

Hartree-Fock Model (not in the text)

HF-1

What we know: Slater determinant gives the wave function for N electrons with Coulomb interaction between them neglected

Question: What if we want to include electron-electron repulsions?

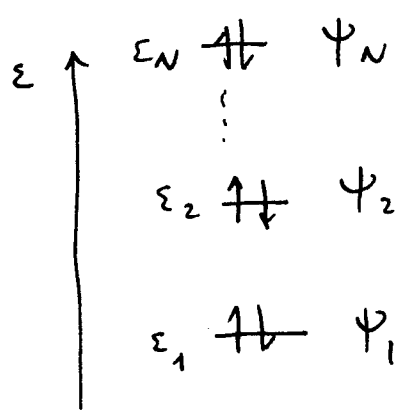
Answer: Try to solve the SE for a single electron (molecular orbital) moving in an average potential of all other electrons (HF model).

HF equation:

$$\hat{h}^{\text{HF}}(1, 2, \dots, i-1, i+1, \dots, N) \Psi_i = \epsilon_i \Psi_i$$

HF operator \nearrow depends on all $N-1$ electrons \nearrow wave function of i th electron

Let's assume we have solved this equation. What is the N -electron wave function?



Configuration in which all HF states are filled by pairs of electrons with opposite spins.

N-electron wave function (Pauli exclusion):

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$$\Psi_e(\vec{r}_1 s_1, \vec{r}_2 s_2, \vec{r}_3 s_3, \dots, \vec{r}_N s_N) =$$

spin variable

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(\vec{r}_1) \chi_+^{(1)} & \Psi_1(\vec{r}_2) \chi_-^{(2)} & \dots & \Psi_1(\vec{r}_N) \chi_-^{(N)} \\ \vdots & \vdots & \ddots & \vdots \\ \Psi_N(\vec{r}_1) \chi_+^{(1)} & \Psi_N(\vec{r}_2) \chi_-^{(2)} & \dots & \Psi_N(\vec{r}_N) \chi_-^{(N)} \end{vmatrix}$$

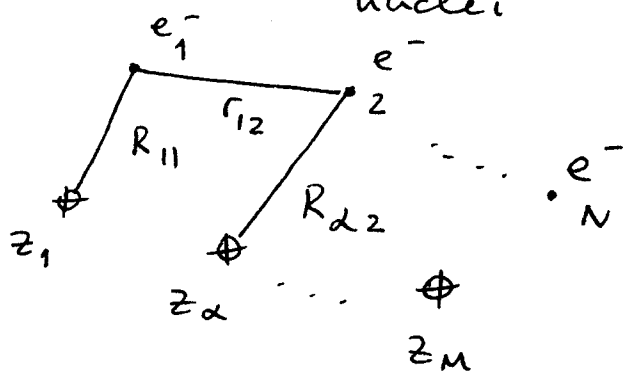
We want to find the best function Ψ_e to minimize the expectation value

$$E_0 \leq E = \langle \Psi_e | H | \Psi_e \rangle$$

Hamiltonian (applies to any molecular system):

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \sum_{\alpha=1}^M \frac{z_\alpha}{R_{\alpha i}} + \underbrace{\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}}_{\text{Coulomb rep. between the electrons}}$$

sum over all nuclei

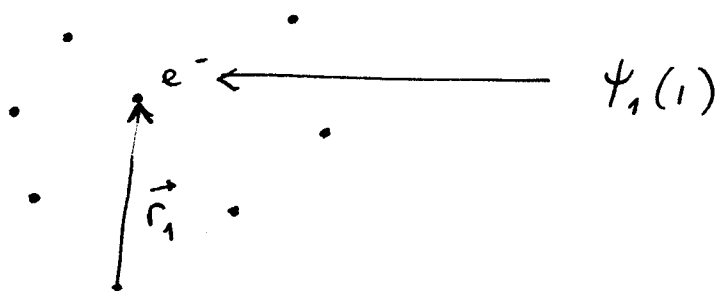


Coulomb rep. between the electrons

The HF operator (physics)

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Let's assume that we have singled out an electron (1) and want to define the potential of the rest of electrons acting on it



Interaction with the nuclei + kinetic energy:

$$h(\vec{r}_1) = \frac{p_1^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \sum_{\alpha=1}^M \frac{Z_{\alpha}}{R_{1\alpha}}$$

Coulomb interaction with all other electrons in states $\chi_b(\vec{r}_i)$, $i \neq 1$

$$v^c(\vec{r}_1) = \frac{e^2}{4\pi\epsilon_0} \sum_{b \neq 1} \int d\vec{r}_2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} \underbrace{e |\psi_b(\vec{r}_2)|^2}_{\text{density of the electronic cloud}}$$

Exchange operator:

$$J_b(1) \psi_a(1) = \left[\int d\vec{r}_2 \psi_b^*(\vec{r}_2) \psi_a(\vec{r}_2) \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} \right] \psi_b(\vec{r}_1)$$

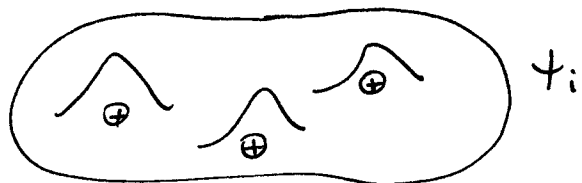
$$\hat{h}^{HF}(1) = h(\vec{r}_1) + v^c(\vec{r}_1) - \sum_{b \neq 1} J_b(1)$$

$$\hat{h}^{\text{HF}}(i) \psi_1(i) = \epsilon_1 \psi_1(i)$$

HF equation is a non-linear integral equation for the set of functions $\psi_1(i) \dots \psi_N(N)$. How do we solve it?

The LCAO procedure

Each HF orbital $\psi_i(i)$ is a molecular orbital. In the LCAO procedure ψ_i is expressed as a linear combination of atomic orbitals χ_μ



$$\psi_i(\vec{r}) = a_{i1} \chi_1(\vec{r}) + a_{i2} \chi_2(\vec{r}) + \dots + a_{in} \chi_n(\vec{r})$$

The idea is to determine the best ψ_i by adjusting the coefficients a_{ik} .

$$|\psi_i\rangle = \sum C_{\mu i} |\chi_\mu\rangle \leftarrow \text{LCAO}$$

HF equation becomes a matrix equation

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

↑
Roothaan equation

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$$

$\uparrow \quad \uparrow$
 indexes of atomic orbitals

Matrix form of Roothaan equations:

$$\boxed{\vec{F} \vec{C} = \vec{S} \vec{C} \epsilon}$$

Fock matrix

This is not a linear algebraic equation because \vec{F} is a functional of coefficients

Eqn: $\vec{F} = \vec{F}[\vec{C}]$

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{\alpha, \lambda, \beta} c_{\lambda\alpha} c_{\beta\alpha} [2(\mu\nu | \beta\lambda) - (\mu\lambda | \beta\nu)]$$

\uparrow core Hamiltonian \uparrow Coulomb integrals \uparrow exchange integrals

$$H_{\mu\nu}^{\text{core}} = \langle \Phi_\mu | \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \sum_{\alpha} \frac{z_\alpha}{R_{\alpha\mu}} | \Phi_\nu \rangle$$

$$(\mu\nu | \lambda\beta) = \int d\vec{r}_1 d\vec{r}_2 \Phi_\mu^*(1) \Phi_\nu(1) \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} \Phi_\lambda^*(2) \Phi_\beta(2)$$

Iterative solution of Roothaan equations is known as self-consistent-field (SCF) procedure.

Basis sets (not in the text)

Variational solutions of HF equations involve calculations of two-electron, four-function integrals:

$$\iint d\vec{r}_1 d\vec{r}_2 \chi_p^*(\vec{r}_1) \chi_q(\vec{r}_1) \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} \chi_\lambda^*(\vec{r}_2) \chi_\beta(\vec{r}_2)$$

This requirement mostly defines which functions to use for $\chi_p(\vec{r})$.

Slater suggested to use simple Bohr-like orbitals

$$N r^{(n^*-1)} \exp\left[-\frac{Z-s}{n^*} \frac{r}{a_0}\right] Y_{lm}(\theta, \phi)$$

screening constant \underline{s} and the effective principle quantum number $\underline{n^*}$ are adjustable parameters (see 14-4 for He)

These are called Slater-type orbitals (STO)

An alternative approach is to use Gaussian-type orbitals (GTOs)

$$\chi(r) \propto \exp\left(-d \frac{r^2}{a_0^2}\right)$$

Why?

1s and 2p GTOs:

$$G_{1s} = \left(\frac{2\alpha}{\pi a_0^2} \right)^{3/4} \exp\left(-\frac{\alpha r^2}{a_0^2}\right)$$

$$G_{2px} = \left(\frac{128\alpha^5}{\pi^3 a_0^{10}} \right)^{1/4} x \exp\left(-\frac{\alpha r^2}{a_0^2}\right)$$

Cartesian GTOs:

$$G \propto x^l y^m z^n \exp\left(-\frac{\alpha r^2}{a_0^2}\right)$$

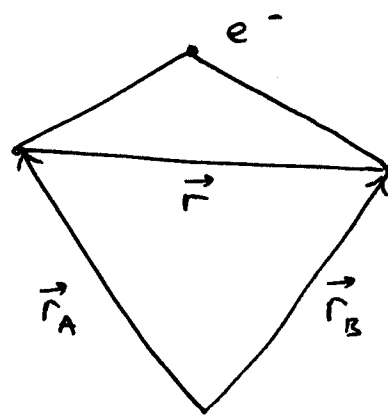
Why GTOs?

Integrals involving GTOs are much faster to calculate than those involving STOs.

$$S_{AB} = \langle \chi_A | \chi_B \rangle$$

$$G_A(\vec{r}) = \left(\frac{2\alpha_A}{\pi a_0^2} \right)^{3/4} \exp\left[-\frac{\alpha_A (\vec{r} - \vec{r}_A)^2}{a_0^2}\right]$$

$$G_B(\vec{r}) = \left(\frac{2\alpha_B}{\pi a_0^2} \right)^{3/4} \exp\left[-\frac{\alpha_B (\vec{r} - \vec{r}_B)^2}{a_0^2}\right]$$



$$G_A G_B \propto \exp\left[-\frac{\alpha_A + \alpha_B}{a_0^2} (\vec{r} - \vec{r}_C)^2\right]$$

$$\vec{r}_C = \frac{1}{\alpha_A + \alpha_B} (\alpha_A \vec{r}_A + \alpha_B \vec{r}_B)$$

The product of two Gaussians is a Gaussian!

The STO/UG philosophy

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Slater orbitals are represented as a fixed linear combination of GTOs:

$$\text{STO}(\zeta) = d_1 \text{GTO}(\alpha_1) + d_2 \text{GTO}(\alpha_2) + d_3 \text{GTO}(\alpha_3)$$

Procedure:

- ①. Assume $\zeta = 1$ and fit $\text{STO}(\zeta = 1)$ to a linear combination of GTOs
- ②. If $\zeta \neq 1$, d_i will be constant, but each d_i is multiplied by ζ^2 .
- ③. Each atomic orbital $1s, 2s, 2p, 3d, \dots$ will be characterized by its own set of d_i 's and each atom will be assigned a set of ζ - values.

α is called Gaussian exponent and d_i are contraction coefficients.

STO-3G set:

$$\Phi_{1s}(\zeta = 1.0) = \sum_{i=1}^3 d_{i,1s} g_{1s}(\alpha_{i,1s})$$

$$\Phi_{2s}(\zeta = 1.0) = \sum_{i=1}^3 d_{i,2s} g_{1s}(\alpha_{i,2sp})$$

$$\Phi_{2p}(\zeta = 1.0) = \sum_{i=1}^3 d_{i,2p} g_{2p}(\alpha_{i,2sp})$$

STO - 3G exponents

Atom	ζ_{1s}	ζ_{2sp}
H	1.24	—
Li	2.69	0.75
Be	3.68	1.10
B	4.68	1.45

These exponents are applied to each atom in a multiatom molecule

4-31G Basis set

4 GTOs are used for inner shells and
3+1 GTOs are used for valence shells

$$\text{Li: } \Phi_{1s}(\vec{r}) = \sum_{i=1}^4 d_{i,1s} g_{1s}(\alpha_{i,1s}, \vec{r})$$

$$\Phi_{2s}'(\vec{r}) = \sum_{i=1}^3 d_{i,2s} g_{2s}(\alpha_{i,2s}, \vec{r})$$

$$\Phi_{2s}''(\vec{r}) = g_{1s}(\alpha_{2s}'', \vec{r})$$

4-31G exponents

Atom	ζ'	ζ''
H	1.20	1.15
C	1.00	1.04
N	0.99	0.98
O	0.99	0.98