Hartree-Fock Theory 1

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  - We built our electronic Hamiltonian from logically thinking about the most relevant physical interactions in our system

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  - We reasoned that our wavefunction for a many electron system is best approximated by a product of one electron wavefunctions (spin-orbitals). But, this is not enough; half-integer spin of electrons requires antisymmetric wavefunction under exchange. So, we make an *antisymmetric product* (Slater determinant) wavefunction.

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  - We built our electronic Hamiltonian from logically thinking about the most relevant physical interactions in our system
  - We reasoned that our wavefunction for a many electron system is best approximated by a product of one electron wavefunctions (spin-orbitals). But, this is not enough; half-integer spin of electrons requires antisymmetric wavefunction under exchange. So, we make an *antisymmetric product* (Slater determinant) wavefunction.
  - Applying this wavefunction and Hamiltonian to the time-independent Schrodinger equation gives us an expression for the **electronic energy**, known as the **first Slater-Condon rule:**

$$E = \sum_i \langle \psi_i^i | \hat{h}(i) | \psi_i^i \rangle + \sum_{i<j} \langle \psi_i^i \psi_j^j | \hat{g}(i,j) | \psi_i^i \psi_j^j \rangle - \langle \psi_i^i \psi_j^j | \hat{g}(i,j) | \psi_j^i \psi_i^j \rangle$$

Know how to derive this equation. There isn't just one way to reason through it, come up with a way that you're comfortable with

Closed-shell case

$$E = \sum_i \langle \psi_i^i | \hat{h}(i) | \psi_i^i \rangle + \sum_{i<j} \langle \psi_i^i \psi_j^j | \hat{g}(i,j) | \psi_i^i \psi_j^j \rangle - \langle \psi_i^i \psi_j^j | \hat{g}(i,j) | \psi_j^i \psi_i^j \rangle$$

Above is a general expression, but if we assume a closed-shell Slater determinant, the sum over N electrons can be converted to sum over the number of doubly-occupied (N/2) molecular orbitals by integrating out the spin functions (derivation in lecture notes):

$$E = 2 \sum_i^{N/2} \langle \phi_i | \hat{h}(i) | \phi_i \rangle + \sum_i^{N/2} \sum_j^{N/2} 2\langle \phi_i \phi_j | \hat{g}(i,j) | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \hat{g}(i,j) | \phi_j \phi_i \rangle$$

Restricted Hartree-Fock

- Our restricted energy expression

$$E = 2 \sum_i^{N/2} \langle \phi_i | \hat{h}(i) | \phi_i \rangle + \sum_i^{N/2} \sum_j^{N/2} 2 \langle \phi_i \phi_j | \hat{g}(i,j) | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \hat{g}(i,j) | \phi_j \phi_i \rangle$$

- We have not specified what our spatial orbitals **are**
- Using any random set of orbitals will give us *some* energy, but it probably won't be very good
- What is the **best set of orbitals** which give the **best single Slater determinant wavefunction** so that our energy is as accurate as possible?

Restricted Hartree-Fock

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- According to the Variational Principle, any trial wavefunction will overestimate the true ground state energy. So, varying our wavefunction's parameters (the orbitals) such that the energy is lowest will give the best wavefunction and the best energy

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$$\delta E = 2 \sum_i^{N/2} \langle \delta\phi_i | \hat{h}(i) | \delta\phi_i \rangle + \sum_i^{N/2} \sum_j^{N/2} 2 \langle \delta\phi_i \delta\phi_j | \hat{g}(i,j) | \delta\phi_i \delta\phi_j \rangle - \langle \delta\phi_i \delta\phi_j | \hat{g}(i,j) | \delta\phi_j \delta\phi_i \rangle$$

- We cannot just vary the orbitals however we want. This energy expression was derived under the assumption the orbitals are orthonormal. So they need to be kept that way!

$$\delta E = 2 \sum_{i}^{N/2} \langle \delta\phi_i | \hat{h}(i) | \delta\phi_i \rangle + \sum_{i}^{N/2} \sum_{j}^{N/2} 2 \langle \delta\phi_i \delta\phi_j | \hat{g}(i,j) | \delta\phi_i \delta\phi_j \rangle - \langle \delta\phi_i \delta\phi_j | \hat{g}(i,j) | \delta\phi_j \delta\phi_i \rangle$$

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- How might we do that?
  - We could minimize the energy brute-force; compute the energy over and over again, using basic optimization algorithms like Newton conjugate gradient, BFGS, …
  - By using the **method of Lagrange multipliers** which can give a general set of equations for finding extrema of a particular function subject to some constraint

Hartree-Fock Equations

$$\delta E = 2 \sum_{i}^{N/2} \langle \delta\phi_i | \hat{h}(i) | \delta\phi_i \rangle + \sum_{i}^{N/2} \sum_{j}^{N/2} 2\langle \delta\phi_i \delta\phi_j | \hat{g}(i,j) | \delta\phi_i \delta\phi_j \rangle - \langle \delta\phi_i \delta\phi_j | \hat{g}(i,j) | \delta\phi_j \delta\phi_i \rangle$$

Minimizing the energy expression under the constraint that the spin orbitals remain orthonormal (using Lagrange's method) gives us a set of equations[1,2,3] describing the conditions the *best possible* spin orbitals satisfy. These *best possible* spin orbitals give the *best possible* single Slater determinant wavefunction and *best possible* energy

$$\hat{f}\,\phi_i = \epsilon_i \phi_i$$

1. C. C. J. Roothaan, "New Developments in Molecular Orbital Theory", 1951
2. Dr. Andreas Copan's Notes (Github → CCQC → chem-8950 → 2017 → 1q-1h-hartree-fock.pdf
3. Szabo and Ostlund "Modern Quantum Chemistry"

$$\hat{f}\,\phi_i = \epsilon_i\phi_i$$

$$\left[\hat{h} + \sum_j (2\hat{J}_j - \hat{K}_j)\right]\phi_i = \epsilon_i\phi_i$$

$$\hat{J}_j|\phi^\mu\rangle = \langle\phi_j^\nu|\hat{g}(\mu,\nu)|\phi_j^\nu\phi^\mu\rangle \qquad \text{Coulomb operator}$$

$$\hat{K}_j|\phi^\mu\rangle = \langle\phi_j^\nu|\hat{g}(\mu,\nu)|\phi^\nu\phi_j^\mu\rangle \qquad \text{Exchange operator}$$

Hartree-Fock Equations

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- For an N-electron system, the Hartree-Fock equations are a set of N-coupled equations for N spin-orbitals (or N/2 equations for N/2 spatial orbitals in the restricted case)

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- "Solving" the HF equations means finding a set of spin-orbitals for which the HF equations are *stationary*, or "self-consistent": the set of orbitals used to construct the Fock operator are no different from the eigenfunctions of the Fock operator

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- "Solving" the HF equations means finding a set of spin-orbitals for which the HF equations are *stationary*, or "self-consistent": the set of orbitals used to construct the Fock operator are no different from the eigenfunctions of the Fock operator
- Trial and error: Assume a set of ϕ_i, calculate $\hat{f}$, solve the above equation for the N/2 lowest eigenvalues and corresponding eigenfunctions, compare the eigenfunctions to the original set, update the orbitals, repeat until consistency

Solving the Hartree-Fock equations is really hard

$$\hat{f} \, \phi_i = \epsilon_i \phi_i$$

- What is the form of ϕ_i ?
- How to apply the Fock operator? Solve for new ϕ_i ?

Hartree-Fock has really only ever been done for single atoms, or very simple diatomics, but even then some approximations are made

Approximating HF: LCAO-MO's

We need to approximate the best MO's given by Hartree-Fock. The most common approximation is by a *linear combination of atomic orbitals* (LCAO) to form the *approximate* Hartree-Fock MO's (LCAO-MO)

$$\hat{f}\,\phi_i = \epsilon_i \phi_i$$

$$\phi_i = \sum_q \chi_q C_{qi}$$

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Left-multiplying by some other AO χ_p^* and integrating both sides:

$$\sum_q \langle \chi_p \mid \hat{f} \mid \chi_q \rangle C_{qi} = \epsilon_i \sum_q \langle \chi_p \mid \chi_q \rangle C_{qi}$$

Approximating HF: LCAO-MO's

$$\hat{f}\,\phi_i = \epsilon_i\,\phi_i$$

$$\hat{f}\,\sum_q \chi_q C_{qi} = \epsilon_i \sum_q \chi_q C_{qi}$$

$$\sum_q \langle \chi_p \mid \hat{f} \mid \chi_q \rangle C_{qi} = \epsilon_i \sum_q \langle \chi_p \mid \chi_q \rangle C_{qi}$$

Approximating HF: LCAO-MO's

$$\hat{f}\,\phi_i = \epsilon_i \phi_i$$

$$\hat{f}\sum_q \chi_q C_{qi} = \epsilon_i \sum_q \chi_q C_{qi}$$

$$\sum_q \langle \chi_p \mid \hat{f} \mid \chi_q \rangle C_{qi} = \epsilon_i \sum_q \langle \chi_p \mid \chi_q \rangle C_{qi}$$

Defining the integrals above $\langle \chi_p \mid \hat{f} \mid \chi_q \rangle$ and $\langle \chi_p \mid \chi_q \rangle$ as F_{pq} and S_{pq},

$$\sum_q F_{pq} C_{qi} = \epsilon_i \sum_q S_{pq} C_{qi} \longrightarrow \boldsymbol{FC} = \boldsymbol{SC\epsilon}$$

True for a single ϕ_i

True for *all* ϕ_i

Approximating HF: LCAO-MO's

Roothaan-Hall equations:

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

For m AO basis functions, $\boldsymbol{C}$ is an m x m matrix with each column containing the expansion coefficients for some LCAO-MO ϕ_i

Approximating HF: LCAO-MO's

Roothaan-Hall equations:

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

$$\boldsymbol{F}_{pq} = \begin{pmatrix} \langle \chi_1 \mid \hat{f} \mid \chi_1 \rangle & \cdots & \langle \chi_1 \mid \hat{f} \mid \chi_m \rangle \\ \vdots & \ddots & \vdots \\ \langle \chi_m \mid \hat{f} \mid \chi_1 \rangle & \cdots & \langle \chi_m \mid \hat{f} \mid \chi_m \rangle \end{pmatrix}$$

$$\boldsymbol{S}_{pq} = \begin{pmatrix} \langle \chi_1 \mid \chi_1 \rangle & \cdots & \langle \chi_1 \mid \chi_m \rangle \\ \vdots & \ddots & \vdots \\ \langle \chi_m \mid \chi_1 \rangle & \cdots & \langle \chi_m \mid \chi_m \rangle \end{pmatrix}$$

Fock Matrix Elements

Applying the definition of the Fock operator, and Coulomb and Exchange operators:

$$\hat{f} = \left[\hat{h} + \sum_j (2\hat{J}_j - \hat{K}_j)\right]$$

$$\langle \chi_p \mid \hat{J}_j \mid \chi_q \rangle = \langle \chi_p \phi_j \mid \hat{g} \mid \chi_q \phi_j \rangle$$

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$$\langle \chi_p \mid \hat{f} \mid \chi_q \rangle = \langle \chi_p \mid \hat{h} \mid \chi_q \rangle + \sum_j^{N/2} 2\langle \chi_p \phi_j \mid \hat{g} \mid \chi_q \phi_j \rangle - \langle \chi_p \phi_j \mid \hat{g} \mid \phi_j \chi_q \rangle$$

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Expand:
$$\langle \phi_j \mid = \sum_{r} \langle \chi_r \mid C_{rj}^* \qquad \mid \phi_j \rangle = \sum_{s} \mid \chi_s \rangle C_{sj}$$

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$$\langle \chi_p \mid \hat{f} \mid \chi_q \rangle = \langle \chi_p \mid \hat{h} \mid \chi_q \rangle + \sum_j^{N/2} \sum_r^m \sum_s^m C_{rj}^* C_{sj} \left[2\langle \chi_p \chi_r \mid \hat{g} \mid \chi_q \chi_s \rangle - \langle \chi_p \chi_r \mid \hat{g} \mid \chi_s \chi_q \rangle \right]$$

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Fock Matrix Elements

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Each element of the Fock matrix is a simple sum of:

- A single electron-kinetic-energy integral over two AO basis functions
- A single electron-nuclear attraction integral over two AO basis functions
- A sum over weighted two-electron integrals

The whole Fock matrix is built from matrices which hold all possible kinetic and potential integrals over the set of AO basis functions, and an array of all possible two electron integrals 'contracted' with the density matrix

Solving the Roothaan-Hall Equations

$$FC = SC\epsilon$$

- If S is an identity matrix, this equation is easy to solve by 'diagonalizing' F

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So, we need to perform a change-of-basis, and this change-of-basis transformation needs to satisfy:

$$U^T S U = I$$

$$U^T S U = I$$

$$U^T SU = I$$

$$U = S^{-1/2}$$

$$U^T S U = I$$

$$U = S^{-1/2}$$

$$U^T S U = S^{-1/2} S S^{-1/2} = I$$

$$U^T S U = I$$

$$U = S^{-1/2}$$

$$U^T S U = S^{-1/2} S S^{-1/2} = I$$

Change our basis to an orthogonalized basis:

$$FC = SC\epsilon \qquad\qquad S^{-1/2} F S^{-1/2} \qquad\qquad S^{-1/2} S S^{-1/2}$$

We can't just stuff $S^{-1/2}$ into this equation wherever we want; we have to do some algebraic manipulations

$$\boldsymbol{FC} = \boldsymbol{SC}\boldsymbol{\epsilon} \qquad \boldsymbol{S}^{-1/2}\boldsymbol{FS}^{-1/2} \qquad \boldsymbol{S}^{-1/2}\boldsymbol{SS}^{-1/2}$$

$$\cdots$$

$$\tilde{\boldsymbol{F}}\tilde{\boldsymbol{C}} = \tilde{\boldsymbol{C}}\boldsymbol{\epsilon}$$

$$\tilde{\boldsymbol{F}} = \boldsymbol{S}^{-1/2}\boldsymbol{FS}^{-1/2} \qquad \tilde{\boldsymbol{C}} = \boldsymbol{S}^{1/2}\boldsymbol{C}$$

RHF Algorithm

1. Collect all one and two-electron integrals in a matrix, form the orthogonalizer $S^{-1/2}$
2. Guess $D = 0$
3. Build F
4. Compute the energy
5. Diagonalize $\tilde{F} = S^{-1/2} F S^{-1/2}$ to get $\tilde{C}$ and ϵ
6. Backtransform to unorthogonalized AO basis $C = S^{-1/2} \tilde{C}$
7. Compute the new density matrix $D = \sum_{j}^{N/2} C_{rj}^* C_{sj}$
8. If new D and old D differ by too much, return to step 3.