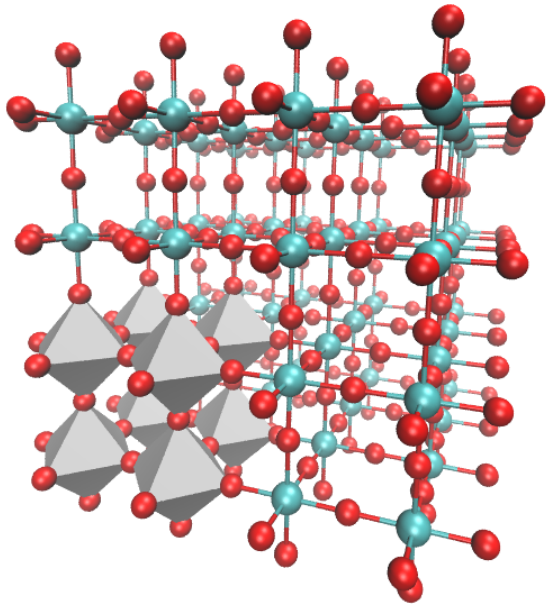
Constructing a Basis: Roothan-Hall Hartree-Fock Theory



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Roothan-Hall Equations

Basis set approximation

- We now know in principle how to construct orbitals to get energy
- We change shape of the orbitals in an iterative calculation
- How do we modify the shape of the orbitals?
- Use a basis expansion to describe orbitals
- "Linear combination of atomic orbitals"

$$|\psi_i\rangle = \sum_{\mu}^{N_{\text{basis}}} C_{\mu i} |\phi_\mu\rangle$$

- "Atomic orbitals" set of known functions (see basis sets lecture)
- Writing Fock equations in terms of atomic orbitals yields Roothan-Hall equations

$$\hat{F}_i \sum_{\mu}^{N_{\text{basis}}} C_{\mu i} |\phi_\mu\rangle = \epsilon_i \sum_{\mu}^{N_{\text{basis}}} C_{\mu i} |\phi_\mu\rangle$$

Roothan-Hall Equations

Reformulation of Fock equation

- Use basis set approximation to re-write Fock equations as matrix eigenvalue problem

$$\sum_{\mu}^{N_{\text{basis}}} C_{\mu i}\langle\phi_\nu|\hat{F}_i|\phi_\mu\rangle = \epsilon_i \sum_{\mu}^{N_{\text{basis}}} C_{\mu i}\langle\phi_\nu|\phi_\mu\rangle$$

$$\sum_{\mu}^{N_{\text{basis}}} F_{\nu\mu}C_{\mu i} = \epsilon_i \sum_{\mu}^{N_{\text{basis}}} S_{\nu\mu}C_{\mu i}$$

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon}$$

1. Construct Fock matrix **F** in the atomic orbital basis set
2. Orthogonalize basis using the overlap matrix **S**
3. Diagonalize **F** to get the "molecular orbital" coefficients" **C**
4. Compare new **C** to old **C** used to build **F** and stop if the same

Roothan-Hall Equations

Formation of the Fock matrix

- Matrix representation of Fock operator in AO basis

$$\langle \phi_\nu | \hat{F}_i | \phi_\mu \rangle = \langle \phi_\nu | \hat{h}_i | \phi_\mu \rangle + \sum_j^{N_{\text{elec}}} \langle \phi_\nu | \hat{J}_j - \hat{K}_j | \phi_\mu \rangle \qquad \hat{F}_i = \hat{h}_i + \sum_j^{N_{\text{elec}}} (\hat{J}_j - \hat{K}_j)$$

$$= \langle \phi_\nu | \hat{h}_i | \phi_\mu \rangle + \sum_j^{N_{\text{elec}}} (\langle \phi_\nu \psi_j | r_{12}^{-1} | \phi_\mu \psi_j \rangle - \langle \phi_\nu \psi_j | r_{12}^{-1} | \psi_j \phi_\mu \rangle)$$

$$= \langle \phi_\nu | \hat{h}_i | \phi_\mu \rangle + \sum_j^{N_{\text{elec}}} \sum_{\lambda\tau}^{N_{\text{basis}}} C_{\lambda j} C_{\tau j} (\langle \phi_\nu \phi_\lambda | r_{12}^{-1} | \phi_\mu \phi_\tau \rangle - \langle \phi_\nu \phi_\lambda | r_{12}^{-1} | \phi_\tau \phi_\mu \rangle)$$

$$= \langle \phi_\nu | \hat{h}_i | \phi_\mu \rangle + \sum_{\lambda\tau}^{N_{\text{basis}}} P_{\lambda\tau} (\langle \phi_\nu \phi_\lambda | r_{12}^{-1} | \phi_\mu \phi_\tau \rangle - \langle \phi_\nu \phi_\lambda | r_{12}^{-1} | \phi_\tau \phi_\mu \rangle)$$

$$F_{\nu\mu} = h_{\nu\mu} + \sum_{\lambda\tau} P_{\lambda\tau} \langle \nu\lambda || \mu\tau \rangle$$

$$P_{\lambda\tau} = \sum_j^{N_{\text{elec}}} C_{\lambda j} C_{\tau j}$$

$$\mathbf{F} = \mathbf{h} + \mathbf{G}(\mathbf{P})$$

Roothan-Hall Equations

Energy expression

- Matrix representation of Fock operator in AO basis

$$P_{\lambda\tau} = \sum_{j}^{N_{\text{elec}}} C_{\lambda j} C_{\tau j} \qquad F_{\nu\mu} = h_{\nu\mu} + \sum_{\lambda\tau} P_{\lambda\tau} \langle \nu\lambda || \mu\tau \rangle \qquad \mathbf{F} = \mathbf{h} + \mathbf{G}(\mathbf{P})$$

$$E_{HF} = \sum_{i}^{N_{\text{elec}}} \langle \psi_i | \hat{h} | \psi_i \rangle + \frac{1}{2} \sum_{ij}^{N_{\text{elec}}} (\psi_i \psi_i || \psi_j \psi_j) + V_{NN}$$

$$= \sum_{i}^{N_{\text{elec}}} \sum_{\mu\nu}^{N_{\text{basis}}} C_{\mu i} C_{\nu i} \langle \phi_\mu | \hat{h} | \phi_\nu \rangle + \frac{1}{2} \sum_{ij}^{N_{\text{elec}}} \sum_{\mu\nu\lambda\tau}^{N_{\text{basis}}} C_{\mu i} C_{\nu i} C_{\lambda j} C_{\tau j} (\phi_\mu \phi_\nu || \phi_\lambda \phi_\tau) + V_{NN}$$

$$= \sum_{\mu\nu}^{N_{\text{basis}}} P_{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\tau}^{N_{\text{basis}}} P_{\mu\nu} P_{\lambda\tau} (\phi_\mu \phi_\nu || \phi_\lambda \phi_\tau) + V_{NN}$$

$$= \frac{1}{2} \sum_{\mu\nu}^{N_{\text{basis}}} P_{\mu\nu} (h_{\mu\nu} + F_{\mu\nu})$$

Roothan-Hall Equations

Orthogonalization of the basis

- Atomic orbital basis set not orthogonal resulting in overlap **S**
- We can transform nonorthogonal basis to orthogonal set by taking linear combination **X**

$$|\phi'_\mu\rangle = \sum_{\nu}^{N_{\text{basis}}} X_{\nu\mu}|\phi_\nu\rangle \qquad S'_{\mu\nu} = \langle\phi'_\mu|\phi'_\nu\rangle = \sum_{\lambda\tau}^{N_{\text{basis}}} X^*_{\lambda\mu}\langle\phi_\lambda|\phi_\tau\rangle X_{\tau\nu} = \delta_{\mu\nu}$$

$$\mathbf{X}^\dagger\mathbf{S}\mathbf{X} = \mathbf{1}$$

- Canonical orthogonalization

$$\mathbf{X} = \mathbf{U}\mathbf{s}^{-1/2} \qquad \mathbf{U}^\dagger\mathbf{S}\mathbf{U} = \mathbf{s}$$

$$\mathbf{X}^\dagger\mathbf{S}\mathbf{X} = (\mathbf{U}\mathbf{s}^{-1/2})^\dagger\mathbf{S}(\mathbf{U}\mathbf{s}^{-1/2}) = \mathbf{s}^{-1/2}\mathbf{U}^\dagger\mathbf{S}\mathbf{U}\mathbf{s}^{-1/2} = \mathbf{s}^{-1/2}\mathbf{s}\mathbf{s}^{-1/2} = \mathbf{1}$$

- To remove linear dependence, throw away basis functions with s=0
- Use transformation matrix to convert matrices to orthogonal basis

$$\mathbf{C} = \mathbf{X}\mathbf{C}' \qquad \mathbf{C}' = \mathbf{X}^{-1}\mathbf{C}$$

$$\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\epsilon} \qquad \mathbf{F}\mathbf{X}\mathbf{C}' = \mathbf{S}\mathbf{X}\mathbf{C}'\boldsymbol{\epsilon} \qquad \mathbf{X}^\dagger\mathbf{F}\mathbf{X}\mathbf{C}' = \mathbf{X}^\dagger\mathbf{S}\mathbf{X}\mathbf{C}'\boldsymbol{\epsilon} \qquad \mathbf{F}'\mathbf{C}' = \mathbf{C}'\boldsymbol{\epsilon}$$

SCF Optimization

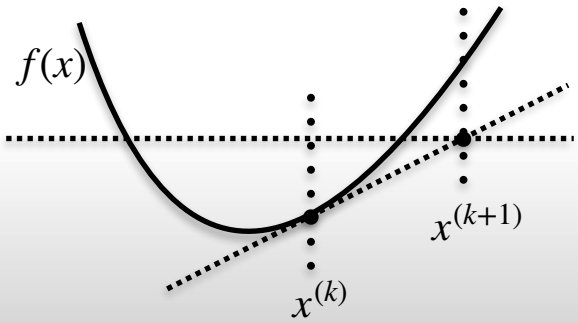
Direct inversion of the iterative subspace (DIIS)

- Hartree-Fock equations non-linear resulting in problematic convergence
- Many different algorithms for SCF optimization developed
- Most successful and widely used is DIIS
- We use SCF optimization as an example, but general for finding solutions to

$$f(x) = 0$$

- Function is a measure of error in optimization, use commutativity of Fock matrix and density matrix

$$f(x) = \mathbf{FPS} - \mathbf{SPF} = \mathbf{0}$$



- From given $x^{(k)}$ we obtain new $x^{(k+1)}$

$$x^{(k+1)} = x^k - \frac{f(x^k)}{f'(x^k)}$$

SCF Optimization

Direct inversion of the iterative subspace (DIIS)

- From n approximations $x^{(1)}$, $x^{(2)}$…$x^{(n)}$ construct linear combination

$$\tilde{x} = \sum_{k=1}^{n} d_k x^{(k)} \qquad \sum_{k=1}^{n} d_k = 1$$

- We thus construct a Lagrangian

$$\Lambda = \sum_{k=1}^{n} d_k f(x^{(k)}) - \lambda\left(\sum_{k=1}^{n} d_k - 1 \right) = 0$$

From which we obtain the set of linear equations to solve

$$\begin{bmatrix} \mathrm{tr}\{f(x^{(1)})f(x^{(1)})\} & \dots & \mathrm{tr}\{f(x^{(1)})f(x^{(n)})\} & -1 \\ \mathrm{tr}\{f(x^{(2)})f(x^{(1)})\} & \dots & \mathrm{tr}\{f(x^{(2)})f(x^{(n)})\} & -1 \\ \vdots & \ddots & \vdots & \vdots \\ \mathrm{tr}\{f(x^{(n)})f(x^{(1)})\} & \dots & \mathrm{tr}\{f(x^{(n)})f(x^{(n)})\} & -1 \\ 1 & \dots & 1 & 0 \end{bmatrix} \begin{bmatrix} d_1 \\ d_2 \\ \vdots \\ d_n \\ \lambda \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix}$$

$$\mathbf{F}^{(n+1)} = \sum_{k=1}^{n} d_k F^{(k)}$$

Summary

- Linear combination of atomic orbitals approach to Hartree-Fock (Roothan-Hall)
- Construct molecular orbital shapes (unknown) by weighted combinations of atomic orbitals
- Form Hartree-Fock equations in atomic orbital basis using “molecular orbital” coefficients
- Density matrix described using molecular orbital coefficients and energy can be expressed using density matrix
- Atomic orbitals are not necessarily orthonormal so have to account for non-orthonormality of basis by similarity transformation and removal of linear dependencies
- Optimization can follow simple procedure comparing density matrix in different iterations
- More advanced optimization algorithms significantly improve convergence - e.g. DIIS