ATOMIC SPECTROSCOPY SUMMARY

TERM SYMBOLS

- Because the total angular momentum and energy commute, we can use the angular momentum (L) to label the energy states.
- Note that electron configurations are ambiguous in that we don't specify which orbital or which spin each electron has. This means that there are a number of different sets of m_ℓ and m_s that are consistent with a given configuration.
- Why are there different energies? Because of electron/electron repulsion and spin-orbit coupling, the ways we can fill the orbitals DO NOT NESCESSARILLY have the same energy. (Remember that we talked about how Hund's rules come from this. How spin up elelctrons interact less with other spin up electrons in the same subshell.)

  Components of a Term Symbol:

$$^{2S+1}L_J$$

RULES FOR TERM SYMBOLS

Term Symbols are assigned based on two main rules:

1. **Unsöld's Rule:** All filled shells/subshells are ignored when calculating L and S. Basically, all of the electrons will have their contributions to spin and orbital angular momentum canceled by other electrons in the same subshell.
2. **"holes":** The state of the "hole" (an empty spot in an orbital where an electron could be but isn't) is the same as the state of an electron. This means that when we look at a p^5 we can pretend it is a p^1. This is incredibly useful as it means that instead of 5 electrons to tinker with, you can just act like it is 1.

CALCULATING L:

- L is the **Total Angular Momentum**

  L= (sum of ℓ values) ….(smallest positive difference of ℓ values)

  - 2 s electrons (different shells)
    L=0+0,…,0-0
    L=0
  - 1 d electron and 1 p electron
    L=2+1,…,2-1
    L=3, 2, 1

- S is the **Total Spin**

  S is the total spin quantum number of the electrons in an atom. Each electron has a value of s=1/2. If the electrons are paired, the spins cancel, and you do not count them. If they are unpaired, the spins add.

  2 d elecctrons:

↑	↑			

S=1

↑	↓			

S=0

- J is the **Total Angular Momentum (Spin-Orbit Coupling)**

  J=L+S,…$|L-S|$

HOW TO DERIVE TERM SYMBOLS FOR A CONFIGURATION

CASE 1: ELECTRONS ARE IN SEPARATE SUBSHELLS

- Because the electrons are in separate subshells, we do not need to worry about the Pauli Exclusion Principal.
- All values of L and S will be fine because of this, and you do not have to worry about writing out configurations that work.

  - $2p^1\ 3d^1$

  L=1,2,3 S= 0,1

  So all the terms that are combinations will be possible:

  ^1F, ^1D, ^1P, ^3F, ^3D, ^3P

  Now, with J:

  $^3F_4$, $^3F_4$, $^3F_4$, $^1F_4$ $^3D_3$, $^3D_2$, $^3D_1$, $^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$, $^1P_1$

CASE 2: DERIVE TERM SYMBOLS WHEN ELECTRONS ARE IN THE SAME SUBSHELL

- Here, you MUST write out all the possible Configurations, as some terms will not be allowed due to the Pauli Exclusion Principle.
- Remember how the projection on the z-axis corresponds to the angular momentum vectors… This will be the same.

p^2 Configuration:

p_1	p_0	p_{-1}	M_L	M_S	Terms:	^1D	^3P	^1S
↑↓			2	0		✓		
↑	↑		1	1			✓	
↑	↓		1	0		✓		
↓	↑		1	0			✓	
↓	↓		1	-1			✓	
↑		↑	0	1			✓	
↑		↓	0	0		✓		
	↑↓		0	0			✓	
↓		↑	0	0				✓
↓		↓	0	-1			✓	
	↑	↑	-1	1			✓	
	↑	↓	-1	0		✓		
	↓	↑	-1	0			✓	
	↓	↓	-1	-1			✓	
		↑↓	-2	0		✓		

Problem Set: Due Wednesday Nov 4

Derive the term symbols for the following configurations:

1. The ground state configuration of Li.
2. d^3
3. p^5
4. p^1
5. d^8
6. d^2