INTRODUCTION

Theoretical chemistry seeks to provide explanations to the chemical and physical observations of molecules. Theoretical chemistry includes the fundamental laws of physics Coulomb's law, Kinetic energy, Potential energy, the virial theorem, Planck's Law, Pauli exclusion principle and many others to explain and predict chemicalobserved phenomena.

In order to explain an observation one has to choose the "appropriate level of theory". For example, some theoretical methods (DFT) may not be appropriate to solve magnetic coupling or electron transitions properties. Instead, there are reports like Multireference configuration interaction (MRCI), which accurately and thoroughly explain the observed phenomena by means of the fundamental interactions.

Major components include quantum chemistry, the application of quantum mechanics to the understanding of valence, molecular dynamics, statistical thermodynamics and theories of electrolyte solutions, reaction networks, polymerization, catalysis, molecular magnetism and spectroscopy.

Quantum chemistry

The application of quantum mechanics or fundamental interactions to chemical and physico-chemical problems. Spectroscopic and magnetic properties are between the most frequently modelled.

Computational chemistry

The application of computer codes to chemistry, involving approximation schemes such as Hartree–Fock, post-Hartree–Fock, density functional theory,semiempirical methods (such as PM3) or force field methods. Molecular shape is the most frequently predicted property. Computers can also predict vibrational spectra and vibronic coupling, but also acquire and Fourier transform Infra-red Data into frequency information. The comparison with predicted vibrations supports the predicted shape.

Molecular modelling

Methods for modelling molecular structures without necessarily referring to quantum mechanics. Examples are molecular docking, protein-protein docking, drug design, combinatorial chemistry. The fitting of shape and electric potential are the driving factor in this graphical approach.

Molecular dynamics

Application of classical mechanics for simulating the movement of the nuclei of an assembly of atoms and molecules. The rearrangement of molecules within an ensemble is controlled by Van der Waals forces and promoted by temperature.

Molecular mechanics

Modeling of the intra- and inter-molecular interaction potential energy surfaces via potentials. The latter are usually parameterized from ab initio calculations.

Mathematical chemistry

Discussion and prediction of the molecular structure using mathematical methods without necessarily referring to quantum mechanics. Topology is a branch of mathematics that allows to predict properties of flexible finite size bodies like clusters.

Theoretical chemical kinetics

Theoretical study of the dynamical systems associated to reactive chemicals, the activated complex and their corresponding differential equations.

Cheminformatics (also known as chemoinformatics)

The use of computer and informational techniques, applied to crop information to solve problems in the field of chemistry.

Historically, the major field of application of theoretical chemistry has been in the following fields of research:

- Atomic physics: The discipline dealing with electrons and atomic nuclei.
- Molecular physics: The discipline of the electrons surrounding the molecular nuclei and of movement of the nuclei. This term usually refers to the study of molecules made of a few atoms in the gas phase. But some consider that molecular physics is also the study of bulk properties of chemicals in terms of molecules.
- Physical chemistry and chemical physics: Chemistry investigated via physical methods like laser techniques, scanning tunneling microscope, etc. The formal distinction between both fields is that physical chemistry is a branch of chemistry while chemical physics is a branch of physics. In practice this distinction is quite vague.
- Many-body theory: The discipline studying the effects which appear in systems with large number of constituents. It is based on quantum physics – mostly second quantization formalism – and quantum electrodynamics.

Hence, theoretical chemistry has emerged as a branch of research. With the rise of the density functional theory and other methods like molecular mechanics, the range of application has been extended to chemical systems which are relevant to other fields of chemistry and physics, including biochemistry, condensed matter physics, nanotechnology or molecular biology.

OPERATORS:

In physics, an operator is a function over a space of physical states to another space of physical states. The simplest example of the utility of operators is the study of symmetry (which makes the concept of a group useful in this context). Because of this, they are a very useful tool in classical mechanics. Operators are even more important in quantum mechanics, where they form an intrinsic part of the formulation of the theory.

OPERATORS IN QUANTUM MECHANICS:

The mathematical formulation of quantum mechanics (QM) is built upon the concept of an operator.

The wavefunction represents the probability amplitude of finding the system in that state. The terms "wavefunction" and "state" in QM context are usually used interchangeably.

Physical pure states in quantum mechanics are represented as unit-norm vectors (probabilities are normalized to one) in a special complex Hilbert space. Time evolution in this vector space is given by the application of the evolution operator.

Any observable, i.e., any quantity which can be measured in a physical experiment, should be associated with a self-adjoint linear operator. The operators must yield real eigenvalues, since they are values which may come up as the result of the experiment. Mathematically this means the operators must be Hermitian. The probability of each eigenvalue is related to the projection of the physical state on the subspace related to that eigenvalue. See below for mathematical details.

In the wave mechanics formulation of QM, the wavefunction varies with space and time, or equivalently momentum and time (see position and momentum space for details), so observables are differential operators.

In the matrix mechanics formulation, the norm of the physical state should stay fixed, so the evolution operator should be unitary, and the operators can be represented as matrices. Any other symmetry, mapping a physical state into another, should keep this restriction.

Basic Notations of Operator Algebra:

We already know that the operators:

$$\hat{x} \qquad \text{and} \qquad \hat{p} = -i\hbar\nabla$$

they are called "**fundamental operators**".

Many operators are constructed from $\hat{x}$ and $\hat{p}$; for example the **Hamiltonian** for a single particle:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x})$$

where $\hat{p}^2/2m$ is the K.E. operator and $\hat{V}$ is the P.E. operator. This example shows that we can **add** operators to get a new operator. So one may ask what other algebraic operations one can carry out with operators?

The product of two operators is defined by operating with them on a function.

Let the operators be $\hat{A}$ and $\hat{B}$, and let us operate on a function $f(x)$ (one-dimensional for simplicity of notation). Then the expression

$$\hat{A}\hat{B}f(x)$$

is a new function. We can therefore say, by the definition of operators, that $\hat{A}\hat{B}$ is an operator which we can denote by $\hat{C}$:

$$\hat{C} \text{ is the product of operators } \hat{A} \text{ and } \hat{B}.$$

The meaning of $\hat{A}\hat{B}f(x)$ should be that $\hat{B}$ is first operating on $f(x)$, giving a new function, and then $\hat{A}$ is operating on that new function.

Example: $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p} = -i\hbar d/dx$, then we have

$$\hat{A}\hat{B}f(x) = \hat{x}\hat{p}f(x)$$

We can of course also construct another new operator:

$$\hat{p}\hat{x}$$

Then, by definition of the operator product,

$$\hat{p}\hat{x}f(x)$$

means that $\hat{x}$ is first operating on $f(x)$ and then $\hat{p}$ is operating on the function $\hat{x}f(x)$.

Compare the results of operating with the products $\hat{p}\hat{x}$ and $\hat{x}\hat{p}$ on $f(x)$:

$$(\hat{x}\hat{p} - \hat{p}\hat{x})f(x) = -i\hbar\left(x\frac{df(x)}{dx} - \frac{d}{dx}(xf(x))\right)$$

and hence by the product rule of differentiation:

$$(\hat{x}\hat{p} - \hat{p}\hat{x})f(x) = i\hbar f(x)$$

and since this must hold for any differentiable function $f(x)$, we can write this as an **operator equation**:

$$\hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar$$

Thus we have shown that the operator product of $\hat{x}$ and $\hat{p}$ is **non-commuting.**

Because combinations of operators of the form

$$\hat{A}\hat{B} - \hat{B}\hat{A}$$

do frequently arise in QM calculations, it is customary to use a short-hand notation:

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

and this is called the **commutator** of $\hat{A}$ and $\hat{B}$ (**in that order!**).
If $[\hat{A}, \hat{B}] \neq 0$, then one says that $\hat{A}$ and $\hat{B}$ do not commute,
if $[\hat{A}, \hat{B}] = 0$, then $\hat{A}$ and $\hat{B}$ are said to commute with each other.
An operator equation of the form of

$$[\hat{A}, \hat{B}] = \text{something}$$

is called a **commutation relation.**

$$[\hat{x}, \hat{p}] = i\hbar$$

is the **fundamental** commutation relation.