10. j-j Coupling

In its ideal form, the j-j coupling is an opposite extreme to the ideal *L-S* coupling and is approached by the heavier atoms, for which the spin-orbit (magnetic) interaction term in the Hamiltonian predominates over the ~~residual~~ electrostatic interaction ~~and the spin-spin corelation~~. This means that the interaction between the orbital and spin momenta of a single electron is much greater than the interaction between the orbital momenta of different electrons or between the spin momenta of different electrons. Therefore, in this case the splitting of the unperturbed energy level due to the introduction of the various perturbations takes place in the following order :

(*a*) *As a result of the stronger spin-orbit interaction, the orbital and spin angular momentum vectors of each individual electron are strongly coupled together to form a resultant angular momentum* *vector* $\vec{\mathbf{j}}$ *of magnitude* $\sqrt{j(j+1)}\,\frac{h}{2\pi}$, *where* $j = l - \frac{1}{2}$ and $l + \frac{1}{2}$, *that is, j takes half-integral values only.* This means that the unperturbed energy level is splitted into a number of well-spaced levels, each corresponding to a different combination of the possible j-values for the individual valence electrons ; the lowest being the one which corresponds to all of the electrons having their smaller j-value ($j = l - \frac{1}{2}$).

(*b*) *As a result of the residual electrostatic interaction and spin-spin corelation, the resultant angular momentum vectors* $\vec{\mathbf{j}}$ *of the individual electrons are less strongly coupled with one another to form the total angular momentum vector* $\vec{\mathbf{J}}$ *of the atom, of magnitude* $\sqrt{J(J+1)}\,\frac{h}{2\pi}$, *where the quantum number J has the values*

$$J = |\vec{\mathbf{j}}_1 + \vec{\mathbf{j}}_2 + \dots|_{min},\ |\vec{\mathbf{j}}_1 + \vec{\mathbf{j}}_2 + \dots|_{min} + 1,\ \dots (j_1 + j_2 + \dots)$$

This means that each of the above levels is further splitted into a number of levels characterised by different values of the total angular momentum quantum number J.

As an illustration, let us consider the terms for the electron configuration $4p\ 4d$, under j-j coupling. (We recall that under L-S coupling this configuration gives the terms $^1P_1$; $^1D_2$; $^1F_3$; $^3P_{0,1,2}$; $^3D_{1,2,3}$; $^3F_{2,3,4}$.)

For the p-electron : $l_1 = 1,\ s_1 = \frac{1}{2}\quad \therefore\ j_1 = \frac{1}{2}, \frac{3}{2}$.

For the d-electron : $l_2 = 2,\ s_2 = \frac{1}{2}\quad \therefore\ j_2 = \frac{3}{2}, \frac{5}{2}$.

This gives rise to four (j_1, j_2) combinations of the possible j_1 and j_2 values, namely $\left(\frac{1}{2}, \frac{3}{2}\right)$; $\left(\frac{1}{2}, \frac{5}{2}\right)$; $\left(\frac{3}{2}, \frac{3}{2}\right)$ and $\left(\frac{3}{2}, \frac{5}{2}\right)$. Thus the spin-orbit effect splits the unperturbed level into four levels, of which $\left(\frac{1}{2}, \frac{3}{2}\right)$ lies lowest and $\left(\frac{3}{2}, \frac{5}{2}\right)$ highest.

The four (j_1, j_2) combinations give J-values as under :

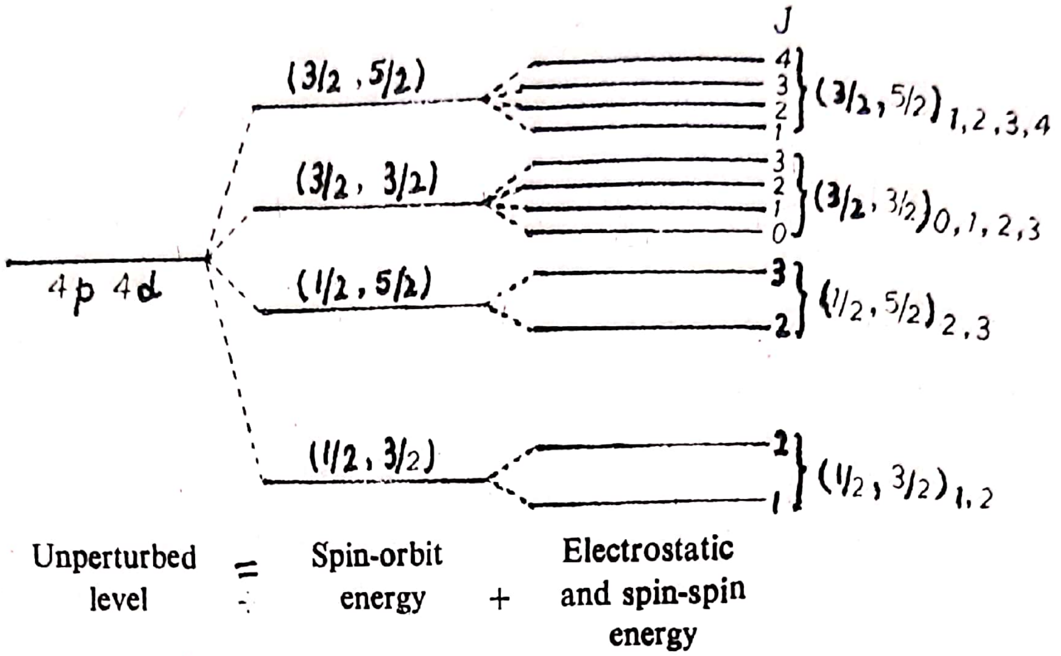
$\left(\frac{1}{2}, \frac{3}{2}\right)$ gives $J = 1, 2.$

$\left(\frac{1}{2}, \frac{5}{2}\right)$ gives $J = 2, 3.$

$\left(\frac{3}{2}, \frac{3}{2}\right)$ gives $J = 0, 1, 2, 3.$

$\left(\frac{3}{2}, \frac{5}{2}\right)$ gives $J = 1, 2, 3, 4.$

Hence each of the above four levels is further splitted by the electrostatic interaction and spin-spin corelation into a number of *J*-levels, equal to the number of integrally spaced values of *J* that can be formed out of the two *j*-values. The complete splitting is shown in Fig. 5.



(Fig. 5)

We see that the total number of final levels is the same (12) as for the *L-S* coupling and that the *J* values also are the same.

Pure *j-j* coupling occurs relatively seldom. In fact, there is a gradual shift from *L-S* coupling *for certain levels* of lighter atoms toward *j-j* coupling for the heavier atoms. An example of such a transition is seen in the levels of the first excited state of the IV-group elements *C*, *Si*, *Ge*, *Sn* and *Pb*. Whereas *C* and *Si* have practically pure *L-S* coupling, *Ge*, *Sn* and *Pb* approach closer and closer to *j-j* coupling. For the ground state of these atoms, however, it is the *L-S* coupling which holds.

11. Selection Rules in j-j Coupling

1. The parity of the configuration must change in an electric-dipole transition (Laporte rule). This means that if only one electron jumps in the transition (as is usually the case) then for this electron we must have $\Delta l = \pm 1$. If two electron jumps then $\Delta l_1 = \pm 1$ and $\Delta l_2 = 0, \pm 2$. This rule is exactly same as in *L–S* coupling.

2. $\Delta j = 0, \pm 1$ for the jumping electron, and $\Delta j = 0$ for all the other electrons.

3. For the atom as a whole,

$$\Delta J = 0, \pm 1 \quad \text{but} \quad J = 0 \nleftrightarrow J = 0.$$

The selection rules $\Delta S = 0$ and $\Delta L = 0, \pm 1$ no longer hold, since *L* and *S* are no longer good quantum numbers.