CHAPTER 13

The Structure of Atoms

SECTION 13.1

13.1 We might expect the configurations of the atoms from Sc–Zn to follow a regular pattern of filling the 3d subshell that characterizes this first row of transition metals: from 1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$4s$^2$3d$^1$ for Sc to 1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$4s$^2$3d$^{10}$ for Zn. Instead, one finds that the trend is followed from Sc through V, but Cr, which one might expect to be 1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$4s$^2$3d$^4$, is found instead to be 1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$4s$^1$3d$^5$. Likewise, Cu is not 1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$4s$^2$3d$^9$, but 1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$4s$^1$3d$^{10}$ instead. These two anomalies are explained by invoking the extra stability of filled and half-filled subshells. Chromium lowers its total energy by moving an expected 4s electron into the 3d subshell, giving each a half-filled configuration. Similarly, Cu moves a 4s electron into 3d to make this subshell full with 10 electrons. Our task in this chapter is to understand why these changes lead to extra stability.

13.2 Elements that comprise the first “g block” ($l = 4$) would number 2($2l + 1$) in all, or, for $l = 4$, 18 in all. The factor of 2 accounts for the two electrons that can be spin paired into any one orbital, and $2l + 1$ is the number of orbitals ($m$ values) that are associated with any $l$ value.

SECTION 13.2

13.3 If $y = x_1 + x_2 - x_3$, the results of applying $\hat{P}_{12}$, $\hat{P}_{13}$, and $\hat{P}_{23}$ to $y$ are

$$\hat{P}_{12} y = x_2 + x_1 - x_3 = (+1)y$$
$$\hat{P}_{13} y = x_3 + x_2 - x_1 \neq (±1)y$$
$$\hat{P}_{23} y = x_1 + x_3 - x_2 \neq (±1)y.$$

Only the $\hat{P}_{12}$ operator gives an eigenvalue relation, with $\hat{P}_{12} y = (+1)y$.  

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13.4 If \( y_1(x_1) = \sin x_1 \) and \( y_2(x_2) = \cos x_2 \), we can construct a function \( f_+(x_1, x_2) \) that is symmetric with respect to exchange (i.e., that has an eigenvalue of +1 with respect to the \( \hat{P}_{12} \) operator):

\[
f_+(x_1, x_2) = y_1(x_1)y_2(x_2) + y_1(x_2)y_2(x_1) = \sin x_1 \cos x_2 + \sin x_2 \cos x_1
\]

\[
\hat{P}_{12}f_+(x_1, x_2) = \sin x_2 \cos x_1 + \sin x_1 \cos x_2 = f_+(x_1, x_2).
\]

Similarly, an antisymmetric function \( f_-(x_1, x_2) \) is

\[
f_-(x_1, x_2) = y_1(x_1)y_2(x_2) - y_1(x_2)y_2(x_1) = \sin x_1 \cos x_2 - \sin x_2 \cos x_1
\]

\[
\hat{P}_{12}f_-(x_1, x_2) = \sin x_2 \cos x_1 - \sin x_1 \cos x_2 = -f_-(x_1, x_2).
\]

13.5 If the two particles are identical spinless bosons that do not interact, the total wavefunction has no spin function factors and it must be symmetric with respect to interchange of the two particle’s coordinates. These requirements are met by the function \( \Psi_+ \) of Eq. (13.4). For two identical particles in a box of length \( L \), this equation is

\[
\Psi_+(x_1, x_2) = \frac{1}{\sqrt{2}} \left[ \psi_1(x_1)\psi_2(x_2) + \psi_1(x_2)\psi_2(x_1) \right]
\]

\[
= \frac{2}{\sqrt{2}L} \left[ \sin \left( \frac{\pi x_1}{L} \right) \sin \left( \frac{2\pi x_2}{L} \right) + \sin \left( \frac{\pi x_2}{L} \right) \sin \left( \frac{2\pi x_1}{L} \right) \right].
\]

Note that the technique used to arrive at a symmetric total function composed of two individual particle functions is identical to that used in the previous problem (with the addition here of the normalization factor \( 1/\sqrt{2} \)). If the particles are identical spin 1/2 fermions, the total wavefunction must be antisymmetric with respect to coordinate interchange. The \( \Psi_- \) function of Eq. (13.4) satisfies this requirement, but it is incomplete in that it does not include the spin wavefunctions of the two particles. If we multiply this function by a spin wavefunction that is symmetric with respect to exchange, we still preserve the antisymmetric character of the entire wavefunction. There are three ways we can do this:

\[
\Psi_1(x_1, x_2) = \frac{1}{\sqrt{2}} \left[ \psi_1(x_1)\psi_2(x_2) - \psi_1(x_2)\psi_2(x_1) \right] \alpha(1)\alpha(2)
\]

\[
\Psi_2(x_1, x_2) = \frac{1}{\sqrt{2}} \left[ \psi_1(x_1)\psi_2(x_2) - \psi_1(x_2)\psi_2(x_1) \right] \beta(1)\beta(2)
\]

\[
\Psi_3(x_1, x_2) = \frac{1}{\sqrt{2}} \left[ \psi_1(x_1)\psi_2(x_2) - \psi_1(x_2)\psi_2(x_1) \right] \frac{1}{\sqrt{2}} \left[ \alpha(1)\beta(2) + \alpha(2)\beta(1) \right].
\]
These three functions include the three spin function combinations we can write that are symmetric, but there is a fourth acceptable function: one with a symmetric spatial part multiplying an antisymmetric spin part:

$$\Psi_4(x_1, x_2) = \frac{1}{\sqrt{2}} \left[ \psi_1(x_1)\psi_2(x_2) + \psi_1(x_2)\psi_2(x_1) \right] \frac{1}{\sqrt{2}} \left[ \alpha(1)\beta(2) - \alpha(2)\beta(1) \right].$$

These four functions are quite general, and we will encounter them again as Equations (13.23a)–(13.23d) where they are used to describe an excited state of helium.

13.6 The symmetric ($\Psi_+$) and antisymmetric ($\Psi_-$) total spatial wavefunctions can be written as in Problem 13.5:

$$\Psi_{\pm}(\phi_1, \phi_2) = \frac{1}{\sqrt{2}} \left[ \psi_1(\phi_1)\psi_2(\phi_2) \pm \psi_1(\phi_2)\psi_2(\phi_1) \right]$$

$$= \frac{1}{\sqrt{2}} \frac{1}{2\pi} \left[ e^{i\phi_1} e^{-i\phi_2} \pm e^{i\phi_2} e^{-i\phi_1} \right]$$

$$= \frac{1}{\sqrt{2}} \frac{1}{2\pi} \left[ e^{i(\phi_1 - \phi_2)} \pm e^{-i(\phi_1 - \phi_2)} \right]$$

$$= \frac{1}{\sqrt{2}} \frac{1}{2\pi} \left[ e^{i\Delta\phi} \pm e^{-i\Delta\phi} \right].$$

Using the identity $e^{\pm i\Delta\phi} = \cos \Delta\phi \pm i \sin \Delta\phi$, we can write

$$\Psi_+ (\phi_1, \phi_2) = \Psi_+(\Delta\phi) = \frac{\sqrt{2}}{2\pi} \cos \Delta\phi \quad \text{and} \quad \Psi_- (\phi_1, \phi_2) = \Psi_-(\Delta\phi) = \frac{i\sqrt{2}}{2\pi} \sin \Delta\phi.$$

The first is symmetric, since particle interchange turns $\Delta\phi$ into $-\Delta\phi$ and $\cos \Delta\phi = \cos(-\Delta\phi)$, and the second is antisymmetric because $\sin \Delta\phi = -\sin(-\Delta\phi)$. If the particles are bosons, $\Psi_+$ is the correct wavefunction (times a symmetric spin part if the bosons are not spinless). If they are fermions, we can either multiply $\Psi_+$ by an antisymmetric spin wavefunction, as in $\Psi_4$ of the previous problem, or we can multiply $\Psi_-$ by a symmetric spin wavefunction, as in $\Psi_1 - \Psi_3$ in the previous problem. If both particles have quantum number $m = 0$, the spatial wavefunction for either one is simply $\psi_0(\phi) = 1/\sqrt{2\pi}$; there is no particle coordinate dependence. All spatial functions we construct from this $\psi_0$ must be symmetric with respect to coordinate interchange, because there are no spatial coordinates!
13.7 Since the ground state energy of a one-electron atom varies like \( Z^2 E_1 \) where \( Z \) is the nuclear charge and \( E_1 \) is the H atom ground state energy, the independent electron energy for a two-electron atom is just \( 2Z^2 E_1 \). The electron–electron repulsion term that is neglected in the independent electron model is just \( e^2/(4\pi\varepsilon_0)r_{12} \) where \( r_{12} \) is the electron–electron separation. It is reasonable to expect this distance to be comparable to the atomic radius, which must be on the order of that for hydrogen. The general expression for \( \langle r \rangle \) on page 431 in the text reduces to \( \langle r \rangle = 3a_0/2 \) for the ground state of a one-electron atom of nuclear charge \( Z \). If we take \( r_{12} \equiv 3a_0/2 \), we can expect the neglected term to raise the independent electron energy by

\[
\frac{e^2}{(4\pi\varepsilon_0)r_{12}} = \frac{2Ze^2}{(4\pi\varepsilon_0)3a_0} = \frac{4Z}{3} \frac{e^2}{2(4\pi\varepsilon_0)a_0} = -\frac{4ZE_1}{3}.
\]

The simpler estimate of the magnitude of this effect given for He (\( Z = 2 \)) on page 456 of the text, \(-2E_1 = 27.2 \text{ eV}\), compares reasonably with this estimate, which is \(-8E_1/3 = 36.3 \text{ eV}\). Adding 36.3 eV to the independent electron energy for He, \(-108.78 \text{ eV}\), gives \(-72.5 \text{ eV}\), in reasonable agreement with the experimental \(-79.0 \text{ eV}\).

**SECTION 13.3**

13.8 Our approach here is to substitute our trial wavefunction \( \phi(x) = N \exp(-\beta x^2) \) and the harmonic oscillator Hamiltonian \( \hat{H} = -(\hat{p}^2/2\mu)(d^2/dx^2) + kx^2/2 \) into Eq. (13.9), the variation expression for the total energy \( \langle E \rangle \), and to find that value of the variation parameter \( \beta \) that minimizes \( \langle E \rangle \). We start with

\[
\langle E \rangle = \int_{-\infty}^{\infty} \phi \hat{H} \phi \, dx = N^2 \int_{-\infty}^{\infty} e^{-\beta x^2} \left( \frac{\hat{p}^2}{2\mu} \frac{d^2}{dx^2} + \frac{kx^2}{2} \right) e^{-\beta x^2} \, dx
\]

\[
= \int_{-\infty}^{\infty} \phi^2 \, dx \quad N^2 \int_{-\infty}^{\infty} e^{-2\beta x^2} \, dx
\]

We evaluate this expression integral by integral (and note that the normalization constant \( N \) cancels in the expression for \( \langle E \rangle \)). The integral in the denominator is one we have seen before, in both Example 12.4 and in Problem 11.22. It is of the form \( \int_{-\infty}^{\infty} e^{-\alpha x^2} \, dx = \sqrt{\pi/\alpha} \) with \( \alpha = 2\beta \) so that
\[
\int_{-\infty}^{\infty} e^{-2\beta x^2} \, dx = \sqrt{\frac{\pi}{2\beta}}.
\]

Next, we operate on the trial wavefunction with the Hamiltonian:

\[
\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{kx^2}{2} \right) e^{-\beta x^2} = \frac{\hbar^2}{2\mu} \left( 4\beta^2 x^2 - 2\beta \right) e^{-\beta x^2} + \frac{k}{2} x^2 e^{-\beta x^2}.
\]

We see that the numerator in the expression for \( <E> \) is a sum of two integrals:

\[
\int_{-\infty}^{\infty} e^{-\beta x^2} \left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{kx^2}{2} \right) e^{-\beta x^2} \, dx
\]

\[
= \left( \frac{k}{2} - \frac{4\beta^2 \hbar^2}{2\mu} \right) \int_{-\infty}^{\infty} x^2 e^{-2\beta x^2} \, dx + \frac{2\beta \hbar^2}{2\mu} \int_{-\infty}^{\infty} e^{-2\beta x^2} \, dx.
\]

The first integral is also known: \( \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} \, dx = \alpha^{-3/2} \sqrt{\pi}/2 \), so that we have

\[
\int_{-\infty}^{\infty} e^{-\beta x^2} \left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{kx^2}{2} \right) e^{-\beta x^2} \, dx
\]

\[
= \left( \frac{k}{2} - \frac{4\beta^2 \hbar^2}{2\mu} \right) \frac{\sqrt{\pi}}{4\sqrt{2}\beta^{3/2}} + \frac{\sqrt{\beta \pi} \hbar^2}{\sqrt{2}\mu}
\]

\[
= \frac{\sqrt{\pi} \left( \frac{4\beta^2 \hbar^2}{\mu} + k \right)}{8\sqrt{2}\beta^{3/2}}.
\]

We divide this expression by the denominator integral and write \( <E> \) as

\[
<E> = \frac{\sqrt{\pi} \left( \frac{4\beta^2 \hbar^2}{\mu} + k \right)}{(\sqrt{\pi/2\beta}) \left( \frac{1}{8\sqrt{2}\beta^{3/2}} \right)} = \frac{\beta \hbar^2}{2\mu} + \frac{k}{8\beta}.
\]
Next, we minimize $<E>$ with respect to $\beta$:

$$\frac{d<E>}{d\beta} = \frac{\hbar^2}{2\mu} - \frac{k}{8\beta^2} = 0 \quad \text{or} \quad \beta = \frac{1}{2} \sqrt{\frac{k\mu}{\hbar^2}}.$$ 

As shown on page 404 in the text, our best variational wavefunction is the exact ground-state wavefunction:

$$\phi(x) = N e^{-\beta x^2} = N \exp \left( -\frac{1}{2} \frac{\sqrt{k\mu}}{\hbar} x^2 \right).$$

13.9 For the trial wavefunction $\phi(x) = N \sin^2 \left( \frac{\pi x}{L} \right)$, the variational energy expression is

$$<E> = \frac{N^2}{3} \int_0^L \sin^2 \left( \frac{\pi x}{L} \right) \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \sin^2 \left( \frac{\pi x}{L} \right) dx$$

As is always the case, the normalization constant cancels from the expression for $<E>$. The integral in the denominator is given in the problem and equals $3L/8$. The integral in the numerator is

$$\int_0^L \sin^2 \left( \frac{\pi x}{L} \right) \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \sin^2 \left( \frac{\pi x}{L} \right) dx = -\frac{\hbar^2}{2mL^2} \int_0^L \sin^2 \left( \frac{\pi x}{L} \right) \left[ \cos^2 \left( \frac{\pi x}{L} \right) - \sin^2 \left( \frac{\pi x}{L} \right) \right] dx$$

$$= -\frac{\hbar^2}{2mL^2} \int_0^L \left[ \sin^2 \left( \frac{\pi x}{L} \right) - 2\sin^4 \left( \frac{\pi x}{L} \right) \right] dx = -\frac{\hbar^2}{2mL^2} \left[ \frac{L}{2} - 2 \left( \frac{3L}{8} \right) \right] = \frac{\hbar^2}{4mL} \frac{\pi^2}{2}$$

where we have used the identity $\cos^2 \left( \frac{\pi x}{L} \right) = 1 - \sin^2 \left( \frac{\pi x}{L} \right)$ to go from the second to third step and the integrals in the problem to go from the third to the fourth. Dividing this by the denominator, $3L/8$, gives $<E> = 2\pi^2 \frac{\hbar^2}{3mL^2}$. The exact energy is $\pi^2 \frac{\hbar^2}{2mL^2}$, which is three-fourths the variation energy.
13.10 We can follow the logic of Problem 13.8 here with only a change in the potential energy portion of the Hamiltonian from \(kx^2/2\) to \(bx^4\) where \(b\) is a constant. We will also need the definite integral \(\int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} \, dx = 3\alpha^{-5/2}\pi/4\). We write

\[
\langle E \rangle = \frac{\int_{-\infty}^{\infty} \phi \hat{H} \phi \, dx}{\int_{-\infty}^{\infty} \phi^2 \, dx} = \frac{N^2 \int_{-\infty}^{\infty} e^{-\alpha x^2} \left( -\frac{\hat{p}^2}{2\mu} \frac{d^2}{dx^2} + bx^4 \right) e^{-\alpha x^2} \, dx}{\int_{-\infty}^{\infty} e^{-2\alpha x^2} \, dx} .
\]

The integral in the denominator equals (from Problem 13.8) \(\sqrt{\pi/2\alpha}\), and the integral in the numerator is

\[
\int_{-\infty}^{\infty} e^{-\alpha x^2} \left( -\frac{\hat{p}^2}{2\mu} \frac{d^2}{dx^2} + bx^4 \right) e^{-\alpha x^2} \, dx
\]

\[
= \frac{\alpha \hat{p}^2}{\mu} \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} \, dx - \frac{\alpha^2 \hat{p}^2}{2\mu} \int_{-\infty}^{\infty} x^4 e^{-2\alpha x^2} \, dx + b \int_{-\infty}^{\infty} x^4 e^{-2\alpha x^2} \, dx
\]

\[
= \frac{\alpha \hat{p}^2}{\mu} \sqrt{\frac{\pi}{2\alpha}} - \frac{\alpha^2 \hat{p}^2}{2\mu} \frac{\sqrt{\pi}}{2(2\alpha)^{3/2}} + b \frac{3\sqrt{\pi}}{4(2\alpha)^{5/2}} .
\]

Thus, \(\langle E \rangle\) is

\[
\langle E \rangle = \frac{\frac{\alpha \hat{p}^2}{\mu} \sqrt{\frac{\pi}{2\alpha}} - \frac{\alpha^2 \hat{p}^2}{2\mu} \frac{\sqrt{\pi}}{2(2\alpha)^{3/2}} + b \frac{3\sqrt{\pi}}{4(2\alpha)^{5/2}}}{\sqrt{\frac{\pi}{2\alpha}}} = \frac{3b}{16\alpha^2} + \frac{\alpha \hat{p}^2}{2\mu} .
\]

We minimize \(\langle E \rangle\) with respect to our parameter \(\alpha\) and find

\[
\frac{d}{d\alpha} \left( \frac{3b}{16\alpha^2} + \frac{\alpha \hat{p}^2}{2\mu} \right) = -\frac{3b}{8\alpha^3} + \frac{\hat{p}^2}{2\mu} = 0 \quad \text{or} \quad \alpha = \left( \frac{3b\mu}{4\hat{p}^2} \right)^{1/3} .
\]
This gives the following variation theory estimate of the ground state energy:

\[
\langle E \rangle = \frac{3b}{16\alpha^2} + \frac{\alpha J^2}{2\mu} = \frac{3b}{16} \left( \frac{3b\mu}{4 J^2} \right)^{1/3} \frac{J^2}{2\mu} = \frac{3}{4} \frac{J}{4\mu^2} \left( \frac{3b\mu}{4 J^2} \right)^{1/3} .
\]

13.11 The first-order energy correction is the expectation value of the perturbation calculated using the zeroth-order wavefunctions, Eq. (13.16):

\[
E_n^{(1)} = \int \psi_n^{(0)*} H' \psi_n^{(0)} d\tau = H'_{nn}.
\]

For potential (a), the perturbation is zero from \( x = 0 \) to \( L/2 \) and constant at \( V_0 \) from \( x = L/2 \) to \( L \). The energy expression in this case is

\[
E_n^{(1)} = \int_0^{L/2} \psi_n^{(0)*} 0 \psi_n^{(0)} d\tau + \int_{L/2}^{L} \psi_n^{(0)*} V_0 \psi_n^{(0)} d\tau = V_0 \int_{L/2}^{L} \left| \psi_n^{(0)} \right|^2 d\tau = \frac{V_0}{2}
\]

where the final integral must equal 1/2, since it represents the probability that the unperturbed system is in the right-hand half of the box and this probability equals 1/2 by symmetry. For potential (b), the perturbation is zero from \( x = 0 \) to \( L/4 \ and from \( x = 3L/4 \) to \( L \). These regions contribute nothing to the energy correction. The region from \( x = L/4 \) to \( 3L/4 \) represents the constant \( V_0 \) perturbation and an energy correction equal to (using the unperturbed wavefunctions for the particle-in-a-box from Chapter 12, page 396 in the text)

\[
E_n^{(1)} = V_0 \int_{L/4}^{3L/4} \left| \psi_n^{(0)} \right|^2 d\tau = V_0 \frac{2}{L} \int_{L/4}^{3L/4} \sin^2 \left( \frac{n\pi x}{L} \right) d\tau.
\]

The integral given in the problem lets us write this as

\[
E_n^{(1)} = \frac{V_0}{2} + \frac{V_0}{2n\pi} \left[ \sin \left( \frac{n\pi}{2} \right) - \sin \left( \frac{3n\pi}{2} \right) \right].
\]
(Note that we cannot jump to the conclusion that our integral here equals 1/2 even though it covers half the box. The particle-in-a-box wavefunctions are symmetric about the middle of the box, but the center half of them is not equivalent to the sum of the outer two quarters.) Note that as $n \to \infty$, both potentials, (a) and (b), have energy corrections that equal $V_0/2$. This is expected, since $n \to \infty$ recovers the classical limit in which the particle simply experiences, on average, an energy change of $V_0/2$ no matter what state it is in and no matter where the potential step is placed. For finite $n$, however, the potential (b) expression takes on one of three values, depending on $n$. If we write $\sin(3n\pi/2) = \sin(n\pi/2 + n\pi)$, then the trigonometric identity $\sin(a + b) = \cos a \sin b + \sin a \cos b$ lets us write

$$E_n^{(1)} = \frac{V_0}{2} + \frac{V_0}{2n\pi} \left[ \sin \left( \frac{n\pi}{2} \right) - \sin \left( \frac{n\pi}{2} + n\pi \right) \right]$$

$$= \frac{V_0}{2} + \frac{V_0}{2n\pi} \left[ \sin \left( \frac{n\pi}{2} \right) - \cos \left( \frac{n\pi}{2} \right) \sin n\pi - \cos n\pi \sin \left( \frac{n\pi}{2} \right) \right]$$

$$= \frac{V_0}{2} + \frac{V_0}{2n\pi} \left[ \sin \left( \frac{n\pi}{2} \right) \left( 1 - \cos n\pi \right) \right],$$

since $\sin n\pi = 0$ if $n$ is an integer, as it is here. The factor in square brackets in the last expression has three distinct values: for $n = \text{any even integer}$, it is zero; for $n = 1, 5, 9, \ldots$, it equals $+2$; for $n = 3, 7, 11, \ldots$, it equals $-2$. Thus, we can summarize the first-order energy correction for potential (b) as

$$E_n^{(0)} = \begin{cases} \frac{V_0}{2}, & n = 2, 4, 6, \ldots \\ \frac{V_0}{2} + \frac{V_0}{n\pi}, & n = 1, 5, 9, \ldots \\ \frac{V_0}{2} - \frac{V_0}{n\pi}, & n = 3, 7, 11, \ldots \end{cases}$$

Note that the $n = \text{even integer}$ result is the same as for potential (a), since the wavefunctions for these states are symmetric about not only the middle of the box but also about the steps in the potential at $x = L/4$ and $3L/4$. The diagram on the next page shows the square of the unperturbed wavefunctions for $n = 1, 2, \text{and} 3$, which are representative of each of these three perturbation energies.
13.12 Following Example 13.4 and exploiting the expressions in the text for the perturbation Hamiltonian matrix elements of a quartic perturbation, we can write, with \( E_0^{(0)} - E_m^{(0)} = -m \bar{p} \omega \),

\[
\psi_0^{(1)} = \sum_{m \neq 0} \frac{H_{0m}'}{E_0^{(0)} - E_m^{(0)}} \psi_0^{(0)} - \frac{1}{2} \bar{p} \omega \sum_{m \neq 0} \frac{H_{0m}'}{E_0^{(0)} - E_m^{(0)}} \psi_0^{(0)} + \frac{1}{4} \bar{p} \omega \sum_{m \neq 0} \frac{H_{0m}'}{E_0^{(0)} - E_m^{(0)}} \psi_0^{(0)}.
\]

The matrix elements are given in the text on page 464. Substituting them into this expression gives

\[
\psi_0^{(1)} = \frac{3b}{-2\sqrt{2} \bar{p} \omega} \left( \frac{\bar{p} \omega}{k} \right)^2 \psi_2^{(0)} + \frac{3b}{-4\sqrt{6} \bar{p} \omega} \left( \frac{\bar{p} \omega}{k} \right)^2 \psi_4^{(0)}
\]

\[
= -\frac{3b \bar{p} \omega}{2\sqrt{2}k} \left( \psi_2^{(0)} + \frac{1}{2\sqrt{3}} \psi_4^{(0)} \right).
\]

The general expressions in the summary to Chapter 12 show us how to write the unperturbed ground-state wavefunction and the two unperturbed excited state wavefunctions used above:
\[ \psi_{0}(0) = \left( \frac{k}{\pi \hbar \omega} \right)^{1/4} e^{-kx^2/2 \hbar \omega} \]

\[ \psi_{2}(0) = \left( \sqrt{\frac{k}{\pi \hbar \omega}} \frac{1}{2^{2.2}} \right)^{1/2} \left( \frac{4kx^2}{\hbar \omega} - 2 \right) e^{-kx^2/2 \hbar \omega} \]

\[ = \sqrt{\pi} \left( \frac{kx^2}{\hbar \omega} - \frac{1}{2} \right)^{1/4} e^{-kx^2/2 \hbar \omega} \]

\[ = \sqrt{\pi} \left( \frac{kx^2}{\hbar \omega} - \frac{1}{2} \right) \psi_{0}(0) \]

\[ \psi_{4}(0) = \left( \sqrt{\frac{k}{\pi \hbar \omega}} \frac{1}{2^{4.24}} \right)^{1/2} \left( 16 \left( \frac{kx^2}{\hbar \omega} \right)^2 \frac{kx^2}{\hbar \omega} + 12 \right) e^{-kx^2/2 \hbar \omega} \]

\[ = \sqrt{\pi} \left( \frac{kx^2}{\hbar \omega} + \frac{1}{4} \right) \psi_{0}(0) \]

The first-order corrected ground-state wavefunction is thus, after some algebra,

\[ \psi_{0} = \psi_{0}^{(0)} + \psi_{0}^{(1)} \]

\[ = \psi_{0}^{(0)} - \frac{3b \hbar \omega}{2 \sqrt{2} k^2} \left( \psi_{2}^{(0)} + \frac{1}{2 \sqrt{3}} \psi_{4}^{(0)} \right) \]

\[ = \psi_{0}^{(0)} \left[ 1 + \frac{b \hbar \omega}{k^2} \left( \frac{9}{16} - \frac{1}{3} \frac{kx^2}{\hbar \omega} - \frac{1}{4} \frac{k^2x^4}{\hbar \omega^2} \right) \right]. \]

13.13 Using the notation of the problem and the second-order energy expressions for the two-level system discussed on page 464 of the text, we can write

\[ E_{0}^{(2)} = \frac{\left| H'_{01} \right|^2}{-\Delta E^{(0)}} \quad \text{and} \quad E_{1}^{(2)} = \frac{\left| H'_{01} \right|^2}{\Delta E^{(0)}}. \]

Thus, the perturbed energies \( E_{0} \) and \( E_{1} \) are
\[ E_0 = E_0^{(0)} + E_0^{(2)} = E_0^{(0)} - \frac{|H'_{01}|^2}{\Delta E^{(0)}} \quad \text{and} \quad E_1 = E_1^{(0)} + E_1^{(2)} = E_1^{(0)} + \frac{|H'_{01}|^2}{\Delta E^{(0)}}. \]

and the perturbed energy difference is

\[ \Delta E = \Delta E^{(0)} + \frac{2|H'_{01}|^2}{\Delta E^{(0)}} = \Delta E^{(0)} \left[ 1 + \frac{2|H'_{01}|^2}{(\Delta E^{(0)})^2} \right]. \]

If \( \Delta E = 2\Delta E^{(0)} \), this expression shows us that

\[ 2 = 1 + \frac{2|H'_{01}|^2}{(\Delta E^{(0)})^2} \quad \text{or} \quad H'_{01} = \frac{\Delta E^{(0)}}{\sqrt{2}}. \]

13.14 As is discussed in more detail in Chapter 15, this problem is related to the system’s dipole moment. We will see there that the dipole moment of a charged system (which is what we have here—the net charge is \( q \)) depends on where we place the coordinate origin in our system. The first-order energy correction is

\[ H'_{nn} = E_n^{(1)} = \int \psi_n^{(0)} x \psi_n^{(0)} \, dx = -qF_0 <\chi>_n. \]

This is independent of \( n \). If the coordinate system is placed so that the box extends from \( x = 0 \) to \( x = L \), as we did in Chapter 12, \( <\chi>_n = L/2 \) for all \( n \), but if the coordinate system is placed so that the origin is at the middle of the box, \( <\chi>_n = 0 \) and the first-order correction vanishes! This seems to be a paradox: how can the energy of the system depend on the location of an abstract coordinate origin? The resolution to this dilemma (and it recurs in the next problem) is the recognition that we can measure only energy differences. Any constant energy added to all the energy levels of the system amounts to no more than a shift of the (arbitrary) definition of the zero of total energy.

13.15 The first-order energy correction is

\[ H'_{nn} = E_n^{(1)} = \int \psi_n^{(0)} x \psi_n^{(0)} \, dx = -qF_0 <\chi>_n. \]
exactly as in the previous problem, but here, the only sensible choice for a coordinate origin is at the minimum of the harmonic potential well. With this choice, $\langle x \rangle = 0$ for all quantum numbers $n$ due to the symmetry of the potential. Since this result, $E_n^{(1)} = 0$, is a constant, any coordinate origin must also give $E_n^{(1)} = a$ constant, and since only energy differences can be measured, this term in the perturbation is not observable. To see if higher order terms are observable, we use the matrix element expressions given in the problem (and that were also derived in Problem 12.13 in terms of the dimensionless harmonic oscillator coordinate $q$ rather than the physical distance coordinate $x$ used here—hence, Problem 12.13 does not include the factor $1/\alpha$) along with the general second-order energy expression:

$$
E_n^{(2)} = \sum_{n \neq m} \frac{|H_{nm}|^2}{E_n^{(0)} - E_m^{(0)}} = q^2 F_0^2 \left( \frac{x_{n,n+1}^2 + x_{n,n-1}^2}{-\beta_0 \omega} \right) - q^2 F_0^2 \left( -\frac{n+1}{2} + \frac{n}{2} \right) = -\frac{q^2 F_0^2}{2k}.
$$

Since this term is also a constant for every state, the second-order energy correction is also not observable.

13.16 Now we consider an exact solution to the system discussed in the previous problem. We are using a simple mathematical trick—completing the square—to rewrite the potential energy. We write, as suggested in the problem, the following potential energy function:

$$
V(x) = \frac{kx^2}{2} - qF_0x + E' - E = a(x - x')^2 - E' = ax^2 - 2ax' + ax'^2 - E'.
$$

Equating coefficients of each power of $x$ in the last expression to those in the original expression for $V(x)$ shows that

$$
\frac{k}{2} = a, \quad 2ax' = kx' = qF_0, \quad x' = \frac{qF_0}{k}, \quad E' = ax'^2 = \frac{q^2 F_0^2}{2k}.
$$

These equalities let us write the potential energy as
\[
V(x) = \frac{1}{2} k(x - x')^2 - \frac{q^2 F_0^2}{2k},
\]

which is just an ordinary harmonic oscillator (define \(y = x - x'\) and recognize the pure harmonic term \(ky^2/2\)) with the zero of energy shifted down by the constant amount \(q^2 F_0^2/2k\) (which must be positive so that the shift is guaranteed to be down). Thus, the energy expression must be

\[
E = \hbar \omega \left( \nu + \frac{1}{2} \right) - \frac{q^2 F_0^2}{2k}
\]

where \(\nu\) is the usual harmonic oscillator quantum number and \(\omega = \sqrt{k/m}\) where \(m\) is the particle mass.

13.17 The unperturbed wavefunctions and energies for the particle-on-a-ring system are derived in Example 12.6:

\[
\psi_m^{(0)} = \frac{e^{im\phi}}{\sqrt{2\pi}}, \quad E_m^{(0)} = \frac{m^2 \hbar^2}{2MR^2}, \quad m = 0, \pm 1, \pm 2, \ldots
\]

and the perturbation from the electric field is

\[
\hat{H}' = -qRF_0 \cos \phi = -qRF_0 \frac{e^{i\phi} + e^{-i\phi}}{2}.
\]

The general matrix element for this perturbation is

\[
H_{mn}' = -\frac{qRF_0}{4\pi} \int_0^{2\pi} e^{-im\phi} \left( e^{i\phi} + e^{-i\phi} \right) e^{in\phi} d\phi
\]

\[
= -\frac{qRF_0}{4\pi} \left[ \int_0^{2\pi} e^{i(n + 1 - m)\phi} d\phi + \int_0^{2\pi} e^{i(n - 1 - m)\phi} d\phi \right].
\]

These integrals are both of the type \(\int_0^{2\pi} e^{ik\phi} d\phi\) where \(k\) is an integer. If \(k = 0\), the integral equals \(2\pi\), but if \(k\) is any other integer, the integral is zero:
Since $e^{2\pi ik} = 1$ for $k$ any nonzero integer. Thus, $H'_{mn} = 0$ unless $n + 1 - m = 0$ (so that the first integral in the final expression above for $H'_{mn}$ equals $2\pi$) or $n - 1 - m = 0$ (so that the second integral equals $2\pi$). Therefore

$$H'_{mn} = \begin{cases} -\frac{qRF_0}{2} & n = m + 1 \text{ or } n = m - 1 \\ 0 & \text{otherwise} \end{cases}$$

This result tells us immediately that the first-order perturbation theory correction to the energy is zero for every state, since $E_{n}^{(1)} = H'_{nn}$ and $H'_{nn} = 0$ for all $n$. The second-order energy expression is given by the sum in Eq. (13.18), which here has only two terms due to the general expression for the perturbation matrix elements we just found:

$$E_{n}^{(2)} = \sum_{m \neq n} \frac{H'_{nm} H'_{mn}}{E_{n}^{(0)} - E_{m}^{(0)}} = \frac{(H'_{n,n+1})^2}{E_{n}^{(0)} - E_{n+1}^{(0)}} + \frac{(H'_{n,n-1})^2}{E_{n}^{(0)} - E_{n-1}^{(0)}}.$$

Substituting the expressions for the unperturbed energies and the perturbation matrix elements into this equation gives

$$E_{n}^{(2)} = \frac{(-qRF_0/2)^2}{[n^2 - (n + 1)^2] (\bar{\eta}^2/2MR^2)^2} + \frac{(-qRF_0/2)^2}{[n^2 - (n - 1)^2] (\bar{\eta}^2/2MR^2)^2} = \frac{(qRF_0)^2}{4(\bar{\eta}^2/2MR^2)} \left[ \frac{1}{-2n - 1} + \frac{1}{2n - 1} \right] = \frac{q^2R^4F_0^2M}{\bar{\eta}^2} \frac{1}{4n^2 - 1}.$$

The total energy, correct through this second-order expression, is thus

$$E_{n} = E_{n}^{(0)} + E_{n}^{(2)} = \frac{n^2 \bar{\eta}^2}{2MR^2} + \frac{q^2R^4F_0^2M}{\bar{\eta}^2} \frac{1}{4n^2 - 1}.$$
If we measure energy in multiples of $\frac{\hbar^2}{2MR^2}$ and measure the strength of the perturbation through the dimensionless ratio $\varepsilon = qRF_0/(\frac{\hbar^2}{2MR^2})$, we can write the total energy in dimensionless form as

$$\frac{E_n}{\frac{\hbar^2}{2MR^2}} = n^2 + \frac{\varepsilon^2}{2(4n^2 - 1)}.$$ 

This expression lets us see clearly that our perturbation term has the properties we expect: for the ground state, $n = 0$, this term is negative—the second-order correction always lowers the ground state energy—but for all other states, the perturbation is positive and decreasing with increasing $n$. A comparison of the unperturbed and perturbed energies for the lowest few states is shown below in a diagram drawn to scale for the case $\varepsilon = 1$ (which is an unreasonably large value for a “perturbation”).

**SECTION 13.4**

13.18 We start with the expression in the problem, written to expose the one-electron atom potential energy operator, the factor in parentheses below, written for a one-electron atom of nuclear charge $Z_e$:

$$- \frac{(2 - Z_e) e^2}{(4\pi\varepsilon_0)r} = - \frac{2 - Z_e}{Z_e} \frac{Ze^2}{(4\pi\varepsilon_0)r} = \frac{2 - Z_e}{Z_e} \left( \frac{Ze^2}{(4\pi\varepsilon_0)r} \right).$$

The Virial Theorem for a one-electron atom tells us that $\langle \hat{E} \rangle = \langle \hat{V} \rangle / 2$ where the average expressed by the angle brackets is taken over the ground state here. Performing this average over the expression above gives us
\[
\left\langle -\frac{(2 - Z_e) e^2}{(4\pi\varepsilon_0)r} \right\rangle = \frac{2 - Z_e}{Z_e} \left\langle -\frac{Z_e e^2}{(4\pi\varepsilon_0)r} \right\rangle = \frac{2 - Z_e}{Z_e} <\hat{V}> = \frac{2 - Z_e}{Z_e} (2E_1)
\]

where \(E_1\) represents the ground-state energy for a one-electron atom of nuclear charge \(Z_e\). Since

\[
E_1 = -\frac{Z_e^2 e^2}{2(4\pi\varepsilon_0)a_0}
\]

from Eq. (12.46b), we have

\[
\left\langle -\frac{(2 - Z_e) e^2}{(4\pi\varepsilon_0)r} \right\rangle = \frac{2 - Z_e}{Z_e} (2E_1) = -\frac{2 - Z_e}{Z_e} \frac{Z_e^2 e^2}{(4\pi\varepsilon_0)a_0} = \left(\frac{Z_e^2}{2} - 2Z_e\right) \frac{Z_e^2 e^2}{(4\pi\varepsilon_0)a_0},
\]

which is the expression we seek.

13.19 For \(H^-\), the real nuclear charge is \(Z = 1\) rather than the He value \(Z = 2\). This changes the expression for \(<E>\) from that on page 470 in the text just before Eq. (13.20) into

\[
<E> = \frac{e^2}{(4\pi\varepsilon_0)a_0} \left[ \frac{Z_e^2}{2} - Z_e^2 + \left(Z_e^2 - Z_e\right) + \frac{Z_e^2}{2} - Z_e^2 + \left(Z_e^2 - Z_e\right) + \frac{5}{8} Z_e \right]
\]

\[
= \frac{e^2}{(4\pi\varepsilon_0)a_0} \left(Z_e^2 - \frac{11}{8} Z_e \right) = (27.196 \text{ eV}) \left(Z_e^2 - \frac{11}{8} Z_e \right).
\]

As in the text, we next minimize \(<E>\) with respect to \(Z_e\) and find

\[
\frac{d<E>}{dZ_e} = (27.196 \text{ eV}) \left(2Z_e - \frac{11}{8}\right) = 0 \quad \text{or} \quad Z_e = \frac{11}{16}.
\]

Thus, the variational energy is

\[
<E> = (27.196 \text{ eV}) \left[\left(\frac{11}{16}\right)^2 - \frac{11}{8} \frac{11}{16}\right] = -12.854 \text{ eV}.
\]
Note that this number is greater than the energy of H + e−, which is just the ground-state H atom energy, −13.598 eV. The experimental H− energy is the negative of the first and second ionization energies: −(13.598 eV + 0.7542 eV) = −14.352 eV. Not only does the variational calculation predict a significantly greater energy for H− than is observed, it predicts an energy greater than that of H + e−, which means it does not predict H− to be stable.

13.20 Figure 12.14c represents the true H atom 3s function with its two characteristic radial nodes. Slater orbitals do not have radial nodes. The diagrams below compare the true 3s wavefunction and radial distribution function to their Slater approximations.

13.21 If we consider Al, with Z = 13 and a 1s22s22p63s23p1 configuration, perfect screening would predict that the 3p Ze would be 1 (the other 12 electrons screen 12 of the nuclear proton charges perfectly), the 3s Ze would be 3 (10 other electrons screening perfectly), the 2p Ze would be 9 (4 other electrons screening perfectly), the 2s Ze would be 11 (perfect screening from the two 1s electrons),
and the 1s $Z_e$ would be 13 (completely unscreened innermost orbital). These predictions and the true values are compared in the table below.

<table>
<thead>
<tr>
<th></th>
<th>1s</th>
<th>2s</th>
<th>2p</th>
<th>3s</th>
<th>3p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfect screening</td>
<td>13</td>
<td>11</td>
<td>9</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Actual screening</td>
<td>12.59</td>
<td>8.21</td>
<td>8.96</td>
<td>4.12</td>
<td>4.07</td>
</tr>
</tbody>
</table>

Comparison shows that penetration is significantly different for s and p orbitals, and that 2p orbitals are almost perfectly screened (in this model), but 3p orbitals are not.

13.22 Before we attack this problem head-on and quickly fill a page or two with algebra, it is helpful to write the Hamiltonian in a slightly simpler way that keeps us from writing too many fundamental constants again and again. We recognize that

$$-\frac{\hbar^2}{2\mu} = a_0^2 E_1 \quad \text{and} \quad -\frac{e^2}{(4\pi\epsilon_0)} = 2a_0 E_1 \quad \text{so that}$$

$$\hat{H} = E_1 \left[ a_0^2 \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + 2a_0 \right].$$

Here, $E_1$ is the H-atom ground state energy and $a_0$ is the Bohr radius. This lets us write the variation integral for $<E>$ as

$$<E> = \left[ \int_0^\infty d\tau \int_0^\infty e^{-\alpha r^2} \left[ a_0^2 \frac{d}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{2a_0}{r} \right] e^{-\alpha r^2} r^2 dr \right].$$

The integral in the denominator equals $\sqrt{\pi/(2\alpha)^3}/4$, and the numerator is a sum of three integrals whose values are known:
\[
E_1 \int_0^\infty e^{-\alpha r^2} \left[ \frac{a_0^2}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{2a_0}{r} \right] e^{-\alpha r^2} r^2 dr
\]

\[
= 2E_1 a_0 \left[ \int_0^\infty e^{-2\alpha r^2} r dr - 3a_0 \alpha \int_0^\infty e^{-2\alpha r^2} r^2 dr + 2a_0 \alpha^2 \int_0^\infty e^{-2\alpha r^2} r^4 dr \right]
\]

\[
= E_1 a_0 \left( \frac{1}{2\alpha} \frac{3a_0 \sqrt{\pi}}{4\sqrt{2\alpha}} + \frac{3a_0 \sqrt{2\pi}}{16\sqrt{\alpha}} \right).
\]

Thus, \( \langle E \rangle \) is, after some simplifying algebra,

\[
\langle E \rangle = E_1 a_0 \left( \frac{4\sqrt{2\alpha}}{\sqrt{\pi}} - 3a_0 \alpha \right).
\]

The best value for \( \alpha \) is the one that minimizes this energy:

\[
\frac{d\langle E \rangle}{d\alpha} = E_1 a_0 \left( \frac{2\sqrt{2}}{\sqrt{\pi} \alpha} - 3a_0 \right) = 0 \text{ or } \alpha = \frac{8}{9a_0^2 \pi}.
\]

Substituting this into the energy expression gives the best energy:

\[
\langle E \rangle = E_1 a_0 \left( \frac{4\sqrt{2}}{\sqrt{\pi}} \frac{8}{9a_0^2 \pi} - 3a_0 \frac{8}{9a_0^2 \pi} \right) = \frac{8E_1}{3\pi} = 0.8489E_1.
\]

Note that, since \( E_1 \) is less than zero, \( \langle E \rangle \) here is greater than \( E_1 \), as we should expect from a variational calculation. If we plot on the same graph this best GTO (with \( N \) equal to \( 16\sqrt{3} / 9a_0^{3/2} \pi \), a value we can find from the normalization integral expression and the value of the integral in the denominator for \( \langle E \rangle \)) along with the \( 1s \) STO, we find the figure shown at the top of the next page, which looks very different from the graph on page 473 in the text. That figure was drawn with \( \alpha \) chosen to represent the STO in a least-squares sense, and its \( \alpha \) value, \( 0.967/a_0^{1/2} \), predicts \( \langle E \rangle = 0.2374E_1 \), a much higher energy than the variational result.
For the 1s$^1$2p$^1$ configuration of He, the electron spins are free to take on either value, $\alpha$ or $\beta$, without violating the Pauli Principle (since they are inequivalent electrons). In the abbreviated Slater determinant notation, the twelve possibilities are:

\[
\begin{align*}
&|| 1s\alpha(1) 1p_x\alpha(2) || || 1s\alpha(1) 1p_y\alpha(2) || || 1s\alpha(1) 1p_z\alpha(2) || \\
&|| 1s\beta(1) 1p_x\beta(2) || || 1s\beta(1) 1p_y\beta(2) || || 1s\beta(1) 1p_z\beta(2) || \\
&|| 1s\alpha(1) 1p_x\beta(2) || || 1s\alpha(1) 1p_y\beta(2) || || 1s\alpha(1) 1p_z\beta(2) || \\
&|| 1s\beta(1) 1p_x\alpha(2) || || 1s\beta(1) 1p_y\alpha(2) || || 1s\beta(1) 1p_z\alpha(2) ||
\end{align*}
\]

Note that the first three have both spins $\alpha$, the next three have both $\beta$, the next have an $\alpha\beta$ assignment, and the last three have a $\beta\alpha$ assignment. The full Slater determinant for the last possibility, for example, is

\[
|| 1s\beta(1) 1p_z\alpha(2) || = \frac{1}{\sqrt{2}} \begin{vmatrix}
1s\beta(1) & 1p_z\alpha(1) \\
1s\beta(2) & 1p_z\alpha(2)
\end{vmatrix}.
\]

The full Slater determinant for the other eleven possibilities follow in analogous fashion.

If we assume a 1s$^3$ configuration for Li, then we have the following Slater determinant:

\[
\frac{1}{\sqrt{6}} \begin{vmatrix}
1s\alpha(1) & 1s\beta(1) & 1s\alpha(1) \\
1s\alpha(2) & 1s\beta(2) & 1s\alpha(2) \\
1s\alpha(3) & 1s\beta(3) & 1s\alpha(3)
\end{vmatrix}
\]
where the final column could as easily have been written with $\beta$ spin as with $\alpha$. Note that either possible determinant has one column duplicated; here, the first and third are the same. If we apply the general expansion of a $3 \times 3$ determinant given in the problem to one with two identical columns, we find that it is identically zero:

$$\begin{vmatrix} a & b & a \\ d & e & d \\ g & h & g \end{vmatrix} = aeg + bdg + adh - aeg - bdg - adh = 0.$$  

13.25 Since $\phi_1 = \phi_2 = 1s$ for the He ground state, the definitions of the $J$ and $K$ integrals (following Eq. (13.26) on page 477 of the text) show us that what we have here is $J_{ii} = J_{11} = J = K_{ii} = K_{11} = K$.

SECTION 13.5

13.26 The spin-orbit energy expression, Eq. (13.31), is

$$E_{so}^{(1)} = \frac{\hbar^2}{2} h_{so} \left[ j(j+1) - l(l+1) - s(s+1) \right],$$

and to find the spin-orbit coupling constant, $h_{so}$, from energy differences (intervals) between terms split by spin-orbit interaction, we must calculate this energy for each level of the interval and subtract them to express the interval in terms of $h_{so}$. For a $^2P_{3/2}$ level, $s = 1/2$, $l = 1$, and $j = 3/2$. For a $^2P_{1/2}$ level, $s = 1/2$, $l = 1$, and $j = 1/2$. This gives us

$$E_{so}^{(1)}(^2P_{3/2}) = \frac{\hbar^2}{2} h_{so} \left[ \frac{3}{2} \frac{5}{2} - \frac{3}{2} \frac{3}{2} \right] = \frac{\hbar^2}{2} h_{so}$$

$$E_{so}^{(1)}(^2P_{1/2}) = \frac{\hbar^2}{2} h_{so} \left[ \frac{1}{2} \frac{3}{2} - \frac{1}{2} \frac{3}{2} \right] = -\frac{\hbar^2}{2} h_{so}$$

so that the interval is $\hbar^2 h_{so}/2 - (-\hbar^2 h_{so}) = 3 \hbar^2 h_{so}/2$. The halogen intervals in Example 13.5 are expressed in cm$^{-1}$ units, and the units for $h_{so}$ in our expressions above are (energy)/(angular momentum)$^2 = J/(J s)^2 = \text{kg}^{-1} \text{m}^{-2}$ in SI units. Thus, we convert the interval energies from cm$^{-1}$ to J units before dividing them by $3 \hbar^2/2$. This gives us the table shown at the top of the next page, which reproduces the data in the text along with the results of our calculations here.
### Table

<table>
<thead>
<tr>
<th>Halogen</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interval/cm⁻¹</td>
<td>404</td>
<td>881</td>
<td>3685</td>
<td>7603</td>
</tr>
<tr>
<td>Interval/10⁻²¹ J</td>
<td>8.025</td>
<td>17.50</td>
<td>73.20</td>
<td>151.0</td>
</tr>
<tr>
<td>( h_{so} )/10⁴⁷ kg⁻¹ m⁻²</td>
<td>4.811</td>
<td>10.49</td>
<td>43.88</td>
<td>90.54</td>
</tr>
</tbody>
</table>

The units we have here for \( h_{so} \) are perfectly acceptable, but somewhat awkward. Often, spin-orbit coupling constants are expressed in cm⁻¹ units directly (as if \( J \) was not in the energy expression and with energy expressed in cm⁻¹ units). With this convention, we would express \( h_{so} \) simply as two-thirds the interval. Finally, note that we have the correct magnitude of \( h_{so} \) here, as the problem requested, but in fact, \( h_{so} \) is negative for the halogens, since their two lowest energy levels are said to be inverted. The higher \( J \) term, \( 2P_{3/2} \), is the ground state. By convention, the “noninverted” energy level ordering is taken to be in increasing order of \( J \).

13.27 Table 13.2 tells us that the d², d⁸ configurations have \(^1S\), \(^1D\), \(^1G\), \(^3P\), and \(^3F\) terms. We assign possible \( J \) values to each as shown in the table below.

<table>
<thead>
<tr>
<th>Term</th>
<th>( S )</th>
<th>( L )</th>
<th>Possible ( J ) values</th>
<th>Complete term symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1S)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(^1S_0)</td>
</tr>
<tr>
<td>(^1D)</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>(^1D_2)</td>
</tr>
<tr>
<td>(^1G)</td>
<td>0</td>
<td>4</td>
<td>4</td>
<td>(^1G_4)</td>
</tr>
<tr>
<td>(^3P)</td>
<td>1</td>
<td>1</td>
<td>0, 1, 2</td>
<td>(^3P_0, ^3P_1, ^3P_2)</td>
</tr>
<tr>
<td>(^3F)</td>
<td>1</td>
<td>3</td>
<td>2, 3, 4</td>
<td>(^3F_2, ^3F_3, ^3F_4)</td>
</tr>
</tbody>
</table>

The \( S \) values come from the relationship between the term symbol multiplicity (the pre-superscript) and \( S \): multiplicity = \( 2S + 1 \); the \( L \) value is coded in the central letter in the usual way: S, P, D, F, G \( \rightarrow \) \( L = 0, 1, 2, 3, 4 \); and the possible \( J \) values range from \( L + S \) down to \( |L − S| \) in unit steps. According to Hund’s rules, the triplets are lower in energy than the singlets; of the triplets, the term of greatest \( L \) is lowest (\( L = 3 \), or \(^3F\)), and of the \(^3F\) possibilities, the minimum \( J \) is lowest for the less-than-half-filled d² configuration (\(^3F_2\)), but the maximum \( J \) is lowest for the greater-than-half-filled d⁸ configuration (\(^3F_4\)). An example of a \(^3F_2\) ground state is \( d^2 \) Ti, and Ni is the example of a \( d^8 \) \(^3F_4\) ground state.

13.28 The ground-state valence configuration of the alkaline earths is \( ns^2 \). The first excited configuration is therefore \( ns^1np^1 \). For this configuration, the s electron has \( l = 0 \) and the p electron has \( l = 1 \) so that \( L \) must equal 1, a P term. The
Electron spins are independent and can pair in an $S = 0$ (singlet) or in an $S = 1$ (triplet) fashion, leading to $1P$ and $3P$ terms. The $1P$ term can only have $J = 1$ (a $1P_1$ term symbol), but the $3P$ can have $J = 0$, 1, or 2 for $3P_0$, $3P_1$, and $3P_2$ term symbols. The triplet with minimum $J$ is lowest, according to Hund’s rules for a less-than-half-filled configuration: $3P_0$ is the lowest energy level of those derived from the $ns^1np^1$ configuration.

13.29 The elements half-way across any $l$ block in the Periodic Table have half-filled subshells: H–Fr are $ns^1$, N–Bi are $np^3$, Mn–Re are $nd^5$, and Eu–Am are $nf^7$. According to Hund’s rules, the maximum spin multiplicity state will be lowest in energy, and for half-filled subshells, the maximum multiplicity comes from all spins aligned. This accounts for the increasing $2S + 1$ multiplicities:

- $ns^1 \rightarrow S = 1/2 \rightarrow$ doublet multiplicity
- $np^3 \rightarrow S = 3/2 \rightarrow$ quartet multiplicity
- $nd^5 \rightarrow S = 5/2 \rightarrow$ sextet multiplicity
- $nf^7 \rightarrow S = 7/2 \rightarrow$ octet multiplicity.

Since all of these electrons have the same $l$ value (s, p, d, or f), the only way to align all these spins and obey the Pauli Principle is to assign each to a unique $m_l$ value. For example, the $np^3$ configuration with all spins aligned must have $m_l = -1$ for one electron, 0 for another, and +1 for the third. With this assignment, the total orbital angular momentum adds to $L = 0$, an S state.

13.30 The table suggested in the problem is shown below:

<table>
<thead>
<tr>
<th>$m$</th>
<th>$m_L$</th>
<th>$m_S$</th>
<th>$m$</th>
<th>$m_L$</th>
<th>$m_S$</th>
<th>$m$</th>
<th>$m_L$</th>
<th>$m_S$</th>
<th>$m$</th>
<th>$m_L$</th>
<th>$m_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>↑↓</td>
<td></td>
<td>+1</td>
<td></td>
<td></td>
<td>+1</td>
<td></td>
<td></td>
<td>+1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>⬇️</td>
<td>⬆️</td>
<td>0</td>
<td>⬇️</td>
<td>⬆️</td>
<td>0</td>
<td>⬇️</td>
<td>⬆️</td>
<td>0</td>
<td>⬇️</td>
<td>⬆️</td>
</tr>
<tr>
<td>−1</td>
<td>⬆️</td>
<td>⬇️</td>
<td>−1</td>
<td>⬆️</td>
<td>⬇️</td>
<td>−1</td>
<td>⬆️</td>
<td>⬇️</td>
<td>−1</td>
<td>⬆️</td>
<td>⬇️</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>−2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>−1</td>
<td>−1</td>
<td>−1</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>−1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>−1</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note that there are 15 columns in the table, and we interpret the $m_L$ and $m_S$ values in the last two rows as coordinates for nonzero entries in a Slater diagram. The entire diagram, given in the problem, is reproduced at the top of the next page with the subdiagrams for each term symbol outlined by a rectangle or square.
The diagram for any one term symbol has a “1” in each circle within the rectangle outlining it above, and the total Slater diagram is simply the sum of all the 1’s in all the overlapping subdiagrams.

13.31 For three equivalent p electrons, Table 13.2 tells us we should find $^2P$, $^2D$, and $^4S$ terms. The table of possible spin combinations for the p$^3$ configuration has 20 columns, as shown below:

<table>
<thead>
<tr>
<th>$m = +1$</th>
<th>$\uparrow$</th>
<th>$\uparrow\downarrow$</th>
<th>$\uparrow\downarrow$</th>
<th>$\uparrow$</th>
<th>$\downarrow$</th>
<th>$\downarrow\uparrow$</th>
<th>$\downarrow\uparrow$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m = 0$</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>$m = -1$</td>
<td>↑</td>
<td>↓</td>
<td>↑</td>
<td>↓</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
</tr>
</tbody>
</table>

The Slater diagram corresponding to this table, with the subdiagrams for each term symbol, is shown at the top of the next page. Note that this diagram is five columns across, as in the previous problem, but it is four rows tall due to the half-integral values for $m_S$ that are due to the odd number of electrons here. Note also the general rule that any subdiagram must extend as far to the right as it does to the left of the diagram’s center, and that each must also extend as far above as below that center. Moreover, the subdiagram’s spin multiplicity tells us its height in rows and its $L$ value tells us its width in columns.
13.32 In the Ce ground-state configuration, 4f\textsuperscript{1}5d\textsuperscript{1}6s\textsuperscript{2}, we see that the 6s subshell is full and can be ignored for the purposes of determining term symbols. The f electron has \( l = 3 \), and the d electron has \( l = 2 \) so that \( L \) is at most \( 3 + 2 = 5 \) and at least \( |3 - 2| = 1 \) with all integral values in between allowed. This gives P, D, F, G, and H terms. Since the electrons are independent, they can be spin-paired for \( S = 0 \), a singlet term, or unpaired for \( S = 1 \), a triplet. These spin multiplicities are allowed for each \( L \) value so that the possible term symbols neglecting \( J \) are \( 1P, 3P, 1D, 3D, 1F, 3F, 1G, 3G, 1H, \) and \( 3H \). Including \( J \) expands this list to read \( 1P_1, 3P_{0,1,2}, 1D_2, 3D_{1,2,3}, 1F_3, 3F_{2,3,4}, 1G_4, 3G_{3,4,5}, 1H_5, \) and \( 3H_{4,5,6} \). That this rather innocuous-looking configuration gives rise to 20 different energy states might help you understand why the lanthanide elements have very complicated energy level patterns and atomic spectra.

13.33 Not all of the singly-charged anions of the elements from H through Ne are stable, but of those that are, we can use isoelectronic analogies to write their ground-state term symbols. For example, H\textsuperscript{–} is isoelectronic to He and thus has a \( 1\text{S}_0 \) term symbol. Continuing, He\textsuperscript{–} is unstable, Li\textsuperscript{–} is like Be: \( 1\text{S}_0 \), Be\textsuperscript{–} is unstable, B\textsuperscript{–} is like C: \( 3\text{P}_0 \), C\textsuperscript{–} is like N: \( 4\text{S}_{3/2} \), N\textsuperscript{–} is unstable, O\textsuperscript{–} is like F: \( 2\text{P}_{3/2} \), F\textsuperscript{–} is like Ne: \( 1\text{S}_0 \), and Ne\textsuperscript{–} is unstable. For the singly-charged cations, H\textsuperscript{+} has no electrons and thus needs no terms symbol, He\textsuperscript{+} is \( 2\text{S}_{1/2} \), Li\textsuperscript{+} is \( 1\text{S}_0 \), Be\textsuperscript{+} is \( 2\text{S}_{1/2} \), B\textsuperscript{+} is \( 1\text{S}_0 \), C\textsuperscript{+} is \( 2\text{P}_{1/2} \), N\textsuperscript{+} is \( 3\text{P}_0 \), O\textsuperscript{+} is \( 4\text{S}_{3/2} \), F\textsuperscript{+} is \( 3\text{P}_2 \), and Ne\textsuperscript{+} is \( 2\text{P}_{3/2} \).

13.34 From Problem 13.27, we know that the possible term symbols for Ti in the 3d\textsuperscript{2}4s\textsuperscript{2} configuration are \( 1\text{S}_0, 1\text{D}_2, 1\text{G}_4, 3\text{P}_0, 3\text{P}_1, 3\text{P}_2, 3\text{F}_2, 3\text{F}_3, \) and \( 3\text{F}_4 \) with the \( 3\text{F}_2 \) term the ground state. The next two levels are quite nearby and must
correspond to $^3\!F_3$ and $^3\!F_4$, respectively. We expect the other set of triplet levels, $^3\!P_0$, $^3\!P_1$, and $^3\!P_2$, to come next and in this order. We then assign the state at 8602 cm$^{-1}$ to $^1\!G_4$, since it is the singlet state of highest $L$. The final observed state at 12 118 cm$^{-1}$ must be the $^1\!D_2$ state, since the $^1\!S_0$ state is as yet unobserved.

**13.35** To couple the $^8\!S$ and $^3\!P$ terms that represent the f and sp electrons, respectively, in the 4f$^7$6s$^1$6p$^1$ configuration of Eu, we first decompose them into their corresponding $S$ and $L$ values: $^8\!S \rightarrow S = 7/2$ and $L = 0$; $^3\!P \rightarrow S = 1, L = 1$. The $L$ values can only couple to give $L = 1$ so that all states must be $P$ states. The $S$ values can couple to a resultant $S$ that has any of the values 5/2, 7/2, or 9/2 so that the multiplicity possibilities are 6, 8, and 10. The nine complete term symbols including $J$ are $^6\!P_{3/2, 5/2, 7/2}$, $^8\!P_{5/2, 7/2, 9/2}$, and $^{10}\!P_{7/2, 9/2, 11/2}$.

**GENERAL PROBLEMS**

**13.36** The trial wavefunction is

$$\phi(x) = c_1\psi_1(x) + c_2\psi_2(x) = \left(\frac{2}{L}\right)^{1/2} \left[ c_1 \sin\left(\frac{\pi x}{L}\right) + c_2 \sin\left(\frac{2\pi x}{L}\right) \right],$$

and the perturbation is zero from $x = 0$ to $x = L/2$ but constant at $V_0 = E_1 = \frac{\hbar^2 \pi^2}{2mL^2}$ from $x = L/2$ to $x = L$. The variational energy expression is given by Eq. (13.13):

$$\langle E \rangle = \frac{\sum_{i=1}^{2} \sum_{j=1}^{2} c_i^* c_j H_{ij}}{\sum_{i=1}^{2} \sum_{j=1}^{2} c_i^* c_j S_{ij}},$$

and it indicates that our first task is to find the matrix elements $S_{ij}$ and $H_{ij}$. The $S$ matrix is particularly easy to find, since our trial wavefunction contains only the orthonormal functions $\psi_1$ and $\psi_2$:

$$S_{ii} = \int_0^L \psi_i^2 \, dx = 1, \quad S_{ij} = \int_0^L \psi_i \psi_j \, dx = 0, \quad S = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$
The Hamiltonian matrix is also easy to calculate. The complete Hamiltonian operator $\hat{H}$ is just the sum of the usual particle-in-a-box kinetic energy term $\hat{T}$ plus the potential energy term that equals zero over one half of the box and $E_1$ over the other. For the $H_{11}$ matrix element, we write

$$H_{11} = \int_0^L \psi_1 \hat{H} \psi_1 \, dx = \frac{2}{L} \int_0^L \sin \left( \frac{\pi x}{L} \right) \hat{H} \sin \left( \frac{\pi x}{L} \right) \, dx$$

$$= \frac{2}{L} \int_0^L \sin \left( \frac{\pi x}{L} \right) \hat{T} \sin \left( \frac{\pi x}{L} \right) \, dx + E_1 \int_{L/2}^L \sin^2 \left( \frac{\pi x}{L} \right) \, dx$$

$$= E_1 + \frac{E_1}{2} = \frac{3}{2} E_1$$

where the integral containing $\hat{T}$ must equal $E_1$ because $\hat{T}$ is the entire Hamiltonian for the ordinary particle-in-a-box problem, for which $\psi_1$ is the eigenfunction with eigenenergy $E_1$. Likewise, the integral from $L/2$ to $L$ represents the only nonzero part of the potential energy, and by symmetry, this integral equals $1/2$, the probability that the ordinary system is found in this region. We find the $H_{22}$ matrix element similarly, taking advantage of the fact that $E_2$, the second energy of the ordinary system, equals $2^2 E_1 = 4E_1$. We have

$$H_{22} = \int_0^L \psi_2 \hat{H} \psi_2 \, dx = \frac{2}{L} \int_0^L \sin \left( \frac{2\pi x}{L} \right) \hat{H} \sin \left( \frac{2\pi x}{L} \right) \, dx$$

$$= \frac{2}{L} \int_0^L \sin \left( \frac{2\pi x}{L} \right) \hat{T} \sin \left( \frac{2\pi x}{L} \right) \, dx + E_1 \int_{L/2}^L \sin^2 \left( \frac{2\pi x}{L} \right) \, dx$$

$$= E_2 + \frac{E_1}{2} = 4E_1 + \frac{E_1}{2} = \frac{9}{2} E_1.$$ 

The so-called “off-diagonal” Hamiltonian matrix elements $H_{12}$ and $H_{21}$ are equal by symmetry. We find them to be
\[ H_{12} = \int_0^L \psi_1 \hat{H} \psi_2 \, dx = \frac{2}{L} \int_0^L \sin \left( \frac{\pi x}{L} \right) \hat{T} \sin \left( \frac{2\pi x}{L} \right) \, dx \]

\[ = \frac{2}{L} \int_0^L \sin \left( \frac{\pi x}{L} \right) \sin \left( \frac{2\pi x}{L} \right) \, dx + \frac{2}{L} \int_{L/2}^L \sin \left( \frac{\pi x}{L} \right) \sin \left( \frac{2\pi x}{L} \right) \, dx \]

\[ = E_2 \frac{2}{L} \int_0^L \sin \left( \frac{\pi x}{L} \right) \sin \left( \frac{2\pi x}{L} \right) \, dx + E_1 \frac{2}{L} \int_{L/2}^L \sin \left( \frac{\pi x}{L} \right) \sin \left( \frac{2\pi x}{L} \right) \, dx \]

\[ = 0 + E_1 \left( -\frac{4}{3\pi} \right) = -\frac{4E_1}{3\pi} \]

where the zero value follows from the orthogonality of \( \psi_1 \) and \( \psi_2 \) and the final integral is given in the problem. Thus, the entire Hamiltonian matrix is

\[
\begin{pmatrix}
\frac{3E_1}{2} & -\frac{4E_1}{3\pi} \\
-\frac{4E_1}{3\pi} & \frac{9E_1}{2}
\end{pmatrix} = E_1 \begin{pmatrix}
\frac{3}{2} & -\frac{4}{3\pi} \\
-\frac{4}{3\pi} & \frac{9}{2}
\end{pmatrix}.
\]

The best energy is the solution to the quadratic expression shown at the bottom of page 460 in the text:

\[ 0 = (H_{11} - <E>S_{11}) (H_{22} - <E>S_{22}) - (H_{12} - <E>S_{12})^2 
= \left( \frac{3}{2} E_1 - <E> \right) \left( \frac{9}{2} E_1 - <E> \right) - E_1^2 \frac{16}{9\pi^2}. \]

Two solutions emerge:

\[ <E> = E_1 \left[ 3 \pm \frac{1}{2} \sqrt{4 \left( \frac{16}{9\pi^2} \right) + 9} \right] = \begin{pmatrix} 1.4411E_1 \\ 4.5589E_1 \end{pmatrix} \]

and we choose the smaller of the two as the best approximation to the true ground-state energy.

13.37 We continue the previous problem here with a look at the variational wavefunction itself. We now must use the best energy found there, 1.4411E_1, to find the
coefficients $c_1$ and $c_2$. These are found from their normalization condition $c_1^2 + c_2^2 = 1$ and the two equations shown on page 460 in the text, which, given our $H$ and $S$ matrices, read

\[
\begin{align*}
  c_1 \left( \frac{3}{2} E_1 - 1.4411 E_1 \right) - c_2 E_1 \frac{4}{3\pi} &= 0, \\
  -c_1 E_1 \frac{4}{3\pi} + c_2 \left( \frac{9}{2} E_1 - 1.4411 E_1 \right) &= 0.
\end{align*}
\]

Simultaneous solution of these equations gives $c_1 = \pm 0.9905$ and $c_2 = \pm 0.1374$ with an ambiguity in sign due to the quadratic nature of the equations. We can decide which signs to choose because we know the best energy from the previous problem. We write

\[
\frac{\langle E \rangle}{E_1} = 1.4411 = \int_0^L \left( c_1 \psi_1 + c_2 \psi_2 \right) \frac{\hat{H}}{E_1} \left( c_1 \psi_1 + c_2 \psi_2 \right) dx
\]

\[
= \int_0^L \left( c_1 \psi_1 + c_2 \psi_2 \right) \left[ \frac{\hat{T}}{E_1} \left( c_1 \psi_1 + c_2 \psi_2 \right) + \frac{\hat{V}}{E_1} \left( c_1 \psi_1 + c_2 \psi_2 \right) \right] dx
\]

\[
= \int_0^L \left( c_1 \psi_1 + c_2 \psi_2 \right) \left( c_1 \psi_1 + 4c_2 \psi_2 \right) dx + \int_{L/2}^L \left( c_1 \psi_1 + c_2 \psi_2 \right)^2 dx
\]

\[
= c_1^2 + 4c_2^2 + c_1^2 + 2c_1c_2 \left( -\frac{4}{3\pi} \right) + \frac{c_2^2}{2} = 3c_1^2 + \frac{3}{2} - \frac{8c_1c_2}{3\pi}
\]

where we have used the integral given in the previous problem as well as the orthonormality and symmetry of $\psi_1$ and $\psi_2$. This expression shows us that $c_1$ and $c_2$ must be both positive or both negative; the choice of opposite signs does not satisfy this equation. Thus, we have, choosing the positive signs,

\[
\phi(x) = c_1 \psi_1 + c_2 \psi_2 = 0.9905 \psi_1 + 0.1374 \psi_2.
\]

This wavefunction is graphed on the next page. Over the potential step, from $x = L/2$ to $L$, the particle has a smaller kinetic energy than it has from 0 to $L/2$. This means it has a greater de Broglie wavelength over the step, and this forces the maximum in $\phi$ to lie between 0 and $L/2$. One can show that the mean posi-
tion of the particle, $\langle x \rangle$, is 0.4510$L$. This is somewhat surprising, since the classical expectation would be that the particle spends more time over the potential step, where it moves slower, so that $\langle x \rangle$ would be $>L/2$.

13.38 For the general case of a two-electron atom of nuclear charge $Z$, we can easily write the expression for $\langle E \rangle$ if we generalize the expression on page 470 in the text. The two factors of 2 in that expression become $Z$, and we introduce the ground-state H-atom energy, $E_1$, to simplify notation. We find

$$\langle E \rangle = -2E_1 \left[ \frac{Z_e^2}{2} - Z_e^2 + \left( Z_e^2 - ZZ_e \right) + \frac{Z_e^2}{2} - Z_e^2 + \left( Z_e^2 - ZZ_e \right) + \frac{5}{8} Z_e \right]$$

$$= -2E_1 \left( Z_e^2 - 2ZZ_e + \frac{5}{8} Z_e \right).$$

We minimize this expression with respect to $Z_e$:

$$\frac{d\langle E \rangle}{dZ_e} = -2E_1 \left( 2Z_e - 2Z + \frac{5}{8} \right) = 0 \quad \text{or} \quad Z_e = Z - \frac{5}{16}.$$  

Substituting this value for $Z_e$ into the general expression for $\langle E \rangle$ gives

$$\langle E \rangle = E_1 \left( 2Z^2 - \frac{5}{4} Z + \frac{25}{128} \right).$$

This energy is the energy of the two-electron atom with respect to a zero of energy that represents the nucleus and the two electrons infinitely far apart. The energy of the one-electron atom with the second electron infinitely far away is $Z^2E_1$ with respect to this energy zero so that the first ionization energy of the two-electron atom is $Z^2E_1 - \langle E \rangle$:  

329
IP = Z^2E_1 - \langle E \rangle = -E_1 \left( Z^2 - \frac{5}{4} Z + \frac{25}{128} \right). 

With \( E_1 = -13.595 \text{ eV} \), this expression becomes \( \text{IP/eV} = 13.595Z^2 - 16.994Z + 2.6553 \). We can use this expression to compare with the experimental IPs as shown in the table below (where IP is expressed in eV units).

<table>
<thead>
<tr>
<th></th>
<th>H^-</th>
<th>He</th>
<th>Li^+</th>
<th>Be^{2+}</th>
<th>B^{3+}</th>
<th>C^{4+}</th>
<th>N^{5+}</th>
<th>O^{6+}</th>
<th>F^{7+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Expt</td>
<td>0.7542</td>
<td>24.596</td>
<td>75.619</td>
<td>153.85</td>
<td>259.298</td>
<td>391.986</td>
<td>551.925</td>
<td>739.114</td>
<td>953.6</td>
</tr>
<tr>
<td>Calc</td>
<td>-0.7535</td>
<td>23.05</td>
<td>74.03</td>
<td>152.2</td>
<td>257.6</td>
<td>390.1</td>
<td>549.9</td>
<td>736.8</td>
<td>950.9</td>
</tr>
</tbody>
</table>

Note that the calculated H^- IP is negative, which means this level of theory predicts H^- is unstable. (This is the result we found in Problem 13.19.) The absolute error is remarkably constant, varying smoothly from about 1.4 eV to about 2.7 eV, but the relative error is decreasing with increasing \( Z \).

13.39 Triplet Ps emits three photons so that two have off-setting angular momenta and the third carries the angular momentum inherent in the triplet. One photon decay could conserve the triplet’s angular momentum, but in the Ps atom’s reference frame, there is no linear momentum before the decay and thus there must be none after the decay. One photon decay would produce linear momentum (that of the photon) where none had existed before, in violation of linear momentum conservation. Three photons can be emitted with linear momenta that point in different directions so that they add, vectorially, to zero.

13.40 It is sufficient here to consider, for simplicity in notation and algebra, only the \( n = 1 \) ground state and an abbreviated expansion of the true wavefunction in the form

\[
\psi_1 = \psi_1^{(0)} + \lambda c_{11} \psi_1^{(0)} + \lambda c_{12} \psi_2^{(0)}
\]

where we have expanded the first-order corrected wavefunction through only the \( n = 2 \) state. The normalization integral is
where we have exploited the orthonormality properties of $\psi^{(0)}_1$ and $\psi^{(0)}_2$ to evaluate the many integrals. If we take $c_{11}$ to be real, then $c_{11} + c_{11}^* = 2c_{11}$. Finally, to be consistent with the idea that we are deriving an expression valid through first order only, we drop the second-order term $\lambda^2$ and end with a normalization expression

$$\int \psi_1^* \psi_1 \, d\tau = 1 + 2\lambda c_{11} .$$

In order to make this integral equal 1, we must have $c_{11} = 0$. 