

# Lecturer 4

Term Symbol Russell Saunders

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## 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  $1s^2 2s^2 2p^2 \ ^3P_1$ . The 0 indicates that  $2S+1 = 1$  and so  $S=0$  and  $1=L$  of notation spectroscopic,  $1$  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  $(2J+1)$ .
- A combination of L, S, J and  $M_J$  determines a single state.

As an example, for  $S = 1$ ,  $L = 2$ , there are 15 different microstates corresponding to the  $3D$  term, of which 7 belong to the  $3D_2$  level ( $J=2$ ) and 8 belong to the  $3D_1$  level ( $J=1$ ). For  $S = 1$ ,  $L = 2$ , there are 15 different microstates corresponding to the  $3D$  term, of which 7 belong to the  $3D_2$  level ( $J=2$ ) and 8 belong to the  $3D_1$  level ( $J=1$ ).

Electrons in an atom reside in shells characterised by a particular value of  $n$ , the Principal Quantum Number. Within each shell an electron can occupy an orbital which is further characterised by an Orbital Quantum Number,  $l$ , where  $l$  can take all values in the range:

$$l = 0, 1, 2, 3, \dots, (n-1),$$

traditionally termed s, p, d, f, etc. orbitals.

Each orbital has a characteristic shape reflecting the motion of the electron in that particular orbital, this motion being characterised by an angular momentum that reflects the angular velocity of the electron moving in its orbital.

A quantum mechanics approach to determining the energy of electrons in an element or ion is based on the results obtained by solving the Schrödinger Wave Equation for the H-atom. The various solutions for the different energy states are characterised by the three quantum numbers,  $n$ ,  $l$  and  $m_l$ .

$m_l$  is a subset of  $l$ , where the allowable values are:  $m_l = l, l-1, l-2, \dots, 1, 0, -1, \dots, -(l-2), -(l-1), -l$ .

There are thus  $(2l + 1)$  values of  $m_l$  for each  $l$  value,  
i.e. one s orbital ( $l = 0$ ), three p orbitals ( $l = 1$ ), five d orbitals ( $l = 2$ ), etc

There is a fourth quantum number,  $m_s$ , that identifies the orientation of the spin of one electron relative to those of other electrons in the system. A single electron in free space has a fundamental property associated with it called spin, originally conceived as the rotation of a particle around some axis. Electrons are not literally spinning balls of charge, but they do have intrinsic angular momentum that may be regarded as being generated by a circulating flow of energy in the wave field of the electron. Likewise, the magnetic moment may be regarded as generated by a circulating flow of charge in the wave field

In summary then, each electron in an orbital is characterised by four quantum numbers:

Quantum Numbers		
symbol	description	range of values
$n$	Principal Quantum Number - largely governs size of orbital and its energy	1,2,3 etc
$l$	Azimuthal/Orbital Quantum Number - largely determines shape of subshell 0 for s orbital, 1 for p orbital etc	$(0 \leq l \leq n-1)$ for $n = 3$ then $l = 0, 1, 2$ (s, p, d)
$m_l$	Magnetic Quantum Number - orientation of subshell's shape for example $p_x$ with $p_y$ and $p_z$	$l \geq m_l \geq -l$ for $l = 2$ , then $m_l = 2, 1, 0, -1, -2$
$m_s$	Spin Quantum Number	either $+\frac{1}{2}$ or $-\frac{1}{2}$ for single electron

The ways in which the angular momenta associated with the orbital and spin motions in many-electron-atoms can be combined together are many and varied. In spite of this seeming complexity, the results are frequently readily determined for simple atom systems and are used to characterise the electronic states of atoms.

The interactions that can occur are of three types.

spin-spin coupling

- orbit-orbit coupling
- spin-orbit coupling

There are two principal coupling schemes used:

- Russell-Saunders (or L - S) coupling
- and j - j coupling.

In the Russell Saunders scheme (named after Henry Norris Russell, 1877-1957 a Princeton Astronomer and Frederick Albert Saunders, 1875-1963 a Harvard Physicist and published in [Astrophysics Journal, 61, 38, 1925](#) ) it is assumed that:  
spin-spin coupling > orbit-orbit coupling > spin-orbit coupling.

This is found to give a good approximation for first row transition series where spin-orbit (J) coupling can generally be ignored, however for elements with atomic number greater than thirty, spin-orbit coupling becomes more significant and the j-j coupling scheme is used.

## Spin-Spin coupling

S - the resultant spin quantum number for a system of electrons. The overall spin S arises from adding the individual  $m_s$  together and is as a result of coupling of spin quantum numbers for the separate electrons.

## Orbit-Orbit coupling

L - the total orbital angular momentum quantum number defines the energy state for a system of electrons. These states or term letters are represented as follows:

Total Orbital Momentum						
L	0	1	2	3	4	5
	S	P	D	F	G	H



## Spin-Orbit coupling

Coupling occurs between the resultant spin and orbital momenta of an electron which gives rise to J the total angular momentum quantum number. Multiplicity occurs when several levels are close together and is given by the formula  $(2S+1)$ .

The Russell Saunders term symbol that results from these considerations is given by:

$$(2S+1)L$$

As an example, for a  $d^1$  configuration:

$$S = +\frac{1}{2}, \text{ hence } (2S+1) = 2$$

$$L = 2$$

and the Ground Term is written as  $^2D$

The Russell Saunders term symbols for the other free ion configurations are given in the Table below.

## Terms for 3d<sup>n</sup> free ion configurations

Configuration	# of quantum states	# of energy levels	Ground Term	Excited Terms
d <sup>1</sup> ,d <sup>9</sup>	10	1	<sup>2</sup> D	-
d <sup>2</sup> ,d <sup>8</sup>	45	5	<sup>3</sup> F	<sup>3</sup> P, <sup>1</sup> G, <sup>1</sup> D, <sup>1</sup> S
d <sup>3</sup> ,d <sup>7</sup>	120	8	<sup>4</sup> F	<sup>4</sup> P, <sup>2</sup> H, <sup>2</sup> G, <sup>2</sup> F, 2 x <sup>2</sup> D, <sup>2</sup> P
d <sup>4</sup> ,d <sup>6</sup>	210	16	<sup>5</sup> D	<sup>3</sup> H, <sup>3</sup> G, 2 x <sup>3</sup> F, <sup>3</sup> D, 2 x <sup>3</sup> P, <sup>1</sup> I, 2 x <sup>1</sup> G, <sup>1</sup> F, 2 x <sup>1</sup> D, 2 x <sup>1</sup> S
d <sup>5</sup>	252	16	<sup>6</sup> S	<sup>4</sup> G, <sup>4</sup> F, <sup>4</sup> D, <sup>4</sup> P, <sup>2</sup> I, <sup>2</sup> H, 2 x <sup>2</sup> G, 2 x <sup>2</sup> F, 3 x <sup>2</sup> D, <sup>2</sup> P, <sup>2</sup> S

Note that d<sup>n</sup> gives the same terms as d<sup>10-n</sup>

# Hund's Rules

The Ground Terms are deduced by using Hund's Rules.

The two rules are:

- 1) The Ground Term will have the maximum multiplicity
- 2) If there is more than 1 Term with maximum multiplicity, then the Ground Term will have the largest value of L.

***A simple graphical method for determining just the ground term alone for the free-ions uses a "fill in the boxes" arrangement.***

$d^n$	2	1	0	-1	-2	L	S	Ground Term
$d^1$	↑					2	1/2	$^2D$
$d^2$	↑	↑				3	1	$^3F$
$d^3$	↑	↑	↑			3	3/2	$^4F$
$d^4$	↑	↑	↑	↑		2	2	$^5D$
$d^5$	↑	↑	↑	↑	↑	0	5/2	$^6S$
$d^6$	↑↓	↑	↑	↑	↑	2	2	$^5D$
$d^7$	↑↓	↑↓	↑	↑	↑	3	3/2	$^4F$
$d^8$	↑↓	↑↓	↑↓	↑	↑	3	1	$^3F$
$d^9$	↑↓	↑↓	↑↓	↑↓	↑	2	1/2	$^2D$

For  $s^1$



$$m_l = 0$$

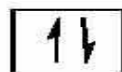
$S = 1/2$ ; thus  $(2S+1) = 2$

$L = 0$ ; thus symbol is S

$J = S = 1/2$  (Since subshell is half filled)

term symbol  $^2S_{1/2}$

For  $s^2$



$$m_l = 0$$

$S = 1/2 + -1/2 = 0$ ; thus  $(2S+1) = 1$

$L = 0$ ; thus symbol is S

$J = S = 0$  (Since subshell is full filled)

term symbol  $^1S_0$

For  $p^1$



$$m_l = +1 \quad 0 \quad -1$$

$S = 1/2$ ; thus  $(2S+1) = 2$

$L = 1$ ; thus symbol is P

$J = (L - S) = 1 - 1/2 = 1/2$  (Since subshell is less than half filled)

term symbol  $^2P_{1/2}$

For  $p^4$



$$m_l = +1 \quad 0 \quad -1$$

$S = 1/2 + 1/2 = 1$ ; thus  $(2S+1) = 3$

$L = 2 + 0 - 1 = 1$ ; thus symbol is P

$J = (L + S) = 1 + 1 = 2$  (Since subshell is more than half filled)

term symbol  $^3P_2$

For  $p^2$



$$m_l = +1 \quad 0 \quad -1$$

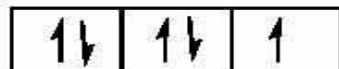
$S = 1/2 + 1/2 = 1$ ; thus  $(2S+1) = 3$

$L = 1 + 0 = 1$ ; thus symbol is P

$J = (L - S) = 1 - 1 = 0$  (Since subshell is less than half filled)

term symbol  $^3P_0$

For  $p^5$



$$m_l = +1 \quad 0 \quad -1$$

$S = 1/2$ ; thus  $(2S+1) = 2$

$L = 1$ ; thus symbol is P

$J = (L + S) = 1 + 1/2 = 3/2$  (Since subshell is more than half filled)

term symbol  $^2P_{3/2}$

For  $p^3$



$$m_l = +1 \quad 0 \quad -1$$

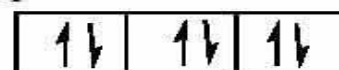
$S = 1/2 + 1/2 + 1/2 = 3/2$ ; thus  $(2S+1) = 4$

$L = 1 + 0 - 1 = 0$ ; thus symbol is S

$J = S = 3/2$  (Since subshell is half filled)

term symbol  $^4S_{3/2}$

For  $p^6$



$$m_l = +1 \quad 0 \quad -1$$

$S = 0$ ; thus  $(2S+1) = 1$

$L = 0$ ; thus symbol is S

$J = S = 0$  (Since subshell is full filled)

term symbol  $^1S_0$

To calculate **S**, simply sum the **unpaired** electrons using a value of  $\frac{1}{2}$  for each.

To calculate **L**, use the labels for each column to determine the value of **L** for that box, then add all the individual box values together.

For a  $d^7$  configuration, then:

in the +2 box are 2 electrons, so **L** for that box is  $2*2= 4$

in the +1 box are 2 electrons, so **L** for that box is  $1*2= 2$

in the 0 box is 1 electron, **L** is 0

in the -1 box is 1 electron, **L** is  $-1*1= -1$

in the -2 box is 1 electron, **L** is  $-2*1= -2$

Total value of **L** is therefore  $+4 +2 +0 -1 -2$  or **L**=3.

Note that for 5 electrons with 1 electron in each box then the total value of **L** is 0.

This is why **L** for a  $d^1$  configuration is the same as for a  $d^6$ .

The other thing to note is the idea of the "hole" approach.

A  $d^1$  configuration can be treated as similar to a  $d^9$  configuration. In the first case there is 1 electron and in the latter there is an absence of an electron ie a hole.

The overall result shown in the Table above is that:

4 configurations ( $d^1, d^4, d^6, d^9$ ) give rise to D ground terms,

4 configurations ( $d^2, d^3, d^7, d^8$ ) give rise to F ground terms

and the  $d^5$  configuration gives an S ground term.