

## Chapter 10

*Electronic Wavefunctions Must Also Possess Proper Symmetry. These Include Angular Momentum and Point Group Symmetries*

### I. Angular Momentum Symmetry and Strategies for Angular Momentum Coupling

Because the total Hamiltonian of a many-electron atom or molecule forms a mutually commutative set of operators with  $S^2$ ,  $S_z$ , and  $A = (\sqrt{1/N!})\sum_p s_p P$ , the exact eigenfunctions of  $H$  must be eigenfunctions of these operators. Being an eigenfunction of  $A$  forces the eigenstates to be odd under all  $P_{ij}$ . Any acceptable model or trial wavefunction should be constrained to also be an eigenfunction of these symmetry operators.

If the atom or molecule has additional symmetries (e.g., full rotation symmetry for atoms, axial rotation symmetry for linear molecules and point group symmetry for non-linear polyatomics), the trial wavefunctions should also conform to these spatial symmetries. This Chapter addresses those operators that commute with  $H$ ,  $P_{ij}$ ,  $S^2$ , and  $S_z$  and among one another for atoms, linear, and non-linear molecules.

As treated in detail in Appendix G, the full non-relativistic  $N$ -electron Hamiltonian of an atom or molecule

$$H = \sum_j (-\hbar^2/2m \nabla_j^2 - \sum_a Z_a e^2/r_{j,a}) + \sum_{j<k} e^2/r_{j,k}$$

commutes with the following operators:

- i. The inversion operator  $i$  and the three components of the total orbital angular momentum  $L_z = \sum_j L_z(j)$ ,  $L_y$ ,  $L_x$ , as well as the components of the total spin angular momentum  $S_z$ ,  $S_x$ , and  $S_y$  **for atoms** (but not the individual electrons'  $L_z(j)$ ,  $S_z(j)$ , etc). Hence,  $L^2$ ,  $L_z$ ,  $S^2$ ,  $S_z$  are the operators we need to form eigenfunctions of, and  $L$ ,  $M_L$ ,  $S$ , and  $M_S$  are the "good" quantum numbers.
- ii.  $L_z = \sum_j L_z(j)$ , as well as the  $N$ -electron  $S_x$ ,  $S_y$ , and  $S_z$  **for linear molecules** (also  $i$ , if the molecule has a center of symmetry). Hence,  $L_z$ ,  $S^2$ , and  $S_z$  are the operators we need to form eigenfunctions of, and  $M_L$ ,  $S$ , and  $M_S$  are the "good" quantum numbers;  $L$  no longer is!
- iii.  $S_x$ ,  $S_y$ , and  $S_z$  as well as all point group operations **for non-linear polyatomic molecules**. Hence  $S^2$ ,  $S_z$ , and the point group operations are used to characterize the