Approximate Methods in Quantum Chemistry
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Lecture-32
Hartree-Fock Roothaan Equations

Hello students! Welcome to this lecture. In the last few lectures, we discussed the Hartree-Fock theory. We have seen how we could obtain the Hartree-Fock equations and the Hartree-Fock energy, the interpretation of the HF orbital energy.

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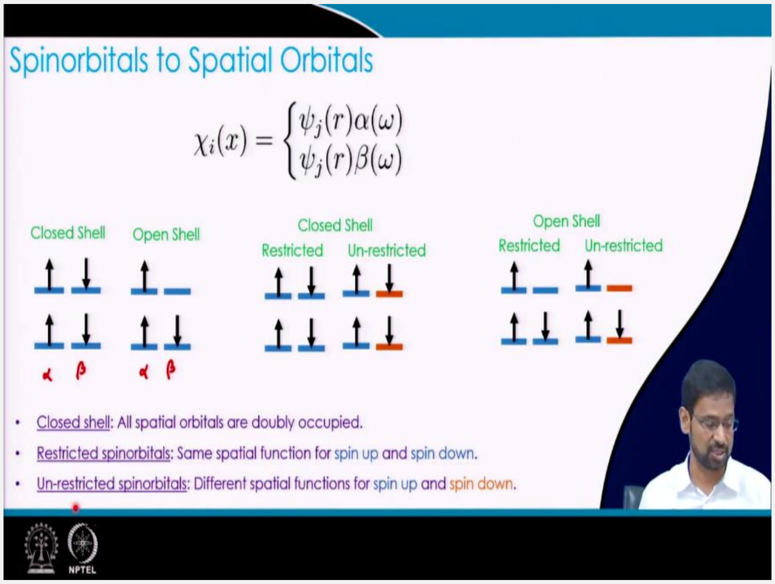

Spinorbitals to Spatial Orbitals

$$\chi_i(x) = \begin{cases} \psi_j(r)\alpha(\omega) \\ \psi_j(r)\beta(\omega) \end{cases}$$

- Closed shell: All spatial orbitals are doubly occupied.
- Restricted spinorbitals: Same spatial function for spin up and spin down.
- Un-restricted spinorbitals: Different spatial functions for spin up and spin down.

If you recall, we have formulated the Hartree-Fock problem in terms of the spinorbitals that have definite spatial identity (r) and spin identity (ω). We defined the spinorbitals $\{\chi_i\}$and (spatial) orbitals $\{\psi_j\}$as following

$$\chi_i(x) = \begin{cases} \psi_j(r)\alpha(\omega) \\ \psi_j(r)\beta(\omega) \end{cases}$$

In the above expression, we state that from a given spatial orbital, we can generate two spinorbitals whose spatial components would be identical while their spins are different. This treatment is called restricted approach. A HF theory following this approach is called restricted HF (RHF) method.

Depending on the number of electrons in a molecule and its electron configuration, we can have closed-shell systems, where all spatial orbitals are fully filled (unless vacant) or can have open-shell systems where at least one spatial orbital is singly occupied.

For closed-shell systems, the number of electrons with up-spin is same as that of the down spin. Hence, the spin multiplicity is zero (or a singlet state). For the open-shell system, the number of electrons of opposite spin are not equal. Since we know that two electrons of same spin have interaction energy (Coulomb and exchange) different from those of opposite spin. Hence, for open-shell systems it is not a good idea to treat the spatial component of two spinorbitals (differing only by spin) as identical (as was done in the restricted HF method). Such a treatment, where the spatial components of the alpha spinorbitals and beta spinorbitals are treated separately is called unrestricted HF (UHF) method. UHF is essential for open-shell systems. However, our present discussion will be restricted to the closed-shell restricted formulation of HF theory.

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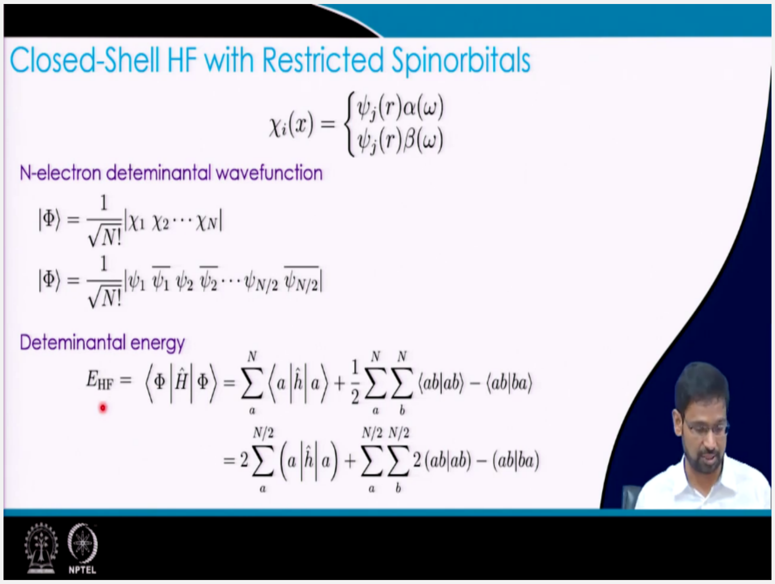

Closed-Shell HF with Restricted Spinorbitals

$$\chi_i(x) = \begin{cases} \psi_j(r)\alpha(\omega) \\ \psi_j(r)\beta(\omega) \end{cases}$$

N-electron deteminantal wavefunction

$$|\Phi\rangle = \frac{1}{\sqrt{N!}}|\chi_1\ \chi_2 \cdots \chi_N|$$

$$|\Phi\rangle = \frac{1}{\sqrt{N!}}|\psi_1\ \overline{\psi_1}\ \psi_2\ \overline{\psi_2} \cdots \psi_{N/2}\ \overline{\psi_{N/2}}|$$

Deteminantal energy

$$E_{\mathrm{HF}} = \left\langle \Phi \middle| \hat{H} \middle| \Phi \right\rangle = \sum_{a}^{N} \left\langle a \middle| \hat{h} \middle| a \right\rangle + \frac{1}{2}\sum_{a}^{N}\sum_{b}^{N} \langle ab|ab\rangle - \langle ab|ba\rangle$$

$$= 2\sum_{a}^{N/2} \left(a \middle| \hat{h} \middle| a \right) + \sum_{a}^{N/2}\sum_{b}^{N/2} 2\,(ab|ab) - (ab|ba)$$

For a closed-shell RHF treatment, the N-electron wave function is given by,

$$|\Phi\rangle = \frac{1}{\sqrt{N!}}|\chi_1\ \chi_2 \cdots \chi_N|$$

$$|\Phi\rangle = \frac{1}{\sqrt{N!}}|\psi_1\ \overline{\psi_1}\ \psi_2\ \overline{\psi_2} \cdots \psi_{N/2}\ \overline{\psi_{N/2}}|$$

In the above expression, the overbar indicated beta spin. In an earlier lecture, we derived the energy expectation value in terms of spinorbitals and (spatial) orbitals as following

$$\begin{aligned} E_{\mathrm{HF}} &= \left\langle \Phi \middle| \hat{H} \middle| \Phi \right\rangle = \sum_{a}^{N} \left\langle a \middle| \hat{h} \middle| a \right\rangle + \frac{1}{2} \sum_{a}^{N} \sum_{b}^{N} \langle ab|ab\rangle - \langle ab|ba\rangle \\ &= 2 \sum_{a}^{N/2} \left(a \middle| \hat{h} \middle| a \right) + \sum_{a}^{N/2} \sum_{b}^{N/2} 2\,(ab|ab) - (ab|ba) \end{aligned}$$

Note the use of round/angular brackets and the limit of the summation sign in the above two expressions.

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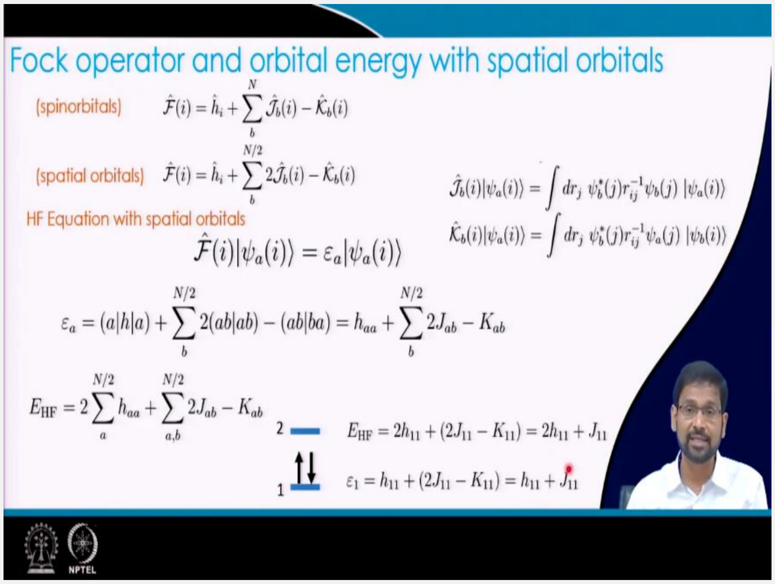


Fock operator and orbital energy with spatial orbitals

(spinorbitals) $\hat{\mathcal{F}}(i) = \hat{h}_i + \sum_{b}^{N} \hat{\mathcal{J}}_b(i) - \hat{\mathcal{K}}_b(i)$

(spatial orbitals) $\hat{\mathcal{F}}(i) = \hat{h}_i + \sum_{b}^{N/2} 2\hat{\mathcal{J}}_b(i) - \hat{\mathcal{K}}_b(i)$

$\hat{\mathcal{J}}_b(i)|\psi_a(i)\rangle = \int dr_j\, \psi_b^*(j) r_{ij}^{-1} \psi_b(j)\, |\psi_a(i)\rangle$

$\hat{\mathcal{K}}_b(i)|\psi_a(i)\rangle = \int dr_j\, \psi_b^*(j) r_{ij}^{-1} \psi_a(j)\, |\psi_b(i)\rangle$

HF Equation with spatial orbitals

$$\hat{\mathcal{F}}(i)|\psi_a(i)\rangle = \varepsilon_a|\psi_a(i)\rangle$$

$$\varepsilon_a = (a|h|a) + \sum_{b}^{N/2} 2(ab|ab) - (ab|ba) = h_{aa} + \sum_{b}^{N/2} 2J_{ab} - K_{ab}$$

$$E_{\mathrm{HF}} = 2\sum_{a}^{N/2} h_{aa} + \sum_{a,b}^{N/2} 2J_{ab} - K_{ab}$$

$E_{\mathrm{HF}} = 2h_{11} + (2J_{11} - K_{11}) = 2h_{11} + J_{11}$

$\varepsilon_1 = h_{11} + (2J_{11} - K_{11}) = h_{11} + J_{11}$

Earlier we expressed the Fock operator in terms the spinorbitals. We can also express the same in terms of the (spatial) orbitals as,

$$\hat{\mathcal{F}}(i) = \hat{h}_i + \sum_{b}^{N} \hat{\mathcal{J}}_b(i) - \hat{\mathcal{K}}_b(i)$$

$$\hat{\mathcal{F}}(i) = \hat{h}_i + \sum_{b}^{N/2} 2\hat{\mathcal{J}}_b(i) - \hat{\mathcal{K}}_b(i)$$

In the 2nd line of the above equation, the Coulomb and exchange operators are defined as

$$\hat{\mathcal{J}}_b(i)|\psi_a(i)\rangle = \int dr_j\ \psi_b^*(j) r_{ij}^{-1} \psi_b(j)\ |\psi_a(i)\rangle$$

$$\hat{\mathcal{K}}_b(i)|\psi_a(i)\rangle = \int dr_j\ \psi_b^*(j) r_{ij}^{-1} \psi_a(j)\ |\psi_b(i)\rangle$$

The corresponding HF equation becomes

$$\hat{\mathcal{F}}(i)|\psi_a(i)\rangle = \varepsilon_a |\psi_a(i)\rangle$$

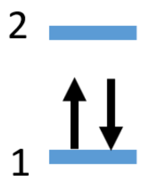
where the orbital energies (ϵ_a) are given by

$$\varepsilon_a = (a|h|a) + \sum_b^{N/2} 2(ab|ab) - (ab|ba) = h_{aa} + \sum_b^{N/2} 2J_{ab} - K_{ab}$$

The energy expectation value with the HF wave function would then become

$$E_{\text{HF}} = 2\sum_a^{N/2} h_{aa} + \sum_{a,b}^{N/2} 2J_{ab} - K_{ab}$$

Considering the above-mentioned results, we can now write down the HF energy and orbital energy of the following electron configuration,



$$E_{\text{HF}} = 2h_{11} + (2J_{11} - K_{11}) = 2h_{11} + J_{11}$$

$$\varepsilon_1 = h_{11} + (2J_{11} - K_{11}) = h_{11} + J_{11}$$

In this exercise, we expressed most of our HF-SCF related results in the (spatial) orbitals. We are now ready to introduce a very important idea in HF theory.

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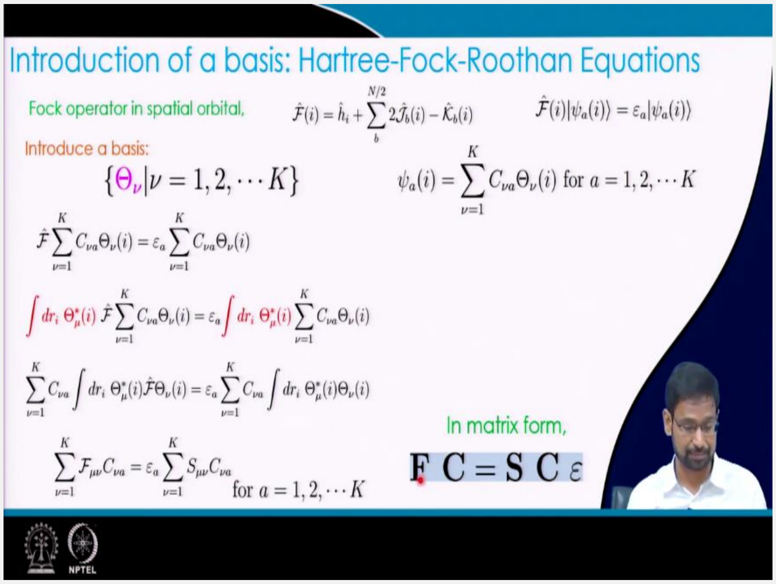

Introduction of a basis: Hartree-Fock-Roothan Equations

Fock operator in spatial orbital, $\hat{\mathcal{F}}(i) = \hat{h}_i + \sum_{b}^{N/2} 2\hat{\mathcal{J}}_b(i) - \hat{\mathcal{K}}_b(i)$ $\quad \hat{\mathcal{F}}(i)|\psi_a(i)\rangle = \varepsilon_a|\psi_a(i)\rangle$

Introduce a basis:

$$\{\Theta_\nu|\nu = 1, 2, \cdots K\} \qquad \psi_a(i) = \sum_{\nu=1}^{K} C_{\nu a}\Theta_\nu(i) \text{ for } a = 1, 2, \cdots K$$

$$\hat{\mathcal{F}}\sum_{\nu=1}^{K} C_{\nu a}\Theta_\nu(i) = \varepsilon_a \sum_{\nu=1}^{K} C_{\nu a}\Theta_\nu(i)$$

$$\int dr_i\, \Theta_\mu^*(i)\, \hat{\mathcal{F}}\sum_{\nu=1}^{K} C_{\nu a}\Theta_\nu(i) = \varepsilon_a \int dr_i\, \Theta_\mu^*(i) \sum_{\nu=1}^{K} C_{\nu a}\Theta_\nu(i)$$

$$\sum_{\nu=1}^{K} C_{\nu a}\int dr_i\, \Theta_\mu^*(i)\hat{\mathcal{F}}\Theta_\nu(i) = \varepsilon_a \sum_{\nu=1}^{K} C_{\nu a}\int dr_i\, \Theta_\mu^*(i)\Theta_\nu(i)$$

$$\sum_{\nu=1}^{K} \mathcal{F}_{\mu\nu}C_{\nu a} = \varepsilon_a \sum_{\nu=1}^{K} S_{\mu\nu}C_{\nu a} \quad \text{for } a = 1, 2, \cdots K$$

In matrix form,

$$\mathbf{F}\ \mathbf{C} = \mathbf{S}\ \mathbf{C}\ \varepsilon$$

The integro-differential HF equations are difficult to solve for large systems. The popularity of quantum chemistry with increasing computational power owes its origin to the idea of Roothan (and Hall) who introduced the concept of a basis to the HF-SCF method. The basic idea is to express the (spatial) orbital as a linear combination of some basis functions $\{\theta\}$,

$$\psi_a(i) = \sum_{\nu=1}^{K} C_{\nu a}\Theta_\nu(i) \text{ for } a = 1, 2, \cdots K$$

Where, $\{\Theta_\nu|\nu = 1, 2, \cdots K\}$

form a complete set of basis functions.

The HF equation in the (spatial) orbital $\hat{\mathcal{F}}\sum_{\nu=1}^{K} C_{\nu a}\Theta_\nu(i) = \varepsilon_a \sum_{\nu=1}^{K} C_{\nu a}\Theta_\nu(i)$

can now be written as

$$\hat{\mathcal{F}}\sum_{\nu=1}^{K} C_{\nu a}\Theta_\nu(i) = \varepsilon_a \sum_{\nu=1}^{K} C_{\nu a}\Theta_\nu(i)$$

where the (spatial) orbitals are expressed in terms of the *K* basis functions.

Let's multiply $\langle\theta_\mu(i)|$ both sides to get,

$$\int dr_i\ \Theta_\mu^*(i)\ \hat{\mathcal{F}} \sum_{\nu=1}^{K} C_{\nu a}\Theta_\nu(i) = \varepsilon_a \int dr_i\ \Theta_\mu^*(i) \sum_{\nu=1}^{K} C_{\nu a}\Theta_\nu(i)$$

which can be rearranged to

$$\sum_{\nu=1}^{K} C_{\nu a} \int dr_i\ \Theta_\mu^*(i)\hat{\mathcal{F}}\Theta_\nu(i) = \varepsilon_a \sum_{\nu=1}^{K} C_{\nu a} \int dr_i\ \Theta_\mu^*(i)\Theta_\nu(i)$$

The term within the integral sign of the LHS is the matrix element of the Fock operator. Defining Fock matrix ($\mathcal{F}$) and overlap matrix (S), we have,

$$\sum_{\nu=1}^{K} \mathcal{F}_{\mu\nu} C_{\nu a} = \varepsilon_a \sum_{\nu=1}^{K} S_{\mu\nu} C_{\nu a} \qquad \text{for } a = 1, 2, \cdots K$$

The above set of K equations can be expressed in matrix form is known as the Hartree-Fock-Roothan (HFR) Equation

$$\mathbf{F\ C = S\ C}\ \varepsilon$$

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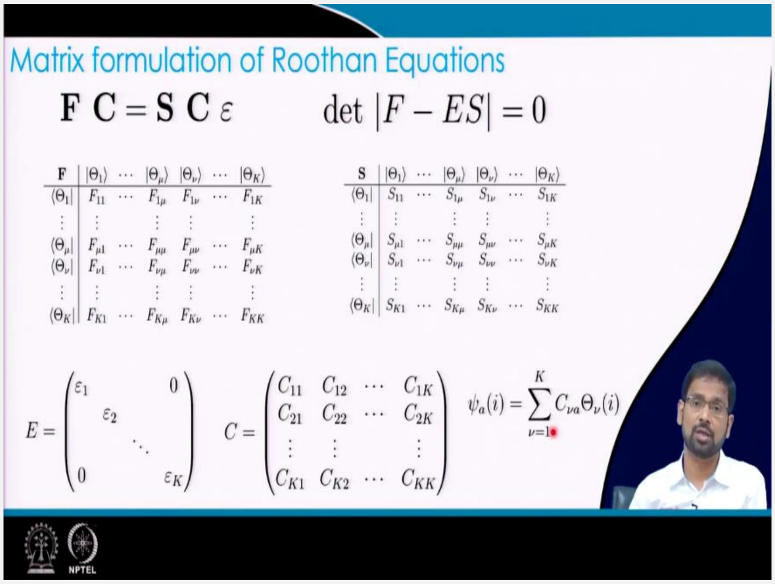

Matrix formulation of Roothan Equations

$$\mathbf{F\ C = S\ C}\ \varepsilon \qquad \det\ |F - ES| = 0$$

$$\begin{array}{c|cccccc} \mathbf{F} & |\Theta_1\rangle & \cdots & |\Theta_\mu\rangle & |\Theta_\nu\rangle & \cdots & |\Theta_K\rangle \\ \hline \langle\Theta_1| & F_{11} & \cdots & F_{1\mu} & F_{1\nu} & \cdots & F_{1K} \\ \vdots & \vdots & & \vdots & \vdots & & \vdots \\ \langle\Theta_\mu| & F_{\mu 1} & \cdots & F_{\mu\mu} & F_{\mu\nu} & \cdots & F_{\mu K} \\ \langle\Theta_\nu| & F_{\nu 1} & \cdots & F_{\nu\mu} & F_{\nu\nu} & \cdots & F_{\nu K} \\ \vdots & \vdots & & \vdots & \vdots & & \vdots \\ \langle\Theta_K| & F_{K1} & \cdots & F_{K\mu} & F_{K\nu} & \cdots & F_{KK} \end{array} \qquad \begin{array}{c|cccccc} \mathbf{S} & |\Theta_1\rangle & \cdots & |\Theta_\mu\rangle & |\Theta_\nu\rangle & \cdots & |\Theta_K\rangle \\ \hline \langle\Theta_1| & S_{11} & \cdots & S_{1\mu} & S_{1\nu} & \cdots & S_{1K} \\ \vdots & \vdots & & \vdots & \vdots & & \vdots \\ \langle\Theta_\mu| & S_{\mu 1} & \cdots & S_{\mu\mu} & S_{\mu\nu} & \cdots & S_{\mu K} \\ \langle\Theta_\nu| & S_{\nu 1} & \cdots & S_{\nu\mu} & S_{\nu\nu} & \cdots & S_{\nu K} \\ \vdots & \vdots & & \vdots & \vdots & & \vdots \\ \langle\Theta_K| & S_{K1} & \cdots & S_{K\mu} & S_{K\nu} & \cdots & S_{KK} \end{array}$$

$$E = \begin{pmatrix} \varepsilon_1 & & & 0 \\ & \varepsilon_2 & & \\ & & \ddots & \\ 0 & & & \varepsilon_K \end{pmatrix} \qquad C = \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1K} \\ C_{21} & C_{22} & \cdots & C_{2K} \\ \vdots & \vdots & & \vdots \\ C_{K1} & C_{K2} & \cdots & C_{KK} \end{pmatrix} \qquad \psi_a(i) = \sum_{\nu=1}^{K} C_{\nu a}\Theta_\nu(i)$$

The solution of the HFR equation can be found by obtaining

$$\det\ |F - ES| = 0$$

Where the Fock matrix and overlap matrix are given by

$$\begin{array}{c|cccccc}
\mathbf{F} & |\Theta_1\rangle & \cdots & |\Theta_\mu\rangle & |\Theta_\nu\rangle & \cdots & |\Theta_K\rangle \\
\hline
\langle\Theta_1| & F_{11} & \cdots & F_{1\mu} & F_{1\nu} & \cdots & F_{1K} \\
\vdots & \vdots & & \vdots & \vdots & & \vdots \\
\langle\Theta_\mu| & F_{\mu 1} & \cdots & F_{\mu\mu} & F_{\mu\nu} & \cdots & F_{\mu K} \\
\langle\Theta_\nu| & F_{\nu 1} & \cdots & F_{\nu\mu} & F_{\nu\nu} & \cdots & F_{\nu K} \\
\vdots & \vdots & & \vdots & \vdots & & \vdots \\
\langle\Theta_K| & F_{K1} & \cdots & F_{K\mu} & F_{K\nu} & \cdots & F_{KK}
\end{array}
\qquad
\begin{array}{c|cccccc}
\mathbf{S} & |\Theta_1\rangle & \cdots & |\Theta_\mu\rangle & |\Theta_\nu\rangle & \cdots & |\Theta_K\rangle \\
\hline
\langle\Theta_1| & S_{11} & \cdots & S_{1\mu} & S_{1\nu} & \cdots & S_{1K} \\
\vdots & \vdots & & \vdots & \vdots & & \vdots \\
\langle\Theta_\mu| & S_{\mu 1} & \cdots & S_{\mu\mu} & S_{\mu\nu} & \cdots & S_{\mu K} \\
\langle\Theta_\nu| & S_{\nu 1} & \cdots & S_{\nu\mu} & S_{\nu\nu} & \cdots & S_{\nu K} \\
\vdots & \vdots & & \vdots & \vdots & & \vdots \\
\langle\Theta_K| & S_{K1} & \cdots & S_{K\mu} & S_{K\nu} & \cdots & S_{KK}
\end{array}$$

For a given system with a given choice of basis, we can construct the Fock matrix and the overlap matrix as shown above. The solution of the HFR equation would yield the energy matrix (diagonal) and coefficient matrix as

$$E = \begin{pmatrix} \varepsilon_1 & & & 0 \\ & \varepsilon_2 & & \\ & & \ddots & \\ 0 & & & \varepsilon_K \end{pmatrix} \qquad C = \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1K} \\ C_{21} & C_{22} & \cdots & C_{2K} \\ \vdots & \vdots & & \vdots \\ C_{K1} & C_{K2} & \cdots & C_{KK} \end{pmatrix}$$

The Hartree-Fock formalism that we discussed in last few classes, when coupled with Roothaan’s idea, provides us with a matrix formulation of Hartree-Fock scheme, also known as the Hartree-Fock Roothaan scheme. This scheme is ideally suited for use in computers where we can easily construct and diagonalize extremely large matrices.

Thank you for your attention.