PHYS852 Quantum Mechanics II, Spring 2010
HOMEWORK ASSIGNMENT 8: Solutions

Topics covered: hydrogen fine structure

1. [10 pts] Let the Hamiltonian H depend on the parameter λ, so that $H = H(\lambda)$. The eigenstates and eigenvalues of H are then also functions of λ, i.e. $E_n = E_n(\lambda)$ and $|n\rangle = |n(\lambda)\rangle$.
Use the property $H|n\rangle = E_n|n\rangle$ to prove the Feynman-Hellmann theorem:

$$\frac{\partial E_n(\lambda)}{\partial \lambda} = \langle n(\lambda)| \frac{\partial H(\lambda)}{\partial \lambda} |n(\lambda)\rangle$$

Start from the definition

$$E_n = \langle n|H|n\rangle$$

Differentiation gives

$$\frac{\partial}{\partial \lambda} E_n = \left(\frac{\partial}{\partial \lambda}\langle n|\right) H|n\rangle + \langle n| \left(\frac{\partial}{\partial \lambda} H\right) |n\rangle + \langle n|H \frac{\partial}{\partial \lambda}|n\rangle$$

Since $H|n\rangle = E_n|n\rangle$ and $\langle n|H = \langle n|E_n$, we can rewrite this as

$$\begin{aligned} \frac{\partial}{\partial \lambda} E_n &= E_n \left(\frac{\partial}{\partial \lambda}\langle n|\right) |n\rangle + \langle n| \left(\frac{\partial}{\partial \lambda}|n\rangle\right) E_n + \langle n| \frac{\partial H}{\partial \lambda}|n\rangle \\ &= E_n \frac{\partial}{\partial \lambda}\langle n|n\rangle + \langle n| \frac{\partial H}{\partial \lambda}|n\rangle \end{aligned}$$

Since $\langle n|n\rangle = 1$, it follows that

$$\frac{\partial E_n(\lambda)}{\partial \lambda} = \langle n(\lambda)| \frac{\partial H(\lambda)}{\partial \lambda} |n(\lambda)\rangle$$

2. [15 pts] The effective Hamiltonian which governs the radial wave equation is

$$H = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2 \ell(\ell+1)}{2Mr^2} - \frac{e^2}{4\pi\epsilon_0 r}.$$

The exact eigenvalues in terms of e and ℓ are

$$E_n = -\frac{Me^4}{32\pi^2\epsilon_0^2\hbar^2 n(\ell)^2,}$$

where $n(\ell) = n_r + \ell + 1$, with n_r being the highest power in the series expansion or $R_{n\ell}(r)$.

Apply the Feynman-Hellman theorem with $\lambda = e$ to derive:

$$\langle n\ell^{(0)}|R^{-1}|n\ell^{(0)}\rangle = \frac{1}{n^2 a_0}.$$

Then use $\lambda = \ell$, with ℓ treated as a continuous parameter, to derive:

$$\langle n\ell^{(0)}|R^{-2}|n\ell^{(0)}\rangle = \frac{1}{(\ell+1/2)n^3 a_0^2}.$$

According to Feynman-Hellman

$$\langle n\ell m_\ell|\frac{\partial H}{\partial e}|n\ell m_\ell\rangle = \frac{\partial E_n}{\partial e}$$

now

$$\frac{\partial H}{\partial e} = -\frac{2e}{4\pi\epsilon_0}\frac{1}{R}$$

and we have

$$E_n = \frac{-\hbar^2}{2m_e a_0^2 n^2}$$

with $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$ this works out to

$$E_n = -\frac{m_e e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$$

so that

$$\frac{\partial E_n}{\partial e} = -\frac{2m_e e^3}{(4\pi\epsilon_0)^2\hbar^2 n^2}$$

Thus Feynman-Hellman gives

$$-\frac{2e}{4\pi\epsilon_0}\langle R^{-1}\rangle = -\frac{2m_e e^3}{(4\pi\epsilon_0)^2\hbar^2 n^2}$$

Solving for $\langle R^{-1}\rangle$ thus gives

$$\langle R^{-1}\rangle = \frac{m_e e^2}{4\pi\epsilon_0\hbar^2 n^2} = \frac{1}{n^2 a_0}.$$

Now

$$\frac{\partial H}{\partial \ell} = \frac{\partial}{\partial \ell} \frac{\hbar^2 \ell(\ell+1)}{2m_e R^2} = \frac{\hbar^2(\ell+1/2)}{m_e R^2}$$

and

$$\frac{\partial E_n}{\partial \ell} = -\frac{\partial}{\partial \ell} \frac{\hbar^2}{2m_e a_0^2 n^2(\ell)} = \frac{\hbar^2}{m_e a_0^3 n^3}$$

where we have used $\frac{\partial}{\partial \ell} n(\ell) = 1$. Putting these results into Feynman-Hellman gives

$$\frac{\hbar^2(\ell+1/2)}{m_e} \langle R^{-2} \rangle = \frac{\hbar^2}{m_e a_0^2 n^3}$$

Solving for $\langle R^{-2} \rangle$ gives

$$\langle R^{-2} \rangle = \frac{1}{(\ell+1/2) n^3 a_0^2}$$

3. [20 pts] Deriving Kramer's relation:

a.) First, show via integration by parts that $\int dr\, ur^s u' = -\frac{s}{2}\int dr\, ur^{s-1}u$. Then use this result to show that $\int dr\, u'r^s u' = -\frac{2}{s+1}\int dr\, u'r^{s+1}u''$.

Let:

$$\begin{array}{cc} f = ur^2 & dg = u'dr \\ df = (u'r^2 + 2r^{2-1})dr & g = u \end{array}$$

Thus we have

$$\int dr\, ur^s u' = \int f\, dg = fg\Big| - \int g df = ur^s u\Big| - \int dr\, (u'r^s - sur^{s-1})u$$

Assuming the boundary term vanishes, this gives

$$\int dr\, ur^s u' = -\int dr\, u'r^s u - s\int dr\, ur^{s-1}u$$

Collecting like terms then gives

$$\int dr\, ur^s u' = -\frac{s}{2}\int dr\, ur^{s-1}u$$

This allows us to eliminate a first-derivative at the cost of reducing the power of r by one.

This result can be rewritten as

$$\int dr\, ur^{s-1}u = -\frac{2}{s}\int dr\, ur^s u'$$

with $u \to u'$ and $s \to s+1$ this becomes

$$\int dr\, u'r^s u' = -\frac{2}{s+1}\int dr\, u'r^{s+1}u''$$

b.) With $R_{n\ell}(r) = u(r)/r$, the radial eigenvalue equation of the hydrogen atom becomes

$$u'' = \left[\frac{\ell(\ell+1)}{r^2} - \frac{2}{a_0 r} + \frac{1}{n^2 a_0^2}\right] u.$$

Use this to express $\int dr\, ur^s u''$ in terms of $\langle n\ell^{(0)}|R^s|n\ell^{(0)}\rangle$, $\langle n\ell^{(0)}|R^{s-1}|n\ell^{(0)}\rangle$, and $\langle n\ell^{(0)}|R^{s-2}|n\ell^{(0)}\rangle$.

From direct substitution we find

$$\begin{aligned} \int drur^2u'' &= \int drur^s \left[\frac{\ell(\ell+1)}{r^2} - \frac{2}{a_0 r} + \frac{1}{n^2 a_0^2}\right] u \\ &= \ell(\ell+1)\langle R^{s-2}\rangle - \frac{2}{a_0}\langle R^{s-1}\rangle + \frac{1}{n^2 a_0^2}\langle R^s\rangle \end{aligned}$$

c.) Set aside your result from part b.), and now integrate $\int dr\, ur^s u''$ by parts, assuming the boundary terms vanish. Apply the identities derived in part a.) to each of the resulting terms in the obvious manner, and then again use the eigenvalue equation to eliminate u''.

With

$$\begin{array}{cc} f = ur^s & dg = u''dr \\ df = (u'r^s + sur^{s-1})dr & g = u' \end{array}$$

we find

$$\int dr\, ur^s u'' = \int f\, dg = fg\Big| - \int g\, df = ur^s u'\Big| - \int dr\, u'r^s u' - s\int dr\, ur^{s-1}u'$$

Assuming the boundary term vanishes and inserting the results from part a.) gives

$$\int drur^s u'' = \frac{2}{s+1}\int dr\, u'r^{s+1}u'' + \frac{s(s-1)}{2}\langle R^{s-2}\rangle$$

inserting the eigenvalue equation on the r.h.s. gives

$$\int drur^s u'' = \frac{2}{s+1}\int dr\, u'r^{s+1}\left[\frac{\ell(\ell+1)}{r^2} - \frac{2}{a_0 r} + \frac{1}{n^2 a_0^2}\right]u + \frac{s(s-1)}{2}\langle R^{s-2}\rangle$$

From part a.), we have $\int dr\, u'r^s u = -\frac{s}{2}\int dr\, ur^{s-1}u = \langle R^{s-1}\rangle$, which gives

$$\int drur^s u'' = -\frac{\ell(\ell+1)(s-1)}{s+1}\langle R^{s-2}\rangle + \frac{2s}{(s+1)a_0}\langle R^{s-1}\rangle - \frac{1}{n^2 a_0^2}\langle R^s\rangle + \frac{s(s-1)}{2}\langle R^{s-2}\rangle$$

d.) You now have two distinct expressions for $\int dr\, ur^s u''$. Equate them and collect like terms to derive a relation between $\langle n\ell^{(0)}|R^s|n\ell^{(0)}\rangle$, $\langle n\ell^{(0)}|R^{s-1}|n\ell^{(0)}\rangle$, and $\langle n\ell^{(0)}|R^{s-2}|n\ell^{(0)}\rangle$. This is called Kramer's relation.

Equating the expression from b.) with the expression from c.) and collecting like terms gives Kramer's relation:

$$\frac{a_0^2 s}{4}\left((2\ell+1)^2 - s^2\right)\langle R^{s-2}\rangle - a_0(2s+1)\langle R^{s-1}\rangle + \frac{s+1}{n^2}\langle R^s\rangle = 0,$$

which allows you to compute the expectation values of successive powers of R^{-1} via iteration.

4. [15 pts] Spin-orbit interaction:

a.) Use Kramer's relation with $s = -1$, together with your results from problem 2, to evaluate $\langle n\ell^{(0)}|R^{-3}|n\ell^{(0)}\rangle$.

Kramers relation with $s = -1$ gives:

$$-a_0^2\ell(\ell+1)\langle R^{-3}\rangle + a_0\langle R^{-2}\rangle = 0$$

Solving for $\langle R^{-3}\rangle$ gives

$$\langle R^{-3}\rangle = \frac{1}{a_0\ell(\ell+1)}\langle R^{-2}\rangle$$

With the expression from problem 2, this becomes

$$\langle R^{-3}\rangle = \frac{1}{\ell(\ell+1/2)(\ell+1)n^3a_0^3}$$

b.) Use this expression to show that the first-order spin-orbit interaction shift, given by the Dirac equation as

$$E^{(1)}_{n\ell j} = \frac{e^2}{8\pi\epsilon_0 M_e^2c^2}\langle n\ell j^{(0)}|\frac{\vec{L}\cdot\vec{S}}{R^3}|n\ell j^{(0)}\rangle,$$

can be expressed as

$$E^{(1)}_{n\ell j} = \frac{\left[E_n^{(0)}\right]^2}{M_ec^2}\frac{n\left[j(j+1)-\ell(\ell+1)-3/4\right]}{\ell(\ell+1/2)(\ell+1)}.$$

We can separate the eigenstate $|n\ell jm_j^{(0)}\rangle$ into the tensor product $|n\ell\rangle^{(R)}\otimes|\ell jm_j\rangle^{(L\otimes S)}$, where the state $|n\ell\rangle$ lives in the radial Hilbert space, and $|\ell jm_j\rangle$ lives in the angular-momentum Hilbert space. Due to symmetry, the result cannot depend on m_j, so we will drop it. The state $|n\ell j^{(0)}\rangle$ is then an arbitrary superposition of m_j states.
This gives

$$\langle n\ell j^{(0)}|\frac{\vec{L}\cdot\vec{S}}{R^3}|n\ell j^{(0)}\rangle = \langle n\ell|R^{-3}|n\ell\rangle\langle\ell j|\vec{L}\cdot\vec{S}|\ell j\rangle$$

Since $J^2 = L^2 + 2\vec{L}\cdot\vec{S} + S^2$ we get $\vec{L}\cdot\vec{S} = \frac{1}{2}\left(J^2 - L^2 - S^2\right)$ which gives

$$\langle\frac{\vec{L}\cdot\vec{S}}{R^3}\rangle = \frac{\hbar^2}{2a_0^3n^3}\frac{(j(j+1)-\ell(\ell+1)-3/4)}{\ell(\ell+1/2)(\ell+1)}$$

so that

$$E^{(1)}_{n\ell j} = \left[E_n^{(0)}\right]^2\frac{1}{M_ec^2}\frac{n\left(j(j+1)-\ell(\ell+1)-3/4\right)}{\ell(\ell+1/2)(\ell+1)}$$

5. [15 pts] From the Dirac equation, it is found that the fine-structure of hydrogen is given by three terms: the relativistic mass correction, the spin-orbit interaction, and the Darwin term. In the atomic physics lecture notes, the Feynman-Hellman theorem is used to show that the first-order relativistic mass-correction is

$$E^{(1)}_{n\ell} = -\frac{\left[E^{(0)}_n\right]^2}{2M_e c^2}\left(\frac{4n}{\ell+1/2} - 3\right).$$

Due to symmetry, the spin-orbit interaction term is exactly zero for $\ell = 0$, while the combined mass-correction and Darwin terms give a net shift of

$$E^{(1)}_{n0\frac{1}{2}} = -\frac{M_e c^2\alpha^4}{4n^4}\left(2n - \frac{3}{2}\right).$$

For $\ell \neq 0$, on the other hand, the Darwin term vanishes, while the spin-orbit shift is non-zero.

Consider separately the two possible cases $j = \ell + 1/2$ and $j = \ell - 1/2$, and show that for $\ell \neq 0$, the full fine-structure shift is given by

$$E^{(1)}_{nj} = -\frac{M_e c^2\alpha^4}{4n^4}\left(\frac{2n}{j+1/2} - \frac{3}{2}\right).$$

Using the above expression for $E^{(1)}_{n0\frac{1}{2}}$, show that this formula also works for the $\ell = 0$ case.

Based on this formula, make a sketch of the hydrogen energy levels for $n = 1, 2, 3$, showing the fine structure splittings. For each n, give the degeneracy of each j sub-level, and compute the level separations in eV.

For $\ell = 0$, we must have $j = 1/2$, so the general formula agrees with the sum of the mass-correction and Darwin terms. For $\ell \neq 0$, we have two terms: mass-correction, and spin-orbit. Adding them together gives,

$$\begin{aligned} E^{(1)}_{n\ell j} &= \frac{M_e c^2\alpha^4}{4n^4}\left[\frac{n\left[j(j+1) - \ell(\ell+1) - 3/4\right]}{\ell(\ell+1)(\ell+1/2)} - \frac{2n}{\ell+1/2} + \frac{3}{2}\right] \\ &= -\frac{M_e c^2\alpha^4}{4n^4}\left[n\frac{3/4 + \ell^2 + \ell - j^2 - j + 2\ell^2 + 2\ell}{\ell(\ell+1/2)(\ell+1)} - \frac{3}{2}\right] \end{aligned}$$

setting $j = \ell \pm 1/2$ gives,

$$\begin{aligned} E^{(1)}_{n\ell j} &= -\%\left[n\frac{3/4 + 3\ell^2 + 3\ell - \ell^2 \mp \ell - 1/4 - \ell \mp 1/2}{\ell(\ell+1/2)(\ell+1)} - \frac{3}{2}\right] \\ &= -\%\left[n\frac{(1\mp 1)1/2 + 2\ell^2 + (2\mp 1)\ell}{\ell(\ell+1/2)(\ell+1)} - \frac{3}{2}\right] \end{aligned}$$

for the case $j = \ell + 1/2$, this reduces to

$$\begin{aligned} E^{(1)}_{n\ell j} &= -\%\left[n\frac{2\ell^2 + \ell}{\ell(\ell+1/2))(\ell+1)} - \frac{3}{2}\right] \\ &= -\%\left[\frac{2n\ell(\ell+1/2)}{\ell(\ell+1/2)(\ell+1)} - \frac{3}{2}\right] \\ &= -\%\left[\frac{2n}{\ell+1} - \frac{3}{2}\right] \\ &= -\frac{M_e c^2\alpha^4}{4n^4}\left[\frac{2n}{j+1/2} - \frac{3}{2}\right] \end{aligned}$$

while for the case $j = \ell - 1/2$, it gives

$$\begin{aligned} E^{(1)}_{n\ell j} &= -\% \left[n \frac{2\ell^2 + 3\ell + 1}{\ell(\ell + 1/2)(\ell + 1)} - \frac{3}{2} \right] \\ &= -\% \left[\frac{2n\left(\ell^2 + \frac{3}{2}\ell + \frac{1}{2}\right)}{\ell(\ell + 1/2)(\ell + 1)} - \frac{3}{2} \right] \\ &= -\% \left[\frac{2n(\ell + 1/2)(\ell + 1)}{\ell(\ell + 1/2)(\ell + 1)} - \frac{3}{2} \right] \\ &= -\% \left[\frac{2n}{\ell} - \frac{3}{2} \right] \\ &= -\frac{M_e c^2 \alpha^4}{4n^4} \left[\frac{2n}{j + 1/2} - \frac{3}{2} \right] \end{aligned} \tag{1}$$

For $n = 1$, we have $\ell = 0$, so that $j = 1/2$. This level is shifted by

$$E^{(1)}_{1\frac{1}{2}} = -\frac{M_e c^2 \alpha^4}{8}$$

and the degeneracy of the level is $d_{1\frac{1}{2}} = 2j + 1 = 2$.

For $n = 2$, the $\ell = 0$ state corresponds to $j = 1/2$, while the $\ell = 1$ state splits into $j = 1/2$ and $j = 3/2$ levels. Because states with the same j, but different ℓ are still degenerate, we see that the $n = 2$ bare energy level splits into to fine-structure sublevels. The energy shifts are given by

$$E^{(1)}_{2\frac{1}{2}} = -\frac{5 M_e c^2 \alpha^4}{128}$$

$$E^{(1)}_{2\frac{3}{2}} = -\frac{M_e c^2 \alpha^4}{128},$$

The fine structure splitting (the splitting is easier to measure than the absolute shifts) is therefore

$$\Delta E_2 = E^{(1)}_{2\frac{3}{2}} - E^{(1)}_{2\frac{1}{2}} = \frac{M_e c^2 \alpha^4}{32}$$

The degeneracies are

$$d_{2\frac{1}{2}} = 2 \cdot (2j + 1) = 4,$$

where the extra factor 2 is the number of degenerate ℓ levels, and

$$d_{2\frac{3}{1}} = 2j + 1 = 4$$

Total number of $n = 2$ states: $4 + 4 = 8 = 2n^2$, as expected.

For $n = 3$, the $\ell = 0$ state again forms a $j = 1/2$ level, the $\ell = 1$ state splits into $j = 1/2$ and $j = 3/2$ sublevels, and the $\ell = 2$ state splits into $j = 3/2$ and $j = 5/2$ sublevels. Thus there are a total of 3 sublevels, corresponding to $j = 1/2, 3/2, 5/2$.
The fine-structure energy shifts are

$$E^{(1)}_{3\frac{1}{2}} = -\frac{M_e c^2 \alpha^4}{72}$$

$$E^{(1)}_{3\frac{3}{2}} = -\frac{M_e c^2 \alpha^4}{3 \cdot 72}$$

$$E^{(1)}_{3\frac{5}{2}} = -\frac{M_e c^2 \alpha^4}{9 \cdot 72}$$

The two fine-structure splittings are

$$\Delta E_{3,lower} = E^{(1)}_{3,\frac{3}{2}} - E^{(1)}_{3\frac{1}{2}} = \frac{2}{3}\frac{M_e c^2 \alpha^4}{72}$$

and

$$\Delta E_{3,upper} = E^{(1)}_{3\frac{5}{2}} - E^{(1)}_{3\frac{3}{2}} = \frac{2}{9}\frac{M_e c^2 \alpha^4}{72}$$

The degeneracies of the levels are

$$d_{3\frac{1}{2}} = 2 \cdot (2j + 1) = 4$$

$$d_{3\frac{3}{2}} = 2 \cdot (2j + 1) = 8$$

$$d_{3\frac{5}{2}} = 2j + 1 = 6$$

Total number of $n = 3$ states is $4 + 8 + 6 = 18 = 2n^2$.

Practice problem:
This problem will not be graded and no points will be awarded. The solution will be included with the solutions to the required problems.

DC Stark Effect to first-order for the $n = 3$ level of the hydrogen atoms: The stark shift is governed by the potential:

$$V_E = -eE_0 Z.$$

a.) List all of the degenerate $|n\ell m_\ell^{(0)}\rangle$ states in the $n = 3$ subspace. Then use the selection rules to group the levels into closed sets of coupled states.

The $n = 3$ manifold consists of nine states:
$|3,0,0\rangle$, $|3,1,-1\rangle$, $|3,1,0\rangle$, $|3,1,1\rangle$, $|3,2,-2\rangle$, $|3,2,-1\rangle$, $|3,2,0\rangle$, $|3,2,1\rangle$, and $|3,2,2\rangle$.

From the selection rule $m' = m$, we see that the $n = 3$ subspace can divided into a closed thee-state manifold, and two closed two-state manifolds. They are:
$|3,0,0\rangle \leftrightarrow |3,1,0\rangle \leftrightarrow |3,2,0\rangle$
$|3,1,1\rangle \leftrightarrow |3,2,1\rangle$
$|3,1,-1\rangle \leftrightarrow |3,2,-1\rangle$
The remaining two states do not couple with any states in the degenerate subspace:
$|2,1,2\rangle$
$|2,1,-2\rangle$

b.) Write the matrix element $\langle 3\ell m_\ell^{(0)}|Z|3\ell' m_\ell'^{(0)}\rangle$ out as an integral over r, θ, ϕ. Evaluate the integral for all transitions which obey the selection rules.

Inserting the projector $I = \int_0^\infty r dr \int_0^\pi \sin(\theta) d\theta \int_0^{2\pi} d\phi \, |r\theta\phi\rangle\langle r\theta\phi|$ gives

$$\langle 3\ell m_\ell|Z|3\ell' m'_\ell\rangle = \int_0^\infty r dr \int_0^\pi \sin(\theta) d\theta \int_0^{2\pi} d\phi \, R_{3\ell}(r) \left[Y_\ell^{m_\ell}(\theta,\phi)\right]^* r\cos\theta R_{3\ell'}(r) Y_{\ell'}^{m'_\ell}(\theta,\phi),$$

The radial wavefunction (from lecture notes) is:

$$R_{n\ell}(r) = \left[\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}\right]^{1/2} \exp\left(-\frac{r}{na_0}\right)\left(\frac{2r}{na_0}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right)$$

Letting Mathematica handle the integrals, we find the matrix-elements which satisfy these selection rules are (labeled as $z_{m_\ell,\ell,\ell'}$):
$z_{001} = \langle 3,0,0|Z|3,1,0\rangle = -3\sqrt{6}a_0$
$z_{012} = \langle 3,1,0|Z|3,2,0\rangle = -3\sqrt{3}a_0$
$z_{-112} = \langle 3,1,-1|Z|3,2,-1\rangle = -(9/2)a_0$
$z_{112} = \langle 3,1,1|Z|3,2,1\rangle = -(9/2)a_0$
from $Z^\dagger = Z$ we then know that:
$z_{010} = z_{001}^* = -3\sqrt{6}a_0$
$z_{021} = z_{012}^* = -3\sqrt{3}a_0$
$z_{-121} = z_{-112}^* = -(9/2)a_0$
$z_{121} = z_{112}^* = -(9/2)a_0$

c.) For each group in part a.) having more than one element, find the 'good' eigenstates, by diagonalizing V_E in the subspace of the states in the group.

The 'good' eigenstates for the $m_\ell = 0$ manifold are found by diagonalizing the 3×3 matrix (in basis $\{|3,0,0\rangle, |3,2,0\rangle, |3,2,0\rangle\}$):

$$V_{30} = -eE_0 \begin{pmatrix} 0 & z_{001} & 0 \\ z_{010} & 0 & z_{012} \\ 0 & z_{021} & 0 \end{pmatrix}$$

The eigenvalues of this matrix are $v_{301} = -9ea_0E_0$, $v_{3,0,2} = 0$ and $v_{3,0,3} = 9ea_0E_0$.

The corresponding eigenvectors are:

$$|3,0,1^{(0)}\rangle = \frac{1}{\sqrt{6}}\left(\sqrt{2}|3,0,0\rangle - \sqrt{3}|3,1,0\rangle + |3,2,0\rangle\right)$$

$$|3,0,2^{(0)}\rangle = \frac{1}{\sqrt{3}}\left(|3,0,0\rangle - \sqrt{2}|3,1,0\rangle\right)$$

$$|3,0,3^{(0)}\rangle = \frac{1}{\sqrt{6}}\left(\sqrt{2}|3,0,0\rangle + \sqrt{3}|3,1,0\rangle + |3,2,0\rangle\right)$$

The 'good' eigenstates for the $m_\ell = \pm 1$ manifolds are found by diagonalizing the 2×2 matrices

$$V_{3\pm1} = -eE_0 \begin{pmatrix} 0 & z_{\pm112} \\ z_{\pm121} & 0 \end{pmatrix}$$

The eigenvalues of this matrix are $v_{3,\pm1,1} = -(9/2)ea_0E_0$ and $v_{2,\pm1,2} = (9/2)ea_0E_0$.
The corresponding eigenvectors are:

$$|3,\pm1,1^{(0)}\rangle = \frac{1}{\sqrt{2}}\left(|3,1,\pm1\rangle - |3,2,\pm1\rangle\right)$$

$$|3,\pm1,2^{(0)}\rangle = \frac{1}{\sqrt{2}}\left(|3,1,\pm1\rangle + |3,2,\pm1\rangle\right)$$

In this new notation $|n, m_\ell, m^{(0)}\rangle$, where m labels the eigenstates in a given m_ℓ manifold, the remaining two 'good' eigenstates are:

$$|3,2,1^{(0)}\rangle = |3,2,2\rangle$$

$$|3,-2,1^{(0)}\rangle = |3,-2,-2\rangle$$

Because of the selection rules, the operator Z does not couple these states to either themselves, or any other states in the $n = 3$ degenerate subspace. This implies that their first-order energy shifts are zero.
Thus we have defined all 9 of the 'good' bare eigenstates $\{|n, m_\ell, m^{(0)}\rangle\}$.

d.) Give the number of distinct sublevels that the $n = 3$ level splits into. State the degeneracy of each sub-level, and list the 'good' basis states which belong to each sub-level. Include a sketch of the energy levels versus E_0.

From first-order perturbation theory and our previous results, we find that the Stark effect splits the $n = 3$ level into 5 sub-levels according to:

level shift	degeneracy	states
$9ea_0E_0$	1	$\|3, 0, 2^{(0)}\rangle$
$(9/2)ea_0E_0$	2	$\|3, -1, 2^{(0)}\rangle$, $\|3, 1, 2^{(0)}\rangle$
0	3	$\|3, -2, 1^{(0)}\rangle$, $\|3, 0, 2^{(0)}\rangle$,$\|3, 2, 1^{(0)}\rangle$
$-(9/2)a_0E_0$	2	$\|3, -1, 1^{(0)}\rangle$, $\|3, 1, 1^{(0)}\rangle$
$-9ea_0E_0$	1	$\|3, 0, 1^{(0)}\rangle$