

## Computational Chemistry 5

### Semi- empirical Methods

Semi- empirical Methods quantum chemistry methods are based on the Hartree- fock method.

Because of the difficulties in applying Ab-initio methods to medium and large molecules many Semi-empirical methods were developed to treat such molecules .

The earliest Semi- empirical treated only the  $\pi$  electrons of conjugated molecules.

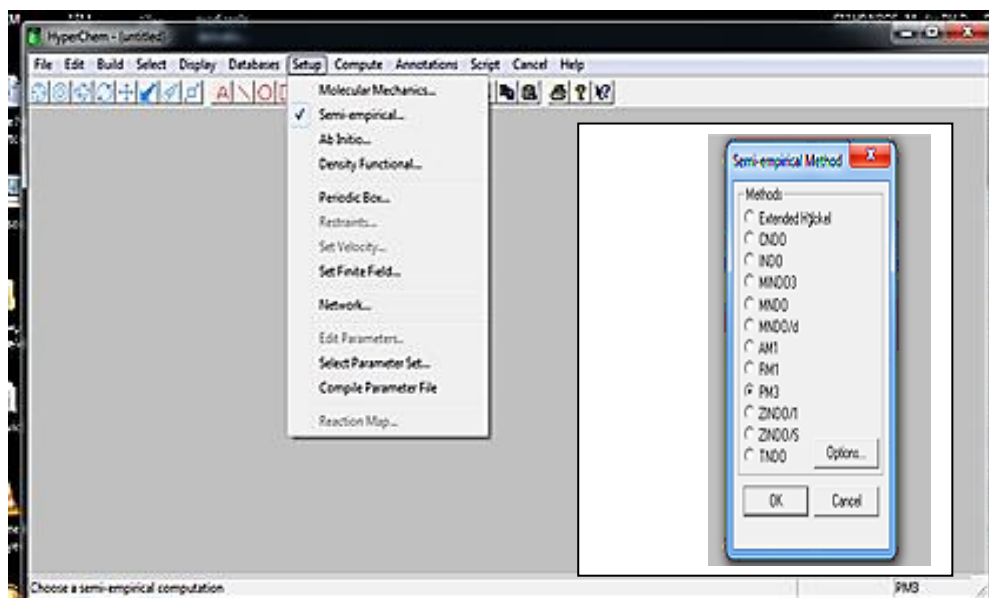
The Semi-empirical MO method apply to all Molecules and treat all the valence electrons.

Semi- empirical MO theories fall into two categories:

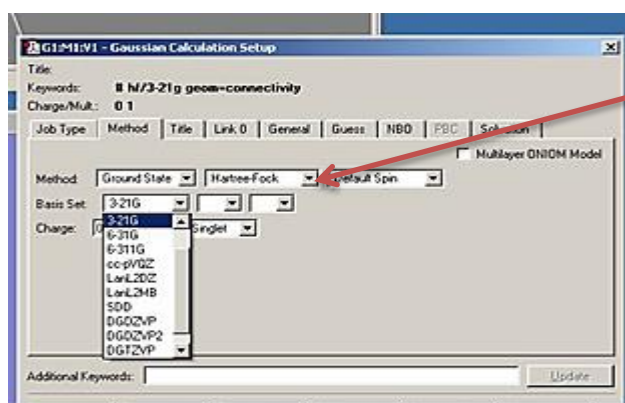
Those using a Hamiltonian that is the sum of **one – electron** terms and those using a Hamiltonian that includes **two electron** repulsion terms as well as one electron terms.

The Huckel Method is a one – electron theory, whereas the Parise- Parr-Pople method is a two –electron Theory.

In HYPER CHEM. program



While in Gaussian program.



يتم اختيار طريقة Semi-empirical بدل من Hatree Fock المؤشرة اعلاه

## Semi-empirical Methods

- 1- The Extended Huckel Method (EH)
- 2- Intermediate neglect of differential overlap (INDO) method
- 3- The complete neglect of differential overlap (CNDO) method
- 4- Modified –Intermediate neglect differential overlap (MINDO) method
- 5- Modified neglect of Diatomic overlap (MNDO) method
- 6- Austin methods Version 1 (AM1)
- 7- parameterized model number 3 (PM3)

### 1-The Extended Huckel Method

The most important one –electron Semi-empirical MO method for non planar molecules is the extended Huckel theory.

An early version was used in treating inorganic complexes .

The Extended Huckel (EH) method begins with the approximation of treating the valence electrons separately from the rest.

The valence –electron Hamiltonian is taken as the sum of one- electron Hamiltonians .

The (EH) treatment of non-planar Hydrocarbons each valence MO contains contribution from four AOs on each carbon atom ( one 2s and three 2p) and 1s AO on each Hydrogen atom.

While the simple Huckel theory of planar Hydrocarbons each  $\pi$  MO contains contribution from one  $2P\pi$  AO on each carbon atom.

All this is similar to simple Huckel theory , However the extended Huckel theory does not neglect overlap.

The EH is give poor predictions of such molecular properties as bond length , dipole moments and energies.

### **2-The complete neglect of differential overlap ( CNDO) method .**

CNDO method treat only the valence electrons and used a minimal basis set of valence Slater AOs .

The repulsion between electrons in different orbitals depends only upon the nature of the atoms involved and not on the particular orbitals.

The CNDO method give fairly good bond lengths and angle.

### **3-Modified –Intermediate neglect differential overlap (MINDO) method**

MINDO is based on the Inter mediate neglect of differential overlap ( INDO) method approximation and is the earliest of the Dewar methods.

It provides more accurate geometries and heats of formation .

### **4-- Modified neglect of Diatomic overlap (MNDO) method**

The MNDO method has been parametrized for compounds containing ( H, Li, Be , B, C , N , O, F , P, and S ) gives substantially improved results as compared with MINDO for the same sample of ( C, H, O, N ) compounds.

It has been used widely to calculate heats of formation , molecular geometries , dipole moments, ionization energies, and other properties.

## **5- Austin methods Version 1 ( AM1)**

AM1 is an improvement over MNDO even though it uses the same basic approximation .

AM1 treatment of phosphorus- oxygen bonds is accurate , nitro compounds and the peroxide bond.

## **6- Parametric Method Versions 3 ( PM3)method**

PM3 is a parameterization of AM1 , which is based on the neglect of diatomic differential overlap ( NDDO) approximation .

PM3 differs from AM1 only in the values of the parameters.

Typically non bonded interactions are less repulsive in PM3 than in AM1

PM3 is primarily used for organic molecules .

A major limitation of the original versions of the AM1 , MNDO , PM3 methods is that they use a basis set of S and P valence AOs only .

Semi-empirical calculations done by traditional methods are limited to molecules with no more than 1000 atoms.