

Derivation of the Hartree–Fock Equation

This appendix is divided into two parts. In the first section we develop the formula for the expectation value $\bar{E} = \langle \psi | H | \psi \rangle$ for the case in which ψ is a single determinantal wavefunction over MOs. In the second section we derive the Hartree–Fock equation by requiring \bar{E} to be stationary with respect to variations in ψ .

A7-1 The Expansion of \bar{E} in Terms of Integrals over MOs

We limit discussion to the case in which ψ is a single, closed-shell determinant. We will develop our arguments by referring to a four-electron example:

$$\psi_4 = (4!)^{-1/2} |\phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4)| \quad (\text{A7-1})$$

Recall that this is the shorthand formula for a Slater determinant. Each ϕ is a normalized MO, the MOs are assumed to be orthogonal, and a bar signifies that an electron possesses β spin. As we develop our arguments within the context of ψ , we will generalize them to apply to the general $2n$ electron closed-shell wavefunction

$$\psi_{2n} = [(2n!)]^{-1/2} |\phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) \cdots \phi_n(2n-1)\bar{\phi}_n(2n)| \quad (\text{A7-2})$$

When ψ_4 is expanded according to the rule for determinants (Appendix 2), we obtain $4!$ products. We note the following features of the expanded form.

1. There is one product, occurring with coefficient $+1$, which is identical to the product appearing in the shorthand form of Eq. (A7-1). We refer to this as the “leading term.”
2. An equivalent way of expressing a Slater determinant is via the expression (for ψ_4)

$$\psi_4 = (4!)^{-1/2} \sum_P (-1)^P P(\phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4)) \quad (\text{A7-3})$$

Here P stands for all the sequences of permutations of electron labels that lead to different products (i.e., P is a permutation *operator*), and p is the number of pairwise permutations in a given sequence. For ψ_4 there are $4!$ sequences P , the simplest being “no permutations” (hence, $p = 0$) which produces the leading term. Then there are single permutations, such as $P_{1,2}$ (with $p = 1$), which produces the term $-\phi_1(2)\bar{\phi}_1(1)\phi_2(3)\bar{\phi}_2(4)$. There are also double permutations, etc. According to Eq. (A7-3), any term differing from the leading term by an odd number of

permutations will appear with coefficient -1 . We will be particularly concerned with products that differ from the leading term by a single permutation.

3. A single permutation may be made to occur between electrons in MO's with the same spins or different spins. In the latter case, two electrons in the singly permuted product will disagree in spin with their counterparts in the leading term. In the former case, no such spin disagreement will exist.
4. Terms also appear in ψ_4 corresponding to more than a single permutation of electron indices.

It is useful to pick a representative example of each type of product mentioned above. For ψ_4 , we have the following:

$$\begin{array}{ll}
 \text{Leading term:} & \phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) \\
 \text{Singly permuted term:} & \phi_1(1)\bar{\phi}_1(4)\phi_2(3)\bar{\phi}_2(2); \quad \text{Spin agreement: } (P_{2,4}) \\
 \text{Singly permuted term:} & \phi_1(2)\bar{\phi}_1(1)\phi_2(3)\bar{\phi}_2(4); \quad \text{Spin disagreement: } (P_{1,2}) \\
 \text{Doubly permuted term:} & \phi_1(2)\bar{\phi}_1(4)\phi_2(3)\bar{\phi}_2(1); \quad (P_{1,2}P_{1,4})
 \end{array}$$

Upon expanding $\langle \psi_4 | \hat{H} | \psi_4 \rangle$, we obtain a set of $4!$ products on both the left and right-hand sides of \hat{H} :

$$\begin{aligned}
 \bar{E} = (4!)^{-1} \int \{ & \phi_1^*(1)\bar{\phi}_1^*(2)\phi_2^*(3)\bar{\phi}_2^*(4) - \phi_1^*(1)\bar{\phi}_1^*(4)\phi_2^*(3)\bar{\phi}_2^*(2) - \dots \} \\
 & \times \hat{H}(1, 2, 3, 4) \{ \phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) - \phi_1(1)\bar{\phi}_1(4)\phi_2(3)\bar{\phi}_2(2) - \dots \} d\tau \quad (\text{A7-4})
 \end{aligned}$$

This can be expanded into a set of integrals, one for each term on the left:

$$\begin{aligned}
 \bar{E} = (4!)^{-1} \left\{ \int & \phi_1^*(1)\bar{\phi}_1^*(2)\phi_2^*(3)\bar{\phi}_2^*(4)\hat{H}(1, 2, 3, 4) [\phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) \right. \\
 & - \phi_1(1)\bar{\phi}_1(4)\phi_2(3)\bar{\phi}_2(2) - \phi_1(2)\bar{\phi}_1(1)\phi_2(3)\bar{\phi}_2(4) - \dots] d\tau \\
 & - \int \phi_1^*(1)\bar{\phi}_1^*(4)\phi_2^*(3)\bar{\phi}_2^*(2)\hat{H}(1, 2, 3, 4) [\phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) \\
 & \left. - \phi_1(1)\bar{\phi}_1(4)\phi_2(3)\bar{\phi}_2(2) - \phi_1(2)\bar{\phi}_1(1)\phi_2(3)\bar{\phi}_2(4) - \dots] d\tau \right\} \quad (\text{A7-5})
 \end{aligned}$$

etc. In Eq. (A7-5), \bar{E} is a sum of $4!$ integrals, each containing one term from the set on the left of \hat{H} and all $4!$ from the set on the right.

At first, it might seem that we must evaluate all of the $4!$ integrals in Eq. (A7-5). But it can be shown that these integrals, times their $+1$ or -1 coefficients, are all equal to each other, enabling us to write \bar{E} as $4!$ times the first integral:

$$\begin{aligned}
 \bar{E} = \int & \phi_1^*(1)\bar{\phi}_1^*(2)\phi_2^*(3)\bar{\phi}_2^*(4)\hat{H}(1, 2, 3, 4) \\
 & \sum_P (-1)^P P(\phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4)) d\tau \quad (\text{A7-6})
 \end{aligned}$$

The demonstration that the various integrals in Eq. (A7-5), times their coefficients, are equal to each other is as follows. Consider the second integral in Eq. (A7-5). Note that, if we permute electrons 2 and 4 in that integral, we restore the term on the left of \hat{H} to its original “leading term” order, thereby making that product identical to its counterpart in the first integral. Furthermore, if we carry out this permutation throughout the whole of the integrand of integral number 2 (i.e., in \hat{H} , in all 4! products to the right of \hat{H} , and in $d\tau$), we will not affect the value of the integral. (Recall that, for example,

$$\int_0^1 x^2 dx \int_1^2 y^3 dy \equiv \int_0^1 y^2 dy \int_1^2 x^3 dx$$

The result of this permutation $P_{2,4}$ on the second integral in Eq. (A7-5) is

$$\int \phi_1^*(1)\bar{\phi}_1^*(2)\phi_2^*(3)\bar{\phi}_2^*(4)\hat{H}(1, 4, 3, 2) [\phi_1(1)\bar{\phi}_1(4)\phi_2(3)\bar{\phi}_2(2) - \phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) - \dots] d\tau \quad (\text{A7-7})$$

Now \hat{H} is invariant under exchange of electron indices, and the set of products to the right of \hat{H} in Eq. (A7-7) is the same set we had before, but their order is changed, and the whole product evidently differs by a factor of -1 from the set in the first integral. Therefore, we can say that the first and second integrals of Eq. (A7-5) have the same absolute value but different signs. However, the fact that these integrals contribute to \bar{E} with opposite signs cancels the sign disagreement. In this way, every integral in Eq. (A7-5) can be compared to the leading integral and Eq. (A7-6) verified. This much simplified expression for \bar{E} is, for the $2n$ -electron case

$$\bar{E} = \int \phi_1^*(1)\bar{\phi}_1^*(2) \cdots \phi_n^*(2n-1)\bar{\phi}_n^*(2n)\hat{H}(1, 2, \dots, 2n) \left[\sum_P (-1)^P P(\phi_1(1)\bar{\phi}_1(2) \cdots \phi_n(2n-1)\bar{\phi}_n(2n)) \right] d\tau \quad (\text{A7-8})$$

At this point we write out \hat{H} more explicitly. It is, in atomic units,

$$\hat{H}(1, 2, \dots, 2n) = \sum_{i=1}^{2n} \left(-\frac{1}{2} \nabla_i^2 - \sum_{\mu}^{\text{nuclei}} Z_{\mu} / r_{\mu i} \right) + \sum_{i=1}^{2n-1} \sum_{j=i+1}^{2n} 1/r_{ij} \quad (\text{A7-9})$$

$$= \sum_{i=1}^{2n} H_{(i)}^{\text{core}} + \sum' 1/r_{ij} \quad (\text{A7-10})$$

Here, \sum' is a shorthand symbol for the double sum in Eq. (A7-9). We see that \hat{H} is composed of one-electron operators, $H_{(i)}^{\text{core}}$, which deal with the kinetic and nuclear-electron attraction energies for electron i , and two-electron operators for interelectronic repulsion. The internuclear repulsion is omitted since, for a given nuclear configuration, it is simply a constant that can be added to the electronic energy. Note for future reference that \hat{H} has no dependence on electron spin coordinates.

If we insert the expression (A7-10) for \hat{H} into Eq. (A7-6) for \bar{E} , it is easy to see that we can expand the result into separate sets of integrals over one- and two-electron operators. We consider first the one-electron integrals. For ψ_4 , these are

$$\int (\phi_1^*(1)\bar{\phi}_1^*(2)\phi_2^*(3)\bar{\phi}_2^*(4)) \times \sum_{i=1}^4 H_{(i)}^{\text{core}} [\phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) - \phi_1(1)\bar{\phi}_1(4)\phi_2(3)\phi_2(2) - \dots] d\tau \quad (\text{A7-11})$$

Upon expanding this, the first set of integrals we obtain is

$$\int \phi_1^*(1)\bar{\phi}_1^*(2)\phi_2^*(3)\bar{\phi}_2^*(4) [H_{(1)}^{\text{core}} + H_{(2)}^{\text{core}} + H_{(3)}^{\text{core}} + H_{(4)}^{\text{core}}] \phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) d\tau \quad (\text{A7-12})$$

This can be expanded again. The first integral contains the operator $H_{(1)}^{\text{core}}$, which does not act on electrons 2-4. This allows a separation into a product of integrals as follows:

$$\int \phi_1^*(1)\bar{\phi}_1^*(2)\phi_2^*(3)\bar{\phi}_2^*(4) H_{(1)}^{\text{core}} \phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) d\tau \quad (\text{A7-13})$$

$$= \int \phi_1^*(1) H_{(1)}^{\text{core}} \phi_1(1) d\tau_1 \int \bar{\phi}_1^*(2)\bar{\phi}_1(2) d\tau_2 \int \phi_2^*(3)\phi_2(3) d\tau_3 \int \bar{\phi}_2^*(4)\bar{\phi}_2(4) d\tau_4 \quad (\text{A7-14})$$

The last three integrals are overlap integrals and are all unity by virtue of normality of the MOs. The first integral, a "core integral," is normally symbolized H_{11} . Here the subscripts refer to the MO index, not the electron index:

$$H_{ii} = \int \phi_i^*(1) H_{(1)}^{\text{core}} \phi_i(1) d\tau_1 \quad (\text{A7-15})$$

Therefore, Eq. (A7-13) equals H_{11} . By continued expansion, Eq. (A7-12) can be shown to be equal to $H_{11} + H_{11} + H_{22} + H_{22} = 2(H_{11} + H_{22})$. In this case, we have been dealing with identical MO products on the two sides of the operator. As we continue evaluating the expansion of Eq. (A7-12), we next encounter an integral in which the products differ by a permutation, namely,

$$- \int \phi_1^*(1)\bar{\phi}_1^*(2)\phi_2^*(3)\bar{\phi}_2^*(4) [H_{(1)}^{\text{core}} + H_{(2)}^{\text{core}} + H_{(3)}^{\text{core}} + H_{(4)}^{\text{core}}] \phi_1(1)\bar{\phi}_1(4)\phi_2(3)\bar{\phi}_2(2) d\tau \quad (\text{A7-16})$$

Again, for $H^{\text{core}}(1)$, this may be written

$$- \int \phi_1^*(1) H_{(1)}^{\text{core}} \phi_1(1) d\tau_1 \int \bar{\phi}_1^*(2)\bar{\phi}_2(2) d\tau_2 \int \phi_2^*(3)\phi_2(3) d\tau_3 \int \bar{\phi}_2^*(4)\bar{\phi}_1(4) d\tau_4 \quad (\text{A7-17})$$

Orbital orthogonality will cause the second and fourth integrals to vanish. In general, if the two products differ by one or more permutations, they will have two or more sites of disagreement. Upon expansion, at least one disagreement will occur in an overlap

integral, causing the integral to vanish. Thus, except for the integral involving identical products [Eq. (A7-12)], all the integrals obtained by expansion of Eq. (A7-11) vanish. Our result, generalized to the $2n$ -electron case, is (see Appendix 11 for bra-ket notation)

$$\left\langle \psi_{2n} \left| \sum_{i=1}^{2n} H_{(1)}^{\text{core}} \right| \psi_{2n} \right\rangle = \sum_{i=1}^n 2H_{ii} \quad (\text{A7-18})$$

We now turn to integrals containing two-electron operators. Consider, for example, an integral that has products differing in two places,

$$-\langle \phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) | 1/r_{13} | \phi_1(3)\bar{\phi}_1(2)\phi_2(1)\bar{\phi}_2(4) \rangle \quad (\text{A7-19})$$

This can be partly separated into a product of integrals over different electron coordinates.

$$(\text{A7-19}) = -\langle \phi_1(1)\phi_2(3) | 1/r_{13} | \phi_1(3)\phi_2(1) \rangle \langle \bar{\phi}_1(2) | \bar{\phi}_1(2) \rangle \langle \bar{\phi}_2(4) | \bar{\phi}_2(4) \rangle \quad (\text{A7-20})$$

Observe that the two disagreements are inside the two-electron integral, and that the overlap terms both show complete internal agreement and are therefore equal to unity. It is clear that, if our two products differed in *more* than two places, at least one such disagreement would appear in an overlap integral, causing the whole integral to vanish. Therefore, two-electron integrals need be considered only if they involve products differing by zero or one permutations. Let us consider these two possibilities separately. If there are no disagreements, we have for ψ_4 ,

$$\begin{aligned} & \left\langle \phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) \left| \sum' 1/r_{ij} \right| \phi_1(1)\bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4) \right\rangle \\ &= \langle \phi_1(1)\bar{\phi}_1(2) | 1/r_{12} | \phi_1(1)\bar{\phi}_1(2) \rangle + \langle \phi_1(1)\phi_2(3) | 1/r_{13} | \phi_1(1)\phi_2(3) \rangle \\ &+ \langle \phi_1(1)\bar{\phi}_2(4) | 1/r_{14} | \phi_1(1)\bar{\phi}_2(4) \rangle + \langle \bar{\phi}_1(2)\phi_2(3) | 1/r_{23} | \bar{\phi}_1(2)\phi_2(3) \rangle \\ &+ \langle \bar{\phi}_1(2)\bar{\phi}_2(4) | 1/r_{24} | \bar{\phi}_1(2)\bar{\phi}_2(4) \rangle + \langle \phi_2(3)\bar{\phi}_2(4) | 1/r_{34} | \phi_2(3)\bar{\phi}_2(4) \rangle \end{aligned} \quad (\text{A7-21})$$

These integrals give the coulombic repulsion between electrons in MOs. They are symbolized J_{ij} , where

$$J_{ij} = \left\langle \phi_i(1)\phi_j(2) | 1/r_{12} | \phi_i(1)\phi_j(2) \right\rangle \equiv \langle ij | ij \rangle \quad (\text{A7-22})$$

Here ϕ_i and ϕ_j may be associated with either spin. Because the operator and MOs commute, the integrand can be rearranged to give

$$J_{ij} = \int \phi_i^*(1)\phi_i(1)(1/r_{12})\phi_j^*(2)\phi_j(2) d\tau_1 d\tau_2 \equiv (ii | jj) \quad (\text{A7-23})$$

Some people prefer this form because it places the two mutually repelling charge clouds on the two sides of the operator. It is important to realize that the parenthetical expression $(ii | jj)$ and the bra-ket shorthand $\langle ij | ij \rangle$ correspond to *different conventions* for electron index order, and are really the same integral. Returning to Eq. (A7-21), we see that it is equal to

$$J_{11} + J_{12} + J_{12} + J_{12} + J_{12} + J_{22} = \sum_{i=1}^2 \left(J_{ii} + \sum_{j \neq i} 2J_{ij} \right) \quad (\text{A7-24})$$

We must now consider the case where the products differ by a single permutation, hence in two places. An example has been provided in Eq. (A7-19). We noted that, when the operator $1/r_{ij}$ corresponds to electrons i and j in the positions of disagreement, the overlap integrals are all unity. Otherwise, at least one overlap integral vanishes. An integral like that in Eq. (A7-20) is called an exchange integral.

Exchange integrals can occur only when the product on the right of the operator differs from the leading term by a single permutation. Hence, exchange integrals always enter with a coefficient of -1 .

We noted earlier that two classes of singly permuted products exist. One class involves permutations between electrons of like spin. In such a case, ϕ_i and ϕ_j appear throughout the integral K_{ij} with spin agreement. For cases where electrons of different spin have been permuted, spin disagreement forces the exchange integral to vanish. (Since $1/r_{ij}$ is not a spin operator, the integration over spin coordinates factors out and produces a vanishing integral if spins disagree.)

The result of all this is that each singly permuted product can give $-K_{ij}$ if the permutation is between electrons of like spin in MOs ϕ_i and ϕ_j , and zero otherwise. For ψ_4 , the acceptable permutations can be seen to be electron 1 with 3 and electron 2 with 4, both of these occurring between ϕ_1 and ϕ_2 space MOs. Hence, the contribution to E is $-2K_{12}$. Combining this with J terms gives

$$\langle \psi_4 | \sum' 1/r_{ij} | \psi_4 \rangle = J_{11} + 4J_{12} - 2K_{12} + J_{22} \quad (\text{A7-25})$$

From the definitions of J and K , it is apparent that

$$J_{ij} = J_{ji}, \quad K_{ij} = K_{ji}, \quad K_{ii} = J_{ii}$$

This allows us to rewrite Eq. (A7-25) as

$$\begin{aligned} & 2J_{11} - K_{11} + 2J_{12} - K_{12} + 2J_{21} - K_{21} + 2J_{22} - K_{22} \\ &= \sum_{i=1}^2 \sum_{j=1}^2 (2J_{ij} - K_{ij}) \end{aligned} \quad (\text{A7-26})$$

Generalizing to the $2n$ -electron, closed-shell case and adding in our one-electron contribution,

$$\bar{E} = \langle \psi_{2n} | \hat{H} | \psi_{2n} \rangle = 2 \sum_{i=1}^n H_{ii} + \sum_{i=1}^n \sum_{j=1}^n (2J_{ij} - K_{ij}) \quad (\text{A7-27})$$

This is the desired expression for \bar{E} in terms of integrals over MOs ϕ_i for a single-determinantal, closed-shell wavefunction.

A7-2 Derivation of the Hartree–Fock Equations

To find the “best” MOs, we seek those that minimize \bar{E} , that is, those MOs ϕ for which \bar{E} is stationary to small variations $\delta\phi$. But there is a restriction in the variations $\delta\phi$. The MOs can only be varied in ways that do not destroy their orthonormality since this property was assumed in deriving Eq. (A7-27). This means that, for proper variations

$\delta\phi$ at the minimum \bar{E} , both \bar{E} and all the MO overlap integrals $S_{ij} \equiv \langle \phi_i | \phi_j \rangle$ must remain constant. (S_{ij} must equal unity when $i = j$, zero otherwise.) If \bar{E} and S_{ij} are constant, any linear combination of them is constant too. Thus, we may write that, at the minimum \bar{E} ,

$$c_0 \bar{E} + \sum_i \sum_j c_{ij} S_{ij} = \text{constant} \quad (\text{A7-28})$$

for our restricted type of $\delta\phi$. This equation will hold for *any* set of coefficients c as long as $\delta\phi$ is of the proper *restricted* nature. However, it is possible to show that, for a particular set of coefficients, Eq. (A7-28) is satisfied at minimum \bar{E} for *any* small variations $\delta\phi$. The particular coefficients are called *Lagrangian multipliers*. They are of undetermined value thus far, but their values will become known in the course of solving the problem. The technique, known as “Lagrange’s method of undetermined multipliers” is from the calculus of variations.¹ The Lagrangian multipliers will ultimately turn out to be essentially the MO energies. For future convenience we write Eq. (A7-28) in the form

$$\bar{E} - 2 \sum_i \sum_j \epsilon_{ij} S_{ij} = \text{constant for } \delta\phi \quad (\text{A7-29})$$

where we now understand $\delta\phi$ to be unrestricted and ϵ_{ij} to be some unknown special set of constants. The stability of the quantity on the left-hand side of Eq. (A7-29) may be expressed as follows:

$$\delta E - 2\delta \sum_i \sum_j \epsilon_{ij} S_{ij} = 0 \quad (\text{A7-30})$$

or, expanding \bar{E} ,

$$2 \sum_{i=1}^n \delta H_{ii} + \sum_{i=1}^n \sum_{j=1}^n (2\delta J_{ij} - \delta K_{ij}) - 2 \sum_{i=1}^n \sum_{j=1}^n \epsilon_{ij} \delta S_{ij} = 0 \quad (\text{A7-31})$$

The variations occur in the MOs ϕ , and so

$$\delta S_{ij} = \int \delta\phi_i^*(1) \phi_j(1) d\tau_1 + \int \phi_i^*(1) \delta\phi_j(1) d\tau_1 \quad (\text{A7-32})$$

$$\delta H_{ii} = \int \delta\phi_i^*(1) H_{(1)}^{\text{core}} \phi_i(1) d\tau_1 + \int \phi_i^*(1) H_{(1)}^{\text{core}} \delta\phi_i(1) d\tau_1 \quad (\text{A7-33})$$

$$\begin{aligned} \delta J_{ij} &= \int \delta\phi_i^*(1) \phi_j^*(2) (1/r_{12}) \phi_i(1) \phi_j(2) d\tau_1 d\tau_2 \\ &+ \int \phi_i^*(1) \delta\phi_j^*(2) (1/r_{12}) \phi_i(1) \phi_j(2) d\tau_1 d\tau_2 + \text{complex conjugates} \end{aligned} \quad (\text{A7-34})$$

It is convenient to define a coulomb operator $\hat{J}_i(1)$ as

$$\hat{J}_i(1) = \int \phi_i^*(2) (1/r_{12}) \phi_i(2) d\tau_2 \quad (\text{A7-35})$$

¹For an introduction to this topic, see Margenau and Murphy [1].

Using this definition we can rewrite Eq. (A7-34) as

$$\delta J_{ij} = \int \delta \phi_i^*(1) \hat{J}_j(1) \phi_i(1) d\tau_1 + \int \delta \phi_j^*(1) \hat{J}_i(1) \phi_j(1) d\tau_1 + \text{complex conjugates} \quad (\text{A7-36})$$

In the same spirit, we define an exchange operator \hat{K}_i , which, because it involves an orbital exchange, must be written in the context of an orbital being operated on:

$$\hat{K}_i(1) \phi_j(1) = \int \phi_i^*(2) (1/r_{12}) \phi_j(2) d\tau_2 \phi_i(1) \quad (\text{A7-37})$$

This enables us to write δK_{ij}

$$\delta K_{ij} = \int \delta \phi_i^*(1) \hat{K}_j(1) \phi_i(1) d\tau_1 + \int \delta \phi_j^*(1) \hat{K}_i(1) \phi_j(1) d\tau_1 + \text{complex conjugates}$$

Employing the operators \hat{J} and \hat{K} , Eq. (A7-31) can be written as follows:

$$\begin{aligned} 2 \sum_i \int \delta \phi_i^*(1) \left[H_{(1)}^{\text{core}} \phi_i(1) + \sum_j (2\hat{J}_j(1) - \hat{K}_j(1)) \phi_i(1) - \sum_j \epsilon_{ij} \phi_j(1) \right] d\tau_1 \\ + 2 \sum_i \int \delta \phi_i(1) \left[H_{(1)}^{\text{core}*} \phi_i^*(1) + \sum_j (2\hat{J}_j^*(1) - \hat{K}_j^*(1)) \phi_i^*(1) \right. \\ \left. - \sum_j \epsilon_{ij}^* \phi_j^*(1) \right] d\tau_1 = 0 \quad (\text{A7-38}) \end{aligned}$$

Here we have made use of the hermitian properties of H^{core} , \hat{J} , and \hat{K} , and also the relation $\epsilon_{ji} \int \delta \phi_j(1) \phi_i^*(1) d\tau_1 = \epsilon_{ij} \int \delta \phi_i(1) \phi_j^*(1) d\tau_1$, which is merely an index interchange.

Since the variations $\delta \phi_i^*$ and $\delta \phi_i$ are independent, each half of Eq. (A7-38) must independently equal zero. Hence, we can select either half for further development. We will select the first half. This equation indicates that the sum of integrals equals zero. Either the integrals are all individually equal to zero or else they are finite but cancel. However the latter possibility is ruled out because the variations $\delta \phi_i^*$ are arbitrary. By appropriately picking $\delta \phi_i^*$, we could always spoil cancellation if the various integrals for different i were nonzero. But the equation states that the sum vanishes for every $\delta \phi_i^*$. Therefore, we are forced to conclude that each integral vanishes.

Continuing in the same spirit, we can conclude that the term in brackets in the integrand is zero. For the integral to vanish requires the integrand either to be identically zero or else to have equal positive and negative parts. If the latter were true for some choice of $\delta \phi_i^*$, it would be possible to change $\delta \phi_i^*$ so as to unbalance the cancellation and produce a nonzero integral. Since the integral is zero for all $\delta \phi_i^*$, it must be that the bracketed term vanishes identically. Thus,

$$\left[H_{(1)}^{\text{core}} + \sum_j (2\hat{J}_j(1) - \hat{K}_j(1)) \right] \phi_i(1) = \sum_j \epsilon_{ij} \phi_j(1) \quad (\text{A7-39})$$

for all $i = 1$ to n and for a certain set of constants ϵ_{ij} .

The original development of SCF equations was performed by Hartree for simple product wavefunctions. Fock later extended the approach to apply to antisymmetrized wavefunctions. For this reason, the collection of operators in brackets in Eq. (A7-39) is called the Fock operator, symbolized \hat{F} , and Eq. (A7-39) becomes

$$\hat{F}(1)\phi_i(1) = \sum_j \epsilon_{ij}\phi_j(1) \quad (\text{A7-40})$$

Equation A7-40 is a differential equation for each MO ϕ_i . But as it stands it is not an eigenvalue equation because, instead of regenerating ϕ_i , we obtain a sum of functions ϕ_j times the various unknown constants ϵ_{ij} . However, there remains a degree of freedom in the problem that can be used to throw Eq. (A7-40) into eigenvalue form. It is pointed out in Appendix 2 that the value of a determinant is unchanged if any row or column, multiplied by a constant, is added to any other row or column. This means that a Slater determinant of “best” MOs is unaffected by such internal rearrangements. In other words, if we were to solve Eq. (A7-40) for a set of “best” MOs, ϕ_i^b , we could form various new orthonormal MOs, (e.g., $\phi_i^b + \lambda_{ik}\phi_k^b$, $\phi_k^b - \lambda_{ki}\phi_i^b$) by mixing them together, and our wavefunction ψ , and all values of observables predicted from ψ , including \bar{E} , would be precisely the same.

A transformation that mixes the MOs ϕ without affecting the property of orthonormality is called a unitary transformation (see Chapter 9). Letting U stand for such a transformation, we have that a transformed set of ϕ 's, called ϕ' , is given by

$$\phi'_i = \sum_j U_{ji}\phi_j, \quad i = 1, \dots, n \quad (\text{A7-41})$$

In matrix notation, this is

$$\tilde{\Phi}' = \tilde{\Phi}U \quad (\text{A7-42})$$

where $\tilde{\Phi}'$ and $\tilde{\Phi}$ are row vectors, viz.

$$\tilde{\Phi}' = (\Phi'_1 \Phi'_2 \dots \Phi'_n), \quad (\text{A7-43})$$

and U is an $n \times n$ matrix, with

$$UU^\dagger = U^\dagger U = 1 \quad (\text{A7-44})$$

In terms of these matrices, Eq. (A7-40) is

$$\hat{F}\tilde{\Phi} = \tilde{\Phi}E \quad (\text{A7-45})$$

where E is an $n \times n$ matrix. If we multiply this from the right by U , we obtain

$$\hat{F}\tilde{\Phi}U = \tilde{\Phi}EU \quad (\text{A7-46})$$

Inserting 1 (in the form UU^\dagger) between $\tilde{\Phi}$ and E gives

$$\hat{F}\tilde{\Phi}U = \tilde{\Phi}UU^\dagger EU \quad (\text{A7-47})$$

or

$$\hat{F}\tilde{\Phi}' = \tilde{\Phi}'U^\dagger EU \quad (\text{A7-48})$$

We can now require that the matrix \mathbf{U} be such that $\mathbf{U}^\dagger \mathbf{E} \mathbf{U}$ is a diagonal matrix \mathbf{E}' . (This requires that \mathbf{E} be a hermitian matrix, which can be shown to be the case.)² This requirement defines \mathbf{U} , and we have

$$\hat{F} \tilde{\Phi}' = \tilde{\Phi}' \mathbf{E}' \quad (\text{A7-49})$$

which corresponds to

$$\hat{F} \phi'_i = \epsilon'_i \phi'_i, \quad i = 1, 2, \dots, n \quad (\text{A7-50})$$

This equation has the desired eigenvalue form, and is commonly referred to as the *Hartree–Fock* equation. It is discussed at length in Chapter 11.

It is important to bear in mind that our transformation \mathbf{U} is for mathematical convenience and has no physical effect. We may imagine that our original basis set spans a certain function space, and that solution of Eq. (A7-50) produces a set of occupied MOs ϕ'_i that span a “best” subspace. Transformations by unitary matrices produce new sets of MOs ϕ'' but these still span the same subspace as ϕ' . However, they are generally not eigenfunctions of \hat{F} , and satisfy the less convenient Eq. (A7-40). Nonetheless, there are occasions when it is useful to use some set of MOs other than ϕ' , and we can always do this without having to worry about introducing physical changes as long as our converted MO's are related to ϕ' by a unitary transformation.

The Hartree–Fock equation is ordinarily used in quantum chemistry in connection with a basis set of AOs, and it is possible to carry through a derivation of the Hartree–Fock equation for this type of basis. Detailed treatments of this derivation may be found in the paper by Roothaan [2] and in the book by Pople and Beveridge [3].

References

- [1] H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry*. Van Nostrand-Reinhold, Princeton, New Jersey, 1956.
- [2] C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951).
- [3] J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*. McGraw-Hill, New York, 1970.

²See Roothaan [2].