Approximate Methods in Quantum Chemistry
Professor Sabyashachi Mishra
Department of Chemistry
Indian Institute of Technology, Kharagpur
Lecture-30
Canonical HF Equations

Hello students! Welcome to this lecture. In the last lecture, we started our discussion on the Hartree-Fock self-consistent field method. We were in the middle of formulation of the HF-SCF method as a variational problem. We will continue our discussion from there.

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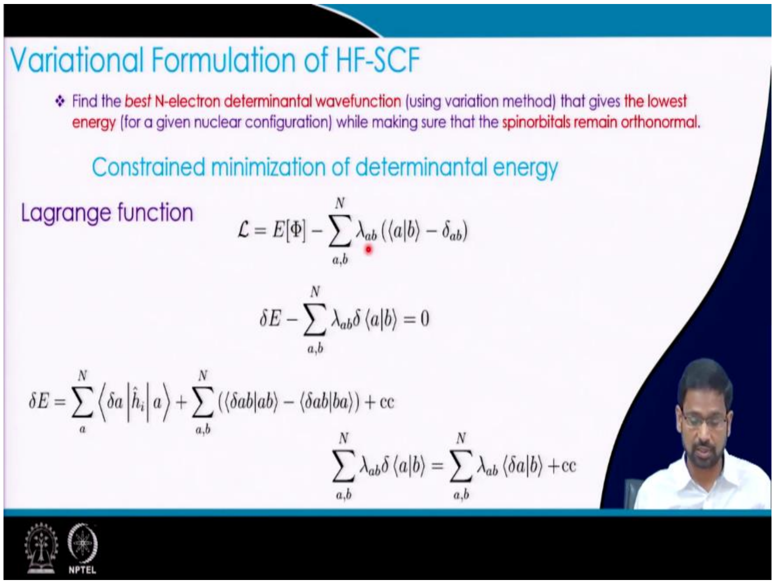

Our overall objective was to find the Slater determinant that minimizes the energy (expressed as a functional of the Slater determinant Φ), while keeping the spinorbitals ($\{\chi_a\}$ or $\{a\}$) orthonormal. Such a constrained minimization was carried out by adopting the Lagrange's method of undetermined multipliers. We defined the Lagrange function

$$\mathcal{L} = E[\Phi] - \sum_{a,b}^{N} \lambda_{ab} \left(\langle a|b \rangle - \delta_{ab} \right)$$

Here, λ_{ab} are the undetermined multipliers. For the constrained minimization, we expect the first variation of the Lagrange function to be come zero. To that end, we need to satisfy

$$\delta E - \sum_{a,b}^{N} \lambda_{ab} \delta \langle a|b \rangle = 0$$

where we have already determined (from previous lecture),

$$\delta E = \sum_{a}^{N} \left\langle \delta a \left| \hat{h}_i \right| a \right\rangle + \sum_{a,b}^{N} \left(\langle \delta ab | ab \rangle - \langle \delta ab | ba \rangle \right) + \mathrm{cc}$$

and

$$\sum_{a,b}^{N} \lambda_{ab} \delta \langle a|b \rangle = \sum_{a,b}^{N} \lambda_{ab} \langle \delta a|b \rangle + \mathrm{cc}$$

Here *cc* represents the complex conjugate.

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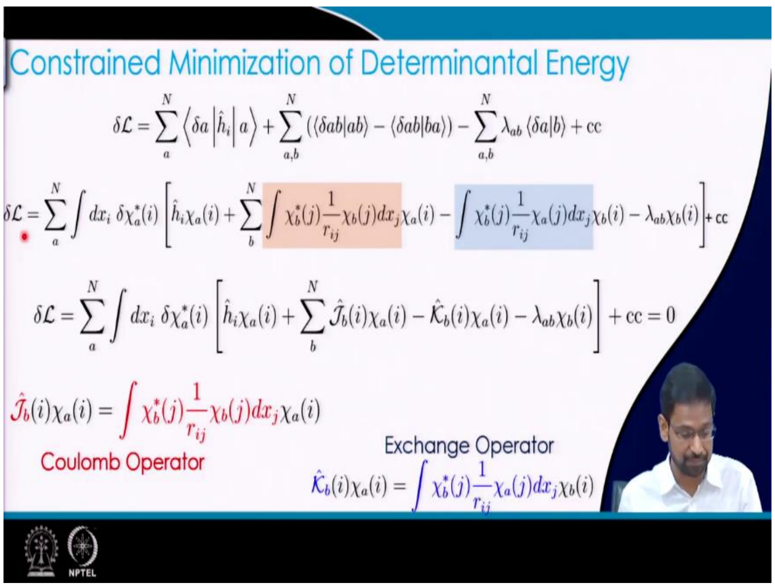

Using the above two expressions, the first variation of the Lagrange function can be expressed as

$$\delta\mathcal{L} = \sum_{a}^{N} \left\langle \delta a \left| \hat{h}_i \right| a \right\rangle + \sum_{a,b}^{N} \left(\langle \delta ab | ab \rangle - \langle \delta ab | ba \rangle \right) - \sum_{a,b}^{N} \lambda_{ab} \langle \delta a|b \rangle + \mathrm{cc}$$

Let us now express the above equation by writing them down in their integral forms:

$$\delta\mathcal{L} = \sum_{a}^{N} \int dx_i \, \delta\chi_a^*(i) \left[\hat{h}_i \chi_a(i) + \sum_{b}^{N} \int \chi_b^*(j) \frac{1}{r_{ij}} \chi_b(j) dx_j \chi_a(i) - \int \chi_b^*(j) \frac{1}{r_{ij}} \chi_a(j) dx_j \chi_b(i) - \lambda_{ab}\chi_b(i) \right]$$

If we define the above shaded regions as Coulomb operator ($\widehat{J_b}$)and exchange operator ($\widehat{K_b}$) as following,

$$\hat{\mathcal{J}}_b(i)\chi_a(i) = \int \chi_b^*(j) \frac{1}{r_{ij}} \chi_b(j) dx_j \chi_a(i) \qquad \hat{\mathcal{K}}_b(i)\chi_a(i) = \int \chi_b^*(j) \frac{1}{r_{ij}} \chi_a(j) dx_j \chi_b(i)$$

The first variation of the Lagrange function then simplifies to

$$\delta\mathcal{L} = \sum_{a}^{N} \int dx_i \; \delta\chi_a^*(i) \left[\hat{h}_i \chi_a(i) + \sum_{b}^{N} \hat{\mathcal{J}}_b(i)\chi_a(i) - \hat{\mathcal{K}}_b(i)\chi_a(i) - \lambda_{ab}\chi_b(i) \right] + \text{cc} = 0$$

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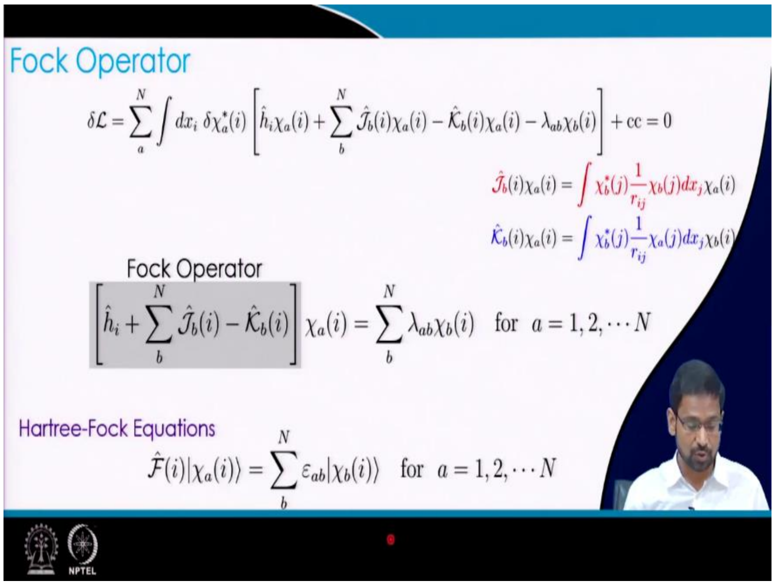

In the above expression, the first variation of the Lagrange function ($\delta\mathcal{L}$) will become zero when the terms shown explicitly and the corresponding complex-conjugate terms become zero independently. Hence, we can drop *cc* from the above equation. The above expression of the $\delta\mathcal{L}$ involves a summation over the spinorbitals (a). For $\delta\mathcal{L}$ to become zero, the above expression must be zero for *each* spinorbital. Hence, the summation sign can be dropped. This leaves us with the terms within the integral sign. We can further simplify the above equation, by requiring the terms in the square brackets to become zero. This results in the following relation,

$$\left[\hat{h}_i + \sum_{b}^{N} \hat{\mathcal{J}}_b(i) - \hat{\mathcal{K}}_b(i) \right] \chi_a(i) = \sum_{b}^{N} \lambda_{ab}\chi_b(i) \quad \text{for} \quad a = 1, 2, \cdots N$$

The operators in the left-hand side (within the square brackets) are known as the Fock operator, which consists of 1-electron core Hamiltonian operators and the Coulomb and exchange operators. Since the Fock operator is an energy operator, we can express the undetermined multipliers λ_{ab} as some energy values ϵ_{ab}.

The action of the Fock operator ($\hat{\mathcal{F}}$) can be expressed as,

$$\hat{\mathcal{F}}(i)|\chi_a(i)\rangle = \sum_b^N \varepsilon_{ab}|\chi_b(i)\rangle \quad \text{for} \quad a = 1, 2, \cdots N$$

The above set of equations are called the Hartree-Fock equations, more accurately, the noncanonical Hartree-Fock equations. We call them noncanonical because the above equation does not represent a standard eigenvalue problem (notice that the functions/spinorbitals in LHS and RHS are different).

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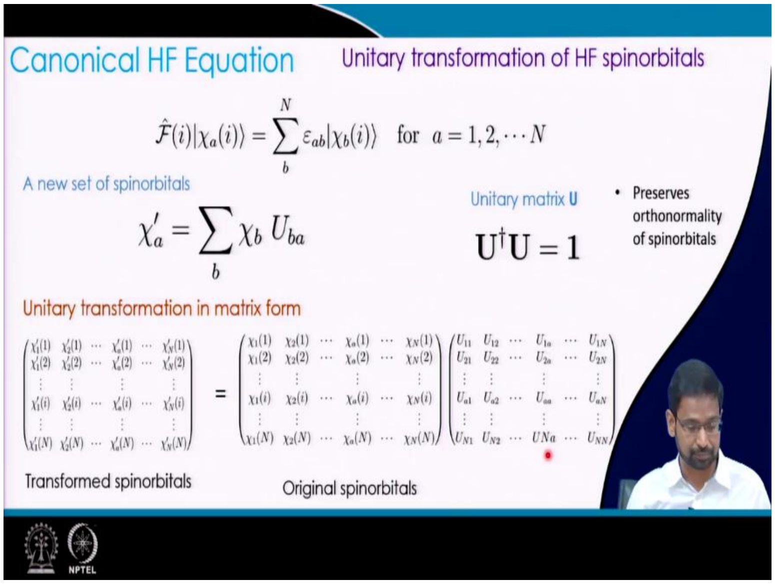

Next, we discuss how to express the Hartree-Fock equations in a canonical form. This can be achieved by carrying out a unitary transformation of the HF spinorbitals. In other words, we obtain a Unitary matrix (**U**) that transforms the noncanonical HF spinorbitals to a different set of spinorbitals, i.e.,

$$\chi'_a = \sum_b \chi_b \, U_{ba}$$

Here the unitary matrix ($U^{+}\mathbf{U} = \mathbf{1}$) preserves the orthonormality of the spinorbitals even after the transformation.

By carrying out this unitary transformation, we are preparing a new set of transformed spinorbitals (χ_a') from the (noncanonical) HF spinorbitals (χ_a),

$$\begin{pmatrix} \chi_1'(1) & \chi_2'(1) & \cdots & \chi_a'(1) & \cdots & \chi_N'(1) \\ \chi_1'(2) & \chi_2'(2) & \cdots & \chi_a'(2) & \cdots & \chi_N'(2) \\ \vdots & \vdots & & \vdots & & \vdots \\ \chi_1'(i) & \chi_2'(i) & \cdots & \chi_a'(i) & \cdots & \chi_N'(i) \\ \vdots & \vdots & & \vdots & & \vdots \\ \chi_1'(N) & \chi_2'(N) & \cdots & \chi_a'(N) & \cdots & \chi_N'(N) \end{pmatrix} = \begin{pmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_a(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_a(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & & \vdots & & \vdots \\ \chi_1(i) & \chi_2(i) & \cdots & \chi_a(i) & \cdots & \chi_N(i) \\ \vdots & \vdots & & \vdots & & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_a(N) & \cdots & \chi_N(N) \end{pmatrix} \begin{pmatrix} U_{11} & U_{12} & \cdots & U_{1a} & \cdots & U_{1N} \\ U_{21} & U_{22} & \cdots & U_{2a} & \cdots & U_{2N} \\ \vdots & \vdots & & \vdots & & \vdots \\ U_{a1} & U_{a2} & \cdots & U_{aa} & \cdots & U_{aN} \\ \vdots & \vdots & & \vdots & & \vdots \\ U_{N1} & U_{N2} & \cdots & UNa & \cdots & U_{NN} \end{pmatrix}$$

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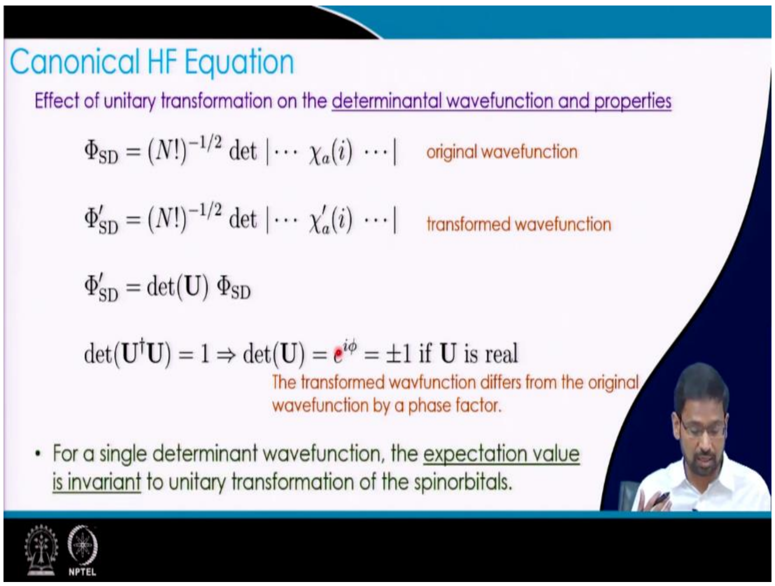

Using the transformed spinorbitals, we can write down the corresponding Slater determinant as following

$$\Phi'_{\text{SD}} = (N!)^{-1/2} \det |\cdots \ \chi'_a(i) \ \cdots|$$

The transformed Slater determinant (Φ_{SD}') is related to the (noncanonical) HF Slater determinant (Φ_{SD}) as following

$$\Phi'_{\text{SD}} = \det(\mathbf{U}) \ \Phi_{\text{SD}}$$

Since **U** is a unitary matrix,

$$\det(\mathbf{U}^\dagger \mathbf{U}) = 1 \Rightarrow \det(\mathbf{U}) = e^{i\phi} = \pm 1 \text{ if } \mathbf{U} \text{ is real}$$

This means Φ'_{SD} is related to Φ_{SD} via a phase factor ($e^{i\phi}$).

If we evaluate any expectation value of any operator using the Slater determinant wave function, we can see that the expectation value will not change (or remain invariant) if we take Φ_{SD} or the transformed Slater determinant Φ'_{SD}. Hence, the expectation value is invariant to unitary transformation of the spinorbital.

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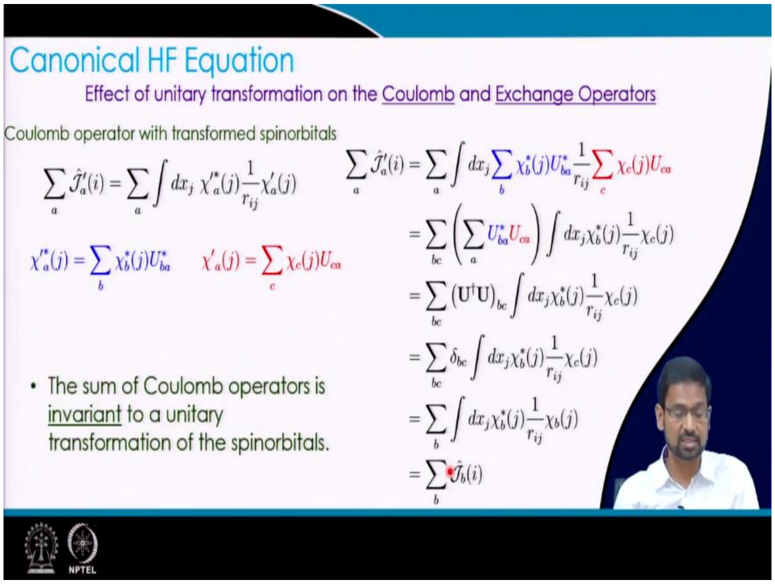

If you recall our earlier discussion, you would realize that the definition of the Coulomb operator and the exchange operator involves the spinorbitals. If we transform the spinorbitals, we need to see how that affects these operators. Let us define the Coulomb operator in the basis of transformed spinorbitals

$$\sum_a \hat{\mathcal{J}}'_a(i) = \sum_a \int dx_j\; \chi'^*_a(j)\frac{1}{r_{ij}}\chi'_a(j)$$

where the transformed spin orbitals are related to the original spinorbitals and the Unitary matrix,

$$\chi'^*_a(j) = \sum_b \chi^*_b(j)U^*_{ba} \qquad \chi'_a(j) = \sum_c \chi_c(j)U_{ca}$$

Using the above relation in the definition of the Coulomb operator, we obtain

$$\begin{aligned}
\sum_a \hat{\mathcal{J}}'_a(i) &= \sum_a \int dx_j \sum_b \chi_b^*(j) U_{ba}^* \frac{1}{r_{ij}} \sum_c \chi_c(j) U_{ca} \\
&= \sum_{bc} \left(\sum_a U_{ba}^* U_{ca} \right) \int dx_j \chi_b^*(j) \frac{1}{r_{ij}} \chi_c(j) \\
&= \sum_{bc} \left(\mathbf{U}^\dagger \mathbf{U} \right)_{bc} \int dx_j \chi_b^*(j) \frac{1}{r_{ij}} \chi_c(j) \\
&= \sum_{bc} \delta_{bc} \int dx_j \chi_b^*(j) \frac{1}{r_{ij}} \chi_c(j) \\
&= \sum_b \int dx_j \chi_b^*(j) \frac{1}{r_{ij}} \chi_b(j) \\
&= \sum_b \hat{\mathcal{J}}_b(i)
\end{aligned}$$

Since U is a unitary matrix, the only the diagonal matrix elements of $\mathbf{U^+U}$ are 1, while all off-diagonal elements are zero. Hence, $(\mathbf{U^+U})_{bc} = \boldsymbol{\delta}_{\mathbf{bc}}$. At the end of the above exercise, I see that the sum of the Coulomb operators is invariant to the unitary transformation of the noncanonical spinorbitals.

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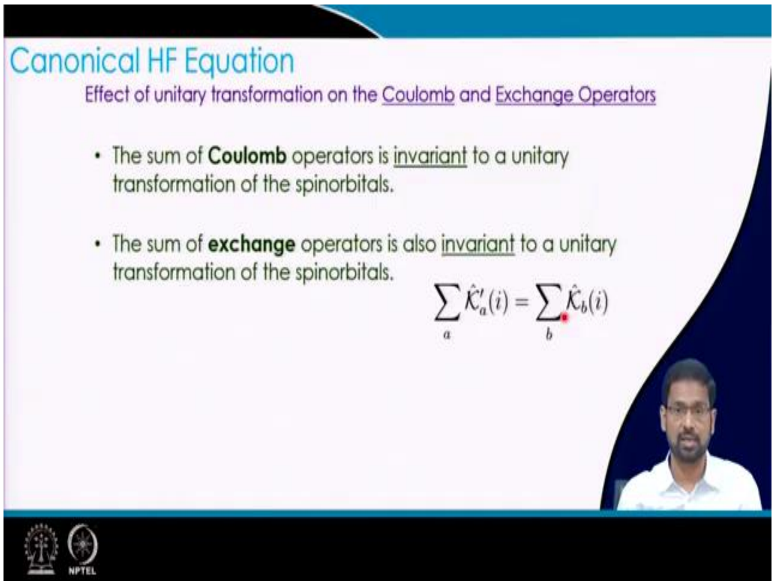

Similarly, we can also show that the sum of the exchange operators is also invariant to unitary transformation, i.e.,

$$\sum_a \hat{\mathcal{K}}'_a(i) = \sum_b \hat{\mathcal{K}}_b(i)$$

In that case, the Fock operator itself is invariant to the unitary transformation.

$$\hat{\mathcal{F}}'(i) = \hat{\mathcal{F}}(i)$$

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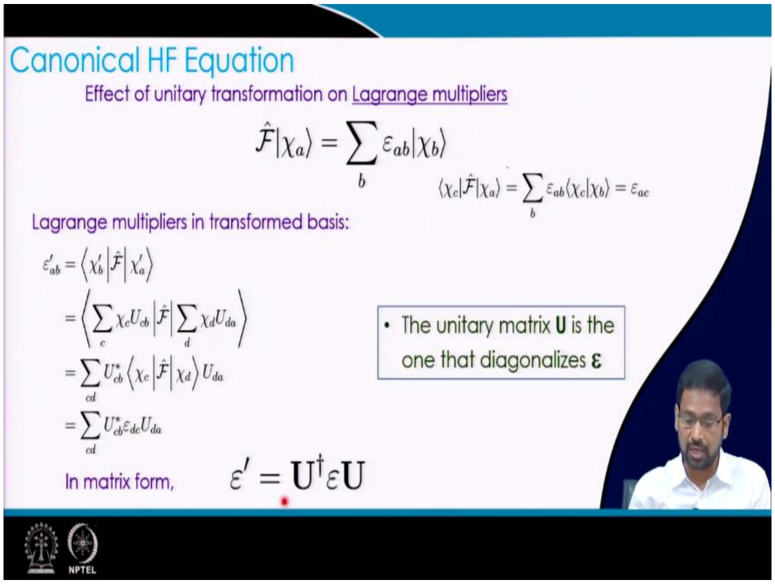

Although we have seen that the unitary transformation leaves the Fock operator invariant, we still do not know two things, namely, what is the effect of unitary transformation on the Lagrange multipliers and how to obtain the unitary matrix. We will discuss them now.

We have the following non-canonical HF equation, $\hat{\mathcal{F}}|\chi_a\rangle = \sum_b \varepsilon_{ab}|\chi_b\rangle$

If we multiply $\langle\chi_c|$ both sides of the above equation we get (using the orthonormality of the spinorbitals),

$$\langle\chi_c|\hat{\mathcal{F}}|\chi_a\rangle = \sum_b \varepsilon_{ab}\langle\chi_c|\chi_b\rangle = \varepsilon_{ac}$$

Now, let us find out the effect of unitary transformation of the spinorbitals on the Lagrange multipliers, i.e.,

$$\begin{aligned}\varepsilon'_{ab} &= \left\langle \chi'_b \middle| \hat{\mathcal{F}} \middle| \chi'_a \right\rangle \\ &= \left\langle \sum_c \chi_c U_{cb} \middle| \hat{\mathcal{F}} \middle| \sum_d \chi_d U_{da} \right\rangle \\ &= \sum_{cd} U^*_{cb} \left\langle \chi_c \middle| \hat{\mathcal{F}} \middle| \chi_d \right\rangle U_{da} \\ &= \sum_{cd} U^*_{cb} \varepsilon_{dc} U_{da}\end{aligned}$$

In the second line of the above equation, we have used the definition of the transformed spinorbitals in terms of the original spinorbitals and the unitary matrix. In the last line we have the used Fock matrix element $\langle\chi_c|\hat{\mathcal{F}}|\chi_d\rangle = \epsilon_{dc}$.

The expression $\epsilon'_{ab} = \sum_{c,d} U^*_{cd}\, \epsilon_{dc} U_{da}$ can be written down in the matrix form as

$$\varepsilon' = \mathbf{U}^{\dagger}\varepsilon\mathbf{U}$$

Where $\boldsymbol{\epsilon}$ and $\boldsymbol{\epsilon}'$ are the Lagrange multiplier matrices before and after the unitary transformation. The above relation also tells us how to obtain the unitary matrix. We can see that the unitary matrix is the one that diagonalizes the Lagrange multiplier matrix $\boldsymbol{\epsilon}$. The transformed Lagrange multiplier matrix $\boldsymbol{\epsilon}'$ is now a diagonal matrix.

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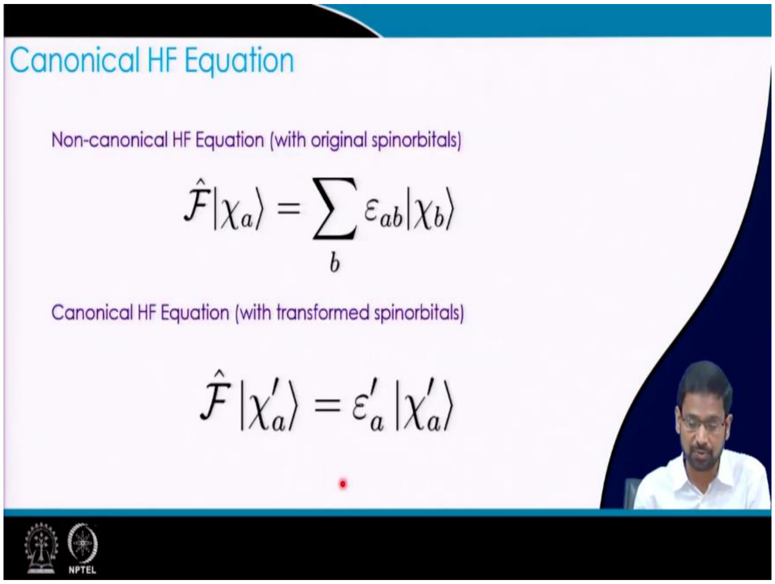

At the end of this exercise, we can now write the non-canonical and canonical HF equations as following

$$\hat{\mathcal{F}}|\chi_a\rangle = \sum_b \varepsilon_{ab}|\chi_b\rangle \qquad\qquad \hat{\mathcal{F}}\,|\chi'_a\rangle = \varepsilon'_a\,|\chi'_a\rangle$$

The canonical HF equation is an eigenvalue problem, where the transformed spinorbitals are the eigenfunctions of the Fock operators with eigenvalues of ϵ'_a.

Since for most practical purposes we will use the canonical form of the HF equation, we can drop the prime symbols in the canonical HF equation and write $\hat{\mathcal{F}}|\chi_a\rangle = \epsilon_a|\chi_a\rangle$ as the HF equation.

Thank you for your attention.