Rizvi College of Arts, Science and Commerce

ELECTRONIC STATES AND TERMS

T.Y. B.Sc. (Chemistry)

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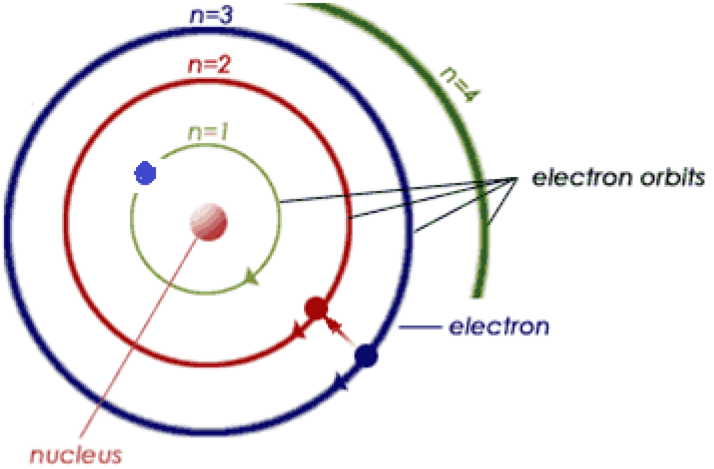
Objectives

- After studying this topic you should be able to predicts the microstate for give electronic system.
- Spin – orbit coupling
- Derive the term symbol for ground state and excited state for transition metal ions.

Description of energy levels of an electron—

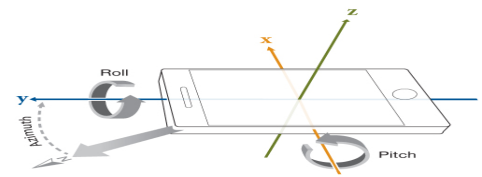
Energy level of an electron can be described in terms of *four* quantum numbers—

A) Principle quantum number (n) — The Rutherford – Bohr Model of an atom simply based on the idea that electrons can only exist on certain fixed levels. It determines the successive major energy levels of electrons in an atom.
'n' can have values 1, 2, 3, …… corresponds to K, L, M, …. shell



B) Azimuthal Quantum Number (Subsidiary Quantum Number) (*l*)–

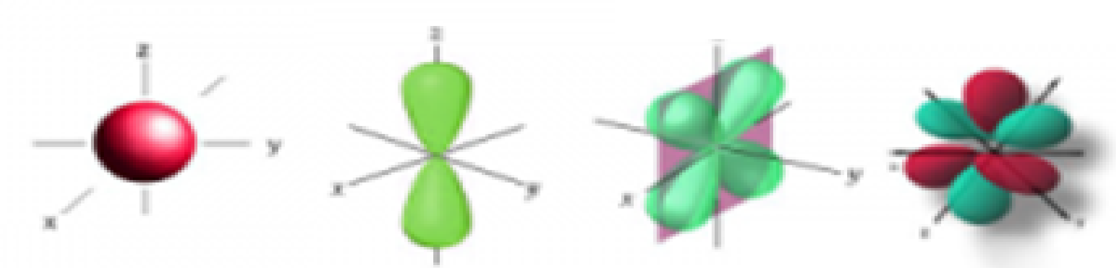
(*azimuth is an angular measurement in a spherical coordinate system. The vector from an observer to a point of interest is projected perpendicularly onto a reference plane; the angle between the projected vector and a reference vector on the reference plane is called the azimuth.*)



The orbital has a total (n-1) nodes : (n - *l* - 1) radial nodes and *l* angular nodes

The acceptable values of (*l*) are related to 'n'. From 0 to (n-1).

l → *0, 1, 2, 3, ….(n-1) that corresponds to shapes of orbital's*



$\ell =$	0	1	2	3
	s	p	d	f

C) The magnetic quantum number (m_l) –

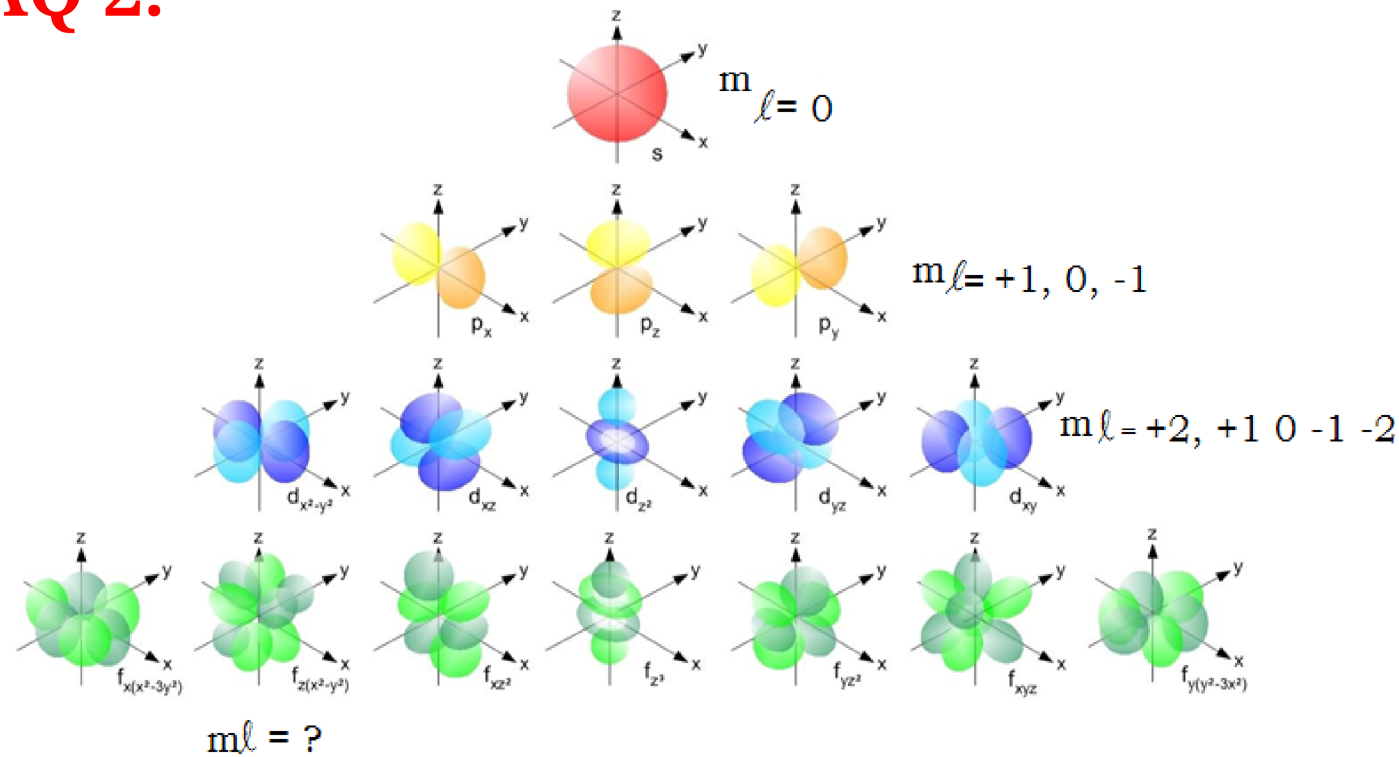
(*since electron is a charged particle, its spin motion would give rise to a magnetic moment*)

- This quantum number determines an orientation of the angular orbital momentum. It specifies certain selected directions (*conventionally z-axis*) in space for orientation of the orbital angular momentum vector of the electron (*or you can say that it signifies the sub-orbitals*). It has all integral values in the range from $+l$ to $-l$.
- i.e. it can take up the total values $(2l+1) = +l, l-1, l-2, \ldots, 0, -l$
- Hence,
- When n=1 → $l = 0$; *i.e. s; therefore,* $m_l = 1$
- When n=2 → $l = 1$; *i.e. 0, 1 (hence, s & p therefore, when l is 0 s orbital & when l is 1 - p orbital l*) $m_l = 3$ (+1, 0 -1) corresponds to p_x, *py* and p_z.

***SAQ 1** – describe the magnetic quantum number for M shell.*

D) Spin Quantum Number (s)—

- Spectral data shown that the value of s along *z*-axis conventionally is always ½
- The magnetic spin quantum number (m_s)= it is the component along the 'z' direction of the spin quantum number and has two values +½ and -½
- **SAQ 2:**



To build up of electrons in an element – follow three simple rules—

1) 'Aufbau Principle

Incoming electrons occupies orbital's of lowest energy levels

2) Pauli Exclusion Principle

No two electrons in an element can have all the four quantum numbers same. (*It restricts the max. no. of electrons which may be assigned to a given orbital*)

3) Hund's Maximum Multiplicity

Electrons occupy the orbital's with parallel spin first before being paired. (*The ground state of an atom should contain maximum number of unpaired electrons within the same subshell with their spins parallel)*

Electronic configuration is an assignment of a given number of electrons to a certain set of orbital's. It does not take into account electrostatic and other interactions between electrons

SAQ 3: State whether the following are true or false. If false, write the correct statement

- 1) The principle quantum number signifies number of electrons present in an given system.
- 2) Principle quantum number signifies energy of an electron from the nucleus.
- 3) Orbital angular momentum is arises from the spinning of an electron.
- 4) Orbital angular momentum signifies nodal planes.
- 5) The magnetic quantum number signifies the shapes of an orbital.
- 6) The magnetic quantum number signifies the shapes of sub-orbital's.

Term and Term Symbol –

- Atomic spectra of many-electron atoms are very complex in nature.
- They contain multiple lines indicating several transitions.
- These spectral lines corresponds to mutual interaction between the electrons.
- There are three kinds of interactions between spin and orbital angular momenta-
- 1) spin – spin coupling
- 2) orbit – orbit coupling
- 3) spin – orbit coupling
- It is assumed that the strength of interaction varies as –

spin-spin coupling > orbit-orbit coupling > spin-orbit coupling

- The single electron of an atomic nucleus can be described in terms of the orbitals of hydrogen like atom. A particular set of values for the quantum numbers n, l, and m_l, , designates a particular orrbital of the electron. The angular momentum contributed by the electron to the atom depends on the value of l , and the angular-momentum component along an imposed direction depends on the value of m_l.
- When another electrons are added to begin the buildup of a many-electron atom, each added electron gets affected by the central field resulting from the average positions of all the other electrons.
- Hence it is necessary to consider the mutual influence of these electrons have on one another. It is observed that the interactions of the magnetic fields, produced by the electrons (orbital and spin angular momenta) gives rise to a series of energy levels.

Russel – Saunders coupling (L-S coupling)—

- When several electrons are present in a subshell—
- Total orbital angular momentum (L) - the individual orbital angular momenta '*l*' are first combined to give a L value of the system.

  i.e. $L = l_1 + l_2 + l_3 + ... = \sum l$ (algebric summation)

The different L values 0,1,2,3, etc. are represented by a letter symbol

L = 0 1 2 3 4 5 6 7

Symbol = S P D F G H I K (note that J is missing)

The individual m_l values represent the component of orbital angular momentum vectors. Just like m_l. There are (2L+1) values for M_L. i.e. +L….0 -L

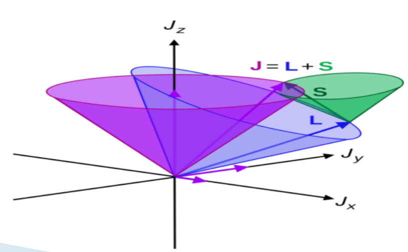
Simlarly,

- The resultant spin quantum number (S) – the individual spin quantum number '*s*' are combined to give S

i.e. $S = s_1 + s_2 + s_3 + ... \sum m_s$ (algebric summation)

Total angular Momentum (J) - In an atom, the magnetic effects of L and S interact to give new quantum number J called the Total Angular Momentum Quantum Number. It is actually results from vectorial combination of L & S. J can take values from |L+S| to |L-S|.

Each J value has (2J+1) fold, degenerate specified by quantum number M_J. It gets removed on application of magnetic field.



Note that only partially filled subshells contribute to L and S. When there are at least two electrons in the valence shell and when there are multiple possible choices in ml and ms for these electrons consistent with the Pauli principle and the particular configuration. But this is not the case for the ground states of the rare gases, alkali metals, alkaline earth metals, group III and the halogens. Atoms in all of these groups have either a filled shell or subshell, or only one electron or one electron fewer than the maximum number of electrons in a subshell. None of these atoms has more than one unpaired electrons in its ground state.

If spin – orbit coupling is neglected, the total energy is independent of M_S and M_L. Therefore, a group of different quantum states that have the same values for L and S but different values of M_L and M_S is degenerate in energy. Such a group of states is called a term, and the L and S values for the term indicated by the symbol $^{(2S+1)}L$.

(*hence, a term is a group of states that has the same L and S values*.)

- **Term symbols** usually represent electronic states in the Russell-Saunders coupling scheme, where a typical atomic term symbol consists of the spin multiplicity, the symmetry label and the total angular momentum of the atom. They have the format of $^{(2S+1)}\mathbf{L}_J$.

Spin multiplicity (2S+1) – when the spins of two electrons couple, the resultant spin quantum number obtained is S = 1or 0. For each value of S there will be 2S+1 values of of M_S, where (2S+1) known as the spin multiplicity.

Microstates (N)—

- Due to spin orbit coupling, the energy levels are further splits to different energy by the application of magnetic or electric field (Zeeman effect), and is called as microstates.
- The number of microstates (N) can be calculate by using the formula-

$$N = \frac{n!}{r!\,(n-r)!}$$

- (Where N- microstates; n – max. no. of electrons that can be accommodate in a given valence orbital's; r – number of electrons present in given valence orbital.)

The main Steps in finding the states—

- 1) Calculate the microstates
- 2) Individual spin angular momenta (m_s) of the electrons combine to give a resultant spin angular momenta (S).
  - $S = \sum m_s$.
- 3) Individual orbital angular momenta (m_l) of the electrons combine to give a resultant orbital angular momenta (S).

$L = \sum m_l$.

& expressed the value of quantum number L by letter (***symbol***) S, P, D, F,… etc.

- 4) L & S couple together to give a total resultant angular momentum 'J'

$J = |L+S| \ldots\ldots\ldots\ldots\ldots |L-S|$

5) Expressed the various states arising from L, S and J by term symbol

.

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

- 6) Select the maximum J value for the ground state if the subshell is more than half-filled and the minimum J value if the subshell is less than half filled.

Deduce the microstates and terms for p^2 configuration as in carbon atom.

- 1) In *p* sub-orbital's we can accommodate maximum 6 electrons. Therefore, n=6
  for given p^2 config. r (no. of e^-)= 2

$$microstates = \frac{n!}{r!\,(n-r)!} = \frac{6!}{2!\,(6-2)!} = 15$$

15 allowed microstates for p^2 configuration.

The electronic configuration for p^2 –

1s	2s	2p		
		p_x	p_y	p_z
		+1	0	-1
↑↓	↑↓	↑	↑	

1) The value of the L quantum number = $\sum m_l$ = (+1+0) = 1
2) The value of S quantum number = $\sum m_s$ = +½+½ = 1
3) Therefore, the spin multiplicity (2S + 1) = (2 x 1 +1) = 3
4) Thus, in carbon atom, L = 1 indicates term symbol 'P'

5) J can take values from $|L+S|...0....|L-S|$

$\therefore J = |1+1|, |1+1-1|, |1+1-2| = 2, 1, 0$

Since p^2 configuration is less than half filled, hence the minimum value of J is to be selected.

Hence, the ground state term symbol for p^2 config. – $^{(2S+1)}L_J$.

i.e. $\boxed{^3P_0}$

Thank you