

Chemistry 137

Introduction to Hartree-Fock

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Resources

- Grant and Richards, Chapter 2
- Foresman and Frisch, *Exploring Chemistry with Electronic Structure Methods* (Gaussian Inc., 1996)
- Cramer, Chapter 4
- Jensen, Chapter 3
- Leach, Chapter 2
- Ostlund and Szabo, *Modern Quantum Chemistry* (McGraw-Hill, 1982)

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Born-Oppenheimer Approximation

- freeze the nuclear positions (nuclear kinetic energy is zero in the electronic Hamiltonian)

$$\hat{H}_{el} = \sum_i^{electrons} \frac{-\hbar^2}{2m_e} \nabla_i^2 + \sum_i^{electrons} \sum_A^{nuclei} \frac{-e^2 Z_A}{r_{iA}} + \sum_{i>j}^{electrons} \frac{e^2}{r_{ij}} + \sum_{A>B}^{nuclei} \frac{e^2 Z_A Z_B}{r_{AB}}$$

- calculate the electronic wavefunction and energy

$$\hat{H}_{el} \Psi_{el} = E \Psi_{el}, \quad E = \frac{\int \Psi_{el}^* \hat{H}_{el} \Psi_{el} d\tau}{\int \Psi_{el}^* \Psi_{el} d\tau}$$

- E depends on the nuclear positions through the nuclear-electron attraction and nuclear-nuclear repulsion terms
- E = 0 corresponds to all particles at infinite separation

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Hartree Approximation

- assume that a many electron wavefunction can be written as a product of one electron functions

$$\Psi(r_1, r_2, r_3, \dots) = \phi(r_1)\phi(r_2)\phi(r_3)\dots$$

- if we use the variational energy, solving the many electron Schrödinger equation is reduced to solving a series of one electron Schrödinger equations
- each electron interacts with the average distribution of the other electrons

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Hartree-Fock Approximation

- the Pauli principle requires that a wavefunction for electrons must change sign when any two electrons are permuted
 - since $|\Psi(1,2)|^2 = |\Psi(2,1)|^2$, $\Psi(1,2) = \pm \Psi(2,1)$ (minus sign for fermions)
- the Hartree-product wavefunction must be antisymmetrized
- can be done by writing the wavefunction as a determinant
 - determinants change sign when any two columns are switched

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \cdots & \phi_1(n) \\ \phi_2(1) & \phi_2(2) & \cdots & \phi_2(n) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_n(1) & \phi_n(2) & \cdots & \phi_n(n) \end{vmatrix} = |\phi_1 \phi_2 \cdots \phi_n|$$

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Spin Orbitals

- each spin orbital ϕ_i describes the distribution of one electron
- in a Hartree-Fock wavefunction, each electron must be in a different spin orbital (or else the determinant is zero)
- an electron has both space and spin coordinates
- an electron can be alpha spin (α , \uparrow , spin up) or beta spin (β , \downarrow , spin down)
- each spatial orbital can be combined with an alpha or beta spin component to form a spin orbital
- thus, at most two electrons can be in each spatial orbital

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Fock Equation

- take the Hartree-Fock wavefunction

$$\Psi = |\phi_1 \quad \phi_2 \quad \cdots \quad \phi_n|$$

- put it into the variational energy expression

$$E_{\text{var}} = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

- minimize the energy with respect to changes in the orbitals while keeping the orbitals orthonormal

$$\partial E_{\text{var}} / \partial \phi_i = 0, \quad \int \phi_i^* \phi_j d\tau = \delta_{ij}$$

- yields the Fock equation

$$\hat{F} \phi_i = \varepsilon_i \phi_i$$

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Fock Equation

$$\hat{F} \phi_i = \varepsilon_i \phi_i$$

- the Fock operator is an effective one electron Hamiltonian for an orbital ϕ
- ε is the orbital energy
- each orbital ϕ sees the average distribution of all the other electrons
- finding a many electron wavefunction is reduced to finding a series of one electron orbitals

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Fock Operator

$$\hat{\mathbf{F}} = \hat{\mathbf{T}} + \hat{\mathbf{V}}_{NE} + \hat{\mathbf{J}} - \hat{\mathbf{K}}$$

- kinetic energy operator

$$\hat{\mathbf{T}} = \frac{-\hbar^2}{2m_e} \nabla^2$$

- nuclear-electron attraction operator

$$\hat{\mathbf{V}}_{ne} = \sum_A^{nuclei} \frac{-e^2 Z_A}{r_{iA}}$$

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Fock Operator

$$\hat{\mathbf{F}} = \hat{\mathbf{T}} + \hat{\mathbf{V}}_{NE} + \hat{\mathbf{J}} - \hat{\mathbf{K}}$$

- Coulomb operator (electron-electron repulsion)

$$\hat{\mathbf{J}}\phi_i = \left\{ \sum_j^{electrons} \int \phi_j \frac{e^2}{r_{ij}} \phi_j d\tau \right\} \phi_i$$

- exchange operator (purely quantum mechanical
-arises from the fact that the wavefunction must
switch sign when you exchange to electrons)

$$\hat{\mathbf{K}}\phi_i = \left\{ \sum_j^{electrons} \int \phi_j \frac{e^2}{r_{ij}} \phi_i d\tau \right\} \phi_j$$

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Solving the Fock Equations

$$\hat{\mathbf{F}}\phi_i = \varepsilon_i\phi_i$$

1. obtain an initial guess for all the orbitals ϕ_i
2. use the current ϕ_i to construct a new Fock operator
3. solve the Fock equations for a new set of ϕ_i
4. if the new ϕ_i are different from the old ϕ_i , go back to step 2.

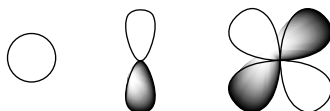
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Hartree-Fock Orbitals

- for atoms, the Hartree-Fock orbitals can be computed numerically
- the ϕ 's resemble the shapes of the hydrogen orbitals
- s, p, d orbitals



- radial part somewhat different, because of interaction with the other electrons (e.g. electrostatic repulsion and exchange interaction with other electrons)

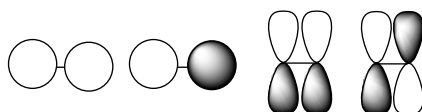
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Hartree-Fock Orbitals

- for homonuclear diatomic molecules, the Hartree-Fock orbitals can also be computed numerically (but with much more difficulty)
- the ϕ 's resemble the shapes of the H_2^+ orbitals
- σ , π , bonding and anti-bonding orbitals



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LCAO Approximation

- numerical solutions for the Hartree-Fock orbitals only practical for atoms and diatomics
- diatomic orbitals resemble linear combinations of atomic orbitals
- e.g. sigma bond in H_2
 $\sigma \approx 1s_A + 1s_B$
- for polyatomics, approximate the molecular orbital by a linear combination of atomic orbitals (LCAO)

$$\phi = \sum_{\mu} c_{\mu} \chi_{\mu}$$

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Basis Functions

$$\phi = \sum_{\mu} c_{\mu} \chi_{\mu}$$

- χ 's are called basis functions
- usually centered on atoms
- can be more general and more flexible than atomic orbitals
- larger number of well chosen basis functions yields more accurate approximations to the molecular orbitals

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Roothaan-Hall Equations

- choose a suitable set of basis functions

$$\phi = \sum_{\mu} c_{\mu} \chi_{\mu}$$

- plug into the variational expression for the energy

$$E_{\text{var}} = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

- find the coefficients for each orbital that minimizes the variational energy

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Roothaan-Hall Equations

- basis set expansion leads to a matrix form of the Fock equations

$$\mathbf{F} \mathbf{C}_i = \varepsilon_i \mathbf{S} \mathbf{C}_i$$

- \mathbf{F} – Fock matrix
- \mathbf{C}_i – column vector of the molecular orbital coefficients
- ε_i – orbital energy
- \mathbf{S} – overlap matrix

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Fock matrix and Overlap matrix

- Fock matrix

$$F_{\mu\nu} = \int \chi_\mu \hat{\mathbf{F}} \chi_\nu d\tau$$

- overlap matrix

$$S_{\mu\nu} = \int \chi_\mu \chi_\nu d\tau$$

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Integrals for the Fock matrix

- Fock matrix involves one electron integrals of kinetic and nuclear-electron attraction operators and two electron integrals of $1/r$

$$h_{\mu\nu} = \int \chi_{\mu} (\hat{\mathbf{T}} + \hat{\mathbf{V}}_{ne}) \chi_{\nu} d\tau$$

- one electron integrals are fairly easy and few in number (only N^2)

$$(\mu\nu | \lambda\sigma) = \int \chi_{\mu}(1) \chi_{\nu}(1) \frac{1}{r_{12}} \chi_{\lambda}(2) \chi_{\sigma}(2) d\tau_1 d\tau_2$$

- two electron integrals are much harder and much more numerous (N^4)

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Solving the Roothaan-Hall Equations

1. choose a basis set
2. calculate all the one and two electron integrals
3. obtain an initial guess for all the molecular orbital coefficients \mathbf{C}_i
4. use the current \mathbf{C}_i to construct a new Fock matrix
5. solve $\mathbf{F} \mathbf{C}_i = \epsilon_i \mathbf{S} \mathbf{C}_i$ for a new set of \mathbf{C}_i
6. if the new \mathbf{C}_i are different from the old \mathbf{C}_i , go back to step 4.

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Solving the Roothaan-Hall Equations

- also known as the self consistent field (SCF) equations, since each orbital depends on all the other orbitals, and they are adjusted until they are all converged
- calculating all two electron integrals is a major bottleneck, because they are difficult (6 dimensional integrals) and very numerous (formally N^4)
- iterative solution may be difficult to converge
- formation of the Fock matrix in each cycle is costly, since it involves all N^4 two electron integrals

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Summary

- start with the Schrödinger equation
- use the variational energy
- Born-Oppenheimer approximation
- Hartree-Fock approximation
- LCAO approximation

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