

upper level has deeper.

l-l coupling (b) As a result of the residual electrostatic interaction, the individual orbital angular momentum vectors of the 'optical' electrons

are strongly coupled with one another to form a resultant orbital angular momentum vector \vec{L} of magnitude $\sqrt{L(L+1)} \frac{h}{2\pi}$ which is a constant of motion. The quantum number L can take the values :

$$L = | \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots |_{min}, | \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots |_{min} + 1, \dots, (l_1 + l_2 + l_3 + \dots).$$

The states with different values of L have fairly large energy differences; the one of largest L value being of lowest energy. This means that each of the levels splitted by spin-spin correlation effect is further splitted by the residual electrostatic effect into a number of less separated levels, equal to the number of different values of L that can be formed from the individual orbital angular momenta of the optical electrons of the atom; and of these levels, the one of largest L lies lowest. The different levels are designated as $S, P, D, F, G,$ according as $L = 0, 1, 2, 3, 4, \dots$. Thus we have :

For $3p\ 3d$ electrons : $l_1 = 1, l_2 = 2.$

$$\therefore L = | l_1 - l_2 |; | l_1 - l_2 | + 1, \dots, (l_1 + l_2) \\ = 1, 2, 3 \text{ (P, D, F, states)}$$

For $2p\ 3p\ 4d$ electrons : Let us first combine the two p electrons which are more tightly bound to the atom. For this

$$l_1 = 1, l_2 = 1 \\ \therefore L' = 0, 1, 2.$$

Now, combining the d electron, $l_3 = 2$, which is less tightly bound, with each of these gives

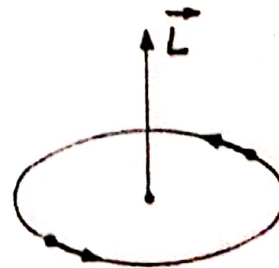
$$L' = 0, l_3 = 2 \\ \therefore L = 2 \text{ (D state),} \\ L' = 1, l_3 = 2. \\ \therefore L = 1, 2, 3 \text{ (P, D, F, states),} \\ L' = 2, l_3 = 2$$

and

$$\therefore L = 0, 1, 2, 3, 4 \text{ (S, P, D, F, G, states)}$$

Thus in all we obtain one S , two P 's, three D 's, two F 's and one G states

That the state of largest L is of lowest energy can be understood by considering two electrons in a Bohr atom. Because of the coulomb repulsion between the electrons, the electrostatic energy will be a minimum when the electrons stay at the opposite ends of a diameter, i.e., at a maximum distance apart (Fig. 2). In this state, the two electrons would be revolving together "in the same direction" about the nucleus, i.e., with their individual orbital angular momentum vectors parallel. The magnitude of the total orbital angular momentum vector, L , would clearly be a maximum in this state of lowest energy.



(Fig. 2)

(c) The dominant spin-spin correlation and the residual electrostatic interaction having been taken into account as a first perturbation, the smaller spin-orbit interaction is included in L - S coupling as an additional perturbation. As a result of spin-orbit interaction, the resultant orbital angular momentum vector \vec{L} and the resultant spin angular momentum vector \vec{S} are less strongly coupled with each other to form a vector \vec{J} ,

$$\vec{J} = \vec{L} + \vec{S}$$

which is the total angular momentum vector of the atom, and the coupling takes place in such a way that the magnitudes of \vec{J} , \vec{L} and \vec{S} remain constant. The magnitude of \vec{J} is $\sqrt{J(J+1)} h/2\pi$, where the quantum number J takes the following values :

$$J = |L-S|, |L-S| + 1, \dots, (L+S).$$

J is integral or half-integral according as S is integral or half-integral. The number of J values is $(2S+1)$ when $L > S$, or $(2L+1)$ when $S > L$. This means that due to spin-orbit magnetic interaction; a level characterised by given values of L and S is further broken up into comparatively closer $(2S+1)$ { or $(2L+1)$ } levels, each characterised by a different J value*. The group of these J -levels forms a 'fine-structure multiplet'. The relative spacing of the fine-structure levels within a multiplet is governed by Lande interval rule.

4. Lande Interval Rule

Under L - S coupling the spin-orbit interaction energy is of the form

$$\Delta E_{sl} = a (\vec{L} \cdot \vec{S}),$$

where a is an interaction constant. Let us write

$$\vec{J} = \vec{L} + \vec{S}.$$

Taking the scalar self product, we have

$$\vec{J} \cdot \vec{J} = \vec{L} \cdot \vec{L} + \vec{S} \cdot \vec{S} + 2 \vec{L} \cdot \vec{S}$$

or $|\vec{J}|^2 = |\vec{L}|^2 + |\vec{S}|^2 + 2 \vec{L} \cdot \vec{S}$

or $\vec{L} \cdot \vec{S} = \frac{1}{2} [|\vec{J}|^2 - |\vec{L}|^2 - |\vec{S}|^2]$

$$\therefore \Delta E_{sl} = \frac{a}{2} [J(J+1) - L(L+1) - S(S+1)] h^2/4\pi^2$$

because $|\vec{J}| = \sqrt{J(J+1)} \hbar/2\pi$ and so on. We can write it as

$$\Delta E_{st} = A [J(J+1) - L(L+1) - S(S+1)],$$
 where A is another constant.

The various fine-structure levels of a Russell-Saunders multiplet have the same values of L and S , and differ only in the value J . Hence the energy difference between two fine-structure levels corresponding to J and $J+1$ is

$$\begin{aligned} E_{J+1} - E_J &= A [(J+1)(J+2) - J(J+1)] \\ &= 2A(J+1). \end{aligned}$$

Thus the energy interval between consecutive levels J and $J+1$ of a fine-structure multiplet is proportional to $J+1$, i.e., to the larger of the two J -values involved. This is 'Lande interval rule.'

Let us take few examples. According to Lande interval rule, the fine-structure levels ${}^3P_0, {}^3P_1, {}^3P_2$ have separations in the ratio 1:2, the levels ${}^3D_1, {}^3D_2, {}^3D_3$ in the ratio 2:3; the levels ${}^4D_{1/2}, {}^4D_{3/2}, {}^4D_{5/2}, {}^4D_{7/2}$ in the ratio 3:5:7; and so on. The excellent agreement between the experimentally observed and the theoretically predicted ratios in lighter atoms provides evidence of L - S coupling in these atoms. Deviations from Lande interval rule occur with increasing deviation from L - S coupling.