QUANTUM CHEMISTRY - 7

HARTREE FOCK MULTYELECTRONIC APPROACH

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$$E_0 \le E_{trial}^{HF}[\Psi^{HF}] = \left\langle \Psi^{HF} \middle| \hat{H} \middle| \Psi^{HF} \right\rangle = \left\langle \Psi^{HF} \middle| \hat{H}^{I} \middle| \Psi^{HF} \right\rangle + \left\langle \Psi^{HF} \middle| \hat{H}^{II} \middle| \Psi^{HF} \right\rangle$$

$$\left\langle \Psi^{HF} \middle| \hat{H}^{I} \middle| \Psi^{HF} \right\rangle$$
$$= N! \left\langle \Psi^{H} \middle| \hat{\wp} \hat{H}^{I} \hat{\wp} \middle| \Psi^{H} \right\rangle$$
$$= N! \left\langle \Psi^{H} \middle| \hat{H}^{I} \hat{\wp}^{2} \middle| \Psi^{H} \right\rangle$$
$$= N! \left\langle \Psi^{H} \middle| \hat{H}^{I} \hat{\wp} \middle| \Psi^{H} \right\rangle$$
$$= \sum_{i=1}^{N} \sum_{P} (-1)^{P} \left\langle \Psi^{H} \middle| \left[-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \right] \hat{\wp} \middle| \Psi^{H} \right\rangle$$
$$\equiv \sum_{i=1}^{N} \sum_{P} (-1)^{P} \left\langle \Psi^{H} \middle| \hat{h}_i(1) \hat{\wp} \middle| \Psi^{H} \right\rangle$$
$$= \sum_{i=1}^{N} \left\langle \Psi^{H} \middle| \hat{h}_i(1) \middle| \Psi^{H} \right\rangle$$
$$= \sum_{i=1}^{N} \left\langle \chi_i^{\sigma}(1) \middle| \hat{h}_i(1) \middle| \chi_i^{\sigma}(1) \right\rangle$$
$$= \sum_{i=1}^{N} \int \chi_i^{\sigma^*}(1) \hat{h}_i(1) \chi_i^{\sigma}(1) d\tau_1$$
$$\equiv \sum_{i=1}^{N} h_{ii}$$
$$\equiv H_{ii} .$$

$$\left\langle \Psi^{HF} \middle| \hat{H}^{II} \middle| \Psi^{HF} \right\rangle$$
$$= N! \left\langle \Psi^{H} \middle| \hat{\wp} \hat{H}^{II} \hat{\wp} \middle| \Psi^{H} \right\rangle$$
$$= N! \left\langle \Psi^{H} \middle| \hat{H}^{II} \hat{\wp}^{2} \middle| \Psi^{H} \right\rangle$$
$$= N! \left\langle \Psi^{H} \middle| \hat{H}^{II} \hat{\wp} \middle| \Psi^{H} \right\rangle$$
$$= \sum_{\substack{i,j=1 \\ i<j}}^{N} \sum_{P} (-1)^{P} \left\langle \Psi^{H} \middle| \frac{1}{r_{ij}} \hat{\wp} \middle| \Psi^{H} \right\rangle$$
$$= \sum_{\substack{i,j=1 \\ i<j}}^{N} \left\langle \Psi^{H} \middle| \frac{1}{r_{ij}} (1 - P_{ij}) \middle| \Psi^{H} \right\rangle$$
$$= \sum_{\substack{i,j=1 \\ i<j}}^{N} \left\langle \Psi^{H} \middle| \frac{1}{r_{ij}} \middle| \Psi^{H} \right\rangle - \sum_{\substack{i,j=1 \\ i<j}}^{N} \left\langle \Psi^{H} \middle| \frac{1}{r_{ij}} P_{ij} \middle| \Psi^{H} \right\rangle$$
$$= \sum_{\substack{i,j=1 \\ i<j}}^{N} \left\langle \chi_i^{\sigma}(1) \chi_j^{\sigma}(2) \middle| \frac{1}{r_{12}} \middle| \chi_i^{\sigma}(1) \chi_j^{\sigma}(2) \right\rangle - \sum_{\substack{i,j=1 \\ i<j}}^{N} \left\langle \chi_i^{\sigma}(1) \chi_j^{\sigma}(2) \middle| \frac{1}{r_{12}} \middle| \chi_j^{\sigma}(1) \chi_i^{\sigma}(2) \right\rangle$$
$$\equiv \sum_{\substack{i,j=1 \\ i<j}}^{N} \left\langle \chi_i^{\sigma}(1) \middle| \hat{J}_j(1) \middle| \chi_i^{\sigma}(1) \right\rangle - \sum_{\substack{i,j=1 \\ i<j}}^{N} \left\langle \chi_i^{\sigma}(1) \middle| \hat{K}_j(1) \middle| \chi_i^{\sigma}(2) \right\rangle$$
$$= \sum_{\substack{i,j=1 \\ i<j}}^{N} \iint \chi_i^{\sigma^*}(1) \chi_j^{\sigma^*}(2) \frac{1}{r_{ij}} \chi_i^{\sigma}(1) \chi_j^{\sigma}(2) d\tau_1 d\tau_2 - \sum_{\substack{i,j=1 \\ i<j}}^{N} \iint \chi_i^{\sigma^*}(1) \chi_j^{\sigma^*}(2) \frac{1}{r_{ij}} \chi_j^{\sigma}(1) \chi_i^{\sigma}(2) d\tau_1 d\tau_2$$
$$\equiv \sum_{\substack{i,j=1 \\ i<j}}^{N} J_{ij} - \sum_{\substack{i,j=1 \\ i<j}}^{N} K_{ij}$$
$$= \frac{1}{2} \sum_{i,j=1}^{N} [J_{ij} - K_{ij}]$$
$$\equiv U_{ee}$$

$$E_{trial}^{HF}[\Psi^{HF}] = \sum_{i=1}^{N} h_{ii} + \frac{1}{2} \sum_{i}^{N} \sum_{i=1}^{N} [J_{ij} - K_{ij}].$$

$$\delta \left\{ E_{trial}^{HF}[\Psi^{HF}] - \sum_{i=1}^{N} \varepsilon_i^{HF} \left(\left\langle \chi_i^{\sigma}(1) \middle| \chi_i^{\sigma}(1) \right\rangle - 1 \right) \right\} = 0$$

$$\hat{F}(1) = -\frac{1}{2} \nabla_i^2 + V_i^{HFeff}(1)$$

$$V_i^{HFeff}(1) = -\sum_A \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} V_j^{ee}(1) - \sum_{i=1}^{N} V_j^{ex}(1)$$

$$\varepsilon_i^{HF} = \int \chi_i^{\sigma^*}(1) \hat{F}(1) \chi_i^{\sigma}(1) d\tau_1 = h_{ii} + \sum_{j=1}^{N} [J_{ij} - K_{ij}]$$

$$E^{HF}[\Psi^{HF}] = \sum_{i=1}^{N} \varepsilon_i^{HF} - U_{ee}$$

Summative Questions:

1. Abordarea Hartree-Fock are la baza:…aproximarea energiei sistemului cu N particule printr-o energie cu doua componente, uni- si bi-particula
2. **Energia uni-particola din abordarea Hartree-Fock este de natura**:…cinetica si Coulombiana pentru interactia electroni-sistemul de nuclee in permutare
3. **In derivarea energiilor Hartree-Fock, operatorul de proiectie are rolul**:…de a reduce sistemul de N-particule la proiectiile uni-particula, indiferent daca este vorba de energie cinetica, sau Coulombiana
4. **Contributiade schimb in Energia Hartree-Fock isi are originea** in:…permutarea interactiei inter-electronice cu priectiile spin orbitale “ij” si “ji”
5. Optimizarea energie Hartree-Fock se face pentru atingerea minimului energetic reprezentand:…energia orbitala Hartree-Fock
6. Sumarea energiilor orbitale Hartree-Fock se poate face pe numarul total al celor N-particole din sistem deoarece:…fiecarei particole ii este asociat un unic [spin-orbital]
7. Optimizarea variationala a energiei Hartree-Fock se face in raport cu :…un spin-orbital arbitrar din sistemul de N-spin-orbitali
8. Diferenta intre energia Hartree-Fock de incercare/trial si energia Hartree-Fock orbital totala este:…factorul “1/2” care se regaseste in primul caz si nu apare in al doilea
9. **Diferenta intre energia Hartree-Fock de incercare/trial si energia Hartree-Fock orbital o face**: termenul de interactie inter-electronica care combina componentele Coulombiene inter-electronice cu energia de schimb inter-electronic