

Self-Consistent Field Hartree Fock Theory: Roothaan Equations

LCAO approach: $\Psi_a = \sum_{i=1}^N c_{ia} \phi_i$ Ψ_a = one-electron molecular orbital

ϕ_i = atomic orbitals for N orbitals (Slater or Gaussian)

c_{ia} = orbital coefficients -- variational parameters

Molecule wavefunctions are Slater determinants of one-electron MO's

$$\Psi = 1/\sqrt{N!} \begin{vmatrix} \Psi_a(1)\alpha(1) & \Psi_a(1)\beta(1) & \Psi_b(1)\alpha(1) & \Psi_b(1)\beta(1) & \dots \\ \Psi_a(2)\alpha(2) & \Psi_a(2)\beta(2) & \Psi_b(2)\alpha(2) & \Psi_b(2)\beta(2) & \dots \\ \Psi_a(3)\alpha(3) & \Psi_a(3)\beta(3) & \Psi_b(3)\alpha(3) & \Psi_b(3)\beta(3) & \dots \\ \vdots & \vdots & \vdots & \vdots & \dots \end{vmatrix}$$

Spin wavefunction: $\sigma(1) = \alpha(1)$ or $\beta(1)$

Variation Theorem: vary c_{ia} 's to find the lowest energy:

Hartree-Fock Equations:

$f_1 \Psi_a(1)\sigma(1) = \epsilon_a \Psi_a(1)\sigma(1)$ ϵ_a = one-electron orbital energy
for MO a, b, c, ...

$f_1 = h_1 + \sum_{j=1}^{n/2} \{2J_j(1) - K_j(1)\}$ j = all the other filled orbitals
for electron 1, 2, 3, ...

core Hamiltonian:
$$h_1 = \frac{-\hbar^2}{2m} \nabla_1^2 - \sum_{k=1}^m \frac{Z_k e^2}{4\pi\epsilon_0 r_{k1}}$$
 k = all nuclei

electron-electron repulsion:

Coulomb operator:
$$J_j(1) \Psi_a(1) = \left(\int \Psi_j^*(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} \Psi_j(2) d\tau_2 \right) \Psi_a(1)$$

Exchange operator:
$$K_j(1) \Psi_a(1) = \left(\int \Psi_j^*(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} \Psi_a(2) d\tau_2 \right) \Psi_j(1)$$

$$\sum_{i=1}^N c_{ia} \int \phi_j(1) f_1 \phi_i(1) d\tau_1 = \epsilon_a \sum_{i=1}^N c_{ia} \int \phi_j(1) \phi_i(1) d\tau_1$$

$$\sum_{i=1}^N c_{ia} F_{ji} = \epsilon_a \sum_{i=1}^N c_{ia} S_{ji} \quad F_{ji} = \int \phi_j(1) f_1 \phi_i(1) d\tau_1$$

Semi-Empirical Molecular Orbital Theory

- only valence electrons: the core electrons are included in the nuclear core.
- minimal basis set: basis set contains only occupied atomic orbitals (*s*, *p* and *d*), e.g., for carbon STO-3G only 2s and 2p functions.
- parameterized integrals: many integrals obtained by fitting the results to experimental data or *ab initio* calculations. Gives training set dependence.
- omission of some of the two electron integrals.

$$\int \phi_i(1) \phi_j(1) \frac{e^2}{4\pi\epsilon_0 r_{12}} \phi_k(2) \phi_l(2) d\tau_1 d\tau_2$$

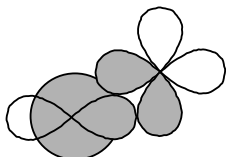
$\phi_i(1)$ = different atomic orbitals
perhaps on different nuclei

$$\int A(1) B(1) \frac{e^2}{4\pi\epsilon_0 r_{12}} C(2) D(2) d\tau_1 d\tau_2$$

CNDO: complete neglect of differential overlap
zero unless A=B C=D two-center integrals only



MNDO: modified neglect of differential overlap
zero unless A, B on same atom C, D on same atom



neglect of diatomic differential overlap

AM1: more diverse training set; no d's for 3rd period or metals.

PM3: more heteroatoms in training set, use for 3rd period atoms and hydrogen bonding.

MNDO/d, PM3/TM: includes d orbitals for 3rd period elements, metals

ZINDO: parameterized to reproduce electronic spectra

- If your molecule is *similar* to molecules in the training set, then the *results may be very good*.
- If your molecule is *significantly different* from anything in the training set, the *results may be very poor*.
- Semi-empirical methods are not as sensitive to the parameterization set as molecular mechanics methods.
- Much caution is warranted for transition states and unstable molecules and ions.