

### ❖ Correlation and Spin-Orbit Coupling in Free Ions for 1st Series of Transition Metals

The energy of different free ion terms primarily depends on the spin-spin interaction, yielding the most stable state with the highest multiplicity. Furthermore, if the values of spin multiplicity for two different states are equivalent, the value of resultant angular momentum will be the deciding factor in the determination of the lower energy term. A higher value of  $L$  gives the lower energy state and the vice-versa is also true. The energy dependence of different terms upon total angular momentum is configuration-specific in nature. The perturbed Hamiltonian of spin-orbital interaction can have both types of effect, stabilization or destabilization, over the energy states and depends upon the magnitude of  $J$ -value. It has been proved that the interaction of spin-orbital motion destabilizes the less than half filled configuration and stabilizes the more than half-filled.

Hence, a lower  $J$ -value for less than half-filled and a higher  $J$ -value for more than half will give the lower energy. However, the actual value of the energies for different terms, and hence their relative ordering, must be determined from the analysis of spectroscopic data. The correlation diagram of different free ion terms and thereafter the effect of  $L$ - $S$  interaction for different ions can be given as:

#### 1. $\text{Sc}^{2+}$ and $\text{Cu}^{2+}$ ( $d^1$ , $d^9$ ):

The number of unpaired electrons and hence microstates in  $\text{Sc}^{2+}$  ( $d^1$ ) and  $\text{Cu}^{2+}$  ( $d^9$ ) are the same. The one and only term symbol containing all the 10 microstates is  ${}^2D$ , which also represents the ground electronic state. However, the splitting pattern of  ${}^2D$  term due to  $L$ - $S$  coupling for  $\text{Cu}^{2+}$  ( $d^9$ ) is just the reverse of what is for  $\text{Sc}^{2+}$  ( $d^1$ ).

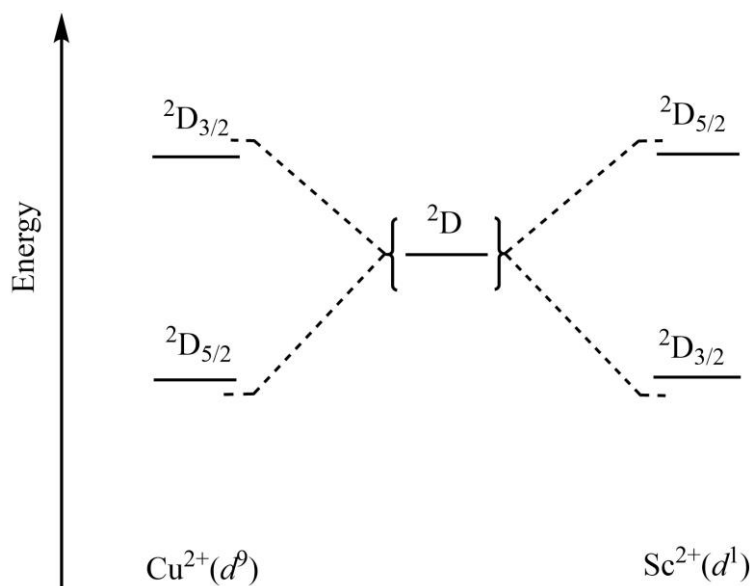


Figure 2. Correlation and spin-orbital coupling of free ion terms of  $\text{Sc}^{2+}$  and  $\text{Cu}^{2+}$ .

## 2. $V^{3+}$ and $Ni^{2+}$ ( $d^2$ , $d^8$ ):

The number of unpaired electrons and hence microstates in  $V^{3+}$  ( $d^2$ ) and  $Ni^{2+}$  ( $d^8$ ) are the same. All the 45 microstates for  $d^2$  and  $d^8$ -configurations are distributed in  $^1S$ ,  $^3P$ ,  $^1D$ ,  $^3F$  and  $^1G$  term symbols with  $^3F$  as the ground electronic state. However, the splitting pattern of  $^3F$  term due to L-S coupling for  $Ni^{2+}$  ( $d^8$ ) is just the reverse of what is for  $V^{3+}$  ( $d^2$ ).

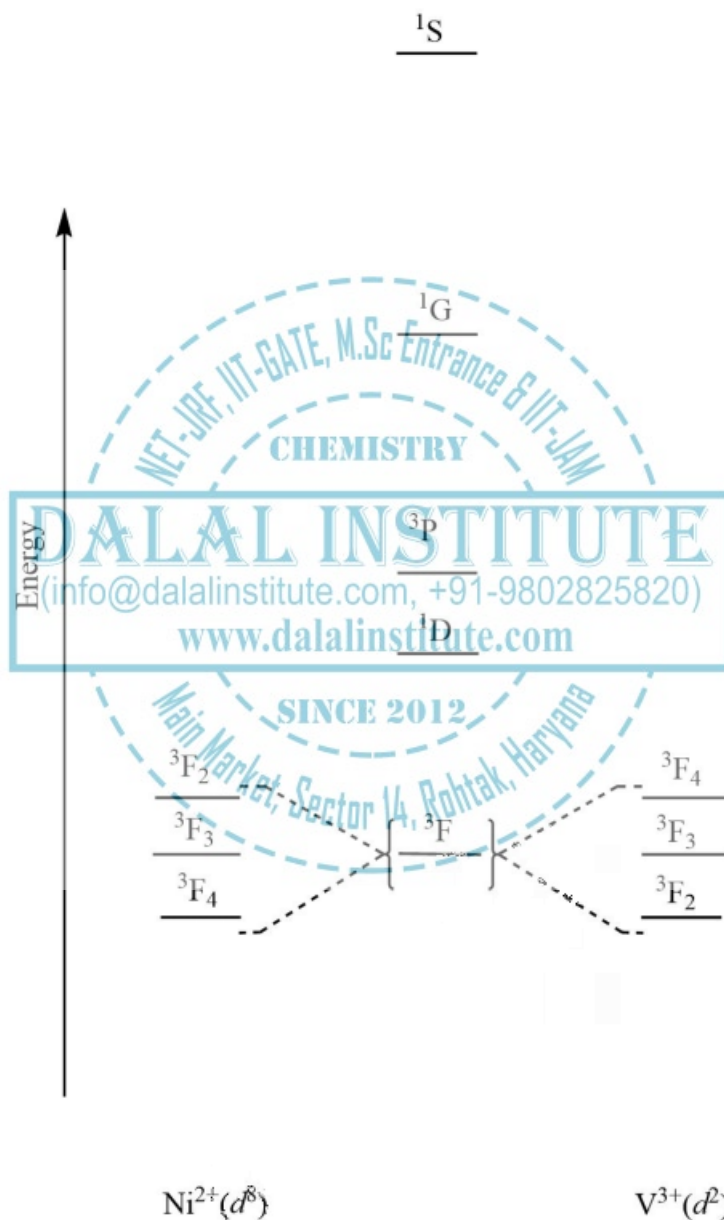


Figure 3. Correlation and spin-orbital coupling of free ion terms of  $V^{3+}$  and  $Ni^{2+}$ .

### 3. $\text{Cr}^{3+}$ and $\text{Co}^{2+}$ ( $d^3$ , $d^7$ ):

The number of unpaired electrons and hence microstates in  $\text{Cr}^{3+}$  ( $d^3$ ) and  $\text{Co}^{2+}$  ( $d^7$ ) are the same. All the 120 microstates for  $d^3$  and  $d^7$ -configurations are distributed in  $^4\text{F}$ ,  $^4\text{P}$ ,  $^2\text{H}$ ,  $^2\text{G}$ ,  $^2\text{F}$ ,  $^2\text{D}$ ,  $^2\text{D}$  and  $^2\text{P}$  term symbols with  $^4\text{F}$  as the ground electronic state. However, the splitting pattern of  $^4\text{F}$  term due to L-S coupling for  $\text{Co}^{2+}$  ( $d^7$ ) is just the reverse of what is for  $\text{Cr}^{3+}$  ( $d^3$ ).

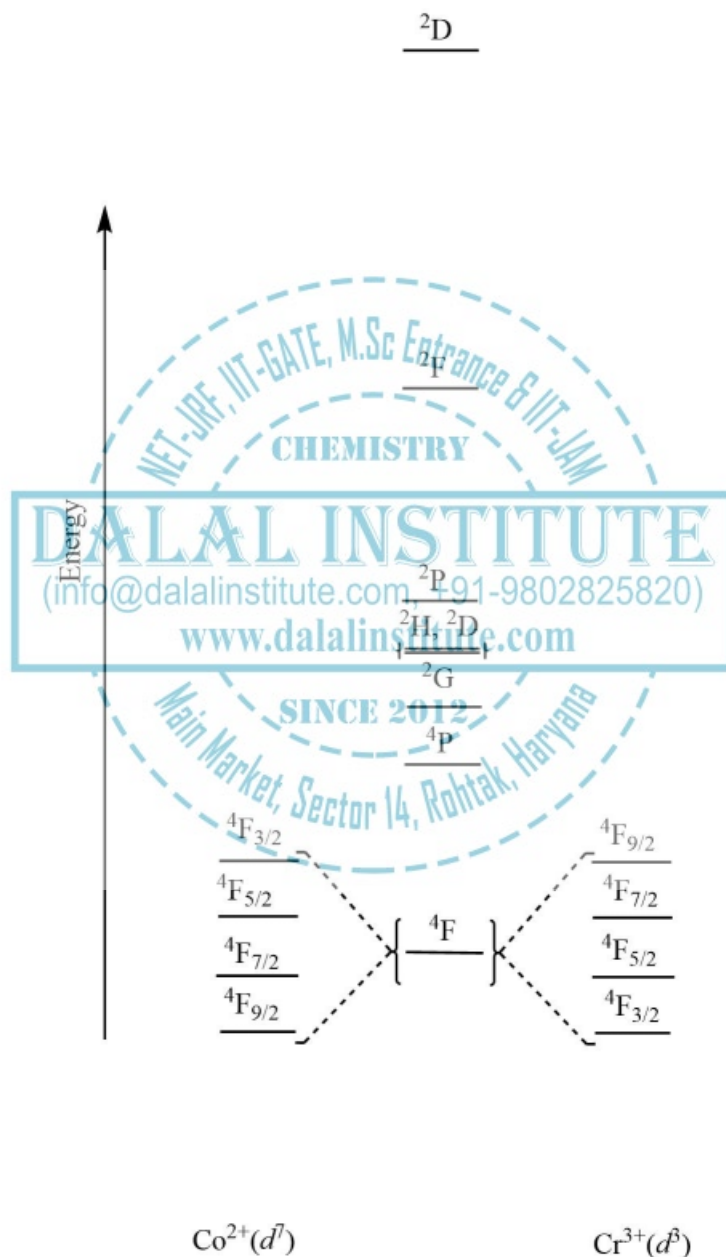


Figure 4. Correlation and spin-orbital coupling of free ion terms of  $\text{Cr}^{3+}$  and  $\text{Co}^{2+}$ .

#### 4. $\text{Mn}^{3+}$ and $\text{Fe}^{2+}$ ( $d^4$ , $d^6$ ):

The number of unpaired electrons and hence microstates in  $\text{Mn}^{3+}$  ( $d^4$ ) and  $\text{Fe}^{2+}$  ( $d^6$ ) are the same. All the 210 microstates for  $d^4$  and  $d^6$ -configurations are distributed in  ${}^5\text{D}$ ,  ${}^3\text{H}$ ,  ${}^3\text{G}$ ,  ${}^3\text{F}$ ,  ${}^3\text{F}$ ,  ${}^3\text{D}$ ,  ${}^3\text{P}$ ,  ${}^3\text{P}$ ,  ${}^1\text{I}$ ,  ${}^1\text{G}$ ,  ${}^1\text{G}$ ,  ${}^1\text{F}$ ,  ${}^1\text{D}$ ,  ${}^1\text{D}$ ,  ${}^1\text{S}$  and  ${}^1\text{S}$  term symbols with  ${}^5\text{D}$  as the ground electronic state. However, the splitting pattern of  ${}^5\text{D}$  term due to L-S coupling for  $\text{Fe}^{2+}$  ( $d^6$ ) is just the reverse of what is for  $\text{Mn}^{3+}$  ( $d^4$ ).

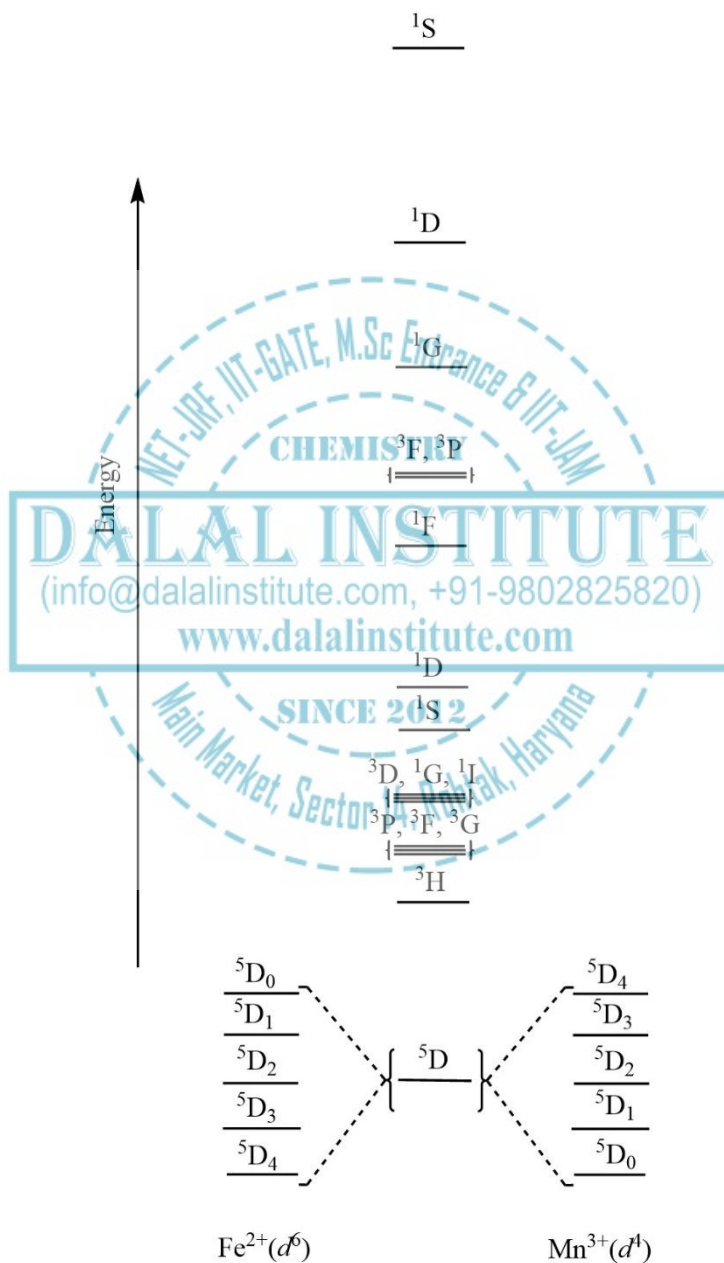


Figure 5. Correlation and spin-orbital coupling of free ion terms of  $\text{Mn}^{3+}$  and  $\text{Fe}^{2+}$ .

**5. Fe<sup>3+</sup> and Mn<sup>2+</sup> (d<sup>5</sup>):**

The number of unpaired electrons and hence microstates in Fe<sup>3+</sup> (d<sup>5</sup>) and Mn<sup>2+</sup> (d<sup>5</sup>) are the same. All the 252 microstates for d<sup>5</sup>-configurations are distributed in <sup>2</sup>I, <sup>2</sup>H, <sup>2</sup>G, <sup>2</sup>G, <sup>2</sup>F, <sup>2</sup>F, <sup>2</sup>D, <sup>2</sup>D, <sup>2</sup>D, <sup>2</sup>D, <sup>2</sup>P, <sup>2</sup>S, <sup>4</sup>G, <sup>4</sup>F, <sup>4</sup>D, <sup>4</sup>P and <sup>6</sup>S term symbols with <sup>6</sup>S as the ground electronic state. Moreover, the splitting of <sup>6</sup>S term due to L-S coupling is not possible because of the absence of resultant orbital motion. However, higher-energy free ion terms with 4 or two multiplicities will get split.

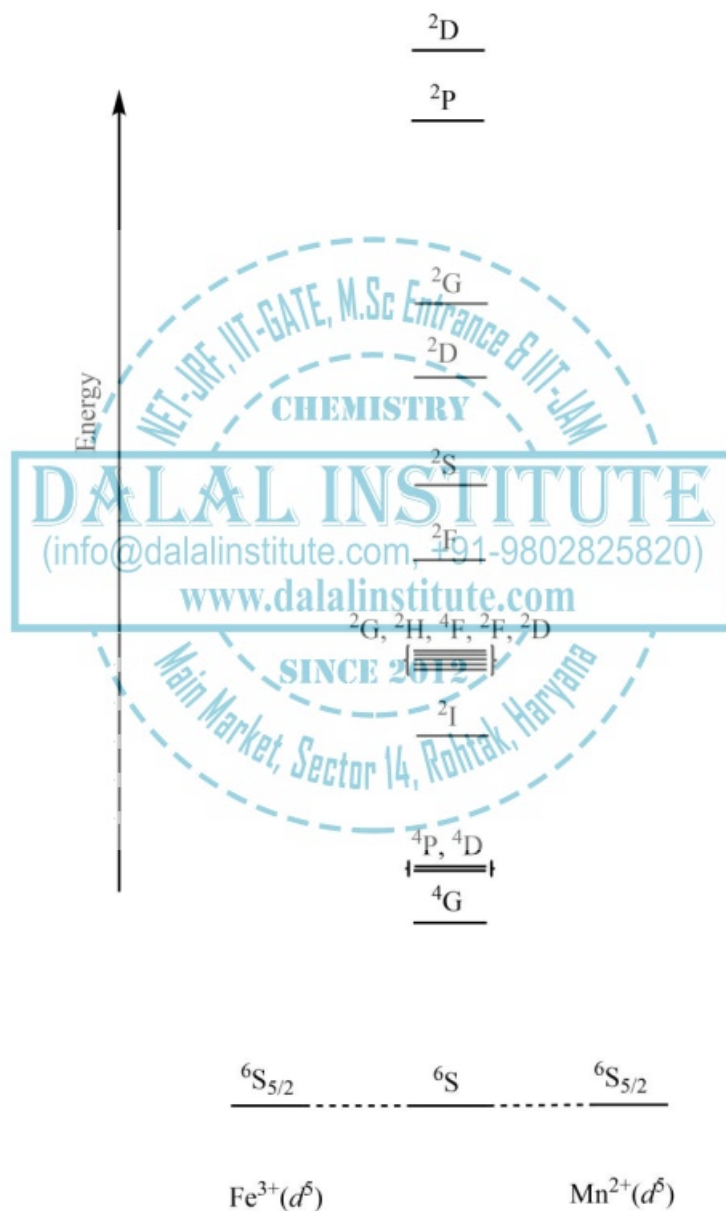


Figure 6. Correlation and spin-orbit coupling of free ion terms of Fe<sup>3+</sup> and Mn<sup>2+</sup>.

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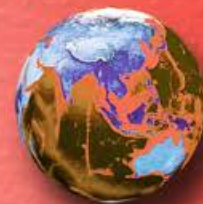
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