

## Phys 487 Discussion 4 – Atomic Structure

Summary of the key elements that you must consider in understanding atomic structure are:

- The **good quantum numbers** of an N-electron atom are
  - the individual  $I_i$  of the individual electrons  $i = 1, \dots, N$   
(thus, “the Carbon ground state is  $1s^2 2s^2 2p^2$ ” is a meaningful thing to say)
  - the total  $L$ ,  $S$ , and  $J$  quantum numbers  
(where total means “of all the electrons”)

We have not proved this yet; coming up. It is called the **LS-coupling scheme** and works well when  $V_{ee} \gg V_{s-o}$  (which is true for all but the heaviest atoms). The term symbol for an atomic state is thus

$$\boxed{^{2S+1}L_J}.$$

This is exactly the same as for a 1-electron atom, except you replace the single-electron quantum numbers  $s$ ,  $l$ , and  $j$  with the total angular momentum quantum numbers  $S$ ,  $L$ , and  $J$ .

- The wavefunction of the atomic electrons must be **antisymmetric** under the exchange of any two of them, which can be accomplished by either of these arrangements :

$$\psi(1,2,3,\dots) = \begin{cases} \psi_S(\vec{r}_1, \vec{r}_2, \dots) \cdot \chi_A(1,2,\dots) \\ \psi_A(\vec{r}_1, \vec{r}_2, \dots) \cdot \chi_S(1,2,\dots) \end{cases}$$

In words: either the **space part** is symmetric and the **spin part** is antisymmetric, or vice versa.

NOTE: Are we certain that the N-electron wavefunction *always factorizes* into a space-only part  $\times$  a spin-only part? Yes, thanks to the LS-coupling scheme, which tells us that total-spin  $S$  and total-OAM  $L$  are separately conserved; the space part of the wavefunction determines  $L$ , and the separate spin part determines  $S$ .

- The main terms in the Hamiltonian that decide the ordering of energy levels are, in order of size,
  1. The **Bohr-model** Hamiltonian  $T + V_{\text{Coulomb}}$ , whose eigenvalues are determined by the quantum #  $n$
  2. The **repulsive**  $V_{ee}$  term we discussed today, whose average size is controlled mainly by  $S$  and  $L$
  3. The **spin-orbit**  $V_{s-o}$  term, whose size is controlled by  $J$

At the end, we went through the **Hund rules**, which specify how to use points 2 and 3 to determine the lowest-lying energy state of an atom:

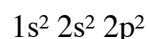
rule #1 First maximize  $S$  to minimize  $V_{ee}$  via the exchange force

rule #2 Then maximize  $L$ , also to minimize  $V_{ee}$  (less dramatically)

rule #3 Then choose  $J$  to minimize the  $V_{s-o}$ : for shells less than half full, minimize  $J$   
for shells more than half full, maximize  $J$

### Problem 1 : 1 x 1

We were about to study the Carbon atom in class but didn't quite make it. Its ground-state configuration is



- (a) The  $1s^2 2s^2$  part comprises two **closed shells**, with total  $S = 0$  and total  $L = 0$ . To be certain that this is the case, check the NIST energy level database for the 4-electron atom Beryllium. Does the term symbol you find there for the ground state match  $S = 0$  and  $L = 0$ ?
- (b) Thus, from the perspective of angular momentum, we ignore the closed-shell part and focus on the two

p-shell electrons of Carbon. Each of them has  $l = 1$ . How many  $ml$  states are associated with each electron, and as a result, how many OAM states  $|m_{l1}, m_{l2}\rangle$  are there for the  $2p^2$  electrons?

(c)  $|m_{l1}, m_{l2}\rangle$  is one possible basis;  $|L, M\rangle$  is another. Enumerate all possible  $|L, M\rangle$  states for the  $2p^2$  electrons of carbon, and check that you have the same number of states as in part (b)!

(d) Each  $L$  value produces a **multiplet** of states  $|L, M\rangle$ . As it happens, whenever you add two equal angular momenta together (such as  $l_1 = 1$  and  $l_2 = 1$  in our example), the  $L$  multiplets have these features :

- every member of an  $L$  multiplet has definite symmetry under exchange (either symm or anti-symm)
- even values of  $L$  produce symmetric states and odd values of  $L$  produce anti-symmetric states

You can readily prove this by constructing the Clebsch-Gordan coefficients as we did last year. We also discussed this in class. Let's make sure it is intuitively clear (and that you remember how to use Clebsch-Gordan tables ☺) : using the Clebsch-Gordan tables on the website,

(i) Write down the states  $|2 +2\rangle_{LM}$ ,  $|2 +1\rangle_{LM}$ ,  $|1 +1\rangle_{LM}$ ,  $|1 0\rangle_{LM}$ , and  $|0 0\rangle_{LM}$  in the basis  $|m_1 m_2\rangle$ .

(ii) Examine the states in the  $|m_1 m_2\rangle$  basis, where the state of the individual electrons (#1 and #2) can be seen, and indicate whether each is symmetric or anti-symmetric under exchange.

See how it works? The highest- $L$  multiplet is always symmetric, the one underneath is antisymmetric by orthogonality with the previous one, etc.

## Problem 2 : Carbon $2p^2$

Now we can construct *all possible* states  $^{2S+1}L_J$  of the two p-shell electrons in carbon, and figure out their energy ordering using the Hund rules.

(a) First list all possible  $^{2S+1}L$  states, i.e. ignore  $J$ . You should get **three**. If you get six, you need to apply an important constraint ... that is on page 1 ... second bullet ... you just did some relevant work in problem 1 ...

(b) Now apply Hund rule #1 to figure out which of those three is the ground state. You do not have to memorized Hund #1 because it is really clear when you remember the exchange force and how it can powerfully affect that repulsive  $V_{ee}$  term!

(c) Next apply Hund rule #2 to figure out the smaller splitting between the other two states: which has lower E?

(d) Finally consider all possible  $J$  values for all the states. There is a 3-fold degeneracy in one of the states ... but it is broken by the spin-orbit interaction. Recalling that  $V_{s-o} \sim +\vec{l} \cdot \vec{s}$ , you won't even have to flip back to read Hund #3, it is very clear which  $J$  value will have the lowest energy and which the highest.

(e) Check your energy-level diagram with NIST! Do you have all five  $^{2S+1}L_J$  states in the right order?