

## 10.7: Review of Atomic Cases

The orbitals of an atom are labeled by  $l$  and  $m_l$  quantum numbers; the orbitals belonging to a given energy and  $l$  value are  $2l + 1$ -fold degenerate. The many-electron Hamiltonian,  $H$ , of an atom and the antisymmetrizer operator  $A = \left(\sqrt{\frac{1}{N!}}\right) \sum_p s_p P$  commute with total  $L_z = \sum_i L_z(i)$ , as in the linear-molecule case. The additional symmetry present in the spherical atom reflects itself in the fact that  $L_x$ , and  $L_y$  now also commute with  $H$  and  $A$ . However, since  $L_z$  does **not** commute with  $L_x$  or  $L_y$ , new quantum numbers can not be introduced as symmetry labels for these other components of  $L$ . A new symmetry label does arise when

$$L^2 = L_z^2 + L_x^2 + L_y^2$$

is introduced;  $L^2$  commutes with  $H$ ,  $A$ , and  $L_z$ , so proper eigenstates (and trial wavefunctions) can be labeled with  $L$ ,  $M_L$ ,  $S$ ,  $M_S$ , and  $H$  quantum numbers.

To identify the states which arise from a given atomic configuration and to construct properly symmetry-adapted determinantal wave functions corresponding to these symmetries, one must employ  $L$  and  $M_L$  and  $S$  and  $M_S$  angular momentum tools. One first identifies those determinants with maximum  $M_S$  (this then defines the maximum  $S$  value that occurs); within that set of determinants, one then identifies the determinant(s) with maximum  $M_L$  (this identifies the highest  $L$  value). This determinant has  $S$  and  $L$  equal to its  $M_S$  and  $M_L$  values (this can be verified, for example for  $L$ , by acting on this determinant with  $L_+$  in the form

$$L^2 = L_- L_+ + L_z^2 + \hbar L_z$$

and realizing that  $L_+$  acting on the state must vanish); other members of this  $L, S$  energy level can be constructed by sequential application of  $S_-$  and  $L_- = \sum_i L_-(i)$ . Having exhausted a set of  $(2L+1)(2S+1)$  combinations of the determinants belonging to the given configuration, one proceeds to apply the same procedure to the remaining determinants (or combinations thereof). One identifies the maximum  $M_S$  and, within it, the maximum  $M_L$  which thereby specifies another  $S, L$  label and a new "maximum" state. The determinantal functions corresponding to these  $L, S$  (and various  $M_L, M_S$ ) values can be constructed by applying  $S_-$  and  $L_-$  to this "maximum" state. This process is continued until all of the states and their determinantal wave functions are obtained.

As illustrated above, any  $p^2$  configuration gives rise to  $^3P^e, ^1D^e$ , and  $^1S^e$  levels which contain nine, five, and one state respectively. The use of  $L$  and  $S$  angular momentum algebra tools allows one to identify the wavefunctions corresponding to these states. As shown in detail in Appendix G, in the event that **spin-orbit** coupling causes the Hamiltonian,  $H$ , not to commute with  $L$  or with  $S$  but only with their vector sum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ , then these  $L^2 S^2 L_z S_z$  eigenfunctions must be coupled (i.e., recombined) to generate  $J^2 J_z$  eigenstates. The steps needed to effect this coupling are developed and illustrated for the above  $p^2$  configuration case in Appendix G.

In the case of a pair of **non-equivalent**  $p$  orbitals (e.g., in a  $2p^1 3p^1$  configuration), even more states would arise. They can also be found using the tools provided above. Their symmetry labels can be obtained by vector coupling (see Appendix G) the spin and orbital angular momenta of the two subsystems. The orbital angular momentum coupling with  $l = 1$  and  $l = 1$  gives  $L = 2, 1$ , and  $0$  or  $D, P$ , and  $S$  states. The spin angular momentum coupling with  $s = 1/2$  and  $s = 1/2$  gives  $S = 1$  and  $0$ , or triplet and singlet states. So, vector coupling leads to the prediction that  $^3D^e, ^1D^e, ^3P^e, ^1P^e, ^3S^e$ , and  $^1S^e$  states can be formed from a pair of non-equivalent  $p$  orbitals. It is seen that more states arise when non-equivalent orbitals are involved; for equivalent orbitals, some determinants vanish, thereby decreasing the total number of states that arise.

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