

## Molecular Orbital Theory – The Hartree-Fock Method

A key development in computational quantum mechanics has been the computation of accurate self-consistent field (SCF) wavefunctions for many diatomic and polyatomic molecules. The starting point for most high-level molecular computations is the Hartree-Fock method. In this lecture, we restrict ourselves to close-shell configurations. For open-shell configurations, the formula are more complicated, and will be discussed in the future.

### 1. The Hartree-Fock method revisited

The expression for the Hartree-Fock energy for closed-shell system ( $N$  electrons,  $N/2$  orbitals)

$$E = 2 \sum_{i=1}^{N/2} H_{ii}^{core} + \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} (2J_{ij} - K_{ij}) \quad (1)$$

The corresponding Fock operator is

$$\hat{F}_i(i) = \hat{H}^{core}(i) + \sum_{j=1}^{N/2} [2\hat{J}_j(i) - \hat{K}_j(i)] \quad (2)$$

where  $\hat{F}_i(i)$  is the Fock operator for the  $i$ -th electron in the system,  $\hat{H}^{core}(i)$  is the core Hamiltonian for the  $i$ -th electron.

$$\hat{H}^{core}(i) = -\frac{1}{2} \nabla_i^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} \quad (3)$$

$\hat{J}_j(i)$  is the Coulomb operator, defining the repulsive force between the  $j$ -th and  $i$ -th electrons in the system;  $\hat{K}_j(i)$  is the exchange operator, defining the electron exchange of two electrons.

Note: In many-electron systems, we have derived the HF equation as follows, (see lecture note 7):

$$\left[ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{2e^2}{r_i} + e^2 \sum_{j \neq i}^N \int \frac{\psi_j^*(r') \psi_j(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - e^2 \sum_{j \neq i}^N \delta_{s_i s_j} \int \frac{\psi_j^*(r') \psi_i(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \psi_i(\mathbf{r}_i) = \epsilon_i \psi_i(\mathbf{r}_i) \quad (4)$$

Finding the Hartree-Fock wavefunctions is now equivalent to solving the HF equations

$$\hat{F}_i \psi_i = \epsilon_i \psi_i \quad (5)$$

where  $\psi_i$  is the corresponding molecular orbital (or spin-orbital).

According to the LCAO-MO treatment. We now write each MO as a linear combination of single atomic orbitals

$$\psi_i(\mathbf{r}_i) = \sum_{v=1}^K c_{vi} \phi_v(\mathbf{r}_i) \quad (6)$$

We are expecting to derive a total of  $K$  Molecular Orbitals. Atomic Orbital  $\phi_v$  is common called basis functions, which will be elaborated on in the next section.

Using LCAO, equation 4 becomes

$$\hat{F}_i \sum_v^K c_{vi} \phi_v(\mathbf{r}_i) = \epsilon_i \sum_v^K c_{vi} \phi_v(\mathbf{r}_i) \quad (7)$$

Pre-multiplying each side by  $\phi_\mu(i)$  (where  $\phi_\mu$  is one of the basis functions), and integrating gives the following matrix equation:

$$\sum_{v=1}^K c_{vi} \int \phi_\mu(\mathbf{r}_i) \hat{F}_i \phi_v(\mathbf{r}_i) d\mathbf{r}_i = \epsilon_i \sum_{v=1}^K c_{vi} \int \phi_\mu(\mathbf{r}_i) \phi_v(\mathbf{r}_i) d\mathbf{r}_i \quad (8)$$

$\int \phi_\mu \phi_\nu d\mathbf{r}_i$  Is the overlap integral between the basis functions  $\mu$  and  $\nu$ , written  $S_{\mu\nu}$ . (they are not necessarily orthogonal). This is called the Roothan-Hall equation.

The element of the *Fock matrix* are given by  $F_{\mu\nu} = \int \phi_\mu \hat{F}_i \phi_\nu d\mathbf{r}_i$ . We now separate the Fock matrix element into different contributions. The elements of the Fock matrix for a closed-shell system can now be written as

$$F_{\mu\nu} = \int \phi_\mu \hat{H}^{core} \phi_\nu d\tau + \sum_{j=1}^{N/2} \int \phi_\mu (2\hat{J}_j - \hat{K}_j) \phi_\nu d\tau \quad (9)$$

The core contribution

$$H_{\mu\nu}^{core} = \int \phi_\mu \hat{H}^{core} \phi_\nu d\tau \quad (10)$$

The Coulomb operator is defined

$$\hat{J}_j = \int \psi_j^*(\mathbf{r}_j) \frac{1}{r_{ij}} \psi_j(\mathbf{r}_j) d\mathbf{r}_j = \int \left( \sum_{\sigma} c_{\sigma j} \phi_{\sigma}(\mathbf{r}_j) \right) \frac{1}{r_{ij}} \left( \sum_{\lambda} c_{\lambda j} \phi_{\lambda}(\mathbf{r}_j) \right) d\mathbf{r}_j \quad (11)$$

The exchange operator is defined as

$$\hat{K}_j \phi_\nu(\mathbf{r}_i) = \psi_j(\mathbf{r}_i) \int \psi_j^*(\mathbf{r}_j) \frac{1}{r_{ij}} \phi_\nu(\mathbf{r}_j) d\mathbf{r}_j = \left[ \sum_{\lambda} c_{\lambda j} \phi_{\lambda}(\mathbf{r}_i) \right] \int \left[ \sum_{\sigma} c_{\sigma j} \phi_{\sigma}(\mathbf{r}_j) \right] \frac{1}{r_{ij}} \phi_\nu(\mathbf{r}_j) d\mathbf{r}_j \quad (12)$$

Therefore

$$\begin{aligned}
& \sum_{j=1}^{N/2} \int \phi_{\mu}(1)(2\hat{J}_j - \hat{K}_j)\phi_{\nu}(1) d\mathbf{r}_i \\
= & \sum_{j=1}^{N/2} \sum_{\sigma}^K \sum_{\lambda}^K c_{\sigma j} c_{\lambda j} \left[ 2 \int \frac{\phi_{\mu}(1)\phi_{\sigma}(2)\phi_{\lambda}(2)\phi_{\nu}(1)}{r_{ij}} d\mathbf{r}_i d\mathbf{r}_j - \int \frac{\phi_{\mu}(1)\phi_{\lambda}(1)\phi_{\sigma}(2)\phi_{\nu}(2)}{r_{ij}} d\mathbf{r} \right] \quad (13) \\
= & \sum_{j=1}^{N/2} \sum_{\sigma}^K \sum_{\lambda}^K c_{\sigma j} c_{\lambda j} [2(\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma)]
\end{aligned}$$

The two-electron integrals may involve up to four different basis functions (  $\mu, \nu, \lambda, \sigma$  ), which may in turn be located at different centers.

By introducing the *charge density matrix*  $\mathbf{P}$  (or bond-order matrix), whose elements are defined as

$$P_{\mu\nu} = 2 \sum_i^K c_{\mu i} c_{\nu i}$$

(sometimes, a density operator is defined as  $\hat{\rho} = \sum_i w_i |\psi_i\rangle \langle \psi_i|$  )

The Fock matrix elements have the formula

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{\lambda=1}^K \sum_{\sigma=1}^K P_{\sigma\lambda} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)] \quad (14)$$

### Other implications for the charge density matrix

The electron density at a point  $\mathbf{r}$  can be expressed in terms of the density matrix

$$\rho(\mathbf{r}) = \sum_{\mu=1}^K \sum_{\nu}^K P_{\mu\nu} \phi_{\mu}(\mathbf{r}) \phi_{\nu}(\mathbf{r}) \quad (15)$$

The expression for the Hartree-Fock energy is given by (not proven here)

$$E_{HF} = \int D^* \hat{H}_{el} D d\tau = 2 \sum_{i=1}^{N/2} H_{ii}^{core} + \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} (2J_{ij} - K_{ij}) \quad (16)$$

$$H_{ii}^{core} = \int \psi_i^*(\mathbf{r}_i) \hat{H}^{core} \psi_i(\mathbf{r}_i) d\mathbf{r}_i \quad (17)$$

The Hartree-Fock energy can also be expressed (not including the nuclei Coulomb energy  $V_{NN}$  )

$$E_{HF} = \sum_i^{N/2} \epsilon_i + \sum_i^{N/2} H_{ii}^{core} \quad (18)$$

This energy can be calculated from the density matrix

$$E_{HF} = \frac{1}{2} \sum_{\mu=1}^K \sum_{\nu=1}^K P_{\mu\nu} (H_{\mu\nu}^{core} + F_{\mu\nu}) \quad (19)$$

The Fock matrix is a  $K \times K$  square matrix that is symmetric if real basis functions are used. The

matrix format of the Roothan-Hall equation (8) is

$$FC = SCE \quad (20)$$

A common scheme to solve the Roothan-Hall equations can be found in lecture note 7.

## 2. Basis Sets

When molecular calculations are performed, it is common to use a basis composed of a finite number of atomic orbitals, centered at each atomic nucleus within the molecule.

### 2.1 Slater-type orbitals

Slater (1930) suggested a simpler analytical form for the radial functions

$$R_{nl}(r) = N r^n e^{-\zeta r} \quad (21)$$

where  $N$  is the normalization factor  $N = \sqrt{\frac{(2\zeta)^{n+1}}{(2n!)}}$ ,  $n$  is the principle quantum number,  $\zeta$  the orbital exponent.

### 2.2 Gaussian-type orbitals

Slater-type orbitals could in turn be approximated as linear combinations of Gaussian orbitals instead. Because it is easier to calculate overlap and other integrals with Gaussian basis functions, this led to huge computational savings.

#### Gaussian Product Theorem

The product of two GTOs centered on two different atoms is a finite sum of Gaussians centered on a point along the axis connecting them.

In this manner, four-center integrals can be reduced to finite sums of two-center integrals, and in a next step to finite sums of one-center integrals. (The speedup by 4--5 orders of magnitude compared to STOs).

The GTOs have the following form  $\psi_{GTO}(x, y, z) = x^l y^m z^n \exp(-\alpha r^2)$  :  $\alpha$  determines the spread of a Gaussian function.

The order of these GTOs is determined by the powers of the Cartesian variables, a zeroth-order function has  $l+m+n=0$ , first-order  $l+m+n=1$ .

Consider two Gaussians  $m$  and  $n$  :  $\exp(-\alpha_m r_m^2) \exp(-\alpha_n r_n^2) = \exp\left(-\frac{\alpha_m \alpha_n}{\alpha_m + \alpha_n} r_{mn}^2\right) \exp(-\alpha r_c^2)$

The product of the two Gaussians  $m$  and  $n$  can now be replaced by another Gaussian centered at  $C$ , which has coordinates:

$$x_c = \frac{\alpha_m x_m + \alpha_n x_n}{\alpha_m + \alpha_n}; \quad y_c = \frac{\alpha_m y_m + \alpha_n y_n}{\alpha_m + \alpha_n}; \quad z_c = \frac{\alpha_m z_m + \alpha_n z_n}{\alpha_m + \alpha_n} \quad (22)$$

$r_{mn}$  is the distance between the centers of  $m$  and  $n$ .

### Gaussian functions and orbital symmetry

The zeroth-order Gaussian function  $g_s$  has s-orbital symmetry; the three first-order Gaussian functions have p-orbital symmetry. In normalized form, they are:

$$g_s(\alpha, r) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2} \quad (23)$$

$$g_x(\alpha, r) = \left(\frac{128\alpha^5}{\pi^3}\right)^{1/4} x e^{-\alpha r^2} \quad (24)$$

$$g_y(\alpha, r) = \left(\frac{128\alpha^5}{\pi^3}\right)^{1/4} y e^{-\alpha r^2} \quad (25)$$

$$g_z(\alpha, r) = \left(\frac{128\alpha^5}{\pi^3}\right)^{1/4} z e^{-\alpha r^2} \quad (26)$$

The six second-order Gaussian functions have the following form, exemplified by two functions

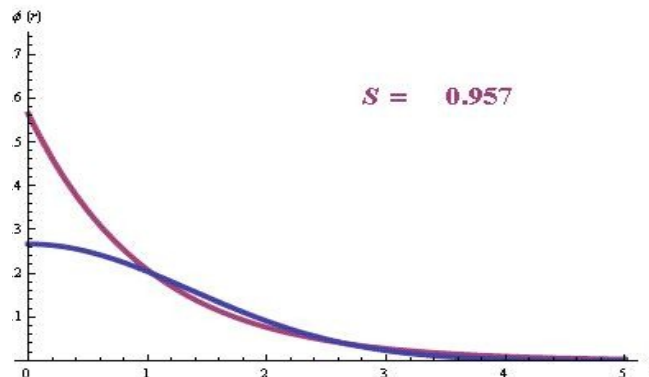
$$g_{xx}(\alpha, r) = \left(\frac{204\alpha^7}{9\pi^3}\right)^{1/4} x^2 e^{-\alpha r^2} \quad (27)$$

$$g_{xy}(\alpha, r) = \left(\frac{204\alpha^7}{9\pi^3}\right)^{1/4} xy e^{-\alpha r^2} \quad (28)$$

$g_{xx}, g_{xz}, g_{yz}$  and  $g_{3zz-rr} = \frac{1}{2}(2g_{zz} - g_{zz} - g_{yy})$ ,  $g_{xx-yy} = \sqrt{3/4}(g_{xx} - g_{yy})$  give the same angular symmetry of d-orbitals.

### Contracted and uncontracted GTOs

Replacing a STO by a single GTO leads to unacceptable errors.



This problem can be overcome by representing each STO with a linear combination of Gaussian functions

$$\phi_{\mu} = \sum_i^L d_{i\mu} \phi_i(\alpha_{i\mu}) \quad (29)$$

The coefficient can be found by least-squares fitting, with a maximized integral (e.g. 1s-STO):

$$S = \frac{1}{\sqrt{(\pi)}} \left( \frac{2\alpha}{\pi} \right)^{3/4} \int d\mathbf{r} e^{-r} e^{-\alpha r^2} \quad (30)$$

If those two parameters are pre-determined prior to calculations, the Gaussian functions are called a *contraction*, with the *contraction length* being the number of terms in the expansion. Each Gaussian function in the expansion is called a *primitive* Gaussian function.

Alternatively, the two parameters (coefficient and  $\alpha$ ) are allowed to vary in computation. Such calculations are said to use *uncontracted* or *primitive* Gaussian functions. Caveats: calculations with primitive Gaussians require a significant computational effort. Normally, contracted Gaussians are preferred.

### Minimum basis set

A minimum basis set is one in which, on each atom in the molecule, a single basis function is used for each orbital in a HF calculation on the free atom.

**Exceptions:** for atoms such as lithium, basis functions of p type are added to the basis functions corresponding to the 1s and 2s orbitals of the free atom. For example, each atom in the first row of the periodic system (Li - Ne) would have a basis set of five functions (two s functions and three p functions).

The most common minimal basis set is STO-nG, where  $n$  is an integer. This  $n$  value represents the

number of Gaussian primitive functions comprising a single basis function.

Commonly used minimal basis sets of this type are:

- STO-3G
- STO-4G
- STO-6G
- STO-3G\* - Polarized version of STO-3G

Some problems with the minimal basis sets: (1) same number of basis functions for one period, (2) Radial functions are not allowed to vary according to the molecular environment, (3) incapable of describing non-spherical charge charge distribution.

How many functions for C<sub>2</sub>H<sub>2</sub> minimum basis set calculations?

### Double-zeta $\zeta$ basis set

More than one function is used for each orbital. A basis set doubles the number of minimal basis set is described as Double-zeta basis. ( $\zeta$  is the STO orbital exponent): The orbital is represented by a contraction and a *diffuse* function. The components of the two functions can be determined on the fly in computation.

Such an approach can provide a solution to the anisotropy problem.

Basis sets in which there are multiple basis functions corresponding to each atomic orbital, including both valence orbitals and core orbitals are called double, triple, or quadruple-zeta basis sets.

### Split-valence basis set

An alternative to the double zeta basis set is to double the number of functions used to describe the valence electrons, but to keep single function for inner shells.

The notation for split valence basis set is typically  $X-YZg$  (due to Nobel laureate John Pople).

$X$ : the number of primitive Gaussians comprising each core atomic orbital basis function.

$Y$  and  $Z$  indicate that the valence orbitals are composed of two basis functions each, the first one composed of a linear combination of  $Y$  primitive Gaussian functions, the other composed of a linear combination of  $Z$  primitive Gaussian functions.

In this case, his basis set is a *split-valence double-zeta* basis set. Split-valence triple- and quadruple-zeta basis sets are also used, denoted as  $X-YZWg$ ,  $X-YZWWg$ , etc. Here is a list of commonly used split-valence basis sets of this type:

- 3-21g
- 3-21g\* - Polarized
- 3-21+g - Diffuse functions
- 3-21+g\* - With polarization *and* diffuse functions
- 6-31g
- 6-31g\*
- 6-31+g\*
- 6-31g(3df, 3pd)
- 6-311g

- 6-311g\*
- 6-311+g\*

### Polarization basis functions

The most common addition to minimal basis sets is probably the addition of **polarization functions**, denoted (in the names of basis sets developed by Pople) by an asterisk, \*. Two asterisks, \*\*, indicate that polarization functions are also added to light atoms (hydrogen and helium).

These are auxiliary functions with one additional node. For example, the only basis function located on a hydrogen atom in a minimal basis set would be a function approximating the 1s atomic orbital. When polarizations added to this basis set, a p-function is also added to the basis set. This adds some additional needed flexibility within the basis set, effectively allowing molecular orbitals involving the hydrogen atoms to be more asymmetric about the hydrogen nucleus. This is an important result when considering accurate representations of bonding between atoms, because the very presence of the bonded atom makes the energetic environment of the electrons spherically asymmetric.

Similarly, d-type functions can be added to a basis set with valence p orbitals, and f-functions to a basis set with d-type orbitals, and so on. Another, more precise notation indicates exactly which and how many functions are added to the basis set, such as (p, d).

### Diffuse functions

Pople-type notation : by a plus sign, +, and Dunning-type notation: by "aug" (from "augmented"). Two plus signs indicate that diffuse functions are also added to light atoms (hydrogen and helium). These are very shallow Gaussian basis functions, which more accurately represent the "tail" portion of the atomic orbitals, which are distant from the atomic nuclei. These additional basis functions can be important when considering anions and other large, "soft" molecular systems.

### Basis set superposition error (BSSE)

## 2.3 Planewave basis set

In addition to localized basis sets, planewave basis sets can also be used in quantum chemical simulations.

- Involving periodic boundary Condition. Certain integrals and operations are much easier to code and carry out with plane wave basis functions, than with their localized counterparts.
- Often used in combination with an 'effective core potential' or pseudopotential so that the plane waves are only used to describe the valence charge density.
- Furthermore, as all functions in the basis are mutually orthogonal, plane wave basis sets do not exhibit basis set superposition error.
- However, they are less well suited to gas-phase calculations (and more..).
- Using Fast Fourier Transforms, one can work with plane wave basis sets in reciprocal space in which not only the aforementioned integrals, such as the kinetic energy, but also derivatives are computationally less demanding to be carried out
- Another important advantage of a plane wave basis is that it is guaranteed to converge to the target wave function while there is no such guarantee for Gaussian type basis sets.

### 3. Approximate Molecular Orbital Theories

Ab initio calculations can be extremely expensive in terms of computer resources. More approximate quantum mechanical methods have been developed to make ab initio methods a widely used computational tool. In some cases, by incorporating parameters derived from experimental data, some approximate methods can calculate certain properties more accurately than even the highest-level of ab initio methods.

#### 3.1 Semi-empirical Methods.

The Roothan-Hall equations for closed shell systems are

$$F C = S C E \quad (31)$$

where the matrix elements have been introduced earlier (see e.g. Equations 9 through 14). Of particular interest are the Fock matrix elements

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{\lambda=1}^K \sum_{\sigma=1}^K P_{\sigma\lambda} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)] \quad (32)$$

It is useful to divide the Fock matrix elements into three groups:

- $F_{\mu\mu}$  : The diagonal elements (same orbital).
- $F_{\mu\nu}$  :  $\phi_{\mu}$  and  $\phi_{\nu}$  are on the same atom.
- $F_{\mu\nu}$  :  $\phi_{\mu}$  and  $\phi_{\nu}$  are on different atoms.

The most efficient way to reduce computational effort is to neglect or approximate some of the integrals. Approaches:

- (a) Consider only the valence electrons. The core electrons are subsumed into the nuclear core.
- (b) The semi-empirical calculations invariably use basis sets comprising STO s, p and some d orbitals. The orthogonality of these orbitals enables further simplification.
- (c) The overlap matrix S is always set equal to identity matrix **I**. The Roothan-Hall equations becomes standard matrix form. However, in calculating  $F_{\mu\nu}$ , some overlap integrals can not be neglected.

#### Zero-differential Overlap (ZDO)

In this approximation, the overlap between pairs of different orbitals is set to zero from all volume elements  $d\nu$  :

$$\phi_{\mu} \phi_{\nu} d\nu = 0 \quad (33)$$

The overlap integrals have the following results

$$S_{\mu\nu} = \delta_{\mu\nu} \quad (34)$$

if  $\phi_{\mu}$  and  $\phi_{\nu}$  are on the same atom, the differential overlap is called monatomic differential

overlap. If  $\phi_\mu$  and  $\phi_\nu$  are on different atoms, the differential overlap is called diatomic differential overlap.

The two-electron integral can be simplified

$$(\mu\nu|\sigma\lambda) = (\mu\mu|\sigma\sigma)\delta_{\mu\nu}\delta_{\sigma\lambda} \quad (35)$$

Under ZDO approximations:

All three-, four center integrals are zero.

The Fock matrix can be considerably simplified:

$$F_{\mu\mu} = H_{\mu\mu}^{core} + \frac{1}{2}P_{\mu\mu}(\mu\mu|\mu\mu) + \sum_{\lambda=1, \lambda \neq \mu}^K P_{\lambda\lambda}(\mu\mu|\lambda\lambda) \quad \text{for } (\mu=\nu) \quad (36)$$

$$F_{\mu\nu} = H_{\mu\mu}^{core} - \frac{1}{2}P_{\mu\nu}(\mu\mu|\nu\nu) \quad \text{for } (\mu \neq \nu) \quad (37)$$

ZDO can not be used to produce meaningful results. (due to the problem of rotational variance).

### Complete neglect of differential overlap (CNDO)

The first method to implement the ZDO approximation in a practical fashion.

The two-electron integrals  $(\mu\mu|\lambda\lambda)$ , where  $\mu$  and  $\lambda$  are on different atoms were set equal to a parameter  $\gamma_{AB}$  which depends on atomic types and interatomic distance. (average electrostatic repulsion between A and B). The Fock matrix equations become:

$$F_{\mu\mu} = H_{\mu\mu}^{core} + \sum_{\lambda=1, \lambda \text{ on } A}^K P_{\lambda\lambda}\gamma_{AA} + \sum_{\lambda=1, \lambda \text{ not on } A}^K P_{\lambda\lambda}\gamma_{AB} \quad (38)$$

$$F_{\mu\nu} = H_{\mu\mu}^{core} - \frac{1}{2}P_{\mu\nu}\gamma_{AA} \quad ; \quad \phi_\mu \text{ and } \phi_\nu \text{ both on atom A} \quad (39)$$

$$F_{\mu\nu} = H_{\mu\mu}^{core} - \frac{1}{2}P_{\mu\nu}\gamma_{AB} \quad \phi_\mu \text{ and } \phi_\nu \text{ on different atoms} \quad (40)$$

CNDO/1 and CNDO/2 (two different versions.. the penetration effect was fixed in the CNDO/2).

### Intermediate Neglect of Differential Overlap (INDO)

This model includes monatomic differential overlap for one-center integrals (basis functions centered on the same atom).

### Neglect of Diatomic Differential Overlap (NDDO)

This theory only neglects differential overlap between atomic orbitals on different atoms. Thus all of the two-electron, two-center integrals of the form  $(\mu\nu|\lambda\sigma)$ , where  $\mu$  and  $\nu$  are on the same atom, and  $\lambda$  and  $\sigma$  are also on the same atom, are retained. (The computation required is

increased by a factor of 100 for NDDO).

### Modified INDO (MINDO/3)

The original CNDO, INDO, NDDO are not little used.

In MINDO/3, the two-center repulsion integrals  $\gamma_{AB}$  are calculated using the following function

$$\gamma_{AB} = \frac{e^2}{\left[ R_{AB}^2 + \frac{1}{4} \left( \frac{e^2}{\bar{g}_A} + \frac{e^2}{\bar{g}_B} \right) \right]^{1/2}} \quad (41)$$

Where  $\bar{g}_A$  is the average of the one-center, two-electron integrals  $g_{\mu\nu}$  on atom A ( $g_{\mu\nu} = (\mu\mu|\nu\nu)$ ). at large  $R_{AB}$  it tends toward Coulomb's law expression  $e^2/R_{AB}$ .

Other parameters including electron-core interaction are parameterized using experimental data.

### Modified NDO (MNDO/3)

Austin Model (AM1) (modifications to core-core interactions)

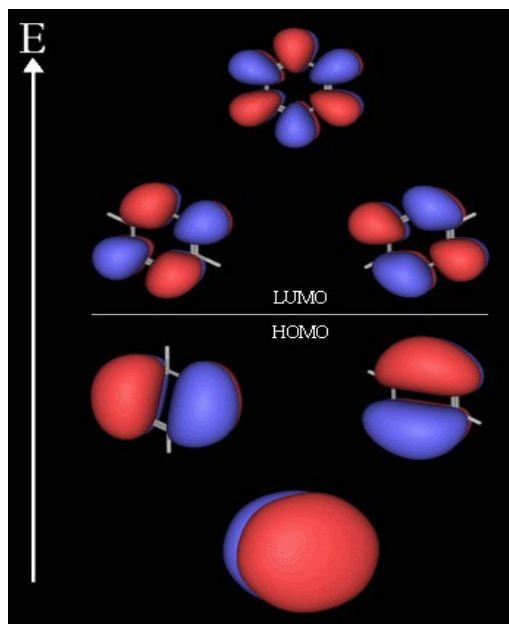
PM3 (the third parametrization of MNDO)

SAM1 (Semi-ab-initio Model 1)

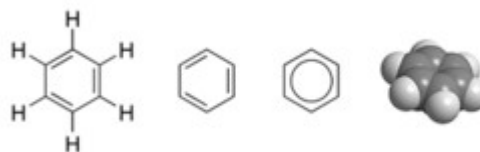
## 3.2 Hückel Theory

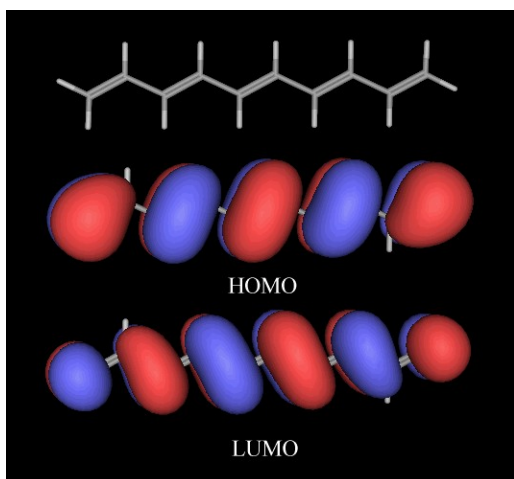
Hückel Theory can be considered the “grandfather” of approximate molecular orbital theory. It is limited to conjugated  $\pi$  systems. (little used in research today. Extensions such as extended Huckel theory are still employed in research - EHT).

A conjugated system is a system of atoms covalently bonded with alternating single and multiple (e.g. double) bonds (e.g., C=C-C=C-C) in a molecule of an organic compound.

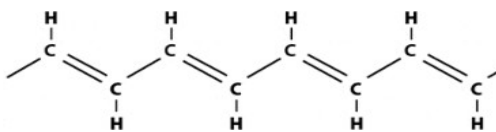


Benzene C<sub>6</sub>H<sub>6</sub>

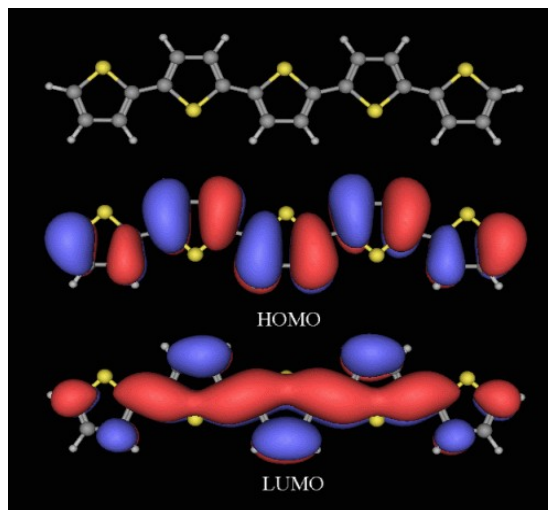




Conjugated oligomer of acetylene



(Trans-polyacetylene)



2,4-thiophene oligomer

- $\pi$  electron approximation. Hückel Theory separates the  $\pi$  system from the  $\sigma$  framework. Molecular Orbitals into which  $\pi$  electrons are filled in.
- The MO are constructed using the LCAO method.

$$\phi_i = \sum_{r=1}^{n_c} c_{ri} f_r, \text{ where } f_r \text{ is a } 2p\pi \text{ atomic orbital.}$$

- Hückel Theory can be explained using the CNDO method.  $\mathbf{HC} = \mathbf{CE}$

$$H_{rr}^{eff} = \int f_r^*(I) \hat{H}^{eff}(i) f_r(i) d\tau_i = \alpha \quad (42)$$

$$H_{rs}^{eff} = \int f_r^*(I) \hat{H}^{eff}(i) f_s(i) d\tau_i = \beta \text{ for } C_s \text{ and } C_r \text{ bonded} \quad (43)$$

$$H_{rs}^{eff} = 0 \text{ for } C_s \text{ and } C_r \text{ not bonded} \quad (44)$$

- $\alpha$  is called Coulomb integral,  $\beta$  is called bond integral or resonance integral.
- The Fock matrix is of the following form (for benzene)

$$\begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix} \quad (45)$$

- The secular equation is

$$\begin{vmatrix} \alpha - \epsilon & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - \epsilon & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - \epsilon & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - \epsilon & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - \epsilon & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - \epsilon \end{vmatrix} = 0 \quad (46)$$

- The results for a few simple molecules are tabulated below:

Molecule	Energy	Frontier orbital	HOMO - LUMO energy gap
<u>Ethylene</u>	$E_1 = \alpha - \beta$	LUMO	$-2\beta$
	$E_2 = \alpha + \beta$	HOMO	
<u>Butadiene</u>	$E_1 = \alpha + 1.62\beta$		
	$E_2 = \alpha + 0.62\beta$	HOMO	$-1.24\beta$
	$E_3 = \alpha - 0.62\beta$	LUMO	
	$E_4 = \alpha - 1.62\beta$		
<u>Benzene</u>	$E_1 = \alpha + 2\beta$		
	$E_2 = \alpha + \beta$		
	$E_3 = \alpha + \beta$	HOMO	$-2\beta$
	$E_4 = \alpha - \beta$	LUMO	
	$E_5 = \alpha - \beta$		
	$E_6 = \alpha - 2\beta$		

*Hückel method results* Lowest energies up top  $\alpha$  and  $\beta$  are both negative values

### 3.3 Extended Hückel Theory

Huckel theory is limited because it is limited to  $\pi$  systems.

The extended Huckel theory (EHT) is a molecular theory that takes account of all valence electrons in the molecule (R. Hoffman 1963, who received the Nobel Prize for his contributions).

The Fock matrix to be solved is still  $\mathbf{FC}=\mathbf{SCE}$ . The extended Huckel theory does not neglect overlap. Rather, all overlap integrals are explicitly evaluated using the forms chosen for the AOs and the internuclear distances. (Formulas for overlap integrals of STOs are readily available).

By Koopmans' theorem, the valence-state orbital energy is taken as equal to minus the valence-state ionization potential energy of the orbital. The one-electron integral  $H_{\mu\mu}$  looks like an average energy of an electron in the AO  $\phi_{\mu}$  on atom A in the molecule. Therefore,  $H_{\mu\mu}$  is empirically taken as the orbital energy of the AO.

The Fock matrix elements taking the following simple forms:

$$F_{\mu\mu}=H_{\mu\mu}=-I_{\mu} \quad (47)$$

$$F_{\mu\nu}=H_{\mu\nu}=-1/2 K(I_{\mu}+I_{\nu})S_{\mu\nu} \quad (48)$$

In these equations  $\mu$  and  $\nu$  are two atomic orbitals,  $I_{\mu}$  is the ionization energy of the orbital and K is a constant, which originally set to 1.75.

These off-diagonal matrix elements are calculated between all pairs of orbitals, so extended Huckel theory is not limited to  $\pi$  systems.

The EH method is often used to provide an initial guess for the valence MO coefficients in ab initio MO calculations.

The EH method was found to give rather accurate bond angles for molecules whose bonds are not highly polar. It is particularly useful for studying systems containing metals. The EH method fails in bond-angle predictions for molecules with very polar bonds, and is not reliable for predicting bond lengths, dipole moments etc (some conclude this method is "obsolete").