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 $A = (\sqrt{1/N!})\Sigma_p s_p P$, 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

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

commutes with the following operators:

i. The inversion operator i and the three components of the total orbital angular momentum $L_z = \Sigma_j L_z(j)$, 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. $L_z = \Sigma_j L_z(j)$, 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