

Chemistry 3P51 – Fall 2013

Quantum Chemistry

Lecture No. 28
Nov 13th, 2013

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Objectives

- To remind the student the main ideas about addition of angular momentum.
- To introduce the concept of term symbols for atomic systems.
- To present a procedure on how to determine the term symbols for an atomic system.
- To show, with an example, how the procedure presented works.

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Addition of quantized vectors: An example

Suppose we have two electrons with $l_1 = 2$ and $l_2 = 1$. What are the possible values of the total angular momentum quantum number L ? The total angular momentum **vector** is $\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2$, where the possible orientations of \mathbf{l}_1 and \mathbf{l}_2 are represented by $2l + 1$ cones of uncertainty which are characterized by the magnetic quantum numbers

$$m_1 = 2, 1, 0, -1, -2 \quad \text{and} \quad m_2 = 1, 0, -1$$

The possible values of the total magnetic quantum number M_L are obtained as all possible combinations (sums) of values of m_1 and m_2 :

$$\begin{aligned} M_L = & 3, 2, 1, 0, -1, \\ & 2, 1, 0, -1, -2, \\ & 1, 0, -1, -2, -3 \end{aligned}$$

This set can be rearranged as three sets of M_L values:

$$\left. \begin{aligned} M_L = & 3, 2, 1, 0, -1, -2, -3 \Rightarrow L=3 \\ M_L = & 2, 1, 0, -1, -2 \Rightarrow L=2 \\ M_L = & 1, 0, -1 \Rightarrow L=1 \end{aligned} \right\} \begin{array}{l} \text{Answer: these are the three} \\ \text{possible values of } L. \text{ The largest} \\ \text{is } l_1 + l_2, \text{ the smallest is } |l_1 - l_2| \end{array} \quad \mathbf{3}$$

Rules for vector addition of angular momenta

In general, when the quantum numbers for the angular momenta of two electrons are l_1 and l_2 , the possible quantum numbers for the **orbital angular momentum** of the two-electron system are

$$L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|$$

Example: If $l_1 = 2$, $l_2 = 3$, then $L = 5, 4, 3, 2, 1$.

Similarly, for the **spin angular momentum**:

$$S = s_1 + s_2, s_1 + s_2 - 1, \dots, |s_1 - s_2|$$

Example: If $s_1 = s_2 = \frac{1}{2}$, then $S = 1, 0$.

If the system (atom) contains more than two electrons, these relations should be applied consecutively for:

electron 1 + electron 2
(the system of electrons 1,2) + electron 3
(the system of electrons 1,2,3) + electron 4
and so on...

Finding the total L , S and J values for an atomic configuration

Specification of the electronic configuration of an atom such as

Carbon: $1s^2 2s^2 2p^2$

does **not** uniquely determine the energy of the atom because depending on how the spin and orbital angular momenta of the electrons combine, the atom may have different energies. For a given electron configuration, the energy of an atom also depends on L , S , and J . For this reason, we need to know how to determine the possible values of L , S , J .

Closed subshells contribute zero to the total orbital and spin angular momenta of an atom because the individual angular momenta of electrons in a closed subshell add up to zero. Thus, *only the open subshells need to be considered*.

Example: What are the possible L , S , J values for lithium and boron in their lowest states?

Li: $1s^2 2s$ $L = 0$; $S = \frac{1}{2}$; $J = \frac{1}{2}$
 B: $1s^2 2s^2 2p$ $L = 1$; $S = \frac{1}{2}$; $J = \frac{3}{2}, \frac{1}{2}$

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Term symbols for atomic states

Because the orbital and spin angular momenta L and S interact, atomic states with different L and S have different energies. Atomic states that have the same electron configuration, same L value, same S value, and same energy constitute a **term**. Atomic terms are classified (and designated) according to L and S . The convention is to report the values of L and S for a given configuration as a **term symbol**

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

in which the value of L is represented by a capital letter as follows:

$L =$	0	1	2	3	4	...
Symbol	S	P	D	F	G	...

The superscript $2S+1$ is the **spin multiplicity**:

$2S+1 =$	1	2	3	4	5	6
Name	singlet	doublet	triplet	quartet	quintet	sextet

Examples of terms: 2S , 3P , 1D .

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Procedure to obtain term symbols: An example

In the coming slides a procedure on how to determine the term symbols of an atomic system. In order to do so, an example will be worked out.

Let us determine the term symbols for an excited state of **Manganese** with electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2 4p^2 5s^1$. This is a very lengthy example and is intended to show all the procedure details.

Step 1. Eliminate the closed subshells. Closed subshells do not contribute to the term; they have $L = S = 0$

Ex. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2 4p^2 5s^1 \rightarrow 3d^2 4p^2 5s^1$

Step 2. Determine if there are any “inequivalent” electrons: electrons with different values of n or l . If so, deal with each set of inequivalent electrons independently and couple them together at the end

Ex. Inequivalent electrons $\rightarrow 3d, 4p$, and $5s$ are inequivalent

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Step 3. For each set of inequivalent electrons, determine the term symbols. To do so:

- a. Construct all the nonzero Slater determinants with the electrons in the orbitals in question.
- b. Calculate M_L and M_S for these states and make a table of microstates.
- c. Find the largest value of M_L and M_S ; that is M_L^{\max} and M_S^{\max} respectively.
- d. There is a $^{2M_S^{\max}+1}A(M_L^{\max})$ term. Eliminate one Slater determinant (it does not matter which one if there are more than one) for each permissible value of M_L and M_S that satisfy the inequality

$$-M_S^{\max} \leq M_S \leq M_S^{\max} \quad ; \quad -M_L^{\max} \leq M_L \leq M_L^{\max}$$

- e. Examining the table of microstates, go back to step (3c). Repeat the procedure until no Slater determinants remain.

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Example: $5s^1$ configuration.

$$\begin{array}{cc} M_S/M_L & 0 \\ \frac{1}{2} & |\psi_{5s}\alpha| \\ -\frac{1}{2} & |\psi_{5s}\beta| \end{array}$$

$M_S^{\max} = 1; M_L^{\max} = 0 \rightarrow {}^2S$. The term symbol is 2S

Example: $4p^2$ configuration.

$$\begin{array}{ccccccc}
M_s/M_L & 2 & 1 & 0 & -1 & -2 \\
1 & 0 & \left| \psi_{4p_1} \alpha \quad \psi_{4p_0} \alpha \right| & \left| \psi_{4p_1} \alpha \quad \psi_{4p-1} \alpha \right| & \left| \psi_{4p-1} \alpha \quad \psi_{4p_0} \alpha \right| & 0 \\
0 & \left| \psi_{4p_1} \alpha \quad \psi_{4p_1} \beta \right| & \left(\begin{array}{cc} \left| \psi_{4p_1} \alpha \quad \psi_{4p_0} \beta \right| \\ \left| \psi_{4p_1} \beta \quad \psi_{4p_0} \alpha \right| \end{array} \right) & \left(\begin{array}{cc} \left| \psi_{4p_1} \alpha \quad \psi_{4p_0} \beta \right| \\ \left| \psi_{4p_1} \alpha \quad \psi_{4p-1} \beta \right| \end{array} \right) & \left(\begin{array}{cc} \left| \psi_{4p-1} \alpha \quad \psi_{4p_0} \beta \right| \\ \left| \psi_{4p-1} \beta \quad \psi_{4p_0} \alpha \right| \end{array} \right) & \left| \psi_{4p-1} \alpha \quad \psi_{4p-1} \beta \right| \\
-1 & 0 & \left| \psi_{4p_1} \beta \quad \psi_{4p_0} \beta \right| & \left| \psi_{4p_1} \beta \quad \psi_{4p-1} \beta \right| & \left| \psi_{4p-1} \beta \quad \psi_{4p_0} \beta \right| & 0 \\
\end{array}$$

Now $M_L^{\max} = M_S^{\max} = 1$. **So we have a 3P state.**

After eliminating the matrix elements for the 3P state, we have

$$\begin{array}{ccccccc}
M_s/M_L & 2 & 1 & 0 & -1 & -2 \\
1 & 0 & - & - & - & 0 \\
0 & \left| \psi_{4p_1} \alpha \quad \psi_{4p_1} \beta \right| & \left(\begin{array}{cc} - & \\ \left| \psi_{4p_1} \beta \quad \psi_{4p_0} \alpha \right| \end{array} \right) & \left(\begin{array}{cc} - & \\ \left| \psi_{4p_1} \alpha \quad \psi_{4p-1} \beta \right| \end{array} \right) & \left(\begin{array}{cc} - & \\ \left| \psi_{4p-1} \beta \quad \psi_{4p_0} \alpha \right| \end{array} \right) & \left| \psi_{4p-1} \alpha \quad \psi_{4p-1} \beta \right| \\
-1 & 0 & - & - & - & 0 \\
\end{array}$$

The dashes show the elements we removed. Now $M_S^{\max} = 0, M_L^{\max} = 2$. **We have a 1D state.**

Now, eliminating these elements (denoted with a + in Eq. (3.140)) we have

$$\begin{array}{ccccccc}
M_s/M_L & 2 & 1 & 0 & -1 & -2 \\
1 & 0 & - & - & - & 0 \\
0 & + & \left(\begin{array}{cc} - & \\ + & \end{array} \right) & \left(\begin{array}{cc} - & \\ + & \end{array} \right) & + & \\
-1 & 0 & - & - & - & 0 \\
\end{array}$$

Now $M_S^{\max} = M_L^{\max} = 0$. **We have a 1S state.**

The term symbols are $^3P, ^1D, ^1S$.

$$\begin{array}{ccccccc}
M_S/M_L & 4 & 3 & 2 & 1 & 0 \\
1 & 0 & - & - & \begin{pmatrix} - \\ + \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix} \\
0 & \left| \psi_{3a_2} \alpha \quad \psi_{3a_2} \beta \right| \begin{pmatrix} - \\ \left| \psi_{3a_2} \beta \quad \psi_{3a_4} \alpha \right| \end{pmatrix} & \begin{pmatrix} - \\ \left| \psi_{3a_2} \beta \quad \psi_{3a_6} \alpha \right| \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix} \\
& & & & & \begin{pmatrix} - \\ + \end{pmatrix}
\end{array}$$

Now $M_S^{\text{max}} = 0$, $M_L^{\text{max}} = 4$. We have a 1G term. Eliminating the appropriate determinants,

$$\begin{array}{ccccccc}
M_S/M_L & 4 & 3 & 2 & 1 & 0 \\
1 & 0 & - & - & \begin{pmatrix} - \\ + \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix}
\end{array}$$

$$\begin{array}{ccccccc}
0 & \pm \begin{pmatrix} - \\ \pm \end{pmatrix} & \begin{pmatrix} - \\ \pm \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix} \\
& & \left| \psi_{3a_4} \beta \quad \psi_{3a_4} \alpha \right| & \left| \psi_{3a_2} \beta \quad \psi_{3a_4} \alpha \right| & \left| \psi_{3a_2} \beta \quad \psi_{3a_2} \alpha \right| & \left| \psi_{3a_6} \alpha \quad \psi_{3a_6} \beta \right| & \left| \psi_{3a_6} \alpha \quad \psi_{3a_6} \beta \right|
\end{array}$$

We now have $M_S^{\text{max}} = 0$, $M_L^{\text{max}} = 2$. This gives a 1D term. Eliminating the determinants,

$$\begin{array}{ccccccc}
M_S/M_L & 4 & 3 & 2 & 1 & 0 \\
1 & 0 & - & - & \begin{pmatrix} - \\ + \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix} \\
0 & \pm \begin{pmatrix} - \\ \pm \end{pmatrix} & \begin{pmatrix} - \\ \pm \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix} & \begin{pmatrix} - \\ + \end{pmatrix} \\
& & \approx & \approx & \approx & \approx
\end{array}$$

which leaves us with just a single remaining microstate, which is 1S .

The terms for the $3d^2$ configuration are thus 3F , 3P , 1G , 1D , 1S .

Step 4. Couple together the nonequivalent terms. This is done by vector addition. Thus, when adding an $L = 2$ term to and $L = 1$ term, it is possible to get a $L = 3$ term, an $L = 2$ term and an $L = 1$ term.

The gist is that one obtains states with

$$L_{coupled} = L_1 + L_2, L_1 + L_2 - 1, \dots, |L_1 - L_2|$$

$$S_{coupled} = S_1 + S_2, S_1 + S_2 - 1, \dots, |S_1 - S_2|$$

Example:

Couple the $3d^2$ ($^3F, ^3P, ^1G, ^1D, ^1S$) and $4p^2$ ($^3P, ^1D, ^1S$) terms.

$$^3F \sim ^3P \rightarrow ^5G, ^3G, ^1G; ^5F, ^3F, ^1F, ^5D, ^3D, ^1D$$

$$^3F \sim ^1D \rightarrow ^3H, ^3G, ^3F, ^3D, ^3P$$

$$^3F \sim ^1S \rightarrow ^3F$$

$$^3P \sim ^3P \rightarrow ^5D, ^3D, ^1D, ^5P, ^3P, ^1P, ^5S, ^3S, ^1S$$

$$^3P \sim ^1D \rightarrow ^3F, ^3D, ^3P$$

$$^3P \sim ^1S \rightarrow ^3P$$

$$^1G \sim ^3P \rightarrow ^3H, ^3G, ^3F$$

$$^1G \sim ^1D \rightarrow ^1I, ^1H, ^1G, ^1F, ^1D$$

$$^1G \sim ^1S \rightarrow ^1G$$

$$^1D \sim ^3P \rightarrow ^3F, ^3D, ^3P$$

$$^1D \sim ^1D \rightarrow ^1G, ^1F, ^1D, ^1P, ^1S$$

$$^1D \sim ^1S \rightarrow ^1D$$

$$^1S \sim ^3P \rightarrow ^3P$$

$$^1S \sim ^1D \rightarrow ^1D$$

$$^1S \sim ^1S \rightarrow ^1S$$

Example: Couple the terms from the $3d^2 4p^2$ configuration to those from the $5s^1$ configuration.

Using the terms from the first example (the grouping parentheses are merely to make it easier to see from which term in the first example these terms are derived)

$$\begin{aligned}
{}^3F &\sim {}^3P \sim {}^2S \rightarrow ({}^6G, {}^4G), ({}^4G, {}^2G'), ({}^2G'); ({}^6F, {}^4F), ({}^4F, {}^2F), ({}^2F), ({}^6D, {}^4D), ({}^4D, {}^2D), ({}^2D) \\
{}^3F &\sim {}^1D \sim {}^2S \rightarrow ({}^4H, {}^2H), ({}^4G, {}^2G), ({}^4F, {}^2F), ({}^4D, {}^2D), ({}^4P, {}^2P) \\
{}^3F &\sim {}^1S \sim {}^2S \rightarrow ({}^4F, {}^2F) \\
{}^3P &\sim {}^3P \sim {}^2S \rightarrow ({}^6D, {}^4D), ({}^4D, {}^2D), ({}^2D), ({}^6P, {}^4P), ({}^4P, {}^2P), ({}^2P), ({}^6S, {}^4S), ({}^4S, {}^2S), ({}^2S) \\
{}^3P &\sim {}^1D \sim {}^2S \rightarrow ({}^4F, {}^2F), ({}^4D, {}^2D), ({}^4P, {}^2P) \\
{}^3P &\sim {}^1S \sim {}^2S \rightarrow ({}^4P, {}^2P) \\
{}^1G &\sim {}^3P \sim {}^2S \rightarrow ({}^4H, {}^2H), ({}^4G, {}^2G), ({}^4F, {}^2F) \\
{}^1G &\sim {}^1D \sim {}^2S \rightarrow {}^2I, {}^2H, {}^2G, {}^2F, {}^2D \\
{}^1G &\sim {}^1S \sim {}^2S \rightarrow {}^2G \\
{}^1D &\sim {}^3P \sim {}^2S \rightarrow ({}^4F, {}^2F), ({}^4D, {}^2D), ({}^4P, {}^2P) \\
{}^1D &\sim {}^1D \sim {}^2S \rightarrow {}^2G, {}^2F, {}^2D, {}^2P, {}^2S \\
{}^1D &\sim {}^1S \sim {}^2S \rightarrow {}^2D \\
{}^1S &\sim {}^3P \sim {}^2S \rightarrow ({}^4P, {}^2P) \\
{}^1S &\sim {}^1D \sim {}^2S \rightarrow {}^2D \\
{}^1S &\sim {}^1S \sim {}^2S \rightarrow {}^2S
\end{aligned}$$

Augmenting these terms with the subscripts appropriate to J is easy, and (in obvious shorthand) gives