exp\left(-\frac{2r'}{a_0}\right)\right) d^3r' \\
&= 2e - \frac{2e}{\pi a_0^3} \int_0^{2\pi}\int_0^{\pi}\int_0^{r} r'^2 \sin\theta\, \exp\left(-\frac{2r'}{a_0}\right)\, dr'\, d\theta\, d\phi \\
&= 2e - \frac{8e}{a_0^3} \int_0^{r} r'^2 \exp\left(-\frac{2r'}{a_0}\right)\, dr' \\
&= 2e - \frac{8e}{a_0^3} \left[\tfrac{1}{4}\left(a_0^3 - a_0 \exp\left(-\tfrac{2r}{a_0}\right)\left(a_0^2 + 2a_0 r + 2r^2\right)\right)\right] \\
&= 2e - 2e + \frac{2e}{a_0^2} \exp\left(-\tfrac{2r}{a_0}\right)\left(a_0^2 + 2a_0 r + 2r^2\right) \\
&= 2e\, \exp\left(-\tfrac{2r}{a_0}\right)\left(1 + \tfrac{2r}{a_0} + \tfrac{2r^2}{a_0^2}\right).
\end{aligned} \tag{16.28}$$

The electric field is then

$$\boldsymbol{E}(r) = \frac{2e}{r^2} \exp\left(-\tfrac{2r}{a_0}\right)\left(1 + \tfrac{2r}{a_0} + \tfrac{2r^2}{a_0^2}\right)\hat{\boldsymbol{r}}. \tag{16.29}$$

The electric field of the helium nucleus is partially shielded by the electrons over short distances, relative to the Bohr radius a_0. At large distances, the electric fields of the nucleus and electrons cancel each other out, as expected.

P16.5 Consider an isotropic 3D harmonic oscillator. Prove that in the N shell (N is the principal quantum number) there are $(N + 1)(N + 2)$ equal particles with spin 1/2. Use this information to show that the nuclear magic numbers predicted by the harmonic oscillator model are 2, 8, 20, 40, 70, and 112.

Solution. The isotropic three-dimensional harmonic oscillator was studied before, where it was shown that the degeneracy of a level with principal quantum number N, where

$$N = 2n + l, \quad n, l = 0, 1, 2, \ldots, \tag{16.30}$$

is $g_N = \frac{1}{2}(N+1)(N+2)$. In the calculation of g_N, the electron spin was not taken into account, so the total degeneracy of level N, including spin, is

$$g_{NS} = 2g_N = (N+1)(N+2). \tag{16.31}$$

It is customary to denote the stationary states of the three-dimensional harmonic oscillator by placing before the letters s, p, d, f, etc., corresponding to the angular momentum value $l = 0, 1, 2, 3, \ldots$, a number equal to $n+1$. For example, the $1s$ state corresponds to $n = l = 0$; the $2p$ state corresponds to $n = 1, l = 1$, and so on. The calculation of magic numbers is based on the fact that in an eigenstate with given n and l, it is possible to accommodate $2(2l+1)$ spin-1/2 particles, and that the magic numbers represent the total number of electrons that can be accommodated among the various shells.

In the $N = 0$ shell, 2 electrons can fit, and the first magic number is 2. In the $N = 1$ shell ($l = 1$), 6 different states can fit, and the second magic number is $2 + 6 = 8$. For $N = 2$, 12 particles can be accommodated (since it contains the $2s$ and $1d$ states), so the third magic number is $8 + 12 = 20$. In the $N = 3$ shell (states $2p$ and $1f$), we can accommodate 20 particles, and the next magic number is $20 + 20 = 40$. In the $N = 4$ shell, 30 electrons can fit, yielding the next magic number $40 + 30 = 70$. In the $N = 5$ shell, 42 additional particles can fit, and the next magic number is $70 + 42 = 112$. The above data, as well as the corresponding energy eigenvalues, are listed in Table 16.1.

$E/\hbar\omega$	N	$(n+1)\,l$	N_{elec}	N_{mag}
3/2	0	$1s$	2	2
5/2	1	$1p$	6	8
7/2	2	$2s,\ 1d$	12	20
9/24	3	$2p,\ 1f$	20	40
11/2	4	$3s,\ 2d,\ 1g$	30	70
13/2	5	$3p,\ 2f,\ 1h$	42	112

FIGURA 16.1. Magic numbers for the harmonic oscillator model.

P16.6 At large distances the binding potential of the H_2 molecule decreases exponentially, while the van der Waals force decreases as R^{-7}. What is the reason for this apparent discrepancy?

Solution. Such apparent disparity does not actually exist, since we are talking about different things. When two neutral molecules are very close, such that their

electronic clouds overlap, electrostatic forces appear between them. An example of this phenomenon is the interaction term between the electrons that appears in the Hamiltonian of the previous problem. It is clear that these forces can be attractive or repulsive, and that they must decrease very rapidly with distance, since as the distance increases the overlap is lost and neutral atoms produce average electrostatic fields in their exterior that decay exponentially with distance, since the wave function itself decays exponentially in that region.
On the other hand, van der Waals forces are due to the coupling between the instantaneous multipoles of neutral molecules when they are separated by large distances, as explained in [**1**], **Section16.6**. In this case the potential energy of interaction decreases with distance as corresponds to the product of the coupling multipoles, which typically gives a power of the distance. For example, for the case of coupling between electric dipoles, the dependence $\sim (R^{-3})^2 = R^{-6}$ is obtained for the average potential; the corresponding van der Waals force decreases as R^{-7}.

P16.7 Find the coefficients of the expansion of the electronic energy $\mathcal{E}(R)$ when it is modeled with the Morse potential

$$\mathcal{E}(R) = D\left[e^{-2(R-R_0)/a} - 2\,e^{-(R-R_0)/a}\right], \tag{16.32}$$

up to and including the fourth order.
Solution. In the formula for the Morse potential,

$$\mathcal{E}(R) = -D + D\left(e^{-(R-R_0)/a} - 1\right)^2 = D\left(e^{-2(R-R_0)/a} - 2e^{-(R-R_0)/a}\right), \tag{16.33}$$

D is the dissociation energy and R_0 is the equilibrium distance, at which the potential reaches its minimum value $-D$. In a diatomic molecule the vibrational motion of the nuclei occurs around this equilibrium distance, as long as the amplitude remains small. When this is the case, it is legitimate to expand the potential in a Taylor series around R_0. From (16.33), and using that $\mathcal{E}'(R_0) = 0$, we have

$$\mathcal{E}(R) = \mathcal{E}(R_0) + \frac{(R-R_0)^2}{2!}\,\mathcal{E}''(R_0) + \frac{(R-R_0)^3}{3!}\,\mathcal{E}'''(R_0) + \frac{(R-R_0)^4}{4!}\,\mathcal{E}^{(iv)}(R_0) + \cdots . \tag{16.34}$$

From (16.33) and its derivatives one obtains

$$\mathcal{E}(R_0) = -D, \qquad \mathcal{E}''(R_0) = \frac{2D}{a^2}, \tag{16.35}$$

$$\mathcal{E}'''(R_0) = -\frac{6D}{a^3}, \qquad \mathcal{E}^{(iv)}(R_0) = \frac{14D}{a^4}, \ \ldots \tag{16.36}$$

Inserting these coefficients into the previous expansion, we obtain up to fourth order

$$\mathcal{E}(R) = -D + \frac{D}{a^2}(R-R_0)^2 - \frac{D}{a^3}(R-R_0)^3 + \frac{7}{12}\frac{D}{a^4}(R-R_0)^4. \tag{16.37}$$

This potential can be identified with that of a perturbed harmonic oscillator, whose vibrational frequency satisfies

$$\frac{1}{2}M\omega_0^2 = \frac{D}{a^2}. \tag{16.38}$$

With this identification we finally get

$$\mathcal{E}(R) = -D + \frac{1}{2}M\omega_0^2(R-R_0)^2 - \frac{M\omega_0^2}{2a}(R-R_0)^3 + \frac{7M\omega_0^2}{24a^2}(R-R_0)^4. \tag{16.39}$$

A slightly more transparent form of this result is

$$\mathcal{E}(R) = -D + \frac{1}{2}M\omega_0^2(R-R_0)^2\left[1 - \frac{R-R_0}{a} + \frac{7}{12}\left(\frac{R-R_0}{a}\right)^2\right]. \tag{16.40}$$

We see that as long as the quantity $(R-R_0)/a$ remains small, the correction to the harmonic potential stays small.

P16.8 Find the order of magnitude of the wavelength of the radiation emitted during a $K=1 \to K=0$ vibrational transition in a LiH molecule. Assume that the equilibrium distance between the atoms in a diatomic molecule is similar to the distance between the atoms in a crystal of the same substance. *Note:* The LiH lattice is cubic and the crystal has an approximate density of 0.83 g/cm^3. *(Solution:* $\lambda \sim 1{,}8 \times 10^{-3}$ cm*)*

Solution. Consider a simple cubic crystal of LiH, with molecular weight M' equal to 7.947 g/g-mol and density ρ of 0.83 g/cm^3. The mass of a LiH molecule is

$$m = \frac{M'}{N_A} = \frac{7{,}947\,\text{g/g-mol}}{6{,}023 \times 10^{23}\,\text{molecules/g-mol}} = 1{,}319 \times 10^{-23}\,\text{g/molecule}, \tag{16.41}$$

where N_A is Avogadro's number. The number of molecules per unit volume is

$$N = \frac{\rho}{m} = \frac{0{,}83\,\text{g/cm}^3}{1{,}319 \times 10^{-23}\,\text{g/molecule}} = 6{,}293 \times 10^{22}\,\text{molecule/cm}^3, \tag{16.42}$$

and since each LiH molecule contains two atoms, the number of atoms per cm^3 is

$$2N = 1{,}259 \times 10^{23}\,\text{atoms/cm}^3. \tag{16.43}$$

If there are n atoms along the edge of a cube of volume 1 cm^3, from $n^3 = 1{,}259 \times 10^{23}\,\text{atoms/cm}^3$ we obtain that

$$n = 5{,}012 \times 10^7\,\text{atoms/cm}. \tag{16.44}$$

The distance between atoms is

$$R_0 = \frac{1}{n}\,\text{cm} = 1{,}995 \times 10^{-8}\,\text{cm}. \tag{16.45}$$

This estimate is not far from the tabulated value, $R_0 = 1{,}595 \times 10^{-8}$ cm. During a vibrational transition $K=1 \to K=0$ the rotational quantum number may

change, so the radiated frequencies are given by

$$\omega^{\pm} = \frac{E(1,L) - E(0,L\pm 1)}{h} = \omega_0 + \begin{cases} 2BL, \\ -2B(L+1), \end{cases} \quad , \tag{16.46}$$

where

$$B = \frac{h}{2MR_0^2} = \frac{h}{2I}, \tag{16.47}$$

with M the reduced mass of the molecule. In the present case we have

$$M = \frac{M_{Li}M_H}{M_{Li}+M_H} = \frac{1{,}00797 \times 6{,}939}{7{,}947}\,\text{uam} = 1{,}461 \times 10^{-27}\,\text{kg}; \tag{16.48}$$

$$B = \frac{1{,}0546 \times 10^{-34}\,\text{kg}\cdot\text{m}^2/\text{s}}{2(1{,}461 \times 10^{-27}\,\text{kg})(1{,}995 \times 10^{-10}\,\text{m})^2} = 9{,}068 \times 10^{11}\,\text{s}^{-1}. \tag{16.49}$$

Additionally, since

$$E_{\text{vib}} \sim \hbar\omega_0 \sim \sqrt{\frac{m}{M}}\,|E_{\text{elect}}| \sim \sqrt{\frac{m}{M}}\frac{\hbar^2}{ma^2} \sim \sqrt{\frac{m}{M}}\frac{\hbar^2}{mR_0^2}, \tag{16.50}$$

with $D = |E_{\text{elect}}|$, we have that

$$D \sim \frac{\hbar^2}{ma^2}, \tag{16.51}$$

$$\hbar\omega_0 \sim \sqrt{\frac{m}{M}\frac{\hbar^2}{ma^2}}, \tag{16.52}$$

with m the electron mass and a the characteristic intermolecular distance, which we will take as R_0 in a first approximation. With this, we obtain

$$D \sim \frac{(1{,}0546 \times 10^{-34}\,\text{kg}\cdot\text{m}^2/\text{s})^2}{(9{,}1091 \times 10^{-31}\,\text{kg})\,(1{,}995 \times 10^{-10}\,\text{m})^2} \tag{16.53}$$

$$= 3{,}068 \times 10^{-19}\,\text{kg}\cdot\text{m}^2/\text{s}^2 = 1{,}915\,\text{eV}. \tag{16.54}$$

From Eq. (16.46) it follows that the frequency of the emitted radiation is given approximately by

$$\omega^{+} \sim \omega_0 + 2B, \tag{16.55}$$

with ω_0 given by (16.38), so that

$$\omega_0 = \sqrt{\frac{2D}{Ma^2}} \sim 1{,}03 \times 10^{14}\,\text{s}^{-1}. \tag{16.56}$$

The frequency of the emitted radiation is of the order of

$$\omega^{+} \sim 1{,}048 \times 10^{14}\,\text{s}^{-1}, \tag{16.57}$$

and corresponds to an infrared wavelength, of the order of

$$\lambda^{+} = \frac{2\pi c}{\omega^{+}} \sim 1{,}8 \times 10^{-5}\,\text{m}. \tag{16.58}$$

P16.9 Based on the absorption spectrum of HCl vapor in the near infrared shown in [**1**], **Figure 16.8(b)**, prove that the equilibrium distance between the H and Cl atoms of this molecule is of the order of $1{,}3 \times 10^{-8}$ cm.

Solution. The spectral lines of HCl in the near infrared correspond to vibrational transitions, for which the emission and absorption spectra coincide, so it is sufficient to study the emissions. During an emission by a diatomic molecule the vibrational quantum number K decreases by one, but the rotational quantum number L can increase ($L \to L+1$) or decrease ($L \to L-1$) ($\Delta L = 0$ corresponds to a forbidden transition). The radiated frequencies are given by the expression

$$\omega^{\pm} = \frac{E(1,L) - E(0,L \pm 1)}{\hbar} = \omega_0 + \begin{cases} 2BL \\ -2B(L+1) \end{cases},$$

which gives, considering two successive lines,

$$\Delta\left(\frac{1}{\lambda}\right) = \frac{\Delta\omega}{2\pi c} = \frac{B}{\pi c} = \frac{\hbar}{2\pi c M R_0^2} = \frac{\hbar}{2\pi c I}. \tag{16.59}$$

This gives for the moment of inertia of the molecule

$$I = M R_0^2 = \frac{\hbar}{2\pi c \Delta(\lambda^{-1})}. \tag{16.60}$$

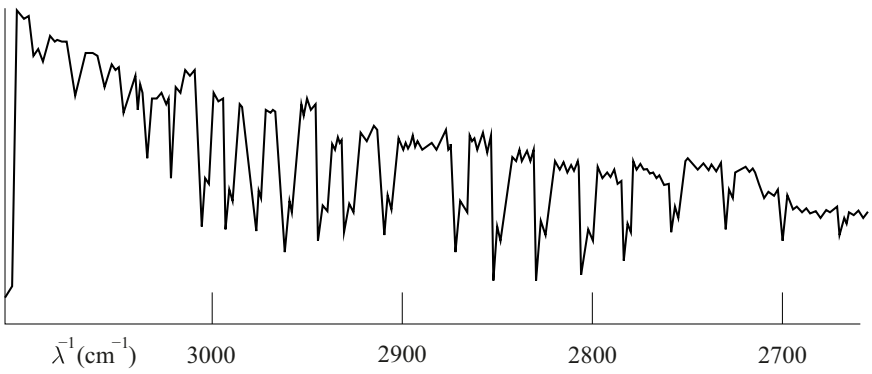

FIGURA 16.2. Absorption of electromagnetic radiation by HCl.

From Fig. 16.2 (which corresponds to part of **Figure 16.8** in [**1**]) it is observed that $\Delta(\lambda^{-1}) \sim 21$ cm^{-1}. With this value introduced in the previous expression, we obtain for the moment of inertia

$$I = \frac{1{,}0546 \times 10^{-34}\ \text{kg}\cdot\text{m}^2/\text{s}}{2\pi(3 \times 10^8\ \text{m/s})(21 \times 10^2\ \text{m}^{-1})} = 2{,}67 \times 10^{-47}\ \text{kg}\cdot\text{m}^2 = 2{,}67 \times 10^{-40}\ \text{g}\cdot\text{cm}^2. \tag{16.61}$$

The reduced mass of the HCl molecule is

$$M = \frac{M_H M_{Cl}}{M_H + M_{Cl}} = \frac{1 \times 35}{1+35} \text{ uam} = \frac{35}{36} \times 1{,}6604 \times 10^{-27} \text{ kg} = 1{,}614 \times 10^{-24} \text{ g}, \tag{16.62}$$

so that

$$R_0^2 = \frac{I}{M} = \frac{2{,}677 \times 10^{-40} \text{ g cm}^2}{1{,}614 \times 10^{-24} \text{ g}} = 1{,}659 \times 10^{-16} \text{ cm}^2, \tag{16.63}$$

from which it follows that the equilibrium distance between the H and Cl atoms of this molecule is

$$R_0 = 1{,}29 \times 10^{-8} \text{ cm}. \tag{16.64}$$

P16.10 Find the dissociation energy of the D_2 molecule, using the fact that the dissociation energy and the minimum vibrational energy of the H_2 molecule are equal to 4.46 eV and 0.26 eV, respectively.

Solution. The total energy of the diatomic molecule within the Morse approximation is

$$E = -D + \hbar\omega_0 \left(K + \tfrac{1}{2}\right) + B\hbar L(L+1). \tag{16.65}$$

The second and third terms, which correspond to the vibrational energy, E_{vib}, and the rotational energy, E_{rot}, respectively, depend on the reduced nuclear mass of the molecule in question. The vibrational term dependence on nuclear mass is given through the frequency

$$\omega_0 = \frac{1}{\sqrt{M}} \left(\frac{\partial^2 \mathcal{E}}{\partial R^2}\bigg|_{R=R_0} \right)^{1/2}. \tag{16.66}$$

Given that the potential $\mathcal{E}(R)$ is solely dependent on the electronic distribution and not on any nuclear parameters, this model yields the same potential for both molecules. This allow us to have

$$\omega_0 \sim \frac{1}{\sqrt{M}}. \tag{16.67}$$

The previous statement also implies that the potential depth $-D$ is the same for both molecules. The energy of the ground state ($K = 0, L = 0$) is given by

$$E_0 = -D + \frac{\hbar\omega_0}{2} = -D + E_{\text{vib0}}. \tag{16.68}$$

The energy required to dissociate the molecule from the ground state, that is, the amount of energy that must be supplied to bring the system from the ground state up to zero (since the potential well has negative depth), is therefore $-E_0 = D_0$. We thus have

$$D = D_0 + E_{\text{vib0}}. \tag{16.69}$$

Using the values provided by the problem for H_2 we obtain

$$D = D_0^{H_2} + E_{vib0}^{H_2} = 4{,}46 \text{ eV} + 0{,}26 \text{ eV} = 4{,}72 \text{ eV}. \tag{16.70}$$

Now, since the vibrational energy is proportional to $1/\sqrt{M}$ and the nuclear mass of D_2 is approximately twice that of H_2,

$$M^{D_2} \approx 2M^{H_2}, \tag{16.71}$$

the vibrational energy of the ground state of D_2 is approximately

$$E_{vib0}^{D_2} \approx \frac{1}{\sqrt{2}} E_{vib0}^{H_2}. \tag{16.72}$$

This allows us to write the equation

$$-D_0^{D_2} = -D + E_{vib0}^{D_2} = -D + \frac{1}{\sqrt{2}} E_{vib0}^{H_2}, \tag{16.73}$$

that is,

$$D_0^{D_2} = D - \frac{1}{\sqrt{2}} E_{vib0}^{H_2} = 4{,}72 \text{ eV} - \frac{1}{\sqrt{2}} (0{,}26 \text{ eV}) = 4{,}53 \text{ eV}. \tag{16.74}$$

This is the minimum energy required to dissociate D_2, since the energy of the ground state is the lowest energy the molecule can possess.

P16.11 Prove that the molecule He_2^{3+} does not exist.
Solution. We will consider the He_3^+ molecule formed by three helium atoms (each with configuration $1s^2$) and a total charge of $+1$. The total number of electrons is

$$3 \times 2 - 1 = 5 \text{ electrons}. \tag{16.75}$$

Assuming an equilateral triangular geometry (D_{3h} symmetry), the molecular orbitals (MOs) are constructed as linear combinations of the $1s$ orbitals of each He. The resulting MOs are: Totally symmetric bonding orbital (σ_g),

$$\psi_1 = \frac{1}{\sqrt{3}}(\phi_A + \phi_B + \phi_C), \quad \text{energy } E_1, \tag{16.76}$$

and degenerate antibonding orbitals (e'),

$$\psi_2 = \frac{1}{\sqrt{6}}(2\phi_A - \phi_B - \phi_C), \tag{16.77}$$

$$\psi_3 = \frac{1}{\sqrt{2}}(\phi_B - \phi_C), \quad \text{energy } E_2. \tag{16.78}$$

The occupation of MOs with 5 electrons is

$$\sigma_g^2 (e')^3. \tag{16.79}$$

The total electronic energy is therefore

$$E_{elec} = 2E_1 + 3E_2, \tag{16.80}$$

and the effective bond order,

$$\mathrm{BO} = \frac{2-3}{3} = -\frac{1}{3}. \tag{16.81}$$

A negative bond order indicates thermodynamic instability. The repulsion energy between the three He nuclei ($Z = 2$) is

$$V_{\mathrm{rep}} = \sum_{i<j} \frac{4e^2}{R_{ij}} \approx \frac{12e^2}{R} \quad (\text{for } R_{ij} \approx R). \tag{16.82}$$

For a typical interatomic distance $R \approx 1{,}0\text{Å} = 1{,}89\,\text{au}$,

$$V_{\mathrm{rep}} \approx \frac{12}{1{,}89}\,\text{hartree} \approx 6{,}35\,\text{hartree} \approx 173\,\text{eV}. \tag{16.83}$$

The energy of He_3^+ must include electronic energy (E_{elec}), dominated by antibonding MO occupation, and nuclear repulsion (V_{rep}), extremely high due to $+6e$ charge. The dissociation energy is given by

$$\mathrm{He}_3^+ \to \mathrm{He}_2^+ + \mathrm{He}, \quad \Delta E = E(\mathrm{He}_2^+) + E(\mathrm{He}) - E(\mathrm{He}_3^+). \tag{16.84}$$

Given that He_2^+ has bond order 0,5 ($\sigma_g^2\sigma_u^1$) and is stable ($D_e \approx 2{,}5\,\text{eV}$) and $E(\mathrm{He}_3^+) > E(\mathrm{He}_2^+) + E(\mathrm{He})$, the process is exothermic ($\Delta E < 0$). Due to all the above reasons, the existence of the He_3^+ molecule is not possible.

P16.12 An empirical formula for the potential of the NaCl molecule is

$$V(R) = -\frac{e^2}{4\pi\epsilon_0 R} + Ae^{-R/a}, \tag{16.85}$$

where R is the internuclear distance. The equilibrium internuclear distance is 2,5Å and the dissociation energy is 3.6 eV. Find the value of A and a/R_0, and explain the physical meaning of the parameters A and a.

Solution. At the equilibrium distance R_0, the potential $V(R)$ acquires its minimum value,

$$\left.\frac{dV}{dR}\right|_{R=R_0} = 0 \quad \Rightarrow \quad \frac{e^2}{4\pi\epsilon_0 R_0^2} - \frac{A}{a}e^{-R_0/a} = 0. \tag{16.86}$$

With the dissociation energy D_e defined as $D_e = -V(R_0)$, and $V(\infty) = 0$, we have

$$D_e = -V(R_0) = \frac{e^2}{4\pi\epsilon_0 R_0} - Ae^{-R_0/a}. \tag{16.87}$$

Introducing (16.86) in this expression we get

$$D_e = \frac{e^2}{4\pi\epsilon_0 R_0} - \frac{e^2 a}{4\pi\epsilon_0 R_0^2} = \frac{e^2}{4\pi\epsilon_0 R_0}\left(1 - \frac{a}{R_0}\right). \tag{16.88}$$

Using $R_0 = 2{,}5$Å and $D_e = 3{,}6\,\text{eV}$ gives

$$\frac{e^2}{4\pi\epsilon_0 R_0} = \frac{14{,}4}{2{,}5} = 5{,}76\,\text{eV}, \tag{16.89}$$

$$3{,}6 = 5{,}76\left(1 - \frac{a}{R_0}\right). \tag{16.90}$$

Solving for a/R_0 we get

$$\frac{a}{R_0} = 1 - 0{,}625 = 0{,}375. \tag{16.91}$$

We now use Eq. (16.86) to calculate

$$A = \frac{e^2 a}{4\pi\epsilon_0 R_0^2} e^{R_0/a}. \tag{16.92}$$

With $a = R_0 \cdot \frac{a}{R_0} = 2{,}5 \times 0{,}375 = 0{,}9375\,\text{Å}$, and $R_0/a = 1/0{,}375 = 8/3 \approx 2{,}6667$, the factor $e^2 a/4\pi\epsilon_0 R_0^2$ has the value

$$\frac{e^2 a}{4\pi\epsilon_0 R_0^2} = \frac{14{,}4 \times 0{,}9375}{(2{,}5)^2} = \frac{13{,}5}{6{,}25} = 2{,}16\,\text{eV} \tag{16.93}$$

With the exponential factor given by $e^{R_0/a} = e^{8/3} \approx e^{2{,}6667} \approx 14{,}384$, we obtain finally,

$$A = 2{,}16 \times 14{,}384 \approx 31{,}07\,\text{eV} \tag{16.94}$$

The factor A of the exponential is related to the strength of the repulsion between the ions at very short distances due to electron cloud overlap. In turn, the length parameter a determines the decay rate of the exponential repulsion..

P16.13 Compare the rotational and vibrational levels of an HCl molecule calculated with the potential

$$V(r) = 4\alpha\left[\left(\frac{d}{r}\right)^{12} - \left(\frac{d}{r}\right)^{6}\right], \qquad \alpha = 3{,}1 \times 10^{-12}\,\text{eV}, \quad d = 3{,}3\,\text{Å}. \tag{16.95}$$

Hint: Since the equilibrium position r_0 depends weakly on angular momentum, the effective potential can be expanded around r_0.

Solution. It is convenient to introduce $b = \hbar^2/md^2$ and express the potential in terms of b and $x_0 = r_0/d$. The potential can be expanded around the equilibrium position r_0, defined by the condition $V'(r_0) = 0$. The Taylor expansion of the potential around r_0 up to second order is

$$V(r) \approx V(r_0) + \frac{1}{2}V''(r_0)(r - r_0)^2. \tag{16.96}$$

The linear term vanishes because $V'(r_0) = 0$, and the potential takes the harmonic approximation

$$V(r) = V(r_0) + \frac{1}{2}M\omega_0^2(r - r_0)^2, \tag{16.97}$$

where the frequency ω_0 is defined by

$$M\omega_0^2 = V''(r_0), \tag{16.98}$$

and M is the reduced nuclear mass of the system. This expression is general and identical to that appearing in [**1**], **Section 16.5**. The procedure for obtaining the energy spectrum is the same, so we proceed to write directly

$$E = V(r_0) + \hbar\omega_0\left(K + \tfrac{1}{2}\right) + B\hbar L(L+1), \;\; K = 0, 1, 2, \ldots \tag{16.99}$$

where K is the vibrational quantum number, L is the rotational quantum number, and the rotational constant B is given by

$$B = \frac{\hbar}{2Mr_0^2}. \tag{16.100}$$

Now we consider the specific potential of the problem. The equilibrium distance r_0 is found by solving $V'(r) = 0$, we take the derivative of the potential

$$\frac{dV}{dr} = 4\alpha\left[-12\,\frac{d^{12}}{r^{13}} + 6\,\frac{d^6}{r^7}\right]. \tag{16.101}$$

From $V'(r_0) = 0$ we get

$$r_0 = 2^{1/6}d, \tag{16.102}$$

and

$$V(r_0) = 4\alpha\left[\frac{1}{4} - \frac{1}{2}\right] = -\alpha. \tag{16.103}$$

From the second derivative,

$$V''(r) = 4\alpha\left(156\frac{d^{12}}{r^{14}} - 42\frac{d^6}{r^8}\right), \tag{16.104}$$

we have

$$V''(r_0) = \frac{4\alpha}{r_0^2}\left(156\frac{1}{4} - 42\frac{1}{2}\right) = \frac{72\alpha}{2^{1/3}d^2}. \tag{16.105}$$

The vibrational frequency is therefore given by

$$\omega_0 = \sqrt{\frac{V''(r_0)}{M}} = \sqrt{\frac{72\alpha}{M2^{1/3}d^2}} = \frac{2^{1/3}6}{d}\sqrt{\frac{\alpha}{M}}, \tag{16.106}$$

and the rotational constant is

$$B = \frac{\hbar}{2Mr_0^2} = \frac{\hbar}{2Md^2\,2^{1/3}}. \tag{16.107}$$

This gives for the complete energy spectrum

$$E = -\alpha + \hbar\frac{2^{1/3}6}{d}\sqrt{\frac{\alpha}{M}}\left(K + \tfrac{1}{2}\right) + \frac{\hbar^2}{2Md^2\,2^{1/3}}L(L+1) \tag{16.108}$$

or, in terms of the parameters $b = \hbar^2/Md^2$ and $x_0 = r_0/d = 2^{1/6}$,

$$E = -\alpha + 6x_0^2\sqrt{\alpha\, b}\,\left(K + \tfrac{1}{2}\right) + \frac{b}{2x_0^2}\,L(L+1). \tag{16.109}$$

The requested comparison reduces to confronting the vibrational scale $\hbar\omega_0 = 6x_0^2\sqrt{\alpha b}$ and the rotational constant $B = \frac{b}{2x_0^2}$. With $b \approx 3{,}917 \times 10^{-4}$ eV we can compute numerically

$$\hbar\omega_0 \approx 2{,}63 \times 10^{-7}\ \text{eV} \quad \left(\approx 2{,}1 \times 10^{-3}\ \text{cm}^{-1}\right), \tag{16.110}$$

$$B \approx 1{,}55 \times 10^{-4}\ \text{eV} \quad \left(\approx 1{,}25\ \text{cm}^{-1}\right), \tag{16.111}$$

so that the ratio of the two characteristic energies is

$$\frac{\hbar\omega_0}{B_e} \approx 1{,}7 \times 10^{-3} \ll 1. \tag{16.112}$$

The potential well is extraordinarily soft physically, given the specified Lenard–Jones parameters. The vibrational level spacing is thousands of times smaller than the rotational spacing, which is the opposite of that observed for a typical covalent molecule (where usually $\hbar\omega_0 \gg B_e$). Furthermore, the depth of the well is

$$D = \alpha = 3{,}1 \times 10^{-12}\ \text{eV}.$$

This is many orders of magnitude smaller than the zero–point energy $\frac{1}{2}\hbar\omega_0 \approx 1{,}31 \times 10^{-7}$ eV,

$$D = \alpha \ll \tfrac{1}{2}\hbar\omega_0, \tag{16.113}$$

For these parameters, the ground vibrational level would lie above the dissociation threshold, so no bound state would exist. In conclusion, the provided Lennard-Jones parameters describe a very weak (van der Waals–type) interaction rather than an intramolecular covalent bond.

P16.14 The vibrational frequency of the CO molecule in its lowest state is $\nu_0 = 2\times 10^{13}$ Hz. What is the wavelength of the radiation emitted by the lowest vibrational excitation? What is the probability that the first vibrational state is excited? Compare your result with the probability that the CO molecule is in its vibrational ground state when the temperature is 300 K.

Solution. The lowest vibrational transition is $K = 1 \to K = 0$. The photon energy equals the energy difference between these levels. For a quantum harmonic oscillator:

$$E_K = h\nu_0\left(K + \frac{1}{2}\right), \tag{16.114}$$

The energy difference is:

$$\Delta E = E_1 - E_0 = h\nu_0\left(1 + \frac{1}{2}\right) - h\nu_0\left(0 + \frac{1}{2}\right) = h\nu_0. \tag{16.115}$$

Relating photon energy to wavelength λ,

$$\Delta E = \frac{hc}{\lambda} \implies \lambda = \frac{c}{\nu_0}, \tag{16.116}$$

we get

$$\lambda = \frac{3 \times 10^8}{2 \times 10^{13}}\,\mathrm{m} = 1{,}5 \times 10^{-5}\ \mathrm{m} = 15\ \mu\mathrm{m}. \tag{16.117}$$

The vibrational level occupation follows a Boltzmann distribution,

$$P_K = (1 - e^{-\beta})e^{-K\beta}, \quad \text{where} \quad \beta = \frac{h\nu_0}{k_B T}, \tag{16.118}$$

with $k_B = 1{,}381 \times 10^{-23}$ J/K. With

$$h\nu_0 = (6{,}626 \times 10^{-34}) \times (2 \times 10^{13}) = 1{,}3252 \times 10^{-20}\ \mathrm{J}, \tag{16.119}$$

$$k_B T = (1{,}381 \times 10^{-23}) \times 300 = 4{,}143 \times 10^{-21}\ \mathrm{J}, \tag{16.120}$$

$$\beta = \frac{1{,}3252 \times 10^{-20}}{4{,}143 \times 10^{-21}} = 3{,}199, \tag{16.121}$$

For $K = 1$,

$$P_1 = (1 - e^{-\beta})e^{-\beta}, \tag{16.122}$$

and for $K = 0$,

$$P_0 = (1 - e^{-\beta})e^{0} = 1 - e^{-\beta}. \tag{16.123}$$

Therefore,

$$\frac{P_1}{P_0} = e^{-h\nu_0/kT}. \tag{16.124}$$

With

$$\frac{h\nu_0}{kT} = \frac{(6{,}626 \times 10^{-34}\ \mathrm{J \cdot s})(2 \times 10^{13}\ \mathrm{Hz})}{(1{,}38 \times 10^{-23}\ \mathrm{J \cdot K^{-1}})(300\ \mathrm{K})} \approx 3{,}2,$$

we finally obtain

$$P_1 \approx \left(1 - e^{-3{,}2}\right) e^{-3{,}2} \approx 0{,}039, \quad \frac{P_1}{P_0} \approx e^{-3{,}2} \approx 0{,}041.$$

The ground state probability is approximately 24.4 times higher than the probability of the first excited state, indicating that the vibrational quantum energy $h\nu_0$ exceeds the thermal energy $k_B T$. At room temperature, most molecules remain in the ground state.

Capítulo 17

Time-Dependent Perturbations. Field Quantization and Second Quantization

P17.1 Show that an adiabatic perturbation produces periodic transitions in a system that has two degenerate states.

Solution. We denote with $\psi_A^{(0)}$ and $\psi_B^{(0)}$ the degenerate wave functions of the unperturbed system and we assume that at $t = 0$, the moment when the adiabatic perturbation with Hamiltonian $\hat{H}'(t)$ is applied, the system is in state A. We aim to calculate the probability that the system makes a transition to state B as a result of the perturbation. If the perturbation is small, all matrix elements $\hat{H}'_{mn}$, with $m \neq n$, are small compared to $E_n^{(0)} - E_m^{(0)}$, except for the matrix elements $\hat{H}'_{AB}$ and $\hat{H}'_{BA}$ for which $E_A^{(0)} - E_B^{(0)} = 0$. This allows us to approximate all coefficients $c_m(t)$ of time-dependent perturbation theory by zero, except $c_A(t)$ and $c_B(t)$, which are given by the usual expressions,

$$\frac{dc_A(t)}{dt} = \frac{1}{i\hbar}\left[c_A(t)\left\langle A \mid \hat{H}' \mid A\right\rangle + c_B(t)\left\langle A \mid \hat{H}' \mid B\right\rangle\right], \tag{17.1}$$

$$\frac{dc_B(t)}{dt} = \frac{1}{i\hbar}\left[c_A(t)\left\langle B \mid \hat{H}' \mid A\right\rangle + c_B(t)\left\langle B \mid \hat{H}' \mid B\right\rangle\right]. \tag{17.2}$$

To simplify the algebra without altering the essence of the problem, we will assume that

$$\left\langle A \mid \hat{H}' \mid A\right\rangle = \left\langle B \mid \hat{H}' \mid B\right\rangle \equiv H'_{AA}, \quad \left\langle A \mid \hat{H}' \mid B\right\rangle = \left\langle B \mid \hat{H}' \mid A\right\rangle \equiv H'_{AB}. \tag{17.3}$$

With this simplification the evolution equations take the form

$$\frac{dc_A(t)}{dt} = \frac{1}{i\hbar}\left[H'_{AA}c_A(t) + H'_{AB}c_B(t)\right], \tag{17.4}$$

$$\frac{dc_B(t)}{dt} = \frac{1}{i\hbar}\left[H'_{AB}c_A(t) + H'_{AA}c_B(t)\right]. \tag{17.5}$$

Adding and subtracting these expressions we obtain

$$\frac{d}{dt}[c_A(t) + c_B(t)] = -\frac{i}{\hbar}(c_A(t) + c_B(t))(H'_{AA} + H'_{AB}), \tag{17.6}$$

$$\frac{d}{dt}(c_A - c_B) = -\frac{i}{\hbar}(c_A(t) - c_B(t))(H'_{AA} - H'_{AB}). \tag{17.7}$$

To integrate these equations we take into account that the perturbation is adiabatic, which means that the matrix elements H'_{AA} and H'_{AB} vary very slowly with time and can be taken as constants in first approximation. This gives

$$c_A(t) + c_B(t) = a \exp\left[-\frac{i}{\hbar}(H'_{AA} + H'_{AB})t\right], \tag{17.8}$$

$$c_A(t) - c_B(t) = b \exp\left[-\frac{i}{\hbar}(H'_{AA} - H'_{AB})t\right]. \tag{17.9}$$

Adding and subtracting again we obtain

$$c_A(t) = \frac{1}{2}\left\{a \exp\left[-\frac{i}{\hbar}(H'_{AA} + H'_{AB})t\right] + b \exp\left[-\frac{i}{\hbar}(H'_{AA} - H'_{AB})t\right]\right\}, \tag{17.10}$$

$$c_B(t) = \frac{1}{2}\left\{a \exp\left[-\frac{i}{\hbar}(H'_{AA} + H'_{AB})t\right] - b \exp\left[-\frac{i}{\hbar}(H'_{AA} - H'_{AB})t\right]\right\}. \tag{17.11}$$

From the initial conditions $c_A(0) = 1$ and $c_B(0) = 0$ it follows that $a = b = 1$, which finally gives

$$c_A(t) = \cos\left(\frac{H'_{AB}}{\hbar}t\right) e^{-\frac{i}{\hbar}H'_{AA}t} \tag{17.12}$$

and

$$c_B(t) = -i \sin\left(\frac{H'_{AB}}{\hbar}t\right) e^{-\frac{i}{\hbar}H'_{AA}t}. \tag{17.13}$$

The probabilities that the system is in state A or in state B at time t are

$$w_{AA} \equiv w_A = |c_A(t)|^2 = \cos^2\frac{H'_{AB}}{\hbar}t, \tag{17.14}$$

$$w_{AB} \equiv w_B = 1 - w_A = |c_B(t)|^2 = \sin^2\frac{H'_{AB}}{\hbar}t, \tag{17.15}$$

respectively. We see that both probabilities vary periodically between the values 0 and 1 over time, that is, periodic transitions occur between the two degenerate states. The frequency of these transitions, $\omega_{AB} = H'_{AB}/\hbar$, is determined by the coupling between the two degenerate states produced by the perturbation. For very weak perturbations and small times compared to ω_{AB}^{-1}, we can write

$$w_A = 1, \quad w_B = \left(\frac{H'_{AB}}{\hbar}\right)^2 t^2, \tag{17.16}$$

which shows that the system practically does not respond at the beginning of the perturbation, since $w_B \ll 1$. However, if the perturbation persists, there will come a time when $\omega_{AB}t \sim 1$ and the probability w_B reaches a value comparable to unity. In other words, no matter how weak an adiabatic perturbation is, if it lasts long enough it will populate all the degenerate (or nearly degenerate) states that it connects.

P17.2 Show that if the potential $V(t) = \hat{A}\delta(t)$ is applied to a system in its ground state, the probability of a transition to any excited state is

$$w = \frac{1}{\hbar^2}\left(\langle 0|A^2|0\rangle - \langle 0|A|0\rangle^2\right). \tag{17.17}$$

Solution. The probability that a transition occurs from state n to state k during the time that a perturbation V lasts is given, to first order in time–dependent perturbation theory by

$$w_{nk} = \left|C_{nk}^{(1)}(\infty)\right|^2 = \frac{1}{\hbar^2}\left|\int_0^\infty e^{i\omega_{kn}t}V_{kn}(t)\,dt\right|^2, \tag{17.18}$$

where, as usual, we have written

$$\omega_{kn} = \frac{E_k - E_n}{\hbar}, \tag{17.19}$$

$$V_{kn}(t) = \langle k|V(t)|n\rangle. \tag{17.20}$$

Since in the present case the perturbation applied to the system is given by $V(t) = \hat{A}\,\delta(t)$, we have

$$V_{kn}(t) = \delta(t)\,\langle k|\hat{A}|n\rangle. \tag{17.21}$$

To avoid indeterminacies in the value of the integral, it will be assumed that the perturbation is applied at a positive time ε, but infinitely small. From expression (17.18), it then follows that the probability of a transition from the ground state to some excited state k is

$$w_{0k} = \frac{1}{\hbar^2}\left|\int_0^\infty e^{i\omega_{k0}(t-\varepsilon)}\delta(t-\varepsilon)\langle k|\hat{A}|0\rangle\,dt\right|^2 \simeq \frac{1}{\hbar^2}\left|\langle k|\hat{A}|0\rangle\right|^2 = \frac{1}{\hbar^2}\langle 0|\hat{A}|k\rangle\langle k|\hat{A}|0\rangle. \tag{17.22}$$

The probability that the transition is to any excited state k is the sum of all the previous probabilities for $k \neq 0$, that is,

$$w = \frac{1}{\hbar^2}\sum_{k\neq 0}\langle 0|\hat{A}|k\rangle\langle k|\hat{A}|0\rangle, \tag{17.23}$$

which gives, using the completeness relation, the required result,

$$w = \frac{1}{\hbar^2}\left(\langle 0|\hat{A}^2|0\rangle - \langle 0|\hat{A}|0\rangle^2\right). \tag{17.24}$$

This shows that an abrupt perturbation on a system in its ground state can induce transitions to all available excited states.

P17.3 A harmonic oscillator in its ground state is perturbed by the sudden application of a uniform electric field of intensity $\mathcal{E}$ (not necessarily small), which

remains constant from that moment on. Show that the probability of transition to the excited state n is given by the Poisson distribution

$$W_{0n} = \frac{\xi_0^{2n}}{2^n n!} e^{-\xi_0^2/2},$$

where $\xi_0 = x_0/\sqrt{\hbar/m\omega}$ and $x_0 = e\mathcal{E}/m\omega^2$. Find the mean value of n.

Solution. Since the possibility that $\mathcal{E}$ is not small must be considered, a non-perturbative method is required to solve this problem. We define $t = 0$ as the moment when the field is connected; for $t \leq 0$, the wave function is (with $\alpha_0 = \sqrt{\hbar/m\omega}$)

$$\psi = \psi_0(x) e^{-iE_0 t/\hbar}, \quad \psi_0(x) = \left(\frac{1}{\sqrt{\pi}\alpha_0}\right)^{1/2} e^{-x^2/2\alpha_0^2}, \quad E_0 = \tfrac{1}{2}\hbar\omega. \tag{17.25}$$

This wave function remains effective for $t = +0$ because the oscillator cannot change its state instantaneously. However, for $t > 0$, the Hamiltonian changes due to the additional term $-e\mathcal{E}x$, shifting the equilibrium position of the oscillator from the origin to $x_0 = e\mathcal{E}/m\omega^2$. Consequently, the new eigenfunctions are $\psi_n(x - x_0)$, which form a suitable basis for describing the oscillator's state after the perturbation is applied. Specifically, for $t = +0$, we can write

$$\psi_0(x) = \sum_{n=0}^{\infty} c_n \psi_n(x - x_0). \tag{17.26}$$

For $t > 0$, the wave function becomes

$$\Psi(x,t) = \sum_{n=0}^{\infty} c_n \psi_n(x - x_0) e^{-iE_n t/\hbar}, \quad E_n = \hbar\omega\left(n + \tfrac{1}{2}\right) - \frac{e^2\mathcal{E}^2}{2m\omega^2}. \tag{17.27}$$

The probability of finding the oscillator in state n at time $t > 0$ is

$$w_n = |c_n|^2, \tag{17.28}$$

so we only need to determine the expansion coefficients c_n. Using $\xi = x/\alpha_0$ and $\xi_0 = x_0/\alpha_0$, we have

$$c_n = \int_{-\infty}^{\infty} \psi_0(x)\psi_n^*(x - x_0)\, dx = \frac{1}{\sqrt{\pi 2^n n!}} \int_{-\infty}^{\infty} \exp\left(\tfrac{1}{2}\left[-\xi^2 - (\xi - \xi_0)^2\right]\right) H_n(\xi - \xi_0)\, d\xi. \tag{17.29}$$

From the previous result, with a change of variables, we obtain

$$\sqrt{\pi 2^n n!}\, c_n = \int_{-\infty}^{\infty} \exp\left[-\tfrac{1}{2}\left((y + \xi_0)^2 + y^2\right)\right] H_n(y)\, dy. \tag{17.30}$$

This integral was evaluated (up to a minor sign change) before using the generating function of Hermite polynomials. The result is

$$c_n = \frac{e^{-\xi_0^2/4}}{\sqrt{2^n n!}} (-\xi_0)^n. \tag{17.31}$$

Therefore, the probability of finding the oscillator in state n at time t is

$$w_n = \frac{e^{-\xi_0^2/2}}{2^n n!}\,\xi_0^{2n}. \tag{17.32}$$

This probability follows a Poisson distribution, whose general form is

$$w(n) = \frac{e^{-\lambda}\lambda^n}{n!}. \tag{17.33}$$

By comparison, we identify the mean value of n as

$$\langle n\rangle = \tfrac{1}{2}\xi_0^2 = \frac{e^2\mathcal{E}^2}{2m\hbar\omega^3}. \tag{17.34}$$

For $\bar{n} \gg 1$, the oscillators can be treated in a semiclassical regime where their average energy is given by $\frac{1}{2}m\omega^2 a^2$, with a being the oscillation amplitude. Equating this with the quantum result yields

$$a = \frac{e\mathcal{E}}{m\omega^2} = |x_0|, \tag{17.35}$$

where x_0 is the equilibrium displacement. This shows that the average oscillation amplitude equals the magnitude of the equilibrium shift x_0, which is identical to the behavior of a classical oscillator initially at rest. For very weak perturbations ($\bar{n} \ll 1$), the probability distribution w_n simplifies to

$$w_n \simeq \frac{\xi_0^{2n}}{2^n n!} = \frac{(\bar{n})^n}{n!}, \tag{17.36}$$

which exhibits rapid decay with increasing n.

P17.4 A physical system having only the states $|1\rangle$ and $|2\rangle$, degenerate and orthogonal, is perturbed by the action of a potential V that is applied in the interval $(0, T)$. Assuming (for simplicity) that the matrix elements of V are $V_{11} = V_{22} = 0$, $V_{12} = V_{21} = V_0$, determine the exact probability of the transition from $|1\rangle$ to $|2\rangle$, if the system is initially in the state $|1\rangle$. Then use perturbation theory to determine the effect of the perturbation to first order and compare the results. When is the perturbative solution valid?

Solution. We write the Hamiltonian in the form $H = \hat{H}_0 + V$, with V the perturbation. We are interested in the solutions of the Schrödinger equation

$$\hat{H}\psi = (\hat{H}_0 + V)\psi = i\hbar\frac{\partial\psi}{\partial t}. \tag{17.37}$$

Since by hypothesis the system has only two eigenstates of $\hat{H}_0$, which we will call $|1\rangle$ and $|2\rangle$, with common eigenvalue E, we can express $|\psi\rangle$ as the superposition

$$|\psi(x,t)\rangle = a_1(t)|1\rangle + a_2(t)|2\rangle, \tag{17.38}$$

where the expansion coefficients are functions of time. It is convenient to factorize in the form

$$a_i(t) = c_i(t)e^{-iEt/\hbar}, \tag{17.39}$$

$$\psi(x,t) = [c_1(t)|1\rangle + c_2(t)|2\rangle]e^{-iEt/\hbar}, \tag{17.40}$$

since, in the absence of perturbations, both coefficients c_i would be constant, which means that in the presence of moderate perturbations they will vary slowly with time. Substituting into (17.37) we obtain, taking into account that $\hat{H}_0\psi = E\psi$,

$$\hat{H}\psi = E(c_1(t)|1\rangle + c_2(t)|2\rangle)e^{-iEt/\hbar} + V(c_1(t)|1\rangle + c_2(t)|2\rangle)e^{-iEt/\hbar} \tag{17.41}$$

$$= i\hbar\left[\frac{dc_1}{dt}|1\rangle + \frac{dc_2}{dt}|2\rangle\right]e^{-iEt/\hbar} + E(c_1(t)|1\rangle + c_2(t)|2\rangle)e^{-iEt/\hbar}, \tag{17.42}$$

or, simplifying,

$$i\hbar\left[\frac{dc_1}{dt}|1\rangle + \frac{dc_2}{dt}|2\rangle\right] = V(c_1(t)|1\rangle + c_2(t)|2\rangle). \tag{17.43}$$

Taking matrix elements of this expression with $\langle 1|$ and $\langle 2|$ successively, we obtain

$$i\hbar\frac{dc_1}{dt} = c_1(t)\langle 1|V|1\rangle + c_2(t)\langle 1|V|2\rangle, \tag{17.44}$$

$$i\hbar\frac{dc_2}{dt} = c_1(t)\langle 2|V|1\rangle + c_2(t)\langle 2|V|2\rangle. \tag{17.45}$$

By hypothesis $\langle 1 \mid V \mid 1\rangle = \langle 2 \mid V \mid 2\rangle = 0$ and $\langle 1 \mid V \mid 2\rangle = \langle 2 \mid V \mid 1\rangle = V_0$, so the previous expressions reduce to the system of coupled equations

$$i\hbar\frac{dc_1}{dt} = c_2(t)V_0, \quad i\hbar\frac{dc_2}{dt} = c_1(t)V_0. \tag{17.46}$$

Adding and subtracting these expressions and integrating, we obtain

$$c_1 + c_2 = Ae^{-iV_0t/\hbar}, \quad c_1 - c_2 = Be^{iV_0t/\hbar}. \tag{17.47}$$

When integrating, it was assumed that V_0 is constant; if it were a function of time, the substitution $V_0t \to \int^t V_0(s)ds$ would have to be made. From this it follows that

$$c_1(t) = \tfrac{1}{2}Ae^{-iV_0t/\hbar} + \tfrac{1}{2}Be^{iV_0t/\hbar}, \tag{17.48}$$

$$c_2(t) = \tfrac{1}{2}Ae^{-iV_0t/\hbar} - \tfrac{1}{2}Be^{iV_0t/\hbar}. \tag{17.49}$$

Introducing the initial conditions $c_1(0) = 1$ and $c_2(0) = 0$, we obtain $A = B = 1$, which gives

$$c_1(t) = \cos\frac{V_0t}{\hbar}, \tag{17.50}$$

$$c_2(t) = -i\sin\frac{V_0t}{\hbar}. \tag{17.51}$$

The solution of the Schrödinger equation is thus

$$\psi(x,t) = \left(\cos\frac{V_0t}{\hbar}|1\rangle - i\sin\frac{V_0t}{\hbar}|2\rangle\right)e^{-iEt/\hbar}. \tag{17.52}$$

The probability of transition from state $|1\rangle$ to $|2\rangle$ is

$$w_{12}(t) = \sin^2\frac{V_0t}{\hbar}, \tag{17.53}$$

while the probability that the system remains in the initial state is

$$w_{11}(t) = \cos^2 \frac{V_0 t}{\hbar}. \tag{17.54}$$

Let us now apply time-dependent perturbation theory to first order. We start from the system of equations, which in the present case is written in the form

$$i\hbar \frac{d}{dt} c_n(t) = \sum_{k=1}^{2} c_k(t) V_{nk}. \tag{17.55}$$

Since at $t = 0$ the system is in state $|1\rangle$, we have $c_n^{(1)}(0) = \delta_{n1}$; if the perturbation is small or the times are sufficiently short so that all coefficients c_m are small, except c_1, the previous system reduces to first order to

$$i\hbar \frac{d}{dt} c_1^{(1)}(t) = V_{11} c_1^{(1)}, \tag{17.56}$$

$$i\hbar \frac{d}{dt} c_2^{(1)}(t) = V_{21} c_1^{(1)}. \tag{17.57}$$

Integrating,

$$c_1^{(1)}(t) = \exp\left[-\frac{i}{\hbar}\int_0^t V_{11}(s)ds\right] \approx 1 - \frac{i}{\hbar}\int_0^t V_{11}(s)ds, \tag{17.58}$$

$$c_2^{(1)}(t) = -\frac{i}{\hbar}\int^t V_{21}(s)ds = -\frac{i}{\hbar} V_0 t \text{ for } V_{21} = V_0 = \text{const.} \tag{17.59}$$

If here we set $V_{11} = 0$, we get $w_{11}^{(1)} = \left|c_1^{(1)}(t)\right|^2 = 1$ for all t, and it becomes necessary to resort to a higher-order calculation. However, the previous results are correct to first order, and correspond to the first terms of the series expansion of the exact solutions, Eqs. (17.50) and (17.51). It is clear that the perturbative result can be applied only to small times, such that $\left|\int^t V_{21}(s)ds\right| \ll \hbar$.

P17.5 Calculate in detail the Einstein coefficient B for resonant absorption processes and show that the Einstein relation $B_{nk} = B_{kn}$ is satisfied.

Solution. The problem can be solved by following exactly the same steps used in [1], **Section 17.2** to determine the Einstein coefficient B for induced emissions. Since the only change is the sign of ω in

$$\hat{\mathcal{H}}^+ = -\frac{e}{mc}\boldsymbol{A}_+(\boldsymbol{r}, t)\cdot\hat{\boldsymbol{p}} = \hat{V}^+ e^{i\omega t}, \tag{17.60}$$

when taking A_- instead of A_+, while at the same time interchanging the initial and final atomic states. The formula $dW_{nk} = \frac{\pi e^2 \rho(\omega)}{m^2\hbar^2\omega^2}\left|\langle n|\hat{\epsilon}\cdot\hat{\boldsymbol{p}}|k\rangle\right|^2 d\Omega_p$ $(\omega = |\omega_{nk}|)$, which determines the transition probability and hence the corresponding Einstein coefficient, is insensitive to these changes, therefore $B_{nm} = B_{mn}$.

For a more formal analysis, one proceeds as follows. The probability per unit time of a dipole atomic transition from state n to state m, in any direction and with any polarization of the emitted radiation , is given by

$$W_{nm} = \frac{4\pi^2 e^2}{3\hbar^2}\,\rho(\omega)\,\left|\langle n|r|m\rangle\right|^2, \tag{17.61}$$

where $\rho(\omega)$ represents the spectral density of the field in which the atom is immersed. For induced transitions,

$$W_{nm} = B_{nm}\,\rho(\omega_{nm}), \tag{17.62}$$

from which it follows that

$$B_{nm} = \frac{4\pi^2 e^2}{3\hbar^2}\,\left|\langle n|r|m\rangle\right|^2 \tag{17.63}$$

and

$$B_{mn} = \frac{4\pi^2 e^2}{3\hbar^2}\,\left|\langle m|r|n\rangle\right|^2. \tag{17.64}$$

Since $\left|\langle n|r|m\rangle\right|^2 = \left|\langle m|r|n\rangle\right|^2$, we conclude that

$$B_{nk} = B_{kn}. \tag{17.65}$$

To increase the didactic value of the present example, we will solve the problem in detail, starting from elementary considerations and avoiding the mechanical use of textbook formulas as much as possible.

Let us consider an atom with Z electrons and two stationary states Ψ_m^0 and Ψ_n^0 in the absence of the perturbation, such that $E_m > E_n$. We suppose that at $t = 0$ the atom is in the lower–energy state n. From $t = 0$ onward, the system is subjected to the perturbative influence of electromagnetic radiation which contains a narrow range of frequencies in the vicinity of $\omega_{mn} = (E_m - E_n)/\hbar$. We are interested in calculating the transition probability to state m as a result of this perturbation. Let us first consider the component in the x- direction of the electric field of the incident radiation. Later, we will take into account the rest of the field. The interaction Hamiltonian due to this perturbation can be written in the dipole approximation (that is, long wavelength, neglecting the spatial variations of the electric field inside the atom) in the form

$$\hat{H}' = E_x \sum_j e_j x_j, \tag{17.66}$$

where e_j represents the charge and x_j the coordinate x of the j-th particle. The expression $\sum_j e_j x_j$ is the x–component of the atomic electric dipole moment. The intensity of the field E_x is given in terms of its spectral components by the general expression

$$E_x = \int E_x^0(\nu)\left(e^{i2\pi\nu t} + e^{-i2\pi\nu t}\right) d\nu. \tag{17.67}$$

Let us consider for the moment only one frequency ν of the perturbation, although in the end it will be necessary to integrate over all frequencies. To apply time–dependent perturbation theory we introduce the initial conditions $c_m(0) = 0$ and $c_n(0) = 1$ on the right–hand side of

$$\dot{c}_l(t) = -\frac{i}{\hbar} \sum_k c_k(t) e^{i(E_l - E_k)t/\hbar} \mathcal{H}_{lk}, \tag{17.68}$$

(the other coefficients in the sum are zero) to obtain

$$\dot{c}_m(t) = -\frac{i}{\hbar} \int \Psi_m^{0*} \hat{H}' \Psi_n^0 \, dx = -\frac{i}{\hbar} \int \psi_m^{0*} e^{iE_m t/\hbar} \left(e^{i\omega t} + e^{-i\omega t} \right) E_x \sum_j e_j x_j \psi_n^0 e^{-iE_n t/\hbar} \, dx. \tag{17.69}$$

We now introduce the matrix elements of the atomic dipole moment, denoted by

$$(D_x)_{mn} = \int \psi_m^{0*} \sum_j e_j x_j \psi_n^0 \, dx, \tag{17.70}$$

and obtain

$$\frac{dc_m(t)}{dt} = -\frac{i}{\hbar} (D_x)_{mn} E_x^0(\nu) \left[e^{i(\omega_{mn}+\omega)t} + e^{i(\omega_{mn}-\omega)t} \right]. \tag{17.71}$$

By integration we obtain

$$c_m(t) = (D_x)_{mn} E_x^0(\nu) \left[\frac{1 - e^{i(\omega_{mn}+\omega)t}}{\hbar(\omega_{mn} + \omega)} + \frac{1 - e^{i(\omega_{mn}-\omega)t}}{\hbar(\omega_{mn} - \omega)} \right]. \tag{17.72}$$

This result shows that there are two contributions whose relative weight may vary considerably from case to case. Normally the coefficient $(D_x)_{mn} E_x^0(\nu)$ is small, so that $c_m(t)$ can reach significant values only when one of the denominators appearing in (17.72) is also small; this happens only if $\omega \sim \omega_{mn}$, or $\omega \sim -\omega_{mn}$. In each case only one of the two terms is important (where the the denominator approaches zero) while the other becomes considerably smaller (with denominator given approximately by $2|\omega_{mn}|$). In other words, induced absorption arises because the presence of the resonance denominator, $\omega_{mn} - \omega$, causes the transition probability from state n to state m to acquire a maximum value when the frequency of the radiation is very close to that given by Bohr's formula. In this case the second term is the important one, and we can neglect the first without introducing a significant error.

For induced emission, $\omega_{mn} < 0$ and the first term is the one that generates resonant transitions, while the second becomes negligible. It is now easy to see that the value of $|c_m(t)|^2$ (which determines the transition probability and thus the Einstein coefficients produced by either the first or the second term, as the case may be) is equal in both cases for the same value of $|\omega_{mn}|$; from this follows the equality of these coefficients for stimulated absorption or emission between a given pair of states m and n.

To complete the exercise we calculate the transition probability at time t. For resonant absorption we have

$$W_{n\to m} = c_m^*(t)c_m(t) = 4(D_x)_{mn}^2 E_x^{02}(\nu_{mn}) \int \frac{\sin^2\left[\pi(E_m - E_n + h\nu)t/\hbar\right]}{(E_m - E_n + h\nu)^2}\, d\nu. \tag{17.73}$$

The integral can be extended from $-\infty$ to ∞, considering that the integrand is very small outside resonance. Using the formula

$$\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2}\, dx = \pi, \tag{17.74}$$

we obtain

$$w_{n\to m} = \frac{1}{\hbar^2}(D_x)_{mn}^2 E_x^{02}(\nu_{mn})\, t. \tag{17.75}$$

The transition probability per unit time, considering the three components of the field, is then

$$W_{n\to m} = \lim_{t\to\infty} \frac{w_{n\to m}}{t} = \frac{1}{\hbar^2}\left[(D_x)_{mn}^2 + (D_y)_{mn}^2 + (D_z)_{mn}^2\right]. \tag{17.76}$$

Once again we verify that $W_{n\to m} = W_{m\to n}$. Except for the factor $\rho(\omega)$ due to the spectral density of the incident field, this statement is equivalent to $B_{nm} = B_{mn}$. It is left to the reader to show that from (17.76) it follows that

$$B_{nm} = \frac{4\pi^2}{3\hbar^2}\,|D_{mn}|^2. \tag{17.77}$$

P17.6 Show that the probability per unit time that an atom makes a spontaneous quadrupole transition between states n and n' is given by

$$A_{nn'}^{(2e)} = \frac{\omega_{nn'}^5}{90\hbar c^5} \sum_{i,j} \left|\langle n|Q_{ij}|n'\rangle\right|^2, \tag{17.78}$$

where Q_{ij} are the components of the electric quadrupole moment,

$$Q_{ij} = e\left(3x_i x_j - r^2\delta_{ij}\right), \quad i,j = 1,2,3. \tag{17.79}$$

Solution. We derive the probability for spontaneous quadrupole transitions by quantizing the corresponding classical formula. The classical radiation intensity for quadrupole radiation is given by

$$W = \frac{1}{180c^5}\left(\ddot{Q}_{ij}\right)^2, \tag{17.80}$$

where Q_{ij} are the components of the electric quadrupole moment tensor

$$Q_{ij} = e\left(3x_i x_j - r^2\delta_{ij}\right), \quad i,j = 1,2,3. \tag{17.81}$$

In quantum theory, radiation results from atomic transitions between quantum states n and n'. The classical variable Q_{ij} is replaced by its quantum counterpart,

$$Q_{ij} \to \left(\dot{Q}_{ij}\right) = \langle \Psi | \dot{Q}_{ij} | \Psi \rangle. \tag{17.82}$$

The radiated power can be expressed in terms of Einstein's spontaneous emission coefficient $A_{nn'}$

$$W = g_n g_{n'} \hbar \omega A_{nn'}, \tag{17.83}$$

where g_n and $g_{n'}$ characterize the occupation of states n and n'. For simplicity , we set $g_n g_{n'} = 1$,

$$W = \hbar \omega A_{nn'}. \tag{17.84}$$

Combining Eqs. (17.80), (17.82), and (17.84), we obtain the Einstein coefficient for electric quadrupole transitions

$$A_{nn'}^{(2e)} = \frac{1}{180 c^5 \hbar \omega_{nn'}} \overline{\left(\ddot{Q}_{ij}\right)^2_{nn'}}^t, \tag{17.85}$$

where the bar with index t indicates a time average. To calculate the required matrix elements, we consider that only the levels n and n', with energies E_n and $E_{n'}$ respectively, are active; this is equivalent to using the two-level atom model. As the two states coexist in the ensemble, we take the wave function as a superposition,

$$\Psi(t) = C_n e^{-iE_n t/\hbar} \psi_n + C_{n'} e^{-iE_{n'} t/\hbar} \psi_{n'}. \tag{17.86}$$

We thus obtain

$$\left\langle \hat{Q}_{ij} \right\rangle = \left\langle \Psi \right| \hat{Q}_{ij} \left| \Psi \right\rangle = |C_n|^2 \left(\hat{Q}_{ij}\right)_{nn} + |C_{n'}|^2 \left(\hat{Q}_{ij}\right)_{n'n'} \tag{17.87}$$

$$+ C_n^* C_{n'} e^{i\omega t} \left(\hat{Q}_{ij}\right)_{nn'} + C_{n'}^* C_n e^{-i\omega t} \left(\hat{Q}_{ij}\right)_{n'n}, \tag{17.88}$$

where $\omega \equiv \omega_{nn'} = (E_n - E_{n'})/\hbar$. Taking into account that $\left(\hat{Q}_{ij}\right)^*_{nn'} = \left(\hat{Q}_{ij}\right)_{n'n}$ and that the diagonal matrix elements are time-independent, we obtain from (17.88):

$$\left\langle \dddot{\hat{Q}}_{ij} \right\rangle = -i\omega^3 \left[C_n^* C_{n'} e^{i\omega t} \left(\hat{Q}_{ij}\right)_{nn'} - C_{n'}^* C_n e^{-i\omega t} \left(\hat{Q}_{ij}\right)_{n'n} \right], \tag{17.89}$$

from which it follows that

$$\left| \left\langle \dddot{\hat{Q}}_{ij} \right\rangle \right|^2 = \omega^6 \left[|C_n|^2 |C_{n'}|^2 \left| \left(\hat{Q}_{ij}\right)_{nn'} \right|^2 - C_n^2 C_{n'}^{*2} e^{-2i\omega t} \left(\hat{Q}_{ij}\right)^*_{nn'} \left(\hat{Q}_{ij}\right)_{n'n} \right. \tag{17.90}$$

$$\left. - C_{n'} C_n^* C_n^* C_{n'} e^{2i\omega t} \left(\hat{Q}_{ij}\right)^*_{n'n} \left(\hat{Q}_{ij}\right)_{nn'} + |C_n|^2 |C_{n'}|^2 \left| \left(\hat{Q}_{ij}\right)_{n'n} \right|^2 \right]. \tag{17.91}$$

Since the time average of the oscillating terms is zero, we obtain upon averaging

$$\overline{\left|\hat{Q}_{ij}\right|^2}^t = 2\omega^6 |C_n|^2 |C_{n'}|^2 \left|\hat{Q}_{ij}\right|^2_{nn'}. \tag{17.92}$$

Substituting this result into (17.85) yields

$$A^{(2e)}_{nn'} = \frac{\omega^5}{90\hbar c^5}|C_n|^2|C_{n'}|^2\left|\hat{Q}_{ij}\right|^2_{nn'}. \tag{17.93}$$

To obtain the numerically correct result we must set $|C_n|^2|C_{n'}|^2 = 1$. A rigorous justification of this choice can only be made within quantum electrodynamics, so the above calculation should be taken as a heuristic guide to understand the relationship between the classical and quantum results, and to estimate the order of magnitude of the latter. With the proposed selection, we finally obtain

$$A^{(2e)}_{nn'} = \frac{\omega^5}{90\hbar c^5}\sum_{i,j}\left|\langle n|\hat{Q}_{ij}|n'\rangle\right|^2. \tag{17.94}$$

To estimate the magnitude of this probability relative to that of electric dipole transitions of similar frequency, we note that (17.94) gives

$$A^{(2e)} \sim \frac{e^2\omega^5 a_0^4}{90\hbar c^5}, \tag{17.95}$$

while for dipole transitions, we should write, with similar approximation:

$$A^{(1e)} \sim \frac{e^2\omega^3 a_0^2}{\hbar c^3}. \tag{17.96}$$

From this it follows that

$$\frac{A^{(2e)}}{A^{(1e)}} \sim \frac{a_0^2\omega^2}{90c^2} = \frac{4\pi^2}{90}\left(\frac{a_0}{\lambda}\right)^2 \sim \left(\frac{a_0}{\lambda}\right)^2, \tag{17.97}$$

where λ is the wavelength of the emitted radiation. The relative probability of quadrupole transitions compared to dipole transitions of similar frequency (and hence their relative intensity) is on the order of the square of the ratio of an atomic radius to the wavelength of the emitted radiation, a quantity that for radiation in the visible spectrum is about 10^{-6}.

P17.7 Find the selection rules for electric quadrupole transitions of: a) particles confined in a one-dimensional infinite rectangular well; b) particles in a one-dimensional harmonic oscillator well; c) a flat rigid rotor.

Solution. a) In the previous problem we saw that the probability of spontaneous quadrupole transitions per unit time is proportional to the square modulus of the matrix elements $\langle n|\,\hat{Q}_{ij}\,|n'\rangle$. The tensor Q_{ij} has only one component in the one-dimensional case, proportional to $\langle n' \mid (x-\overline{x})^2 \mid n\rangle$. Placing the origin at one end of the well of width a, we have $\bar{x} = a/2$. Using the eigenfunctions of the infinite

well and taking $n \neq n'$, we have

$$\langle n'|(x-\overline{x})^2|n\rangle = \frac{2}{a}\int_0^a \left(x-\frac{a}{2}\right)^2 \sin\left(\frac{\pi n' x}{a}\right)\sin\left(\frac{\pi n x}{a}\right)dx \tag{17.98}$$

$$= \frac{1}{a}\int_0^a \left(x^2 - ax + \frac{a^2}{4}\right)\left[\cos\frac{\pi(n'-n)x}{a} - \cos\frac{\pi(n'+n)x}{a}\right]dx \tag{17.99}$$

$$= \frac{a^2}{\pi^2(n'-n)^2}\left[\cos\pi(n'-n)+1\right] - \frac{a^2}{\pi^2(n'+n)^2}\left[\cos\pi(n'+n)+1\right] \tag{17.100}$$

$$= \frac{a^2}{\pi^2(n'-n)^2}\left[(-1)^{n'-n}+1\right] - \frac{a^2}{\pi^2(n'+n)^2}\left[(-1)^{n'+n}+1\right], \tag{17.101}$$

that is,

$$\langle n'|(x-\overline{x})^2|n\rangle = \frac{a^2}{\pi^2}\left[(-1)^{n'+n}+1\right]\left[\frac{1}{(n'-n)^2} - \frac{1}{(n'+n)^2}\right]. \tag{17.102}$$

This result shows that the selection rule for quadrupole transitions for the one-dimensional infinite well coincides with that for dipole transitions for this same system, that is,

$$|\Delta n| = |n'-n| = \text{ an even number.} \tag{17.103}$$

A consequence of this coincidence is that the dipole and quadrupole energy spectra coincide, and their lines merely overlap. It is important to emphasize that these results refer to the one-dimensional case; for the spherical infinite well (as for any problem in more than one dimension) the selection rules generated by angular momentum appear, which for electric quadrupole transitions are $\Delta l = 0, \pm 2$; $\Delta m = 0, \pm 1, \pm 2$ (the latter is demonstrated in a particular case in part c) of this problem). Since electric dipole transitions occur for $\Delta l = \pm 1$, dipole and quadrupole transitions never compete in multidimensional problems.

b) For particles confined in a one-dimensional harmonic oscillator well centered at the origin $\overline{x} = 0$, the probability of quadrupole transitions is proportional to the matrix element $\langle n' \mid x^2 \mid n\rangle$, with $|n\rangle$ the harmonic oscillator eigenfunctions. From the above problems, we have that

$$x^2|n\rangle = \frac{\hbar}{2m\omega}\left[\sqrt{n(n-1)}\,|n-2\rangle + (2n+1)\,|n\rangle + \sqrt{(n+1)(n+2)}\,|n+2\rangle\right], \tag{17.104}$$

from which it follows that the matrix elements $\langle n' \mid x^2 \mid n\rangle$ differ from zero only for $n' = n$ and $n' = n \pm 2$, which determines the selection rules for electric quadrupole transitions in the present case. When dealing with spontaneous emissions, which occur only for $n' < n$, the selection rule reduces to $n' = n-2$, which corresponds to

the emission of an energy $2\hbar\omega$. This constitutes the quantum equivalent of second harmonic radiation.
c) The probability of electric quadrupole transitions for a rigid rotor of radius R is determined by the matrix elements $\langle m' \mid xy \mid m\rangle$, $\langle m' \mid x^2 \mid m\rangle$ and $\langle m' \mid y^2 \mid m\rangle$, calculated with the eigenfunctions

$$|m\rangle = \frac{1}{\sqrt{2\pi}} e^{im\varphi}, \quad m = 0, \pm 1, \pm 2, \ldots \tag{17.105}$$

We thus have

$$\langle m'|xy|m\rangle = R^2 \langle m'|\sin\varphi\cos\varphi|m\rangle \tag{17.106}$$

$$= \frac{R^2}{4\pi}\int_0^{2\pi} \sin 2\varphi\, e^{i(m-m')\varphi} d\varphi \tag{17.107}$$

$$= \begin{cases} \pm iR^2/4, & m - m' = \pm 2 \\ 0, & m - m' \neq \pm 2 \end{cases}. \tag{17.108}$$

$$\langle m'|y^2|m\rangle = R^2 \langle m'|\sin^2\varphi|m\rangle \tag{17.109}$$

$$= \frac{R^2}{4\pi}\int_0^{2\pi} (1 - \cos 2\varphi) e^{i(m-m')\varphi} d\varphi \tag{17.110}$$

$$= \frac{R^2}{2}\delta_{mm'} - \frac{R^2}{4\pi}\begin{cases} 0, & |m - m'| \neq 2 \\ \pi, & |m - m'| = 2 \end{cases}. \tag{17.111}$$

$$\langle m'|x^2|m\rangle = R^2 \langle m'|\cos^2\varphi|m\rangle \tag{17.112}$$

$$= R^2\langle m'|m\rangle - R^2\langle m'|\sin^2\varphi|m\rangle \tag{17.113}$$

$$= \frac{R^2}{2}\delta_{mm'} + \frac{R^2}{4\pi}\begin{cases} 0, & m - m' \neq \pm 2 \\ \pi, & m - m' = \pm 2 \end{cases}. \tag{17.114}$$

From these results follow the quadrupole selection rules $\Delta m = m' - m = 0, \pm 2$. Unlike the two previous cases, for which the selection rules had to do only with energy (the equivalent of the principal quantum number), the selection rules here are angular.

P17.8 Determine the direction in which an electron is most likely to be emitted by the absorption of 50-keV γ radiation.
Solution. The differential cross section used (as given in [1], Section 17.2.7) for the photoelectric process in the regime $\hbar\omega \gg I$ is

$$\frac{d\sigma}{d\Omega} = \frac{32\,\alpha\,\hbar}{mc\,k}\left(\frac{\hbar Z}{a_0\,p}\right)^5 \frac{\sin^2\theta\,\sin^2\phi}{\left(1 - \frac{v}{c}\cos\theta\right)^4}, \tag{17.115}$$

where α is the fine structure constant, m the electron mass, c the speed of light, $k = \omega/c$ the photon wave number, Z the atomic number of the target, a_0 the Bohr

radius, p and v the momentum and speed of the emitted electron. $\theta \in [0,\pi], \phi \in [0,2\pi]$ are the polar and azimuthal angles, with θ measured from $\boldsymbol{k}$ and ϕ the angle between the polarization direction and the component of $\boldsymbol{p}$ perpendicular to $\boldsymbol{k}$. The kinematic quantities k, p and v depend on the incident photon energy $E_\gamma = \hbar\omega$ which is transferred to the electron as kinetic energy. In particular we have, using the relativistic relation for the kinetic energy

$$K = (\gamma - 1)mc^2, \quad \gamma = \frac{1}{\sqrt{1-\beta^2}}, \tag{17.116}$$

that the velocity ratio $\beta = v/c$ is given by

$$\beta = \frac{v}{c} = \sqrt{1 - \left(\frac{K}{mc^2} + 1\right)^{-2}}. \tag{17.117}$$

For the purpose of locating the direction of maximum probability we may factor out the positive prefactor that contains Z and the constants and study the angular function

$$f(\theta,\phi) \;=\; \frac{\sin^2\theta\,\cos^2\phi}{\big(1-\beta\cos\theta\big)^4}, \tag{17.118}$$

with $0 < \beta < 1$. The prefactor $A = \dfrac{32\alpha\hbar}{mck}\big(\dfrac{\hbar Z}{a_0 p}\big)^5$ scales the magnitude but does not change the location of extrema in θ, ϕ. Differentiation of f with respect to ϕ keeping θ fixed gives

$$\frac{\partial f}{\partial \phi} \propto \sin\phi\cos\phi = 0.$$

Thus the azimuthal stationary points are $\phi = 0, \frac{\pi}{2}, \pi, \frac{3\pi}{2}, 2\pi$. Because f contains $\cos^2\phi$ in the numerator, the azimuthal maxima occur at

$$\phi^* = n\pi, \qquad n \in \mathbb{Z}. \tag{17.119}$$

Physically, ϕ^* corresponds to the direction for which the transverse component of $\boldsymbol{p}$ is aligned with the polarization vector $\boldsymbol{\epsilon}$ (in the convention used in [**1**]). Now we set $\phi = \pi/2$ and define the one-variable function

$$g(\theta) = \frac{\sin^2\theta}{(1-\beta\cos\theta)^4}.$$

With $x = \cos\theta$, $x \in [-1,1]$, we have

$$g(x) = \frac{1-x^2}{(1-\beta x)^4}.$$

Now we differentiate with respect to x and set the derivative to zero,

$$\frac{dg}{dx} = 0 \quad \Longrightarrow \quad \beta x^2 + x - 2\beta = 0.$$

This quadratic equation yields the physically admissible root,

$$\cos\theta^* \;=\; \frac{-1+\sqrt{1+8\beta^2}}{2\beta}. \tag{17.120}$$

The second algebraic root lies outside the interval $[-1,1]$ for $0<\beta<1$ and is therefore discarded.

Taking limits of (17.120), we have: For $\beta\to 0$ (low electron speed), $\cos\theta^*\to 0$, hence $\theta^*\to 90^\circ$. This recovers the dipole-dominated pattern in which emission is preferentially in the plane perpendicular to $\boldsymbol{k}$ and aligned with the polarization $\boldsymbol{\epsilon}$. For $\beta\to 1$ (ultrarelativistic electrons) $\cos\theta^*\to 1$, so $\theta^*\to 0^\circ$: the distribution becomes strongly forward-peaked along $\boldsymbol{k}$. Using $mc^2 = 511$ keV and $K = E_\gamma = 50$ keV, we evaluate β from (17.117)

$$\beta \approx 0{,}413 \tag{17.121}$$

ans substitute this value into (17.120) to obtain

$$\cos\theta^* \approx 0{,}651 \quad\Longrightarrow\quad \theta^* \approx 49{,}4^\circ, \tag{17.122}$$

and from (17.119), $\phi^* = \pi/2 \pmod{\pi}$. Therefore the direction of maximum emission predicted by (17.115) under the stated approximations is

$$(\theta^*, \phi^*) \approx (49{,}4^\circ,\ 90^\circ). \tag{17.123}$$

The location of the maximum (θ^*, ϕ^*) depends only on the kinematic parameter β (hence on the emitted-electron kinetic energy) and *not* on Z within the model based on (17.115), because Z appears only in the positive prefactor A. Thus the angular position of the maximum is independent of Z so long as the approximations behind (17.115) hold. In practice, if the binding energy I of the shell from which the electron is ejected is not negligible compared with E_γ, one should use $K = E_\gamma - I$ and recompute β from (17.117) using K instead of E_γ. For deep shells of heavy atoms this correction can be significant.

P17.9 Calculate the probability of an electron in an atom making a transition between stationary states under the influence of a charged particle passing close to the atom.

Solution. Consider a charged particle (charge Ze) passing near an atom with impact parameter b and constant velocity v along a straight-line trajectory. The Coulomb interaction between the particle and atomic electron acts as a time-dependent perturbation, inducing transitions between atomic stationary states. We use first-order time-dependent perturbation theory. The Coulomb interaction potential between the incident particle (position $\vec{R}(t)$) and the electron (position $\vec{r}$) is

$$H'(t) = -\frac{Ze^2}{|\boldsymbol{r}-\boldsymbol{R}(t)|}. \tag{17.124}$$

The transition probability from initial state $|i\rangle$ to final state $|f\rangle$ is given by

$$P_{i\to f} = \frac{1}{\hbar^2}\left|\int_{-\infty}^{\infty} \langle f|\, H'(t)\, |i\rangle\, e^{i\omega_{fi}t} dt\right|^2, \tag{17.125}$$

where $\omega_{fi} = (E_f - E_i)/\hbar$.

Using the Fourier expansion of the Coulomb potential,

$$\frac{1}{|\vec{r} - \vec{R}(t)|} = \frac{1}{(2\pi)^3}\int \frac{4\pi}{k^2} e^{i\vec{k}\cdot(\boldsymbol{r}-\boldsymbol{R}(t))} d^3k, \tag{17.126}$$

the matrix element becomes

$$\langle f|\, H'(t)\, |i\rangle = -\frac{Ze^2}{(2\pi)^3}\int \frac{4\pi}{k^2}\, \langle f|\, e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\, |i\rangle\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}(t)} d^3k. \tag{17.127}$$

Assuming the trajectory $\vec{R}(t) = (vt, b, 0)$ for a particle moving parallel to the x-axis with impact parameter b along y-axis,

$$\vec{k}\cdot\vec{R}(t) = k_x vt + k_y b, \tag{17.128}$$

the time integral yields

$$\int_{-\infty}^{\infty} e^{-i(k_x vt + k_y b)} e^{i\omega_{fi}t} dt = 2\pi e^{-ik_y b}\delta(\omega_{fi} - k_x v). \tag{17.129}$$

The transition probability becomes thus

$$P_{i\to f} = \frac{4Z^2e^4}{\hbar^2}\left|\langle f|\, x\, |i\rangle\, \frac{\omega_{fi}}{v} K_0\left(\frac{|\omega_{fi}|b}{v}\right) - i\, \langle f|\, y\, |i\rangle\, \frac{|\omega_{fi}|}{v} K_1\left(\frac{|\omega_{fi}|b}{v}\right)\right|^2, \tag{17.130}$$

where K_0 and K_1 are modified Bessel functions of the second kind, the $\langle f|\, x\, |i\rangle$ and $\langle f|\, y\, |i\rangle$ are electric dipole matrix elements and $\omega_{fi} = (E_f - E_i)/\hbar$.
For randomly oriented atoms, we average over all directions,

$$\overline{P}_{i\to f}(b) = \frac{4Z^2e^4}{3\hbar^2v^2} |\, \langle f|\, \boldsymbol{r}\, |i\rangle\, |^2 \left[\left(\frac{\omega_{fi}}{v} K_0\left(\frac{|\omega_{fi}|b}{v}\right)\right)^2 + \left(\frac{|\omega_{fi}|}{v} K_1\left(\frac{|\omega_{fi}|b}{v}\right)\right)^2\right], \tag{17.131}$$

where $|\, \langle f|\, \boldsymbol{r}\, |i\rangle\, |^2 = |\, \langle f|\, x\, |i\rangle\, |^2 + |\, \langle f|\, y\, |i\rangle\, |^2 + |\, \langle f|\, z\, |i\rangle\, |^2$.

P17.10 A 1D HO originally at rest is subjected to a force $f(t)$. Find the equation of motion of the center of the wave packet using first-order perturbation theory and compare with the exact result.

Solution. We considerf a one-dimensional harmonic oscillator with unperturbed Hamiltonian

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \tag{17.132}$$

initially in its ground state $|0\rangle$, with $\langle x\rangle(0) = 0$ and $\langle p\rangle(0) = 0$. A force $f(t)$ is applied, modeled as a time-dependent perturbation

$$\hat{H}'(t) = -f(t)\hat{x}, \tag{17.133}$$

so that the total Hamiltonian is

$$\hat{H} = \hat{H}_0 + \hat{H}'(t). \tag{17.134}$$

In time-dependent perturbation theory, the wave function is expanded to first order

$$|\psi(t)\rangle = e^{-iE_0 t/\hbar}\left(|0\rangle + \sum_n c_n^{(1)}(t)|n\rangle\right), \tag{17.135}$$

where $E_0 = (1/2)\hbar\omega$ is the ground state energy, and the coefficients $c_n^{(1)}(t)$ are given by

$$c_n^{(1)}(t) = -\frac{i}{\hbar}\int_0^t e^{i\omega_{n0}t'}\langle n|\hat{H}'(t')|0\rangle\, dt', \quad \omega_{n0} = \frac{E_n - E_0}{\hbar}. \tag{17.136}$$

For the harmonic oscillator, the operator $\hat{x}$ connects only adjacent states. In particular, $\langle 1|\hat{x}|0\rangle = \sqrt{\hbar/2m\omega}$. Thus,

$$\langle 1|\hat{H}'(t')|0\rangle = -f(t')\langle 1|\hat{x}|0\rangle = -f(t')\sqrt{\frac{\hbar}{2m\omega}}. \tag{17.137}$$

Substituting into the expression for $c_1^{(1)}(t)$,

$$c_1^{(1)}(t) = -\frac{i}{\hbar}\int_0^t e^{i\omega t'}\left(-f(t')\sqrt{\frac{\hbar}{2m\omega}}\right)dt' = \frac{i}{\hbar}\sqrt{\frac{\hbar}{2m\omega}}\int_0^t e^{i\omega t'}f(t')\, dt'. \tag{17.138}$$

With the wave function to first order

$$|\psi(t)\rangle = e^{-iE_0 t/\hbar}\left(|0\rangle + c_1^{(1)}(t)|1\rangle\right), \tag{17.139}$$

the expectation value of $\hat{x}$ is given to first order by

$$\langle x\rangle = c_1^{(1)}\langle 0|\hat{x}|1\rangle + c_1^{(1)*}\langle 1|\hat{x}|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(c_1^{(1)} + c_1^{(1)*}\right). \tag{17.140}$$

From Eq. (17.136) we have

$$c_1^{(1)} + c_1^{(1)*} = \frac{i}{\hbar}\sqrt{\frac{\hbar}{2m\omega}}\int_0^t e^{i\omega t'}f(t')\, dt' - \frac{i}{\hbar}\sqrt{\frac{\hbar}{2m\omega}}\int_0^t e^{-i\omega t'}f(t')\, dt' \tag{17.141}$$

$$= \frac{i}{\hbar}\sqrt{\frac{\hbar}{2m\omega}}\int_0^t \left(e^{i\omega t'} - e^{-i\omega t'}\right)f(t')\, dt'. \tag{17.142}$$

$$= -\frac{2}{\hbar}\sqrt{\frac{\hbar}{2m\omega}}\int_0^t \sin(\omega t')f(t')\, dt'. \tag{17.143}$$

Therefore, the center of the wave packet is given by

$$\langle x\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(-\frac{2}{\hbar}\sqrt{\frac{\hbar}{2m\omega}}\int_0^t \sin(\omega t')f(t')\, dt'\right) = -\frac{1}{m\omega}\int_0^t \sin(\omega t')f(t')\, dt'. \tag{17.144}$$

We now differentiate this equation two times with respect to t,

$$\frac{d}{dt}\langle x\rangle_{\rm pert} = -\frac{1}{m\omega}\sin(\omega t)f(t), \tag{17.145}$$

$$\frac{d^2}{dt^2}\langle x\rangle_{\rm pert} = -\frac{1}{m\omega}\left(\omega\cos(\omega t)f(t) + \sin(\omega t)\frac{df}{dt}\right), \tag{17.146}$$

therefore,

$$\frac{d^2}{dt^2}\langle x\rangle_{\rm pert} + \omega^2\langle x\rangle_{\rm pert} == -\frac{1}{m}\cos(\omega t)f(t) - \frac{1}{m\omega}\sin(\omega t)\frac{df}{dt} - \frac{\omega}{m}\int_0^t \sin(\omega t')f(t')\,dt'. \tag{17.147}$$

This expression is not equal to $f(t)/m$ in general, so the equation of motion obtained from perturbation theory is not correct.

On the other hand, according to Ehrenfest's theorem, the time evolution of the expectation values follows the classical equations. For the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}'(t)$, we have

$$\frac{d}{dt}\langle x\rangle = \frac{1}{m}\langle p\rangle, \quad \frac{d}{dt}\langle p\rangle = -m\omega^2\langle x\rangle + f(t), \tag{17.148}$$

whence

$$\frac{d^2}{dt^2}\langle x\rangle + \omega^2\langle x\rangle = \frac{f(t)}{m}. \tag{17.149}$$

This is the exact equation of motion for the center of the wave packet. With the initial conditions $\langle x\rangle(0) = 0$ and $\frac{d}{dt}\langle x\rangle(0) = 0$, the exact solution is

$$\langle x\rangle_{\rm exact} = \frac{1}{m\omega}\int_0^t \sin(\omega(t-t'))f(t')\,dt'. \tag{17.150}$$

The first-order perturbation theory provides an approximation for $\langle x\rangle$ that is linear in $f(t)$, but does not capture the full dynamics of the system. The exact equation of motion is obtained via Ehrenfest's theorem and coincides with the classical equation of the forced oscillator. The discrepancy arises because first-order perturbation theory only includes transitions to the first excited state, while the exact solution involves all states (coherent states).

P17.11 The free-particle Lamb effect can be identified with the contribution of the (free-space) ZPF to the particle's energy, given by

$$\delta E_{fp} = \frac{e^2\hbar}{\pi m c^3}\int_0^{\omega_C} d\omega\,\omega, \tag{17.151}$$

where the usual cutoff frequency $\omega_C = mc^2/\hbar$ (equal to Compton's frequency of the electron) has been introduced. Assume that the distribution of ZPF modes can be reduced by introducing the particle in a cavity that filters out all modes of frequency ω smaller than Ω without altering the isotropy of the field and write down the formula for the resulting energy shift.

a) Estimate the minimum value of Ω needed to produce an energy shift of the order of the atomic Lamb effect.

b) Estimate the size of the cavity needed to filter out the frequencies $\omega < \Omega$ and compare it with the size of the H atom. Considering 5 nm as the minimum size of current solid-state nanoelectronic devices, could such an energy shift be detectable? Discuss your answer.

Solution. Starting from (17.151), if the particle is placed in a cavity that filters out all modes with $\omega < \Omega$ while preserving the isotropy of the field, the remaining contribution is obtained by replacing the lower integration limit with Ω,

$$\delta E_{\rm fp}(\Omega) = \frac{e^2\hbar}{\pi m c^3}\int_{\Omega}^{\omega_C} \omega\, d\omega = \frac{e^2\hbar}{2\pi m c^3}\left(\omega_C^2 - \Omega^2\right). \tag{17.152}$$

Therefore, the cavity-induced shift relative to free space is

$$\delta E_{\rm cav}(\Omega) \equiv \delta E_{\rm fp}(0) - \delta E_{\rm fp}(\Omega) = \frac{e^2\hbar}{2\pi m c^3}\,\Omega^2 = \frac{\alpha\,\hbar^2}{2\pi m c^2}\,\Omega^2, \tag{17.153}$$

where we used $\alpha = \frac{e^2}{\hbar c}$. To answer part (a), we require that the magnitude of (17.153) be of the order of an atomic Lamb shift E_L (e.g., the canonical hydrogen $2s_{1/2} - 2_{1/2}$ value: 4.372×10^{-6} eV). Setting $\delta E_{\rm cav}(\Omega) \approx \delta E_{Ln}$ and solving for Ω yields

$$\Omega \;=\; \left(\frac{2\pi m c^2}{\alpha\hbar^2}\,\delta E_L\right)^{1/2}. \tag{17.154}$$

Numerically, this gives

$$\Omega \;\approx\; 6.7 \times 10^{16}\ \mathrm{s}^{-1}, \tag{17.155}$$

which corresponds to a frequency $f = \Omega/2\pi \approx 1.1 \times 10^{16}$ Hz in the extreme-UV/soft-X range.

For part (b), a simple geometrical criterion to suppress all standing-wave modes with $\omega < \Omega$ is to make sure that no wavelength longer than $\lambda_{\rm cut} = 2\pi c/\Omega$ fits in the cavity. A conservative estimate is then

$$L \;\lesssim\; \frac{\lambda_{\rm cut}}{2} \;=\; \frac{\pi c}{\Omega}, \tag{17.156}$$

which, using (17.155), gives

$$L \;\approx\; 1.4 \times 10^{-8}\ \mathrm{m} \;=\; 14\ \mathrm{nm}. \tag{17.157}$$

Compared to the size of the H atom (~ 0.05 nm), this cavity is roughly 2.6×10^2 times larger—well within the nanoscale, yet comfortably larger than an atom. Since (17.153) implies $|\delta E_{\rm cav}| \propto \Omega^2 \propto 1/L^2$, going down to state-of-the-art solid-state dimensions (e.g., $L \sim 5\,\mathrm{nm}$) would increase the shift by nearly an order of magnitude, reaching the $10\,\mu$eV range.

In conclusion, starting from the free-space expression (17.151) and implementing the spectral filtering described in the problem, we obtain the cavity-induced shift (17.153). Matching it to an atomic Lamb shift fixes the cutoff (17.154) at the value (17.155), and the corresponding cavity size (17.157). The quadratic scaling

with Ω (or $1/L$) shows that nanometric cavities can, in principle, generate shifts at or above atomic-Lamb-shift scales, with detectability ultimately limited by how ideal the mode filtering and isotropy preservation can be made in a realistic device.

P17.12 Use the fact that the normal field amplitudes used in [**1**], **Section 17.5** are independent from each other, to prove that $[\hat{\mathrm{q}}, \hat{\mathrm{p}}]_{\mathrm{nn}'} = i\hbar\delta_{\mathrm{nn}'}$.

Solution. The Poisson bracket of a given pair of canonical variables (q, p) associated to field modes of frequency $\pm\omega$ satisfies

$$[\mathrm{q}, \mathrm{p}]_{\{\mathrm{q},\mathrm{p}\}} = 1,$$

where $\{\mathrm{q}, \mathrm{p}\}$ denotes the canonical variables of the full set of field modes (of all frequences). These variables are related to the normal field amplitudes $\{a, a^*\}$ by the general transformation rule given in [**1**], **Eq. (17.221)**. Therefore taking the derivatives with respect to $\{a, a^*\}$ instead of $\{\mathrm{q}, \mathrm{p}\}$ introduces a factor $i\hbar$ to the right side of the Poisson bracket,

$$[\mathrm{q}, \mathrm{p}]_{\{a,a^*\}} = i\hbar.$$

Let us now assume that the field in question (of frequency $\pm\omega$) is in a given state n at time t. The variables of this field must satisfy the condition

$$[\mathrm{q_n}(t), \mathrm{p_n}(t)]_{[a,a^*]} = i\hbar.$$

Since $\dot{\mathrm{q}}_\mathrm{n}(t) = \mathrm{p_n}(t)$, this condition implies that both $\mathrm{q_n}(t), \mathrm{p_n}(t)$ are linear functions of the normal field variables, as expressed in **Eqs. (17.217)** and **(17.218)**,

$$\mathrm{q_n}(t) = \mathrm{q_{nn+1}} a_+ e^{-i\omega t} + \mathrm{q_{nn-1}} a_- e^{i\omega t} + c.c.,$$

$$\mathrm{p_n}(t) = \mathrm{p_{nn+1}} a_+ e^{-i\omega t} + \mathrm{p_{nn-1}} a_- e^{i\omega t} + c.c.,$$

where a_+ is associated to the mode of frequency $\omega_{\mathrm{n+1n}} = +\omega$, and a_- is associated to the mode of frequency $\omega_{\mathrm{n-1n}} = -\omega$. In taking the derivatives with respect to the normal field amplitudes one must consider that the amplitudes associated with different frequencies ω are independent of each other. (Note, by contrast, that both q and p mix modes of frequencies $+\omega$ and $-\omega$).This means that the terms that contribute to the Poisson bracket are those that involve derivation with respect to a_+, a_+^*, and with respect to a_-, a_-^*. We thus obtain

$$\sum_{\mathrm{k=n\pm1}} (\mathrm{q_{nk}} \mathrm{p}^*_{\mathrm{nk}} - \mathrm{p_{nk}} \mathrm{q}^*_{\mathrm{nk}}) \;\; = i\hbar. \tag{17.158}$$

Further, since $\mathrm{q_n}(t)$ and $\mathrm{p_n}(t)$ must be real, q^*_{nk}=$\mathrm{q_{kn}}$ and $\mathrm{p}^*_{\mathrm{nk}}$=$\mathrm{p_{kn}}$. This allows us to write (17.158) in the form

$$\sum_{\mathrm{k=n\pm1}} (\mathrm{q_{nk}} \mathrm{p_{kn}} - \mathrm{p_{nk}} \mathrm{q_{kn}}) \;\; = i\hbar,$$

which is the matrix form of the commutator

$$[\hat{\mathrm{q}}, \hat{\mathrm{p}}]_{\mathrm{nn}} = i\hbar.$$

Note that the derivatives of $\mathrm{q_n}(t), \mathrm{p_n}(t)$ in the Poisson bracket must be taken as a rule with respect to pairs a, a^* pertaining to the same mode —in the present case, the pairs a_+, a_+^*,and a_-, a_-^*, which pertain to the modes of frequencies $+\omega$ and $-\omega$, respectively. By contrast, a commutator $[\hat{\mathrm{q}}, \hat{\mathrm{p}}]_{\mathrm{nn'}}$ with $\mathrm{n'} \neq \mathrm{n}$ would imply taking derivatives of $\mathrm{q_n}(t), \mathrm{p_{n'}}(t)$ with respect to field amplitudes pertaining to different modes, which are independent from each other and hence do not contribute to the Poisson bracket. Summarizing, we conclude that $[\hat{\mathrm{q}}, \hat{\mathrm{p}}]_{\mathrm{nn'}} = i\hbar\delta_{\mathrm{nn'}}$.

P17.13 By making repeated use of

$$[A, BC] = B[A, C] + [A, B]C, \tag{17.159}$$

determine the commutator of the densities $[A(x), A(x')]$, where $A(x)$ is the boson density operator.

Solution. The boson density operator is defined as $\hat{A}(x) = \hat{\psi}^\dagger(x)\hat{\psi}(x)$, where $\hat{\psi}(x)$ and $\hat{\psi}^\dagger(x)$ are the bosonic field operators satisfying the commutation relations

$$[\hat{\psi}(x), \hat{\psi}(x')] = 0, \quad [\hat{\psi}^\dagger(x), \hat{\psi}^\dagger(x')] = 0, \quad [\hat{\psi}(x), \hat{\psi}^\dagger(x')] = \delta(x - x'). \tag{17.160}$$

We wish to compute the commutator

$$[\hat{A}(x), \hat{A}(x')] = [\hat{\psi}^\dagger(x)\hat{\psi}(x), \hat{\psi}^\dagger(x')\hat{\psi}(x')]. \tag{17.161}$$

To simplify, we define

$$\hat{\psi}_x = \hat{\psi}(x), \quad \hat{\psi}_{x'} = \hat{\psi}(x'), \quad \hat{\psi}_x^\dagger = \hat{\psi}^\dagger(x), \quad \hat{\psi}_{x'}^\dagger = \hat{\psi}^\dagger(x'). \tag{17.162}$$

The commutator thus takes the form

$$[\hat{A}(x), \hat{A}(x')] = [\hat{\psi}_x^\dagger\hat{\psi}_x, \hat{\psi}_{x'}^\dagger\hat{\psi}_{x'}]. \tag{17.163}$$

We will repeatedly use the identity (17.159). First, we apply this identity to the $[\hat{\psi}_x^\dagger\hat{\psi}_x, \hat{\psi}_{x'}^\dagger\hat{\psi}_{x'}]$, taking $\hat{A} = \hat{\psi}_x^\dagger\hat{\psi}_x$, $\hat{B} = \hat{\psi}_{x'}^\dagger$, and $\hat{C} = \hat{\psi}_{x'}$,

$$[\hat{\psi}_x^\dagger\hat{\psi}_x, \hat{\psi}_{x'}^\dagger\hat{\psi}_{x'}] = \hat{\psi}_{x'}^\dagger[\hat{\psi}_x^\dagger\hat{\psi}_x, \hat{\psi}_{x'}] + [\hat{\psi}_x^\dagger\hat{\psi}_x, \hat{\psi}_{x'}^\dagger]\hat{\psi}_{x'}. \tag{17.164}$$

Now, we compute the commutators $[\hat{\psi}_x^\dagger\hat{\psi}_x, \hat{\psi}_{x'}]$ and $[\hat{\psi}_x^\dagger\hat{\psi}_x, \hat{\psi}_{x'}^\dagger]$ using the identity (17.159) and applying with $\hat{A} = \hat{\psi}_x^\dagger\hat{\psi}_x$, $\hat{B} = \hat{\psi}_x^\dagger$, and $\hat{C} = \hat{\psi}_x$,

$$[\hat{\psi}_x^\dagger\hat{\psi}_x, \hat{\psi}_{x'}] = \hat{\psi}_x^\dagger[\hat{\psi}_x, \hat{\psi}_{x'}] + [\hat{\psi}_x^\dagger, \hat{\psi}_{x'}]\hat{\psi}_x. \tag{17.165}$$

By applying the commutation rules

$$[\hat{\psi}_x, \hat{\psi}_{x'}] = 0, \quad [\hat{\psi}_x^\dagger, \hat{\psi}_{x'}] = -\delta(x - x'), \tag{17.166}$$

where the last one follows from $[\hat{\psi}_{x'}, \hat{\psi}_x^\dagger] = \delta(x - x')$ and the antisymmetry of the commutator, we get

$$[\hat{\psi}_x^\dagger\hat{\psi}_x, \hat{\psi}_{x'}] = \hat{\psi}_x^\dagger \cdot 0 + (-\delta(x - x'))\hat{\psi}_x = -\delta(x - x')\hat{\psi}_x. \tag{17.167}$$

Applying the identity with $\hat{A} = \hat{\psi}_x^\dagger\hat{\psi}_x$, $\hat{B} = \hat{\psi}_x^\dagger$, and $\hat{C} = \hat{\psi}_x$

$$[\hat{\psi}_x^\dagger\hat{\psi}_x, \hat{\psi}_{x'}^\dagger] = \hat{\psi}_x^\dagger[\hat{\psi}_x, \hat{\psi}_{x'}^\dagger] + [\hat{\psi}_x^\dagger, \hat{\psi}_{x'}^\dagger]\hat{\psi}_x \tag{17.168}$$

and using the commutation rules

$$[\hat{\psi}_x, \hat{\psi}^\dagger_{x'}] = \delta(x - x'), \quad [\hat{\psi}^\dagger_x, \hat{\psi}^\dagger_{x'}] = 0, \tag{17.169}$$

we get

$$[\hat{\psi}^\dagger_x \hat{\psi}_x, \hat{\psi}^\dagger_{x'}] = \hat{\psi}^\dagger_x \delta(x - x') + 0 \cdot \hat{\psi}_x = \delta(x - x')\hat{\psi}^\dagger_x. \tag{17.170}$$

Substituting (17.167) and (17.170) into (17.164), we obtain

$$[\hat{\psi}^\dagger_x \hat{\psi}_x, \hat{\psi}^\dagger_{x'} \hat{\psi}_{x'}] = \hat{\psi}^\dagger_{x'}(-\delta(x-x')\hat{\psi}_x) + (\delta(x-x')\hat{\psi}^\dagger_x)\hat{\psi}_{x'} = -\delta(x-x')\hat{\psi}^\dagger_{x'}\hat{\psi}_x + \delta(x-x')\hat{\psi}^\dagger_x\hat{\psi}_{x'} \tag{17.171}$$

that is,

$$[\hat{A}(x), \hat{A}(x')] = \delta(x - x') \left(\hat{\psi}^\dagger_x \hat{\psi}_{x'} - \hat{\psi}^\dagger_{x'} \hat{\psi}_x \right). \tag{17.172}$$

Now we have two cases: first, if $x \neq x'$, then $\delta(x - x') = 0$, so the commutator is zero.

Second, if $x = x'$, then $\hat{\psi}^\dagger_x \hat{\psi}_{x'} = \hat{\psi}^\dagger_x \hat{\psi}_x = \hat{A}(x)$ and $\hat{\psi}^\dagger_{x'} \hat{\psi}_x = \hat{\psi}^\dagger_x \hat{\psi}_x = \hat{A}(x)$, so the expression in parentheses is $\hat{A}(x) - \hat{A}(x) = 0$. Therefore, in all cases,

$$[\hat{A}(x), \hat{A}(x')] = 0. \tag{17.173}$$

CHAPTER 18

Elastic Scattering Theory

P18.1 Derive the relations [1] (18.1) and (18.2) that are used to transition between the laboratory and CM reference frames in a two-particle problem.

Solution. For the analysis of the collision of two particles it is very convenient to use the relative and center-of-mass coordinates, defined in terms of the positions $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ of the particles 1 and 2 of masses m_1, m_2, respectively, in the usual form

$$\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2, \qquad \boldsymbol{R} = \frac{m_1\boldsymbol{r}_1 + m_2\boldsymbol{r}_2}{M} = \frac{m}{m_2}\boldsymbol{r}_1 + \frac{m}{m_1}\boldsymbol{r}_2, \tag{18.1}$$

where $M = m_1 + m_2$ is the total mass of the system and $m = m_1m_2/M$ is its reduced mass. Inverting these expressions we obtain

$$\boldsymbol{r}_1 = \boldsymbol{R} + \frac{m}{m_1}\boldsymbol{r}, \qquad \boldsymbol{r}_2 = \boldsymbol{R} - \frac{m}{m_2}\boldsymbol{r}. \tag{18.2}$$

The positions of the particles referred to the CM system, $\boldsymbol{r}_1^*$ and $\boldsymbol{r}_2^*$, are defined by the relations

$$\boldsymbol{r}_1 = \boldsymbol{R} + \boldsymbol{r}_1^*, \qquad \boldsymbol{r}_2 = \boldsymbol{R} + \boldsymbol{r}_2^*, \tag{18.3}$$

and they follow immediately, using (18.2),

$$\boldsymbol{r}_1^* = \frac{m}{m_1}\boldsymbol{r}, \qquad \boldsymbol{r}_2^* = -\frac{m}{m_2}\boldsymbol{r}. \tag{18.4}$$

The velocities of the particles in a laboratory system L are $\mathbf{v}_1 = \dot{\boldsymbol{r}}_1$ and $\mathbf{v}_2 = \dot{\boldsymbol{r}}_2$, so the velocity of the center of mass and the relative velocity result

$$\boldsymbol{V} = \frac{m_1\boldsymbol{v}_1 + m_2\boldsymbol{v}_2}{M}, \qquad \boldsymbol{v} = \boldsymbol{v}_1 - \boldsymbol{v}_2. \tag{18.5}$$

From here it follows that

$$\boldsymbol{v}_1 = \boldsymbol{V} + \frac{m}{m_1}\boldsymbol{v}, \qquad \boldsymbol{v}_2 = \boldsymbol{V} - \frac{m}{m_2}\boldsymbol{v}. \tag{18.6}$$

Differentiating with respect to time the expressions (18.3), we obtain

$$\boldsymbol{v}_1 = \boldsymbol{V} + \boldsymbol{v}_1^*, \qquad \boldsymbol{v}_2 = \boldsymbol{V} + \boldsymbol{v}_2^*. \tag{18.7}$$

Comparing with (18.6) (or, equivalently, differentiating (18.4)),

$$\boldsymbol{v}_1^* = \frac{m}{m_1}\boldsymbol{v}, \qquad \boldsymbol{v}_2^* = -\frac{m}{m_2}\boldsymbol{v}. \tag{18.8}$$

The total linear momentum of the system follows from (18.5), and is

$$\boldsymbol{P} = \boldsymbol{p}_1 + \boldsymbol{p}_2 = m_1\boldsymbol{v}_1 + m_2\boldsymbol{v}_2 = M\boldsymbol{V}. \tag{18.9}$$

In turn, the momentum associated with the relative motion can be written in the alternative forms

$$m\boldsymbol{v} = \boldsymbol{p}_1^* = -\boldsymbol{p}_2^* = \frac{m}{m_1}\boldsymbol{p}_1 - \frac{m}{m_2}\boldsymbol{p}_2, \tag{18.10}$$

with $\boldsymbol{p}_1^* = m_1\boldsymbol{v}_1^*$, $\boldsymbol{p}_2^* = m_2\boldsymbol{v}_2^*$. From (18.10) it follows, in particular, that $\boldsymbol{p}_1^* + \boldsymbol{p}_2^* = 0$, as expected. The previous relations can be applied both to the initial system (before the collision) and to the final system (after it). To establish the relation between the scattering angle as seen from the L and CM systems we write, with the help of Fig. 18.1, where θ_{1L} represents the scattering angle of particle 1 in the L system and $\theta_{CM} \equiv \theta^*$ represents this angle in the CM system,

$$v_1^* \sin\theta^* = v_1 \sin\theta_{1L}, \tag{18.11}$$

$$v_1^* \cos\theta^* + V = v_1 \cos\theta_{1L}. \tag{18.12}$$

The quotient of these two expressions leads to

$$\tan\theta_{1L} = \frac{\sin\theta^*}{\cos\theta^* + V/v_1^*}. \tag{18.13}$$

From relations (18.8) and (18.9) it follows that

$$\frac{V}{v_1^*} = \frac{P}{m_2 v} = \frac{m_1}{m_2}\left[\frac{\left(v_1 + (m_2/m_1)v_2\right)^2}{(v_1 - v_2)^2}\right]^{1/2}. \tag{18.14}$$

We assume that the target, taken as particle 2, is initially at rest, so that $v_2 = 0$; from the last equation it follows that

$$\frac{V}{v_1^*} = \frac{m_1}{m_2}, \tag{18.15}$$

and (18.13) takes the form

$$\tan\theta_{1L} = \frac{\sin\theta^*}{\cos\theta^* + m_1/m_2}, \tag{18.16}$$

which coincides with the equation (18.1) that had to be demonstrated. It follows, in particular, that when $m_1/m_2 > 1$, the scattering angle θ_{1L} cannot reach the value $\pi/2$.

In the absence of external or internal forces, the total energy is purely kinetic and is given by

$$E_L = \tfrac{1}{2}m_1 v_1^2 + \tfrac{1}{2}m_2 v_2^2 = \tfrac{1}{2}MV^2 + \tfrac{1}{2}mv^2 = E_{CM} + E_r. \tag{18.17}$$

The energy $E_{CM} = \frac{1}{2}MV^2$ is associated with the center of mass, while $E_r = \frac{1}{2}mv^2$ is due to the relative motion. In the particular case analyzed above, where $v_2 = 0$, we have

$$E_L = \tfrac{1}{2}m_1 v_1^2, \qquad E_r = \tfrac{1}{2}mv_1^2 \;\Rightarrow\; E_r = \frac{m}{m_1}E_L \tag{18.18}$$

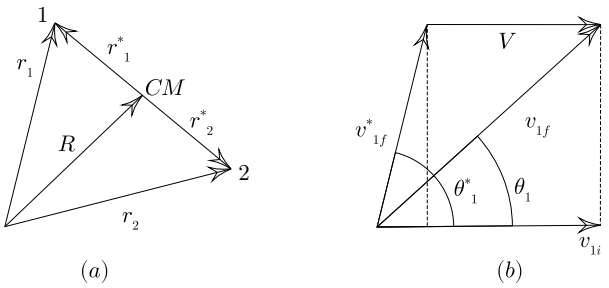

FIGURE 18.1. Laboratory and CM coordinates; (a) shows the position vectors and (b) shows the velocities.

and the previous equation reduces to

$$E_L = E_{CM} + \frac{m_2}{M} E_L. \tag{18.19}$$

We see that in this case the energy associated with the motion of the center of mass can be written in terms of the energy defined in the laboratory system in the form

$$E_{CM} = \left(1 - \frac{m_2}{M}\right) E_L = \frac{m_1}{M} E_L. \tag{18.20}$$

This is the equation (18.2) that was requested to be proved. Notice that in extreme cases, such as $m_2 \ll m_1$, the CM can carry away a very significant part of the available energy; for equal masses, $E_{CM} = E_L/2$.

P18.2 Derive [**1**], **Eq. (18.3),** which relates the number of particles per unit area in both reference frames.

Solution. We seek to find the relationship connecting the elastic scattering cross section expressed in the laboratory system with the corresponding expression in the center-of-mass system. The differential scattering cross section in a given direction is written in the form $d\sigma(\Omega) = \sigma'(\Omega) d\Omega$, where $\sigma'(\Omega) \equiv d\sigma(\Omega)/d\Omega$, and is defined as

$$d\sigma(\Omega) = \frac{\text{number of particles scattered into } d\Omega \text{ per unit time}}{\text{incident flux on target}}, \tag{18.21}$$

and $d\Omega$ is the solid angle element in direction Ω. To simplify the following description, we will consider that the scattering potential is central; the resulting symmetry about the axis describing the incident particle's trajectory allows writing the solid angle element as

$$d\Omega = 2\pi \sin\theta \, d\theta, \tag{18.22}$$

where θ is the angle between the outgoing and incident directions, that is, the scattering angle. From (18.22) it follows that the number of particles scattered

into solid angle $d\Omega$ per unit time is

$$dn(\theta) = J_{\text{inc}}\sigma'(\theta)2\pi\sin\theta|d\theta|, \tag{18.23}$$

where the absolute value ensures that $dn(\theta)$ remains positive. Since the number of particles scattered into a given solid angle element is independent of the reference frame (lab or CM), we must have

$$2\pi J_{\text{inc}}\sigma'(\theta_L)\sin\theta_L|d\theta_L| = 2\pi J_{\text{inc}}\sigma'(\theta^*)\sin\theta^*|d\theta^*|, \tag{18.24}$$

which simplifies to

$$\sigma'(\theta_L) = \sigma'(\theta^*)\frac{\sin\theta^*}{\sin\theta_L}\left|\frac{d\theta^*}{d\theta_L}\right| = \sigma'(\theta^*)\left|\frac{d\cos\theta^*}{d\cos\theta_L}\right|. \tag{18.25}$$

To determine the required derivative without excessive complication, we consider the same special case as in the previous problem, assuming particle 2 initially at rest ($v_2 = 0$). Defining $\gamma = m_1/m_2$, we obtain

$$\cos^2\theta_{1L} = \frac{1}{1+\tan^2\theta_{1L}} = \frac{(\cos\theta^*+\gamma)^2}{1+\gamma^2+2\gamma\cos\theta^*}, \tag{18.26}$$

which, with $\theta_{1L} = \theta_L$, gives

$$\cos\theta_L = \frac{\cos\theta^*+\gamma}{\sqrt{1+2\gamma\cos\theta^*+\gamma^2}}, \tag{18.27}$$

$$\frac{d\cos\theta_L}{d\cos\theta^*} = \frac{1+\gamma\cos\theta^*}{(1+2\gamma\cos\theta^*+\gamma^2)^{3/2}}, \tag{18.28}$$

and, finally,

$$\sigma'(\theta_L) = \frac{(1+2\gamma\cos\theta^*+\gamma^2)^{3/2}}{1+\gamma\cos\theta^*}\sigma'(\theta^*), \quad \gamma = \frac{m_1}{m_2}. \tag{18.29}$$

P18.3 Prove that for a collision process of the type $P_1 + P_2 \to P_3 + P_4$, which can be elastic or inelastic so that the quantity $Q = E_{\text{kyn.final}} - E_{\text{kyn.initial}}$ can be different from zero, in

$$n(\theta_L) = \frac{\left[1+2\frac{m_1}{m_2}\cos\theta_{CM}+\left(\frac{m_1}{m_2}\right)^2\right]^{3/2}}{1+\frac{m_1}{m_2}\cos\theta_{CM}}n(\theta_{CM}). \tag{18.3}$$

the factor $\gamma = m_1/m_2$ must be replaced by

$$\gamma = \left(\frac{m_1}{m_2}\frac{m_3}{m_4}\frac{E_r}{E_r+Q}\right)^{1/2}, \quad E_r = \frac{1}{2}m_{\text{red}}v^2. \tag{18.30}$$

Solution. Consider a binary collision in which a particle of mass m_1 collides with another at rest, of mass m_2, and which results in two particles, of masses m_3 and m_4. It is clear that $m_1 + m_2 = m_3 + m_4$. In this generalization of problem P18.1, Eq. (18.16) remains valid, even if the collision is inelastic, as long as the ratio

$\gamma = V/v_1^*$ still represents the ratio between the velocity of the center of mass in the laboratory system and the velocity of the observed particle (with mass m_3) in the CM system; in other words, we must set $\gamma = V/v_3^*$. This is the quantity to be determined in the new situation.

We define the initial energy associated with the relative motion in the CM system (with $v = v_1 = v_0$, since $v_2 = 0$ by hypothesis), according to equation

$$E_L = \frac{1}{2}m_1\mathbf{v}_1^2 + \frac{1}{2}m_2\mathbf{v}_2^2 = \frac{1}{2}M\mathbf{V}^2 + \frac{1}{2}m\mathbf{v}^2 = E_{\text{CM}} + E_r.$$

as

$$E_r = \frac{1}{2}\frac{m_1 m_2}{m_1 + m_2}v_0^2. \tag{18.31}$$

In turn, the energy absorbed during the collision is given by

$$Q = T_f - T_i = E_{\text{final kinetic}} - E_{\text{initial kinetic}} = \frac{1}{2}\frac{m_3 m_4}{m_3 + m_4}v^2 - E_r. \tag{18.32}$$

From this it follows that the relative velocity of particles 3 and 4 after the collision is

$$v^2 = \frac{2M}{m_3 m_4}(E_r + Q), \tag{18.33}$$

where $M = m_1 + m_2 = m_3 + m_4$. Using

$$\boldsymbol{v}_1^* = \frac{m}{m_1}\boldsymbol{v}, \qquad \boldsymbol{v}_2^* = -\frac{m}{m_2}\boldsymbol{v},$$

we can write (with $m_1 \to m_3$, $m \to m_{34} = m_3 m_4/M$)

$$v_3^* = \frac{m_4}{M}v. \tag{18.34}$$

Combining the last two expressions we obtain

$$v_3^{*2} = \frac{m_4^2}{M^2}v^2 = \frac{2m_4}{Mm_3}(E_r + Q). \tag{18.35}$$

Since $v_2 = 0$, we have $MV = m_1 v_1 = m_1 v_0$, that is,

$$V^2 = \frac{m_1^2}{M^2}v_0^2 = \frac{2m_1}{m_2 M}\left(\frac{1}{2}\frac{m_1 m_2}{m_1 + m_2}v_0^2\right) = \frac{2m_1}{m_2 M}E_r. \tag{18.36}$$

Combining this result with (18.35) yields

$$\gamma^2 = \frac{V^2}{v_3^{*2}} = \frac{m_1 m_3}{m_2 m_4}\frac{E_r}{E_r + Q}, \tag{18.37}$$

which leads to the requested expression

$$\gamma = \sqrt{\frac{m_1 m_3}{m_2 m_4}\frac{E_r}{E_r + Q}}. \tag{18.38}$$

P18.4 A particle of mass m collides elastically with a particle of mass M at rest (in the laboratory frame). Suppose that the scattering has spherical symmetry in the CM frame. What is the angular distribution of the target particles in the laboratory frame?

Solution. We must study what happens to the target particle after the collision. (Note the change of notation compared to previous problems: $m_1 \to m$, $m_2 \to M$.) We denote by V the velocity of the center of mass, by v_2 the velocity of the particle of mass M after the collision, as seen from the laboratory system, and by v_2^* the same velocity as seen from the CM system. We call θ_2 the angle formed by v_2 with respect to the incident direction, that is, the recoil angle of the target, and ϕ_{CM} this same angle, but measured in the CM system. It is clear that

$$\phi_{CM} = \pi - \theta^*, \tag{18.39}$$

where θ^* is the scattering angle of particle 1, studied in problem P18.1. Applying the appropriate changes to Eq. (18.13) for particle 2 ($\theta_{1L} \to \theta_{2L} \equiv \theta_2$; $\theta^* \to \pi - \theta^*$; $v_1^* \to v_2^*$), we obtain

$$\tan\theta_2 = \frac{\sin(\pi - \theta^*)}{\cos(\pi - \theta^*) + V/v_2^*}. \tag{18.40}$$

On the other hand, since $v_2 = 0$, it follows from (18.9), mutatis mutandis, that

$$P = (m + M)V = mv_0 = m\frac{m + M}{m}v_2^* = (m + M)v_2^*, \tag{18.41}$$

that is,

$$\frac{V}{v_2^*} = 1. \tag{18.42}$$

Equation (18.40) thus reduces to

$$\tan\theta_2 = \frac{\sin(\pi - \theta^*)}{\cos(\pi - \theta^*) + 1} = \tan\tfrac{1}{2}(\pi - \theta^*), \tag{18.43}$$

whence

$$\theta_2 = \tfrac{1}{2}(\pi - \theta^*). \tag{18.44}$$

Since θ^* can take any value between 0 and π, the target particle, which was initially at rest in the laboratory system, according to this result can only move within an angle contained in the interval $\theta_2 \in [0, \pi/2]$, that is, within the forward hemisphere. In the CM system, before the collision, the two particles, target and projectile, approach each other along the same line with equal magnitude momentum, and separate in opposite directions after the collision. Thus, if the projectile, seen from this reference frame, is scattered at an angle θ^* with respect to the incident direction, the target will recoil forming an angle $\theta_{2CM} = \pi - \theta^*$. It follows that the scattering cross section for the target is

$$\sigma'(\theta_{2CM}) = \sigma'(\pi - \theta^*). \tag{18.45}$$

As in problem P18.2, we have assumed that the scattering potential is central, so that there is symmetry around the axis of incidence. Proceeding with the target as we did with particle 1 in problem P18.3, we obtain

$$\sigma'(\theta_2) = \sigma'(\theta_{2CM}) \left| \frac{\sin\theta_{2CM}}{\sin\theta_2} \right| \left| \frac{d\theta_{2CM}}{d\theta_2} \right|, \tag{18.46}$$

where θ_2 is the recoil angle of the target as seen in the laboratory system. On the other hand, in the previous problem it was shown that the recoil angle of the target in the laboratory system is related to θ^* by the expression

$$\theta_2 = \tfrac{1}{2}(\pi - \theta^*) = \tfrac{1}{2}\theta_{2CM}. \tag{18.47}$$

From this it follows that

$$\frac{\sin\theta_{2CM}}{\sin\theta_2} = \frac{\sin 2\theta_2}{\sin\theta_2} = 2\cos\theta_2, \tag{18.48}$$

that is,

$$\frac{d\theta_{2CM}}{d\theta_2} = 2. \tag{18.49}$$

Substituting these results in (18.46) we obtain

$$\sigma'(\theta_2) = 4\sigma'(\theta_{2CM})\cos\theta_2. \tag{18.50}$$

Since in the CM system the scattering is spherically symmetric, it does not depend on θ^*; consequently, $\sigma'(\theta_{2CM})$ also does not depend on this angle, and the angular cross section for the target takes the form

$$\sigma'(\theta_2) = A\cos\theta_2, \tag{18.51}$$

with A a constant. It is interesting to note that this expression predicts that the target particles recoil with maximum probability in the incident direction; for recoils close to $\pi/2$ the probability is practically zero.

P18.5 A beam of particles with density n_0 part/cm^3 is fired at a target with total effective cross section σ. Show that if the thickness of the target is d, the beam that crosses it comes out with density $n = n_0 e^{-\mu d}$, where $\mu = N\sigma$ is the so-called linear attenuation coefficient and N is the number of collision centers that the target contains per unit volume.

Solution. In a scattering experiment, particles are typically counted within the solid angle $d\Omega$ defined by the detector window placed in a predetermined direction. If, as usual, the scattering cross section $\sigma = \int \sigma' d\Omega$ is written as $\sigma = \pi a^2$ (i.e., as an effective area around the target with scattering radius a), then incident particles approaching the target with impact parameter $b \leq a$ will be scattered at angles $\geq \theta$ and thus will not be detected by a detector placed at that angle relative to the incidence direction.

Consider a target consisting of a homogeneous sheet with area A and thickness δz sufficiently small that the individual scattering cross sections σ of constituent

particles don't overlap and each projectile particle experiences only one scattering event when crossing the target. If the sheet contains N scattering centers per unit volume, the total number of scatterers is $NA\delta z$. The effective area presented for scattering at angles $\geq \theta$ is

$$A_{\text{ef}} = \sigma N A \delta z. \tag{18.52}$$

Assuming the target area A is uniformly illuminated by the incident beam, the fraction of incident particles scattered at angles $\geq \theta$ is

$$f = \frac{\text{Number of particles scattered at angles } \geq \theta}{\text{Number of incident particles}} = \frac{\sigma N A \delta z}{A} = \sigma N \delta z. \tag{18.53}$$

Consider now a target of finite thickness d, where projectiles may experience multiple scattering events before emerging. To determine the number of emerging projectiles, we model the finite thickness target as a series of infinitesimal layers of thickness dz, each thin enough to apply formula (18.53). Each collision between z and $z + dz$ removes one projectile from the incident beam, reducing the number of particles n_0 reaching subsequent layers. Denoting this reduction by $dn_0(z)$ and applying (18.53), we obtain

$$\frac{dn_0(z)}{n_0(z)} = -\sigma N dz. \tag{18.54}$$

Integrating over the entire target thickness yields the emerging beam density

$$n = n_0 e^{-\sigma N d} = n_0 e^{-\mu d}, \tag{18.55}$$

where $\mu = N\sigma$ is the *linear attenuation coefficient* $\mu = N\sigma$. This shows that the beam intensity decreases exponentially with target thickness.

P18.6 Show that the differential scattering cross section in the Born approximation due to a spherical barrier of radius R and constant height V_0 is

$$\frac{d\sigma}{d\Omega} = \left(\frac{2mV_0}{\hbar^2}\right)^2 \frac{(\sin qR - qR\cos qR)^2}{q^6}. \tag{18.56}$$

Solution. In the Born approximation, the scattering amplitude is given by

$$f(\theta, \varphi) = -\frac{m}{2\pi\hbar^2} \int V(r)\, e^{i\mathbf{q}\cdot\mathbf{r}}\, d^3r. \tag{18.57}$$

In turn, the differential scattering cross section is given in general by the expression

$$\frac{d\sigma}{d\Omega} = |f(\theta, \varphi)|^2. \tag{18.58}$$

Consider a uniform spherical barrier; the corresponding potential can be written in the form

$$V(r) = \begin{cases} V_0, & r \leq R; \\ 0, & r > R. \end{cases} \tag{18.59}$$

From (18.57) it follows that the corresponding scattering amplitude is given by

$$f(\theta,\varphi) = -\frac{mV_0}{2\pi\hbar^2}\int_0^R\int_0^\pi\int_0^{2\pi} e^{i\mathbf{q}\cdot\mathbf{r}} r^2\sin\theta\, d\varphi\, d\theta\, dr. \tag{18.60}$$

The integral

$$I = \int_0^\pi\int_0^{2\pi} e^{iqr\cos\theta}\sin\theta\, d\varphi\, d\theta \tag{18.61}$$

is common to all central potentials and is easily performed if the z-axis of the reference system is oriented in the direction of the vector $\boldsymbol{q}$ and the change of variable $x = \cos\theta$ is made, which leads to

$$I = 2\pi\int_0^\pi e^{iqr\cos\theta}\sin\theta\, d\theta = 2\pi\int_{-1}^1 e^{iqrx}\, dx \tag{18.62}$$

$$= 2\pi\frac{e^{iqr} - e^{-iqr}}{iqr} = \frac{4\pi\sin qr}{qr}. \tag{18.63}$$

With this result in (18.57) we obtain the formula for the scattering amplitude by central potentials,

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int V(r)\, e^{i\mathbf{q}\cdot\mathbf{r}}\, d^3r = -\frac{2m}{\hbar^2 q}\int_0^\infty rV(r)\sin qr\, dr. \tag{18.64}$$

Inserting here the potential (18.59) or, alternatively, substituting in (18.60), we arrive at an integral that is easily performed by parts,

$$f(\theta) = -\frac{2mV_0}{\hbar^2 q}\int_0^R r\sin qr\, dr \tag{18.65}$$

$$= -\frac{2mV_0}{\hbar^2 q}\left[-\frac{r}{q}\cos qr\Big|_0^R + \frac{1}{q}\int_0^R \cos qr\, dr\right] \tag{18.66}$$

$$= -\frac{2mV_0}{\hbar^2 q}\left(-\frac{R}{q}\cos qR + \frac{1}{q^2}\sin qR\right), \tag{18.67}$$

that is,

$$f(\theta) = -\frac{2mV_0}{\hbar^2}\cdot\frac{\sin qR - qR\cos qR}{q^3}, \tag{18.68}$$

where the dependence on the scattering angle (and on the collision energy) is given through the transferred momentum $q = 2k\sin\frac{1}{2}\theta$, $k = \sqrt{2mE}/\hbar$. Substituting this result into (18.58) we obtain the differential scattering cross section for a homogeneous spherical barrier of radius R and constant height V_0 in the first Born approximation,

$$\frac{d\sigma}{d\Omega} = \left(\frac{2mV_0}{\hbar^2}\right)^2\frac{(\sin qR - qR\cos qR)^2}{q^6}. \tag{18.69}$$

P18.7 For the Ramsauer–Townsend effect to occur (see [1], Section 5.3.2), the cross section must vanish at very small bombardment energies (which can be assumed to be zero). Using a uniform spherical well as a model for the interaction potential, find the value that should be assigned to the product a^2V_0. *Hint:* Consider at least the s and p waves.

Solution. We first study the problem in a general form, and then we restrict ourselves to the case of low energies (s wave). The uniform spherical well has the form

$$V(r) = \begin{cases} -V_0, & r \le a, \\ 0, & r > a, \end{cases} \qquad V_0 > 0. \tag{18.70}$$

To analyze the problem in terms of partial waves we start from the radial Schrödinger equation for a component of angular momentum l,

$$\frac{\hbar^2}{2m}\frac{d^2R}{dr^2} + \frac{\hbar^2}{2mr}\frac{dR}{dr} + \left[-\frac{\hbar^2 l(l+1)}{2mr^2} - V(r) + E\right] R = 0, \tag{18.71}$$

with $E > 0$. With the change of variable

$$\rho \equiv \rho_< = k_1 r, \qquad k_1 = \sqrt{\frac{2m(V_0+E)}{\hbar^2}}, \tag{18.72}$$

for the interior region, and

$$\rho_> = kr, \qquad k = \sqrt{\tfrac{2mE}{\hbar^2}} \tag{18.73}$$

for the exterior region, the Schrödinger equation (18.71) can be rewritten as

$$\frac{d^2R}{d\rho_<^2} + \frac{2}{\rho_<}\frac{dR}{d\rho_<} + \left[1 - \frac{l(l+1)}{\rho_<^2}\right] R = 0, \qquad r \le a, \tag{18.74}$$

$$\frac{d^2R}{d\rho_>^2} + \frac{2}{\rho_>}\frac{dR}{d\rho_>} + \left[1 - \frac{l(l+1)}{\rho_>^2}\right] R = 0, \qquad r > a. \tag{18.75}$$

Both equations have as regular solutions the spherical Bessel functions $j_l(\rho)$; the other linearly independent solutions are the spherical Neumann functions $n_l(\rho)$. The solution in the interior ($r \le a$) must be regular at the origin; this eliminates the Neumann functions, and we must write

$$R(r) = Aj_l(k_1 r), \qquad r \le a, \tag{18.76}$$

with A a constant that can be adjusted to normalize the wave function. The solution for the exterior ($r > a$) takes the general form

$$R(r) = Bj_l(kr) + Cn_l(kr), \qquad r > a. \tag{18.77}$$

The ratio B/C is determined from the continuity condition of the logarithmic derivative of R at $r = a$ (the prime denotes differentiation with respect to the

argument itself in each case),

$$k_1 \frac{j_l'(k_1 r)}{j_l(k_1 r)}\Big|_{r=a} = k \frac{B j_l'(kr) + C n_l'(kr)}{B j_l(kr) + C n_l(kr)}\Big|_{r=a}. \tag{18.78}$$

If we write

$$B = \alpha_l \cos\delta_l, \qquad C = -\alpha_l \sin\delta_l, \tag{18.79}$$

then condition (18.78)—that is, the scattering potential—determines the phase shifts δ_l, while the coefficient α_l is determined by A, that is, by the continuity of the amplitude. With this new parametrization, Eq. (18.78) takes the form

$$k_1 \frac{j_l'(k_1 a)}{j_l(k_1 a)} = k \frac{j_l'(ka)\cos\delta_l - n_l'(ka)\sin\delta_l}{j_l(ka)\cos\delta_l - n_l(ka)\sin\delta_l}, \tag{18.80}$$

or

$$k_1 \frac{j_l'(k_1 a)}{j_l(k_1 a)} = k \frac{j_l'(ka) - n_l'(ka)\tan\delta_l}{j_l(ka) - n_l(ka)\tan\delta_l}, \tag{18.81}$$

from which it follows that

$$\tan\delta_l = \frac{k j_l(k_1 a) j_l'(ka) - k_1 j_l(ka) j_l'(k_1 a)}{k j_l(k_1 a) n_l'(ka) - k_1 n_l(ka) j_l'(k_1 a)}. \tag{18.82}$$

The expression (18.82) simplifies considerably for low values of l, since in such a case the explicit forms of the spherical Bessel functions in terms of trigonometric functions can be conveniently used. For example, the formulas

$$j_0(z) = \frac{\sin z}{z}, \qquad j_1(z) = \frac{\sin z}{z^2} - \frac{\cos z}{z} = -j_0'(z); \tag{18.83}$$

$$n_0(z) = -\frac{\cos z}{z}, \qquad n_1(z) = -\frac{\sin z}{z^2} - \frac{\cos z}{z} = -n_0'(z), \tag{18.84}$$

substituted into (18.82) with $l = 0$, give the following (exact) expression for the phase shift of the s wave

$$\tan\delta_0 = \frac{k}{k_1} \frac{\tan k_1 a - (k_1/k)\tan ka}{1 + (k/k_1)\tan ka \tan k_1 a}. \tag{18.85}$$

In turn, the solution (18.77), taking into account (18.79), reduces for the s wave to

$$R = \frac{\alpha_0}{ka} \left(\sin ka \cos\delta_0 + \cos ka \sin\delta_0\right), \tag{18.86}$$

that is,

$$R = \frac{\alpha_0}{ka} \sin(ka + \delta_0). \tag{18.87}$$

Since in the absence of the scattering potential one must take $k_1 = k$, from (18.76) and (18.77) it follows that $C = 0$ and from (18.79) that $\delta_0 = 0$. This shows that δ_0 plays the role of a phase shift of the s wave generated by the presence of the scattering potential.

At sufficiently low energies the condition $ka \ll 1$ holds, and it is possible to simplify considerably Eq. (18.82). Using the asymptotic expressions of the Bessel functions

$$j_l(z) \sim \frac{z^l}{(2l+1)!!}, \qquad j_l'(z) \sim \frac{lz^{l-1}}{(2l+1)!!} = \frac{l}{z} j_l(z), \tag{18.88}$$

$$n_l(z) \sim -\frac{(2l-1)!!}{z^{l+1}}, \qquad n_l'(z) \sim -\frac{(2l-1)!!(l+1)}{z^{l+2}} = -\frac{l+1}{z} n_l(z), \tag{18.89}$$

substituting and simplifying we arrive at

$$\tan\delta_l = \frac{(ka)^{2l+1}}{(2l+1)!!(2l-1)!!} \frac{l j_l(k_1a) - k_1 a j_l'(k_1a)}{(l+1) j_l(k_1a) + k_1 a j_l'(k_1a)}. \tag{18.90}$$

The factor $(ka)^{2l+1}$ in front of this expression implies that $\tan\delta_l$ decreases as the energy is reduced, and decreases more rapidly as l increases. This means, in particular, that the total scattering cross section at low energies is essentially determined only by the first values of l, that is, the s and p waves; the other terms can be ignored. For the case $l = 0$, (18.90) gives

$$\tan\delta_0 = ka \cdot \frac{-k_1 a j_0'(k_1a)}{j_0(k_1a) + k_1 a j_0'(k_1a)} = \frac{k}{k_1} \frac{\sin k_1a - k_1a\cos k_1a}{\cos k_1a} = -ka\left(1 - \frac{\tan k_1a}{k_1a}\right), \tag{18.91}$$

or equivalently,

$$\tan\delta_0 = -ka + \frac{k}{k_1}\tan k_1a. \tag{18.92}$$

Naturally, the same result is obtained by approximating (18.85) to first order in ka,

$$\tan\delta_0 = \frac{k}{k_1}\frac{\tan k_1a - (k_1/k)\tan ka}{1 + (k/k_1)\tan ka \tan k_1a} \approx \frac{k}{k_1}\frac{\tan k_1a - \left(\frac{k_1}{k}\right)ka}{1 + \left(\frac{ka}{k_1a}\right)ka\tan k_1a} \approx \frac{k}{k_1}\left[\tan k_1a - (k_1/k)ka\right]. \tag{18.93}$$

For the p wave, that is $l = 1$, we obtain

$$\tan\delta_1 = \frac{(ka)^3}{3}\frac{j_1(k_1a) - k_1 a j_1'(k_1a)}{2j_1(k_1a) + k_1 a j_1'(k_1a)}, \tag{18.94}$$

or, using (18.88),

$$\tan\delta_1 = ka\left[\left(\frac{k}{k_1}\right)^2 - \tfrac{1}{3}(ka)^2\right] - \frac{(ka)^3}{3k_1a}\cot k_1a. \tag{18.95}$$

The total cross section is given by

$$\sigma = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l. \tag{18.96}$$

Assuming that the energy is sufficiently low so that only the s and p waves are needed to calculate the total cross section, we obtain

$$\sigma = \frac{4\pi}{k^2}\left(\sin^2\delta_0 + 3\sin^2\delta_1\right). \tag{18.97}$$

We see that this cross section will be small only if each of the two contributions is itself small. Since δ_1 is third order in ka, while δ_0 is first order, it follows from (18.90) that for low energies with $ka \ll 1$ we can approximate $\sin\delta_j \sim \tan\delta_j \sim \delta_j$, and write

$$\sigma = 4\pi a^2\left(\frac{1}{k_1 a}\tan k_1 a - 1\right)^2 + 4\pi a^2 \frac{(ka)^4}{9}\left[\frac{3}{(k_1 a)^2} - \frac{1}{k_1 a}\cot k_1 a - 1\right]^2, \tag{18.98}$$

which for the s wave gives

$$\sigma = 4\pi a^2\left(\frac{1}{k_1 a}\tan k_1 a - 1\right)^2. \tag{18.99}$$

This cross section vanishes whenever

$$k_1 a = \tan k_1 a, \tag{18.100}$$

where $k_1 = \sqrt{2m(V_0+E)}/\hbar \approx \sqrt{2mV_0}/\hbar$ (to write the last equality it has been assumed that the energy is very low and can be neglected compared to V_0). The roots of this equation determine the values of a^2V_0 that cancel the s-wave cross section, thus producing the Ramsauer–Townsend effect. The first values are

$$\sqrt{2ma^2V_0}/\hbar = 4.493,\ 7.725,\ 10.904,\ 14.066, \ldots$$

On the other hand, an asymptotic expression for the roots of the equation $\tan x - x = 0$ is

$$x^{(n)} \sim \frac{\pi}{2}\left(2n + 1 - \frac{1}{2n+1} + \cdots\right). \tag{18.101}$$

P18.8 Find the differential cross section for the case where both the target and the projectile have structure.

Solution. To be more specific, we will consider the electric case and assume that the target is an extended electric charge with density $ep(r)$ ($\int \rho(r) d^3r = 1$); in turn, the projectile, also with extended charge, has density $e'\rho'(r)$ ($\int \rho'(r) d^3r = 1$). The interaction between both charges is Coulombian. Denoting with $\boldsymbol{r}$ the position of the projectile's center of mass, with $\boldsymbol{r'}$ the position of each charge element constituting the projectile relative to its center of mass, and with $\boldsymbol{r''}$ the position of the charge elements of the target particle, the interaction potential between target and projectile is

$$V(\boldsymbol{r}) = ee' \int\int \frac{\rho(\boldsymbol{r'})\,\rho'(\boldsymbol{r''})}{|\boldsymbol{r} + \boldsymbol{r'} - \boldsymbol{r''}|} d^3r'\, d^3r'', \tag{18.102}$$

where the integrals extend over the volume occupied by the particles. Substituting this expression into

$$f(\theta,\varphi) = -\frac{m}{2\pi\hbar^2}\int V(\boldsymbol{r})\, e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\, d^3r, \tag{18.103}$$

yields for the scattering amplitude of extended particles in the first Born approximation

$$f\,(\theta) = -\frac{mee'}{2\pi\hbar^2}\int\int\int \frac{\rho\,(\boldsymbol{r}')\,\rho\,(\boldsymbol{r}'')}{|\boldsymbol{r}+\boldsymbol{r}'-\boldsymbol{r}''|}\, e^{iq\cdot\boldsymbol{r}}\; d^3r\; d^3r'\;\; d^3r''. \tag{18.104}$$

With the change of variables $\boldsymbol{r} \to \boldsymbol{R} = \boldsymbol{r}+\boldsymbol{r}'-\boldsymbol{r}''$, the integrand factors conveniently,

$$f(\theta) = -\frac{mee'}{2\pi\hbar^2}\int\int\int \frac{\rho(\boldsymbol{r}')\rho(\boldsymbol{r}'')}{|\boldsymbol{R}|}\, e^{iq\cdot(\boldsymbol{R}-\boldsymbol{r}'+\boldsymbol{r}'')}\; d^3R\; d^3r'\;\; d^3r'' \tag{18.105}$$

$$= -\frac{mee'}{2\pi\hbar^2}\int \frac{e^{iq\cdot\boldsymbol{R}}}{R}\; d^3R \int \rho(\boldsymbol{r}')\, e^{-iq\cdot\boldsymbol{r}'}\; d^3r' \int \rho(\boldsymbol{r}'')e^{iq\cdot\mathbf{r}''}\; d^3r''. \tag{18.106}$$

The second and third integrals are proportional to the Fourier transforms of the charge distributions of the target and projectile, respectively, that is, the corresponding electric form factors

$$F(\mathbf{q}) = \int \rho(\boldsymbol{r}')e^{-iq\cdot\mathbf{r}'}\, d^3r', \tag{18.107}$$

$$G(\mathbf{q}) = \int \rho'(\boldsymbol{r}'')e^{iq\cdot\mathbf{r}''}\, d^3r''. \tag{18.108}$$

When the charge distributions have spherical symmetry, the form factors depend only on the magnitude of $\boldsymbol{q}$. Assuming this is the case, the scattering amplitude becomes (changing the integration variable $\boldsymbol{R} \to \boldsymbol{r}$)

$$f(\theta) = -\frac{me^c}{2\pi\hbar^2}F(q^2)G(q^2)\int \frac{e^{iq\cdot r}}{|r|}d^3r. \tag{18.109}$$

Identifying here the quantity $V(r) = ee'/r$ as the interaction potential between two point charges e and e', the above result can be rewritten as

$$f(\theta) = -\frac{m}{2\pi\hbar^2}F(q^2)G(q^2)\int V(r)e^{iq\cdot r}d^3r, \tag{18.110}$$

or more precisely,

$$f(\theta) = F(q^2)G(q^2)f_{\text{punctual}}(\theta,\varphi). \tag{18.111}$$

It is clear that this result is general, in the sense that it provides the relationship between the point-like scattering amplitude and the corresponding amplitude for the problem with structure. From this it follows that the differential scattering cross section for particles with structure is

$$\left.\frac{d\sigma}{d\Omega}\right|_{\text{extended}} = |F(q^2)|^2\left|G(q^2)\right|^2\left.\frac{d\sigma}{d\Omega}\right|_{\text{point-like}}. \tag{18.112}$$

P18.9 Protons with energy of 0.3 MeV are scattered by a thin sheet of aluminum. The number of backscattered protons is observed to be 0.96 times the predicted value for a Coulomb potential. Interpreting this discrepancy as due to shielding effects and assuming that the corresponding potential change appreciably affects only the s wave, determine the change in the value of δ_0. Indicate whether the interaction is attractive or repulsive.

Solution. The shielding effect causes a change $\Delta\delta_l$ in the phase shifts due to the Coulomb potential. This modifies the scattering amplitude, which instead of being given by

$$f(\theta) = \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)\left(e^{2i\delta_l}-1\right)P_l(\cos\theta), \tag{18.113}$$

is transformed into

$$f(\theta) = \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)\left(e^{2i(\delta_l+\Delta\delta_l)}-1\right)P_l(\cos\theta). \tag{18.114}$$

The factor $e^{2i(\delta_l+\Delta\delta_l)}-1$ can be rewritten as follows

$$e^{2i(\delta_l+\Delta\delta_l)}-1 = e^{2i\delta_l}e^{2i\Delta\delta_l}-1+e^{2i\delta_l}-e^{2i\delta_l} \tag{18.115}$$

$$= \left(e^{2i\delta_l}-1\right)+e^{2i\delta_l}\left(e^{2i\Delta\delta_l}-1\right) \tag{18.116}$$

$$= \left(e^{2i\delta_l}-1\right)+e^{i(2\delta_l+\Delta\delta_l)}\left(e^{i\Delta\delta_l}-e^{-i\Delta\delta_l}\right) \tag{18.117}$$

$$= \left(e^{2i\delta_l}-1\right)+2ie^{i(2\delta_l+\Delta\delta_l)}\sin\Delta\delta_l, \tag{18.118}$$

which allows rewriting (18.114) in the form

$$f(\theta) = \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)\left(e^{2i\delta_l}-1\right)P_l(\cos\theta) \tag{18.119}$$

$$+\frac{1}{k}\sum_{l=0}^{\infty}(2l+1)e^{i(2\delta_l+\Delta\delta_l)}\sin\Delta\delta_l P_l(\cos\theta). \tag{18.120}$$

The first term on the right side corresponds to the scattering amplitude produced by the Coulomb potential (or any other that can be treated similarly); denoting this amplitude by $f_c(\theta)$, we can write

$$f(\theta) = f_c(\theta)+\frac{1}{k}\sum_{l=0}^{\infty}(2l+1)e^{i(2\delta_l+\Delta\delta_l)}\sin\Delta\delta_l P_l(\cos\theta). \tag{18.121}$$

Since by hypothesis the shielding only significantly affects the s wave, we can ignore the corrections for $l \geq 1$ and write

$$f(\theta) = f_c(\theta)+\frac{1}{k}e^{i(2\delta_0+\Delta\delta_0)}\sin\Delta\delta_0. \tag{18.122}$$

Putting this result in the general formula for the differential cross section

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2, \tag{18.123}$$

and setting $\theta = \pi$, we obtain for the backward cross section

$$\left(\frac{d\sigma}{d\Omega}\right)_{\theta=\pi} = \left(\frac{d\sigma}{d\Omega}\right)_{\theta=\pi}^{\text{Ruther}} + \frac{1}{k^2}\sin^2\Delta\delta_0 + 2\text{Re}\left[\frac{1}{k}f_c(\pi)e^{-i(2\delta_0+\Delta\delta_0)}\sin\Delta\delta_0\right]. \tag{18.124}$$

In the s-wave approximation, we can write

$$f_c(\pi) = -\left[\left(\frac{d\sigma}{d\Omega}\right)_{\theta=\pi}^{\text{Ruther}}\right]^{1/2} e^{2i\delta_0}, \tag{18.125}$$

so we obtain

$$\left(\frac{d\sigma}{d\Omega}\right)_{\theta=\pi} = \left(\frac{d\sigma}{d\Omega}\right)_{\theta=\pi}^{\text{Ruther}} + \frac{1}{k^2}\sin^2\Delta\delta_0 - \frac{1}{k}\left[\left(\frac{d\sigma}{d\Omega}\right)_{\theta=\pi}^{\text{Ruther}}\right]^{1/2}\sin 2\Delta\delta_0. \tag{18.126}$$

From the numerical values $m_p = 1.67\times10^{-27}\,\text{kg}$, $E = 0.3\,\text{MeV} = 4.806\times10^{-14}\,\text{J}$, it follows that

$$\frac{1}{k^2} = \frac{\hbar^2}{2mE} = \frac{(1.054\times10^{-34}\,\text{J}\cdot\text{s})^2}{2(1.67\times10^{-27}\,\text{kg})(4.806\times10^{-14}\,\text{J})} = 6.921\times10^{-29}\,\text{m}^2 = 0.692\,\text{barn}, \tag{18.127}$$

$$\frac{1}{k} = 8.319\times10^{-15}\,\text{m}. \tag{18.128}$$

Writing also $e^2 \simeq \hbar c/137 = 2.308\times10^{-28}\,\text{J}\cdot\text{m}$, and approximating the differential Rutherford scattering cross section with the expression

$$\left(\frac{d\sigma}{d\Omega}\right)^{\text{Ruther}} = \left[\frac{Z_1Z_2e^2}{4E\sin^2(\theta/2)}\right]^2, \tag{18.129}$$

we obtain for $Z_2 = Z_{\text{Al}} = 13$,

$$\left(\frac{d\sigma}{d\Omega}\right)_{\theta=\pi}^{\text{Ruther}} = \left[\frac{13\,(2.308\times10^{-28}\,\text{J.m})}{4\,(4.806\times10^{-14}\,\text{J})}\right]^2 = 2.436\times10^{-28}\,\text{m}^2/\text{sr} = 2.436\,\text{barn/sr}. \tag{18.130}$$

From the experimental data we know that

$$\left(\frac{d\sigma}{d\Omega}\right)_{\theta=\pi} = 0.96\left(\frac{d\sigma}{d\Omega}\right)_{\theta=\pi}^{\text{Ruther}}, \tag{18.131}$$

from which

$$\left(\frac{d\sigma}{d\Omega}\right)_{\theta=\pi} = 2.339\,\text{barn/sr}. \tag{18.132}$$

Substituting (18.127), (18.128), (18.130) and (18.132) into (18.126), we obtain $2.339 \times 10^{-28} = 2.436 \times 10^{-28} + 0.692 \times 10^{-28} \sin^2 \Delta\delta_0 - 1.298 \times 10^{-27} \sin 2\Delta\delta_0$, which can be rewritten as

$$\sin 2\Delta\delta_0 - 0.5331 \sin^2 \Delta\delta_0 - 7.473 \times 10^{-2} = 0. \tag{18.133}$$

The roots of this equation in $[0, \pi]$ determine the value of $\Delta\delta_0$. These roots are

$$\Delta\delta_0 = 2.2^\circ, \quad \Delta\delta_0 = 72.9^\circ, \tag{18.134}$$

of which only the first should be considered, since the value of δ_0 for the Coulomb phase shift is very small. Given the small value of $\Delta\delta_0$, it is possible to approximate in (18.133) the sine with the arc, which quickly leads to the previous numerical solution. The positive phase shift indicates that it is an attractive interaction.

P18.10 Consider scattering by a uniform spherical well of radius a and (large) depth V_0. Show that the condition for bound states to exist is

$$k_1 a = \left(n + \frac{1}{2}(l+1) \right) \pi,$$

where $k_1^2 = 2m(E + V_0)/\hbar^2$.

Solution. Let us consider the attractive spherical potential well defined by Eq.(18.70); the radial Schrödinger equation is

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} - \frac{l(l+1)}{r^2}R + \frac{2m}{\hbar^2}(V_0 + E)R = 0, \qquad r \le a, \tag{18.135}$$

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} - \frac{l(l+1)}{r^2}R + \frac{2m}{\hbar^2}ER = 0, \qquad r > a. \tag{18.136}$$

We are only interested in the solutions for $E < 0$, since we are looking for bound states. Defining the constants

$$k_1^2 = \frac{2m}{\hbar^2}(V_0 - |E|), \qquad \alpha^2 = \frac{2m|E|}{\hbar^2}, \tag{18.137}$$

we can write

$$\frac{d^2R}{d(k_1 r)^2} + \frac{2}{k_1 r}\frac{dR}{d(k_1 r)} + \left[1 - \frac{l(l+1)}{k_1^2 r^2}\right] R = 0, \qquad r \le a, \tag{18.138}$$

$$\frac{d^2R}{d(i\alpha r)^2} + \frac{2}{i\alpha r}\frac{dR}{d(i\alpha r)} + \left[1 - \frac{l(l+1)}{(i\alpha r)^2}\right] R = 0, \qquad r > a. \tag{18.139}$$

Both equations have as solutions the spherical Bessel functions. To ensure that the appropriate boundary conditions are met, we proceed as follows. The solution for $r \le a$ must be regular at the origin, which eliminates the Neumann functions, and we are left with

$$R(r) = A j_l(k_1 r), \qquad r \le a, \tag{18.140}$$

where A is the normalization constant. The solution for $r > a$ must vanish exponentially as $r \to \infty$; since the spherical Hankel functions of the first kind are the only Bessel functions that behave as e^{iz}, we take as solution

$$R(r) = Bh_l^{(1)}(i\alpha r), \qquad r > a. \tag{18.141}$$

With this choice we have that, indeed, when $r \to \infty$, $h_l^{(1)}(i\alpha r) \sim e^{i(i\alpha r)} = e^{-\alpha r}$. The continuity conditions at $r = a$ lead to the relation

$$\frac{k_1}{j_l(\rho)}\frac{dj_l(\rho)}{d\rho}\Big|_{\rho=k_1 a} = \frac{i\alpha}{h_l^{(1)}(\rho)}\frac{dh_l^{(1)}(\rho)}{d\rho}\Big|_{\rho=i\alpha a}. \tag{18.142}$$

This equation determines the possible bound states, but its exact solution is in general unattainable. Suppose that the potential is so deep that $k_1 a \gg l$; in this case we can use the asymptotic form of the Bessel functions

$$j_l(\rho) \sim \frac{1}{\rho}\cos\left[\rho - \frac{\pi}{2}(l+1)\right], \tag{18.143}$$

$$h_l^{(1)}(\rho) = j_l(\rho) + in_l(\rho) \sim \frac{1}{\rho}\cos\left[\rho - \frac{\pi}{2}(l+1)\right] + i\frac{1}{\rho}\sin\left[\rho - \frac{\pi}{2}(l+1)\right], \tag{18.144}$$

so that

$$\frac{1}{j_l(\rho)}\frac{dj_l(\rho)}{d\rho} \sim -\frac{1}{\rho} - \tan\left[\rho - \frac{\pi}{2}(l+1)\right], \tag{18.145}$$

$$\frac{1}{h_l^{(1)}(\rho)}\frac{dh_l^{(1)}(\rho)}{d\rho} \sim -\frac{1}{\rho} + i. \tag{18.146}$$

With this, equation (18.142) reduces to

$$-\frac{k_1}{\rho} - k_1 \tan\left[\rho - \tfrac{\pi}{2}(l+1)\right]\Big|_{\rho=k_1 a} = -\frac{i\alpha}{\rho} - \alpha\Big|_{\rho=i\alpha a}, \tag{18.147}$$

that is,

$$\tan\left[k_1 a - \tfrac{\pi}{2}(l+1)\right] = \frac{\alpha}{k_1}. \tag{18.148}$$

This is the condition that determines the position of the bound states. To solve it approximately let us note that $\alpha/k_1 = \sqrt{|E|/(V_0 - |E|)}$ becomes very small if $|E| \ll V_0$, so that the condition $k_1 a \gg l$ implies that the tangent must have a value very close to zero. Therefore, as a first approximation we can write

$$k_1 a - \tfrac{\pi}{2}(l+1) \simeq n\pi, \tag{18.149}$$

or

$$k_1 a = \left(n + \tfrac{1}{2}(l+1)\right)\pi, \qquad V_0 \gg \frac{\hbar^2 l^2}{2ma^2}. \tag{18.150}$$

Combining this result with (18.137) we obtain the approximate eigenvalues of the energy,

$$E_{nl} = -V_0 + \frac{\pi^2\hbar^2}{2ma^2}\left(n + \tfrac{1}{2}(l+1)\right)^2. \tag{18.151}$$

P18.11 By solving the radial Schrödinger equation with the scattering potential as a perturbation, derive Eq. [**1**], **(18.110)** for the phase shift when it is small,

$$\delta_l = -\frac{\pi m}{\hbar^2}\int_0^\infty rV(r)J^2_{l+1/2}(kr)\,dr. \tag{18.152}$$

Note that with this procedure we avoid using Eq. [**1**], **(18.109)** .

Solution. Since the unperturbed problem is degenerate (scattered particles all have the same energy regardless of direction), we must apply degenerate perturbation theory, which complicates the treatment. A simpler and more direct approach is as follows.

We start from the original radial Schrödinger equation

$$\frac{d^2R_l(r)}{dr^2} + \left[k^2 - \frac{l(l+1)}{r^2} - \frac{2m}{\hbar^2}V(r)\right]R_l(r) = 0, \quad R_l(0) = 0 \tag{18.153}$$

and the corresponding free-particle equation

$$\frac{d^2g_l(r)}{dr^2} + \left[k^2 - \frac{l(l+1)}{r^2}\right]g_l(r) = 0, \quad g_l(0) = 0. \tag{18.154}$$

Multiplying (18.153) by g_l and (18.154) by R_l, then subtracting, we obtain

$$R_l(r)\frac{d^2g_l(r)}{dr^2} - g_l(r)\frac{d^2R_l(r)}{dr^2} = \frac{2m}{\hbar^2}V(r)R_l(r)g_l(r). \tag{18.155}$$

Integrating over $r \in [0, \rho]$ yields

$$\left[g_l\frac{dR_l}{dr} - R_l\frac{dg_l}{dr}\right]_{r=\rho} = \frac{2m}{\hbar^2}\int_0^\rho V(\tau)R_l(\tau)g_l(\tau)d\tau. \tag{18.156}$$

The free radial solution has the form

$$g_l(r) = krj_l(kr), \tag{18.157}$$

where $j_l(kr)$ is the spherical Bessel function. Since (18.156) is homogeneous (bilinear) in g_l and R_l, the results are independent of normalization factors. For the asymptotic solution ($\rho \to \infty$), we approximate

$$g_l(r) = \sin(kr - \tfrac{1}{2}l\pi), \tag{18.158}$$

$$R_l(r) = \sin\left(kr - \tfrac{1}{2}l\pi + \delta_l\right). \tag{18.159}$$

With these substitutions, Eq. (18.156) reduces to

$$k\sin\delta_l = -\frac{2m}{\hbar^2}\int_0^\infty V(r)R_l(r)g_l(r)dr. \tag{18.160}$$

This result is exact but formal, since the sought phase δ_l is expressed in terms of itself through $R_l(r)$. To obtain a useful expression, although approximate, for δ_l, let us observe that the difference between the radial functions $R_l(r)$ and $g_l(r)$ is due

to the presence of the scattering potential; if we consider this as a perturbation, to lowest order we can replace $R_l(r)$ with $g_l(r)$, which leads to

$$\sin\delta_l \approx -\frac{2m}{\hbar^2 k}\int_0^\infty V\left(r\right) g_l^2\left(r\right)\, dr = -\frac{2mk}{\hbar^2}\int_0^\infty V\left(r\right) j_l^2\left(kr\right)\, r^2 dr. \tag{18.161}$$

The requested form for δ_l is obtained from here by introducing the relation

$$j_l\left(kr\right) = \sqrt{\frac{\pi}{2kr}} J_{l+1/2}\left(kr\right), \tag{18.162}$$

and approximating for small phase shifts $\sin\delta_l \sim \delta_l$.

P18.12 Show that the condition: incident wave flux = outgoing wave flux, implies that $|\widehat{S}|^2 = 1$.

Solution. The condition, flux of the incident wave = flux of the outgoing wave, means that if we calculate the total flux of particles through a spherical surface in the asymptotic region centered at the origin of coordinates, the result must be zero. We write this condition in the form

$$J = \int\limits_{\Omega} J_r r^2 d\Omega = 0, \tag{18.163}$$

with the radial flux given by

$$J_r = \frac{\hbar}{2im}\left(\psi^*\frac{\partial\psi}{\partial r} - \psi\frac{\partial\psi^*}{\partial r}\right). \tag{18.164}$$

To perform the calculation we start from the general expression for the asymptotic solution, which we write for convenience in the form

$$\psi(r,\theta) = \sum_{l=0}^{\infty}(2l+1)i^l\frac{\chi_l(r)}{kr}P_l(\cos\theta). \tag{18.165}$$

The function $\chi_l(r)$ can be expressed in the asymptotic region as

$$\chi_l(r) \sim \sin(kr - \frac{\pi}{2}l + \delta_l)e^{i\delta_l}, \tag{18.166}$$

with δ_l the phase shift of the l wave. From (18.165) it follows that

$$\frac{\partial\psi}{\partial r} = \sum_{l=0}^{\infty}(2l+1)i^l\frac{1}{kr}\left[\frac{d\chi_l(r)}{dr} - \frac{1}{r}\chi_l(r)\right]P_l(\cos\theta). \tag{18.167}$$

The second term on the right side is of order $O(r^{-2})$, which implies that multiplying it by $r^2\psi^*$ gives a contribution of order $O(r^{-1})$, which when integrated over a sphere of infinite radius vanishes. For the determination of the flux it is then sufficient to

retain the first term, so we write

$$\psi^*\frac{\partial\psi}{\partial r}=\sum_{l=0}^{\infty}\sum_{l'=0}^{\infty}(2l+1)(2l'+1)\frac{i^l(-i)^{l'}}{k^2r^2}\chi_l^*(r)\frac{d\chi_{l'}(r)}{dr}P_l(\cos\theta)P_{l'}(\cos\theta)+\cdots; \tag{18.168}$$

$$\psi\frac{\partial\psi^*}{\partial r}=\sum_{l=0}^{\infty}\sum_{l'=0}^{\infty}(2l+1)(2l'+1)\frac{i^l(-i)^{l'}}{k^2r^2}\chi_l(r)\frac{d\chi_{l'}^*(r)}{dr}P_l(\cos\theta)P_{l'}(\cos\theta)+\cdots. \tag{18.169}$$

The total flux is then given by

$$J=-\frac{i\hbar}{2m}\int\left(\psi^*\frac{\partial\psi}{\partial r}-\psi\frac{\partial\psi^*}{\partial r}\right)r^2\sin\theta\,d\theta\,d\varphi \tag{18.170}$$

$$=-\frac{i\hbar}{2mk^2}2\pi\left\{\sum_{l=0}^{\infty}\sum_{l'=0}^{\infty}\left[(2l+1)(2l'+1)i^l(-i)^{l'}\right]\times\left[\chi_l^*(r)\frac{d\chi_{l'}(r)}{dr}-(-1)^{l-l'}\chi_l(r)\frac{d\chi_{l'}^*(r)}{dr}\right]\right.$$
$$\left.\times\int_0^{\pi}P_l(\cos\theta)P_{l'}(\cos\theta)\sin\theta\,d\theta\right\}. \tag{18.171}$$

With the orthogonality condition of the Legendre polynomials

$$\int_0^{\pi}P_l(\cos\theta)P_{l'}(\cos\theta)\sin\theta\,d\theta=\frac{2}{2l+1}\delta_{ll'}, \tag{18.172}$$

the previous result reduces to

$$J=\frac{2\pi\hbar}{imk^2}\sum_{l=0}^{\infty}(2l+1)\left[\chi_l^*(r)\frac{d\chi_l(r)}{dr}-\chi_l(r)\frac{d\chi_l^*(r)}{dr}\right], \tag{18.173}$$

an expression that must be evaluated at $r\to\infty$. From (18.166) and its derivative, both valid in the asymptotic region,

$$\frac{d\chi_l(r)}{dr}\sim k\cos\left(kr-\frac{\pi}{2}l+\delta_l\right)e^{i\delta_l}, \tag{18.174}$$

it follows that

$$\chi_l^*(r)\frac{d\chi_l(r)}{dr}-\chi_l(r)\frac{d\chi_l^*(r)}{dr} \tag{18.175}$$

$$=ke^{i(\delta_l-\delta_l^*)}\left[\sin\left(kr-\frac{\pi}{2}l+\delta_l^*\right)\cos\left(kr-\frac{\pi}{2}l+\delta_l\right)-\sin\left(kr-\frac{\pi}{2}l+\delta_l\right)\cos\left(kr-\frac{\pi}{2}l+\delta_l^*\right)\right], \tag{18.176}$$

$$=-ke^{i(\delta_l-\delta_l^*)}\sin(\delta_l-\delta_l^*). \tag{18.177}$$

The total flux over the sphere at infinity results in thus given by

$$J=\frac{2\pi i\hbar}{mk}\sum_{l=0}^{\infty}(2l+1)e^{i(\delta_l-\delta_l^*)}\sin(\delta_l-\delta_l^*). \tag{18.178}$$

The condition $J = 0$, Eq. (18.163), is satisfied only if $\delta_l = \delta_l^*$, that is, for real phase shifts. This condition corresponds to elastic scattering, since, as demonstrated in [**1**], **Section 20.7**, complex phase shifts are equivalent to the introduction of absorption and, as follows from the present discussion, imply a non-unitary S matrix. In this case, from the definition for the l element of the (elastic) scattering matrix,

$$S_l(k) = e^{2i\delta_l}, \tag{18.179}$$

it follows that

$$S_l^*(k) = e^{-2i\delta_l}, \tag{18.180}$$

$$|S_l|^2 = 1, \tag{18.181}$$

which is the requested result.

An alternate way to reach the same conclusion is the following. We write (18.165) in the asymptotic region in the following form, with $S_l = e^{2i\delta_l}$,

$$\psi(r,\theta) = \sum_{l=0}^{\infty}(2l+1)i^l \frac{e^{i\delta_l}}{kr} \sin\left(kr - \frac{1}{2}l\pi + \delta_l\right) P_l(\cos\theta) \tag{18.182}$$

$$= \sum_{l=0}^{\infty}(2l+1)i^l \frac{1}{2ikr}\left[S_l e^{i(kr-l\pi/2)} - e^{-i(kr-l\pi/2)}\right] P_l(\cos\theta). \tag{18.183}$$

This expression includes both outgoing and incoming waves, which can be identified as

$$\psi_l^{\text{in}} = -(2l+1)\frac{i^l e^{-i(kr-\frac{l\pi}{2})}}{2i} P_l(\cos\theta), \tag{18.184}$$

$$\psi_l^{\text{out}} = (2l+1)\frac{i^l S_l e^{i(kr-\frac{l\pi}{2})}}{2i} P_l(\cos\theta). \tag{18.185}$$

With this identification and (18.164) we obtain for the incoming and outgoing radial flux

$$|J_{\text{in}}| = \frac{\hbar k}{4m}\frac{(2l+1)^2}{k^2r^2} P_l^2(\cos\theta), \tag{18.186}$$

$$|J_{\text{out}}| = \frac{\hbar k}{4m}\frac{(2l+1)^2}{k^2r^2} |S_l|^2 P_l^2(\cos\theta). \tag{18.187}$$

As in the previous demonstration, we can ignore terms that go as r^{-3}, since in the asymptotic limit $r \to \infty$ they do not contribute to the total flux. The condition $|J_{\text{in}}| = |J_{\text{out}}|$ now leads directly to (18.181), $|S_l|^2 = 1$.

P18.13 Show that the flux J through a spherical surface of radius $r \to \infty$ is given, in the case of elastic scattering, by

$$J = v\left(\sigma - \frac{4\pi}{k}\,\text{Im}\, f(0)\right). \tag{18.188}$$

Solution. From (18.113) we have with $\theta = 0$ and $P_l(1) = 1$,

$$f(0) = \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)\left(e^{2i\delta_l}-1\right). \tag{18.189}$$

It follows that

$$\operatorname{Im} f(0) = \frac{f(0)-f^*(0)}{2i} = -\frac{1}{4k}\sum_{l=0}^{\infty}(2l+1)\left(e^{2i\delta_l}+e^{-2i\delta_l}-2\right). \tag{18.190}$$

On the other hand, from Eq. (18.95) and the equalities

$$\sin^2\delta_l = \left|e^{i\delta_l}\sin\delta_l\right|^2 = \left|\frac{e^{2i\delta_l}-1}{2i}\right|^2, \tag{18.191}$$

it follows that the total (elastic) scattering cross section can be written as

$$\sigma = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\frac{1}{4}\left(e^{2i\delta_l}-1\right)\left(e^{-2i\delta_l^*}-1\right), \tag{18.192}$$

$$\sigma = \frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\left(e^{2i(\delta_l-\delta_l^*)}+1\right) - \frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\left(e^{2i\delta_l}+e^{-2i\delta_l^*}\right). \tag{18.193}$$

Combining with (18.190) we obtain

$$\sigma - \frac{4\pi}{k}\operatorname{Im} f(0) = \frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\left(e^{2i(\delta_l-\delta_l^*)}-1\right) \tag{18.194}$$

$$= \frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)e^{i(\delta_l-\delta_l^*)}\left(e^{i(\delta_l-\delta_l^*)}-e^{-i(\delta_l-\delta_l^*)}\right) \tag{18.195}$$

$$= \frac{2\pi i}{k^2}\sum_{l=0}^{\infty}(2l+1)e^{i(\delta_l-\delta_l^*)}\sin(\delta_l-\delta_l^*). \tag{18.196}$$

Since the velocity of the incident particles is $v = \hbar k/m$, it is possible to write this result in the form

$$v\left(\sigma - \frac{4\pi}{k}\operatorname{Im} f(0)\right) = \frac{2\pi i\hbar}{mk}\sum_{l=0}^{\infty}(2l+1)e^{i(\delta_l-\delta_l^*)}\sin(\delta_l-\delta_l^*). \tag{18.197}$$

Comparing with (18.178) we recognize that the right-hand side of this expression represents the flux integrated over the surface of the sphere at infinity, so that we can write

$$J = v\left(\sigma - \frac{4\pi}{k}\operatorname{Im} f(0)\right), \tag{18.198}$$

which is the required result. As we saw in the previous exercise, conservation of flux implies that $J = 0$, an observation which leads directly to the optical theorem,

$$\sigma = \frac{4\pi}{k} \operatorname{Im} f(0). \tag{18.199}$$

Since for this proof it was not required that the phase shifts be real, the optical theorem is demonstrated for both elastic and inelastic collisions.

An illustrative application of the optical theorem is the following. From (18.58) it follows that

$$\left(\frac{d\sigma}{d\Omega}\right)_{\theta=0} = |f(0)|^2, \tag{18.200}$$

and taking into account that $|f(0)|^2 \geq [\operatorname{Im} f(0)]^2$, it follows immediately from (18.199) that

$$\left(\frac{d\sigma}{d\Omega}\right)_{\theta=0} \geq \left(\frac{k}{4\pi}\right)^2 \sigma_{\text{total}}^2. \tag{18.201}$$

P18.14 Determine the scattering amplitude and the differential cross section in Born's first approximation for the potential $V_0\delta(r - R)$.
Solution. The given potential is

$$V(r) = V_0\delta(r - R). \tag{18.202}$$

In the first Born approximation, the scattering amplitude for a central potential is

$$f(\theta) = -\frac{2m}{\hbar^2 q} \int_0^\infty rV(r) \sin(qr)\, dr, \tag{18.203}$$

where $q = 2k \sin(\theta/2)$ is the momentum transfer, $k = \sqrt{2mE}/\hbar$ is the incident wave number and E is the incident particle energy. Substituting $V(r) = V_0\delta(r - R)$ into the integral

$$\int_0^\infty rV_0\delta(r - R) \sin(qr)\, dr, \tag{18.204}$$

and using the key property of Dirac's delta

$$\int_{-\infty}^\infty f(x)\delta(x - a)\, dx = f(a), \tag{18.205}$$

we write

$$\int_0^\infty r\delta(r - R) \sin(qr)\, dr = R \sin(qR), \tag{18.206}$$

since the delta "selects" the value at $r = R$. Substituting the integral result into $f(\theta)$

$$f(\theta) = -\frac{2m}{\hbar^2 q} \cdot V_0 R \sin(qR) \tag{18.207}$$

and simplifying, we get

$$f(\theta) = -\frac{2mV_0R}{\hbar^2 q}\sin(qR). \tag{18.208}$$

The differential cross section is defined as

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2. \tag{18.209}$$

Calculating the squared modulus of $f(\theta)$, we obtain the final result,

$$\frac{d\sigma}{d\Omega} = \left(\frac{2mV_0R}{\hbar^2 q}\right)^2 \sin^2(qR). \tag{18.210}$$

P18.15 Find the differential and total cross sections in Born's first approximation for the Gaussian potential $V_0 \exp(-\alpha^2 r^2)$.

Solution. For the Gaussian potential $V(r) = V_0 e^{-a^2 r^2}$, in the first Born approximation the scattering amplitude $f(\theta)$ is calculated using

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int V(r) e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\, d^3r. \tag{18.211}$$

Since the potential is spherically symmetric, the integral is evaluated in spherical coordinates,

$$f(\theta) = -\frac{2mV_0}{\hbar^2 q}\int_0^\infty e^{-a^2r^2}\sin(qr)\, r\, dr \tag{18.212}$$

The integral gives

$$\int_0^\infty e^{-a^2r^2}\sin(qr)\, r\, dr = \frac{\sqrt{\pi}q}{4a^3}e^{-q^2/(4a^2)}. \tag{18.213}$$

Substituting this result into the expression for $f(\theta)$, we get

$$f(\theta) = -\frac{2mV_0}{\hbar^2 q}\cdot\frac{\sqrt{\pi}q}{4a^3}e^{-q^2/(4a^2)} = -\frac{mV_0\sqrt{\pi}}{2\hbar^2 a^3}e^{-q^2/(4a^2)}. \tag{18.214}$$

The differential cross section $d\sigma/d\Omega$ is given by $|f(\theta)|^2$, so

$$\frac{d\sigma}{d\Omega} = \left(\frac{mV_0\sqrt{\pi}}{2\hbar^2 a^3}\right)^2 e^{-q^2/(2a^2)} = \frac{m^2V_0^2\pi}{4\hbar^4 a^6}e^{-q^2/(2a^2)}, \tag{18.215}$$

where $q = 2k\sin(\theta/2)$ is the magnitude of the momentum transfer vector, and $k = (\sqrt{2mE})/\hbar$ is the wave number.

For the total cross section σ, we integrate $d\sigma/d\Omega$ over all solid angles,

$$\sigma = \int \frac{d\sigma}{d\Omega}\, d\Omega = 2\pi\int_0^\pi \frac{d\sigma}{d\Omega}\sin\theta\, d\theta. \tag{18.216}$$

Changing the integration variable to q, with $\sin\theta\, d\theta = q/k^2\, dq$, and limits from $q = 0$ to $q = 2k$,

$$\sigma = 2\pi \int_0^{2k} \frac{m^2 V_0^2 \pi}{4\hbar^4 a^6} e^{-q^2/(2a^2)} \frac{q}{k^2}\, dq = \frac{\pi^2 m^2 V_0^2}{2\hbar^4 k^2 a^6} \int_0^{2k} e^{-q^2/(2a^2)} q\, dq. \tag{18.217}$$

The integral gives

$$\int_0^{2k} e^{-q^2/(2a^2)} q\, dq = a^2 \left(1 - e^{-2k^2/a^2}\right), \tag{18.218}$$

therefore,

$$\sigma = \frac{\pi^2 m^2 V_0^2}{2\hbar^4 k^2 a^6} \cdot a^2 \left(1 - e^{-2k^2/a^2}\right) = \frac{\pi^2 m^2 V_0^2}{2\hbar^4 k^2 a^4} \left(1 - e^{-2k^2/a^2}\right). \tag{18.219}$$

Expressing k^2 in terms of the energy E, we obtain the final result,

$$\sigma = \frac{\pi^2 m^2 V_0^2}{2\hbar^4} \cdot \frac{\hbar^2}{2mEa^4} \left(1 - e^{-2k^2/a^2}\right) = \frac{\pi^2 m V_0^2}{4\hbar^2 E a^4} \left(1 - e^{-4mE/(\hbar^2 a^2)}\right), \tag{18.220}$$

where $2k^2/a^2 = 4mE/(\hbar^2 a^2)$.

P18.16 Particles of mass m are incident on a central potential of the form

$$V(r) = \begin{cases} \infty, & r < a, \\ -V_0, & a \le r \le 2a, \\ 0, & r > 2a, \end{cases}$$

$V_0 > 0$. Show that the cross section σ is such that

$$\lim_{v \to 0} \sigma = 4\pi \left[k_0^{-1} \tan(k_0 a) - 2a\right]^2,$$

with $k_0 = (2mV_0/\hbar^2)^{1/2}$.

Solution. In low-energy scattering, only the s-wave ($l = 0$) contributes significantly. The cross section is related to the scattering length a_s by

$$\sigma = 4\pi a_s^2. \tag{18.221}$$

Our goal is to compute a_s for this potential. The radial wave function $u(r) = rR(r)$ satisfies the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + V(r)u = Eu. \tag{18.222}$$

For $l = 0$, this simplifies to

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2}[E - V(r)]u = 0. \tag{18.223}$$

We consider the low-energy limit: $E = \frac{\hbar^2 k^2}{2m} \to 0$, so $k \to 0$.

Region I: $r < a$. Since $V(r) = \infty$, the wave function must vanish,

$$u(r) = 0. \tag{18.224}$$

Region II: $a \leq r \leq 2a$. Here, $V(r) = -V_0$, and $E \approx 0$, so the equation becomes

$$\frac{d^2u}{dr^2} + k_0^2 u = 0, \quad \text{where } k_0 = \sqrt{\frac{2mV_0}{\hbar^2}}. \tag{18.225}$$

The general solution is

$$u(r) = A\sin[k_0(r-a)] + B\cos[k_0(r-a)]. \tag{18.226}$$

Applying the boundary condition $u(a) = 0$, we get $B = 0$, so:

$$u(r) = A\sin[k_0(r-a)]. \tag{18.227}$$

Region III: $r > 2a$. Here, $V(r) = 0$, and $k \to 0$, so the equation becomes

$$\frac{d^2u}{dr^2} = 0. \tag{18.228}$$

The general solution is

$$u(r) = C(r - a_s), \tag{18.229}$$

where a_s is the scattering length.

We require continuity of $u(r)$ and $u'(r)$ at $r = 2a$. From Region II,

$$u(2a) = A\sin(k_0 a) \tag{18.230}$$

$$u'(2a) = Ak_0\cos(k_0 a). \tag{18.231}$$

From Region III,

$$u(2a) = C(2a - a_s) \tag{18.232}$$

$$u'(2a) = C. \tag{18.233}$$

Matching values and derivatives,

$$A\sin(k_0 a) = C(2a - a_s) \tag{18.234}$$

$$Ak_0\cos(k_0 a) = C. \tag{18.235}$$

Dividing Eq. (18.234) by (18.235)

$$\frac{\sin(k_0 a)}{k_0\cos(k_0 a)} = 2a - a_s \quad \Rightarrow \quad \frac{\tan(k_0 a)}{k_0} = 2a - a_s, \tag{18.236}$$

and solving for a_s,

$$a_s = 2a - \frac{\tan(k_0 a)}{k_0}. \tag{18.237}$$

we get for the low-energy cross section

$$\sigma = 4\pi a_s^2 = 4\pi\left(\frac{\tan(k_0 a)}{k_0} - 2a\right)^2. \tag{18.238}$$

P18.17 The scattering amplitude for a certain interaction is given by

$$f(\theta) = \frac{1}{k}\left(e^{ika}\sin ka + 3ie^{2ika}\cos\theta\right), \tag{18.239}$$

where a is the characteristic length of the interaction potential and k is the wavenumber of the incident particles. Find the differential cross section for s-waves for this interaction.

Solution. Given the scattering amplitude (18.239) we isolate the s-wave ($\ell = 0$) contribution to find the differential cross section. The s-wave scattering amplitude is angle-independent and corresponds to the a_0 coefficient in the partial wave expansion,

$$f_s(\theta) = a_0. \tag{18.240}$$

This coefficient is obtained by integrating $f(\theta)$ over the solid angle, using the property of Legendre polynomials $P_0(\cos\theta) = 1$,

$$a_0 = \frac{1}{2}\int_{-1}^{1} f(\theta)d(\cos\theta). \tag{18.241}$$

We substitute $x = \cos\theta$ and $dx = d(\cos\theta)$,

$$a_0 = \frac{1}{2}\int_{-1}^{1}\frac{1}{k}\left(e^{ika}\sin(ka) + 3ie^{2ika}x\right)dx. \tag{18.242}$$

and separate into two integrals,

$$a_0 = \frac{1}{2k}\left[e^{ika}\sin(ka)\int_{-1}^{1}dx + 3ie^{2ika}\int_{-1}^{1}xdx\right]. \tag{18.243}$$

Since $\int_{-1}^{1}dx = 2$ and $\int_{-1}^{1}xdx = 0$, we get

$$a_0 = \frac{1}{2k}\left[e^{ika}\sin(ka)\cdot 2 + 0\right] = \frac{1}{k}e^{ika}\sin(ka). \tag{18.244}$$

The s-wave scattering amplitude is

$$f_s(\theta) = \frac{1}{k}e^{ika}\sin(ka), \tag{18.245}$$

and the s-wave differential cross section is

$$\frac{d\sigma_s}{d\Omega} = |f_s(\theta)|^2 = \left|\frac{1}{k}e^{ika}\sin(ka)\right|^2. \tag{18.246}$$

Since $|e^{ika}| = 1$ and $\sin(ka)$ is real, the result is

$$\frac{d\sigma_s}{d\Omega} = \frac{1}{k^2}\sin^2(ka). \tag{18.247}$$

P18.18 Determine the phase shifts δ_l produced by the potential $V(r) = g/r^2$. Find the effective differential cross section and verify that it is inversely proportional to

the energy.

Solution. For the potential $V(r) = g/r^2$, the phase shifts δ_l are determined using the Born approximation for small phase shifts, given by

$$\delta_l = -\frac{2mk}{\hbar^2} \int_0^\infty r^2 j_l^2(kr) V(r)\, dr. \tag{18.248}$$

Substituting $V(r) = g/r^2$, we have

$$\delta_l = -\frac{2mk}{\hbar^2} \int_0^\infty r^2 j_l^2(kr) \frac{g}{r^2}\, dr = -\frac{2mkg}{\hbar^2} \int_0^\infty j_l^2(kr)\, dr. \tag{18.249}$$

The integral $\int_0^\infty j_l^2(kr)\, dr$ is evaluated using the property of spherical Bessel functions,

$$\int_0^\infty j_l^2(x)\, dx = \frac{\pi}{2(2l+1)}. \tag{18.250}$$

With the change of variable $x = kr$, $dr = dx/k$, we obtain

$$\int_0^\infty j_l^2(kr)\, dr = \frac{1}{k} \int_0^\infty j_l^2(x)\, dx = \frac{1}{k} \cdot \frac{\pi}{2(2l+1)} = \frac{\pi}{2k(2l+1)}. \tag{18.251}$$

Substituting into the expression for δ_l, we obtain

$$\delta_l = -\frac{mg\pi}{\hbar^2(2l+1)}. \tag{18.252}$$

These phase shifts are constant, independent of the energy E, and depend only on the quantum number l.

The differential cross section is obtained from the scattering amplitude $f(\theta)$, given by equation

$$f(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1)(e^{2i\delta_l} - 1) P_l(\cos\theta). \tag{18.253}$$

Substituting δ_l,

$$f(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) \left(e^{-\frac{2img\pi}{\hbar^2(2l+1)}} - 1 \right) P_l(\cos\theta). \tag{18.254}$$

The differential cross section is given by $d\sigma/d\Omega = |f(\theta)|^2$,

$$\frac{d\sigma}{d\Omega} = \left| \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) \left(e^{-\frac{2img\pi}{\hbar^2(2l+1)}} - 1 \right) P_l(\cos\theta) \right|^2 \tag{18.255}$$

$$= \frac{1}{4k^2} \left| \sum_{l=0}^{\infty} (2l+1) \left(e^{-\frac{2img\pi}{\hbar^2(2l+1)}} - 1 \right) P_l(\cos\theta) \right|^2. \tag{18.256}$$

Since $k = \sqrt{2mE}/\hbar$, we have $k^2 = 2mE/\hbar^2$, so $1/k^2 \propto 1/E$. The sum in the expression for $d\sigma/d\Omega$ is independent of E, since δ_l does not depend on E. Therefore, the differential cross section is inversely proportional to the energy,

$$\frac{d\sigma}{d\Omega} \propto \frac{1}{E}. \tag{18.257}$$

This verifies that the differential cross section is inversely proportional to the energy.

CHAPTER 19

Relativistic Equations. An Introduction

P19.1 Solve the Klein-Gordon equation for an isotropic attractive potential of depth V_0 and radius a; find the continuity conditions at $r = a$. Obtain the minimum value of V_0 needed to bind a particle of mass m.

Solution. The Klein–Gordon equation for a free particle

$$\Box\Psi - \frac{m^2c^2}{\hbar^2}\Psi = 0, \tag{19.1}$$

with

$$\Box = \nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}, \tag{19.2}$$

can be reexpressed in terms of the four-vector

$$\hat{p}_\mu = -i\hbar\partial_\mu \tag{19.3}$$

in the form

$$\left(\hat{p}_\mu\hat{p}_\mu + m^2c^2\right)\Psi = 0, \tag{19.4}$$

where the index μ takes the values $\mu = 1, 2, 3, 4$ and $x_4 = ict$, so that it follows that $\Box = -\hat{p}_\mu\hat{p}_\mu/\hbar^2$. The present problem requires extending this equation to the case where the particle is under the action of a central scalar potential. To construct this generalization we can apply the principle of minimal coupling, which is known to be effective both in the classical case and in nonrelativistic quantum mechanics, and is also applicable in the relativistic context. This principle consists of making the substitutions

$$\hat{E} = i\hbar\frac{\partial}{\partial t} \;\rightarrow\; i\hbar\frac{\partial}{\partial t} - e\phi = i\hbar\frac{\partial}{\partial t} + ieA_4, \tag{19.5}$$

$$\hat{\boldsymbol{p}} = -i\hbar\nabla \;\rightarrow\; -i\hbar\nabla - \frac{e}{c}\boldsymbol{A}, \tag{19.6}$$

with $A_4 = i\phi$; note that the commonly called "scalar potential" ϕ is in fact the fourth component of the four-vector $A_\mu = (\boldsymbol{A}, i\phi)$. In terms of this four-vector, the principle of minimal coupling is expressed as

$$\hat{p}_\mu \rightarrow \hat{p}_\mu - \frac{e}{c}A_\mu, \tag{19.7}$$

and it leads directly to the Klein–Gordon equation, which describes the behavior of a particle in the presence of an electromagnetic field,

$$\left(\hat{p}_\mu - \frac{e}{c}A_\mu\right)\left(\hat{p}_\mu - \frac{e}{c}A_\mu\right)\Psi + m^2c^2\Psi = 0. \tag{19.8}$$

For the study of stationary states it is convenient to separate the spatial derivatives from the time derivative, so we write

$$\sum_{i=1}^{3}\left(\hat{p}_i-\frac{e}{c}A_i\right)^2\Psi+\left(\hat{p}_4-\frac{e}{c}A_4\right)^2\Psi+m^2c^2\Psi=0, \tag{19.9}$$

and look for a solution of the form

$$\Psi(r,t)=\psi(r)e^{-iEt/\hbar}. \tag{19.10}$$

With

$$\left(\hat{p}_4-\frac{e}{c}A_4\right)^2\Psi=\left(-\frac{\hbar}{c}\frac{\partial}{\partial t}-\frac{e}{c}A_4\right)^2\Psi=\left(i\frac{E}{c}-\frac{e}{c}A_4\right)^2\Psi=-\left(\frac{E}{c}+\frac{ie}{c}A_4\right)^2\Psi, \tag{19.11}$$

equation (19.9) takes the form (eliminating the common factor $e^{-iEt/\hbar}$)

$$\left(\hat{\boldsymbol{p}}-\frac{e}{c}\boldsymbol{A}\right)^2\psi(r)-\left(\frac{E}{c}+\frac{ie}{c}A_4\right)^2\psi(r)+m^2c^2\psi(r)=0. \tag{19.12}$$

For a central scalar potential

$$eA_4=iV(r),\qquad \boldsymbol{A}=0, \tag{19.13}$$

equation (19.11) reduces to

$$c^2\hat{\boldsymbol{p}}^2\psi(r)-\left[(E-V(r))^2-m^2c^4\right]\psi(r)=0, \tag{19.14}$$

or equivalently,

$$\nabla^2\psi(r)+\frac{1}{\hbar^2c^2}\left[(E-V(r))^2-m^2c^4\right]\psi(r)=0. \tag{19.15}$$

This is the form taken by the stationary Klein–Gordon equation for a static central potential. Equation (19.15) can be solved by comparison with the Schrödinger problem, making the substitution

$$\frac{2m}{\hbar^2}\left[E-V(r)\right]\;\longrightarrow\;\frac{1}{\hbar^2c^2}\left[(E-V(r))^2-m^2c^4\right]. \tag{19.16}$$

Expanding, the correspondence between the relativistic and nonrelativistic values results in

$$E_{\text{non rel}}\;\longrightarrow\;\frac{E^2-m^2c^4}{2mc^2}, \tag{19.17}$$

$$V_{\text{non rel}}\;\longrightarrow\;\frac{2E-V}{2mc^2}V. \tag{19.18}$$

The second of these equivalences is particularly interesting, since it shows how the transition is made from the scalar potential $V_{\text{non rel}}$ to the relativistic potential $V=-ieA_4$ (time component of a four-vector). In particular, the spherical uniform well continues to be a spherical uniform well, although with a slightly modified depth; for other potentials, however, the dependence on r is different in the two

theories. Nevertheless, the modifications are generally small, as can be seen by writing $E = mc^2 + E_{\text{non rel}}$, from which it follows that

$$\begin{aligned}\frac{E^2 - m^2c^4}{2mc^2} &= \frac{1}{2mc^2}(E + mc^2)(E - mc^2) \\ &= \frac{1}{2mc^2}(2mc^2 + E_{\text{non rel}})E_{\text{non rel}} \\ &= \left(1 + \frac{E_{\text{non rel}}}{2mc^2}\right) E_{\text{non rel}}, \end{aligned} \tag{19.19}$$

$$\frac{2E - V}{2mc^2}V = \left(1 + \frac{2E_{\text{non rel}} - V}{2mc^2}\right) V. \tag{19.20}$$

It is clear that in both cases, for small energies compared to the rest energy, the relativistic expressions reduce essentially to the nonrelativistic ones.

We now proceed to solve Eq. (19.15), although omitting details widely covered in [**1**]. Since V depends only on the radial coordinate, it is convenient to use spherical coordinates, in terms of which this equation is written as

$$\begin{aligned}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\psi(r) \\ + \frac{1}{\hbar^2c^2}\left[(E - V(r))^2 - m^2c^4\right]\psi(r) = 0. \end{aligned} \tag{19.21}$$

To separate variables we set

$$\psi(\mathbf{r}) = R(r)Y(\theta, \varphi), \tag{19.22}$$

which leads to

$$\frac{1}{R}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r} + \frac{r^2}{\hbar^2c^2}\left[(E - V(r))^2 - m^2c^4\right] = -\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta} - \frac{1}{Y\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}. \tag{19.23}$$

This equation is equivalent to the pair of differential equations

$$\hbar^2c^2\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r} + \left[(E - V(r))^2 - m^2c^4 - \frac{\lambda}{r^2}\right]R = 0, \tag{19.24}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2} + \frac{\lambda}{\hbar^2c^2}Y = 0, \tag{19.25}$$

where λ is the separation constant. The angular equation (19.25) is exactly the same as the one for the Schrödinger problem, and its solutions are the spherical harmonics with $\lambda = \hbar^2c^2l(l+1)$, $l = 0, 1, 2, \ldots$, and $m = 0, \pm1, \pm2, \ldots$. With this value of λ the radial equation takes the form

$$R'' + \frac{2}{r}R' + \frac{1}{\hbar^2c^2}\left[(E - V(r))^2 - m^2c^4\right]R - \frac{l(l+1)}{r^2}R = 0. \tag{19.26}$$

The change of variable $R = u(r)/r$ leads to a relativistic version of the (one-dimensional) radial Schrödinger equation; however, as follows from (19.26), in this

case, instead of the effective potential associated with the centrifugal term, it is more appropriate to speak of an effective mass, given by the combination of the last two terms. In the present case, we have, with $V_0 > 0$,

$$V(r) = \begin{cases} -V_0, & r \le a, \\ 0, & r > a, \end{cases} \tag{19.27}$$

For $r \le a$, we have that $(E - V(r))^2 - m^2c^4 > 0$ (assuming that the depth of the well exceeds the binding energy), so that Eq. (19.26) reduces to

$$\frac{\partial^2 R}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial R}{\partial \rho} + \left(1 - \frac{l(l+1)}{\rho^2}\right) R = 0, \tag{19.28}$$

where we have set

$$\rho = k_1 r, \qquad k_1^2 = \frac{(E + V_0)^2 - m^2c^4}{\hbar^2 c^2}, \qquad \rho \le k_1 a. \tag{19.29}$$

For $r > a$, we have that $(E - V(r))^2 - m^2c^4 = E^2 - m^2c^4 < 0$, since the binding energy is negative, so the total energy must be less than mc^2. This makes it convenient to write the radial equation in the form

$$\frac{\partial^2 R}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial R}{\partial \rho} + \left(1 - \frac{l(l+1)}{\rho^2}\right) R = 0, \tag{19.30}$$

with

$$\rho = ik_0 r, \qquad k_0^2 = \frac{m^2c^4 - E^2}{\hbar^2 c^2}, \qquad |\rho| > k_0 a. \tag{19.31}$$

As has been discussed, these equations have as solutions the spherical Bessel functions $j_l(\rho)$, the spherical Neumann functions $n_l(\rho)$, and the spherical Hankel functions of the first and second kind $h_l^{(1)}(\rho), h_l^{(2)}(\rho)$. For $r \le a$, one can take $j_l(\rho)$ and $n_l(\rho)$ as linearly independent solutions and write the general solution in the form

$$R(r) = Aj_l(k_1 r) + Bn_l(k_1 r). \tag{19.32}$$

The condition that $R(r)$ be regular at the origin eliminates the Neumann functions $n_l(\rho)$, so that we take $B = 0$,

$$R(r) = Aj_l(\rho), \qquad r \le a. \tag{19.33}$$

For $r > a$, the solutions that correspond to bound states must converge as $r \to \infty$, a behavior that corresponds to the functions $h_l^{(1)}(\rho)$, which decay exponentially at infinity for $\rho = ik_0 r$,

$$R(r) = B\left[j_l(\rho) + in_l(\rho)\right] = Bh_l^{(1)}(\rho), \qquad r > a. \tag{19.34}$$

The function $h_l^{(2)}(\rho)$ cannot appear in the solution because it grows exponentially with r. The energy eigenvalues are obtained from the condition of continuity of the wave function and its derivative at $r = a$. As usual, these two conditions lead

to the condition of continuity of the logarithmic derivative (the prime indicates derivative with respect to the argument),

$$k_1 \frac{j_l'(\rho)}{j_l(\rho)}\bigg|_{\rho=k_1 a} = ik_0 \frac{h_l^{(1)\prime}(\rho)}{h_l^{(1)}(\rho)}\bigg|_{\rho=ik_0 a}. \tag{19.35}$$

Analyzing this boundary condition for arbitrary l is quite complicated. However, we can consider the special case of the s-states, for which $l = 0$. Using the expressions given in [1], **Appendix A.1.5**, we can write for this case

$$j_0(\rho) = \frac{\sin\rho}{\rho}, \qquad j_0'(\rho) = \frac{\cos\rho}{\rho} - \frac{\sin\rho}{\rho^2}, \tag{19.36}$$

$$h_0^{(1)}(\rho) = j_0(\rho) + in_0(\rho) = \frac{\sin\rho}{\rho} - i\frac{\cos\rho}{\rho} = -\frac{i}{\rho}e^{-i\rho}, \tag{19.37}$$

$$h_0^{(1)\prime}(\rho) = \frac{e^{i\rho}}{\rho}\left(1 + \frac{i}{\rho}\right), \tag{19.38}$$

so that the condition (19.35) for $l = 0$ becomes

$$\left(\cos k_1 a - \frac{\sin k_1 a}{k_1 a}\right)\frac{k_1}{\sin k_1 a} = -k_0 e^{-k_0 a}\left(1 + \frac{1}{k_0 a}\right)e^{k_0 a},$$

which reduces to

$$k_1 a \cot(k_1 a) = -k_0 a. \tag{19.39}$$

This result is analogous to that obtained for the nonrelativistic uniform spherical well in [1]. From the analysis carried out there we know that the energy eigenvalues and the number of bound states are given by the intersections of the curves (we set $x = k_1 a$),

$$y_1(x) = \cot x, \qquad y_2(x) = -\frac{k_0 a}{x}.$$

For at least one s-state to exist, at least one intersection must occur, which imposes the condition

$$x = k_1 a = \frac{a}{\hbar c}\sqrt{(E + V_0)^2 - m^2c^4} \geq \frac{\pi}{2}. \tag{19.40}$$

When the binding energy is small compared to the electron rest energy, this equation gives the approximate condition

$$2mc^2 V_0 + V_0^2 \geq \frac{\pi^2\hbar^2 c^2}{4a^2}. \tag{19.41}$$

Writing $E = mc^2 + \Delta E$ ($\Delta E < 0$ is the binding energy), we obtain

$$k_1 = \frac{1}{\hbar c}\sqrt{(mc^2 + \Delta E + V_0)^2 - m^2c^4} = \frac{1}{\hbar c}\sqrt{2mc^2(\Delta E + V_0) + (\Delta E + V_0)^2}, \tag{19.42}$$

and neglecting $\Delta E + V_0$ compared to $2mc^2$,

$$k_1 \approx \frac{\sqrt{2m(\Delta E + V_0)}}{\hbar},$$

which is precisely the nonrelativistic expression appropriate for this variable, so that Eq. (19.40) reduces to the corresponding nonrelativistic condition.

P19.2 Use the method suggested in Problem P19.1 and the approximate equivalence

$$\frac{2m}{\hbar^2}\left[E - V(r)\right] \to \frac{1}{\hbar^2 c^2}\left[\left(E - V(r)\right)^2 - m^2c^4\right], \tag{19.43}$$

to obtain the Klein-Gordon solution for the spherical uniform well from the solution of the corresponding Schrödinger problem.

Solution. Consider a uniform spherical well of radius a and depth V_0,

$$V(r) = \begin{cases} -V_0 & \text{for } r < a \text{ (interior)} \\ 0 & \text{for } r > a \text{ (exterior).} \end{cases} \tag{19.44}$$

For s-waves ($\ell = 0$), the radial Schrödinger equation for $u(r) = rR(r)$ is

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + V(r)u = Eu \tag{19.45}$$

Inside the well ($r < a$),

$$\frac{d^2u}{dr^2} + k^2u = 0, \quad \text{where } k^2 = \frac{2m}{\hbar^2}(E + V_0). \tag{19.46}$$

with general solution $u_{\text{int}}(r) = A\sin(kr)$. Outside the well ($r > a$),

$$\frac{d^2u}{dr^2} - \kappa^2 u = 0, \quad \text{where } \kappa^2 = -\frac{2mE}{\hbar^2} \quad (E < 0), \tag{19.47}$$

with solution: $u_{\text{ext}}(r) = Be^{-\kappa r}$.

Using the equivalence

$$\frac{2m}{\hbar^2}[E - V(r)] \to \frac{1}{\hbar^2 c^2}[(E - V(r))^2 - m^2c^4], \tag{19.48}$$

the Klein-Gordon equation becomes

$$\frac{d^2u}{dr^2} + \frac{1}{\hbar^2 c^2}[(E - V(r))^2 - m^2c^4]u = 0. \tag{19.49}$$

Inside the well ($r < a$),

$$\frac{d^2u}{dr^2} + k_{\text{kg}}^2 u = 0, \quad k_{\text{kg}}^2 = \frac{(E + V_0)^2 - m^2c^4}{\hbar^2 c^2}, \tag{19.50}$$

with solution$u_{\text{int}}(r) = A\sin(k_{\text{kg}}r)$. Outside the well ($r > a$),

$$\frac{d^2u}{dr^2} - \kappa_{\text{kg}}^2 u = 0, \quad \kappa_{\text{kg}}^2 = \frac{m^2c^4 - E^2}{\hbar^2 c^2}, \tag{19.51}$$

with solution $u_{\text{ext}}(r) = Be^{-\kappa_{\text{kg}}r}$. The physical solutions mut meet the conditions of continuity at $r = a$,

$$A\sin(k_{\text{kg}}a) = Be^{-\kappa_{\text{kg}}a},$$

and continuity of the derivative,

$$Ak_{\rm kg}\cos(k_{\rm kg}a) = -B\kappa_{\rm kg}e^{-\kappa_{\rm kg}a},$$

which combined give the quantization condition

$$k_{\rm kg}\cot(k_{\rm kg}a) = -\kappa_{\rm kg}, \tag{19.52}$$

that is,

$$\sqrt{(E+V_0)^2 - m^2c^4}\cot\left(\frac{a}{\hbar c}\sqrt{(E+V_0)^2 - m^2c^4}\right) = -\sqrt{m^2c^4 - E^2}. \tag{19.53}$$

The transcendental equation determines the allowed values of E Solutions exist when

$$|E| < mc^2 \quad \text{and} \quad (E+V_0)^2 > m^2c^4. \tag{19.54}$$

For $E \approx mc^2 + \epsilon$ with $\epsilon \ll mc^2$, we recover the Schrödinger equation, and

$$\sqrt{2m\epsilon}\cot\left(\frac{a}{\hbar}\sqrt{2m\epsilon}\right) = -\sqrt{2m(V_0-\epsilon)}. \tag{19.55}$$

The complete radial wavefunction $R(r) = u(r)/r$ is

$$R(r) = \begin{cases} A\dfrac{\sin(k_{\rm kg}r)}{r} & \text{for } r < a \\ B\dfrac{e^{-\kappa_{\rm kg}r}}{r} & \text{for } r > a \end{cases} \tag{19.56}$$

where the constants A and B are determined by normalization and boundary conditions.

P19.3 Show that the expectation values of E and p^2 for a general packet solution of the Klein-Gordon equation satisfy the equation $\langle E^2\rangle = c^2\langle p^2\rangle + m^2c^4$.
Solution. To show this we begin by recalling the Klein-Gordon equation for a free particle

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2 + \frac{m^2c^2}{\hbar^2}\right)\psi = 0. \tag{19.57}$$

In terms of operators, this is written as

$$\hat{E}^2\psi = c^2\hat{p}^2\psi + m^2c^4\psi, \tag{19.58}$$

where $\hat{E} = i\hbar\frac{\partial}{\partial t}$ and $\hat{p} = -i\hbar\nabla$. Therefore, for any solution ψ,

$$\left(\hat{E}^2 - c^2\hat{p}^2 - m^2c^4\right)\psi = 0. \tag{19.59}$$

Consider a general wave packet $\psi(\mathbf{r}, t)$ that is a solution of the Klein-Gordon equation. To compute expectation values, we must use the appropriate inner product for the Klein-Gordon equation. For positive-energy solutions, the conserved and positive-definite inner product is

$$\langle\phi|\psi\rangle = i\hbar\int\left(\phi^*\frac{\partial\psi}{\partial t} - \frac{\partial\phi^*}{\partial t}\psi\right)d^3x. \tag{19.60}$$

We assume that ψ is normalized, $\langle\psi|\psi\rangle = 1$. The expectation value of an operator $\hat{O}$ is defined as $\langle\hat{O}\rangle = \langle\psi|\hat{O}\psi\rangle$. Applying this to the operator equation, we have

$$\langle\psi|\left(\hat{E}^2 - c^2\hat{p}^2 - m^2c^4\right)\psi\rangle = 0, \tag{19.61}$$

which expands as

$$\langle\psi|\hat{E}^2\psi\rangle - c^2\langle\psi|\hat{p}^2\psi\rangle - m^2c^4\langle\psi|\psi\rangle = 0. \tag{19.62}$$

Substituting the definitions of the expectation values and the normalization, we obtain

$$\langle E^2\rangle = c^2\langle p^2\rangle + m^2c^4. \tag{19.63}$$

This shows that the relation holds for any general wave packet solution of the Klein-Gordon equation, provided the correct inner product is used and the solution is normalized.

P19.4 Show explicitly that the matrices γ_μ and α_μ satisfy the appropriate anti-commutation rules, given in **[1]**, **Eqs. (19.36) and (19.52)**.

Solution. The 4×4 Dirac algebra matrices can be constructed from the following elements.

a) The three 2×2 Pauli matrices (the 2×2 matrices are denoted here with a prime, to distinguish them from the 4×4 matrices),

$$\hat{\sigma}'_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \hat{\sigma}'_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \hat{\sigma}'_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{19.64}$$

$$\hat{\sigma}'^2_i = \mathbb{I}', \qquad \hat{\sigma}'_i\hat{\sigma}'_j = \mathbb{I}'\delta_{ij} + i\varepsilon_{ijk}\hat{\sigma}'_k; \tag{19.65}$$

b) The three 4×4 matrices $\hat{\rho}_i$, defined as

$$\hat{\rho}_1 = \begin{pmatrix} \mathbb{O}' & \mathbb{I}' \\ \mathbb{I}' & \mathbb{O}' \end{pmatrix}, \qquad \hat{\rho}_2 = \begin{pmatrix} \mathbb{O}' & -i\mathbb{I}' \\ i\mathbb{I}' & \mathbb{O}' \end{pmatrix}, \qquad \hat{\rho}_3 = \begin{pmatrix} \mathbb{I}' & \mathbb{O}' \\ \mathbb{O}' & -\mathbb{I}' \end{pmatrix}, \tag{19.66}$$

with the properties

$$\hat{\rho}_i^2 = \mathbb{I}, \qquad \hat{\rho}_i^\dagger = \hat{\rho}_i, \qquad \hat{\rho}_i\hat{\rho}_j = -\hat{\rho}_j\hat{\rho}_i; \tag{19.67}$$

c) The three 4×4 matrices $\hat{\sigma}_i$ defined as

$$\hat{\sigma}_i = \begin{pmatrix} \hat{\sigma}'_i & 0' \\ 0' & \hat{\sigma}'_i \end{pmatrix}, \tag{19.68}$$

with the properties

$$\hat{\sigma}_i^2 = \mathbb{I}, \qquad \hat{\sigma}_i^\dagger = \hat{\sigma}_i, \qquad \hat{\sigma}_i\hat{\sigma}_j + \hat{\sigma}_j\hat{\sigma}_i = 2\mathbb{I}\delta_{ij}, \qquad \hat{\sigma}_i\hat{\sigma}_j = \mathbb{I}\delta_{ij} + i\varepsilon_{ijk}\hat{\sigma}_k. \tag{19.69}$$

In addition, the matrices $\hat{\sigma}_i$ and $\hat{\rho}_j$ commute,

$$\hat{\sigma}_i\hat{\rho}_j = \hat{\rho}_j\hat{\sigma}_i. \tag{19.70}$$

From now on, the identity operator $\mathbb{I}$ will simply be written as 1. We adopt the convention that Roman indices take the values $1, 2, 3$, and Greek subscripts take the values $1, 2, 3, 4$.

a) In the Dirac–Pauli representation, the matrices $\hat{\alpha}_\mu$ and $\hat{\gamma}_\mu$ are defined as

$$\hat{\alpha}_i = \hat{\rho}_1\hat{\sigma}_i, \qquad \hat{\alpha}_4 = -\hat{\beta}, \qquad \hat{\beta} = \hat{\rho}_3; \tag{19.71}$$

$$\hat{\gamma}_i = \hat{\rho}_2\hat{\sigma}_i, \qquad \hat{\gamma}_4 = \hat{\rho}_3. \tag{19.72}$$

From the previous definitions and properties, it follows that

$$\hat{\alpha}_i\hat{\alpha}_j + \hat{\alpha}_j\hat{\alpha}_i = \hat{\rho}_1\hat{\sigma}_i\hat{\rho}_1\hat{\sigma}_j + \hat{\rho}_1\hat{\sigma}_j\hat{\rho}_1\hat{\sigma}_i = \hat{\rho}_1^2\left(\hat{\sigma}_i\hat{\sigma}_j + \hat{\sigma}_j\hat{\sigma}_i\right), \tag{19.73}$$

which, with the help of (19.67) and (19.69), reduces to

$$\hat{\alpha}_i\hat{\alpha}_j + \hat{\alpha}_j\hat{\alpha}_i = 2\delta_{ij}. \tag{19.74}$$

In an analogous way,

$$\begin{aligned}\hat{\alpha}_i\hat{\alpha}_4 + \hat{\alpha}_4\hat{\alpha}_i &= -\hat{\rho}_1\hat{\sigma}_i\hat{\rho}_3 - \hat{\rho}_3\hat{\rho}_1\hat{\sigma}_i = -\hat{\rho}_1\hat{\rho}_3\hat{\sigma}_i - \hat{\rho}_3\hat{\rho}_1\hat{\sigma}_i \\ &= \hat{\rho}_3\hat{\rho}_1\hat{\sigma}_i - \hat{\rho}_3\hat{\rho}_1\hat{\sigma}_i = 0,\end{aligned} \tag{19.75}$$

and finally,

$$\hat{\alpha}_4\hat{\alpha}_4 + \hat{\alpha}_4\hat{\alpha}_4 = 2\hat{\rho}_3^2 = 2. \tag{19.76}$$

The results (19.74), (19.75), and (19.76) can be summarized in the anticommutation property

$$\hat{\alpha}_\mu\hat{\alpha}_\nu + \hat{\alpha}_\nu\hat{\alpha}_\mu = 2\delta_{\mu\nu}. \tag{19.77}$$

To obtain the properties of the $\hat{\gamma}_\mu$ matrices one can proceed in a similar way. Using (19.70) we write

$$\hat{\gamma}_i\hat{\gamma}_j + \hat{\gamma}_j\hat{\gamma}_i = \hat{\rho}_2\hat{\sigma}_i\hat{\rho}_2\hat{\sigma}_j + \hat{\rho}_2\hat{\sigma}_j\hat{\rho}_2\hat{\sigma}_i = \hat{\rho}_2^2\left(\hat{\sigma}_i\hat{\sigma}_j + \hat{\sigma}_j\hat{\sigma}_i\right), \tag{19.78}$$

from which it follows that

$$\hat{\gamma}_i\hat{\gamma}_j + \hat{\gamma}_j\hat{\gamma}_i = 2\delta_{ij}. \tag{19.79}$$

On the other hand,

$$\hat{\gamma}_i\hat{\gamma}_4 + \hat{\gamma}_4\hat{\gamma}_i = \hat{\rho}_2\hat{\sigma}_i\hat{\rho}_3 + \hat{\rho}_3\hat{\rho}_2\hat{\sigma}_i = \hat{\rho}_2\hat{\rho}_3\hat{\sigma}_i + \hat{\rho}_2\hat{\rho}_3\hat{\sigma}_i \tag{19.80}$$

$$= \hat{\rho}_2\hat{\rho}_3\hat{\sigma}_i - \hat{\rho}_2\hat{\rho}_3\hat{\sigma}_i = 0, \tag{19.81}$$

and finally,

$$\hat{\gamma}_4\hat{\gamma}_4 + \hat{\gamma}_4\hat{\gamma}_4 = 2\hat{\rho}_3^2 = 2. \tag{19.82}$$

The properties (19.79), (19.81), and (19.82) can be summarized in the anticommutation relation

$$\hat{\gamma}_\mu\hat{\gamma}_\nu + \hat{\gamma}_\nu\hat{\gamma}_\mu = 2\delta_{\mu\nu}. \tag{19.83}$$

b) The Kramers or Weyl representation uses the alternate definitions

$$\hat{\alpha}_i = \hat{\rho}_3\hat{\sigma}_i, \qquad \hat{\alpha}_4 = -\hat{\beta} = -\hat{\rho}_1; \tag{19.84}$$

$$\hat{\gamma}_i = -\hat{\rho}_2\hat{\sigma}_i, \qquad \hat{\gamma}_4 = \hat{\rho}_1. \tag{19.85}$$

Proceeding as in the previous case, we obtain

$$\hat{\alpha}_i\hat{\alpha}_j + \hat{\alpha}_j\hat{\alpha}_i = \hat{\rho}_3\hat{\sigma}_i\hat{\rho}_3\hat{\sigma}_j + \hat{\rho}_3\hat{\sigma}_j\hat{\rho}_3\hat{\sigma}_i = \hat{\rho}_3^2(\hat{\sigma}_i\hat{\sigma}_j + \hat{\sigma}_j\hat{\sigma}_i) = 2\delta_{ij}, \tag{19.86}$$

$$\hat{\alpha}_i\hat{\alpha}_4 + \hat{\alpha}_4\hat{\alpha}_i = -\hat{\rho}_3\hat{\sigma}_i\hat{\rho}_1 - \hat{\rho}_1\hat{\rho}_3\hat{\sigma}_i = -\hat{\rho}_3\hat{\rho}_1\hat{\sigma}_i - \hat{\rho}_1\hat{\rho}_3\hat{\sigma}_i = \hat{\rho}_1\hat{\rho}_3\hat{\sigma}_i - \hat{\rho}_1\hat{\rho}_3\hat{\sigma}_i = 0, \tag{19.87}$$

$$\hat{\alpha}_4\hat{\alpha}_4 + \hat{\alpha}_4\hat{\alpha}_4 = 2\hat{\rho}_1^2 = 2. \tag{19.88}$$

We see that in this representation the same anticommutation property (19.77) is satisfied. Similarly, we obtain

$$\hat{\gamma}_i\hat{\gamma}_j + \hat{\gamma}_j\hat{\gamma}_i = \hat{\rho}_2\hat{\sigma}_i\hat{\rho}_2\hat{\sigma}_j + \hat{\rho}_2\hat{\sigma}_j\hat{\rho}_2\hat{\sigma}_i = \hat{\rho}_2^2(\hat{\sigma}_i\hat{\sigma}_j + \hat{\sigma}_j\hat{\sigma}_i) = 2\delta_{ij}, \tag{19.89}$$

$$\hat{\gamma}_i\hat{\gamma}_4 + \hat{\gamma}_4\hat{\gamma}_i = -\hat{\rho}_2\hat{\sigma}_i\hat{\rho}_1 - \hat{\rho}_1\hat{\rho}_2\hat{\sigma}_i = -\hat{\rho}_2\hat{\rho}_1\hat{\sigma}_i - \hat{\rho}_1\hat{\rho}_2\hat{\sigma}_i = 0, \tag{19.90}$$

$$\hat{\gamma}_4\hat{\gamma}_4 + \hat{\gamma}_4\hat{\gamma}_4 = 2\hat{\rho}_1^2 = 2, \tag{19.91}$$

recovering the anticommutation rule (19.83).

c) In the Majorana representation we define

$$\hat{\alpha}_1 = \hat{\rho}_3\hat{\sigma}_1, \qquad \hat{\alpha}_2 = -\hat{\rho}_1, \qquad \hat{\alpha}_3 = \hat{\rho}_3\hat{\sigma}_3, \qquad \hat{\alpha}_4 = -\hat{\beta} = -\hat{\rho}_3\hat{\sigma}_2; \tag{19.92}$$

$$\hat{\gamma}_1 = -\hat{\sigma}_3, \qquad \hat{\gamma}_2 = \hat{\rho}_2\hat{\sigma}_2, \qquad \hat{\gamma}_3 = \hat{\sigma}_1, \qquad \hat{\gamma}_4 = \hat{\rho}_3\hat{\sigma}_2. \tag{19.93}$$

From these definitions it follows that

$$2\hat{\alpha}_1\hat{\alpha}_1 = 2\hat{\rho}_3\hat{\sigma}_1\hat{\rho}_3\hat{\sigma}_1 = 2\hat{\rho}_3^2\hat{\sigma}_1^2 = 2, \tag{19.94}$$

$$2\hat{\alpha}_2\hat{\alpha}_2 = 2\hat{\rho}_1^2 = 2, \tag{19.95}$$

$$2\hat{\alpha}_3\hat{\alpha}_3 = 2\hat{\rho}_3\hat{\sigma}_3\hat{\rho}_3\hat{\sigma}_3 = 2\hat{\rho}_3^2\hat{\sigma}_3^2 = 2, \tag{19.96}$$

$$2\hat{\alpha}_4\hat{\alpha}_4 = 2\hat{\beta}^2 = 2, \tag{19.97}$$

$$\hat{\alpha}_1\hat{\alpha}_2 + \hat{\alpha}_2\hat{\alpha}_1 = -\hat{\rho}_3\hat{\sigma}_1\hat{\rho}_1 - \hat{\rho}_1\hat{\rho}_3\hat{\sigma}_1 = -\hat{\rho}_3\hat{\rho}_1\hat{\sigma}_1 - \hat{\rho}_1\hat{\rho}_3\hat{\sigma}_1 = 0, \tag{19.98}$$

$$\hat{\alpha}_1\hat{\alpha}_3 + \hat{\alpha}_3\hat{\alpha}_1 = \hat{\rho}_3\hat{\sigma}_1\hat{\rho}_3\hat{\sigma}_3 + \hat{\rho}_3\hat{\sigma}_3\hat{\rho}_3\hat{\sigma}_1 = \hat{\rho}_3^2(\hat{\sigma}_1\hat{\sigma}_3 + \hat{\sigma}_3\hat{\sigma}_1) = 0, \tag{19.99}$$

$$\hat{\alpha}_1\hat{\alpha}_4 + \hat{\alpha}_4\hat{\alpha}_1 = -\hat{\rho}_3\hat{\sigma}_1\hat{\rho}_3\hat{\sigma}_2 - \hat{\rho}_3\hat{\sigma}_2\hat{\rho}_3\hat{\sigma}_1 = -\hat{\rho}_3^2(\hat{\sigma}_1\hat{\sigma}_2 + \hat{\sigma}_2\hat{\sigma}_1) = 0, \tag{19.100}$$

$$\hat{\alpha}_2\hat{\alpha}_3 + \hat{\alpha}_3\hat{\alpha}_2 = -\hat{\rho}_1\hat{\rho}_3\hat{\sigma}_3 - \hat{\rho}_3\hat{\sigma}_3\hat{\rho}_1 = \hat{\rho}_3\hat{\rho}_1\hat{\sigma}_3 - \hat{\rho}_3\hat{\rho}_1\hat{\sigma}_3 = 0, \tag{19.101}$$

$$\hat{\alpha}_2\hat{\alpha}_4 + \hat{\alpha}_4\hat{\alpha}_2 = \hat{\rho}_1\hat{\rho}_3\hat{\sigma}_2 + \hat{\rho}_3\hat{\sigma}_2\hat{\rho}_1 = \hat{\rho}_1\hat{\rho}_3\hat{\sigma}_2 - \hat{\rho}_1\hat{\rho}_3\hat{\sigma}_2 = 0, \tag{19.102}$$

$$\hat{\alpha}_3\hat{\alpha}_4 + \hat{\alpha}_4\hat{\alpha}_3 = -\hat{\rho}_3\hat{\sigma}_3\hat{\rho}_3\hat{\sigma}_2 - \hat{\rho}_3\hat{\sigma}_2\hat{\rho}_3\hat{\sigma}_3 = -\hat{\rho}_3^2(\hat{\sigma}_3\hat{\sigma}_2 + \hat{\sigma}_2\hat{\sigma}_3) = 0. \tag{19.103}$$

Thus, in this representation the anticommutation rule (19.77) is also satisfied. In an entirely similar way one obtains

$$2\hat{\gamma}_1\hat{\gamma}_1 = 2\hat{\sigma}_3^2 = 2, \tag{19.104}$$

$$2\hat{\gamma}_2\hat{\gamma}_2 = 2\hat{\rho}_2\hat{\sigma}_2\hat{\rho}_2\hat{\sigma}_2 = 2\hat{\rho}_2^2\hat{\sigma}_2^2 = 2, \tag{19.105}$$

$$2\hat{\gamma}_3\hat{\gamma}_3 = 2\hat{\sigma}_1^2 = 2, \tag{19.106}$$

$$2\hat{\gamma}_4\hat{\gamma}_4 = 2\hat{\rho}_3\hat{\sigma}_2\hat{\rho}_3\hat{\sigma}_2 = 2\hat{\rho}_3^2\hat{\sigma}_2^2 = 2, \tag{19.107}$$

$$\hat{\gamma}_1\hat{\gamma}_2 + \hat{\gamma}_2\hat{\gamma}_1 = -\hat{\sigma}_3\hat{\rho}_2\hat{\sigma}_2 - \hat{\rho}_2\hat{\sigma}_2\hat{\sigma}_3 = -\hat{\rho}_2(\hat{\sigma}_3\hat{\sigma}_2 + \hat{\sigma}_2\hat{\sigma}_3) = 0, \tag{19.108}$$

$$\hat{\gamma}_1\hat{\gamma}_3 + \hat{\gamma}_3\hat{\gamma}_1 = -\hat{\sigma}_3\hat{\sigma}_1 - \hat{\sigma}_1\hat{\sigma}_3 = 0, \tag{19.109}$$

$$\hat{\gamma}_1\hat{\gamma}_4 + \hat{\gamma}_4\hat{\gamma}_1 = -\hat{\sigma}_3\hat{\rho}_3\hat{\sigma}_2 - \hat{\rho}_3\hat{\sigma}_2\hat{\sigma}_3 = -\hat{\rho}_3(\hat{\sigma}_3\hat{\sigma}_2 + \hat{\sigma}_2\hat{\sigma}_3) = 0, \tag{19.110}$$

$$\hat{\gamma}_2\hat{\gamma}_3 + \hat{\gamma}_3\hat{\gamma}_2 = \hat{\rho}_2\hat{\sigma}_2\hat{\sigma}_1 + \hat{\sigma}_1\hat{\rho}_2\hat{\sigma}_2 = \hat{\rho}_2(\hat{\sigma}_2\hat{\sigma}_1 + \hat{\sigma}_1\hat{\sigma}_2) = 0, \tag{19.111}$$

$$\hat{\gamma}_2\hat{\gamma}_4 + \hat{\gamma}_4\hat{\gamma}_2 = \hat{\rho}_2\hat{\sigma}_2\hat{\rho}_3\hat{\sigma}_2 + \hat{\rho}_3\hat{\sigma}_2\hat{\rho}_2\hat{\sigma}_2 = \hat{\rho}_2\hat{\rho}_3 + \hat{\rho}_3\hat{\rho}_2 = 0, \tag{19.112}$$

$$\hat{\gamma}_3\hat{\gamma}_4 + \hat{\gamma}_4\hat{\gamma}_3 = \hat{\sigma}_1\hat{\rho}_3\hat{\sigma}_2 + \hat{\rho}_3\hat{\sigma}_2\hat{\sigma}_1 = \hat{\rho}_3(\hat{\sigma}_1\hat{\sigma}_2 + \hat{\sigma}_2\hat{\sigma}_1) = 0. \tag{19.113}$$

Once again, the properties are summarized in the anticommutation rule (19.83).

P19.5 In applications, the matrix γ_5, defined as the product of the four matrices γ_μ,

$$\gamma_5 = \gamma_1\gamma_2\gamma_3\gamma_4,$$

is frequently used. Prove that γ_5 is Hermitian, that it anticommutes with the matrices γ_μ,

$$\gamma_5\gamma_\mu + \gamma_\mu\gamma_5 = 0 \quad (\mu = 1, 2, 3, 4),$$

and that

$$\gamma_5 = \begin{pmatrix} 0 & -I \\ -I & 0 \end{pmatrix}, \quad \gamma_5^2 = 1.$$

Solution. Given $\gamma^5 = \gamma^1\gamma^2\gamma^3\gamma^4$, we compute its Hermitian adjoint

$$(\gamma^5)^\dagger = (\gamma^1\gamma^2\gamma^3\gamma^4)^\dagger = \gamma^{4\dagger}\gamma^{3\dagger}\gamma^{2\dagger}\gamma^{1\dagger}. \tag{19.114}$$

In the standard Dirac representation γ^i are Hermitian for $i = 1, 2, 3$: $\gamma^{i\dagger} = \gamma^i$ and γ^4 is anti-Hermitian, $\gamma^{4\dagger} = -\gamma^4$. Thus,

$$(\gamma^5)^\dagger = (-\gamma^4)\gamma^3\gamma^2\gamma^1. \tag{19.115}$$

Rearranging terms (noting that theγ^i anti-commute for $i \neq j$),

$$(\gamma^5)^\dagger = (-1)^3\gamma^1\gamma^2\gamma^3\gamma^4 = \gamma^1\gamma^2\gamma^3\gamma^4 = \gamma^5. \tag{19.116}$$

Therefore, γ^5 is Hermitian,

$$(\gamma^5)^\dagger = \gamma^5. \tag{19.117}$$

Using the Clifford algebra relation $\{\gamma^\mu, \gamma^\nu\} = 2\delta^{\mu\nu}$, we analyze $\{\gamma^5, \gamma^\mu\}$. For $\mu = 1$,

$$\gamma^5\gamma^1 = \gamma^1\gamma^2\gamma^3\gamma^4\gamma^1 \tag{19.118}$$

$$= -\gamma^1\gamma^2\gamma^3\gamma^1\gamma^4 \tag{19.119}$$

$$= +\gamma^1\gamma^2\gamma^1\gamma^3\gamma^4 \tag{19.120}$$

$$= -\gamma^1\gamma^1\gamma^2\gamma^3\gamma^4 \tag{19.121}$$

$$= -\gamma^2\gamma^3\gamma^4 \tag{19.122}$$

and

$$\gamma^1\gamma^5 = \gamma^1\gamma^1\gamma^2\gamma^3\gamma^4 = \gamma^2\gamma^3\gamma^4. \tag{19.123}$$

Therefore,

$$\{\gamma^5, \gamma^1\} = -\gamma^2\gamma^3\gamma^4 + \gamma^2\gamma^3\gamma^4 = 0. \tag{19.124}$$

A similar calculation for $\mu = 2, 3, 4$ gives

$$\{\gamma^5, \gamma^\mu\} = 0 \quad \text{for } \mu = 1, 2, 3, 4. \tag{19.125}$$

In the standard Dirac representation

$$\gamma^4 = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \quad \gamma^i = \begin{pmatrix} 0 & \sigma^i \\ -\sigma^i & 0 \end{pmatrix}, \tag{19.126}$$

$\gamma^5 = \gamma^1\gamma^2\gamma^3\gamma^4$ is

$$\gamma^1\gamma^2\gamma^3 = i\begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix}, \quad \gamma^5 = i\begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}. \tag{19.127}$$

The more common convention is

$$\gamma^5 = \begin{pmatrix} 0 & -I \\ -I & 0 \end{pmatrix}, \tag{19.128}$$

which satisfies

$$(\gamma^5)^2 = \begin{pmatrix} 0 & -I \\ -I & 0 \end{pmatrix}\begin{pmatrix} 0 & -I \\ -I & 0 \end{pmatrix} = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix} = I. \tag{19.129}$$

With this we have demonstrated that γ^5 is Hermitian because it anti-commutes with all γ^μ matrices and its matrix form satisfies $(\gamma^5)^2 = 1$.

P19.6 Solve Problem P19.1, this time using Dirac's equation. Compare and discuss your results.

Solution. The Dirac equation for central potentials has as solution the spinor given by equation

$$\psi(r,\theta,\varphi) = \begin{pmatrix} g(r)\,\mathcal{Y}^{j_3}_{jl_A} \\ if(r)\,\mathcal{Y}^{j_3}_{jl_B} \end{pmatrix}, \tag{19.130}$$

where the radial functions $g(r)$ and $f(r)$ satisfy the coupled differential equations

$$-f' + \frac{k-1}{r}f = \frac{1}{\hbar c}\left[E - V(r) - mc^2\right]g, \tag{19.131}$$

$$g' + \frac{k+1}{r}g = \frac{1}{\hbar c}\left[E - V(r) + mc^2\right]f. \tag{19.132}$$

The number k takes the value $j + \frac{1}{2}$ if $l_A = l_B + 1 = j + \frac{1}{2}$ and $-(j + \frac{1}{2})$ if $l_A = l_B - 1 = j - \frac{1}{2}$, as shown in [**1**]. In the present problem we must solve the previous system of radial equations for the potential

$$V(r) = \begin{cases} -V_0, & r \le a, \\ 0, & r > a. \end{cases} \quad V_0 > 0. \tag{19.133}$$

For $r \le a$ we obtain

$$-f' + \frac{k-1}{r}f = \frac{1}{\hbar c}\left(E + V_0 - mc^2\right)g, \tag{19.134}$$

$$g' + \frac{k+1}{r}g = \frac{1}{\hbar c}\left(E + V_0 + mc^2\right)f. \tag{19.135}$$

To decouple these equations we differentiate (19.134),

$$-f''+\frac{k-1}{r}f'-\frac{k-1}{r^2}f=\frac{1}{\hbar c}\left(E+V_0-mc^2\right)g', \tag{19.136}$$

and substitute (19.135) into the result,

$$-f''+\frac{k-1}{r}f'-\frac{k-1}{r^2}f=\frac{(E+V_0)^2-m^2c^4}{\hbar^2c^2}f-\frac{1}{\hbar c}\left(E+V_0-mc^2\right)\frac{k+1}{r}g. \tag{XXII.193}$$

We eliminate g from here with the help of (19.134), to obtain

$$f''+\frac{2}{r}f'+\left[\frac{k(1-k)}{r^2}+\frac{(E+V_0)^2-m^2c^4}{\hbar^2c^2}\right]f=0. \tag{19.137}$$

Introducing the quantity

$$\lambda_1^2=\frac{(E+V_0)^2-m^2c^4}{\hbar^2c^2}, \tag{19.138}$$

we get $\lambda_1^2>0$ for bound states (in problem P19.7.1 this quantity was called k_1^2) and the previous equation can be written as

$$f''+\frac{2}{r}f'+\left[\lambda_1^2-\frac{k(k-1)}{r^2}\right]f=0. \tag{19.139}$$

With the change of variable $\rho=\lambda_1 r$, (19.139) is transformed into

$$\frac{d^2f}{d\rho^2}+\frac{2}{\rho}\frac{df}{d\rho}+\left[1-\frac{k(k-1)}{\rho^2}\right]f=0, \tag{19.140}$$

whose solutions are the spherical Bessel functions. The possible cases are:

a) $k=j+1/2$: we have $k(k-1)=(j-1/2)(j-1/2+1)=(l_A-1)l_A$.

b) $k=-(j+1/2)$: we have $k(k-1)=(j+1/2)(j+1/2+1)=l_B(l_B+1)$.

We write the solution in the form

$$f=a_1j_{l_B}(\rho)+a_2n_{l_B}(\rho), \tag{19.141}$$

with

$$l_B=\begin{cases}j-\frac{1}{2}, & \text{if } k=j+\frac{1}{2},\\ j+\frac{1}{2}, & \text{if } k=-(j+\frac{1}{2}).\end{cases} \tag{19.142}$$

To find the corresponding function g we substitute (19.141) into (19.131),

$$-\lambda_1\left[a_1\frac{dj_{l_B}(\rho)}{d\rho}+a_2\frac{dn_{l_B}(\rho)}{d\rho}\right]+\frac{k-1}{r}\left[a_1j_{l_B}(\rho)+a_2n_{l_B}(\rho)\right]=\frac{1}{\hbar c}\left(E+V_0-mc^2\right)g. \tag{19.143}$$

Using the recurrence relations of the spherical Bessel functions that appear in [**1**], **Appendix A.6**, this expression can be put in the form

$$-\lambda_1\frac{l_B}{2l_B+1}\left[a_1j_{l_B-1}(\rho)+a_2n_{l_B-1}(\rho)\right]+\lambda_1\frac{l_B+1}{2l_B+1}\left[a_1j_{l_B+1}(\rho)+a_2n_{l_B+1}(\rho)\right]$$

$$+\lambda_1 \frac{k-1}{2l_B+1}\left[a_1 j_{l_B-1}(\rho)+a_2 n_{l_B-1}(\rho)\right]+\lambda_1 \frac{k-1}{2l_B+1}\left[a_1 j_{l_B+1}(\rho)+a_2 n_{l_B+1}(\rho)\right]$$
$$=\frac{1}{\hbar c}\left(E+V_0-mc^2\right)g. \tag{19.144}$$

For $k=j+\frac{1}{2}$ we have $l_B=j-\frac{1}{2}=k-1$, which gives

$$g=\frac{\hbar c\lambda_1}{E+V_0-mc^2}\left[a_1 j_{l_B+1}(\rho)+a_2 n_{l_B+1}(\rho)\right]. \tag{19.145}$$

In turn, for $k=-(j+\frac{1}{2})$, we have $l_B=j+\frac{1}{2}$, that is $k-1=-l_B-1$, which gives

$$g=-\frac{\hbar c\lambda_1}{E+V_0-mc^2}\left[a_1 j_{l_B-1}(\rho)+a_2 n_{l_B-1}(\rho)\right]. \tag{19.146}$$

The results (19.145) and (19.146) can be written in the more compact form

$$g=\frac{k}{|k|}\frac{\hbar c\lambda_1}{E+V_0-mc^2}[a_1 j_{l_A}(\lambda_1 r)+a_2 n_{l_A}(\lambda_1 r)], \tag{19.147}$$

with

$$l_A=\begin{cases} j+\frac{1}{2}, & \text{if } k=j+\frac{1}{2},\\ j-\frac{1}{2}, & \text{if } k=-(j+\frac{1}{2}).\end{cases} \tag{19.148}$$

To obtain the solution in the external region $r>a$, it is sufficient to substitute $V_0=0$ in (19.137), which gives

$$f''+\frac{2}{r}f'-\left[\frac{k(k-1)}{r^2}+\frac{m^2c^4-E^2}{\hbar^2c^2}\right]f=0. \tag{19.149}$$

Defining

$$\lambda_2^2=\frac{m^2c^4-E^2}{\hbar^2c^2} \tag{19.150}$$

(this was called k_0^2 in problem P19.1), for bound states $\lambda_2^2>0$, and with the change of variable $\rho=i\lambda_2 r$, Eq. (19.149) can be written as

$$\frac{d^2f}{d\rho^2}+\frac{2}{\rho}\frac{df}{d\rho}+\left[1-\frac{k(k-1)}{\rho^2}\right]f=0. \tag{19.151}$$

As in the internal region $r\le a$, we have the two possibilities.

a) $k=j+\frac{1}{2}$; it follows that $k(k-1)=(j-\frac{1}{2})(j-\frac{1}{2}+1)=l_B(l_B+1)$,

b) $k=-(j+\frac{1}{2})$ and consequently $k(k-1)=(j+\frac{1}{2})(j+\frac{1}{2}+1)$.

Equation (19.151) has as solutions the spherical Hankel functions of the first and second kind, and we can write the general solution in the form

$$f=b_1 h_{l_B}^{(1)}(i\lambda_2 r)+b_2 h_{l_B}^{(2)}(i\lambda_2 r). \tag{19.152}$$

The corresponding function $g(r)$ is obtained by substituting this result into (19.131),

$$-i\lambda_2\left[b_1\frac{dh_{l_B}^{(1)}(\rho)}{d\rho}+b_2\frac{dh_{l_B}^{(2)}(\rho)}{d\rho}\right]+i\lambda_2\frac{k-1}{\rho}\left[b_1 h_{l_B}^{(1)}(\rho)+b_2 h_{l_B}^{(2)}(\rho)\right] \tag{19.153}$$

$$= \frac{1}{\hbar c}\left(E - mc^2\right) g. \tag{19.154}$$

Using the pertinent recurrence relations leads to

$$- i\lambda_2 \frac{l_B}{2l_B+1}\left[b_1 h^{(1)}_{l_B-1}(i\lambda_2 r) + b_2 h^{(2)}_{l_B-1}(i\lambda_2 r)\right] \tag{19.155}$$

$$+ i\lambda_2 \frac{l_B+1}{2l_B+1}\left[b_1 h^{(1)}_{l_B+1}(i\lambda_2 r) + b_2 h^{(2)}_{l_B+1}(i\lambda_2 r)\right] \tag{19.156}$$

$$+ i\lambda_2 \frac{k-1}{2l_B+1}\left[b_1 h^{(1)}_{l_B-1}(i\lambda_2 r) + b_2 h^{(2)}_{l_B-1}(i\lambda_2 r)\right] \tag{19.157}$$

$$+ i\lambda_2 \frac{k-1}{2l_B+1}\left[b_1 h^{(1)}_{l_B+1}(i\lambda_2 r) + b_2 h^{(2)}_{l_B+1}(i\lambda_2 r)\right] = \frac{1}{\hbar c}\left(E - mc^2\right) g. \tag{19.158}$$

For $k = j + \frac{1}{2}, l_B = j - \frac{1}{2} = k - 1$ and

$$g = \frac{i\hbar c\lambda_2}{E - mc^2}\left[b_1 h^{(1)}_{l_B+1}(i\lambda_2 r) + b_2 h^{(2)}_{l_B+1}(i\lambda_2 r)\right]. \tag{19.159}$$

For $k = -(j + \frac{1}{2}), l_B = j + \frac{1}{2}$, $k - 1 = -l_B - 1$ and

$$g = -\frac{\hbar c i\lambda_2}{E - mc^2}\left[b_1 h^{(1)}_{l_B-1}(i\lambda_2 r) + b_2 h^{(2)}_{l_B-1}(i\lambda_2 r)\right]. \tag{19.160}$$

Equations (19.159) and (19.160) can be written in the form

$$g = \frac{k}{|k|}\frac{\hbar c i\lambda_2}{E - mc^2}\left[b_1 h^{(1)}_{l_A}(i\lambda_2 r) + b_2 h^{(2)}_{l_A}(i\lambda_2 r)\right], \tag{19.161}$$

with

$$l_A = \begin{cases} j + \frac{1}{2}, & \text{if } k = j + \frac{1}{2}, \\ j - \frac{1}{2}, & \text{if } k = -(j + \frac{1}{2}). \end{cases} \tag{19.162}$$

The above are general solutions, so it is still necessary to impose the appropriate boundary conditions for the problem. At $r = 0$ the wave function must remain regular, which requires setting $a_2 = 0$. For the wave function to decay exponentially at $r \to \infty$, the restriction $b_2 = 0$ must be imposed. This results in the solution for the bound state having the form, for $r \leq a$,

$$f = a_1 j_{l_B}(\lambda_1 r), \tag{19.163}$$

$$g = a_1 \frac{k}{|k|}\frac{\hbar c\lambda_1}{E + V_0 - mc^2} j_{l_A}(\lambda_1 r), \tag{19.164}$$

and for $r > a$,

$$f = b_1 h^{(1)}_{l_B}(i\lambda_2 r), \tag{19.165}$$

$$g = b_1 \frac{k}{|k|}\frac{\hbar c i\lambda_2}{E - mc^2} h^{(1)}_{l_A}(i\lambda_2 r), \tag{19.166}$$

with l_A and l_B given by (19.142) and (19.148). To ensure that the solution matches correctly at $r = a$ it is required that

$$a_1 j_{l_B}(\lambda_1 a) = b_1 h^{(1)}_{l_B}(i\lambda_2 a), \tag{19.167}$$

$$\frac{\lambda_1 a_1}{E + V_0 - mc^2} j_{l_A}(\lambda_1 a) = \frac{i\lambda_2 b_1}{E - mc^2} h^{(1)}_{l_A}(i\lambda_2 a). \tag{19.168}$$

From this pair of equations follows the consistency condition

$$\frac{j_{l_B}(\lambda_1 a)}{j_{l_A}(\lambda_1 a)} = -\frac{i\lambda_1(E - mc^2)}{\lambda_2(E + V_0 - mc^2)} \frac{h^{(1)}_{l_B}(i\lambda_2 a)}{h^{(1)}_{l_A}(i\lambda_2 a)}. \tag{19.169}$$

The energy eigenvalues for the bound states are obtained from the solutions of this equation. However, the expression is very complicated for arbitrary l_A and l_B, so we will restrict ourselves to the simplest possible case, $|k| = 1$.

a) For $k = -1$ we have $l_A = 0$, $l_B = 1$, and the previous expression reduces to

$$\frac{j_1(\lambda_1 a)}{j_0(\lambda_1 a)} = -\frac{i\lambda_1(E - mc^2)}{\lambda_2(E + V_0 - mc^2)} \frac{h^{(1)}_1(i\lambda_2 a)}{h^{(1)}_0(i\lambda_2 a)}. \tag{19.170}$$

With the use of the required expressions for the Bessel functions, see **[1]**, **Appendix A**, this equation reduces to

$$\frac{1}{\lambda_1 a} - \cot \lambda_1 a = -\frac{\lambda_1}{\lambda_2} \frac{E - mc^2}{E + V_0 - mc^2} \left(1 + \frac{1}{\lambda_2 a}\right), \tag{19.171}$$

that is,

$$\lambda_1 a \cot \lambda_1 a = 1 + \frac{\lambda_1^2}{\lambda_2^2} \frac{E - mc^2}{E + V_0 - mc^2} (\lambda_2 a + 1). \tag{19.172}$$

Substituting the values of λ_1 and λ_2 we obtain

$$\lambda_1 a \cot \lambda_1 a = 1 - \frac{E + V_0 + mc^2}{E + mc^2} \left(\frac{a}{\hbar c}\sqrt{m^2c^4 - E^2} + 1\right), \tag{19.173}$$

whose solutions give the allowed energy values and the number of bound states of the well.

b) For $k = 1$ we have $l_A = 1$ and $l_B = 0$, and

$$\frac{j_0(\lambda_1 a)}{j_1(\lambda_1 a)} = \frac{\lambda_1(E - mc^2)}{i\lambda_2(E + V_0 - mc^2)} \frac{h^{(1)}_0(i\lambda_2 a)}{h^{(1)}_1(i\lambda_2 a)}, \tag{19.174}$$

which can be rewritten in the form

$$\lambda_1 a \cot \lambda_1 a = 1 + \frac{E + V_0 - mc^2}{mc^2 - E} \left(\frac{a}{\hbar c}\sqrt{m^2c^4 - E^2} + 1\right), \tag{19.175}$$

from which the allowed energy values and the number of bound states for this case are obtained.

Making the approximation $(E + V_0 + mc^2)/(E + mc^2) \sim 1$ in (19.173), we get

$$\lambda_1 a \cot \lambda_1 a = -\frac{a}{\hbar c}\sqrt{m^2c^4 - E^2} = -\lambda_2 a. \tag{19.176}$$

With the identification $\lambda_1 = k_1$, $\lambda_2 = k_0$, this expression coincides with that obtained for the same case with the Klein-Gordon theory in problem P19.1. Thus, the effect of the electron spin reduces for this problem essentially to the correction introduced by the factor that has been approximated in going from (19.175) to (19.176). The discrepancy is significant only for very deep wells, with V_0/mc^2 not too small compared to unity.

P19.7 Prove that $\left[\widehat{H}, \boldsymbol{a}\cdot\hat{\boldsymbol{\sigma}}\right] = -2ic\hat{\boldsymbol{\alpha}}\cdot(\hat{\boldsymbol{p}}\times\boldsymbol{a})$, for $\boldsymbol{a}$ a fixed vector and $\widehat{H}$ the free-particle Dirac Hamiltonian.

Solution. If $\hat{H}$ is the Dirac Hamiltonian for a free particle and $\boldsymbol{a}$ represents a fixed vector, $\boldsymbol{a}\cdot\hat{\boldsymbol{\sigma}} = a_j\hat{\sigma}_j$ and the commutator is

$$\left[\widehat{H}, \boldsymbol{a}\cdot\hat{\boldsymbol{\sigma}}\right] = [\hat{H}, a_j\hat{\sigma}_j] = ca_j[\hat{\alpha}_i\hat{p}_i, \hat{\sigma}_j] + mc^2a_j[\hat{\beta}, \hat{\sigma}_j]. \tag{19.177}$$

Since the Pauli matrices $\hat{\sigma}_j$ and the components of the linear momentum operator act on different spaces, they commute,

$$[\hat{p}_i, \hat{\sigma}_j] = 0, \tag{19.178}$$

and furthermore, since $\hat{\beta} = \hat{\rho}_3$, from relation (19.70) it follows that $[\hat{\beta}, \hat{\sigma}_j] = 0$. With this, (19.177) reduces to

$$\left[\widehat{H}, \boldsymbol{a}\cdot\hat{\boldsymbol{\sigma}}\right] = ca_j[\hat{\alpha}_i, \hat{\sigma}_j]\hat{p}_i = ca_j\hat{\rho}_1[\hat{\sigma}_i, \hat{\sigma}_j]\hat{p}_i = 2ica_j\varepsilon_{ijk}\hat{\rho}_1\hat{\sigma}_k\hat{p}_i \tag{19.179}$$

$$= 2ic\varepsilon_{kij}\hat{\alpha}_k\hat{p}_ia_j = 2ic\,\hat{\alpha}\cdot(\hat{\boldsymbol{p}}\times\boldsymbol{a}), \tag{19.180}$$

which is the required result.

P19.8 Consider the sign operator for the free-particle Dirac equation given by the equation

$$\hat{\Lambda} = \frac{\widehat{H}_D}{E_+} = \frac{c\hat{\boldsymbol{\alpha}}\cdot\hat{\boldsymbol{p}} + \hat{\beta}mc^2}{E_+}, \quad E_+ = +c\sqrt{\boldsymbol{p}^2 + m^2c^2}. \tag{19.181}$$

Show that this operator is Hermitian and unitary, with eigenvalues $\lambda = \pm 1$, and that these eigenvalues are integrals of motion for the free particle. Construct with its help the projectors $\hat{\Pi}^{\pm} = \frac{1}{2}(1 \pm \hat{\Lambda})$ and show that these operators project the positive and negative energy states, respectively, for the free particle.

Solution. The $\hat{\Lambda}$ operator is defined as

$$\hat{\Lambda} = \frac{\hat{H}_D}{E_+}, \quad \text{where} \quad \hat{H}_D = c\hat{\boldsymbol{\alpha}}\cdot\hat{\boldsymbol{p}} + \hat{\beta}mc^2 \tag{19.182}$$

and $E_+ = +\sqrt{c^2p^2 + m^2c^4}$. Given that $\hat{\boldsymbol{\alpha}}$ and $\hat{\beta}$ are Hermitian Dirac matrices ($\hat{\alpha}_i^\dagger = \hat{\alpha}_i$, $\hat{\beta}^\dagger = \hat{\beta}$), $\hat{\boldsymbol{p}}$ is Hermitian and E_+ is real and positive. Therefore, $\hat{\Lambda}$ is Hermitian,

$$\hat{\Lambda}^\dagger = \left(\frac{\hat{H}_D}{E_+}\right)^\dagger = \frac{\hat{H}_D^\dagger}{E_+^\dagger} = \frac{\hat{H}_D}{E_+} = \hat{\Lambda}. \tag{19.183}$$

An operator is unitary if $\hat{\Lambda}^\dagger\hat{\Lambda} = I$. Since $\hat{\Lambda}$ is Hermitian, we only need to show that $\hat{\Lambda}^2 = I$,

$$\hat{\Lambda}^2 = \left(\frac{\hat{H}_D}{E_+}\right)^2 = \frac{\hat{H}_D^2}{E_+^2}. \tag{19.184}$$

Using properties of the free Dirac Hamiltonian,

$$\hat{H}_D^2 = (c\hat{\boldsymbol{\alpha}}\cdot\hat{\boldsymbol{p}} + \hat{\beta}mc^2)^2 = c^2(\hat{\boldsymbol{\alpha}}\cdot\hat{\boldsymbol{p}} + mc^3(\hat{\boldsymbol{\alpha}}\cdot\hat{\boldsymbol{p}})\hat{\beta} + \hat{\beta}(\hat{\boldsymbol{\alpha}}\cdot\hat{\boldsymbol{p}})$$
$$= (c^2p^2 + m^2c^4)I \quad (\text{using } \{\hat{\alpha}_i, \hat{\alpha}_j\} = 2\delta_{ij}I \text{ and } \hat{\beta}^2 = I).$$

Since $E_+^2 = c^2(p^2 + m^2c^2)$, we have

$$\hat{\Lambda}^2 = \frac{(c^2p^2 + m^2c^4)I}{c^2(p^2 + m^2c^2)} = I \tag{19.185}$$

Therefore, $\hat{\Lambda}$ is unitary,

$$\hat{\Lambda}^\dagger\hat{\Lambda} = I, \tag{19.186}$$

and its eigenvalues λ satisfy

$$\lambda^2 = 1 \implies \lambda = \pm 1. \tag{19.187}$$

These eigenvalues are conserved because $\hat{\Lambda}$ commutes with $\hat{H}_D$ for a free particle,

$$[\hat{H}_D, \hat{\Lambda}] = \left[\hat{H}_D, \frac{\hat{H}_D}{E_+}\right] = \frac{1}{E_+}[\hat{H}_D, \hat{H}_D] = 0. \tag{19.188}$$

The projection operators are defined as

$$\hat{\Pi}_+ = \frac{1}{2}(1 + \hat{\Lambda}), \quad \hat{\Pi}_- = \frac{1}{2}(1 - \hat{\Lambda}). \tag{19.189}$$

They project onto positive and negative energy states. For a positive energy state ψ_+ ($E = +E_+$, $\hat{\Lambda}$ eigenvalue $+1$),

$$\hat{\Pi}_+\psi_+ = \frac{1}{2}(1 + \hat{\Lambda})\psi_+ = \psi_+, \quad \hat{\Pi}_-\psi_+ = 0 \tag{19.190}$$

and for a negative energy state ψ_- ($E = -E_+$, $\hat{\Lambda}$ eigenvalue -1),

$$\hat{\Pi}_-\psi_- = \frac{1}{2}(1 - \hat{\Lambda})\psi_- = \psi_-, \quad \hat{\Pi}_+\psi_- = 0. \tag{19.191}$$

Thus,

$$\hat{\Pi}_\pm \text{ project onto } \lambda = \pm 1 \text{ eigenstates.} \tag{19.192}$$

P19.9 Given the Dirac Hamiltonian with minimal coupling (in units $c = \hbar = 1$)

$$\hat{H}_D = \hat{\boldsymbol{\alpha}} \cdot \hat{\boldsymbol{\pi}} + \hat{\beta} m + e\phi, \tag{19.193}$$

where $\hat{\boldsymbol{\pi}} = \hat{\boldsymbol{p}} - e\boldsymbol{A}$, prove that

$$\dot{\hat{\boldsymbol{r}}} = \hat{\boldsymbol{\alpha}}, \quad \ddot{\hat{\boldsymbol{r}}} = \dot{\hat{\boldsymbol{\alpha}}} = 2i \left[\hat{\boldsymbol{\pi}} - \hat{\boldsymbol{\alpha}} (\hat{H}_D - e\phi) \right], \tag{19.194}$$

$$\dot{\hat{\boldsymbol{\pi}}} = e\boldsymbol{E} + e\hat{\boldsymbol{\alpha}} \times \boldsymbol{B}. \tag{19.195}$$

Note that the Lorentz force is expressed in terms of $\hat{\boldsymbol{\alpha}}$.

Solution. The canonical momentum for a Dirac particle in an electromagnetic field with minimal coupling is $\hat{\boldsymbol{\pi}} = \hat{\boldsymbol{p}} - e\boldsymbol{A}$, and $A_4(x) = i\phi$. Applying the Heisenberg equation

$$\frac{d\hat{F}}{dt} = \frac{\partial \hat{F}}{\partial t} + i \left[\hat{H}_D, \hat{F} \right] \tag{19.196}$$

to the i component of the position vector, we obtain

$$\frac{dx_i}{dt} = i \left[\hat{\alpha}_j \hat{\pi}_j + \hat{\beta} m + e\phi,\, x_i \right]. \tag{19.197}$$

Since both the Coulomb potential ϕ (which depends only on the coordinates) and the Dirac matrices commute with the position variables, $[\phi, x_i] = 0, [\hat{\alpha}_j, x_i] = [\hat{\beta}, x_i] = 0$, the previous expression reduces to

$$\frac{dx_i}{dt} = i \left[\hat{\alpha}_j \hat{\pi}_j, x_i \right] = i\hat{\alpha}_j \left[\hat{\pi}_j, x_i \right] = i\hat{\alpha}_j \left[\hat{p}_j - eA_j, x_i \right]. \tag{19.198}$$

Since it also holds that $[A_j, x_i] = 0$, we are left with

$$\frac{dx_i}{dt} = i\hat{\alpha}_j \left[\hat{p}_j, x_i \right] = \hat{\alpha}_j \delta_{ij} = \hat{\alpha}_i, \tag{19.199}$$

that is,

$$\dot{\boldsymbol{r}} = \hat{\boldsymbol{\alpha}}. \tag{19.200}$$

To determine the time evolution of $\dot{\boldsymbol{r}}$ we write

$$\frac{d\dot{\boldsymbol{r}}}{dt} = \dot{\hat{\boldsymbol{\alpha}}} = i \left[\hat{H}_D, \hat{\boldsymbol{\alpha}} \right] = i \left(\hat{H}_D \hat{\boldsymbol{\alpha}} - \hat{\boldsymbol{\alpha}} \hat{H}_D \right) \tag{19.201}$$

$$= i \left(\hat{H}_D \hat{\boldsymbol{\alpha}} + \hat{\boldsymbol{\alpha}} \hat{H}_D - 2\hat{\boldsymbol{\alpha}} \hat{H}_D \right) = i \left(\left\{ \hat{H}_D, \hat{\boldsymbol{\alpha}} \right\} - 2\hat{\boldsymbol{\alpha}} \hat{H}_D \right). \tag{19.202}$$

Since

$$\left\{ \hat{H}_D, \hat{\alpha}_i \right\} = \left\{ \hat{\alpha}_j \hat{\pi}_j + \hat{\beta} m + e\phi, \hat{\alpha}_i \right\} = \{ \hat{\alpha}_j \hat{\pi}_j, \hat{\alpha}_i \} + 2\hat{\alpha}_i e\phi \tag{19.203}$$

$$= \{ \hat{\alpha}_j, \hat{\alpha}_i \} \hat{\pi}_j + 2\hat{\alpha}_i e\phi = 2\delta_{ij} \hat{\pi}_j + 2\hat{\alpha}_i e\phi = 2\hat{\pi}_i + 2\hat{\alpha}_i e\phi, \tag{19.204}$$

we obtain

$$\left\{ \hat{H}_D, \hat{\boldsymbol{\alpha}} \right\} = 2\hat{\boldsymbol{\pi}} + 2\hat{\boldsymbol{\alpha}} e\phi \tag{19.205}$$

and

$$\frac{d\dot{\boldsymbol{r}}}{dt} = 2i\left[\hat{\boldsymbol{\pi}} - \hat{\boldsymbol{\alpha}}(\hat{H}_D - e\phi)\right]. \tag{19.206}$$

Finally, the equation of motion for the canonical momentum $\hat{\boldsymbol{\pi}} = \hat{\boldsymbol{p}} - e\boldsymbol{A}$ is

$$\frac{d\hat{\boldsymbol{\pi}}}{dt} = \frac{\partial\hat{\boldsymbol{\pi}}}{\partial t} + i\left[\hat{H}_D, \hat{\boldsymbol{\pi}}\right], \tag{19.207}$$

where $\boldsymbol{A}$ may depend on time. From this it follows that

$$\frac{d\hat{\boldsymbol{\pi}}}{dt} = i\left[\hat{H}_D, \hat{\boldsymbol{\pi}}\right] - e\frac{\partial\boldsymbol{A}}{\partial t} = i\left[\hat{H}_D, \hat{\boldsymbol{p}}\right] - ie\left[\hat{H}_D, \boldsymbol{A}\right] - e\frac{\partial\boldsymbol{A}}{\partial t}. \tag{19.208}$$

To calculate the commutator $\left[\hat{H}_D, \hat{\boldsymbol{p}}\right]$ we proceed as follows,

$$\left[\hat{H}_D, \hat{\boldsymbol{p}}\right] = \left[\hat{\boldsymbol{\alpha}}\cdot\hat{\boldsymbol{\pi}}, \hat{\boldsymbol{p}}\right] + m\left[\hat{\beta}, \hat{\boldsymbol{p}}\right] + e\left[\phi, \hat{\boldsymbol{p}}\right] = \left[\hat{\boldsymbol{\alpha}}\cdot\hat{\boldsymbol{\pi}}, \hat{\boldsymbol{p}}\right] + e\left[\phi, \hat{\boldsymbol{p}}\right], \tag{19.209}$$

and since $e\left[\phi, \hat{\boldsymbol{p}}\right] = -ie\left[\phi, \nabla\right] = ie(\nabla\phi)$, we are left with

$$\left[\hat{H}_D, \hat{\boldsymbol{p}}\right] = \left[\hat{\boldsymbol{\alpha}}\cdot\hat{\boldsymbol{\pi}}, \hat{\boldsymbol{p}}\right] + ie(\nabla\phi) = \left[\hat{\boldsymbol{\alpha}}\cdot\hat{\boldsymbol{\pi}}, \hat{\boldsymbol{p}}\right] - e[\hat{\boldsymbol{\alpha}}\cdot\boldsymbol{A}, \hat{\boldsymbol{p}}] + ie(\nabla\phi) \tag{19.210}$$

$$= -e[\hat{\alpha}_j A_j, \hat{p}_i]\hat{e}_i + ie(\nabla\phi) = -e\hat{\alpha}_j[A_j, \hat{p}_i]\hat{e}_i + ie(\nabla\phi). \tag{19.211}$$

In turn,

$$\left[\hat{H}_D, \boldsymbol{A}\right] = \left[\hat{\boldsymbol{\alpha}}\cdot\hat{\boldsymbol{\pi}}, \boldsymbol{A}\right] + m\left[\hat{\beta}, \boldsymbol{A}\right] + e\left[\phi, \boldsymbol{A}\right] = \left[\hat{\boldsymbol{\alpha}}\cdot\hat{\boldsymbol{\pi}}, \boldsymbol{A}\right] = \hat{\alpha}_j[\hat{p}_j, A_i]\hat{e}_i. \tag{19.212}$$

Substituting these last two expressions into (19.208) we obtain

$$\frac{d\hat{\boldsymbol{\pi}}}{dt} = i(-e\hat{\alpha}_j[A_j, \hat{p}_i]\hat{e}_i + ie\nabla\phi) - ie\hat{\alpha}_j[\hat{p}_j, A_i]\hat{e}_i - e\frac{\partial\boldsymbol{A}}{\partial t} \tag{19.213}$$

$$= ie\hat{\alpha}_j\left\{[\hat{p}_i, A_j] - [\hat{p}_j, A_i]\right\}\hat{e}_i + e\left(-\nabla\phi - \frac{\partial\boldsymbol{A}}{\partial t}\right). \tag{19.214}$$

Introducing the electric field vector given by

$$\boldsymbol{E} = -\nabla\phi - \frac{\partial\boldsymbol{A}}{\partial t}, \tag{19.215}$$

we obtain

$$\frac{d\hat{\boldsymbol{\pi}}}{dt} = ie\hat{\alpha}_j\left\{[\hat{p}_i, A_j] - [\hat{p}_j, A_i]\right\}\hat{e}_i + e\boldsymbol{E}. \tag{19.216}$$

Tking into account that

$$[\hat{p}_i, A_j] - [\hat{p}_j, A_i] = i\left(\frac{\partial A_i}{\partial x_j} - \frac{\partial A_j}{\partial x_i}\right) = i\left(\nabla\times\mathbf{A}\right)_k = iB_k, \tag{19.217}$$

where the indices i, j, k must be taken in cyclic order and B_k represents the k component of the magnetic field given by

$$\boldsymbol{B} = \nabla\times\boldsymbol{A}, \tag{19.218}$$

we obtain

$$\frac{d\hat{\boldsymbol{\pi}}}{dt} = e\boldsymbol{E} - e\epsilon_{ijk}\hat{e}_i\hat{\alpha}_j B_k = e\boldsymbol{E} + e\hat{\boldsymbol{\alpha}} \times \boldsymbol{B}. \tag{19.219}$$

The right-hand side of this equation can be considered as the form that the Lorentz force takes in Dirac theory, with $\boldsymbol{v}/c \to \hat{\boldsymbol{\alpha}}$, which is consistent with Eq. (19.200). In other words, $\hat{\boldsymbol{\pi}}$ satisfies an evolution equation that has the "classical" form, in which the operator $\hat{\boldsymbol{\alpha}}$ plays the role of velocity. However, Eq. (19.200), which determines the evolution of $\boldsymbol{x}$, that is, the analogue of velocity, has no classical analogue in any form, not even within special relativity. As discussed in [**1**], this is directly related to the phenomenon of zitterbewegung.

P19.10 Prove the equation

$$(\boldsymbol{\alpha}\cdot\boldsymbol{p})(\boldsymbol{\sigma}\cdot\boldsymbol{J}) = \rho_1(\boldsymbol{\sigma}\cdot\boldsymbol{p})(\boldsymbol{\sigma}\cdot\boldsymbol{J}) = \rho_1\,\boldsymbol{p}\cdot\boldsymbol{J} + i\,\boldsymbol{\alpha}\cdot(\boldsymbol{p}\times\boldsymbol{J}). \tag{19.220}$$

(For simplicity in writing, we omit the carets over the operators.)
Solution. Using the Dirac–Pauli representation, $\boldsymbol{\alpha}_i \equiv \rho_1\sigma_i$ and the fact that ρ_1 commutes with σ_i, $\boldsymbol{p}$ and $\boldsymbol{J}$, we have $(\boldsymbol{\alpha}\cdot\boldsymbol{p})(\boldsymbol{\sigma}\cdot\boldsymbol{J}) = \hat{\rho}_1(\boldsymbol{\sigma}\cdot\boldsymbol{p})(\boldsymbol{\sigma}\cdot\boldsymbol{J})$. We now use the Pauli identity

$$(\boldsymbol{\sigma}\cdot\boldsymbol{A})(\boldsymbol{\sigma}\cdot\boldsymbol{B}) = \boldsymbol{A}\cdot\boldsymbol{B} + i\,\boldsymbol{\sigma}\cdot(\boldsymbol{A}\times\boldsymbol{B}), \qquad [\boldsymbol{\sigma},\boldsymbol{A}] = [\boldsymbol{\sigma},\boldsymbol{B}] = 0, \tag{19.221}$$

with $\boldsymbol{A} = \boldsymbol{p}$ and $\boldsymbol{B} = \boldsymbol{J}$. Since $[\hat{\boldsymbol{\sigma}},\boldsymbol{p}] = [\hat{\boldsymbol{\sigma}},\boldsymbol{J}] = 0$, Eq.(19.221) gives $(\boldsymbol{\sigma}\cdot\boldsymbol{p})(\boldsymbol{\sigma}\cdot\boldsymbol{J}) = \boldsymbol{p}\cdot\boldsymbol{J} + i\,\boldsymbol{\sigma}\cdot(\boldsymbol{p}\times\boldsymbol{J})$. Multiplying on the left by ρ_1 and recalling $\rho_1\boldsymbol{\sigma} = \boldsymbol{\alpha}$, we obtain the desired identity,

$$(\boldsymbol{\alpha}\cdot\boldsymbol{p})(\boldsymbol{\sigma}\cdot\boldsymbol{J}) = \rho_1(\boldsymbol{\sigma}\cdot\boldsymbol{p})(\boldsymbol{\sigma}\cdot\boldsymbol{J}) = \rho_1\,\boldsymbol{p}\cdot\boldsymbol{J} + i\,\boldsymbol{\alpha}\cdot(\boldsymbol{p}\times\boldsymbol{J}). \tag{19.222}$$

P19.11 The selection rules for dipole transitions that apply to Dirac's theory are $\Delta l = \pm 1$, $\Delta j = 0, \pm 1$. Determine the frequencies of the transitions allowed between the states with $n = 2$ and $n = 3$ for the H atom in Dirac's theory, and compare with the results predicted by Schrödinger's theory.
Solution. The exact formula for the energy levels of a hydrogen-like atom given by Dirac's theory, is

$$E_{nj} = \frac{mc^2}{\sqrt{1 + \frac{\alpha^2 Z^2}{(n-j-\frac{1}{2}+\sqrt{k^2-\alpha^2Z^2})^2}}}, \tag{19.223}$$

where $\alpha = e^2/\hbar c$. Expanding this expression in a power series of $(Z\alpha)^2$ and retaining only up to second-order terms, we get

$$E_{nj} = mc^2\left[1 - \frac{Z^2\alpha^2}{2n^2} - \frac{Z^4\alpha^4}{2n^4}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right) + \cdots\right], \tag{19.224}$$

where

$$n = n' + |k|, \quad n = 0, 1, 2, \ldots. \tag{19.225}$$

is the principal quantum number that determines the energy in the non-relativistic expression

$$E_n = -\frac{Z^2 m e^4}{2\hbar^2 n^2} = -\frac{Z^2 \alpha^2 m c^2}{2n^2}. \tag{19.226}$$

In comparison, the corresponding expression predicted by the Klein-Gordon equation, sometimes called the *relativistic Schrödinger expression*, is given by

$$E_{nl} = mc^2 \left[1 - \frac{Z^2\alpha^2}{2n^2} - \frac{Z^4\alpha^4}{2n^4}\left(\frac{n}{l+\frac{1}{2}} - \frac{3}{4}\right)\right]. \tag{19.227}$$

In both equation (19.224) and (19.227), the third term on the right represents the relativistic correction to the energy (19.226), which is degenerate with respect to l and j. It is clear that this formula is valid only for $k^2 > Z^2\alpha^2$, that is, for not very heavy atoms or highly excited states in heavy atoms. The comparison between (19.224) and (19.227) shows that the introduction of spin generates the substitution $l \to j$; however, this is not merely a numerical change, since for a given j there are two possible values of l, $l = j \pm 1/2$, so Dirac's theory predicts a richer spectrum than that derived using the Klein-Gordon equation. In particular, the Dirac equation breaks the degeneracy with respect to j, but not with respect to l (up to second order).

To study transitions from states with $n = 3$, we consider that in the formula $n = n' + |k|$, n' can only take the values 0, 1, 2, since $|k| \geq 0$, while k can take the values $k = \pm(3 - n')$, except for $n' = 0$, in which case it can only be $k = 3$. Taking into account that

$$k = j(j+1) - l\,(l+1) + \frac{1}{4} = \begin{cases} l+1, & \text{if } j = l + \frac{1}{2}, \\ -l, & \text{if } j = l - \frac{1}{2}, \end{cases} \tag{19.228}$$

we can construct the following table for Dirac eigenstates corresponding to $n = 3$ (the term notation is nL_j),

n'	k	l	j	term
0	3	2	5/2	$3d_{5/2}$
1	−2	2	3/2	$3d_{3/2}$
1	2	1	3/2	$3p_{3/2}$
2	−1	1	1/2	$3p_{1/2}$
2	1	0	1/2	$3s_{1/2}$

(19.229)

For $n = 2$ we obtain analogously

n'	k	l	j	term
0	2	1	3/2	$2p_{3/2}$
1	−1	1	1/2	$2p_{1/2}$
1	1	0	3/2	$2s_{3/2}$

(19.230)

With the selection rules for dipole transitions that apply to Dirac's theory, $\Delta l = \pm 1$, $\Delta j = 0, \pm 1$, the allowed transitions $n = 3 \to n = 2$ result in

$$3d_{5/2} \to 2p_{3/2}, \quad 3d_{3/2} \to 2p_{3/2}, \tag{19.231}$$

$$3d_{3/2} \to 2p_{1/2}, \quad 3p_{3/2} \to 2s_{3/2}, \tag{19.232}$$

$$3p_{1/2} \to 2s_{3/2}, \quad 3s_{1/2} \to 2p_{3/2}, \tag{19.233}$$

$$3s_{1/2} \to 2p_{1/2}. \tag{19.234}$$

Each transition corresponds to the frequency

$$\omega_{3j' \to 2j} = \frac{E_{3j'} - E_{2j}}{\hbar} \tag{19.235}$$

$$= \frac{mc^2 Z^2 \alpha^2}{2\hbar} \left(\frac{1}{2^2} - \frac{1}{3^2} \right) + \frac{3}{8} \frac{mc^2 Z^4 \alpha^4}{\hbar} \left(\frac{1}{3^4} - \frac{1}{2^4} \right) \tag{19.236}$$

$$+ \frac{mc^2 Z^4 \alpha^4}{2\hbar} \left(\frac{1}{2^3 (j + \frac{1}{2})} - \frac{1}{3^3 (j' + \frac{1}{2})} \right) \tag{19.237}$$

$$= A - \frac{65}{64 \cdot 27} B + \left(\frac{1}{2^3 (j + \frac{1}{2})} - \frac{1}{3^3 (j' + \frac{1}{2})} \right) B, \tag{19.238}$$

where we introduced the abbreviations

$$A = \frac{5}{72} Z^2 \alpha^2 \frac{mc^2}{\hbar}, \quad B = \frac{1}{2} Z^4 \alpha^4 \frac{mc^2}{\hbar}. \tag{19.239}$$

The constant A essentially corresponds to the transition frequency given by Schrödinger's theory; the contribution proportional to B gives the correction predicted by Dirac's equation, to second order. These corrections are of order $Z^2 \alpha^2 \sim Z^2 \times 10^{-4}$ relative to the non-relativistic values given by A.

The frequency of the transition $3d_{5/2} \to 2p_{3/2}$ is

$$\omega_1 = A - \frac{65}{64 \cdot 27} B + \left(\frac{1}{24} - \frac{1}{34} \right) B = A - \frac{65}{64 \cdot 81} B. \tag{19.240}$$

For the transition $3d_{3/2} \to 2p_{3/2}$ we obtain

$$\omega_2 = A - \frac{65}{64 \cdot 27} B + \left(\frac{1}{24} - \frac{1}{32} \right) B = A + \frac{11}{64 \cdot 27} B. \tag{19.241}$$

The transition $3d_{3/2} \to 2p_{1/2}$ gives

$$\omega_3 = A - \frac{65}{64 \cdot 27} B + \left(\frac{1}{23} - \frac{1}{32} \right) B = A + \frac{119}{64 \cdot 27} B. \tag{19.242}$$

The energy of the transition $3p_{3/2} \to 2s_{3/2}$ is degenerate with that of the transition $3d_{3/2} \to 2p_{3/2}$, since the value of l does not appear in the second-order formulas. Therefore,

$$\omega_4 = A + \frac{11}{64 \cdot 27} B. \tag{19.243}$$

For the transition $3p_{1/2} \to 2s_{3/2}$ we have

$$\omega_5 = A - \frac{65}{64 \cdot 27} B + \left(\frac{1}{24} - \frac{1}{32} \right) B = A - \frac{19}{64 \cdot 27} B. \tag{19.244}$$

The transition $3s_{1/2} \to 2p_{3/2}$ is degenerate with the previous one, therefore

$$\omega_6 = A - \frac{19}{64 \cdot 27} B. \tag{19.245}$$

Finally, for the frequency of the transition $3s_{1/2} \to 2p_{1/2}$ we obtain

$$\omega_7 = A - \frac{65}{64 \cdot 27} B + \left(\frac{1}{2^3} - \frac{1}{3^3} \right) B = A + \frac{29}{64 \cdot 9} B. \tag{19.246}$$

From these results we conclude that the non-relativistic line of frequency $\sim A$ actually consists of five slightly separated lines, with the frequencies given above. For comparison purposes, let us consider the predictions of the Klein-Gordon equation that follow from Eq. (19.227). With $n = n' + l + 1$, the eigenstates corresponding to $n = 3$ and $n = 2$ are those listed in the accompanying tables,

$$n = 3: \quad \begin{array}{ccc} n' & l & \text{term} \\ 0 & 2 & 3d \\ 1 & 1 & 3p \\ 2 & 0 & 3s \end{array} \tag{19.247}$$

$$n = 2: \quad \begin{array}{ccc} n' & l & \text{term} \\ 0 & 1 & 2p \\ 1 & 0 & 2s \end{array} \tag{19.248}$$

For dipole transitions the selection rule is $\Delta l = \pm 1$, which allows 3 lines in the transition $n = 3 \to n = 2$,

$$3d \to 2p, \quad 3p \to 2s, \quad 3s \to 2p. \tag{19.249}$$

The corresponding frequencies are

$$\omega_{3l'2l} = \frac{E_{3l'} - E_{2l}}{h} \tag{19.250}$$

$$= A - \frac{65}{64 \cdot 27} B + \left(\frac{1}{2^3 (l + \frac{1}{2})} - \frac{1}{3^3 (l' + \frac{1}{2})} \right) B. \tag{19.251}$$

Comparing with (19.238) we see that the difference with Dirac's theory lies in the last term, which differs by the substitution $j \to l$, $j' \to l'$, that is, the loss of spin effects. The three transition frequencies are:

a) $3d \to 2p$,

$$\omega_1' = A - \frac{65}{64 \cdot 27} B + \left(\frac{1}{2^3 \cdot \frac{3}{2}} - \frac{1}{3^3 \cdot \frac{5}{2}} \right) B = A - \frac{801}{15 \cdot 64 \cdot 27} B. \tag{19.252}$$

b) $3p \to 2s$,

$$\omega_2' = A - \frac{65}{64 \cdot 27}B + \left(\frac{1}{2^3 \cdot \frac{1}{2}} - \frac{1}{3^3 \cdot \frac{3}{2}}\right) B = A + \frac{973}{3 \cdot 64 \cdot 27}B. \tag{19.253}$$

c) $3s \to 2p$,

$$\omega_3' = A - \frac{65}{64 \cdot 27}B + \left(\frac{1}{2^3 \cdot \frac{3}{2}} - \frac{1}{3^3 \cdot \frac{1}{2}}\right) B = A - \frac{49}{64 \cdot 27}B. \tag{19.254}$$

The Klein-Gordon equation thus predicts only three lines with a somewhat larger separation between them than that given by Dirac's theory. It is clear that detailed observation of the atom's emission spectrum allows discrimination between the three theories. The above calculation shows that the purely relativistic corrections (common to both Klein-Gordon and Dirac theories) are of the same order as those due to the electron's spin (which appear only in the second of these theories). This is why the first relativistic calculations, performed using the Klein-Gordon equation, proved manifestly insufficient to solve the problem of correctly determining the hydrogen-like spectrum.

Appendix. Complementary Simulations and Graphics

As part of the additional resources for the solutions, we are providing this GitHub repository, which will continue to be updated. There, you can find Python programs to support some of the problems.

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