

## Worksheet AM1: Coupling Interactions

In complex atoms, the electrons interact with each other. Naturally, the interactions affect the energy. Also, due to these interactions, the individual electrons can change their individual orbital and spin angular momenta (specified by quantum numbers  $l$ ,  $m_l$ , and  $m_s$  for each electron;  $s$  of course is always  $\frac{1}{2}$  and cannot change). Consequently, each atom has many different possible states. Even the ground electron configuration itself may correspond to several different states: some have different energies, some are degenerate.

Why is this important? For many reasons. For example, because there are many states, atomic spectra are complex. Some states may be more reactive than others. Later we will see that the same issues are important for molecules. In order to understand spectra and reactivity, we need to understand the diversity of states accessible to an atom or molecule.

To get a handle on this, we need to understand how the electron-electron interactions lead to different states, develop a method for determining the states accessible to an atom, and of course develop a terminology for describing the states of atoms.

### Critical Thinking Questions

- As a macroscopic analogy, think of an idealized pool table on which there is no friction. Let's consider a few scenarios.
  - There is *one* ball on the table. The ball constitutes "the system." You hit the ball with your cue stick. It rolls across the table, occasionally bouncing off the walls. Describe what happens. Is the ball's kinetic energy conserved? Is its momentum conserved?
  - There are *two* balls on the table. Together, the two balls constitute "the system." With your cue stick you hit one ball, which rolls toward the other ball and hits it head-on. Describe what happens. Are the kinetic energy and momentum of the individual balls conserved? Are the kinetic energy and momentum of the system conserved?
- We described the electron in a hydrogenic atom with the quantum numbers  $l$ ,  $m_l$ ,  $s$ , and  $m_s$ . Suppose we used the same set of quantum numbers to describe each electron in a complex atom ( $l_1, m_{l1}, s_1, m_{s1}, l_2, m_{l2}, s_2, m_{s2}$ , etc.). In view of the answers to CTQ 1, would you expect these individual-electron quantum numbers to be conserved over time? Why or why not?
- Suppose we describe the total momentum of all the electrons in our complex atom. It turns out that there are quantum numbers to describe the total angular momentum ( $J, M_J$ ). Would you expect  $J$  and  $M_J$  to be conserved over time? Why or why not?
- Because the balls in the macroscopic system interact, we say their motion is "coupled." Likewise, the electrons in the microscopic system are coupled by their interactions. List the different ways in which electrons "interact" or are "coupled." Be as complete as you can.

5. The picture for electrons is more complicated than for the pool balls. Electrons possess two kinds of angular momentum. (i) What are they? (ii) Does the Earth possess more than one kind of angular momentum?
6. Even for a single electron in a hydrogenic atom, the orbital and the spin behaviors are coupled. We call this “spin-orbit coupling.” (i) What is the interaction that provides this coupling? (ii) What general word would you use to describe it (gravitational, electrostatic, magnetic, etc.)? (iii) Draw a picture to depict the interaction. (You can consult your text, of course. It will be very helpful if you understand the picture well enough to remember it.)
7. Consider your list of interactions between electrons in CTQ 4. (i) Which interaction(s) “couple” the orbital angular momenta of individual electrons (i.e. which interactions couple  $l_1, l_2, m_{l1}, m_{l2}$  etc.)? (ii) Which interaction(s) “couple” the spin angular momenta of individual electrons? (iii) Which interaction(s) “couple” the orbital with the spin angular momenta of electrons?
8. Let’s put some meat on these bones, so to speak. Consider the following ways to place 3 electrons in a p subshell (a  $p^3$  configuration). Each possibility is a “state” (sometimes we say “microstate”). (i) Predict the ordering of energies. Will any of the microstates be degenerate? (ii) What interactions cause the energies to be different (name them)?

1.  $\uparrow \quad \uparrow \quad \uparrow$

2.  $\uparrow \quad \downarrow \quad \uparrow$

3.  $\uparrow\downarrow \quad \uparrow \quad \underline{\quad}$

4.  $\downarrow \quad \downarrow \quad \downarrow$

## Worksheet AM2: Coupling Angular Momentum

The interactions that couple electrons with each other involve angular momentum (orbital and spin). Consequently, we can distinguish the different states of atoms by the way in which individual angular momenta are coupled. The angular momenta are described by quantum numbers, so we will begin by considering the appropriate quantum numbers to use. Then we will develop rules for analyzing the states of complex atoms.

The wavefunction for a system,  $\psi$ , is often called a “stationary state.” That does not mean that the system does not move. It means that important properties of the system do not change over time, for example the total energy and the total angular momentum. As long as the system does not interact with other systems, these properties are conserved. This is in direct analogy to macroscopic systems. For an isolated macroscopic system, the total energy and the total angular momentum are conserved. In the quantum world, quantum numbers correspond to conserved properties like the total energy (hence the quantum number  $n$  for a hydrogenic atom: the value of  $n$  specifies the total energy,  $E_n$ ).

### Critical Thinking Questions

1. We sometimes speak of “good” quantum number and “bad” quantum numbers. Can you guess what “good” and “bad” mean? Hint: a “good” quantum number corresponds to a property that is strictly conserved. (i) What would it mean for a quantum number to be “bad”? (ii) What might it mean for a quantum number to be “pretty good”? (iii) What might cause a quantum number to be only “pretty good” or “bad”?
2. Electrostatic interactions and spin correlation effects between electrons are pretty strong. What do you conclude about the quantum numbers  $l$ ,  $m_l$ , and  $m_s$  (which describe individual electrons in atoms)?
3. The individual orbital angular momenta of electrons in an atom can be coupled to give a total orbital angular momentum (described by the quantum numbers  $L$  and  $M_L$ ), and the individual spin angular momenta can be coupled to give a total spin angular momentum (described by the quantum numbers  $S$  and  $M_S$ ). (i) Suppose there were no spin-orbit interaction. Would these quantum numbers be “good”, “pretty good”, or “bad”? (ii) In fact, there *is* a spin-orbit interaction. But for light atoms, it is very small compared to the electrostatic interactions and spin correlation effects. Which category do  $L$ ,  $M_L$ ,  $S$ , and  $M_S$  really fall into for light atoms: “good”, “pretty good”, or “bad”?

Comment: You should now understand why we use the quantum numbers  $L$ ,  $M_L$ ,  $S$ ,  $M_S$ ,  $J$  and  $M_J$  to describe the states of light atoms. We will now discuss a method for determining these quantum numbers that is called either “Russell-Saunders coupling” or “L-S coupling.”

4.  $L$  and  $S$  are determined with the Clebsch-Gordan series:

$$L = l_1 + l_2, \dots, |l_1 - l_2|$$

The same idea works for any kind of angular momentum, hence:

$$S = s_1 + s_2, \dots, |s_1 - s_2|$$

Determine the values of  $L$  and  $S$  possible for the electron configurations (i)  $p^1d^1$ , (ii)  $p^2d^1$ .  
Hint: when there are three electrons, first choose any two and couple them. Then couple the third electron to the result. [See your text to understand why the Clebsch-Gordan series works.]

5. For any given value of  $L$  or  $S$ , the allowed values of  $M_L$  and  $M_S$  are:

$$M_L = \pm L, \pm(L-1), \dots, 0$$

$$M_S = \pm S, \pm(S-1), \dots, \pm\frac{1}{2} \text{ (if } S \text{ is half-integral) or } 0 \text{ (if } S \text{ is integral)}$$

For each of the  $L$  and  $S$  values you determined for the  $p^1d^1$  configuration (CTQ 4), determine all the allowed values of  $M_L$  and  $M_S$ .

6. Once you have determined  $L$  and  $S$ , you can couple them to determine  $J$ . Why do you think we have done things in this order (first couple  $l_1, l_2$  etc to give  $L$  and  $s_1, s_2$  etc. to give  $S$ , and only then couple  $L$  and  $S$  to give  $J$ )?
7. Couple  $L$  and  $S$  to give  $J$  for the  $p^1d^1$  configurations (CTQ 4).
8. The spin-orbit interaction is proportional to  $Z^4$ , where  $Z$  is the atomic number. What does this mean for  $L$  and  $S$ ? (i) Are they “good”, “pretty good”, or “bad” quantum numbers for heavy atoms like transition metals? (ii) Do you think Russell-Saunders coupling is a good way to figure out the possible states of heavy atoms?
10. There is an alternative coupling scheme, called  $jj$ -coupling, often used for heavy atoms. In this coupling scheme, the  $l$  and  $s$  for each individual electron are coupled to give a  $j$  for that electron. Then the  $j$  values for each electron are coupled to give a total  $J$ . Why is this done? Hint: think about the relative strengths of the interactions.
11. A note of caution: Russell-Saunders coupling can over-count the possible states when there are equivalent electrons. Equivalent electrons are electrons that occupy the same subshell. Here is an example. Determine the maximum value of  $L$  for a  $p^4$  configuration using Russell-Saunders coupling. Is it actually possible? Why or why not?

Comment: Do not worry. We are going to treat this possibility as “for experts.” You should just be aware that the possibility of over-counting exists. If you need to treat equivalent electrons, there are methods you can learn to avoid over-counting. We will not learn them in this course.

### Worksheet AM3: Term symbols

Now you understand that an atom can have many states, even for one electron configuration. A compact notation is needed to describe the states. We call the states “Terms”; the symbols for them are “Term Symbols.” The rules are simple:

1. Represent L with a capital letter, in analogy to the way we name orbitals. An orbital with  $l=0$  is called s; with  $l=1$ , p; with  $l=2$ , d, etc. A term with  $L=0$  is called S; with  $L=1$ , P; with  $L=2$ , D, etc.
2. Represent total spin using the “multiplicity”, represented with a capital M and defined as  $M = 2S+1$ . (If this seems weird, note that there are  $2S+1$  different allowed values of  $M_S$  for any given value of S. Hence M is the “multiplicity” of spin states for a given value of S.) Give M as a left superscript to the capital letter.
3. Give the value of J as a right subscript to the capital letter. Sometimes we give several values of J together for compactness. This is because, often, the energies of terms with a given M and L are degenerate or very closely spaced in energy.

Examples:  $L=1, S=1, J=2: {}^3P_2$        $L=0, S=1/2, D=1/2: {}^2S_{1/2}$

Note that the term symbol alone does not define a state unambiguously. Each electron configuration gives rise to a set of terms, but the terms may not be unique to that configuration. For example,  $[\text{He}]2s^1$  and  $[\text{Ne}]3s^1$  both give rise to a  ${}^2S_1$  term. If you need to be specific, give both the configuration and the term symbol.

### Critical Thinking Questions

1. Write the term symbols for: (i)  $L=0, S=0, J=0$ , (ii)  $L=2, S=1, J=1$ , (iii)  $L=1, S=3/2, J=1/2$
2. Write all the term symbols for terms arising from an  $s^1p^1$  configuration (It could be  $2s^12p^1$  or  $3s^13p^1$  or .... The terms would have the same symbols.)
3. With lots of electrons, it can get tricky. There is a simplifying rule. Any filled subshell is irrelevant for the term symbol. Can you explain why this is?
4. Write all the term symbols for terms arising from a  $1s^22s^23s^13d^1$  configuration (note this an excited configuration).
5. There is a set of rules for arranging the terms in a given configuration in order of energy. There is a catch, though. It only works well for the ground configuration. Here are the rules:
  - (a) The term with larger M is lower in energy. **Can you think of an explanation?**
  - (b) For terms with identical multiplicity, the term with larger L is lower in energy. **Can you think of an explanation? Hint: think about how far apart electrons can keep themselves from each other.**
  - (c) For the case that M and L are identical, there is also a rule about J. It is not used so much, but here it is: if the shell is less than half filled, the term with lower J is lower in energy; if the shell is more than half filled, the term with higher J is lower in energy.

6. Write the term symbols for terms arising from the  $[\text{Ne}]3s^23p^2$  configuration and arrange them in order of energy. Do not worry about J for now. [*Is this a case when Russell-Saunders coupling will over-count? If so, don't worry about it, but we will discuss the matter.*]
7. When an atom absorbs or emits a photon, the photon brings (or carries away) a unit of energy and also a unit of angular momentum. Consequently the values of L, S and J can change, and thus the term can change. There are rules governing which transitions are possible ("allowed") and which are impossible ("forbidden"). The rules are called "selection rules":

$$\Delta S = 0 \quad \Delta L = 0, \pm 1 \quad \Delta J = 0, \pm 1 \text{ but } J=0 \leftarrow | \rightarrow J=0 \text{ (forbidden)}$$

8. Which of these transitions are allowed, and why (note that the upper term precedes the lower by convention, so  $\rightarrow$  is an emission and  $\leftarrow$  is an absorption)?

