## Lecture IV: The Hartree-Fock method

## I. THE HARTREE METHOD

We have seen in the previous lecture that the many-body Hamiltonian for an electronic system may be written in atomic units as

$$
\begin{equation*}
\hat{H}=-\frac{1}{2} \sum_{i}^{N_{e}} \nabla_{i}^{2}-\sum_{i}^{N_{e}} \sum_{I}^{N_{n}} \frac{Z_{I}}{\left|\vec{r}_{i}-\vec{R}_{I}\right|}+\frac{1}{2} \sum_{i}^{N_{e}} \sum_{j \neq i}^{N_{e}} \frac{1}{\left|\vec{r}_{i}-\vec{r}_{j}\right|}+\frac{1}{2} \sum_{I}^{N_{n}} \sum_{J \neq I}^{N_{n}} \frac{Z_{I} Z_{J}}{\left|\vec{R}_{I}-\vec{R}_{J}\right|} \tag{1}
\end{equation*}
$$

For the time being we take the final term to be a constant and we only consider the electronic Hamiltonian, which is just

$$
\begin{equation*}
\hat{H}_{e}=-\frac{1}{2} \sum_{i}^{N_{e}} \nabla_{i}^{2}-\sum_{i}^{N_{e}} \sum_{I}^{N_{n}} \frac{Z_{I}}{\left|\vec{r}_{i}-\vec{R}_{I}\right|}+\frac{1}{2} \sum_{i}^{N_{e}} \sum_{j \neq i}^{N_{e}} \frac{1}{\left|\vec{r}_{i}-\vec{r}_{j}\right|} \tag{2}
\end{equation*}
$$

In Eq. 2 the kinetic energy term and the nucleus-electron interaction term are sums of single-particle operators, each of which act on a single electronic coordinate. The electron-electron interaction term on the other hand is a pair interaction and acts on pairs of electrons. To facilitate the upcoming math, let's make the following definition

$$
\begin{equation*}
\hat{H}_{e}=\sum_{i} \hat{h}_{1}\left(\vec{x}_{i}\right)+\frac{1}{2} \sum_{i \neq j} \hat{h}_{2}\left(\vec{x}_{i}, \vec{x}_{j}\right) \tag{3}
\end{equation*}
$$

where $\vec{x}_{i}$ is now a generalized coordinate that includes spatial as well as spin degrees of freedom.
The Hartree-Fock method is a variational, wavefunction-based approach. Although it is a many-body technique, the approach followed is that of a single-particle picture, i.e. the electrons are considered as occupying single-particle orbitals making up the wavefunction. Each electron feels the presence of the other electrons indirectly through an effective potential. Each orbital, thus, is affected by the presence of electrons in other orbitals.

The starting point of the Hartree-Fock method is to write a variational wavefunction, which is built from these singleparticle orbitals. Once we make a suitable ansatz to the wavefunction, all that is left is the application of the variational principle as described in Lecture 1. The simplest wavefunction that can be formed from these orbitals is their direct product

$$
\begin{equation*}
\Phi\left(\vec{x}_{1}, \cdots, \vec{x}_{N}\right)=\phi_{1}\left(\vec{x}_{1}\right) \phi_{2}\left(\vec{x}_{2}\right) \cdots \phi_{N}\left(\vec{x}_{N}\right) . \tag{4}
\end{equation*}
$$

This is the Hartree approximation and it is a straightforward task to calculate the variational lowest energy from Eq. 4. However, the Hartree wavefunction has a very important shortcoming, which is that it fails to satisfy antisymmetry, which states that a fermion wavefunction changes sign under odd permutations of the electronic variables. The permutation operator is defined by its action on the wavefunction

$$
\begin{equation*}
\hat{P}_{i j} \Phi\left(\vec{x}_{1}, \cdots, \vec{x}_{i}, \cdots, \vec{x}_{j}, \cdots, \vec{x}_{N}\right)=\Phi\left(\vec{x}_{1}, \cdots, \vec{x}_{j}, \cdots, \vec{x}_{i}, \cdots, \vec{x}_{N}\right)=-\Phi\left(\vec{x}_{1}, \cdots, \vec{x}_{i}, \cdots, \vec{x}_{j}, \cdots, \vec{x}_{N}\right) \tag{5}
\end{equation*}
$$

If an odd number of such permutation operators are applied to the wavefunction, it picks up a minus sign while no change in sign occurs under an even number of permutations. In order to satisfy the antisymmetry condition, a more sophisticated form than that of the Hartree wavefunction is needed.

## II. THE SLATER DETERMINANT

If, for example, we have a two-electron system with orbitals $\phi_{1}\left(\vec{x}_{1}\right)$ and $\phi_{2}\left(\vec{x}_{2}\right)$, the following variational wavefunction satisfies the antisymmetry condition, at the same time preserving the single-particle picture

$$
\begin{equation*}
\Phi\left(\vec{x}_{1}, \vec{x}_{2}\right)=c\left[\phi_{1}\left(\vec{x}_{1}\right) \phi_{2}\left(\vec{x}_{2}\right)-\phi_{1}\left(\vec{x}_{2}\right) \phi_{2}\left(\vec{x}_{1}\right)\right] \tag{6}
\end{equation*}
$$

where $c$ is the normalization constant. For three electrons, the equivalent antisymmetrized wavefunction would be

$$
\begin{align*}
\Phi\left(\vec{x}_{1}, \vec{x}_{2}, \vec{x}_{3}\right)= & c\left[\phi_{1}\left(\vec{x}_{1}\right) \phi_{2}\left(\vec{x}_{2}\right) \phi_{3}\left(\vec{x}_{3}\right)-\phi_{1}\left(\vec{x}_{1}\right) \phi_{2}\left(\vec{x}_{3}\right) \phi_{3}\left(\vec{x}_{2}\right)+\phi_{1}\left(\vec{x}_{3}\right) \phi_{2}\left(\vec{x}_{1}\right) \phi_{3}\left(\vec{x}_{2}\right)\right. \\
& \left.-\phi_{1}\left(\vec{x}_{2}\right) \phi_{2}\left(\vec{x}_{1}\right) \phi_{3}\left(\vec{x}_{3}\right)+\phi_{1}\left(\vec{x}_{3}\right) \phi_{2}\left(\vec{x}_{2}\right) \phi_{3}\left(\vec{x}_{1}\right)-\phi_{1}\left(\vec{x}_{2}\right) \phi_{2}\left(\vec{x}_{3}\right) \phi_{3}\left(\vec{x}_{1}\right)\right] . \tag{7}
\end{align*}
$$

Upon closer inspection, we notice that the same permutations of orbitals with matching signs are obtained by the following determinant

$$
\Phi=c\left|\begin{array}{lll}
\phi_{1}\left(\vec{x}_{1}\right) & \phi_{2}\left(\vec{x}_{1}\right) & \phi_{3}\left(\vec{x}_{1}\right)  \tag{8}\\
\phi_{1}\left(\vec{x}_{2}\right) & \phi_{2}\left(\vec{x}_{2}\right) & \phi_{3}\left(\vec{x}_{2}\right) \\
\phi_{1}\left(\vec{x}_{3}\right) & \phi_{2}\left(\vec{x}_{3}\right) & \phi_{3}\left(\vec{x}_{3}\right)
\end{array}\right|
$$

Generalizing this to an $N$-electron system where the orbitals are taken to satisfy orthonormality, we have

$$
\Phi=\frac{1}{\sqrt{N!}}\left|\begin{array}{cccc}
\phi_{1}\left(\vec{x}_{1}\right) & \phi_{2}\left(\vec{x}_{1}\right) & \cdots & \phi_{N}\left(\vec{x}_{1}\right)  \tag{9}\\
\phi_{1}\left(\vec{x}_{2}\right) & \phi_{2}\left(\vec{x}_{2}\right) & \cdots & \phi_{N}\left(\vec{x}_{2}\right) \\
\vdots & \vdots & & \vdots \\
\phi_{1}\left(\vec{x}_{N}\right) & \phi_{2}\left(\vec{x}_{N}\right) & \cdots & \phi_{N}\left(\vec{x}_{N}\right)
\end{array}\right|
$$

where the factor in front ensures normalization. For an arbitrary number of electrons the wavefunction form in Eq. 9 can be shown to satisfy the desired antisymmetry condition. The determinant, referred to as a Slater determinant in literature, has $N$ ! terms each multiplied by -1 or 1 depending on the parity of the permutation. Each term has each orbital $\phi_{i}$ only once and each of the arguments $\vec{x}_{i}$ only once. Thus, each term may be written as follows :

$$
\begin{equation*}
(-1)^{P\left(i_{1}, i_{2}, \cdots, i_{N}\right)} \phi_{i_{1}}\left(\vec{x}_{1}\right) \phi_{i_{2}}\left(\vec{x}_{2}\right) \cdots \phi_{i_{N}}\left(\vec{x}_{N}\right) \tag{10}
\end{equation*}
$$

where the indices $i_{1}, i_{2}, \cdots$ take values between 1 and $N$ and the exponent of -1 in front refers to the order of appearance of the orbital indices in the term. The term picks up a -1 in front if the corresponding permutation is odd and +1 if it is even. For ease of notation, we replace $P\left(i_{1}, i_{2}, \cdots, i_{N}\right)$ by the shorthand notation $P(i)$, where $i$ now refers to a particular arrangement (or sequence) of the $N$ indices. The Slater determinant may then be written as

$$
\begin{equation*}
\sum_{i}^{N!}(-1)^{P(i)} \phi_{i_{1}}\left(\vec{x}_{1}\right) \phi_{i_{2}}\left(\vec{x}_{2}\right) \cdots \phi_{i_{N}}\left(\vec{x}_{N}\right) \tag{11}
\end{equation*}
$$

where the sum $i$ runs over the $N$ ! terms. Nothing has been said so far about the form of the orbitals $\phi_{i}\left(\vec{x}_{j}\right)$ and they are left to be found as a result of the minimization procedure associated by the variation. In order to achieve that we now calculate the expectation value of the Hamiltonian for this variational wavefunction

$$
\begin{equation*}
E_{H}=\langle\Phi| \hat{H}_{e}|\Phi\rangle \tag{12}
\end{equation*}
$$

## III. ELECTRONIC ENERGY FOR THE SLATER DETERMINANT

First, we tackle the single-particle terms in Eq. 2.

$$
\begin{equation*}
\langle\Phi| \sum_{n} \hat{h}_{1}\left(\vec{x}_{n}\right)|\Phi\rangle=\frac{1}{N!} \sum_{n} \sum_{i, j}(-1)^{P(i)}(-1)^{P(j)}\left\langle\phi_{j_{1}}\left(\vec{x}_{1}\right) \phi_{j_{2}}\left(\vec{x}_{2}\right) \cdots \phi_{j_{N}}\left(\vec{x}_{N}\right)\right| \hat{h}_{1}\left(\vec{x}_{n}\right)\left|\phi_{i_{1}}\left(\vec{x}_{1}\right) \phi_{i_{2}}\left(\vec{x}_{2}\right) \cdots \phi_{i_{N}}\left(\vec{x}_{N}\right)\right\rangle \tag{13}
\end{equation*}
$$

Because each orbital making up the Slater determinant depends only on a single coordinate, we can pair up those orbitals that have the same argument and separate them into individual inner products, except for the one that has the same argument as the operator :

$$
\begin{align*}
\langle\Phi| \sum_{n} \hat{h}_{1}\left(\vec{x}_{n}\right)|\Phi\rangle=\frac{1}{N!} \sum_{n} \sum_{i, j} & (-1)^{P(i)}(-1)^{P(j)} \times \\
& \left\langle\phi_{j_{1}}\left(\vec{x}_{1}\right) \mid \phi_{i_{1}}\left(\vec{x}_{1}\right)\right\rangle \cdots\left\langle\phi_{j_{n-1}}\left(\vec{x}_{n-1}\right) \mid \phi_{i_{n-1}}\left(\vec{x}_{n-1}\right)\right\rangle\left\langle\phi_{j_{n}}\left(\vec{x}_{n}\right)\right| \hat{h}_{1}\left(\vec{x}_{n}\right)\left|\phi_{i_{n}}\left(\vec{x}_{n}\right)\right\rangle \times \\
& \left\langle\phi_{j_{n+1}}\left(\vec{x}_{n+1}\right) \mid \phi_{i_{n+1}}\left(\vec{x}_{n+1}\right)\right\rangle \cdots\left\langle\phi_{j_{N}}\left(\vec{x}_{N}\right) \mid \phi_{i_{N}}\left(\vec{x}_{N}\right)\right\rangle \tag{14}
\end{align*}
$$

Due to orthonormality of the chosen orbitals, all the inner products yield delta functions

$$
\begin{equation*}
\langle\Phi| \sum_{n} \hat{h}_{1}\left(\vec{x}_{n}\right)|\Phi\rangle=\frac{1}{N!} \sum_{n} \sum_{i, j}(-1)^{P(i)}(-1)^{P(j)} \delta_{j_{1} i_{1}} \cdots \delta_{j_{n-1} i_{n-1}}\left\langle\phi_{j_{n}}\left(\vec{x}_{n}\right)\right| \hat{h}_{1}\left(\vec{x}_{n}\right)\left|\phi_{i_{n}}\left(\vec{x}_{n}\right)\right\rangle \delta_{j_{n+1} i_{n+1}} \cdots \delta_{j_{N} i_{N}} \tag{15}
\end{equation*}
$$

Due to the Kronecker delta's all $i_{k}$ are equal to $j_{k}$ except for $i_{n}$. But because all terms appear exactly once in the products, $i_{n}=j_{n}$ is also automatically satisfied. Thus, the sequence of indices labeled $i$ is identical to that labeled $j$, making the permutations yield identical signs. We have, as a result,

$$
\begin{equation*}
\langle\Phi| \sum_{n} \hat{h}_{1}\left(\vec{x}_{n}\right)|\Phi\rangle=\frac{1}{N!} \sum_{n} \sum_{i}\left\langle\phi_{i_{n}}\left(\vec{x}_{n}\right)\right| \hat{h}_{1}\left(\vec{x}_{n}\right)\left|\phi_{i_{n}}\left(\vec{x}_{n}\right)\right\rangle \tag{16}
\end{equation*}
$$

Now, for a given sequence labeled by $i$ and for a fixed $i_{n}$, there are $(N-1)$ ! terms in the sum. The sum over sequence index $i$ may then be reduced to the sum of a single index $i_{n}$

$$
\begin{equation*}
\langle\Phi| \sum_{n} \hat{h}_{1}\left(\vec{x}_{n}\right)|\Phi\rangle=\frac{1}{N!}(N-1)!\sum_{n} \sum_{i_{n}}^{N}\left\langle\phi_{i_{n}}\left(\vec{x}_{n}\right)\right| \hat{h}_{1}\left(\vec{x}_{n}\right)\left|\phi_{i_{n}}\left(\vec{x}_{n}\right)\right\rangle \tag{17}
\end{equation*}
$$

Because the expectation value is an integration over the variable $\vec{x}_{n}$, each term yields the same result and there are $N$ such terms. Finally we replace the now arbitrary index $i_{n}$ by a generic index $i$. The final expression is then

$$
\begin{equation*}
\langle\Phi| \sum_{n} \hat{h}_{1}\left(\vec{x}_{n}\right)|\Phi\rangle=\sum_{i}^{N}\left\langle\phi_{i}\right| \hat{h}_{1}\left|\phi_{i}\right\rangle \tag{18}
\end{equation*}
$$

Next, we deal with the more complicated case of the two-particle terms. The starting point is identical to the case of the single-body part of the Hamiltonian where orbitals sharing the same argument are paired up into inner products except for the ones that have the same argument as the operator. In the case of the two-body part of the Hamiltonian there are two such orbitals. Assuming without loss of generality that $n<m$ we thus have
$\langle\Phi| \frac{1}{2} \sum_{n \neq m} \hat{h}_{2}\left(\vec{x}_{n}, \vec{x}_{m}\right)|\Phi\rangle=\frac{1}{N!} \frac{1}{2} \sum_{n \neq m} \sum_{i, j}(-1)^{P(i)}(-1)^{P(j)} \delta_{j_{1} i_{1}} \cdots \delta_{j_{n-1} i_{n-1}} \delta_{j_{n+1} i_{n+1}} \cdots \delta_{j_{m-1} i_{m-1}} \delta_{j_{m+1} i_{m+1}} \cdots \delta_{j_{N} i_{N}} \times$

$$
\begin{equation*}
\left\langle\phi_{j_{n}}\left(\vec{x}_{n}\right) \phi_{j_{m}}\left(\vec{x}_{m}\right)\right| \hat{h}_{2}\left(\vec{x}_{n}, \vec{x}_{m}\right)\left|\phi_{i_{n}}\left(\vec{x}_{n}\right) \phi_{i_{m}}\left(\vec{x}_{m}\right)\right\rangle \tag{19}
\end{equation*}
$$

This time, there are two cases regarding the values $i_{n}$ and $i_{m}$ can take:

$$
\begin{aligned}
& \text { i. } j_{n}=i_{n} \text { and } j_{m}=i_{m} \\
& \text { ii. } j_{n}=i_{m} \text { and } j_{m}=i_{n}
\end{aligned}
$$

The first case is very similar to the situation in the treatment of the single-body term and causes the sequences $i$ and $j$ to be equal. For the second case however, the sequences differ by a single pair, where one has $i_{m}$ and $i_{n}$ interchanged. This term then picks up a minus sign. We may now reduce one of the sums over the sequences and obtain

$$
\begin{array}{r}
\langle\Phi| \frac{1}{2} \sum_{n \neq m} \hat{h}_{2}\left(\vec{x}_{n}, \vec{x}_{m}\right)|\Phi\rangle=\frac{1}{N!} \frac{1}{2} \sum_{n \neq m} \sum_{i}^{N!}\left[\left\langle\phi_{i_{n}}\left(\vec{x}_{n}\right) \phi_{i_{m}}\left(\vec{x}_{m}\right)\right| \hat{h}_{2}\left(\vec{x}_{n}, \vec{x}_{m}\right)\left|\phi_{i_{n}}\left(\vec{x}_{n}\right) \phi_{i_{m}}\left(\vec{x}_{m}\right)\right\rangle-\right. \\
\left.\left\langle\phi_{i_{m}}\left(\vec{x}_{n}\right) \phi_{i_{n}}\left(\vec{x}_{m}\right)\right| \hat{h}_{2}\left(\vec{x}_{n}, \vec{x}_{m}\right)\left|\phi_{i_{n}}\left(\vec{x}_{n}\right) \phi_{i_{m}}\left(\vec{x}_{m}\right)\right\rangle\right] \tag{20}
\end{array}
$$

By a similar argument to the one that leads to Eq. 18, we notice that for a fixed sequence $i$ and for fixed $i_{n}$ and $i_{m}$, there are $(N-2)$ ! terms in the sum. We do not divide by two because this factor is already included. We do however, make sure that $i_{n} \neq i_{m}$ because each term shows up only once in the sum. Eq. 21 then becomes

$$
\begin{array}{r}
\langle\Phi| \frac{1}{2} \sum_{n \neq m} \hat{h}_{2}\left(\vec{x}_{n}, \vec{x}_{m}\right)|\Phi\rangle=\frac{1}{N!}(N-2)!\frac{1}{2} \sum_{n \neq m} \sum_{i_{n} \neq i_{m}}^{N}\left[\left\langle\phi_{i_{n}}\left(\vec{x}_{n}\right) \phi_{i_{m}}\left(\vec{x}_{m}\right)\right| \hat{h}_{2}\left(\vec{x}_{n}, \vec{x}_{m}\right)\left|\phi_{i_{n}}\left(\vec{x}_{n}\right) \phi_{i_{m}}\left(\vec{x}_{m}\right)\right\rangle-\right. \\
\left.\left\langle\phi_{i_{m}}\left(\vec{x}_{n}\right) \phi_{i_{n}}\left(\vec{x}_{m}\right)\right| \hat{h}_{2}\left(\vec{x}_{n}, \vec{x}_{m}\right)\left|\phi_{i_{n}}\left(\vec{x}_{n}\right) \phi_{i_{m}}\left(\vec{x}_{m}\right)\right\rangle\right] \tag{21}
\end{array}
$$

If $n$ is not equal to $m$, for each $n$ there are $N-1$ different values for $m$. Thus the number of $(n, m)$ pairs is $N(N-1)$ and we may replace the sum over such pairs with this factor. Finally, we replace $i_{n}$ and $i_{m}$ by more conventional indices such as $i$ and $j$ and the two-body term reduces to

$$
\begin{equation*}
\langle\Phi| \frac{1}{2} \sum_{n \neq m} \hat{h}_{2}\left(\vec{x}_{n}, \vec{x}_{m}\right)|\Phi\rangle=\sum_{i, j}^{N} \frac{1}{2} \sum_{i, j}^{N}\left[\left\langle\phi_{i} \phi_{j}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle-\left\langle\phi_{j} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle\right] \tag{22}
\end{equation*}
$$

where we have once again removed the dependence on orbitals. Notice the important fact that the term $i=j$ does not give any contribution to the sum because the two terms exactly cancel in that case. This is going to be a major difference between the Hartree-Fock method and density functional theory.

Putting together Eq. 18 and Eq. 22, the expectation value of the Hamiltonian for the Slater determinant is

$$
\begin{equation*}
\langle\Phi| \hat{H}_{e}|\Phi\rangle=\sum_{i}^{N}\left\langle\phi_{i}\right| \hat{h}_{1}\left|\phi_{i}\right\rangle+\frac{1}{2} \sum_{i, j}^{N}\left[\left\langle\phi_{i} \phi_{j}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle-\left\langle\phi_{j} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle\right] \tag{23}
\end{equation*}
$$

Next, we would like to apply the variational principle to the value in Eq. 23 to obtain the best possible estimate.

## IV. THE HARTREE-FOCK EQUATIONS

The variational principle that we will apply here is rather different from the linear variation that we saw in the first lecture. There the form of our approximate wavefunction was written as an expansion over a collection of predetermined functions and we minimized the expectation value (at the same time obeying the normalization constraint) with respect to the coefficients of the basis functions. Here however we employ a much more general treatment where we minimize with respect to the basis functions themselves! Needless to say, this requires functional differentiation where any change affected in the expectation value in Eq. 23 due to an infinitesimal change in any of the orbitals $\phi_{k}$ should be zero.

$$
\begin{equation*}
\phi_{k} \rightarrow \phi_{k}+\delta \phi_{k} \quad \Rightarrow \quad \delta\langle\Phi| \hat{H}_{e}|\Phi\rangle=0 \tag{24}
\end{equation*}
$$

In addition, we demand through Lagrange multipliers that the set of oritals $\phi_{k}$ remain orthogonal throughout the minimization process. The condition to be satisfied is then

$$
\begin{equation*}
\delta F \equiv \delta\left[\langle\Phi| \hat{H}_{e}|\Phi\rangle-\sum_{i, j} \lambda_{i j}\left(\left\langle\phi_{i} \mid \phi_{j}\right\rangle-\delta_{i j}\right)\right]=0 \tag{25}
\end{equation*}
$$

where the number of the Lagrange multipliers is now $N^{2}$ and we demand that the derivatives ith respect to all the Lagrange multipliers vanish.
First, let's see how the single-body term changes under an infinitesimal change in one of the orbitals, $\phi_{k}$.

$$
\begin{equation*}
\delta\langle\Phi| \sum_{i} \hat{h}_{1}\left(\vec{x}_{i}\right)|\Phi\rangle=\left\langle\delta \phi_{k}\right| \hat{h}_{1}\left|\phi_{k}\right\rangle+\left\langle\phi_{k}\right| \hat{h}_{1}\left|\delta \phi_{k}\right\rangle=\left\langle\delta \phi_{k}\right| \hat{h}_{1}\left|\phi_{k}\right\rangle+\left\langle\delta \phi_{k}\right| \hat{h}_{1}\left|\phi_{k}\right\rangle^{*} \tag{26}
\end{equation*}
$$

The last equality of Eq. 26 has been written making use of the hermiticity of the single-particle operator.
Similarly, the variation of the two-body term yields

$$
\begin{align*}
\delta\langle\Phi| \frac{1}{2} \sum_{i \neq j} \hat{h}_{2}\left(\vec{x}_{i}, \vec{x}_{j}\right)|\Phi\rangle & =\delta \frac{1}{2} \sum_{i, j}\left\{\left\langle\phi_{i} \phi_{j}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle-\left\langle\phi_{j} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle\right\} \\
& =\frac{1}{2} \sum_{i}\left\{\left\langle\phi_{i} \delta \phi_{k}\right| \hat{h}_{2}\left|\phi_{i} \phi_{k}\right\rangle+\left\langle\phi_{i} \phi_{k}\right| \hat{h}_{2}\left|\phi_{i} \delta \phi_{k}\right\rangle-\left\langle\delta \phi_{k} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{k}\right\rangle-\left\langle\phi_{k} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \delta \phi_{k}\right\rangle\right\} \\
& +\frac{1}{2} \sum_{j}\left\{\left\langle\delta \phi_{k} \phi_{j}\right| \hat{h}_{2}\left|\phi_{k} \phi_{j}\right\rangle+\left\langle\phi_{k} \phi_{j}\right| \hat{h}_{2}\left|\delta \phi_{k} \phi_{j}\right\rangle-\left\langle\phi_{j} \delta \phi_{k}\right| \hat{h}_{2}\left|\phi_{k} \phi_{j}\right\rangle-\left\langle\phi_{j} \phi_{k}\right| \hat{h}_{2}\left|\delta \phi_{k} \phi_{j}\right\rangle\right\} \tag{27}
\end{align*}
$$

where it is understood that in the second line $\hat{h}_{2}$ carries indices $i$ and $k$ and in the third line it carries indices $j$ and $k$. We can simplify the equation in Eq. 27 by making use of the hermiticity of $\hat{h}_{2}$ and the identity

$$
\begin{equation*}
\left\langle f_{1} f_{2}\right| \hat{A}\left|f_{3} f_{4}\right\rangle=\left\langle f_{2} f_{1}\right| \hat{A}\left|f_{4} f_{3}\right\rangle \tag{28}
\end{equation*}
$$

which holds if both of the functions on either side of the two-body operator are interchanged simultaneously. Interchanging the order of orbitals on the third line yields the same terms as in the second line except for the summation indices $i$ and $j$ which are arbitrary and interchangable. Having two identical sums, the factor of $\frac{1}{2}$ cancels. Applying finally the Hermiticy, we reduce the two-body term to

$$
\begin{align*}
\delta\langle\Phi| \frac{1}{2} \sum_{i \neq j} \hat{h}_{2}\left(\vec{x}_{i}, \vec{x}_{j}\right)|\Phi\rangle=\sum_{i} & {\left[\left\langle\phi_{i} \delta \phi_{k}\right| \hat{h}_{2}\left|\phi_{i} \phi_{k}\right\rangle+\left\langle\phi_{i} \delta \phi_{k}\right| \hat{h}_{2}\left|\phi_{i} \phi_{k}\right\rangle^{*}\right.} \\
& \left.-\left\langle\delta \phi_{k} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{k}\right\rangle-\left\langle\delta \phi_{k} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{k}\right\rangle^{*}\right] \tag{29}
\end{align*}
$$

The functional derivative of the Lagrange multipliers proceeds in exactly the same way with the Hermicity considered again at the end. Putting everything together the variation turns out to be

$$
\begin{align*}
\delta F= & \left\langle\delta \phi_{k}\right| \hat{h}_{1}\left|\phi_{k}\right\rangle+\left\langle\delta \phi_{k}\right| \hat{h}_{1}\left|\phi_{k}\right\rangle^{*}+\sum_{i}\left[\left\langle\phi_{i} \delta \phi_{k}\right| \hat{h}_{2}\left|\phi_{i} \phi_{k}\right\rangle+\left\langle\phi_{i} \delta \phi_{k}\right| \hat{h}_{2}\left|\phi_{i} \phi_{k}\right\rangle^{*}\right. \\
& \left.-\left\langle\delta \phi_{k} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{k}\right\rangle-\left\langle\delta \phi_{k} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{k}\right\rangle^{*}\right]-\sum_{i}\left[\lambda_{i k}\left\langle\delta \phi_{k} \mid \phi_{i}\right\rangle^{*}+\lambda_{k i}\left\langle\delta \phi_{k} \mid \phi_{i}\right\rangle\right] \tag{30}
\end{align*}
$$

For reasons which will become clear shortly, we shall evaluate the variation with respect to $\phi_{k}^{*}$ and not $\phi_{k}$. (For a proof that variation with respect to $\phi_{k}$ and $\phi_{k}^{*}$ are equivalent, see the appendix at the end.) Written as an integral, terms in Eq. 30 would read, for instance,

$$
\begin{equation*}
\left\langle\delta \phi_{k} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{k}\right\rangle=\iint \delta \phi_{k}^{*}\left(\vec{x}_{1}\right) \phi_{i}^{*}\left(\vec{x}_{2}\right) \hat{h}_{2}\left(\vec{x}_{1}, \vec{x}_{2}\right) \phi_{i}\left(\vec{x}_{1}\right) \phi_{k}\left(\vec{x}_{2}\right) d \vec{x}_{1} d \vec{x}_{2} \tag{31}
\end{equation*}
$$

Moreover, since we are considering the variation ith respect to only $\delta \phi_{k}^{*}$, we would completely disregard terms with $\delta \phi$ in the ket. As we saw in the section on functional integrals, evaluating $\frac{\delta F}{\delta \phi_{k}^{*}}$ basically amounts to getting rid of $\delta \phi_{k}$ in the bras in Eq. 30 and also the integral over its argument. This leaves

$$
\begin{equation*}
\hat{h}_{1} \phi_{k}\left(\vec{x}_{1}\right)+\sum_{i}\left\{\int \phi_{i}^{*}\left(\vec{x}_{2}\right) \hat{h}_{2}\left[\phi_{i}\left(\vec{x}_{2}\right) \phi_{k}\left(\vec{x}_{1}\right)\right] d \vec{x}_{2}-\int \phi_{i}^{*}\left(\vec{x}_{2}\right) \hat{h}_{2}\left[\phi_{i}\left(\vec{x}_{1}\right) \phi_{k}\left(\vec{x}_{2}\right)\right] d \vec{x}_{2}\right\}=\sum_{i} \lambda_{k i} \phi_{i}\left(\vec{x}_{1}\right) \tag{32}
\end{equation*}
$$

It is customary to write Eq. 32 using the orbital-dependent operators $\hat{J}_{i}$ and $\hat{K}_{i}$ as

$$
\begin{equation*}
\left[\hat{h}_{1}+\sum_{i}\left(\hat{J}_{i}-\hat{K}_{i}\right)\right] \phi_{k}=\sum_{i} \lambda_{k i} \phi_{i} \tag{33}
\end{equation*}
$$

where the first and the second term are straightforward, single-body operators and the third term is an integral operator. This is now a set of interdependent single-particle eigenvalue equations. The operator $\hat{J}$ corresponds to the classical interaction of an electron distributions given by $\left|\phi_{i}\right|^{2}$ and $\left|\phi_{k}\right|^{2}$ and is called the direct term while $\hat{K}$, called the exchange term, has no classical analogue and is a direct result of the antisymmetry property of the wavefunction. The Fock operator is defined as

$$
\begin{equation*}
\hat{F}=\hat{h}_{1}+\sum_{i}\left(\hat{J}_{i}-\hat{K}_{i}\right) \tag{34}
\end{equation*}
$$

and using this definition Eq. 33 takes the simple form

$$
\begin{equation*}
\hat{F} \phi_{k}=\sum_{i=1}^{N} \lambda_{k i} \phi_{i} \tag{35}
\end{equation*}
$$

There are several different solutions to the equations in Eq. 35 each corresponding to a different set of $\lambda_{k i}$. We have the freedom to concentrate upon those $\lambda_{k i}$ which satisfies

$$
\begin{equation*}
\lambda_{k i}=\delta_{k i} \epsilon_{k} \tag{36}
\end{equation*}
$$

where $\epsilon_{k}$ is essentially a new name for the Lagrange multipliers[1]. With this, Eq. 35 may be written as

$$
\begin{equation*}
\hat{F} \phi_{k}=\epsilon_{k} \phi_{k} . \tag{37}
\end{equation*}
$$

In this form, Eq. 37 is a traditional eigenvalue equation. For each $k$ there is an equivalent equation defining a system of Schrödinger-like, one-particle equations. Although it's tempting to interpret the eigenvalues $\epsilon_{k}$ as the energy levels of an interacting system, this is in fact not justified because the single-electron picture is not correct. However, if interpreted correctly the Hartree-Fock eigenvalues do correspond to certain physical entities.

## V. TOTAL ENERGY AND KOOPMANS' THEOREM

The total Hartree-Fock energy, $E_{H F}$, of the system of $N$ electrons discussed above may be written as

$$
\begin{equation*}
E_{H F}=\sum_{i}^{N}\left\langle\phi_{i}\right| \hat{h}_{1}\left|\phi_{i}\right\rangle+\frac{1}{2} \sum_{i, j}^{N}\left[\left\langle\phi_{i} \phi_{j}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle-\left\langle\phi_{j} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle\right. \tag{38}
\end{equation*}
$$

making use of Eq. 18 an Eq. 22. On the other hand the eigenergies, $\epsilon_{k}$, of the Hartree-Fock equations given in Eq. 37 may be summed to give

$$
\begin{equation*}
\sum_{k} \epsilon_{k}=\sum_{i}^{N}\left\langle\phi_{i}\right| \hat{h}_{1}\left|\phi_{i}\right\rangle+\sum_{i, j}^{N}\left[\left\langle\phi_{i} \phi_{j}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle-\left\langle\phi_{j} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle .\right. \tag{39}
\end{equation*}
$$

Eq. 38 and Eq. 39 demonstrate that the total energy cannot be given as a simple sum over the eigenenergies of the Fock operator but are closely related by

$$
\begin{equation*}
E_{H F}=\sum_{k} \epsilon_{k}-\frac{1}{2} \sum_{i, j}^{N}\left[\left\langle\phi_{i} \phi_{j}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle-\left\langle\phi_{j} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle\right] \tag{40}
\end{equation*}
$$

This "discrepancy" stems from the description of a true many-body system in terms of single-particle orbitals. Next, let's compare the energy of two systems, one with $N$ electrons and one with $N-1$, where an electron has been removed from the $n$th level from the system with $N$ electrons to obtain the system with $N-1$ electrons. The energy required to remove the electron is given by

$$
\begin{align*}
\Delta E_{N} \equiv & E_{H F}(N-1)-E_{H F}(N) \\
= & \sum_{i \neq n}^{N}\left\langle\phi_{i}\right| \hat{h}_{1}\left|\phi_{i}\right\rangle+\frac{1}{2} \sum_{i, j \neq n}^{N}\left[\left\langle\phi_{i} \phi_{j}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle-\left\langle\phi_{j} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle\right] \\
& \quad-\sum_{i}^{N}\left\langle\phi_{i}\right| \hat{h}_{1}\left|\phi_{i}\right\rangle-\frac{1}{2} \sum_{i, j}^{N}\left[\left\langle\phi_{i} \phi_{j}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle-\left\langle\phi_{j} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{j}\right\rangle\right] \\
= & -\left\langle\phi_{i}\right| \hat{h}_{n}\left|\phi_{i}\right\rangle-\frac{1}{2} \sum_{i}^{N}\left[\left\langle\phi_{i} \phi_{n}\right| \hat{h}_{2}\left|\phi_{i} \phi_{n}\right\rangle-\left\langle\phi_{n} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{n}\right\rangle\right]-\frac{1}{2} \sum_{j}^{N}\left[\left\langle\phi_{n} \phi_{j}\right| \hat{h}_{2}\left|\phi_{n} \phi_{j}\right\rangle-\left\langle\phi_{j} \phi_{n}\right| \hat{h}_{2}\left|\phi_{n} \phi_{j}\right\rangle\right] . \tag{41}
\end{align*}
$$

which is obtained by evaluating the difference in a straightforward manner. In the final sum $i$ can be substituted by $j$ since the index is aritrary. We then obtain

$$
\begin{equation*}
\Delta E_{N}=-\left\langle\phi_{i}\right| \hat{h}_{n}\left|\phi_{i}\right\rangle-\frac{1}{2} \sum_{i}^{N}\left[\left\langle\phi_{i} \phi_{n}\right| \hat{h}_{2}\left|\phi_{i} \phi_{n}\right\rangle-\left\langle\phi_{n} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{n}\right\rangle\right]-\frac{1}{2} \sum_{i}^{N}\left[\left\langle\phi_{n} \phi_{i}\right| \hat{h}_{2}\left|\phi_{n} \phi_{i}\right\rangle-\left\langle\phi_{i} \phi_{n}\right| \hat{h}_{2}\left|\phi_{n} \phi_{i}\right\rangle\right] . \tag{42}
\end{equation*}
$$

In Eq. 42, it is permissible to exchange the indices $i$ and $n$ if done simultaneously on either side of the operator, we have

$$
\Delta E_{N}=-\left\langle\phi_{i}\right| \hat{h}_{n}\left|\phi_{i}\right\rangle-\frac{1}{2} \sum_{i}^{N}\left[\left\langle\phi_{i} \phi_{n}\right| \hat{h}_{2}\left|\phi_{i} \phi_{n}\right\rangle-\left\langle\phi_{n} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{n}\right\rangle\right]-\frac{1}{2} \sum_{i}^{N}\left[\left\langle\phi_{i} \phi_{n}\right| \hat{h}_{2}\left|\phi_{i} \phi_{n}\right\rangle-\left\langle\phi_{n} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{n}\right\rangle\right]
$$

The two sums at the end are identical. Thus

$$
\begin{equation*}
\Delta E_{N}=-\left\langle\phi_{i}\right| \hat{h}_{n}\left|\phi_{i}\right\rangle-\sum_{i}^{N}\left[\left\langle\phi_{i} \phi_{n}\right| \hat{h}_{2}\left|\phi_{i} \phi_{n}\right\rangle-\left\langle\phi_{n} \phi_{i}\right| \hat{h}_{2}\left|\phi_{i} \phi_{n}\right\rangle\right] \tag{43}
\end{equation*}
$$

By comparing Eq. 43 and Eq. 35, we see that the right hand side is nothing but $-\epsilon_{n}$

$$
\begin{equation*}
E_{H F}(N-1)-E_{H F}(N)=-\epsilon_{n} \tag{44}
\end{equation*}
$$

We thus arrive at Koopmans' theorem, which states that each eigenvalue of the Fock operator gives the energy required to remove an electron from the corresponding single-electron state. Similarly the energy required to add an electron to orbital $m$ can be proven to be given by

$$
\begin{equation*}
E_{H F}(N+1)-E_{H F}(N)=\epsilon_{m} \tag{45}
\end{equation*}
$$

In Eq. 44 and Eq. 45, level $n$ is assumed to be occupied and level $m$ is assumed to be empty. Therefore $\epsilon_{k}$ may be interpreted as orbital energies in the approximation that the changes in the orbitals when the electron is removed or added is small.

## VI. HARTREE-FOCK-ROOTHAAN EQUATIONS

Solving the Fock equations given in Eq. 33 involves the evaluation of the orbitals at every single point in space, which is a rather daunting task. Instead, Roothaan proposed a limited variation instead where the orbitals are expanded in terms of a known basis set and the variation is conducted over the coefficients of the basis functions. This is slightly different from the usual variational principle that we discussed in Lecture 1 since there the approximate wavefunction was directly expanded in terms of the known basis without the extra step of the Slater determinant inbetween. In Roothaan's expansion, each orbital is written as

$$
\begin{equation*}
\phi_{l}(\vec{x})=\sum_{p}^{N_{b}} c_{p l} \chi_{p}(\vec{x}) \tag{46}
\end{equation*}
$$

where $N_{b}$ is the number of basis sets used. Most of the time, the basis that we use is going to be a truncated set and $N_{b}$ is going to be finite. When substituted into Eq. 25, this expansion yields

$$
\begin{align*}
\hat{F}= & \sum_{i=1}^{N} \sum_{m, n=1}^{N_{b}} c_{m i}^{*} c_{n i}\left\langle\chi_{m}\right| \hat{h}_{1}\left|\chi_{n}\right\rangle+ \\
& \frac{1}{2} \sum_{i, j}^{N} \sum_{m, n, p, q}^{N_{b}} c_{m i}^{*} c_{p i} c_{n j}^{*} c_{q j}\left[\left\langle\chi_{m} \chi_{p}\right| \hat{h}_{2}\left|\chi_{n} \chi_{q}\right\rangle-\left\langle\chi_{p} \chi_{m}\right| \hat{h}_{2}\left|\chi_{n} \chi_{q}\right\rangle\right]-\sum_{i}^{N} \epsilon_{i}\left[\sum_{n, m}^{N_{b}} c_{m i}^{*} c_{n i}\left\langle\chi_{m} \mid \chi_{n}\right\rangle-1\right] \tag{47}
\end{align*}
$$

where we once again make use of diagonal Lagrange multipliers. Since we conduct the variation over the coefficients rather than the orbitals, we have

$$
\begin{equation*}
\delta F=0 \quad \Rightarrow \quad \frac{\partial F}{\partial c_{r k}^{*}}=0 \tag{48}
\end{equation*}
$$

The first term will yield a nonzero result only if $m=r$ and $k=i$, which reduces to

$$
\begin{equation*}
\sum_{n}^{N_{b}} c_{n k}\left\langle\chi_{r}\right| \hat{h}_{1}\left|\chi_{n}\right\rangle \tag{49}
\end{equation*}
$$

The second term brings two contributions, one for each of the $c^{*}$ coefficients. By previous experience (and also by a quite straighforward yet tedious calculation) we foresee that these two contributions will be equal. Let's then look at the case where $m=r$ and $k=i$ and multiply by two to obtain the entire contribution from the two-body term

$$
\begin{equation*}
\sum_{j}^{N} \sum_{p, q}^{N_{b}} c_{p k} c_{n j}^{*} c_{q j}\left[\left\langle\chi_{r} \chi_{p}\right| \hat{h}_{2}\left|\chi_{n} \chi_{q}\right\rangle-\left\langle\chi_{p} \chi_{r}\right| \hat{h}_{2}\left|\chi_{n} \chi_{q}\right\rangle\right] \tag{50}
\end{equation*}
$$

For further use, let's exchange the summation indices $p$ and $n$ to obtain

$$
\begin{equation*}
\sum_{j}^{N} \sum_{p, q}^{N_{b}} c_{n k} c_{p j}^{*} c_{q j}\left[\left\langle\chi_{r} \chi_{n}\right| \hat{h}_{2}\left|\chi_{p} \chi_{q}\right\rangle-\left\langle\chi_{n} \chi_{r}\right| \hat{h}_{2}\left|\chi_{p} \chi_{q}\right\rangle\right] \tag{51}
\end{equation*}
$$

Finally the term with the Lagrange multipliers can be evaluated quite simply to result in

$$
\begin{equation*}
\epsilon_{k} \sum_{n}^{N_{b}} c_{n k}\left\langle\chi_{r} \mid \chi_{n}\right\rangle \tag{52}
\end{equation*}
$$

The minimization then yields, putting everything together and collecting all terms under a single sum

$$
\begin{equation*}
\sum_{n}^{N_{b}}\left\{\left\langle\chi_{r}\right| \hat{h}_{1}\left|\chi_{n}\right\rangle+\sum_{j}^{N} \sum_{p, q}^{N_{b}} c_{p j}^{*} c_{q j}\left[\left\langle\chi_{k} \chi_{n}\right| \hat{h}_{2}\left|\chi_{p} \chi_{q}\right\rangle-\left\langle\chi_{n} \chi_{k}\right| \hat{h}_{2}\left|\chi_{p} \chi_{q}\right\rangle\right]\right\} c_{n k}=\epsilon_{k} \sum_{n}^{N_{b}}\left\langle\chi_{r} \mid \chi_{n}\right\rangle c_{n k} \tag{53}
\end{equation*}
$$

If now, we call the term in the large curly braces $F_{r n}$ and recognize the inner product on the right-hand side as an element of the overlap matrix, namely $S_{r n}$ then Eq. 53 turns into the following matrix equation

$$
\begin{equation*}
F \cdot C=\epsilon C \tag{54}
\end{equation*}
$$

where $C$ is the usual vector of coefficients.
Eq. 54, although very similar to the matrix equation that we obtained when dealing with the variational principle, differs in that the representation of the matrix $F$ in any basis depends again on the coefficients that we are trying to calculate. This is again a result of the description of the many-body wavefunction as formed by noninteracting single-particle orbitals where the effect of the orbitals come out indirectly in the operator that defines the eigenvalue equation. A very similar problem ill be encountered when we deal with DFT and standard methods of tackling with such so called self-consistent field problems will be illustrated.

## VII. SPIN PROPERTIES

Because the Slater determinant is a product of imagination, it is no guaranteed to satisfy all the properties of the exact wavefunction. Let us, for instance, look at the spin properties of the Slater determinant. We shall consider two operators : $\hat{S}_{z}$ and $\hat{S}^{2}$. The total spin in any one direction is the sum of the spins of individual electrons

$$
\begin{equation*}
\hat{S}_{x}=\sum_{i}^{N} \hat{s}_{i, x} \quad \hat{S}_{y}=\sum_{i}^{N} \hat{s}_{i, y} \quad \text { and } \quad \hat{S}_{z}=\sum_{i}^{N} \hat{s}_{i, z} \tag{55}
\end{equation*}
$$

and the total spin is given by

$$
\begin{equation*}
\hat{S}^{2}=\hat{S}_{x}^{2}+\hat{S}_{y}^{2}+\hat{S}_{z}^{2} \tag{56}
\end{equation*}
$$

In order to find out about the spin properties of the approximate function, we need to explicitly specify the spin dependence of the individual orbitals. Let's assume that $n$ of the orbitals have $\alpha$ spin while $m$ of them have $\beta$ spin. Then the determinant may be written in shorthand notation as

$$
\begin{equation*}
\Phi\left(\vec{x}_{1}, \vec{x}_{2}, \cdots, \vec{x}_{N}\right)=\left|\phi_{1}^{+} \alpha, \phi_{2}^{+} \alpha, \cdots \phi_{n}^{+} \alpha, \phi_{1}^{-} \beta \phi_{2}^{-} \beta \cdots \phi_{m}^{-} \beta\right| \tag{57}
\end{equation*}
$$

where we have allowed the position-dependent $\phi^{+}$and $\phi^{-}$orbitals to be different. If the function, $\Phi$ in Eq. 57 is written down explicitly as a sum, we have

$$
\begin{equation*}
\Phi=\frac{1}{\sqrt{N!}} \sum_{i=1}^{N!}(-1)^{P(i)} \phi_{i_{1}}^{+}\left(\vec{r}_{1}\right) \alpha(1) \cdots \phi_{i_{n}}^{+}\left(\vec{r}_{n}\right) \alpha(n), \phi_{i_{n+1}}^{-}\left(\vec{r}_{n+1}\right) \beta(n+1) \cdots \phi_{i_{N}}^{+}\left(\vec{r}_{N}\right) \tag{58}
\end{equation*}
$$

Using the $\hat{S}_{z}$ operator in Eq. 55, the wavefunction in Eq. 58 is clearly seen to be an eigenstate of the $\hat{S}_{z}$ operator with

$$
\begin{equation*}
\hat{S}_{z} \Phi=\frac{n-m}{2} \Phi \tag{59}
\end{equation*}
$$

One can prove, however, through some straighforward (but somewhat lengthy) algebra that $\Phi$ is an eigenfunction of $S^{2}$ only if $m=n$ and $\phi^{-}=\phi^{+}$. If we impose these constraints on the Slater determinant, this amounts to the restricted Hartree-Fock method. Alternatively, we may either ignore the problem and use unrestricted Hartree-Fock or resort to the projected Hartree-Fock method where the linear combination of more than one Slater determinant is taken as the approximate wavefunction, which is also an eigenfunction of the operator $\hat{S}^{2}$.

## VIII. APPENDIX

Consider a real function, $f\left(z, z^{*}\right)$, of the complex variable $z$ and its complex conjugate $z^{*}$. The real and imaginary parts of the variable $z$ can be written as linear combinations of $z$ and $z^{*}$ as

$$
\begin{align*}
& z_{r}=\frac{z+z^{*}}{2} \\
& z_{i}=\frac{z-z^{*}}{2 i} . \tag{60}
\end{align*}
$$

If we consider now the derivatives with respect to $z$ and make use of the chain rule, we obtain

$$
\begin{equation*}
\left.\frac{\partial f}{\partial z}\right|_{z^{*}}=\frac{\partial f}{\partial z_{r}} \frac{\partial z_{r}}{\partial z}+\frac{\partial f}{\partial z_{i}} \frac{\partial z_{i}}{\partial z}=\frac{1}{2}\left(\frac{\partial f}{\partial z_{r}}-i \frac{\partial f}{\partial z_{i}}\right) \tag{61}
\end{equation*}
$$

where the last inequality has been written using Eq. 60. Similarly the derivative with respect to $z^{*}$ yields

$$
\begin{equation*}
\left.\frac{\partial f}{\partial z^{*}}\right|_{z}=\frac{\partial f}{\partial z_{r}} \frac{\partial z_{r}}{\partial z^{*}}+\frac{\partial f}{\partial z_{i}} \frac{\partial z_{i}}{\partial z^{*}}=\frac{1}{2}\left(\frac{\partial f}{\partial z_{r}}+i \frac{\partial f}{\partial z_{i}}\right) . \tag{62}
\end{equation*}
$$

Since $f$ is real, the derivatives $\frac{\partial f}{\partial z_{r}}$ and $\frac{\partial f}{\partial z_{i}}$ in Eq. 61 and Eq. 62 are also real. Equating both of these equations to zero at the minimum then yields the conditions

$$
\begin{equation*}
\frac{\partial f}{\partial z_{r}}=0 \quad \text { and } \quad \frac{\partial f}{\partial z_{i}}=0 \tag{63}
\end{equation*}
$$

and are thus equivalent.
[1] One can prove that this it is possible to move between the diagonal form of the Lagrange multipliers and the more general non-diagonal form through a unitary transform

