

## 2. Derivation of the Hartree-Fock Method

### I. The Hartree Product

Look back at Eq. **Error! Reference source not found.**: in order to calculate find the “lowest-energy” Slater determinant, we need to be able to calculate the energy of a Slater determinant. That is, we need to be able to evaluate integrals like

$$E \equiv \left\langle \begin{vmatrix} \psi_1 & \psi_2 & \dots & \psi_N \end{vmatrix} \middle| \hat{Q} \middle| \begin{vmatrix} \psi_1 & \psi_2 & \dots & \psi_N \end{vmatrix} \right\rangle \quad (1.1)$$

where  $\hat{Q}$  is an operator. The most important cases are the identity operator (for normalization),

$$\hat{I} = 1 \quad (1.2)$$

the kinetic-energy operator,

$$\hat{T} = \sum_{i=1}^N -\frac{\nabla_i^2}{2}, \quad (1.3)$$

the electron-electron repulsion energy operator,

$$\hat{V}_{ee} \equiv \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (1.4)$$

and the electron-nuclear attraction energy operator,

$$\hat{V}_{ne} \equiv \sum_{i=1}^N v(\mathbf{r}_i) \quad (1.5)$$

where the external potential,  $v(\mathbf{r})$ , in a  $P$ -atom molecule is

$$v(\mathbf{r}_i) \equiv \sum_{\alpha=1}^P -\frac{Z_{\alpha}}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|}. \quad (1.6)$$

We write the total Hamiltonian as a sum of the one-electron and two-electron pieces, namely,

$$\hat{H} \equiv \sum_{i=1}^N \hat{h}(\mathbf{r}_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \quad (1.7)$$

where the electron-electron repulsion between electrons  $i$  and  $j$  is given by

$$\hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (1.8)$$

and

$$\hat{h}(\mathbf{r}_i) \equiv \hat{t}(\mathbf{r}_i) + v(\mathbf{r}_i) \quad (1.9)$$

is the sum of the kinetic energy operator for electron  $i$ ,

$$\hat{t}(\mathbf{r}_i) = -\frac{\nabla_i^2}{2} \quad (1.10)$$

and the external potential which “binds” this electron to the atom,  $v(\mathbf{r}_i)$  (cf. Eq. (1.6)). Don’t worry quite yet if all this notation isn’t clicking—it will become more familiar once it is used, and the parts that are used least are the least important.

In order to evaluate properties of Slater determinants, it is useful to remember what a Slater determinant is: it is simply an “antisymmetric sum” of all the possible ways to distribute electrons in a system. For example,

$$\begin{aligned} \begin{vmatrix} \psi_1 & \psi_2 & \psi_3 \end{vmatrix} &= \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_1(\mathbf{z}_1) & \psi_2(\mathbf{z}_1) & \psi_3(\mathbf{z}_1) \\ \psi_1(\mathbf{z}_2) & \psi_2(\mathbf{z}_2) & \psi_3(\mathbf{z}_2) \\ \psi_1(\mathbf{z}_3) & \psi_2(\mathbf{z}_3) & \psi_3(\mathbf{z}_3) \end{vmatrix} \\ &= \frac{1}{\sqrt{6}} \begin{pmatrix} \psi_1(\mathbf{z}_1)\psi_2(\mathbf{z}_2)\psi_3(\mathbf{z}_3) \\ \psi_1(\mathbf{z}_2)\psi_2(\mathbf{z}_1)\psi_3(\mathbf{z}_3) \\ -\psi_1(\mathbf{z}_3)\psi_2(\mathbf{z}_2)\psi_3(\mathbf{z}_1) \\ +\psi_1(\mathbf{z}_1)\psi_2(\mathbf{z}_3)\psi_3(\mathbf{z}_2) \\ +\psi_1(\mathbf{z}_2)\psi_2(\mathbf{z}_3)\psi_3(\mathbf{z}_1) \\ +\psi_1(\mathbf{z}_3)\psi_2(\mathbf{z}_1)\psi_3(\mathbf{z}_2) \end{pmatrix} \end{aligned} \quad (1.11)$$

Note the trend: we take the product of the diagonal elements of the Slater determinant, then we do all the “single exchanges” (which get a negative sign by the Pauli antisymmetry principle), and then form all the “unique” double exchanges (which get a positive sign”. The total number of terms is the number of different ways to pick a coordinate for  $\psi_1$  (three),  $\psi_2$  (two), and  $\psi_3$  (one). Each term in Eq. (1.11) is referred to as a Hartree-product wave function, and can be denoted as, for instance,

$$\psi_1(\mathbf{z}_1)\psi_2(\mathbf{z}_2)\psi_3(\mathbf{z}_3) = \begin{vmatrix} \psi_1 & \psi_2 & \psi_3 \end{vmatrix} \quad (1.12)$$

So we can write the expression in Eq. (1.11) as:

$$\begin{vmatrix} \psi_1 & \psi_2 & \psi_3 \end{vmatrix} = \frac{1}{\sqrt{6}} \begin{pmatrix} \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \\ -\begin{vmatrix} \psi_2\psi_1\psi_3 \end{vmatrix} - \begin{vmatrix} \psi_3\psi_2\psi_1 \end{vmatrix} - \begin{vmatrix} \psi_1\psi_3\psi_2 \end{vmatrix} \\ +\begin{vmatrix} \psi_3\psi_1\psi_2 \end{vmatrix} + \begin{vmatrix} \psi_2\psi_3\psi_1 \end{vmatrix} \end{pmatrix} \quad (1.13)$$

We often find it convenient to denote “exchanges” of coordinates explicitly. We do this by introducing the permutation operator,  $\mathcal{P}_{i,j}$ , which means “exchange the coordinates of orbitals  $i$  and  $j$  in the Hartree product. Thus, Eq. (1.13) becomes

$$\begin{vmatrix} \psi_1 & \psi_2 & \psi_3 \end{vmatrix} = \frac{1}{\sqrt{6}} \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \begin{vmatrix} \psi_1 \psi_2 \psi_3 \end{vmatrix} \quad (1.14)$$

Note that  $\mathcal{P}_{i,j} = \mathcal{P}_{j,i}$  and that the order of permutations does not matter. The Pauli antisymmetry principle indicates that when there are an odd number of permutations, the Hartree product has a negative coefficient.

## II. Integrals of Hartree-Product Wave Functions

Based on the above considerations, it is clear that evaluating integrals between Slater determinants requires merely that we be able to evaluate integrals between Hartree-product wave functions. We have the following results, which are summarized in Table 7.1.

### A. One-electron integrals

#### 1. Identical Hartree products, $|\psi_1 \psi_2 \dots \psi_N\rangle$ .

$$\begin{aligned} & \left\langle \left( \psi_1 \psi_2 \dots \psi_N \middle| \hat{h}(\mathbf{r}_i) \middle| \psi_1 \psi_2 \dots \psi_N \right) \right\rangle \\ & \equiv \int \psi_1^*(\mathbf{z}_1) \psi_2^*(\mathbf{z}_2) \dots \psi_N^*(\mathbf{z}_N) \hat{h}(\mathbf{r}_i) \psi_1(\mathbf{z}_1) \psi_2(\mathbf{z}_2) \dots \psi_N(\mathbf{z}_N) d\mathbf{z}_1 \dots d\mathbf{z}_N \\ & = \left( \int \psi_1^*(\mathbf{z}_1) \psi_1(\mathbf{z}_1) d\mathbf{z}_1 \dots \right. \\ & \quad \times \int \psi_{i-1}^*(\mathbf{z}_{i-1}) \psi_{i-1}(\mathbf{z}_{i-1}) d\mathbf{r}_{i-1} \int \psi_i^*(\mathbf{z}_i) \hat{h}(\mathbf{r}_i) \psi_i(\mathbf{z}_i) d\mathbf{r}_i \int \psi_{i+1}^*(\mathbf{z}_{i+1}) \psi_{i+1}(\mathbf{z}_{i+1}) d\mathbf{z}_{i+1} \dots \\ & \quad \left. \times \int \psi_N^*(\mathbf{z}_N) \psi_N(\mathbf{z}_N) d\mathbf{z}_N \right) \quad (1.15) \\ & = \left\langle \psi_i \middle| \hat{h} \middle| \psi_i \right\rangle \prod_{\substack{k=1 \\ k \neq i}}^N \langle \psi_k | \psi_k \rangle \end{aligned}$$

Here,  $\prod_{\substack{k=1 \\ k \neq i}}^N \langle \psi_k | \psi_k \rangle$  denotes the product of “normalization integrals” for all

the orbitals except  $\psi_i$ . For example, for four electrons,

$$\left\langle \left( \psi_1 \psi_2 \psi_3 \psi_4 \middle| \hat{h}(\mathbf{r}_2) \middle| \psi_1 \psi_2 \psi_3 \psi_4 \right) \right\rangle = \left\langle \psi_2 \middle| \hat{h} \middle| \psi_2 \right\rangle \langle \psi_1 | \psi_1 \rangle \langle \psi_3 | \psi_3 \rangle \langle \psi_4 | \psi_4 \rangle \quad (1.16)$$

If the orbitals are normalized, then  $\langle \psi_k | \psi_k \rangle = 1$  and

$$\left\langle \left( \psi_1 \psi_2 \dots \psi_N \middle| \hat{h}(\mathbf{r}_i) \middle| \psi_1 \psi_2 \dots \psi_N \right) \right\rangle = \left\langle \psi_i \middle| \hat{h} \middle| \psi_i \right\rangle \quad (1.17)$$

- 2. Two Hartree-products differing by the orbital for the  $\alpha^{th}$  electron.**  
**That is, the two Hartree products are given by  $|\psi_1 \dots \psi_\alpha \dots \psi_N\rangle$  and  $|\psi_1 \dots \psi'_\alpha \dots \psi_N\rangle$ , where  $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$ .**

There are two cases.

**Case I.** When the one-electron integral operates on an electron,  $i$ , other than electron  $\alpha$ , then the result is a simple generalization of Eq. (1.15):

$$\left\langle (\psi_1 \dots \psi'_\alpha \dots \psi_N | \hat{h}(\mathbf{r}_i) | \psi_1 \dots \psi_\alpha \dots \psi_N) \right\rangle = \langle \psi_i | \hat{h} | \psi_i \rangle \langle \psi'_\alpha | \psi_\alpha \rangle \prod_{\substack{k=1 \\ k \neq \alpha \\ k \neq i}}^N \langle \psi_k | \psi_k \rangle \quad (1.18)$$

For example, for four electrons

$$\left\langle (\psi_1 \psi_2 \psi_3 \psi_4 | \hat{h}(\mathbf{r}_1) | \psi_1 \psi'_2 \psi_3 \psi_4) \right\rangle = \langle \psi_1 | \hat{h} | \psi_1 \rangle \langle \psi'_2 | \psi_2 \rangle \langle \psi_3 | \psi_3 \rangle \langle \psi_4 | \psi_4 \rangle \quad (1.19)$$

In the important case where  $\psi_\alpha(\mathbf{r})$  and  $\psi'_\alpha(\mathbf{r})$  are orthogonal (so  $\langle \psi'_\alpha | \psi_\alpha \rangle = 0$ ) then

$$\left\langle (\psi_1 \dots \psi'_\alpha \dots \psi_N | \hat{h}(\mathbf{r}_i) | \psi_1 \dots \psi_\alpha \dots \psi_N) \right\rangle = 0 \quad (\alpha \neq i) \quad (1.20)$$

**Case II.** When the one-electron integral operates on electron  $\alpha$ , then a simple generalization of the argument in Equation (1.15) shows that

$$\left\langle (\psi_1 \dots \psi'_\alpha \dots \psi_N | \hat{h}(\mathbf{r}_\alpha) | \psi_1 \dots \psi_\alpha \dots \psi_N) \right\rangle = \langle \psi'_\alpha | \hat{h} | \psi_\alpha \rangle \prod_{\substack{k=1 \\ k \neq \alpha}}^N \langle \psi_k | \psi_k \rangle \quad (1.21)$$

For example, for four electrons we have that

$$\left\langle (\psi_1 \psi_2 \psi_3 \psi_4 | \hat{h}(\mathbf{r}_2) | \psi_1 \psi'_2 \psi_3 \psi_4) \right\rangle = \langle \psi_2 | \hat{h} | \psi_2 \rangle \langle \psi_1 | \psi_1 \rangle \langle \psi_3 | \psi_3 \rangle \langle \psi_4 | \psi_4 \rangle \quad (1.22)$$

In the important case where the orbitals are all normalized, we have

$$\left\langle (\psi_1 \dots \psi'_\alpha \dots \psi_N | \hat{h}(\mathbf{r}_\alpha) | \psi_1 \dots \psi_\alpha \dots \psi_N) \right\rangle = \langle \psi'_\alpha | \hat{h} | \psi_\alpha \rangle \quad (1.23)$$

There is no simplification resulting from the assumption that  $\psi_\alpha(\mathbf{r})$  and  $\psi'_\alpha(\mathbf{r})$  are orthogonal.

- 3. Two Hartree-products differing by the orbitals for the  $\alpha^{th}$  electron and the orbital for the  $\beta^{th}$  electron. The two Hartree products are given by  $|\psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N\rangle$  and  $|\psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N\rangle$ , with  $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$  and  $\psi_\beta(\mathbf{r}) \neq \psi'_\beta(\mathbf{r})$ .**

There are, as before two cases.

**Case I.** The electron under consideration is neither electron  $\alpha$  nor electron  $\beta$ . Then, similar to Eq. (1.18), we have

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{h}(\mathbf{r}_i) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle = \left\langle \psi_i \left| \hat{h} \right| \psi_i \right\rangle \left\langle \psi'_\alpha \left| \psi_\alpha \right\rangle \left\langle \psi'_\beta \left| \psi_\beta \right\rangle \prod_{\substack{k=1 \\ k \neq \alpha, \beta, i}}^N \left\langle \psi_k \left| \psi_k \right\rangle \right. \quad (1.24)$$

and if the primed and unprimed orbitals are orthogonal ( $\langle \psi'_\alpha \left| \psi_\alpha \right\rangle = \langle \psi'_\beta \left| \psi_\beta \right\rangle = 0$ ), then

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \right) \left| \hat{h}(\mathbf{r}_i) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right\rangle = 0 \quad (1.25)$$

**Case II.** The electron under consideration is electron  $\alpha$  (the answer is similar for electron  $\beta$ ). Then

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{h}(\mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle = \left\langle \psi'_\alpha \left| \hat{h} \right| \psi_\alpha \right\rangle \left\langle \psi'_\alpha \left| \psi_\alpha \right\rangle \left\langle \psi'_\beta \left| \psi_\beta \right\rangle \prod_{\substack{k=1 \\ k \neq \alpha, \beta}}^N \left\langle \psi_k \left| \psi_k \right\rangle \right. \quad (1.26)$$

and in the important case where the primed and unprimed orbitals are orthogonal ( $\langle \psi'_\alpha \left| \psi_\alpha \right\rangle = \langle \psi'_\beta \left| \psi_\beta \right\rangle = 0$ ), then

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{h}(\mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle = 0 \quad (1.27)$$

4. For Hartree products differing by more than two orbitals, the one-electron integrals are zero as long as different orbitals are orthogonal.

## B. for two-electron integrals.

### 1. Identical Hartree-products, $|\psi_1\psi_2\ldots\psi_N\rangle$ .

$$\begin{aligned}
& \left\langle (\psi_1\psi_2\ldots\psi_N | \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) | \psi_1\psi_2\ldots\psi_N) \right\rangle \\
& \equiv \int \psi_1^*(\mathbf{z}_1)\psi_2^*(\mathbf{z}_2)\cdots\psi_N^*(\mathbf{z}_N) \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \psi_1(\mathbf{z}_1)\psi_2(\mathbf{z}_2)\cdots\psi_N(\mathbf{z}_N) d\mathbf{z}_1\ldots d\mathbf{z}_N \\
& = \left( \begin{aligned} & \int \psi_1^*(\mathbf{r}_1)\psi_1(\mathbf{r}_1) d\mathbf{r}_1 \cdots \\ & \times \int \psi_{i-1}^*(\mathbf{z}_{i-1})\psi_{i-1}(\mathbf{z}_{i-1}) d\mathbf{z}_{i-1} \left( \int \psi_i^*(\mathbf{z}_i)\psi_j^*(\mathbf{z}_j) \hat{v}_{ee}(\mathbf{z}_i, \mathbf{z}_j) \psi_j(\mathbf{z}_j)\psi_i(\mathbf{z}_i) d\mathbf{z}_i d\mathbf{z}_j \right) \\ & \times \int \psi_{i+1}^*(\mathbf{z}_{i+1})\psi_{i+1}(\mathbf{z}_{i+1}) d\mathbf{z}_{i+1} \cdots \\ & \times \int \psi_{j-1}^*(\mathbf{z}_{j-1})\psi_{j-1}(\mathbf{z}_{j-1}) d\mathbf{r}_{j-1} \int \psi_{j+1}^*(\mathbf{z}_{j+1})\psi_{j+1}(\mathbf{z}_{j+1}) d\mathbf{z}_{j+1} \cdots \\ & \times \int \psi_N^*(\mathbf{z}_N)\psi_N(\mathbf{z}_N) d\mathbf{z}_N \end{aligned} \right) \quad (1.28) \\
& = \left\langle (\psi_i\psi_j | \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) | \psi_i\psi_j) \right\rangle \prod_{\substack{k=1 \\ k \neq i,j}}^N \langle \psi_k | \psi_k \rangle
\end{aligned}$$

For example, for five electrons,

$$\left\langle (\psi_1\psi_2\psi_3\psi_4\psi_5 | \hat{v}_{ee}(\mathbf{r}_2, \mathbf{r}_4) | \psi_1\psi_2\psi_3\psi_4\psi_5) \right\rangle = \langle \psi_2\psi_4 | \hat{v}_{ee} | \psi_2\psi_4 \rangle \langle \psi_1 | \psi_1 \rangle \langle \psi_3 | \psi_3 \rangle \langle \psi_5 | \psi_5 \rangle \quad (1.29)$$

Notice the introduction of a useful “shorthand” for the integrals in Eq. (1.29). It is understood that

$$\langle \psi_i\psi_j | \hat{v}_{ee} | \psi_i\psi_j \rangle \equiv \left\langle \psi_i(\mathbf{z}_i)\psi_j(\mathbf{z}_j) | \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) | \psi_i(\mathbf{z}_i)\psi_j(\mathbf{z}_j) \right\rangle. \quad (1.30)$$

If the orbitals are normalized, then  $\langle \psi_k | \psi_k \rangle = 1$  and

$$\left\langle (\psi_1\psi_2\ldots\psi_N | \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) | \psi_1\psi_2\ldots\psi_N) \right\rangle = \langle (\psi_i\psi_j | \hat{v}_{ee} | \psi_i\psi_j) \rangle \quad (1.31)$$

### 2. Two Hartree-products differing by the orbital for the $\alpha^{th}$ electron.

That is, the two Hartree products are given by  $|\psi_1\ldots\psi_\alpha\ldots\psi_N\rangle$  and  $|\psi_1\ldots\psi'_\alpha\ldots\psi_N\rangle$ , where  $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$ .

There are two cases.

**Case I.** When the electron-electron repulsion operator does not operate on electron  $\alpha$ . Then, generalizing Eq. (1.28), we see that

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \middle| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \middle| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle = \left\langle \left( \psi_i \psi_j \middle| \hat{v}_{ee} \middle| \psi_i \psi_j \right) \right\rangle \langle \psi'_\alpha | \psi_\alpha \rangle \prod_{\substack{k=1 \\ k \neq i, j, \alpha}}^N \langle \psi_k | \psi_k \rangle \quad (1.32)$$

Returning to our 5-electron example,

$$\left\langle \left( \psi_1 \psi_2 \psi'_3 \psi_4 \psi_5 \middle| \hat{v}_{ee}(\mathbf{r}_2, \mathbf{r}_4) \middle| \psi_1 \psi_2 \psi_3 \psi_4 \psi_5 \right) \right\rangle = \langle \psi_2 \psi_4 | \hat{v}_{ee} | \psi_2 \psi_4 \rangle \langle \psi'_3 | \psi_3 \rangle \langle \psi_1 | \psi_1 \rangle \langle \psi_5 | \psi_5 \rangle. \quad (1.33)$$

In the important case where  $\psi_\alpha(\mathbf{r})$  and  $\psi'_\alpha(\mathbf{r})$  are orthogonal (so  $\langle \psi'_\alpha | \psi_\alpha \rangle = 0$ ) then

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \middle| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \middle| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle = 0 \quad \alpha \neq i, j \quad (1.34)$$

**Case II.** When the electron-electron repulsion energy of electron  $\alpha$  is being considered, then a simple generalization of the argument in Equation (1.28) shows that

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \middle| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_\alpha) \middle| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle = \left\langle \left( \psi_i \psi'_\alpha \middle| \hat{v}_{ee} \middle| \psi_i \psi_\alpha \right) \right\rangle \prod_{\substack{k=1 \\ k \neq i, \alpha}}^N \langle \psi_k | \psi_k \rangle \quad (1.35)$$

For example, for four electrons we have that

$$\left\langle \left( \psi_1 \psi_2 \psi_3 \psi'_4 \psi_5 \middle| \hat{v}_{ee}(\mathbf{r}_2, \mathbf{r}_4) \middle| \psi_1 \psi_2 \psi_3 \psi_4 \psi_5 \right) \right\rangle = \langle \psi_2 \psi'_4 | \hat{v}_{ee} | \psi_2 \psi_4 \rangle \langle \psi_3 | \psi_3 \rangle \langle \psi_1 | \psi_1 \rangle \langle \psi_5 | \psi_5 \rangle \quad (1.36)$$

In the important case where the orbitals are all normalized, we have

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \middle| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_\alpha) \middle| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle = \left\langle \left( \psi_i \psi'_\alpha \middle| \hat{v}_{ee} \middle| \psi_i \psi_\alpha \right) \right\rangle \quad (1.37)$$

No simplification results from the assumption that  $\psi_\alpha(\mathbf{r})$  and  $\psi'_\alpha(\mathbf{r})$  are orthogonal.

**3. Two Hartree-products differing by the orbitals for the  $\alpha^{th}$  electron and the orbital for the  $\beta^{th}$  electron. The two Hartree products are given by  $|\psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N\rangle$  and  $|\psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N\rangle$ , with  $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$  and  $\psi_\beta(\mathbf{r}) \neq \psi'_\beta(\mathbf{r})$ .**

There are three cases.

**Case I.** The electron-electron repulsion operator does not include the coordinates for electron  $\alpha$  or the coordinates for electron  $\beta$ . Then,

$$\begin{aligned} & \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \middle| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \middle| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right) \right\rangle \\ &= \left\langle \left( \psi_i \psi_j \middle| \hat{v}_{ee} \middle| \psi_i \psi_j \right) \right\rangle \langle \psi'_\alpha | \psi_\alpha \rangle \langle \psi'_\beta | \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq i, j, \alpha, \beta}}^N \langle \psi_k | \psi_k \rangle \end{aligned} \quad (1.38)$$

and if the primed and unprimed orbitals are orthogonal ( $\langle \psi'_\alpha | \psi_\alpha \rangle = \langle \psi'_\beta | \psi_\beta \rangle = 0$ ), then

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle = 0 \quad (1.39)$$

**Case II.** The electron-electron repulsion between electron  $i$  ( $i \neq \beta$ ) and electron  $\alpha$  is being considered. (The situation is similar when we replace the roles of electrons  $\alpha$  and  $\beta$ .) Then

$$\begin{aligned} & \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle \\ &= \left\langle \left( \psi_i \psi'_\alpha \right) \left| \hat{v}_{ee} \right| \psi_i \psi_\alpha \right\rangle \langle \psi'_\beta | \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq i, \alpha, \beta}}^N \langle \psi_k | \psi_k \rangle \end{aligned} \quad (1.40)$$

and in the important case where the primed and unprimed orbitals are orthogonal ( $\langle \psi'_\alpha | \psi_\alpha \rangle = \langle \psi'_\beta | \psi_\beta \rangle = 0$ ), then

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle = 0 \quad i \neq \beta \quad (1.41)$$

**Case III.** The electron-electron repulsion between electrons  $\alpha$  and electrons  $\beta$  is being considered. Then,

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{v}_{ee}(\mathbf{r}_\alpha, \mathbf{r}_\beta) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle = \left\langle \left( \psi'_\alpha \psi'_\beta \right) \left| \hat{v}_{ee} \right| \psi_\alpha \psi_\beta \right\rangle \prod_{\substack{k=1 \\ k \neq \alpha, \beta}}^N \langle \psi_k | \psi_k \rangle \quad (1.42)$$

and in the important case where the orbitals are normalized, then

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{v}_{ee}(\mathbf{r}_\alpha, \mathbf{r}_\beta) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle = \left\langle \left( \psi'_\alpha \psi'_\beta \right) \left| \hat{v}_{ee} \right| \psi_\alpha \psi_\beta \right\rangle \quad (1.43)$$

No simplification is obtained by assuming the primed and unprimed orbitals to be orthogonal.

**4. For Hartree products differing by more than two orbitals, the two-electron integrals are zero as long as different orbitals are orthogonal.**



**Table 7.1: Integrals Between Hartree-Product Wave-Functions.**

# of different orbitals	a. Operator	General Result	Orthonormal Orbitals
0 $ \psi_1 \dots \psi_N\rangle$	$\hat{h}(\mathbf{r}_i)$	$\langle \psi_i   \hat{h}   \psi_i \rangle \prod_{\substack{k=1 \\ k \neq i}}^N \langle \psi_k   \psi_k \rangle$	$\langle \psi_i   \hat{h}   \psi_i \rangle$
0 $ \psi_1 \dots \psi_N\rangle$	$\hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j)$	$\langle \psi_i \psi_j   \hat{v}_{ee}   \psi_i \psi_j \rangle \prod_{\substack{k=1 \\ k \neq i, j}}^N \langle \psi_k   \psi_k \rangle$	$\langle \psi_i \psi_j   \hat{v}_{ee}   \psi_i \psi_j \rangle$
1 $ \psi_1 \dots \psi'_\alpha \dots \psi_N\rangle;  \psi_1 \dots \psi_\alpha \dots \psi_N\rangle$	$\hat{h}(\mathbf{r}_i)$ $i \neq \alpha$	$\langle \psi_i   \hat{h}   \psi_i \rangle \langle \psi'_\alpha   \psi_\alpha \rangle \prod_{\substack{k=1 \\ k \neq i, \alpha}}^N \langle \psi_k   \psi_k \rangle$	<b>0</b>
1 $ \psi_1 \dots \psi'_\alpha \dots \psi_N\rangle;  \psi_1 \dots \psi_\alpha \dots \psi_N\rangle$	$\hat{h}(\mathbf{r}_\alpha)$	$\langle \psi'_\alpha   \hat{h}   \psi_\alpha \rangle \prod_{\substack{k=1 \\ k \neq \alpha}}^N \langle \psi_k   \psi_k \rangle$	$\langle \psi'_\alpha   \hat{h}   \psi_\alpha \rangle$
1 $ \psi_1 \dots \psi'_\alpha \dots \psi_N\rangle;  \psi_1 \dots \psi_\alpha \dots \psi_N\rangle$	$\hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j)$ $i, j \neq \alpha$	$\langle \psi_i \psi_j   \hat{v}_{ee}   \psi_i \psi_j \rangle \langle \psi'_\alpha   \psi_\alpha \rangle \prod_{\substack{k=1 \\ k \neq i, j, \alpha}}^N \langle \psi_k   \psi_k \rangle$	<b>0</b>
1 $ \psi_1 \dots \psi'_\alpha \dots \psi_N\rangle;  \psi_1 \dots \psi_\alpha \dots \psi_N\rangle$	$\hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_\alpha)$	$\langle \psi_i \psi'_\alpha   \hat{v}_{ee}   \psi_i \psi_\alpha \rangle \prod_{\substack{k=1 \\ k \neq i, \alpha}}^N \langle \psi_k   \psi_k \rangle$	$\langle \psi_i \psi'_\alpha   \hat{v}_{ee}   \psi_i \psi_\alpha \rangle$
2 $ \dots \psi'_\alpha \dots \psi'_\beta \dots\rangle;  \dots \psi_\alpha \dots \psi_\beta \dots\rangle$	$\hat{h}(\mathbf{r}_i)$ $i \neq \alpha, \beta$	$\langle \psi_i   \hat{h}   \psi_i \rangle \langle \psi'_\alpha   \psi_\alpha \rangle \langle \psi'_\beta   \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq i, \alpha, \beta}}^N \langle \psi_k   \psi_k \rangle$	<b>0</b>
2 $ \dots \psi'_\alpha \dots \psi'_\beta \dots\rangle;  \dots \psi_\alpha \dots \psi_\beta \dots\rangle$	$\hat{h}(\mathbf{r}_\alpha)$	$\langle \psi'_\alpha   \hat{h}   \psi_\alpha \rangle \langle \psi'_\beta   \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq \alpha, \beta}}^N \langle \psi_k   \psi_k \rangle$	<b>0</b>
2 $ \dots \psi'_\alpha \dots \psi'_\beta \dots\rangle;  \dots \psi_\alpha \dots \psi_\beta \dots\rangle$	$\hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j)$ $i, j \neq \alpha, \beta$	$\langle \psi_i \psi_j   \hat{v}_{ee}   \psi_i \psi_j \rangle \langle \psi'_\alpha   \psi_\alpha \rangle \langle \psi'_\beta   \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq i, j, \alpha, \beta}}^N \langle \psi_k   \psi_k \rangle$	<b>0</b>
2 $ \dots \psi'_\alpha \dots \psi'_\beta \dots\rangle;  \dots \psi_\alpha \dots \psi_\beta \dots\rangle$	$\hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_\alpha)$ $i \neq \beta$	$\langle \psi_i \psi'_\alpha   \hat{v}_{ee}   \psi_i \psi_\alpha \rangle \langle \psi'_\beta   \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq i, j, \beta}}^N \langle \psi_k   \psi_k \rangle$	<b>0</b>
2 $ \dots \psi'_\alpha \dots \psi'_\beta \dots\rangle;  \dots \psi_\alpha \dots \psi_\beta \dots\rangle$	$\hat{v}_{ee}(\mathbf{r}_\alpha, \mathbf{r}_\beta)$	$\langle \psi'_\alpha \psi'_\beta   \hat{v}_{ee}   \psi_\alpha \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq \alpha, \beta}}^N \langle \psi_k   \psi_k \rangle$	$\langle \psi'_\alpha \psi'_\beta   \hat{v}_{ee}   \psi_\alpha \psi_\beta \rangle$
3 or more	$\hat{h}(\mathbf{r})$ ; any $i$	(more complicated, but similar)	<b>0</b>
3 or more	$v_{ee}(\mathbf{r}_i, \mathbf{r}_j)$ ; any $i, j$	(more complicated, but similar)	<b>0</b>

Using the results in the previous table, we can now construct the integrals for more complicated operators, notably the sums of the 1-electron and 2-electron operators. We have the following key results

## C. Sums of One-Electron Operators

### 1. Identical Hartree products, $|\psi_1\psi_2\ldots\psi_N\rangle$ .

$$\begin{aligned} \left\langle \left( \psi_1\psi_2\ldots\psi_N \left| \sum_{i=1}^N \hat{h}(\mathbf{r}_i) \right| \psi_1\psi_2\ldots\psi_N \right) \right\rangle &\equiv \sum_{i=1}^N \left\langle \psi_i \left| \hat{h} \right| \psi_i \right\rangle \left( \prod_{\substack{k=1 \\ k \neq i}}^N \langle \psi_k | \psi_k \rangle \right) \\ &\stackrel{\text{orthonormal}}{=} \sum_{i=1}^N \left\langle \psi_i \left| \hat{h} \right| \psi_i \right\rangle \end{aligned} \quad (1.44)$$

### 2. Two Hartree products differing by the orbital for the $\alpha^{th}$ electron.

That is, the two Hartree products are given by  $|\psi_1\ldots\psi_\alpha\ldots\psi_N\rangle$  and  $|\psi_1\ldots\psi'_\alpha\ldots\psi_N\rangle$ , where  $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$ .

$$\begin{aligned} &\left\langle \left( \psi_1\ldots\psi'_\alpha\ldots\psi_N \left| \sum_{i=1}^N \hat{h}(\mathbf{r}_i) \right| \psi_1\ldots\psi_\alpha\ldots\psi_N \right) \right\rangle \\ &= \left\langle \left( \psi_1\ldots\psi'_\alpha\ldots\psi_N \left| \hat{h}(\mathbf{r}_\alpha) \right| \psi_1\ldots\psi_\alpha\ldots\psi_N \right) \right\rangle + \sum_{\substack{i=1 \\ i \neq \alpha}}^N \left\langle \left( \psi_1\ldots\psi'_\alpha\ldots\psi_N \left| \hat{h}(\mathbf{r}_i) \right| \psi_1\ldots\psi_\alpha\ldots\psi_N \right) \right\rangle \\ &= \left\langle \psi'_\alpha \left| \hat{h} \right| \psi_\alpha \right\rangle \prod_{\substack{k=1 \\ k \neq \alpha}}^N \langle \psi_k | \psi_k \rangle + \sum_{i=1}^N \left\langle \psi_i \left| \hat{h} \right| \psi_i \right\rangle \left\langle \psi'_\alpha | \psi_\alpha \right\rangle \prod_{\substack{k=1 \\ k \neq \alpha \\ k \neq i}}^N \langle \psi_k | \psi_k \rangle \\ &\stackrel{\text{orthonormal}}{=} \left\langle \psi'_\alpha \left| \hat{h} \right| \psi_\alpha \right\rangle \end{aligned} \quad (1.45)$$

3. **Two Hartree products differing by the orbitals for the  $\alpha^{th}$  electron and the orbital for the  $\beta^{th}$  electron. The two Hartree products are given by  $|\psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N\rangle$  and  $|\psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N\rangle$ , with  $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$  and  $\psi_\beta(\mathbf{r}) \neq \psi'_\beta(\mathbf{r})$ .**

$$\begin{aligned}
& \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \left| \sum_{i=1}^N \hat{h}(\mathbf{r}_i) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right) \right\rangle \\
&= \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \left| \hat{h}(\mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right) \right\rangle \\
&\quad + \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \left| \hat{h}(\mathbf{r}_\beta) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right) \right\rangle \\
&\quad + \sum_{\substack{i=1 \\ i \neq \alpha, \beta}}^N \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \left| \hat{h}(\mathbf{r}_i) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right) \right\rangle \\
&= \left( \langle \psi'_\alpha | \hat{h} | \psi_\alpha \rangle \langle \psi'_\beta | \psi_\beta \rangle + \langle \psi'_\beta | \hat{h} | \psi_\beta \rangle \langle \psi'_\alpha | \psi_\alpha \rangle \right) \left( \prod_{\substack{k=1 \\ k \neq \alpha, \beta, i}}^N \langle \psi_k | \psi_k \rangle \right) \\
&\quad + \sum_{\substack{i=1 \\ i \neq \alpha, \beta}}^N \langle \psi_i | \hat{h} | \psi_i \rangle \langle \psi'_\alpha | \psi_\alpha \rangle \langle \psi'_\beta | \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq \alpha, \beta, i}}^N \langle \psi_k | \psi_k \rangle \\
&\quad \text{orthonormal} \\
&\quad \text{orbitals} \\
&= 0
\end{aligned} \tag{1.46}$$

4. **For orthonormal orbitals, sums of one-electron integrals of Hartree-product wave functions differing by three or more orbitals are also zero.**

## D. Sums of Two-Electron Operators

1. **Identical Hartree-products,  $|\psi_1 \psi_2 \dots \psi_N\rangle$ .**

$$\begin{aligned}
& \left\langle \left( \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \psi_2 \dots \psi_N \right) \right\rangle = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \langle (\psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j) \rangle \prod_{\substack{k=1 \\ k \neq i, j}}^N \langle \psi_k | \psi_k \rangle \\
&\quad \text{orthonormal} \\
&\quad \text{orbitals} \\
&= \sum_{i=1}^{N-1} \sum_{j=i+1}^N \langle (\psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j) \rangle
\end{aligned} \tag{1.47}$$

**2. Two Hartree-products differing by the orbital for the  $\alpha^{th}$  electron.**

That is, the two Hartree products are given by  $|\psi_1 \dots \psi_\alpha \dots \psi_N\rangle$  and  $|\psi_1 \dots \psi'_\alpha \dots \psi_N\rangle$ , where  $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$ .

$$\begin{aligned}
& \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&= \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \sum_{i=1}^{\alpha-1} \sum_{\substack{j=i+1 \\ j \neq \alpha}}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&\quad + \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \sum_{i=1}^{\alpha-1} \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&\quad + \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \sum_{j=\alpha+1}^N \hat{v}_{ee}(\mathbf{r}_\alpha, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&\quad + \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \sum_{i=\alpha+1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&= \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \sum_{i=1}^{\alpha-1} \sum_{\substack{j=i+1 \\ j \neq \alpha}}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&\quad + \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \sum_{i=1}^{\alpha+1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&\quad + \sum_{\substack{i=1 \\ i \neq \alpha}}^N \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&= \sum_{\substack{i=1 \\ i \neq \alpha}}^{N-1} \sum_{\substack{j=i+1 \\ j \neq \alpha}}^N \left\langle \left( \psi_i \psi_j \left| \hat{v}_{ee} \right| \psi_i \psi_j \right) \right\rangle \langle \psi'_\alpha | \psi_\alpha \rangle \prod_{\substack{k=1 \\ k \neq i, j, \alpha}}^N \langle \psi_k | \psi_k \rangle \\
&\quad + \sum_{\substack{i=1 \\ i \neq \alpha}}^N \left\langle \left( \psi_i \psi'_\alpha \left| \hat{v}_{ee} \right| \psi_i \psi_\alpha \right) \right\rangle \prod_{\substack{k=1 \\ k \neq i, \alpha}}^N \langle \psi_k | \psi_k \rangle \\
&\stackrel{\text{orthonormal}}{\stackrel{\text{orbitals}}{=}} \sum_{\substack{i=1 \\ i \neq \alpha}}^N \left\langle \left( \psi_i \psi'_\alpha \left| \hat{v}_{ee} \right| \psi_i \psi_\alpha \right) \right\rangle
\end{aligned} \tag{1.48}$$

- 3. Two Hartree products differing by the orbitals for the  $\alpha^{th}$  electron and the orbital for the  $\beta^{th}$  electron. The two Hartree products are given by  $|\psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N\rangle$  and  $|\psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N\rangle$ , with  $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$  and  $\psi_\beta(\mathbf{r}) \neq \psi'_\beta(\mathbf{r})$ .**

$$\begin{aligned}
& \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right) \right\rangle \\
&= \sum_{\substack{i=1 \\ i \neq \alpha, \beta}}^{N-1} \sum_{\substack{j=i+1 \\ j \neq \alpha, \beta}}^N \left\langle \left( \psi_i \psi_j \left| \hat{v}_{ee} \right| \psi_i \psi_j \right) \right\rangle \langle \psi'_\alpha | \psi_\alpha \rangle \langle \psi'_\beta | \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq i, j, \alpha, \beta}}^N \langle \psi_k | \psi_k \rangle \\
&\quad + \sum_{\substack{i=1 \\ i \neq \alpha, \beta}}^N \left( \left\langle \left( \psi_i \psi'_\alpha \left| \hat{v}_{ee} \right| \psi_i \psi_\alpha \right) \right\rangle \langle \psi'_\beta | \psi_\beta \rangle \right. \\
&\quad \left. + \left\langle \left( \psi_i \psi'_\beta \left| \hat{v}_{ee} \right| \psi_i \psi_\beta \right) \right\rangle \langle \psi'_\alpha | \psi_\alpha \rangle \right) \left( \prod_{\substack{k=1 \\ k \neq i, \alpha, \beta}}^N \langle \psi_k | \psi_k \rangle \right) \\
&\quad + \left\langle \left( \psi'_\alpha \psi'_\beta \left| \hat{v}_{ee} \right| \psi_\alpha \psi_\beta \right) \right\rangle \prod_{\substack{k=1 \\ k \neq \alpha, \beta}}^N \langle \psi_k | \psi_k \rangle \\
&\stackrel{\text{orthonormal}}{\stackrel{\text{orbitals}}{=}} \left\langle \left( \psi'_\alpha \psi'_\beta \left| \hat{v}_{ee} \right| \psi_\alpha \psi_\beta \right) \right\rangle
\end{aligned} \tag{1.49}$$

- 4. For orthonormal orbitals, sums of two-electron integrals of Hartree-product wave functions differing by three or more orbitals are also zero.**

While the preceding analysis is tedious, it is not difficult. An important point to remember is that, for orthonormal orbitals, the integral will vanish if the number of “different orbitals” is greater than the number of electrons the operator acts on. This is obvious on “intuitive” grounds, since if the operator links  $k$  electrons, then if there are more than  $k$  different orbitals there will be at least one set of orthogonal orbitals,  $\psi'_\lambda(\mathbf{z})$  and  $\psi_\lambda(\mathbf{z})$ , that are not “operated on”, and the presence of a factor of  $\langle \psi'_\lambda | \psi_\lambda \rangle = 0$  renders the expression zero.

**Table: Integrals Between Hartree-Product Wave-Functions and Many-Electron Operators.**

# of different orbitals	a. Operator	General Result	Orthonormal Orbitals
0; $ \psi_1 \dots \psi_N\rangle$	$\sum_{i=1}^N \hat{h}(\mathbf{r}_i)$	Eq. (1.44)	$\sum_{i=1}^N \langle \psi_i   \hat{h}   \psi_i \rangle$
0; $ \psi_1 \dots \psi_N\rangle$	$\sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j)$	Eq. (1.47)	$\sum_{i=1}^N \sum_{j=i+1}^N \langle \psi_i \psi_j   \hat{v}_{ee}   \psi_i \psi_j \rangle$
1; $ \psi_1 \dots \psi'_\alpha \dots \psi_N\rangle;  \psi_1 \dots \psi_\alpha \dots \psi_N\rangle$	$\sum_{i=1}^N \hat{h}(\mathbf{r}_i)$	Eq. (1.45)	$\langle \psi'_\alpha   \hat{h}   \psi_\alpha \rangle$
1; $ \psi_1 \dots \psi'_\alpha \dots \psi_N\rangle;  \psi_1 \dots \psi_\alpha \dots \psi_N\rangle$	$\sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j)$	Eq. (1.48)	$\sum_{i=1}^N \sum_{\substack{j=i+1 \\ i \neq \alpha}} \langle \psi_i \psi'_\alpha   \hat{v}_{ee}   \psi_i \psi_\alpha \rangle$
2; $ \dots \psi'_\alpha \dots \psi'_\beta \dots\rangle;  \dots \psi_\alpha \dots \psi_\beta \dots\rangle$	$\sum_{i=1}^N \hat{h}(\mathbf{r}_i)$	Eq. (1.46)	<b>0</b>
2; $ \dots \psi'_\alpha \dots \psi'_\beta \dots\rangle;  \dots \psi_\alpha \dots \psi_\beta \dots\rangle$	$\sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j)$	Eq. (1.49)	$\langle \psi'_\alpha \psi'_\beta   \hat{v}_{ee}   \psi_\alpha \psi_\beta \rangle$
3 or more	$\sum_{i=1}^N \hat{h}(\mathbf{r}_i)$	(more complicated, but similar)	<b>0</b>
3 or more	$\sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j)$	(more complicated, but similar)	<b>0</b>

### III. One-Electron Integrals Between Slater Determinants

We are now, at long last, ready to compute the energy of a Slater determinant. We'll start with a simple example, and then move to the general case. For three electrons, we had (cf. Eq. (1.14))

$$\begin{vmatrix} \psi_1 & \psi_2 & \psi_3 \end{vmatrix} = \frac{1}{\sqrt{6}} \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \quad (1.50)$$

and so

$$\begin{aligned} & \left\langle \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \right\rangle \\ &= \frac{1}{6} \left\langle \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \right\rangle \end{aligned} \quad (1.51)$$

To understand the result, we need only note that every time one permutes two coordinates the new Hartree-product differs from the original Hartree product by two orbitals. Since the orbitals are orthonormal, both single permutations

$$\left\langle \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \mathcal{P}_{1,2} \right| \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \right\rangle = \left\langle \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \begin{vmatrix} \psi_2\psi_1\psi_3 \end{vmatrix} \right\rangle = 0 \quad (1.52)$$

and double permutations

$$\left\langle \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \mathcal{P}_{1,2}\mathcal{P}_{2,3} \right| \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \right\rangle = \left\langle \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \begin{vmatrix} \psi_2\psi_3\psi_1 \end{vmatrix} \right\rangle = 0 \quad (1.53)$$

are zero. It follows that all the “cross terms” between the permutations in Eq. (1.51) vanish, and one is left with

$$\begin{aligned}
& \left\langle \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \\
&= \frac{1}{6} \left( \left\langle \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \right. \\
&\quad + (-1)^2 \left\langle \mathcal{P}_{1,2} \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \mathcal{P}_{1,2} \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \\
&\quad + (-1)^2 \left\langle \mathcal{P}_{1,3} \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \mathcal{P}_{1,3} \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \\
&\quad + (-1)^2 \left\langle \mathcal{P}_{2,3} \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \mathcal{P}_{2,3} \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \\
&\quad + \left\langle \mathcal{P}_{1,2} \mathcal{P}_{2,3} \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \mathcal{P}_{1,2} \mathcal{P}_{2,3} \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \\
&\quad \left. + \left\langle \mathcal{P}_{1,3} \mathcal{P}_{2,3} \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \mathcal{P}_{1,3} \mathcal{P}_{2,3} \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \right) \tag{1.54}
\end{aligned}$$

However, because the operator,  $\sum_{i=1}^N h(\mathbf{r}_i)$  is symmetric with respect to permutations of the coordinates, all six terms are equal. We compute just one of these six terms and “cancel out” the normalization factor. Then, using Eq. (1.44) to evaluate the integral of the first term, we obtain

$$\begin{aligned}
\left\langle \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle &= \left\langle \left( \psi_1 \psi_2 \psi_3 \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \psi_1 \psi_2 \psi_3 \right) \right\rangle \\
&= \langle \psi_1 | \hat{h} | \psi_1 \rangle + \langle \psi_2 | \hat{h} | \psi_2 \rangle + \langle \psi_3 | \hat{h} | \psi_3 \rangle \\
&= \sum_{i=1}^3 \langle \psi_i | \hat{h} | \psi_i \rangle \tag{1.55}
\end{aligned}$$

The analysis is similar for arbitrary numbers of electrons. One has<sup>1</sup>

---

<sup>1</sup> The general form of Eq. (1.56) is that one starts with the “reference” Hartree product, then constructs all ways of permuting two electronic coordinates, and then constructs the more complicated permutations, which consist of several sequential “exchanges” of electrons between orbitals. The “higher order” terms give Hartree-products that differ by more than two orbitals from the “reference” Hartree product, and so when the orbitals are orthogonal, they do not effect the value of 2-body operators.



$$\begin{aligned}
& \left\langle \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^N \hat{h}(\mathbf{r}_i) \right| \psi_1 \psi_2 \dots \psi_N \right\rangle \\
&= \frac{1}{N!} \left\langle \left( \begin{array}{c} 1 - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \mathcal{P}_{i,j} \\ \text{+ (higher-order} \\ \text{permutations)} \end{array} \right) \psi_1 \dots \psi_N \left| \sum_{i=1}^N \hat{h}(\mathbf{r}_i) \right| \left( \begin{array}{c} 1 - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \mathcal{P}_{i,j} \\ \text{+ (higher-order} \\ \text{permutations)} \end{array} \right) \psi_1 \dots \psi_N \right\rangle. \quad (1.56)
\end{aligned}$$

- Because a permutation always changes two orbitals, all the “cross-terms” (that is, all the integrals where the Hartree product on the left-hand-side and right-hand-side are not equal) are zero.
- There are  $N!$  different permutations: there are  $N$  ways to pick orbital for the first electron,  $N-1$  ways to pick the orbital for the second electron, .... and one way to pick the orbital for the  $N^{\text{th}}$  electron.
- Because the operator,  $\sum_{i=1}^N h(\mathbf{r}_i)$ , is totally symmetric, it is invariant to permutations of the electronic coordinates. Consequently, all  $N!$  of the non-vanishing integrals have the same value.
- The final result, then, is  $N!$  times the integral of *any* of the Hartree-products occurring in the Slater determinant. For simplicity, we take the first such product and use Eq. (1.44) to evaluate the integral, obtaining

$$\begin{aligned}
\left\langle \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^N \hat{h}(\mathbf{r}_i) \right| \psi_1 \psi_2 \dots \psi_N \right\rangle &= \frac{1}{N!} (N!) \left\langle \psi_1 \dots \psi_N \left| \sum_{i=1}^N \hat{h}(\mathbf{r}_i) \right| \psi_1 \dots \psi_N \right\rangle \\
&= \sum_{i=1}^N \left\langle \psi_i \left| \hat{h} \right| \psi_i \right\rangle \prod_{\substack{j=1 \\ j \neq i}}^N \langle \psi_j | \psi_j \rangle \\
&\stackrel{\text{normalized}}{\text{orbitals}} = \sum_{i=1}^N \left\langle \psi_i \left| \hat{h} \right| \psi_i \right\rangle. \quad (1.57)
\end{aligned}$$

The normalization integral can be evaluated as a special case of Eq. (1.57). In particular, take  $\hat{h}(\mathbf{r}) = \frac{1}{N}$ . Then:

$$\begin{aligned}
\langle \psi_1 \psi_2 \dots \psi_N | 1 | \psi_1 \psi_2 \dots \psi_N \rangle &= \left\langle \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^N \frac{1}{N} \right| \psi_1 \psi_2 \dots \psi_N \right\rangle \\
&= \frac{1}{N!} (N!) \left\langle \psi_1 \dots \psi_N \left| \sum_{i=1}^N \frac{1}{N} \right| \psi_1 \dots \psi_N \right\rangle \\
&= \sum_{i=1}^N \langle \psi_i | \frac{1}{N} | \psi_i \rangle \prod_{\substack{j=1 \\ j \neq i}}^N \langle \psi_j | \psi_j \rangle \\
&= \sum_{i=1}^N \frac{1}{N} \langle \psi_i | \psi_i \rangle \prod_{\substack{j=1 \\ j \neq i}}^N \langle \psi_j | \psi_j \rangle \\
&= \left( \sum_{i=1}^N \frac{1}{N} \right) \prod_{j=1}^N \langle \psi_j | \psi_j \rangle \\
&= 1 \cdot \prod_{\substack{j=1 \\ \text{normalized} \\ \text{orbitals}}}^N \langle \psi_j | \psi_j \rangle \\
&= 1
\end{aligned} \tag{1.58}$$

## IV. Two-Electron Integrals Between Slater Determinants

The analysis for the two-electron integrals is a bit more complicated. Again, we start with the example of a three-electron system. We have

$$\begin{aligned}
&\left\langle \psi_1 \psi_2 \psi_3 \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \psi_2 \psi_3 \right\rangle \\
&= \frac{1}{6} \left\langle \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \psi_1 \psi_2 \psi_3 \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \psi_1 \psi_2 \psi_3 \right\rangle
\end{aligned} \tag{1.59}$$

We expect, as before, that because  $\sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j)$  is invariant to permutations of the electronic coordinates, that there will be  $N! = 6$  terms that are identical.

This could be shown using methods similar to those employed for one-electron integrals, but let's use a different method. (In general, the more tools you know for doing this sort of integral, the better.) Let  $\hat{Q}(\mathbf{r}_1, \dots, \mathbf{r}_N)$  be the operator that represents any property of an electronic system. Because electrons are indistinguishable, they can be labeled in any order we choose, electronic operators cannot depend on the “order” in which we label the electrons. It follows that  $\hat{Q}(\mathbf{r}_1, \dots, \mathbf{r}_N)$  is *invariant* to permutations of the electrons. That is,

$$\hat{Q}(\dots \mathbf{r}_i \dots \mathbf{r}_j \dots) \equiv \hat{Q}(\dots \mathbf{r}_j \dots \mathbf{r}_i \dots) \tag{1.60}$$

Now let's evaluate the expectation value of  $\hat{Q}$  for a Slater determinant. For simplicity, consider the three electron case. Expanding the Slater determinant gives:<sup>2</sup>

$$\begin{aligned}
& \left\langle \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \middle| \psi_1\psi_2\psi_3 \right\rangle \hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \left| \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \right\rangle \psi_1\psi_2\psi_3 \rangle \\
&= \left\langle \begin{pmatrix} \psi_1\psi_2\psi_3 \middle| \hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \middle| \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \right\rangle \right\rangle \\
&\quad + \left\langle \begin{pmatrix} \psi_2\psi_1\psi_3 \middle| \hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \middle| \begin{pmatrix} -\mathcal{P}_{1,2} \\ +1 + \mathcal{P}_{1,2}\mathcal{P}_{1,3} + \mathcal{P}_{1,2}\mathcal{P}_{2,3} \\ -\mathcal{P}_{2,3} - \mathcal{P}_{1,3} \end{pmatrix} \right\rangle \right\rangle \\
&\quad + \left\langle \begin{pmatrix} \psi_3\psi_2\psi_1 \middle| \hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \middle| \begin{pmatrix} -\mathcal{P}_{1,3} \\ +\mathcal{P}_{1,3}\mathcal{P}_{1,2} + 1 + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \\ -\mathcal{P}_{2,3} - \mathcal{P}_{1,2} \end{pmatrix} \right\rangle \right\rangle \\
&\quad + \left\langle \begin{pmatrix} \psi_1\psi_3\psi_2 \middle| \hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \middle| \begin{pmatrix} -\mathcal{P}_{2,3} \\ +\mathcal{P}_{2,3}\mathcal{P}_{1,2} + \mathcal{P}_{2,3}\mathcal{P}_{1,3} + 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} \end{pmatrix} \right\rangle \right\rangle \\
&\quad + \left\langle \begin{pmatrix} \psi_2\psi_3\psi_1 \middle| \hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \middle| \begin{pmatrix} \mathcal{P}_{1,3}\mathcal{P}_{2,3} \\ -\mathcal{P}_{2,3} - \mathcal{P}_{1,2} - \mathcal{P}_{1,3} \\ +1 + \mathcal{P}_{1,2}\mathcal{P}_{2,3} \end{pmatrix} \right\rangle \right\rangle \\
&\quad + \left\langle \begin{pmatrix} \psi_3\psi_1\psi_2 \middle| \hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \middle| \begin{pmatrix} \mathcal{P}_{1,2}\mathcal{P}_{2,3} \\ -\mathcal{P}_{1,3} - \mathcal{P}_{2,3} - \mathcal{P}_{1,2} \\ +\mathcal{P}_{1,3}\mathcal{P}_{2,3} + 1 \end{pmatrix} \right\rangle \right\rangle
\end{aligned} \tag{1.61}$$

which shows that every term in the expansion has the same form—the only thing that has changed is that we have permuted the orbitals. However, because  $\hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$  is invariant to permutation of the electronic coordinates, all six terms in Eq. (1.61) must be equal.

This general scenario occurs for any number of electrons, and we write the general result as a theorem:

---

<sup>2</sup> If you don't understand where Eq. (1.61) comes from, evaluate the permutation operators and verify the result by comparing to the “long form” for the integral. Doing this will help you master the notation and, more importantly, the key ideas.

**Theorem 7.1:** Let  $|\psi_1 \dots \psi_N|$  be a Slater determinant and  $\hat{Q}(\mathbf{r}_1, \dots, \mathbf{r}_N)$  be an electronic operator. Then

$$\langle |\psi_1 \dots \psi_N| | \hat{Q} | |\psi_1 \dots \psi_N| \rangle = \sqrt{N!} \langle (\psi_1 \dots \psi_N | \hat{Q} | \psi_1 \dots \psi_N) \rangle \quad (1.62)$$

where  $(\psi_1 \dots \psi_N |$  is the Hartree product,

$$(\psi_1 \dots \psi_N | \equiv \psi_1^*(\mathbf{z}_1) \psi_2^*(\mathbf{z}_2) \dots \psi_N^*(\mathbf{z}_N). \quad (1.63)$$

Next, note that in the derivation of the preceding theorem we never used the fact that the orbitals in the “ket” Slater determinant were identical to those in the “bra” Slater determinant. It follows that we actually have the more general (and *very* useful) theorem,

**Theorem 2:** Let  $|\psi_1 \dots \psi_N|$  and  $|\psi'_1 \dots \psi'_N|$  be a Slater determinants and  $\hat{Q}(\mathbf{r}_1, \dots, \mathbf{r}_N)$  be an electronic operator. Then

$$\langle |\psi_1 \dots \psi_N| | \hat{Q} | |\psi'_1 \dots \psi'_N| \rangle = \sqrt{N!} \langle (\psi_1 \dots \psi_N | \hat{Q} | \psi'_1 \dots \psi'_N) \rangle \quad (1.64)$$

where  $(\psi_1 \dots \psi_N |$  is the Hartree product,

$$(\psi_1 \dots \psi_N | \equiv \psi_1^*(\mathbf{z}_1) \psi_2^*(\mathbf{z}_2) \dots \psi_N^*(\mathbf{z}_N). \quad (1.65)$$

Returning to the two-electron case, we can use Theorem 1 to evaluate

$$\begin{aligned} & \left\langle |\psi_1 \psi_2 \psi_3| \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| |\psi_1 \psi_2 \psi_3| \right\rangle \\ &= \sqrt{6} \left\langle (\psi_1 \psi_2 \psi_3 | \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| |\psi_1 \psi_2 \psi_3) \right\rangle \\ &= \frac{\sqrt{6}}{\sqrt{6}} \left\langle (\psi_1 \psi_2 \psi_3 | \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} |\psi_1 \psi_2 \psi_3) \right\rangle \\ &= \left[ \left\langle (\psi_1 \psi_2 \psi_3 | \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| |\psi_1 \psi_2 \psi_3) \right\rangle - \left\langle (\psi_1 \psi_2 \psi_3 | \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| |\psi_2 \psi_1 \psi_3) \right\rangle \right. \\ &\quad \left. - \left\langle (\psi_1 \psi_2 \psi_3 | \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| |\psi_3 \psi_2 \psi_1) \right\rangle - \left\langle (\psi_1 \psi_2 \psi_3 | \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| |\psi_1 \psi_3 \psi_2) \right\rangle \right. \\ &\quad \left. + \left\langle (\psi_1 \psi_2 \psi_3 | \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| |\psi_2 \psi_3 \psi_1) \right\rangle + \left\langle (\psi_1 \psi_2 \psi_3 | \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| |\psi_3 \psi_1 \psi_2) \right\rangle \right] \quad (1.66) \end{aligned}$$

The first term contains two identical Hartree products, the second three terms contain Hartree products have two different orbitals, and the last two terms have Hartree-products that differ in more than two orbitals. Using the rules in the Table, then, we have that

$$\begin{aligned}
& \left\langle \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \\
&= \left( \begin{aligned} & \sum_{i=1}^2 \sum_{j=i+1}^3 \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle \\ & - \langle \psi_1 \psi_2 | \hat{v}_{ee} | \psi_2 \psi_1 \rangle - \langle \psi_1 \psi_3 | \hat{v}_{ee} | \psi_3 \psi_1 \rangle - \langle \psi_2 \psi_3 | \hat{v}_{ee} | \psi_3 \psi_2 \rangle \\ & + 0 + 0 \end{aligned} \right) \tag{1.67} \\
&= \sum_{i=1}^2 \sum_{j=i+1}^3 \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \sum_{i=1}^2 \sum_{j=i+1}^3 \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle \\
&= \sum_{i=1}^2 \sum_{j=i+1}^3 \left( \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle \right)
\end{aligned}$$

After understanding this derivation, we can proceed to the general case. Namely,

$$\begin{aligned}
& \left\langle \left| \psi_1 \psi_2 \dots \psi_N \right| \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \left| \psi_1 \psi_2 \dots \psi_N \right| \right\rangle \\
& \stackrel{Th. 1}{=} \left\langle \left( \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \psi_2 \dots \psi_N \right) \right\rangle \\
& = \left\langle \left( \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \left( 1 - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \mathcal{P}_{i,j} \right. \right. \right. \\
& \quad \left. \left. \left. + \begin{pmatrix} \text{higher-order} \\ \text{permutations} \end{pmatrix} \right) \psi_1 \dots \psi_N \right) \right\rangle \\
& = \left\langle \left( \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_N \right) \right\rangle \\
& \quad + \left\langle \left( \psi_1 \psi_2 \dots \psi_N \left| \sum_{A=1}^{N-1} \sum_{B=A+1}^N \hat{v}_{ee}(\mathbf{r}_A, \mathbf{r}_B) \right| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \mathcal{P}_{i,j} \right| \psi_1 \dots \psi_N \right) \right\rangle \\
& \quad + \left\langle \left( \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \begin{pmatrix} \text{higher-order} \\ \text{permutations} \end{pmatrix} \right| \psi_1 \dots \psi_N \right) \right\rangle \\
& = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle \prod_{\substack{k=1 \\ k \neq i,j}}^N \langle \psi_k | \psi_k \rangle \\
& \quad - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left\langle \left( \psi_1 \psi_2 \dots \psi_N \left| \sum_{A=1}^{N-1} \sum_{B=A+1}^N \hat{v}_{ee}(\mathbf{r}_A, \mathbf{r}_B) \right| \mathcal{P}_{i,j} \right| \psi_1 \dots \psi_N \right) \right\rangle \prod_{\substack{k=1 \\ k \neq i,j}}^N \langle \psi_k | \psi_k \rangle \\
& \quad + 0 \\
& = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle \prod_{\substack{k=1 \\ k \neq i,j}}^N \langle \psi_k | \psi_k \rangle - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle \prod_{\substack{k=1 \\ k \neq i,j}}^N \langle \psi_k | \psi_k \rangle \\
& = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left[ \left( \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle \right) \prod_{\substack{k=1 \\ k \neq i,j}}^N \langle \psi_k | \psi_k \rangle \right]
\end{aligned} \tag{1.68}$$

## V. The Energy of a Slater Determinant.

We now have all the tools we require to evaluate the energy of a Slater determinant.

We have that,

$$\begin{aligned}
E_{Sl}[\Phi] & \equiv \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \\
& = \frac{\left\langle \left| \psi_1 \dots \psi_N \right| \left| \sum_{i=1}^N h(\mathbf{r}_i) \right| \left| \psi_1 \dots \psi_N \right| \right\rangle + \left\langle \left| \psi_1 \dots \psi_N \right| \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \left| \psi_1 \dots \psi_N \right| \right\rangle}{\langle \psi_1 \dots \psi_N | \psi_1 \dots \psi_N \rangle}
\end{aligned} \tag{1.69}$$

and, substituting in the results from Eqs. (1.57), (1.58), and (1.68)

$$\begin{aligned}
E_{Sl}[\Phi] &= \frac{\left( \sum_{i=1}^N \langle \psi_i | \hat{h} | \psi_i \rangle \prod_{\substack{k=1 \\ k \neq i}}^N \langle \psi_k | \psi_k \rangle \right. \\
&\quad \left. + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left[ \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle \right] \prod_{\substack{k=1 \\ k \neq i, j}}^N \langle \psi_k | \psi_k \rangle \right) \\
&\quad \prod_{k=1}^N \langle \psi_k | \psi_k \rangle} \\
&= \left( \sum_{i=1}^N \frac{\langle \psi_i | \hat{h} | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left( \frac{\langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_j | \psi_j \rangle} \right) \right)
\end{aligned} \tag{1.70}$$

If the orbitals are not only orthogonal, but normalized, then we have

$$E_{Sl}[\Phi] = \sum_{i=1}^N \langle \psi_i | \hat{h} | \psi_i \rangle + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left( \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle \right). \tag{1.71}$$

For convenience, we introduce notation for the one-electron integrals,

$$\begin{aligned}
h_i &\equiv \langle \psi_i | \hat{h} | \psi_i \rangle \\
&= \left\langle \psi_i \left| -\frac{\nabla_i^2}{2} + v(\mathbf{r}_i) \right| \psi_i \right\rangle \\
&= \int \psi_i^*(\mathbf{r}) \left( -\frac{\nabla^2}{2} + v(\mathbf{r}) \right) \psi_i(\mathbf{r}) d\mathbf{r}
\end{aligned} \tag{1.72}$$

and two-electron integrals, which we name the *Coulomb integrals*,

$$\begin{aligned}
J_{ij} &\equiv \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle \\
&= \iint \frac{\psi_i^*(\mathbf{z}_i) \psi_j^*(\mathbf{z}_j) \psi_i(\mathbf{z}_i) \psi_j(\mathbf{z}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{z}_i d\mathbf{z}_j
\end{aligned} \tag{1.73}$$

and the *exchange integrals*,

$$\begin{aligned}
K_{ij} &\equiv \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle \\
&= \iint \frac{\psi_i^*(\mathbf{z}_i) \psi_j^*(\mathbf{z}_j) \psi_j(\mathbf{z}_i) \psi_i(\mathbf{z}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{z}_i d\mathbf{z}_j
\end{aligned} \tag{1.74}$$

The above formulae are all correct when the orbitals are real (which is the usual case), and when the orbitals are complex the only change is that the exchange integral should be replaced by

$$K_{ij} \xrightarrow{\text{complex orbitals}} \frac{K_{ij} + K_{ji}}{2}. \tag{1.75}$$

We will assume the orbitals are real in all subsequent work, but by making the change in Eq. (1.75), the following treatment is easily generalized.

It is helpful to reverse the notational change in Eq. **Error! Reference source not found.** and show the spin coordinates of the orbitals explicitly. Denoting the spin of electron  $i$  when it is in the spin-orbital  $\psi_k(\mathbf{z})$  as  $\sigma_k(i)$ , we have

$$\begin{aligned}
J_{ij} &= \iint \frac{\psi_i^*(\mathbf{z}_i)\psi_j^*(\mathbf{z}_j)\psi_i(\mathbf{z}_i)\psi_j(\mathbf{z}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{z}_i d\mathbf{z}_j \\
&= \iint \frac{\psi_i^*(\mathbf{r}_i)\psi_j^*(\mathbf{r}_j)\psi_i(\mathbf{r}_i)\psi_j(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_i d\mathbf{r}_j \cdot \langle \sigma_i(i) \sigma_j(j) | \sigma_i(i) \sigma_j(j) \rangle \\
&= \iint \frac{\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r})\psi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \cdot \langle \sigma_i | \sigma_i \rangle \langle \sigma_j | \sigma_j \rangle \\
&= \iint \frac{|\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'
\end{aligned} \tag{1.76}$$

which reveals that the  $J_{ij}$  is the classical Coulomb repulsion energy between two charge distributions: one due to the electron in  $\psi_i(\mathbf{r})$  one from the electron in  $\psi_j(\mathbf{r})$ . Because this is a classical electrostatic interaction, there is no dependence on the spin. In addition, we note that

$$J_{ij} = J_{ji} \tag{1.77}$$

This allows us to rewrite the sum of the Coulomb integrals,<sup>3</sup>

---

<sup>3</sup> This sort of analysis is typical of the sort of “index games” we play in quantum chemistry. Here, because  $J_{ij} = J_{ji}$ , we can calculate the Coulomb energy by evaluating the Coulomb repulsion between orbital  $i$  and orbital  $j$  when  $i < j$  or, equivalently, evaluate the interactions between orbitals  $i$  and  $j$  when  $i > j$ . We can even, as we do here, take the sum of both possibilities and divide by two (since we have counted the “interaction” between the orbitals twice. Indeed, we would have obtained the “symmetric” formula if we had used the “symmetric” for the electron-electron repulsion operator, that is, used

$$\hat{V}_{ee} \equiv \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

instead of

$$\hat{V}_{ee} \equiv \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}.$$



$$\begin{aligned}
\sum_{1 \leq i < j}^N J_{ij} &= \sum_{i=1}^{N-1} \sum_{j=i+1}^N J_{ij} \\
&= \sum_{i=1}^{N-1} \sum_{j=i+1}^N J_{ji} \\
&= \sum_{j=1}^N \sum_{i=1}^{j-1} J_{ji} \\
&= \sum_{i=2}^N \sum_{j=1}^{i-1} J_{ij} \\
&= \sum_{i > j > 1}^N J_{ij}
\end{aligned} \tag{1.78}$$

which allows us to write

$$\sum_{i=1}^{N-1} \sum_{j=i+1}^N J_{ij} = \sum_{i=2}^N \sum_{j=1}^{i-1} J_{ij} = \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N J_{ij} . \tag{1.79}$$

The analysis for the exchange integrals is similar. Analogous to Eq. (1.76) we have (assuming real orbitals)

$$\begin{aligned}
K_{ij} &= \iint \frac{\psi_i(\mathbf{z}_i) \psi_j(\mathbf{z}_j) \psi_j(\mathbf{z}_i) \psi_i(\mathbf{z}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{z}_i d\mathbf{z}_j \\
&= \iint \frac{\psi_i(\mathbf{r}_i) \psi_j(\mathbf{r}_j) \psi_j(\mathbf{r}_i) \psi_i(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_i d\mathbf{r}_j \cdot \langle \sigma_i(i) \sigma_j(j) | \sigma_j(i) \sigma_i(j) \rangle \\
&= \iint \frac{\psi_i(\mathbf{r}) \psi_j(\mathbf{r}') \psi_j(\mathbf{r}) \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \cdot \langle \sigma_i | \sigma_j \rangle \langle \sigma_j | \sigma_i \rangle \\
&= \delta_{\sigma_j \sigma_i} \iint \frac{(\psi_i(\mathbf{r}) \psi_j(\mathbf{r})) (\psi_j(\mathbf{r}') \psi_i(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'
\end{aligned} \tag{1.80}$$

Unlike the Coulomb integral, the exchange integral does depend on the spins and, in particular, is zero unless the orbitals,  $\psi_i(\mathbf{z})$  and  $\psi_j(\mathbf{z})$ , have the same spin. Just like Eq. (1.77)

$$K_{ij} = K_{ji} \tag{1.81}$$

and, tracing through the analysis in Eq. (1.78) with  $K_{ij}$  replacing  $J_{ij}$ , we find that we can again write

$$\underbrace{\sum_{i=1}^{N-1} \sum_{j=i+1}^N K_{ij}}_{i < j \text{ form}} = \underbrace{\sum_{i=2}^N \sum_{j=1}^{i-1} K_{ij}}_{i > j \text{ form}} = \underbrace{\frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N K_{ij}}_{i \neq j \text{ form}} \tag{1.82}$$

and if we recognize that

$$K_{ii} = J_{ii} \tag{1.83}$$

we can write the energy expression for a Slater determinant, (1.71), as

$$\begin{aligned}
E_{Sl}[\Phi] &\equiv \left\langle \psi_1 \dots \psi_N \left| \hat{H} \right| \psi_1 \dots \psi_N \right\rangle \\
&= \sum_{i=1}^N h_i + \sum_{i=1}^{N-1} \sum_{j=i+1}^N (J_{ij} - K_{ij}) \\
&= \sum_{i=1}^N h_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) \\
&= \sum_{i=1}^N \left( h_i + \frac{1}{2} \sum_{j=1}^N (J_{ij} - K_{ij}) \right).
\end{aligned} \tag{1.84}$$

The Coulomb integrals are always positive, as is clear because the integrand is always positive. The integrand in the exchange integrals is not always positive, but the exchange integrals are still positive whenever the orbitals therein have the same spin. On a mathematical level, this is because  $\iint d\mathbf{r} d\mathbf{r}' \left[ \frac{1}{|\mathbf{r}-\mathbf{r}'|} \times \right]$  is a positive-definite integral operator (often we just say that  $\frac{1}{|\mathbf{r}-\mathbf{r}'|}$  is a positive-definite “kernel”), and so

$$\iint f(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} f(\mathbf{r}') d\mathbf{r} d\mathbf{r}' > 0 \tag{1.85}$$

(provided  $f(\mathbf{r}) \neq 0$ ) for just the same reason that, for any positive definite matrix,  $P$ ,

$$\mathbf{x}^T P \mathbf{x} > 0 \tag{1.86}$$

for any non-zero vector  $\mathbf{x}$ . (There is also a proof using Poisson’s equation<sup>4</sup> and Green’s first identity.) Intuitively, the exchange integral,  $K_{ij}$ , is positive because it is the Coulomb interaction energy between a charge distribution,  $\psi_i(\mathbf{r})\psi_j(\mathbf{r})$ , and itself. Rewriting the exchange integral using the substitution  $\mathbf{x} = \mathbf{r}' - \mathbf{r}$ , we have

$$K_{ij} = \delta_{\sigma_j \sigma_i} \iint \frac{(\psi_i(\mathbf{r})\psi_j(\mathbf{r}))(\psi_j(\mathbf{r}+\mathbf{x})\psi_i(\mathbf{r}+\mathbf{x}))}{|\mathbf{x}|} d\mathbf{r} d\mathbf{x} \tag{1.87}$$

For small  $x \equiv |\mathbf{x}|$ , we see that the integrand will tend to be large (the denominator is small) and positive,<sup>5</sup> since  $\psi_i(\mathbf{r})\psi_j(\mathbf{r})$  and  $\psi_i(\mathbf{r}+\mathbf{x})\psi_j(\mathbf{r}+\mathbf{x})$  will tend to have the same sign for small  $x$ . For larger interelectron distances,  $x$ , it is possible to have a favorable interaction between the charge distribution (the integrand can be negative), but this is mitigated by the fact the denominator is larger. That is, a charge distribution is most sensitive, owing to the  $\frac{1}{r}$  nature of the Coulomb force, to what is happening “nearby”, and for the interaction of a

---

<sup>4</sup> Poisson’s equation indicates that for any well-behaved charge density,  $q(\mathbf{r})$ ,

$$\nabla^2 \left( \int \frac{q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \right) = -4\pi q(\mathbf{r}).$$

<sup>5</sup> Remember that the interaction energy is positive (unfavorable/repulsive) for “like charges” and negative (favorable/attractive) for unlike charges,

charge distribution with itself, this is always “unfavorable”, resulting in a repulsive interaction.

The magnitude of the exchange-integral is smaller than that of the associated Coulomb integral, and so

$$J_{ij} - K_{ij} > 0 \quad (1.88)$$

for all  $i$  and  $j$ . Equation (1.88) is plausible because  $J_{ij}$  represents the interaction between two distributions with unit charge (because  $\int |\psi_i(\mathbf{r})|^2 d\mathbf{r} = \int |\psi_j(\mathbf{r})|^2 d\mathbf{r} = 1$ ), while  $K_{ij}$  represents the interaction between two distributions with zero charge (because  $\int \psi_i(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} = 0$ ).

To prove Eq. (1.88), we start by noting that.

$$\iint \frac{|\psi_i(\mathbf{r})\psi_j(\mathbf{r}')| |\psi_i(\mathbf{r}')\psi_j(\mathbf{r})|}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' > \iint \frac{\psi_i(\mathbf{r})\psi_j(\mathbf{r})\psi_i(\mathbf{r}')\psi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \equiv K_{ij} \quad (1.89)$$

To derive Eq. (1.89), use the fact that  $|x| \geq x$ , with the equality holding only for non-negative numbers,  $x$ . (The inequality is strict because the spatial portions of orbitals with the same spin must be orthogonal,  $\int \psi_i(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} = 0$ , which implies that  $\psi_i(\mathbf{r}) \psi_j(\mathbf{r})$  will not be positive for all choices of  $\mathbf{r}$  and  $\mathbf{r}'$ .) Next, we use the Cauchy inequality,<sup>6</sup>

$$2|x||y| \leq x^2 + y^2, \quad (1.90)$$

to obtain

$$\begin{aligned} 2K_{ij} &< 2 \iint \frac{|\psi_i(\mathbf{r})\psi_j(\mathbf{r}')| |\psi_i(\mathbf{r}')\psi_j(\mathbf{r})|}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &< \iint \frac{|\psi_i(\mathbf{r})\psi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \iint \frac{|\psi_i(\mathbf{r}')\psi_j(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &< \iint \frac{|\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \iint \frac{|\psi_i(\mathbf{r}')|^2 |\psi_j(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &< J_{ij} + J_{ji} \\ &< 2J_{ij}. \end{aligned} \quad (1.91)$$

For molecules composed of “light” atoms (H-Ar), the exchange integrals tend to be, on average, about an order of magnitude smaller than the Coulomb integrals.

We conclude this section by briefly discussing the energy formula for the Slater determinant, Eq. (1.84), which we repeat for convenience.

---

<sup>6</sup> The Cauchy inequality just says that the “cross-term” in  $(x+y)^2$  is less than the sum of the “direct terms.” It is most easily proved using polar coordinates. Then

$$2xy = 2r^2 \cos(\theta) \sin(\theta) = r^2 \sin(2\theta) \leq r^2 |\sin(2\theta)| = 2|x||y| \leq r^2 = x^2 + y^2.$$

$$\begin{aligned}
E_{sl}[\Phi] &\equiv \left\langle |\psi_1 \dots \psi_N| \left| \hat{H} \right| |\psi_1 \dots \psi_N| \right\rangle \\
&= \sum_{i=1}^N \left( h_i + \frac{1}{2} \sum_{j=1}^N (J_{ij} - K_{ij}) \right).
\end{aligned} \tag{1.92}$$

The energy of a Slater determinant, then, consists of

- The sum of the kinetic energy and electron-nuclear attraction energies for each orbital,  $h_i$ .
- The Coulomb repulsion,  $J_{ij}$ , between each orbital,  $\psi_i(\mathbf{z})$  and every other orbital. Note that  $J_{ij} = J_{ji}$ .
- An “exchange energy” that diminishes the Coulomb repulsion between orbitals with the same spin. However, because  $K_{ij} = 0$  if the spins of orbitals  $\psi_i(\mathbf{z})$  and  $\psi_j(\mathbf{z})$ ,  $\sigma_i$  and  $\sigma_j$ , are different, there is no exchange effect when electrons have opposite spin. This provides further evidence for the fact “exchange” measures the energetic effects of the Pauli exclusion principle. In addition,  $K_{ij} < J_{ij}$  in all cases, so the Pauli exclusion principle never completely “cancels out” the Coulomb repulsion between electrons. The exchange is an energetically important effect however, lowering the energy by approximately 10 eV per electron pair (for molecules formed with atoms from the first row of the periodic table).

## VI. Digression on the Calculus of Variations

Recall that the Hartree-Fock method is obtained by finding the Slater determinant of orbitals with the lowest energy, Eq. **Error! Reference source not found.** This requires that one be able to determine how the energy changes as the orbitals change, so that we can construct a method for revising the orbitals from an initial “guess” approximation towards the exact answer.

As motivation for the approach we shall take, consider the similar problem of minimizing a function,  $f(\mathbf{x})$ , where  $\mathbf{x} = \begin{bmatrix} x_1 & x_2 & \dots & x_d \end{bmatrix}^T$  is a  $d$ -dimensional vector. Given an initial guess for the minimizing value of  $\mathbf{x}$ , which we call  $\tilde{\mathbf{x}}$ , the minimum value of the function can be found by computing the gradient of the function at the point  $\tilde{\mathbf{x}}$ ,  $\nabla f(\tilde{\mathbf{x}})$ , and moving in the direction of decrease, changing  $\tilde{\mathbf{x}}$  to  $\tilde{\mathbf{x}} - \varepsilon \nabla f(\tilde{\mathbf{x}})$  ( $\varepsilon > 0$ ), until the minimum is found. Alternatively, if the function is *convex*,<sup>7</sup> so that there is only one place

---

<sup>7</sup> A function is convex if, for any points  $\mathbf{x}$  and  $\mathbf{y}$  and any value  $0 \leq t \leq 1$ , then

where  $\nabla f(\tilde{\mathbf{x}}) = 0$ , then, instead of minimizing the function  $f(\mathbf{x})$ , we can solve for the point,  $\mathbf{x}_{\min}$ , where

$$\nabla f(\mathbf{x}_{\min}) = 0. \quad (1.93)$$

This suggests that, in order to find the optimum Slater determinant, we need a way to generalize the concept of a derivative from functions whose arguments are variables, like  $f(\mathbf{x})$ , to functions whose arguments are other functions, like the energy of a Slater determinant, (we revise (1.70) in accord with Eqs. (1.79) and (1.82)),

$$E_{sl}[\Phi] = \left[ \sum_{i=1}^N \frac{\langle \psi_i | \hat{h} | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left( \frac{\langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_j | \psi_j \rangle} \right) \right]. \quad (1.94)$$

Some nomenclature: A function of a function is called a *functional*, and its argument is enclosed in brackets (instead of parentheses). When a functional is a function of both functions and variables, the arguments are traditionally separated by a semicolon, with the functions listed first. E.g.,  $F[f; \mathbf{x}]$  is a functional of  $f(\mathbf{x})$  and a function of  $\mathbf{x}$ . Often the arguments of functionals are omitted when they are clear from context, just as we often just write the wave function as  $\Psi$ , conveniently “forgetting” to write out its dependence on the spatial and spin coordinates of the electrons.

The *functional derivative* describes how a functional changes when the functions on which it depends change, just as the usual derivative describes how a function changes when the variables on which it depends changes. Suppose we change the argument of a function from  $\mathbf{x}$  to  $\mathbf{x} + d\mathbf{x}$ . Then the value of the function changes according to

$$\begin{aligned} df &\equiv f(\mathbf{x} + d\mathbf{x}) - f(\mathbf{x}) \\ &= \nabla f(\mathbf{x}) \cdot d\mathbf{x} + \mathcal{O}(d\mathbf{x} \cdot d\mathbf{x}) \\ &= \sum_{i=1}^d \frac{\partial f(\mathbf{x})}{\partial x_i} dx_i + \mathcal{O}\left(\sum_{i=1}^d (dx_i)^2\right) \end{aligned} \quad (1.95)$$

where the first line is the definition of the derivative—the derivative maps changes in  $\mathbf{x}$  to changes in  $f(\mathbf{x})$  with errors proportional to the magnitude of the change squared (for small

$$tf(\mathbf{x}) + (1-t)f(\mathbf{y}) > f(t\mathbf{x} + (1-t)\mathbf{y}).$$

A convex function looks (very roughly) like a bowl, with a single minimum at the “bottom” of the bowl. This is the generalization of the criterion that the second derivative must be positive at a minimum, as is apparent from the fact the formula for the second derivative

$$\frac{d^2 f}{dx^2} = \lim_{h \rightarrow 0} \frac{f(r-h) + f(r+h) - 2f(r)}{h^2} > 0$$

has the same form as the convexity condition. (Take  $x = r - h$ ,  $y = r + h$ , and  $t = \frac{1}{2}$ .)

changes). The second line uses the definition of the dot product, and the notation  $\mathcal{O}(d\mathbf{x} \cdot d\mathbf{x})$  indicates that the formula is exact, except for errors proportional to  $d\mathbf{x} \cdot d\mathbf{x}$ .

The formula for the functional derivative is similar. Changing the argument of the functional,  $Q[f]$ , from  $f(\mathbf{r})$  to  $f(\mathbf{r}) + \delta f(\mathbf{r})$  gives

$$Q[f + \delta f] - Q[f] = \int \frac{\delta Q[f]}{\delta f(\mathbf{r})} \delta f(\mathbf{r}) d\mathbf{r} + \left( \begin{array}{l} \text{errors of proportional} \\ \text{to the size of } (\delta f(\mathbf{r}))^2 \end{array} \right), \quad (1.96)$$

and the functional derivative,  $\frac{\delta Q[f]}{\delta f(\mathbf{r})}$ , is defined as the function that maps changes in  $f(\mathbf{r})$  to changes in  $Q[f]$  according to Eq. (1.96), with the remaining error being proportional to the square of the size of the change in the function,  $\|\delta f(\mathbf{r})\|^2$ . The similarity between the functional derivative and the gradient is striking: just as there are multiple terms in the sum in (1.95) because it is possible to change  $\mathbf{x}$  in different “directions”, so also it is possible to change a function at many different “points”, and so we must integrate over all the possible places the function might change, as in Eq. (1.96).<sup>8</sup>

From this argument, we suspect that if we change the function at only one point in space, then we will obtain a “direct” formula for the functional derivative, just as when we change a function  $f(\mathbf{x})$ , in only one direction,  $x_i$ , we obtain a more conventional form for the usual derivative ( $\nabla f \cdot d\mathbf{x} \rightarrow \frac{df}{dx_i} dx_i$ ). To this end, consider the case where

$$\delta f(\mathbf{r}) = \varepsilon \delta(\mathbf{r} - \mathbf{x}). \quad (1.97)$$

Substituting Eq. (1.97) into Eq. (1.96), we find that

---

<sup>8</sup> The similarity is even more striking if you remember the Riemann sum definition of the integral, whereby we can write

$$Q[f + \delta f] - Q[f] \approx \lim_{N \rightarrow \infty} \left[ \sum_{i=0}^N \left( \frac{\delta Q[f]}{\delta f\left(a + i \frac{(b-a)}{N}\right)} \delta f\left(a + i \frac{(b-a)}{N}\right) \right) \left( \frac{(b-a)}{N} \right) \right] \equiv \int_a^b \frac{\delta Q[f]}{\delta f(x)} \delta f(x) dx$$

$$\begin{aligned}
Q[f + \varepsilon \delta(\mathbf{r} - \mathbf{x})] - Q[f] &= \int \frac{\delta Q}{\delta f(\mathbf{r})} \varepsilon \delta(\mathbf{r} - \mathbf{x}) d\mathbf{r} + \left( \begin{array}{l} \text{errors proportional} \\ \text{to } \varepsilon^2 \end{array} \right) \\
Q[f + \varepsilon \delta(\mathbf{r} - \mathbf{x})] - Q[f] &= \varepsilon \frac{\delta Q}{\delta f(\mathbf{x})} + \left( \begin{array}{l} \text{errors proportional} \\ \text{to } \varepsilon^2 \end{array} \right) \\
\frac{Q[f + \varepsilon \delta(\mathbf{r} - \mathbf{x})] - Q[f]}{\varepsilon} &= \frac{\delta Q[f]}{\delta f(\mathbf{x})} + \left( \begin{array}{l} \text{errors} \\ \text{proportional} \\ \text{to } \varepsilon \end{array} \right) \\
\lim_{\varepsilon \rightarrow 0} \frac{Q[f(\mathbf{r}) + \varepsilon \delta(\mathbf{r} - \mathbf{x})] - Q[f]}{\varepsilon} &= \frac{\delta Q[f]}{\delta f(\mathbf{x})} + 0 \\
\left( \frac{\partial Q[f(\mathbf{r}) + \varepsilon \delta(\mathbf{r} - \mathbf{x})]}{\partial \varepsilon} \right)_{\varepsilon=0} &= \frac{\delta Q[f]}{\delta f(\mathbf{x})}.
\end{aligned} \tag{1.98}$$

Equation (1.98) is a key formula,<sup>9</sup> and is very useful for evaluating functional derivatives.

Another method for evaluating functional derivatives is to use the definition, Eq. (1.96), directly. Take the difference between  $Q[f + \delta f]$  and  $Q[f]$  and find the coefficient of  $\delta f(\mathbf{r})$  in the expression

$$Q[f + \delta f] - Q[f] = \int q(\mathbf{r}) \delta f(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint q^{(2)}(\mathbf{r}, \mathbf{r}') \delta f(\mathbf{r}) \delta f(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \dots \tag{1.99}$$

Then, from Eq. (1.96), we have that  $q(\mathbf{r}) = \frac{\delta Q[f]}{\delta f(\mathbf{r})}$ . Incidentally,  $q^{(2)}(\mathbf{r}, \mathbf{r}')$  is the second functional derivative,  $\frac{\delta^2 Q[f]}{\delta f(\mathbf{r}) \delta f(\mathbf{r}')} = \frac{\delta}{\delta f(\mathbf{r}')} \left( \frac{\delta Q[f]}{\delta f(\mathbf{r})} \right)$ . (In fact, Eq. (1.99) is analogous to the Taylor series for functions,

$$f(\mathbf{x} + d\mathbf{x}) - f(\mathbf{x}) = \nabla f(\mathbf{x}) \cdot d\mathbf{x} + \frac{1}{2} d\mathbf{x} \cdot (\nabla \nabla f(\mathbf{x})) \cdot d\mathbf{x} + \dots \tag{1.100}$$

Finally, there is a useful identity that I call the Gelfand-Fomin identity, which states that for a functional that can be written as an integral of a functional,  $\mathcal{F}$ , which is a simple function of  $f(x)$ ,  $\frac{df}{dx}$ ,  $\frac{d^2 f(x)}{dx^2}$ , etc.,

---

<sup>9</sup> The last line in Eq. (1.98) uses a somewhat non-standard definition of the derivative. It is equivalent to the usual definition. In particular, from the “usual” definition of the derivative we have

$$\begin{aligned}
\lim_{\varepsilon \rightarrow 0} \frac{f(x+\varepsilon h) - f(\varepsilon)}{\varepsilon} &= \lim_{\varepsilon h \rightarrow 0} \frac{f(x+\varepsilon h) - f(\varepsilon)}{\varepsilon} \\
&= \lim_{\varepsilon h \rightarrow 0} \frac{f(x+\varepsilon h) - f(\varepsilon)}{\varepsilon} \left( \frac{h}{h} \right) \\
&= h \lim_{\varepsilon h \rightarrow 0} \frac{f(x+\varepsilon h) - f(\varepsilon)}{\varepsilon h} \\
&= h \left. \frac{df(y)}{dy} \right|_{y=x}.
\end{aligned}$$

and from the “special” definition we have

$$\left. \frac{df(x+\varepsilon h)}{d\varepsilon} \right|_{\varepsilon=0} = \left. \frac{df(x+\varepsilon h)}{d(x+\varepsilon h)} \frac{d(x+\varepsilon h)}{d\varepsilon} \right|_{\varepsilon=0} = \left. \frac{df(x+\varepsilon h)}{d(x+\varepsilon h)} h \right|_{\varepsilon=0} = h \left. \frac{df(y)}{dy} \right|_{y=x}.$$

$$F[f] \equiv \int \mathcal{F}\left(f, \frac{df}{dx}, \frac{d^2f}{dx^2} \dots\right) dx \quad (1.101)$$

that

$$\frac{\delta F[f]}{\delta f(x)} = \frac{\partial \mathcal{F}\left[f, \frac{df}{dx}, \frac{d^2f}{dx^2}, \dots\right]}{\partial f(x)} - \frac{d}{dx} \left( \frac{\partial \mathcal{F}\left[f, \frac{df}{dx}, \frac{d^2f}{dx^2}, \dots\right]}{\partial \left(\frac{df}{dx}\right)} \right) + \frac{d^2}{dx^2} \left( \frac{\partial \mathcal{F}\left[f, \frac{df}{dx}, \frac{d^2f}{dx^2}, \dots\right]}{\partial \left(\frac{d^2f}{dx^2}\right)} \right) - \dots \quad (1.102)$$

Equation (1.102) is derived using integration by parts.

From any of these methods, it is easy to derive a number of useful results, chief among them the

- sum rule. The functional derivative of a sum is the sum of the functional derivatives,

$$\frac{\delta F[f] + G[f]}{\delta f(x)} = \frac{\delta F[f]}{\delta f(x)} + \frac{\delta G[f]}{\delta f(x)} \quad (1.103)$$

- product rule. The functional derivative of a product is given by the formula

$$\frac{\delta F[f] G[f]}{\delta f(x)} = F[f] \frac{\delta G[f]}{\delta f(x)} + G[f] \frac{\delta F[f]}{\delta f(x)} \quad (1.104)$$

- chain rules. If  $F$  is a functional of  $g(x)$ , which is a functional of  $f(x)$ , then

$$\frac{\delta F[g(f(x))]}{\delta f(x)} = \int \frac{\delta F}{\delta g(x')} \frac{\delta g(x')}{\delta f(x)} dx' \quad (1.105)$$

- If  $F$  is a function of  $G$ , which is a functional of  $f(x)$ , then

$$\frac{\delta F[G[f]]}{\delta f(x)} = \frac{dF}{dG} \frac{\delta G[f]}{\delta f(x)} \quad (1.106)$$

- If  $F$  is a functional of  $f(y)$ , and  $y$  is a function of  $x$ , then

$$\frac{\delta F[f]}{\delta f(y(x))} = \frac{\delta F}{\delta f(y)} \frac{dy}{dx}. \quad (1.107)$$

Each of these results resembles the usual results for “normal” derivatives, as should be expected from the “normal derivative” expression for the functional derivative, Eq. (1.98).

. In particular, remember that the chain rule for a function depending on several variables—say, the Gibb’s free energy as a function of  $T$  and  $P$ , is

$$\frac{\partial G}{\partial V} = \frac{\partial G}{\partial T} \cdot \frac{\partial T}{\partial V} + \frac{\partial G}{\partial P} \cdot \frac{\partial P}{\partial V} \quad (1.108)$$

and, in the general case,

$$\frac{\partial G(\mathbf{x})}{dy} = \sum_{i=1}^d \frac{\partial G}{\partial x_i} \frac{dx_i}{dy}. \quad (1.109)$$



The sums in Eqs. (1.108) and (1.109) (which are just “dot products”) are directly analogous (if you use the Riemann sum again) to the integral in chain rule for the functional derivative, Eq. (1.105).

These concepts are most easily demonstrated using examples. For example, choosing

$$F[f] \equiv \int (f(\mathbf{x}))^k d\mathbf{x}, \quad (1.110)$$

we can use the technique based on Eq. (1.99) to obtain

$$\begin{aligned} F[f + \delta f] - F[f] &= \int (f(\mathbf{x}) + \delta f(\mathbf{x}))^k d\mathbf{x} - \int (f(\mathbf{x}))^k d\mathbf{x} \\ &= \int (f(\mathbf{x}))^k + k(f(\mathbf{x}))^{k-1} \delta f(\mathbf{x}) + \frac{k(k-1)}{2} (f(\mathbf{x}))^{k-2} (\delta f(\mathbf{x}))^2 + \dots d\mathbf{x} - \int (f(\mathbf{x}))^k d\mathbf{x} \\ &= \int k(f(\mathbf{x}))^{k-1} \delta f(\mathbf{x}) + \frac{k(k-1)}{2} (f(\mathbf{x}))^{k-2} (\delta f(\mathbf{x}))^2 + \dots d\mathbf{x}, \end{aligned} \quad (1.111)$$

where we have used the binomial theorem in the second line. It follows from Eq. (1.99) that

$$\frac{\delta \int (f(\mathbf{r}))^k d\mathbf{r}}{\delta f(\mathbf{x})} = k f(\mathbf{x}). \quad (1.112)$$

As a second example, we can take

$$G[f] \equiv \int \mathbf{E}(\mathbf{r}) \cdot \nabla f(\mathbf{r}) d\mathbf{r}. \quad (1.113)$$

We can evaluate this using any of the above methods, but the method using the “delta-function” technique in Eq. (1.98) is particularly elegant. We have that

$$\begin{aligned} \frac{\delta G[f]}{\delta f(\mathbf{x})} &= \left( \frac{dG[f + \varepsilon \delta(\mathbf{r} - \mathbf{x})]}{d\varepsilon} \right)_{\varepsilon=0} \\ &= \frac{d}{d\varepsilon} \int \mathbf{E}(\mathbf{r}) \cdot \nabla (f(\mathbf{r}) + \varepsilon \delta(\mathbf{r} - \mathbf{x})) d\mathbf{r} \\ &= \int \frac{d}{d\varepsilon} \mathbf{E}(\mathbf{r}) \cdot (\nabla f(\mathbf{r}) + \varepsilon \nabla \delta(\mathbf{r} - \mathbf{x})) d\mathbf{r} \\ &= \int \mathbf{E}(\mathbf{r}) \cdot (0 + \nabla \delta(\mathbf{r} - \mathbf{x})) d\mathbf{r} \\ &= -\nabla \cdot \mathbf{E}(\mathbf{x}) \end{aligned} \quad (1.114)$$

where we have used the result for the derivative of the delta function,

$$\int \mathbf{E}(\mathbf{r}) \cdot \nabla \delta(\mathbf{r} - \mathbf{x}) = -\nabla \cdot \mathbf{E}(\mathbf{x}). \quad (1.115)$$

which is the generalization of the result

$$\int f(r) \frac{d(\delta(r - x))}{dr} dr = -f'(r). \quad (1.116)$$

You will get a lot of practice using these tools in the following sections!

## VII. The Hartree-Fock Equations

We now have all the tools we need to derive the Hartree-Fock Equations. In particular, we know how the energy depends on the orbitals, Eq. (1.94), and how to

compute the way the energy changes as the orbitals change using the functional derivative. Returning, then, to the definition of the Hartree-Fock energy, Eq. **Error! Reference source not found.**, we need to minimize the energy of the Slater determinant with respect to all possible choice of orthonormal orbitals. Thus,

$$E_{HF} = \min_{\{\psi_i\}_{i=1}^N} E_{Sl}[\Phi] \\ = \min_{\{\psi_i\}_{i=1}^N} \left( \sum_{i=1}^N \frac{\langle \psi_i | \hat{h} | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left( \frac{\langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_j | \psi_j \rangle} \right) \right) \quad (1.117)$$

and, just as we can find the stationary points,  $\mathbf{x}_{stat}$ , and values,  $f(\mathbf{x}_{stat})$  of a function of  $d$  variables by solving the simultaneous equations,

$$\left( \frac{\partial f(\mathbf{x}_{stat})}{\partial x_\alpha} \right)_{x_{j \neq \alpha}} = 0 \quad 1 \leq \alpha \leq d, \quad (1.118)$$

we can find the stationary values of the energy as a functional of the  $N$ -orbitals in a Slater determinant by solving the simultaneous equations

$$\left( \frac{\delta E_{Sl} \left[ \left\{ \psi_k^{stat} \right\}_{k=1}^N \right]}{\delta \psi_\alpha(\mathbf{r})} \right)_{\psi_{j \neq \alpha}} = 0 \quad 1 \leq \alpha \leq N \quad (1.119)$$

subject to the constraint that the orbitals be orthogonal.<sup>10</sup> Looking at expression (1.99) for the functional derivative, we see that it is necessary not only that  $\psi_\alpha(\mathbf{z})$  be orthogonal to the other orbitals in the Slater determinant,  $\{\psi_j\}_{j=1; j \neq \alpha}^N$ , but also the  $\psi_\alpha(\mathbf{z}) + \delta\psi_\alpha(\mathbf{z})$  be orthogonal to the other orbitals. To construct such a variation, let  $\{\psi_i\}_{i=1}^\infty$  denote a complete set of spin-orbitals, with the first  $N$  elements of the set chosen so that

$$\Phi_{Sl} \equiv |\psi_1 \dots \psi_N|. \quad (1.120)$$

Then we can write<sup>11</sup>

$$\delta\psi_\alpha(\mathbf{z}) \equiv \sum_{j=N+1}^\infty d_{j\alpha} \psi_j(\mathbf{z}). \quad (1.121)$$

Inserting Eq. (1.121) into Eq. (1.117), we have that

<sup>10</sup> By including the form with the appropriate normalization constants in the denominator, we have obviated the need to require the orbitals to be normalized—we need only require orthogonality.

<sup>11</sup> Usually it is understood that  $d_{j\alpha}$  will be zero unless  $\psi_j(\mathbf{z})$  and  $\psi_\alpha(\mathbf{z})$  have the same spin, that is, unless  $\sigma_j = \sigma_\alpha$ . This ensures that the perturbed orbital,  $\psi_\alpha(\mathbf{z}) + \delta\psi_\alpha(\mathbf{z})$ , can still be written as a simple product of a “spin” part and a “spatial” part. We need not worry about the normalization of the modified orbital because of the terms in the denominator of Eq. (1.117).

$$\begin{aligned}
& E_{Sl}[\{\psi_k\}_{k \neq \alpha}; \psi_\alpha + \delta\psi_\alpha] - E_{Sl}[\{\psi_k\}_{k \neq \alpha}; \psi_\alpha] \\
&= \left[ \sum_{\substack{i=1 \\ i \neq \alpha}}^N \frac{\langle \psi_i | \hat{h} | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} + \frac{\langle \psi_\alpha + \delta\psi_\alpha | \hat{h} | \psi_\alpha + \delta\psi_\alpha \rangle}{\langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle} \right. \\
&\quad + \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq \alpha}}^N \left( \frac{\langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_j | \psi_j \rangle} \right) \\
&\quad + \frac{1}{2} \sum_{i=1}^N \left( \frac{\langle \psi_i (\psi_\alpha + \delta\psi_\alpha) | \hat{v}_{ee} | \psi_i (\psi_\alpha + \delta\psi_\alpha) \rangle - \langle \psi_i (\psi_\alpha + \delta\psi_\alpha) | \hat{v}_{ee} | (\psi_\alpha + \delta\psi_\alpha) \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle} \right) \\
&\quad + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq \alpha}}^N \sum_{j=1}^N \left( \frac{\langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_j | \psi_j \rangle} \right) \\
&\quad + \frac{1}{2} \sum_{j=1}^N \left( \frac{\langle (\psi_\alpha + \delta\psi_\alpha) \psi_j | \hat{v}_{ee} | (\psi_\alpha + \delta\psi_\alpha) \psi_j \rangle - \langle (\psi_\alpha + \delta\psi_\alpha) \psi_j | \hat{v}_{ee} | \psi_j (\psi_\alpha + \delta\psi_\alpha) \rangle}{\langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle \langle \psi_j | \psi_j \rangle} \right) \\
&\quad + \frac{1}{2} \frac{\langle (\psi_\alpha + \delta\psi_\alpha) (\psi_\alpha + \delta\psi_\alpha) | \hat{v}_{ee} | (\psi_\alpha + \delta\psi_\alpha) (\psi_\alpha + \delta\psi_\alpha) \rangle - \langle (\psi_\alpha + \delta\psi_\alpha) (\psi_\alpha + \delta\psi_\alpha) | \hat{v}_{ee} | (\psi_\alpha + \delta\psi_\alpha) \psi_\alpha \rangle}{\langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle \langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle} \Bigg] \\
&\quad - \left[ \sum_{i=1}^N \frac{\langle \psi_i | \hat{h} | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left( \frac{\langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_j | \psi_j \rangle} \right) \right] \\
&\quad \left. \begin{array}{l} \text{1 el.} \\ \text{term} \\ j \neq \alpha \\ \text{term} \\ j = \alpha \\ \text{term} \\ i \neq \alpha \\ \text{term} \\ i = \alpha \\ \text{term} \\ i = \alpha, \\ j = \alpha \\ \text{term} \end{array} \right] \quad (1.122)
\end{aligned}$$

Simplifying, we have

$$\begin{aligned}
& E_{Sl}[\{\psi_k\}_{k \neq \alpha}; \psi_\alpha + \delta\psi_\alpha] - E_{Sl}[\{\psi_k\}_{k \neq \alpha}; \psi_\alpha] \\
&= \frac{\langle \psi_\alpha + \delta\psi_\alpha | \hat{h} | \psi_\alpha + \delta\psi_\alpha \rangle}{\langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle} - \frac{\langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle} \\
&\quad + \frac{1}{2} \sum_{i=1}^N \left[ \frac{\langle \psi_i (\psi_\alpha + \delta\psi_\alpha) | \hat{v}_{ee} | \psi_i (\psi_\alpha + \delta\psi_\alpha) \rangle - \langle \psi_i (\psi_\alpha + \delta\psi_\alpha) | \hat{v}_{ee} | (\psi_\alpha + \delta\psi_\alpha) \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle} \right. \\
&\quad \left. - \frac{\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle - \langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_\alpha \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_\alpha | \psi_\alpha \rangle} \right] \\
&\quad + \frac{1}{2} \sum_{j=1}^N \left[ \frac{\langle (\psi_\alpha + \delta\psi_\alpha) \psi_j | \hat{v}_{ee} | (\psi_\alpha + \delta\psi_\alpha) \psi_j \rangle - \langle (\psi_\alpha + \delta\psi_\alpha) \psi_j | \hat{v}_{ee} | \psi_j (\psi_\alpha + \delta\psi_\alpha) \rangle}{\langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle \langle \psi_j | \psi_j \rangle} \right. \\
&\quad \left. - \frac{\langle \psi_\alpha \psi_j | \hat{v}_{ee} | \psi_\alpha \psi_j \rangle - \langle \psi_\alpha \psi_j | \hat{v}_{ee} | \psi_j \psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle \langle \psi_j | \psi_j \rangle} \right] \quad (1.123)
\end{aligned}$$

where we have used the fact that the  $i = j = \alpha$  term is identically zero. In Eq. (1.123), the electron-electron repulsion terms on the second and third lines are identical,<sup>12</sup> and so

$$\begin{aligned}
& E_{Sl}[\{\psi_k\}_{k \neq \alpha}; \psi_\alpha + \delta\psi_\alpha] - E_{Sl}[\{\psi_k\}_{k \neq \alpha}; \psi_\alpha] \\
&= \frac{\langle \psi_\alpha + \delta\psi_\alpha | \hat{h} | \psi_\alpha + \delta\psi_\alpha \rangle}{\langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle} - \frac{\langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle} \\
&+ \sum_{i=1}^N \left[ \frac{\langle \psi_i(\psi_\alpha + \delta\psi_\alpha) | \hat{v}_{ee} | \psi_i(\psi_\alpha + \delta\psi_\alpha) \rangle - \langle \psi_i(\psi_\alpha + \delta\psi_\alpha) | \hat{v}_{ee} | (\psi_\alpha + \delta\psi_\alpha) \psi_i \rangle}{\frac{\langle \psi_i | \psi_i \rangle \langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle}{\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle - \langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_\alpha \psi_i \rangle}} \right] \\
&= \frac{\langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle + \langle \delta\psi_\alpha | \hat{h} | \psi_\alpha \rangle + \langle \psi_\alpha | \hat{h} | \delta\psi_\alpha \rangle + \langle \delta\psi_\alpha | \hat{h} | \delta\psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle + \langle \delta\psi_\alpha | \psi_\alpha \rangle + \langle \psi_\alpha | \delta\psi_\alpha \rangle + \langle \delta\psi_\alpha | \delta\psi_\alpha \rangle} - \frac{\langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle} \\
&+ \sum_{i=1}^N \left[ \frac{\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle + \langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i(\delta\psi_\alpha) \rangle + \langle \psi_i(\delta\psi_\alpha) | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle + \langle \psi_i(\delta\psi_\alpha) | \hat{v}_{ee} | \psi_i(\delta\psi_\alpha) \rangle}{\frac{\langle \psi_i | \psi_i \rangle (\langle \psi_\alpha | \psi_\alpha \rangle + \langle \delta\psi_\alpha | \psi_\alpha \rangle + \langle \psi_\alpha | \delta\psi_\alpha \rangle + \langle \delta\psi_\alpha | \delta\psi_\alpha \rangle)}{\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle - \langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_\alpha \psi_i \rangle}} \right] \quad (1.124)
\end{aligned}$$

Because the operators in Eq. (1.124) are Hermitian and the orbitals are chosen to be real, we have, for example that,

$$\langle \psi_\alpha | \hat{h} | \delta\psi_\alpha \rangle \overset{\text{Hermitian operators}}{=} \langle \hat{h} \psi_\alpha | \delta\psi_\alpha \rangle = \langle \delta\psi_\alpha | \hat{h} | \psi_\alpha \rangle \overset{\text{real orbitals}}{=} \langle \delta\psi_\alpha | \hat{h} | \psi_\alpha \rangle. \quad (1.125)$$

Thus, Eq. (1.124) simplifies to

$$\begin{aligned}
& E_{Sl}[\{\psi_k\}_{k \neq \alpha}; \psi_\alpha + \delta\psi_\alpha] - E_{Sl}[\{\psi_k\}_{k \neq \alpha}; \psi_\alpha] \\
&= \frac{\langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle + 2\langle \delta\psi_\alpha | \hat{h} | \psi_\alpha \rangle + \langle \delta\psi_\alpha | \hat{h} | \delta\psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle + 2\langle \delta\psi_\alpha | \psi_\alpha \rangle + \langle \delta\psi_\alpha | \delta\psi_\alpha \rangle} - \frac{\langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle} \\
&+ \sum_{i=1}^N \left[ \frac{\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle + 2\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i(\delta\psi_\alpha) \rangle + \langle \psi_i(\delta\psi_\alpha) | \hat{v}_{ee} | \psi_i(\delta\psi_\alpha) \rangle}{\frac{\langle \psi_i | \psi_i \rangle (\langle \psi_\alpha | \psi_\alpha \rangle + 2\langle \delta\psi_\alpha | \psi_\alpha \rangle + \langle \delta\psi_\alpha | \delta\psi_\alpha \rangle)}{\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle - \langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_\alpha \psi_i \rangle}} \right]. \quad (1.126)
\end{aligned}$$

Remember that the orbitals in the Slater determinant,  $\{\psi_i(\mathbf{z})\}_{i=1}^N$ , can be chosen to be normalized. By contrast, no such assurance can be made for  $\psi_\alpha(\mathbf{z}) + \delta\psi_\alpha(\mathbf{z})$ , which may or

---

<sup>12</sup> This is true for real orbitals. Otherwise the treatment must be revised to accommodate the substitution in Eq. (1.75), with similar results.

may not be normalized. Choosing the orbitals to be normalized and using the  $n = -1$  case of the binomial theorem,

$$(1+x)^n = 1 + n \cdot x + \frac{n(n-1)}{2} x^2 + \dots \quad (1.127)$$

gives

$$\begin{aligned} & E_{Sl}[\{\psi_k\}_{k \neq \alpha}; \psi_\alpha + \delta\psi_\alpha] - E_{Sl}[\{\psi_k\}_{k \neq \alpha}; \psi_\alpha] \\ &= \frac{\langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle + 2\langle \delta\psi_\alpha | \hat{h} | \psi_\alpha \rangle + \langle \delta\psi_\alpha | \hat{h} | \delta\psi_\alpha \rangle}{1 + 2\langle \delta\psi_\alpha | \psi_\alpha \rangle + \langle \delta\psi_\alpha | \delta\psi_\alpha \rangle} - \frac{\langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle}{1} \\ &+ \sum_{i=1}^N \left[ \frac{\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle + 2\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i (\delta\psi_\alpha) \rangle + \langle \psi_i (\delta\psi_\alpha) | \hat{v}_{ee} | \psi_i (\delta\psi_\alpha) \rangle}{1(1 + 2\langle \delta\psi_\alpha | \psi_\alpha \rangle + \langle \delta\psi_\alpha | \delta\psi_\alpha \rangle)} \right. \\ &\quad \left. - \frac{\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_\alpha \psi_i \rangle - 2\langle \psi_i \psi_\alpha | \hat{v}_{ee} | (\delta\psi_\alpha) \psi_i \rangle - \langle \psi_i (\delta\psi_\alpha) | \hat{v}_{ee} | (\delta\psi_\alpha) \psi_i \rangle}{1 \cdot 1} \right] \\ &= \langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle + 2\langle \delta\psi_\alpha | \hat{h} | \psi_\alpha \rangle + \langle \delta\psi_\alpha | \hat{h} | \delta\psi_\alpha \rangle (1 - 2\langle \delta\psi_\alpha | \psi_\alpha \rangle - \langle \delta\psi_\alpha | \delta\psi_\alpha \rangle + \dots) - \langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle \\ &+ \sum_{i=1}^N \left[ \frac{\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle + 2\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i (\delta\psi_\alpha) \rangle}{1} \right. \\ &\quad \left. - \frac{\langle \psi_i (\delta\psi_\alpha) | \hat{v}_{ee} | \psi_i (\delta\psi_\alpha) \rangle - \langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_\alpha \psi_i \rangle}{1} \right] ((1 - 2\langle \delta\psi_\alpha | \psi_\alpha \rangle - \langle \delta\psi_\alpha | \delta\psi_\alpha \rangle + \dots)) \\ &= 2\langle \delta\psi_\alpha | \hat{h} | \psi_\alpha \rangle - 2\langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle \langle \delta\psi_\alpha | \psi_\alpha \rangle + \mathcal{O}(\langle \delta\psi_\alpha | \delta\psi_\alpha \rangle) \\ &+ \sum_{i=1}^N \left[ \frac{2(\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i (\delta\psi_\alpha) \rangle - \langle \psi_i \psi_\alpha | \hat{v}_{ee} | (\delta\psi_\alpha) \psi_i \rangle)}{1} \right. \\ &\quad \left. - 2(\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle - \langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_\alpha \psi_i \rangle) \langle \delta\psi_\alpha | \psi_\alpha \rangle \right] \\ &\quad \left[ \mathcal{O}(\langle \delta\psi_\alpha | \delta\psi_\alpha \rangle) \right] \end{aligned} \quad (1.128)$$

Referring to Eq. (1.99), we find that for variations that preserve the orthogonality of the orbitals, we have

$$\begin{aligned} & \left( \frac{\delta E_{Sl}[\{\psi_k^{stat}\}_{k=1}^N]}{\delta\psi_\alpha(\mathbf{z})} \right)_{\psi_{j \neq \alpha}} = 2\hat{h}(\mathbf{r})\psi_\alpha(\mathbf{z}) - 2\langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle \psi_\alpha(\mathbf{z}) \\ &+ 2 \sum_{i=1}^N \left( \int \frac{\psi_i^*(\mathbf{z}')\psi_i(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \psi_\alpha^*(\mathbf{z}) - \int \frac{\psi_i(\mathbf{z}')\psi_\alpha^*(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{z}' \psi_i^*(\mathbf{z}) \right) \psi_\alpha(\mathbf{z}) \quad (1.129) \\ &- 2 \left( \sum_{i=1}^N \langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle - \langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_\alpha \psi_i \rangle \right) \psi_\alpha(\mathbf{z}) \end{aligned}$$

Using the notation for the one-electron and two-electron integrals, cf. Eqs. (1.72)-(1.74), we have

$$\begin{aligned} \left( \frac{\delta E_{Sl} \left[ \left\{ \psi_k^{stat} \right\}_{k=1}^N \right]}{\delta \psi_\alpha(\mathbf{z})} \right)_{\psi_{j \neq \alpha}} &= 2\hat{h}(\mathbf{r}) \psi_\alpha(\mathbf{z}) - 2h_\alpha \psi_\alpha(\mathbf{z}) - 2 \left( \sum_{i=1}^N J_{\alpha i} - K_{\alpha i} \right) \psi_\alpha(\mathbf{z}) \\ &+ 2 \sum_{i=1}^N \left( \int \frac{\psi_i^*(\mathbf{z}') \psi_i(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \psi_\alpha^*(\mathbf{z}) - \int \frac{\psi_i(\mathbf{z}') \psi_\alpha^*(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{z}' \psi_i^*(\mathbf{z}) \right) \psi_\alpha(\mathbf{z}) \end{aligned} \quad (1.130)$$

In order for the energy to be stationary with respect to orthogonalization-preserving changes in the  $\alpha^{th}$  orbital, it is necessary that the functional derivative be zero. Then, from Eq. (1.130), we obtain the equation

$$\begin{aligned} \left[ \hat{h}(\mathbf{r}) + \sum_{i=1}^N \left( \int \frac{\psi_i^*(\mathbf{z}') \psi_i(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \psi_\alpha^*(\mathbf{z}) - \int \frac{\psi_i(\mathbf{z}') \psi_\alpha^*(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{z}' \psi_i^*(\mathbf{z}) \right) \right] \psi_\alpha(\mathbf{z}) \\ = \left( h_\alpha + \sum_{i=1}^N (J_{\alpha i} - K_{\alpha i}) \right) \psi_\alpha(\mathbf{z}) \end{aligned} \quad (1.131)$$

which is immediately recognized as a one-electron Schrödinger equation with potential

$$v(\mathbf{r}) + j(\mathbf{r}) - \hat{k}(\mathbf{r}) \quad (1.132)$$

and energy eigenvalue

$$\varepsilon_\alpha = h_\alpha + \sum_{i=1}^N (J_{\alpha i} - K_{\alpha i}), \quad (1.133)$$

where we have defined the Coulomb potential operator as

$$\begin{aligned} j(\mathbf{r}) &\equiv \sum_{i=1}^N \int \frac{\psi_i^*(\mathbf{z}') \psi_i(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \\ &= \int \frac{\sum_{i=1}^N \psi_i^*(\mathbf{z}') \psi_i(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \end{aligned} \quad (1.134)$$

and the exchange potential operator as

$$\begin{aligned} \hat{k}(\mathbf{r}) \psi_\alpha(\mathbf{z}) &\equiv \sum_{i=1}^N \int \frac{\psi_i^*(\mathbf{z}') \psi_\alpha(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{z}' \psi_i(\mathbf{z}) \\ &= \int \frac{\sum_{i=1}^N \psi_i^*(\mathbf{z}') \psi_i(\mathbf{z}) \psi_\alpha(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{z}' \\ &= \sum_{i=1}^N \delta_{\sigma_i \sigma_\alpha} \int \frac{\psi_i^*(\mathbf{r}') \psi_\alpha(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \cdot \psi_i(\mathbf{z}) \end{aligned} \quad (1.135)$$

where, in analogy to expression (1.80) for the exchange energy, we have explicitly noted that there is no contribution to the exchange potential from orbitals,  $i$ , with spin,  $\sigma_i$ , that is different from the spin of the orbital being operated on,  $\sigma_\alpha$ .

With this notation, we can write the Hartree-Fock equations as the eigenvalue problem,

$$\left[ \hat{h}(\mathbf{r}) + j\left[\{\psi_i\}_{i=1}^N; \mathbf{r}\right] - \hat{k}\left[\{\psi_i\}_{i=1}^N; \mathbf{z}\right] \right] \psi_\alpha(\mathbf{z}) \equiv \varepsilon_\alpha \psi_\alpha(\mathbf{z}) \quad 1 \leq \alpha < \infty \quad (1.136)$$

or, if we write out the operator  $\hat{h}(\mathbf{r})$  in its explicit form,

$$\left[ -\frac{\nabla^2}{2} + v(\mathbf{r}) + j\left[\{\psi_i\}_{i=1}^N; \mathbf{r}\right] - \hat{k}\left[\{\psi_i\}_{i=1}^N; \mathbf{z}\right] \right] \psi_\alpha(\mathbf{z}) \equiv \varepsilon_\alpha \psi_\alpha(\mathbf{z}) \quad 1 \leq \alpha < \infty \quad (1.137)$$

Note, in particular, that both the Coulomb and the exchange operators depend on all the orbitals in the Slater determinant, and not just the orbital under question,  $\psi_\alpha(\mathbf{z})$ . Note that

$$\varepsilon_\alpha = \left\langle \psi_\alpha \left| \hat{h}(\mathbf{r}) + j\left[\{\psi_i\}_{i=1}^N; \mathbf{r}\right] - \hat{k}\left[\{\psi_i\}_{i=1}^N; \mathbf{z}\right] \right| \psi_\alpha \right\rangle \quad (1.138)$$

The entire one-electron Hamiltonian in Eq. (1.137) is often called the *one-electron Fock operator*, and denoted

$$\hat{f}[\{\psi_i\}; \mathbf{r}] \equiv \hat{h}(\mathbf{r}) + j[\{\psi_i\}; \mathbf{r}] - \hat{k}[\{\psi_i\}; \mathbf{r}]. \quad (1.139)$$

The many-electron system is then described using the “many-electron Fock” operator, with

$$\hat{F} = \sum_{i=1}^N f(\mathbf{r}_i) \quad (1.140)$$

and

$$(\hat{F})|\psi_1 \dots \psi_N| = \left( \sum_{i=1}^N \varepsilon_i \right) |\psi_1 \dots \psi_N| \quad (1.141)$$

While minimizing the energy of  $\langle \Psi | \hat{F} | \Psi \rangle$  gives the Hartree-Fock wave function, this does not reproduced the Hartree-Fock energy, as is clear from the right-hand-side of Eq. (1.141).<sup>13</sup>

---

<sup>13</sup> This is because the Hartree-Fock energy is not simply the sum of the Hartree-Fock orbital energies