

Lecture 4

Electronic Microstates & Term Symbols

Suggested reading: Shriver and Atkins, Chapter 20.3
or Douglas, 1.4-1.5

Recap from last class: Quantum Numbers

Four quantum numbers: “n”, “l”, “m_l”, and “m_s”

Or, equivalently: “n”, “l”, “j”, and “m_j”

Orbital angular
momentum:



Associated with
rotation of electron
cloud around
nucleus

Spin angular
momentum:



Associated with
rotation/spin of
electron around it's
axis

Total angular
momentum:



Vector sum of
orbital and spin
angular
momentum

Recap from last class: Quantum Numbers

Four quantum numbers: “n”, “l”, “m_l”, and “m_s”

Or, equivalently: “n”, “l”, “j”, and “m_j”

Orbital angular
momentum:

$$L = \hbar \sqrt{\ell(\ell + 1)}$$

$$L_z = m_\ell \hbar$$

$$\ell = 0, 1, 2, \dots, n-1$$

$$m_\ell = -\ell, \dots, 0, \dots, +\ell$$

Spin angular
momentum:

$$S = \hbar \sqrt{s(s+1)}$$

$$S_z = m_s \hbar$$

$$s = 1/2$$

$$m_s = \pm 1/2$$

Total angular
momentum:

$$J = \hbar \sqrt{j(j+1)}$$

$$J_z = m_j \hbar$$

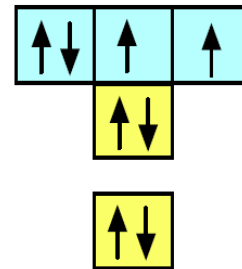
$$j = \ell - s, \dots, \ell + s$$

$$m_j = -j, \dots, 0, \dots, +j$$

Electronic Configurations and Microstates

- Electronic configurations tell us the number of electrons in each orbital, but they don't tell us how the electrons occupy the orbitals.

i.e., don't always want to draw:



- “Terms”: the energy levels and configurations of atoms and ions (and molecules)
- Useful in understanding ionic and coordination compound spectra

General Form of Terms

$$n^a T_b$$

- n: principle quantum number

- $a = 2S+1$ “multiplicity”

(S is the total spin angular momentum of all electrons)

****a number****

For example, if two electrons are in two different orbitals we might have antiparallel spins:

$$\begin{aligned} S &= s_1 + s_2 \\ &= \frac{1}{2} - \frac{1}{2} = 0 \end{aligned}$$

Or parallel spins: $S = s_1 + s_2 = \frac{1}{2} + \frac{1}{2} = 1$

General Form of Terms

$$n^a T_b$$

- n: principle quantum number of valence electrons

- $a = 2S+1$ “multiplicity”

- (S is the total spin angular momentum of all electrons)

- **a number**

- T=L (total orbital angular momentum of all electrons; vector sum of ℓ , the orbital momentum of individual electrons)

- **a letter**

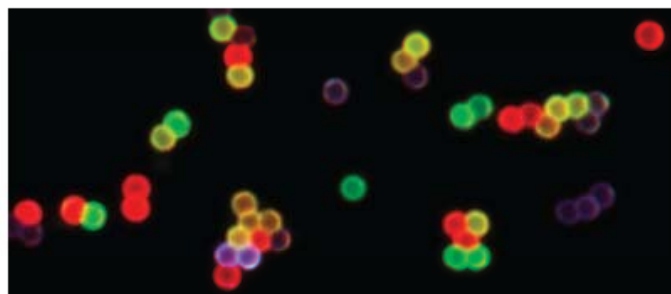
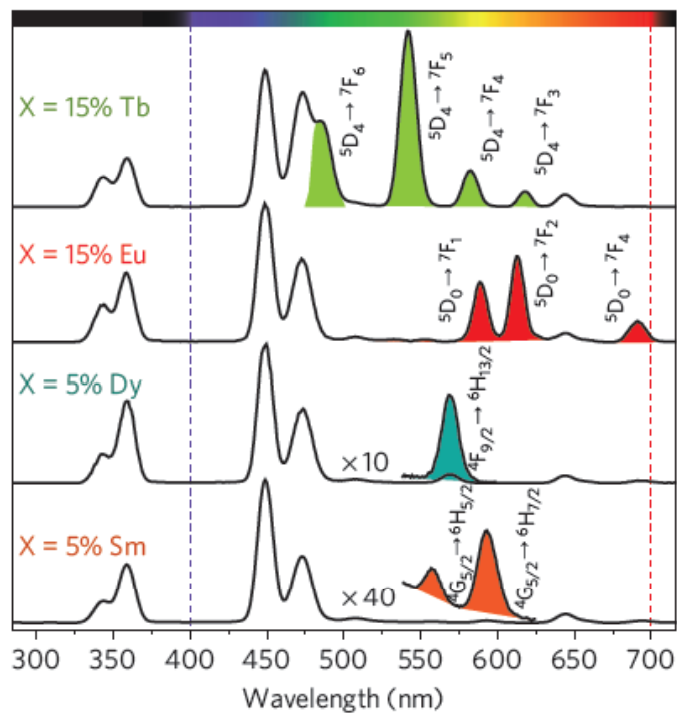
- L=0, 1, 2, 3, 4 \rightarrow S, P, D, F, G

- b=J (total angular momentum)

- **a number**

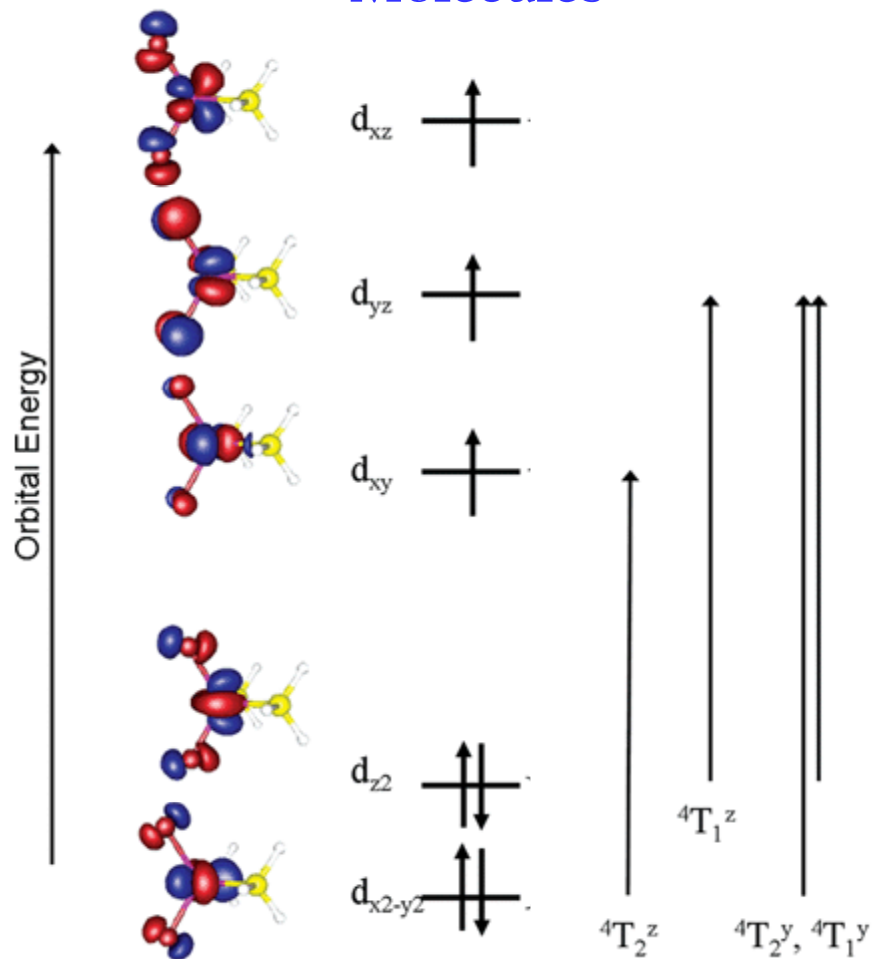
Examples of Term Symbols in the literature

Free Ions/ Atoms



Wang, *Nature Materials* 10 (2011)

Molecules



Sundararajan, *Dalton Trans.*, 2009, 6021-6036

$\text{Co}(\text{PPH}_3)_2\text{Cl}_2 \rightarrow$ Used in palladium-catalyzed coupling reactions, 2010 Nobel Prize

Hydrogen (1 electron atom)

Ground state: $1s$

$$n=1; \ell=0$$

$$L = \ell = 0$$

$$S = s = 1/2$$

$$J = L + S \text{ (vector sum)}$$
$$= 0 + 1/2$$

Only one term is possible
(i.e., only one energy level
for the one microstate)

$^2S_{1/2}$ (read “doublet S”)

In a magnetic field, due to the Zeeman effect, the $1^2S_{1/2}$ term yields two closely-spaced energy levels ($m_j = 1/2, -1/2$)

Multiplicity terms

$S = \frac{1}{2} \rightarrow 2S+1 = a = 2$ doublet (electron can be spin up or spin down)

$S = 1 \rightarrow 2S+1 = a = 3$ triplet (three different spin configurations, with spin wavefunction χ)

$\chi = \uparrow\uparrow$ (both electrons spin up)

$\chi = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$ (electrons are indistinguishable)

$\chi = \downarrow\downarrow$ (both electrons spin down)

Multiplicity terms

$S = 1/2 \rightarrow 2S+1=a=2$ doublet (electron can be spin up or spin down)

$S = 1 \rightarrow 2S+1=a=3$ triplet (three different spin configurations, with spin wavefunction χ)

$S = 3/2 \rightarrow 2S+1=a=4$ quartet (four different spin configurations)

$$\chi = \uparrow\uparrow\uparrow$$

$$\chi = \frac{1}{\sqrt{3}} (\uparrow\downarrow\downarrow + \downarrow\downarrow\uparrow + \downarrow\uparrow\downarrow)$$

$$\chi = \frac{1}{\sqrt{3}} (\uparrow\uparrow\downarrow + \uparrow\downarrow\uparrow + \downarrow\uparrow\uparrow)$$

$$\chi = \downarrow\downarrow\downarrow$$

Hydrogen (1 electron atom)

Excited state: $2p^1$

$$n=2; \ell=1$$

$$L = \ell = 1$$

$$S = s = 1/2$$

$$J = L + S$$

$$= 1 + 1/2 \text{ or } 1 - 1/2$$

$$= 1/2 \text{ or } 3/2$$

Two terms are possible
(i.e., two energy levels,
depending on the
orientations of the electron
spin with respect to the
orbital angular momentum
of the electron)

$${}^2P_{1/2} \text{ or } {}^2P_{3/2}$$

In a magnetic field, due to the Zeeman effect, the ${}^2P_{1/2}$ term yields two closely-spaced energy levels ($m_j = 1/2, -1/2$) while the ${}^2P_{3/2}$ yields four ($m_j = 3/2, 1/2, -1/2, -3/2$)

Helium (2 electron atom)

$$L = \ell_1 + \ell_2$$

$$S = s_1 + s_2$$

Ground state: $1s^2$

$$n=1; \ell_1=\ell_2=0$$

$$L = \ell_1 + \ell_2 = 0$$

$$S = s_1 + s_2 = 1/2 - 1/2 \text{ (Pauli)} = 0$$

$$J = L + S \text{ (vector sum)} = 0$$

1S_0



Helium (2 electron atom)

$$L = \ell_1 + \ell_2$$

$$S = s_1 + s_2$$

Ground state: $1s^1 2p^1$

$$\ell_1=0; \ell_2=1$$

$$L = \ell_1 + \ell_2 = 1$$

$$S = s_1 + s_2 = 1/2 - 1/2 \text{ or } 1/2 + 1/2 \\ = 0 \text{ or } 1$$

$$J = L + S (\text{vector sum}) = 0$$

1P_0 “singlet P”

3P_0 “triplet P”

Carbon (6 electron atom)

$$L = l_1 + l_2 + l_3 + l_4 + l_5 + l_6$$

$$S = s_1 + s_2 + s_3 + s_4 + s_5 + s_6$$

Ground state: $1s^2 2s^2 2p^2$

$$l_1=0; l_2=0; l_3=0; l_4=0; l_5=1; l_6=1$$

$$L = 2, 1, 0 \rightarrow D, P, S$$

$$S = 0 \text{ or } 1 \rightarrow 2S+1 = 1, 3$$

$$J = L+S(\text{vector sum}) = 3, 2, 1$$

The electrons in the $1s$ and $2s$ states will be spin paired. The two electrons in p can be either in p_x , p_y , or p_z orbitals, and either paired or unpaired:

$$m_\ell = -1 \quad m_\ell = 0 \quad m_\ell = +1$$

Microstates

Microstates: the different ways in which electrons can occupy certain orbitals

Grouping together the microstates that have the same energy when electron-electron repulsions are taken into account, yields the terms (i.e., the spectroscopically distinguishable energy levels)

Number of microstates: $\Gamma = \frac{2N_0!}{(2N_0 - N_e)!N_e!}$

$N_0 = \#$ degenerate orbitals (i.e., three degenerate p orbitals)

$N_e = \#$ electrons

Carbon, continued: [He]2p²

$$\Gamma = \frac{2N_0!}{(2N_0 - N_e)!N_e!} = \frac{2(3!)}{(2 \cdot 3 - 2)!2!} = 15$$

$N_0 = \#$ degenerate orbitals for $p=3$

$N_e = \#$ electrons in $p=2$

What are the microstates, and which has the lowest energy?

Carbon, continued: $[\text{He}]2p^2$

m_l	$m_s = +1/2$			$m_s = -1/2$			$M_L = \sum m_l$	$M_S = \sum m_s$
	+1	0	-1	+1	0	-1		
1	↑	↑					1	1
2	↑		↑				0	1
3		↑	↑				-1	1
4				↓	↓		1	-1
5				↓		↓	0	-1
6					↓	↓	-1	-1
7	↑			↓			2	0
8	↑				↓		1	0
9	↑					↓	0	0
10		↑		↓			1	0
11		↑			↓		0	0
12		↑				↓	-1	0
13			↑	↓			0	0
14			↑		↓		-1	0
15			↑			↓	-2	0

Carbon, continued: $[\text{He}]2p^2$

		$M_S = \sum m_s$		
		+1	0	-1
$M_L = \sum m_l$	-2	0	1	0
	-1	1	2	1
	0	1	3	1
	+1	1	2	1
	+2	0	1	0

Note: the array is symmetric about the lines through $M_L=0$ and $M_S=0$, providing a check of the tabulation

$$M_L = 2, 1, 0, -1, -2 \rightarrow L=2 \rightarrow \text{a D term}$$

The values in the array occur only for $M_S=0 \rightarrow S=0$

****a 1D term!****

Subtracting out the 1D term:

	$M_S = \Sigma m_s$		
	+1	0	-1
$M_L = \Sigma m_l$			
-2			
-1	1	1	1
0	1	2	1
+1	1	1	1
+2			

$M_L = 1, 0, -1 \rightarrow L=1 \rightarrow$ a P term

The values in the array occur $M_S = 1, 0, -1 \rightarrow S=1$

****a 3P term!****

Subtracting out the 3P term:

	$M_S = \sum m_s$		
	+1	0	-1
$M_L = \sum m_l$	-2		
	-1	0	0
	0	0	1
	+1	0	0
	+2		

$M_L=0 \rightarrow L=0 \rightarrow$ a S term

$M_S=0 \rightarrow S=0$

****a 1S term!****

The energies of the terms

1. Hund's rule: For a given configuration, the term with the greatest multiplicity lies lowest in energy
→ the triplet term of a configuration (if one is permitted) will have a lower energy than a singlet term
2. L_Rule: For a term of a given multiplicity, the term with the greatest value of L lies lowest in energy
→ if L is high, the electrons can effectively avoid each other
3. J-Rule: if subshell is less than half filled, lowest J is lowest energy.
If greater than half filled, highest J is lowest energy
If equal to half-filled, only one J possible

Energy Diagram for Carbon

Ground state of Carbon: 3P_0 (“triplet P_0 ”)



Beyond Russell-Saunders coupling

For light atoms and the 3d series ($Z \leq 30$), the energies of the microstates are determined first by the electron spin (S), then their orbital angular momentum (L).

i.e, as before, total momentum J is determined by summing first the orbital angular momenta, then the spins, and then combining both: Russell-Saunders coupling

For heavier atoms, must consider spin-orbit coupling: “jj-coupling”. For each electron, find $j = \ell + s$, then sum j 's of each electron to find total J of atom/ion

For this class, knowledge of Russell-Saunders coupling is sufficient