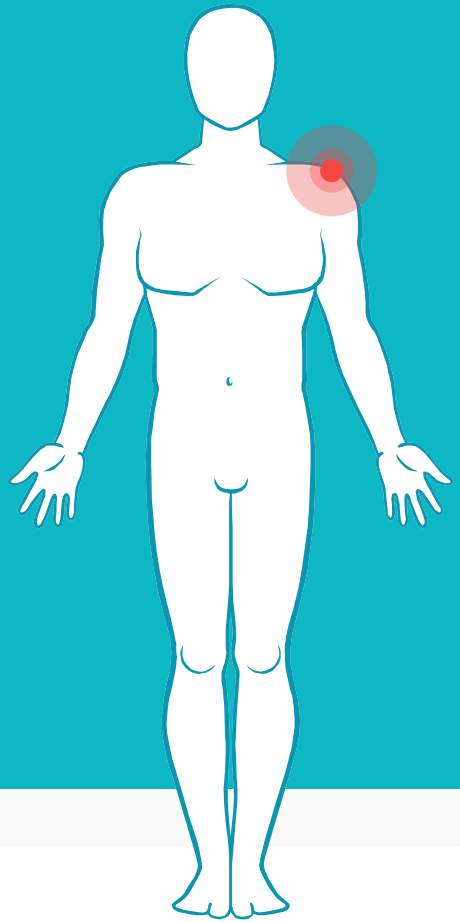
Computational Chemistry Methods



Lecture – 6

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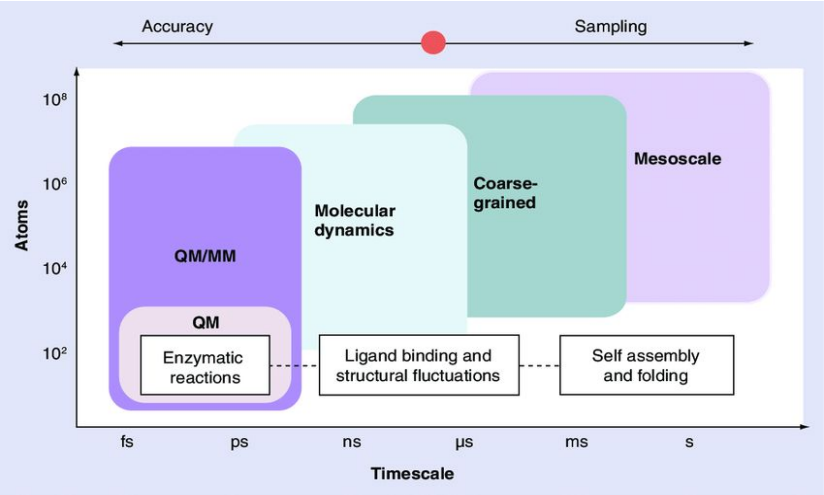
Definition

The main objective of computational chemistry is to solve chemical problems by simulating chemical systems (molecular, biological, materials) in order to provide reliable, accurate and comprehensive information at an atomic level.
To this end, there are two main methodological families: those based on **quantum chemical methods** and those based on **molecular mechanics**.

The former are methods in which the electrons are explicitly accounted for, while in the latter their presence is hidden in the force field.



Computational Chemistry Methods

1. Classical Methods
2. Quantum chemistry method

Classical Methods

1. Molecular Mechanics

Molecular mechanics is **an empirical method for calculation of properties of molecules such as molecular geometry, heat of formation, strain energy, dipole moment, and vibrational frequencies**

2. Molecular Dynamics

Molecular dynamics (MD) is **a computer simulation method for analyzing the physical movements of atoms and molecules**.

Quantum chemistry method:-

1. Semi empirical Methods.

Semiempirical Methods are **simplified versions of Hartree-Fock theory using empirical (= derived from experimental data) corrections in order to improve performance**.

2. Ab initio Methods.

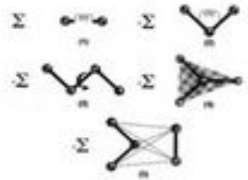
Ab initio methods, as the name implies, require no empirical information about the molecular system being considered but rather **apply various approximations to solve Schrödinger's equation through the use of wave functions to describe atomic orbitals for the calculation of molecular properties**.

3. Density functional Theory.

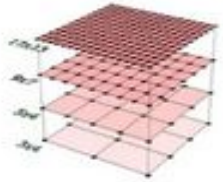
Density-functional theory is a computational quantum mechanical modelling method used in physics, chemistry and materials science to investigate the electronic structure of many-body systems, in particular atoms, molecules, and the condensed phases.

Computational Chemistry

Quantum Mechanics (QM)



Molecular Mechanics (MM)



Hybrid QM / MM

Semi-empirical (SE)

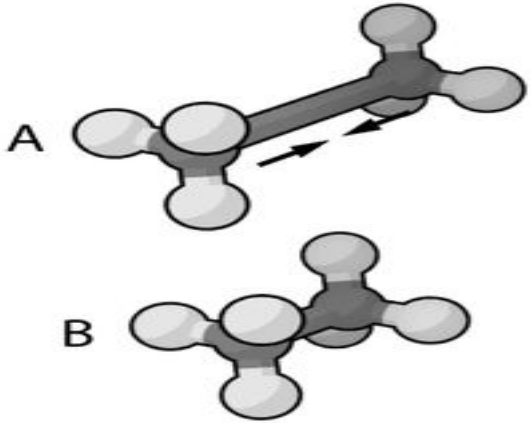
Molecular Mechanics

- **Molecular Mechanics** • Molecular mechanics programs use equations based on classical physics to calculate force fields.
- • Atoms treated as spheres, bonds as springs and electron are ignored.
- • It assume that the total potential energy (Etotal) of molecule is given by sum of all the energies of attractive and repulsive forces between atom in structure
- The molecular mechanics equation E = EB+EA+ED+ENB*

*EB = The energy involved in the deformation bond either by stretching or compression. EA = The energy involved in the angle bending . ED = The torsional angle energy. ENB = The energy involved in the interaction between atoms that are not directly bonded.

Force Field

Force field refers to calculation of the interaction and energies between different atoms between bond stretching, angle bending



Molecular Dynamics

- • Molecular dynamics is a molecular mechanics program designed to mimic the movement of atoms within a molecule.

- • Molecular dynamics can be carried out o a molecule to generate different conformation which on energy minimization, give a range of stable conformation. Alternatively bonds can be rotated in a stepwise process to generate different conformation
  - https://www.youtube.com/watch?v=lLFEqKl3sm4

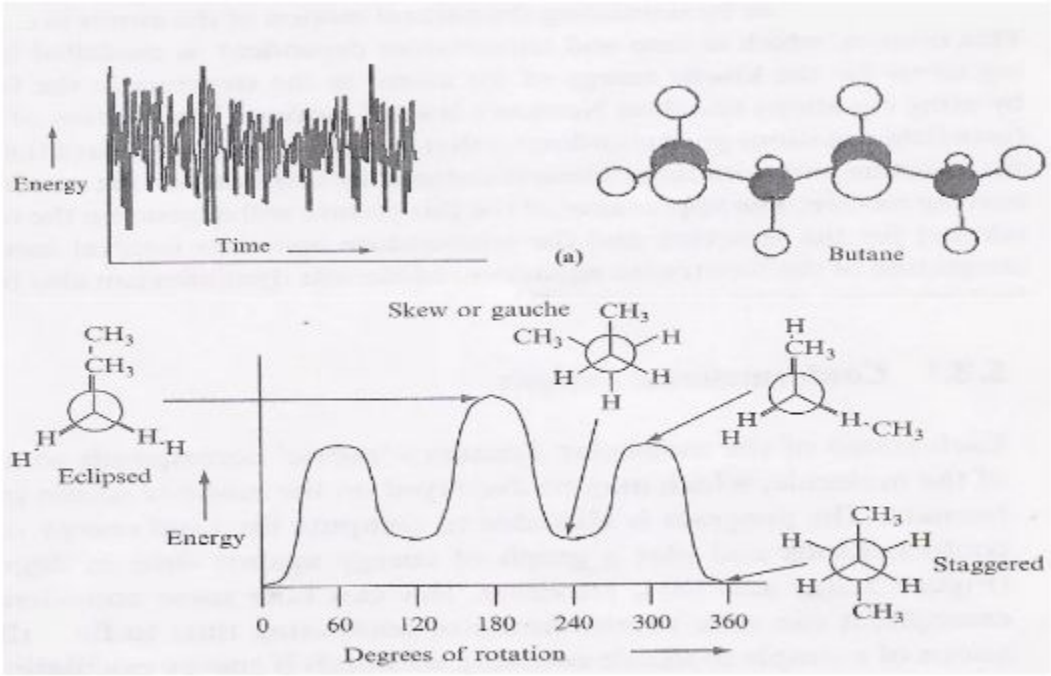


Fig-: Plot of change in the energy with the rotation about C_2-C_3 bond In butane

Quantum mechanics

- Quantum mechanics is based on arrangement of electrons of molecule and interaction of those electron with electron and nuclei of other molecule.
- It based on the realization that electron and all material exhibit wave like properties.
- The Quantum mechanics based on finding solution to Schrödinger wave equation.

Schrödinger's Equation

The Schrödinger equation is the basis of quantum mechanics and gives a complete description of the electronic structure of a molecule.

$$H\psi = E\psi$$

Where H=Hamiltonian operator Ψ =wave function E =Energy system

Ab Initio method

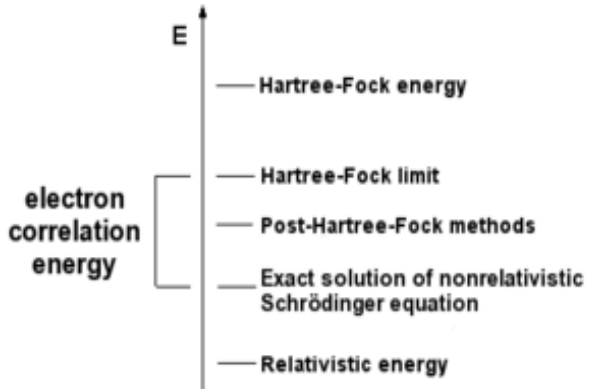
- Ab initio translated from Latin means from “first principles”.

- This refers to the fact that no experimental data is used and computations are based on quantum mechanics.

- It derived directly from theoretical principle

Different Levels of Ab Initio Calculations

1. Hartree-Fock (HF)
2. Density Functional Theory (DFT)



Hartree-Fock (HF)

The simplest ab initio calculation.

• It based on Central field approximation.

• The major disadvantage of HF calculations is that electron correlation is not taken into consideration.

Density Functional Theory

Considered an ab initio method, but different from other ab initio methods because the wave function is not used to describe a molecule.

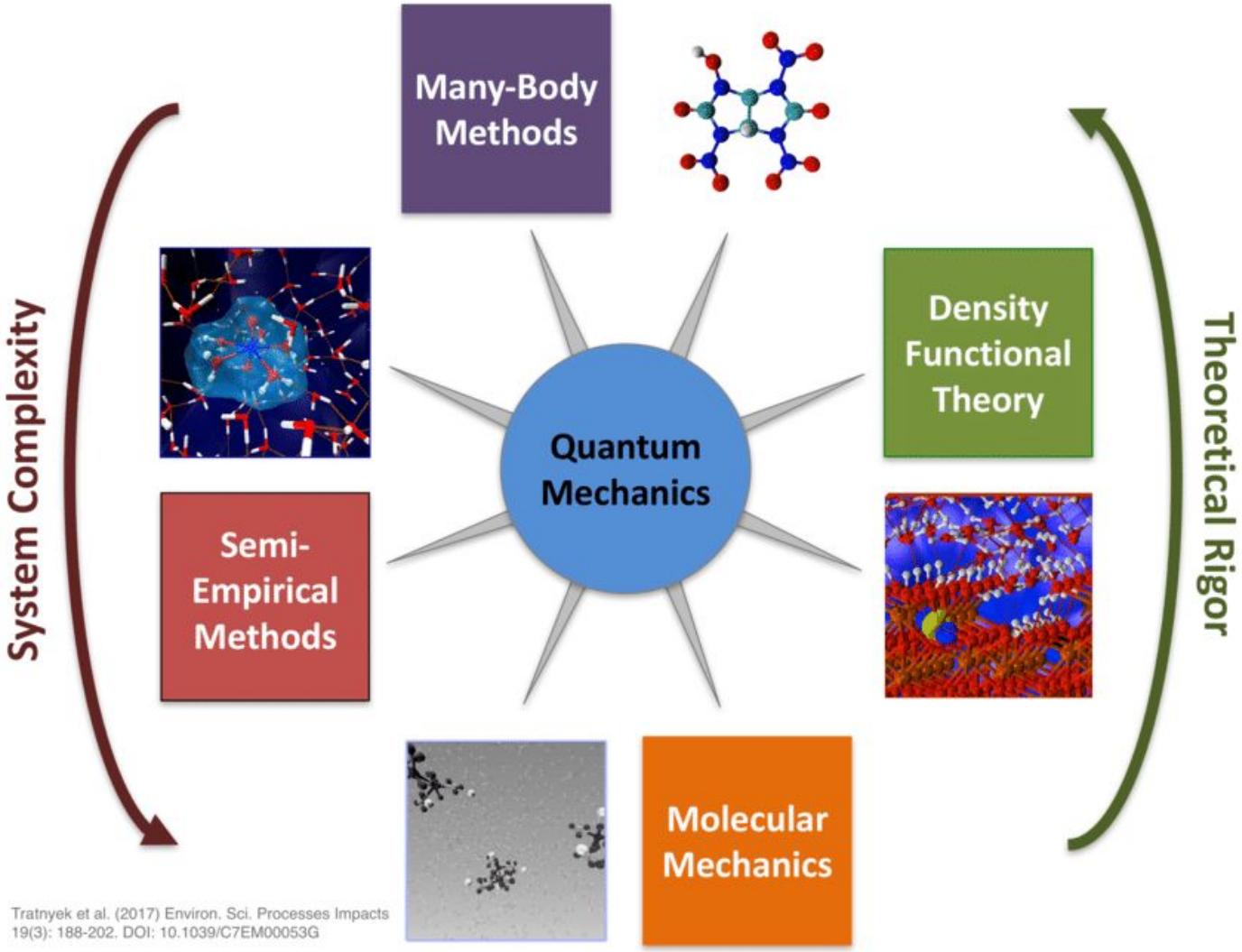
• Density functional theory in which total energy is expressed in term of total electron density is used.

• DFT methods take less computational time than HF calculations and are considered more accurate.

Semi-empirical quantum methods,

represents a middle road between the mostly qualitative results available from molecular mechanics and the high computationally demanding quantitative results from ab initio methods.

- Semi empirical methods use experimental data to parameterize equations.
- Like the ab initio methods, a Hamiltonian and wave function are used.
- Less accurate than ab initio methods but also much faster.



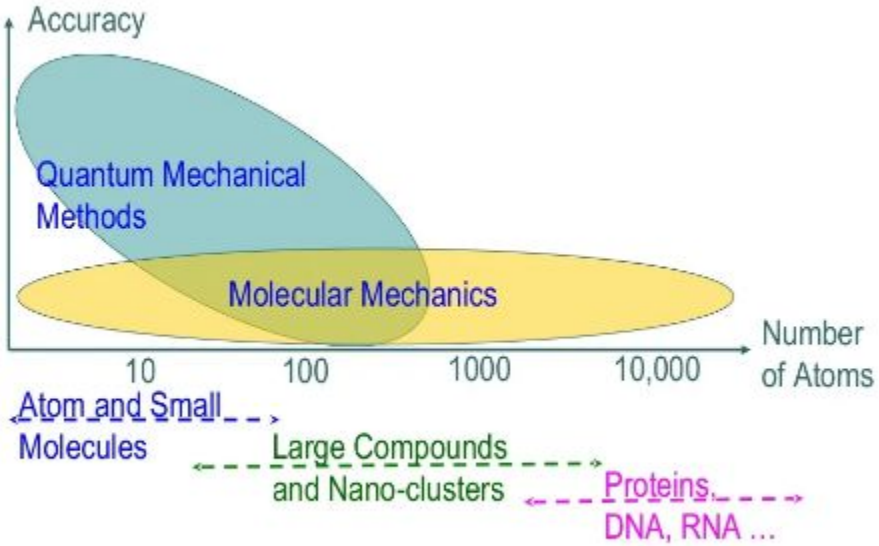
Tratnyek et al. (2017) Environ. Sci. Processes Impacts 19(3): 188-202. DOI: 10.1039/C7EM00053G

Choice of Method

The method of calculation based on what calculation needs to done and size of molecule. Molecular mechanics useful for

- Energy minimization
- Identifying stable conformation
- Energy calculation for specific conformations
- Studying molecular motion
- Studying different conformation.

Computational Cost vs. Accuracy

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