1. For this case, the perturbation is $\hat{H}^{(1)} \longrightarrow -\lambda \sin(\pi x/a)$ for $0 < x < a$ and 0 elsewhere. The ground state wavefunction of the unperturbed square well is $\psi_0(x) = \sqrt{2/a}\sin(\pi x/a)$, so the first order energy shift is

$$E_0^{(1)} = \langle\psi_0|\hat{H}^{(1)}|\psi_0\rangle = -\frac{2\lambda}{a}\int_0^a \sin^3(\pi x/a)\mathrm{d}x = -\frac{8\lambda}{3\pi}.$$

(The integral can be done by writing $\sin^3 y = \sin y\,(1-\cos^2 y)$.) The answer is negative as expected since the potential energy is everywhere lower in the perturbed well than in the unperturbed one. In Q4 though, we will see that it is still an over-estimate.

2. In these problems $\hat{H}^{(0)} = \hat{H}(\lambda = 0)$ has only diagonal elements, $E_1^{(0)}$ and $E_2^{(0)}$ (with $E_1^{(0)} = 0$ in (ii)). Since $\hat{H}^{(0)}$ is already diagonal, the (non-degenerate) eigenvectors are $|1^{(0)}\rangle = \binom{1}{0}$ and $|2^{(0)}\rangle = \binom{0}{1}$. Then $\hat{H}^{(1)} = \hat{H} - \hat{H}^{(0)}$ consists of all the λ-dependent terms. The required matrix elements can be read off directly from the matrix form of $\hat{H}^{(1)}$, since it is already given in the basis $\{|1^{(0)}\rangle, |2^{(0)}\rangle\}$:

$$\hat{H}^{(1)} \longrightarrow \begin{pmatrix} \langle 1^{(0)}|\hat{H}^{(1)}|1^{(0)}\rangle & \langle 1^{(0)}|\hat{H}^{(1)}|2^{(0)}\rangle \\ \langle 2^{(0)}|\hat{H}^{(1)}|1^{(0)}\rangle & \langle 2^{(0)}|\hat{H}^{(1)}|2^{(0)}\rangle \end{pmatrix}.$$

The energy shifts to second order are as follows:

$$E_1 = E_1^{(0)} + \langle 1^{(0)}|\hat{H}^{(1)}|1^{(0)}\rangle - \frac{\left|\langle 2^{(0)}|\hat{H}^{(1)}|1^{(0)}\rangle\right|^2}{\Delta}, \qquad E_2 = E_2^{(0)} + \langle 2^{(0)}|\hat{H}^{(1)}|2^{(0)}\rangle + \frac{\left|\langle 2^{(0)}|\hat{H}^{(1)}|1^{(0)}\rangle\right|^2}{\Delta},$$

where $\Delta = E_2^{(0)} - E_1^{(0)}$.

i) In this case, the first-order shifts vanish since $\hat{H}^{(1)}$ has no diagonal elements:

$$\hat{H}^{(1)} \longrightarrow \begin{pmatrix} 0 & \lambda \\ \lambda^* & 0 \end{pmatrix}; \qquad E_1 = E_1^{(0)} + 0 - \frac{|\lambda|^2}{\Delta} + \ldots, \qquad E_2 = E_2^{(0)} + 0 + \frac{|\lambda|^2}{\Delta} + \ldots.$$

For comparison the exact eigenvalues are

$$\tfrac{1}{2}\left(E_2^{(0)} + E_1^{(0)} \mp \sqrt{\Delta^2 + 4|\lambda|^2}\right) = \tfrac{1}{2}(E_2^{(0)} + E_1^{(0)}) \mp \tfrac{1}{2}\Delta\left(1 + \tfrac{1}{2}\tfrac{4|\lambda|^2}{\Delta^2} + \ldots\right).$$

which agrees with the result of perturbation theory.

The first-order shifts in the states are

$$|1^{(1)}\rangle = -\frac{\lambda^*}{\Delta}|2^{(0)}\rangle \Rightarrow |1\rangle \longrightarrow \begin{pmatrix} 1 \\ -\frac{\lambda^*}{\Delta} \end{pmatrix}, \qquad |2^{(1)}\rangle = \frac{\lambda}{\Delta}|1^{(0)}\rangle \Rightarrow |2\rangle \longrightarrow \begin{pmatrix} \frac{\lambda}{\Delta} \\ 1 \end{pmatrix},$$

while the (unnormalised) exact results are

$$|1\rangle \longrightarrow \begin{pmatrix} 1 \\ \frac{-2\lambda^*}{\Delta + \sqrt{4|\lambda|^2 + \Delta^2}} \end{pmatrix}, \qquad |2\rangle \longrightarrow \begin{pmatrix} \frac{2\lambda}{\Delta + \sqrt{4|\lambda|^2 + \Delta^2}} \\ 1 \end{pmatrix}.$$

which match our perturbative results if we drop terms of order $|\lambda|^2$. The error in the normalisation of each state is clearly of order λ^2.

ii) In this case, $E_1^{(0)} = 0$ and so $\Delta = E_2^{(0)}$; the perturbative results are

$$\hat{H}^{(1)} \longrightarrow \begin{pmatrix} 2\lambda & \lambda \\ \lambda & 0 \end{pmatrix}; \qquad E_1 = 2\lambda - \frac{\lambda^2}{\Delta} + \ldots, \qquad E_2 = \Delta + 0 + \frac{\lambda^2}{\Delta} + \ldots,$$

while the exact eigenvalues are

$$\begin{aligned} \tfrac{1}{2}\left(\Delta + 2\lambda \mp \sqrt{\Delta^2 - 4\lambda\Delta + 8\lambda^2}\right) &= \tfrac{1}{2}\Delta + \lambda \mp \tfrac{1}{2}\Delta\left(1 + \tfrac{1}{2}\left(-4\tfrac{\lambda}{\Delta} + 8\left(\tfrac{\lambda}{\Delta}\right)^2\right) - \tfrac{1}{8}\left(-4\tfrac{\lambda}{\Delta}\right)^2 + \ldots\right) \\ &= \tfrac{1}{2}\Delta + \lambda \mp \left(\tfrac{1}{2}\Delta - \lambda + \tfrac{\lambda^2}{\Delta}\ldots\right). \end{aligned}$$

which again agrees with perturbation theory.

3. Here we need to find the eigenvectors of $\hat{H}^{(0)}$ each time before we can apply perturbation theory. In the first case it is trivial (as in the question above) but in the second case it has to be done explicitly. As a result the matrix elements of the perturbation also have to be calculated explicitly in this case and not just "read off".

For $a \gg b$, the eigenstates of $\hat{H}^{(0)} = \hat{H}_0 + \hat{H}_a$ are $|1^{(0)}\rangle = \binom{1}{0}$ and $|2^{(0)}\rangle = \binom{0}{1}$, with energies $E_0 \mp a$. These are not degenerate, so we can use ordinary perturbation theory to find that the first-order energy shifts due to $\hat{H}_b$ are both just b, and the second-order shifts are

$$E_1^{(2)} = -E_2^{(2)} = \frac{|\langle 2^{(0)}|\hat{H}_b|1^{(0)}\rangle|^2}{(E_0 - a) - (E_0 + a)} = -\frac{b^2}{2a} \qquad \Rightarrow \begin{cases} E_1 = E_0 - a + b - \frac{b^2}{2a} + \ldots \\ E_2 = E_0 + a + b + \frac{b^2}{2a} + \ldots. \end{cases}$$

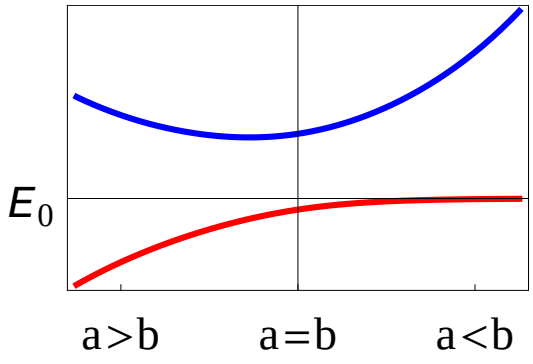
For $a \ll b$, the eigenstates of $\hat{H}^{(0)} = \hat{H}_0 + \hat{H}_b$ are

$$|1^{(0)}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \text{and} \qquad |2^{(0)}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix},$$

with energies E_0 and $E_0 + 2b$. Again these are not degenerate and we can use ordinary perturbation theory. Explicit calculation gives $\langle 1^{(0)}|\hat{H}_a|1^{(0)}\rangle = 0 = \langle 2^{(0)}|\hat{H}_a|2^{(0)}\rangle$, so this time the first-order energy shifts vanish. The second-order shifts are

$$E_1^{(2)} = -E_2^{(2)} = \frac{|\langle 2^{(0)}|\hat{H}_a|1^{(0)}\rangle|^2}{E_0 - (E_0 + 2b)} = -\frac{a^2}{2b} \qquad \Rightarrow \begin{cases} E_1 = E_0 - \frac{a^2}{2b} + \ldots \\ E_2 = E_0 + 2b + \frac{a^2}{2b} + \ldots. \end{cases}$$

The eigenvalues of the full $\hat{H}_0 + \hat{H}_a + \hat{H}_b$ are $E_0 + b \mp \sqrt{a^2 + b^2}$ which when expanded in powers of a/b or b/a give to second order the values found in the two calculations above. The (unnormalised) eigenvectors are $(a + \sqrt{a^2 + b^2}, b)$ and $(-b, a + \sqrt{a^2 + b^2})$ which could also be used to check the first order shifts in the states. The energy eigenvalues are shown below as functions of b.

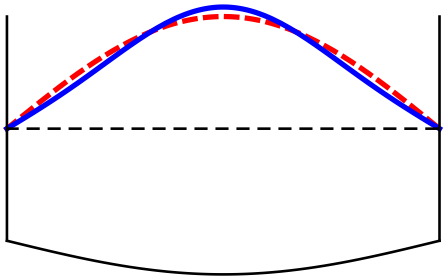


The problem with the perturbative calculations if a and b are around the same size, is that $|E^{(0)}|$, $|E^{(1)}|$ and $|E^{(2)}|$ are all of the same order, and an expansion in a/b or b/a will not converge. In general, even if the unperturbed states are not actually degenerate, if they are close in energy they give rise to small energy denominators which spoil the convergence.

4. Here I switch back to the "traditional" labelling of the states of the infinite square well, $E_m^{(0)} = m^2 E_1^{(0)}$, $|m^{(0)}\rangle \underset{x}{\longrightarrow} \sqrt{\frac{2}{a}} \sin \frac{m\pi}{a}$, with $m = 1, 2, 3, \ldots$. Defining the dimensionless small parameter $\beta \equiv \lambda / E_1^{(0)}$ for the perturbation of Q1, the first-order shift in the ground state is

$$\begin{aligned} |1^{(1)}\rangle &= \sum_{m>1} \frac{\langle m^{(0)}|\hat{H}^{(1)}|1^{(0)}\rangle}{E_1^{(0)} - E_m^{(0)}} |m^{(0)}\rangle \\ &\underset{x}{\longrightarrow} \sum_{m>1} \frac{1}{E_1^{(0)}(1-m^2)} \left(-\lambda \frac{2}{a} \int_0^a \sin \frac{m\pi x'}{a} \sin^2 \frac{\pi x'}{a} \mathrm{d}x' \right) \sqrt{\frac{2}{a}} \sin \frac{m\pi x}{a} \\ &= - \sum_{m=3,5\ldots} \frac{8\beta}{m(m^2-4)(m^2-1)\pi} \sqrt{\frac{2}{a}} \sin \frac{m\pi x}{a}. \end{aligned}$$

Only odd terms appear since, by symmetry about the point $x = a/2$, the integral vanishes for even m. The denominator here grows very rapidly with m, and so the wave function shift will be dominated by the first term, $-\frac{\beta}{15\pi} \sqrt{\frac{2}{a}} \sin \frac{3\pi x}{a}$. Noting that the prefactor is negative, this will tend to cancel the zeroth order wave function at the sides of the box and reinforce it in the middle, thereby increasing the probability of finding the particle in the region where the well is deepest. The picture below is not to scale; the effect on the wave function (blue, solid, where red dashed is unperturbed) is magnified for visibility.



The second-order energy shift calculated with only this term in $|1^{(1)}\rangle$ is

$$E_1^{(2)} = \sum_{m>1} \frac{|\langle m^{(0)}|\hat{H}^{(1)}|1^{(0)}\rangle|^2}{E_1^{(0)} - E_m^{(0)}} = - \sum_{m=3,5\ldots} \frac{E_1^{(0)}}{m^2-1} \left(\frac{8\beta}{m(m^2-4)\pi} \right)^2 \approx -\frac{8E_1^{(0)}\beta^2}{225\pi^2}.$$

The full sum can actually be done, giving

$$E_1^{(2)} = -\frac{(448 - 45\pi^2)E_1^{(0)}\beta^2}{108\pi^2}.$$

The ratio of the full and one-term results is 1.007, so the assumption of dominance of the $\sin \frac{3\pi x}{a}$ correction is very good.

5. The 1D harmonic oscillator has non-degenerate energy levels and so we do not need to worry about degeneracy. On Examples 1 we found that

$$\langle m^{(0)}|\hat{x}|n^{(0)}\rangle = (x_0/\sqrt{2})\langle m^{(0)}|\hat{a}^\dagger + \hat{a}|n^{(0)}\rangle = (x_0/\sqrt{2})(\sqrt{m}\delta_{(n+1),m} + \sqrt{n}\delta_{(n-1),m}).$$

Hence the diagonal matrix elements are zero and there is no first-order shift in the energy. As the off-diagonal matrix elements vanish unless unless $m = n \pm 1$, in which case $E_n^{(0)} - E_m^{(0)} = \mp\hbar\omega$, the sum over all states in the first-order shift in the eigenstates reduces to two terms (and similarly for the second-order shift in the energy):

$$|n^{(1)}\rangle = \sum_{m=n\pm1} \frac{\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}|m^{(0)}\rangle = \frac{x_0\lambda}{\sqrt{2}\hbar\omega}\left(-\sqrt{n+1}|(n+1)^{(0)}\rangle + \sqrt{n}|(n-1)^{(0)}\rangle\right),$$

$$E_n^{(2)} = \sum_{m=n\pm1} \frac{\left|\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}} = -\frac{\lambda^2 x_0^2}{2\hbar\omega} = -\frac{\lambda^2}{2m\omega^2}.$$

For $n = 0$ there is no state $|(n-1)^{(0)}\rangle$, but that doesn't matter as the coefficient is zero; so $E_0^{(2)}$ is as above and

$$|0^{(1)}\rangle = -\frac{x_0\lambda}{\sqrt{2}\hbar\omega}|1^{(0)}\rangle.$$

Exact results may be obtained by "completing the square" to write the potential as $V(x) = \frac{1}{2}m\omega^2x^2 + \lambda x = \frac{1}{2}m\omega^2(x-\delta)^2 - \epsilon$, where $\delta = -\lambda/(m\omega^2)$ and $\epsilon = \lambda^2/(2m\omega^2)$. So all energies are simply lowered by ϵ, and the wave functions are obtained from the unperturbed ones by replacing $x \to x - \delta$. For the ground state,

$$\phi_0(x-\delta) = (\pi x_0^2)^{-1/4}\mathrm{e}^{-(x-\delta)^2/2x_0^2} = \frac{1}{(\pi x_0^2)^{1/4}}\left(1 + \delta\frac{x}{x_0^2} + \ldots\right)\mathrm{e}^{-x^2/2x_0^2} = \phi_0(x) + \frac{\delta}{\sqrt{2}x_0}\phi_1(x) + \ldots.$$

Comparing the perturbative and exact results we see that $E_n^{(2)}$ is in fact $-\epsilon$, the exact energy shift. The first-order state shift also agrees. Obviously there are higher-order state shifts which we have not calculated, but as the exact energy shift is proportional to λ^2 and to no other power of λ, all higher-order energy shifts must vanish.

For the perturbation $\lambda\hat{x}^3$, we need

$$\begin{aligned}\langle m^{(0)}|\hat{x}^3|n^{(0)}\rangle = \frac{x_0^3}{2\sqrt{2}}\big(&\sqrt{m(m-1)(m-2)}\delta_{m,(n+3)} + 3m\sqrt{m}\delta_{m,(n+1)} \\ &+ 3n\sqrt{n}\delta_{m,(n-1)} + \sqrt{n(n-1)(n-2)}\delta_{m,(n-3)}\big).\end{aligned}$$

The shift in the states is

$$\begin{aligned}|n^{(1)}\rangle = \frac{x_0^3\lambda}{2\sqrt{2}\hbar\omega}\Big(&-\tfrac{1}{3}\sqrt{(n+3)(n+2)(n+1)}\,|(n+3)^{(0)}\rangle - 3(n+1)\sqrt{n+1}\,|(n+1)^{(0)}\rangle \\ &+ 3n\sqrt{n}\,|(n-1)^{(0)}\rangle + \tfrac{1}{3}\sqrt{n(n-1)(n-2)}\,|(n-3)^{(0)}\rangle\Big),\end{aligned}$$

and so $|0^{(1)}\rangle = \dfrac{x_0^3\lambda}{2\sqrt{2}\hbar\omega}\Big(-\tfrac{1}{3}\sqrt{6}\,|(3)^{(0)}\rangle - 3\,|(1)^{(0)}\rangle\Big)$.

Also $E_n^{(2)} = -\dfrac{(11 + 30n + 30n^2)\hbar^2\lambda^2}{8m^3\omega^4}$ and so $E_0^{(2)} = -\dfrac{11\hbar^2\lambda^2}{8m^3\omega^4}$.

However small λ is, there will be some value of x for which $\lambda x^3 \geq \frac{1}{2}m\omega^2 x^2$. Hence for highly excited states which probe these values of x, λx^3 cannot be treated as small, and so the perturbation series must break down. In fact the potential goes to $-\infty$ as $x \to -\infty$, which means that highly excited states are not even bound, and the lowest-lying states have a possibility of decaying through tunnelling. If that probability is small enough, though, the perturbative calculation can still be very reliable for low-lying states.

6. In this problem the matrices are again written in the eigenbasis of $\hat{H}^{(0)}$:

$$|1^{(0)}\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \qquad |2^{(0)}\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \qquad |3^{(0)}\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix},$$

and so matrix elements between these states can be "read-off" straightforwardly.

i) Non-degenerate: There are no first-order energy shifts since $\hat{H}^{(1)}$ has no diagonal elements. However all off-diagonal elements are non-zero, and so each state has a first-order shift involving both of the others; to first order in a and b (defining $\Delta_{ij} = E_i^{(0)} - E_j^{(0)}$) we get

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + \frac{b}{\Delta_{12}}\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + \frac{a}{\Delta_{13}}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \; |2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} - \frac{b}{\Delta_{12}}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + \frac{a}{\Delta_{23}}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix},$$
$$|3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} - \frac{a}{\Delta_{13}}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} - \frac{a}{\Delta_{23}}\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}.$$

ii) Degenerate ($E_1^{(0)} = E_2^{(0)}$): Because $\hat{H}^{(1)}$ has a non-vanishing matrix element between the degenerate states in the current basis, we need to choose a new basis. In this 2D space, we need to use as our new zeroth-order states the eigenvectors of the matrix

$$\begin{pmatrix} E_1^{(0)} & b \\ b & E_1^{(0)} \end{pmatrix}.$$

These are $|1'^{(0)}\rangle = \sqrt{\frac{1}{2}}\left(|1^{(0)}\rangle - |2^{(0)}\rangle\right)$ and $|2'^{(0)}\rangle = \sqrt{\frac{1}{2}}\left(|1^{(0)}\rangle + |2^{(0)}\rangle\right)$. (The non-degenerate third state is unaffected: $|3'^{(0)}\rangle = |3^{(0)}\rangle$).

The first-order energy shifts are $E_{n'}^{(1)} = \langle n'^{(0)}|\hat{H}^{(1)}|n'^{(0)}\rangle$, namely $\mp b$ for the first two states and 0 for the third. In the new basis, $\hat{H}^{(1)}$ mixes only the new second state with the third (that is, only $\langle 2'^{(0)}|\hat{H}^{(1)}|3^{(0)}\rangle$ and its complex conjugate are non-zero); we get

$$|1'\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}, \quad |2'\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} - \frac{\sqrt{2}a}{\Delta}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad |3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} + \frac{a}{\Delta}\begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix},$$

where the energy denominator is, strictly, $E_3^{(0)} - E_1^{(0)}$. However at this order we can replace it by $\Delta = E_3^{(0)} - (E_1^{(0)} + b)$ which happens to give a closer match to the exact result discussed below. We can easily see that $|1'^{(0)}\rangle$ is an exact eigenvector of the full Hamiltonian with eigenvalue $E_1^{(0)} - b$.

The other two eigenvalues are $(E_1^{(0)} + b + E_3^{(0)} \pm \sqrt{\Delta^2 + 8a^2})/2$. (Hence we can see immediately that a contributes to the energies only at second order.) The exact (unnormalised) eigenvectors are

$$|2'\rangle = \frac{\Delta + \sqrt{\Delta^2 + 8a^2}}{2\sqrt{2}\Delta} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} - \frac{\sqrt{2}a}{\Delta} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad |3\rangle = \frac{\Delta + \sqrt{\Delta^2 + 8a^2}}{2\Delta} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} + \frac{a}{\Delta} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}.$$

(The overall normalisation is the same in both cases and has been chosen to make clear the relation with the first-order results; it differs from 1 only by terms of order a^2.)

7. The perturbation can be written $\hat{H}^{(1)} = \lambda \hat{x}\hat{y} = \frac{1}{2}\lambda x_0^2 (\hat{a}_x + \hat{a}_x^\dagger)(\hat{a}_y + \hat{a}_y^\dagger)$. For the ground-state $\hat{H}^{(1)}|0,0\rangle = \frac{1}{2}\lambda x_0^2 |1,1\rangle$ and so its first-order energy shift is zero.

There are two states with $E = 2\hbar\omega$, $|1,0\rangle$ and $|0,1\rangle$, and for them

$$\hat{H}^{(1)}|1,0\rangle = \frac{\lambda x_0^2}{2}\left(\sqrt{2}|2,1\rangle + |0,1\rangle\right), \qquad \hat{H}^{(1)}|0,1\rangle = \frac{\lambda x_0^2}{2}\left(\sqrt{2}|1,2\rangle + |1,0\rangle\right).$$

The degenerate states $|1,0\rangle$ and $|0,1\rangle$ are therefore mixed by the perturbation $\hat{H}^{(1)}$, and to find the correct basis we need to diagonalise $\hat{H}^{(1)}$. The matrix representing $\hat{H}^{(1)}$ in this 2D subspace is

$$\begin{pmatrix} \langle 1,0|\hat{H}^{(1)}|1,0\rangle & \langle 1,0|\hat{H}^{(1)}|0,1\rangle \\ \langle 0,1|\hat{H}^{(1)}|1,0\rangle & \langle 0,1|\hat{H}^{(1)}|0,1\rangle \end{pmatrix} = \frac{\hbar\lambda}{2m\omega} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

Its eigenvectors are $\frac{1}{\sqrt{2}}\binom{1}{1}$ and $\frac{1}{\sqrt{2}}\binom{1}{-1}$, so the eigenstates in this subspace are $|A\rangle = \sqrt{\frac{1}{2}}(|1,0\rangle + |0,1\rangle)$ and $|A\rangle = \sqrt{\frac{1}{2}}(|1,0\rangle - |0,1\rangle)$, with eigenvalues $\pm\hbar\lambda/(2m\omega)$. Thus to first order in λ the energies are $\hbar\omega(2 \pm \lambda/(2m\omega^2))$.

The second-order shift in energy of the ground state is

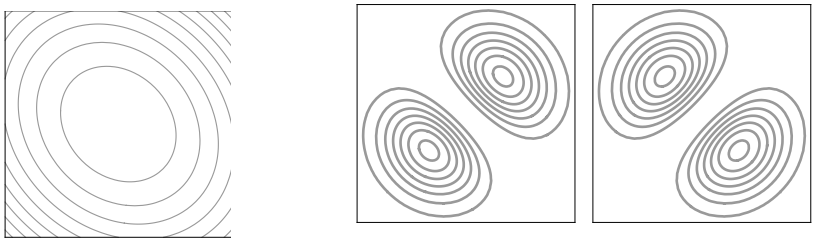
$$E_{0,0}^{(2)} = \sum_{m,n\neq 0} \frac{|\langle m,n|\hat{H}^{(1)}|0,0\rangle|^2}{(-m-n)\hbar\omega} = \frac{|\langle 1,1|\hat{H}^{(1)}|00\rangle|^2}{-2\hbar\omega} = -\tfrac{1}{2}\left(\frac{\lambda}{2m\omega^2}\right)^2 \hbar\omega.$$

The second-order shift in energy of state $|A\rangle$ is

$$\begin{aligned} E_A^{(2)} &= \sum_{m,n} \frac{|\langle m,n|\hat{H}^{(1)}|A\rangle|^2}{(1-m-n)\hbar\omega} \quad \text{where } \{m,n\} \neq \{1,0\},\{0,1\} \\ &= \frac{|\langle 2,1|\hat{H}^{(1)}|A\rangle|^2}{-2\hbar\omega} + \frac{|\langle 1,2|\hat{H}^{(1)}|A\rangle|^2}{-2\hbar\omega} = -\left(\frac{\lambda}{2m\omega^2}\right)^2 \hbar\omega, \end{aligned}$$

and that of state $|B\rangle$ is the same.

In this problem, the perturbation, no matter how small, breaks the rotational symmetry in the $x-y$ plane. The term $\delta V = \lambda xy$ is highest along the line $x = y$ and lowest along $x = -y$. The linear combinations $\sqrt{\frac{1}{2}}(|1,0\rangle \pm |0,1\rangle)$ have probability densities proportional to $(x \pm y)^2 \mathrm{e}^{-r^2/x_0^2}$, and so clearly the first is concentrated in the region where the potential is highest while the second is concentrated where the potential is lowest. Hence these are obviously the best starting points to construct the eigenstates of the perturbed Hamiltonian. Contour plots of the potential (left) and probability densities for the two eigenstates (right) are shown below. (In terms of angles, the probability densities are proportional to $\cos^2(\phi - \frac{\pi}{4})$ and $\sin^2(\phi - \frac{\pi}{4})$.)



In fact, working with rotated coordinates $x' = \sqrt{\frac{1}{2}}(x+y)$ and $y' = \sqrt{\frac{1}{2}}(x-y)$, the perturbation is $\frac{1}{2}\lambda\Big((x')^2 - (y')^2\Big)$ and the full perturbed potential can be written $\frac{1}{2}m\omega_+^2(x')^2 + \frac{1}{2}m\omega_-^2(y')^2$, with $\omega_\pm^2 = \omega^2(1 \pm \lambda/m\omega^2)$, which is elliptical. Hence the exact energies are $(n_{x'} + \frac{1}{2})\hbar\omega_+ + (n_{y'} + \frac{1}{2})\hbar\omega_-$, and the perturbative results can be obtained from expanding this in powers of λ, as in section 4.1.3:

$$E = (n_{x'} + n_{y'} + 1)\hbar\omega + \frac{\lambda}{2m\omega^2}(n_{x'} - n_{y'})\hbar\omega - \tfrac{1}{2}\left(\frac{\lambda}{2m\omega^2}\right)^2 (n_{x'} + n_{y'} + 1)\hbar\omega \ldots$$

8. $^3\mathrm{Li}^{++}$ is a hydrogenic atom with a single electron and a nuclear charge $Z = 3$. In hydrogen, the electromagnetic parameter α enters only as the coefficient of the Coulomb interaction, $V_C = \hbar c\alpha/r$; in lithium this is replaced by $V_C = \hbar c Z\alpha/r$, so all calculations follow through as in the hydrogen case but with $\alpha \to Z\alpha$. The unperturbed energy levels are $-\frac{1}{2}(Z\alpha)^2 m_e c^2/n^2 = -Z^2 E_{\mathrm{Ry}}/n^2$ and the Bohr radius $\hbar/(mcZ\alpha) = a_0/Z$; the fine structure energy shift is

$$E^{(1)}_{nj} = \frac{Z^4\alpha^2 E_{\mathrm{Ry}}}{n^3}\left(\frac{3}{4n} - \frac{2}{2j+1}\right); \qquad E^{(1)}_{4,3/2} = -E_{\mathrm{Ry}}\alpha^2\frac{81\times 5}{1024} = -287\,\mu\mathrm{eV}.$$

Positronium has a Hamiltonian that differs from hydrogen only in the replacement of the electron mass m_e (strictly, the reduced mass of the electron-proton system) by the reduced mas of positronium, $m_e/2$. In the final result for the fine structure of hydrogen, the mass only enters through E_{Ry}, which will be halved in positronium, giving $-\frac{1}{2}E_{\mathrm{Ry}}\alpha^2\frac{5}{1024} = -1.77\,\mu\mathrm{eV}$.

9. Expanding the relativistic energy to order p^4, we get the leading correction to the non-relativistic Hamiltonian:

$$\hat{H}^{(1)} = -\frac{\hat{p}^4}{8m^3c^2},$$

Using $\hat{p}^2 = -\dfrac{\hbar^2}{2x_0^2}\Big(\hat{a}^\dagger\hat{a}^\dagger + \hat{a}\hat{a} - (2\hat{a}^\dagger\hat{a} + 1)\Big)$ we get

$$\begin{aligned}\langle n^{(0)}|p^4|n^{(0)}\rangle &= \frac{\hbar^4}{4x_0^4}\langle n^{(0)}|\Big(\hat{a}^\dagger\hat{a}^\dagger\hat{a}\hat{a} + \hat{a}\hat{a}\hat{a}^\dagger\hat{a}^\dagger + (2\hat{a}^\dagger\hat{a}+1)^2\Big)|n^{(0)}\rangle \\ &= \tfrac{1}{4}(\hbar\omega m)^2\Big(n(n-1) + (n+1)(n+2) + (2n+1)^2\Big) = \tfrac{3}{4}(\hbar\omega m)^2(2n(n+1)+1),\end{aligned}$$

where we have dropped all terms which give zero because the numbers of creation and annihilation operators don't match. Thus $E^{(1)}_n = -\frac{3(\hbar\omega)^2}{32mc^2}(2n(n+1)+1)$. [Using the trick, $p^2 = 2m\Big(\hat{H}^{(0)} - V(x)\Big)$, doesn't simplify things here; for eigenstates of the HO $\langle V\rangle = \frac{1}{2}\langle\hat{H}^{(0)}\rangle$, giving $\langle p^4\rangle = \langle V^2\rangle$ which just leads to the same set of terms as considered above.]

10. The two electrons have orbital angular momenta $l = 0$ and 1, and hence a total of $L = 1$. The spins of the electrons can add to give a total of $S = 0$ or $S = 1$. However the spin-orbit interaction would have no effect on states with $S = 0$ and so these levels presumably have $S = 1$. (Experiments with laser excitations typically do not see $S = 1$ and $S = 0$ states at the same time, as spin-flip interactions are suppressed.) Adding $L = 1$ and $S = 1$ can give $J = 0,\ 1,\ 2$. This agrees with the observed pattern of three levels. The spin-orbit energies of the levels are

$$E_J = \tfrac{1}{2}\mathcal{E}\Big(J(J+1) - L(L+1) - S(S+1)\Big),$$

and so the two splittings are $E_1 - E_0 = \mathcal{E}$, $E_2 - E_1 = 2\mathcal{E}$ and their ratio is 2. Comparing this prediction with the observed value,

$$\frac{E_2 - E_1}{E_1 - E_0} = \frac{0.01313}{0.00647} = 2.03,$$

we see that it agrees to better than 2%.

11. With $j = l \pm \frac{1}{2}$ and the decompositions given in the question, and writing $|j, m_j\rangle$ as a shorthand for $|l, \frac{1}{2}; j, m_j\rangle$,

$$\langle j, m_j|\hat{S}_z|jm_j\rangle = \frac{l + \frac{1}{2} \pm m_j}{2l+1}\tfrac{1}{2}\hbar + \frac{l + \frac{1}{2} \mp m_j}{2l+1}(-\tfrac{1}{2}\hbar) = \pm\frac{\hbar m_j}{2l+1}$$

Also using $\hat{\mathbf{L}} = \hat{\mathbf{J}} - \hat{\mathbf{S}}$ to reexpress the scalar product, we get

$$\frac{\langle j, m_j|\hat{\mathbf{S}}\cdot\hat{\mathbf{J}}|j, m_j\rangle}{\langle j, m_j|\hat{\mathbf{J}}^2|j, m_j\rangle} = \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)},$$

and for $j = l \pm \frac{1}{2}$ this simplifies to $\pm 1/(2l+1)$. Hence the equality is shown.

12. Defiing the total spin as $\hat{\mathbf{S}} = \hat{\mathbf{S}}^{(p)} + \hat{\mathbf{S}}^{(n)}$, we can write

$$\hat{H}^{(0)} = -A\hat{\mathbf{S}}^{(p)}\cdot\hat{\mathbf{S}}^{(n)} = -\tfrac{1}{2}A\Big(\hat{\mathbf{S}}^2 - (\hat{\mathbf{S}}^{(p)})^2 - (\hat{\mathbf{S}}^{(n)})^2\Big) = -\tfrac{1}{2}A\Big(\hat{\mathbf{S}}^2 - \tfrac{3}{2}\hbar^2\Big).$$

The eigenstates of this Hamiltonian are $\{|S, M\rangle\}$, the eigenstates of $\hat{\mathbf{S}}^2$ and $\hat{S}_z$, with quantum numbers S and M, where $S = 1$ or 0: $\{|1,1\rangle, |1,0\rangle, |1,-1\rangle\}$ with energy $-A\hbar^2/4$ and $|0,0\rangle$ with energy $3A\hbar^2/4$.

When we introduce a magnetic field, we have to consider whether the three-fold degeneracy of the spin-1 states will be a problem. It is not, because the operator $\Big(g_p\hat{S}_z^{(p)} + g_n\hat{S}_z^{(n)}\Big)$ has no off-diagonal elements between these three states. We can check this explicitly, or note that for a non-zero result, $\hat{H}^{(1)}$ would need to flip individual spins, which the $S_z^{(i)}$ do not. (We could even invoke the Wigner-Eckart theorem which says that the $m = 0$ element of a vector operator can connect only states with the same M.)

The first-order energy shifts can therefore be calculated directly:

$$\begin{aligned}
E^{(1)}_{1,1} &= \frac{\mu_N B}{\hbar}\langle 1,1|\Big(g_p\hat{S}^{(p)}_z + g_n\hat{S}^{(n)}_z\Big)|1,1\rangle \\
&= \frac{\mu_N B}{\hbar}\Big(\langle+|\otimes\langle+|\Big)\Big(g_p\hat{S}^{(p)}_z + g_n\hat{S}^{(n)}_z\Big)\Big(|+\rangle\otimes|+\rangle\Big) = \tfrac{1}{2}\mu_N B(g_p+g_n), \\
E^{(1)}_{1,0} &= \frac{\mu_N B}{2\hbar}\Big(\langle+|\otimes\langle-|+\langle-|\otimes\langle+|\Big)\Big(g_p\hat{S}^{(p)}_z + g_n\hat{S}^{(n)}_z\Big)\Big(|+\rangle\otimes|-\rangle+|-\rangle\otimes|+\rangle\Big) = 0, \\
E^{(1)}_{1,-1} &= \frac{\mu_N B}{\hbar}\Big(\langle-|\otimes\langle-|\Big)\Big(g_p\hat{S}^{(p)}_z + g_n\hat{S}^{(n)}_z\Big)\Big(|-\rangle\otimes|-\rangle\Big) = -\tfrac{1}{2}\mu_N B(g_p+g_n), \\
E^{(1)}_{0,0} &= \frac{\mu_N B}{2\hbar}\Big(\langle+|\otimes\langle-|-\langle-|\otimes\langle+|\Big)\Big(g_p\hat{S}^{(p)}_z + g_n\hat{S}^{(n)}_z\Big)\Big(|+\rangle\otimes|-\rangle-|-\rangle\otimes|+\rangle\Big) = 0.
\end{aligned}$$

13. For the nucleons $g_s \neq 2$, but the proof goes through as in lectures, except that we first write

$$\hat{\boldsymbol{\mu}} = -(\mu_B/\hbar)(g_l\hat{\mathbf{L}} + g_s\hat{\mathbf{S}}) = g_l\hat{\mathbf{J}} + (g_s - g_l)\hat{\mathbf{S}},$$

where $g_l = 1$ for a proton and 0 for a neutron. Then the Landé g-factor is

$$\begin{aligned}
g &= \left(g_l + (g_s-g_l)\frac{j(j+1)-l(l+1)+s(s+1)}{2j(j+1)}\right) \\
&= \frac{(g_s+g_l)j(j+1)+(g_s-g_l)\Big(s(s+1)-l(l+1)\Big)}{2j(j+1)}.
\end{aligned}$$

To add the noments of two nucleons, we express both $\langle\hat{J}^{(1)}_z\rangle$ and $\langle\hat{J}^{(2)}_z\rangle$ in terms of $\langle\hat{J}_z\rangle$:

$$\langle\hat{J}^{(1)}_z\rangle = \langle\hat{J}_z\rangle\frac{\langle\hat{\mathbf{J}}\cdot\hat{\mathbf{J}}^{(1)}\rangle}{\langle\hat{\mathbf{J}}^2\rangle} = \hbar M\frac{\langle\hat{\mathbf{J}}^2+(\hat{\mathbf{J}}^{(1)})^2-(\hat{\mathbf{J}}^{(2)})^2\rangle}{2\langle\hat{\mathbf{J}}^2\rangle} = \hbar M\frac{J(J+1)+j_1(j_1+1)-j_2(j_2+1)}{2J(J+1)},$$

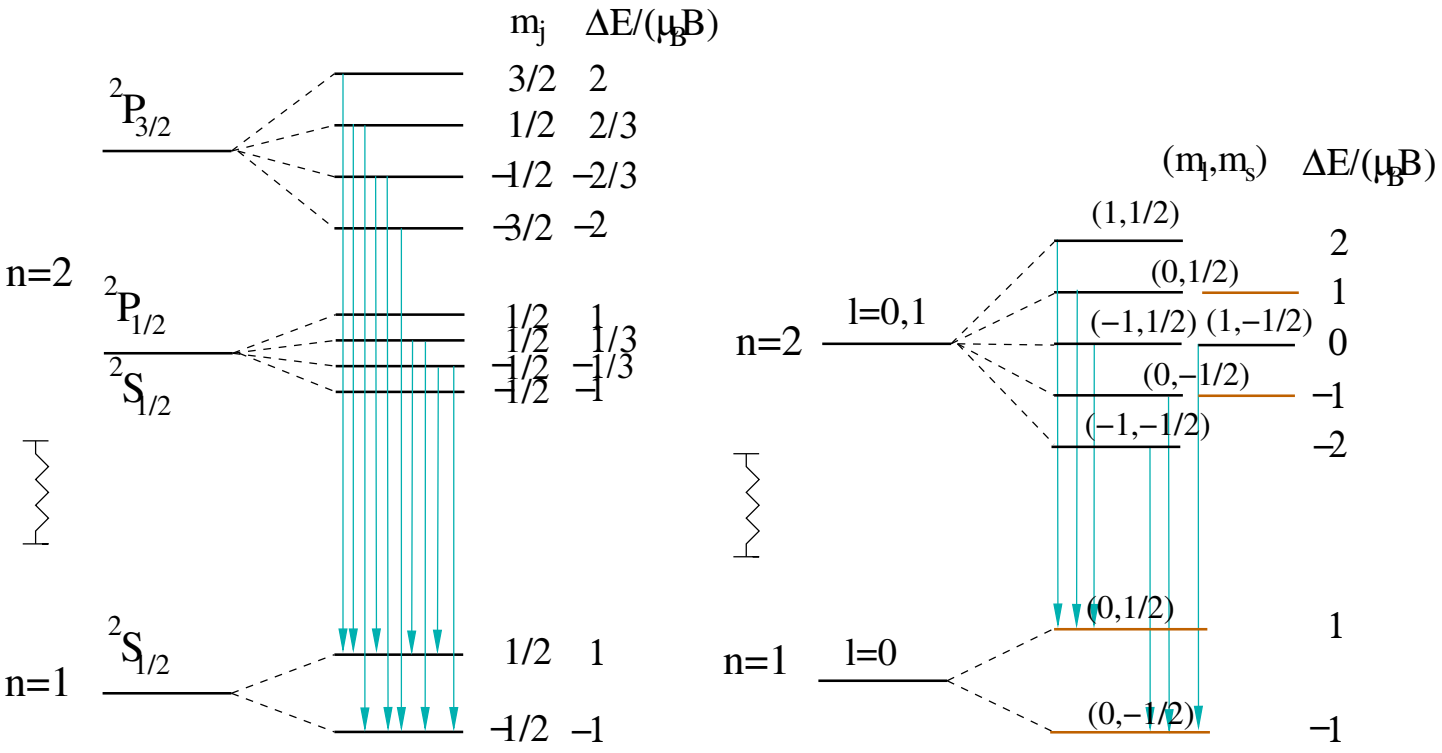
and similarly for $\langle\hat{J}^{(2)}_z\rangle$. Combining these, we get

$$\langle g_1\hat{J}^{(1)}_z + g_2\hat{J}^{(2)}_z\rangle = \hbar M\frac{(g_1+g_2)J(J+1)+(g_1-g_2)\Big(j_1(j_1+1)-j_2(j_2+1)\Big)}{2J(J+1)} \equiv \hbar M g.$$

Note that this is symmetric if we swap both $j_1 \leftrightarrow j_2$ and $g_1 \leftrightarrow g_2$, as it must be!

14. The energy shift for a general state in the weak field limit is $g_{lsj}\mu_B B m_j$. Thus $1s_{1/2}$ and $2s_{1/2}$ states are shifted by $\pm\mu_B B$, the $2p_{1/2}$ states by $\pm\mu_B B/3$ and the $2p_{3/2}$ states by $\pm 2\mu_B B/3$ or $\pm 2\mu_B B$ (depending on m_j). We take $E_{1/2}$ and $E_{3/2}$ to be the $2p \to 1s$ transition energies, including fine-structure splitting but in the absence of the external magnetic field. In the field, the transition energies are, in the order shown in the diagram on the left below:

$$\begin{aligned}
&E_{3/2}+\mu_B B, \quad E_{3/2}-\mu_B B/3, \quad E_{3/2}+5\mu_B B/3, \quad E_{3/2}-5\mu_B B/3, \quad E_{3/2}+\mu_B B/3, \\
&E_{3/2}-\mu_B B, \quad E_{1/2}-2\mu_B B/3, \quad E_{1/2}+4\mu_B B/3, \quad E_{1/2}-4\mu_B B/3, \quad E_{1/2}+2\mu_B B/3
\end{aligned}$$



Note that there are no transitions from the $2s_{1/2}$ states, since they cannot decay via electric dipole transitions.

In the strong-field limit, the fine structure splitting is much smaller than the effect of the external magnetic field, and we can treat states with different values of j, for the same l, as degenerate. The states with different j are mixed by the external field and so the basis $\{|l, \frac{1}{2}; j, m_j\rangle\}$ is not appropriate. Instead we need to work with eigenstates of $\hat{L}_z$ and $\hat{S}_z$: $\{|l, m_l\rangle \otimes |\frac{1}{2}, m_s\rangle\}$.

For these states, the first-order energy shift is $\mu_B B(m_l + 2m_s)$. This again gives $\pm\mu_B B$ for the $l = 0$ states with $m_s = \pm\frac{1}{2}$. For the $l = 1$ states it is $2\mu_B B$ for $(m_l, m_s) = (1, \frac{1}{2})$, $\mu_B B$ for $(m_l, m_s) = (0, \frac{1}{2})$, 0 for $(m_l, m_s) = (1, -\frac{1}{2})$ and $(-1, \frac{1}{2})$, and so on. Purely for completeness, in the diagram on the right above the allowed transitions have been shown. The selection rules are $\Delta l = 1$, $\Delta m_l = -1, 0, 1$, and $\Delta m_s = 0$. The $n = 2$ states with $(m_l, m_s) = (0, \pm\frac{1}{2})$ can have $l = 0$ or 1; those with $l = 0$ are shown in brown, and they cannot decay via an electric dipole transition.

15. We need $3|e|\mathcal{E}a_0 = 1$ meV, so $|e|\mathcal{E} = 0.630$ meV Å^{-1} and $\mathcal{E} = 6.3 \times 10^6$ V m^{-1}. Note that this field (around the breakdown strength of air) is very achievable in the lab, and it gives an energy shift much larger than the neglected fine-structure shifts.
The second-order shift of the ground state can be written $E^{(2)} = (3e\mathcal{E}a_0)^2 a_0/(4\hbar c\alpha)$. Using $\hbar c/a_0 = 1973/0.529$ eV, we get $E^{(2)} = -9.18 \times 10^{-9}$ eV.

16. We start with the four degenerate states with $j = \frac{1}{2}$ ($2s_{1/2}$ and $2p_{1/2}$). Using the notation $|l, \frac{1}{2}; j, m_j\rangle$ and $|l, m_l\rangle \otimes |\frac{1}{2}, m_s\rangle$ we have:

$$
\begin{aligned}
|0, \tfrac{1}{2}; \tfrac{1}{2}, \pm\tfrac{1}{2}\rangle &= |0, 0\rangle \otimes |\tfrac{1}{2}, \pm\tfrac{1}{2}\rangle \\
|1, \tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2}\rangle &= \sqrt{\tfrac{2}{3}}|1, 1\rangle \otimes |\tfrac{1}{2}, -\tfrac{1}{2}\rangle - \sqrt{\tfrac{1}{3}}|1, 0\rangle \otimes |\tfrac{1}{2}, \tfrac{1}{2}\rangle \\
|1, \tfrac{1}{2}; \tfrac{1}{2}, -\tfrac{1}{2}\rangle &= \sqrt{\tfrac{1}{3}}|10\rangle \otimes |\tfrac{1}{2}, -\tfrac{1}{2}\rangle - \sqrt{\tfrac{2}{3}}|1, -1\rangle \otimes |\tfrac{1}{2}, \tfrac{1}{2}\rangle
\end{aligned}
$$

For an external electric field $\mathbf{E} = \mathcal{E}\mathbf{e}_z$, the Hamiltonian is $\hat{H}^{(1)} = |e|\mathcal{E}\hat{z}$. Within this set of states, we see that z mixes only states with the same m_j and different l. Also, as $\hat{H}^{(1)}$ is spin-independent, the matrix elements for the states $|l, \frac{1}{2}; j, m_j\rangle$ reduce to those for the states $|l, m_l\rangle$:

$$
\langle 1, \tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2}|z|0, \tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2}\rangle = -\sqrt{\tfrac{1}{3}}\langle 1, 0|z|0, 0\rangle \qquad\qquad \langle 1, \tfrac{1}{2}; \tfrac{1}{2}, -\tfrac{1}{2}|z|0, \tfrac{1}{2}; \tfrac{1}{2}, -\tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{3}}\langle 1, 0|z|0, 0\rangle
$$

and the other matrix elements (other than the complex conjugates) vanish. The states with different m_j ($\pm\frac{1}{2}$) therefore decouple and we can consider them separately. For each pair with the same m_j the algebra is the same as in lectures except for the overall factor of $\mp\sqrt{\frac{1}{3}}$:

$$
\hat{H}^{(1)} = \pm\sqrt{3}a_0|e|\mathcal{E}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},
$$

with eigenvalues $\mp\sqrt{3}a_0|e|\mathcal{E}$ in both cases. Thus the four degenerate states with $j = \frac{1}{2}$ are split into two degenerate doublets, with a spacing $2\sqrt{3}a_0|e|\mathcal{E}$.

(There are also four degenerate states with $j = \frac{3}{2}$ but these all have $l = 1$, and hence there is no mixing and no first-order Stark effect for them.)

17. We can assume that our system is in a large box, so that even the unbound states are discrete, and then we don't need to distinguish between bound and unbound states. Denoting all states by $|m^{(0)}\rangle$, where the unperturbed ground state is $|0^{(0)}\rangle$, we have

$$
\begin{aligned}
E_0^{(2)} &= \sum_{m\neq 0} \frac{\langle 0^{(0)}|\hat{H}^{(1)}|m^{(0)}\rangle\langle m^{(0)}|\hat{H}^{(1)}|0^{(0)}\rangle}{E_0^{(0)} - E_m^{(0)}} \\
&= \sum_{m\neq 0} \frac{\langle 0^{(0)}|\hat{H}^{(1)}|m^{(0)}\rangle\langle m^{(0)}|[\hat{\Omega}, \hat{H}^{(0)}]|0^{(0)}\rangle}{E_0^{(0)} - E_m^{(0)}} \\
&= \sum_{m\neq 0} \frac{\langle 0^{(0)}|\hat{H}^{(1)}|m^{(0)}\rangle\langle m^{(0)}|(\hat{\Omega}E_0^{(0)} - E_m^{(0)}\hat{\Omega})|0^{(0)}\rangle}{E_0^{(0)} - E_m^{(0)}} \\
&= \sum_{m\neq 0} \langle 0^{(0)}|\hat{H}^{(1)}|m^{(0)}\rangle\langle m^{(0)}|\hat{\Omega}|0^{(0)}\rangle = \langle 0^{(0)}|\hat{H}^{(1)}\Big(\hat{I} - |0^{(0)}\rangle\langle 0^{(0)}|\Big)\hat{\Omega}|0^{(0)}\rangle \\
&= \langle 0^{(0)}|\hat{H}^{(1)}\hat{\Omega}|0^{(0)}\rangle - E_0^{(1)}\langle 0^{(0)}|\hat{\Omega}|0^{(0)}\rangle.
\end{aligned}
$$

In the penultimate line we have used completeness: $\sum_m |m^{(0)}\rangle\langle m^{(0)}| = 1$. For the Stark effect, $E_0^{(1)} = 0$ so the second term in the last line vanishes.

To show that $\hat{\Omega} \longrightarrow (ma_0 q_e \mathcal{E}/\hbar^2)(\frac{1}{2}r^2 + a_0 r)\cos\theta$ works, we need to calculate $[\hat{\Omega}, \hat{H}^{(0)}]|0^{(0)}\rangle$. Clearly $V(r)$ commutes with $\hat{\Omega}$, so we can drop that. In the following we use $\nabla^2 = \nabla_r^2 - \hat{\mathbf{L}}^2/(\hbar^2 r^2)$, define $\omega(r) = (\frac{1}{2}r^2 + a_0 r)$, and drop the subscripts on ψ_{100}:

$$\begin{aligned}
\left[\hat{\Omega}, -\frac{\hbar^2}{2m}\nabla^2\right]\psi &= \tfrac{1}{2}a_0 q_e \mathcal{E}[\nabla_r^2 - \tfrac{1}{\hbar^2 r^2}\hat{\mathbf{L}}^2, \omega(r)\cos\theta]\psi \\
&= \tfrac{1}{2}a_0 q_e \mathcal{E}\left(\cos\theta[\nabla_r^2, \omega(r)] - \frac{\omega(r)}{\hbar^2 r^2}[\hat{\mathbf{L}}^2, \cos\theta]\right)\psi \\
&= \tfrac{1}{2}a_0 q_e \mathcal{E}\cos\theta\Big(\nabla_r^2(\omega\psi) - \omega\nabla_r^2\psi - \tfrac{2}{r^2}\omega\psi\Big) \\
&= \tfrac{1}{2}a_0 q_e \mathcal{E}\cos\theta\Big((\omega'' + \tfrac{2}{r}\omega' - \tfrac{2}{r^2}\omega)\psi + 2\omega'\psi'\Big) \\
&= -q_e \mathcal{E} r\cos\theta\psi = \hat{H}^{(1)}\psi
\end{aligned}$$

In the third line, we used the fact that ψ_{100} is spherically symmetric and $\cos\theta \propto Y_1^0(\theta,\phi)$, and in the last line, $\psi'_{100} = -\psi_{100}/a_0$. Both of these steps work only for this particular hydrogenic wave function, and are not general.

Finally we calculate $\langle 0^{(0)}|\hat{H}^{(1)}\hat{\Omega}|0^{(0)}\rangle$; writing $\omega\cos\theta = z\,\omega/r$, we have

$$\langle 100|z^2(\tfrac{1}{2}r + a_0)|100\rangle = \tfrac{1}{3}\langle 100|r^2(\tfrac{1}{2}r + a_0)|100\rangle = \tfrac{9}{4}a_0^3,$$

and using $a_0 mc^2 = \hbar c/\alpha$, we get

$$E_0^{(2)} = -\frac{9(e\mathcal{E})^2 a_0^3}{4\hbar c\alpha}.$$