Time-Independent Perturbation Theory: Solved Problems

1. Use first-order nondegenerate perturbation theory to compute the first-order corrections to the energies of the bound states of the infinitely deep square well due to a delta function perturbation in the center of the well

$$H_1 = \alpha\ \delta(x\ -\ a/2).$$

(a) To do this problem you must remember how to do integrals with delta functions inside the integral. In this problem, you must integrate the wavefunction squared against a delta function in the center of the well. Note that this problem is formulated so that the well goes from 0 to a. Therefore, the normalized wavefunctions are all sines, namely

$$\psi_n^0(x) = \sqrt{\frac{2}{a}}\ \sin\ \left(\frac{n\pi x}{a}\right),$$

instead of our usual sine and cosine wavefunctions in symmetric wells....

Write down the integral in position space that corresponds to the matrix element that you will need to evaluate, namely $< n \mid H_1 \mid n >$.

(b) Evaluate this integral. Because of the delta function, this integral just becomes equal to α times the value of the wavefunction squared at the position of the delta function. Hence you should find ${E_n}^1 = 0$ if n is even, and ${E_n}^1 = \alpha\ (2/a)$ if n is odd.

(c) Sketch the first three even-n wavefunctions squared in the square well with the delta function potential perturbation. Use your sketch to describe physically why the delta function potential **does not** shift the energy. Remember that the classical electrostatic potential energy density is given by the charge density times the electrostatic potential $\rho(x)V(x)dx$ and that the charge density is given by the square of the wavefunction $\rho(x) = e \mid \psi(x) \mid^2$.

(d) Sketch the first three odd-n wavefunctions squared in the square well with the delta function potential perturbation. Use your sketch to describe physically why the delta function potential **does** shift the energy.

(e) Where would you put the delta function to produce the maximum first-order perturbation theory correction to the energies for the first three even-n states? How does the first-order correction vary as you move the delta function across the well starting at the left hand side (*i.e.,* at $x = 0$) and moving to the right hand side (*i.e.,* to $x = a$). Sketch the behavior of the first-order correction versus the position of the delta function for the $n = 2$ state.

(f) Where would you put a delta function to produce the minimum first-order perturbation theory correction to the energies for the first three odd-n states? How does the first-order correction vary as you move the delta function across the well starting at the left hand side (*i.e.,* at $x = 0$) and moving to the right hand side (*i.e.,* to $x = a$). Sketch the behavior of the first-order correction versus the position of the delta function for the $n = 3$ state.

1.(a) For

$$H_1 = \alpha\delta\left(x - \frac{a}{2}\right) \qquad \text{and} \qquad \psi_n^0(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right),$$

the integral of interest in position space is given by

$$E_n^1 = \,<\!n|H|n\!>\, = \,<\!\psi_n^0(x)|H|\psi_n^0(x)\!>$$
$$= \int_{-\infty}^{\infty}\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)\alpha\delta\left(x - \frac{a}{2}\right)\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)\,dx$$

$$\Rightarrow \quad E_n^1 = \frac{2\alpha}{a}\int_0^a \sin^2\left(\frac{n\pi x}{a}\right)\delta\left(x - \frac{a}{2}\right)\,dx$$

for the well that goes from zero to a.

1.(b) Since the integrand includes a δ function, the integral has the value of the included function at $x = a/2$, since $a/2$ is between the limits of integration, or

$$E_n^1 = \frac{2\alpha}{a}\int_0^a \sin^2\left(\frac{n\pi x}{a}\right)\delta\left(x - \frac{a}{2}\right)\,dx = \frac{2\alpha}{a}\sin^2\left(\frac{n\pi}{a}\frac{a}{2}\right)$$

$$\Rightarrow \quad E_n^1 = \frac{2\alpha}{a}\sin^2\left(\frac{n\pi}{2}\right).$$

Note the $\sin^2$ term will have the value 1 or zero for integer n, *i.e.*,

n	$\sin^2\left(\frac{n\pi}{2}\right)$	E_n^1
1	1	$2\alpha/a$
2	0	0
3	1	$2\alpha/a$
4	0	0
$\vdots$	$\vdots$	$\vdots$

so the possible values of E_n^1 are given by

$$E_n^1 = 0 \quad \text{if } n \text{ is even, and} \quad E_n^1 = \frac{2\alpha}{a} \quad \text{if } n \text{ is odd.}$$

1.(c) Sketches of the first four even n wave functions look like this

The perturbation

$$H_1 = \alpha\delta\left(x - \frac{a}{2}\right)$$

is a δ function in the center of the well, and is also illustrated in the sketches. The unperturbed wave functions for all even n wave functions have the value zero in the center of the well. The effect is $0 \cdot \text{anything} = 0$. The perturbation has nothing to perturb at that location so the entire wave function remains unperturbed. If the wave function is unperturbed, the energies are unperturbed.

Another view is that the δ function acts like a barrier. the wave function may be perturbed as it goes over the barrier, or it can have a node at the barrier. The even n wave functions have a node at the barrier so the perturbation does not occur.

1.(d) Sketches of the first three odd n wave functions look like this

The δ function is in a location where the odd n wave functions are non-zero. If the δ function barrier were infinite, the wave function could not alter itself by going over so would have to adjust by having a zero value at the location of the δ function, *i.e.*, by having a node in the center. For our problem this is not the case, assuming $\alpha < 1$. The wave function is altered by the perturbation to go over the barrier. The effect is to raise the level of the energy by $2\alpha/a$ evenly all along the well. We may then, want to look at higher order corrections since we might expect more effect in the vicinity of the perturbation and less effect away from the perturbation. The first order, linear correction, however, describes a linear response, and the linear response described is the wave function goes over the barrier by raising itself to the top of the barrier and is otherwise unchanged.

1.(e) Since

$$E_n^1(x) = \frac{2\alpha}{a}\sin^2\left(\frac{n\pi}{a}x\right),$$

the maxima will occur at positions where the $\sin^2$ term is a maximum. For even n, or $n = 2, 4, 6, \ldots,$ this means

$$\frac{n\pi}{a}x = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}, \ldots = \frac{k\pi}{2}, \quad k = 1, 3, 5, \ldots, (2n-1)$$

$$\boxed{\Rightarrow \quad x = \frac{ka}{2n}, \quad k = 1, 3, 5, \ldots, (2n-1) \quad \text{for even } n.}$$

A sketch of variation as a function of position for $n = 2$ is simply a sketch of

$$E_n^1(x) = \frac{2\alpha}{a}\sin^2\left(\frac{2\pi}{a}x\right),$$

which looks like this

1.(f) A similar rationale is applied to find the minima for odd n, *i.e.,* $n = 1, 3, 5, \ldots$. The minima will occur at the positions where the sine is zero. This means that

$$\frac{n\pi}{z}x = 0, \pi, 2\pi, 3\pi, \ldots = k\pi, \quad k = 0, 1, 2, 3, \ldots, n$$

$$\boxed{\Rightarrow \quad x = \frac{ka}{n}, \quad k = 0, 1, 2, 3, \ldots, n \quad \text{for odd } n.}$$

A sketch of variation as a function of position for $n = 3$ is a sketch of

$$E_n^1(x) = \frac{2\alpha}{a} \sin^2\left(\frac{3\pi}{a}x\right),$$

which looks like this

The minima occur at both walls, at $a/3$, and at $2a/3$.

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2. First, use second-order nondegenerate perturbation theory to compute the second-order corrections to the energies of the bound states of the infinitely deep square well with a delta function perturbation in the center of the well:

(a) Write down the integral that corresponds to the matrix element $< m \mid H_1 \mid n >$ that you need to evaluate to compute the second-order corrections to the energy E_n^2. Note that this integral now has the form wavefunction-m times the delta function times wavefunction-n and is equal to α times the value of the product of the two wavefunctions at the position of the delta function.

(b) Evaluate this integral. Explain why it is equal to zero unless both m and n are odd, and why it can be positive or negative if both m and n are odd. You should find, that when m and n are both odd, that the value of the integral is $\pm\alpha\ (2/a)$.

(c) Write down the sum of the squares of the matrix element divided by the energy differences. You should find

$$E_n^2 = \sum_{m\ odd}{}' \frac{(2\alpha/a)^2}{E_n^0 - E_m^0}.$$

(d) Carefully remind yourself how to calculate the energy levels of the infinitly deep square well (and write it down on your exam sheets!). Substitute in the quadratic dependence of the unperturbed energies on n and m and mess around with your sum until you get it in the form

$$E_n^2 = 2m \left(\frac{2\alpha}{\pi\hbar}\right)^2 \sum_{m\ odd}{}' \frac{1}{n^2 - m^2}.$$

(e) Sum this series for the first three odd values of n. You may find it helpful to write

$$\frac{1}{n^2 - m^2} = \frac{1}{2n}\left[\frac{1}{n+m} - \frac{1}{m-n}\right].$$

Note that you'll then get sums like

$$\frac{1}{2}\left[\frac{1}{4} + \frac{1}{6} + \frac{1}{8} + \ \ldots\ - \frac{1}{2} - \frac{1}{4} - \frac{1}{6} - \frac{1}{8} - \ \ldots\right] = \frac{1}{2}\,(-\frac{1}{2}) = -\frac{1}{4} \quad \text{for } n = 1$$

and

$$\frac{1}{6}\left[\frac{1}{4} + \frac{1}{8} + \frac{1}{10} + \ \ldots\ + \frac{1}{2} - \frac{1}{2} - \frac{1}{4} - \frac{1}{6} - \frac{1}{8} - \frac{1}{10} - \ \ldots\right] = \frac{1}{6}\,(-\frac{1}{6}) = -\frac{1}{36} \quad \text{for } n = 3.$$

So, the first two are already done....

(f) Use induction to conclude that general result for the sum of the series is given by $-(1/(2n)^2)$.

(g) Put it all together to show that $E_n^2 = 0$ if n is even, and that $E_n^2 = -2m(\alpha/\pi\hbar n)^2$ if n is odd.

Now use second-order nondegenerate perturbation theory to compute the second-order corrections to the energies of the bound states of Problem 6.2, *i.e.,* the one-dimensional harmonic oscillator with a small shift in the spring constant $k' = k + \epsilon k$:

(h) Write down the integral that corresponds to the matrix element $< m \mid H_1 \mid n >$ that you need to evaluate to compute the second-order correction to the energy E_n^2. Note that this integral now has the form of wavefunction-m times x^2 times wavefunction-n. It is equal to the matrix element of the x^2 operator between the unperturbed states of the harmonic oscillator.

(i) **Do not** evaluate all of these integrals!!! It is much easier to use the ladder operator formalism to evaluate the matrix element. Show that the matrix element you need to evaluate is given by

$$< m \mid x^2 \mid n > = < m \mid \ (a^\dagger)^2 + a^\dagger a + a a^\dagger + a^2 \ \mid n > .$$

(j) Evaluate the matrix element by using the properties of the ladder operators. You should find that

$$< m \mid x^2 \mid n > = \left(\frac{\hbar}{2m\omega}\right) \left[\sqrt{(n+1)(n+2)}\ \delta_{m,n+2} \ + \ \sqrt{(n)(n-1)}\ \delta_{m,n-2} \right] .$$

(k) Write down the sum of the squares of the matrix elements divided by the energy differences. You should find

$$E_n^{\ 2} \ = \ \left(\frac{\epsilon\hbar\omega}{4}\right)^2 \sum_m{}' \frac{[\ \sqrt{(n+1)(n+2)}\ \delta_{m,n+2} + \ \sqrt{(n)(n-1)}\ \delta_{m,n-2}]^2}{[(n+\frac{1}{2})\ \hbar\omega \ - \ (m+\frac{1}{2})\ \hbar\omega]} .$$

(l) Use the properties of the Kronecker delta symbols to sum this series. You should find that

$$E_n^2 = \left(\frac{\epsilon^2\hbar\omega}{16}\right) \left[\frac{(n+1)(n+2)}{(n)-(n+2)} \ + \ \frac{(n)(n-1)}{(n)-(n-2)} \right] .$$

(m) Put it all together to show that $E_n^2 = -\frac{1}{8}\ \epsilon^2\ \hbar\omega\ (n+\frac{1}{2})$.

(n) Show that the second-order perturbative correction agrees with the corresponding ϵ^2 term in the exact solution. To find the exact solution start with the expression for the exact energy $E_n = (n+\frac{1}{2})\hbar\omega'$ and the expression for the exact frequency $\omega' = \sqrt{k'/m} = \sqrt{k(1+\epsilon)/m} = \omega\ \sqrt{1+\epsilon}$. Then use the small ϵ expansion of $\sqrt{1+\epsilon}$ to find a power series expansion for the exact energy E_n in terms of powers of ϵ. You should find that the exact energy is given by $E_n = (n+\frac{1}{2})\ \hbar\omega\ \sqrt{1+\epsilon} = (n+\frac{1}{2})\ \hbar\omega\ (1+\frac{1}{2}\epsilon - \frac{1}{8}\epsilon^2 + \frac{1}{16}\epsilon^3 + \ \ldots)$.

2.(a) Using the potential, the wave functions, and the perturbation of Problem 1, we find that the position space integrals are given by

$$<m|H_1|n> = \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right) \alpha\delta\left(x - \frac{a}{2}\right) \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) dx$$

$$\Rightarrow \quad <m|H_1|n> = \frac{2\alpha}{a} \int_0^a \sin\left(\frac{m\pi x}{a}\right) \delta\left(x - \frac{a}{2}\right) \sin\left(\frac{n\pi x}{a}\right) dx.$$

2.(b) This integral can be evaluated by substituting the value of x which makes the argument of the δ function zero for the independent variable x in the integrand so we find

$$<m|H_1|n> = \frac{2\alpha}{a} \sin\left(\frac{m\pi}{2}\right) \sin\left(\frac{n\pi}{2}\right).$$

We can obtain the value for each matrix element by noting that m and n are integers, and so the values of the sines will be either 0 or ± 1. So, we find

m	$\sin\left(\frac{m\pi}{2}\right)$	n	$\sin\left(\frac{n\pi}{2}\right)$
1	1	1	1
2	0	2	0
3	-1	3	-1
4	0	4	0
5	1	5	1
$\vdots$	$\vdots$	$\vdots$	$\vdots$

where the sequences continue indefinitely. So if either m or n are even, the integral is zero. It can be nonzero only if neither m or n are even, or equivalently, only if both m or n are odd. If both m or n are odd, the product of the sine terms is ± 1. The overall product then is

$$<m|H_1|n> = \frac{2\alpha}{a} \sin\left(\frac{m\pi x}{2}\right) \sin\left(\frac{n\pi x}{2}\right) = \frac{2\alpha}{a}(\pm 1)$$

$$\Rightarrow \quad <m|H_1|n> = \pm\frac{2\alpha}{a}$$

2.(c) The sum of the squares of the energy differences are the second order energy corrections. These are given by

$$E_n^2 = \sum_{\substack{m \\ m \neq n}} \frac{\left| <m|H_1|n> \right|^2}{E_n^0 - E_m^0} = \sum_{m \text{ odd}}{}' \frac{\left| \pm 2\alpha/a \right|^2}{E_n^0 - E_m^0}$$

$$\Rightarrow \quad E_n^2 = \sum_{m\ \text{odd}}{}' \frac{\left(2\alpha/a\right)^2}{E_n^0 - E_m^0},$$

where the prime on the last two summations indicates $m \neq n$.

2.(d) The eigenenergies for an infinite square well of width a are given by

$$E_n = n^2 \left(\frac{\pi^2\hbar^2}{2ma^2}\right),$$

where n is the quantum number. Combining this with the result from part (c), we obtain

$$\begin{aligned} E_n^2 &= \sum_{m\ \text{odd}}{}' \frac{\left(2\alpha/a\right)^2}{n^2\left(\frac{\pi^2\hbar^2}{2ma^2}\right) - m^2\left(\frac{\pi^2\hbar^2}{2ma^2}\right)} \\ &= \frac{2ma^2}{\pi^2\hbar^2}\left(\frac{2\alpha}{a}\right)^2 \sum_{m\ \text{odd}}{}' \frac{1}{n^2 - m^2} \end{aligned}$$

$$\Rightarrow \quad E_n^2 = 2m\left(\frac{2\alpha}{\pi\hbar}\right)^2 \sum_{m\ \text{odd}}{}' \frac{1}{n^2 - m^2}.$$

2.(e) Examining just the series, we find

$$\begin{aligned} \sum_{m\ \text{odd}}{}' \frac{1}{n^2 - m^2} &= \sum_{m\ \text{odd}}{}' \frac{-1}{m^2 - n^2} = \sum_{m\ \text{odd}}{}' \frac{1}{2n}\frac{-2n}{m^2 - n^2} \\ &= \frac{1}{2n}\sum_{m\ \text{odd}}{}' \frac{m - 2n - m}{m^2 - n^2} = \frac{1}{2n}\sum_{m\ \text{odd}}{}' \frac{m - n - m - n}{(m+n)(m-n)} \\ &= \frac{1}{2n}\sum_{m\ \text{odd}}{}' \frac{(m-n) - (m+n)}{(m+n)(m-n)} = \frac{1}{2n}\sum_{m\ \text{odd}}{}' \left[\frac{(m-n)}{(m+n)(m-n)} - \frac{(m+n)}{(m+n)(m-n)}\right] \\ &= \frac{1}{2n}\sum_{m\ \text{odd}}{}' \left[\frac{1}{(m+n)} - \frac{1}{(m-n)}\right]. \end{aligned}$$

We are going to sum this series for the first three values of n. The summation index reminds us that m must be odd, but we need to remember that n must also be odd for the second-order correction to be non-zero. This means the first three values of n will be $n = 1, 3, 5$. For $n = 1$, we find

$$\frac{1}{2n}\sum_{m\ \text{odd}}{}' \left[\frac{1}{(m+n)} - \frac{1}{(m-n)}\right] = \frac{1}{2}\left[\cancel{\frac{1}{4}} + \cancel{\frac{1}{6}} + \cancel{\frac{1}{8}} + \cancel{\frac{1}{10}} + \cancel{\frac{1}{12}} + \cdots - \frac{1}{2} - \cancel{\frac{1}{4}} - \cancel{\frac{1}{6}} - \cancel{\frac{1}{8}} - \cancel{\frac{1}{10}} - \cancel{\frac{1}{12}} - \cdots\right]$$

where all the terms except $-1/2$ are struck because there is a corresponding term of equal magnitude and opposite sign. Also notice that the term $+1/2$ is not included, because $n \neq m$ is indicated by the prime on the summation. So, the summation simplifies to

$$\boxed{n = 1 \quad \Rightarrow \quad \frac{1}{2n} \sum_{m \text{ odd}}{}' \left[\frac{1}{(m+n)} - \frac{1}{(m-n)} \right] = \frac{1}{2}\left(-\frac{1}{2}\right) = -\frac{1}{4}.}$$

For $n = 3$, we obtain

$$\frac{1}{2n} \sum_{m \text{ odd}}{}' \left[\frac{1}{(m+n)} - \frac{1}{(m-n)} \right] = \frac{1}{6}\left[\cancel{\frac{1}{4}} + \cancel{\frac{1}{8}} + \cancel{\frac{1}{10}} + \cancel{\frac{1}{12}} + \cdots + \cancel{\frac{1}{2}} - \cancel{\frac{1}{2}} - \cancel{\frac{1}{4}} - \frac{1}{6} - \cancel{\frac{1}{8}} - \cancel{\frac{1}{10}} - \cancel{\frac{1}{12}} - \cdots \right]$$

where the term $+1/6$ is not included because $n \neq m$ and the term $+1/2$ comes from $-1/(m-n)$ for $m = 1$ and $n = 3$. Simplifying this,

$$\boxed{n = 3 \quad \Rightarrow \quad \frac{1}{2n} \sum_{m \text{ odd}}{}' \left[\frac{1}{(m+n)} - \frac{1}{(m-n)} \right] = \frac{1}{6}\left(-\frac{1}{6}\right) = -\frac{1}{36}.}$$

For $n = 5$, we obtain

$$\frac{1}{2n} \sum_{m \text{ odd}}{}' \left[\frac{1}{(m+n)} - \frac{1}{(m-n)} \right]$$
$$= \frac{1}{10}\left[\cancel{\frac{1}{6}} + \cancel{\frac{1}{8}} + \cancel{\frac{1}{12}} + \cancel{\frac{1}{14}} \cdots + \cancel{\frac{1}{4}} + \cancel{\frac{1}{2}} - \cancel{\frac{1}{2}} - \cancel{\frac{1}{4}} - \cancel{\frac{1}{6}} - \cancel{\frac{1}{8}} - \frac{1}{10} - \cancel{\frac{1}{12}} - \cancel{\frac{1}{14}} - \cdots \right]$$

where the term $+1/10$ is not included because $n \neq m$ and two positive terms come from the $-1/(m-n)$ expression. Simplifying this,

$$\boxed{n = 5 \quad \Rightarrow \quad \frac{1}{2n} \sum_{m \text{ odd}}{}' \left[\frac{1}{(m+n)} - \frac{1}{(m-n)} \right] = \frac{1}{10}\left(-\frac{1}{10}\right) = -\frac{1}{100}.}$$

Notice that in all three cases the sum is of the form $-1/(2n)^2$.

2.(f) The series will have the general form $\displaystyle \frac{1}{2n}\sum_{m \text{ odd}}{}' \left[\frac{1}{(m+n)} - \frac{1}{(m-n)}\right]$

$$= \frac{1}{2n}\left[\frac{1}{1+n} + \frac{1}{3+n} + \frac{1}{5+n} + \cdots + \frac{1}{(n-4)+n} + \frac{1}{(n-2)+n} + \frac{1}{(n+2)+n} + \frac{1}{(n+4)+n} + \cdots\right.$$

$$\left. - \frac{1}{1-n} - \frac{1}{3-n} - \frac{1}{5-n} - \cdots - \frac{1}{(n-4)-n} - \frac{1}{(n-2)-n} - \frac{1}{(n+2)-n} - \frac{1}{(n+4)-n} - \cdots\right]$$

where $m = n$ is avoided. Terms from the $1/(m+n)$ expression are on the top line, and terms from the $1/(m-n)$ expression are on the lower line, just so we can keep things organized. Neither expression is fully developed yet. As larger values of m are used, and realizing the value of $2n$ is even and m must be odd, m will have values like $2n-1$ and $2n+1$ in the vicinity of $m = 2n$. Putting these terms into the summation explicitly and simplifying where possible,

$$= \frac{1}{2n}\left[\frac{1}{1+n} + \frac{1}{3+n} + \frac{1}{5+n} + \cdots + \frac{1}{2n-4} + \frac{1}{2n-2} + \frac{1}{2n+2} + \frac{1}{2n+4} + \cdots\right.$$

$$\left. - \frac{1}{1-n} - \frac{1}{3-n} - \frac{1}{5-n} - \cdots - \frac{1}{-4} - \frac{1}{-2} - \frac{1}{2} - \frac{1}{4} - \cdots - \frac{1}{(2n-3)-n} - \frac{1}{(2n-1)-n} - \frac{1}{(2n+1)-n} - \cdots\right]$$

$$= \frac{1}{2n}\left[\frac{1}{1+n} + \frac{1}{3+n} + \frac{1}{5+n} + \cdots + \frac{1}{2n-4} + \frac{1}{2n-2} + \frac{1}{2n+2} + \frac{1}{2n+4} + \cdots\right.$$

$$\left. \left\{ + \frac{1}{n-1} + \frac{1}{n-3} + \frac{1}{n-5} + \cdots + \frac{1}{4} + \frac{1}{2} - \frac{1}{2} - \frac{1}{4} - \cdots - \frac{1}{n-3} - \frac{1}{n-1} \right\} - \frac{1}{n+1} - \frac{1}{n+3} - \cdots\right]$$

where the terms in the curly braces, all from the $1/(m-n)$ expression, sum to zero. Each term has a corresponding term of equal magnitude and opposite sign. As values $m \to 3n$, and $3n$ is always odd, are used explicitly, the summation is

$$= \frac{1}{2n}\left[\frac{1}{1+n} + \frac{1}{3+n} + \frac{1}{5+n} + \cdots + \frac{1}{2n-4} + \frac{1}{2n-2} + \frac{1}{2n+2} + \frac{1}{2n+4} + \cdots\right.$$

$$\left. - \frac{1}{n+1} - \frac{1}{n+3} - \frac{1}{n+5} - \cdots - \frac{1}{(3n-4)-n} - \frac{1}{(3n-2)-n} - \frac{1}{(3n)-n} - \frac{1}{(3n+2)-n} - \frac{1}{(3n+4)-n} - \cdots\right]$$

$$= \frac{1}{2n}\left[\left(\frac{1}{1+n} + \frac{1}{3+n} + \frac{1}{5+n} + \cdots + \frac{1}{2n-4} + \frac{1}{2n-2}\right) + \left\{\frac{1}{2n+2} + \frac{1}{2n+4} + \cdots\right\}\right.$$

$$\left. + \left(-\frac{1}{1+n} - \frac{1}{3+n} - \frac{1}{5+n} - \cdots - \frac{1}{2n-4} - \frac{1}{2n-2}\right) - \frac{1}{2n} + \left\{-\frac{1}{2n+2} - \frac{1}{2n+4} - \cdots\right\}\right]$$

where the two expressions in parenthesis sum to zero term by term, and the two expressions in curly braces also sum to zero term-by-term. The only term left is $-1/2n$, so we obtain

$$\boxed{\frac{1}{2n}\sum_{m \text{ odd}}{}' \left[\frac{1}{(m+n)} - \frac{1}{(m-n)}\right] = \frac{1}{2n}\left[-\frac{1}{2n}\right] = -\frac{1}{(2n)^2}.}$$

2.(g) Combining part f with of part d, we obtain

$$E^2_{n\ \text{odd}} = 2m\left(\frac{2\alpha}{\pi\hbar}\right)^2\left(-\frac{1}{(2n)^2}\right) = -8m\left(\frac{\alpha}{\pi\hbar}\right)^2\left(\frac{1}{4n^2}\right)$$

$$\Rightarrow \quad E^2_n \begin{array}{ccl} = & -2m\left(\frac{\alpha}{\pi\hbar n}\right)^2 & \text{for } n \text{ odd,} \\ = & 0 & \text{for } n \text{ even.} \end{array}$$

2.(h) In the general case, we find

$$E^2_n = \sum_{\substack{m \\ m \neq n}} \frac{\left| <m|H_1|n> \right|^2}{E^0_n - E^0_m}.$$

So for a one dimensional harmonic oscillator with a small shift in in the spring constant $k' = k + \epsilon k$, we find

$$H = H_0 + H_1 \quad \Rightarrow \quad H_1 = \frac{1}{2}\epsilon k x^2 \qquad \text{where} \qquad E_n = \left(n + \frac{1}{2}\right)\hbar\omega,$$

$$\begin{aligned} \Rightarrow \quad E^2_n &= \sum_m{}' \frac{\left| <m|\frac{1}{2}\epsilon k x^2|n> \right|^2}{\left(n+\frac{1}{2}\right)\hbar\omega - \left(m+\frac{1}{2}\right)\hbar\omega} \\ &= \left(\frac{1}{2}\epsilon k\right)^2 \sum_m{}' \frac{\left| <m|x^2|n> \right|^2}{n\hbar\omega + \frac{1}{2}\hbar\omega - m\hbar\omega - \frac{1}{2}\hbar\omega} \\ &= \frac{\epsilon^2 k^2}{4\hbar\omega} \sum_m{}' \frac{\left| <m|x^2|n> \right|^2}{n-m}. \end{aligned} \tag{1}$$

In integral form this is given by

$$E^2_n = \frac{\epsilon^2 k^2}{4\hbar\omega} \sum_m{}' \frac{1}{n-m} \int_{-\infty}^{\infty} \left(\psi^{0*}_m x^2 \psi^0_n\right)^2 \, dx.$$

2.(i) To evaluate the $<m|x^2|n>$ matrix elements, consider

$$X_{\text{op}} = \left(\frac{\hbar}{2m\omega}\right)^{1/2}\left(a + a^\dagger\right)$$

$$\Rightarrow \quad X_{\text{op}}^2 = \left(\frac{\hbar}{2m\omega}\right)^{1/2}\left(a+a^\dagger\right)\left(\frac{\hbar}{2m\omega}\right)^{1/2}\left(a+a^\dagger\right)$$
$$= \frac{\hbar}{2m\omega}\left(a^2 + aa^\dagger + a^\dagger a + a^{\dagger^2}\right)$$
$$\Rightarrow \quad <m|x^2|n> = <m|\frac{\hbar}{2m\omega}\left(a^2 + aa^\dagger + a^\dagger a + a^{\dagger^2}\right)|n> \quad \text{or}$$

$$\boxed{<m|x^2|n> = \frac{\hbar}{2m\omega}<m|a^2 + aa^\dagger + a^\dagger a + a^{\dagger^2}|n>.}$$

2.(j) Remember the ladder operators

$$a|n> = \sqrt{n}|n-1>, \qquad \text{and} \qquad a^\dagger|n> = \sqrt{n+1}|n+1>, \qquad \text{so}$$

$$<m|a^2+aa^\dagger+a^\dagger a+a^{\dagger^2}|n> = <m|a^2|n> + <m|aa^\dagger|n> + <m|a^\dagger a|n> + <m|a^{\dagger^2}|n>$$
$$= <m|a\sqrt{n}|n-1> + <m|a\sqrt{n+1}|n+1> + <m|a^\dagger\sqrt{n}|n-1> + <m|a^\dagger\sqrt{n+1}|n+1>$$
$$= \sqrt{n}<m|a|n-1> + \sqrt{n+1}<m|a|n+1> + \sqrt{n}<m|a^\dagger|n-1> + \sqrt{n+1}<m|a^\dagger|n+1>$$
$$= \sqrt{n}<m|\sqrt{n-1}|n-2> + \sqrt{n+1}<m|\sqrt{n+1}|n> + \sqrt{n}<m|\sqrt{n}|n> + \sqrt{n+1}<m|\sqrt{n+2}|n+2>$$
$$= \sqrt{n}\sqrt{n-1}<m|n-2> + (n+1)<m|n> + n<m|n> + \sqrt{n+1}\sqrt{n+2}<m|n+2>$$
$$= \sqrt{(n)(n-1)}\,\delta_{m,n-2} + (n+1)\,\delta_{m,n} + n\,\delta_{m,n} + \sqrt{(n+1)(n+2)}\,\delta_{m,n+2}.$$

The terms $(n+1)\,\delta_{m,n}$ and $n\,\delta_{m,n}$ will be dropped because $m = n$ is specifically excluded, and that is the only time they would be non zero. So

$$\boxed{<m|x^2|n> = \frac{\hbar}{2m\omega}\left(\sqrt{(n+1)(n+2)}\,\delta_{m,n+2} + \sqrt{(n)(n-1)}\,\delta_{m,n-2}\right).}$$

2.(k) Combining the result of part j with equation (1) of part h, we obtain

$$E_n^2 = \frac{\epsilon^2 k^2}{4\hbar\omega}\sum_m{}' \frac{\left|<m|x^2|n>\right|^2}{n-m}$$

$$= \frac{\epsilon^2 k^2}{4\hbar\omega}\sum_m{}' \frac{\left|\frac{\hbar}{2m\omega}\left(\sqrt{(n+1)(n+2)}\,\delta_{m,n+2} + \sqrt{(n)(n-1)}\,\delta_{m,n-2}\right)\right|^2}{n-m}$$

$$= \frac{\epsilon^2 k^2 \hbar^2}{16m^2\omega^2}\sum_m{}' \frac{\left(\sqrt{(n+1)(n+2)}\,\delta_{m,n+2} + \sqrt{(n)(n-1)}\,\delta_{m,n-2}\right)^2}{n\hbar\omega - m\hbar\omega}.$$

Here the magnitude symbols have been dropped because the numerator is non-negative, given the integer nature of n, the possible values of the Kronecker delta, and the index on the second Kronecker delta which prevents a value of m less than $n = 2$. Remember that

$$\omega = \sqrt{\frac{k}{m}} \qquad \Rightarrow \qquad \frac{k^2}{m^2} = \omega^4,$$

and adding and subtracting $\hbar\omega/2$ in the denominator of the summation, we find

$$\Rightarrow \quad E_n^2 = \frac{\epsilon^2\hbar^2\omega^2}{16} \sum_m{}' \frac{\left(\sqrt{(n+1)(n+2)}\,\delta_{m,n+2} + \sqrt{(n)(n-1)}\,\delta_{m,n-2}\right)^2}{\left(n+\frac{1}{2}\right)\hbar\omega - \left(m+\frac{1}{2}\right)\hbar\omega}$$

$$\Rightarrow \quad E_n^2 = \left(\frac{\epsilon\hbar\omega}{4}\right)^2 \sum_m{}' \frac{\left(\sqrt{(n+1)(n+2)}\,\delta_{m,n+2} + \sqrt{(n)(n-1)}\,\delta_{m,n-2}\right)^2}{\left(n+\frac{1}{2}\right)\hbar\omega - \left(m+\frac{1}{2}\right)\hbar\omega}$$

2.(l) Examining this in the form

$$E_n^2 = \frac{\epsilon^2\hbar^2\omega^2}{16\hbar\omega} \sum_m{}' \frac{\left(\sqrt{(n+1)(n+2)}\,\delta_{m,n+2} + \sqrt{(n)(n-1)}\,\delta_{m,n-2}\right)^2}{n-m},$$

the summation is

$$\sum_m{}' \frac{\left(\sqrt{(n+1)(n+2)}\,\delta_{m,n+2} + \sqrt{(n)(n-1)}\,\delta_{m,n-2}\right)^2}{n-m} = \frac{(n+1)(n+2)}{n-m} = \frac{(n+1)(n+2)}{n-(n+2)}$$

for all $m = n+2$. If $m = n+2$, the second term in the numerator vanishes because $m \neq n-2$. The summation is removed because m is the index of the summation, and for E_n^2, we are addressing a specific value of n. Similarly,

$$\sum_m{}' \frac{\left(\sqrt{(n+1)(n+2)}\,\delta_{m,n+2} + \sqrt{(n)(n-1)}\,\delta_{m,n-2}\right)^2}{n-m} = \frac{(n)(n-1)}{n-m} = \frac{(n)(n-1)}{n-(n-2)}$$

for all $m = n-2$. There will generally be a value of m such that $m = n+2$ and $m = n-2$ for a specific value of n so we need both of the above expressions in E_n^2. Using these sums in the initial expression

$$E_n^2 = \frac{\epsilon^2\hbar\omega}{16}\left[\frac{(n+1)(n+2)}{n-(n+2)} + \frac{(n)(n-1)}{n-(n-2)}\right].$$

2.(m) Simply reducing the above expression, we obtain

$$\begin{aligned}
E_n^2 &= \frac{\epsilon^2\hbar\omega}{16}\left[\frac{n^2+3n+2}{n-n-2}+\frac{n^2-n}{n-n+2}\right]\\
&= \frac{\epsilon^2\hbar\omega}{16}\left[-\frac{n^2+3n+2}{2}+\frac{n^2-n}{2}\right]\\
&= \frac{\epsilon^2\hbar\omega}{16}\left[\frac{-n^2-3n-2+n^2-n}{2}\right]\\
&= \frac{\epsilon^2\hbar\omega}{16}\left[\frac{-4n-2}{2}\right]\\
&= -\frac{\epsilon^2\hbar\omega}{16}\left[2n+1\right]
\end{aligned}$$

$$\boxed{\Rightarrow \quad E_n^2 = -\frac{1}{8}\epsilon^2\hbar\omega\left(n+\frac{1}{2}\right).}$$

2.(n) For the exact solution, remember that

$$V(x)=\frac{1}{2}kx^2 \qquad \text{and} \qquad k'=(1+\epsilon)k \quad \Rightarrow \quad V(x)=\frac{1}{2}(1+\epsilon)kx^2=\frac{1}{2}kx^2+\frac{1}{2}\epsilon kx^2.$$

The altered eigenenergies may be expressed

$$\begin{aligned}
E_n' &= \left(n+\frac{1}{2}\right)\hbar\omega' = \left(n+\frac{1}{2}\right)\hbar\sqrt{\frac{(1+\epsilon)k}{m}}\\
&= \left(n+\frac{1}{2}\right)\hbar\sqrt{\frac{k+\epsilon k}{m}} = \left(n+\frac{1}{2}\right)\hbar\sqrt{\omega^2+\epsilon\omega^2}\\
&= \left(n+\frac{1}{2}\right)\hbar\omega(1+\epsilon)^{1/2}.
\end{aligned}$$

This is exact. Using the binomial series expansion in powers of ϵ, we find

$$\begin{aligned}
E_n' &= \left(n+\frac{1}{2}\right)\hbar\omega\left[1+\frac{1}{2}\epsilon+\frac{\left(\frac{1}{2}\right)\left(-\frac{1}{2}\right)}{2!}\epsilon^2+\frac{\left(\frac{1}{2}\right)\left(-\frac{1}{2}\right)\left(-\frac{3}{2}\right)\epsilon^3}{3!}+\cdots\right]\\
&= \left(n+\frac{1}{2}\right)\hbar\omega\left[1+\frac{1}{2}\epsilon-\frac{1}{8}\epsilon^2+\frac{1}{16}\epsilon^3-\cdots\right]
\end{aligned}$$

This is also exact. We are interested only in the second-order correction, however, which is given by

$$\boxed{E_n^2 = -\frac{1}{8}\epsilon^2\hbar\omega\left(n+\frac{1}{2}\right)}.$$

This is the same result as that obtained in part m.

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3. Two-by-two, three-by-three, and four-by-four problems can always be solved exactly because we can solve all quadratic, cubic, and quartic characteristic equations exactly. The unperturbed Hamiltonian of this cute three-by-three problem has two degenerate eigenvalues and one unique eigenvalue. Consequently, you can use nondegenerate perturbation theory for the perturbations of the unique eigenvalue, but you will need to use degenerate perturbation theory for the perturbations of the two degenerate eigenvalues. One of the main pedagogical intentions of this problem is to teach you how to handle a problem with some degenerate eigenvalues and some unique eigenvalues. You will solve this problem exactly and compare the exact solution in detail with the predictions of nondegenerate and degenerate perturbation theory.

(a) I'm sure you can all find the eigenvalues and eigenvectors of the unperturbed Hamiltonian

$$H_0 = V_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} .$$

However, to define the notation we will use later, you should find the following eigenvectors and eigenvalues for H_0:

$$\vec{ev}_1 = |\, 1 > = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad \text{with} \quad ev_1 = {E_1}^0 = V_0 \,,$$

$$\vec{ev}_2 = |\, 2 > = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \text{with} \quad ev_2 = {E_2}^0 = V_0 \,,$$

$$\vec{ev}_3 = |\, 3 > = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad \text{with} \quad ev_3 = {E_3}^0 = 2\, V_0 \,.$$

(b) Note that the characteristic equation you will extract to find the exact eigenvalues of the full perturbed Hamiltonian $H = H_0 + H_1$ factors into a linear term times a quadratic term. So you can find the eigenvalue corresponding to the linear term by inspection and you can find the two eigenvalues corresponding to the quadratic term by using the quadratic equation. Of course, you could multiply it all out and use the cubic equation, but that would be silly! You should find that the exact eigenvalues are given by $ev_1 = E_1 = V_0(1-\epsilon)$, $ev_2 = E_2 = (V_0/2)\,[\,3 - \sqrt{1+4\epsilon^2}\,]$, and $ev_3 = E_3 = (V_0/2)\,[\,3 + \sqrt{1+4\epsilon^2}\,]$.

(c) Now expand the $\sqrt{1+4\epsilon^2}$ terms to show that $ev_2 = E_2 \simeq V_0(1-\epsilon^2)$, and $ev_3 = E_3 \simeq V_0(2+\epsilon^2)$. Note that the exact energy eigenvalue E_1 has a shift that is linear in ϵ, but that the shifts in the exact energy eigenvalues E_2 and E_3 are both quadratic in ϵ.

(d) The third eigenvalue of the unperturbed Hamiltonian is nondegenerate, so you can use nondegenerate perturbation theory to find the shift in the energy of this state even though the first and second eigenvalues are degenerate and you will need to use degenerate perturbation theory to find the shifts in the first and second eigenvalues!!! Calculate the first-order correction to the unperturbed energy ${E_3}^1 = < 3 \mid H_1 \mid 3 >$. You should find ${E_3}^1 = 0$.

(e) Now calculate the second-order correction to the unperturbed energy

$$ {E_3}^2 \ = \ \sum_m{}' \frac{|< m \mid H_1 \mid 3 >|^2}{{E_3}^0 \ - \ E_m^0} \ . $$

You should find ${E_3}^2 \ = \epsilon^2 \ V_0$. Show that this agrees with the exact calculation.

(f) Now it's time to do the degenerate perturbation theory on the first and second states. Calculate the matrix elements W_{aa}, W_{ab} and W_{bb} that go into the quadratic equation [Griffiths' equation 6.26]. You should find $W_{aa} = < 1 \mid H_1 \mid 1 > = -\epsilon \ V_0$, $W_{ab} = < 1 \mid H_1 \mid 2 > = 0$, and $W_{bb} = < 2 \mid H_1 \mid 2 > = 0$.

(g) Solve the quadratic equation [6.26] to obtain the corresponding first-order corrections to the energy $E_\pm^1$. You should find $E_+^1 \ = \ 0$ and $E_-^1 \ = \ -\epsilon \ V_0$. Show that these perturbative results agree with the exact results to first-order in ϵ. Why does E_-^1 correspond to state $\mid 1 >$ whereas E_+^1 corresponds to state $\mid 2 >$?

3.(a) We are given

$$ H = V_0 \begin{pmatrix} (1-\epsilon) & 0 & 0 \\ 0 & 1 & \epsilon \\ 0 & \epsilon & 2 \end{pmatrix} , $$

so the unperturbed Hamiltonian would be

$$ H_0 = V_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} . $$

This is diagonal, so by inspection the eigenvalues and eigenvectors of this matrix are

$$ |ev_1 = V_0 > = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} , \quad |ev_2 = V_0 > = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} , \quad \text{and} \quad |ev_3 = 2V_0 > = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} . $$

Notice that ev_1 and ev_2 are degenerate.

3.(b) We can obtain the eigenvalues of the perturbed Hamiltonian by solving the characteristic equation, so we have

$$ \det \frac{H}{V_0} = \det \begin{pmatrix} (1-\epsilon)-\omega & 0 & 0 \\ 0 & 1-\omega & \epsilon \\ 0 & \epsilon & 2-\omega \end{pmatrix} = (1-\epsilon-\omega)(1-\omega)(2-\omega) = (1-\epsilon-\omega)(\omega^2-3\omega+2-\epsilon^2) = 0 $$

$$\Rightarrow \quad \omega_1 = 1-\epsilon, \qquad \omega_{2,3} = \frac{3 \pm \sqrt{9-4(1)(2-\epsilon^2)}}{2} = \frac{3}{2} \pm \frac{1}{2}\sqrt{9-8+4\epsilon^2} = \frac{3}{2} \pm \frac{1}{2}\sqrt{1+4\epsilon^2}$$

$$\boxed{\begin{aligned} & ev_1 = V_0(1-\epsilon) \\ \Rightarrow \quad & ev_2 = \frac{V_0}{2}\left(3-\sqrt{1+4\epsilon^2}\right) \\ & ev_2 = \frac{V_0}{2}\left(3+\sqrt{1+4\epsilon^2}\right). \end{aligned}}$$

3.(c) Using the binomial theorem to expand the square root, we find

$$\begin{aligned} ev_2 &= \frac{V_0}{2}\left(3-\left[1+4\epsilon^2\right]^{1/2}\right) \\ &= \frac{V_0}{2}\left(3-\left[1+\frac{4\epsilon^2}{2}+\frac{\frac{1}{2}\left(-\frac{1}{2}\right)\left(4\epsilon^2\right)^2}{2!}+\frac{\frac{1}{2}\left(-\frac{1}{2}\right)\left(-\frac{3}{2}\right)\left(4\epsilon^2\right)^3}{3!}+\cdots\right]\right) \\ &= \frac{V_0}{2}\left(3-\left[1+2\epsilon^2-2\epsilon^4+4\epsilon^6+\cdots\right]\right) \\ &= \frac{V_0}{2}\left(2-2\epsilon^2+2\epsilon^4-4\epsilon^6+\cdots\right) \\ &= V_0\left(1-\epsilon^2+\epsilon^4-2\epsilon^6+\cdots\right). \end{aligned}$$

For $\epsilon \ll 1$ we can treat all terms of powers greater than quadratic as negligible, and so we find

$$\boxed{ev_2 \approx V_0\left(1-\epsilon^2\right).}$$

Treating ev_3 similarly, we find

$$\begin{aligned} ev_3 &= \frac{V_0}{2}\left(3+\left[1+4\epsilon^2\right]^{1/2}\right) \\ &= \frac{V_0}{2}\left(3+\left[1+\frac{4\epsilon^2}{2}+\frac{\frac{1}{2}\left(-\frac{1}{2}\right)\left(4\epsilon^2\right)^2}{2!}+\cdots\right]\right) \\ &= \frac{V_0}{2}\left(3+\left[1+2\epsilon^2-2\epsilon^4+\cdots\right]\right) \\ &= \frac{V_0}{2}\left(4+2\epsilon^2-2\epsilon^4+\cdots\right) \\ &= V_0\left(2+\epsilon^2-\epsilon^4+\cdots\right). \end{aligned}$$

$$\boxed{\Rightarrow \quad ev_3 \approx V_0\left(2+\epsilon^2\right).}$$

3.(d) $H = H_0 + H_1 \quad \Rightarrow \quad H_1 = H - H_0,$

$$\Rightarrow \quad H_1 = V_0 \begin{pmatrix} (1-\epsilon) & 0 & 0 \\ 0 & 1 & \epsilon \\ 0 & \epsilon & 2 \end{pmatrix} - V_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} = V_0 \begin{pmatrix} -\epsilon & 0 & 0 \\ 0 & 0 & \epsilon \\ 0 & \epsilon & 0 \end{pmatrix}.$$

The first-order energy shift for the non-degenerate ev_3 is given by

$$E_3^1 = < ev_3 | H_1 | ev_3 > = \ (0,\ 0,\ 1) V_0 \begin{pmatrix} -\epsilon & 0 & 0 \\ 0 & 0 & \epsilon \\ 0 & \epsilon & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = (0,\ 0,\ 1) \begin{pmatrix} 0 \\ \epsilon \\ 0 \end{pmatrix}$$

$$\boxed{\Rightarrow \quad E_3^1 = 0.}$$

3.(e) The second-order correction for the non-degenerate ev_3 is given by

$$E_3^2 = \sum_m{}' \frac{\left| < ev_m | H_1 | ev_3 > \right|^2}{E_3^0 - E_m^0} = \frac{\left| < ev_1 | H_1 | ev_3 > \right|^2}{E_3^0 - E_1^0} + \frac{\left| < ev_2 | H_1 | ev_3 > \right|^2}{E_3^0 - E_2^0}$$

$$= \frac{\left| (1,\ 0,\ 0) V_0 \begin{pmatrix} -\epsilon & 0 & 0 \\ 0 & 0 & \epsilon \\ 0 & \epsilon & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \right|^2}{2V_0 - V_0} + \frac{\left| (0,\ 1,\ 0) V_0 \begin{pmatrix} -\epsilon & 0 & 0 \\ 0 & 0 & \epsilon \\ 0 & \epsilon & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \right|^2}{2V_0 - V_0}$$

$$= V_0 \left| (1,\ 0,\ 0) \begin{pmatrix} 0 \\ \epsilon \\ 0 \end{pmatrix} \right|^2 + V_0 \left| (0,\ 1,\ 0) \begin{pmatrix} 0 \\ \epsilon \\ 0 \end{pmatrix} \right|^2$$

$$= V_0 (0)^2 + V_0 (\epsilon)^2$$

$$\boxed{\Rightarrow \quad E_3^2 = \epsilon^2 V_0.}$$

From part (c), we find

$$ev_3 = E_3 = E_3^0 + E_3^1 + E_3^2 + \cdots = 2V_0 + \epsilon^2 V_0 - \epsilon^4 V_0 + \cdots = 2V_0 + (0)\epsilon + \epsilon^2 V_0 + (0)\epsilon^3 - \epsilon^4 V_0 + \cdots.$$

If an infinite number of terms are retained, this expansion is exact. Here $E_3^0 = 2V_0$, which is the unperturbed energy and the first term in the expansion. The linear term in the expansion is 0, which is in exact agreement with part (d). Part (e) gives the second-order correction for $\epsilon^2 V_0$, which agrees exactly with the quadratic term of the expansion.

3.(f) The matrix elements for the two-fold degenerate eigenvalues are given by

$$W_{aa} = < ev_1 | H_1 | ev_1 > = \ (1,\ 0,\ 0) V_0 \begin{pmatrix} -\epsilon & 0 & 0 \\ 0 & 0 & \epsilon \\ 0 & \epsilon & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = V_0 (1,\ 0,\ 0) \begin{pmatrix} -\epsilon \\ 0 \\ 0 \end{pmatrix}$$

$$\Rightarrow \quad W_{aa} = -\epsilon V_0.$$

$$W_{ab} = <ev_1|H_1|ev_2> = \ (1,\ 0,\ 0)V_0 \begin{pmatrix} -\epsilon & 0 & 0 \\ 0 & 0 & \epsilon \\ 0 & \epsilon & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = V_0(1,\ 0,\ 0) \begin{pmatrix} 0 \\ 0 \\ \epsilon \end{pmatrix}$$

$$\Rightarrow \quad W_{ab} = 0.$$

$$W_{bb} = <ev_2|H_1|ev_2> = \ (0,\ 1,\ 0)V_0 \begin{pmatrix} -\epsilon & 0 & 0 \\ 0 & 0 & \epsilon \\ 0 & \epsilon & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = V_0(0,\ 1,\ 0) \begin{pmatrix} 0 \\ 0 \\ \epsilon \end{pmatrix}$$

$$\Rightarrow \quad W_{bb} = 0.$$

3.(g) Using these results, we find

$$\begin{aligned} E^1_{\pm} &= \frac{1}{2}\left[W_{aa} + W_{bb} \pm \sqrt{\left(W_{aa} - W_{bb}\right)^2 + 4\left|W_{ab}\right|^2}\right] \\ &= \frac{1}{2}\left[-\epsilon V_0 + 0 \pm \sqrt{\left(-\epsilon V_0 - 0\right)^2 + 4\left|0\right|^2}\right] \\ &= \frac{1}{2}\left[-\epsilon V_0 \pm \epsilon V_0\right] \end{aligned}$$

$$\Rightarrow \quad E^1_+ = 0 \quad \text{and} \quad E^1_- = -\epsilon V_0.$$

In part (b) we found $E_1 = V_0(1-\epsilon) = V_0 - \epsilon V_0$ from the perturbed Hamiltonian. The unperturbed Hamiltonian tells us that $E^0_1 = V_0$. Subtracting this from the eigenenergy of the perturbed Hamiltonian yields $-\epsilon V_0$, which is exactly the result for the perturbative method obtained in part (f). From part (c), the coefficient of the term linear in ϵ of ev_2 is zero, which agrees exactly the result for E^1_+. And from the argument at the end of part (e), the term linear in ϵ is zero which also agrees exactly with the perturbative result from part (d).

We anticipate that $E^1_- = -\epsilon V_0$ corresponds to the energy change in $ev_1 = E_1$ because there is only one perturbation on the diagonal, and that would be in the eigenvector associated with $ev_1 = E_1$. The effect should be lower order, for example linear instead of quadratic or higher order. This is exactly what is seen. Since there is no perturbation on the diagonal for $ev_2 = E_2$, the perturbative effects will be the result of "mixing" and only higher order effects, quadratic and above, are anticipated.

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4. This problem has at least four pedagogical intentions: (1) You must learn to calculate all of the energy levels of the unperturbed levels of the hydrogen atom. (2) You must learn how to use the energies of the levels to calculate the wavelength and the frequency of the light that would be emitted or absorbed in transitions between the levels. (3) You must learn how to calculate the energy corrections to the unperturbed levels due to the fine structure Hamiltonian. (4) You must learn how to make an energy level diagram for hydrogen including the fine structure, and you must understand how to label this diagram with the relevant quantum numbers, namely n and j.

(a) Calculate the energy difference between the $n = 2$ and $n = 3$ unperturbed levels of hydrogen. Convert this energy difference into the corresponding photon wavelength and frequency. You should find ${E_3}^0 - {E_2}^0 = -\frac{5}{36}$ Rydbergs, $\lambda = 655$ nanometers, and $\nu = 4.58 \times 10^{14}$ Hz.

(b) Calculate fine structure splittings of the $n = 2$ state. Recall that for $n = 2$ either $l = 0$ or $l = 1$. So for $n = 2$, we will have either $j = \frac{1}{2}$ or $j = \frac{3}{2}$ and the unperturbed $n = 2$ level splits into two levels. Use equation [6.65] to calculate the fine structure splittings. Note that this equation only depends on n and j. You should find $E^1_{fs}(n = 2\ ,\ j = \frac{1}{2}) = -5.66 \times 10^{-5}$ ev, and $E^1_{fs}(n = 2\ ,\ j = \frac{3}{2}) = -1.13 \times 10^{-5}$ ev.

(c) Calculate fine structure splittings of the $n = 3$ state. Recall that for $n = 3$ either $l = 0$, $l = 1$ or $l = 2$. So for $n = 3$, we will have either $j = \frac{1}{2}$, $j = \frac{3}{2}$, or $j = \frac{5}{2}$ and the unperturbed $n = 3$ level splits into three levels. Again use equation [6.65] to calculate the fine structure splittings. You should find $E^1_{fs}(n = 3\ ,\ j = \frac{1}{2}) = -2.01 \times 10^{-5}$ ev, $E^1_{fs}(n = 3\ ,\ j = \frac{3}{2}) = -6.70 \times 10^{-6}$ ev, and $E^1_{fs}(n = 3\ ,\ j = \frac{5}{2}) = -2.23 \times 10^{-6}$ ev.

(d) Because the upper $n = 3$ level has split into three levels and the lower $n = 2$ level has split into two levels, there are six possible transitions since each upper level can decay into both of the lower levels. To calculate the energies of the photons that will be emitted you need all of the energy differences between the three upper levels and the two lower levels. You need the total energy of the three upper levels and the two lower levels so you better use an equation like [6.66] instead of an equation like [6.65]. You should find

$$\Delta E(n = 3, j = \frac{5}{2} \Rightarrow n = 2, j = \frac{3}{2}) = 9.08 \times 10^{-6} \text{ eV},$$

$$\Delta E(n = 3, j = \frac{3}{2} \Rightarrow n = 2, j = \frac{3}{2}) = 4.61 \times 10^{-6} \text{ eV},$$

$$\Delta E(n = 3, j = \frac{1}{2} \Rightarrow n = 2, j = \frac{3}{2}) = -8.80 \times 10^{-6} \text{ eV},$$

$$\Delta E(n = 3, j = \frac{5}{2} \Rightarrow n = 2, j = \frac{1}{2}) = 54.33 \times 10^{-6} \text{ eV},$$

$$\Delta E(n = 3, j = \frac{3}{2} \Rightarrow n = 2, j = \frac{1}{2}) = 49.86 \times 10^{-6} \text{ eV},$$

$$\Delta E(n = 3, j = \frac{1}{2} \Rightarrow n = 2, j = \frac{1}{2}) = 36.45 \times 10^{-6} \text{ eV}.$$

(e) There are six lines, so there are five frequency spacings between these lines. The frequency spacing $\Delta\nu_{a,b} = (\nu_a - \nu_b) = (\Delta E_a - \Delta E_b)/h$. So you should find the following frequency differences: 3.23, 1.08, 6.60, 3.23, and 1.08 gigahertz. Note that if you mixed the light with a square law detector and measured the difference frequencies, they would all be in the easily measurable microwave range!

4.(a) The energy difference between the $n = 2$ and $n = 3$ unperturbed level of hydrogen are

$$E_3^0 - E_2^0 = 13.6\left(\frac{1}{3^2} - \frac{1}{2^2}\right) = 13.6\left(\frac{1}{9} - \frac{1}{4}\right) = 13.6\left(\frac{4}{36} - \frac{9}{36}\right)$$

$$\boxed{= -\frac{5}{36}(13.6 \text{ eV}) = \frac{5}{36} \text{ Rydberg} = 1.89 \text{ eV}.}$$

In terms of wavelength this is

$$\boxed{h\nu = \frac{hc}{\lambda} \quad \Rightarrow \quad \lambda = \frac{1.24 \times 10^3 \text{ eV} \cdot \text{nm}}{1.89 \text{ eV}} = 656 \text{ nm},}$$

and this corresponds to a frequency of

$$\boxed{\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{656 \times 10^{-9} \text{ m}} = 4.57 \times 10^{14} \text{ Hz}.}$$

4.(b) To calculate fine structure splitting, we use the equation

$$E_{\text{fs}}^1 = \frac{E_n^2}{2mc^2}\left(3 - \frac{4n}{j + 1/2}\right).$$

For $n = 2$, there are two terms to calculate

$$E_{\text{fs}}^1\left(n = 2,\ j = \frac{1}{2}\right) = \frac{\left(13.6 \text{ eV}/2^2\right)^2}{2\left(0.511 \times 10^6 \ \frac{\text{eV}}{\text{c}^2}\right)\text{c}^2}\left(3 - \frac{4 \cdot 2}{\frac{1}{2} + \frac{1}{2}}\right) = \frac{11.56 \text{ eV}}{2\left(0.511 \times 10^6\right)}(3 - 8)$$

$$\boxed{\Rightarrow \quad E_{\text{fs}}^1\left(n = 2,\ j = \frac{1}{2}\right) = -5.66 \times 10^{-5} \text{ eV}.}$$

$$E^1_{\text{fs}}\left(n=2,\ j=\frac{3}{2}\right)=\frac{\left(13.6\text{ eV}/2^2\right)^2}{2\left(0.511\times10^6\ \frac{\text{eV}}{\text{c}^2}\right)\text{c}^2}\left(3-\frac{4\cdot2}{\frac{3}{2}+\frac{1}{2}}\right)=\frac{11.56\text{ eV}}{2\left(0.511\times10^6\right)}(3-4)$$

$$\boxed{\Rightarrow\quad E^1_{\text{fs}}\left(n=2,\ j=\frac{3}{2}\right)=-1.13\times10^{-5}\text{ eV},}$$

4.(c) For the $n=3$ state, there are three terms to calculate

$$E^1_{\text{fs}}\left(n=3,\ j=\frac{1}{2}\right)=\frac{\left(13.6\text{ eV}/3^2\right)^2}{2\left(0.511\times10^6\ \frac{\text{eV}}{\text{c}^2}\right)\text{c}^2}\left(3-\frac{4\cdot3}{\frac{1}{2}+\frac{1}{2}}\right)=\frac{2.283\text{ eV}}{2\left(0.511\times10^6\right)}(3-12)$$

$$\boxed{\Rightarrow\quad E^1_{\text{fs}}\left(n=3,\ j=\frac{1}{2}\right)=-2.01\times10^{-5}\text{ eV},}$$

$$\boxed{E^1_{\text{fs}}\left(n=3,\ j=\frac{3}{2}\right)=2.234\times10^{-6}\left(3-\frac{4\cdot3}{\frac{3}{2}+\frac{1}{2}}\right)\text{ eV}=-6.70\times10^{-6}\text{ eV},}$$

$$\boxed{E^1_{\text{fs}}\left(n=3,\ j=\frac{5}{2}\right)=2.234\times10^{-6}\left(3-\frac{4\cdot3}{\frac{5}{2}+\frac{1}{2}}\right)\text{ eV}=-2.23\times10^{-6}\text{ eV}.}$$

4.(d) There are six possible transitions from $n=3$ to $n=2$. A diagram which illustrates these transitions may be helpful

To calculate the energy shifts due to the fine structure we will use the equation

$$E_{nj} = -\frac{13.6}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right] \text{ eV} \quad \text{where} \quad \alpha = \frac{1}{137.036} \quad \text{and} \quad \Delta E = E_{3j_i} - E_3 - (E_{3j_k} - E_2)\,.$$

Here E_3 and E_2 are the unperturbed energies. We can get an equivalent expression by excluding the 1 to the immediate right of the left square bracket. This general expression can be simplified since we are examining the $n = 3$ to $n = 2$ transitions.

$$\Delta E = \left[-\frac{13.6}{3^2} - \frac{13.6\alpha^2}{3^2 \cdot 3^2}\left(\frac{3}{j_i+\frac{1}{2}} - \frac{3}{4}\right)\right] + \frac{13.6}{3^2} + \left[\frac{13.6}{2^2} + \frac{13.6\alpha^2}{2^2 \cdot 2^2}\left(\frac{2}{j_k+\frac{1}{2}} - \frac{3}{4}\right)\right] - \frac{13.6}{2^2}$$

$$= -\left(8.94 \times 10^{-6}\right)\left(\frac{3}{j_i+\frac{1}{2}} - \frac{3}{4}\right) + \left(4.53 \times 10^{-5}\right)\left(\frac{2}{j_k+\frac{1}{2}} - \frac{3}{4}\right) \text{ in eV.}$$

$$\Delta E\left(n=3,\ j=\frac{5}{2} \;\rightarrow\; n=2, j=\frac{3}{2}\right) = -\left(8.94 \times 10^{-6}\right)\left(\frac{3}{\frac{5}{2}+\frac{1}{2}} - \frac{3}{4}\right) + \left(4.53 \times 10^{-5}\right)\left(\frac{2}{\frac{3}{2}+\frac{1}{2}} - \frac{3}{4}\right)$$

$$\boxed{\Rightarrow \quad \Delta E\left(n=3,\ j=\frac{5}{2} \;\rightarrow\; n=2, j=\frac{3}{2}\right) = 9.09 \times 10^{-6} \text{ eV.}}$$

$$\Delta E\left(n=3,\ j=\frac{3}{2} \;\rightarrow\; n=2, j=\frac{3}{2}\right) = -\left(8.94 \times 10^{-6}\right)\left(\frac{3}{\frac{3}{2}+\frac{1}{2}} - \frac{3}{4}\right) + \left(4.53 \times 10^{-5}\right)\left(\frac{2}{\frac{3}{2}+\frac{1}{2}} - \frac{3}{4}\right)$$

$$\boxed{\Rightarrow \quad \Delta E\left(n=3,\ j=\frac{3}{2} \;\rightarrow\; n=2, j=\frac{3}{2}\right) = 4.61 \times 10^{-6} \text{ eV.}}$$

$$\Delta E\left(n=3,\ j=\frac{1}{2} \;\rightarrow\; n=2, j=\frac{3}{2}\right) = -\left(8.94 \times 10^{-6}\right)\left(\frac{1}{\frac{5}{2}+\frac{1}{2}} - \frac{3}{4}\right) + \left(4.53 \times 10^{-5}\right)\left(\frac{2}{\frac{3}{2}+\frac{1}{2}} - \frac{3}{4}\right)$$

$$\boxed{\Rightarrow \quad \Delta E\left(n=3,\ j=\frac{1}{2} \;\rightarrow\; n=2, j=\frac{3}{2}\right) = -8.79 \times 10^{-6} \text{ eV.}}$$

$$\Delta E\left(n=3,\ j=\frac{5}{2} \;\rightarrow\; n=2, j=\frac{1}{2}\right) = -\left(8.94 \times 10^{-6}\right)\left(\frac{3}{\frac{5}{2}+\frac{1}{2}} - \frac{3}{4}\right) + \left(4.53 \times 10^{-5}\right)\left(\frac{2}{\frac{1}{2}+\frac{1}{2}} - \frac{3}{4}\right)$$

$$\boxed{\Rightarrow \quad \Delta E\left(n=3,\ j=\frac{5}{2} \;\rightarrow\; n=2, j=\frac{1}{2}\right) = 5.43 \times 10^{-5} \text{ eV.}}$$

$$\Delta E\left(n=3,\ j=\frac{3}{2} \;\rightarrow\; n=2, j=\frac{1}{2}\right) = -\left(8.94 \times 10^{-6}\right)\left(\frac{3}{\frac{3}{2}+\frac{1}{2}} - \frac{3}{4}\right) + \left(4.53 \times 10^{-5}\right)\left(\frac{2}{\frac{1}{2}+\frac{1}{2}} - \frac{3}{4}\right)$$

$$\Rightarrow \quad \Delta E\left(n=3,\ j=\frac{3}{2}\ \rightarrow\ n=2, j=\frac{1}{2}\right) = 4.99\times 10^{-5}\ \text{eV}.$$

$$\Delta E\left(n=3,\ j=\frac{1}{2}\ \rightarrow\ n=2, j=\frac{1}{2}\right) = -\left(8.94\times 10^{-6}\right)\left(\frac{3}{\frac{1}{2}+\frac{1}{2}}-\frac{3}{4}\right)+\left(4.53\times 10^{-5}\right)\left(\frac{2}{\frac{1}{2}+\frac{1}{2}}-\frac{3}{4}\right)$$

$$\Rightarrow \quad \Delta E\left(n=3,\ j=\frac{1}{2}\ \rightarrow\ n=2, j=\frac{1}{2}\right) = 3.65\times 10^{-5}\ \text{eV}.$$

4.(e) The corresponding frequencies are given by

$$\Delta\nu_{a,b} = \nu_a - \nu_b = \frac{\Delta E_a - \Delta E_b}{h} \quad \text{where} \quad h = 4.14\times 10^{-15}\ \text{eV}\cdot\text{s}.$$

$$\frac{\Delta E\left(n=3,\ j=\frac{5}{2}\ \rightarrow\ n=2,\ j=\frac{3}{2}\right) - \Delta E\left(n=3,\ j=\frac{3}{2}\ \rightarrow\ n=2,\ j=\frac{3}{2}\right)}{h} = 1.08\times 10^{9}\ \text{Hz}$$

$$\frac{\Delta E\left(n=3,\ j=\frac{3}{2}\ \rightarrow\ n=2,\ j=\frac{3}{2}\right) - \Delta E\left(n=3,\ j=\frac{1}{2}\ \rightarrow\ n=2,\ j=\frac{3}{2}\right)}{h} = 3.24\times 10^{9}\ \text{Hz}$$

$$\frac{\Delta E\left(n=3,\ j=\frac{5}{2}\ \rightarrow\ n=2,\ j=\frac{1}{2}\right) - \Delta E\left(n=3,\ j=\frac{3}{2}\ \rightarrow\ n=2,\ j=\frac{1}{2}\right)}{h} = 1.08\times 10^{9}\ \text{Hz}$$

$$\frac{\Delta E\left(n=3,\ j=\frac{3}{2}\ \rightarrow\ n=2,\ j=\frac{1}{2}\right) - \Delta E\left(n=3,\ j=\frac{1}{2}\ \rightarrow\ n=2,\ j=\frac{1}{2}\right)}{h} = 3.24\times 10^{9}\ \text{Hz}$$

$$\frac{\Delta E\left(n=3,\ j=\frac{1}{2}\ \rightarrow\ n=2,\ j=\frac{1}{2}\right) - \Delta E\left(n=3,\ j=\frac{5}{2}\ \rightarrow\ n=2,\ j=\frac{3}{2}\right)}{h} = 6.61\times 10^{9}\ \text{Hz}$$

5. The Zeeman splitting of the energy levels due to an applied magnetic field is extremely important! Static magnetic fields are one of the best tools we have for controlling the level splitting of a great variety of systems... In this problem, you will calculate the Zeeman splitting for the $n = 2$ level of hydrogen. We learned that the unperturbed $n = 2$ level of hydrogen is split into two j levels by the fine structure Hamiltonian. These two fine structure levels have $j = \frac{1}{2}$ and $j = \frac{3}{2}$. Each of these two j levels is still four-fold degenerate. The magnetic Zeeman splitting will remove all of the degeneracy. So what are these final eight states, and how do they split in an applied magnetic field?

(a) Write down the eight states $| \, n, l, j, m_j >$. For $n = 2$, recall that either $l = 0$ (and then $j = \frac{1}{2}$) or $l = 1$ (and then either $j = \frac{1}{2}$ or $j = \frac{3}{2}$). Therefore you should find three kinds of states: the first group has two states with $| \, 2, 0, \frac{1}{2}, ? >$, the second group has two states with $| \, 2, 1, \frac{1}{2}, ? >$, and the third group has four states with $| \, 2, 1, \frac{3}{2}, ? >$.

(b) The Zeeman splitting calculated using first-order perturbation theory $E^1_{zee} = \mu_B g_J m_j B_{ext}$ depends on m_j and on the Lande g-factor g_J. Within the three groups of states noted above, the Lande g-factor is the same for all of the states within the group. Calculate these three Lande g-factors. You should find g_J (group 1) = 2, g_J (group 2) = $\frac{2}{3}$, and g_J (group 3) = $\frac{4}{3}$.

(c) Before you calculate the field dependent splitting, you should calculate the zero-field splitting of the states due to the fine structure Hamiltonian. Note that all of the states in the first two groups have the same fine structure correction relative to the unperturbed $n = 2$ state because they all have the same value of j, namely $j = \frac{1}{2}$ and the fine structure shift only depends on j (of course, it also depends on n, but all the states we are considering have $n = 2$). So the first two groups combine to form the upper four $j = \frac{1}{2}$ states, and the third group contains all of the states in the lower four $j = \frac{3}{2}$ states. Calculate the fine structure shifts for the upper four and for the lower four states. You should find $E^1_{fs}(\text{upper}) = \frac{1}{4} \left[1 + \frac{5}{16} \alpha^2 \right]$ Rydbergs, and $E^1_{fs}(\text{lower}) = \frac{1}{4} \left[1 + \frac{1}{16} \alpha^2 \right]$ Rydbergs.

(d) Note that the magnetic field dependence of the Zeeman splitting is linear in the field and that the slope is set by the coefficient $(g_J m_j \mu_B)$. Since the Bohr magneton μ_B is the same for all the states, the slopes are controlled by the coefficient $(g_J m_j)$. Work out these coefficients and use them to make a plot of the Zeeman splitting versus applied magnetic field of the four upper levels and of the four lower levels. Also show the initial zero field fine structure splitting.

(e) Finally, write down the energy of these eight levels versus the applied magnetic field. For the upper group, you should find

$$E(\,2\,,\,0\,,\,\frac{1}{2}\,,\,\frac{1}{2}\,) = -3.4 \text{ eV } (1 + \frac{5}{16}\alpha^2) \;+\; \mu_B \, B_{ext}\,,$$

$$E(\,2\,,\,0\,,\,\frac{1}{2}\,,\,-\frac{1}{2}\,) = -3.4 \text{ eV } (1 + \frac{5}{16}\alpha^2) \;-\; \mu_B \, B_{ext}\,,$$

$$E(\,2\,,\,1\,,\,\frac{1}{2}\,,\,\frac{1}{2}\,) = -3.4 \text{ eV } (1 + \frac{5}{16}\alpha^2) \;+\; \frac{1}{3}\,\mu_B \, B_{ext}\,,$$

$$E(\,2\,,\,1\,,\,\frac{1}{2}\,,\,-\frac{1}{2}\,) = -3.4 \text{ eV } (1+\frac{5}{16}\alpha^2) \;-\; \frac{1}{3}\,\mu_B\,B_{ext}.$$

For the lower group you should find

$$E(\,2\,,\,1\,,\,\frac{3}{2}\,,\,\frac{3}{2}\,) = -3.4 \text{ eV } (1+\frac{1}{16}\alpha^2) \;+\; 2\,\mu_B\,B_{ext}\,,$$

$$E(\,2\,,\,1\,,\,\frac{3}{2}\,,\,-\frac{3}{2}\,) = -3.4 \text{ eV } (1+\frac{1}{16}\alpha^2) \;-\; 2\,\mu_B\,B_{ext}\,,$$

$$E(\,2\,,\,1\,,\,\frac{3}{2}\,,\,\frac{1}{2}\,) = -3.4 \text{ eV } (1+\frac{1}{16}\alpha^2) \;+\; \frac{2}{3}\,\mu_B\,B_{ext}\,,$$

$$E(\,2\,,\,1\,,\,\frac{3}{2}\,,\,-\frac{1}{2}\,) = -3.4 \text{ eV } (1+\frac{1}{16}\alpha^2) \;-\; \frac{2}{3}\,\mu_B\,B_{ext}\,.$$

5.(a) The eight states for $n = 2$ in $|n,\ l,\ j,\ m_j>$ format are

$\|2,\ 0,\ 1/2,\ 1/2>$,	$\|2,\ 0,\ 1/2,\ -1/2>$	group 1
$\|2,\ 1,\ 1/2,\ 1/2>$,	$\|2,\ 1,\ 1/2,\ -1/2>$	group 2
$\|2,\ 1,\ 3/2,\ 3/2>$,	$\|2,\ 1,\ 3/2,\ -3/2>$	group 3
$\|2,\ 1,\ 3/2,\ 1/2>$,	$\|2,\ 1,\ 3/2,\ -1/2>$	group 3

where the eight states are divided into three groups. Each group will have a different Lande g-factor which will be calculated in part (b).

5.(b) We calculate the Lande g-factor using the equation

$$|n,\ l,\ j> \;\;\Rightarrow\;\; g_j = 1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)}.$$

Since this equation does not depend on m_j, we can use the first three quantum numbers to specify the state—in fact, we could use just the middle two. The three groups in part (a) are the states with the same l and j values. For group 1, we find

$$|2,\ 0,\ 1/2> \;\;\Rightarrow\;\; g_j = 1 + \frac{\frac{1}{2}\left(\frac{1}{2}+1\right) - 0(0+1) + \frac{3}{4}}{2\left(\frac{1}{2}\right)\left(\frac{1}{2}+1\right)} = 1 + \frac{\frac{3}{4}+\frac{3}{4}}{3/2} = 1 + \frac{3/2}{3/2}$$

$$\boxed{|2,\ 0,\ 1/2> \ \Rightarrow \quad g_j = 2.}$$

For group 2, we find

$$|2,\ 1,\ 1/2> \ \Rightarrow \quad g_j = 1 + \frac{\frac{1}{2}\left(\frac{1}{2}+1\right) - 1(1+1) + \frac{3}{4}}{2\left(\frac{1}{2}\right)\left(\frac{1}{2}+1\right)} = 1 + \frac{\frac{3}{4} - 2 + \frac{3}{4}}{3/2} = 1 - \frac{1/2}{3/2}$$

$$\boxed{|2,\ 1,\ 1/2> \ \Rightarrow \quad g_j = \frac{2}{3}.}$$

For group 3, we find

$$|2,\ 1,\ 3/2> \ \Rightarrow \quad g_j = 1 + \frac{\frac{3}{2}\left(\frac{3}{2}+1\right) - 1(1+1) + \frac{3}{4}}{2\left(\frac{3}{2}\right)\left(\frac{3}{2}+1\right)} = 1 + \frac{\frac{15}{4} - 2 + \frac{3}{4}}{15/2} = 1 + \frac{10/4}{15/2}$$

$$\boxed{|2,\ 1,\ 1/2> \ \Rightarrow \quad g_j = \frac{4}{3}.}$$

5.(c) The zero-field splitting can be calculated using the equation

$$E_{nj} = \frac{\text{Ry}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right]$$

For $n = 2$ and $j = 1/2$, we find

$$E_{2,\,1/2} = \frac{\text{Ry}}{4}\left[1 + \frac{\alpha^2}{4}\left(\frac{2}{1/2+1/2} - \frac{3}{4}\right)\right] = \frac{\text{Ry}}{4}\left[1 + \frac{\alpha^2}{4}\left(2 - \frac{3}{4}\right)\right]$$

$$\boxed{\Rightarrow \quad E^1_{fs}(\text{upper}) = E_{2,\,1/2} = \frac{1}{4}\left[1 + \frac{5\alpha^2}{16}\right]\text{Ry}}$$

For $n = 2$ and $j = 3/2$, we find

$$E_{2,\,3/2} = \frac{\text{Ry}}{4}\left[1 + \frac{\alpha^2}{4}\left(\frac{2}{3/2+1/2} - \frac{3}{4}\right)\right] = \frac{\text{Ry}}{4}\left[1 + \frac{\alpha^2}{4}\left(1 - \frac{3}{4}\right)\right]$$

$$\Rightarrow \quad E^1_{fs}(\text{lower}) = E_{2,\,3/2} = \frac{1}{4}\left[1 + \frac{\alpha^2}{16}\right] \text{Ry}$$

5.(d) Note that the product $g_j m_j$ is different for each of the eight states. Using the values of g_j from part (b), we find

$$|2,\ 0,\ 1/2,\ 1/2> \ \Rightarrow \ g_j m_j = 2\left(\frac{1}{2}\right) = 1$$

$$|2,\ 0,\ 1/2,\ -1/2> \ \Rightarrow \ g_j m_j = 2\left(-\frac{1}{2}\right) = -1$$

$$|2,\ 1,\ 1/2,\ 1/2> \ \Rightarrow \ g_j m_j = \frac{2}{3}\left(\frac{1}{2}\right) = \frac{1}{3}$$

$$|2,\ 1,\ 1/2,\ -1/2> \ \Rightarrow \ g_j m_j = \frac{2}{3}\left(-\frac{1}{2}\right) = -\frac{1}{3}$$

$$|2,\ 1,\ 3/2,\ 3/2> \ \Rightarrow \ g_j m_j = \frac{4}{3}\left(\frac{3}{2}\right) = 2$$

$$|2,\ 1,\ 3/2,\ -3/2> \ \Rightarrow \ g_j m_j = \frac{4}{3}\left(-\frac{3}{2}\right) = -2$$

$$|2,\ 1,\ 3/2,\ 1/2> \ \Rightarrow \ g_j m_j = \frac{4}{3}\left(\frac{1}{2}\right) = \frac{2}{3}$$

$$|2,\ 1,\ 3/2,\ -1/2> \ \Rightarrow \ g_j m_j = \frac{4}{3}\left(-\frac{1}{2}\right) = -\frac{2}{3}$$

A plot of the Zeeman splitting versus applied magnetic field for the four upper and for the four lower levels—including the initial zero-field fine structure splitting—looks like this

5.(e) The energy of these eight levels including the applied magnetic field will be given by the sums of the fine structure splitting from part (c) and the Zeeeman splittings $g_j m_j \mu_B B_{\text{ext}}$ given by part (d). Evaluating the fine structure energies in part c, we find

$$E_{2,\,1/2} = \frac{1}{4}\left[1+\frac{5\alpha^2}{16}\right]\text{Ry} = E_{2,\,1/2} = \frac{-13.6\text{ eV}}{4}\left[1+\frac{5\alpha^2}{16}\right] = -3.4\left[1+\frac{5\alpha^2}{16}\right]\ \text{eV}\quad\text{for } j=\frac{1}{2}\text{ states,}$$

$$\text{and}\qquad E_{2,\,3/2} = \frac{1}{4}\left[1+\frac{\alpha^2}{16}\right]\text{Ry} = -3.4\left[1+\frac{\alpha^2}{16}\right]\ \text{eV}\quad\text{for } j=\frac{3}{2}\text{ states.}$$

The resulting sums are given by

$$\boxed{\begin{aligned}
E\left(2,\ 0,\ \frac{1}{2},\ \frac{1}{2}\right) &= -3.4\left[1+\frac{5\alpha^2}{16}\right]\ \text{eV} + \mu_B B_{\text{ext}}\\
E\left(2,\ 0,\ \frac{1}{2},\ -\frac{1}{2}\right) &= -3.4\left[1+\frac{5\alpha^2}{16}\right]\ \text{eV} - \mu_B B_{\text{ext}}\\
E\left(2,\ 1,\ \frac{1}{2},\ \frac{1}{2}\right) &= -3.4\left[1+\frac{5\alpha^2}{16}\right]\ \text{eV} + \frac{1}{3}\mu_B B_{\text{ext}}\\
E\left(2,\ 1,\ \frac{1}{2},\ -\frac{1}{2}\right) &= -3.4\left[1+\frac{5\alpha^2}{16}\right]\ \text{eV} - \frac{1}{3}\mu_B B_{\text{ext}}\\
E\left(2,\ 1,\ \frac{3}{2},\ \frac{3}{2}\right) &= -3.4\left[1+\frac{\alpha^2}{16}\right]\ \text{eV} + 2\mu_B B_{\text{ext}}\\
E\left(2,\ 1,\ \frac{3}{2},\ -\frac{3}{2}\right) &= -3.4\left[1+\frac{\alpha^2}{16}\right]\ \text{eV} - 2\mu_B B_{\text{ext}}\\
E\left(2,\ 1,\ \frac{3}{2},\ \frac{1}{2}\right) &= -3.4\left[1+\frac{\alpha^2}{16}\right]\ \text{eV} + \frac{2}{3}\mu_B B_{\text{ext}}\\
E\left(2,\ 1,\ \frac{3}{2},\ -\frac{1}{2}\right) &= -3.4\left[1+\frac{\alpha^2}{16}\right]\ \text{eV} - \frac{2}{3}\mu_B B_{\text{ext}}
\end{aligned}}$$