

# Physics 137B (Professor Shapiro) Spring 2010

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## Homework 6 Solutions

1. For  $t < 0$ , eigenstates are  $\psi_n(x) = \sqrt{\frac{2}{L}} \sin(\frac{n\pi x}{L})$ . For  $t > 0$  the well has width  $2L$  and the eigenstates are  $\phi_n(x) = \sqrt{\frac{2}{2L}} \sin(\frac{n\pi x}{2L})$ . For  $t < 0$  the system is in the state  $\psi_1(x)$ . Since the well increases in size suddenly at  $t=0$ , the sudden approximation tells us that the system is still in the state  $\psi_1(x)$  just after  $t=0$ . That is, at  $t = 0$  the wavefunction is:

$$|\psi_1\rangle = \sum_n |\phi_n\rangle \langle \phi_n | \psi_1\rangle \quad (\text{using the completeness relation})$$

Therefore the probability of the system being found in the eigenstate  $|\phi_n\rangle$  is  $|\langle \phi_n | \psi_1\rangle|^2$ .

$$\begin{aligned} \langle \phi_n | \psi_1\rangle &= \int_0^{2L} \phi_n^*(x) \psi_1(x) dx \\ &= \int_0^L \sqrt{\frac{2}{2L}} \sin(\frac{n\pi x}{2L}) \sqrt{\frac{2}{L}} \sin(\frac{\pi x}{L}) dx \\ &= \frac{\sqrt{2}}{L} \int_0^L \frac{1}{2} (\cos(\frac{(n-2)\pi x}{2L}) - \cos(\frac{(n+2)\pi x}{2L})) dx \\ &= \frac{1}{L\sqrt{2}} \left( \frac{2L \sin(\frac{(n-2)\pi x}{2L})}{(n-2)\pi} - \frac{2 \sin(\frac{(n+2)\pi x}{2L})}{(n+2)\pi} \right) \Bigg|_{x=0}^{x=L} \\ &= \frac{\sqrt{2}}{\pi} \left( \frac{\sin(\frac{(n-2)\pi}{2})}{(n-2)} - \frac{\sin(\frac{(n+2)\pi}{2})}{(n+2)} \right) \end{aligned}$$

If  $n$  is even and  $n \neq 2$  then this is zero. If  $n = 2$  then this equals  $\frac{1}{\sqrt{2}}$ . If  $n = 2k + 1$  then:

$$\begin{aligned} \langle \phi_n | \psi_1 \rangle &= \frac{\sqrt{2}}{\pi} \left( \frac{\sin(\frac{(2k-1)\pi}{2})}{(2k-1)} - \frac{\sin(\frac{(2k+3)\pi}{2})}{(2k+3)} \right) \\ &= \frac{\sqrt{2}}{\pi} \left( \frac{(-1)^{k+1}}{(2k-1)} - \frac{(-1)^{k+1}}{(2k+3)} \right) \\ &= \frac{\sqrt{2}}{\pi} (-1)^k \frac{4}{(n^2-4)} \end{aligned}$$

So the probabilities are:

$$\begin{aligned} P_n &= \frac{1}{2} \delta_{n2} \quad (\text{for } n \text{ even}) \\ P_n &= \frac{32}{\pi^2 (n^2-4)^2} \quad (\text{for } n \text{ odd}) \end{aligned}$$

2. The potential is  $V = K(a_1 + a_1^\dagger - a_2 - a_2^\dagger)^2$  where  $K = \frac{\lambda \hbar}{2m\omega}$ .

(a) The eigenstates of the unperturbed system must be symmetric under interchange of the bosons. Therefore the ground state is  $|00\rangle$  and the first excited state is  $\frac{1}{\sqrt{2}}(|01\rangle + |10\rangle)$ . So the first order energy corrections are:

$$\begin{aligned} E_0^{(1)} &= \langle 00 | V | 00 \rangle \\ &= K (\langle 10 | - \langle 01 |) (|10\rangle - |01\rangle) \\ &= 2K \\ E_1^{(1)} &= \frac{1}{\sqrt{2}} (\langle 01 | + \langle 10 |) V \frac{1}{\sqrt{2}} (|01\rangle + |10\rangle) \\ &= \frac{K}{2} (\sqrt{2} \langle 20 | - \sqrt{2} \langle 02 |) (\sqrt{2} |20\rangle - \sqrt{2} |02\rangle) \\ &= 2K \end{aligned}$$

So, to first order in perturbation theory, the ground state has energy  $\hbar\omega + 2K$ , while the first excited has energy  $2\hbar\omega + 2K$ .

(b) The eigenstates of the unperturbed system must now be antisymmetric under interchange of the fermions. The the ground state is  $\frac{1}{\sqrt{2}}|00\rangle$  ( $|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$ ). The first excited state has degeneracy 4 and has basis  $\frac{1}{2}(|01\rangle + |10\rangle)(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ , and  $\frac{1}{\sqrt{2}}(|01\rangle + |10\rangle)|\phi\rangle$ ,

where  $|\phi\rangle = |\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle$  or  $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ . These four states all have different eigenvalues under the symmetry operators  $S$  or  $S_z$  and therefore this is a good basis for the perturbation  $V$ . Therefore, we can apply non-degenerate perturbation theory to this degenerate subspace. Thus the first order energy corrections are (note: the spin part of the wavefunction never contributes since  $V$  does not contain spin terms):

$$\begin{aligned}
E_0^{(1)} &= \langle 00|V|00\rangle \\
&= K(\langle 10| - \langle 01|)(|10\rangle - |01\rangle) \\
&= 2K \\
E_1^{(1)} &= \frac{1}{\sqrt{2}}(\langle 10| + \langle 01|)V\frac{1}{\sqrt{2}}(|10\rangle + |01\rangle) \\
&= \frac{K}{2}(\sqrt{2}\langle 20| - \sqrt{2}\langle 02|)(\sqrt{2}|20\rangle - \sqrt{2}|02\rangle) \\
&= 2K \\
\tilde{E}_1^{(1)} &= \frac{1}{\sqrt{2}}(\langle 10| - \langle 01|)V\frac{1}{\sqrt{2}}(|10\rangle - |01\rangle) \\
&= \frac{K}{2}(\sqrt{2}\langle 20| + \sqrt{2}\langle 02| + 2\langle 00| - 2\langle 11|) \cdot \\
&\quad (\sqrt{2}|20\rangle + \sqrt{2}|02\rangle + 2|00\rangle - 2|11\rangle) \\
&= 6K
\end{aligned}$$

So, to first order in perturbation theory, the ground state has energy  $\hbar\omega + 2K$ . The four first excited states get split by the perturbation, with one state having energy  $2\hbar\omega + 2K$  and the other three states having energy  $2\hbar\omega + 6K$ .

3. Sodium has electron configuration  $1s^2 2s^2 2p^6 3s^1$ . The outer shell has just one electron in it, which therefore determines the spin and angular momentum of the whole atom. That is,  $L = 0$  and  $S = 1/2$  (since the lone electron is in the  $s$  ( $L = 0$ ) level and has spin  $1/2$ ). Therefore  $J = 1/2$  also. So the only possible angular momentum state for sodium is  $^2S_{1/2}$ . Since there is only one possible state, Hund's rules are trivially satisfied.

Magnesium has electron configuration  $1s^2 2s^2 2p^6 3s^2$ . Since the outer shell of magnesium is filled, the only possible state consistent with Pauli exclusion is  $S = L = J = 0$ , that is,  $^1S_0$ . Once again, since there is only one possible state, Hund's rules are trivially satisfied.

Aluminium has electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^1$ . The one outer  $p$  electron determines the spin and angular momentum to be  $L = 1, S = 1/2$ .

Therefore  $J$  can be either  $1/2$  or  $3/2$ . So energy levels are  ${}^2P_{1/2}$ ,  ${}^2P_{3/2}$ . Hund's third rule then tells us that the lowest energy level of these two is  ${}^2P_{1/2}$ , which is also what is found experimentally.

4. Please see the excerpt from the lecture notes by E. Commins attached to the end of this document for details about calculating the possible total angular momentum.

(a) Boron has configuration  $1s^2 2s^2 2p^1$ . Carbon has configuration  $1s^2 2s^2 2p^2$ . Nitrogen has configuration  $1s^2 2s^2 2p^3$ .

(b) Boron has 1 p electron in the outer shell, so Boron must have  $L=1$ ,  $S=1/2$ . Therefore the total angular momentum can be either  $J = 3/2$  or  $J = 1/2$ . So the possible states are  ${}^2P_{1/2}$  or  ${}^2P_{3/2}$ .

Carbon has 2 p electrons, and they must be in an antisymmetric state because they are identical fermions. Both electrons have orbital angular momentum  $l = 1$ . When we add the orbital angular momentum of the two electrons, we obtain  $L = 0, 1$  or  $2$ . The  $L = 2$  state is symmetric, the  $L = 1$  state is antisymmetric and the  $L = 0$  state is symmetric. Both electrons have spin  $s = 1/2$ . When we add these two spins we obtain  $S = 0$  or  $1$ .  $S=1$  is a symmetric state and  $S=0$  is an antisymmetric state. We require the total wavefunction to be symmetric, so the only possible states are  $(L = 2, S = 0)$ ,  $(L = 1, S = 1)$  and  $(L = 0, S = 0)$ , that is,  ${}^1D$ ,  ${}^3P$  and  ${}^1S$ . Using the angular momentum addition of  $L$  and  $S$  we can then find the possible values of  $J$ . The possible states are  ${}^1D_2$ ,  ${}^3P_0$ ,  ${}^3P_1$ ,  ${}^3P_2$  or  ${}^1S_0$ .

Nitrogen has 3 p electrons and so the possible states are  ${}^2D$ ,  ${}^2P$ ,  ${}^4S$  (see lecture notes at the end of this document). Calculating the corresponding  $J$  values then leads to the following possible states:

${}^2D_{5/2}$ ,  ${}^2D_{3/2}$ ,  ${}^2P_{3/2}$ ,  ${}^2P_{1/2}$ , or  ${}^4S_{3/2}$ .

(c) Applying Hund's rules to the possible states found above, we predict that the ground state of Boron is  ${}^2P_{1/2}$ , the ground state of Carbon is  ${}^3P_0$  and the ground state of Nitrogen is  ${}^4S_{3/2}$ . This agrees with experiment.

## LECTURE NOTES ON MANY-ELECTRON ATOMS (E. Commins):

the Hamiltonian, it gives rise to an effective spin-spin coupling from the Coulomb interaction, as we discussed in the previous chapter.

To summarize, if we ignore the spin-orbit interaction,  $S = \sum_i S_i$  and  $L = \sum_i L_i$  separately commute with  $H$ , as does  $J$ . Therefore energy eigenstates simultaneously have definite values of  $J, L$ , and  $S$ . Our next task is to determine the possible values of  $J, L$ , and  $S$  for a given configuration, and establish reasons for energy ordering of states of given  $J, L, S$ .

### 13.6 Theory of multiplets in the Russell-Saunders scheme

In the central field approximation, the energy of an atom is determined solely by the configuration (assignment of  $n, \ell$  values to individual orbitals). Thus there is in general a great deal of degeneracy in each configuration. To see this consider a given  $\ell$  shell which can contain up to  $N_0 = 2(2\ell + 1)$  electrons. Suppose that in fact it contains  $n_0 < N_0$  electrons. For example, if  $\ell = 1$  ( $p$  shell),  $N_0 = 6$ . For carbon, we have 2 equivalent  $p$  electrons, so  $n_0 = 2$ . For nitrogen,  $n_0 = 3$ , for oxygen,  $n_0 = 4$ , and so on. The first electron may be placed in any one of the  $N_0$  orbitals, the second in  $N_0 - 1$ , the third in  $N_0 - 2$ , and so forth. Therefore, a priori there are:

$$\frac{N_0!}{(N_0 - n_0)!}$$

possibilities. However, some of these are equivalent because the electrons are indistinguishable: we must divide by the number of ways the electrons can be permuted among themselves, which is  $n_0!$ . Thus the degeneracy is:

$$g = \frac{N_0!}{n_0!(N_0 - n_0)!} = \binom{N_0}{n_0} \quad (13.32)$$

For example,

$$\begin{aligned} g(\text{carbon}) &= \binom{6}{2} = 15 \\ g(\text{nitrogen}) &= \binom{6}{3} = 20 \\ g(\text{oxygen}) &= \binom{6}{4} = 15 \\ g(\text{iron}) &= \binom{10}{6} = 210 \\ g(\text{gadolinium}) &= \binom{14}{8} = 3003 \end{aligned}$$

Thus in the central field approximation there are 15 degenerate states associated with the ground configuration of carbon, 210 in iron, etc. However, because of the electrostatic interaction the potential is not truly central and much of this degeneracy is lifted. Since  $L, S, J$  are still good quantum numbers, all states with given  $L, S, J$  remain degenerate (they form a *term*), but terms with distinct values of  $L, S, J$  in general have distinct energies. (The word *multiplet* is reserved for states with given  $L, S$ . Here, there can sometimes be several values of  $J$ . For example the ground multiplet of oxygen is  $^3P$  which consists of the terms  $J=2, 1$ , and  $0$ .) We have already seen the simplest example in Chapter 12: in helium the  $1s2s$  configuration has a degeneracy of 4, and it breaks up into two distinct terms:

$$^1S_0 : g = 1$$

$$^3S_1 : g = 3$$

Let us now see how the Pauli principle determines which multiplets correspond to a given configuration.

- a) If an atom contains only closed shells (e.g. the rare gas atoms and the group II elements Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg) the Pauli principle requires a pairing off of spins and orbital angular momenta to give  $S=0, L=0$ . Thus we must have a  $^1S_0$  ground state.
- b) If there is one electron outside of closed shells, the total spin  $S (=1/2)$  and the total orbital angular momentum  $L$  are that of the valence electron. Thus we obtain the following ground states:

$$H, Li, Na, K, Rb, Cs, Fr : ^2S_{1/2}$$

$$Ag, Au : ^2S_{1/2}$$

$$Ga, In, Tl : ^2P_{1/2}$$

Note that for  $Ga, In, Tl$  we have written  $J=1/2$  for the ground state. In fact we need some knowledge of the spin-orbit interaction to determine that  $J=1/2$  has lower energy than  $J=3/2$ .

- c) Atoms that lack just one electron to complete a shell (for example, the halogens which have 5 equivalent p electrons) may be treated as having one "hole", and the total spin and orbital angular momentum are that of the hole. Thus the halogen ground states are  $^2P_{3/2}$ ; (once again  $J$  is determined from knowledge of the spin-orbit interaction).
- d) If there are two electrons in the outermost incomplete shell, we can employ the following theorem: the wave function describing these electrons, which must be anti-symmetric with respect to exchange, can always be written as a product of a spatial part and a spin part. If the spatial part is symmetric, the spin part is anti-symmetric; and vice-versa. The proof of this theorem is exactly the same as for the  $1s2s$  configuration in helium (see Sec. 12.7) and we do not repeat it. The theorem may also be used if we have two equivalent holes in an incomplete shell.

For example, consider carbon, which has two equivalent  $p$  ( $\ell=1$ ) electrons. Then, the possible values of  $S$  are 1 and 0, while the possible values of  $L$  are 2, 1, and 0. Then, a priori we may form the multiplets:  ${}^3D, {}^3P, {}^3S, {}^1D, {}^1P, {}^1S$ . However, because of the symmetry properties of vector coupling coefficients,  $L=0, 2$  are symmetric spatial states, while  $L=1$  is anti-symmetric. Also  $S=1$  is a symmetric spin state, while  $S=0$  is anti-symmetric. Therefore the multiplets  ${}^3D, {}^3S$ , and  ${}^1P$  are excluded, and we are left with the multiplets:

$${}^3P \text{ (9 states), } {}^1D \text{ (5 states), } {}^1S \text{ (1 state)}$$

for a total of 15 states. The same remarks hold for oxygen, which has two equivalent  $\ell=1$  holes.

e) If there are more than 2 equivalent electrons, it is no longer possible to factor the wave function into space and spin parts with opposite exchange symmetry. However the multiplets can be enumerated in a systematic, if somewhat laborious way, by constructing a table. We illustrate with the example of 3 equivalent  $p$  electrons. The columns of the table (shown on the following page) are labeled:

$$m_{\ell_1}, m_{\ell_2}, m_{\ell_3}, m_{s_1}, m_{s_2}, m_{s_3}, M_L, M_S, L, \text{ and } S$$

We start by entering in the first row the maximum possible values of  $m_{\ell_i}$ ,  $i=1,2,3$ . For 3 equivalent  $p$  electrons this would be +1, +1, +1, yielding  $M_L=3$ . Now each of the  $m_{s_i}$  can only be  $\pm 1/2$  a priori. However, since  $m_{\ell_1}=m_{\ell_2}=m_{\ell_3}$ , no two of the  $m_{s_i}$  can be the same. Therefore we cannot have a state with  $M_L=3$ . Hence we cannot form an  $L=3$  multiplet; the largest possible value is  $L=2$ . Accordingly we try to construct a state with  $M_L=2$ , (the next row in the table). As can be seen, this is possible provided that not all values of  $m_s$  are the same; hence for this particular state we have  $M_S=1/2$ . Therefore this line of the table corresponds to a  ${}^2D$  multiplet, which has altogether 10 distinct states. Since the total degeneracy of a  $p^3$  configuration is 20, we must identify 10 more states. In the next lines of the table we write out those configurations associated with  $M_L=1$ . It can be seen that there are two independent possibilities. One linear combination must correspond to the  ${}^2D$ ,  $M_L=1$  state. The orthogonal combination must be the  $M_L=1$  component of a new multiplet with  $M_S=1/2$ , hence  $S=1/2$ . This is obviously  ${}^2P$ , and contains altogether 6 states. It remains to identify 4 of the 20 states. To this end we start to write out the lines of the table corresponding to  $M_L=0$ . It can be seen that there is one state with  $M_S=3/2$ . Since  $M_S=3/2$  did not occur in any of the previous lines, it must be associated with  $L=0$ ,  $S=3/2$  (a  ${}^4S_{3/2}$  multiplet with 4 states). We have now identified all 20 states, and it is unnecessary to fill in any more lines of the table. To recapitulate, a  $p^3$  configuration contains the multiplets  ${}^2D, {}^2P$ , and  ${}^4S$ .

Multiplet Table for  $p^3$

$m_{\ell 1}$	$m_{\ell 2}$	$m_{\ell 3}$	$m_{s1}$	$m_{s2}$	$m_{s3}$	$M_L$	$M_S$	$L$	$S$
1	1	1							Impossible
1	1	0	+	-	+	2	$\frac{1}{2}$	2	$\frac{1}{2}$
1	1	-1	+	-	+			2	$\frac{1}{2}$
1	0	0	+	-	+	1	$\frac{1}{2}$	1	$\frac{1}{2}$
1	0	-1	+	+	+	0	$\frac{3}{2}$	0	$\frac{3}{2}$

This method can be extended in a routine way to more complicated cases.

Now that we have a procedure for constructing the possible multiplets of a given configuration, how are they to be ordered in energy? There are several rules, named after the German spectroscopist F. Hund, who worked in the early decades of the 20<sup>th</sup> century and arrived at the rules empirically.

Hund's first rule: *Terms with the highest spin multiplicity lie lowest in energy.*

This owes its origin to the same phenomenon that causes  $^3S_1$  to lie lower than  $^1S_0$  in helium. Recall that the spatial wave function of the 2 electrons in  $^3S_1$  is anti-symmetric; thus the probability that both electrons are found in the same small region of space is vanishingly small. Hence the average value of the repulsive interaction  $1/r_{12}$  is much smaller than for  $^1S_0$ , where the spatial wave function is symmetric. More generally, given a many-electron configuration, a multiplet with large  $S$  has a more anti-symmetric spatial wave function than a multiplet with small  $S$ .

Hund's second rule: *For multiplets of the same  $S$ , those with higher  $L$  lie lower in energy.*

For given spin, multiplets with larger  $L$  tend to have electrons further apart than those with smaller  $L$ .

Several simple examples of these rules are provided by carbon, oxygen, and nitrogen. In carbon and oxygen,  $^3P$  lies lowest, followed by  $^1D$  and then  $^1S$ . In nitrogen, the ground multiplet is  $^4S$ , followed by  $^2D$  and then  $^2P$ .

However, while Hund's rules provide a very useful general guide, they are not always valid. Configuration mixing and other effects can alter the energy ordering of multiplets.

### 13.7 Calculation of multiplet energies in the L-S coupling scheme

Quantitative calculations of multiplet splittings are not trivial, even for relatively simple atoms. The basic approach is to start with the central field approximation, assume only a single configuration, and use first-order perturbation theory with the *Slater sum rule*. Let