

Phys 487 Discussion 5 – Atomic Structure

Now that we are studying **multi-electron atoms**, it is important to distinguish between the operators and quantum numbers of single electrons as compared to the total for all electrons. As in classical mechanics, we use lower-case letters to refer to single-particle properties and CAPITAL letters to refer to TOTAL properties of the system. For a system of N electrons,

$\hat{L} = \hat{l}_1 + \hat{l}_2 + \dots + \hat{l}_N$ = operator for TOTAL orbital angular momentum of atom,
obtained by summing over the angular momenta of the atom's N electrons

$\hat{S} = \hat{s}_1 + \hat{s}_2 + \dots + \hat{s}_N$ = operator for TOTAL spin angular momentum of atom,
obtained by summing over the angular momenta of the atom's N electrons

$\hat{J} = \hat{L} + \hat{S}$ = operator for TOTAL angular momentum of all types (orbital + spin)

We've grown accustomed to considering only single particles, so watch out for capital vs lower-case letters in the problems below.

Here is a summary of the key elements needed to understand atomic structure.

- The **good quantum numbers** of an N -electron atom are
 - the individual l_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 discussed this yet; coming up. It is called the **LS-coupling scheme**. It is approximate but it works very well when $V_{ee} \gg V_{s-o}$ (which is true for all but the heaviest atoms). The term symbol for the state of a multi-electron atom 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 (or linear combinations thereof):

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

In words: either the **space part** is symmetric and the **spin part** is antisymmetric, or vice versa. (FYI ¹)

- 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

¹ Just FYI: There are additional ways of constructing fully-antisymmetric wavefunctions. They appear when **more than two** identical particles are involved. We won't be working with such systems in this course, but so that you are aware, you can/will get so-called **mixed symmetry** terms that can be combined. E.g. You can combine a spatial wavefunction that is symmetric only in the first two particle indices with a spin wavefunction that is antisymmetric in the same two indices. Also, so you know, the basic procedure for adding three spins together is simple: you first add #1 and #2 (using our CG tables), then add #3 to the combined #12 system.

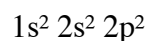
At the end, we went through the **Hund rules**, which specify how to use points 2 and 3 to determine the lowest-lying energy state of an atom:

rule #1 First **maximize S** \rightarrow minimizes V_{ee} via the exchange force
 rule #2 Then **maximize L** \rightarrow also minimizes V_{ee} (less dramatically)
 rule #3 Then choose J to minimize V_{s-o} :
 for shells less than half full, **minimize J** (we discussed this case today)
 for shells more than half full, **maximize J**

The ultimate source of atomic physics data is the **NIST Atomic Spectra Database**. (NIST = National Institute of Science and Technology, a world-class institute in the DC area that specializes in precision measurements.) You will check your answers today on atomic energy levels against this database. To find it, just google “NIST atomic levels”, will take you right there. (FYI: The database has a “levels” section and also a “lines” section, you’ll see the tabs at the top. We only want “levels” = energy levels for the next while.) When you specify an atom to research, you must also give the ionization state you want. The easiest notation to use to look for e.g. neutral iron is “Fe 0”; singly-ionized iron is “Fe 1+”, doubly-ionized is “Fe 2+”, etc. There is an equivalent roman numeral notation they seem to prefer, but it confuses me. :-)

Problem 1 : 1 x 1

Consider the neutral carbon atom, with 6 electrons ($Z=6$). 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 ($Z=4$). 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 m_l 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? (see footnote if you’re disturbed²)

(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 $|L, M\rangle$. 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 (CG) coefficients as we did last year. We also discussed this in class for two spin- $\frac{1}{2}$ particles. Let’s make sure it is intuitively clear (and that you remember how to use CG tables ☺) : using the CG tables on our website,

(i) Write down the states $|2+2\rangle_{LM}$, $|2+1\rangle_{LM}$, $|1+1\rangle_{LM}$, $|10\rangle_{LM}$, and $|00\rangle_{LM}$ 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.

² Are you disturbed that we are tabulating states of m_l when these are not good quantum numbers in the presence of the spin-orbit interaction? GOOD JOB! ☺ You are quite correct. I am just using this as an example to practice angular momentum addition.

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 correct order?