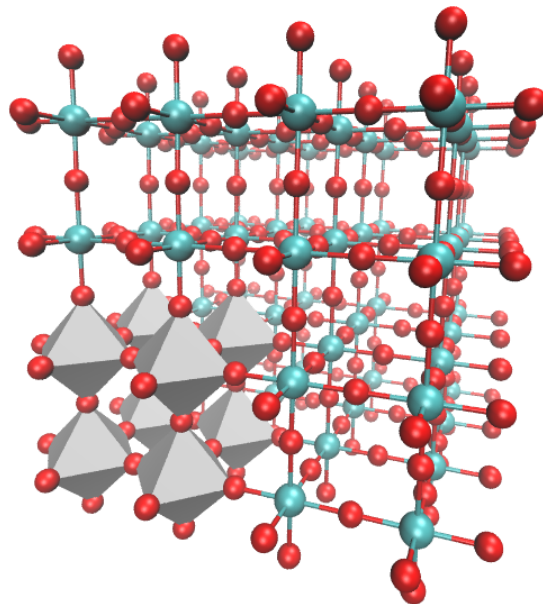




Hartree-Fock Molecular Orbital Theory



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Introduction

Schrödinger equation

- Recall:

$$\hat{H}\Psi = E\Psi$$

- Born-Oppenheimer approximated Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_{iA} \frac{Z_A}{r_{iA}} + \sum_{i<j} \frac{1}{r_{ij}} = \sum_{i=1}^n \hat{h}_i + \sum_{i<j} \frac{1}{r_{ij}}$$

- Wavefunction approximated as single Slater determinant

$$|\Psi\rangle = \frac{1}{\sqrt{n!}} \begin{bmatrix} \psi_1(1) & \psi_2(1) & \dots & \psi_n(1) \\ \psi_1(2) & \psi_2(2) & \dots & \psi_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(n) & \psi_2(n) & \dots & \psi_n(n) \end{bmatrix}$$

- Orthonormal spin orbitals

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

- But we still have no idea as to the form of the spin orbitals



Variational Theorem

Guiding principles

- Hartree-Fock - minimize the energy of a Slater determinant

$$E_{HF} = \min_{\Phi} \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

- Exact ground state is lower energy than any approximation
- If approximate wavefunction decreases energy it is an improvement
- Molecular orbitals should be orthonormal

Lagrangian Minimization

Objective function

- Achieved by optimizing spatial orbitals subject to orthonormality

$$E_{HF} = \min_{\{\psi_i\}} \langle \Phi | \hat{H} | \Phi \rangle \quad \text{such that} \quad \langle \psi_i | \psi_j \rangle = \delta_{ij}$$

- Use Lagrange multipliers to enforce orthogonality of orbitals

$$E_{HF} = \min_{\{\psi_i\}} \Lambda$$

$$\Lambda = \langle \Phi | \hat{H} | \Phi \rangle - \sum_{ij} \epsilon_{ij} [\langle \psi_i | \psi_j \rangle - \delta_{ij}]$$

$$\Lambda = \sum_i \langle \psi_i | \hat{h} | \psi_i \rangle + \frac{1}{2} \sum_{ij} \langle \psi_i \psi_j | r_{ij}^{-1} (1 - \hat{\pi}_{ij}) | \psi_i \psi_j \rangle - \sum_{ij} \epsilon_{ij} [\langle \psi_i | \psi_j \rangle - \delta_{ij}]$$

$$\Lambda = \sum_i \langle \psi_i | \hat{h} | \psi_i \rangle + \frac{1}{2} \sum_{ij} \langle \psi_j | \hat{J}_i - \hat{K}_i | \psi_j \rangle - \sum_{ij} \epsilon_{ij} [\langle \psi_i | \psi_j \rangle - \delta_{ij}]$$

Lagrangian Minimization

Minimization procedure

- Minimize Lagrangian by setting derivative equal to zero

$$\delta\Lambda = \delta E - \sum_j \epsilon_{kj} (\langle \delta\psi_k | \psi_j \rangle + \langle \psi_j | \delta\psi_k \rangle) = 0$$

$$\begin{aligned} \delta E = & \sum_i (\langle \delta\psi_i | \hat{h} | \psi_i \rangle + \langle \psi_k | \hat{h} | \delta\psi_k \rangle) + \frac{1}{2} \sum_{ij} (\langle \delta\psi_i | \hat{J}_j - \hat{K}_j | \psi_i \rangle + \langle \psi_i | \hat{J}_j - \hat{K}_j | \delta\psi_i \rangle) \\ & + \frac{1}{2} \sum_{ij} (\langle \delta\psi_j | \hat{J}_i - \hat{K}_i | \psi_j \rangle + \langle \psi_j | \hat{J}_i - \hat{K}_i | \delta\psi_j \rangle) \end{aligned}$$

$$\delta E = 2 \sum_i \langle \delta\psi_i | \hat{h} | \psi_i \rangle + 2 \sum_{ij} \langle \delta\psi_i | \hat{J}_j - \hat{K}_j | \psi_i \rangle$$

$$\frac{1}{2} \frac{\delta E}{\delta \psi_k} = \hat{h} | \psi_k \rangle + \sum_j (\hat{J}_j - \hat{K}_j) | \psi_k \rangle$$

$$\frac{1}{2} \frac{\delta \Lambda}{\delta \psi_k} = \hat{h} | \psi_k \rangle + \sum_j (\hat{J}_j - \hat{K}_j) | \psi_k \rangle - \sum_j \epsilon_{kj} | \psi_j \rangle = 0$$

Fock Equations

Fock Operator

- Operator for effective one-electron energy

$$\hat{F}_i = \hat{h}_i + \sum_j^{N_{\text{elec}}} (\hat{J}_j - \hat{K}_j)$$

- Rewrite Lagrangian derivative using the Fock operator

$$\frac{1}{2} \frac{\delta \Lambda}{\delta \psi_k} = \hat{F}_k |\psi_k\rangle - \sum_j \epsilon_{kj} |\psi_j\rangle = 0$$

$$\hat{F}_k |\psi_k\rangle = \sum_j \epsilon_{kj} |\psi_j\rangle$$

- Energy is minimized when orbitals are eigenfunction of Fock operator

$$\hat{F}_k |\psi_k\rangle = \epsilon_k |\psi_k\rangle \qquad \epsilon_{kj} = \delta_{kj} \epsilon_k$$

- These are the “canonical” orbitals and eigenvalues are orbital energies

Canonical Orbitals

Energy expression

- A Fock equation for each molecular orbital
- But Fock equation requires form of all other occupied orbitals
- Need to use an iterative approach to solve - “self-consistent field”
- Can write energy of Slater determinant using Fock eigenvalues

$$E_{HF} = \sum_i^{N_{\text{elec}}} h_{ii} + \frac{1}{2} \sum_{ij}^{N_{\text{elec}}} (J_{ij} - K_{ij}) + V_{NN} \qquad \epsilon_i = \langle \psi_i | \hat{F} | \psi_i \rangle = h_i + \sum_j^{N_{\text{elec}}} (J_{ij} - K_{ij})$$

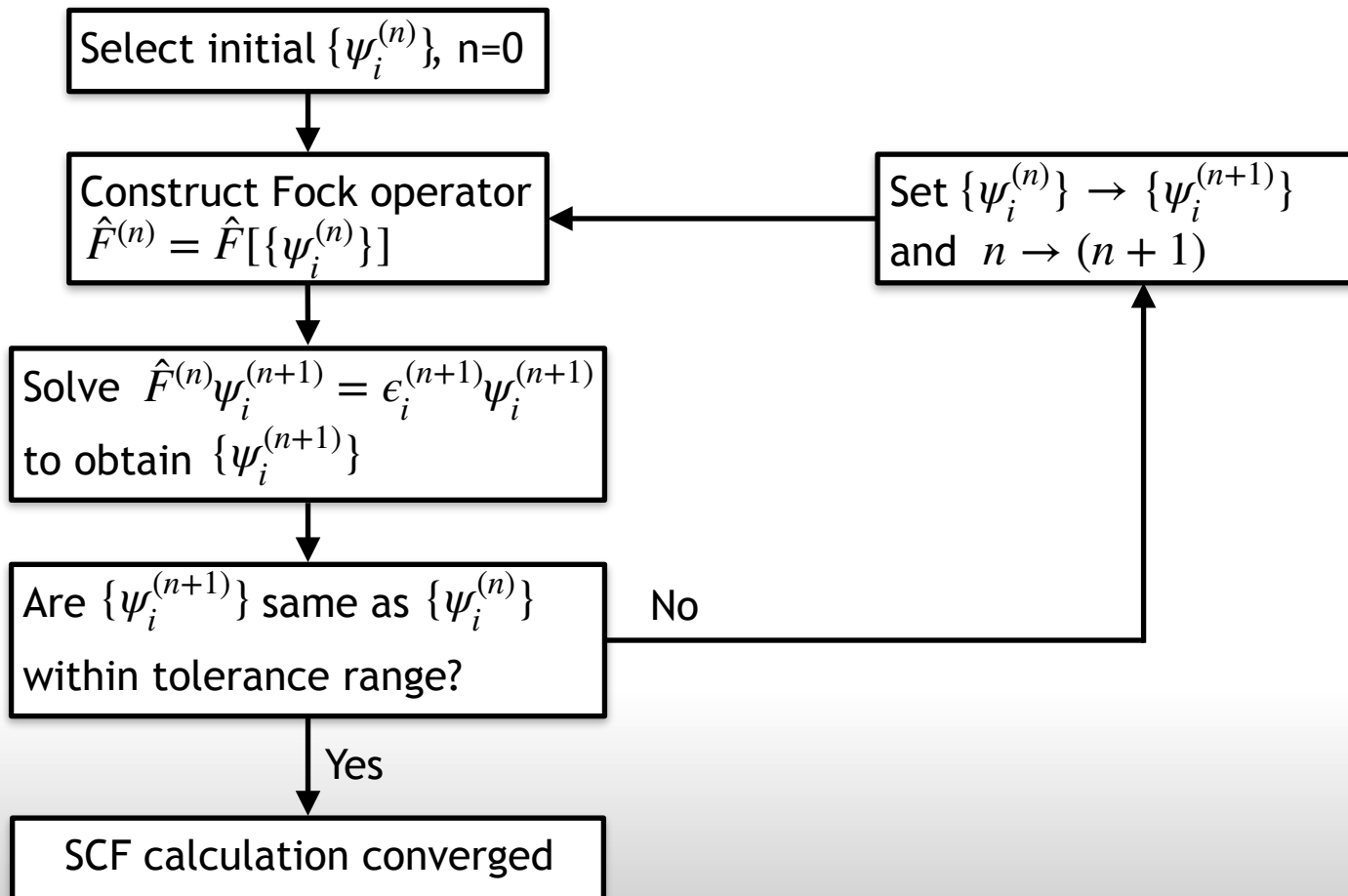
$$E_{HF} = \sum_i^{N_{\text{elec}}} \epsilon_i - \frac{1}{2} \sum_{ij}^{N_{\text{elec}}} (J_{ij} - K_{ij}) + V_{NN}$$

- Hartree-Fock energy not just a sum of orbital energies
- Energy cannot be exact as it describes electron-electron interaction assuming spatial distribution described by set of orbitals - “mean-field approximation”
- Result of using a single Slater determinant as guess for the energy



Self-Consistent Field

Iterative procedure



Koopmans' Theorem

- Physical interpretation of orbital energies (Lagrange multipliers) from Koopmans' theorem

$$E_{HF}^{N\text{elec}} = \sum_i^{N\text{elec}} h_{ii} + \frac{1}{2} \sum_{ij}^{N\text{elec}} (J_{ij} - K_{ij}) + V_{NN}$$

$$E_{HF}^{N\text{elec}-1} = \sum_i^{N\text{elec}-1} h_{ii} + \frac{1}{2} \sum_{ij}^{N\text{elec}-1} (J_{ij} - K_{ij}) + V_{NN}$$

$$E_{HF}^{N\text{elec}} - E_{HF}^{N\text{elec}-1} = h_{kk} + \frac{1}{2} \sum_i^{N\text{elec}} (J_{ik} - K_{ik}) + \frac{1}{2} \sum_j^{N\text{elec}} (J_{kj} - K_{kj})$$

$$E_{HF}^{N\text{elec}} - E_{HF}^{N\text{elec}-1} = h_{kk} + \sum_i^{N\text{elec}} (J_{ik} - K_{ik}) = \epsilon_k$$

- Ionization energy from “frozen” Hartree-Fock orbital is equal to the orbital energy



Summary

- Slater determinant wavefunction constructed from antisymmetric combinations of one-electron wavefunctions
- We needed to develop approach for optimizing one-electron wavefunctions simultaneously for all electrons (i.e. orbital shapes)
- Variational principle shows that decreasing the energy necessarily gives a better wavefunction approximation
- Lagrangian minimization of energy with respect to orbital shape subject to orthonormality constraint gives optimization procedure
- Fock operator is the one-electron operator accounting for interaction with other electrons at the “mean-field” level
- Canonical orbitals are those that diagonalize the Fock operator matrix representation, energy has two-electron contribution in addition to sum of orbital energies.
- Hartree-Fock cannot be exact as interaction is with averaged charge of all other electrons (orbital approximation)
- Iterative procedure required to optimize Hartree-Fock energy