

(A) For most atoms, mainly the lighter ones, the residual (non-spherical) electrostatic interaction effect of the term (iii) and the spin-spin correlation effect of the term (iv) are the largest of the remaining terms; the spin-orbit magnetic interaction term (v) is considerably smaller, while the rest are negligible. Such atoms are governed by  $L-S$  coupling.

(B) For some atoms, mainly the heavier ones, the spin-orbit term (v) predominates over others. Such atoms are governed by  $j-j$  coupling.

### 3. $L-S$ Coupling

The  $L-S$  coupling is also known as 'Russell-Saunders' coupling after the two astronomers who first used it in studying atomic spectra emitted by stars. In atoms which obey this coupling we

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\* The energy of the core is constant because the core electrons do not take part in optical excitations.

introduce the various perturbations in the order : (a) spin-spin correlation, (b) residual electrostatic interaction, (c) spin-orbit interaction.

*S-S coupling*

(a) As a result of spin-spin correlation effect, the individual spin angular momentum vectors of the 'optical' electrons are strongly coupled with one another to form a resultant spin angular momentum vector  $\vec{S}$  of magnitude  $\sqrt{S(S+1)} \frac{h}{2\pi}$  which is a constant of motion.

The quantum number  $S$  can take the values :

$$S = | \vec{s}_1 + \vec{s}_2 + \vec{s}_3 + \dots |_{min}, | \vec{s}_1 + \vec{s}_2 + \vec{s}_3 + \dots |_{max} + 1, \dots, (s_1 + s_2 + s_3 + \dots)$$

The states with different values of  $S$  have considerable energy difference ; the one of highest  $S$  being of lowest energy. This means that the (unperturbed) energy level of the central field model is splitted into a number of well-separated levels, equal to the number of different values of  $S$  that can be formed from the individual spins of the optical electrons of the atom ; and of these levels, the one of highest  $S$  lies lowest. The different levels are designated by their multiplicity,  $(2S+1)$ .

**For one electron—**  $S = s = \frac{1}{2}$  (Doublets).

**For two electrons—**  $s_1 = \frac{1}{2}, s_2 = \frac{1}{2}$ .

$$\therefore S = |s_1 - s_2| ; |s_1 - s_2| + 1, \dots, (s_1 + s_2) = 0, 1 \text{ (Singlets and Triplets).}$$

**For three electrons—**  $s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, s_3 = \frac{1}{2}$ .

To combine three spins, we first combine two of them to obtain  $S' = 0, 1$ , and then combine the third  $s_3 = \frac{1}{2}$  to each of them. Thus if we couple  $s_3 = \frac{1}{2}$  to  $S' = 0$  ; we get  $S = \frac{1}{2}$  ; and if we couple  $s_3 = \frac{1}{2}$  to  $S' = 1$ , we get  $S = \frac{1}{2}, \frac{3}{2}$ . Thus for three electrons, we get

$$S = \frac{1}{2}, \frac{1}{2}, \frac{3}{2}$$

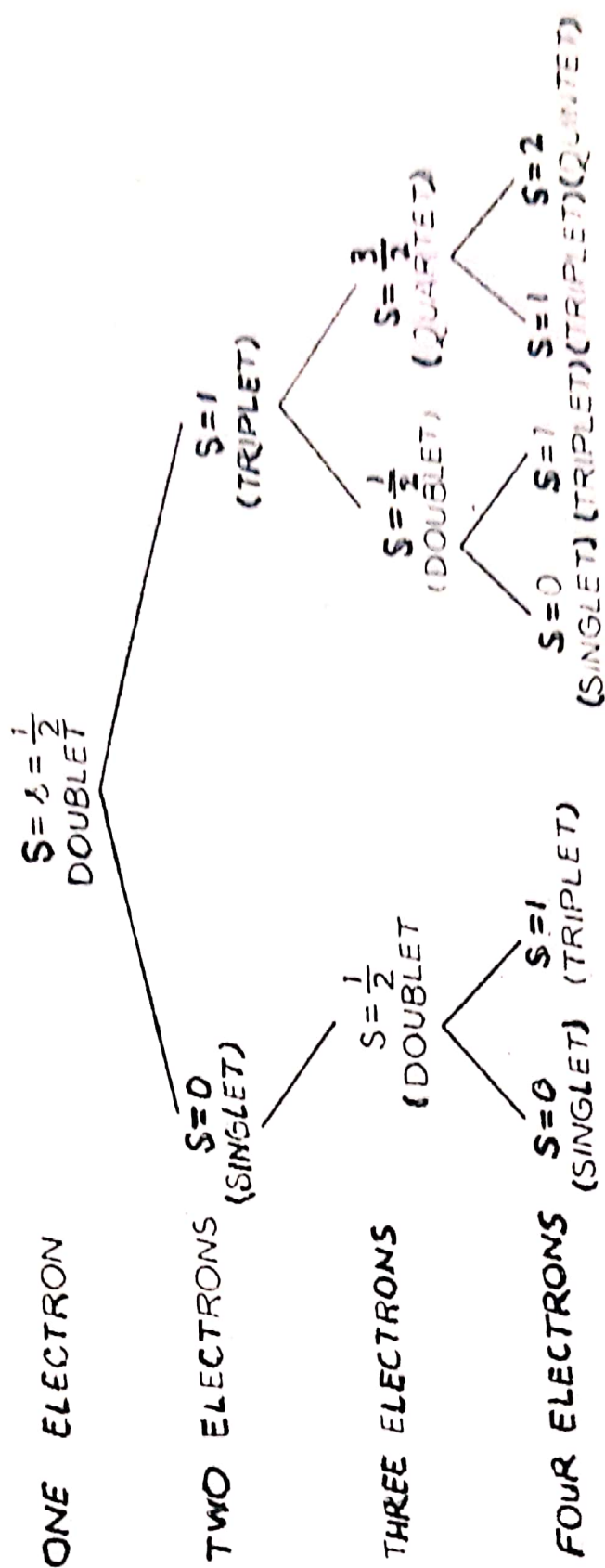
(two sets of doublets, and one set of quartets).

The following branching diagram (Fig. 1) illustrates the possible total spin quantum numbers which can be obtained by combining several independent electron spins.

In the general case of  $N$  electrons, the possible values of  $S$  are

$$S = 0, 1, 2, \dots, \frac{N}{2} \text{ for even } N.$$

$$S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots, \frac{N}{2} \text{ for odd } N.$$



(Fig. 1)

That the state of largest  $S$  is of lowest energy can be understood by considering the case of two electrons. The spin correlation effect splits the unperturbed level into two: a singlet level and a triplet level. Because of the total eigenfunction being anti-symmetric with respect to an exchange of the electrons, the average distance between the two electrons is larger in the triplet state (parallel spins) than it is in the singlet state (antiparallel spins). Therefore the (positive) electrostatic repulsion energy is smaller in the triplet state than it is in the singlet state. Hence triplet level lies deeper.