Homework 3: #'s 5.13, 5.14, 5.17, 5.20, 5.21

Michael Good

Feb 20, 2005

Problem 5.13
Compute the Stark effect for the $2S_{1/2}$ and $2P_{1/2}$ levels of hydrogen for a field ϵ sufficiently weak so that $e\epsilon a_0$ is small compared to the fine structure, but take the Lamb shift δ ($\delta = 1057$MHz) into account (that is, ignore $2P_{3/2}$ in this calculation). Show that for $e\epsilon a_0 \ll \delta$, the energy shifts are quadratic in ϵ, whereas for $e\epsilon a_0 \gg \delta$ they are linear in ϵ. (The radial integral is $\langle 2s|r|2pra = 3\sqrt{3}a_0$.) Briefly discuss the consequences if any of time reversal for this problem.

Solution:

We are looking to diagonalize the perturbation matrix. The Hamiltonian is $H = H_0 + e\epsilon z$. I know from parity that

$$\langle 2s|z|2p\rangle = \langle 2p|z|2s\rangle = 0$$

Including the lamb shift, δ, and recognizing $\langle 2p|H_\delta|2p\rangle = 0$ for the lamb shift elements, we may construct the perturbation matrix. Using the ever popular equation (3.7.64) in Sakurai and the radial integral given in the problem, the elements for the perturbation can be found.

$$|2s_{1/2}\ m = +1/2\rangle = R_{20}Y_0^0 \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad |2s_{1/2}\ m = -1/2\rangle = R_{20}Y_0^0 \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The $2p$ states are:

$$|2p_{1/2}\ m = +1/2\rangle = R_{21}\frac{1}{\sqrt{3}} \begin{pmatrix} -Y_1^0 \\ \sqrt{2}Y_1^1 \end{pmatrix}$$

$$|2p_{1/2}\ m = -1/2\rangle = R_{21}\frac{1}{\sqrt{3}} \begin{pmatrix} -\sqrt{2}Y_1^{-1} \\ Y_1^0 \end{pmatrix}$$

Where I used equation (5.3.8):

$$\psi_{nlm} = R_{nl}\mathcal{Y}_l^{j=l\pm\frac{1}{2},m}$$

Sandwiching them together yields, (using the radial integral) and some calculus

$$\langle 2s_{1/2}m = \pm 1/2|V|2p_{1/2}m = \pm 1/2\rangle = \pm\sqrt{3}e\epsilon a_0$$

My perturbation matrix can be:

$$V = \begin{pmatrix} \delta & \sqrt{3}e\epsilon a_0 \\ \sqrt{3}e\epsilon a_0 & 0 \end{pmatrix}$$

Therefore

$$\begin{vmatrix} \delta - \lambda & \sqrt{3}e\epsilon a_0 \\ \sqrt{3}e\epsilon a_0 & -\lambda \end{vmatrix} = 0$$

the eigenvalue equation is:

$$\lambda = \frac{\delta \pm \sqrt{\delta^2 - 4(-3e^2\epsilon^2 a_0^2)}}{2}$$

$$\lambda = \frac{\delta}{2} \pm \sqrt{\frac{\delta^2}{4} + 3e^2\epsilon^2 a_0^2}$$

These are the shifts. Let me show that for $e\epsilon a_0 \ll \delta$ the energy shifts are quadratic. If

$$e\epsilon a_0 \ll \delta$$

then the shifts become

$$\Delta_\pm = \frac{\delta}{2} \pm \frac{\delta}{2}\sqrt{1 + \frac{12e^2\epsilon^2 a_0^2}{\delta^2}}$$

$$\Delta_\pm \approx \frac{\delta}{2} \pm \frac{\delta}{2}[1 + \frac{1}{2}\frac{12e^2\epsilon^2 a_0^2}{\delta^2}]$$

$$\Delta_\pm = \frac{\delta}{2} \pm [\frac{\delta}{2} + \frac{3e^2\epsilon^2 a_0^2}{\delta}]$$

So we have the shifts being quadratic in ϵ:

$$\Delta_+ = \delta + \frac{3e^2\epsilon^2 a_0^2}{\delta} \qquad \Delta_- = -\frac{3e^2\epsilon^2 a_0^2}{\delta}$$

Now let me show that for $e\epsilon a_0 \gg \delta$ the energy shifts are linear. If

$$e\epsilon a_0 \gg \delta$$

then the shifts become

$$\Delta_\pm = \frac{\delta}{2} \pm \sqrt{\frac{\delta^2}{4} + 3e^2\epsilon^2 a_0^2}$$

$$\Delta_\pm \approx \frac{\delta}{2} \pm \sqrt{3e^2\epsilon^2 a_0^2}$$

and we the shifts being linear in ϵ:

$$\Delta_+ = \frac{\delta}{2} + \sqrt{3}e\epsilon a_0 \qquad \Delta_- = \frac{\delta}{2} - \sqrt{3}e\epsilon a_0$$

Time reversal invariance does not restrict the Hamiltonian as parity conservation did.

Problem 5.14
Work out the Stark effect to lowest non vanishing order for the $n = 3$ level of the hydrogen atom. Ignoring the spin-orbit force and relativistic correction (Lamb shift), obtain not only the energy shifts to lowest non vanishing order but also the corresponding zeroth-order eigenket.

Solution:

This problem is very similar to problem 6.32 in Griffiths. We have 9 states. Thus we are going to end up having a huge $9x9$ matrix. The states are

$$l = 0: \ |300\rangle = R_{30}Y_0^0$$

and

$$l = 1: \ |311\rangle = R_{31}Y_1^1 \quad |310\rangle = R_{31}Y_1^0 \quad |31-1\rangle = R_{31}Y_1^{-1}$$

and

$$l = 2: \ |322\rangle = R_{32}Y_2^2 \quad |321\rangle = R_{32}Y_2^1 \quad |320\rangle = R_{32}Y_2^0 \quad |32{-}1\rangle = R_{32}Y_2^{-1} \quad |32{-}2\rangle = R_{32}Y_2^{-2}$$

Using formula (5.1.65) saves a great deal of time, (which I had to learn the hard way). It says:

$$\langle 3l'm'|z|3lm\rangle = 0$$

unless $m = m'$, $l' = l \pm 1$. This means that the huge $9x9$ matrix will have zero's on the diagonal. There will also be zeros everywhere else except in three cases. Those are:

$$\boxed{\langle 300|z|310\rangle \neq 0} \qquad \boxed{\langle 310|z|320\rangle \neq 0}$$

where $m = m' = 0$.(I am excluding the tricky one, $\langle 300|z|320\rangle$ because $l' \neq l \pm 1$) and

$$\boxed{\langle 31 \pm 1|z|32 \pm 1\rangle \neq 0}$$

where $m = m' = \pm 1$. The majority of this problem is evaluating these three values. After plugging them in to the huge $9x9$ matrix, we can just diagonalize each subspace to find the shifts and eigenstates. So let's begin taking integrals.

- First value:

$$\langle 300| - e\epsilon z|310\rangle = -e\epsilon \int R_{30}R_{31}r^3\ dr \int Y_0^0 Y_1^0 \cos\theta \sin\theta d\theta d\phi$$

In these integrals I'm pulling the values from Griffith's tables, 4.2 and 4.6.

$$\int R_{30}R_{31}r^3\ dr = \int \frac{2}{\sqrt{27}}a^{-3/2}(1 - \frac{2}{3}\frac{r}{a} + \frac{2}{27}(\frac{r}{a})^2)e^{-r/3a}\ \frac{8}{27\sqrt{6}}a^{-3/2}(1 - \frac{r}{6a})(\frac{r}{a})e^{-r/3a}r^3\ dr$$

Now it's time to watch our algebra, as you can see. To do this integral(and the other integrals in the rest of the problem) more simply, introduce these substitutions.

$$x = \frac{2}{3}\frac{r}{a} \quad dx = \frac{2}{3a}dr \quad \frac{3}{2}x = \frac{r}{a} \quad \frac{3a}{2}x = r \quad dr = \frac{3a}{2}dx$$

Now you can just plug these in like you're a machine and then turn your own crank.

$$\int R_{30}R_{31}r^3\ dr = \int \frac{2}{\sqrt{27}}a^{-3/2}[1 - x + \frac{2}{27}(\frac{3}{2})^2x^2]e^{-x}\ \frac{8}{27\sqrt{6}}a^{-3/2}(1 - \frac{1}{6}\frac{3}{2}x)(\frac{3}{2}x)(\frac{3}{2}a)^3x^3\frac{3a}{2}\ dx$$

$$\int R_{30}R_{31}r^3\ dr = \frac{9a}{2\sqrt{27}\sqrt{6}}\int [1 - x + \frac{x^2}{6}](1 - \frac{x}{4})x^4e^{-x}\ dx$$

$$\int R_{30}R_{31}r^3\ dr = \frac{a}{2\sqrt{2}}\int [1 - \frac{5}{4}x + \frac{5}{12}x^2 - \frac{1}{24}x^3]x^4e^{-x}\ dx$$

Using the integral given in problem 5.20, which I'll use for all the rest of the problem, I obtain:

$$\int R_{30}R_{31}r^3\ dr = \frac{a}{2\sqrt{2}} = \frac{a}{2\sqrt{2}}[4! - \frac{5}{4}5! + \frac{5}{12}6! - \frac{1}{24}7!]$$

$$\int R_{30}R_{31}r^3\ dr = \frac{a}{2\sqrt{2}} = \frac{a}{2\sqrt{2}}[-36]$$

$$\int R_{30}R_{31}r^3\ dr = \frac{a}{2\sqrt{2}} = \boxed{-9\sqrt{2}a}$$

Now for this one:

$$\int Y_0^0 Y_1^0 \cos\theta \sin\theta d\theta d\phi = \frac{1}{\sqrt{4\pi}}\frac{\sqrt{3}}{\sqrt{4\pi}}\int \cos^2\theta \sin\theta d\theta d\phi$$

$$= \frac{\sqrt{3}}{4\pi}\int_0^{2\pi}\int_0^{\pi} \cos^2\theta \sin\theta d\theta d\phi$$

$$= \frac{\sqrt{3}}{2}\int_0^\pi \cos^2\theta \sin\theta d\theta$$

by a quick u substitution if you need it:

$$= \frac{\sqrt{3}}{2}[\frac{2}{3}]$$

$$\int Y_0^0 Y_1^0 \cos\theta \sin\theta d\theta d\phi = \boxed{\tfrac{\sqrt{3}}{3}}$$

So we have for our first value:

$$\langle 300| - e\epsilon z|310\rangle = -e\epsilon[-9\sqrt{2}a][\frac{\sqrt{3}}{3}]$$

$$\langle 300| - e\epsilon z|310\rangle = \boxed{3\sqrt{6}e\epsilon a}$$

- Second value:

$$\langle 310| - e\epsilon z|320\rangle = -e\epsilon \int R_{31}R_{32}r^3\ dr \int Y_1^0 Y_2^0 \cos\theta \sin\theta d\theta d\phi$$

Taking appropriate values from the tables:

$$\int R_{31}R_{32}r^3\ dr = \int \frac{8}{27\sqrt{6}}a^{-3/2}(1-\frac{1}{6}\frac{r}{a})(\frac{r}{a})e^{-r/3a}\ \frac{4}{81\sqrt{30}}a^{-3/2}(\frac{r}{a})^2 e^{-r/3a}r^3\ dr$$

Doing the substitutions again:

$$\int R_{31}R_{32}r^3\ dr = \frac{32a^{-3}}{27\sqrt{6}\sqrt{30}81}\int_0^\infty [1-\frac{1}{6}\frac{3}{2}x][\frac{3}{2}]e^{-x}(\frac{3}{2}x)^2(\frac{3}{2}ax)^3\frac{3a}{2}\ dx$$

$$\int R_{31}R_{32}r^3\ dr = \frac{1}{4\sqrt{56}}a\int_0^\infty [1-\frac{1}{4}x]x^6 e^{-x}\ dx$$

$$\int R_{31}R_{32}r^3\ dr = \frac{a}{24\sqrt{5}}[6! - \frac{1}{4}7!]$$

$$\int R_{31}R_{32}r^3\ dr = \frac{a\sqrt{5}}{120}[-540]$$

$$\int R_{31}R_{32}r^3\ dr = \boxed{-\tfrac{9}{2}\sqrt{5}a}$$

Next one:

$$\int Y_1^0 Y_2^0 \cos\theta \sin\theta d\theta d\phi = \int_0^{2\pi}\int_0^\pi \frac{\sqrt{3}}{\sqrt{4\pi}}\cos\theta\frac{\sqrt{5}}{\sqrt{16\pi}}(3\cos^2\theta - 1)\cos\theta\sin\theta\ d\theta d\phi$$

$$\int Y_1^0 Y_2^0 \cos\theta \sin\theta d\theta d\phi = \frac{\sqrt{3}\sqrt{5}}{2\sqrt{4}} \int_0^\pi \cos^2\theta \sin\theta (3\cos^2\theta - 1) d\theta$$

$$\int Y_1^0 Y_2^0 \cos\theta \sin\theta d\theta d\phi = \frac{\sqrt{3}\sqrt{5}}{4} \int_0^\pi 3\cos^4\theta \sin\theta - \cos^2\theta \sin\theta d\theta$$

$$\int Y_1^0 Y_2^0 \cos\theta \sin\theta d\theta d\phi = \frac{\sqrt{3}\sqrt{5}}{4} [3\frac{\cos^5\theta}{5} - \frac{\cos^3\theta}{3}]\Big|_0^\pi$$

$$\int Y_1^0 Y_2^0 \cos\theta \sin\theta d\theta d\phi = \frac{\sqrt{3}\sqrt{5}}{4}[-\frac{3}{5} - \frac{2}{3}]$$

$$\int Y_1^0 Y_2^0 \cos\theta \sin\theta d\theta d\phi = \boxed{\frac{2}{\sqrt{15}}}$$

So we have for our second value:

$$\langle 310| - e\epsilon z|320\rangle = -e\epsilon[-\frac{9}{2}\sqrt{5}a][\frac{2}{\sqrt{15}}]$$

$$\langle 310| - e\epsilon z|320\rangle = \boxed{3\sqrt{3}e\epsilon a}$$

- Third value:

$$\langle 31\pm1| - e\epsilon z|32\pm1\rangle = -e\epsilon \int R_{31}R_{32}r^3\ dr \int Y_1^{\pm1*} Y_2^{\pm1} \cos\theta \sin\theta d\theta d\phi$$

This one is trickier because of the $\pm$ options. But fortunately we've already done the first integral.

$$\int R_{31}R_{32}r^3\ dr = -\sqrt{5}\frac{9}{2}a$$

So only one to go:

$$\int Y_1^{\pm1*} Y_2^{\pm1} \cos\theta \sin\theta d\theta d\phi = (\mp\frac{\sqrt{3}}{\sqrt{8\pi}}(\mp\frac{\sqrt{15}}{\sqrt{8\pi}}) \int_0^{2\pi}\int_0^\pi \sin\theta e^{\mp i\phi} \sin\theta\cos\theta e^{\pm i\phi} \cos\theta \sin\theta d\theta d\phi$$

$$\int Y_1^{\pm1*} Y_2^{\pm1} \cos\theta \sin\theta d\theta d\phi = +\frac{\sqrt{3}\sqrt{15}}{4} \int_0^\pi \sin^3\theta \cos^2\theta\ d\theta$$

$$= \frac{\sqrt{3}\sqrt{15}}{4} \int_0^\pi \sin\theta (1 - \cos^2\theta)\cos^2\theta\ d\theta$$

$$= \frac{\sqrt{3}\sqrt{15}}{4} \int_0^\pi \cos^2\theta \sin\theta - \cos^4\theta \sin\theta\ d\theta$$

$$= \frac{\sqrt{3}\sqrt{15}}{4}[\frac{2}{3} - \frac{2}{5}]$$

$$= \frac{3\sqrt{5}}{4}[\frac{4}{15}]$$

$$\int Y_1^{\pm 1*} Y_2^{\pm 1} \cos\theta \sin\theta d\theta d\phi = \boxed{\tfrac{1}{\sqrt{5}}}$$

So we have for our third value:

$$\langle 31 \pm 1 | - e\epsilon z | 32 \pm 1 \rangle = -e\epsilon[-\frac{9}{2}\sqrt{5}a][\frac{1}{\sqrt{5}}]$$

$$\langle 31 \pm 1 | - e\epsilon z | 32 \pm 1 \rangle = \boxed{\tfrac{9}{2} e\epsilon a}$$

There we go. All three values here:

$$\langle 300 | - e\epsilon z | 310 \rangle = \boxed{3\sqrt{6} e\epsilon a}$$

$$\langle 310 | - e\epsilon z | 320 \rangle = \boxed{3\sqrt{3} e\epsilon a}$$

$$\langle 31 \pm 1 | - e\epsilon z | 32 \pm 1 \rangle = \boxed{\tfrac{9}{2} e\epsilon a}$$

Now we are in a position to construct a huge $9x9$. I'll start with rows from top to bottom in this order, 300, 310, 320, 311, 321, 31-1, 32-1, 322, 32-2. Since all of the elements are zero except our known three values above, we have

$$V = \begin{pmatrix} 0 & 3\sqrt{6}e\epsilon a & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 3\sqrt{6}e\epsilon a & 0 & 3\sqrt{3}e\epsilon a & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3\sqrt{3}e\epsilon a & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{9}{2}e\epsilon a & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{9}{2}e\epsilon a & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{9}{2}e\epsilon a & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{9}{2}e\epsilon a & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

Diagonalizing the subspaces:
First the $3x3$ subspace,

$$\begin{vmatrix} -\lambda & 3\sqrt{6}e\epsilon a & 0 \\ 3\sqrt{6}e\epsilon a & -\lambda & 3\sqrt{3}e\epsilon a \\ 0 & 3\sqrt{3}e\epsilon a & -\lambda \end{vmatrix} = 0$$

yields $\lambda(\lambda^2 - 81e^2\epsilon^2a^2) = 0$

$$\lambda = \pm 9e\epsilon a, 0$$

with eigenstates, after normalizing

$$|\pm\rangle = \frac{1}{\sqrt{6}}(\sqrt{2}|300\rangle \pm \sqrt{3}|310\rangle + |320\rangle)$$

Next, the $2x2$ subspace:

$$\begin{vmatrix} -\lambda & \frac{9}{2}e\epsilon a \\ \frac{9}{2}e\epsilon a & -\lambda \end{vmatrix} = 0$$

yields $\lambda^2 - \frac{81}{4}e^2\epsilon^2a^2 = 0$

$$\lambda = \pm\frac{9}{2}e\epsilon a$$

with normalized eigenstates

$$|\pm\rangle = \frac{1}{\sqrt{2}}(|311\rangle \pm |321\rangle)$$

The next $2x2$ is obviously the same, but with different eigenstates:

$$\begin{vmatrix} -\lambda & \frac{9}{2}e\epsilon a \\ \frac{9}{2}e\epsilon a & -\lambda \end{vmatrix} = 0$$

$$\lambda = \pm\frac{9}{2}e\epsilon a$$

with

$$|\pm\rangle = \frac{1}{\sqrt{2}}(|31-1\rangle \pm |32-1\rangle)$$

The last subspaces are $1x1$ and have $\Delta = 0$. These are the ones with $m = \pm 2$, those of $|32-2\rangle$ and $|322\rangle$.

All in all, we have to the lowest non vanishing order, with zeroth order eigenstates:

$$\Delta = 0 \qquad \begin{cases} |32-2\rangle \\ \frac{1}{\sqrt{3}}(|300\rangle - \sqrt{2}|320\rangle \\ |322\rangle \end{cases} \qquad \boxed{\text{3 degeneracy}}$$

$$\Delta = \begin{cases} \frac{9}{2}e\epsilon a \\ -\frac{9}{2}e\epsilon a \end{cases} \qquad \begin{cases} \frac{1}{\sqrt{2}}(|31\pm 1\rangle + |32\pm 1\rangle \\ \frac{1}{\sqrt{2}}(|31\pm 1\rangle - |32\pm 1\rangle) \end{cases} \qquad \boxed{\text{2 degeneracy}}$$

$$\Delta = \begin{cases} 9e\epsilon a \\ -9e\epsilon a \end{cases} \qquad \begin{cases} \frac{1}{\sqrt{6}}(\sqrt{2}|300\rangle + \sqrt{3}|310\rangle + |320\rangle) \\ \frac{1}{\sqrt{6}}(\sqrt{2}|300\rangle - \sqrt{3}|310\rangle + |320\rangle) \end{cases} \qquad \boxed{\text{1 degeneracy}}$$

Problem 5.17

a. Suppose the Hamiltonian of a rigid rotator in a magnetic field perpendicular to the axis is of the form

$$A\boldsymbol{L}^2 + BL_z + CL_y$$

if terms quadratic in the field are neglected. Assuming $B \gg C$, use perturbation theory to lowest nonvanishing order to get approximate energy eigenvalues. b. Consider the matrix elements

$$\langle n'l'm_l'm_s'|(3z^2 - r^2)|nlm_lm_s\rangle$$

$$\langle n'l'm_l'm_s'|xy|nlm_lm_s\rangle$$

of a one electron (e.g., alkali) atom. Write the selection rules for Δl, Δm_l and Δm_s. Justify your answer.

Solution:

The perturbation will be CL_y. With the unperturbed Hamiltonian of

$$H_0 = A\boldsymbol{L}^2 + BL_z$$

with energies

$$E_0 = A\hbar^2 l(l+1) + Bm\hbar$$

Apply perturbation theory, the first order shift vanishes:

$$\Delta^{(1)} = \langle lm|CL_y|lm\rangle = 0$$

This is because

$$L_y = \frac{1}{2i}(L_+ - L_-)$$

and we can see that the perturbation is off diagonal.
I used here:

$$\langle l'm'|L_\pm|lm\rangle = \sqrt{(l \mp m)(l \pm m + 1)}\hbar\delta_{l,l'}\delta_{m',m\pm 1}$$

So for example:

$$\langle 1,0|CL_y|1,0\rangle = \langle 1,0|C\frac{L_+ - L_-}{2i}|1,0\rangle = 0$$

The second order shift does not vanish:

$$\Delta^{(2)} = C^2 \sum_{m'} \frac{|\langle l'm'|\frac{L_+ - L_-}{2i}|lm\rangle|^2}{E^{(0)}_{lm} - E^{(0)}_{l'm'}}$$

and the l's must be the same or the numerator vanishes. The elements left are:

$$\Delta^{(2)} = C^2\hbar^2\frac{(l-m)(l+m+1)}{-4B\hbar} + C^2\hbar^2\frac{(l+m)(l-m+1)}{4B\hbar}$$

$$\Delta^{(2)} = C^2\hbar^2\frac{l^2+lm+l-ml-m^2-m}{-4B\hbar} + C^2\hbar^2\frac{l^2-lm+l+ml-m^2+m}{4B\hbar}$$

$$\Delta^{(2)} = \frac{C^2\hbar}{4B}[(-l^2-l+m^2+m)+(l^2+l-m^2+m)]$$

so

$$\Delta^{(2)} = \frac{C^2\hbar}{4B}2m = \frac{C^2\hbar m}{2B}$$

The approximate energy eigenvalues to lowest non vanishing order are therefore

$$E = E_0 + \frac{C^2\hbar m}{2B}$$

$$E = A\hbar^2 l(l+1) + Bm\hbar + \frac{C^2\hbar m}{2B}$$

b.

• For $(3z^2-r^2)$ there is no spin dependency, $\Delta m_s = 0$. Converting coordinates

$$3z^2 - r^2 = 3r^2\cos^2\theta - r^2 = r^2(3\cos^2\theta - 1) = r^2(\frac{16\pi}{5})^{1/2}Y_2^0$$

We have

$$\langle n'l'm_l'm_s'|r^2(\frac{16\pi}{5})^{1/2}Y_2^0|nlm_lm_s\rangle$$

So $\Delta m_l = 0$ and $-2 \leq \Delta l \leq 2$. Including parity $\Delta l \neq 1$. So the selection rules for the elements

$$\langle n'l'm_l'm_s'|(3z^2-r^2)|nlm_lm_s\rangle$$

are

$$\boxed{\Delta m_s = 0,\ \Delta m_l = 0,\ \Delta l = 0, \pm 2}$$

• For xy there is also no spin dependency, $\Delta m_s = 0$. Representing this in spherical harmonics:

$$Y_2^2 = (\frac{15}{32\pi})^{1/2}\sin^2\theta e^{2i\phi}$$

This is

$$Y_2^2 = (\frac{15}{32\pi})^{1/2} \sin^2\theta[\cos\phi + i\sin\phi]^2 = (\frac{15}{32\pi})^{1/2}[\sin\theta\cos\phi + i\sin\theta\sin\phi]^2$$

$$r^2 Y_2^2 = (\frac{15}{32\pi})^{1/2}[x+iy]^2$$

and the same goes for

$$r^2 Y_2^{-2} = (\frac{15}{32\pi})^{1/2}[-x+iy]^2$$

Subtracting the two get us xy:

$$r^2[Y_2^2 - Y_2^{-2}] = (\frac{15}{32\pi})^{1/2}[x^2 - 2xy - y^2 - (x^2 + 2xy - y^2)] = (\frac{15}{32\pi})^{1/2}(-4xy)$$

I am concerned with:

$$\langle n'l'm_l'm_s'|xy|nlm_lm_s\rangle = K\langle n'l'm_l'm_s'|Y_2^2 - Y_2^{-2}|nlm_lm_s\rangle$$

where K is just the proportionality constant. This shows the selection rules similar to above with $\Delta m_l = \pm 2$ and $\Delta l = 0, \pm 2$ disregarding $\Delta l = \pm 1$ because of parity again. So the selection rules for the elements:

$$\langle n'l'm_l'm_s'|xy|nlm_lm_s\rangle$$

are

$$\boxed{\Delta m_s = 0,\ \Delta m_l = \pm 2,\ \Delta l = 0, \pm 2}$$

Problem 5.20
Estimate the ground state energy of a one dimensional simple harmonic oscillator using

$$\langle x|\widetilde{0}\rangle = e^{-\beta|x|}$$

as a trial function with β to be varied. Use

$$\int_0^\infty e^{-\alpha x} x^n \, dx = \frac{n!}{\alpha^{n+1}}$$

Solution:

Solving for

$$\overline{H} = \frac{\langle\widetilde{0}|H|\widetilde{0}\rangle}{\langle\widetilde{0}|\widetilde{0}\rangle}$$

with

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

First the denominator

$$\langle\widetilde{0}|\widetilde{0}\rangle = \int_{-\infty}^{\infty} e^{-2\beta|x|}\ dx = 2\int_0^{\infty} e^{-2\beta x} = \frac{1}{\beta}$$

Now the numerator

$$\langle\widetilde{0}|H|\widetilde{0}\rangle = \int_{-\infty}^{\infty} e^{-\beta|x|}[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2]e^{-\beta x}\ dx$$

$$\langle\widetilde{0}|H|\widetilde{0}\rangle = \int_{-\infty}^{\infty} e^{-\beta|x|}[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}]e^{-\beta|x|}\ dx + 2\int_0^{\infty}\frac{1}{2}m\omega^2 x^2 e^{-\beta x}\ dx$$

Lets break this up so its easier to understand. The second integral is:

$$2\int_0^{\infty}\frac{1}{2}m\omega^2 x^2 e^{-\beta x}\ dx = m\omega^2[\frac{2!}{(2\beta)^3}] = \frac{m\omega^2}{4\beta^3}$$

But the first integral is tricky. We must remember the first derivative contribution and bring in a Dirac delta function. Here are the steps:

$$\frac{d^2}{dx^2}e^{-\beta|x|} = \frac{d}{dx}[-\beta e^{-\beta|x|}\frac{d|x|}{dx}]$$

where because of the absolute value

$$\frac{d|x|}{dx} = \begin{cases} +1 & \text{for } x > 0\ , \\ -1 & \text{for } x < 0\ . \end{cases}$$

If we look at this integral, with e a really small number close to zero:

$$\int_{-e}^{e}\frac{d^2|x|}{dx^2}\ dx = \frac{d|x|}{dx}\bigg|_e - \frac{d|x|}{dx}\bigg|_{-e} = 2$$

So, using Dirac's nice function, we see that

$$\frac{d^2|x|}{dx^2} = 2\delta(x)$$

must be true. So we have

$$\frac{d^2}{dx^2}e^{-\beta|x|} = -\beta[e^{-\beta|x|}\frac{d^2|x|}{dx^2} + \frac{d|x|}{dx}(-\beta e^{-\beta|x|}\frac{d|x|}{dx})]$$

$$\frac{d^2}{dx^2}e^{-\beta|x|} = -\beta e^{-\beta|x|}2\delta(x) + \beta^2 e^{-\beta|x|}(\frac{d|x|}{dx})^2$$

$$\frac{d^2}{dx^2}e^{-\beta|x|} = [\beta^2 - \beta 2\delta(x)]e^{-\beta|x|}$$

because

$$(\frac{d|x|}{dx})^2 = 1$$

So finally the first integral is

$$\int_{-\infty}^{\infty} e^{-\beta|x|}[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}]e^{-\beta|x|}\ dx = \int_{-\infty}^{\infty} e^{-\beta|x|}[-\frac{\hbar^2}{2m}[\beta^2 - 2\beta\delta(x)]e^{-2\beta|x|}\ dx$$

$$= -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\beta^2 e^{-2\beta x} + -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty} -2\beta\delta(x)e^{-2\beta x}\ dx$$

$$= \frac{-\hbar^2\beta}{2m} + -\frac{\hbar^2}{2m}(-2\beta)$$

$$= \frac{\hbar^2\beta}{2m}$$

Constructing everything:

$$\overline{H} = [\frac{\hbar^2\beta}{2m} + \frac{m\omega^2}{4\beta^3}]\beta$$

$$\overline{H} = \frac{\hbar^2\beta^2}{2m} + \frac{m\omega^2}{4\beta^2}$$

and running quickly through the variational method...

$$\frac{d\overline{H}}{d\beta} = \frac{\hbar^2\beta_0}{m} - \frac{m\omega^2}{2\beta_0^3} = 0$$

$$\frac{\hbar^2\beta_0}{m} = \frac{m\omega^2}{2\beta_0^3}$$

$$\beta_0^2 = \frac{m\omega}{\sqrt{2}\hbar}$$

So

$$\overline{H}_{min} = \frac{\hbar^2}{2m}\frac{m\omega}{\sqrt{2}\hbar} + \frac{m\omega^2}{4}\frac{\sqrt{2}\hbar}{m\omega}$$

$$\overline{H}_{min} = \sqrt{2}\frac{\hbar\omega}{2}$$

Which, since I know the real answer is

$$E_0 = \frac{\hbar\omega}{2}$$

this satisfies the variational theorem for an upper bound:

$$\overline{H} \geq E_0 \qquad \rightarrow \qquad \sqrt{2}\frac{\hbar\omega}{2} \geq \frac{\hbar\omega}{2}$$

Problem 5.21
Estimate the lowest eigenvalue (λ) of the differential equation

$$\frac{d^2\psi}{dx^2} + (\lambda - |x|)\psi = 0, \qquad \psi \rightarrow 0 \text{ for } |x| \rightarrow \infty$$

using the variational method with

$$\psi = \begin{cases} c(\alpha - |x|) & \text{for } |x| < \alpha \ , \\ 0 & \text{for } |x| > \alpha. \end{cases}$$

as a trial function. (α to be varied). (Caution: $d\psi/dx$ is discontinuous at $x = 0$)
Numerical data that may be useful for this problem are:

$$3^{1/3} = 1.442 \quad 5^{1/3} = 1.710 \quad 3^{2/3} = 2.080 \quad \pi^{2/3} = 2.145$$

Solution:

To use the variational method, we first solve

$$\overline{H} = \frac{\langle\widetilde{0}|H|\widetilde{0}\rangle}{\langle\widetilde{0}|\widetilde{0}\rangle}$$

Then take the derivative with respect to the varying parameter, in this case, α, and set to zero.

$$\frac{d\overline{H}}{d\alpha} = 0$$

This allows us to solve for α_0 that will give the lowest energy eigenvalue, by plugging the α_0 into $\overline{H}$. In this problem we have a tricky discontinuity at $x = 0$, which requires us to bring in the delta function. Lets solve for H first:

$$\frac{d^2\psi}{dx^2} + (\lambda - |x|)\psi = 0$$

$$\frac{d^2\psi}{dx^2} - |x|\psi = -\lambda\psi$$

$$-\frac{d^2\psi}{dx^2} + |x|\psi = \lambda\psi$$

$$[-\frac{d^2}{dx^2} + |x|]\psi = \lambda\psi \rightarrow H\psi = \lambda\psi$$

So

$$H = -\frac{d^2}{dx^2} + |x|$$

Solving for $\overline{H}$:

$$\overline{H} = \frac{\langle\widetilde{0}|H|\widetilde{0}\rangle}{\langle\widetilde{0}|\widetilde{0}\rangle}$$

First

$$\langle\widetilde{0}|H|\widetilde{0}\rangle = \int_{-\alpha}^{\alpha} c^*(\alpha - |x|)(-\frac{d^2}{dx^2} + |x|)c(\alpha - |x|)\ dx$$

$$\langle\widetilde{0}|H|\widetilde{0}\rangle = \int_{-\alpha}^{\alpha} c^*(\alpha - |x|)\left(-\frac{d^2}{dx^2}[c(\alpha - |x|)]\right)\ dx + 2\int_0^{\alpha} c^*(\alpha - |x|)|x|c(\alpha - |x|)\ dx$$

Lets leave the first term alone for now, its more difficult mathematically.

$$\langle\widetilde{0}|H|\widetilde{0}\rangle = \int_{-\alpha}^{\alpha} c^*(\alpha - |x|)\left(-\frac{d^2\psi}{dx^2}\right)\ dx + 2|c|^2\int_0^{\alpha} |x|(\alpha - |x|)^2\ dx$$

$$\langle\widetilde{0}|H|\widetilde{0}\rangle = \int_{-\alpha}^{\alpha} c^*(\alpha - |x|)\left(-\frac{d^2\psi}{dx^2}\right)\ dx + 2|c|^2\int_0^{\alpha} \alpha^2|x| - 2\alpha|x|^2 + |x|^3\ dx$$

Now, the discontinuity is at $x = 0$ for $d\psi/dx$, where for $0 < x < \alpha$, $d\psi/dx = -c$ and for $-\alpha < x < 0$, $d\psi/dx = c$. If we take the integral

$$\int_{-e}^{e} \frac{d^2\psi}{dx^2}\ dx = \frac{d\psi}{dx}|_{x=e} - \frac{d\psi}{dx}|_{x=e} = -2c$$

where e is a number really really close to zero, we get

$$\frac{d^2\psi}{dx^2} = -2c\delta(x)$$

So our expression now is:

$$\langle\widetilde{0}|H|\widetilde{0}\rangle = \int_{-\alpha}^{\alpha} c^*(\alpha - |x|)2c\delta(x)\ dx + 2|c|^2\int_0^{\alpha} \alpha^2|x| - 2\alpha|x|^2 + |x|^3\ dx$$

$$\langle\widetilde{0}|H|\widetilde{0}\rangle = 2|c|^2\int_{-\alpha}^{\alpha} (\alpha - |x|)2\delta(x)\ dx + 2|c|^2\int_0^{\alpha} \alpha^2|x| - 2\alpha|x|^2 + |x|^3\ dx$$

$$\langle\widetilde{0}|H|\widetilde{0}\rangle = 2|c|^2\alpha + 2|c|^2\ [\frac{\alpha^2|x|^2}{2} - \frac{2\alpha|x|^3}{3} + \frac{|x|^4}{4}]\Big|_0^{\alpha}$$

$$\langle\widetilde{0}|H|\widetilde{0}\rangle = 2|c|^2\alpha + 2|c|^2[\frac{\alpha^4}{2} - \frac{2\alpha^4}{3} + \frac{\alpha^4}{4}]$$

$$\langle\widetilde{0}|H|\widetilde{0}\rangle = 2|c|^2[\alpha + \frac{3\alpha^4}{4} - \frac{2\alpha^4}{3}]$$

That's good enough for now. Lets solve for the denominator now.

$$\langle\widetilde{0}|\widetilde{0}\rangle = \int_{-\alpha}^{\alpha} |c(\alpha - |x|)|^2 \, dx = 2|c|^2 \int_0^{\alpha} \alpha^2 - 2\alpha|x| + |x|^2 \, dx$$

$$\langle\widetilde{0}|\widetilde{0}\rangle = 2|c|^2[\alpha^2 x - \alpha x^2 + \frac{x^3}{3}\Big|_0^{\alpha}] = 2|c|^2[\alpha^3 - \alpha^3 + \frac{\alpha^3}{3}]$$

$$\langle\widetilde{0}|\widetilde{0}\rangle = 2|c|^2\frac{\alpha^3}{3}$$

Constructing $\overline{H}$

$$\overline{H} = \frac{\langle\widetilde{0}|H|\widetilde{0}\rangle}{\langle\widetilde{0}|\widetilde{0}\rangle} = [\alpha + \frac{3\alpha^4}{4} - \frac{2\alpha^4}{3}]\frac{3}{\alpha^3}$$

$$\overline{H} = \frac{3}{\alpha^2} + \frac{9}{4}\alpha - 2\alpha = \frac{3}{\alpha^2} + \frac{\alpha}{4}$$

Now

$$\frac{d\overline{H}}{d\alpha} = 0 = -6\alpha_0^{-3} + \frac{1}{4}$$

$$\alpha_0 = 24^{1/3}$$

Plugging back in

$$\overline{H}_{min} = \frac{3}{24^{2/3}} + \frac{24^{1/3}}{4} = 1.082$$

and according to the variational principle

$$\overline{H}_{min} \geq E_0$$

$$1.082 \geq 1.019$$