

### 3.3 The Energy of a Slater Determinant

We will first evaluate the energy of a single Slater determinant. It is convenient to write it as a sum of permutations over the “diagonal” of the determinant. We will denote the diagonal product by  $\Pi$ , and use the symbol  $\Phi$  to represent the determinant wave function.

$$\Phi = \mathbf{A}[\phi_1(1)\phi_2(2) \dots \phi_N(N)] = \mathbf{A}\Pi$$

$$\mathbf{A} = \frac{1}{\sqrt{N!}} \sum_{p=0}^{N-1} (-1)^p \mathbf{P} = \frac{1}{\sqrt{N!}} [1 - \sum_{ij} \mathbf{P}_{ij} + \sum_{ijk} \mathbf{P}_{ijk} - \dots] \quad (3.21)$$

The  $\mathbf{1}$  operator is the identity, while  $\mathbf{P}_{ij}$  generates all possible permutations of two electron coordinates,  $\mathbf{P}_{ijk}$  all possible permutations of three electron coordinates etc. It may be shown that the *antisymmetrizing operator*  $\mathbf{A}$  commutes with  $\mathbf{H}$ , and that  $\mathbf{A}$  acting twice gives the same as  $\mathbf{A}$  acting once, multiplied by the square root of  $N$  factorial.

$$\mathbf{A}\mathbf{H} = \mathbf{H}\mathbf{A}$$

$$\mathbf{A}\mathbf{A} = \sqrt{N!}\mathbf{A} \quad (3.22)$$

Consider now the Hamilton operator. The nuclear–nuclear repulsion does not depend on electron coordinates and is a constant for a given nuclear geometry. The nuclear–electron attraction is a sum of terms, each depending only on one electron coordinate. The same holds for the electron kinetic energy. The electron–electron repulsion, however, depends on two electron coordinates.

$$\mathbf{H}_e = \mathbf{T}_e + \mathbf{V}_{ne} + \mathbf{V}_{ee} + \mathbf{V}_{nn}$$

$$\mathbf{T}_e = - \sum_i^N \frac{1}{2} \nabla_i^2$$

$$\mathbf{V}_{ne} = - \sum_i^N \sum_a \frac{Z_a}{|\mathbf{R}_a - \mathbf{r}_i|}$$

$$\mathbf{V}_{ee} = \sum_i^N \sum_{j>i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\mathbf{V}_{nn} = \sum_a \sum_{b>a} \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|} \quad (3.23)$$

The operators may be collected according to the number of electron indices.

$$\begin{aligned} \mathbf{h}_i &= -\frac{1}{2}\nabla_i^2 - \sum_a \frac{Z_a}{|\mathbf{R}_a - \mathbf{r}_i|} \\ \mathbf{g}_{ij} &= \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\ \mathbf{H}_e &= \sum_{i=1}^N \mathbf{h}_i + \sum_{i=1}^N \sum_{j>i}^N \mathbf{g}_{ij} + \mathbf{V}_{nn} \end{aligned} \quad (3.24)$$

The one electron operator  $\mathbf{h}_i$  describes the motion of electron  $i$  in the field of all the nuclei, and  $\mathbf{g}_{ij}$  is a two electron operator giving the electron–electron repulsion. We note that the zero point of the energy corresponds to the particles being at rest ( $\mathbf{T}_e = 0$ ) and infinitely removed from each other ( $\mathbf{V}_{ne} = \mathbf{V}_{ee} = \mathbf{V}_{nn} = 0$ ).

The energy may be written in terms of the permutation operator as (using eqs. (3.21)–(3.22))

$$\begin{aligned} E &= \langle \Phi | \mathbf{H} | \Phi \rangle \\ &= \langle \mathbf{A}\Pi | \mathbf{H} | \mathbf{A}\Pi \rangle \\ &= \sqrt{N!} \langle \Pi | \mathbf{H} | \mathbf{A}\Pi \rangle \\ &= \sum_p (-1)^p \langle \Pi | \mathbf{H} | \mathbf{P}\Pi \rangle \end{aligned} \quad (3.25)$$

The nuclear repulsion operator does not depend on electron coordinates and can immediately be integrated to yield a constant.

$$\langle \Phi | \mathbf{V}_{nn} | \Phi \rangle = V_{nn} \langle \Phi | \Phi \rangle = V_{nn} \quad (3.26)$$

For the one-electron operator only the identity operator can give a non-zero contribution. For coordinate 1 this yields

$$\begin{aligned} \langle \Pi | \mathbf{h}_1 | \Pi \rangle &= \langle \phi_1(1)\phi_2(2)\dots\phi_N(N) | \mathbf{h}_1 | \phi_1(1)\phi_2(2)\dots\phi_N(N) \rangle \\ &= \langle \phi_1(1) | \mathbf{h}_1 | \phi_1(1) \rangle \langle \phi_2(2) | \phi_2(2) \rangle \dots \langle \phi_N(N) | \phi_N(N) \rangle \\ &= \langle \phi_1(1) | \mathbf{h}_1 | \phi_1(1) \rangle = h_1 \end{aligned} \quad (3.27)$$

as all the MOs  $\phi_i$  are normalized. All matrix elements involving a permutation operator give zero. Consider for example

$$\begin{aligned} \langle \Pi | \mathbf{h}_1 | \mathbf{P}_{12}\Pi \rangle &= \langle \phi_1(1)\phi_2(2)\dots\phi_N(N) | \mathbf{h}_1 | \phi_2(1)\phi_1(2)\dots\phi_N(N) \rangle \\ &= \langle \phi_1(1) | \mathbf{h}_1 | \phi_2(1) \rangle \langle \phi_2(2) | \phi_1(2) \rangle \dots \langle \phi_N(N) | \phi_N(N) \rangle \end{aligned} \quad (3.28)$$

This is zero as the integral over electron 2 is an overlap of two different MOs, which are orthogonal (eq. (3.20)).

For the two electron operator, only the identity and  $\mathbf{P}_{ij}$  operators can give a non-zero contribution. A three electron permutation will again give at least one overlap integral between two different MOs, which will be zero. The term arising from the identity

operator is

$$\begin{aligned} \langle \Pi | \mathbf{g}_{12} | \Pi \rangle &= \langle \phi_1(1) \phi_2(2) \dots \phi_N(N) | \mathbf{g}_{12} | \phi_1(1) \phi_2(2) \dots \phi_N(N) \rangle \\ &= \langle \phi_1(1) \phi_2(2) | \mathbf{g}_{12} | \phi_1(1) \phi_2(2) \rangle \dots \langle \phi_N(N) | \phi_N(N) \rangle \\ &= \langle \phi_1(1) \phi_2(2) | \mathbf{g}_{12} | \phi_1(1) \phi_2(2) \rangle = J_{12} \end{aligned} \quad (3.29)$$

and is called a *Coulomb* integral. It represents a classical repulsion between two charge distributions described by  $\phi_1^2(1)$  and  $\phi_2^2(2)$ . The term arising from the  $\mathbf{P}_{ij}$  operator is

$$\begin{aligned} \langle \Pi | \mathbf{g}_{12} | \mathbf{P}_{12} \Pi \rangle &= \langle \phi_1(1) \phi_2(2) \dots \phi_N(N) | \mathbf{g}_{12} | \phi_2(1) \phi_1(2) \dots \phi_N(N) \rangle \\ &= \langle \phi_1(1) \phi_2(2) | \mathbf{g}_{12} | \phi_2(1) \phi_1(2) \rangle \dots \langle \phi_N(N) | \phi_N(N) \rangle \\ &= \langle \phi_1(1) \phi_2(2) | \mathbf{g}_{12} | \phi_2(1) \phi_1(2) \rangle = K_{12} \end{aligned} \quad (3.30)$$

and is called an *exchange* integral, which has no classical analogy. Note that the order of the MOs in the  $J$  and  $K$  matrix elements is according to the electron indices. The energy can thus be written as

$$E = \sum_{i=1}^N h_i + \sum_{i=1}^N \sum_{j>i}^N (J_{ij} - K_{ij}) + V_{nn} \quad (3.31)$$

where the minus sign for the exchange term comes from the factor of  $(-1)^P$  in the antisymmetrizing operator, eq. (3.21). The energy may also be written in a more symmetrical form as

$$E = \sum_{i=1}^N h_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) + V_{nn} \quad (3.32)$$

where the factor of 1/2 allows the double sum to run over all electrons (it is easily seen from eqs. (3.29) and (3.30) that the Coulomb "self-interaction"  $J_{ii}$  is exactly canceled by the corresponding "exchange" element  $K_{ii}$ ).

For the purpose of deriving the variation of the energy, it is convenient to express the energy in terms of Coulomb and Exchange operators.

$$E = \sum_i^N \langle \phi_i | \mathbf{h}_i | \phi_i \rangle + \frac{1}{2} \sum_{ij}^N (\langle \phi_j | \mathbf{J}_i | \phi_j \rangle - \langle \phi_j | \mathbf{K}_i | \phi_j \rangle) + V_{nn} \quad (3.33)$$

$$\mathbf{J}_i | \phi_j(2) \rangle = \langle \phi_i(1) | \mathbf{g}_{12} | \phi_i(1) \rangle | \phi_j(2) \rangle$$

$$\mathbf{K}_i | \phi_j(2) \rangle = \langle \phi_i(1) | \mathbf{g}_{12} | \phi_j(1) \rangle | \phi_i(2) \rangle$$

Note that the  $\mathbf{J}$  operator involves "multiplication" by a matrix element with the same orbital on both sides, while the  $\mathbf{K}$  operator "exchanges" the two functions on the right-hand side of the  $\mathbf{g}_{12}$  operator.

The objective is now to determine a set of MOs which makes the energy a minimum, or at least stationary with respect to a change in the orbitals. The variation, however, must be carried out in such a way that the MOs remain orthogonal and normalized. This is a constrained optimization, and can be handled by means of *Lagrange multipliers* (see Section 14.6). The condition is that a small change in the orbitals should not change the Lagrange function, i.e. the Lagrange function is stationary with respect to an orbital

variation.

$$L = E - \sum_{ij}^N \lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}) \quad (3.34)$$

$$\delta L = \delta E - \sum_{ij}^N \lambda_{ij} (\langle \delta \phi_i | \phi_j \rangle + \langle \phi_i | \delta \phi_j \rangle) = 0$$

The variation of the energy is given by

$$\delta E = \sum_i^N (\langle \delta \phi_i | \mathbf{h}_i | \phi_i \rangle + \langle \phi_i | \mathbf{h}_i | \delta \phi_i \rangle) \quad (3.35)$$

$$+ \frac{1}{2} \sum_{ij}^N (\langle \delta \phi_i | \mathbf{J}_j - \mathbf{K}_j | \phi_i \rangle + \langle \phi_i | \mathbf{J}_j - \mathbf{K}_j | \delta \phi_i \rangle)$$

$$+ \langle \delta \phi_j | \mathbf{J}_i - \mathbf{K}_i | \phi_j \rangle + \langle \phi_j | \mathbf{J}_i - \mathbf{K}_i | \delta \phi_j \rangle$$

The third and fifth terms are identical (since the summation is over all  $i$  and  $j$ ), as are the fourth and sixth terms. They may be collected to cancel the factor of 1/2, and the variation can be written in terms of a *Fock operator*,  $\mathbf{F}_i$ .

$$\delta E = \sum_i^N \langle \delta \phi_i | \mathbf{h}_i | \phi_i \rangle + \langle \phi_i | \mathbf{h}_i | \delta \phi_i \rangle + \sum_{ij}^N (\langle \delta \phi_i | \mathbf{J}_j - \mathbf{K}_j | \phi_i \rangle + \langle \phi_i | \mathbf{J}_j - \mathbf{K}_j | \delta \phi_i \rangle)$$

$$\delta E = \sum_i^N (\langle \delta \phi_i | \mathbf{F}_i | \phi_i \rangle + \langle \phi_i | \mathbf{F}_i | \delta \phi_i \rangle)$$

$$\mathbf{F}_i = \mathbf{h}_i + \sum_j^N (\mathbf{J}_j - \mathbf{K}_j) \quad (3.36)$$

The Fock operator is an effective one-electron energy operator, describing the kinetic energy of an electron, the attraction to all the nuclei and the repulsion to all the other electrons (via the  $\mathbf{J}$  and  $\mathbf{K}$  operators). Note that the Fock operator is associated with the variation of the total energy, not the energy itself. The Hamilton operator (3.23) is not a sum of Fock operators.

The variation of the Lagrange function (3.34) now becomes

$$\delta L = \sum_i^N (\langle \delta \phi_i | \mathbf{F}_i | \phi_i \rangle + \langle \phi_i | \mathbf{F}_i | \delta \phi_i \rangle) - \sum_{ij}^N \lambda_{ij} (\langle \delta \phi_i | \phi_j \rangle + \langle \phi_i | \delta \phi_j \rangle) \quad (3.37)$$

The variational principle states that the desired orbitals are those that make  $\delta L = 0$ . Making use of the fact that  $\langle \phi | \delta \phi \rangle = \langle \delta \phi | \phi \rangle^*$  and  $\langle \phi | \mathbf{F} | \delta \phi \rangle = \langle \delta \phi | \mathbf{F} | \phi \rangle^*$  we get

$$\delta L = \sum_i^N \langle \delta \phi_i | \mathbf{F}_i | \phi_i \rangle - \sum_{ij}^N \lambda_{ij} \langle \delta \phi_i | \phi_j \rangle \quad (3.38)$$

$$+ \sum_i^N \langle \delta \phi_i | \mathbf{F}_i | \phi_i \rangle^* - \sum_{ij}^N \lambda_{ij} \langle \delta \phi_j | \phi_i \rangle^* = 0$$

The variation of either  $\langle \delta\phi |$  or  $\langle \delta\phi |^*$  should make  $\delta L = 0$ . The first two terms in (3.38) should thus be zero, and the last two terms should be zero. Taking the complex conjugate of the last two terms and subtracting them from the first two gives

$$\sum_{ij}^N (\lambda_{ij} - \lambda_{ji}^*) \langle \delta\phi_i | \phi_j \rangle = 0 \quad (3.39)$$

which means that the Lagrange multipliers are elements of a Hermitian matrix ( $\lambda_{ij} = \lambda_{ji}^*$ ). The final set of *Hartree-Fock equations* may be written as

$$\mathbf{F}_i \phi_i = \sum_j^N \lambda_{ij} \phi_j \quad (3.40)$$

The equations may be simplified by choosing a unitary transformation (Chapter 13) which makes the matrix of Lagrange multipliers diagonal, i.e.  $\lambda_{ij} \rightarrow 0$  and  $\lambda_{ii} \rightarrow \varepsilon_i$ . This special set of molecular orbitals ( $\phi'$ ) are called *canonical* MOs, and they transform eq. (3.40) into a set of pseudo-eigenvalue equations.

$$\mathbf{F}_i \phi'_i = \varepsilon_i \phi'_i \quad (3.41)$$

The Lagrange multipliers can be interpreted as MO energies, i.e. they are the expectation value of the Fock operator in the MO basis (multiply eq. (3.41) by  $\phi'_i{}^*$  from the left and integrate).

$$\varepsilon_i = \langle \phi'_i | \mathbf{F}_i | \phi'_i \rangle \quad (3.42)$$

The Hartree-Fock equations form a set of pseudo-eigenvalue equations, as the Fock operator depends on all the occupied MOs (via the Coulomb and Exchange operators, eqs. (3.36) and (3.33)). A specific Fock orbital can only be determined if all the other occupied orbitals are known, and iterative methods must therefore be employed for determining the orbitals. A set of functions which is a solution to eq. (3.41) are called *Self-Consistent Field* (SCF) orbitals.

The canonical MOs may be considered as a convenient set of orbitals for carrying out the variational calculation. The total energy, however, depends only on the total wave function, which is a Slater determinant written in terms of the occupied MOs, eq. (3.20). The total wave function is unchanged by a unitary transformation of the occupied MOs among themselves (rows and columns in a determinant can be added and subtracted without affecting the determinant itself). After having determined the canonical MOs, other sets of MOs may be generated by forming linear combinations, such as localized MOs, or MOs displaying hybridization, to be discussed in more detail in Chapter 9.

The orbital energies can be considered as matrix elements of the Fock operator with the MOs (dropping the prime notation and letting  $\phi$  be the canonical orbitals). The total energy can be written either as eq. (3.32) or in terms of MO energies (using the definition of  $\mathbf{F}$  in eqs. (3.36) and (3.42)).

$$E = \sum_i^N \varepsilon_i - \frac{1}{2} \sum_{ij}^N (J_{ij} - K_{ij}) + V_{nn} \quad (3.43)$$

$$\varepsilon_i = \langle \phi_i | \mathbf{F}_i | \phi_i \rangle = h_i + \sum_j^N (J_{ij} - K_{ij})$$

The total energy is not simply a sum of MO orbital energies. The Fock operator contains terms describing the repulsion to all other electrons ( $J$  and  $K$  operators), and the sum over MO energies therefore counts the electron–electron repulsion twice, which must be corrected for. It is also clear that the total energy cannot be exact, as it describes the repulsion between an electron and all the other electrons, assuming that their spatial distribution is described by a set of orbitals. The electron–electron repulsion is only accounted for in an average fashion, and the HF method is therefore also referred to as a *Mean Field* approximation. As mentioned previously, this is due to the approximation of a single Slater determinant as the trial wave function.

### 3.4 Koopmans' Theorem

The canonical MOs are convenient for the physical interpretation of the Lagrange multipliers. Consider the energy of a system with one electron removed from orbital number  $k$ , and assume that the MOs are identical for the two systems (eq. (3.32)).

$$E_N = \sum_{i=1}^N h_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) + V_{nn} \quad (3.44)$$

$$E_{N-1}^k = \sum_{i=1}^{N-1} h_i + \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} (J_{ij} - K_{ij}) + V_{nn}$$

Subtracting the two total energies gives

$$E_N - E_{N-1}^k = h_k + \frac{1}{2} \sum_{i=1}^N (J_{ik} - K_{ik}) + \frac{1}{2} \sum_{j=1}^N (J_{kj} - K_{kj}) \quad (3.45)$$

The last two sums are identical and the energy difference becomes

$$E_N - E_{N-1}^k = h_k + \sum_{i=1}^N (J_{ki} - K_{ki}) = \varepsilon_k \quad (3.46)$$

which is seen (eq. (3.43)) to be exactly the orbital energy  $\varepsilon_k$ . The ionization energy within the “frozen MO” approximation is given simply as the orbital energy, a result known as *Koopmans' theorem*.<sup>4</sup> Similarly, the electron affinity of a neutral molecule is given as the orbital energy of the corresponding anion, or, since the MOs are assumed constant, as the energy of the  $k$ th unoccupied orbital energy in the neutral species.

$$E_{N+1}^k - E_N = \varepsilon_k \quad (3.47)$$

Computationally, however, there is a significant difference between the eigenvalue of an occupied orbital for the anion and the eigenvalue corresponding to an unoccupied orbital in the neutral species when the orbitals are expanded in a set of basis functions (Section 3.5). Eigenvalues corresponding to occupied orbitals are well defined and they converge to a specific value as the size of the basis set is increased. In contrast, unoccupied orbitals in a sense are only the “left over” functions in a given basis set, and their number increases as the basis set is made larger. The lowest unoccupied eigenvalue usually converges to zero, corresponding to a solution for a free electron, described by a linear combination of the most diffuse basis functions. Equating ionization potentials to

occupied orbital energies is therefore justified based on the frozen MO approximation, but taking unoccupied orbital energies as electron affinities is somewhat questionable, since continuum solutions are mixed in.

### 3.5 The Basis Set Approximation

For small highly symmetric systems, like atoms and diatomic molecules, the Hartree–Fock equations may be solved by mapping the orbitals on a set of grid points. These are referred to as *numerical Hartree–Fock* methods.<sup>5</sup> However, essentially all calculations use a basis set expansion to express the unknown MOs in terms of a set of known functions. Any type of basis function may in principle be used: exponential, Gaussian, polynomial, cube, plane wave etc. There are two guidelines for choosing the basis functions. One is that they should have a behaviour which agrees with the physics of the problem, this ensures that the convergence as more basis functions are added is reasonably rapid. For bound atomic and molecular systems this means that the functions should go towards zero as the distance between the nucleus and the electron becomes large. The second guideline is practical: the chosen functions should make it easy to calculate all the required integrals. The first criterion suggests the use of exponential functions located on the nuclei, such functions are known to be exact solutions for the hydrogen atom. Unfortunately exponential functions turn out to be computationally difficult. Gaussian functions are computationally much easier to handle, and although they are poorer at describing the electronic structure on a one-to-one basis, the computational advantages more than make up for this. We will return to the precise description of basis sets in Chapter 5, but for now simply assume that a set of  $M$  basis functions located on the nuclei has been chosen.

Each MO is expanded in terms of the basis functions, conventionally called *atomic orbitals* (MO=LCAO, *Linear Combination of Atomic Orbitals*), although they are generally not solutions to the atomic HF problem.

$$\phi_i = \sum_{\alpha}^M c_{\alpha i} \chi_{\alpha} \quad (3.48)$$

The Hartree–Fock equations (3.41) may be written as:

$$\mathbf{F}_i \sum_{\alpha}^M c_{\alpha i} \chi_{\alpha} = \epsilon_i \sum_{\alpha}^M c_{\alpha i} \chi_{\alpha} \quad (3.49)$$

Multiplying from the left by a specific basis function and integrating yields the *Roothaan–Hall* equations (for a closed shell system).<sup>6</sup> These are the Fock equations in the atomic orbital basis, and all the  $M$  equations may be collected in a matrix notation.

$$\begin{aligned} \mathbf{FC} &= \mathbf{SC}\epsilon \\ F_{\alpha\beta} &= \langle \chi_{\alpha} | \mathbf{F} | \chi_{\beta} \rangle \\ S_{\alpha\beta} &= \langle \chi_{\alpha} | \chi_{\beta} \rangle \end{aligned} \quad (3.50)$$

The  $\mathbf{S}$  matrix contains the overlap elements between basis functions, and the  $\mathbf{F}$  matrix contains the Fock matrix elements. Each  $F_{\alpha\beta}$  element contains two parts from the Fock operator (eq. (3.36)), integrals involving the one-electron operators, and a sum over

occupied MOs of coefficients multiplied with two-electron integrals involving the electron–electron repulsion operator. The latter is often written as a product of a *density* matrix and two-electron integrals:

$$\begin{aligned}
 \langle \chi_\alpha | \mathbf{F} | \chi_\beta \rangle &= \langle \chi_\alpha | \mathbf{h} | \chi_\beta \rangle + \sum_j^{\text{occ. MO}} \langle \chi_\alpha | \mathbf{J}_j - \mathbf{K}_j | \chi_\beta \rangle \\
 &= \langle \chi_\alpha | \mathbf{h} | \chi_\beta \rangle + \sum_j^{\text{occ. MO}} (\langle \chi_\alpha \phi_j | \mathbf{g} | \chi_\beta \phi_j \rangle - \langle \chi_\alpha \phi_j | \mathbf{g} | \phi_j \chi_\beta \rangle) \\
 &= \langle \chi_\alpha | \mathbf{h} | \chi_\beta \rangle + \sum_j^{\text{occ. MO}} \sum_\gamma^{\text{AO}} \sum_\delta^{\text{AO}} c_{\gamma j} c_{\delta j} (\langle \chi_\alpha \chi_\gamma | \mathbf{g} | \chi_\beta \chi_\delta \rangle - \langle \chi_\alpha \chi_\gamma | \mathbf{g} | \chi_\delta \chi_\beta \rangle) \\
 &= \langle \chi_\alpha | \mathbf{h} | \chi_\beta \rangle + \sum_\gamma^{\text{AO}} \sum_\delta^{\text{AO}} D_{\gamma\delta} (\langle \chi_\alpha \chi_\gamma | \mathbf{g} | \chi_\beta \chi_\delta \rangle - \langle \chi_\alpha \chi_\gamma | \mathbf{g} | \chi_\delta \chi_\beta \rangle) \\
 D_{\gamma\delta} &= \sum_j^{\text{occ. MO}} c_{\gamma j} c_{\delta j} \tag{3.51}
 \end{aligned}$$

For use in Section 3.8, it can also be written in a more compact notation

$$\begin{aligned}
 F_{\alpha\beta} &= h_{\alpha\beta} + \sum_{\gamma\delta} G_{\alpha\beta\gamma\delta} D_{\gamma\delta} \\
 \mathbf{F} &= \mathbf{h} + \mathbf{G} \cdot \mathbf{D} \tag{3.52}
 \end{aligned}$$

where  $\mathbf{G} \cdot \mathbf{D}$  denotes the contraction of the  $\mathbf{D}$  matrix with the four-dimensional  $\mathbf{G}$  tensor.

The total energy (3.32) in term of integrals over basis functions is given as

$$\begin{aligned}
 E &= \sum_i^N \langle \phi_i | \mathbf{h} | \phi_i \rangle + \frac{1}{2} \sum_{ij}^N (\langle \phi_i \phi_j | \mathbf{g} | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \mathbf{g} | \phi_j \phi_i \rangle) + V_{\text{nn}} \\
 E &= \sum_i^N \sum_{\alpha\beta}^M c_{\alpha i} c_{\beta i} \langle \chi_\alpha | \mathbf{h} | \chi_\beta \rangle + \frac{1}{2} \sum_{ij}^N \sum_{\alpha\beta\gamma\delta}^M c_{\alpha i} c_{\gamma j} c_{\beta i} c_{\delta j} (\langle \chi_\alpha \chi_\gamma | \mathbf{g} | \chi_\beta \chi_\delta \rangle \\
 &\quad - \langle \chi_\alpha \chi_\gamma | \mathbf{g} | \chi_\delta \chi_\beta \rangle) + V_{\text{nn}} \\
 E &= \sum_{\alpha\beta}^M D_{\alpha\beta} h_{\alpha\beta} + \frac{1}{2} \sum_{\alpha\beta\gamma\delta}^M D_{\alpha\beta} D_{\gamma\delta} (\langle \chi_\alpha \chi_\gamma | \mathbf{g} | \chi_\beta \chi_\delta \rangle - \langle \chi_\alpha \chi_\gamma | \mathbf{g} | \chi_\delta \chi_\beta \rangle) + V_{\text{nn}} \tag{3.53}
 \end{aligned}$$

The latter expression may also be written as

$$E = \sum_{\alpha\beta}^M D_{\alpha\beta} h_{\alpha\beta} + \frac{1}{2} \sum_{\alpha\beta\gamma\delta}^M (D_{\alpha\beta} D_{\gamma\delta} - D_{\alpha\delta} D_{\beta\gamma}) \langle \chi_\alpha \chi_\gamma | \mathbf{g} | \chi_\beta \chi_\delta \rangle + V_{\text{nn}} \tag{3.54}$$

The one- and two-electron integrals in the atomic basis are given as (eq. (3.24))

$$\langle \chi_\alpha | \mathbf{h} | \chi_\beta \rangle = \int \chi_\alpha(1) \left( -\frac{1}{2} \nabla^2 \right) \chi_\beta(1) \mathbf{d}\mathbf{r}_1 + \sum_a \int \chi_\alpha(1) \frac{Z_a}{|\mathbf{R}_a - \mathbf{r}_1|} \chi_\beta(1) \mathbf{d}\mathbf{r}_1$$

$$\langle \chi_\alpha \chi_\gamma | \mathbf{g} | \chi_\beta \chi_\delta \rangle = \int \chi_\alpha(1) \chi_\gamma(2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_\beta(1) \chi_\delta(2) \mathbf{d}\mathbf{r}_1 \mathbf{d}\mathbf{r}_2 \quad (3.55)$$

The two-electron integrals are often written in a notation without the  $\mathbf{g}$  operator present.

$$\int \chi_\alpha(1) \chi_\gamma(2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_\beta(1) \chi_\delta(2) \mathbf{d}\mathbf{r}_1 \mathbf{d}\mathbf{r}_2 = \langle \chi_\alpha \chi_\gamma | \mathbf{g} | \chi_\beta \chi_\delta \rangle \quad (3.56)$$

$$= \langle \chi_\alpha \chi_\gamma | \chi_\beta \chi_\delta \rangle$$

This is known as the *physicist's* notation, where the ordering of the functions is given by the electron indices. They may also be written in an alternative order with both functions depending on electron 1 on the left, and the functions depending on electron 2 on the right; this is known as the *Mulliken* or *chemist's* notation.

$$\int \chi_\alpha(1) \chi_\beta(1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_\gamma(2) \chi_\delta(2) \mathbf{d}\mathbf{r}_1 \mathbf{d}\mathbf{r}_2 = (\chi_\alpha \chi_\beta | \chi_\gamma \chi_\delta) \quad (3.57)$$

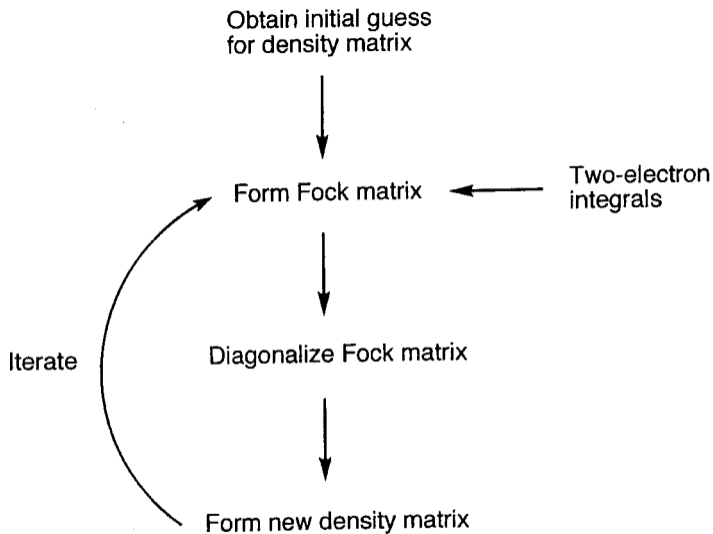
The bracket notation has the electron indices  $\langle 12 | 12 \rangle$  while the parenthesis notation has the order  $(11|22)$ . In many cases the integrals are written with only the indices given, i.e.  $\langle \chi_\alpha \chi_\gamma | \chi_\beta \chi_\delta \rangle = \langle \alpha \gamma | \beta \delta \rangle$ . Since Coulomb and exchange integrals often are used as their difference, the following double bar notations are also used frequently.

$$\langle \chi_\alpha \chi_\beta || \chi_\gamma \chi_\delta \rangle = \langle \chi_\alpha \chi_\beta | \chi_\gamma \chi_\delta \rangle - \langle \chi_\alpha \chi_\beta | \chi_\delta \chi_\gamma \rangle \quad (3.58)$$

$$(\chi_\alpha \chi_\beta || \chi_\gamma \chi_\delta) = (\chi_\alpha \chi_\beta | \chi_\gamma \chi_\delta) - (\chi_\alpha \chi_\gamma | \chi_\beta \chi_\delta)$$

The Roothaan–Hall equation (3.50) is a determination of the eigenvalues of the Fock matrix, see Chapter 13 for details. To determine the unknown MO coefficients  $c_{\alpha i}$ , the Fock matrix must be diagonalized. However, the Fock matrix is only known if all the MO coefficients are known, eq. (3.51). The procedure therefore starts off by some guess of the coefficients, forms the F matrix, and diagonalizes it. The new set of coefficients is then used for calculating a new Fock matrix etc., as illustrated in Figure 3.3. This is continued until the set of coefficients used for constructing the Fock matrix is equal to those resulting from the diagonalization (to within a certain threshold). This set of coefficients determines an SCF solution. The potential (or field) generated by the SCF electron density is identical to that produced by solving for the electron distribution. The Fock matrix, and therefore the total energy, depends only on the occupied MO. Solving the Roothaan–Hall equations produces a total of  $M$  ( $=$  number of basis functions) MOs, i.e. there are  $N$  occupied and  $M - N$  unoccupied, or *virtual*, MOs. The virtual orbitals are orthogonal to all the occupied orbitals, but have no direct physical interpretation, except as electron affinities (via Koopmans' theorem).

To construct the Fock matrix, eq. (3.51), integrals over all pairs of basis functions and the one-electron operator  $\mathbf{h}$  are needed. For  $M$  basis functions there are of the order of  $M^2$  of such *one-electron integrals*. These one-integrals are also known as *core* integrals, they describe the interaction of an electron with the whole frame of bare nuclei. The second part of the Fock matrix involves integrals over four basis functions and the  $\mathbf{g}$  two-electron operator. There are of the order of  $M^4$  of these *two-electron integrals*. In conventional HF methods the two-electron integrals are calculated and saved before the



**Figure 3.3** Illustration of the SCF procedure