Semi-Empirical Methods

The major limitation of *ab initio* methods is the complexity of the calculations. This complexity puts a limit on the size of molecular system that may be practically treated using even the simplest HF theory.

Much effort has been put into finding ways of overcoming this barrier and semi-empirical methods are one of the most successful to come out of this effort. As the name suggests, these methods include a certain amount of pre-calculated data in the calculation to both reduce the computational effort and increase the accuracy of the results.

Theory

Firstly, it is worth remembering that semi-empirical methods are a form of HF method with some of the Hartree-Fock calculations replaced by the use of empirical (experimental or *ab initio*) data.

Semi-empirical methods are all based around two basic schemes for reducing the amount of calculation:

- Elimination of the core electrons from the calculation.
- Reduction of the number of two-electron integrals.

The removal of the core electrons from the calculation has some good chemical grounds in that we would not expect them to be involved in any chemical activity. They are replaced by parameterized function which describes the core region (nucleus and core electrons) of a particular atom type. This has the effect of drastically reducing the complexity of the calculation without a huge impact on the accuracy.

The second approximation is introduced on practical rather than chemical grounds. The majority of the work in *ab initio* calculations is in the evaluation of the two electron integrals (Coulomb and exchange, see *ab initio* section) it makes sense to concentrate on this part of the calculation. All modern semi-empirical methods are based on the Modified Negelect of Differential Overlap (MNDO) approach. In this method parameters are assigned for different atomic types and are fitted to reproduce heats of formation, geometrical variables, dipole moments and first ionization energies. The parameterization was carried out separately for hydrocarbons, CHO systems and CHN systems.

The latest versions of the MNDO method are referred to as AM1 and PM3. All semi-empirical methods have been specifically designed for organic systems.

Advantages

- Ability to treat larger molecules than would be possible using even simple *ab initio* methods with a comparative level of accuracy.
- Faster throughput of calculations.
- Particularly good for organic molecules and reactions.
- Molecular orbitals allow for prediction of reactions and properties.

Disadvantages

- Accuracy is not as good as higher *ab initio* methods (DFT, MP2).
- Do not work as well for:
  - Molecules that involve hydrogen bonding.
  - Some transition states.
  - Molecule types for which atoms have not been parameterized.
  - Atoms that are poorly parameterized (*e.g.* nitrogen).
- Unavailable for some atoms.

Applications

- Calculation and stability of organic structures: equilibrium, transition state and reaction intermediates.
- Characterization of the MOs – predictions of reactivity.
- Vibrational analysis – calculating IR and Raman spectra.
- Charge distribution.

Software Available on the EaStCHEM RCF

- **Gaussian 03** – Includes implementations of a number of different semi-empirical methods including AM1 and PM3.