Hartree-Fock Method

Tutor: Edrick

Roadmap

0. Define the Hamiltonian of the system

1. Propose trial wave functions $\Psi_{HF}[\{\psi\}]$

2. Compute $E[\{\psi\}]$

3. (Constrained) Stationary condition of $E[\{\psi\}]$ to find $\{\psi\}$

System

- Nuclei-Electron System

$$\mathcal{H} = -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e}\nabla_i^2$$

$$+ \frac{1}{4\pi\varepsilon_0}\sum_{i<j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\varepsilon_0}\sum_{I,i}\frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \frac{1}{4\pi\varepsilon_0}\sum_{I<J}\frac{e^2 Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

- Fix Nuclei

- In atomic units

$$\mathcal{H} = \sum_{i=1} \left(-\tfrac{1}{2}\nabla_i^2\right) + \sum_{i=1} v(\mathbf{r}_i) + \sum_{i<j}\frac{1}{r_{ij}}$$

Slater Determinants (of N electrons)

(r_1, σ_1)

$\phi_1(\mathbf{r}_1)\alpha(s_1)$

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \cdots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \cdots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \cdots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

Spinorbitals

- Antisymmetric
- Pauli Principle
- (Anti)Parallel spins are (un)correlated
- If the spinorbitals are orthonormal then $\langle \Psi_{HF} | \Psi_{HF} \rangle = 1$

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$$
$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$$

(Canonical) Hartree-Fock Equations

$$\hat{F}\lambda_m(\mathbf{r}) = \varepsilon_m \lambda_m(\mathbf{r})$$

- Choice of Spin orbitals -> Restricted vs Unrestricted
- Exchange is zero for antiparallel spins
- Restricted Closed-Shell HF + Basis = Roothaan Equations

  Unrestricted Open-Shell HF + Basis = Pople-Nesbet Equations

- ε_k can be associated with the ionization energy of electron in orbital k — Koopmans theorem
- $\Sigma_k \varepsilon_k \neq E_{HF}$ $E_{HF} \geq E_0$ $E_0 - E_{HF}$

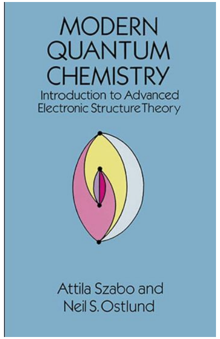
Correlation Energy

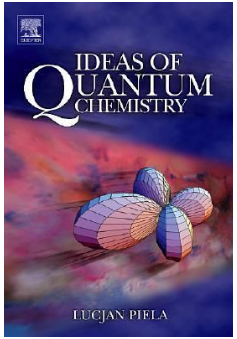
References

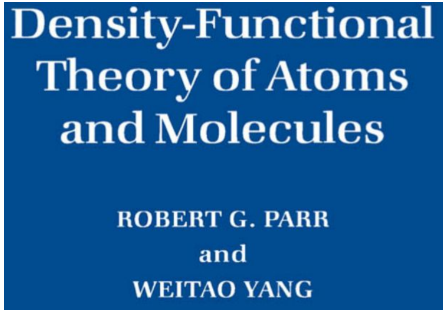
Homework

Feedback! (Positive and Negative)

- Books:







- Sara's notes

Thank you for your attention!