Problem 1

{a}

For \( t \leq 0 \):
\[
\Psi(r, t) = \psi(r)e^{-iEt/\hbar}
\]
where
\[
E = \frac{1}{2}mc^2\alpha^2 \quad (\alpha \simeq 1/137)
\]
\[
\psi(r) = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}
\]

Here we have used the ground state wavefunction for \( Z = 1 \). For \( t \geq 0 \), \( \Psi(r, t) \) can be written as a superposition of \( Z = 2 \) hydrogenic wavefunctions \( \psi_n(r) \):

\[
\Psi(r, t) = \sum_n c_n \psi_n(r)e^{-iE_nt/\hbar}
\]
where
\[
E_n = -\frac{1}{2}mc^2\alpha^2Z^2n^2
\]

In the “sudden” approximation, \( \Psi \) is continuous at \( t = 0 \), so eqns. (1) and (2) give

\[
\psi(r) = \sum_n c_n \psi_n(r)
\]

\[\Rightarrow \]
\[
c_n = \int \psi_n^*(r)\psi(r) \, d^3x
\]

In particular,

\[
c_1 = \int \psi_1^*(r)\psi(r) \, d^3x
\]

\[= \int \frac{1}{\sqrt{\pi}} \left( \frac{2}{a_0} \right)^{3/2} e^{-2r/a_0} \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}4\pi r^2 \, dr
\]

\[= \frac{2^{3/2}4}{a_0^3} \int_0^{\infty} e^{-3r/a_0}r^2 \, dr
\]

\[= \frac{2^{9/2}}{3^3}
\]

So the probability the \(^3\text{He}\) ion is in the ground state is

\[|c_1|^2 = 2^9/3^6 = 0.702\]

{b} Using the hint, the mean energy radiated is

\[\bar{E}_{\text{rad}} = |c_1|^2(E_1 - E_1) + |c_2|^2(E_2 - E_1) + |c_3|^2(E_3 - E_1) + \cdots
\]

Each term is the probability of the \(^3\text{He}\) winding up in an excited state times the energy it would radiate in returning to the ground state. (The first term is zero.) Rewrite this as

\[\bar{E}_{\text{rad}} = \sum_n |c_n|^2E_n - E_1 \sum_n |c_n|^2
\]

\[= \langle \Psi|H|\Psi \rangle_{t \geq 0} - E_1
\]

Here we have used the fact that second sum is unity. Now

\[H = \frac{p^2}{2m} - \frac{2e^2}{r}
\]

where the 2 is in the potential term since \( Z = 2 \) for \( t = 0^+ \). Since \( \Psi(t = 0^+) = \Psi(t = 0^-) = \psi(r) \), we get

\[\bar{E}_{\text{rad}} = \int \psi^*(r) \left( \frac{p^2}{2m} - \frac{2e^2}{r} \right) \psi(r) \, d^3x - E_1
\]

\[= \int \psi^*(r) \left( H_{t=0^-} - \frac{e^2}{r} \right) \psi(r) \, d^3x - E_1
\]
Now
\[ \int \psi^*(r) H_{t=0} \psi(r) \, d^3x = \int \psi^*(r) E_1^{(Z=1)} \psi(r) \, d^3x \]
\[ = E_1^{(Z=1)} \]
and
\[ \int \psi^*(r) - e^2 \psi(r) \, d^3x = \frac{4e^2}{a_0} \int_0^\infty e^{-2r/a_0} \, dr \]
\[ = -\frac{e^2}{a_0} \]
\[ = -mc^2 \alpha^2 \quad (= 2E_1^{(Z=1)}) \]
So
\[ \bar{\mathcal{E}}_{\text{rad}} = \frac{1}{2} mc^2 \alpha^2 - mc^2 \alpha^2 + 2mc^2 \alpha^2 \]
\[ = \frac{1}{4} mc^2 \alpha^2 \quad (= 13.6 \text{ eV}) \]

**Problem 2**

The initial state is \( \Psi(x, t = 0) = \Psi(x, t = 0^-) \), the ground state of the harmonic oscillator. After \( t = 0 \), the state is a free particle, with general solution a superposition of plane waves (eqn. 2.100 in Griffiths):
\[ \Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty A(k) e^{ikx - \Omega t} \, dk \quad (3) \]
where \( \Omega = \hbar k^2 / 2m \). (We need to distinguish \( \Omega \) from the symbol \( \omega \) used to describe the oscillator.) So
\[ \Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty A(k) e^{ikx} \, dk \]

Inverting the Fourier transform:
\[ A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty \Psi(x, 0) e^{-ikx} \, dx \]
\[ = \frac{1}{\sqrt{2\pi}} \left( \frac{m\omega}{\hbar \pi} \right)^{1/4} \int_{-\infty}^\infty \exp \left( -\frac{m\omega}{2\hbar} x^2 \right) e^{-ikx} \, dx \]
\[ = \frac{1}{\sqrt{2\pi}} \left( \frac{m\omega}{\hbar \pi} \right)^{1/4} \left( \frac{2\pi \hbar}{m\omega} \right)^{1/2} e^{-\hbar k^2 / 2m\omega}, \]
where we have used the integral in the hint. Substitute this in eqn. (3):
\[ \Psi(x, t) = \frac{1}{2\pi} \left( \frac{m\omega}{\hbar \pi} \right)^{1/4} \left( \frac{2\pi \hbar}{m\omega} \right)^{1/2} \int_{-\infty}^\infty \exp \left( -\frac{\hbar k^2}{2m\omega} + ikx - \frac{ihk^2t}{2m} \right) \, dk \]
\[ = \frac{1}{2\pi} \left( \frac{m\omega}{\hbar \pi} \right)^{1/4} \left( \frac{2\pi \hbar}{m\omega} \right)^{1/2} \int_{-\infty}^\infty \exp \left[ -\frac{\hbar}{2m\omega}(1 + i\omega t)k^2 + ikx \right] \, dk \]
\[ = \frac{1}{2\pi} \left( \frac{m\omega}{\hbar \pi} \right)^{1/4} \sqrt{\frac{\pi}{\hbar(1 + i\omega t)/2m\omega}} \exp \left[ -\frac{m\omega x^2}{2\hbar(1 + i\omega t)} \right] \]
where we have used the integral in the hint again. Note that \( |\Psi(x, t)|^2 \) is a Gaussian centered on the origin whose width increases with time: the probability distribution spreads.
Problem 3

{a} By property (i),
\[ |\Psi(t = 0)\rangle = c_0 |\psi_0\rangle + c_1 |\psi_1\rangle \]
Since an energy measurement yields \( E_0 \) and \( E_1 \) with equal probability, \( |c_0|^2 = |c_1|^2 = 1/2 \). The overall phase of a state is arbitrary, so let’s choose \( c_0 \) real:
\[ c_0 = \frac{1}{\sqrt{2}}, \quad c_1 = \frac{1}{\sqrt{2}} e^{i\phi} \]
\[ |\Psi(t = 0)\rangle = \frac{1}{\sqrt{2}} \left( |\psi_0\rangle + e^{i\phi} |\psi_1\rangle \right) \]

Now let’s use property (ii):
\[ \langle x \rangle = \frac{1}{2} \left( \langle \psi_0 | + e^{-i\phi} \langle \psi_1 | \right) \hat{x} \left( |\psi_0\rangle + e^{i\phi} |\psi_1\rangle \right) \]
Substitute eqn. (??) for \( \hat{x} \). Now the matrix elements of \( \hat{x} \) between the same states give zero because \( \langle \psi_1 | \hat{a} | \psi_1 \rangle = 0 \) etc. So
\[ \langle x \rangle = \frac{1}{2} \sqrt{\frac{\hbar}{2m\omega}} \left[ e^{i\phi} \langle \psi_0 | \hat{a} + \hat{a}^\dagger | \psi_1 \rangle + e^{-i\phi} \langle \psi_1 | \hat{a} + \hat{a}^\dagger | \psi_0 \rangle \right) \]
Note that \( \langle \psi_1 | \hat{a} + \hat{a}^\dagger | \psi_0 \rangle = \langle \psi_0 | \hat{a}^\dagger + \hat{a} | \psi_1 \rangle \), so the second term is the complex conjugate of the first.
\[ \langle x \rangle = \frac{1}{2} \sqrt{\frac{\hbar}{2m\omega}} \left[ e^{i\phi} \langle \psi_0 | \hat{a} | \psi_1 \rangle + \langle \psi_0 | \hat{a}^\dagger | \psi_1 \rangle \right] + \text{c.c.} \]
Since \( \hat{a} | \psi_1 \rangle = | \psi_0 \rangle \) and \( \hat{a}^\dagger | \psi_1 \rangle = \sqrt{2} | \psi_2 \rangle \), only the first term is nonzero.
\[ \langle x \rangle = \frac{1}{2} \sqrt{\frac{\hbar}{2m\omega}} \left[ e^{i\phi} + \text{c.c.} \right] \]
\[ = \sqrt{\frac{\hbar}{2m\omega}} \cos \phi \]
The largest positive value is for \( \phi = 0 \), so
\[ |\Psi(t = 0)\rangle = \frac{1}{\sqrt{2}} \left( |\psi_0\rangle + |\psi_1\rangle \right) \]

{b} Now put in the time dependence:
\[ |\Psi(t)\rangle = \frac{1}{\sqrt{2}} \left( e^{-iE_0t/\hbar} |\psi_0\rangle + e^{-iE_1t/\hbar} |\psi_1\rangle \right) \]
\[ = \frac{1}{\sqrt{2}} \left( e^{-i\omega t/2} |\psi_0\rangle + e^{-3i\omega t/2} |\psi_1\rangle \right) \]

{c}
\[ \langle p \rangle = \langle \Psi(t)|\hat{p}|\Psi(t)\rangle = \frac{\sqrt{m\omega\hbar}}{2} (\hat{a}^\dagger - \hat{a}) |\Psi(t)\rangle \]
\[ = \frac{\sqrt{m\omega\hbar}}{2} \left( e^{i\omega t/2} \langle \psi_0 | + e^{3i\omega t/2} \langle \psi_1 | \right) (\hat{a}^\dagger - \hat{a}) \left( e^{-i\omega t/2} \langle \psi_0 | + e^{-3i\omega t/2} \langle \psi_1 | \right) \]
The only terms that contribute are \( \langle \psi_1 | \hat{a}^\dagger | \psi_0 \rangle = \langle \psi_1 | \psi_1 \rangle = 1 \) and \( \langle \psi_0 | \hat{a} | \psi_1 \rangle = \langle \psi_0 | \psi_0 \rangle = 1 \), so
\[ \langle p \rangle = \frac{\sqrt{m\omega\hbar}}{2} \left( e^{i\omega t/2} e^{-3i\omega t/2} + e^{3i\omega t/2} e^{-i\omega t/2} \right) \]
\[ = -\sqrt{\frac{m\omega\hbar}{2}} \sin \omega t \]
The largest positive value occurs when \( \sin \omega t = -1 \). The smallest \( t \) for which this is true is

\[
\omega T = \frac{3\pi}{2} \quad \text{and} \quad T = \frac{3\pi}{2\omega}
\]

**Problem 4**

In classical mechanics, the motion of a particle with energy \( E \) in a potential \( V(r) \) is constrained by the equation \( E = T + V \). The maximum distance attainable from the center of an attractive potential is a turning point of the motion, found by setting \( T = 0 \), so that all the energy is potential energy. Any distance greater than this is the classically forbidden region.

\[
E = V |_{r_{\text{max}}} \implies -\frac{1}{2}mc^2 \alpha^2 = -\frac{e^2}{r_{\text{max}}}
\]

Here we want to replace the expression for the ground-state energy of hydrogen with the equivalent expression \( e^2/2a_0 \), so

\[
r_{\text{max}} = 2a_0 \\
\text{Prob}(r > r_{\text{max}}) = \int_{2a_0}^{\infty} R_{10}^2(rr) r^2 dr \\
= \frac{4}{a_0^2} \int_{2a_0}^{\infty} e^{-2r/a_0} r^2 dr \\
= \frac{1}{2} \int_4^{\infty} e^{-y^2} dy \quad (y = 2r/a_0) \\
= \frac{1}{2} e^{-y} \bigg[ -y^2 - 2y - 2 \bigg] \bigg|_4^{\infty} = 13/e^4 = 0.238
\]

**Problem 5**

\{a\}

\[
S^2 = (s_1 + s_2)^2 = s_1^2 + s_2^2 + 2s_1 \cdot s_2
\]

so \( H = \frac{1}{2}c^2(S^2 - s_1^2 - s_2^2) \)

Now the states \( \hat{p}_x sm \) are really states \( |s_1 s_2 s m\rangle \) with \( s_1 \) and \( s_2 \) fixed (in this case, \( s_1 = s_2 = \frac{1}{2} \)). So

\[
H \hat{p}_x sm = \frac{1}{2}ch^2 \left[ s(s + 1) - \frac{3}{4} - \frac{3}{4} \right] \hat{p}_x sm
\]

For \( \hat{p}_x 00 \), we get

\[
E_0 = \frac{1}{2}ch^2 \left[ 0 - \frac{3}{2} \right] = -\frac{3}{4}ch^2
\]

For \( \hat{p}_x 1m \), we get

\[
E_1 = \frac{1}{2}ch^2 \left[ 1 \cdot 2 - \frac{3}{2} \right] = -\frac{1}{4}ch^2
\]

(triply degenerate)

\{b\} In the \( \hat{p}_x m_1 m_2 \) basis, we have

\[
s_1 \cdot s_2 = s_{1x}s_{2x} + s_{1y}s_{2y} + s_{1z}s_{2z} \\
= \frac{1}{4}(s_{1+} + s_{1-})(s_{2+} + s_{2-}) - \frac{1}{4}(s_{1+} - s_{1-})(s_{2+} - s_{2-}) + s_{1z}s_{2z} \\
= \frac{1}{2}s_{1+}s_{2-} + \frac{1}{2}s_{1-}s_{2+} + s_{1z}s_{2z}
\]

Recall that

\[
s_+ |\frac{1}{2}\rangle = 0, \quad s_+ |\frac{3}{2}\rangle = \hbar |\frac{1}{2}\rangle, \quad s_- |\frac{1}{2}\rangle = \hbar |\frac{1}{2}\rangle, \quad s_- |\frac{3}{2}\rangle = 0
\]

So

\[
H \hat{p}_x \frac{1}{2} \frac{1}{2} = \frac{1}{4}ch^2 \hat{p}_x \frac{1}{2} \frac{1}{2} \\
H \hat{p}_x \frac{1}{2} - \frac{1}{2} = \frac{1}{2}ch^2 \hat{p}_x \frac{1}{2} - \frac{1}{2} - \frac{1}{4}ch^2 \hat{p}_x \frac{1}{2} - \frac{1}{2} \\
H \hat{p}_x - \frac{1}{2} \frac{1}{2} = \frac{1}{2}ch^2 \hat{p}_x - \frac{1}{2} - \frac{1}{4}ch^2 \hat{p}_x - \frac{1}{2} \\
H \hat{p}_x - \frac{1}{2} - \frac{1}{2} = \frac{1}{4}ch^2 \hat{p}_x - \frac{1}{2} - \frac{1}{2}
\]
So for example $\langle \frac{1}{2} \left| \frac{1}{2} \right| H \hat{p}_x \frac{1}{2} \rangle = \frac{1}{4} \hbar^2$ and the matrix representation of $H$ in this basis is

$$
H = \frac{1}{4} \hbar^2 \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & -1 & 2 & 0 \\
0 & 2 & -1 & 0 \\
0 & 0 & 0 & 1
\end{bmatrix}
$$

The eigenvalues of this are the energy levels (solutions of $H\psi = E\psi$):

$$\det \begin{bmatrix}
1 - E & 0 & 0 & 0 \\
0 & -1 - E & 2 & 0 \\
0 & 2 & -1 - E & 0 \\
0 & 0 & 0 & 1 - E
\end{bmatrix} = 0$$

gives $E = 1$ twice and

$$
\begin{bmatrix}
-1 - E \\
2 \\
-1 - E
\end{bmatrix} = 0, \quad (1 + E)^2 = 4, \quad E = -3 \quad \text{or} \quad 1
$$

Putting back the factor of $\frac{1}{4} \hbar^2$, we have the same answer as part (a):

$$
E = -\frac{1}{4} \hbar^2 \quad \text{or} \quad \frac{1}{4} \hbar^2 \quad \text{(3 times)}
$$

{c} Write the general solution as a superposition of stationary states:

$$
|\Psi(t)\rangle = \sum_n c_n |\psi_n\rangle e^{-iE_n t/H}
$$

$$
= c_1 \hat{p}_x 00 e^{-iE_0 t/H} + c_2 \hat{p}_x 11 e^{-iE_1 t/H} + c_3 \hat{p}_x 10 e^{-iE_1 t/H} + c_4 \hat{p}_x 01 e^{-iE_0 t/H}
$$

{d} The easiest way to do this is to rewrite the solution (c) in terms of the states $\hat{p}_x \frac{1}{2} \frac{1}{2}$ etc. using

$$
\hat{p}_x 11 = \hat{p}_x \frac{1}{2} \frac{1}{2}
$$

$$
\hat{p}_x 00 = \frac{1}{\sqrt{2}} \left( \hat{p}_x \frac{1}{2} \frac{1}{2} + \hat{p}_x \frac{1}{2} \frac{1}{2} \right)
$$

(remember that we are being lazy here: $\hat{p}_x 11$ really means $\frac{1}{2} \frac{1}{2} 1 1$, but since the first two quantum numbers $s_1 = s_2 = \frac{1}{2}$ stay fixed, we’re omitting them. Similarly, $\hat{p}_x \frac{1}{2} \frac{1}{2}$ really means the product state $\hat{p}_x \frac{1}{2} \frac{1}{2} \hat{p}_x \frac{1}{2} \frac{1}{2}$ where we drop the first quantum number in each ket.) So solution (c) becomes

$$
|\Psi(t)\rangle = A \left( \hat{p}_x \frac{1}{2} \frac{1}{2} - \frac{1}{2} \frac{1}{2} \right) e^{-iE_0 t/H} + \left[ B \hat{p}_x \frac{1}{2} \frac{1}{2} + C \left( \hat{p}_x \frac{1}{2} \frac{1}{2} + \hat{p}_x \frac{1}{2} \frac{1}{2} \right) + D \hat{p}_x \frac{1}{2} \frac{1}{2} \right] e^{-iE_1 t/H}
$$

where we have redefined some constants to absorb the factor of $1/\sqrt{2}$.

Now at $t = 0$,

$$
|\Psi(0)\rangle = \hat{p}_x \frac{1}{2} \frac{1}{2} \quad \implies \quad B = D = 0, \quad A + C = 1, \quad -A + C = 0
$$

Thus $A = C = \frac{1}{2}$ and

$$
|\Psi(t)\rangle = \frac{1}{2} \left( \hat{p}_x \frac{1}{2} \frac{1}{2} - \frac{1}{2} \frac{1}{2} \right) e^{-iE_0 t/H} + \frac{1}{2} \left( \hat{p}_x \frac{1}{2} \frac{1}{2} + \hat{p}_x \frac{1}{2} \frac{1}{2} \right) e^{-iE_1 t/H}
$$

{e}

$$
P(\frac{1}{2}, \frac{1}{2}) = |\langle \frac{1}{2} \frac{1}{2} | \Psi(t)\rangle|^2 = 0
$$

$$
P(\frac{1}{2}, -\frac{1}{2}) = |\langle \frac{1}{2} -\frac{1}{2} | \Psi(t)\rangle|^2
$$

$$
= \left| \frac{1}{2} \left( e^{-iE_0 t/H} + e^{-iE_1 t/H} \right) \right|^2
$$

$$
= \frac{1}{4} \left| e^{3i\hbar t/4} + e^{-i\hbar t/4} \right|^2
$$

$$
= \frac{1}{4} \left| e^{i\hbar t/4} - e^{-i\hbar t/4} \right|^2
$$

$$
= \cos^2 \left( \frac{\chi t}{2} \right)
$$
Problem 6
The first-order correction to the ground state energy is
\[ \Delta E = \langle 1\ 0\ 0 | H' | 1\ 0\ 0 \rangle \] (4)
where |1 0 0⟩ is the ground state ket. To find \( H' \), we need to first find the potential inside and outside a uniform spherical charge distribution of radius \( R \). The perturbation \( H' \) is the difference between this potential and the Coulomb potential used when the proton is treated as a point particle. (More precisely, the difference in the potential energies.) The quickest way to find the potential is to use Gauss’s Law to get the \( \mathbf{E} \) field and then integrate the field to get the potential. Gauss’s Law is
\[
\oint_S \mathbf{E} \cdot d\mathbf{S} = 4\pi \int_V \rho \, d^3x
\]
In spherical symmetry the \( \mathbf{E} \) field is radial and we choose the Gaussian surface to be a sphere of radius \( r \). This gives
\[
4\pi r^2 E(r) = 4\pi \int_0^r \rho(r) \, d^3x \quad \Rightarrow \quad E(r) = \frac{q(r)}{r^2}
\]
where \( q(r) \) is the charge enclosed by a sphere of radius \( r \). Since
\[
q(r) = \begin{cases} 
  e, & r > R \\
  e \left( \frac{r}{R} \right)^3, & r < R 
\end{cases}
\]
we get
\[
E(r) = \begin{cases} 
  \frac{e}{r^2}, & r > R \\
  e \frac{r}{R^3}, & r < R 
\end{cases}
\]
(Note that \( e \) is positive. The charge on an electron is \( -e \) and on a proton is \( +e \).) The potential energy of the electron is
\[
V(r) = (-e) \left( -\int_{\infty}^{r} E(r') \, dr' \right)
\]
For \( r < R \) we get
\[
V(r) = e^2 \int_{\infty}^{R} \frac{dr'}{r'^2} + e^2 \int_{R}^{r} \frac{r'}{R^3} \, dr' \\
= e^2 \left( -\frac{1}{R} + \frac{1}{2} \frac{r^2}{R^3} - \frac{1}{2} \frac{1}{R} \right)
\]
while for \( r > R \) we have \( V(r) = -e^2/r \). So
\[
H' = V(r) - \left( -\frac{e^2}{r} \right) \\
= \begin{cases} 
  0, & r > R \\
  e^2 \left( \frac{1}{r} + \frac{r^2}{2R^3} - \frac{3}{2R} \right), & r < R 
\end{cases}
\]
Eqn. (4) gives
\[
\Delta E = \int_0^R 4\pi r^2 \, dr \left( \frac{1}{\pi a_0^3} e^{-2r/a_0} \right) e^2 \left( \frac{1}{r} + \frac{r^2}{2R^3} - \frac{3}{2R} \right)
\]
Since \( R \ll a_0, r \ll a_0 \) throughout the region of integration. So we can set the exponential term to unity. This gives
\[
\Delta E = \frac{4e^2}{a_0^3} \int_0^R dr \left( r + \frac{r^4}{2R^3} - \frac{3r^2}{2R} \right) \\
= \frac{2}{5} \frac{e^2 R^2}{a_0^3}
\]
Since $e^2/2a_0 = 13.6 \text{ eV}$ and $R/a_0 = 10^{-13} \text{ cm}/0.529 \times 10^{-8} \text{ cm}$, we get

$$\Delta E = 3.9 \times 10^{-9} \text{ eV}$$

Note that since this is much smaller than the distance between the ground state energy and the first excited state, perturbation theory is a good approximation. (In fact, $\Delta E$ is much smaller even than the hyperfine splitting of the ground state, as we will see.)

**Problem 7**
The unperturbed Hamiltonian of a 3-d rotator is

$$H_0 = \frac{L^2}{2I}$$

where $I$ is the moment of inertia. Adding the perturbation

$$H' = -E \cdot d = -\mathcal{E} d \cos \theta$$

gives the full Hamiltonian $H = H_0 + H'$. The unperturbed energies satisfy

$$\frac{L^2}{2I} \psi = E \psi$$

The energy levels and eigenfunctions are

$$E_l = \frac{l(l + 1)}{2I} \hbar^2, \quad \langle r|\psi_{lm} \rangle = Y_{lm}(\theta, \phi)$$

(Note that there is no radial dependence.) Although each state is $(2l + 1)$-fold degenerate, since the perturbation doesn’t depend on $\phi$, it couples only the $m = 0$ states (as we’ll see explicitly below.) So we can use non-degenerate perturbation theory.

To second order, the ground state energy is

$$E = E_0 + \langle \psi_{00} | H' | \psi_{00} \rangle + \sum_{l,m} \frac{|\langle \psi_{lm} | H' | \psi_{00} \rangle|^2}{E_0 - E_l}$$

Note that we can write $H'$ in terms of spherical harmonics as

$$H' = -\mathcal{E} d \sqrt{\frac{4\pi}{3}} Y_{10}$$

So the first-order correction is

$$\langle \psi_{00} | H' | \psi_{00} \rangle = -\mathcal{E} d \sqrt{\frac{4\pi}{3}} \int Y_{00}^* Y_{10} Y_{00} \, d\Omega \propto \int Y_{00}^* Y_{10} \, d\Omega = 0$$

Here $d\Omega = \sin \theta \, d\theta \, d\phi$ and we have used the orthogonality of the $Y_{lm}$’s. (Note that $Y_{00} = 1/\sqrt{4\pi}$ is a constant.)

The leading order correction to the ground state energy is therefore second-order. The matrix elements are

$$\langle \psi_{lm} | H' | \psi_{00} \rangle = -\mathcal{E} d \sqrt{\frac{4\pi}{3}} \int Y_{lm}^* Y_{10} Y_{00} \, d\Omega$$

$$= -\mathcal{E} d \sqrt{\frac{1}{3}} \delta_{l1} \delta_{m0}$$

where we have used orthogonality again. So

$$\Delta E = \sum_{l,m} \left| \frac{\langle \psi_{lm} | H' | \psi_{00} \rangle}{E_0 - E_l} \right|^2 = \frac{\mathcal{E}^2 d^2}{3} \frac{1}{0 - \hbar^2/I} = \frac{\mathcal{E}^2 d^2 I}{3\hbar^2}$$

Second-order perturbation theory is a good approximation provided

$$|\Delta E| \ll |E_0 - E_1| \quad \Rightarrow \quad \left| \frac{\mathcal{E}^2 d^2 I}{3\hbar^2} \right| \ll \frac{\hbar^2}{I} \quad \Rightarrow \quad \mathcal{E} \ll \frac{\hbar^2}{dI}$$

where we have dropped the factor of $1/3$.

**Problem 8**
The interaction energy of a charge $-e$ in an external potential $\phi$ is $H' = -e\phi$. Here the electric field is

$$E = \mathcal{E}e_z = -\nabla\phi \quad \Rightarrow \quad \phi = -\mathcal{E}z$$

(Adding a constant doesn’t change the physics.) So

$$H' = e\mathcal{E}z = e\mathcal{E}r\cos\theta$$

The first-order correction to the ground state energy is

$$\Delta E = \langle 1\ 0\ 0 | e\mathcal{E}r\cos\theta | 1\ 0\ 0 \rangle$$

There are several ways to see this is zero:

1. It is $E$ times the expectation value of a dipole moment in a state of definite parity, which we showed in class is zero using a parity argument.
2. It involves the integral of $Y_{00}^* Y_{10} Y_{00}$. Treat the last factor, $Y_{00}$, as a constant. Then the first two terms give zero by orthogonality.
3. Do the $\theta$ integral explicitly. (Needless to say, this is not the recommended method.)

The second-order correction to the ground-state energy is

$$\Delta E = \sum_{l,m}^\infty \frac{|\langle n\ l\ m|H'|1\ 0\ 0 \rangle|^2}{E_1 - E_n}$$

(5)

The matrix element is

$$\langle n\ l\ m|H'|1\ 0\ 0 \rangle = \langle n\ l\ m|e\mathcal{E}r\cos\theta|1\ 0\ 0 \rangle$$

$$= e\mathcal{E} \frac{4\pi}{3} \langle n\ l\ m|rY_{10}|1\ 0\ 0 \rangle$$

$$= e\mathcal{E} \frac{4\pi}{3} \int Y_{lm}^* Y_{10}\ d\Omega \int_0^\infty R_{nl} R_{10} r^3\ dr$$

$$= \delta_{l1} \delta_{m0} \frac{e\mathcal{E}}{\sqrt{3}} \int_0^\infty R_{nl} R_{10} r^3\ dr$$

Using the Kronecker deltas to do the $l$ and $m$ sums in (5) gives

$$\Delta E = e^2\mathcal{E}^2 \sum_{n=2}^\infty \frac{|z_{n1}|^2}{E_1 - E_n} \quad \text{with} \quad z_{n1} = \frac{1}{\sqrt{3}} \int_0^\infty R_{nl} R_{10} r^3\ dr$$

$$\text{and} \quad \alpha = \frac{2\Delta E}{\mathcal{E}^2} = \frac{2e^2 \sum_{n=2}^\infty \frac{|z_{n1}|^2}{E_1 - E_n}}{E_1 - E_n}$$

In a matrix element like $z_{n1}$, the states are normalized and so their dimensions drop out of the integral. The dimensions are just the dimensions of $z$, and the scale is set by the size of the atom: $z_{n1} \sim a_0$. The energies scale as $E_1 - E_n \sim E_{1} \sim -e^2/a_0$. (This is a better expression to use here than the equivalent $-m\alpha^2$.) Thus

$$\alpha \sim e^2 \frac{a_0^2}{-e^2/a_0} \sim -a_0^3$$

Problem 9
The perturbation Hamiltonian is

$$H' = e\mathcal{E}z = e\mathcal{E}r\cos\theta$$

We need to find the eigenvalues of the matrix of $H'$ in the basis of $n = 2$ degenerate eigenstates. Label the states as

$$|1\rangle = |2\ 0\ 0\rangle, \quad |2\rangle = |2\ 1\ 1\rangle, \quad |3\rangle = |2\ 1\ 0\rangle, \quad |4\rangle = |2\ 1\ -1\rangle$$
where the 3 quantum numbers are \( n, l, m \). We want to find \( H'_{ij} = \langle i | H' | j \rangle \). We use symmetry arguments to determine which of these matrix elements must be zero.

Consider the parity operator \( P \). This is not a symmetry operator for \( H' \), but \( H' \) has a definite transformation property:

\[
P | n \, l \, m \rangle = (-1)^l | n \, l \, m \rangle \quad \text{(from the } Y_{lm} \text{)}
\]

\[
PH'P = -H' \quad \text{(from the } z \text{)}
\]

So

\[
\langle n \, l \, m | H' | n' \, l' \, m' \rangle = -\langle n \, l \, m | (PH'P) | n' \, l' \, m' \rangle = -\left( \langle n \, l \, m | P | H' (P | n' \, l' \, m') \rangle \right) = (-1)^{l+l'+1} \langle n \, l \, m | H' | n' \, l' \, m' \rangle
\]

Thus

\[
\langle n \, l \, m | H' | n' \, l' \, m' \rangle = 0 \quad \text{if } (l + l') \text{ is even.}
\]

Another way of seeing this is from the explicit integral for the matrix element. Since \( \cos \theta \propto Y_{10} \), the angular part of the integral involves

\[
\int Y_{l'm'}^* Y_{lm} \, d\Omega
\]

Under an inversion, each \( Y_{lm} \) gives a factor of \((-1)^l\), giving a total of \((-1)^{l+l'+1}\) as before. So the possible nonzero matrix elements are \{ \( H'_{12}, H'_{13}, H'_{14} \) \} and their Hermitian conjugates.

There is also a selection rule from the \( \phi \)-integral, which involves

\[
\int_0^{2\pi} e^{i(-m+m')\phi} \, d\phi = 0 \quad \text{unless } m = m'
\]

Another way to see this is from the symmetry of the perturbation under rotations about the \( z \)-axis. The generator of these rotations is \( J_z \), and the symmetry is expressed by \([H', J_z] = 0\). (This is just the statement that \([z, J_z] = 0\), one of the equations saying that \((x, y, z)\) form the components of a vector operator.) Now

\[
\langle n \, l \, m | H' J_z | n' \, l' \, m' \rangle = m' \hbar \langle n \, l \, m | H' | n' \, l' \, m' \rangle
\]

Using the commutator relation, this is also equal to

\[
\langle n \, l \, m | J_z H' | n' \, l' \, m' \rangle = m \hbar \langle n \, l \, m | H' | n' \, l' \, m' \rangle
\]

So the matrix element is nonzero only if \( m = m' \). This reduces the set of nonzero matrix elements to just \( H'_{13} = \langle 2 \, 0 \, 0 \langle H' | 2 \, 1 \, 0 \rangle \). So we have only one integral to compute explicitly:

\[
H'_{13} = \varepsilon E \int \frac{4\pi}{3} Y_{10}^* Y_{10} \, d\Omega \int_0^\infty R_{20} r R_{21} r^2 \, dr
\]

\[
= \varepsilon E \sqrt{\frac{4\pi}{3}} \frac{1}{\sqrt{4\pi}} \int Y_{10}^* Y_{10} \, d\Omega \int_0^\infty \frac{1}{\sqrt{4\alpha_0^2}} \left[ \frac{r}{a} - \frac{1}{2} \left( \frac{r}{a_0} \right)^2 \right] e^{-r/a_0} r^3 \, dr
\]

Here we have used the fact that \( Y_{10} \) is real so we can easily see that the angular integral is unity. Put \( x = r/a_0 \) in the radial integral to get

\[
H'_{13} = \frac{1}{12} \varepsilon E a_0 \int_0^\infty \left( x^4 - \frac{x^5}{2} \right) e^{-x} dx = \frac{1}{12} \varepsilon E a_0 \left( 4! - \frac{5!}{2} \right) = -3\varepsilon E a_0
\]

So finally

\[
H' = \begin{pmatrix}
0 & 0 & -3\varepsilon E a_0 & 0 \\
0 & 0 & 0 & 0 \\
-3\varepsilon E a_0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}
\]

Diagonalizing the matrix yields the eigenvalues

\[
\Delta E = 0, 0, \pm 3\varepsilon E a_0
\]

Thus in the presence of the external electric field, the states \( |2 \, 1 \, 1 \rangle \) and \( |2 \, 1 \, -1 \rangle \) receive no first-order correction to their energies. The two linear combinations of \( |2 \, 0 \, 0 \rangle \) and \( |2 \, 1 \, 0 \rangle \) that are the “good” eigenstates are split, one with a positive correction and one with a negative correction.
The way to understand these results without all the formalism is as follows: The $2s$ state has even parity ($l = 0$), the $2p$ states have odd parity ($l = 1$). The perturbation couples states of different parity, since it’s a polar vector. So only matrix elements of $2s$ with $2p$ are nonzero. In addition, rotational symmetry about the $z$-axis means angular momentum about that axis is conserved. So the $m$ value of a state isn’t changed by the perturbation—only states with the same $m$ are coupled.