

## **Chapter-7**

### **INNOVATIVE METHOD FOR THE PREDICTION OF SPIN MULTIPLICITY**

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In the previous chapter 6, formulae-based mnemonics have been discussed to predict the magnetic properties and bond order of diatomic species having the total number of electrons (1-20) without drawing their electronic configurations through molecular orbital theory (M.O.T.). In this chapter 7, spin multiplicity values have been predicted by other innovative method without calculating total spin quantum numbers ( $S$ ) of elements, molecules or ions, and coordination compounds. Spin multiplicity is also very essential to constitute atomic term symbol, ( $^{2S+1}L_J$ ), along with resultant vectors  $L$  and  $J$  in co-ordination chemistry<sup>1</sup>.  $L$  is also known as resultant orbital angular momentum quantum number.

**Spin multiplicity value and its corresponding spin state, first discovered by Friedrich Hund in 1925.** The formula which is generally used for the prediction of spin multiplicity value is  $[(2S+1)]$ , where  $S = \sum s$  = total spin quantum no] is time-consuming<sup>2</sup>. To keep the matter in mind some simple innovative mnemonics has to be introduced for calculation of spin-multiplicity value and thus its corresponding spin state in the easiest way by ignoring the calculation of total spin quantum number ( $S = \sum s$ ).

### **METHODOLOGY**

#### **A. Conventional method for prediction of the spin multiplicity of elements and compounds**

The formula, which is generally used for the prediction of spin multiplicity value is  $(2S+1)$ , where,  $S = \sum s$  = total spin quantum number.

#### **B. Innovative method for prediction of the spin multiplicity of elements and compounds**

First, classify the unpaired electrons of species (atoms, molecules, ions or complexes) for which the spin

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1. J. E. Huheey, et.al. *Inorganic Chemistry* (Pearson, 4<sup>th</sup> ed., India: 2006), 711-715.

2.T. Engel and P. Reid *Physical Chemistry* (Pearson Benjamin-Cummings: 2006), 473, 477–479

multiplicity value should be evaluated into three types based on the nature of alignments <sup>3,4,5,6</sup>.

**i) Species having unpaired electrons in upward alignment ( $\uparrow$ ):**

**In this case, spin multiplicity =  $(n+1)$ ; where  $n$  = number of unpaired electrons**

**ii) Species having unpaired electrons in downward alignment ( $\downarrow$ ):**

**In this case spin multiplicity =  $(-n+1)$ ; Here (-ve) sign indicate downward arrow.**

**iii) Species having unpaired electrons in both mixed alignments ( $\uparrow\downarrow$ ):**

**In this case spin multiplicity =  $[(+n) + (-n) + 1]$ ;**

**where  $n$  = number of unpaired electrons. Here, (+ve) and (-ve) sign indicate upward and downward alignment of electrons, respectively.**

## RESULTS AND DISCUSSION

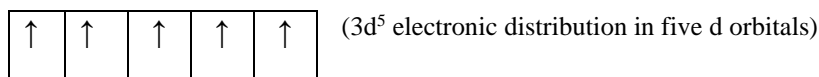
### A. Prediction of the spin multiplicity of elements, molecules, and compounds by the conventional method

The formula, which is generally used for the prediction of spin multiplicity value is  $(2S+1)$ , where,  $S = \sum s$  = total spin quantum number.

In case of element, molecules or ions and coordination compounds, first, draw electronic configurations with the help of Aufbau principle, Molecular orbital theory (MOT) and CFT (crystal field theory) respectively, then calculate the total spin quantum number ( $S$ ) for unpaired electrons present in them, then, evaluated spin multiplicity value by putting the value of  $S$  in  $(2S+1)$  and thus get the corresponding spin state as follows:

**Ex.a. Prediction of spin multiplicity value for manganese Mn ( $Z = 25$ )**

Electronic configuration of Mn, using Aufbau principle, is  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$

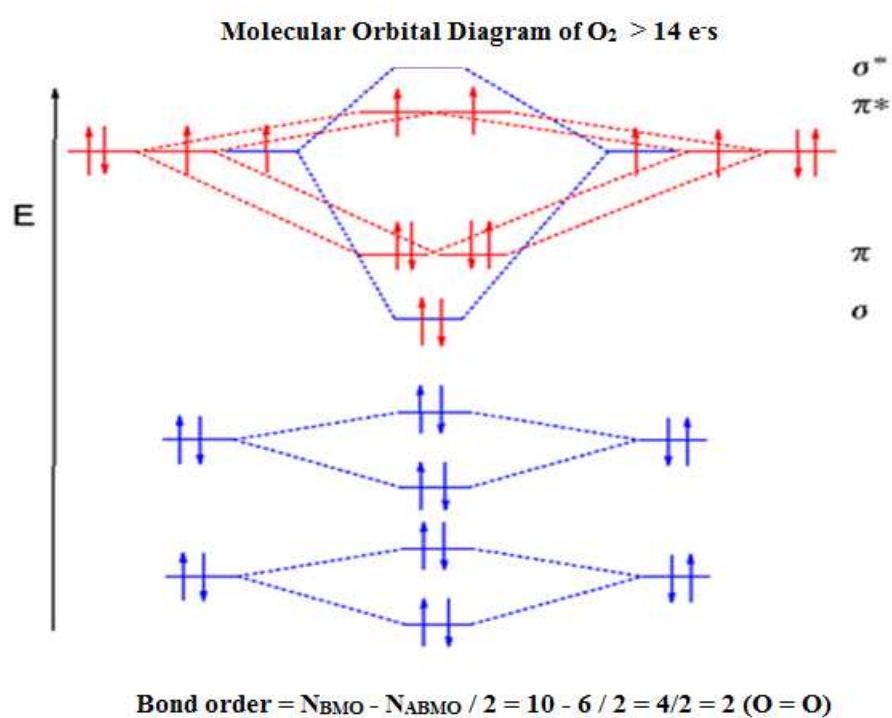


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3. A. Das, "A Review of Time Economic Innovative Mnemonics In Chemical Education", *International Journal of Physics & Chemistry Education* 10 (June 2018): 27-40, doi: 10.12973/ijpce/81589, <http://www.ijpce.org/A-Review-of-Time-Economic-Innovative-Mnemonics-in-Chemical-Education,81589,0,2.html>.
4. A. Das, "Innovative Mnemonics Make Chemical Education Time Economic – A Pedagogical Review Article", *World Journal of Chemical Education* 6(Sept 2018):154-174, doi:10.12691/wjce-6-4-2, <http://pubs.sciepub.com/wjce/6/4/2/index.html>.
5. A. Das, "Innovative Mnemonics in Chemical Education - A Review Article", *American Journal of Chemistry and Applications* 5(April 2018): 19-32, <http://www.openscienceonline.com/journal/archive2?journalId=711&paperId=4221>.
6. A. Das, "Chemical Bonding: Time Economic Innovative Pedagogies - A Review Article", *Global Journal of Science Frontier Research Chemistry* 17 (Nov 2017): 1-16, <https://journalofscience.org/index.php/GJSFR/article/view/2110>.
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Here,  $s = +1/2 + 1/2 + 1/2 + 1/2 + 1/2$ ,  $s$  = spin quantum number, which is  $(+1/2)$  and  $(-1/2)$  for upward and alignment of electrons respectively. Here  $S = \Sigma s$  = total spin quantum number  $= (+5/2)$ , hence, spin multiplicity value  $= 2S + 1 = 2 (+5/2) + 1 = 6$  (spin state – sextet).

**Ex.b.** Prediction of spin multiplicity value for oxygen molecule  $O_2$  ( $16e^-$ s)

Electronic configuration of  $O_2$  having 16 electrons, using molecular orbital theory (M.O.T.), is  $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2pz}^2, \pi_{2px}^2, \pi_{2py}^2, \pi_{2px}^{*1}, \pi_{2py}^{*1}$  (**Fig.4.23**). From this electronic configuration, it is clear that, in  $O_2$ , there is two (02) unpaired electrons in two anti bonding molecular orbitals ( $\pi_{2px}^*, \pi_{2py}^*$ ), for which  $S = \Sigma s$  = total spin quantum number  $= (+1/2) + (1/2) = 1$ , hence, spin multiplicity value  $= 2S + 1 = 2 (1) + 1 = 3$  (spin state – triplet).



**Fig.4.23: Molecular orbital diagram of  $O_2$**

**Ex.c.** Prediction of spin multiplicity value for molecular ion  $O_2^+$  ( $15e^-$ s)

Electronic configuration of  $O_2^+$  having 15 electrons, using molecular orbital theory (M.O.T.), is  $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2pz}^2, \pi_{2px}^2, \pi_{2py}^2, \pi_{2px}^{*1}, \pi_{2py}^{*0}$ . From this electronic configuration, it is clear that, in  $O_2^+$ , there is one (01) unpaired electron in one anti bonding molecular orbital ( $\pi_{2px}^*$ ), for which  $S = \Sigma s$  = total spin quantum number  $= +1/2$ , hence, spin multiplicity value  $= 2S + 1 = 2 (+1/2) + 1 = 2$  (spin state – doublet).

**Ex.d.** Prediction of spin multiplicity value for a high spin  $\text{Mn}^{2+}$  octahedral complex ( $3d^5$ ). Electronic configuration for a high spin  $\text{Mn}^{2+}$  octahedral complex ( $3d^5$ ), using crystal field theory (CFT), is  $t_{2g}^3, e_g^2$ , where, number of unpaired electrons in upward alignment  $n = 5$ . Here  $S = \Sigma s = \text{total spin quantum number} = +5/2$ , hence, spin multiplicity value  $= 2S + 1 = 2 (+5/2) + 1 = 6$  (spin state – sextet).

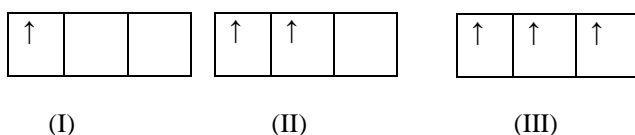
## B. Prediction of the spin multiplicity of elements, molecules, and compounds by innovative method

First of all, classify the species (atoms, molecules, ions or complexes) for which spin multiplicity value and its corresponding spin state should be evaluated into three types based on the nature of alignment of unpaired electrons (upward, downward, or mixed alignment) present in them.

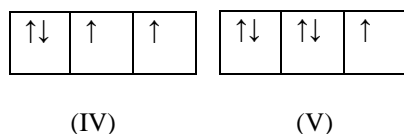
### i) For upward alignment of electrons

**Spin multiplicity  $= (n + 1)$ , where,  $n$  = number of unpaired electrons.**

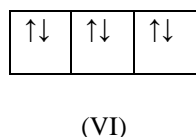
**Ex.**



For above three electronic representations, (I), (II) and (III), spin multiplicity  $= (n + 1) = (1 + 1) = 2$  (spin state = doublet);  $(2 + 1) = 3$  (spin state = triplet) and  $(3 + 1) = 4$  (spin state = quartet) respectively.



For above two electronic representations, (IV) and (V), spin multiplicity  $= (n + 1) = (2 + 1) = 3$  (in this case ignore paired electrons) (spin state = triplet) and  $(1 + 1) = 2$  (spin state = doublet) respectively.

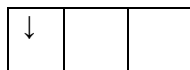


For above electronic representation (VI), spin multiplicity  $= (n + 1) = (0 + 1) = 1$  (spin state = singlet).

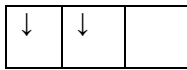
## ii) For downward alignment of electrons

**Spin multiplicity =  $(-n + 1)$ , where,  $n$  = number of unpaired electrons.**

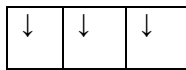
**Ex.**



(VII)

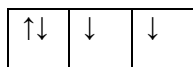


(VIII)

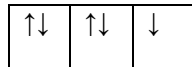


(IX)

For above three electronic representations, (VII), (VIII) and (IX), spin multiplicity =  $(-1 + 1) = 0$ ;  $(-2 + 1) = -1$  and  $(-3 + 1) = -2$  respectively.



(X)



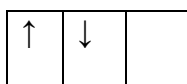
(XI)

For above two electronic representations, (X) and (XI), spin multiplicity =  $(-n + 1) = (-2 + 1) = -1$  (ignore paired electrons) and  $(-1 + 1) = 0$  respectively.

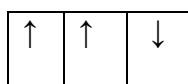
## iii) For mixed (upward & downward) alignment of electrons (completely hypothetical assumption)

**Spin multiplicity =  $[(+n) + (-n) + 1]$ , where,  $(+n)$  = upward directed unpaired electron and  $(-n)$  = downward directed unpaired electron.**

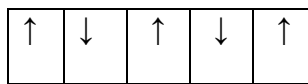
**Ex.**



(XII)



(XIII)



(XIV)

For above three electronic representations, (XII), (XIII) and (XIV), spin multiplicity =  $[(+n) + (-n) + 1] = [(+1) + (-1) + 1] = 1$  (spin state = singlet);  $[(+2) + (-1) + 1] = 2$  (spin state = doublet) and  $[(+3) + (-2) + 1] = 2$  (spin state = doublet) respectively.

For 1, 2, 3, 4, 5, 6 or  $> 6$  spin multiplicity values  $(n+1)$ , the corresponding spin state will be a singlet, doublet, triplet, quartet, quintet, sextet or multiplet, respectively.

**Spin multiplicity and spin state value**

Number of Unpaired electrons (n)	Spin multiplicity value	Spin State
01	02	Doublet
02	03	Triplet
03	04	Quartet
04	05	Quintet
05	06	Sextet
> 05	> 06	Multiplet

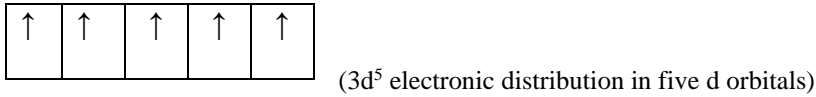
**APPLICATION OF INNOVATIVE METHOD FOR THE PREDICTION OF SPIN MULTIPLICITY VALUE OF ELEMENTS, MOLECULES OR IONS AND CO-ORDINATION COMPOUNDS:**

In case of element, molecules or ions and coordination compounds, first, draw electronic configurations with the help of Aufbau principle, Molecular orbital theory (MOT) and CFT (crystal field theory) respectively, then calculate the number of unpaired electrons (n) present in them, then evaluated spin multiplicity value by putting the value of ‘n’ in the innovative formulae and thus get the corresponding spin state as follows:

**Prediction of the spin multiplicity of the element:**

**Ex.** Prediction of spin multiplicity value for manganese Mn (Z = 25) by drawing electronic configuration with the help of the Aufbau principle and Hund's rule.

Electronic configuration of Mn using Aufbau principle, is  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$



Here, n = number of unpaired electrons = 5, hence, spin multiplicity value =  $(n + 1) = (5 + 1) = 6$  (spin state – sextet).

**Prediction of the spin multiplicity of molecule:**

**Ex.** Prediction of spin multiplicity value for oxygen molecule O<sub>2</sub> (16e<sup>-</sup>s) by drawing electronic configuration with the help of molecular orbital theory (MOT).

Electronic configuration of  $O_2$  having 16 electrons, using molecular orbital theory (M.O.T.), is  $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2pz}^2, \pi_{2px}^2, \pi_{2py}^2, \pi_{2px}^{*1}, \pi_{2py}^{*1}$  (Fig.4.23). From this electronic configuration,  $n$  = number of unpaired electrons = 2, hence, spin multiplicity value =  $(n + 1) = 2 + 1 = 3$  (spin state – triplet).

**Prediction of the spin multiplicity of molecular ion:**

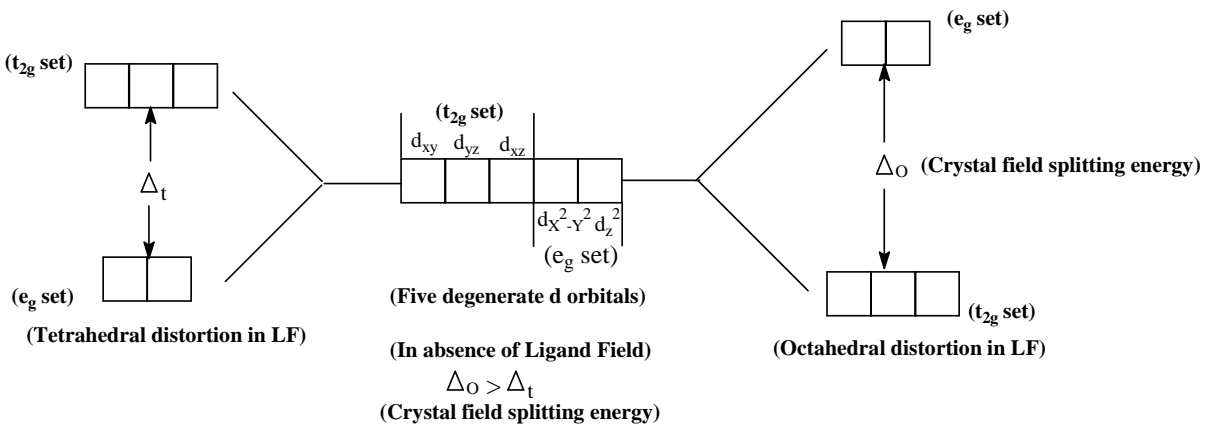
**Ex.** Prediction of spin multiplicity value for molecular ion  $O_2^+$  ( $15e^-$ s) by drawing electronic configuration with the help of molecular orbital theory (MOT).

Electronic configuration of  $O_2^+$  having 15 electrons, using molecular orbital theory (M.O.T.), is  $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2pz}^2, \pi_{2px}^2, \pi_{2py}^2, \pi_{2px}^{*1}, \pi_{2py}^{*0}$ . From this electronic configuration,  $n$  = number of unpaired electrons = 1, hence, spin multiplicity value =  $(n + 1) = 1 + 1 = 2$  (spin state – doublet).

**Prediction of the spin multiplicity of high spin and low spin coordination compounds:**

**Ex.a.** Prediction of spin multiplicity value for high spin and low spin octahedral complexes (coordination no 6) of first-row transition series elements ( $3d^1$  to  $3d^{10}$ ).

As per CFT, the five degenerate (same energy) d orbitals of octahedral complexes in presence of ligand field (LF) splits into two set  $t_{2g}$  and  $e_g$ . Three-d orbitals ( $d_{xy}, d_{yz}, d_{xz}$ ) form  $t_{2g}$  set and rest two d orbitals ( $d_{x^2-y^2}, d_{z^2}$ ) form  $e_g$  set. In octahedral splitting, a  $t_{2g}$  set will be lower in energy than  $e_g$  set. The energy difference between  $t_{2g}$  and  $e_g$  set is to be treated as crystal field splitting energy of octahedral distortion and it is represented by  $\Delta_o$  (Fig.7.24).



**Fig.7.24: Splitting of d orbitals in Crystal Field Theory (CFT)**

***Electronic configuration (E.C.) for low spin (LS) octahedral complexes with CFT and their corresponding spin multiplicity value and spin state can be calculated as follows:***

For  $3d^1(\text{LS})$ , electronic representation –  $(t_{2g}^1, e_g^0)$ , E.C. –  $(t_{2g}^1, e_g^0)$ , number of unpaired electron (n) = 1, spin multiplicity value  $(n+1) = (1+1) = 2$ , spin state is doublet.

For  $3d^2(\text{LS})$ , electronic representation –  $(t_{2g}^{1,2}, e_g^0)$ , E.C. –  $t_{2g}^2, e_g^0$ , number of unpaired electron (n) = 2, spin multiplicity value  $(n+1) = (2+1) = 3$ , spin state is triplet.

For  $3d^3(\text{LS})$ , electronic representation –  $(t_{2g}^{1,2,3}, e_g^0)$ , E.C. –  $t_{2g}^3, e_g^0$ , number of unpaired electron (n) = 3, spin multiplicity value  $(n+1) = (3+1) = 4$ , spin state is quartet.

For  $3d^4(\text{LS})$ , electronic representation –  $(t_{2g}^{1,2,3,4}, e_g^0)$ , E.C. –  $t_{2g}^4, e_g^0$ , number of unpaired electron (n) = 2, spin multiplicity value  $(n+1) = (2+1) = 3$ , spin state is triplet.

For  $3d^5(\text{LS})$ , electronic representation –  $(t_{2g}^{1,2,3,4,5}, e_g^0)$ , E.C. –  $t_{2g}^5, e_g^0$ , number of unpaired electron (n) = 1, spin multiplicity value  $(n+1) = (1+1) = 2$ , spin state is doublet.

For  $3d^6(\text{LS})$ , electronic representation –  $(t_{2g}^{1,2,3,4,5,6}, e_g^0)$ , E.C. –  $t_{2g}^6, e_g^0$ , number of unpaired electron (n) = 0, spin multiplicity value  $(n+1) = (0+1) = 1$ , spin state is **singlet (lowest spin state)**.

For  $3d^7(\text{LS})$ , electronic representation –  $(t_{2g}^{1,2,3,4,5,6}, e_g^1)$ , E.C. –  $t_{2g}^6, e_g^1$ , number of unpaired electron (n) = 1, spin multiplicity value  $(n+1) = (1+1) = 2$ , spin state is doublet.

For  $3d^8(\text{LS})$ , electronic representation –  $(t_{2g}^{1,2,3,4,5,6}, e_g^{7,8})$ , E.C. –  $t_{2g}^6, e_g^2$ , number of unpaired electron (n) = 2, spin multiplicity value  $(n+1) = (2+1) = 3$ , spin state is triplet.

For  $3d^9(\text{LS})$ , electronic representation –  $(t_{2g}^{1,2,3,4,5,6}, e_g^{7,8,9})$ , E.C. –  $t_{2g}^6, e_g^3$ , number of unpaired electron (n) = 1, spin multiplicity value  $(n+1) = (1+1) = 2$ , spin state is doublet.

For  $3d^{10}(\text{LS})$ , electronic representation –  $(t_{2g}^{1,2,3,4,5,6}, e_g^{7,8,9,10})$ , E.C. –  $t_{2g}^6, e_g^4$ , number of unpaired electron (n) = 0, spin multiplicity value  $(n+1) = (0+1) = 1$ , spin state is **singlet (lowest spin state)**.

***Electronic configuration (E.C.) for high spin (HS) octahedral complexes with CFT and their corresponding spin multiplicity value and spin state can be calculated as follows:***

For  $3d^1(\text{HS})$ , electronic representation –  $(t_{2g}^1, e_g^0)$ , E.C. –  $(t_{2g}^1, e_g^0)$ , number of unpaired electron (n) = 1, spin multiplicity value  $(n+1) = (1+1) = 2$ , spin state is doublet.

For  $3d^2(\text{HS})$ , electronic representation –  $(t_{2g}^{1,2}, e_g^0)$ , E.C. –  $(t_{2g}^2, e_g^0)$ , number of unpaired electron (n) = 2, spin multiplicity value  $(n+1) = (2+1) = 3$ , spin state is triplet.



For  $3d^3(\text{HS})$ , electronic representation –  $(t_{2g}^{1,2,3}, e_g^0)$ , E.C. –  $(t_{2g}^3, e_g^0)$ , number of unpaired electron ( $n$ ) = 3, spin multiplicity value  $(n+1) = (3+1) = 4$ , spin state is quartet.

For  $3d^4(\text{HS})$ , electronic representation –  $(t_{2g}^{1,2,3}, e_g^4)$ , E.C. –  $(t_{2g}^3, e_g^1)$ , number of unpaired electron ( $n$ ) = 4, spin multiplicity value  $(n+1) = (4+1) = 5$ , spin state is quintet.

For  $3d^5(\text{HS})$ , electronic representation –  $(t_{2g}^{1,2,3}, e_g^{4,5})$ , E.C. –  $(t_{2g}^3, e_g^2)$ , number of unpaired electron ( $n$ ) = 5, spin multiplicity value  $(n+1) = (5+1) = 6$ , spin state is **sextet (highest spin state)**.

For  $3d^6(\text{HS})$ , electronic representation –  $(t_{2g}^{1,2,3}, e_g^{4,5}, t_{2g}^6)$ , E.C. –  $(t_{2g}^4, e_g^2)$ , number of unpaired electron ( $n$ ) = 4, spin multiplicity value  $(n+1) = (4+1) = 5$ , spin state is quintet.

For  $3d^7(\text{HS})$ , electronic representation –  $(t_{2g}^{1,2,3}, e_g^{4,5}, t_{2g}^{6,7})$ , E.C. –  $(t_{2g}^5, e_g^2)$ , number of unpaired electron ( $n$ ) = 3, spin multiplicity value  $(n+1) = (3+1) = 4$ , spin state is quartet.

For  $3d^8(\text{HS})$ , electronic representation –  $(t_{2g}^{1,2,3}, e_g^{4,5}, t_{2g}^{6,7,8})$ , E.C. –  $(t_{2g}^6, e_g^2)$ , number of unpaired electron ( $n$ ) = 2, spin multiplicity value  $(n+1) = (2+1) = 3$ , spin state is triplet.

For  $3d^9(\text{HS})$ , electronic representation –  $(t_{2g}^{1,2,3}, e_g^{4,5}, t_{2g}^{6,7,8}, e_g^9)$ , E.C. –  $(t_{2g}^6, e_g^3)$ , number of unpaired electron ( $n$ ) = 1, spin multiplicity value  $(n+1) = (1+1) = 2$ , spin state is doublet.

For  $3d^{10}(\text{HS})$ , electronic representation –  $(t_{2g}^{1,2,3}, e_g^{4,5}, t_{2g}^{6,7,8}, e_g^{9,10})$ , E.C. –  $(t_{2g}^6, e_g^4)$ , number of unpaired electron ( $n$ ) = 0, spin multiplicity value  $(n+1) = (0+1) = 1$ , spin state is **singlet (lowest spin state)**.

**Ex.b. Prediction of spin multiplicity value for high spin and low spin tetrahedral complexes (coordination no 4) of first-row transition series elements ( $3d^1$  to  $3d^{10}$ ).**

As per CFT, the five degenerate (same energy) d orbitals of tetra complexes in presence of ligand field (LF) splits into two set  $t_{2g}$  and  $e_g$ . Three-d orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ) form  $t_{2g}$  set and rest two d orbitals ( $d_{x^2-y^2}$ ,  $d_z^2$ ) form  $e_g$  set. In tetrahedral splitting, a  $t_{2g}$  set will be higher in energy than  $e_g$  set. The energy difference between  $e_g$  and  $t_{2g}$  set is to be treated as crystal field splitting energy of tetrahedral distortion and it is represented by  $\Delta_t$  (**Fig.7.24**).

***Electronic configuration (E.C.) for high spin (HS) tetrahedral complexes with CFT and their corresponding spin multiplicity value and spin state can be calculated as follows:***

For  $3d^1(\text{HS})$ , electronic representation –  $(e_g^1, t_{2g}^0)$ , E.C. –  $(t_{2g}^0, e_g^1)$ , number of unpaired electron ( $n$ ) = 1, spin multiplicity value  $(n+1) = (1+1) = 2$ , spin state is doublet.

For  $3d^2(\text{HS})$ , electronic representation –  $(e_g^{1,2}, t_{2g}^0)$ , E.C. –  $(t_{2g}^0, e_g^2)$ , number of unpaired electron ( $n$ ) = 2, spin multiplicity value  $(n+1) = (2+1) = 3$ , spin state is triplet.

For  $3d^3(\text{HS})$ , electronic representation –  $(e_g^{1,2}, t_{2g}^3)$ , E.C. –  $(t_{2g}^1, e_g^2)$ , number of unpaired electron  $(n) = 3$ , spin multiplicity value  $(n+1) = (3+1) = 4$ , spin state is quartet.

For  $3d^4(\text{HS})$ , electronic representation –  $(e_g^{1,2}, t_{2g}^{3,4})$ , E.C. –  $(t_{2g}^2, e_g^2)$ , number of unpaired electron  $(n) = 4$ , spin multiplicity value  $(n+1) = (4+1) = 5$ , spin state is quintet.

For  $3d^5(\text{HS})$ , electronic representation –  $(e_g^{1,2}, t_{2g}^{3,4,5})$ , E.C. –  $(t_{2g}^3, e_g^2)$ , number of unpaired electron  $(n) = 5$ , spin multiplicity value  $(n+1) = (5+1) = 6$ , spin state is **sextet (highest spin state)**.

For  $3d^6(\text{HS})$ , electronic representation –  $(e_g^{1,2}, t_{2g}^{3,4,5}, e_g^6)$ , E.C. –  $(t_{2g}^3, e_g^3)$ , number of unpaired electron  $(n) = 4$ , spin multiplicity value  $(n+1) = (4+1) = 5$ , spin state is quintet.

For  $3d^7(\text{HS})$ , electronic representation –  $(e_g^{1,2}, t_{2g}^{3,4,5}, e_g^{6,7})$ , E.C. –  $(t_{2g}^3, e_g^4)$ , number of unpaired electron  $(n) = 3$ , spin multiplicity value  $(n+1) = (3+1) = 4$ , spin state is quartet.

For  $3d^8(\text{HS})$ , electronic representation –  $(e_g^{1,2}, t_{2g}^{3,4,5}, e_g^{6,7}, t_{2g}^8)$ , E.C. –  $(t_{2g}^4, e_g^4)$ , number of unpaired electron  $(n) = 2$ , spin multiplicity value  $(n+1) = (2+1) = 3$ , spin state is triplet.

For  $3d^9(\text{HS})$ , electronic representation –  $(e_g^{1,2}, t_{2g}^{3,4,5}, e_g^{6,7}, t_{2g}^{8,9})$ , E.C. –  $(t_{2g}^5, e_g^4)$ , number of unpaired electron  $(n) = 1$ , spin multiplicity value  $(n+1) = (1+1) = 2$ , spin state is doublet.

For  $3d^{10}(\text{HS})$ , electronic representation –  $(e_g^{1,2}, t_{2g}^{3,4,5}, e_g^{6,7}, t_{2g}^{8,9,10})$ , E.C. –  $(t_{2g}^6, e_g^4)$ , number of unpaired electron  $(n) = 0$ , spin multiplicity value  $(n+1) = (0+1) = 1$ , spin state is **singlet (lowest spin state)**.

***Electronic configuration (E.C.) for low spin (LS) tetrahedral complexes with CFT and their corresponding spin multiplicity value and spin state can be calculated as follows:***

For  $3d^1(\text{LS})$ , electronic representation –  $(e_g^1, t_{2g}^0)$ , E.C. –  $(t_{2g}^0, e_g^1)$ , number of unpaired electron  $(n) = 1$ , spin multiplicity value  $(n+1) = (1+1) = 2$ , spin state is doublet.

For  $3d^2(\text{LS})$ , electronic representation –  $(e_g^{1,2}, t_{2g}^0)$ , E.C. –  $(t_{2g}^0, e_g^2)$ , number of unpaired electron  $(n) = 2$ , spin multiplicity value  $(n+1) = (2+1) = 3$ , spin state is triplet.

For  $3d^3(\text{LS})$ , electronic representation –  $(e_g^{1,2,3}, t_{2g}^0)$ , E.C. –  $(t_{2g}^0, e_g^3)$ , number of unpaired electron  $(n) = 1$ , spin multiplicity value  $(n+1) = (1+1) = 2$ , spin state is doublet.

For  $3d^4(\text{LS})$ , electronic representation –  $(e_g^{1,2,3,4}, t_{2g}^0)$ , E.C. –  $(t_{2g}^0, e_g^4)$ , number of unpaired electron  $(n) = 0$ , spin multiplicity value  $(n+1) = (0+1) = 1$ , spin state is **singlet (lowest spin state)**.

For  $3d^5(\text{LS})$ , electronic representation –  $(e_g^{1,2,3,4}, t_{2g}^5)$ , E.C. –  $(t_{2g}^1, e_g^4)$ , number of unpaired electron  $(n) = 1$ , spin multiplicity value  $(n+1) = (1+1) = 2$ , spin state is doublet.

For  $3d^6(\text{LS})$ , electronic representation –  $(e_g^{1,2,3,4}, t_{2g}^{5,6})$ , E.C. –  $(t_{2g}^2, e_g^4)$ , number of unpaired electron  $(n) = 2$ , spin multiplicity value  $(n+1) = (2+1) = 3$ , spin state is triplet.

For  $3d^7(\text{LS})$ , electronic representation –  $(e_g^{1,2,3,4}, t_{2g}^{5,6,7})$ , E.C. –  $(t_{2g}^3, e_g^4)$ , number of unpaired electron  $(n) = 3$ , spin multiplicity value  $(n+1) = (3+1) = 4$ , spin state is quartet.

For  $3d^8(\text{LS})$ , electronic representation –  $(e_g^{1,2,3,4}, t_{2g}^{5,6,7,8})$ , E.C. –  $(t_{2g}^4, e_g^4)$ , number of unpaired electron  $(n) = 2$ , spin multiplicity value  $(n+1) = (2+1) = 3$ , spin state is triplet.

For  $3d^9(\text{LS})$ , electronic representation –  $(e_g^{1,2,3,4}, t_{2g}^{5,6,7,8,9})$ , E.C. –  $(t_{2g}^5, e_g^4)$ , number of unpaired electron  $(n) = 1$ , spin multiplicity value  $(n+1) = (1+1) = 2$ , spin state is doublet.

For  $3d^{10}(\text{LS})$ , electronic representation –  $(e_g^{1,2,3,4}, t_{2g}^{5,6,7,8,9,10})$ , E.C. –  $(t_{2g}^6, e_g^4)$ , number of unpaired electron  $(n) = 0$ , spin multiplicity value  $(n+1) = (0+1) = 1$ , spin state is **singlet (lowest spin state)**.

From the above data of spin multiplicity values, both  $3d^5(\text{HS})$  octahedral and tetrahedral complexes, can exhibit highest spin state, 'sextet', corresponding to spin multiplicity value '6' and number of unpaired electrons 5, among all. On the other hand,  $3d^6(\text{LS})$  octahedral,  $3d^{10}(\text{LS})$  octahedral,  $3d^{10}(\text{HS})$  octahedral,  $3d^{10}(\text{HS})$  tetrahedral,  $3d^4(\text{LS})$  tetrahedral and  $3d^{10}(\text{LS})$  tetrahedral complexes can exhibit lowest spin state, 'singlet', corresponding to spin multiplicity value '1' and number of unpaired electron 0, among all.

## PROBLEMS ON SPIN MULTIPLICITY

**Q.1. The spectroscopic ground state term symbols for the octahedral aqua complexes of Mn(II), Cr(III) and Cu(II), respectively, are** (NET 2016)

- a)  $^2H$ ,  $^4F$  and  $^2D$       b)  $^6S$ ,  $^4F$  and  $^2D$       c)  $^2H$ ,  $^2H$  and  $^2D$       d)  $^6S$ ,  $^4F$  and  $^2P$

Ans: b)  $^6S$ ,  $^4F$  and  $^2D$  [E.C. of Mn(II) is  $3d^5$ , number of unpaired electrons  $(n) = 5$ , spin multiplicity  $= (n+1) = (5+1) = 6$ ; E.C. of Cr(III) is  $3d^3$ , number of unpaired electrons  $(n) = 3$ , spin multiplicity  $= (n+1) = (3+1) = 4$  and E.C. of Cu(II) is  $3d^9$ , number of unpaired electrons  $(n) = 1$ , spin multiplicity  $= (n+1) = (1+1) = 2$ ].

**Q.2. The lowest energy term for the  $d^6$  configuration is** (NET 2016)

- a)  $^2D$       b)  $^5D$       c)  $^1P$       d)  $^1D$

Ans: b)  $^5D$  [for E.C.  $d^6$ , number of unpaired electrons  $(n) = 4$ , spin multiplicity  $= (n+1) = (4+1) = 5$ ].

## Conclusion

It may be expected that these time economic innovative mnemonics, described in this chapter 7, will help students and educators, in chemical education at Undergraduate, Senior Undergraduate and Post-Graduate level, to predict the spin multiplicity values and thus the corresponding spin state, from the number of unpaired electrons ( $n$ ) only, without calculating total spin quantum numbers ( $S$ ). **It will help to constitute a rapidly atomic term symbol in the group theory of inorganic chemistry.** Experiments, *in vitro*, on 100 students, showed that by using these innovative formulae students can save up to 2-3 minutes' time in the examination hall to solve different problems related spin multiplicity and its related properties like spin state, atomic term symbol etc. in inorganic chemistry. Based on this, I can strongly recommend using these time economic innovative mnemonics in inorganic chemistry.

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