The perturbing Hamiltonian $\hat{H}_1$ may arise from external perturbations such as those that come from applying electric fields—the Stark effect (Example 11.1 and Sections 11.3 and 11.4)—or those that come from applying magnetic fields—the Zeeman effect (Section 11.7)—to the system, or from internal perturbations such as those causing the fine structure of the hydrogen atom (Section 11.5). If the state $|\varphi_n^{(0)}\rangle$ is not degenerate, the first-order and second-order corrections to the energy are given by

$$E_n^{(1)} = \langle \varphi_n^{(0)} | \hat{H}_1 | \varphi_n^{(0)} \rangle \tag{11.114}$$

and

$$E_n^{(2)} = \sum_{k \neq n} \frac{|\langle \varphi_k^{(0)} | \hat{H}_1 | \varphi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}} \tag{11.115}$$

When the unperturbed energy eigenstates are degenerate, formula (11.114) [as well as (11.115)] does *not* apply. Rather, the first-order corrections to the energy are the eigenvalues of the eigenvalue equation for the operator $\hat{H}_1$ using the degenerate eigenstates of $\hat{H}_0$ as a basis (see Section 11.2). Often we can take advantage of a symmetry of the perturbing Hamiltonian $\hat{H}_1$ to reduce the size of the degenerate subspace in which we need to work. In particular, if $[\hat{H}_1, \hat{A}] = 0$ (where $\hat{A}$ may be the generator of a symmetry operation for $\hat{H}_1$), only states that have both the same energy $E_n^{(0)}$ and the same eigenvalue a of the operator $\hat{A}$ are mixed together by the perturbation. See Sections 11.3 and 11.5 for illustrations.

Problems

11.1. Consider a perturbation $\hat{H}_1 = b\hat{x}^4$ to the simple harmonic oscillator Hamiltonian

$$\hat{H}_0 = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$

This is an example of an anharmonic oscillator, one with a nonlinear restoring force.

(a) Show that the first-order shift in the energy is given by

$$E_n^{(1)} = \frac{3\hbar^2 b}{4m^2\omega^2}(1 + 2n + 2n^2)$$

(b) Argue that no matter how small b is, the perturbation expansion will break down for some sufficiently large n. What is the physical reason?

11.2. For Example 11.1 use the series expansion for the exponential in the translation operator in

$$|\psi_n\rangle = \hat{T}(q|\mathbf{E}|/m\omega^2)|n\rangle = e^{-iq|\mathbf{E}|\hat{p}_x/m\omega^2\hbar}|n\rangle$$

to evaluate the first-order correction to the state of the harmonic oscillator due to an applied electric field. Compare your results with the perturbative result.

11.3. For the simple harmonic oscillator, for which

$$\hat{H}_0 = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$

take the perturbing Hamiltonian to be

$$\hat{H}_1 = \frac{1}{2}m\omega_1^2\hat{x}^2$$

where $\omega_1 \ll \omega$. Calculate the energy shifts through second order and compare with the exact eigenvalues.

11.4. Calculate the first-order shift to the energy of the ground state and first excited state of a particle of mass m in the one-dimensional infinite square well

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{elsewhere} \end{cases}$$

of (a) the constant perturbation $\hat{H}_1 = V_1$ and (b) the linearly increasing perturbation $\hat{H}_1 = \varepsilon E_1^{(0)}\hat{x}/L$, where $E_1^{(0)}$ is the unperturbed energy of the ground state and $\varepsilon \ll 1$.

11.5.
(a) Calculate the exact energy eigenstates of the Hamiltonian (11.7) of the ammonia molecule in an external electric field.

(b) Assuming that $\mu_e|\mathbf{E}| \ll A$, use perturbation theory to determine the first-order correction to the unperturbed eigenstates $|I\rangle$ and $|II\rangle$ and compare with the results of (a).

11.6. The spin Hamiltonian for a spin-$\frac{1}{2}$ particle in an external magnetic field is

$$\hat{H} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B} = -\frac{gq}{2mc}\hat{\mathbf{S}} \cdot \mathbf{B}$$

Take $\mathbf{B} = B_0\mathbf{k} + B_2\mathbf{j}$, with $B_2 \ll B_0$. Determine the energy eigenvalues exactly and compare with the results of perturbation theory through second order in B_2/B_0.

11.7. Assume that the proton is a uniformly charged sphere of radius R.

(a) Show for the hydrogen atom that the potential energy of the electron in the field of the proton is given by

$$V(r) = \begin{cases} -\dfrac{3e^2}{2R^3}\left(R^2 - \dfrac{1}{3}r^2\right) & r < R \\ -\dfrac{e^2}{r} & r > R \end{cases}$$

Hint: Use Gauss's law and remember that the potential energy $V(r)$ must be continuous.

(b) Calculate the energy shift for the $1s$ and $2p$ states of hydrogen if the potential energy in (a) is used. What effect does this shift have upon the Lyman α wavelength? *Suggestion:* You can use the fact that $R \ll a_0$ to simplify the integrand *before* evaluating the integrals.

11.8. Use the form of the $Y_{l,m}(\theta, \phi)$'s to verify that $\langle n, l', m' | \hat{z} | n, l, m \rangle = 0$ for $m \neq m'$.

11.9. A particle of mass m is confined in the three-dimensional potential energy box

$$V(x, y, z) = \begin{cases} 0 & 0 < x < L, \ 0 < y < L, \ 0 < z < L \\ \infty & \text{elsewhere} \end{cases}$$

Determine the first-order shift in the energies of the ground state and the first excited states due to the perturbation

$$\hat{H}_1 = \begin{cases} V_1 & 0 < x < L/2, \ 0 < y < L/2, \ 0 < z < L \\ 0 & \text{elsewhere} \end{cases}$$

which raises the potential energy by an amount V_1 in one quarter of the box.

11.10. The spin Hamiltonian of a spin-1 ion in a crystal is given by

$$\hat{H} = \frac{a}{\hbar^2}\hat{S}_z^2 + \frac{b}{\hbar^2}(\hat{S}_x^2 - \hat{S}_y^2)$$

Assume $b \ll a$ and treat

$$\frac{b}{\hbar^2}(\hat{S}_x^2 - \hat{S}_y^2)$$

as a perturbation. Calculate the unperturbed energies and the first-order corrections using perturbation theory. Beware of the degeneracy. Compare your perturbative results with the exact eigenvalues.

11.11. For the two-dimensional harmonic oscillator, the unperturbed Hamiltonian is given by

$$\hat{H}_0 = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \frac{\hat{p}_y^2}{2m} + \frac{1}{2}m\omega^2\hat{y}^2$$

Determine the first-order energy shifts to the ground state and the degenerate first excited states due to the perturbation

$$\hat{H}_1 = b\hat{x}\hat{y}$$

11.12.

(a) Determine how the energy levels of the hydrogen atom for the $1s$ and $2p$ states would appear in the absence of any intrinsic spin for the electron, with the only contribution to the fine structure coming from the relativistic correction to the kinetic energy.

(b) What happens to these energy levels if the atom is placed in an external magnetic field?

(c) What is the resulting spectrum?

11.13. Show for a general potential energy $V(r)$ that the form of the spin-orbit Hamiltonian (11.78) becomes

$$\hat{H}_{\text{S-O}} = \frac{1}{2m_e^2 c^2 |\hat{r}|} \frac{d\hat{V}}{dr} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

Suggestion: Start with (11.77).

11.14. Obtain the states (11.92a) and (11.92b).

11.15. Determine the effect of an external magnetic field on the energy levels of the $n = 2$ states of hydrogen when the applied magnetic field B has a magnitude much greater than 10^4 gauss, in which case the spin-orbit interaction may be neglected as a first approximation. This is the **Paschen–Bach effect**.

The following four problems provide us with some techniques for evaluating some of the hydrogen-atom expectation values that we have used in this chapter. These "tricks" are given by R. Shankar, *Principles of Quantum Mechanics*.

11.16. In order to evaluate $\langle 1/r \rangle$ consider γ/r as a perturbation for the hydrogenic atom, where we can think of γ as some "small" constant. The first-order shift in the energy is given by

$$E_n^{(1)} = \left\langle \frac{\gamma}{r} \right\rangle_{n,l,m}$$

which is clearly linear in γ.

(a) First show that the exact eigenvalues are given by

$$E_n = -\frac{\mu(Ze^2 - \gamma)^2}{2\hbar^2 n^2}$$

Suggestion: Examine (10.32).

(b) Since $E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots$, we can obtain $E_n^{(1)}$ either by explicitly finding the contribution to E_n that is linear in γ, or, more generally, noting that

$$E_n^{(1)} = \gamma \left(\frac{dE_n}{d\gamma} \right)_{\gamma=0}$$

since $E_n^{(0)}$ is of course independent of γ and the higher order terms in the expansion are at least of order γ^2. In this way show that

$$\left\langle \frac{1}{r} \right\rangle_{n,l,m} = \frac{\mu Z e^2}{\hbar^2 n^2} = \frac{Z \mu c \alpha}{\hbar n^2} = \frac{Z}{a_0 n^2}$$

11.17.

(a) Treat $\gamma \mathbf{p}^2 / 2\mu$ as a perturbation for the hydrogen-like atom and, using the techniques of Problem 11.16, show that

$$\left\langle \frac{\mathbf{p}^2}{2\mu} \right\rangle_{n,l,m} = \frac{\mu c^2 Z^2 \alpha^2}{2n^2}$$

(b) Use the results of (a) and Problem 11.16 to show that for the hydrogen atom

$$\langle K \rangle = -\frac{1}{2} \langle V \rangle$$

in agreement with the virial theorem in quantum mechanics. See Problem 10.13.

11.18. In order to evaluate $\langle 1/r^2 \rangle$ take γ/r^2 as a perturbation for the hydrogen atom. Here again we can obtain the exact solution since the perturbation modifies the centrifugal potential in (10.12) as follows:

$$\frac{l(l+1)\hbar^2}{2\mu r^2} + \frac{\gamma}{r^2} = \frac{l'(l'+1)\hbar^2}{2\mu r^2}$$

Thus the exact energy is given by

$$E = -\frac{\mu c^2 Z^2 \alpha^2}{2(n_r + l' + 1)^2}$$

Show that

$$\left\langle \frac{\gamma}{r^2} \right\rangle_{n,l,m} = E_{n,l,m}^{(1)} = \gamma \left(\frac{dE}{d\gamma} \right)_{\gamma=0} = \gamma \left(\frac{dE}{dl'} \right)_{l'=l} \left(\frac{dl'}{d\gamma} \right)_{l'=l} = \frac{\gamma Z^2}{n^3 a_0^2 (l + \frac{1}{2})}$$

11.19. We cannot use the techniques of Problem 11.16 to evaluate $\langle 1/r^3 \rangle$, since there is no term in the Coulomb Hamiltonian that involves $1/r^3$. However, use the fact that

$$\langle n, l, m | [\hat{H}_0, \hat{p}_r] | n, l, m \rangle = 0$$

where $\hat{p}_r$ is the radial momentum operator introduced in (9.92) and $\hat{H}_0$ is the unperturbed hydrogenic Hamiltonian (11.65), to show that

$$\left\langle \frac{1}{r^3} \right\rangle_{n,l,m} = \frac{Z}{a_0 l (l+1)} \left\langle \frac{1}{r^2} \right\rangle_{n,l,m} = \frac{Z^3}{a_0^3 n^3 l (l+1)(l+\frac{1}{2})}$$