

MATHEMATICAL METHODS OF CALCULATION USED IN COMPUTATIONAL CHEMISTRY

By
Traian-Nicolae Ursaleş

Abstract: In this paper I wanted to present the mains mathematical methods used in computational chemistry to establish the values of some physical size structures characteristics of the chemical systems relied on calix[4]arene.

Keywords: computational chemistry; chemical systems

1. INTRODUCTION

Mathematical model and their use with the help of different computer programmers to estimate the values of different physical sizes, make them very usefully to describe mathematically some chemical procedures. Thus the boundary between mathematics, physics and chemistry is very small and lead to the appearance of the Computational Chemistry¹, which includes:

- a). **Molecular Modeling;**
- b). **Mechanical statistics;**
- c). **Thermodynamics statistics;**
- d). **Solid state modeling;**
- e). **The structure – property relationships investigation;**
- f). **The symbol calculation;**
- g). **Artificial intelligence.**

Following is presented the first class, Molecular Modeling, which includes four branches:

- ab initio methods;**
- semiempirical methods;**
- molecular mechanics;**
- molecular dynamics.**

As follows all these four methods are described separately, because they are also used very much to determine some physical constants for different chemical systems.

2. AB INITIUM METHODS²

Are those cuantic chemistry methods, which always approach to the accurate solution counting on the theoretical integrals, the variations and the perturbations characteristic of the studied chemical systems. The most usefully ab initio methods are

those of this (Hartree-Fock, HF), which derived from the settlement of the Schrodinger equation: $H\Psi = E\Psi$ (1), where

E – the figure value of the energy in basic state; Ψ - wave function; H – the differential operator which represent the total energy from the molecule.

The Hamiltonian includes both the kinetics energy of the particles and neutrons and the repulsion energy between electrons. The essence of the Hartree-Fock ab initio methods is that it doesn't consider the electron – electron interaction, which forecast then as equal to the interaction between one electron and the others electrons taken together. Knowing that the first term I from the above Hamiltonian equation is null, because it was considered an multiple electrons systems, the total energy of the system it: $E_{\text{total}} = E_{\text{electrons}} + E_V$ (the repulsion between nuclei), where $E_{\text{electrons}} = E_{\text{II}} + E_{\text{III}} + E_{\text{IV}}$.

These ab initio methods have an big advantage because almost always tend to the accurate solution, even they are very expensive, comparatively to others calculation methods.

3. SEMIEMPIRICAL METHODS^{3,4}

Were introduced to reduce the costs which implies ab initio method. The semiempirical methods follows the HF calculation scheme, but some of the integrals are either completely eliminated or estimated by experimental data. The results are good enough, because the integrals which are not eliminated are estimated in such a way to compensate those eliminated. It was done an parameterization namely it was chose an “school” molecules set and it was establish the parameters thus through calculation were found the methods used. The advantage of these methods consist in the speed with which they take place comparatively to ab initio methods. The semiempirical methods are applied with priority to the organic systems, because there are an limited member of elements and so there are big chances for the studies molecules to be alike the “school” molecules.

The semiempirical methods are used for molecular study, to determine the structure and the reactivity of the studied chemical system. With these methods we can study: the orbital symmetry, nodal structures, the orbital energy, the charges distribution, the chemical bond order or it can discuss the “frontier” orbital. The semiempirical methods are presented by:

- **MNDO method**⁵ which takes in account the repellencies between the electrons pairs and the electron-electron perellence directions; **ZDO method** (zero differential overlap) is based on the Huckel method for the π electrons;
- **CNDO method** (Complete Neglect of Differential Overlap) which takes in account only the atomic orbital of spherical symmetry and assesses the repulsion integrals as the orbital would be sphere. In this case are two methods CNDO/1 and CNDO/2 which are used for the spectrum parameters;

- **-INDO method**⁶ (Intermediate Neglect of Differential Overlap) which includes the mono-electronic repulsion integrals between atomic orbitals of the same atom;
- **-NDDO method** (Neglect of Differential diatomic overlap) which takes into account the orientation direction of the orbital;
- **-MINDO/3 method** is a particular case of the NDDO method which assesses the mono-electronic repulsion integrals;
- **-PM3 and AM1 methods** which are the most performance in the geometry's optimization and in the minimum energy reaching. These methods study the hypervalent systems, which contain the atoms which use their "d" orbital to form chemical bonds. The methods assess with big accuracy the rotation and repulsion barriers which appear because of the non-participating electron pairs. The performances of the semiempirical method consist in the smaller cost of them and in their speed, but also in the fact they can determine some properties that cannot be established experimentally.

4. MOLECULAR MECHANIC METHODS⁷

Are an ensemble of methods through which the molecular energy of the molecule will be expressed without taking into account the wave function, in other words with this method it is possible to determine the energy of the molecule depending on the atoms configuration without considering the electrons position. The molecular mechanics methods are also formed by:

- **-OPLS** (Optimized Potentials for Liquid Simulation) which considers the Lennard-Jones potential; electrostatic interactions and the energies of the torsion angles; - **-AMBER** (Assisted Model Building with Energy Refinement) includes the energies which are due to the hydrogen bonds, nonbonding interactions, deformations and torsion;

- **-CHARM** (Chemistry at Harvard using Molecular Mechanics) includes the parameters due to their own torsion and the parameters due to the Huck torsion.

The total energy of the studied system by molecular mechanics methods represents the sum of energies on: bonds, angles, torsion, Van der Waals interactions. The molecular mechanics methods are applied on some molecules too big even for a semiempirical approach, the advantage of these methods is the fact that they allow the modeling of gigantic molecules such as some macromolecules and some proteins.

5. THE MOLECULAR DYNAMICS METHODS

Consist in the fact that they follow in time the behavior of one molecule or an ensemble of molecules.

6. CONCLUSION

All these calculation methods had been successfully use to establish the conformational stability of some different chemical systems relayed on calix[4]arenes and calix[4]arenes derivatives. For the majority of the cases the obtained results by these calculation methods were confirmed by the experimental data.

References

1. N.Allingar, V.Burkhart, *Molecular Mechanics, A.C.S.* **1981**.
2. R.Doudel, G.Ieroy, D.Paeters, M.Sana, *Chimie Cuantică*, Ed.Didactică Bucureşti, **1988**.
3. T.Clark, *A Handbook of Computational Chemistry*, John Wiley & Sons New-York, **1985**.
4. M.C.Zerner, *Chem.Revs*, **1992**, 313.
5. M.J.S.Dewar, G.L.Glady, J.J.P.Stewart, *J.Am.Chem.Soc.*, **1978**, 106, 6771.
6. W.P.Anderson, T.Cundari, R.Dargo, M.C.Zerner, *Inorg.Chem.*, **1990**, 29, 1.
7. I.Silaghi-Dumitrescu, D.Horvarth, *Mecanică Moleculară*, Ed. Dacia Cluj-Napoca, **1996**.

Author: Drd. Traian-Nicolae Ursaleş, Department of Chemistry from Cluj-Napoca, România