UNIT-4 (ADVANCED CONCEPTS/TOPICS IN CHEMISTRY)

Computational chemistry: Introduction, Ab Initio studies

Molecular switches: characteristics of molecular motors and machines, Rotaxanes and Catenanes as artificial molecular machines, prototypes – linear motions in rotaxanes, an acid-base controlled molecular shuttle, a molecular elevator, an autonomous light-powered molecular motor

➢ Computational chemistry:-

▪ Introduction:-

- Computational chemistry is a branch of chemistry that uses computer simulation to assist in solving chemical problems.
- It uses methods of theoretical chemistry, incorporated into efficient computer programs, to calculate the structures and properties of molecules and solids.
- It is necessary because, apart from relatively recent results concerning the hydrogen molecular ion (dihydrogen caution, see references therein for more details), the quantum many-body problem cannot be solved analytically, much less in closed form.
- While computational results normally complement the information obtained by chemical experiments, it can in some cases predict hitherto unobserved chemical phenomena.
- It is widely used in the design of new drugs and materials.
- Examples of such properties are structure (i.e., the expected positions of the constituent atoms), absolute and relative (interaction) energies, electronic charge density distributions, dipoles and higher multipolar moments, vibrational frequencies, reactivity, or other spectroscopic quantities, and cross sections for collision with other particles.

▪ Ab Initio studies:-

- *Ab initio* methods are based entirely on quantum mechanics and basic physical constants.
- The programs used in computational chemistry are based on many different quantum-chemical methods that solve the molecular Schrödinger equation associated with the molecular Hamiltonian.
- Methods that do not include any empirical or semi-empirical parameters in their equations – being derived directly from theoretical principles, with no inclusion of experimental data – are called *ab initio methods*.

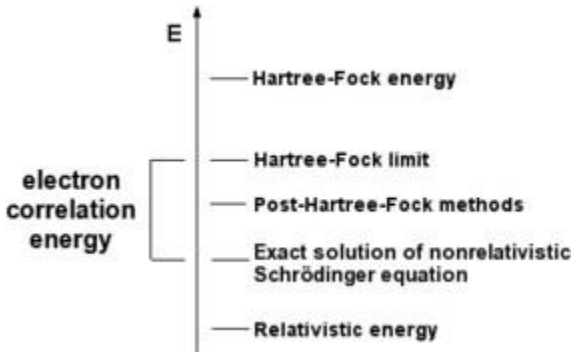


Fig: ab intio methods

- **Molecular switches: -** A molecular switch is a molecule that can be reversibly shifted between two or more stable states.
  - **characteristics of molecular motors and machines:-**
- **Molecular motors**:-
  - Molecular motors are natural (biological) or artificial molecular machines that are the essential agents of movement in living organisms.
  - In general terms, a motor is a device that consumes energy in one form and converts it into motion or mechanical work;
  - For example, many protein-based molecular motors harness the chemical free energy released by the hydrolysis of ATP in order to perform mechanical work.
  - In terms of energetic efficiency, this type of motor can be superior to currently available man-made motors.
  - One important difference between molecular motors and macroscopic motors is that molecular motors operate in the thermal bath, an environment in which the fluctuations due to thermal noise are significant.
- **Molecular machines**:-
  - A molecular machine, nanite, or Nano machine, is a molecular component that produces quasi-mechanical movements (output) in response to specific stimuli (input).
  - In biology, macromolecular machines frequently perform tasks essential for life such as DNA replication and ATP synthesis.
  - The expression is often more generally applied to molecules that simply mimic functions that occur at the macroscopic level.
  - The term is also common in nanotechnology where a number of highly complex molecular machines have been proposed that are aimed at the goal of constructing a molecular assembler.

- **Rotaxanes and Catenanes as artificial molecular machines:-**

- **Rotaxanes**:-
  - A rotaxane is a mechanically interlocked molecular architecture consisting of a "dumbbell shaped molecule" which is threaded through a "macro cycle" (see graphical representation).
  - The name is derived from the Latin for wheel (rota) and axle (axis).
  - The two components of a rotaxane are kinetically trapped since the ends of the dumbbell (often called stoppers) are larger than the internal diameter of the ring and prevent dissociation (unthreading) of the components since this would require significant distortion of the covalent bonds.

- **Catenanes as artificial molecular machines:-**
  - An artificial molecular machine consists of molecule or substituent components jointed together in a specific way so that their mutual displacements could be initiated using appropriate outside stimuli.
  - Such an ability of performing mechanical motions by consuming external energy has endowed these tiny machines with vast fascinating potential applications in areas such as actuators, manipulating atoms/molecules, drug delivery, molecular electronic devices, etc.
  - To date, although vast kinds of molecular machine archetypes have been synthesized in facile ways, they are inclined to be defined as switches but not true machines in most cases because no useful work has been done during a working cycle.

➢ Prototype:-

- A **prototype** is an early sample, model, or release of a product built to test a concept or process.
- It is a term used in a variety of contexts including semantics, design, electronics, and software programming.
- A prototype is generally used to evaluate a new design to enhance precision by system analysts and user.

Basic prototype categories:-

Prototypes explore different aspects of an intended design:

- A **Proof-of-Principle Prototype** serves to verify some key functional aspects of the intended design, but usually does not have all the functionality of the final product.
- A **Working Prototype** represents all or nearly all of the functionality of the final product.
- A **Visual Prototype** represents the size and appearance, but not the functionality, of the intended design.
- A **Form Study Prototype** is a preliminary type of visual prototype in which the geometric features of a design are emphasized, with less concern for color, texture, or other aspects of the final appearance.
- A **User Experience Prototype** represents enough of the appearance and function of the product that it can be used for user research.
- A **Functional Prototype** captures both function and appearance of the intended design, though it may be created with different techniques and even different scale from final design.

➢ Rotaxane:-

- A **rotaxane** is a mechanically interlocked molecular architecture consisting of a "dumbbell shaped molecule" which is threaded through a "macrocycle" .
- The name is derived from the Latin for wheel (rota) and axle (axis).
- The two components of a rotaxane are kinetically trapped since the ends of the dumbbell (often called stoppers) are larger than the internal diameter of the ring and prevent dissociation (unthreading) of the components since this would require significant distortion of the covalent bonds.

➢ An acid-base controlled molecular shuttle:-

- This paper describes the acid/base-mediated three-state translational isomerization of two [2]rotaxanes, each containing *N*-alkylaniline and *N*,*N*-dialkylamine centers as binding sites for threaded dibenzo[24]crown-8 units.
- Under neutral conditions, the dialkylamine unit predominantly recognized the crown ether component through cooperative binding of a proton; when both amino units were protonated under acidic conditions, both translational isomers were generated; the addition of a strong base caused aniline–crown ether interactions to dominate.
- The three states of the rotaxane featuring the 3,5-diphenylaniline terminus in its dumbbell-shaped component were accompanied by distinct absorptive outputs that were detectable using UV spectroscopy.

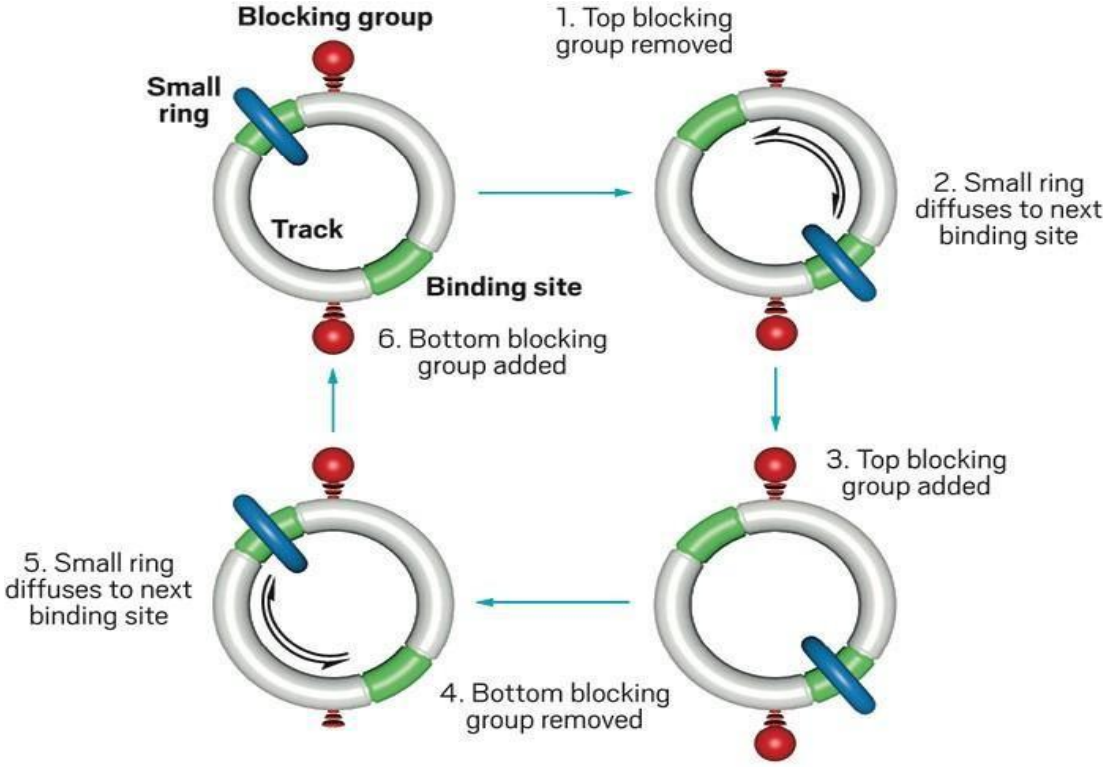
➢ A molecular elevator:-

- We report the incrementally staged design, synthesis, characterization, and operation of a molecular machine that behaves like a nano scale elevator.

- The operation of this device, which is made of a platform like component interlocked with a trifurcated riglike component and is only 3.5 nanometers by 2.5 nanometers in size, relies on the integration of several structural and functional molecular subunits.
- This molecular elevator is considerably more complex and better organized than previously reported artificial molecular machines.

➢ **An autonomous light-powered molecular motor:-**

- Molecular motor runs all by itself, without external intervention, on a tank of chemical fuel



Motor proteins are essential for moving muscles in animals and transporting molecules across cell membranes.

Researchers have now mimicked them by designing and creating the first synthetic motor that runs autonomously—without further intervention—on chemical fuel.

Mother Nature isn't easy to emulate, so an artificial chemically powered motor that works like a motor protein "is a major advance,"

Earlier non autonomous chemically powered motors required constant intervention they had to be fed a sequence of compounds to complete each operating cycle.