

24. Atomic Spectra, Term Symbols and Hund's Rules

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Suggested Reading: Chapters 8-8 to 8-11 of the text.

Introduction

Electron configurations, at least in the forms used in general chemistry are ambiguous. For example for carbon $1s^2 2s^2 2p^2$, where to the two electrons in the p orbitals reside? In which of the three p orbitals, p_{-1} , p_0 , p_{+1} ? What is the spin on the electrons.

As we saw in the last lecture, all of the various quantum numbers affect the energy of the state, not just the principle quantum number, in multi-electron systems. We need a new way to designate a state unambiguously. The scheme presented here is based on the total angular momentum, J, formed by adding the total orbital angular momentum, L, and the total spin angular momentum, S. The symbol used to designate a state by this means is called a term symbol and is of the form

$$^{2S+1}L_J \quad (24-1)$$

The scheme is called Russell-Saunders coupling and is performed as follows: The total orbital angular momentum is given by

$$\vec{L} = \sum_j \vec{l}_j \quad (24-2)$$

a vector addition. The total spin angular momentum is given by

$$\vec{S} = \sum_j \vec{s}_j \quad (24-3)$$

another vector addition. The z components of \vec{L} and \vec{S} are given by the scalar sums

$$L_z = \sum_i l_{z,i} = \sum_i m_i = M_L \quad (24-4)$$

and

$$S_z = \sum_i s_{z,i} = \sum_i m_{s,i} = M_S \quad (24-5)$$

Thus there are $2L + 1$ values of M_L spanning $-L, -L+1, -L+2, \dots, L-1, L$ and $2S + 1$ values of M_S for S spanning $-S, -S+1, -S+2, \dots, S-1, S$.

The leading $2S+1$ superscript in the term symbol is called the spin multiplicity.

Table 24-1: Names for the leading superscripts of atomic term symbols.

$2S+1$	Name
1	singlet
2	doublet
3	triplet

The value of L is substituted as in the hydrogen-like orbitals but with a capital letter. That is,

Table 24-2: Letter conversions for atomic term symbols.

Value of L	Letter
0	S
1	P
2	D
3	F
4	G
5	H

The value of J is kept as a number. Thus for example:

3S_1 - "triplet S one"

1D_3 - "singlet D three"

Examples

Hydrogen: $H 1s^1$, The maximum value of M_S is

$$\begin{aligned}M_{S, max} &= \sum_i m_{s, i} \\ &= \frac{1}{2}\end{aligned}\tag{24-6}$$

to give $S = 1/2$. The maximum value of L is

$$\begin{aligned}M_{L, max} &= \sum_i m_i \\ &= 0\end{aligned}\tag{24-7}$$

thus $L = 0$ and $J = L + S = 1/2$. The term symbol for the ground state of hydrogen is

$${}^2S_{\frac{1}{2}}\tag{24-8}$$

The ground state of He, $1s^2$:

$$\begin{aligned}M_{S, max} &= \sum_i m_{s, i} \\ &= \frac{1}{2} - \frac{1}{2} \\ &= 0\end{aligned}\tag{24-9}$$

$$\begin{aligned}
 M_{L, max} &= \sum_i m_i \\
 &= 0 + 0 \\
 &= 0
 \end{aligned}
 \tag{24-10}$$

Therefore, the term symbol is

$${}^1S_0
 \tag{24-11}$$

An excited state of He, $1s^1 2s^1$:

$$\begin{aligned}
 M_{S, max} &= \sum_i m_{s, i} \\
 &= \frac{1}{2} + \frac{1}{2} \\
 &= 1
 \end{aligned}
 \tag{24-12}$$

therefore $M_S = 1, 0, -1$ but what value of S?

$$\begin{aligned}
 M_{L, max} &= \sum_i m_i \\
 &= 0 + 0 \\
 &= 0
 \end{aligned}
 \tag{24-13}$$

Microstates

To answer our question above, there are two methods. One involves inspection of the problem and works quickly but is not reliable, the second is

perhaps tedious, but always works. It is this second methods that is given in the text and will be used here.

Lets create a table

M_L	M_S		
	1	0	-1
0	$(0^+,0^+)$	$(0^+,0^-), (0^-,0^+)$	$(0^-,0^-)$

The notation $(0^+,0^+)$ means that $(m = 0, m_s = +1/2; m = 0, m_s = +1/2)$ for the two electrons. $(0^+,0^-)$ and $(0^-,0^+)$ are not equivalent because the two electrons are in separate orbitals. The four entries are called microstates. Lets loot at $L = 0, S=1,$

$$L = 0 \rightarrow M_L = 0$$

$$S = 1 \rightarrow M_S = 1, 0, -1$$

This corresponds to the microstates $(0^+,0^+), (0^+,0^-)$ and $(0^-,0^-)$. We have one unaccounted for microstate, $(0^-,0^+)$. This microstate has $S = 0, L = 0$.

Thus there are two possible states for He $1s^1 2s^1$:

$${}^3S_1 \quad {}^1S_0 \quad (24-14)$$

The allowed values of J are $J = L+S, L+S-1, L+S-2, \dots, |L-S|$.

Beryllium $1s^2 2s^2$:

$$\begin{aligned}M_{S, max} &= \sum_i m_{s, i} \\ &= \frac{1}{2} - \frac{1}{2} + \frac{1}{2} - \frac{1}{2} \\ &= 0\end{aligned}\tag{24-15}$$

therefore $M_S = 0$.

$$\begin{aligned}M_{L, max} &= \sum_i m_i \\ &= 0 + 0 + 0 + 0 \\ &= 0\end{aligned}\tag{24-16}$$

therefore the term symbol is

$${}^1S_0\tag{24-17}$$

Filled subshells have total angular momentum of zero and make no contribution to the determination of the term symbol.

Back to carbon. We have six possible spin orbitals in which to place the two electrons

$$2p_0\alpha, 2p_0\beta, 2p_{-1}\alpha, 2p_{-1}\beta, 2p_1\alpha, 2p_1\beta$$

This is “6 choose 2”

$$\begin{aligned}\binom{6}{2} &= \frac{6!}{2!4!} \\ &= \frac{6(5)}{2} \\ &= 15\end{aligned}\tag{24-18}$$

There will be 15 microstates to deal with. In general, if we have j spin orbitals and need to place k electrons we have

$$\binom{j}{k} = \frac{j!}{k!(j-k)!}\tag{24-19}$$

microstates. For example $3d^2$ has

$$\begin{aligned}\binom{10}{2} &= \frac{10!}{2!8!} \\ &= 45\end{aligned}\tag{24-20}$$

microstates. How about $3d^8$?

$$\begin{aligned}\binom{10}{8} &= \frac{10!}{8!2!} \\ &= 45\end{aligned}\tag{24-21}$$

microstates. d^{10-j} has the same number of microstates as d^j .

Back to carbon:

The two electrons may go in the $m = -1, 0, 1$ orbitals. Thus M_L ranges from 2 to -2. The spins may be paired or unpaired, hence $M_S \rightarrow 1, 0, -1$.

M_L	M_S		
	1	0	-1
2		$(1^+, 1^-)$	
1	$(0^+, 1^+)$	$(1^+, 0^-), (0^+, 1^-)$	$(0^-, 1^-)$
0	$(1^+, -1^+)$	$(1^+, -1^-), (-1^+, 1^-), (0^+, 0^-)$	$(1^-, -1^-)$
-1	$(0^+, -1^+)$	$(-1^+, 0^-), (0^+, -1^-)$	$(0^-, -1^-)$
-2		$(-1^+, -1^-)$	

Since the electrons are in the same shell $(1^+, 1^-)$ and $(1^-, 1^+)$ are indistinguishable and hence only one is included. Combinations that are excluded by the Pauli Principle do not make up the table entries.

The largest value of M_L is 2 and has $M_S = 0$, therefore $L = 2, S = 0, J = 2$ to give

$${}^1D_2 \quad (24-22)$$

This state has $M_S = 0, M_L = 2, 1, 0, -1, -2$ for five microstates.

The next largest value of M_L remaining is $M_L = 1$. The largest value of M_S associated with this is $M_S = 1$. Therefore $L = 1, S = 1$

$${}^3P \quad (24-23)$$

with $M_L = 1, 0, -1$ and $M_S = 1, 0, -1$ for nine microstates. The possible values of J are $J = (1+1), (1+1-1), (1-1)$ or $J = 2, 1, 0$ hence we have ${}^3P_2, {}^3P_1$ and 3P_0 with 5, 3, and 1 microstates respectively.

This leaves a single microstate remaining with $M_L = 0$ and $M_S = 0$ to give

$${}^1S_0 \quad (24-24)$$

Thus the states for the ground state configuration of carbon are

$${}^1D_2, {}^3P_2, {}^3P_1 \text{ and } {}^3P_0, {}^1S_0$$

The degeneracy of each state is $2J+1$ for 5, 1, 3, 5, 1 for 15 microstates.

The term symbols for a given electron configuration correspond to that with the same number of holes. For example $2p^2$ and $2p^4$ or $3d^4$ and $3d^6$ (see Table 8.4 in the text).

Hund's Rules

Each of the states designated by a term symbol corresponds to a determinantal wave function that is an eigenfunction of \hat{L}^2 and \hat{S}^2 . Thus each state corresponds to a given energy.

The spectroscopist Fredrich Hund worked out a set of empirical rules to order the energies of the states.

1. The state with the largest value of S is the most stable (has the lowest energy) and stability decreases with decreasing S .
2. For states with the same value of S , the state with the largest value of L is the most stable.
3. If the states have the same value of L and S , then for a subshell that is less than half filled, the state with the smallest value of J is the most stable. For a subshell that is more than half filled, the state with the largest value of J is the most stable.

For example for carbon, 3P_0 is the lowest energy state.

[As an exercise work out the state for d^2 using the microstate method.]

The term symbols are used to describe atomic spectra. Thus far in our development of the Hamiltonian operator for atoms we have included kinetic energy and electrostatic potential energy terms. That is,

$$\hat{H} = -\frac{1}{2} \sum_j \nabla_j^2 - \sum_j \frac{Z}{r_j} + \sum_{i < j} \frac{1}{r_{ij}} \quad (24-25)$$

We need to include spin and magnetic terms as well. The most important is the “spin-orbit interaction term” which results from the interaction of the magnetic moment associated with the spin of an electron with the magnetic field generated by the electric current produced by the electron’s own orbital motion. Other terms include spin-spin and orbit-orbit interaction (in multi-electron systems) but spin-orbit interactions are the most important.

$$\hat{H} = -\frac{1}{2} \sum_j \nabla_j^2 - \sum_j \frac{Z}{r_j} + \sum_{i < j} \frac{1}{r_{ij}} + \sum_j \xi(r_j) \vec{l}_j \cdot \vec{s}_j \quad (24-26)$$

If the effect of the spin-orbit coupling is small, as it is for light atoms (approximately $Z < 30$) the effect may be treated as a perturbation. For heavier atoms, the effect is not small and must be dealt with explicitly.

Selection Rules for Atomic Spectra

Transitions involving light are allowed with atoms for the following

$$\begin{aligned} \Delta L &= \pm 1 \\ \Delta S &= 0 \\ \Delta J &= 0, \pm 1 \end{aligned} \quad (24-27)$$

expect that a transition from a state with $J = 0$ to another state with $J = 0$ is not allowed (forbidden).

Suggested Reading for Next Lecture: Chapter 9 of the text.