3.1.2 The Fock Operator

The Hartree-Fock equation, as we have written it up to this point, is

$$\left[h(1) + \sum_{b \neq a} \mathcal{J}_b(1) - \sum_{b \neq a} \mathcal{K}_b(1) \right] \chi_a(1) = \varepsilon_a \chi_a(1) \qquad (3.14)$$

This is of the eigenvalue form. However, the operator in square brackets appears to be different for every spin orbital χ_a on which it operates (because of the restricted summation over $b \neq a$). Inspecting Eqs. (3.10) and (3.11), it is obvious, however, that

$$[\mathcal{J}_a(1) - \mathcal{K}_a(1)]\chi_a(1) = 0 \qquad (3.15)$$

It is thus possible to add this term to (3.14), eliminate the restriction on the summation, and define a *Fock operator* f by

$$f(1) = h(1) + \sum_b \mathcal{J}_b(1) - \mathcal{K}_b(1) \qquad (3.16)$$

so that the Hartree-Fock equations become

$$f|\chi_a\rangle = \varepsilon_a|\chi_a\rangle \qquad (3.17)$$

This is the usual form of the Hartree-Fock equations. The Fock operator $f(1)$ is the sum of a *core-Hamiltonian operator* $h(1)$ and an effective one-electron potential operator called the *Hartree-Fock potential* $v^{HF}(1)$,

$$v^{HF}(1) = \sum_b \mathcal{J}_b(1) - \mathcal{K}_b(1) \qquad (3.18)$$

That is,

$$f(1) = h(1) + v^{HF}(1) \qquad (3.19)$$

Sometimes it is convenient to write the exchange potential in terms of an operator $\mathcal{P}_{12}$, which, operating to the right, interchanges electron 1 and electron 2. Thus

$$\mathcal{K}_b(1)\chi_a(1) = \left[\int d\mathbf{x}_2 \, \chi_b^*(2) r_{12}^{-1} \chi_a(2) \right] \chi_b(1)$$

$$= \left[\int d\mathbf{x}_2 \, \chi_b^*(2) r_{12}^{-1} \mathcal{P}_{12}\chi_b(2) \right] \chi_a(1) \qquad (3.20)$$

The Fock operator is thus written, using $\mathcal{P}_{12}$, as

$$f(1) = h(1) + v^{HF}(1)$$

$$= h(1) + \sum_b \int d\mathbf{x}_2 \, \chi_b^*(2) r_{12}^{-1}(1 - \mathcal{P}_{12})\chi_b(2) \qquad (3.21)$$

The Hartree-Fock equation

$$f|\chi_a\rangle = \varepsilon_a|\chi_a\rangle \qquad (3.22)$$

is an eigenvalue equation with the spin orbitals as eigenfunctions and the energy of the spin orbitals as eigenvalues. The exact solutions to this integro-differential equation correspond to the "exact" Hartree-Fock spin orbitals. In practice it is only possible to solve this equation exactly (i.e., as an integro-differential equation) for atoms. One normally, instead, introduces a set of basis functions for expansion of the spin orbitals and solves a set of matrix equations, as will be described subsequently. Only as the basis set approaches completeness, i.e., as one approaches the Hartree-Fock limit, will the spin orbitals that one obtains approach the exact Hartree-Fock spin orbitals.

While (3.22) is written as a linear eigenvalue equation, it might best be described as a pseudo-eigenvalue equation since the Fock operator has a functional dependence, through the coulomb and exchange operators, on the solutions $\{\chi_a\}$ of the pseudo-eigenvalue equation. Thus the Hartree-Fock equations are really nonlinear equations and will need to be solved by iterative procedures.

Exercise 3.1 Show that the general matrix element of the Fock operator has the form

$$\langle \chi_i | f | \chi_j \rangle = \langle i|h|j \rangle + \sum_b [ij|bb] - [ib|bj] = \langle i|h|j \rangle + \sum_b \langle ib||jb \rangle \quad (3.23)$$

3.2 DERIVATION OF THE HARTREE-FOCK EQUATIONS

In this section we derive the Hartree-Fock equations in their general spin orbital form, i.e., we obtain the eigenvalue equation (3.17) by minimizing the energy expression for a single Slater determinant. The derivation makes no assumptions about the spin orbitals. Later, we will specialize to restricted and unrestricted spin orbitals and introduce a basis set, in order to generate algebraic equations (matrix equations) that can be conveniently solved on a computer. In the meantime, we are concerned only with the derivation of the general integro-differential equations (the Hartree-Fock eigenvalue equations), the nature of these equations, and the nature of their formal solution. To derive the equations we will use the general and useful technique of functional variation.

3.2.1 Functional Variation

Given any trial function $\tilde{\Phi}$, the expectation value $E[\tilde{\Phi}]$ of the Hamiltonian operator $\mathscr{H}$ is a number given by

$$E[\tilde{\Phi}] = \langle \tilde{\Phi} | \mathscr{H} | \tilde{\Phi} \rangle \quad (3.24)$$

We say that $E[\tilde{\Phi}]$ is a functional of $\tilde{\Phi}$ since its value depends on the form of