Term symbol

In quantum mechanics, the **term symbol** is an abbreviated description of the angular momentum quantum numbers in a multi-electron atom. It is related with the energy level of a given electron configuration. LS coupling is assumed. The ground state term symbol is predicted by Hund's rules.

The term symbol has the form

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

where
S is the total spin quantum number. $2S+1$ is the **spin multiplicity**: the maximum number of different possible states of J for a given (L,S) combination.
L is the total orbital quantum number in spectroscopic notation. The symbols for L = 0,1,2,3,4,5 are S,P,D,F,G,H respectively.
J is the total angular momentum quantum number.

When used to describe electron states in an atom, the term symbol usually follows the electron configuration, e.g., in the case of carbon, the ground state is $1s^2 2s^2 2p^2\ ^3P_0$. The 3 indicates that 2S+1=3 and so S=1, the P is spectroscopic notation for L=1, and 0 is the value of J.

The term symbol is also used to describe compound systems such as mesons or atomic nuclei, or even molecules (see molecular term symbol). In that last case, Greek letters are used to designate the (molecular) orbital angular momenta.

For a given electron configuration

- The combination of an S value and an L value is called a **term**, and has a statistical weight (i.e., number of possible microstates) of $(2S+1)(2L+1)$;
- A combination of S, L and J is called a **level**. A given level has a statistical weight of $(2J+1)$, which is the number of possible microstates associated with this level in the corresponding term;
- A combination of L, S, J and M_J determines a single **state**.

As an example, for $S = 1$, $L = 2$, there are $(2\times1+1)(2\times2+1) = 15$ different microstates corresponding to the ^{3}D term, of which $(2\times3+1) = 7$ belong to the $^3D_3$ (J=3) level. The sum of $(2J+1)$ for all levels in the same term equals $(2S+1)(2L+1)$. In this case, J can be 1, 2, or 3, so 3 + 5 + 7 = 15.

Term symbol parity

The parity of a term symbol is calculated as

$$P = (-1)^{\sum_i l_i},$$

where l_i is the orbital quantum number for each electron. In fact, only electrons in odd orbitals contribute to the total parity: an odd number of electrons in odd orbitals (those with an odd l such as in p, f,...) will make an odd term symbol, while an even number of electrons in odd orbitals will make an even term symbol, irrespective of the number of electrons in even orbitals.

When it is odd, the parity of the term symbol is indicated by a superscript letter "o", otherwise it is omitted:

$^2\mathrm{P}^o_{1/2}$ has odd parity, but $^3\mathrm{P}_0$ has even parity.

Alternatively, parity may be indicated with a subscript letter "g" or "u", standing for *gerade* (German for 'even') or *ungerade* ('odd'):

$^2\mathrm{P}_{1/2,u}$ for odd parity and $^3\mathrm{P}_{0,g}$ for even.

Ground state term symbol

It is relatively easy to calculate the term symbol for the ground state of an atom. It corresponds with a state with maximal S and L.

1. Start with the most stable electron configuration. Full shells and subshells do not contribute to the overall angular momentum, so they are discarded.
    - If all shells and subshells are full then the term symbol is $^1S_0$.
2. Distribute the electrons in the available orbitals, following the Pauli exclusion principle. First, we fill the orbitals with highest m_l value with one electron each, and assign a maximal m_s to them (i.e. +1/2). Once all orbitals in a subshell have one electron, add a second one (following the same order), assigning $m_s = -1/2$ to them.
3. The overall S is calculated by adding the m_s values for each electron. That is the same as multiplying ½ times the number of **unpaired** electrons. The overall L is calculated by adding the m_l values for each electron (so if there are two electrons in the same orbital, then we add twice that orbital's m_l).
4. Calculate J as:
    - if less than half of the subshell is occupied, take the minimum value $J = |L - S|$;
    - if more than half-filled, take the maximum value $J = L + S$;
    - if the subshell is half-filled, then L will be 0, so $J = S$.

As an example, in the case of fluorine, the electronic configuration is: $1s^2 2s^2 2p^5$.

1. Discard the full subshells and keep the $2p^5$ part. So we have five electrons to place in subshell p ($l = 1$).

2. There are three orbitals ($m_l = 1, 0, -1$) that can hold up to $2(2l+1) = 6$ electrons. The first three electrons can take $m_s = 1/2$ (↑) but the Pauli exclusion principle forces the next two to have $m_s = -1/2$ (↓) because they go to already occupied orbitals.

	m_l		
	+1	0	−1
m_s:	↑↓	↑↓	↑

3. $S = 1/2 + 1/2 + 1/2 - 1/2 - 1/2 = 1/2$; and $L = 1 + 0 - 1 + 1 + 0 = 1$, which is "P" in spectroscopic notation;

4. As fluorine 2p subshell is more than half filled, $J = L + S = 3/2$. Its ground state term symbol is then $^{2S+1}L_J = {}^2\mathrm{P}_{3/2}$.

Term symbols for an electron configuration

To calculate all possible term symbols for a given electron configuration the process is a bit longer.

- First, calculate the total number of possible microstates N for a given electron configuration. As before, we discard the filled (sub)shells, and keep only the partially-filled ones. For a given orbital quantum number l the total number of electrons that can be fitted is $t = 2(2l+1)$. If there are e electrons in a given subshell, the number of possible microstates is

$$N = \binom{t}{e} = \frac{t!}{e!\,(t-e)!}.$$

As an example, lets take the carbon electron structure: $1s^2 2s^2 2p^2$. After removing full subshells, there are 2 electrons in a p-level ($l = 1$), so we have

$$N = \frac{6!}{2!\,4!} = 15$$

different microstates.

- Second, draw all possible microstates. Calculate M_L and M_S for each microstate, with $M = \sum_{i=1}^{e} m_i$ where m_i is either m_l or m_s for the i-th electron, and M represents the resulting M_L or M_S respectively:

	m_l				
	+1	**0**	**−1**	M_L	M_S
	↑	↑		1	1
all up	↑		↑	0	1
		↑	↑	−1	1
	↓	↓		1	−1
all down	↓		↓	0	−1
		↓	↓	−1	−1
	↑↓			2	0
	↑	↓		1	0
	↑		↓	0	0
one up	↓	↑		1	0
		↑↓		0	0
one down		↑	↓	−1	0
	↓		↑	0	0
		↓	↑	−1	0
			↑↓	−2	0

- Third, count the number of microstates for each M_L—M_S possible combination

		M_S		
		+1	**0**	**−1**
	+2		1	
	+1	1	2	1
M_L	**0**	1	3	1
	−1	1	2	1
	−2		1	

- Fourth, extract smaller tables representing each possible term. Each table will be $(2L+1)(2S+1)$, and will contain "1"s as entries. The first table extracted corresponds to M_L ranging from −2 to +2 (so $L = 2$), with a single value for M_S (implying $S = 0$). This corresponds to a ^{1}D term. The remaining table is 3×3. Then we extract a second table, removing the entries for M_L and M_S both ranging from −1 to +1 (and so $S = L = 1$, a ^{3}P term). The remaining table is a 1×1 table, with $L = S = 0$, i.e., a ^{1}S term.

S=0, L=2, J=2

$^1D_2$

M_l \ M_s	**0**
+2	1
+1	1
0	1
−1	1
−2	1

S=1, L=1, J=2,1,0

$^3P_2$, $^3P_1$, $^3P_0$

M_l \ M_s	**+1**	**0**	**−1**
+1	1	1	1
0	1	1	1
−1	1	1	1

S=0, L=0, J=0

$^1S_0$

M_l \ M_s	**0**
0	1

- Fifth, applying Hund's rules, deduce which is the ground state (or the lowest state for the configuration of interest.) Hund's rules should not be used to predict the order of states other than the lowest for a given configuration.