8.5: Summary

In summary, the dynamical interactions among electrons give rise to instantaneous spatial correlations that must be handled to arrive at an accurate picture of atomic and molecular structure. The simple, single-configuration picture provided by the mean-field model is a useful starting point, but improvements are often needed. In Section 6, methods for treating electron correlation will be discussed in greater detail.

For the remainder of this Section, the primary focus is placed on forming proper Nelectron wavefunctions by occupying the orbitals available to the system in a manner that guarantees that the resultant N-electron function is an eigenfunction of those operators that commute with the N-electron Hamiltonian.

For polyatomic molecules, these operators include point-group symmetry operators (which act on all N electrons) and the spin angular momentum (S^2 and S_z) of all of the electrons taken as a whole (this is true in the absence of spin-orbit coupling which is treated later as a perturbation). For linear molecules, the point group symmetry operations involve rotations R_z of all N electrons about the principal axis, as a result of which the total angular momentum L_z of the N electrons (taken as a whole) about this axis commutes with the Hamiltonian, H. Rotation of all N electrons about the x and y axes does not leave the total coulombic potential energy unchanged, so L_x and L_y do not commute with H. Hence for a linear molecule, L_z, S^2, and S_z are the operators that commute with H. For atoms, the corresponding operators are L^2, L_z, S^2, and S_z (again, in the absence of spin-orbit coupling) where each operator pertains to the total orbital or spin angular momentum of the N electrons.

To construct N-electron functions that are eigenfunctions of the spatial symmetry or orbital angular momentum operators as well as the spin angular momentum operators, one has to "couple" the symmetry or angular momentum properties of the individual spinorbitals used to construct the N-electrons functions. This coupling involves forming direct product symmetries in the case of polyatomic molecules that belong to finite point groups, it involves vector coupling orbital and spin angular momenta in the case of atoms, and it involves vector coupling spin angular momenta and axis coupling orbital angular momenta when treating linear molecules. Much of this Section is devoted to developing the tools needed to carry out these couplings.