18.2: The Single-Determinant Wavefunction

The simplest trial function of the form given above is the single Slater determinant function:

$$|\Psi\rangle = |\phi_1\phi_2\phi_3\ldots\phi_N|.$$

For such a function, the CI part of the energy minimization is absent (the classic papers in which the SCF equations for closed- and open-shell systems are treated are C. C. J. Roothaan, Rev. Mod. Phys. 23 , 69 (1951); 32 , 179 (1960)) and the density matrices simplify greatly because only one spin-orbital occupancy is operative. In this case, the orbital optimization conditions reduce to:

$$\hat{F}\phi_i = \sum_j \epsilon_{i,j}\phi_j,$$

where the so-called Fock operator $\hat{F}$ is given by

$$\hat{F}\phi_i = h\phi_i + \sum_{j(occupied)} \left[\hat{J}_j - \hat{K}_j\right]\phi_i.$$

The coulomb ($\hat{J}_j$) and exchange ($\hat{K}_j$) operators are defined by the relations:

$$\hat{J}_j\phi_i = \int \phi_j^*(r')\phi_j(r')\frac{1}{|r-r'|}d\tau'\phi_i(r)$$

and

$$\hat{K}_j\phi_i = \int \phi_j^*(r')\phi_i(r')\frac{1}{|r-r'|}d\tau'\phi_j(r).$$

Again, the integration implies integration over the spin variables associated with the ϕ_j (and, for the exchange operator, ϕ_i), as a result of which the exchange integral vanishes unless the spin function of ϕ_j is the same as that of ϕ_i ; the coulomb integral is non-vanishing no matter what the spin functions of ϕ_j and ϕ_i .

The sum over coulomb and exchange interactions in the Fock operator runs only over those spin-orbitals that are occupied in the trial Ψ. Because a unitary transformation among the orbitals that appear in $|\Psi\rangle$ leaves the determinant unchanged (this is a property of determinants- det (UA) = det (U) det (A) = 1 det (A), if U is a unitary matrix), it is possible to choose such a unitary transformation to make the $\epsilon_{i,j}$ matrix diagonal. Upon so doing, one is left with the so-called **canonical Hartree-Fock equations**:

$$\hat{F}\phi_i = \epsilon_i\phi_j,$$

where ϵ_i is the diagonal value of the $\epsilon_{i,j}$ matrix after the unitary transformation has been applied; that is, ϵ_i is an eigenvalue of the $\epsilon_{i,j}$ matrix. These equations are of the eigenvalue-eigenfunction form with the Fock operator playing the role of an effective one-electron Hamiltonian and the ϕ_i playing the role of the one-electron eigenfunctions.

It should be noted that the Hartree-Fock equations $\hat{F}\phi_i = \epsilon_i\phi_j$ possess solutions for the spin-orbitals which appear in Ψ (the so-called **occupied** spin-orbitals) as well as for orbitals which are not occupied in Ψ (the so-called **virtual** spin-orbitals). In fact, the F operator is hermitian, so it possesses a complete set of orthonormal eigenfunctions; only those which appear in Ψ appear in the coulomb and exchange potentials of the Fock operator. The physical meaning of the occupied and virtual orbitals will be clarified later in this Chapter (Section VII.A).