Approximate Methods in Quantum Chemistry
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Lecture-33
The Density Matrix

Hello students! Welcome to this lecture. After discussing HF-SCF theory followed by Hartree-Fock-Roothaan scheme, we have now formulated the *N*-electron problem in a matrix form. In this class, we will introduce the density matrix which plays a critical role in Hartree-Fock calculation.

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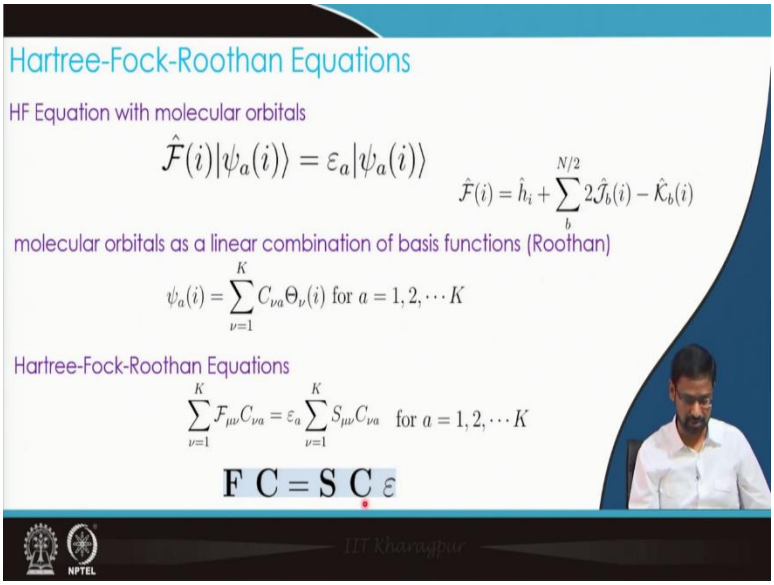

If we express (spatial) orbitals $\psi_a(i)$ in terms of a basis $\theta_\nu(i)$, i.e.,

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

the Hartree-Fock equation becomes,

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

The above set of equations can be converted to a matrix equation in the basis of $\theta_\nu(i)$

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

Here **F** is the Fock matrix, **S** is the overlap matrix, and **C** is the coefficient matrix.

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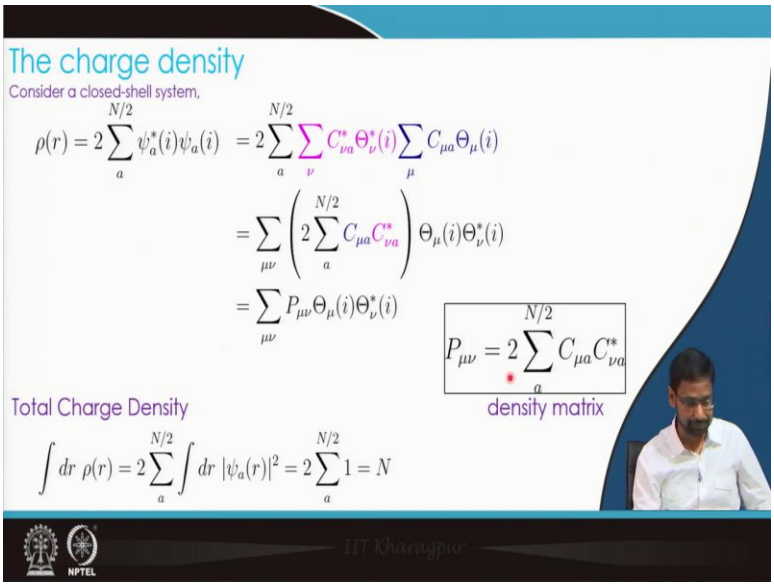

For a closed-shell system, the *N*-electron HF wave function is given by the Slater determinant in terms of *N*/2 spatial orbitals. The charge density for this system is given by the sum of the probability distribution function of the *N*/2 (spatial) orbital, multiplied by 2 (electron occupancy), i.e.,

$$\rho(r) = 2\sum_{a}^{N/2} \psi_a^*(i)\psi_a(i)$$

If we integrate the above equation over all space, we get the total number of electrons (*N*)

$$\int dr\ \rho(r) = 2\sum_{a}^{N/2}\int dr\ |\psi_a(r)|^2 = 2\sum_{a}^{N/2} 1 = N$$

Introducing Roothan's basis to the charge-density equation, we obtain $\rho(r)$ as,

$$= 2\sum_{a}^{N/2}\sum_{\nu} C_{\nu a}^*\Theta_\nu^*(i)\sum_{\mu} C_{\mu a}\Theta_\mu(i)$$

$$= \sum_{\mu\nu}\left(2\sum_{a}^{N/2} C_{\mu a}C_{\nu a}^*\right)\Theta_\mu(i)\Theta_\nu^*(i)$$

$$= \sum_{\mu\nu} P_{\mu\nu}\Theta_\mu(i)\Theta_\nu^*(i)$$

In the last line, we defined a new matrix **P** (density matrix) in terms the Coefficient matrix **C**. The matrix elements of the density matrix are given by,

$$\boxed{P_{\mu\nu} = 2\sum_{a}^{N/2} C_{\mu a} C_{\nu a}^{*}}$$

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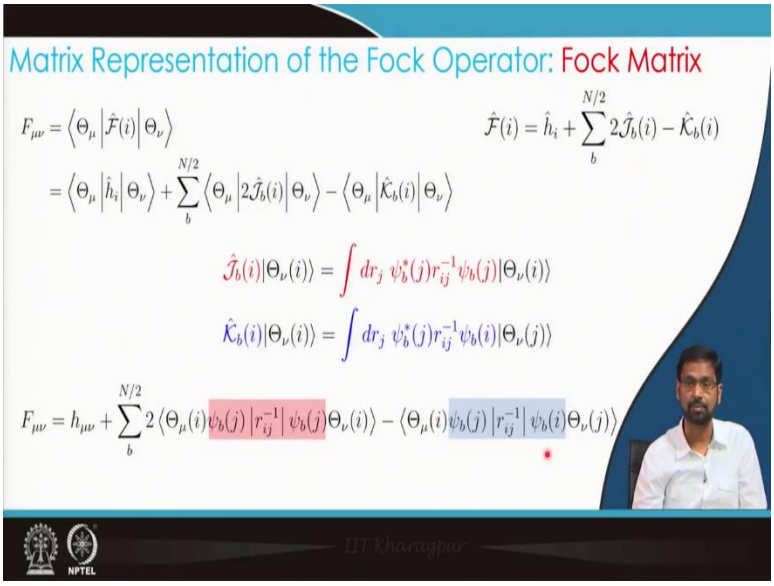

We know, in the basis of spatial orbitals, the Fock operator is given by

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

Now let us formulate the Fock matrix by evaluating its matrix elements in the basis of the $\{\theta_\upsilon\}$

$$F_{\mu\nu} = \left\langle \Theta_\mu \left| \hat{\mathcal{F}}(i) \right| \Theta_\nu \right\rangle$$

$$= \left\langle \Theta_\mu \left| \hat{h}_i \right| \Theta_\nu \right\rangle + \sum_{b}^{N/2} \left\langle \Theta_\mu \left| 2\hat{\mathcal{J}}_b(i) \right| \Theta_\nu \right\rangle - \left\langle \Theta_\mu \left| \hat{\mathcal{K}}_b(i) \right| \Theta_\nu \right\rangle$$

We can express the action of Coulomb and exchange operators on the basis functions as,

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

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

The red/blue parts of the above two equations are the operators themselves that are defined in terms of (spatial) orbitals. Using the above definition of the Coulomb/exchange operators, the Fock matrix can be written as,

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{b}^{N/2} 2\left\langle \Theta_\mu(i)\psi_b(j)\left|r_{ij}^{-1}\right|\psi_b(j)\Theta_\nu(i)\right\rangle - \left\langle \Theta_\mu(i)\psi_b(j)\left|r_{ij}^{-1}\right|\psi_b(i)\Theta_\nu(j)\right\rangle$$

The first term is the matrix element of the core Hamiltonian.

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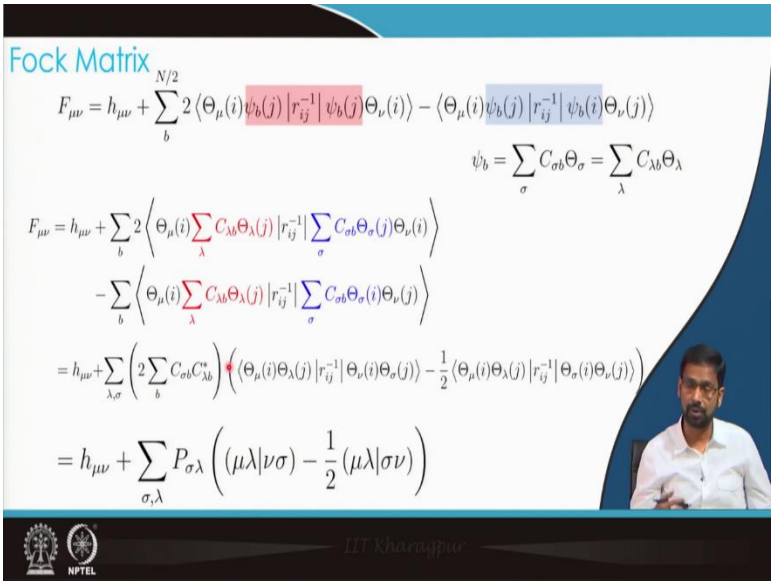

Expanding the spatial orbitals in terms of the basis functions, i.e.,

$$\psi_b = \sum_\sigma C_{\sigma b}\Theta_\sigma = \sum_\lambda C_{\lambda b}\Theta_\lambda$$

we can express the Fock matrix as,

$$F_{\mu\nu} = h_{\mu\nu} + \sum_b 2\left\langle \Theta_\mu(i)\sum_\lambda C_{\lambda b}\Theta_\lambda(j)\left|r_{ij}^{-1}\right|\sum_\sigma C_{\sigma b}\Theta_\sigma(j)\Theta_\nu(i)\right\rangle$$
$$-\sum_b\left\langle \Theta_\mu(i)\sum_\lambda C_{\lambda b}\Theta_\lambda(j)\left|r_{ij}^{-1}\right|\sum_\sigma C_{\sigma b}\Theta_\sigma(i)\Theta_\nu(j)\right\rangle$$

By removing the coefficients from the integration, we have $F_{\mu\nu}$

$$= h_{\mu\nu} + \sum_{\lambda,\sigma} \left(2 \sum_{b} C_{\sigma b} C^{*}_{\lambda b} \right) \left(\left\langle \Theta_{\mu}(i)\Theta_{\lambda}(j) \left| r_{ij}^{-1} \right| \Theta_{\nu}(i)\Theta_{\sigma}(j) \right\rangle - \frac{1}{2} \left\langle \Theta_{\mu}(i)\Theta_{\lambda}(j) \left| r_{ij}^{-1} \right| \Theta_{\sigma}(i)\Theta_{\nu}(j) \right\rangle \right)$$

which can be expressed in terms of the density matrix as, $F_{\mu\nu}$

$$= h_{\mu\nu} + \sum_{\sigma,\lambda} P_{\sigma\lambda} \left((\mu\lambda|\nu\sigma) - \frac{1}{2} (\mu\lambda|\sigma\nu) \right)$$

Here the shorthand notation $(\Theta_{\mu}(i)\Theta_{\lambda}(j) = \mu\lambda$ is used. The round brackets should remind that the basis functions are replacing the spatial orbitals.

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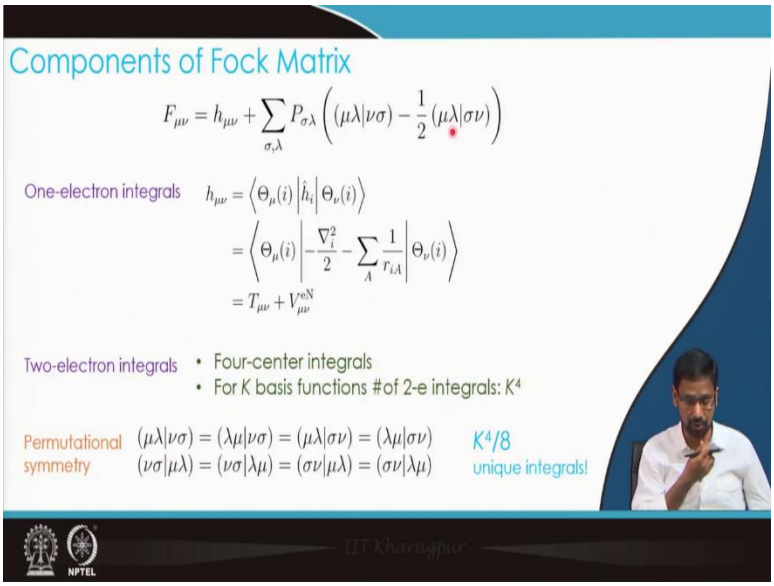

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma,\lambda} P_{\sigma\lambda} \left((\mu\lambda|\nu\sigma) - \frac{1}{2} (\mu\lambda|\sigma\nu) \right)$$

The Fock matrix shown above has got 1-electron and 2-electron integrals. The 1-electron integrals are given as,

$$h_{\mu\nu} = \left\langle \Theta_{\mu}(i) \left| \hat{h}_i \right| \Theta_{\nu}(i) \right\rangle$$
$$= \left\langle \Theta_{\mu}(i) \left| -\frac{\nabla_i^2}{2} - \sum_A \frac{1}{r_{iA}} \right| \Theta_{\nu}(i) \right\rangle$$
$$= T_{\mu\nu} + V_{\mu\nu}^{\mathrm{eN}}$$

The 1-electron integrals have two terms: electron kinetic energy and electron-nuclear potential energy. Both these integrals are rather easy to evaluate, once the basis functions are defined.

Now, let us discuss the two-electron integrals. The two-electron integral $(\mu\lambda|\nu\sigma)$ can be a (up to) 4-centre integral, i.e., when these four basis functions are centered on four different atoms of a molecule. If our basis set has K basis functions, we can construct K^4 number of 2-electron integrals $(\mu\lambda|\nu\sigma)$. For a small molecule, say, with 5 atoms where each atom defined by 4 basis functions, thus making $K = 20$, can have $20^4 = 1{,}60{,}000$ number of 2-electron integrals. The evaluation of such a large number of integrals is quite expensive. However, we can immediately see that not all K^4 integrals are unique. We can use permutational symmetry and show

$$(\mu\lambda|\nu\sigma) = (\lambda\mu|\nu\sigma) = (\mu\lambda|\sigma\nu) = (\lambda\mu|\sigma\nu)$$
$$(\nu\sigma|\mu\lambda) = (\nu\sigma|\lambda\mu) = (\sigma\nu|\mu\lambda) = (\sigma\nu|\lambda\mu)$$

This relation reduces the number of unique integrals to $K^4/8$.

The computation of these 2-electron (4-centre) integrals are the most time-consuming part of a HF-SCF calculation. Several approximations and innovating ideas have been developed to make this part of the computation tractable.

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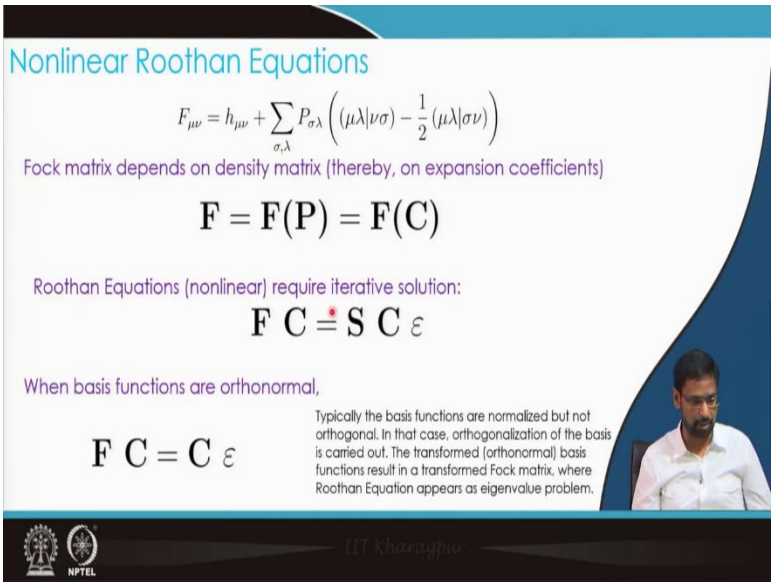

Now since we know how to evaluate the Fock matrix and the overlap matrix, we can easily solve the (Hartree-Fock-) Roothan equation, $\mathbf{F}\ \mathbf{C} = \mathbf{S}\ \mathbf{C}\ \varepsilon$

Typically, the basis functions used are normalized but not orthogonal. In such a case, an orthogonalization of the basis can be carried out. The transformed (orthonormal) basis functions result in a transformed Fock matrix, where the Roothan Equation appears as eigenvalue problem. $\mathbf{F}\ \mathbf{C} = \mathbf{C}\ \varepsilon$

The solution of the above problem would give us the diagonal energy matrix (from the eigenvalues) and the expansion coefficients (from the eigenvectors). However, a careful observation will point out a problem. While constructing the Fock matrix, we used the following relation

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma,\lambda} P_{\sigma\lambda} \left((\mu\lambda|\nu\sigma) - \frac{1}{2} (\mu\lambda|\sigma\nu) \right)$$

Here the Fock matrix depends on the density matrix (**F**(**P**)) and the density matrix is built from the expansion coefficient matrix (**C**), hence we need the coefficient matrix to build the Fock matrix, i.e., **F**(**C**). But the coefficient matrix is obtained from solving the Roothan equation! Hence, we have a non-linear problem that needs to be solved in a self-consistent (iterative) method.

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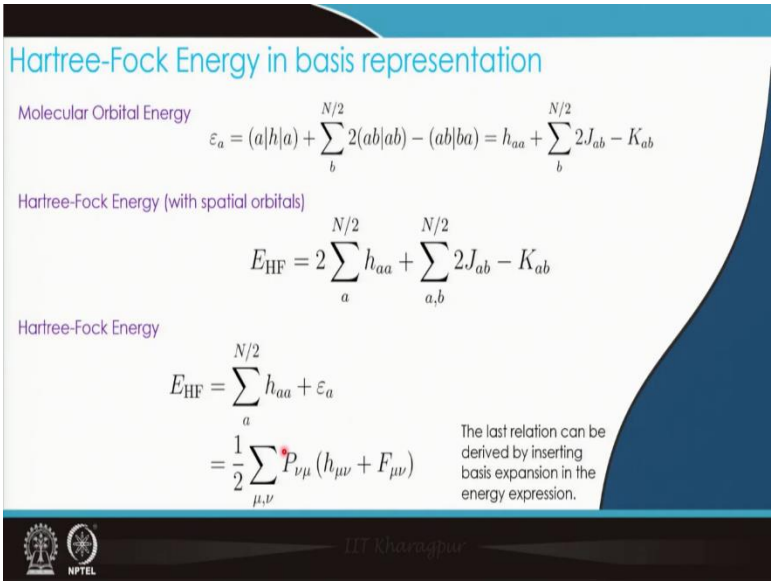

From our previous lectures, we have seen how to express orbital energy (ϵ_a) and HF energy (E_{HF}) in terms of the spatial orbitals:

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

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

$$E_{\mathrm{HF}} = \sum_a^{N/2} h_{aa} + \varepsilon_a$$

Now since we have expressed our integrals in terms of basis functions (within Hartree-Fock-Roothan scheme), we would like to express the energy in terms of the basis functions. If we use the basis expansion relation in the last equation (the exercise is similar to the ones we used to get Fock matrix), we would obtain E_{HF} as

$$= \frac{1}{2}\sum_{\mu,\nu} P_{\nu\mu}\left(h_{\mu\nu} + F_{\mu\nu}\right)$$

The above expression shows that the HF energy can be obtained from the core-Hamiltonian matrix, the Fock matrix, and the density matrix. We also know that we need the density matrix to get the Fock matrix. Hence, it appears that the density matrix is crucial in the solution of Hartree-Fock-Roothan problem.

Thank you for your attention.