

## Homework Set #5 – Solutions

1. This problem is essentially Merzbacher, Chapter 18, Problem 4 [or Sakurai, Chapter 5, Problem 1]. Consider a one-dimensional harmonic oscillator perturbed by a constant force

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 - Fx$$

- a) Show that the first order perturbation in the energy levels vanishes

*Since we will need to find the second order perturbation in part b), let us consider the general matrix element*

$$V_{mn} = -F \langle m^{(0)} | x | n^{(0)} \rangle$$

*The operator  $x$  is given in terms of creation and annihilation operators by  $x = \sqrt{\hbar/(2m\omega)}(a^\dagger + a)$ . Thus*

$$\begin{aligned} V_{mn} &= -F \sqrt{\frac{\hbar}{2m\omega}} \langle m^{(0)} | (a^\dagger + a) | n^{(0)} \rangle \\ &= -F \sqrt{\frac{\hbar}{2m\omega}} [\sqrt{n+1} \delta_{m,n+1} + \sqrt{n} \delta_{j,n-1}] \end{aligned}$$

*This indicates that the  $x$  operator changes the oscillator number by  $\pm 1$ . In particular,  $V_{nn} = 0$ , which demonstrates that the first order energy perturbation vanishes.*

- b) Now calculate the eigenenergies  $E_n$  up to second order in the perturbation.

*Using the matrix element calculated above, we find*

$$\begin{aligned} E_n^{(2)} &= \sum_{k \neq n} \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}} = \frac{|V_{n+1,n}|^2}{E_n^{(0)} - E_{n+1}^{(0)}} + \frac{|V_{n-1,n}|^2}{E_n^{(0)} - E_{n-1}^{(0)}} \\ &= F^2 \frac{\hbar}{2m\omega} \left[ \frac{n+1}{-\hbar\omega} + \frac{n}{\hbar\omega} \right] = -\frac{F^2}{2m\omega^2} \end{aligned}$$

*Combined with the zeroth order energy, this gives*

$$E_n = (n + \frac{1}{2})\hbar\omega - \frac{F^2}{2m\omega^2}$$

- c) Show that the second-order perturbation result gives the exact eigenenergies (which may be obtained by completing the square in  $H$ ). Explain why this happens.

By completing the square, we find

$$\begin{aligned} H &= \frac{p^2}{2m} + \frac{1}{2}m\omega^2\left(x - \frac{F}{m\omega^2}\right)^2 - \frac{F^2}{2m\omega^2} \\ &= \frac{p^2}{2m} + \frac{1}{2}m\omega^2\bar{x}^2 - \frac{F^2}{2m\omega^2} \end{aligned}$$

where  $\bar{x} = x - F/(m\omega^2)$  is a shifted coordinate. In terms of this new coordinate, we have an ordinary harmonic oscillator, however with a constant offset in the potential. We easily read off the eigenenergies as

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega - \frac{F^2}{2m\omega^2} \quad (1)$$

which is identical to the perturbation result of b). Of course, in general we would apply perturbation theory only when we do not know the exact answer. However, in this toy example, after completing the square, we see that  $F$  enters the Hamiltonian only quadratically as an overall offset. In particular, we know that the correct energies, (1), only has  $F^2$ , and no other powers of  $F$  in it. Now recall that each order in the perturbation theory corresponds to precisely that order in a series expansion of the small perturbation parameter (which would be  $F$  in this case); first order perturbation gives  $\mathcal{O}(F)$ , second order gives  $\mathcal{O}(F^2)$ , and so on. As a result, only the second order perturbation to the energy can contribute towards the correct answer, and this is in fact what happens.

2. Sakurai, Chapter 5, Problem 2. In nondegenerate time-independent perturbation theory, what is the probability of finding in a perturbed energy eigenstate  $|\psi_n\rangle$  the corresponding unperturbed eigenstate  $|\psi_n^{(0)}\rangle$ ? Solve this up to terms of order  $g^2$ .

We recall that the perturbed eigenstate is not necessarily normalized, and may be written as

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + g|\psi_n^{(1)}\rangle + g^2|\psi_n^{(2)}\rangle + \dots$$

Since the probability is the amplitude squared, we want to calculate (to second order in  $g$ )

$$P = \left| \frac{\langle \psi_n^{(0)} | \psi_n \rangle}{\sqrt{\langle \psi_n | \psi_n \rangle}} \right|^2 = \frac{|\langle \psi_n^{(0)} | \psi_n \rangle|^2}{\langle \psi_n | \psi_n \rangle}$$

Since all the higher order  $|\psi_n^{(i>0)}\rangle$  states are orthogonal to  $|\psi_n^{(0)}\rangle$ , it is easy to see that

$$\langle \psi_n^{(0)} | \psi_n \rangle = \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1$$

and

$$\begin{aligned} \langle \psi_n | \psi_n \rangle &= \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + g \left( \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle \right) \\ &\quad + g^2 \left( \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(2)} | \psi_n^{(0)} \rangle \right) + \dots \\ &= 1 + g^2 \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle + \dots = 1 + g^2 \sum_{k \neq n} \frac{|V_{kn}|^2}{|E_n^{(0)} - E_k^{(0)}|^2} + \dots \end{aligned}$$

Using  $1/(1+x) = 1 - x + \dots$ , we find

$$P = 1 - g^2 \sum_{k \neq n} \frac{|V_{kn}|^2}{|E_n^{(0)} - E_k^{(0)}|^2} + \dots$$

which we verify is less than or equal to one. Clearly, the only possibility of finding 100% probability is if  $|\psi_n\rangle$  is identical to  $|\psi_n^{(0)}\rangle$ , indicating that the initial eigenstate remains an eigenstate of the perturbation.

[Yes, this is the same as Wave-function Renormalization on p. 293 of Sakurai!]

3. Consider the  $2p$  levels of hydrogen ( $m = 0, \pm 1$ ) subject to a perturbation

$$V = Ax^2 + By^2 - (A + B)z^2$$

- a) Write  $V$  in terms of components of a rank-2 spherical tensor.

Using the spherical harmonic ‘trick’, we can write out the appropriate rank-2 tensor as

$$\begin{aligned} T_{\pm 2}^{(2)} &= \frac{1}{2}(x \pm iy)^2 \\ T_{\pm 1}^{(2)} &= \mp(x \pm iy)z \\ T_0^{(2)} &= -\frac{1}{\sqrt{6}}(x^2 + y^2 - 2z^2) \end{aligned}$$

Of course, the actual normalization is arbitrary. I have removed a factor of  $\sqrt{15\pi/8}$  when compared to the  $Y_{l=2}^m$  spherical harmonics. In this case, we may reexpress

$$x^2 - y^2 = T_2^{(2)} + T_{-2}^{(2)}, \quad x^2 + y^2 - 2z^2 = -\sqrt{6}T_0^{(2)}$$

This allows us to rewrite the perturbation

$$\begin{aligned} V &= \frac{1}{2}(A + B)(x^2 + y^2) + \frac{1}{2}(A - B)(x^2 - y^2) - (A + B)z^2 \\ &= \frac{1}{2}(A + B)(x^2 + y^2 - 2z^2) + \frac{1}{2}(A - B)(x^2 - y^2) \\ &= -\sqrt{\frac{3}{2}}(A + B)T_0^{(2)} + \frac{1}{2}(A - B)(T_2^{(2)} + T_{-2}^{(2)}) \end{aligned} \tag{1}$$

Note that the coefficients of  $x^2$ ,  $y^2$  and  $z^2$  had to work out just right for this to be possible. If instead of  $(A + B)z^2$ , we had something like  $Cz^2$ , then we would have an added term left over which would be proportional to  $r^2 = x^2 + y^2 + z^2$ . This would correspond to a scalar perturbation in addition to a pure rank-2 tensor perturbation.

- b) Neglecting electron spin, find the ‘correct’ zeroth-order eigenstates and their corresponding energies. It is sufficient to give the energies in terms of a reduced matrix element  $\langle 2p || T^{(2)} || 2p \rangle$ .

We denote the  $2p$  states as  $|nlm\rangle = |211\rangle$ ,  $|210\rangle$  and  $|21-1\rangle$ . We first observe that the perturbation will not mix  $|210\rangle$  with the other two states [because of the

$\Delta m = 0, \pm 2$  selection rule evident from (1)]. So, although all three states are degenerate, the perturbation is block diagonal in the  $|210\rangle$  and  $\{|211\rangle, |21-1\rangle\}$  subspaces. This simplification allows us to immediately write down, for the  $|210\rangle$  state

$$\begin{aligned}\Delta E_{210} &= \langle 210|V|210\rangle = -\sqrt{\frac{3}{2}}(A+B)\langle 210|T_0^{(2)}|210\rangle \\ &= -\sqrt{\frac{3}{2}}(A+B)\langle 1200|1210\rangle\langle 2p||T^{(2)}||2p\rangle \\ &= \sqrt{\frac{3}{5}}(A+B)\langle 2p||T^{(2)}||2p\rangle\end{aligned}$$

For the remaining two states, we write out the matrix

$$\begin{aligned}\mathbf{V} &= \begin{pmatrix} \langle 211|V|211\rangle & \langle 211|V|21-1\rangle \\ \langle 21-1|V|211\rangle & \langle 21-1|V|21-1\rangle \end{pmatrix} \\ &= -\sqrt{\frac{3}{2}}(A+B) \begin{pmatrix} \langle 211|T_0^{(2)}|211\rangle & 0 \\ 0 & \langle 21-1|T_0^{(2)}|21-1\rangle \end{pmatrix} \\ &\quad + \frac{1}{2}(A-B) \begin{pmatrix} 0 & \langle 211|T_2^{(2)}|21-1\rangle \\ \langle 21-1|T_{-2}^{(2)}|211\rangle & 0 \end{pmatrix} \\ &= -\sqrt{\frac{3}{2}}(A+B)\langle 2p||T^{(2)}||2p\rangle \begin{pmatrix} \langle 1210|1211\rangle & 0 \\ 0 & \langle 12-10|121-1\rangle \end{pmatrix} \\ &\quad + \frac{1}{2}(A-B)\langle 2p||T^{(2)}||2p\rangle \begin{pmatrix} 0 & \langle 12-12|1211\rangle \\ \langle 121-2|121-1\rangle & 0 \end{pmatrix} \\ &= \frac{1}{2}\sqrt{\frac{3}{5}}\langle 2p||T^{(2)}||2p\rangle \begin{pmatrix} -(A+B) & (A-B) \\ (A-B) & -(A+B) \end{pmatrix}\end{aligned}$$

Working out the eigenvalues and eigenstates, we find a simple result

$$\begin{aligned}\Delta E_{21x} &= -\sqrt{\frac{3}{5}}A\langle 2p||T^{(2)}||2p\rangle & |21x\rangle &\equiv \frac{1}{\sqrt{2}}(|211\rangle - |21-1\rangle) \\ \Delta E_{21y} &= -\sqrt{\frac{3}{5}}B\langle 2p||T^{(2)}||2p\rangle & |21y\rangle &\equiv \frac{1}{\sqrt{2}}(|211\rangle + |21-1\rangle)\end{aligned}$$

Here, the labels  $x$  and  $y$  were chosen to be suggestive of  $p_x$  and  $p_y$  orbitals. However, of course, this is just an arbitrary labeling of the eigenstates. To summarize, the perturbation splits all three  $2p$  states (ignoring spin) to

$$\begin{aligned}\Delta E_{210} &= \sqrt{\frac{3}{5}}(A+B)\langle 2p||T^{(2)}||2p\rangle, & |210\rangle \\ \Delta E_{21x} &= -\sqrt{\frac{3}{5}}A\langle 2p||T^{(2)}||2p\rangle, & |21x\rangle = \frac{1}{\sqrt{2}}(|211\rangle - |21-1\rangle) \\ \Delta E_{21y} &= -\sqrt{\frac{3}{5}}B\langle 2p||T^{(2)}||2p\rangle, & |21y\rangle = \frac{1}{\sqrt{2}}(|211\rangle + |21-1\rangle)\end{aligned}$$

Note that the energy shifts are proportional to  $A$ ,  $B$  and  $-(A+B)$ , the factors multiplying  $x^2$ ,  $y^2$  and  $z^2$ , respectively. The corresponding eigenstates,  $|21x\rangle$ ,

$|21y\rangle$  and  $|210\rangle$  are simply the  $p_x$ ,  $p_y$  and  $p_z$  orbitals (which are aligned along the  $x$ ,  $y$  and  $z$  axis). So this makes perfect physical sense.

c) Show that the expectation value of  $L_z$  vanishes in each eigenstate found above.

Of course the expectation values of  $L_z$  take on the values  $0, \pm\hbar$  in the original basis states  $|210\rangle$  and  $|21 \pm 1\rangle$ . Here, however, we consider

$$\begin{aligned}\langle 210|L_z|210\rangle &= 0 \\ \langle 21x|L_z|21x\rangle &= \frac{1}{2}(\langle 211| - \langle 21 - 1|)L_z(|211\rangle - |21 - 1\rangle) \\ &= \frac{1}{2}(\langle 211|L_z|211\rangle + \langle 21 - 1|L_z|21 - 1\rangle) = 0 \\ \langle 21y|L_z|21y\rangle &= \frac{1}{2}(\langle 211| + \langle 21 - 1|)L_z(|211\rangle + |21 - 1\rangle) \\ &= \frac{1}{2}(\langle 211|L_z|211\rangle + \langle 21 - 1|L_z|21 - 1\rangle) = 0\end{aligned}$$

so that the expectation values indeed vanish. It is important to keep in mind that the expectation values are not the same thing as eigenvalues! The eigenvalues of  $L_z$  are always  $0, \pm\hbar$  for the  $2p$  states.

4. Merzbacher, Chapter 18, Problem 14.

For the Hamiltonian  $H = A\vec{L}^2 + B\hbar^2 \cos 2\varphi$  with  $A \gg B$ , we may take the second term as a perturbation. Hence

$$H_0 = A\vec{L}^2 = A\hbar^2 \ell(\ell + 1)$$

for states of angular momentum  $\ell$ . For the perturbation, we find it convenient to write

$$V = B\hbar^2 \cos 2\varphi = \frac{1}{2}B\hbar^2(e^{2i\varphi} + e^{-2i\varphi})$$

Although the perturbation breaks rotational invariance (after all, it is a hindered rotation), we may nevertheless consider its effect on angular momentum states  $|\ell m\rangle$ . In this case, since  $Y_\ell^m(\theta, \varphi) \sim e^{im\varphi} P_\ell^m(\cos\theta)$ , we see that

$$\langle \ell' m' | V | \ell m \rangle = \int (Y_{\ell'}^{m'})^* V Y_\ell^m d\Omega \sim \int_0^{2\pi} e^{-im'\varphi} (e^{2i\varphi} + e^{-2i\varphi}) e^{im\varphi} d\varphi \times (\text{rest})$$

Hence we may deduce that  $m'$  and  $m$  obey a selection rule  $\Delta m = \pm 2$ . This provides an important simplification, as it indicates that most of the matrix elements of the perturbation actually vanish. We are now ready to examine the  $S$ ,  $P$  and  $D$  levels one at a time.

For the  $S$  level ( $\ell = 0$ )

This state is non-degenerate, and has vanishing zeroth order energy,  $E^{(0)} = 0$ . In addition, the first order shift in the energy also vanishes since  $\langle 00|V|00\rangle = 0$  by the  $\Delta m$  selection rule. We thus have, for the  $S$  level

$$E = 0, \quad |00\rangle$$

Note that, while the energy vanishes up to first order,  $|00\rangle$  is not an eigenstate of  $H$ .

For the  $P$  levels ( $\ell = 1$ )

At zeroth order, the  $P$  levels are three-fold degenerate with  $E^{(0)} = 2A\hbar^2$ . For the first order perturbation, use of the  $\Delta m$  selection rule indicates that  $|10\rangle$  cannot mix with the other states. Hence it is already the “correct” eigenstate, and does not get shifted in energy

$$E = 2A\hbar^2, \quad |10\rangle$$

For the remaining  $|11\rangle$  and  $|1 -1\rangle$  states, we have to diagonalize the perturbation

$$\mathbf{V} = \begin{pmatrix} 0 & \langle 11|V|1 -1\rangle \\ \langle 1 -1|V|11\rangle & 0 \end{pmatrix}$$

The two non-trivial matrix elements are complex conjugates of each other. So we only need to compute

$$\begin{aligned} \langle 11|V|1 -1\rangle &= \frac{1}{2}B\hbar^2 \int (Y_1^1)^* e^{2i\varphi} Y_1^{-1} d\varphi d\cos\theta \\ &= \frac{1}{2}B\hbar^2 \left(-\frac{3}{8\pi}\right) \int \sin^2\theta d\varphi d\cos\theta = -\frac{1}{2}B\hbar^2 \end{aligned}$$

Hence

$$\mathbf{V} = -\frac{1}{2}B\hbar^2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

By now, it should be obvious what the eigenvalues and eigenvectors of this matrix are. Including the zeroth order energy, we have

$$\begin{aligned} E &= 2A\hbar^2 - \frac{1}{2}B\hbar^2, & \frac{1}{\sqrt{2}}(|11\rangle + |1 -1\rangle) \\ E &= 2A\hbar^2 + \frac{1}{2}B\hbar^2, & \frac{1}{\sqrt{2}}(|11\rangle - |1 -1\rangle) \end{aligned}$$

We see that the perturbation completely lifts the degeneracy of the  $P$  states.

For the  $D$  levels ( $\ell = 2$ )

The  $D$  levels are five-fold degenerate at the zeroth order, with  $E^{(0)} = 6A\hbar^2$ . In general, we may have to work out a  $5 \times 5$  matrix for the perturbation. However, the  $\Delta m$  selection rule again helps, and indicates that the five states split up into two subspaces, one with  $\{|21\rangle, |2 -1\rangle\}$  and the other with  $\{|22\rangle, |20\rangle, |2 -2\rangle\}$ . For the former, we have

$$\mathbf{V} = \begin{pmatrix} 0 & \langle 21|V|2 -1\rangle \\ \langle 2 -1|V|21\rangle & 0 \end{pmatrix}$$

where

$$\begin{aligned}\langle 21|V|2-1\rangle &= \frac{1}{2}B\hbar^2 \int (Y_2^1)^* e^{2i\varphi} Y_2^{-1} d\varphi d\cos\theta \\ &= \frac{1}{2}B\hbar^2 \left(-\frac{15}{8\pi}\right) \int (\sin\theta \cos\theta)^2 d\varphi d\cos\theta = -\frac{1}{2}B\hbar^2\end{aligned}$$

The eigenenergies and eigenstates in this subspace are hence

$$\begin{aligned}E &= 6A\hbar^2 - \frac{1}{2}B\hbar^2, & \frac{1}{\sqrt{2}}(|21\rangle + |2-1\rangle) \\ E &= 6A\hbar^2 + \frac{1}{2}B\hbar^2, & \frac{1}{\sqrt{2}}(|21\rangle - |2-1\rangle)\end{aligned}$$

Finally, turning to the three-dimensional subspace, we have

$$\mathbf{V} = \begin{pmatrix} 0 & \langle 22|V|20\rangle & 0 \\ \langle 20|V|22\rangle & 0 & \langle 20|V|2-2\rangle \\ 0 & \langle 2-2|V|20\rangle & 0 \end{pmatrix}$$

We evaluate

$$\begin{aligned}\langle 22|V|20\rangle &= \frac{1}{2}B\hbar^2 \int (Y_2^2)^* e^{2i\varphi} Y_2^0 d\varphi d\cos\theta \\ &= \frac{1}{2}B\hbar^2 \left(\frac{5}{16\pi}\sqrt{\frac{3}{2}}\right) \int \sin^2\theta(3\cos^2\theta - 1)d\varphi d\cos\theta = -\frac{1}{2\sqrt{6}}B\hbar^2\end{aligned}$$

and note that  $\langle 20|V|2-2\rangle$  gives the same result. Thus

$$\mathbf{V} = -\frac{1}{2\sqrt{6}}B\hbar^2 \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

It is easy to check that the matrix of ones and zeros has eigenvalues  $\sqrt{2}$ , 0 and  $-\sqrt{2}$ , with eigenvectors  $(1 \ \sqrt{2} \ 1)^T$ ,  $(1 \ 0 \ -1)^T$  and  $(1 \ -\sqrt{2} \ 1)^T$ . Hence the correct eigenenergies and eigenstates are

$$\begin{aligned}E &= 6A\hbar^2 - \frac{1}{2\sqrt{3}}B\hbar^2, & \frac{1}{2}(|22\rangle + \sqrt{2}|20\rangle + |2-2\rangle) \\ E &= 6A\hbar^2, & \frac{1}{\sqrt{2}}(|21\rangle - |2-2\rangle) \\ E &= 6A\hbar^2 + \frac{1}{2\sqrt{3}}B\hbar^2, & \frac{1}{2}(|22\rangle - \sqrt{2}|20\rangle + |2-2\rangle)\end{aligned}$$

Finally, to summarize, we find, for the  $S$ ,  $P$  and  $D$  levels

$$\begin{aligned}
 S : \quad E &= 0, & |00\rangle \\
 P : \quad E &= 2A\hbar^2 - \frac{1}{2}B\hbar^2, & \frac{1}{\sqrt{2}}(|11\rangle + |1 -1\rangle) \\
 & E = 2A\hbar^2, & |10\rangle \\
 & E = 2A\hbar^2 + \frac{1}{2}B\hbar^2, & \frac{1}{\sqrt{2}}(|11\rangle - |1 -1\rangle) \\
 D : \quad E &= 6A\hbar^2 - \frac{1}{2}B\hbar^2, & \frac{1}{\sqrt{2}}(|21\rangle + |2 -1\rangle) \\
 & E = 6A\hbar^2 - \frac{1}{2\sqrt{3}}B\hbar^2, & \frac{1}{2}(|22\rangle + \sqrt{2}|20\rangle + |2 -2\rangle) \\
 & E = 6A\hbar^2, & \frac{1}{\sqrt{2}}(|21\rangle - |2 -2\rangle) \\
 & E = 6A\hbar^2 + \frac{1}{2\sqrt{3}}B\hbar^2, & \frac{1}{2}(|22\rangle - \sqrt{2}|20\rangle + |2 -2\rangle) \\
 & E = 6A\hbar^2 + \frac{1}{2}B\hbar^2, & \frac{1}{\sqrt{2}}(|21\rangle - |2 -1\rangle)
 \end{aligned}$$

Note that the  $P$  states are split just as they were in problem 3).