

18.5: The LCAO-MO Expansion

The HF equations $F\phi_i = \epsilon_i\phi_i$ comprise a set of integro-differential equations; their differential nature arises from the kinetic energy operator in h , and the coulomb and exchange operators provide their integral nature. The solutions of these equations must be achieved iteratively because the J_i and K_i operators in F depend on the orbitals ϕ_i which are to be solved for. Typical iterative schemes begin with a 'guess' for those ϕ_i which appear in Ψ , which then allows F to be formed. Solutions to $F\phi_i = \epsilon_i\phi_i$ are then found, and those ϕ_i which possess the space and spin symmetry of the occupied orbitals of Ψ and which have the proper energies and nodal character are used to generate a new F operator (i.e., new J_i and K_i operators). The new \hat{F} operator then gives new ϕ_i and ϵ_i via solution of the new equations:

$$\hat{F}\phi_i = \epsilon_i\phi_i. \quad (18.5.1)$$

This iterative process is continued until the ϕ_i and ϵ_i do not vary significantly from one iteration to the next, at which time one says that the process has converged. This iterative procedure is referred to as the Hartree-Fock **self-consistent field** (SCF) procedure because iteration eventually leads to coulomb and exchange potential fields that are consistent from iteration to iteration.

In practice, solution of Equation 18.5.1 as an integro-differential equation can be carried out only for atoms (C. Froese-Fischer, Comp. Phys. Commun. 1, 152 (1970)) and linear molecules (P. A. Christiansen and E. A. McCullough, J. Chem. Phys. 67, 1877 (1977)) for which the angular parts of the ϕ_i can be exactly separated from the radial because of the axial- or full- rotation group symmetry (e.g., $\phi_i = Y_{l,m}R_{n,l}(r)$ for an atom and $\phi_i = e^{im\phi}R_{n,l,m}(r, \theta)$ for a linear molecule). In such special cases, $F\phi_i = \epsilon_i\phi_i$ gives rise to a set of coupled equations for the $R_{n,l}(r)$ or $R_{n,l,m}(r, \theta)$ which can and have been solved. However, for non-linear molecules, the HF equations have not yet been solved in such a manner because of the three-dimensional nature of the ϕ_i and of the potential terms in F .

In the most commonly employed procedures used to solve the HF equations for non-linear molecules, the ϕ_i are expanded in a basis of functions χ_m according to the LCAO-MO procedure:

$$\phi_i = \sum_{\mu} C_{\mu,i}\chi_{\mu}.$$

Doing so then reduces $F\phi_i = \epsilon_i\phi_i$ to a matrix eigenvalue-type equation of the form:

$$\sum_{\nu} F_{\mu,\nu}C_{\nu,i} = \epsilon_i \sum_{\nu} S_{\mu,\nu}C_{\nu,i},$$

where $S_{\mu,\nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle$ is the overlap matrix among the atomic orbitals (aos) and

$$F_{\mu,\nu} = \langle \chi_{\mu} | h | \chi_{\nu} \rangle + \sum_{\delta,\kappa} \left[\gamma_{\delta,\kappa} \langle \chi_{\mu}\chi_{\delta} | g | \chi_{\nu}\chi_{\kappa} \rangle - \gamma_{\delta,\kappa}^{ex} \langle \chi_{\mu}\chi_{\delta} | g | \chi_{\kappa}\chi_{\nu} \rangle \right]$$

is the matrix representation of the Fock operator in the ao basis. The coulomb and exchange-density matrix elements in the ao basis are:

$$\gamma_{\delta,\kappa} = \sum_{i(\text{occupied})} C_{\delta,i}C_{\kappa,i}, \text{ and}$$

$$\gamma_{\delta,\kappa}^{ex} = \sum_{i(\text{occ., and same spin})} C_{\delta,i}C_{\kappa,i},$$

where the sum in $\gamma_{\delta,\kappa}^{ex}$ runs over those occupied spin-orbitals whose m_s value is equal to that for which the Fock matrix is being formed (for a closed-shell species, $\gamma_{\delta,\kappa}^{ex} = \frac{1}{2}\gamma_{\delta,\kappa}$).

It should be noted that by moving to a matrix problem, one does not remove the need for an iterative solution; the $F_{\mu,\nu}$ matrix elements depend on the $C_{\nu,i}$ LCAO-MO coefficients which are, in turn, solutions of the so-called Roothaan matrix Hartree-Fock equations:

$$\sum_{\nu} F_{\mu,\nu}C_{\nu,i} = \epsilon_i \sum_{\nu} S_{\mu,\nu}C_{\nu,i}. \quad (18.5.2)$$

One should also note that, just as $F\phi_i = \epsilon_i\phi_j$ possesses a complete set of eigenfunctions, the matrix $F_{\mu,\nu}$, whose dimension M is equal to the number of atomic basis orbitals used in the LCAO-MO expansion, has M eigenvalues ϵ_i and M eigenvectors whose elements are the $C_{\nu,i}$. Thus, there are occupied and virtual molecular orbitals (mos) each of which is described in the LCAO-MO form with $C_{\nu,i}$ coefficients obtained via solution of Equations [18.5.2](#)

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