

10.1 The Hamiltonian is

$$H \doteq \frac{\hbar}{2} \begin{pmatrix} \omega_0 + \omega_1 & \omega_2 \\ \omega_2 & -\omega_0 - \omega_1 \end{pmatrix}$$

Find the eigenvalues λ using the secular equation

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

The secular equation for this Hamiltonian is

$$\begin{vmatrix} \frac{\hbar}{2}(\omega_0 + \omega_1) - \lambda & \frac{\hbar}{2}\omega_2 \\ \frac{\hbar}{2}\omega_2 & -\frac{\hbar}{2}(\omega_0 + \omega_1) - \lambda \end{vmatrix} = 0$$

and solving yields the eigenvalues

$$\begin{aligned} \lambda^2 - \left(\frac{\hbar}{2}\right)^2 (\omega_0 + \omega_1)^2 - \left(\frac{\hbar}{2}\omega_2\right)^2 &= 0 \\ \lambda^2 = \left(\frac{\hbar}{2}\right)^2 (\omega_0 + \omega_1)^2 + \left(\frac{\hbar}{2}\omega_2\right)^2 \\ \lambda = \pm \frac{\hbar}{2} \sqrt{(\omega_0 + \omega_1)^2 + \omega_2^2} \end{aligned}$$

10.2 Assume the perturbation expansions:

$$\begin{aligned} E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + \dots \\ |n\rangle &= |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \lambda^3 |n^{(3)}\rangle + \dots \end{aligned}$$

Substitute these into the eigenvalue equation $(H_0 + \lambda H')|n\rangle = E_n|n\rangle$ to get

$$(H_0 + \lambda H')|n\rangle = E_n|n\rangle$$

$$\begin{aligned} (H_0 + \lambda H')(|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots) &= \left\{ \begin{array}{l} (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) \times \\ (|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots) \end{array} \right\} \\ \left\{ \begin{array}{l} H_0 |n^{(0)}\rangle + \lambda H_0 |n^{(1)}\rangle + \lambda^2 H_0 |n^{(2)}\rangle + \dots \\ + \lambda H' |n^{(0)}\rangle + \lambda^2 H' |n^{(1)}\rangle + \lambda^3 H' |n^{(2)}\rangle + \dots \end{array} \right\} &= \left\{ \begin{array}{l} E_n^{(0)} |n^{(0)}\rangle + \lambda E_n^{(1)} |n^{(0)}\rangle + \lambda^2 E_n^{(2)} |n^{(0)}\rangle + \dots \\ + \lambda E_n^{(0)} |n^{(1)}\rangle + \lambda^2 E_n^{(1)} |n^{(1)}\rangle + \lambda^3 E_n^{(2)} |n^{(1)}\rangle + \dots \\ + \lambda^2 E_n^{(0)} |n^{(2)}\rangle + \lambda^3 E_n^{(1)} |n^{(2)}\rangle + \lambda^4 E_n^{(2)} |n^{(2)}\rangle + \dots \end{array} \right\} \end{aligned}$$

Collect terms of the same order or power of the parameter λ

$$\left\{ H_0 |n^{(0)}\rangle + \lambda (H_0 |n^{(1)}\rangle + H' |n^{(0)}\rangle) \right\} = \left\{ E_n^{(0)} |n^{(0)}\rangle + \lambda (E_n^{(1)} |n^{(0)}\rangle + E_n^{(0)} |n^{(1)}\rangle) + \right. \\ \left. + \lambda^2 (H_0 |n^{(2)}\rangle + H' |n^{(1)}\rangle) + \dots \right\} = \left\{ E_n^{(0)} |n^{(0)}\rangle + \lambda^2 (E_n^{(2)} |n^{(0)}\rangle + E_n^{(1)} |n^{(1)}\rangle + E_n^{(0)} |n^{(2)}\rangle) + \dots \right\}$$

and then rearrange

$$\left\{ \lambda^0 (H_0 |n^{(0)}\rangle - E_n^{(0)} |n^{(0)}\rangle) + \lambda (H_0 |n^{(1)}\rangle - E_n^{(0)} |n^{(1)}\rangle) \right\} = \left\{ \lambda (E_n^{(1)} |n^{(0)}\rangle - H' |n^{(0)}\rangle) + \right. \\ \left. + \lambda^2 (H_0 |n^{(2)}\rangle - E_n^{(0)} |n^{(2)}\rangle) + \dots \right\} = \left\{ \lambda (E_n^{(1)} - H') |n^{(0)}\rangle + \right. \\ \left. + \lambda^2 (H_0 - E_n^{(0)}) |n^{(1)}\rangle + \dots \right\} = \left\{ \lambda (E_n^{(1)} - H') |n^{(0)}\rangle + \right. \\ \left. + \lambda^2 \{ (E_n^{(1)} - H') |n^{(1)}\rangle + E_n^{(2)} |n^{(0)}\rangle \} + \dots \right\}$$

For the eigenvalue equation to hold for any value of λ , the coefficients of like orders on the two sides of the equation must be equal, and we can isolate an equation for each order in the expansion parameter. The result is the following set of equations:

$$O(\lambda^0): (H_0 - E_n^{(0)}) |n^{(0)}\rangle = 0$$

$$O(\lambda^1): (H_0 - E_n^{(0)}) |n^{(1)}\rangle = (E_n^{(1)} - H') |n^{(0)}\rangle$$

$$O(\lambda^2): (H_0 - E_n^{(0)}) |n^{(2)}\rangle = (E_n^{(1)} - H') |n^{(1)}\rangle + E_n^{(2)} |n^{(0)}\rangle$$

We can infer the last equation

$$O(\lambda^3): (H_0 - E_n^{(0)}) |n^{(3)}\rangle = (E_n^{(1)} - H') |n^{(2)}\rangle + E_n^{(2)} |n^{(1)}\rangle + E_n^{(3)} |n^{(0)}\rangle$$

10.3 We solve the first-order perturbation equation that contains the first-order corrections $E_n^{(1)}$ and $|n^{(1)}\rangle$ to the eigenvalues and eigenstates, respectively, as unknowns:

$$(H_0 - E_n^{(0)}) |n^{(1)}\rangle = (E_n^{(1)} - H') |n^{(0)}\rangle$$

For a 3-state system, the matrices representing the Hamiltonians H_0 and H' are

$$H_0 \doteq \begin{pmatrix} E_1^{(0)} & 0 & 0 \\ 0 & E_2^{(0)} & 0 \\ 0 & 0 & E_3^{(0)} \end{pmatrix}$$

$$H' \doteq \begin{pmatrix} H'_{11} & H'_{12} & H'_{13} \\ H'_{21} & H'_{22} & H'_{23} \\ H'_{31} & H'_{32} & H'_{33} \end{pmatrix}$$

The zeroth-order energy eigenstate $|2^{(0)}\rangle$ is

$$|2^{(0)}\rangle \doteq \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

The first-order correction to the eigenstate $|2^{(1)}\rangle$ is not yet known, and we characterize it in terms of a set of yet-to-be-found first-order coefficients $c_{2m}^{(1)} = \langle m^{(0)} | 2^{(1)} \rangle$ in the zeroth-order basis

$$|2^{(1)}\rangle \doteq \begin{pmatrix} c_{21}^{(1)} \\ c_{22}^{(1)} \\ c_{23}^{(1)} \end{pmatrix}$$

For the choice $n = 2$, the left-hand side of the first-order perturbation equation is

$$(H_0 - E_2^{(0)})|2^{(1)}\rangle \doteq \begin{pmatrix} E_1^{(0)} - E_2^{(0)} & 0 & 0 \\ 0 & \boxed{0} & 0 \\ 0 & 0 & E_3^{(0)} - E_2^{(0)} \end{pmatrix} \begin{pmatrix} c_{31}^{(1)} \\ c_{32}^{(1)} \\ c_{33}^{(1)} \end{pmatrix} = \begin{pmatrix} (E_1^{(0)} - E_2^{(0)})c_{21}^{(1)} \\ \boxed{0} \\ (E_3^{(0)} - E_2^{(0)})c_{23}^{(1)} \end{pmatrix}$$

The right-hand side of the first-order perturbation equation is

$$(E_2^{(1)} - H')|2^{(0)}\rangle \doteq \begin{pmatrix} E_2^{(1)} - H'_{11} & -H'_{12} & -H'_{13} \\ -H'_{21} & \boxed{E_2^{(1)} - H'_{22}} & -H'_{23} \\ -H'_{31} & -H'_{32} & E_2^{(1)} - H'_{33} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = \begin{pmatrix} -H'_{12} \\ \boxed{E_2^{(1)} - H'_{22}} \\ -H'_{32} \end{pmatrix}$$

Equating the two sides of the first-order perturbation equation yields

$$\begin{pmatrix} (E_1^{(0)} - E_2^{(0)})c_{21}^{(1)} \\ \boxed{0} \\ (E_3^{(0)} - E_2^{(0)})c_{23}^{(1)} \end{pmatrix} = \begin{pmatrix} -H'_{12} \\ \boxed{E_2^{(1)} - H'_{22}} \\ -H'_{32} \end{pmatrix}$$

The second row, which we have been highlighting all along, yields the solution for the first-order energy correction to the $n = 2$ state:

$$\begin{aligned} E_2^{(1)} - H'_{22} &= 0 \\ E_2^{(1)} = H'_{22} &= \langle 2^{(0)} | H' | 2^{(0)} \rangle \end{aligned}$$

10.4 The first-order perturbation is

$$\begin{aligned}
 E_n^{(1)} &= \langle n^{(0)} | \hat{H}' | n^{(0)} \rangle = V_0 \int_{L/2}^L |\varphi_n(x)|^2 dx = V_0 \int_{L/2}^L \left[\frac{2}{L} \sin^2\left(\frac{\pi x}{L}\right) \right] dx \\
 &= V_0 \frac{2}{L} \int_{L/2}^L \left(\frac{1}{2} \left[1 - \cos\left(\frac{2\pi x}{L}\right) \right] \right) dx = \frac{V_0}{L} \left[x - \left(\frac{L}{2\pi} \right) \sin\left(\frac{2\pi x}{L}\right) \right]_{L/2}^L \\
 &= \frac{V_0}{L} \left[L - \left(\frac{L}{2\pi} \right) \sin(2\pi) - \frac{L}{2} + \left(\frac{L}{2\pi} \right) \sin(\pi) \right] = \frac{V_0}{L} \left[\frac{L}{2} \right] \\
 &= \frac{V_0}{2}
 \end{aligned}$$

10.5 The first-order state vector correction is

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

The zeroth-order eigenvalues and eigenstates are

$$\begin{aligned}
 E_n^{(0)} &= n^2 \frac{\pi^2 \hbar^2}{2mL^2} \\
 |n^{(0)}\rangle &\doteq \varphi_n^{(0)}(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)
 \end{aligned}$$

For the ground state, the first-order state vector correction is

$$|1^{(1)}\rangle = \sum_{m \neq 1} \frac{\langle m^{(0)} | H' | 1^{(0)} \rangle}{(E_1^{(0)} - E_m^{(0)})} |m^{(0)}\rangle$$

The required matrix elements are

$$\begin{aligned}
 \langle m^{(0)} | H' | 1^{(0)} \rangle &= \int_{-\infty}^{\infty} \varphi_m^{(0)*}(x) V(x) \varphi_1^{(0)}(x) dx \\
 &= \int_0^{L/2} \varphi_m^{(0)*}(x) 0 \varphi_1^{(0)}(x) dx + \int_{L/2}^L \varphi_m^{(0)*}(x) V_0 \varphi_1^{(0)}(x) dx \\
 &= V_0 \int_{L/2}^L \varphi_m^{(0)*}(x) \varphi_1^{(0)}(x) dx = V_0 \frac{2}{L} \int_{L/2}^L \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{\pi x}{L}\right) dx \\
 &= V_0 \frac{2}{L} \left\{ -\frac{L \sin\left(\frac{(m-1)\pi}{2}\right)}{2\pi(m-1)} + \frac{L \sin\left(\frac{(m+1)\pi}{2}\right)}{2\pi(m+1)} \right\} \\
 &= \frac{V_0}{\pi} \left\{ \frac{\cos\left(\frac{m\pi}{2}\right)}{(m-1)} + \frac{\cos\left(\frac{m\pi}{2}\right)}{(m+1)} \right\} = \frac{V_0}{\pi} \left\{ \frac{2m \cos\left(\frac{m\pi}{2}\right)}{(m^2-1)} \right\} \\
 &= \frac{2V_0}{\pi} \left\{ \frac{-4}{3}, 0, \frac{8}{15}, 0, \frac{-12}{35} \right\}; \quad m = 2, 3, 4, 5, 6, \dots
 \end{aligned}$$

Hence, the first three terms in the corrections are

$$\begin{aligned}
 |1^{(1)}\rangle &= \frac{\langle 2^{(0)} | H' | 1^{(0)} \rangle}{(E_1^{(0)} - E_2^{(0)})} |2^{(0)}\rangle + \frac{\langle 4^{(0)} | H' | 1^{(0)} \rangle}{(E_1^{(0)} - E_4^{(0)})} |4^{(0)}\rangle + \frac{\langle 6^{(0)} | H' | 1^{(0)} \rangle}{(E_1^{(0)} - E_6^{(0)})} |6^{(0)}\rangle + \dots \\
 &= \frac{-8V_0/3\pi}{\frac{\pi^2\hbar^2}{2mL^2}(1-4)} |2^{(0)}\rangle + \frac{16V_0/15\pi}{\frac{\pi^2\hbar^2}{2mL^2}(1-16)} |4^{(0)}\rangle + \frac{-24V_0/35\pi}{\frac{\pi^2\hbar^2}{2mL^2}(1-36)} |6^{(0)}\rangle + \dots \\
 &= \frac{16mV_0L^2}{\pi^3\hbar^2} \left\{ \frac{1}{3^2} |2^{(0)}\rangle - \frac{2}{15^2} |4^{(0)}\rangle + \frac{3}{35^2} |6^{(0)}\rangle + \dots \right\}
 \end{aligned}$$

10.6 The first-order state vector correction is

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

The perturbation matrix is

$$H' = -\mu \cdot \mathbf{B}' = \omega_2 S_x \doteq \begin{pmatrix} 0 & \frac{\sqrt{3}}{2} \hbar \omega_2 & 0 & 0 \\ \frac{\sqrt{3}}{2} \hbar \omega_2 & 0 & \frac{\sqrt{4}}{2} \hbar \omega_2 & 0 \\ 0 & \frac{\sqrt{4}}{2} \hbar \omega_2 & 0 & \frac{\sqrt{3}}{2} \hbar \omega_2 \\ 0 & 0 & \frac{\sqrt{3}}{2} \hbar \omega_2 & 0 \end{pmatrix}$$

For the $|2^{(0)}\rangle$ state, the first-order state correction

$$\begin{aligned}
 |2^{(1)}\rangle &= \sum_{m \neq 2} \frac{\langle m^{(0)} | H' | 2^{(0)} \rangle}{(E_2^{(0)} - E_m^{(0)})} |m^{(0)}\rangle = \frac{\langle 1^{(0)} | H' | 2^{(0)} \rangle}{(E_2^{(0)} - E_1^{(0)})} |1^{(0)}\rangle + \frac{\langle 3^{(0)} | H' | 2^{(0)} \rangle}{(E_2^{(0)} - E_3^{(0)})} |3^{(0)}\rangle \\
 &= \frac{\frac{\sqrt{3}}{2} \hbar \omega_2}{\left(\frac{1}{2} \hbar \omega_0 - \frac{3}{2} \hbar \omega_0\right)} |1^{(0)}\rangle + \frac{\frac{\sqrt{4}}{2} \hbar \omega_2}{\left(\frac{1}{2} \hbar \omega_0 - \frac{-1}{2} \hbar \omega_0\right)} |3^{(0)}\rangle \\
 &= -\frac{\sqrt{3} \omega_2}{2 \omega_0} |1^{(0)}\rangle + \frac{\omega_2}{\omega_0} |3^{(0)}\rangle
 \end{aligned}$$

For the $|3^{(0)}\rangle$ state, the first-order state correction

$$\begin{aligned}
 |3^{(1)}\rangle &= \sum_{m \neq 3} \frac{\langle m^{(0)} | H' | 3^{(0)} \rangle}{(E_3^{(0)} - E_m^{(0)})} |m^{(0)}\rangle = \frac{\langle 2^{(0)} | H' | 3^{(0)} \rangle}{(E_3^{(0)} - E_2^{(0)})} |2^{(0)}\rangle + \frac{\langle 4^{(0)} | H' | 3^{(0)} \rangle}{(E_3^{(0)} - E_4^{(0)})} |4^{(0)}\rangle \\
 &= \frac{\frac{\sqrt{4}}{2} \hbar \omega_2}{\left(\frac{-1}{2} \hbar \omega_0 - \frac{1}{2} \hbar \omega_0\right)} |2^{(0)}\rangle + \frac{\frac{\sqrt{3}}{2} \hbar \omega_2}{\left(\frac{-1}{2} \hbar \omega_0 - \frac{-3}{2} \hbar \omega_0\right)} |4^{(0)}\rangle \\
 &= -\frac{\omega_2}{\omega_0} |2^{(0)}\rangle + \frac{\sqrt{3} \omega_2}{2 \omega_0} |4^{(0)}\rangle
 \end{aligned}$$

For the $|4^{(0)}\rangle$ state, the first-order state correction

$$\begin{aligned}
 |4^{(1)}\rangle &= \sum_{m \neq 4} \frac{\langle m^{(0)} | H' | 4^{(0)} \rangle}{(E_4^{(0)} - E_m^{(0)})} |m^{(0)}\rangle = \frac{\langle 3^{(0)} | H' | 4^{(0)} \rangle}{(E_4^{(0)} - E_3^{(0)})} |3^{(0)}\rangle \\
 &= \frac{\frac{\sqrt{3}}{2} \hbar \omega_2}{\left(\frac{-3}{2} \hbar \omega_0 - \frac{-1}{2} \hbar \omega_0\right)} |3^{(0)}\rangle \\
 &= -\frac{\sqrt{3} \omega_2}{2 \omega_0} |3^{(0)}\rangle
 \end{aligned}$$

The resultant corrected states are

$$\begin{aligned}
 |2\rangle &= |2^{(0)}\rangle - \frac{\sqrt{3} \omega_2}{2 \omega_0} |1^{(0)}\rangle + \frac{\omega_2}{\omega_0} |3^{(0)}\rangle \\
 |3\rangle &= |3^{(0)}\rangle - \frac{\omega_2}{\omega_0} |2^{(0)}\rangle + \frac{\sqrt{3} \omega_2}{2 \omega_0} |4^{(0)}\rangle \\
 |4\rangle &= |4^{(0)}\rangle - \frac{\sqrt{3} \omega_2}{2 \omega_0} |3^{(0)}\rangle
 \end{aligned}$$

10.7 For a spin-1 system

$$H_0 = -\mu \cdot \mathbf{B}_0 = \omega_0 S_z \doteq \begin{pmatrix} \hbar\omega_0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\hbar\omega_0 \end{pmatrix}$$

where we have defined the Larmor frequency $\omega_0 = g_N e B_0 / 2m_p$. The zeroth-order energies are $E_1^{(0)} = \hbar\omega_0$, $E_2^{(0)} = 0$, and $E_3^{(0)} = -\hbar\omega_0$. The perturbation Hamiltonian H' is determined by the field $\mathbf{B}' = B_1 \hat{\mathbf{z}}$ and is characterized by a different Larmor frequency $\omega_1 = g_N e B_1 / 2m_p$:

$$H' = -\mu \cdot \mathbf{B}' = \omega_1 S_z \doteq \begin{pmatrix} \hbar\omega_1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\hbar\omega_1 \end{pmatrix}$$

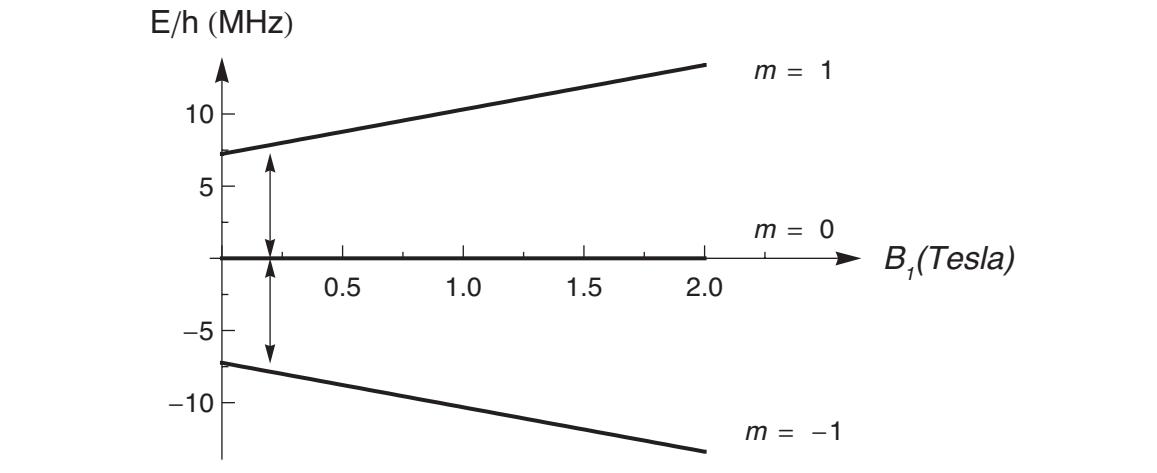
Perturbation theory tells us that the first-order correction to the energy is the expectation value of the perturbation in the unperturbed state:

$$E_n^{(1)} = H'_{nn} = \langle n^{(0)} | H' | n^{(0)} \rangle$$

These are the diagonal elements of the matrix representing H' in the basis of zeroth-order energy eigenstates. The matrix above thus yields the first-order energy shifts due to the perturbation:

$$\begin{aligned} E_1^{(1)} &= \hbar\omega_1 \\ E_2^{(1)} &= 0 \\ E_3^{(1)} &= -\hbar\omega_1 \end{aligned}$$

Plot:



10.8 For a spin-1 system

$$H_0 = -\mu \cdot \mathbf{B}_0 = \omega_0 S_z \doteq \begin{pmatrix} \hbar\omega_0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\hbar\omega_0 \end{pmatrix}$$

where we have defined the Larmor frequency $\omega_0 = g_N e B_0 / 2m_p$. The zeroth-order energies are $E_1^{(0)} = \hbar\omega_0$, $E_2^{(0)} = 0$, and $E_3^{(0)} = -\hbar\omega_0$. The perturbation Hamiltonian H' is determined by the field $\mathbf{B}' = B_2 \hat{\mathbf{x}}$ and is characterized by a different Larmor frequency $\omega_2 = g_N e B_2 / 2m_p$:

$$H' = -\mu \cdot \mathbf{B}' = \omega_2 S_x \doteq \begin{pmatrix} 0 & \frac{1}{\sqrt{2}}\hbar\omega_2 & 0 \\ \frac{1}{\sqrt{2}}\hbar\omega_2 & 0 & \frac{1}{\sqrt{2}}\hbar\omega_2 \\ 0 & \frac{1}{\sqrt{2}}\hbar\omega_2 & 0 \end{pmatrix}$$

This perturbation Hamiltonian has no diagonal elements, so there are no first-order energy corrections. The second-order correction to the energy is

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

For the $|1^{(0)}\rangle$ state, the energy shift is given by a sum, but there is only one term in the sum because only $H'_{12} \neq 0$:

$$E_1^{(2)} = \sum_{m \neq 1} \frac{|\langle 1^{(0)} | H' | m^{(0)} \rangle|^2}{(E_1^{(0)} - E_m^{(0)})} = \frac{|\langle 1^{(0)} | H' | 2^{(0)} \rangle|^2}{(E_1^{(0)} - E_2^{(0)})} = \frac{|\frac{1}{\sqrt{2}}\hbar\omega_2|^2}{(\hbar\omega_0 - 0)} = \frac{\hbar\omega_2^2}{2\omega_0}$$

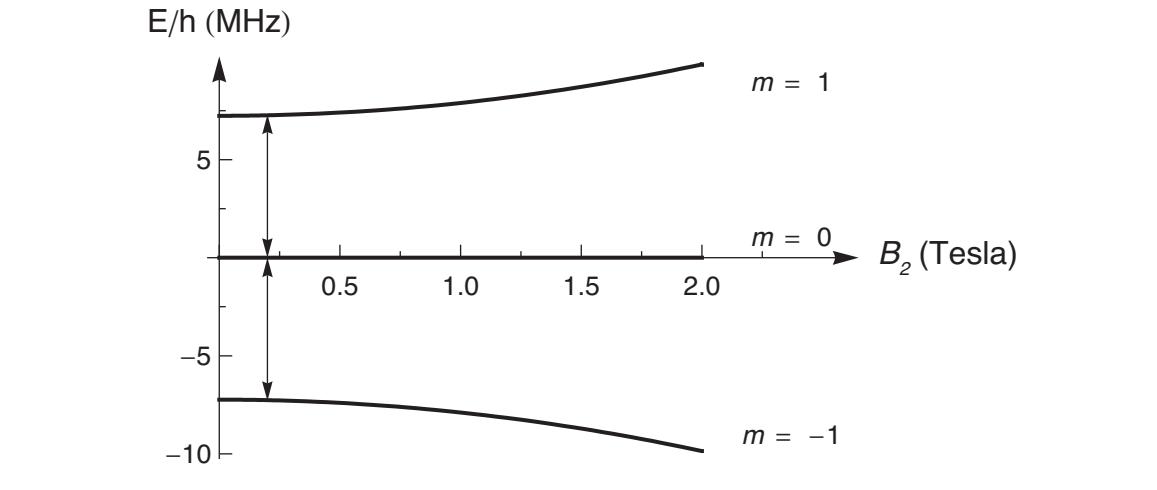
For the $|2^{(0)}\rangle$ state, the energy shift is

$$\begin{aligned} E_2^{(2)} &= \sum_{m \neq 2} \frac{|\langle 2^{(0)} | H' | m^{(0)} \rangle|^2}{(E_2^{(0)} - E_m^{(0)})} = \frac{|\langle 2^{(0)} | H' | 1^{(0)} \rangle|^2}{(E_2^{(0)} - E_1^{(0)})} + \frac{|\langle 2^{(0)} | H' | 3^{(0)} \rangle|^2}{(E_2^{(0)} - E_3^{(0)})} \\ &= \frac{|\frac{1}{\sqrt{2}}\hbar\omega_2|^2}{(0 - \hbar\omega_0)} + \frac{|\frac{1}{\sqrt{2}}\hbar\omega_2|^2}{(0 + \hbar\omega_0)} = 0 \end{aligned}$$

For the $|3^{(0)}\rangle$ state, the energy shift is

$$E_3^{(2)} = \sum_{m \neq 3} \frac{|\langle 3^{(0)} | H' | m^{(0)} \rangle|^2}{(E_3^{(0)} - E_m^{(0)})} = \frac{|\langle 3^{(0)} | H' | 2^{(0)} \rangle|^2}{(E_3^{(0)} - E_2^{(0)})} = \frac{|\frac{1}{\sqrt{2}}\hbar\omega_2|^2}{(-\hbar\omega_0 - 0)} = -\frac{\hbar\omega_2^2}{2\omega_0}$$

Plot:



10.9 The zeroth-order Hamiltonian of a particle on a sphere is the kinetic energy, as we found in Sect. 7.6:

$$H_{sphere} = \frac{\mathbf{L}^2}{2I}$$

The zeroth-order eigenstates are the angular momentum eigenstates

$$|\ell m\rangle \doteq Y_\ell^m(\theta, \phi)$$

and the zeroth-order energies are

$$E_\ell = \frac{\hbar^2}{2I} \ell(\ell+1)$$

The energy is independent of the magnetic quantum number m , so each energy level is degenerate except the $\ell=0$ ground state, with $(2\ell+1)$ possible m states for a given ℓ . Hence the need for degenerate perturbation theory, which means that we must diagonalize the perturbation Hamiltonian in each degenerate subspace, that is, for each value of ℓ .

The perturbation Hamiltonian is the potential energy of interaction $H' = -\boldsymbol{\mu}_L \cdot \mathbf{B}'$ between the applied magnetic field and the magnetic moment of the electron due to its orbital angular momentum (we ignore spin angular momentum here). The electron magnetic moment associated with the orbital motion is

$$\boldsymbol{\mu}_L = -\frac{e}{2m_e} \mathbf{L}$$

and the resultant perturbation Hamiltonian is

$$\begin{aligned} H' &= \frac{e}{2m_e} \mathbf{L} \cdot \mathbf{B}' = \frac{e}{2m_e} B_1 L_y \\ &= \omega_1 L_y \end{aligned}$$

The Larmor frequency in this case is $\omega_1 = eB_1/2m_e$. Diagonalizing the perturbation Hamiltonian is equivalent to diagonalizing the angular momentum component L_y . Hence, the eigenstates of the perturbation Hamiltonian are the L_y eigenstates $|1m_y\rangle$. The L_y eigenstates are thus the "correct" basis for the perturbation problem. In this basis, the perturbation is diagonal in the degenerate subspace, and degenerate perturbation theory reduces to nondegenerate theory: the energy corrections are the diagonal elements $H'_{nn} = \langle n^{(0)} | H' | n^{(0)} \rangle$:

$$E_n^{(1)} = H'_{nn} = \langle n^{(0)} | H' | n^{(0)} \rangle = \langle \ell m_y | \omega_1 L_y | \ell m_y \rangle = m_y \hbar \omega_1$$

Each energy state is split into the $(2\ell+1)$ possible m_y states for that ℓ state.

- 10.10 a) The first-order correction to the energy is zero because the perturbation x^3 is odd and the energy eigenstates are either even or odd so that their squares are even. This is true for all states.

$$E_n^{(1)} = \langle n^{(0)} | \hat{H}' | n^{(0)} \rangle = \langle n^{(0)} | \gamma x^3 | n^{(0)} \rangle = \int_{-\infty}^{\infty} \varphi_n^{(0)*}(x) \gamma x^3 \varphi_n^{(0)}(x) dx = \gamma \int_{-\infty}^{\infty} x^3 |\varphi_n^{(0)}(x)|^2 dx = 0$$

- b) The second-order correction to the energy is

$$E_n^{(2)} = \sum_{k \neq n} \frac{|\langle n^{(0)} | \hat{H}' | k^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

Use the ladder operators to find the required matrix elements:

$$\begin{aligned} x &= \sqrt{\frac{\hbar}{2m\omega}} (a^\dagger + a) \\ x^3 &= \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} (a^\dagger + a)^3 \\ &= \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} (a^\dagger a^\dagger a^\dagger + a^\dagger a^\dagger a + a^\dagger a a^\dagger + a^\dagger a a + a a^\dagger a^\dagger + a a^\dagger a + a a a^\dagger + a a a) \end{aligned}$$

This combination of ladder operators means that matrix elements of the x^3 operator are zero unless the two states differ in n by ± 1 or ± 3 . Hence the energy shifts are

$$\begin{aligned}
 E_0^{(2)} &= \sum_{k \neq 0} \frac{\left| \langle 0^{(0)} | \hat{H}' | k^{(0)} \rangle \right|^2}{E_0^{(0)} - E_k^{(0)}} = \frac{\left| \langle 0^{(0)} | \gamma x^3 | 1^{(0)} \rangle \right|^2}{E_0^{(0)} - E_1^{(0)}} + \frac{\left| \langle 0^{(0)} | \gamma x^3 | 3^{(0)} \rangle \right|^2}{E_0^{(0)} - E_3^{(0)}} \\
 E_1^{(2)} &= \sum_{k \neq 1} \frac{\left| \langle 1^{(0)} | \hat{H}' | k^{(0)} \rangle \right|^2}{E_1^{(0)} - E_k^{(0)}} = \frac{\left| \langle 1^{(0)} | \gamma x^3 | 0^{(0)} \rangle \right|^2}{E_1^{(0)} - E_0^{(0)}} + \frac{\left| \langle 1^{(0)} | \gamma x^3 | 2^{(0)} \rangle \right|^2}{E_1^{(0)} - E_2^{(0)}} + \frac{\left| \langle 1^{(0)} | \gamma x^3 | 4^{(0)} \rangle \right|^2}{E_1^{(0)} - E_4^{(0)}} \\
 E_2^{(2)} &= \sum_{k \neq 2} \frac{\left| \langle 2^{(0)} | \hat{H}' | k^{(0)} \rangle \right|^2}{E_2^{(0)} - E_k^{(0)}} = \frac{\left| \langle 2^{(0)} | \gamma x^3 | 1^{(0)} \rangle \right|^2}{E_2^{(0)} - E_1^{(0)}} + \frac{\left| \langle 2^{(0)} | \gamma x^3 | 3^{(0)} \rangle \right|^2}{E_2^{(0)} - E_3^{(0)}} + \frac{\left| \langle 2^{(0)} | \gamma x^3 | 5^{(0)} \rangle \right|^2}{E_2^{(0)} - E_5^{(0)}}
 \end{aligned}$$

The required matrix elements are

$$\begin{aligned}
 \langle 0^{(0)} | \hat{H}' | 1^{(0)} \rangle &= \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} \langle 0^{(0)} | \left(a^\dagger a^\dagger a^\dagger + a^\dagger a^\dagger a + a^\dagger a a^\dagger + a^\dagger a a + a a^\dagger a^\dagger + \boxed{a a^\dagger a + a a a^\dagger} + a a a^\dagger \right) | 1^{(0)} \rangle \\
 &= \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} \left(\sqrt{1} \sqrt{1} \sqrt{1} + \sqrt{1} \sqrt{2} \sqrt{2} \right) = \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} 3 \\
 \langle 0^{(0)} | \hat{H}' | 3^{(0)} \rangle &= \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} \langle 0^{(0)} | (a a a) | 3^{(0)} \rangle = \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} (\sqrt{1} \sqrt{2} \sqrt{3}) = \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} \sqrt{6} \\
 \langle 1^{(0)} | \hat{H}' | 0^{(0)} \rangle &= \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} \langle 1^{(0)} | (a^\dagger a a^\dagger + a a^\dagger a^\dagger) | 0^{(0)} \rangle = \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} (\sqrt{1} \sqrt{1} \sqrt{1} + \sqrt{2} \sqrt{2} \sqrt{1}) = \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} 3 \\
 \langle 1^{(0)} | \hat{H}' | 2^{(0)} \rangle &= \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} \langle 1^{(0)} | (a^\dagger a a + a a^\dagger a + a a a^\dagger) | 2^{(0)} \rangle \\
 &= \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} (\sqrt{1} \sqrt{1} \sqrt{2} + \sqrt{2} \sqrt{2} \sqrt{2} + \sqrt{2} \sqrt{3} \sqrt{3}) = \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} 6\sqrt{2} \\
 \langle 1^{(0)} | \hat{H}' | 4^{(0)} \rangle &= \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} \langle 1^{(0)} | (a a a) | 4^{(0)} \rangle = \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} (\sqrt{2} \sqrt{3} \sqrt{4}) = \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} 2\sqrt{6} \\
 \langle 2^{(0)} | \hat{H}' | 1^{(0)} \rangle &= \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} \langle 2^{(0)} | (a^\dagger a^\dagger a + a^\dagger a a^\dagger + a a^\dagger a^\dagger) | 1^{(0)} \rangle \\
 &= \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} (\sqrt{2} \sqrt{1} \sqrt{1} + \sqrt{2} \sqrt{2} \sqrt{2} + \sqrt{3} \sqrt{3} \sqrt{2}) = \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} 6\sqrt{2} \\
 \langle 2^{(0)} | \hat{H}' | 3^{(0)} \rangle &= \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} \langle 2^{(0)} | (a^\dagger a a + a a^\dagger a + a a a^\dagger) | 3^{(0)} \rangle \\
 &= \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} (\sqrt{2} \sqrt{2} \sqrt{3} + \sqrt{3} \sqrt{3} \sqrt{3} + \sqrt{3} \sqrt{4} \sqrt{4}) = \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} 9\sqrt{3} \\
 \langle 2^{(0)} | \hat{H}' | 5^{(0)} \rangle &= \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} \langle 2^{(0)} | (a a a) | 5^{(0)} \rangle = \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} (\sqrt{3} \sqrt{4} \sqrt{5}) = \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} 2\sqrt{15}
 \end{aligned}$$

The energy shifts are

$$\begin{aligned}
 E_0^{(2)} &= \gamma^2 \left(\frac{\hbar}{2m\omega} \right)^3 \left(\frac{9}{-\hbar\omega} + \frac{6}{-3\hbar\omega} \right) = \gamma^2 \left(\frac{\hbar}{2m\omega} \right)^3 \left(\frac{-11}{\hbar\omega} \right) \\
 E_1^{(2)} &= \gamma^2 \left(\frac{\hbar}{2m\omega} \right)^3 \left(\frac{9}{+\hbar\omega} + \frac{72}{-\hbar\omega} + \frac{24}{-3\hbar\omega} \right) = \gamma^2 \left(\frac{\hbar}{2m\omega} \right)^3 \left(\frac{-71}{\hbar\omega} \right) \\
 E_2^{(2)} &= \gamma^2 \left(\frac{\hbar}{2m\omega} \right)^3 \left(\frac{72}{+\hbar\omega} + \frac{243}{-\hbar\omega} + \frac{60}{-3\hbar\omega} \right) = \gamma^2 \left(\frac{\hbar}{2m\omega} \right)^3 \left(\frac{-191}{\hbar\omega} \right)
 \end{aligned}$$

c) The first-order corrections to the eigenstates are

$$|n^{(1)}\rangle = \sum_{k \neq n} c_{nk} |n^{(0)}\rangle$$

where the expansion coefficients are the same matrix elements from above (note that they are all real)

$$c_{nk} = \frac{\langle k^{(0)} | H' | n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}$$

Thus

$$\begin{aligned} |0^{(1)}\rangle &= \frac{\langle 1^{(0)} | H' | 0^{(0)} \rangle}{E_0^{(0)} - E_1^{(0)}} |1^{(0)}\rangle + \frac{\langle 3^{(0)} | H' | 0^{(0)} \rangle}{E_0^{(0)} - E_3^{(0)}} |3^{(0)}\rangle \\ &= \gamma \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} \left(\frac{1}{\hbar\omega} \right) \left(-3 |1^{(0)}\rangle - \sqrt{\frac{2}{3}} |3^{(0)}\rangle \right) \\ |1^{(1)}\rangle &= \frac{\langle 0^{(0)} | H' | 1^{(0)} \rangle}{E_1^{(0)} - E_0^{(0)}} |0^{(0)}\rangle + \frac{\langle 2^{(0)} | H' | 1^{(0)} \rangle}{E_1^{(0)} - E_2^{(0)}} |2^{(0)}\rangle + \frac{\langle 4^{(0)} | H' | 1^{(0)} \rangle}{E_1^{(0)} - E_4^{(0)}} |4^{(0)}\rangle \\ &= \gamma \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} \left(\frac{1}{\hbar\omega} \right) \left(+3 |0^{(0)}\rangle - 6\sqrt{2} |2^{(0)}\rangle - 2\sqrt{\frac{2}{3}} |4^{(0)}\rangle \right) \\ |2^{(1)}\rangle &= \frac{\langle 1^{(0)} | H' | 2^{(0)} \rangle}{E_2^{(0)} - E_1^{(0)}} |1^{(0)}\rangle + \frac{\langle 3^{(0)} | H' | 2^{(0)} \rangle}{E_2^{(0)} - E_3^{(0)}} |3^{(0)}\rangle + \frac{\langle 5^{(0)} | H' | 2^{(0)} \rangle}{E_2^{(0)} - E_5^{(0)}} |5^{(0)}\rangle \\ &= \gamma \left(\frac{\hbar}{2m\omega} \right)^{\frac{3}{2}} \left(\frac{1}{\hbar\omega} \right) \left(+6\sqrt{2} |1^{(0)}\rangle - 9\sqrt{3} |3^{(0)}\rangle - 2\sqrt{\frac{5}{3}} |5^{(0)}\rangle \right) \end{aligned}$$

10.11 The first-order energy correction is:

$$E_n^{(1)} = \langle n^{(0)} | \hat{H}' | n^{(0)} \rangle = \langle n^{(0)} | \eta x^4 | n^{(0)} \rangle$$

Use the ladder operators to make our life easy:

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

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

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

Hence

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

10.12 The first-order perturbed energy in the Stark effect example is

$$\begin{aligned}
 E_1^{(1)} &= \langle 100^{(0)} | H' | 100^{(0)} \rangle = \langle 100^{(0)} | e\mathcal{E}z | 100^{(0)} \rangle = e\mathcal{E} \langle 100^{(0)} | z | 100^{(0)} \rangle \\
 &= e\mathcal{E} \int z |\psi_{100}^{(0)}(r, \theta, \phi)|^2 dV
 \end{aligned}$$

Now do the integral:

$$E_1^{(1)} = e\mathcal{E} \int z |\psi_{100}^{(0)}(r, \theta, \phi)|^2 dV$$

The wave function is

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \frac{1}{(a_0)^{3/2}} e^{-r/a_0}$$

The integral is

$$\begin{aligned}
 E_1^{(1)} &= e\mathcal{E} \int z |\psi_{100}^{(0)}(r, \theta, \phi)|^2 dV = e\mathcal{E} \int r \cos \theta |\psi_{100}^{(0)}(r, \theta, \phi)|^2 r^2 \sin \theta d\theta d\phi dr \\
 &= \frac{1}{\pi} \frac{1}{a_0^3} \int_0^\infty \int_0^{2\pi} \int_0^\pi e^{-2r/a_0} r^3 \cos \theta \sin \theta d\theta d\phi dr \\
 &= \frac{1}{\pi} \frac{1}{a_0^3} \left\{ \left(\int_0^\infty r^3 e^{-2r/a_0} dr \right) \left(\int_0^\pi \cos \theta \sin \theta d\theta \right) \left(\int_0^{2\pi} d\phi \right) \right\}
 \end{aligned}$$

The polar angle integral is the one that makes the energy correction zero:

$$\int_0^\pi \cos \theta \sin \theta d\theta = \frac{1}{2} [\sin^2 \theta]_0^\pi = \frac{1}{2} [0 - 0] = 0$$

10.13 The angular integrals in Eq. (10.147) are

$$I_1 = \int_0^\pi \cos^2 \theta \sin \theta d\theta$$

$$I_2 = \int_0^{2\pi} d\phi$$

The results are

$$I_1 = \int_0^\pi \cos^2 \theta \sin \theta d\theta = -\frac{1}{3} [\cos^3 \theta]_0^\pi = -\frac{1}{3} [-1 - 1] = \frac{2}{3}$$

and

$$I_2 = \int_0^{2\pi} d\phi = [\phi]_0^{2\pi} = 2\pi$$

10.14 Find the eigenstates:

$$H' |\psi_{\pm}\rangle = E_{\pm} |\psi_{\pm}\rangle$$

It is sufficient to work in the reduced space of the two coupled states $|200\rangle$ and $|210\rangle$:

$$\begin{pmatrix} 0 & -3e\mathcal{E}a_0 \\ -3e\mathcal{E}a_0 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \pm 3e\mathcal{E}a_0 \begin{pmatrix} a \\ b \end{pmatrix}$$

$$-3e\mathcal{E}a_0 b = \pm 3e\mathcal{E}a_0 a$$

$$b_{\pm} = \mp a$$

Using the normalization requirement yields

$$|\psi_+\rangle \doteq \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$|\psi-\rangle \doteq \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

or

$$|\psi_+\rangle = \frac{1}{\sqrt{2}} [|200\rangle - |210\rangle]$$

$$|\psi-\rangle = \frac{1}{\sqrt{2}} [|200\rangle + |210\rangle]$$

10.15 The state $|\psi_-\rangle$ is

$$|\psi_-\rangle = \frac{1}{\sqrt{2}}(|200\rangle + |210\rangle)$$

The expectation value of the dipole moment $\mathbf{d} = -e\mathbf{r}$ is

$$\begin{aligned}\langle \psi_- | \mathbf{d} | \psi_- \rangle &= \langle \psi_- | -e\mathbf{r} | \psi_- \rangle = -e \frac{1}{\sqrt{2}} (\langle 200 | + \langle 210 |) \mathbf{r} \frac{1}{\sqrt{2}} (\langle 200 \rangle + \langle 210 \rangle) \\ &= -e \frac{1}{2} (\langle 200 | \mathbf{r} | 200 \rangle + \langle 200 | \mathbf{r} | 210 \rangle + \langle 210 | \mathbf{r} | 200 \rangle + \langle 210 | \mathbf{r} | 210 \rangle)\end{aligned}$$

The first and last terms are zero by symmetry and the other two terms are complex conjugates of each other. Hence we need to find

$$\begin{aligned}\langle 200 | \mathbf{r} | 210 \rangle &= \int \psi_{200}^{(0)*}(r, \theta, \phi) (x\hat{\mathbf{i}} + y\hat{\mathbf{j}} + z\hat{\mathbf{k}}) \psi_{210}^{(0)}(r, \theta, \phi) r^2 \sin \theta dr d\theta d\phi \\ &= \frac{2}{(2a_0)^{3/2}} \frac{1}{\sqrt{4\pi}} \frac{1}{\sqrt{3}a_0 (2a_0)^{3/2}} \sqrt{\frac{3}{4\pi}} \int_0^\infty r \left(1 - \frac{r}{2a_0}\right) e^{-r/a_0} (x\hat{\mathbf{i}} + y\hat{\mathbf{j}} + z\hat{\mathbf{k}}) r^2 dr \\ &\quad \int_0^\pi \cos \theta \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{1}{16\pi a_0^4} \int_0^\infty \int_0^{2\pi} \int_0^\pi r^4 \left(1 - \frac{r}{2a_0}\right) e^{-r/a_0} (\sin \theta \cos \phi \hat{\mathbf{i}} + \sin \theta \sin \phi \hat{\mathbf{j}} + \cos \theta \hat{\mathbf{k}}) \cos \theta \sin \theta d\theta d\phi dr\end{aligned}$$

The azimuthal integrals $\int_0^{2\pi} \cos \phi d\phi$ and $\int_0^{2\pi} \sin \phi d\phi$ are both zero. The remaining polar integral gives 2/3, yielding

$$\begin{aligned}\langle 200 | \mathbf{r} | 210 \rangle &= \frac{\hat{\mathbf{k}}}{16\pi a_0^4} \frac{2}{3} 2\pi \int_0^\infty r^4 \left(1 - \frac{r}{2a_0}\right) e^{-r/a_0} dr \\ &= \frac{\hat{\mathbf{k}}}{12a_0^4} \left[\int_0^\infty r^4 e^{-r/a_0} dr - \frac{1}{2a_0} \int_0^\infty r^5 e^{-r/a_0} dr \right] = \frac{\hat{\mathbf{k}}}{12a_0^4} \left[4!a_0^5 - \frac{1}{2a_0} 5!a_0^6 \right] \\ &= -3a_0 \hat{\mathbf{k}}\end{aligned}$$

The expectation value of the dipole moment is

$$\begin{aligned}\langle \psi_- | \mathbf{d} | \psi_- \rangle &= -e \frac{1}{2} (\langle 200 | \mathbf{r} | 210 \rangle + \langle 210 | \mathbf{r} | 200 \rangle) \\ &= -e \frac{1}{2} (-3a_0 \hat{\mathbf{k}} + -3a_0 \hat{\mathbf{k}}) \\ &= 3ea_0 \hat{\mathbf{k}}\end{aligned}$$

which means it is aligned with the applied electric field, as expected [see Fig. 8.9(b)].

10.16. The second-order correction is:

$$\begin{aligned}
 E_n^{(2)} &= \sum_{k \neq n} \frac{\left| \langle n^{(0)} | \hat{H}' | k^{(0)} \rangle \right|^2}{E_n^{(0)} - E_k^{(0)}} = \sum_{k \neq n} \frac{\left| \int_{L/2}^L \varphi_n^{(0)*}(x) V_0 \varphi_k^{(0)}(x) dx \right|^2}{E_n^{(0)} - E_k^{(0)}} \\
 &= (V_0)^2 \sum_{k \neq n} \frac{\left| \frac{2}{L} \int_{L/2}^L \sin \frac{n\pi x}{L} \sin \frac{k\pi x}{L} dx \right|^2}{(n^2 - k^2) \frac{\pi^2 \hbar^2}{2mL^2}} \\
 &= (V_0)^2 \frac{2mL^2}{\pi^2 \hbar^2} \frac{4}{L^2} \sum_{k \neq n} \frac{\left| \frac{L \sin \left(\frac{(n-k)\pi}{2} \right)}{2\pi(n-k)} - \frac{L \sin \left(\frac{(n+k)\pi}{2} \right)}{2\pi(n+k)} \right|^2}{(n^2 - k^2)}
 \end{aligned}$$

For the ground state we get

$$\begin{aligned}
 E_1^{(2)} &= (V_0)^2 \frac{2mL^2}{\pi^2 \hbar^2} \frac{4}{L^2} \sum_{k \neq 1} \frac{\left| \frac{L \sin \left(\frac{(1-k)\pi}{2} \right)}{2\pi(1-k)} - \frac{L \sin \left(\frac{(1+k)\pi}{2} \right)}{2\pi(1+k)} \right|^2}{(1-k^2)} \\
 &= (V_0)^2 \frac{2mL^2}{\pi^2 \hbar^2} \frac{4}{L^2} \frac{L^2}{4\pi^2} \sum_{k \neq 1} \frac{\left| \frac{\cos \left(\frac{k\pi}{2} \right)}{(1-k)} - \frac{\cos \left(\frac{k\pi}{2} \right)}{(1+k)} \right|^2}{(1-k^2)} \\
 &= (V_0)^2 \frac{2mL^2}{\pi^2 \hbar^2} \frac{4}{L^2} \frac{L^2}{4\pi^2} \sum_{k \neq 1} \left(\cos \left(\frac{k\pi}{2} \right) \right)^2 \frac{\left| \frac{2k}{(k^2 - 1)} \right|^2}{(1-k^2)} \\
 &= -(V_0)^2 \frac{2mL^2}{\pi^4 \hbar^2} \sum_{k \neq 1} \left(\cos \left(\frac{k\pi}{2} \right) \right)^2 \frac{4k^2}{(k^2 - 1)^3} = -(V_0)^2 \frac{2mL^2}{\pi^4 \hbar^2} \sum_{j=1} \frac{16j^2}{(4j^2 - 1)^3} \\
 &= -(V_0)^2 \frac{mL^2}{\pi^4 \hbar^2} \frac{\pi^2}{8} \quad ; \text{ do sum in Maple or Mathematica}
 \end{aligned}$$

10.17 The first-order energy correction to the n th state is:

$$E_n^{(1)} = \langle n^{(0)} | H' | n^{(0)} \rangle$$

With $H' = \beta x$ and $\varphi_n^{(0)} = \sqrt{2/L} \sin(n\pi x/L)$, we find for the ground state

$$\begin{aligned}
 E_1^{(1)} &= \int_0^L \frac{2}{L} \sin\left(\frac{\pi x}{L}\right) \beta x \sin\left(\frac{\pi x}{L}\right) dx = \frac{2\beta}{L} \int_0^L x \sin^2\left(\frac{\pi x}{L}\right) dx \\
 &= \frac{2\beta}{L} \left[\frac{x^2}{4} - \frac{x \sin\left(\frac{2\pi x}{L}\right)}{4(\pi/L)} - \frac{\cos\left(\frac{2\pi x}{L}\right)}{8(\pi/L)^2} \right]_0^L \\
 &= \frac{2\beta}{L} \left[\frac{L^2}{4} - \frac{L \sin(2\pi)}{4(\pi/L)} - \frac{\cos(2\pi)}{8(\pi/L)^2} - \left(-\frac{\cos(2\pi)}{8(\pi/L)^2} \right) \right] \\
 &= \frac{2\beta}{L} \left[\frac{L^2}{4} - \frac{L^2}{8\pi^2} - \left(-\frac{L^2}{8\pi^2} \right) \right] = \frac{\beta L}{2}
 \end{aligned}$$

10.18 a) The first-order energy correction to the n th state is:

$$E_n^{(1)} = \langle n^{(0)} | H' | n^{(0)} \rangle$$

With $H' = LV_0\delta(x - L/2)$ and $\varphi_n^{(0)} = \sqrt{2/L} \sin(n\pi x/L)$, we find

$$E_n^{(1)} = \int_0^L \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right) LV_0\delta\left(x - \frac{L}{2}\right) dx = 2V_0 \sin^2\left(\frac{n\pi}{2}\right)$$

For odd values of n , the correction is $2V_0$, while for even values of n , it is zero:

$$E_n^{(1)} = \begin{cases} 2V_0 & ; n \text{ odd} \\ 0 & ; n \text{ even} \end{cases}$$

b) The wave function for a state with an even value of n is zero at the location of the delta function, so it does not "sample" the perturbation, and the energy is therefore unaffected. Not so for states with odd values of n , where the energy levels are indeed shifted.

c) The new wavefunction, correct to first order is:

$$|1\rangle = |1^{(0)}\rangle + \sum_{k \neq 1} \frac{\langle k^{(0)} | H' | 1^{(0)} \rangle}{E_1^{(0)} - E_k^{(0)}} |k^{(0)}\rangle$$

The matrix element in the numerator in the sum is:

$$\begin{aligned}
 \langle k^{(0)} | H' | 1^{(0)} \rangle &= \int_0^L \frac{2}{L} \sin\left(\frac{k\pi x}{L}\right) \sin\left(\frac{\pi x}{L}\right) LV_0\delta\left(x - \frac{L}{2}\right) dx = 2V_0 \sin\left(\frac{k\pi}{2}\right) \sin\left(\frac{\pi}{2}\right) \\
 &= 2V_0 \sin\left(\frac{k\pi}{2}\right)
 \end{aligned}$$

We see that for k even, there is no contribution – the states with even labels do not mix. For k odd, all terms have the same numerator (modulo a sign), but the denominator becomes progressively larger as k increases, because the energy difference between the

ground state and the state in question increases. Thus the largest contribution comes from the $\boxed{k=3}$ state, and it is

$$c_{1k,\max} = c_{13} = \frac{2V_0 \sin\left(\frac{3\pi}{2}\right)}{E_1^{(0)} - E_3^{(0)}} = \frac{-2V_0}{(1-9)\frac{\pi^2\hbar^2}{2mL^2}}$$

$$\left| 1^{(1)} \right\rangle \equiv \frac{V_0 mL^2}{2\pi^2\hbar^2} \left| 3^{(0)} \right\rangle$$

$$\boxed{\left| 1 \right\rangle \equiv \left| 1^{(0)} \right\rangle + \frac{V_0 mL^2}{2\pi^2\hbar^2} \left| 3^{(0)} \right\rangle}$$

d) For this square bump the first-order perturbation is

$$\begin{aligned} E_n^{(1)} &= \left\langle n^{(0)} \left| \hat{H}' \right| n^{(0)} \right\rangle = \int_{L/2-\varepsilon L/2}^{L/2+\varepsilon L/2} \varphi_n^*(x) \frac{V_0}{\varepsilon} \varphi_n(x) dx = \int_{L/2-\varepsilon L/2}^{L/2+\varepsilon L/2} \left[\varphi_1^*(x) \frac{V_0}{\varepsilon} \varphi_1(x) \right] dx \\ &= \frac{V_0}{\varepsilon} \int_{L/2-\varepsilon L/2}^{L/2+\varepsilon L/2} \left[\frac{2}{L} \sin^2\left(\frac{\pi x}{L}\right) \right] dx = \frac{V_0}{\varepsilon} \frac{2}{L} \int_{L/2-\varepsilon L/2}^{L/2+\varepsilon L/2} \left(\frac{1}{2} \left[1 - \cos\left(\frac{2\pi x}{L}\right) \right] \right) dx \\ &= \frac{V_0}{\varepsilon L} \left[x - \left(\frac{L}{2\pi} \right) \sin\left(\frac{2\pi x}{L}\right) \right]_{L/2-\varepsilon L/2}^{L/2+\varepsilon L/2} \\ &= \frac{V_0}{\varepsilon L} \left[\frac{L}{2} + \varepsilon \frac{L}{2} - \left(\frac{L}{2\pi} \right) \sin\left(\frac{2\pi}{L} \left(\frac{L}{2} + \varepsilon \frac{L}{2} \right) \right) - \left(\frac{L}{2} - \varepsilon \frac{L}{2} \right) + \left(\frac{L}{2\pi} \right) \sin\left(\frac{2\pi}{L} \left(\frac{L}{2} - \varepsilon \frac{L}{2} \right) \right) \right] \\ &= \frac{V_0}{\varepsilon L} \left[\varepsilon L - \left(\frac{L}{2\pi} \right) \sin(\pi + \varepsilon\pi) + \left(\frac{L}{2\pi} \right) \sin(\pi - \varepsilon\pi) \right] \\ &= \frac{V_0}{\varepsilon L} \left[\varepsilon L + \left(\frac{L}{2\pi} \right) \sin(\varepsilon\pi) + \left(\frac{L}{2\pi} \right) \sin(\varepsilon\pi) \right] \\ &\boxed{E_1^{(1)} = V_0 \left[1 + \frac{\sin(\varepsilon\pi)}{\varepsilon\pi} \right]} \end{aligned}$$

e) In the limit of small ε , we get

$$E_1^{(1)} \cong V_0 \left[1 + \frac{1}{\varepsilon\pi} \varepsilon\pi \right] = 2V_0$$

$$E_1^{(1)} \cong 2V_0$$

just as we got in part (a). This is to be expected because in the limit of $\varepsilon \rightarrow 0$, the square bump looks like a delta function, and we arranged its parameters at the beginning so that the area of the bump $((V_0/\varepsilon)\varepsilon L = LV_0)$ is the same as the area of the delta function.

10.19 a) The first-order energy correction to the n th state is:

$$E_n^{(1)} = \langle n^{(0)} | H' | n^{(0)} \rangle$$

With $H' = V_0 \sin(\pi x/L)$ and $\varphi_n^{(0)} = \sqrt{2/L} \sin(n\pi x/L)$, we find

$$\begin{aligned} E_n^{(1)} &= \int_0^L \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right) V_0 \sin\left(\frac{\pi x}{L}\right) dx = \frac{2V_0}{L} \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) \sin\left(\frac{\pi x}{L}\right) dx \\ &= \frac{2V_0}{L} \left[-\frac{L \cos\left[\frac{\pi x}{L}\right]}{2\pi} - \frac{L \cos\left[\frac{(2n-1)\pi x}{L}\right]}{4(2n-1)\pi} + \frac{L \cos\left[\frac{(2n+1)\pi x}{L}\right]}{4(2n+1)\pi} \right]_0^L \\ &= \frac{2V_0}{L} \left[\frac{2L}{2\pi} - \frac{L \cos[(2n-1)\pi] - L}{4(2n-1)\pi} + \frac{L \cos[(2n+1)\pi] - L}{4(2n+1)\pi} \right] \\ &= V_0 \left[\frac{2}{\pi} + \frac{1}{(2n-1)\pi} - \frac{1}{(2n+1)\pi} \right] = V_0 \frac{8n^2}{\pi(4n^2-1)} \end{aligned}$$

10.20 The first-order energy correction to the n th state is:

$$E_n^{(1)} = \langle n^{(0)} | H' | n^{(0)} \rangle$$

With $H' = \gamma x(L-x)$ and $\varphi_n^{(0)} = \sqrt{2/L} \sin(n\pi x/L)$, we find

$$\begin{aligned} E_n^{(1)} &= \int_0^L \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right) \gamma x(L-x) dx = \frac{2\gamma}{L} \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) (xL - x^2) dx \\ &= \frac{2\gamma}{L} \left[\frac{L(-L^2 \cos[\frac{2n\pi x}{L}] + 2n\pi x(n\pi x - L \sin[\frac{2n\pi x}{L}]))}{8n^2\pi^2} - \frac{x^3}{6} \right]_0^L \\ &\quad + \frac{L^2 x \cos[\frac{2n\pi x}{L}]}{4n^2\pi^2} + \frac{L(-L^2 + 2n^2\pi^2 x^2) \sin[\frac{2n\pi x}{L}]}{8n^3\pi^3} \\ &= \frac{2\gamma}{L} \left[\frac{L(2n\pi L(n\pi L))}{8n^2\pi^2} - \frac{L^3}{6} + \frac{L^3}{4n^2\pi^2} \right] = L^2 \gamma \left[\frac{1}{6} + \frac{1}{2n^2\pi^2} \right] \end{aligned}$$

10.21 a) The first-order correction to the energy is zero because the perturbation x is odd and the energy eigenstates are either even or odd so that their squares are even. This is true for all states.

$$\begin{aligned} E_n^{(1)} &= \langle n^{(0)} | H' | n^{(0)} \rangle = \langle n^{(0)} | -q\mathcal{E}x | n^{(0)} \rangle = -q\mathcal{E} \int_{-\infty}^{\infty} \varphi_n^*(x) x \varphi_n(x) dx \\ &= -q\mathcal{E} \int_{-\infty}^{\infty} x |\varphi_n(x)|^2 dx = 0 \end{aligned}$$

The second-order correction is

$$E_n^{(2)} = \sum_{k \neq n} \frac{|\langle n^{(0)} | H' | k^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}} = q^2 \mathcal{E}^2 \sum_{k \neq n} \frac{|\langle n^{(0)} | x | k^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

Use ladder operators to calculate the matrix elements

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

$$\begin{aligned} \langle n^{(0)} | x | k^{(0)} \rangle &= \langle n | x | k \rangle = \sqrt{\frac{\hbar}{2m\omega}} \langle n | (a^\dagger + a) | k \rangle = \sqrt{\frac{\hbar}{2m\omega}} [\langle n | a^\dagger | k \rangle + \langle n | a | k \rangle] \\ &= \sqrt{\frac{\hbar}{2m\omega}} [\langle n | \sqrt{k+1} | k+1 \rangle + \langle n | \sqrt{k} | k-1 \rangle] = \sqrt{\frac{\hbar}{2m\omega}} [\sqrt{k+1} \delta_{n,k+1} + \sqrt{k} \delta_{n,k-1}] \end{aligned}$$

Put this back into the energy correction to get

$$\begin{aligned} E_n^{(2)} &= q^2 \mathcal{E}^2 \frac{\hbar}{2m\omega} \sum_{k \neq n} \frac{[\sqrt{k+1} \delta_{n,k+1} + \sqrt{k} \delta_{n,k-1}]^2}{(n + \frac{1}{2})\hbar\omega - (k + \frac{1}{2})\hbar\omega} = \frac{q^2 \mathcal{E}^2}{2m\omega^2} \sum_{k \neq n} \frac{[\sqrt{k+1} \delta_{n,k+1} + \sqrt{k} \delta_{n,k-1}]^2}{n - k} \\ &= \frac{q^2 \mathcal{E}^2}{2m\omega^2} \left[\frac{n}{n - (n-1)} + \frac{n+1}{n - (n+1)} \right] = \frac{q^2 \mathcal{E}^2}{2m\omega^2} [n - (n+1)] \\ E_n^{(2)} &= -\frac{q^2 \mathcal{E}^2}{2m\omega^2} \end{aligned}$$

The new energy levels to second order are thus

$$\begin{aligned} E_n &= E_n^{(0)} + E_n^{(1)} + E_n^{(2)} = \left(n + \frac{1}{2}\right)\hbar\omega + 0 + \left(-\frac{q^2 \mathcal{E}^2}{2m\omega^2}\right) \\ E_n &= \left(n + \frac{1}{2}\right)\hbar\omega - \frac{q^2 \mathcal{E}^2}{2m\omega^2} \end{aligned}$$

b) Now solve the problem exactly by completing the square in the Hamiltonian:

$$\begin{aligned} H &= H_0 + H' = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 - q\mathcal{E}x \\ &= \frac{p^2}{2m} + \frac{1}{2}m\omega^2 \left(x^2 - \frac{2q\mathcal{E}}{m\omega^2} x + \left(\frac{q\mathcal{E}}{m\omega^2}\right)^2 \right) - \frac{1}{2}m\omega^2 \left(\frac{q\mathcal{E}}{m\omega^2}\right)^2 \\ &= \frac{p^2}{2m} + \frac{1}{2}m\omega^2 \left(x - \frac{q\mathcal{E}}{m\omega^2} \right)^2 - \frac{q^2 \mathcal{E}^2}{2m\omega^2} \\ &= \frac{p^2}{2m} + \frac{1}{2}m\omega^2 y^2 - \frac{q^2 \mathcal{E}^2}{2m\omega^2} \quad ; \text{ where } y \equiv x - \frac{q\mathcal{E}}{m\omega^2} \end{aligned}$$

This Hamiltonian represents a system with the position shifted and the energy levels shifted, both by constants. The energy spectrum is thus still a harmonic oscillator spectrum but shifted by the energy shift in the Hamiltonian:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega - \frac{q^2\mathcal{E}^2}{2m\omega^2},$$

which is exactly the same as the perturbation result above. Thus we know that all other orders in perturbation theory will yield zero (or at least all sum to zero).

10.22 The $n = 3$ state of the hydrogen atom is ninefold degenerate, with one $3s$ state and three $3p$ states and five $3d$ states. Degenerate perturbation theory tells us to *diagonalize the perturbation Hamiltonian in the degenerate subspace*. To do this, we need to find the matrix representing the Stark effect perturbation within the subspace of the nine degenerate states. The nine $n = 3$ states of hydrogen are given in Table 8.2. There are 81 matrix elements:

$$\langle 3\ell m^{(0)} | H' | 3\ell' m'^{(0)} \rangle$$

with the perturbation being $H' = e\mathcal{E}z = e\mathcal{E}r \cos\theta$. The Hamiltonian for the perturbation has odd parity, so the matrix elements between states of the same parity give an integrand that is odd and hence a zero integral. The only non-zero matrix elements are those between states of different parity, which are the s and p states or the p and d states. We can reduce our task even further by considering the ϕ part of the integrals for these cases. There is no ϕ dependence in the perturbation Hamiltonian, so the matrix elements have azimuthal integrals

$$\int_0^{2\pi} e^{-im\phi} e^{im'\phi} d\phi = \int_0^{2\pi} e^{i(m'-m)\phi} d\phi$$

This integral is zero unless the magnetic quantum numbers m and m' are the same, which only happens for the matrix elements between the $3s$ and $3p_0$ states, the $3p_0$ and $3d_0$ states, the $3p_1$ and $3d_1$ states, and the $3p_{-1}$ and $3d_{-1}$ states. The last two are the same, so we need do only 3 integrals:

$$\langle 300^{(0)} | H' | 310^{(0)} \rangle, \langle 310^{(0)} | H' | 320^{(0)} \rangle, \langle 31, \pm 1^{(0)} | H' | 32, \pm 1^{(0)} \rangle$$

The first matrix element is

$$\begin{aligned} \langle 300^{(0)} | H' | 310^{(0)} \rangle &= \int \psi_{300}^{(0)*}(r, \theta, \phi) e\mathcal{E}r \cos\theta \psi_{310}^{(0)}(r, \theta, \phi) r^2 \sin\theta dr d\theta d\phi \\ &= e\mathcal{E} \frac{1}{\sqrt{\pi} (3a_0)^{3/2}} \frac{2\sqrt{2}}{3\sqrt{3\pi} (3a_0)^{3/2}} \int_0^\infty \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) \frac{r}{a_0} \left(1 - \frac{r}{6a_0}\right) e^{-2r/3a_0} r^3 dr \\ &\quad \int_0^\pi \cos^2\theta \sin\theta d\theta \int_0^{2\pi} d\phi \end{aligned}$$

The θ and ϕ angular integrals are straightforward and give $2/3$ and 2π , as in the $n = 2$ case. Doing the radial integral gives

$$\begin{aligned}\langle 300^{(0)} | H' | 310^{(0)} \rangle &= e\mathcal{E} \frac{1}{(3a_0)^3} \frac{8\sqrt{2}}{9a_0\sqrt{3}} \int_0^\infty \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) \left(1 - \frac{r}{6a_0}\right) e^{-2r/3a_0} r^4 dr \\ &= e\mathcal{E} \frac{1}{(3a_0)^3} \frac{8\sqrt{2}}{9a_0\sqrt{3}} \left[-\frac{2187}{8} a_0^5 \right] = -e\mathcal{E} a_0 3\sqrt{6}\end{aligned}$$

The second matrix element is

$$\begin{aligned}\langle 310^{(0)} | H' | 320^{(0)} \rangle &= \int \psi_{310}^{(0)*}(r, \theta, \phi) e\mathcal{E} r \cos\theta \psi_{320}^{(0)}(r, \theta, \phi) r^2 \sin\theta dr d\theta d\phi \\ &= e\mathcal{E} \frac{2\sqrt{2}}{3\sqrt{3\pi}(3a_0)^{3/2}} \frac{1}{27\sqrt{2\pi}(3a_0)^{3/2}} \int_0^\infty \frac{r}{a_0} \left(1 - \frac{r}{6a_0}\right) \frac{r^2}{a_0^2} e^{-2r/3a_0} r^3 dr \\ &\quad \int_0^\pi \cos^2\theta \sin\theta (3\cos^2\theta - 1) d\theta \int_0^{2\pi} d\phi\end{aligned}$$

The ϕ integral again gives 2π . The θ integral is

$$\begin{aligned}\int_0^\pi \cos^2\theta \sin\theta (3\cos^2\theta - 1) d\theta &= \int_0^\pi \sin\theta (3\cos^4\theta - \cos^2\theta) d\theta \\ &= \left[-\frac{3}{5} \cos^5\theta + \frac{1}{3} \cos^3\theta \right]_0^\pi = \frac{3}{5} - \frac{1}{3} + \frac{3}{5} - \frac{1}{3} = \frac{8}{15}\end{aligned}$$

Doing the radial integral gives the result

$$\begin{aligned}\langle 310^{(0)} | H' | 320^{(0)} \rangle &= e\mathcal{E} \frac{2}{81\pi\sqrt{3}(3a_0)^3 a_0^3} \frac{8}{15} 2\pi \int_0^\infty \left(1 - \frac{r}{6a_0}\right) e^{-2r/3a_0} r^6 dr \\ &= e\mathcal{E} \frac{2}{\sqrt{3}(3)^7 a_0^6} \frac{16}{15} \left[-\frac{295245}{32} a_0^7 \right] = -e\mathcal{E} a_0 3\sqrt{3}\end{aligned}$$

The third matrix element is

$$\begin{aligned}\langle 31, \pm 1^{(0)} | H' | 32, \pm 1^{(0)} \rangle &= \int \psi_{31,\pm 1}^{(0)*}(r, \theta, \phi) e\mathcal{E} r \cos\theta \psi_{32,\pm 1}^{(0)}(r, \theta, \phi) r^2 \sin\theta dr d\theta d\phi \\ &= e\mathcal{E} \frac{\mp 2}{3\sqrt{3\pi}(3a_0)^{3/2}} \frac{\mp\sqrt{3}}{27\sqrt{\pi}(3a_0)^{3/2}} \int_0^\infty \frac{r}{a_0} \left(1 - \frac{r}{6a_0}\right) \frac{r^2}{a_0^2} e^{-2r/3a_0} r^3 dr \\ &\quad \int_0^\pi \cos^2\theta \sin^3\theta d\theta \int_0^{2\pi} d\phi\end{aligned}$$

The ϕ integral again gives 2π . The θ integral is

$$\begin{aligned}\int_0^\pi \cos^2\theta \sin^3\theta d\theta &= \int_0^\pi \sin\theta \cos^2\theta (1 - \cos^2\theta) d\theta = \int_0^\pi \sin\theta (\cos^2\theta - \cos^4\theta) d\theta \\ &= \left[-\frac{1}{3} \cos^3\theta + \frac{1}{5} \cos^5\theta \right]_0^\pi = \frac{1}{3} - \frac{1}{5} + \frac{1}{3} - \frac{1}{5} = \frac{4}{15}\end{aligned}$$

Doing the radial integral gives the result

$$\begin{aligned}\langle 31, \pm 1^{(0)} | H' | 32, \pm 1^{(0)} \rangle &= e\mathcal{E} \frac{2}{81\pi(3a_0)^3 a_0^3} \frac{4}{15} 2\pi \int_0^\infty \left(1 - \frac{r}{6a_0}\right) e^{-2r/3a_0} r^6 dr \\ &= e\mathcal{E} \frac{16}{3^8 a_0^6} \frac{1}{5} \left[-\frac{295245}{32} a_0^7 \right] = -e\mathcal{E} a_0 \frac{9}{2}\end{aligned}$$

The perturbation matrix thus

$$H' \doteq -ea_0\mathcal{E} \left(\begin{array}{ccccccccc|c} 0 & 0 & 3\sqrt{6} & 0 & 0 & 0 & 0 & 0 & 0 & 300 \\ 0 & 0 & 0 & 0 & 0 & 9/2 & 0 & 0 & 0 & 311 \\ 3\sqrt{6} & 0 & 0 & 0 & 0 & 0 & 3\sqrt{3} & 0 & 0 & 310 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 9/2 & 0 & 31,-1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 322 \\ 0 & 9/2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 321 \\ 0 & 0 & 3\sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 & 320 \\ 0 & 0 & 0 & 9/2 & 0 & 0 & 0 & 0 & 0 & 32,-1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 32,-2 \end{array} \right)$$

To diagonalize this, it is useful to relabel the rows and columns to place the nonzero elements close to the diagonal:

$$H' \doteq -ea_0\mathcal{E} \left(\begin{array}{ccc|cc|cc|cc} 0 & 3\sqrt{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 300 \\ 3\sqrt{6} & 0 & 3\sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 & 310 \\ 0 & 3\sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 320 \\ \hline 0 & 0 & 0 & 0 & 9/2 & 0 & 0 & 0 & 0 & 311 \\ 0 & 0 & 0 & 9/2 & 0 & 0 & 0 & 0 & 0 & 321 \\ \hline 0 & 0 & 0 & 0 & 0 & 0 & 9/2 & 0 & 0 & 31,-1 \\ 0 & 0 & 0 & 0 & 0 & 9/2 & 0 & 0 & 0 & 32,-1 \\ \hline 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 322 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 32,-2 \end{array} \right)$$

This matrix is block-diagonal, so we diagonalize each block independently. First the 3x3 block:

$$\begin{vmatrix} -\lambda & -3\sqrt{6}ea_0\mathcal{E} & 0 \\ 3\sqrt{6}ea_0\mathcal{E} & -\lambda & 3\sqrt{3}ea_0\mathcal{E} \\ 0 & 3\sqrt{3}ea_0\mathcal{E} & -\lambda \end{vmatrix} = 0$$

$$-\lambda(\lambda^2 - (3\sqrt{3}ea_0\mathcal{E})^2) + 3\sqrt{6}ea_0\mathcal{E}(-\lambda 3\sqrt{6}ea_0\mathcal{E}) = 0$$

$$-\lambda(\lambda^2 - (9ea_0\mathcal{E})^2) = 0 \Rightarrow E_1^{(1)} = 0, E_2^{(1)} = 9ea_0\mathcal{E}, E_3^{(1)} = -9ea_0\mathcal{E}$$

Then the two equivalent 2x2 blocks:

$$\begin{vmatrix} -\lambda & 9ea_0\mathcal{E}/2 \\ 9ea_0\mathcal{E}/2 & -\lambda \end{vmatrix} = 0 \Rightarrow \lambda^2 - (9ea_0\mathcal{E}/2)^2 = 0$$

$$E_4^{(1)} = E_5^{(1)} = 9ea_0\mathcal{E}/2, E_6^{(1)} = E_7^{(1)} = -9ea_0\mathcal{E}/2$$

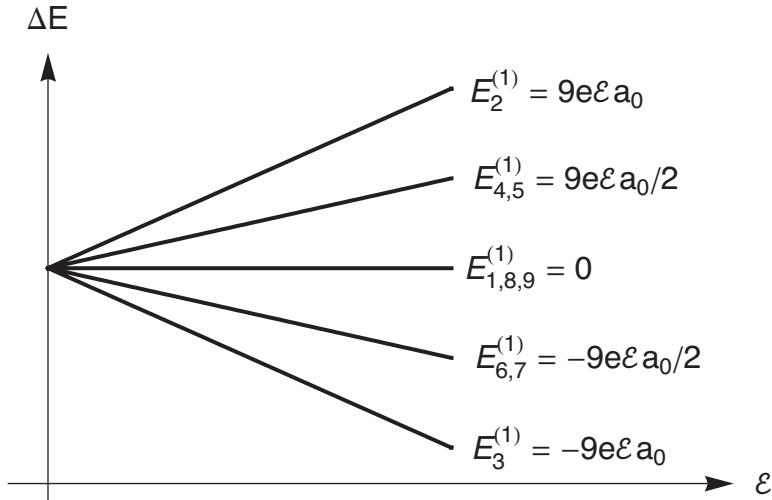
The last two we obtain by inspection:

$$E_8^{(1)} = E_9^{(1)} = 0$$

The eigenvectors are

$$\begin{aligned} |1\rangle &= \frac{1}{\sqrt{3}}|300^{(0)}\rangle - \frac{1}{\sqrt{2}}|310^{(0)}\rangle + \frac{1}{\sqrt{6}}|320^{(0)}\rangle \\ |2\rangle &= \frac{1}{\sqrt{3}}|300^{(0)}\rangle + \frac{1}{\sqrt{2}}|310^{(0)}\rangle + \frac{1}{\sqrt{6}}|320^{(0)}\rangle \\ |3\rangle &= -\frac{1}{\sqrt{3}}|300^{(0)}\rangle + \frac{\sqrt{2}}{\sqrt{3}}|320^{(0)}\rangle \\ |4\rangle &= \frac{1}{\sqrt{2}}|311^{(0)}\rangle + \frac{1}{\sqrt{2}}|321^{(0)}\rangle \\ |5\rangle &= \frac{1}{\sqrt{2}}|311^{(0)}\rangle - \frac{1}{\sqrt{2}}|321^{(0)}\rangle \\ |6\rangle &= \frac{1}{\sqrt{2}}|31,-1^{(0)}\rangle + \frac{1}{\sqrt{2}}|32,-1^{(0)}\rangle \\ |7\rangle &= \frac{1}{\sqrt{2}}|31,-1^{(0)}\rangle - \frac{1}{\sqrt{2}}|32,-1^{(0)}\rangle \\ |8\rangle &= |322^{(0)}\rangle \\ |9\rangle &= |32,-2^{(0)}\rangle \end{aligned}$$

The energy level splitting appears as shown:



The dipole moment is $\mathbf{d} = -e\mathbf{r}$. The perturbation is $H' = -\mathbf{d} \cdot \mathbf{E} = -d_z E_z$, so we can get the dipole moment from the energy shift:

$$\langle d_z \rangle = \langle \psi | d_z | \psi \rangle = -\frac{1}{\epsilon} \langle \psi | H' | \psi \rangle = -\frac{E^{(1)}}{\epsilon}$$

Thus we get

$$\begin{aligned}\langle d_z \rangle_{1,8,9} &= 0 \\ \langle d_z \rangle_2 &= -9ea_0 \\ \langle d_z \rangle_3 &= +9ea_0 \\ \langle d_z \rangle_{4,5} &= -9ea_0/2 \\ \langle d_z \rangle_{6,7} &= +9ea_0/2\end{aligned}$$

The lower energy states are aligned with the field, the higher ones are anti-aligned.

10.23 a) For the unperturbed case ($\epsilon = 0$) we have

$$H_0 \doteq V_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 4 \end{pmatrix}$$

with eigenvalues $E_1 = V_0$, $E_2 = V_0$, $E_3 = 4V_0$ and eigenvectors

$$|1\rangle \doteq \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad |2\rangle \doteq \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad |3\rangle \doteq \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

Note that $|1\rangle$ and $|2\rangle$ are degenerate and $|3\rangle$ is nondegenerate.

b) Now look at the perturbation of the nondegenerate $|3\rangle$ state. First we need to write the perturbation Hamiltonian $H' = H - H_0$

$$H' \doteq V_0 \begin{pmatrix} 0 & 2\epsilon & 0 \\ 2\epsilon & 0 & 3\epsilon \\ 0 & 3\epsilon & 0 \end{pmatrix}$$

The first-order energy correction is

$$\begin{aligned} E_n^{(1)} &= \langle n^{(0)} | H' | n^{(0)} \rangle \\ E_3^{(1)} &= \langle 3^{(0)} | H' | 3^{(0)} \rangle = 0 \\ \boxed{E_3^{(1)} = 0} \end{aligned}$$

The second-order energy correction is

$$\begin{aligned} E_3^{(2)} &= \sum_{k \neq 3} \frac{|\langle 3^{(0)} | H' | k^{(0)} \rangle|^2}{E_3^{(0)} - E_k^{(0)}} = \frac{|\langle 3^{(0)} | H' | 1^{(0)} \rangle|^2}{E_3^{(0)} - E_1^{(0)}} + \frac{|\langle 3^{(0)} | H' | 2^{(0)} \rangle|^2}{E_3^{(0)} - E_2^{(0)}} \\ &= \frac{|0|^2}{4V_0 - V_0} + \frac{|3\epsilon V_0|^2}{4V_0 - V_0} = 3\epsilon^2 V_0 \end{aligned}$$

Hence the corrected energy is

$$\begin{aligned} E_3 &= E_3^{(0)} + E_3^{(1)} + E_3^{(2)} = 4V_0 + 0 + 3\epsilon^2 V_0 \\ \boxed{E_3 = V_0 [4 + 3\epsilon^2]} \end{aligned}$$

c) Now look at the perturbation of the degenerate $|1\rangle$ and $|2\rangle$ states. Here we need to diagonalize the perturbation Hamiltonian within that 2x2 space:

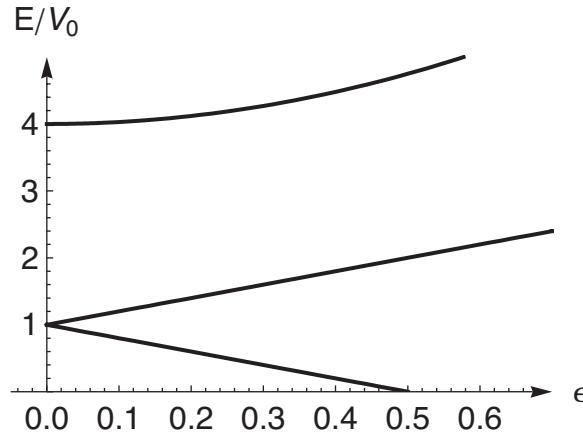
$$H' \doteq V_0 \begin{pmatrix} 0 & 2\epsilon & 0 \\ 2\epsilon & 0 & 3\epsilon \\ 0 & 3\epsilon & 0 \end{pmatrix} \Rightarrow H'_{1,2} \doteq V_0 \begin{pmatrix} 0 & 2\epsilon \\ 2\epsilon & 0 \end{pmatrix}$$

Diagonalizing gives

$$\begin{aligned} \begin{vmatrix} -\lambda & 2\epsilon V_0 \\ 2\epsilon V_0 & -\lambda \end{vmatrix} &= 0 \\ (-\lambda)(-\lambda) - (2\epsilon V_0)^2 &= 0 \\ (\lambda^2 - 4\epsilon^2 V_0^2) &= 0 \\ \lambda &= \pm 2\epsilon V_0 \end{aligned}$$

$$\begin{aligned} \boxed{E_1 = E_1^{(0)} + E_1^{(1)} = V_0 + 2\epsilon V_0 = V_0 (1 + 2\epsilon)} \\ \boxed{E_2 = E_2^{(0)} + E_2^{(1)} = V_0 - 2\epsilon V_0 = V_0 (1 - 2\epsilon)} \end{aligned}$$

- d) The degenerate levels split linearly, while the nondegenerate level has a quadratic dependence and is repelled by the one lower level it is coupled to, as expected.



10.24

$$H \doteq V_0 \begin{pmatrix} 3 & \epsilon & 0 & 0 \\ \epsilon & 3 & 2\epsilon & 0 \\ 0 & 2\epsilon & 5 & \epsilon \\ 0 & 0 & \epsilon & 7 \end{pmatrix}$$

a) For the unperturbed case we have

$$H_0 \doteq V_0 \begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 \\ 0 & 0 & 5 & 0 \\ 0 & 0 & 0 & 7 \end{pmatrix}$$

with eigenvalues $E_1 = 3V_0$, $E_2 = 3V_0$, $E_3 = 5V_0$, $E_4 = 7V_0$ and eigenvectors

$$|1\rangle \doteq \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad |2\rangle \doteq \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad |3\rangle \doteq \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad |4\rangle \doteq \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

Note that $|1\rangle$ and $|2\rangle$ are degenerate and $|3\rangle$ and $|4\rangle$ are nondegenerate.

b) Let's first do nondegenerate perturbation theory for the $|3\rangle$ and $|4\rangle$ states. First we need to write the perturbation Hamiltonian:

$$H' \doteq V_0 \begin{pmatrix} 0 & \epsilon & 0 & 0 \\ \epsilon & 0 & 2\epsilon & 0 \\ 0 & 2\epsilon & 0 & \epsilon \\ 0 & 0 & \epsilon & 0 \end{pmatrix}$$

The first-order corrections are

$$\begin{aligned} E_n^{(1)} &= \langle n^{(0)} | \hat{H}' | n^{(0)} \rangle \\ E_3^{(1)} &= \langle 3^{(0)} | \hat{H}' | 3^{(0)} \rangle = 0 \\ E_4^{(1)} &= \langle 4^{(0)} | \hat{H}' | 4^{(0)} \rangle = 0 \end{aligned}$$

So we need to go to second order for these states

$$\begin{aligned} E_n^{(2)} &= \sum_{k \neq n} \frac{\left| \langle n^{(0)} | \hat{H}' | k^{(0)} \rangle \right|^2}{E_n^{(0)} - E_k^{(0)}} \\ E_3^{(2)} &= \sum_{k \neq n} \frac{\left| \langle 3^{(0)} | \hat{H}' | k^{(0)} \rangle \right|^2}{E_3^{(0)} - E_k^{(0)}} = \frac{\left| \langle 3^{(0)} | \hat{H}' | 1^{(0)} \rangle \right|^2}{E_3^{(0)} - E_1^{(0)}} + \frac{\left| \langle 3^{(0)} | \hat{H}' | 2^{(0)} \rangle \right|^2}{E_3^{(0)} - E_2^{(0)}} + \frac{\left| \langle 3^{(0)} | \hat{H}' | 4^{(0)} \rangle \right|^2}{E_3^{(0)} - E_4^{(0)}} \\ &= \frac{|0|^2}{5V_0 - 3V_0} + \frac{|2\epsilon V_0|^2}{5V_0 - 3V_0} + \frac{|\epsilon V_0|^2}{5V_0 - 7V_0} = \epsilon^2 V_0 \left(\frac{4}{2} + \frac{1}{-2} \right) = \frac{3}{2} \epsilon^2 V_0 \\ E_4^{(2)} &= \sum_{k \neq n} \frac{\left| \langle 4^{(0)} | \hat{H}' | k^{(0)} \rangle \right|^2}{E_4^{(0)} - E_k^{(0)}} = \frac{\left| \langle 4^{(0)} | \hat{H}' | 1^{(0)} \rangle \right|^2}{E_4^{(0)} - E_1^{(0)}} + \frac{\left| \langle 4^{(0)} | \hat{H}' | 2^{(0)} \rangle \right|^2}{E_4^{(0)} - E_2^{(0)}} + \frac{\left| \langle 4^{(0)} | \hat{H}' | 3^{(0)} \rangle \right|^2}{E_4^{(0)} - E_3^{(0)}} \\ &= \frac{|0|^2}{7V_0 - 3V_0} + \frac{|0|^2}{7V_0 - 3V_0} + \frac{|\epsilon V_0|^2}{7V_0 - 5V_0} = \frac{1}{2} \epsilon^2 V_0 \end{aligned}$$

Thus the energies to second order are

$$E_3 = V_0 \left[5 + \frac{3}{2} \epsilon^2 \right]$$

$$E_4 = V_0 \left[7 + \frac{1}{2} \epsilon^2 \right]$$

Now look at the perturbation of the degenerate $|1\rangle$ and $|2\rangle$ states. Here we need to diagonalize the perturbation Hamiltonian within that 2x2 space:

$$H' \doteq V_0 \begin{pmatrix} 0 & \epsilon & 0 & 0 \\ \epsilon & 0 & 2\epsilon & 0 \\ 0 & 2\epsilon & 0 & \epsilon \\ 0 & 0 & \epsilon & 0 \end{pmatrix} \Rightarrow H'_{1,2} \doteq V_0 \begin{pmatrix} 0 & \epsilon \\ \epsilon & 0 \end{pmatrix}$$

Diagonalize this

$$\begin{vmatrix} -\lambda & \varepsilon V_0 \\ \varepsilon V_0 & -\lambda \end{vmatrix} = 0$$

$$\lambda^2 - (\varepsilon V_0)^2 = 0$$

$$\lambda = \pm \varepsilon V_0$$

The corrected energies are

$$\boxed{\begin{aligned} E_1 &= E_1^{(0)} + E_1^{(1)} = 3V_0 + \varepsilon V_0 \\ E_2 &= E_2^{(0)} + E_2^{(1)} = 3V_0 - \varepsilon V_0 \end{aligned}}$$
