18.4 The Russell Saunders Coupling Scheme:

- **Quantum Numbers**

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,.. , (n-1),

traditionally termed s, p, d, f, etc. orbitals after the lines in alkali metal spectra: sharp, principal, diffuse, and fundamental.

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 ml.

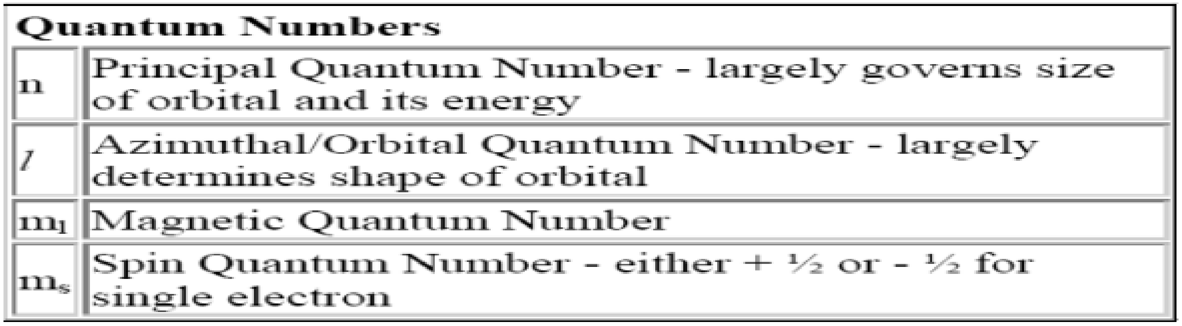
ml is a subset of *l*, where the allowable values are: ml = *l*, *l*-1, *l*-2, ... 1, 0, -1, ... , - (*l*-2), -(*l*-1), -*l*.

There are thus (2*l* +1) values of ml 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, ms, 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, arising from the spinning of an asymmetrical charge distribution about its own axis. Like an electron moving in its orbital around a nucleus, the electron spinning about its axis has associated with its motion a well defined angular momentum. The value of ms is either + ½ or - ½.

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



Quantum Numbers	
n	Principal Quantum Number - largely governs size of orbital and its energy
l	Azimuthal/Orbital Quantum Number - largely determines shape of orbital
m_l	Magnetic Quantum Number
m_s	Spin Quantum Number - either + ½ or - ½ for single electron

❖ Russell Saunders coupling:

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 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 J coupling is 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 ms 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

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

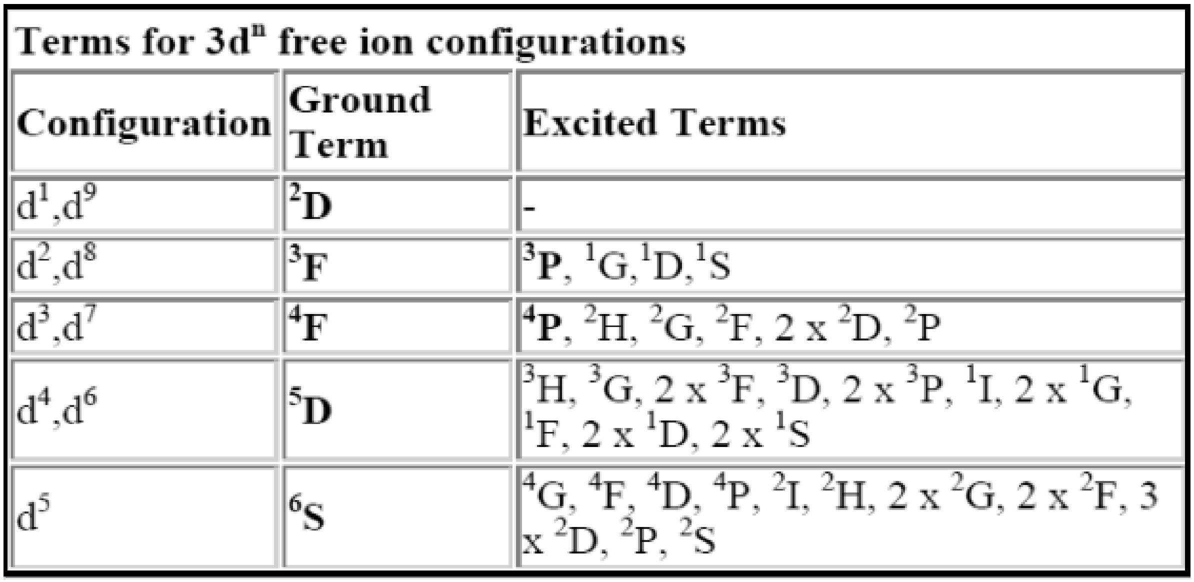
As an example, for a d^1 configuration:

S= + ½, hence (2S+1) = 2

L=2

and the Russell Saunders 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 $3d^n$ free ion configurations

Configuration	Ground Term	Excited Terms
d^1, d^9	**^2D**	-
d^2, d^8	**^3F**	**^3P**, ^1G, ^1D, ^1S
d^3, d^7	**^4F**	**^4P**, ^2H, ^2G, ^2F, 2 x ^2D, ^2P
d^4, d^6	**^5D**	^3H, ^3G, 2 x ^3F, ^3D, 2 x ^3P, ^1I, 2 x ^1G, ^1F, 2 x ^1D, 2 x ^1S
d^5	**^6S**	^4G, ^4F, ^4D, ^4P, ^2I, ^2H, 2 x ^2G, 2 x ^2F, 3 x ^2D, ^2P, ^2S

❖ 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 multipicity, then the Ground Term will have the largest value of L.