Chem221a : Solution Set 9

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Problem 1

As always (even when a Podolsky transformation is needed), quantum operators are created by analogy with classical operators. So let's start out by calculating the classical kinetic energy in cylindrical coordinates.

There are a couple of ways of doing this. Shankar illustrates a visual way of doing it. I don't want to draw the appropriate picture here, so I'm going to instead calculate it using the chain rule.

In Cartesian coordinates, the kinetic energy is given by $T = \frac{m}{2}\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right)$. So all I need is to determine the time derivatives of the Cartesian coordinates as a function of the cylindrical coordinates (and, of course, their time derivatives).

$$\dot{x} = \dot{\rho}\cos(\theta) - \rho\sin(\theta)\dot{\theta} \tag{1}$$

$$\dot{y} = \dot{\rho}\sin(\theta) + \rho\cos(\theta)\dot{\theta} \tag{2}$$

$$\dot{z} = \dot{z} \tag{3}$$

As a brief aside, let's find the squares of the first two of those time derivatives:

$$\dot{x}^2 = \dot{\rho}^2\cos^2(\theta) + \rho^2\sin^2(\theta)\dot{\theta}^2 - 2\dot{\rho}\rho\dot{\theta}\sin(\theta)\cos(\theta) \tag{4}$$

$$\dot{y}^2 = \dot{\rho}^2\sin^2(\theta) + \rho^2\cos^2(\theta)\dot{\theta}^2 + 2\dot{\rho}\rho\dot{\theta}\sin(\theta)\cos(\theta) \tag{5}$$

So when we put all of this together to get the kinetic energy, we obtain:

$$T_{\text{classical}} = \frac{m}{2}\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right) \tag{6}$$

$$= \frac{m}{2}\left(\dot{\rho}^2 + \rho^2\dot{\theta}^2 + \dot{z}^2\right) \tag{7}$$

At this point, we ought to take a look at what we need to find in order to get the Podolsky transformation. The Podolsky transformation, as we saw it in class, is given by the formula

$$T_{\text{QM}} = \frac{1}{2}s^{-1/2}g^{1/4}\left(\sum_{i,j} p_i g^{-1/2} g_{ij} p_j\right) g^{1/4}s^{1/2} \tag{8}$$

where s is the Jacobian connecting the new coordinate system to the Cartesian coordinates, and g is the determinant of the matrix g_{ij}, defined by

$$T_{\text{classical}} = \frac{1}{2}\sum_{ij} p_i g_{ij} p_j \tag{9}$$

Note that we don't yet have our g_{ij} matrix, since we calculated the the classical kinetic energy in terms of velocities instead of in terms of momenta. To fix this, we need to find the appropriate conjugate momenta. Assuming that the potential is only dependent on the coordinates, that's easy enough to do:

$$p_\rho = \frac{\mathrm{d}}{\mathrm{d}\dot{\rho}} T_{\text{classical}} = m\dot{\rho} \qquad \Longrightarrow \qquad \dot{\rho}^2 = \frac{p_\rho^2}{m^2} \tag{10}$$

$$p_\theta = \frac{\mathrm{d}}{\mathrm{d}\dot{\theta}} T_{\text{classical}} = m\rho^2\dot{\theta} \qquad \Longrightarrow \qquad \dot{\theta}^2 = \frac{p_\theta^2}{m^2\rho^4} \tag{11}$$

$$p_z = \frac{\mathrm{d}}{\mathrm{d}\dot{z}} T_{\text{classical}} = m\dot{z} \qquad \Longrightarrow \qquad \dot{z}^2 = \frac{p_z^2}{m^2} \tag{12}$$

Plugging these back into the classical kinetic energy, we get the classical kinetic energy in terms of momenta:

$$T_{\text{classical}} = \frac{1}{2m}\left(p_\rho^2 + \frac{p_\theta^2}{\rho^2} + p_z^2\right) \tag{13}$$

Now we can identify the matrix g_{ij}. Since there are no cross terms in the classical kinetic energy expression, it is a diagonal matrix. Writing the coordinates in the order $\{\rho, \theta, z\}$, the matrix is

$$G = \begin{pmatrix} \frac{1}{m} & 0 & 0 \\ 0 & \frac{1}{m\rho^2} & 0 \\ 0 & 0 & \frac{1}{m} \end{pmatrix} \tag{14}$$

It is easy to see that its determinant is

$$g = \det(G) = \frac{1}{m^3\rho^2} \tag{15}$$

Now we need to calculate the Jacobian determinant. Many of you just "knew" the Jacobian for the transformation to cylindrical coordinates, which is okay. However, I want to take a few lines to explain how one gets the Jacobian.

The Jacobian determinant is the determinant of the Jacobian matrix (duh). The Jacobian matrix is formed by taking the derivatives of the old coordinates with repect to the new coordinates. So the s we need is given by:

$$s = \det \begin{pmatrix} \partial x/\partial\rho & \partial x/\partial\theta & \partial x/\partial z \\ \partial y/\partial\rho & \partial y/\partial\theta & \partial y/\partial z \\ \partial z/\partial\rho & \partial z/\partial\theta & \partial z/\partial z \end{pmatrix} \tag{16}$$

$$= \det \begin{pmatrix} \cos(\theta) & -\rho\sin(\theta) & 0 \\ \sin(\theta) & \rho\cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{17}$$

$$= \rho\left(\cos^2(\theta) + \sin^2(\theta)\right) = \rho \tag{18}$$

Now we have everything we need in order to determine the Podolsky transformation. Plugging

everything into equation (8):

$$T_{\mathrm{QM}} = \frac{1}{2}\rho^{-1/2}\left(\frac{1}{m^3\rho^2}\right)^{1/4}\left(\sum_{i,j} p_i \left(\frac{1}{m^3\rho^2}\right)^{-1/2} g_{ij}p_j\right)\left(\frac{1}{m^3\rho^2}\right)^{1/4}\rho^{1/2} \tag{19}$$

$$= \frac{1}{2}\rho^{-1}\left(\sum_i p_i \rho g_{ii} p_i\right) \tag{20}$$

$$= \frac{1}{2\rho}\left(p_\rho \frac{\rho}{m} p_\rho + p_\theta \frac{1}{m\rho} p_\theta + p_z \frac{\rho}{m} p_z\right) \tag{21}$$

Since a coordinate α commutes with p_β for $\beta \neq \alpha$, we end up with the following:

$$T_{\mathrm{QM}} = \frac{1}{2m}\left(\frac{1}{\rho} p_\rho \, \rho \, p_\rho + \frac{1}{\rho^2} p_\theta^2 + p_z^2\right) \tag{22}$$

Writing the momenta as differential operators (namely, $p_\alpha \doteq -i\hbar\partial/\partial\alpha$) we obtain:

$$T_{\mathrm{QM}} = -\frac{\hbar^2}{2m}\left(\frac{1}{\rho}\frac{\mathrm{d}}{\mathrm{d}\rho}\rho\frac{\mathrm{d}}{\mathrm{d}\rho} + \frac{1}{\rho^2}\frac{\mathrm{d}^2}{\mathrm{d}\theta^2} + \frac{\mathrm{d}^2}{\mathrm{d}z^2}\right) \tag{23}$$

Problem 2

For this problem, we're just looking at a particle in a sphere with the following characteristics for the system:

$$r_0 = 17 \times 10^{-10}\ \mathrm{m} \tag{24}$$

$$m = 9.11 \times 10^{-31}\ \mathrm{kg} \tag{25}$$

$$\tag{26}$$

The energy levels for the particle in a sphere are given by

$$E_{nl} = \frac{\hbar^2}{2mr_0^2}\beta_{nl}^2 = \kappa\beta_{nl}^2 \tag{27}$$

where κ is defined by the set of constants in that equation, and β_{nl} is the nth root of the lth spherical Bessel function, and is unitless.

First let's get a value for κ, and get it into our desired units (eV):

$$\kappa = \frac{\hbar^2}{2mr_0^2} \tag{28}$$

$$= \left(\frac{1.054 \times 10^{-34}\ \mathrm{J\cdot s}}{17 \times 10^{-10}\ \mathrm{m}}\right)^2 \frac{1}{9.11 \times 10^{-31}\ \mathrm{kg}} \tag{29}$$

$$= 4.22 \times 10^{-21}\ \mathrm{J} = 0.0263\ \mathrm{eV} \tag{30}$$

Now let's talk about those β_{nl}. If we're starting out in the "1s" state, then we're starting with β_{10}. It happens that the $l = 0$ spherical Bessel function is just $\sin(x)/x$, so its first zero is when $x = \pi$. Therefore, $\beta_{10} = \pi$.

The first optical transition will be to the lowest state with $l = 1$ (because a photon must impart angular momentum). However, we don't have to change n, since the function $j_1(x)$ will have a first root. There are several ways of finding that first root: look up the root in Abramowitz and Stegun, look up a formula for $j_1(x)$ (it is $(\sin(x) - x\cos(x))/x^2$) and find the root numerically, or find the root numerically with some program that knows the spherical Bessel functions. However you do it, you should find that the first root of j_1 is approximately 4.493.

This means that the energy change is

$$\Delta E = \kappa \left(\beta_{11}^2 - \beta_{10}^2\right) \tag{31}$$

$$= 0.0263 \text{ eV}(4.493^2 - \pi^2) \tag{32}$$

$$= 0.267 \text{ eV} \tag{33}$$

We see that this gives an estimate of the energy which is 2.5 times off from the experimental value. This is probably due to the crudeness of the model. The infinitely sharp walls cause the level spacing to grow much faster than realistic potential would,[1] and so it is not surprising that it would overestimate the energy.

If you really want to know more about this problem, I think it is well described in Griffiths, section 4.1.3. It might also help to review how the quantization of energy comes about in the particle in a box, since the same ideas show up in the justification for doing a root search of the spherical Bessel functions.

Problem 3

(a) This is easy enough: we just take the expression for the position operator in terms of the annihilation and creation operators, and plug it into the expression for the perturbation:

$$W = \sigma\hbar\omega \left(\frac{m\omega}{\hbar}\right)^{3/2} \left(\sqrt{\frac{\hbar}{2m\omega}}\left(a^\dagger + a\right)\right)^3 \tag{34}$$

$$= \sigma\hbar\omega \left(\frac{m\omega}{\hbar}\right)^{3/2} \left(\frac{\hbar}{2m\omega}\right)^{3/2} \left(a^\dagger + a\right)\left(a^\dagger + a\right)\left(a^\dagger + a\right) \tag{35}$$

$$= \frac{\sigma\hbar\omega}{2^{3/2}} \left(a^\dagger + a\right)\left(a^{\dagger 2} + a^\dagger a + aa^\dagger + a^2\right) \tag{36}$$

$$= \frac{\sigma\hbar\omega}{2^{3/2}} \left(a^{\dagger 3} + a^{\dagger 2}a + a^\dagger a a^\dagger + a^\dagger a^2 + aa^{\dagger 2} + aa^\dagger a + a^2 a^\dagger + a^3\right) \tag{37}$$

$$= \frac{\sigma\hbar\omega}{2^{3/2}} \left(a^{\dagger 3} + a^3 + a^\dagger N + Na^\dagger + Na + (aa^\dagger)a^\dagger + (aa^\dagger)a + a(aa^\dagger)\right) \tag{38}$$

[1] If this isn't already a part of your intuition, consider a few examples you're familiar with. The particle in a box has the most sharp walls, and the levels get further apart as you get higher up. The harmonic oscillator has infinite walls which are less sharp, and the levels are all equally spaced. The hydrogen atom has the more realistic feature that the walls are not infinite, and its energy levels get closer as quantum number increases.

Now we recall that $[a, a^\dagger] = 1$, which means that $aa^\dagger = 1 + a^\dagger a = 1 + N$. This gives us:

$$W = \frac{\sigma\hbar\omega}{2^{3/2}}\left({a^\dagger}^3 + a^3 + a^\dagger N + Na^\dagger + Na + (1+N)a^\dagger + (1+N)a + a(1+N)\right) \tag{39}$$

$$= \frac{\sigma\hbar\omega}{2^{3/2}}\left({a^\dagger}^3 + a^3 + a^\dagger N + Na^\dagger + Na + a^\dagger + Na^\dagger + 2a + Na + aN\right) \tag{40}$$

$$= \frac{\sigma\hbar\omega}{2^{3/2}}\left({a^\dagger}^3 + a^3 + 2Na^\dagger + 2Na + 2a + a^\dagger N + a^\dagger + aN\right) \tag{41}$$

Another commutation relation will help us get to the end. As you may remember, in general a raising operator $a^\dagger$ for a number operator N satisfies the relation $[N, a^\dagger] = a^\dagger$ (for the lowering operator, it is $[N, a] = -a$). These give us the relations:

$$aN = Na + a \tag{42}$$

$$a^\dagger N = Na^\dagger - a^\dagger \tag{43}$$

Plugging into our equation for W:

$$W = \frac{\sigma\hbar\omega}{2^{3/2}}\left({a^\dagger}^3 + a^3 + 2Na^\dagger + 2Na + 2a + Na^\dagger - a^\dagger + a^\dagger + Na + a\right) \tag{44}$$

$$= \frac{\sigma\hbar\omega}{2^{3/2}}\left({a^\dagger}^3 + a^3 + 3Na^\dagger + 3(N+1)a\right) \quad \square \tag{45}$$

(b) We're to find the energy to second order. Remember that this is not the same as the second order correction to the energy: the energy to second order includes the zeroth order energy, as well as the first and second order corrections.

We already know the zeroth order energy: that's the energy of the unperturbed harmonic oscillator: $E^{(0)} = \hbar\omega\left(n + \frac{1}{2}\right)$. It's also very easy to determine the first order correction. As we can see from equation (45), all terms in the perturbation involve either only raising operators or only lowering operators. This means that after operating on the ket $|n\rangle$, the result has no components which will have a nonzero overlap with the bra $\langle n|$. Therefore, the expectation value $\langle n|W|n\rangle$ (which is the first order energy correction) is zero.

So all we have to calculate is the second order energy correction. It is given by

$$E^{(2)} = \sum_{p \neq n} \frac{|\langle p|W|n\rangle|^2}{E_p^{(0)} - E_n^{(0)}} \tag{46}$$

We'll begin by calculating the matrix element $\langle p|W|n\rangle$ (because we'll also use that when

calculating the wavefunction in part (c)).

$$\langle p|W|n\rangle = \left\langle p\left|\frac{\sigma\hbar\omega}{2^{3/2}}\left(a^{\dagger 3}+a^3+3Na^\dagger+3(N+1)a\right)\right|n\right\rangle \tag{47}$$

$$= \frac{\sigma\hbar\omega}{2^{3/2}}\left(\sqrt{\frac{(n+3)!}{n!}}\delta_{p,n+3}+\sqrt{\frac{n!}{(n-3)!}}\delta_{p,n-3}+3(n+1)\sqrt{n+1}\delta_{p,n+1}\right.$$

$$\left.+3(n-1)\sqrt{n}\delta_{p,n-1}+3\sqrt{n}\delta_{p,n-1}\right) \tag{48}$$

$$= \frac{\sigma\hbar\omega}{2^{3/2}}\left(\sqrt{\frac{(n+3)!}{n!}}\delta_{p,n+3}+\sqrt{\frac{n!}{(n-3)!}}\delta_{p,n-3}+3(n+1)^{3/2}\delta_{p,n+1}+3n^{3/2}\delta_{n,p-1}\right) \tag{49}$$

When we square those matrix elements, we see that the Kronecker deltas from cross terms will contradict each other, so only the squares of each term remain. Plugging this into our expression for the second order correction, and remembering that $E_p^{(0)}-E_n^{(0)}=\hbar\omega(p-n)$ for the harmonic oscillator, we obtain

$$E^{(2)} = \frac{\sigma^2\hbar^2\omega^2}{8}\left(\frac{(n+3)(n+2)(n+1)}{-3\hbar\omega}+\frac{n(n-1)(n-2)}{3\hbar\omega}+\frac{9(n+1)^2}{-\hbar\omega}+\frac{9n^3}{\hbar\omega}\right) \tag{50}$$

$$= -\frac{\sigma^2\hbar\omega}{8}\left(\frac{1}{3}\left((n^3+6n^2+11n+6)-(n^3-3n^2+2n)\right)+9\left((n^3+3n^2+3n+1)-(n^3)\right)\right) \tag{51}$$

$$= -\frac{\sigma^2\hbar\omega}{8}\left(\frac{1}{3}\left(9n^2+9n+6\right)+9\left(3n^2+3n+1\right)\right) \tag{52}$$

$$= -\frac{\sigma^2\hbar\omega}{8}\left(30n^2+30n+11\right) \tag{53}$$

$$= -\sigma^2\hbar\omega\frac{15}{4}\left(n^2+n+\frac{11}{30}\right) \tag{54}$$

Now we just complete the square:

$$E^{(2)} = -\sigma^2\hbar\omega\frac{15}{4}\left(n^2+n+\frac{1}{4}+\frac{11}{30}-\frac{1}{4}\right) \tag{55}$$

$$= -\sigma^2\hbar\omega\frac{15}{4}\left(\left(n+\frac{1}{2}\right)^2+\frac{22}{60}-\frac{15}{60}\right) \tag{56}$$

$$= -\sigma^2\hbar\omega\frac{15}{4}\left(\left(n+\frac{1}{2}\right)^2+\frac{7}{60}\right) \tag{57}$$

$$= -\sigma^2\hbar\omega\left(\frac{15}{4}\left(n+\frac{1}{2}\right)^2+\frac{7}{16}\right) \tag{58}$$

With that as our correction, and the standard harmonic oscillator $E=\hbar\omega\left(n+\frac{1}{2}\right)$ as our

unperturbed energy, the total energy to second order is:

$$E_n = E^{(0)} + E^{(1)} + E^{(2)} \tag{59}$$

$$= \hbar\omega\left(n+\frac{1}{2}\right) + 0 - \sigma^2\hbar\omega\left(\frac{15}{4}\left(n+\frac{1}{2}\right)^2 + \frac{7}{16}\right) \tag{60}$$

$$= \left(n+\frac{1}{2}\right)\hbar\omega - \frac{15}{4}\sigma^2\left(n+\frac{1}{2}\right)^2\hbar\omega - \frac{7}{16}\sigma^2\hbar\omega \tag{61}$$

(c) Most of what we need for this one was calculated in the previous part. In fact, it would probably have made more sense to calculate the first order correction to the wavefunction before calculating the second order correction to the energy. But whatever, we'll just reuse the relevant parts of the previous part.

The first order correction to the wavefunction is:

$$\left|\psi_n^{(1)}\right\rangle = \sum_{p\neq n}\frac{\langle p|W|n\rangle}{E_p^{(0)} - E_n^{(0)}}\left|p\right\rangle \tag{62}$$

$$= \frac{\sigma\hbar\omega}{2^{3/2}}\left(\sqrt{\frac{(n+3)!}{n!}}\frac{1}{-3\hbar\omega}\left|n+3\right\rangle + \sqrt{\frac{n!}{(n-3)!}}\frac{1}{3\hbar\omega} + 3(n+1)^{3/2}\left|n+1\right\rangle + 3n^{3/2}\left|n-1\right\rangle\right) \tag{63}$$

$$= -\sigma\left(\frac{1}{3}\sqrt{\frac{(n+3)(n+2)(n+1)}{8}}\left|n+3\right\rangle - \frac{1}{3}\sqrt{\frac{n(n-1)(n-2)}{8}}\left|n-3\right\rangle \right.$$
$$\left. + 3\left(\frac{n+1}{2}\right)^{3/2}\left|n+1\right\rangle - 3\left(\frac{n-1}{2}\right)^{3/2}\left|n-1\right\rangle\right) \tag{64}$$

The state to first order is just the unperturbed state, $|n\rangle$, plus the first order correction:

$$|\psi_n\rangle = |n\rangle + \left|\psi_n^{(1)}\right\rangle \tag{65}$$

$$= |n\rangle - 3\sigma\left(\frac{n+1}{2}\right)^{3/2}|n+1\rangle + 3\sigma\left(\frac{n}{2}\right)^{3/2}|n-1\rangle$$
$$- \frac{\sigma}{3}\left(\frac{(n+3)(n+2)(n+1)}{8}\right)^{1/2}|n+3\rangle + \frac{\sigma}{3}\left(\frac{n(n-1)(n-2)}{8}\right)^{1/2}|n-3\rangle \tag{66}$$

That's what we were to show.

Problem 4

The trick in this problem is to get the right perturbation. The trick to that is remembering how we got the rigid rotor approximation in the first place.

Assuming that we've "exactly" represented the vibrational motion as a harmonic oscillator, the Hamiltonian is

$$H = T + \frac{1}{2}k(r-r_e)^2 + \frac{\hbar^2 J(J+1)}{2\mu r^2} \tag{67}$$

The second term in this gives us the potential due to rotation at a given internuclear separation r. We expand this in a Taylor series about r_e:

$$\frac{\hbar^2 J(J+1)}{2\mu r^2} \sim \frac{\hbar^2 J(J+1)}{2\mu r_e^2} - \left.\frac{\hbar^2 J(J+1)}{\mu r^3}\right|_{r_e} (r - r_e) + O\left((r-r_e)^2\right) \tag{68}$$

$$\sim \frac{\hbar^2 J(J+1)}{2\mu r_e^2} - \frac{\hbar^2 J(J+1)}{\mu r_e^3}(r - r_e) \tag{69}$$

The first term in this expansion gives us the rigid rotor approximation. The second term will be our perturbation for this problem.

Switching from using the coordinate r to the coordinate q, we have the Hamiltonian (including perturbation) as:

$$H = T + \frac{1}{2}kq^2 + \frac{\hbar^2 J(J+1)}{2\mu r_e^2} - \frac{\hbar^2 J(J+1)}{\mu r_e^3} q \tag{70}$$

The first three terms are H_{RRHO}, and form our exact Hamiltonian, with energy $E = \left(n + \frac{1}{2}\right)\hbar\omega + \frac{\hbar^2 J(J+1)}{2\mu r_e^2}$ and eigenstates $|n, J, m\rangle$ – the product of the harmonic oscillator states $|n\rangle$ and the spherical harmonic states $|J, m\rangle$. The last term is our perturbation.

It's pretty easy to show that first order perturbation theory gives a correction of zero for this perturbation:

$$E^{(1)} = \left\langle n \middle| \frac{\hbar^2 J(J+1)}{2\mu r_e^3} q \middle| n \right\rangle \tag{71}$$

$$= \frac{\hbar^2 J(J+1)}{2\mu r_e^3} \sqrt{\frac{\hbar}{2\mu\omega}} \left\langle n \middle| a^\dagger + a \right\rangle n \tag{72}$$

$$= 0 \tag{73}$$

The raising and lowering operators prevent the bra from having any overlap with the resulting ket.

Now let's try taking this thing to second order. In that case, we have

$$E^{(2)} = \sum_{p \neq n} \frac{|\langle p|W|n\rangle|^2}{E_p^{(0)} - E_n^{(0)}} \tag{74}$$

We'll start out by calculating the matrix elements:

$$\left\langle p \middle| \frac{-\hbar^2 J(J+1)}{2\mu r_e^3} q \middle| n \right\rangle = -\frac{\hbar^2 J(J+1)}{2\mu r_e^3} \sqrt{\frac{\hbar}{2\mu\omega}} \left\langle p \middle| a^\dagger + a \middle| n \right\rangle \tag{75}$$

$$= -\frac{\hbar^2 J(J+1)}{2\mu r_e^3} \sqrt{\frac{\hbar}{2\mu\omega}} \left(\sqrt{n+1}\delta_{p,n+1} + \sqrt{n}\delta_{p,n-1}\right) \tag{76}$$

Plugging that (and the fact that the energy spacing is $\hbar\omega$) into the equation for the second order

correction:

$$E^{(2)} = \frac{\hbar^4 J^2(J+1)^2}{\mu^2 r_e^6} \frac{\hbar}{2\mu\omega} \left(-\frac{n+1}{\hbar\omega} + \frac{n}{\hbar\omega} \right) \tag{77}$$

$$= -\frac{\hbar^4}{2\mu^3 r_e^6 \omega^2} J^2(J+1)^2 \tag{78}$$

$$= -\frac{\hbar^6}{8\mu^3 r_e^6} \frac{4}{\hbar^2\omega^2} J^2(J+1)^2 \tag{79}$$

$$= -B_e^3 \frac{4}{\hbar^2\omega^2} J^2(J+1)^2 \tag{80}$$

$$= -DJ^2(J+1) \tag{81}$$

Problem 5

For a hydrogen atom with $n = 3$, we have a total of 9 states: 1 s state, 3 p states, and 5 d states. That lists the states according with the value of l. We can also organize them according to the value of m: we have 3 $m = 0$ states (s, p, d), 2 each of $m = \pm 1$ (p, d), and 1 each of $m = \pm 2$ (d).

Since the Stark effect has effective selection rules which determine which states are coupled, we'll use these to our advantage. In particular, we have the $\Delta m = 0$, which means that we'll organize our states according to their values of m, and $\Delta l = \pm 1$, which will make a lot of the remaining matrix elements zero.

The matrix for the perturbation will be block diagonal when organized by m, due to the $\Delta m = 0$ rule. So we have 1×1 blocks for $m = \pm 2$. However, those blocks cannot satisfy the $\Delta l = \pm 1$ selection rule, so they are zero.

We have 2×2 blocks for $m = \pm 1$. Labelling the kets in the order $\{|3,1,m\rangle, |3,2,m\rangle\}$, we have the matrices:

$$A_{-1} = \begin{pmatrix} 0 & \alpha_{12} \\ \alpha_{21} & 0 \end{pmatrix} \qquad B_{+1} = \begin{pmatrix} 0 & \beta_{12} \\ \beta_{21} & 0 \end{pmatrix} \tag{82}$$

where the elements marked as zero are the ones that don't satisfy the $\Delta l = \pm 1$ selection rule.

Finally we'll prepare the matrix for the $m = 0$ subspace, which is a 3×3 block. We'll write the kets in the order $\{|3,0,0\rangle, |3,1,0\rangle, |3,2,0\rangle\}$, and again anything which violates the $\Delta l = \pm 1$ selection rule will be zero:

$$C_0 = \begin{pmatrix} 0 & \gamma_{01} & 0 \\ \gamma_{10} & 0 & \gamma_{12} \\ 0 & \gamma_{21} & 0 \end{pmatrix} \tag{83}$$

Since these matrices must be Hermitian, we know that $X_{ij} = X_{ji}^*$, so we only need to calculate 4 of our 8 nonzero elements. Let's do that, choosing the elements labelled α_{12}, β_{12}, γ_{01}, and γ_{21} above. To get these integrals, we'll just need the recursion relation for spherical harmonics (derived on a previous problem set) and the following integral:

$$\int_{\mathbb{R}_+} \mathrm{d}x\, x^n e^{-\alpha x} = \frac{n!}{\alpha^{n+1}} \tag{84}$$

when n is an integer (this formula can be derived using integration by parts or found — and massaged into useful forms — from a table of integrals).

$$\begin{aligned}
\alpha_{12} &= \langle 3,1,-1|W|3,2,1\rangle && (85)\\
&= |\mu|\, E_0 \,\langle 3,1,-1|r\cos(\theta)|3,2,-1\rangle && (86)\\
&= |\mu|\, E_0 \left\langle R_{31}\ Y_1^{-1}\middle|r\cos(\theta)\middle|R_{32}\ Y_2^{-1}\right\rangle && (87)\\
&= |\mu|\, E_0 \,\langle R_{31}|r|R_{32}\rangle \left\langle Y_1^{-1}\middle|\cos(\theta)\middle|Y_2^{-1}\right\rangle && (88)\\
&= |\mu|\, E_0 \,\langle R_{31}|r|R_{32}\rangle \left\langle Y_1^{-1}\middle|\left(\sqrt{\frac{2^2-1}{4(2)^2-1}}\middle|Y_1^{-1}\right\rangle + \sqrt{\frac{3^2-1}{4(3)^2-1}}\middle|Y_3^{-1}\right\rangle\right) && (89)\\
&= \frac{|\mu|\, E_0}{\sqrt{5}} \,\langle R_{31}|r|R_{32}\rangle && (90)\\
&= \frac{|\mu|\, E_0}{\sqrt{5}} \int_{\mathbb{R}_+} r^2 R_{31}(r) r R_{32}(r) && (91)\\
&= \frac{|\mu|\, E_0}{\sqrt{5}} \int_{\mathbb{R}_+} r^3 \left(\frac{8}{27\sqrt{6{a_0}^3}}\left(1-\frac{r}{6a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\right)\left(\frac{4}{81\sqrt{30{a_0}^3}}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}\right) && (92)\\
&= \frac{|\mu|\, E_0}{5}\frac{2^4}{3^8}\frac{1}{{a_0}^6}\int_{\mathbb{R}_+} \mathrm{d}r\, r^6\left(1-\frac{r}{6a_0}\right)e^{-2r/3a_0} && (93)\\
&= \frac{|\mu|\, E_0}{5}\frac{2^4}{3^8}\frac{1}{{a_0}^6}\left(\int_{\mathbb{R}_+} \mathrm{d}r\, r^6 e^{-2r/3a_0} - \frac{1}{6a_0}\int_{\mathbb{R}_+} \mathrm{d}r\, r^7 e^{-2r/3a_0}\right) && (94)\\
&= \frac{|\mu|\, E_0}{5}\frac{2^4}{3^8}\frac{1}{{a_0}^6}\left(\frac{6!}{(2/3a_0)^7} - \frac{1}{6a_0}\frac{7!}{(2/3a_0)^8}\right) && (95)\\
&= \frac{|\mu|\, E_0}{5}\frac{2^4}{3^8}\frac{1}{{a_0}^6}{a_0}^7\frac{3^7}{2^7}6!\left(1-\frac{7}{4}\right) && (96)\\
&= |\mu|\, E_0 a_0 3\cdot 2\left(-\frac{3}{4}\right) && (97)\\
&= -\,|\mu|\, E_0 a_0 \frac{9}{2} && (98)
\end{aligned}$$

We actually don't even have to calculate β_{12}: since the value of m only comes in as the square, it will be the same as α_{12}.

Now to calculate the ugliest of these:

$$\gamma_{01} = |\mu|\, E_0 \,\langle R_{30}|r|R_{31}\rangle \,\langle Y_0^0|\cos(\theta)|Y_1^0\rangle \tag{99}$$

$$= |\mu|\, E_0 \,\langle R_{30}|r|R_{31}\rangle \left\langle Y_0^0 \middle| \left(\sqrt{\frac{1-0}{4-1}} \middle| Y_0^0 \right\rangle + \sqrt{\frac{2^2-0}{4(2)^2-1}} \middle| Y_2^0 \right\rangle \right) \tag{100}$$

$$= \frac{|\mu|\, E_0}{\sqrt{3}} \,\langle R_{30}|r|R_{31}\rangle \tag{101}$$

$$= \frac{|\mu|\, E_0}{\sqrt{3}} \int_{\mathbb{R}_+} \mathrm{d}r\, r^3 \left(\frac{2}{\sqrt{27{a_0}^3}} \left(1 - \frac{2r}{3a_0} + \frac{2}{27} \left(\frac{r}{a_0} \right)^2 \right) e^{-2/3a_0} \right) \left(\frac{8}{27\sqrt{6{a_0}^3}} \left(1 - \frac{r}{6a_0} \right) \frac{r}{a_0} e^{-r/3a_0} \right) \tag{102}$$

$$= \frac{|\mu|\, E_0}{\sqrt{6}{a_0}^4} \frac{2^4}{3^5} \int_{\mathbb{R}_+} \mathrm{d}r\, r^4 \left(1 - \frac{2r}{3a_0} + \frac{2}{27} \left(\frac{r}{a_0} \right)^2 \right) \left(1 - \frac{r}{6a_0} \right) e^{-2r/3a_0} \tag{103}$$

$$= \frac{|\mu|\, E_0}{\sqrt{6}{a_0}^4} \frac{2^4}{3^5} \int_{\mathbb{R}_+} \mathrm{d}r\, r^4 \left(1 - \frac{5r}{6a_0} + \frac{5}{27} \left(\frac{r}{a_0} \right)^2 - \frac{1}{3^4} \left(\frac{r}{a_0} \right)^3 \right) e^{-2r/3a_0} \tag{104}$$

$$= \frac{|\mu|\, E_0}{\sqrt{6}{a_0}^4} \frac{2^4}{3^5} \left(\int_{\mathbb{R}_+} \mathrm{d}r\, r^4 e^{-2r/3a_0} - \frac{5}{6a_0} \int_{\mathbb{R}_+} \mathrm{d}r\, r^5 e^{-2r/3a_0} + \frac{5}{27{a_0}^2} \int_{\mathbb{R}_+} \mathrm{d}r\, r^6 e^{-2r/3a_0} \right.$$
$$\left. - \frac{1}{81{a_0}^3} \int_{\mathbb{R}_+} \mathrm{d}r\, r^7 e^{-2r/3a_0} \right) \tag{105}$$

$$= \frac{|\mu|\, E_0}{\sqrt{6}{a_0}^4} \frac{2^4}{3^5} \left(\frac{4!}{(2/3a_0)^5} - \frac{5}{6a_0} \frac{5!}{(2/3a_0)^6} + \frac{5}{27{a_0}^2} \frac{6!}{(2/3a_0)^7} - \frac{1}{81{a_0}^3} \frac{7!}{(2/3a_0)^8} \right) \tag{106}$$

$$= \frac{|\mu|\, E_0}{\sqrt{6}{a_0}^4} \frac{2^4}{3^5} 3 \cdot 2^3 {a_0}^5 \frac{3^5}{2^5} \left(1 - \frac{25}{6} \frac{3}{2} + \frac{25 \cdot 6}{27} \frac{3^2}{2^2} - \frac{(5)(6)(7)}{81} \frac{3^3}{2^3} \right) \tag{107}$$

$$= \frac{|\mu|\, E_0 a_0}{\sqrt{6}} 3 \cdot 2^2 \left(1 - \frac{25}{4} + \frac{25}{2} - \frac{35}{4} \right) \tag{108}$$

$$= -3\,|\mu|\, E_0 a_0 \sqrt{6} \tag{109}$$

The only calculation left is for γ_{21}, but it is a little easier. Looking at equation (100), we see that we can replace the bra as appropriate and this time we'll keep the second term in the angular integral instead of the first term. So we get

$$\gamma_{21} = \frac{2}{\sqrt{3}} \frac{|\mu|\, E_0}{\sqrt{5}} \,\langle R_{32}|r|R_{31}\rangle \tag{110}$$

However, the radial wavefunctions are real, so the integral to be calculated is the one we calculated for α_{12}. The result gives us

$$\gamma_{21} = \frac{2}{\sqrt{3}} \left(-\,|\mu|\, E_0 a_0 \frac{9}{2} \right) \tag{111}$$

$$= -\,|\mu|\, E_0 a_0 3\sqrt{3} \tag{112}$$

With all that done, the trick to finding the energy level shifts for these perturbations is to diagonalize the matrix. So let's do it, block by block.

The blocks associated with $m = \pm 2$ are trivial: they don't correspond to a shift.

The blocks associated with $m = \pm 1$ should be pretty familiar by now:

$$A_{-1} = B_{+1} = \begin{pmatrix} 0 & -a \\ -a & 0 \end{pmatrix} \tag{113}$$

with $a = 9\,|\mu|\,E_0 a_0/2$. The eigenvalues are $\pm a$, with eigenvectors:

$$\left\{ |-9\,|\mu|\,E_0 a_0/2\rangle \doteq \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} |+9\,|\mu|\,E_0 a_0/2\rangle \doteq \begin{pmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix} \right\} \tag{114}$$

The block with $m = 0$ is given by the matrix

$$C_0 = 3\sqrt{3}\,|\mu|\,E_0 a_0 \begin{pmatrix} 0 & -\sqrt{2} & 0 \\ -\sqrt{2} & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} \tag{115}$$

Letting $a = 3\sqrt{3}\,|\mu|\,E_0 a_0$, the eigenvalues are determined by

$$0 = \det \begin{pmatrix} \lambda & \sqrt{2}a & 0 \\ \sqrt{2}a & \lambda & a \\ 0 & a & \lambda \end{pmatrix} \tag{116}$$

$$= \lambda^3 - 3a^2\lambda = \lambda(\lambda - a\sqrt{3})(\lambda + a\sqrt{3}) \tag{117}$$

giving the values of 0, $a\sqrt{3}$, and $-a\sqrt{3}$.

Let's find some eigenvectors. For eigenvalue 0:

$$x_2 = 0 \tag{118}$$

$$x_3 = -\sqrt{2}x_1 \tag{119}$$

So the normalized eigenvector is:

$$|0\rangle = \begin{pmatrix} \sqrt{1/3} \\ 0 \\ -\sqrt{2/3} \end{pmatrix} \tag{120}$$

For eigenvalue $+a\sqrt{3}$:

$$x_2 = -\sqrt{\frac{3}{2}}x_1 \tag{121}$$

$$x_3 = -\sqrt{\frac{1}{3}}x_2 = \left(-\sqrt{\frac{1}{3}}\right)\left(-\sqrt{\frac{3}{2}}x_1\right) \tag{122}$$

$$= \sqrt{\frac{1}{2}}x_1 \tag{123}$$

resulting in the normalized eigenvector

$$|9\,|\mu|\,E_0 a_0\rangle = \begin{pmatrix} \sqrt{1/3} \\ -\sqrt{1/2} \\ \sqrt{1/6} \end{pmatrix} \tag{124}$$

Finally, eigenvalue $-a\sqrt{3}$:

$$x_2 = \sqrt{\frac{3}{2}}x_1 \tag{125}$$

$$x_3 = \sqrt{\frac{1}{3}}x_2 = \sqrt{\frac{1}{2}}x_1 \tag{126}$$

with normalized eigenvector

$$|-9\,|\mu|\,E_0 a_0\rangle = \begin{pmatrix} \sqrt{1/3} \\ \sqrt{1/2} \\ \sqrt{1/6} \end{pmatrix} \tag{127}$$

That gives you the main idea — if I have a chance, I'll come back to draw the energy level diagram. Note that it can by drawn to scale by using energy in units of $|mu|\,E_0 a_0$.

Problem 6

. . . coming soon . . .