collisions, and the return to the $F = 0$ ground state can be detected. From an analysis of the intensity of the 21 cm radiation received, astronomers have learned a great deal about the density distribution of neutral hydrogen in interstellar space, as well as the motion and the temperature of the gas clouds containing the hydrogen. The average number of neutral hydrogen atoms appears to be about 1 cm^{-3} in the galactic plane near the sun, and the temperature is of the order of 100° K.

Problems

1. What effect does the addition of a constant to the Hamiltonian have on the wave function?

2. If the general form of a spin-orbit coupling for a particle of mass m and spin $\mathbf{S}$ moving in a potential $V(r)$ is

$$H_{SO} = \frac{1}{2m^2c^2} \mathbf{S}\cdot\mathbf{L} \frac{1}{r} \frac{dV(r)}{dr}$$

what is the effect of that coupling on the spectrum of a three-dimensional harmonic oscillator?

3. Consider the $n = 2$ states in the real hydrogen atom. What is the spectrum in the absence of a magnetic field? How is that spectrum changed when the atom is placed in a magnetic field of 25,000 gauss?

4. Show that

$$\nabla^2 \frac{1}{r} = -4\pi\delta(\mathbf{r})$$

Use the procedure outlined in the footnote to Eq. 17-34.

5. Consider a gas of hydrogen atoms at low temperature and density. At what temperature will the $F = 1$ and the $F = 0$ states be equally occupied? (*Note.* The Boltzmann factor

$$ge^{-E/kT}$$

gives the relative probability of occupation of a given state with degeneracy g when the system is in equilibrium, at temperature T.)

6. Consider a harmonic oscillator in three dimensions. If the relativistic expression for the kinetic energy is used, what is the shift in the ground state energy?

7. The deuteron consists of a proton (charge $+e$) and a neutron (charge 0)

in a state of total spin 1 and total angular momentum $J = 1$. The g-factors for the proton and neutron are

$$g_P = 2(2.7896)$$
$$g_N = 2(-1.9103)$$

(a) What are the possible orbital angular momentum states for this system? If it is known that the state is primarily $^3S_1$, what admixture is allowed given that parity is conserved?

(b) Write an expression for the interaction of the deuteron with an external magnetic field and calculate the Zeeman splitting. Show that if the interaction with the magnetic field is written in the form

$$V = -\mu_{\text{eff}} \cdot \mathbf{B}$$

then the effective magnetic moment of the deuteron is the sum of the proton and neutron magnetic moments, and any deviation from that result is due to an admixture of non-S state to the wave function.

8. Consider positronium, a hydrogenlike atom consisting of an electron and a positron (same mass, opposite charge). Calculate (a) the ground state energy, and that for the $n = 2$ states; (b) the relativistic kinetic energy effect and the spin-orbit coupling; (c) the hyperfine splitting of the ground state. Compare your results with those for the hydrogen atom and explain major differences.

References

The most detailed discussion of the physics of hydrogenlike atoms may be found in

H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*, Springer Verlag, 1957.

The Thomas precession is discussed in

R. M. Eisberg, *Fundaments of Modern Physics*, Wiley, New York (1961)

Problems

15–1. The ground state of positronium, the hydrogenlike system composed of a positron and an electron bound together by their coulomb interaction, consists of one singlet and three triplet substates. The singlet level is the most stable and lies 8×10^{-4} ev below the triplet levels, which are degenerate in zero field. Calculate the effects of a magnetic field on this system. (A positron has a charge and a magnetic moment equal in magnitude but opposite in sign to those of an electron.)

15–2. An electron moves in a central electrostatic field. Each negative energy state is characterized by a definite value of the orbital angular momentum. The degeneracy of each level is $2(2l + 1)$. Show that the inclusion of the spin-orbit interaction and an interaction with an external uniform magnetic field completely removes the degeneracy but does not change the "center of gravity" of each unperturbed energy level.

15–3. An atom with no permanent magnetic moment is said to be *diamagnetic*. Neglect the spin of the electron and proton, and show how to calculate the induced diamagnetic moment for a hydrogen atom in its ground state when a weak magnetic field is applied.

15–4. (a) Show that the dielectric constant of HCl gas depends only upon the population of the ground rotational level. (b) Assuming that the molecules consist of two ions (H^+ and Cl^-) a fixed distance d apart, with each ion carrying one electric charge, calculate the temperature dependence of the dielectric constant. (c) Assume a reasonable value for d and compute the dielectric constant. (d) Compare this result with the experimental value.

15–5. A radiofrequency field acts upon HCl gas. (a) Assuming that the frequency is in the neighborhood of the resonant frequency for transitions between the ground and first excited rotational states, calculate the rate at which the gas absorbs the radio energy. Make the following assumptions: (1) the HCl molecule consists of two ions held a fixed distance d apart; each ion carries one electric charge; (2) a collision between two molecules establishes thermal equilibrium; the cross section for a collision is σ. (b) Show how the absorption varies with frequency, pressure, and temperature.

15–6. Describe the Zeeman effect in atomic hydrogen.

15–7. If the nucleus of an atom possesses a spin $\mathbf{I}$ and associated magnetic moment $\boldsymbol{\mu}$, the interaction of this moment with the magnetic moment associated with the electronic angular momentum $\mathbf{J}$ can split the levels into various sublevels corresponding to different total angular-momentum $\mathbf{F} = \mathbf{J} + \mathbf{I}$ states. Such splittings, which are generally very small, are known as *hyperfine splittings*. The proton in a hydrogen atom has $I = \frac{1}{2}$, leading to a ground state composed of two levels, corresponding to $F = 1$ and $F = 0$. The hyperfine separation of the ground state of hydrogen is 1420 Mc/sec. (a) Calculate the probability that a transition will be induced from one hyperfine energy level to another by a radiofrequency magnetic pulse. (b) Show that if the magnetic field vector is polarized parallel to the axis of quantization, the only transition which can occur is from $m_F = 0$ to $m_F = 0$. (c) Show that if the radiofrequency pulse is followed $(n/2.84) \times 10^{-9}$ sec later (n is an odd integer) by an identical pulse, no first-order transitions can occur.

b. Solve this problem *exactly* and compare with your result obtained in (a).
[You may assume without proof

$$\langle u_{n'}|x|u_n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n+1}\,\delta_{n',n+1} + \sqrt{n}\,\delta_{n',n-1}\right).\Big]$$

2. In nondegenerate time-independent perturbation theory, what is the probability of finding in a perturbed energy eigenstate ($|k\rangle$) the corresponding unperturbed eigenstate ($|k^{(0)}\rangle$)? Solve this up to terms of order g^2.
3. Consider a particle in a two-dimensional potential

$$V_0 = \begin{cases} 0 & \text{for } 0 \le x \le L, 0 \le y \le L, \\ \infty & \text{otherwise.} \end{cases}$$

Write the energy eigenfunctions for the ground and first excited states. We now add a time-independent perturbation of the form

$$V_1 = \begin{cases} \lambda xy & \text{for } 0 \le x \le L, 0 \le y \le L, \\ 0 & \text{otherwise.} \end{cases}$$

Obtain the zeroth-order energy eigenfunctions and the first-order energy shifts for the ground and first excited states.
4. Consider an isotropic harmonic oscillator in *two* dimensions. The Hamiltonian is given by

$$H_0 = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{m\omega^2}{2}\left(x^2 + y^2\right).$$

a. What are the energies of the three lowest-lying states? Is there any degeneracy?
b. We now apply a perturbation

$$V = \delta m\omega^2 xy,$$

where δ is a dimensionless real number much smaller than unity. Find the zeroth-order energy eigenket and the corresponding energy to first order [that is, the unperturbed energy obtained in (a) plus the first-order energy shift] for each of the three lowest-lying states.
c. Solve the $H_0 + V$ problem *exactly*. Compare with the perturbation results obtained in (b).
[You may use $\langle n'|x|n\rangle = \sqrt{\hbar/2m\omega}\left(\sqrt{n+1}\,\delta_{n',n+1} + \sqrt{n}\,\delta_{n',n-1}\right)$.]
5. Establish (5.1.54) for the one-dimensional harmonic oscillator given by (5.1.50) with an additional perturbation $V = \frac{1}{2}\varepsilon m\omega^2 x^2$. Show that all other matrix elements V_{k0} vanish.
6. A slightly anisotropic three-dimensional harmonic oscillator has $\omega_z \approx \omega_x = \omega_y$. A charged particle moves in the field of this oscillator and is at the same time exposed to a uniform magnetic field in the x-direction. Assuming that the Zeeman splitting is comparable to the splitting produced by the anisotropy, but small compared to $\hbar\omega$, cal-

culate to first order the energies of the components of the first excited state. Discuss various limiting cases. (From Merzbacher, *Quantum Mechanics, 2/e*, © 1970. Reprinted by permission of Ellis Horwood, Ltd.)

7. A one-electron atom whose ground state is nondegenerate is placed in a uniform electric field in the z-direction. Obtain an approximate expression for the induced electric dipole moment of the ground state by considering the expectation value of ez with respect to the perturbed state vector computed to first order. Show that the same expression can also be obtained from the energy shift $\Delta = -\alpha|\mathbf{E}|^2/2$ of the ground state computed to second order. (*Note*: α stands for the polarizability.) Ignore spin.
8. Evaluate the matrix elements (or expectation values) given below. If any vanishes, explain why it vanishes using simple symmetry (or other) arguments.
   a. $\langle n=2, l=1, m=0|x|\, n=2, l=0, m=0\rangle$.
   b. $\langle n=2, l=1, m=0|p_z|\, n=2, l=0, m=0\rangle$.
   [In (a) and (b), $|nlm\rangle$ stands for the energy eigenket of a nonrelativistic hydrogen atom with spin ignored.]
   c. $\langle L_z\rangle$ for an electron in a central field with $j=\frac{9}{2}$, $m=\frac{7}{2}$, $l=4$.
   d. $\langle \text{singlet}, m_s=0|S_z^{(e-)} - S_z^{(e+)}|\text{triplet}, m_s=0\rangle$ for an s-state positronium.
   e. $\langle \mathbf{S}^{(1)}\cdot\mathbf{S}^{(2)}\rangle$ for the ground state of a hydrogen *molecule*.
9. A p-orbital electron characterized by $|n, l=1, m=\pm 1, 0\rangle$ (ignore spin) is subjected to a potential

$$V = \lambda(x^2 - y^2) \quad (\lambda = \text{constant}).$$

   a. Obtain the "correct" zeroth-order energy eigenstates that diagonalize the perturbation. You need not evaluate the energy shifts in detail, but show that the original threefold degeneracy is now completely removed.
   b. Because V is invariant under time reversal and because there is no longer any degeneracy, we expect each of the energy eigenstates obtained in (a) to go into itself (up to a phase factor or sign) under time reversal. Check this point explicitly.
10. Consider a spinless particle in a two-dimensional infinite square well:

$$V = \begin{cases} 0 & \text{for } 0 \le x \le a, 0 \le y \le a, \\ \infty & \text{otherwise.} \end{cases}$$

   a. What are the energy eigenvalues for the three lowest states? Is there any degeneracy?
   b. We now add a potential

$$V_1 = \lambda xy, \quad 0 \le x \le a, 0 \le y \le a.$$

the perturbed eigenvalues. (Is this procedure correct?) Then diagonalize the matrix to find the exact eigenvalues. Finally, use the second-order degenerate perturbation theory. Compare the three results obtained.

13. Compute the Stark effect for the $2S_{1/2}$ and $2P_{1/2}$ levels of hydrogen for a field ε sufficiently weak so that $e\varepsilon a_0$ is small compared to the fine structure, but take the Lamb shift δ ($\delta = 1057$ MHz) into account (that is, ignore $2P_{3/2}$ in this calculation). Show that for $e\varepsilon a_0 \ll \delta$, the energy shifts are quadratic in ε, whereas for $e\varepsilon a_0 \gg \delta$ they are linear in ε. (The radial integral you need is $\langle 2s|r|2p\rangle = 3\sqrt{3}\,a_0$.) Briefly discuss the consequences (if any) of time reversal for this problem. This problem is from Gottfried 1966, Problem 7-3.
14. Work out the Stark effect to lowest nonvanishing order for the $n = 3$ level of the hydrogen atom. Ignoring the spin-orbit force and relativistic correction (Lamb shift), obtain not only the energy shifts to lowest nonvanishing order but also the corresponding zeroth-order eigenket.
15. Suppose the electron had a very small intrinsic *electric* dipole moment analogous to the spin magnetic moment (that is, $\boldsymbol{\mu}_{el}$ proportional to $\boldsymbol{\sigma}$). Treating the hypothetical $-\boldsymbol{\mu}_{el}\cdot\mathbf{E}$ interaction as a small perturbation, discuss qualitatively how the energy levels of the Na atom ($Z = 11$) would be altered in the absence of any external electromagnetic field. Are the level shifts first order or second order? State explicitly which states get mixed with each other. Obtain an expression for the energy shift of the lowest level that is affected by the perturbation. Assume throughout that only the valence electron is subjected to the hypothetical interaction.
16. Consider a particle bound to a fixed center by a spherically symmetric potential $V(r)$.
    a. Prove
    $$|\psi(0)|^2 = \left(\frac{m}{2\pi\hbar^2}\right)\left\langle \frac{dV}{dr}\right\rangle$$
    for all s states, ground and excited.
    b. Check this relation for the ground state of a three-dimensional isotropic oscillator, the hydrogen atom, and so on.
    (*Note*: This relation has actually been found to be useful in guessing the form of the potential between a quark and an antiquark.)
17. a. Suppose the Hamiltonian of a rigid rotator in a magnetic field perpendicular to the axis is of the form (Merzbacher 1970, Problem 17-1)
    $$A\mathbf{L}^2 + BL_z + CL_y$$
    if terms quadratic in the field are neglected. Assuming $B \gg C$, use perturbation theory to lowest nonvanishing order to get approximate energy eigenvalues.