17.2.1 The first-order energy correction is:

$$E_n^1 = \left\langle n^0 \middle| H^1 \middle| n^0 \right\rangle = \left\langle n^0 \middle| \lambda x^4 \middle| n^0 \right\rangle$$

Use the ladder operators to make our life easy:

$$x = \sqrt{\frac{\hbar}{2m\omega}}\left(a^\dagger + a\right)$$

$$x^4 = \left(\frac{\hbar}{2m\omega}\right)^2 \left(a^\dagger + a\right)^4$$

$$x^4 = \left(\frac{\hbar}{2m\omega}\right)^2 \left\{a^\dagger a^\dagger a^\dagger a^\dagger + a^\dagger a^\dagger a a^\dagger + a^\dagger a a^\dagger a^\dagger + a^\dagger a a a^\dagger + a a^\dagger a^\dagger a^\dagger + a a^\dagger a a^\dagger + a a a^\dagger a^\dagger + a a a a^\dagger + \right.$$
$$\left. + a^\dagger a^\dagger a^\dagger a + a^\dagger a^\dagger a a + a^\dagger a a^\dagger a + a^\dagger a a a + a a^\dagger a^\dagger a + a a^\dagger a a + a a a^\dagger a + a a a a\right\}$$

When we take diagonal matrix elements, the only terms that survive are those that have two raising and two lowering operators. Thus we are left with

$$\left\langle n^0 \middle| \lambda x^4 \middle| n^0 \right\rangle = \lambda\left(\frac{\hbar}{2m\omega}\right)^2 \left\langle n^0 \middle| \left(a^\dagger a a a^\dagger + a a^\dagger a a^\dagger + a a a^\dagger a^\dagger + a^\dagger a^\dagger a a + a^\dagger a a^\dagger a + a a^\dagger a^\dagger a\right) \middle| n^0 \right\rangle$$
$$= \lambda\left(\frac{\hbar}{2m\omega}\right)^2 \left[n(n+1) + (n+1)^2 + (n+1)(n+2) + n(n-1) + n^2 + n(n+1)\right]$$
$$= \lambda\left(\frac{\hbar}{2m\omega}\right)^2 \left(6n^2 + 6n + 3\right) = 3\lambda\left(\frac{\hbar}{2m\omega}\right)^2 \left(2n^2 + 2n + 1\right)$$

Hence

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

Dimensionally, the parameter λ must scale like $m^2\omega^2/\hbar^2 \times \hbar\omega$, so that the perturbation λx^4 has units of energy. If we let ε be a dimensionless scale for the perturbation

$$\lambda = \varepsilon\hbar\omega\frac{m^2\omega^2}{\hbar^2} = \varepsilon\frac{m^2\omega^3}{\hbar}$$

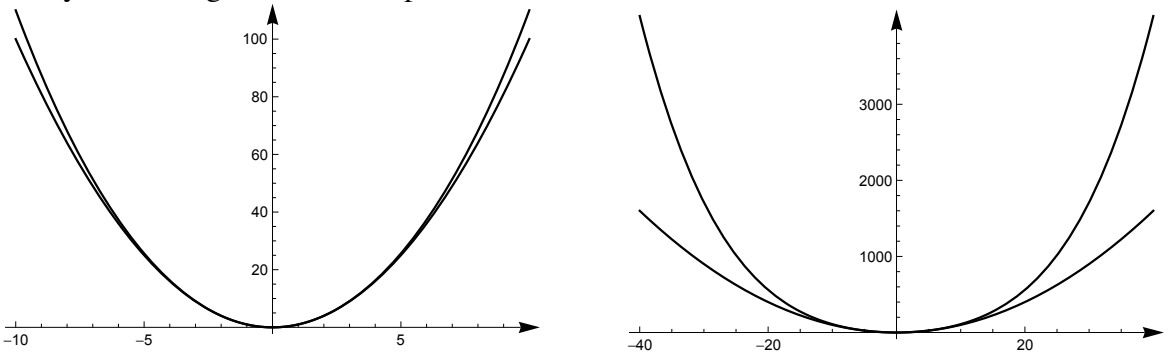
then the energy shift is

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

A small perturbation has the shift much less than the energy level separation

$$E_n^1 \ll \hbar\omega \;\Rightarrow\; \varepsilon\frac{3}{4}\hbar\omega\left(2n^2 + 2n + 1\right) \ll \hbar\omega$$
$$\Rightarrow \varepsilon\left(2n^2 + 2n + 1\right) \ll 1$$

No matter how small ε is, we can always find a large enough n that violates this inequality. You can see this effect also by looking at the potential energies of the perturbed and unperturbed cases. For small ε, the two look very similar near the origin, but as you look farther from the origin, the differences grow quickly. The harmonic oscillator well goes to infinity, so we can always find a region where the perturbation is dominant.



17.2.2 For a spin-1/2 system, the Hamiltonian of the unperturbed spin in a magnetic field $\mathbf{B} = B_0\hat{\mathbf{z}}$ is

$$H^0 = -\boldsymbol{\mu}\bullet\mathbf{B} = -\gamma\mathbf{S}\bullet\mathbf{B} = -\gamma B_0 S_z = -\omega_0 S_z \doteq \begin{pmatrix} -\hbar\omega_0/2 & 0 \\ 0 & \hbar\omega_0/2 \end{pmatrix}$$

where the Larmor freuqency $\omega_0 = \gamma B_0 = -geB_0/2mc$. The zeroth-order energies are $E_1^0 = -\hbar\omega_0/2$ and $E_2^0 = \hbar\omega_0/2$. The perturbation Hamiltonian H^1 is determined by the additional field $\mathbf{B}^1 = B\hat{\mathbf{x}}$ and is characterized by a different Larmor frequency $\omega_1 = \gamma B = -geB/2mc$:

$$H^1 = -\boldsymbol{\mu}\bullet\mathbf{B}_1 = -\gamma\mathbf{S}\bullet\mathbf{B}_1 = -\gamma B S_x = -\omega_1 S_x \doteq \begin{pmatrix} 0 & -\hbar\omega_1/2 \\ -\hbar\omega_1/2 & 0 \end{pmatrix}$$

Perturbation theory tells us that the first-order correction to the energy is the expectation value of the perturbation in the unperturbed state:

$$E_n^1 = \left\langle n^0 \middle| H^1 \middle| n^0 \right\rangle$$

These are the diagonal elements of the matrix representing H^1 in the basis of zeroth-order energy eigenstates. The matrix above has zeroes on the diagonal, and thus yields the first-order energy shifts due to the perturbation:

$$E_1^1 = 0$$
$$E_2^1 = 0$$

The second-order correction to the energy is

$$E_n^2 = \sum_{m \neq n} \frac{\left|\left\langle n^0 \middle| H^1 \middle| m^0 \right\rangle\right|^2}{\left(E_n^0 - E_m^0\right)}$$

For this simple two-state system, the sum reduces to just one term. For the $\left|1^0\right\rangle$ state, the energy shift is

$$E_1^0 = \frac{\left|\left\langle 1^0 \middle| H' \middle| 2^0 \right\rangle\right|^2}{\left(E_1^0 - E_2^0\right)} = \frac{\left|-\hbar\omega_1/2\right|^2}{\left(-\hbar\omega_0/2 - \hbar\omega_0/2\right)} = -\frac{\hbar\omega_1^2}{4\omega_0}$$

For the $\left|2^0\right\rangle$ state, the energy shift is

$$E_2^0 = \frac{\left|\left\langle 2^0 \middle| H' \middle| 1^0 \right\rangle\right|^2}{\left(E_2^0 - E_1^0\right)} = \frac{\left|-\hbar\omega_1/2\right|^2}{\left(\hbar\omega_0/2 - \left(-\hbar\omega_0/2\right)\right)} = \frac{\hbar\omega_1^2}{4\omega_0}$$

We can solve the problem exactly by diagonalizing the full Hamiltonian

$$H = H^0 + H^1 \doteq \frac{\hbar}{2}\begin{pmatrix} -\omega_0 & -\omega_1 \\ -\omega_1 & \omega_0 \end{pmatrix}$$

Find the eigenvalues λ using the secular equation

$$\det\left|H - \lambda I\right| = 0$$

The secular equation for this Hamiltonian is

$$\begin{vmatrix} -\frac{\hbar\omega_0}{2} - \lambda & \frac{\hbar}{2}\omega_1 \\ \frac{\hbar}{2}\omega_1 & \frac{\hbar\omega_0}{2} - \lambda \end{vmatrix} = 0$$

and solving yields the eigenvalues

$$\lambda^2 - \left(\frac{\hbar}{2}\omega_0\right)^2 - \left(-\frac{\hbar}{2}\omega_1\right)^2 = 0$$

$$\lambda^2 = \left(\frac{\hbar\omega_0}{2}\right)^2 + \left(\frac{\hbar\omega_1}{2}\right)^2$$

$$\lambda = \pm\frac{\hbar}{2}\sqrt{\omega_0^2 + \omega_1^2}$$

This is the exact solution, which we now expand in a power series to second order in the small parameter ω_1/ω_0 to compare with the perturbation calculation:

$$E = \pm\frac{\hbar\omega_0}{2}\sqrt{1+\frac{\omega_1^2}{\omega_0^2}} = \pm\frac{\hbar\omega_0}{2}\left[1+\frac{\omega_1^2}{\omega_0^2}\right]^{1/2}$$
$$= \pm\frac{\hbar\omega_0}{2}\left[1+\frac{\omega_1^2}{2\omega_0^2}+\cdots\right]$$
$$\cong \begin{cases} \dfrac{\hbar\omega_0}{2}+\dfrac{\hbar\omega_1^2}{4\omega_0} \\ -\dfrac{\hbar\omega_0}{2}-\dfrac{\hbar\omega_1^2}{4\omega_0} \end{cases}$$

Compared to the previous results

$$E_1 \cong E_1^0 + E_1^1 + E_1^2 = -\frac{\hbar\omega_0}{2} + 0 - \frac{\hbar\omega_1^2}{4\omega_0}$$
$$E_2 \cong E_2^0 + E_2^1 + E_2^2 = \frac{\hbar\omega_0}{2} + 0 + \frac{\hbar\omega_1^2}{4\omega_0}$$

So the exact answer, to second order, agrees with the perturbation calculation to the same order.

17.2.5 The helium ground state has a zeroth-order energy of

$$E_{1s,1s}^0 = -Ryd\left(\frac{Z^2}{1^2}+\frac{Z^2}{1^2}\right) = -4\ Ryd\left(\frac{1}{1^2}+\frac{1}{1^2}\right) = -8\ Ryd = -108.8eV$$

The helium ground state is non-degenerate, so we find the shift caused by the perturbation by finding the expectation value of the perturbation in the zeroth-order state

$$E_{1s,1s}^1 = \left\langle \psi_{1s,1s}^{SA}\middle| H^1 \middle|\psi_{1s,1s}^{SA}\right\rangle = \left\langle \psi_{1s,1s}^{S}\middle| \frac{e^2}{r_{12}} \middle|\psi_{1s,1s}^{S}\right\rangle$$
$$= \iint \psi_{100}^*(\mathbf{r}_1)\psi_{100}^*(\mathbf{r}_2)\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\psi_{100}(\mathbf{r}_2)\psi_{100}(\mathbf{r}_1)d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

The ground state wave function is ($Z = 2$)

$$\psi_{100}(r,\theta,\phi) = \sqrt{\frac{Z^3}{\pi a_0^3}}e^{-Zr/a_0}$$

Use the spherical harmonic addition theorem

$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\frac{4\pi}{2\ell+1}\frac{r_<^\ell}{r_>^{\ell+1}}Y_\ell^{m*}(\theta_1,\phi_1)\,Y_\ell^m(\theta_2,\phi_2)$$

where $r_>$ stands for the larger of the two distances r_1 and r_2, and $r_<$ the smaller . Putting this all together gives

$$E^1_{1s,1s} = \frac{Z^6e^2}{\pi^2 a_0^6}\iint e^{-2Zr_1/a_0}e^{-2Zr_2/a_0}\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\frac{4\pi}{2\ell+1}\frac{r_<^\ell}{r_>^{\ell+1}}Y^*_{\ell m}(\theta_1,\phi_1)\,Y_{\ell m}(\theta_2,\phi_2)d^3\mathbf{r}_1 d^3\mathbf{r}_2$$
$$= \frac{Z^6e^2}{\pi^2 a_0^6}\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\frac{4\pi}{2\ell+1}\iint e^{-2Z(r_1+r_2)/a_0}\frac{r_<^\ell}{r_>^{\ell+1}}Y^*_{\ell m}(\theta_1,\phi_1)Y_{\ell m}(\theta_2,\phi_2)d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

Recall that $Y_0^0(\theta,\phi) = 1/\sqrt{4\pi}$ and separate the integrals to get

$$E^1_{1s,1s} = \frac{Z^6e^2}{\pi^2 a_0^6}\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\frac{(4\pi)^2}{2\ell+1}\int_0^\infty\int_0^\infty e^{-2Z(r_1+r_2)/a_0}\frac{r_<^\ell}{r_>^{\ell+1}}r_1^2\,dr_1 r_2^2\,dr_1$$
$$\times\int Y_\ell^{m*}(\theta_1,\phi_1)Y_0^{0*}(\theta_1,\phi_1)d\Omega_1\int Y_0^{0*}(\theta_2,\phi_2)Y_\ell^m(\theta_2,\phi_2)d\Omega_2$$

The spherical harmonics are orthonormal, so the angular integrals require that $\ell = 0$ and $m = 0$, giving

$$E^1_{1s,1s} = \frac{16Z^6e^2}{a_0^6}\int_0^\infty\int_0^\infty e^{-2Z(r_1+r_2)/a_0}\frac{1}{r_>}r_1^2\,dr_1 r_2^2\,dr_2$$
$$= \frac{16Z^6e^2}{a_0^6}\int_0^\infty e^{-2Zr_1/a_0}r_1^2\,dr_1\left[\frac{1}{r_1}\int_0^{r_1}e^{-2Zr_2/a_0}r_2^2\,dr_2 + \int_{r_1}^\infty e^{-2Zr_2/a_0}\frac{1}{r_2}r_2^2\,dr_2\right]$$
$$= \frac{16Z^6e^2}{a_0^6}\int_0^\infty e^{-2Zr_1/a_0}r_1^2\,dr_1\left[\begin{array}{l}\frac{1}{r_1}\left(\frac{a_0}{4Z^3}\right)\left(a_0^2 - e^{-2Zr_1/a_0}\left\{a_0^2+2a_0r_1Z+2r_1^2Z^2\right\}\right)\\ +\left(\frac{a_0}{4Z^2}\right)e^{-2Zr_1/a_0}\left\{a_0+2r_1Z\right\}\end{array}\right]$$
$$= \frac{4Z^3e^2}{a_0^5}\left[\begin{array}{l}\int_0^\infty\left(a_0^2e^{-2Zr_1/a_0} - e^{-4Zr_1/a_0}\left\{a_0^2+2a_0r_1Z+2r_1^2Z^2\right\}\right)r_1\,dr_1 +\\ +\int_0^\infty e^{-4Zr_1/a_0}\left(a_0Z+2r_1Z^2\right)r_1^2\,dr_1\end{array}\right]$$
$$= \frac{4Z^3e^2}{a_0^5}\left[\frac{a_0^4}{4Z^2}-\frac{a_0^4}{16Z^2}-\frac{a_0^4}{16Z^2}-\frac{3a_0^4}{64Z^2}+\frac{a_0^4}{32Z^2}+\frac{3a_0^4}{64Z^2}\right]$$
$$= \frac{5Ze^2}{8a_0} = \frac{5}{8}\left(\frac{Ze^2}{a_0}\right)$$

Numerically, we get

$$E^1_{1s,1s} = \frac{5}{8}Z\left(\frac{e^2}{a_0}\right) = \frac{5}{8}2(2Ryd) = \frac{5}{2}Ryd = \frac{5}{2}13.6eV = 34eV$$

The new energy is

$$E \cong E^0_{1s,1s} + E^1_{1s,1s} = -8Ryd + \frac{5}{2}Ryd = -5.5Ryd = -5.5(13.6eV) = -74.8eV$$

Another way to solve it is to follow the author's hint, which only works for spherically symmetric wave functions. The idea is to find the electrostatic interaction energy between the

two spherically symmetric charge distributions $\rho_1(r_1)$ and $\rho_2(r_2)$ of the two electrons. From Gauss's law, we know that a charge $dq_1 = \rho_1(r_1)dV_1$ interacts with the charge $q_2(r_1) = \int dq_2$ enclosed within its radius, but not with the charge outside its radius. This energy is

$$E_1 = \int \frac{q_2(r_1)dq_1}{r_1} = \int \frac{\left\{\int dq_2\right\}dq_1}{r_1}$$

Of course, we can make the same argument with 1 and 2 swapped, so we get twice this energy. The key aspect is to get the limits right. We integrate dq_2 from 0 to r_1 and then we integrate dq_1 from 0 to ∞. Hence the energy shift is

$$\begin{aligned}
E^1_{1s,1s} &= 2\int \frac{\left\{\int dq_2\right\}dq_1}{r_1} = 2\int_0^\infty \frac{\left\{\int_0^{r_1} \rho_2(r_2)dV_2\right\}\rho_1(r_1)dV_1}{r_1} \\
&= 2\int_0^\infty \frac{1}{r_1} e\left|\psi_{100}(r_1)^2\right| 4\pi r_1^2 dr_1 \left\{\int_0^{r_1} e\left|\psi_{100}(r_2)^2\right| 4\pi r_2^2\, dr_2\right\} \\
&= \frac{32e^2Z^6}{a_0^6}\int_0^\infty \frac{1}{r_1} e^{-2Zr_1/a_0} r_1^2 dr_1 \left\{\int_0^{r_1} e^{-2Zr_2/a_0} r_2^2\, dr_2\right\} \\
&= \frac{32e^2Z^6}{a_0^6}\int_0^\infty \frac{1}{r_1} e^{-2Zr_1/a_0} r_1^2 \left\{\frac{a_0^3}{4Z^3}\left(1 - e^{-2Zr_1/a_0}\left[1 + \frac{2Zr_1}{a_0} + \frac{2Z^2r_1^2}{a_0^2}\right]\right)\right\} dr_1 \\
&= \frac{8e^2Z^3}{a_0^3}\int_0^\infty e^{-2Zr_1/a_0} r_1 \left\{\left(1 - e^{-2Zr_1/a_0}\left[1 + \frac{2Zr_1}{a_0} + \frac{2Z^2r_1^2}{a_0^2}\right]\right)\right\} dr_1 \\
&= \frac{8e^2Z^3}{a_0^3}\left(\frac{5a_0^2}{64Z^2}\right) \\
&= \frac{5e^2Z}{8a_0}
\end{aligned}$$

as above.

17.3.2 For a spin-1 system with a Hamiltonian

$$H = AS_z^2 + B\left(S_x^2 - S_y^2\right)$$

with $A >> B$, we identify the first term as the unperturbed Hamiltonian and the second term as the perturbation Hamiltonian. Hence

$$H^0 = AS_z^2 \doteq A\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Because the unperturbed Hamiltonian is diagonal, we know the zeroth-order energies and eigenstates by inspection:

$$E_1^0 = A\hbar^2 \quad \left|1^0\right\rangle = \left|m=1\right\rangle$$
$$E_2^0 = 0 \quad \left|2^0\right\rangle = \left|m=0\right\rangle$$
$$E_3^0 = A\hbar^2 \quad \left|3^0\right\rangle = \left|m=-1\right\rangle$$

So the system is degenerate. For the nondegenerate state $\left|2^0\right\rangle$, the first-order correction to the energy is the expectation value of the perturbation in the unperturbed state:

$$E_2^1 = \left\langle 2^0 \middle| H^1 \middle| 2^0 \right\rangle$$

For the degenerate states, we must diagonalize the matrix representing H^1 in the degenerate subspace. The full matrix of the perturbation is

$$H^1 = B\left(S_x^2 - S_y^2\right) \doteq B\frac{\hbar^2}{2}\left\{\begin{pmatrix} 1 & 0 & 1 \\ 0 & 2 & 0 \\ 1 & 0 & 1 \end{pmatrix} - \begin{pmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & 1 \end{pmatrix}\right\}$$
$$\doteq B\hbar^2 \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

By inspection, we get

$$E_2^1 = \left\langle 2^0 \middle| H^1 \middle| 2^0 \right\rangle = 0$$

In the degenerate subspace, we have

$$H^1 \doteq B\hbar^2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Diagonalize:

$$\begin{vmatrix} 0-\lambda & B\hbar^2 \\ B\hbar^2 & 0-\lambda \end{vmatrix} = 0$$

and solving yields the eigenvalues

$$\lambda^2 - \left(B\hbar^2\right)^2 = 0$$
$$E^1_{1,3} = \pm B\hbar^2$$

The perturbed energies to first order in B are

$$E_1 \cong E^0_1 + E^1_1 = A\hbar^2 + B\hbar^2$$
$$E_2 \cong E^0_2 + E^1_2 = 0$$
$$E_3 \cong E^0_3 + E^1_3 = A\hbar^2 - B\hbar^2$$

We can solve the problem exactly by diagonalizing the full Hamiltonian

$$H = H_0 + H^1 = AS_z^2 + B\left(S_x^2 - S_y^2\right) \doteq A\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + B\hbar^2 \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$
$$\doteq \begin{pmatrix} A\hbar^2 & 0 & B\hbar^2 \\ 0 & 0 & 0 \\ B\hbar^2 & 0 & A\hbar^2 \end{pmatrix}$$

Diagonalize:

$$\begin{vmatrix} A\hbar^2 - \lambda & 0 & B\hbar^2 \\ 0 & -\lambda & 0 \\ B\hbar^2 & 0 & A\hbar^2 - \lambda \end{vmatrix} = 0$$

and solving yields the eigenvalues

$$-\lambda\left(A\hbar^2 - \lambda\right)^2 + \lambda\left(B\hbar^2\right)^2 = 0$$
$$\lambda\left[\left(A\hbar^2 - \lambda\right)^2 - \left(B\hbar^2\right)^2\right] = 0 \;\Rightarrow\; \lambda = 0 \quad or$$
$$A\hbar^2 - \lambda = \pm B\hbar^2$$
$$\lambda = A\hbar^2 \pm B\hbar^2$$

The exact energies are

$$E_1 = A\hbar^2 + B\hbar^2$$
$$E_2 = 0$$
$$E_3 = A\hbar^2 - B\hbar^2$$

Hence the perturbation calculation to first order gives the exact values.