

SEMIEMPIRICAL METHODS IN COMPUTATIONAL CHEMISTRY

Introduction-From ab initio to semiempirical methods

- High cost and the need for greater computing power of ab initio calculations is largely due to the many integrals that need to be calculated
- Semi-empirical methods start with the general form of ab initio Hartree-Fock calculations, but make numerous approximations for the various integrals
- In short, we can say that
 - The method is "parameterized"
 - The programme works on a library of integrals that are combined by finding the best possible values
 - The approximated or omitted information's are parameterized using available integrals by determining the best suit.
 - It is thus a mixing of experimental data and theoretical data
 - It is fast and accurate if the given molecule is similar to the molecule in the database
- ❖ It is thus an approximated version of Hartree-Fock

How it works

- Core orbitals are not treated by semiempirical methods, since they do not change much during chemical reactions
- Only a minimal set of valence orbitals are considered on each atom
- Many Integrals are neglected to speed up the computation
- Empirical parameters are inserted to make up for the neglected integrals

Common Semiempirical Methods

Huckels Methods

- ❖ The Huckels method is one of the earliest and simplest semiempirical methods.
- ❖ Huckels calculation models only the π valence electrons in a planar conjugated hydrocarbon.
- ❖ A parameter is used to describe the interaction between bonded atoms.
- ❖ There are no second atom effects.

- ❖ Huckels calculations do reflect orbital symmetry and qualitatively predict orbital coefficients.
- ❖ Huckels calculations can give crude quantitative information or qualitative insight into conjugated compounds, *but are seldom used today*.
- ❖ The primary use of Huckels calculations now is as a class exercise because it is a calculation that can be done by hand.

Extended Huckel Methods

- ❖ An extended Huckel calculation is a simple means for modelling the valence orbitals based on the orbital overlaps and experimental electron affinities and ionization potentials.
- ❖ Orbital overlaps can be obtained from a single STO representation based on the atomic radius.
- ❖ The advantage of extended Huckel calculations over Huckels calculations is that they model all the valence orbitals. (unlike Huckels calculation which consider only π electrons)
- ❖ The primary reason for interest in extended Huckel today is because the method is general enough to use for *all the elements in the periodic table*.
- ❖ This is not an extremely accurate or sophisticated method; however, it is still used for inorganic modelling due to the scarcity of full periodic table methods with reasonable CPU time requirements.
- ❖ Another current use is for computing band structures, which are extremely computation-intensive calculations.
- ❖ Because of this, extended Huckel is often the method of choice for band structure calculations.
- ❖ It is also a very convenient way to view orbital symmetry.

Pariser-Parr-Pople (PPP) method

- ❖ Extension of the Huckel method that allows heteroatoms other than hydrogen.
- ❖ It is still occasionally used when very minimal amounts of electronic effects are required.
- ❖ PPP based terms have been incorporated in molecular mechanics calculations to describe aromaticity.

Complete Neglect of Differential Overlap (CNDO) Method

- ❖ This method models valence orbitals only using a minimal basis set of Slater type orbitals.
- ❖ The CNDO method has proven useful for some hydrocarbon results.
- ❖ CNDO is still sometimes used to generate the initial guess for ab initio calculations on hydrocarbons
- ❖ The original version was CNDO/1 and a modified method CNDO/2 is now available
- ❖ There is a CNDO/S method that is parameterized to reproduce electronic spectra which does yield improved prediction of excitation energies, but at the expense of the poorer prediction of molecular geometry.
- ❖ There have also been extensions of the CNDO/2 method to include elements with occupied d-orbitals.

Zero Differential Overlap (ZDO)

- ❖ Two electron repulsion integrals are one of the most expensive parts of ab initio MO calculations
- ❖ ZDO neglect these integrals if orbitals are not the same
- ❖ All 3 & 4 center 2- electron integrals (most numerous ones) are neglected
- ❖ Approximate integrals by using 's' orbitals only

Advantages and Disadvantages of Semiempirical Methods

- The advantage of semiempirical calculations is that they are much faster than ab initio calculations.
- The disadvantage of semiempirical calculations is that the results can be erratic
- Only some properties can be predicted reliably.
- If the molecule being computed is similar to molecules in the database used to parameterize the method, then the results may be very good.
- If the molecule being computed is significantly different from any molecule in the parameterization set, the answers may be very erratic.
- Semiempirical methods are parameterized to reproduce various results.
- Most often, geometry and energy (usually the heat of formation) are used.
- This is now extended by including dipole moments, heats of reaction, and ionization potentials in the parameterization set.

- Some methods have been parameterized to reproduce properties such as electronic spectra or NMR chemical shifts.
- Semiempirical calculations have been very successful in the description of organic chemistry.
- Only some semiempirical methods have been devised specifically for the description of inorganic molecules.