

COMPUTATIONAL CHEMISTRY

Computational chemistry may be simply defined as a set of techniques used in chemistry to investigate problems with the help of a computer. The main applications of computational chemistry stretch over a wide range.

- 1) Determination of molecular geometry
- 2) Determination of energies of molecules and transition states
- 3) Study chemical reactivity
- 4) Predict molecular spectra
- 5) Study enzyme-substrate interactions
- 6) Determination of physical properties of substances
- 7) Calculation of ionisation energy and electron affinity
- 8) Determination of conformational energies
- 9) Determination of heat of formations
- 10) Determination of strain energy in cyclic compounds

Methods in computational chemistry

1) Molecular mechanics

It considers a molecule as collection of balls (atoms) held together by springs (bonds). If we know the normal spring length, angle and energy required for stretching and bending vibrations, then we can calculate the energy of the molecule.

Also changing the geometry until we obtain the configuration with minimum energy and this process is called geometry optimisation.

Molecular Mechanics is based on hooks law $F = K (r-r_e)^2$

Geometry Optimisation

Its objective is to find an atomic arrangement (geometry) which makes the molecule most stable. ie Lowest energy

Force Field

It refers to the parameters set and functional form used to calculate the potential energy of a system of atoms in MM simulations.

The parameters may be derived from experiments in physics or chemistry or QM calculations.

2) **Ab Initio Method (from the beginning)**

- a) It is a Q.M model based on S.W.E
- b) Derived from theoretical principles with no experimental data.
- c) It refers to an approximate Q.M calculation
- d) It stresses on approximate solutions
- e) Most common Ab Initio calculation is the Hartree-Fock calculation which is based on central force field approximation. (ie coulombic electron-electron repulsion is not specifically taken into account. But its net effect is included in calculation)
- f) Due to central force field approximations the energies from HF calculations are always greater than the true values and tend to a limiting value called the "Hartree-Fock Limit"

3) **Semi Empirical Methods**

- a) Q.M method based on SWE
- b) More approximations are made
- c) Certain information's like 2e- integrals are approximated or omitted
- d) The method is "parameterized"
- e) The programme works on a library of integrals that are combined by finding the best possible values
- f) The approximated or omitted information's are parameterized using available integrals by determining the best suit.
- g) It is thus a mixing of experimental data and theoretical data
- h) It is fast and accurate if the given molecule is similar to the molecule in the database
- i) If the molecule doesn't match any molecule in the database erratic results will be obtained.
- j) Organic molecules of similar size and properties give good results but inorganic molecules give a lot of errors.

4) **Density Functional Theory**

- a) Q.M method based on SWE
- b) Electron density functional is used which has some physical significance.

- c) Ψ don't have any significance here
- d) DFT derives electron distribution
- e) It is faster than Ab Initio but slower than Semi Empirical

Note:

Function is rule that transforms one number to another number

$$\text{eg } 2 \xrightarrow{x^3} 8$$

Functional (function of a function) is a rule that transforms a function into a number

$$f(x) = x^3$$

$$\int_0^2 f(x) dx = \frac{16}{4} = 4$$

In DFT the function is the electron density which is a function of space and time.

5) Molecular dynamics

- a) It applies laws of motions to molecules
- b) Used to track reactions and rearrangements
- c) Molecular motions can be simulated using this method
- d) Main application is in the field of enzyme action, enzyme- substrate binding etc

POTENTIAL ENERGY SURFACE (PES)

- a) In geometry optimisation we check for the lowest possible energy of a molecule.
This is achieved by creating a PES
- b) PES is a mathematical relationship between various molecular geometries and their corresponding single point energies
- c) The values are displayed on a 3D graph
- d) The 3 dimensions represent bond length, bond angle and Hartree-Fock Energy.

The born Oppenheimer approximation says that the nucleus in a molecule are stationary compared to the electrons. This makes the basis of molecular geometry. So we can create a PES and apply SWE to calculate the energy.

Consider a vibrating diatomic molecule

Let r_0 be the equilibrium bond length. If we stretch or compress the bond then P.E increases. It is given in Fig 1

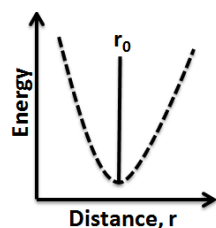


Fig 1

Fig 1 represents 1D PES on a 2 D graph of Energy versus bond length

Note that a diatomic molecule has only one geometric parameter to vary (bond length)

Consider the case of water. Here geometry is defined by two bond length and one bond angle. If we stick on to C_{2v} symmetry the PES for water will be a graph of Energy versus O-H bond length and H-O-H bond angle. That is we get a 2D PES on a 3D Graph

Now consider HOF which is of lower symmetry

It has three geometric parameters, O-H and O-F bond lengths and H-O-F bond angle along with H-O-F bond angle

In order to plot this, we need 4 mutually perpendicular axes. since we cannot construct 4D in 3D space we cannot accurately draw it.

HOF PES is a 3D surface in 4D space that is it is a "Hyper Surface"

We can define the equation $E=f(r_1 r_2 r_3)$ as the PES for HOF. Here f is a function describing how E varies with r values and treat hypersurface mathematically.

The minimum energy point corresponds to equilibrium values of $r_1 r_2 r_3$ given as

$$\frac{dE}{dr_1} = \frac{dE}{dr_2} = \frac{dE}{dr_3} = 0$$

Stationary Points

A stationary point on a PES is a point at which the surface is flat, parallel to the horizontal line corresponding to one geometric parameter or to the plane

corresponding to two parameters or to a hyperplane corresponding to more parameters. A ball placed on a stationary point will remain balanced. At any other point on PES the ball will roll down to lower potential. Stationary points help us to visualise the relationship between potential energy and molecular geometry.

Consider the reaction

It is reasonable that ozone has an isomer (iso ozone) and they are interconvertible through a transition state.

Depicting this on PES, the energy should be plotted against 2 geometric parameters ie O-O bond length and O-O-O bond angle.

It depicts how a 2D slice from a 3D diagram gives the energy coordinate. The slice goes along the lowest energy path connecting ozone, iso ozone and T.S. ie along the reaction coordinate and the horizontal axis is a composite of bond length and bond angle. The reaction coordinates indicates the progress of a reaction.

Stationary points corresponds to actual molecules with finite life time like ozone, isoozone etc are minima or energy minima each occupying the lowest energy point in its region of the PES and any small change in geometry increases the energy as indicated in Fig 2.

Here ozone is a "*global minimum*"_Since it is the lowest point on the PES.

Iso Ozone is a "*relative minimum*", a minimum compared to only nearby points.

The lowest energy pathway linking two minima is called "*Intrinsic reaction coordinate*"(IRC). It is the path followed by the molecule in going from one minimum to another.

Note that a molecule with excess energy may stray out of IRC.

In Fig 2 T.S is the maximum point on IRC. But it along all other directions (except IRC) is a minimum. This is the characteristic of a saddle shaped surface and such a transition state is called a saddle point.

The saddle point lies in the centre of the saddle shaped region and like a minimum, as stationary point since PES at that point is parallel.

Saddle Point

A point on a PES which is a maximum in one direction and minimum in all other directions is called a saddle point. They represent transition structures connecting two equilibrium states.

Note

Both Minima and saddle points are stationary points. Minima is a minimum in all directions but saddle point is a maximum along IRC and minimum along all other directions.

Note

Transition state is thermodynamic concept, it obeys Eyrings transition state theory

Transition structure is a saddle point on a theoretically calculated PES

A saddle point with 2nd order derivative of energy w.r.t one geometric parameter is -ve corresponds to a transition state.

In some PES the 2nd derivative of energy corresponding to more than one geometric parameter may be -ve. These are called higher-order saddle points or hill tops.

A hilltop is a point on a PES which is a maximum along two paths connecting stationary points.