Target: Computer simulations are employed to study the structure and reactivity of single molecules and molecular systems (molecule in solution on in a macromolecular cavity).

Tools: We need a series of software technologies to describe the electronic and geometrical structure of molecules and their time evolution.

(visit http://www.lcpp.bgsu.edu)
The Electronic Energy: Quantum Chemical Technologies

**Physics**: Total Charge Density (electronic wavefunction)

\[ \delta(r) = N \sum_{s1} \ldots \sum_{sN} \int dr_1 \ldots \int dr_N |\psi(r_1, s_1, r_2, s_2, \ldots, r_N, s_N)|^2 \]

**Technology**: all-electron wavefunction

The “technological” wavefunction is a mathematical expression containing “hydrogen-like orbitals”
Ab-initio Quantum Chemical Technologies:
The Pople Diagram

Better description of the HF Coulomb hole and Nuclear cusps

increasing size of basis set

increasing level of theory

increasing accuracy, increasing cpu time

Fermi hole

Homolysis

Coulomb hole

Wavefunction

HF CIS CISD CISDT MP2 MP3 MP4 FCI full e correlation ca. DFT
How to get a good wavefunction: The Variational Principle

\[ E_{el}(R)_{\text{trial}} = \frac{\langle \psi_{\text{trial}} | H_{el} | \psi_{\text{trial}} \rangle}{\langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle} \geq E_{el}(R)_{\text{true}} \]

Rayleigh ratio

nuclear coord.

\[ \frac{\partial E_{el}(R,c)_{\text{trial}}}{\partial c} = 0 \]

\[ \frac{\partial^2 E_{el}(R,c)_{\text{trial}}}{\partial c^2} > 0 \]

\[ \Psi(c)_{\text{trial}} \quad E_{el}(R,c)_{\text{trial}} \]

\[ \Psi(c)_{\text{best}} \quad E_{el}(R,c)_{\text{best}} \]

\[ c_{\text{trial}} \quad c_{\text{best}} \]
How to get a good wavefunction: The Variational Principle

\[ E_{el}(R)_{\text{trial}} = \frac{\langle \psi_{\text{trial}} | H_{el} | \psi_{\text{trial}} \rangle}{\langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle} \geq E_{el}(R)_{\text{true}} \]

Basis of the HF and Post-HF Methods:

\[ E_{el}(R)_{\text{trial}} = \frac{\langle \psi_{\text{trial}} | H_{el} | \psi_{\text{trial}} \rangle}{\langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle} \]

\[ \psi_{\text{trial}} = \sum_{i} c_i \xi_i \]

Orthonormal set

Variational coefficients (variable)

(Basis functions (fixed))

(e.g. in the following \( \xi_i \) can be either an atomic orbital or a determinant)

Notice that \( \xi_i = \text{any basis function} \). It can be an atomic orbital, a Slater determinant or a CSF.

Variational coefficients (variable)

Basis functions (fixed)
How to get a good wavefunction: The Variational Principle

Matrix elements of the Hamiltonian operator

Basis function (a complete set of orthonormal functions)

Linear variational coefficients

\[ E_{el}(R)_{\text{trial}} = \sum_{ij} c_i c_j \langle \xi_i | H_{el} | \xi_j \rangle = \sum_{ij} c_i c_j H_{ij} \]

\[ = \frac{\sum_{ij} c_i c_j \langle \xi_i | \xi_j \rangle}{\sum_{ij} c_i c_j S_{ij}} \]
The Variational Principle: the Ritz Method

Linear variational coefficients (variable)

if the coefficients are not linear (e.g. exponential) the Ritz method cannot be applied

$$E_{el}(R)_{trial} = \frac{\sum_{ij} c_i c_j H_{ij}}{\sum_{ij} c_i c_j S_{ij}}$$

$$E_{el}(R)_{trial} = \frac{c^t H_{el} c}{c^t 1 c}$$

The matrix S for a set of orthonormal basis functions = the Unit matrix
The Variational Principle:
the Ritz Method (valid for linear variational coeff)

\[
E_{el}(R)_{\text{trial}} = \frac{c^t H_{el} c}{c^t 1 c}
\]

small and arbitrary variation of c

\[
\delta E_{el}(R)_{\text{trial}} = \delta c^t (H_{el} - E_{el} 1) c + c^t (H_{el} - E_{el} 1) \delta c = 0
\]

H_{el} is Hermitian, \( \delta c \) arbitrary

Secular Equation \( \rightarrow \) \( (H_{el} - E_{el} 1) c = 0 \)

non-trivial solution only if

\[
\text{Det} |H_{el} - E_{el} 1| = 0
\]
The Variational Principle: the Ritz Method

\[ E_{el}(R)_{\text{trial}} = \sum_{ij} c_i c_j H_{ij} \]

\[ \sum_{ij} c_i c_j S_{ij} \]

\[
\begin{vmatrix}
H_{11} - E_{el}(R)_{\text{trial}} & H_{12} & \cdots & H_{1n} \\
H_{21} & H_{22} - E_{el}(R)_{\text{trial}} & \cdots & H_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
H_{n1} & H_{n2} & \cdots & H_{nn} - E_{el}(R)_{\text{trial}}
\end{vmatrix} = 0
\]

diagonalization \rightarrow \text{eigenvectors & eigenvalues}
One way of getting a good wavefunction: The Independent Particle Model

\[
\hat{H}_{el} = -\frac{1}{2} \sum_i N_{el} \nabla_i^2 + \sum_i \sum_{j<i} \frac{N_{el} N_{el}}{|r_i - r_j|} - \sum_i \sum_{j<i} \frac{N_{el} N_{nuc}}{|r_i - R_j|} 
\]

\[
\hat{H}_{el} = -\frac{1}{2} \sum_i \nabla_i^2 \sum_i \sum_{j<i} \frac{N_{el} N_{nuc}}{|r_i - r_j|} = \sum_i \hat{h}_{el}(r_i) 
\]

\[
\hat{h}_{el}(r_i) = -\frac{1}{2} \nabla_i^2 \sum_j \frac{N_{nuc}}{|r_i - R_j|} 
\]

Hartree product (no spin functions)

\[
\Psi(c)_{trial} = \phi_1(r_1)\phi_2(r_2)\phi_3(r_3)\phi_4(r_4)\ldots\phi_N(r_{N_{el}})
\]
Electronic Energy Computation with the Independent Particle Model: HF

The Fermi hole is correctly described in Hartree-Fock wavefunction but the Coulomb hole and the Homolysis are poorly described (> 5% of the electron-electron repulsion is missing). Far too large for chemical accuracy.

\[ \psi_{HF} = \text{Det} \begin{pmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \cdots & \phi_n(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \cdots & \phi_n(2)\beta(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(n)\alpha(n) & \phi_1(n)\beta(n) & \cdots & \phi_n(n)\beta(n) \end{pmatrix} \]
## The Determinant

The determinant is a \( n \times n \) matrix

\[
\psi_{HF} = \text{Det} \begin{bmatrix}
\phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \ldots & \phi_n(1)\beta(1) \\
\phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \ldots & \phi_n(2)\beta(2) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_1(n)\alpha(n) & \phi_1(n)\beta(n) & \ldots & \phi_n(n)\beta(n)
\end{bmatrix}
\]

\( \psi_{HF} = \begin{vmatrix}
\phi(1)_1\overline{\phi(1)}_1\phi(2)_2\overline{\phi(2)}_2\ldots\phi(n)_n\overline{\phi(n)}_n
\end{vmatrix}
\]

or

\[
\psi_{HF} = \begin{vmatrix}
\phi(1)\phi(2)\ldots\phi(n)
\end{vmatrix}
\]

The mono-electronic wavefunction (molecular orbital) electronic coordinates spin wavefunction spin coordinate spin-orbital

simplified notations
Describe the relationship between the variational principle and the Fock equations.

\[ \psi_{HF} = \text{Det} \begin{pmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \ldots & \phi_n(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \ldots & \phi_n(2)\beta(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(n)\alpha(n) & \phi_1(n)\beta(n) & \ldots & \phi_n(n)\beta(n) \end{pmatrix} \]

\[ E_{el}(R)_{HF} = \frac{\langle \psi_{HF} | H_{el} | \psi_{HF} \rangle}{\langle \psi_{HF} | \psi_{HF} \rangle} \geq E_{el}(R)_{true} \]

\[ \hat{f} \cdot \phi_k = \varepsilon_k \phi_k \]

size of basis set
(one equation for each occupied molecular orbital)
The Slater-Condon Rules

\[ \mathbf{H}_{el} = \left( -\frac{1}{2} \sum_{i}^{{N_{el}}} \nabla_i^2 - \sum_{i}^{{N_{el}}} \sum_{j<i}^{{N_{nuc}}} \frac{Z_j}{|r_i - r_j|} + \sum_{i}^{{N_{el}}} \sum_{j<i}^{{N_{el}}} \frac{1}{|r_i - r_j|} \right) \]

\[ \text{F (one-electron) \qquad G (two-electrons)} \]

(i) If two determinants | > and | ' > are identical and F and G are one-electron and two-electron additive operators, then:

\[ \langle | F + G | \rangle = \sum_i \langle \Phi_i | F | \Phi_i \rangle + \sum_j [\langle \Phi_i \Phi_j | G | \Phi_i \Phi_j \rangle - \langle \Phi_i | G | \Phi_j \Phi_i \rangle] \]

(ii) If | > and | ' > differ by a single spin-orbital ( \( \Phi_p \neq \Phi'_p \)),

\[ \langle | F + G | \rangle = \langle \Phi_p | F | \Phi'_p \rangle + \sum_i [\langle \Phi_p \Phi_i | G | \Phi'_p \Phi_i \rangle - \langle \Phi_p \Phi_i | G | \Phi'_p \Phi_i \rangle] \]

(iii) If | > and | ' > differ by two ( \( \Phi_p \neq \Phi'_p \) and \( \Phi_q \neq \Phi'_q \)),

\[ \langle | F + G | \rangle = \langle \Phi_p \Phi_q | G | \Phi'_p \Phi'_q \rangle - \langle \Phi_p \Phi_q | G | \Phi'_q \Phi'_p \rangle \]

(iv) If | > and | ' > differ by three or more spin orbitals, then

\[ \langle | F + G | \rangle = 0 \]

(v) For the identity operator I, \( \langle I | I \rangle = 0 \) if | > and | ' > differ by one or more spin-orbitals.
How does one find a good $V_{MF}$? One way is the \textit{single} determinant trial function $\psi = |\phi_1 \phi_2 \phi_3 ... \phi_n|$, and write down $\langle \psi | H_{el} | \psi \rangle$ using the \textbf{Slater-Condon rules}

$$
\langle \psi | H_{el} | \psi \rangle = \sum_{k=\text{occ.}} \langle \phi_k | T_e + V_{e,n} | \phi_k \rangle + 1/2 \sum_{k,j=\text{occ.}} [\langle \phi_k(1) \phi_j(2)|e^2/r_{1,2}| \phi_k(1)\rangle - \langle \phi_k(1) \phi_j(2)|e^2/r_{1,2}| \phi_j(1) \phi_k(2)\rangle]
$$

and observe that Coulomb ($J_{k,j}$) and exchange ($K_{k,j}$) integrals among \textit{occupied} orbitals arise.

If one minimizes this energy with respect to the $\phi_j$'s coefficients ($c$), with the constraint that

$$
\langle \phi_j | \phi_K \rangle = \delta_{j,K}
$$

one obtains the HF system of equations:

$$
f \phi_j = \varepsilon_j \phi_j = [T_e + V_{e,n}] \phi_j + \sum_k [\langle \phi_k(1)|e^2/r_{1,2}| \phi_k(1)\rangle \phi_j(2) - \langle \phi_k(1)|e^2/r_{1,2}| \phi_j(1) \phi_k(2)\rangle]
$$

therefore $f$ contains the $J_k (1) = \langle \phi_k(1)|e^2/r_{1,2}| \phi_k(1)\rangle$ and $K_k (1) = \langle \phi_k(1)|e^2/r_{1,2}| \phi_j(1) \phi_k(2)\rangle$ integral operators.
A physical picture of Coulomb and Exchange interactions:

$$J_{1,2} = \int |\phi_1(r)|^2 \frac{e^2}{|r-r'|} |\phi_2(r')|^2 \, dr \, dr' = \int J_1(r) |\phi_2(r')|^2 \, dr' = \int |\phi_1(r)|^2 \, J_2(r') \, dr$$

$$J_k = \int \frac{|\phi_k(r)|^2}{r-r'} \, dr$$
Coulomb operator
operates on $\Phi_j(r')$

$$K_{1,2} = \int \phi_1(r) \phi_2(r') e^2/|r-r'| \phi_2(r) \phi_1(r') \, dr \, dr'$$

$$K_k = \int \frac{|\phi_j(r)\phi_k(r)|}{r-r'} \, dr$$
Exchange operator
operates on $\Phi_j(r')$ and $\Phi_k(r')$
Electronic Energy Computation: HF

\[ H = T_e + V_{e,n} + V_{e,e} \]

So, one can define \( V_{MF} \) in terms of the J and K interactions. This is the Hartree-Fock definition of \( V_{MF} \).

It has the characteristic that

\[ E^{HF} = \langle \psi | H^{HF} | \psi \rangle \geq E^{true} \]

if \( H^{HF} \) is defined as

\[ H^{HF} = T_e + V_{e,n} + (J-K). \]

In this case,

\[ H - H^{HF} = V_{e,e} - (J-K). \]

Notice that it is by making a mean-field model that our (chemists’) concepts of orbitals \( \phi_j \) and of electronic configurations (e.g., \( 1s \alpha 1s \beta 2s \alpha 2s \beta 2p_1 \alpha \)) arise.
Electronic Energy Computation: HF

How to compute the molecular orbitals efficiently?

There are $N$ MOs

\[ f \phi_k = \varepsilon_k \phi_k \]

Fock operator (for each $k$ orbital)

\[
f = -\frac{1}{2} \nabla_k^2 - \sum_i \frac{Z_i}{r_{ki}} + \sum_j \left( 2J_j(k) - K_j(k) \right)
\]

Coulomb-

\[
J_i(k) = \int \int \phi_i \phi_i \frac{1}{r_{12}} \phi_k \phi_k \, dr_1 \, dr_2
\]

Exchange-

\[
K_i(k) = \int \int \phi_i \phi_k \frac{1}{r_{12}} \phi_i \phi_k \, dr_1 \, dr_2
\]
Electronic Energy Computation: HF

- **Secular equations:**

\[
f_{\mu\nu} = \langle \xi_\mu | f | \xi_\nu \rangle \quad S_{\mu\nu} = \langle \xi_\mu | \xi_\nu \rangle
\]

\[
\sum_\mu (f_{\mu\nu} - \varepsilon \ S_{\mu\nu}) c_\mu = 0
\]

The number of orbitals

- equal the number of basis functions ("atomic" orbitals).

- **Molecular orbital energies (eigenvalues):**

\[
\varepsilon_0, \quad \phi_0 = c_{0,0} \xi_0 + c_{0,1} \xi_1 + \cdots + c_{0,\mu} \xi_\mu + \cdots + \cdots
\]

- **Molecular orbitals coefficients (eigenvectors):**

\[
\varepsilon_i, \quad \phi_i = c_{i,0} \xi_0 + c_{i,1} \xi_1 + \cdots + c_{i,\mu} \xi_\mu + \cdots + \cdots
\]
Electronic Energy Computation: HF

- Orbital energies: kinetic energy of the electron + the energy resulting from the averaged interaction of the electron with the other 2N-1 electrons.

\[
E_{el}(R) = \sum_{k=1}^{N} [2\varepsilon_k - \sum_{j=1}^{N} (2J_{kj} - K_{kj})]
\]

- Electron density \(\rho\) = \(\sum_{k} |\phi_k|^2\)

Orbitals: linear combinations of atomic orbitals with \(c_{ik}\) being the variational coefficients.
Electronic Energy Computation: HF

ENIAC, short for Electronic Numerical Integrator and Computer

Douglas Hartree
27 March 1897 – 12 February 1958
Hardware Technologies

IBM 701 was formally announced on May 21, 1952. It could perform more than 16,000 addition or subtraction operations a second.

MIPS
(Millions of Operation/Sec)

FLOPS
(Floating Point Operation/Sec)

R. Mulliken

IBM RoadRunner, 1 petaflops (6,912 AMD Opteron 2210 + 12,960 IBM Power XCell), November, 2008.

CRAY Y-MP C90, 16 CPUs 1 gigaflop each

Dual-core Intel Xeon Woodcrest 64 CPUs 30 gigaflop each, 2006

LCPP@BGSU

Present speed

PostDoc in London

IBM 701 was formally announced on May 21, 1952. It could perform more than 16,000 addition or subtraction operations a second.
"Atomic" Basis (Basis Sets)

\[ \phi_i = \sum_j c_{ij} \xi_j \]

- \( \xi_i \): must form a \( \approx \) complete set of orthonormal functions

HOMO (benzene)

Hydrogen-like orbitals

- \( n \): principal quantum number \( \rightarrow \) shell \( n \geq 1 \)
- \( l \): angular momentum \( \rightarrow \) sub-shell \( 0 \leq l \leq n-1 \)
- \( m_l \): projection of \( l \) \( \rightarrow \) energy shift \( -l \leq m_l \leq l \)
"Atomic" Basis (Basis Sets)

\[ \xi_i \] must form a \( \approx \) complete set of orthonormal functions

\[
J_{kj} = \left\langle \phi_k(1)\phi_j(2) \left| \frac{1}{r_1 - r_2} \right| \phi_k(1)\phi_j(2) \right\rangle = \sum_{\alpha\beta\gamma\delta}^{M_{basis}} c_{\alpha k} c_{\gamma j} c_{\beta k} c_{\delta j} \left( \left\langle \xi_\alpha(1)\xi_\gamma(2) \left| \frac{1}{r_1 - r_2} \right| \xi_\beta(1)\xi_\delta(2) \right\rangle \right)
\]

Coulomb

atomic integrals! no variational coefficients

one-center
two-centers
three-centers
four-centers

HOMO (benzene)
Atomic Basis (Basis Sets)

Hydrogen-like orbitals

\[ \xi_{n,l,m_l}(r,\theta,\varphi) = NY_{l,m_l}(\theta,\varphi)r^{n-1}e^{-\zeta r} \]

Slater Type Orbitals (STO):

\[ \zeta = \frac{Z-s}{n} \]

Shape (spherical harmonics):

\[ Y_{l,m_l}(\theta,\varphi) \]

Integrals \((J_{kj} \text{ and } K_{kj})\) are fast to compute but not accurate.

Three-centers four-centers integrals are very time-consuming to compute with the STO radial part.

No radial nodes for the STO radial part.

Radial behavior (critical) for the STO radial part.

Exponent determined variationally.

Screening constant.

STO vs. GTO (distance from nucleus).
"Atomic" Basis (Basis Sets)

Gaussian Type Orbitals (GTO):

\[ \xi_{\xi, n, l, m_\ell} (r, \theta, \varphi) = NY_{l, m_l} (\theta, \varphi) r^{2n-2-l} e^{-\xi r^2} \]

Radial nodes

Smaller exponent (\(\zeta\))
more diffuse

Larger exponent (\(\zeta\))
less diffuse
“Atomic” Basis (Basis Sets)

John Edward Lennard-Jones (Cambridge, UK) 1894-1854

Samuel Francis Boys was born in 1911, he died in 1972.

S.F. Boys, G.B. Cook, C.M. Reeves and I. Shavvitt,

Automatic fundamental calculations of molecular structure.

"Atomic" Basis (Basis Sets)

Minimal Basis: enough functions to accommodate all the electrons

STO-3G Basis Set

\[
\text{H} \quad (1S) \quad (12 \text{ different functions. 27 in total})
\]

\[
\text{H} \quad \text{C} \quad (1S) + (2S) + (2P_x, 2P_y, 2P_z)
\]

Decreasing $\zeta$

GTO-3

GTO-2

GTO-1

STO

STO-3G

Chemistry

distance from nucleus (au)
End
Lecture 2