



NPTEL ONLINE CERTIFICATION COURSES

Approximate Methods in Quantum Chemistry

Sabyashachi Mishra
Department of Chemistry, IIT Kharagpur

Lecture 29: Self-Consistent Field Method

Self-Consistent Field

For He atom

$$\begin{aligned}\hat{H} &= \sum_{i=1}^2 \left(-\frac{\nabla_i^2}{2} - \frac{2}{r_{iA}} \right) + \frac{1}{r_{12}} \\ &= \sum_{i=1}^2 \hat{h}_i + \frac{1}{r_{12}}\end{aligned}$$

$$\psi(1, 2) = \chi_a(1)\chi_b(2) \quad \text{Hartree Product}$$

$$\int \chi_b^*(2)\chi_b(2) dx_2 = p(2)$$

Interaction energy of electron 1 with the charge density (field) of electron 2:

$$U_1^{\text{eff}} = \frac{-e \cdot -ep(2)}{r_{12}} = \int \chi_b^*(2) \frac{1}{r_{12}} \chi_b(2) dx_2$$

New Hamiltonian for electron 1

$$\hat{H}_1^{\text{eff}} = \hat{h}_1 + U_1^{\text{eff}}$$



Self-Consistent Field

For He atom

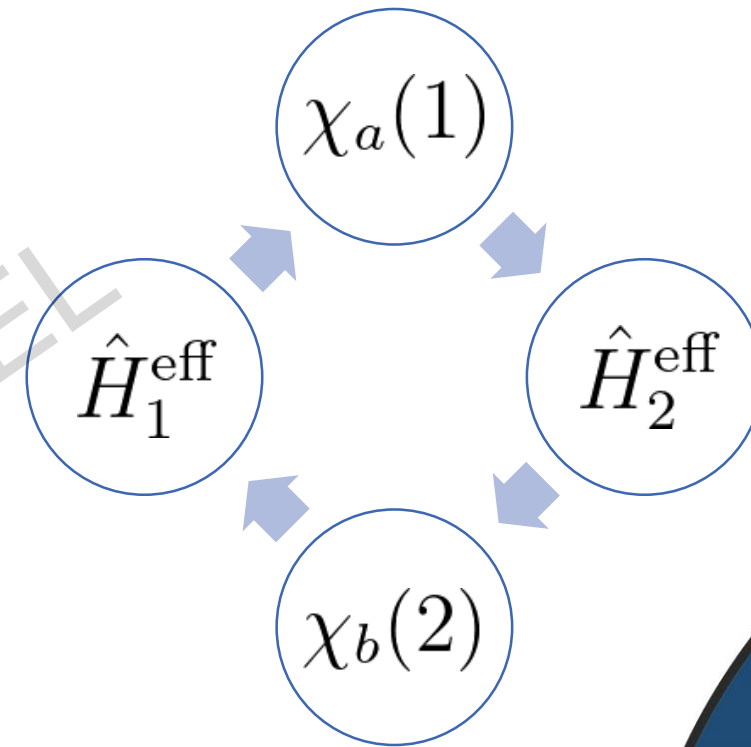
Effective one-electron Hamiltonian

$$\hat{H}_1^{\text{eff}} = \hat{h}_1 + \int \chi_b^*(2) \frac{1}{r_{12}} \chi_b(2) dx_2$$

$$\hat{H}_2^{\text{eff}} = \hat{h}_2 + \int \chi_a^*(1) \frac{1}{r_{12}} \chi_a(1) dx_1$$

$$\hat{H}_1^{\text{eff}} \chi_a(1) = \varepsilon_a \chi_a(1)$$

$$\hat{H}_2^{\text{eff}} \chi_b(2) = \varepsilon_b \chi_b(2)$$



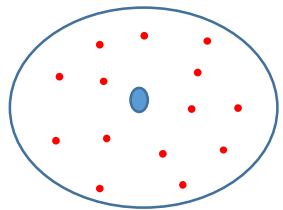
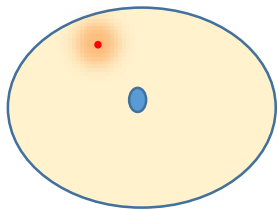
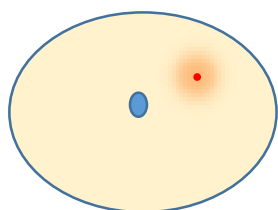
Iterative Solution

Self-Consistent Solution

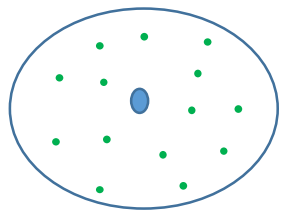
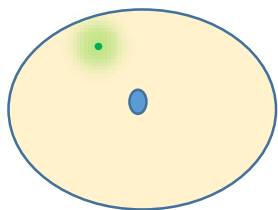
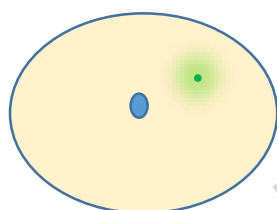


Self-Consistent Field

For N-electron System

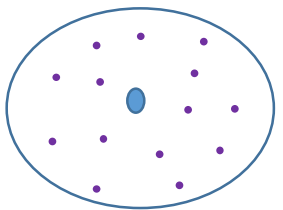


... .. repeat for each electron



... .. repeat for each electron

⋮
iterate the process till convergence (no change in spinorbitals)



Proposed by Hartree (Hartree's SCF)

Hartree-Fock SCF

SCF Scheme of Hartree, improved by Fock (and Slater)

$$\Phi_{\text{HP}}(1, 2, \dots, N) = \chi_1(1)\chi_2(2) \cdots \chi_a(i)\chi_b(j) \cdots \chi_N(N)$$

Hartree SCF

$$\Phi_{\text{SD}}(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} |\chi_1(1)\chi_2(2) \cdots \chi_a(i)\chi_b(j) \cdots \chi_N(N)|$$

Hartree-Fock SCF

- ❖ Find the best N-electron determinantal wavefunction (using variation method) that gives the lowest energy (for a given nuclear configuration) while making sure that the spinorbitals remain orthonormal.



Variational Formulation of HF-SCF

- ❖ Find the **best N-electron determinantal wavefunction** (using variation method) that gives the **lowest energy** (for a given nuclear configuration) while making sure that the **spinorbitals remain orthonormal**.

N-electron determinantal wavefunction

$$\Phi_{\text{SD}}(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} |\chi_1(1)\chi_2(2) \cdots \chi_a(i)\chi_b(j) \cdots \chi_N(N)|$$

Energy

$$\langle \Phi | \hat{H} | \Phi \rangle = E = \sum_a^N \langle a | \hat{h}_i | a \rangle + \frac{1}{2} \sum_{a,b}^N \left(\langle \chi_a(i)\chi_b(j) | \frac{1}{r_{ij}} | \chi_a(i)\chi_b(j) \rangle - \langle \chi_a(i)\chi_b(j) | \frac{1}{r_{ij}} | \chi_b(i)\chi_a(j) \rangle \right)$$

Orthonormal spinorbitals

$$\langle \chi_a | \chi_b \rangle = \langle a | b \rangle = \delta_{ab}$$

- Functional Variation
- Minimization with a constrain

Functional Variation in HF-SCF

$$E(\Phi) = E[\Phi(\{\chi_a\})]$$

$$E(\Phi(\{\chi_a\})) = E[\Phi]$$

○ Minimization with a constrain

$$\langle \chi_a | \chi_b \rangle - \delta_{ab} = 0$$

$$\Phi \rightarrow \Phi + \delta\Phi$$

$$\begin{aligned} E[\Phi + \delta\Phi] &= \langle \Phi + \delta\Phi | \hat{H} | \Phi + \delta\Phi \rangle \\ &= \langle \Phi | \hat{H} | \Phi \rangle + \langle \delta\Phi | \hat{H} | \Phi \rangle + \langle \Phi | \hat{H} | \delta\Phi \rangle + \dots \\ &= E[\Phi] + \delta(E[\Phi]) \end{aligned}$$

Minimum energy is obtained when, $\delta E = 0$



Functional Variation in HF-SCF

constrained minimization of energy by Lagrange's method of undetermined multipliers

- Minimize $f(x)$ $\delta f(x) = 0$

- Minimize $f(x)$ such that $g(x)=0$

$$\mathcal{L}(x, \lambda) = f(x) - \lambda g(x)$$

$$\delta \mathcal{L}(x, \lambda) = 0$$

Lagrange (undetermined) multiplier
Lagrange function

In the present case,

$$f(x) : \quad E = \sum_a^N \langle a | \hat{h}_i | a \rangle + \frac{1}{2} \sum_{a,b}^N \langle ab | ab \rangle - \langle ab | ba \rangle$$

$$g(x)=0 : \quad \sum_{a,b}^N \langle a | b \rangle - \delta_{ab} = 0$$

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



Constrained Minimization of Energy

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

$$\delta \mathcal{L} = 0$$

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

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



Minimization of the Energy of a Slater Determinant

$$E = \sum_a^N \langle a | \hat{h}_i | a \rangle + \frac{1}{2} \sum_{a,b}^N \langle ab | ab \rangle - \langle ab | ba \rangle$$

$$\delta E = \sum_a^N \delta \langle a | \hat{h}_i | a \rangle + \frac{1}{2} \sum_{a,b}^N \delta \langle ab | ab \rangle - \delta \langle ab | ba \rangle$$

$$\begin{aligned} \delta E = \sum_a^N & \left(\langle \delta a | \hat{h}_i | a \rangle + \langle a | \hat{h}_i | \delta a \rangle \right) + \frac{1}{2} \sum_{a,b}^N \left(\langle \delta a b | ab \rangle + \langle a \delta b | ab \rangle + \langle ab | \delta a b \rangle + \langle ab | a \delta b \rangle \right) \\ & - \frac{1}{2} \sum_{a,b}^N \left(\langle \delta a b | ba \rangle + \langle a \delta b | ba \rangle + \langle ab | \delta b a \rangle + \langle ab | b \delta a \rangle \right) \end{aligned}$$

$$= \sum_a^N \langle \delta a | \hat{h}_i | a \rangle + \sum_{a,b}^N (\langle \delta a b | ab \rangle - \langle \delta a b | ba \rangle) + \text{complex conjugate}$$

Constrained Minimization of Determinantal Energy

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

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

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





NPTEL ONLINE CERTIFICATION COURSES

Approximate Methods in Quantum Chemistry

Sabyashachi Mishra
Department of Chemistry, IIT Kharagpur

Lecture 30: Canonical HF Equations

Variational Formulation of HF-SCF

- ❖ Find the **best** N-electron determinantal wavefunction (using variation method) that gives the lowest energy (for a given nuclear configuration) while making sure that the **spinorbitals** remain orthonormal.

Constrained minimization of determinantal energy

Lagrange function

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

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

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

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



Constrained Minimization of Determinantal Energy

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

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

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

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

Coulomb Operator

Exchange Operator

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



Fock Operator

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

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

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

Fock Operator

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

Hartree-Fock Equations

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



Canonical HF Equation

Unitary transformation of HF spinorbitals

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

A new set of spinorbitals

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

Unitary matrix **U**

$$\mathbf{U}^\dagger \mathbf{U} = \mathbf{1}$$

- Preserves orthonormality of spinorbitals

Unitary transformation in matrix form

$$\begin{pmatrix} \chi'_1(1) & \chi'_2(1) & \cdots & \chi'_a(1) & \cdots & \chi'_N(1) \\ \chi'_1(2) & \chi'_2(2) & \cdots & \chi'_a(2) & \cdots & \chi'_N(2) \\ \vdots & \vdots & & \vdots & & \vdots \\ \chi'_1(i) & \chi'_2(i) & \cdots & \chi'_a(i) & \cdots & \chi'_N(i) \\ \vdots & \vdots & & \vdots & & \vdots \\ \chi'_1(N) & \chi'_2(N) & \cdots & \chi'_a(N) & \cdots & \chi'_N(N) \end{pmatrix} = \begin{pmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_a(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_a(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & & \vdots & & \vdots \\ \chi_1(i) & \chi_2(i) & \cdots & \chi_a(i) & \cdots & \chi_N(i) \\ \vdots & \vdots & & \vdots & & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_a(N) & \cdots & \chi_N(N) \end{pmatrix} \begin{pmatrix} U_{11} & U_{12} & \cdots & U_{1a} & \cdots & U_{1N} \\ U_{21} & U_{22} & \cdots & U_{2a} & \cdots & U_{2N} \\ \vdots & \vdots & & \vdots & & \vdots \\ U_{a1} & U_{a2} & \cdots & U_{aa} & \cdots & U_{aN} \\ \vdots & \vdots & & \vdots & & \vdots \\ U_{N1} & U_{N2} & \cdots & U_{Na} & \cdots & U_{NN} \end{pmatrix}$$

Transformed spinorbitals

Original spinorbitals



Canonical HF Equation

Effect of unitary transformation on the determinantal wavefunction and properties

$$\Phi_{\text{SD}} = (N!)^{-1/2} \det | \cdots \chi_a(i) \cdots | \quad \text{original wavefunction}$$

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

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

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

The transformed wavefunction differs from the original wavefunction by a phase factor.

- For a single determinant wavefunction, the expectation value is invariant to unitary transformation of the spinorbitals.



Canonical HF Equation

Effect of unitary transformation on the Coulomb and Exchange Operators

Coulomb operator with transformed spinorbitals

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

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

- The sum of Coulomb operators is invariant to a unitary transformation of the spinorbitals.

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



Canonical HF Equation

Effect of unitary transformation on the Coulomb and Exchange Operators

- The sum of **Coulomb** operators is invariant to a unitary transformation of the spinorbitals.
- The sum of **exchange** operators is also invariant to a unitary transformation of the spinorbitals.

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

- The **Fock** operator is invariant to a unitary transformation of the spinorbitals.

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



Canonical HF Equation

Effect of unitary transformation on Lagrange multipliers

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

Lagrange multipliers in transformed basis:

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

- The unitary matrix **U** is the one that diagonalizes **ε**

In matrix form,

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



Canonical HF Equation

Non-canonical HF Equation (with original spinorbitals)

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

Canonical HF Equation (with transformed spinorbitals)

$$\hat{\mathcal{F}}|\chi'_a\rangle = \varepsilon'_a |\chi'_a\rangle$$





NPTEL ONLINE CERTIFICATION COURSES

Approximate Methods in Quantum Chemistry

Sabyashachi Mishra
Department of Chemistry, IIT Kharagpur

Lecture 31: Hartree-Fock Energy

HF-SCF Method

N-electron Hamiltonian

$$\begin{aligned}\hat{H} &= \sum_i^N \left(-\frac{\nabla_i^2}{2} - \sum_A \frac{Z_A}{r_{iA}} \right) + \sum_{i>j}^N \frac{1}{r_{ij}} \\ &= \sum_i^N \hat{h}_i + \sum_{i>j}^N \frac{1}{r_{ij}}\end{aligned}$$

N-electron determinantal wavefunction

$$|\Phi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(1) & \chi_j(1) & \dots & \chi_k(1) \\ \chi_i(2) & \chi_j(2) & \dots & \chi_k(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(N) & \chi_j(N) & \dots & \chi_k(N) \end{vmatrix}$$

Determinantal energy

$$\begin{aligned}\langle \Phi | \hat{H} | \Phi \rangle &= \sum_a^N \langle a | \hat{h} | a \rangle + \frac{1}{2} \sum_a^N \sum_b^N \langle ab | ab \rangle - \langle ab | ba \rangle && \text{(spinorbitals)} \\ &= 2 \sum_a^{N/2} \left(a | \hat{h} | a \right) + \sum_a^{N/2} \sum_b^{N/2} 2 (ab | ab) - (ab | ba) && \text{(spatial orbitals)}\end{aligned}$$

HF-SCF Method

Constrained minimization of determinantal energy (Lagrange method of undetermined multipliers)

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

Hartree-Fock Equations (non-canonical)

$$\underbrace{\left[\hat{h}_i + \sum_b^N \hat{\mathcal{J}}_b(i) - \hat{\mathcal{K}}_b(i) \right]}_{\hat{\mathcal{F}}} \chi_a(i) = \sum_b^N \varepsilon_{ab} \chi_b(i) \quad \text{for } a = 1, 2, \dots, N$$
$$\hat{\mathcal{J}}_b(i) \chi_a(i) = \int \chi_b^*(j) \frac{1}{r_{ij}} \chi_b(j) dx_j \chi_a(i)$$
$$\hat{\mathcal{K}}_b(i) \chi_a(i) = \int \chi_b^*(j) \frac{1}{r_{ij}} \chi_a(j) dx_j \chi_b(i)$$



HF-SCF Method

Unitary transformation of spinorbitals

$$\chi'_a = \sum_b \chi_b U_{ba} \qquad \mathbf{U}^\dagger \mathbf{U} = \mathbf{1}$$

Effect on wavefunction $\Phi'_{\text{SD}} = e^{i\phi} \Phi_{\text{SD}} \Rightarrow |\Phi'_{\text{SD}}|^2 = |\Phi_{\text{SD}}|^2$

Effect on operators $\sum_a \hat{\mathcal{J}}'_a(i) = \sum_b \hat{\mathcal{J}}_b(i) \quad \sum_a \hat{\mathcal{K}}'_a(i) = \sum_b \hat{\mathcal{K}}_b(i) \quad \hat{\mathcal{F}}'(i) = \hat{\mathcal{F}}(i)$

Effect on Lagrange multipliers $\varepsilon' = \mathbf{U}^\dagger \varepsilon \mathbf{U}$

Canonical Hartree-Fock Equations $\hat{\mathcal{F}} |\chi'_a\rangle = \varepsilon'_a |\chi'_a\rangle$

$$\hat{\mathcal{F}}(i) |\chi_a(i)\rangle = \epsilon_a |\chi_a(i)\rangle$$



Molecular Hamiltonian vs HF-Hamiltonian

N-electron Hamiltonian
and its true solution

$$\hat{H} = \sum_i^N \hat{h}_i + \sum_{i>j}^N \frac{1}{r_{ij}} \quad \hat{H}\Psi = E\Psi$$

HF Solution

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

$$|\Phi\rangle = |\chi_1(1) \cdots \chi_a(i) \chi_b(j) \cdots \chi_N(N)\rangle$$

Comparison of Molecular Hamiltonian and HF Hamiltonian

$$\begin{aligned} \hat{H}_{\text{HF}} &= \sum_i^N \hat{\mathcal{F}}_i \\ &= \sum_i^N \left(\hat{h}_i + \sum_j \hat{\mathcal{J}}_j(i) - \hat{\mathcal{K}}_j(i) \right) \\ &= \sum_i^N \left(\hat{h}_i + \hat{v}_{\text{HF}}(i) \right) \end{aligned}$$

$$\hat{H} - \hat{H}_{\text{HF}} = \sum_{i>j} \frac{1}{r_{ij}} - \sum_i \hat{v}_{\text{HF}}(i)$$

Partial treatment of electron correlation



HF-Energy

HF wavefunction $|\Phi\rangle = |\chi_1(1) \cdots \chi_a(i) \chi_b(j) \cdots \chi_N(N)\rangle$

HF Energy

$$E_{\text{HF}} = \langle \Phi | \hat{H} | \Phi \rangle = \sum_a^N \langle a | \hat{h} | a \rangle + \frac{1}{2} \sum_{a,b}^N \langle ab | ab \rangle - \langle ab | ba \rangle$$

Energy of spinorbital

$$\varepsilon_a = \langle \chi_a(i) | \hat{\mathcal{F}}_i | \chi_a(i) \rangle = \langle a | \hat{h} | a \rangle + \sum_b^N \langle ab | ab \rangle - \langle ab | ba \rangle$$

Sum of HF orbital energy is NOT the HF energy

$$\sum_a^N \varepsilon_a = \sum_a^N \langle a | \hat{h} | a \rangle + \sum_{a,b}^N \langle ab | ab \rangle - \langle ab | ba \rangle \neq E_{\text{HF}}$$



Ionization potential

HF wavefunction

$$|\Phi_0^N\rangle = |\chi_1 \cdots \chi_{c-1} \chi_c \chi_{c+1} \cdots \chi_N\rangle$$

$$|\Phi_c^{N-1}\rangle = |\chi_1 \cdots \chi_{c-1} \chi_{c+1} \cdots \chi_N\rangle$$

$$E_c^{N-1} = \langle \Phi_c^{N-1} | \hat{H} | \Phi_c^{N-1} \rangle = \sum_{a \neq c} \langle a | \hat{h} | a \rangle + \frac{1}{2} \sum_{a \neq c, b \neq c} \langle ab | ab \rangle - \langle ab | ba \rangle$$

$$E_{\text{HF}} - E_c^{N-1} = \langle c | \hat{h} | c \rangle + \sum_b \langle cb | cb \rangle - \langle cb | bc \rangle = \varepsilon_c$$

Koopmans' Theorem

$$\text{IP} = E_c^{N-1} - E_{\text{HF}} = -\varepsilon_c$$

- Ionization potential for removing an electron from an orbital is the negative of that orbital energy



Electron Affinity

$$|\Phi_0^N\rangle = |\chi_1 \cdots \chi_N\rangle$$

$$|\Phi_r^{N+1}\rangle = |\chi_1 \cdots \chi_N \chi_r\rangle$$

Koopmans' Theorem

$$\text{EA} = E_{\text{HF}} - E_r^{N+1} = - \left(\langle r | \hat{h} | r \rangle + \sum_b \langle rb | rb \rangle - \langle rb | br \rangle \right) = -\varepsilon_r$$

Koopmans' theorem, operating within 'frozen orbital' approximation, provides a reasonable first approximation of IP, but EA estimations are often poor.





NPTEL ONLINE CERTIFICATION COURSES

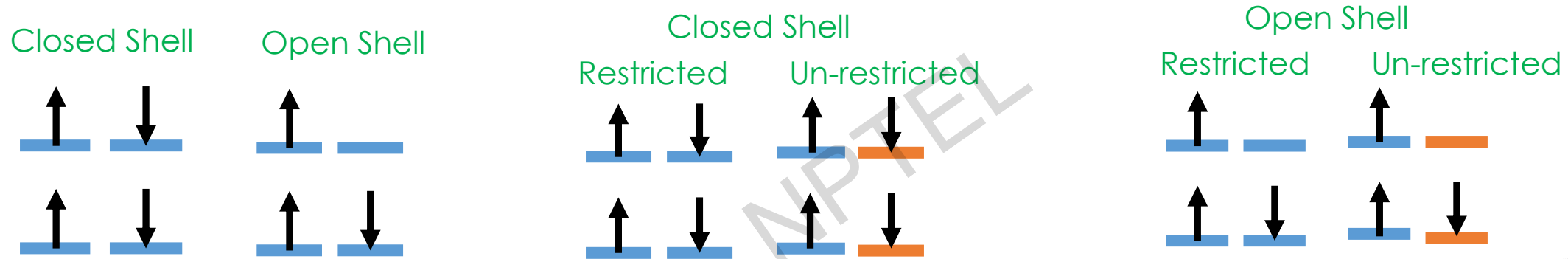
Approximate Methods in Quantum Chemistry

Sabyashachi Mishra
Department of Chemistry, IIT Kharagpur

Lecture 32: Hartree-Fock-Roothan Equations

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.

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 determinantal wavefunction

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

$$|\Phi\rangle = \frac{1}{\sqrt{N!}} |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \cdots \psi_{N/2} \bar{\psi}_{N/2}|$$

Determinantal energy

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



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

HF Equation with spatial orbitals

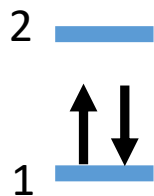
$$\hat{\mathcal{F}}(i)|\psi_a(i)\rangle = \varepsilon_a|\psi_a(i)\rangle$$

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

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

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

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



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

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



Introduction of a basis: Hartree-Fock-Roothan Equations

Fock operator in spatial orbital,

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

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

Introduce a basis:

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

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

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

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

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

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

In matrix form,

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

Matrix formulation of Roothan Equations

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

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

$\mathbf{F}$	$ \Theta_1\rangle$	$\cdots$	$ \Theta_\mu\rangle$	$ \Theta_\nu\rangle$	$\cdots$	$ \Theta_K\rangle$
$\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}

$\mathbf{S}$	$ \Theta_1\rangle$	$\cdots$	$ \Theta_\mu\rangle$	$ \Theta_\nu\rangle$	$\cdots$	$ \Theta_K\rangle$
$\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}

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