

Introduction to Hartree-Fock Molecular Orbital Theory

C. David Sherrill

School of Chemistry and Biochemistry

Georgia Institute of Technology

Origins of Mathematical Modeling in Chemistry

- ◆ Plato (ca. 428-347 BC): The world around us is made of imperfect shadows of the perfect forms constituting the ultimate reality
- ◆ "We may even judge the degree of perfection to which a science has arrived by the facility with which it may be submitted to calculation."
A. Quetelet, 1828

The One Equation... $H\Psi = E\Psi$

“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble” ---P.A.M. Dirac, *Proc. Roy. Soc. (London)* **123**, 714 (1929).

Robert S. Mulliken

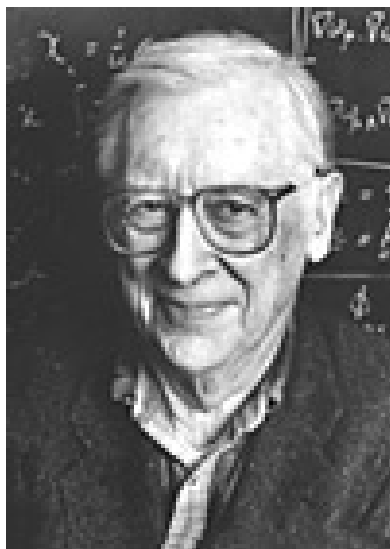
1966 Nobel Prize in Chemistry



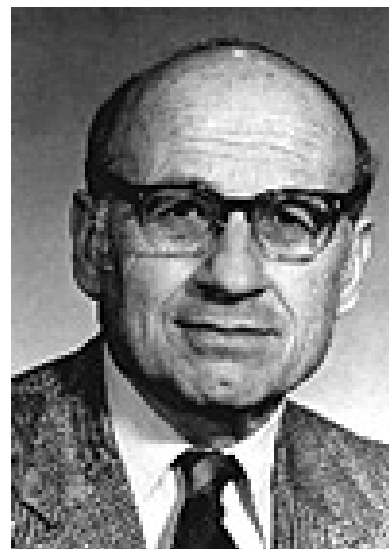
"...the era of computing chemists, when hundreds if not thousands of chemists will go to the computing machine instead of the laboratory...is already at hand. There is only one obstacle, namely, that someone must pay for the computing time."

John Pople and Walter Kohn

1998 Nobel Prize in Chemistry



“for his development of computational methods in quantum chemistry”



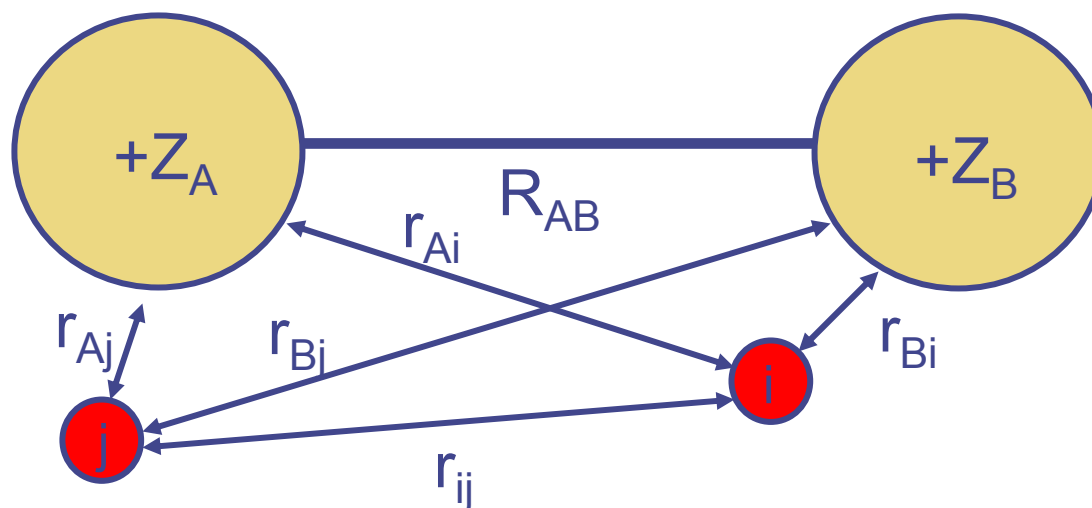
“for his development of the density-functional theory”

The Schrödinger Equation for Molecules

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

$$\Psi = \Psi(x_1, y_1, z_1, \omega_1, x_2, y_2, z_2, \omega_2, \dots)$$

The Molecular Hamiltonian



$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

Electronic
kinetic E

Nuclear
kinetic E

Electron/nuc
attraction

Nuc/nuc
repulsion

Elec/elec
repulsion

Simplified Notation

◆ In atomic units, the Hamiltonian goes from

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}},$$

to

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_{A,i} \frac{Z_A}{r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} + \sum_{i>j} \frac{1}{r_{ij}}$$

◆ Shorthand:

$$\hat{H} = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

Born-Oppenheimer Approximation

- ◆ Nuclei are much more massive than electrons ($\sim 2,000:1$ or more)
- ◆ Electron motions much faster than nuclear motions
- ◆ To a first approximation, assume electrons move “instantly” compared to nuclei. Equivalently, nuclei frozen compared to electrons

$$\hat{H}_{el} = \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$



Max Born



J. Robert Oppenheimer

Born-Oppenheimer Mathematics

$$\hat{H}_{el} \Psi(\mathbf{r}; \mathbf{R}) = E_{el} \Psi(\mathbf{r}; \mathbf{R})$$

Electronic Schrödinger equation

$$\Psi^i(\mathbf{r}, \mathbf{R}) = \sum_{kl} c_{kl}^i \underbrace{\Psi_k(\mathbf{r}; \mathbf{R})}_{\text{electronic}} \underbrace{\chi_{kl}(\mathbf{R})}_{\text{nuclear}}$$

$$\left[\hat{T}_N + \hat{T}'_{kk} + T''_{kk} + U_{kk} - E \right] \chi_k(\mathbf{R}) = - \sum_{k' \neq k} \left[U_{kk'} + \hat{T}'_{kk'} + T''_{kk'} \right] \chi_{k'}(\mathbf{R})$$

$$\left[\hat{T}_N + T''_{kk} + U_{kk} \right] \chi_k(\mathbf{R}) = E \chi_k(\mathbf{R})$$

The nuclei move in a potential set up by the electrons

Born-Oppenheimer Corrections

$$\left[\hat{T}_N + T''_{kk} + U_{kk} \right] \chi_k(\mathbf{R}) = E \chi_k(\mathbf{R})$$



DBOC = Diagonal Born-Oppenheimer Correction

$$E_{\text{DBOC}} = \sum_I^{N_{\text{coord}}} \left\langle \Psi_e \left| -\frac{1}{2M_I} \nabla_I^2 \right| \Psi_e \right\rangle$$

$$= \sum_I^{N_{\text{coord}}} \frac{1}{2M_I} \left\langle \frac{\partial \Psi_e}{\partial \mathbf{R}_I} \left| \frac{\partial \Psi_e}{\partial \mathbf{R}_I} \right\rangle \right\rangle,$$

DBOC correction to barrier to
linearity in H₂O (cm⁻¹)

	bent	linear	ΔE
CISD/cc-pVTZ	612	597	-15

E. F. Valeev and C. D. Sherrill, *J. Chem. Phys.*
118, 3921 (2003)

First Things First!

- ◆ Solve the Electronic Schrödinger Equation to get the potential energy surface,

$$\hat{H}_{el}\Psi(\mathbf{r}; \mathbf{R}) = E_{el}\Psi(\mathbf{r}; \mathbf{R})$$

- ◆ ... and then solve for the nuclear motion by quantum or classical means!
- ◆ Note: $E_{el}(\mathbf{R})$ is the potential energy surface!
- ◆ *The Electronic Schrödinger Equation is the equation that Quantum Chemistry seeks to solve!*

How do we solve the Electronic Schrödinger Equation?

- ◆ Hartree: Try a product of orbitals!
- ◆ Actually need to include a “spin coordinate” ω in addition to spatial coordinates



Douglas Hartree

$$\Psi_{HP}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \cdots \phi_N(\mathbf{r}_N) \quad \mathbf{r} = \{x, y, z\}$$

$$\Psi_{HP}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \cdots \chi_N(\mathbf{x}_N) \quad \mathbf{x} = \{\mathbf{r}, \omega\}$$

Problem with the Hartree Product

- ❖ Electrons are supposed to be mathematically indistinguishable
- ❖ Wavefunction is supposed to change sign upon interchange of two sets of electron coordinates

$$\Psi_{HP}(\mathbf{x}_1, \mathbf{x}_2) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)$$

$$\Psi_{HP}(\mathbf{x}_2, \mathbf{x}_1) = \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1)$$

$$\Psi_{HP}(\mathbf{x}_1, \mathbf{x}_2) \neq -\Psi_{HP}(\mathbf{x}_2, \mathbf{x}_1)$$

A Brute-Force Solution

- ◆ *Make the wavefunction antisymmetric by construction*

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1)]$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1)$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) \end{vmatrix}$$

The Slater Determinant

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

Shorthand: $|\chi_i \chi_j \cdots \chi_k\rangle$ or $|ij \cdots k\rangle$



John Slater

Enforces an antisymmetric wavefunction. Excellent! But....
where do we get the orbitals from??

The Variational Theorem

- ◆ The expectation value of the energy is always greater than or equal to the true energy

$$\begin{aligned} E_{el}(\mathbf{R}) &= \langle \Psi(\mathbf{r}; \mathbf{R}) | \hat{H}_{el} | \Psi(\mathbf{r}; \mathbf{R}) \rangle \\ &= \int_{-\infty}^{\infty} d\mathbf{r} \Psi^*(\mathbf{r}; \mathbf{R}) \hat{H}_{el} \Psi(\mathbf{r}; \mathbf{R}) \\ &\geq \mathcal{E}_0 \end{aligned}$$

- ◆ ...so, vary the orbitals until the energy is a minimum!

Hartree-Fock Molecular Orbital Theory

- ◆ 1. Invoke the Born-Oppenheimer approximation
- ◆ 2. Express the electronic wavefunction as a single Slater Determinant
- ◆ 3. Solve for those orbitals which minimize the electronic energy (variational method)
- ◆ This winds up being mathematically equivalent to assuming *each electron interacts only with the average charge cloud of the other electrons*



Douglas Hartree



V. A. Fock

The Operators

$$h(i) = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}$$

One-electron operator

$$v(i, j) = \frac{1}{r_{ij}}.$$

Two-electron operator

$$\hat{H}_{el} = \sum_i h(i) + \sum_{i < j} v(i, j) + V_{NN}.$$

Electronic Hamiltonian

The Hartree-Fock Energy

- ◆ If the variational theorem says to minimize the energy, *what is* the energy of a Slater determinant?

$$\begin{aligned} E_{el}(\mathbf{R}) &= \langle \Psi(\mathbf{r}; \mathbf{R}) | \hat{H}_{el} | \Psi(\mathbf{r}; \mathbf{R}) \rangle \\ &= \int_{-\infty}^{\infty} d\mathbf{r} \Psi^*(\mathbf{r}; \mathbf{R}) \hat{H}_{el} \Psi(\mathbf{r}; \mathbf{R}) \end{aligned}$$

$$E_{HF} = \sum_i \langle i | h | i \rangle + \frac{1}{2} \sum_{ij} [ii|jj] - [ij|ji],$$

$$\langle i | h | j \rangle = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1)$$

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

Hartree-Fock Equations

- ◆ Minimizing the Hartree-Fock energy with respect to the orbitals leads to the Hartree-Fock equations for the orbitals:

$$h(\mathbf{x}_1)\chi_i(\mathbf{x}_1) + \sum_{j \neq i} \left[\int d\mathbf{x}_2 |\chi_j(\mathbf{x}_2)|^2 r_{12}^{-1} \right] \chi_i(\mathbf{x}_1) - \sum_{j \neq i} \left[\int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_2) \chi_i(\mathbf{x}_2) r_{12}^{-1} \right] \chi_j(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1)$$

$$f(\mathbf{x}_1) = h(\mathbf{x}_1) + \sum_j \mathcal{J}_j(\mathbf{x}_1) - \mathcal{K}_j(\mathbf{x}_1)$$

$$f(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1)$$

- ◆ Problem: This is a very complicated integro-differential equation!

Roothan to the Rescue!

- ◆ If we introduce a basis set, we convert the equation into a much simpler linear algebra problem

$$f(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \epsilon_i\chi_i(\mathbf{x}_1)$$

$$\chi_i = \sum_{\mu=1}^K C_{\mu i} \tilde{\chi}_{\mu}$$

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i}$$

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

$$S_{\mu\nu} = \int d\mathbf{x}_1 \tilde{\chi}_{\mu}^*(\mathbf{x}_1) \tilde{\chi}_{\nu}(\mathbf{x}_1),$$

$$F_{\mu\nu} = \int d\mathbf{x}_1 \tilde{\chi}_{\mu}^*(\mathbf{x}_1) f(\mathbf{x}_1) \tilde{\chi}_{\nu}(\mathbf{x}_1)$$



Clemens C. J. Roothan

Summary of Hartree-Fock-Roothan Equations

$$\mathbf{FC} = \mathbf{SC}\epsilon$$
$$S_{\mu\nu} = \int d\mathbf{x}_1 \tilde{\chi}_\mu^*(\mathbf{x}_1) \tilde{\chi}_\nu(\mathbf{x}_1),$$
$$F_{\mu\nu} = \int d\mathbf{x}_1 \tilde{\chi}_\mu^*(\mathbf{x}_1) f(\mathbf{x}_1) \tilde{\chi}_\nu(\mathbf{x}_1)$$

- ◆ Pseudo-eigenvalue equation
- ◆ C collects the expansion coefficients for each orbital expressed as a linear combination of the basis functions (each column of C is a molecular orbital)
- ◆ Note: C depends on F, which depends on... C!

Self-consistent-field procedure

- ◆ 1. Specify molecule, basis functions, *and electronic state of interest* (i.e., singlet, triplet, etc)
- ◆ 2. Form overlap matrix S
- ◆ 3. Guess initial MO coefficients C
- ◆ 4. Form Fock matrix F
- ◆ 5. Solve $FC = SC\epsilon$
- ◆ 6. Use new MO coefficients C to build new Fock matrix F
- ◆ 7. Go to step 5; repeat until C no longer changes from one iteration to the next

Practical considerations

- ◆ Hartree-Fock self-consistent-field (HF SCF) usually converges fairly well with a good initial guess
- ◆ Stretched bonds, diradicals, transition metals, high-spin states, etc., can cause problems for convergence
- ◆ In high-symmetry cases, the program can guess the wrong orbital occupations, and then have trouble recovering from this to get the desired solution
- ◆ Not guaranteed to land on a local minimum in C space; can check by running a Hartree-Fock stability analysis (useful but not commonly done). However, even this doesn't guarantee you're not in some other local minimum (esp. for high-symmetry cases)
- ◆ User is responsible for making sure the orbital occupations are reasonable and the spin state is correct. Many students don't know that the ground state of O₂ is a triplet, not a singlet. The programs don't know about this!