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

a function, i.e., the function $\tilde{\Phi}$ rather than any single independent variable. Suppose we vary $\tilde{\Phi}$ by, an arbitrarily small amount, by changing the parameters upon which $\tilde{\Phi}$ depends, for example. That is,

$$\tilde{\Phi} \rightarrow \tilde{\Phi} + \delta\tilde{\Phi}$$

The energy then becomes

$$
\begin{aligned}
E[\tilde{\Phi} + \delta\tilde{\Phi}] &= \langle\tilde{\Phi} + \delta\tilde{\Phi}|\mathscr{H}|\tilde{\Phi} + \delta\tilde{\Phi}\rangle \\
&= E[\tilde{\Phi}] + \{\langle\delta\tilde{\Phi}|\mathscr{H}|\tilde{\Phi}\rangle + \langle\tilde{\Phi}|\mathscr{H}|\delta\tilde{\Phi}\rangle\} + \cdots \\
&= E[\tilde{\Phi}] + \delta E + \cdots
\end{aligned}
\tag{3.26}
$$

where δE, which is called the first variation in E, includes all terms that are linear, i.e., first-order, in the variation $\delta\tilde{\Phi}$. Notice that we can treat "δ" just like a differential operator, i.e., $\delta\langle\tilde{\Phi}|\mathscr{H}|\tilde{\Phi}\rangle = \langle\delta\tilde{\Phi}|\mathscr{H}|\tilde{\Phi}\rangle + \langle\tilde{\Phi}|\mathscr{H}|\delta\tilde{\Phi}\rangle$. In the variation method, we are looking for that $\tilde{\Phi}$ for which $E[\tilde{\Phi}]$ is a minimum. In other words, we wish to find that $\tilde{\Phi}$ for which the first variation in $E[\tilde{\Phi}]$ is zero, i.e.,

$$\delta E = 0 \tag{3.27}$$

This condition only ensures that E is *stationary* with respect to any variation in $\tilde{\Phi}$. Normally, however, the stationary point will also be a minimum.

We will illustrate the variational technique by rederiving the matrix eigenvalue equation of the linear variational problem given in Subsection 1.3.2. Given a linear variational trial wave function,

$$|\tilde{\Phi}\rangle = \sum_{i=1}^{N} c_i|\Psi_i\rangle \tag{3.28}$$

we want to minimize the energy

$$E = \langle\tilde{\Phi}|\mathscr{H}|\tilde{\Phi}\rangle = \sum_{ij} c_i^* c_j \langle\Psi_i|\mathscr{H}|\Psi_j\rangle \tag{3.29}$$

subject to the constraint that the trial wave function remains normalized, i.e.,

$$\langle\tilde{\Phi}|\tilde{\Phi}\rangle - 1 = \sum_{ij} c_i^* c_j \langle\Psi_i|\Psi_j\rangle - 1 = 0 \tag{3.30}$$

Using Lagrange's method of undetermined multipliers described in Chapter 1, we therefore minimize, with respect to the coefficients c_i, the following functional

$$
\begin{aligned}
\mathscr{L} &= \langle\tilde{\Phi}|\mathscr{H}|\tilde{\Phi}\rangle - E(\langle\tilde{\Phi}|\tilde{\Phi}\rangle - 1) \\
&= \sum_{ij} c_i^* c_j \langle\Psi_i|\mathscr{H}|\Psi_j\rangle - E\left(\sum_{ij} c_i^* c_j \langle\Psi_i|\Psi_j\rangle - 1\right)
\end{aligned}
\tag{3.31}
$$

where E is the Lagrange multiplier. Therefore, we set the first variation in $\mathscr{L}$ equal to zero.

$$
\begin{aligned}
\delta\mathscr{L} = {} &\sum_{ij} \delta c_i^* c_j \langle\Psi_i|\mathscr{H}|\Psi_j\rangle - E\sum_{ij} \delta c_i^* c_j \langle\Psi_i|\Psi_j\rangle \\
&+ \sum_{ij} c_i^* \delta c_j \langle\Psi_i|\mathscr{H}|\Psi_j\rangle - E\sum_{ij} c_i^* \delta c_j \langle\Psi_i|\Psi_j\rangle = 0
\end{aligned}
\tag{3.32}
$$

Since E is real ($\mathscr{L}$ is real), after collecting terms and interchanging indices, we get

$$\sum_i \delta c_i^* \left[\sum_j H_{ij} c_j - E S_{ij} c_j \right] + \text{complex conjugate} = 0 \tag{3.33}$$

where $H_{ij} = \langle\Psi_i|\mathscr{H}|\Psi_j\rangle$. The linear expansion functions $|\Psi_i\rangle$ are not assumed to be orthonormal, but are assumed to overlap according to

$$\langle\Psi_i|\Psi_j\rangle = S_{ij} \tag{3.34}$$

Since δc_i^* is arbitrary (c_i^* and c_i are both independent variables), the quantity in square brackets in (3.33) must be zero, or

$$\sum_j H_{ij} c_j = E \sum_j S_{ij} c_j$$

$$\mathbf{Hc} = E\mathbf{Sc} \tag{3.35}$$

Essentially the same result (with $\mathbf{S} = \mathbf{1}$ and real coefficients) was previously obtained in Subsection 1.3.2. The functional variation technique thus leads to the same result as is obtained by differentiating with respect to the coefficients. Functional variation is a more general technique, however, and we now proceed to derive the Hartree-Fock equations using it.

3.2.2 Minimization of the Energy of a Single Determinant

Given the single determinant $|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_a\chi_b\cdots\chi_N\rangle$, the energy $E_0 = \langle\Psi_0|\mathscr{H}|\Psi_0\rangle$ is a functional of the spin orbitals $\{\chi_a\}$. To derive the Hartree-Fock equations we need to minimize $E_0[\{\chi_a\}]$ with respect to the spin orbitals, subject to the constraint that the spin orbitals remain orthonormal,

$$\int d\mathbf{x}_1\, \chi_a^*(1)\chi_b(1) = [a|b] = \delta_{ab} \tag{3.36}$$

That is, the constraints are of the form

$$[a|b] - \delta_{ab} = 0 \tag{3.37}$$

We therefore consider the functional $\mathscr{L}[\{\chi_a\}]$ of the spin orbitals

$$\mathscr{L}[\{\chi_a\}] = E_0[\{\chi_a\}] - \sum_{a=1}^{N}\sum_{b=1}^{N} \varepsilon_{ba}([a|b] - \delta_{ab}) \tag{3.38}$$