Hartree-Fock

Core idea

Mean-field theory to solve the electronic Schrödinger equation (similar to DFT)

$$\Big[\underbrace{\hat{T}_e}_{\text{Kinetic energy of the electrons}}(\mathbf{r}) + \underbrace{\hat{V}_{eN}}_{\text{Coulomb electron-nuclei}}(\mathbf{r};\mathbf{R}) + \overbrace{\hat{V}_{NN}}^{\text{Nuclear repulsion}}(\mathbf{R}) + \overbrace{\hat{V}_{ee}}^{\text{Electron repulsion}}(\mathbf{r})\Big]\underbrace{\Psi}_{\text{All-electron wavefunction}}(\mathbf{r};\mathbf{R}) = E_{\text{el}}\Psi(\mathbf{r};\mathbf{R}) \tag{77}$$

explicitly:

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_{A,i}\frac{\overbrace{Z_A}^{\text{Nuclear charges}}}{\underbrace{r_{Ai}}_{\text{Distance nucleus-electron}}} + \sum_{A>B}\frac{Z_A Z_B}{\underbrace{R_{AB}}_{\text{Distance nucleus-nucleus}}} + \sum_{i>j}\frac{1}{\underbrace{r_{ij}}_{\text{Distance electron-electron}}}\right]\Psi(\mathbf{r};\mathbf{R}) = E_{\text{el}}\Psi(\mathbf{r};\mathbf{R}) \tag{78}$$

Hartree Product

Assuming non-interacting electrons yields Hartree product

$$\underbrace{\Psi}_{\text{All-electron wavefunction}}{}_{\mathrm{HP}}(\overbrace{\mathbf{x}_1}^{\text{Position of electron 1}}, \mathbf{x}_2, \cdots, \mathbf{x}_N) = \overbrace{\chi_1}^{\text{One-electron orbital}}(\mathbf{x}_1)\,\chi_2(\mathbf{x}_2)\cdots\chi_N(\mathbf{x}_N) \tag{79}$$

But this approach does not satisfy the antisymmetry principle

$$\chi_1(\mathbf{x}_2)\,\chi_2(\mathbf{x}_1) = -\chi_1(\mathbf{x}_1)\,\chi_2(\mathbf{x}_2) \tag{80}$$

Slater Determinant

Determinant

- Enables antisymmetry: row and column exchanges switch sign
- Electrons are indistinguishable: contains all $N!$ permutations
- Every electron in every orbital
- Equivalent to mean field treatment
- Satisfies Pauli exclusion

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathsf{x}_1) & \chi_2(\mathsf{x}_1) & \cdots & \chi_N(\mathsf{x}_1) \\ \chi_1(\mathsf{x}_2) & \chi_2(\mathsf{x}_2) & \cdots & \chi_N(\mathsf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathsf{x}_N) & \chi_2(\mathsf{x}_N) & \cdots & \chi_N(\mathsf{x}_N) \end{vmatrix} = \frac{1}{\underbrace{\sqrt{N!}}_{\text{Normalises } \langle\Psi|\Psi\rangle = 1}} \sum_P (-1)^P \chi_{P_1}(\mathsf{x}_1) \cdots \chi_{P_N}(\mathsf{x}_N) \tag{81}$$

Energy derivation

Electronic energy expression

$$E_{el} = \langle \Psi | \hat{H}_{el} | \Psi \rangle \tag{82}$$

$$\hat{H}_{el} = \sum_i h(i) + \sum_{i<j} v(i,j) + V_{NN} \qquad \underbrace{h(i)}_{\text{Core Hamiltonian}} = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \qquad v(i,j) = \frac{1}{r_{ij}} \tag{83}$$

Orthonormality

$$\langle \chi_i | \chi_j \rangle = \underbrace{\delta_{ij}}_{\text{Kronecker-Delta: 1 if and only if } i=j} \tag{84}$$

Energy derivation (cont’d)

In integral form

$$E_{HF} = \sum_i \langle i|\underbrace{h}_{\text{Core Hamiltonian}}|i\rangle + \frac{1}{2}\sum_{ij}[ii|jj] - [ij|ji] \tag{85}$$

Core Hamiltonian: One electron, two center

$$\langle i|h|i\rangle \equiv \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1) h(\mathbf{x}_1) \chi_i(\mathbf{x}_1) \tag{86}$$

Electron-repulsion integral (ERI): two electron, four center

$$[ij|kl] \equiv \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) \frac{1}{r_{12}} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2) \tag{87}$$

Rewriting

For non-interacting particles:

$$h(\mathbf{x}_1)\chi_i(\mathbf{x}_1) + \sum_{j\neq i}\left[\underbrace{\mathcal{J}_j}_{\text{Coulomb term}}(\mathbf{x}_1)\right]\chi_i(\mathbf{x}_1) - \sum_{j\neq i}\left[\underbrace{\mathcal{K}_j}_{\text{Exchange term}}(\mathbf{x}_1)\right]\chi_j(\mathbf{x}_1) = \epsilon_i\chi_i(\mathbf{x}_1) \tag{88}$$

With

$$\mathcal{J}_j(\mathbf{x}_1) \equiv \int d\mathbf{x}_2 |\chi_j(\mathbf{x}_2)|^2 r_{12}^{-1} \tag{89}$$

$$\mathcal{K}_j(\mathbf{x}_1) \equiv \int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_2)\chi_i(\mathbf{x}_2) r_{12}^{-1} \tag{90}$$

More rewriting

$$\left[h(\mathbf{x}_1) + \sum_{j\neq i} \mathcal{J}_j(\mathbf{x}_1) - \sum_{j\neq i} \mathcal{K}_j(\mathbf{x}_1)\right] \chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1) \tag{91}$$

With $\left[\mathcal{J}_i(\mathbf{x}_1) - \mathcal{K}_i(\mathbf{x}_1)\right] \chi_i(\mathbf{x}_1) = 0$

$$\underbrace{f(\mathbf{x}_1)}_{\text{Fock operator}} \chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1) \qquad f(\mathbf{x}_1) \equiv h(\mathbf{x}_1) + \sum_{j} \mathcal{J}_j(\mathbf{x}_1) - \mathcal{K}_j(\mathbf{x}_1) \tag{92}$$

Solved numerically by optimizing orthonormal orbitals

Roothaan equations

Solve $f(\mathsf{x}_1)\chi_i(\mathsf{x}_1) = \epsilon_i \chi_i(\mathsf{x}_1)$ in basis set

$$\chi_i = \sum_{\mu=1}^{\overbrace{K}^{\text{Number of basis functions}}} C_{\mu i}\, \underbrace{\tilde{\chi}}_{\text{Basis function}}{}_{\mu} \qquad f(\mathsf{x}_1)\sum_{\nu} C_{\nu i}\tilde{\chi}_{\nu}(\mathsf{x}_1) = \epsilon_i \sum_{\nu} C_{\nu i}\tilde{\chi}_{\nu}(\mathsf{x}_1) \tag{93}$$

$$\sum_{\nu} \underbrace{F_{\mu\nu}}_{\text{Fock matrix element}} C_{\nu i} = \epsilon_i \sum_{\nu} \overbrace{S_{\mu\nu}}^{\text{Overlap matrix element}} C_{\nu i} \qquad \Rightarrow \underbrace{\mathsf{F}}_{\text{Fock matrix} \in \mathbb{R}^{K\times K}} \overbrace{\mathsf{C}}^{\text{Coefficient matrix} \in \mathbb{R}^{K\times N_e}} = \underbrace{\mathsf{S}}_{\text{Overlap matrix} \in \mathbb{R}^{K\times K}} \mathsf{C}\epsilon \tag{94}$$

$$F_{\mu\nu} \equiv \int d\mathsf{x}_1 \tilde{\chi}_{\mu}^{*}(\mathsf{x}_1) f(\mathsf{x}_1) \tilde{\chi}_{\nu}(\mathsf{x}_1) \qquad S_{\mu\nu} \equiv \int d\mathsf{x}_1 \tilde{\chi}_{\mu}^{*}(\mathsf{x}_1) \tilde{\chi}_{\nu}(\mathsf{x}_1) \tag{95}$$

Procedure

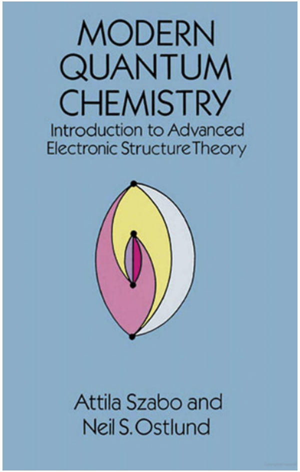
Preparation

- Choose system and K basis functions $\tilde{\chi}_\mu$
- Evaluate operators h and r_{ij}^{-1} in that basis (each operator is a $K \times K$ matrix)
- Initial guess (many ways, e.g. *Superposition of Atomic Densities* (SAD))

Self-Consistent Iterations

- Build density from $\mathbf{C}$
- Calculate $\mathbf{F}[\mathbf{C}]$
- Solve $\mathbf{F}\,\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon$ for new $\mathbf{C}$

Suggested literature



MODERN QUANTUM CHEMISTRY
Introduction to Advanced Electronic Structure Theory

Attila Szabo and
Neil S. Ostlund

Summary

Implications

- Replace the many-body wave function with a single Slater determinant of molecular orbitals.
- Mean-field approximation: each electron moves in the average field of all other electrons.
- Key components:
    - Coulomb interaction: $\mathcal{J}_j$ (classical electron-electron repulsion)
    - Exchange interaction: $\mathcal{K}_j$ (quantum mechanical, no classical analog)
- Self-consistent field (SCF) method: orbitals depend on all other orbitals.
- Roothaan equations: $\mathbf{FC} = \mathbf{SC}\epsilon$ solve HF in finite basis set.
- Foundation for post-HF methods (MP2, CCSD, etc.) and hybrid DFT functionals.