

Foundation of Quantum Chemistry

ELECTRONIC STRUCTURE THEORY

What is Quantum Chemistry?

- Quantum mechanical principles applied to Chemistry
- Chemical systems (Atoms, Molecules, bulk...)
- Properties (Energetic, Spectral, Thermal...)
- Phenomena (Reaction or Interaction...)
- And much more...

It provides

1. Basis for understanding chemical bonding at the molecular level (association and dissociation of molecules)
2. Basis for understanding interaction between molecules (chemical reaction)
3. Basis for understanding interactions of molecules with em radiation (spectroscopy i.e. how to detect quantitatively any chemical species!)

Historical perspectives

- Planck's law : $E = h\nu$ [h -Planck's constant] (concept of quantum of (em) energy)
- Einstein's explanation of *Photoelectric Effect* (application of Planck's law)
- de Broglie's hypothesis : $\lambda = h/p$ (idea of matter waves)

Planck's law

Planck's relation for the energy released by material body at high temperature

$$E = h\nu \text{ [h-Planck's constant]}$$

The Black body radiations was difficult to explain by classical mechanics, so Max Planck gave this revolutionary idea of the release of energy by a material body at high T in light packets. The discreteness in the energy was extremely small (as the value of h is so small) but enough to be discrete and not continuous as was thought earlier.

This was the first idea of a quantum of energy.

Einstein's explanation of *Photoelectric Effect*

- Einstein came up with a brilliant explanation of the Photoelectric effect. To summarize he said that light (em radiation) itself consists of packets of energy now called photons. He gave the relation for the energy associated with em radiation whose frequency is ν ($E = h\nu$) and " h " was exactly the same as that of Planck.
- This was the year when Einstein was awarded Nobel Prize for one out of his three seminal works in Physics namely Photoelectric effect the other two being Theory of Special Relativity and Brownian motion.

de Broglie's hypothesis

Another important discovery by a french Physicist de Broglie was, the proposal of a relationship,

$$\lambda = h/p$$

which says that all material particles moving can be treated as matter with a certain wavelength λ , Here h is again the same constant as Planck's constant and this also gave fundamental importance to " h " in physics and chemistry through Schrödinger equation.

Schrödinger equation

- Conceptualization of above 3 ideas by Erwin Schrödinger

$$i \hbar \frac{\partial \Psi}{\partial t} = H \Psi \quad [\text{Time dependent}]$$

$$H \Psi = E \Psi \quad [\text{Time independent}]$$

- In Newtonian Mechanics, we make use of the relation $F = m \cdot a$ to describe the dynamics of objects. In order to solve the dynamics of atoms/molecules, these are used.

Schrödinger equation

- While solving the equation $H\Psi = E\Psi$, the Hamiltonian H can have various forms, Ψ corresponds to all possible solutions, E are the energies that one can observe.
- A Hamiltonian is not a Quantum Mechanical quantity, it is a classical quantity represented by total energy (KE+PE)

Schrödinger equation

- " H " The Hamiltonian (of whatever system we wish to study) \rightarrow The total energy of the system just as in classical expressions but in QM Systems, the momentum p is to be replaced by a derivative expression

$$p = -i \hbar \frac{\partial}{\partial x} \quad [\text{x component of momentum}]$$

$$p = -i \hbar \frac{\partial}{\partial \theta} \quad [\text{momentum about angle } \theta]$$

Here momentum is in terms of the derivative of the word used to define the classical momentum vector hence, derivative is an operator.

Schrödinger equation

Thus, Hamiltonian is an operator apart from being the total energy.

Ψ - wavefunction associated with the system and depends on coordinate and time.

- it can be a complex function
- does not have a physical interpretation

So, the interesting thing here is that we are told to solve an equation which we do not know and we arrive at a result which can not be interpreted physically.

Schrödinger equation

$$H \Psi = E \Psi \quad [\text{Here } \Psi \text{ does not necessarily have a physical meaning or interpretation}]$$

If Ψ is a complex then its complex conjugate is Ψ^* is such that its absolute square has a meaning

Therefore, the purpose is to find out the absolute square, i.e., square of $|\Psi| d\zeta = \Psi^* \Psi d\zeta$, Which has a meaning.

Thanks to Max Born!

Schrödinger equation

Physical Interpretation- It represents the probability of finding the system in a small space $d\zeta$ [Particle in a box, Hydrogen atom]

[When we make measurements of energy of a system in an experiment we get some values]

Experiments may measure other quantities also such as-

- Momentum of system in motion
- Angular momentum of a system moving around a point
- Electric or magnetic properties
- Molecular Structure
- Bond lengths etc

The basic idea

- To solve Schrödinger Equation $\hat{H}\Psi = E\Psi$
- Schrödinger Equation can only be solved exactly for simple systems.
 - Rigid Rotor, Harmonic Oscillator, Particle in a Box, Hydrogen Atom etc.
- For molecular system

$$\hat{H} = T_n + T_e + V_m + V_{ne} + V_{ee}$$

How to solve it? Wait....

The basic idea

- For more complex systems (i.e. many electron atoms/molecules) we need to make some simplifying assumptions/approximations and solve it numerically.
- This is what results in a rapidly growing field, "Computational Quantum Chemistry"
- As Computers are getting faster. Algorithms and programs are maturing.

Computational Quantum Chemistry

- Uses the results of **Quantum Chemistry** (solution of SWE) incorporated into efficient computer programs
- To calculate the structures and properties of molecules and solids.
- It can deal with system of a single molecule, a group of molecules, a liquid or solid.
- It calculates properties such as structure, relative energies, charge distributions, dipoles and multipole moments, vibrational frequencies, reactivity and other spectroscopic quantities, etc.....

Solving time independent part of $\hat{H}\Psi = E\Psi$

- For molecular system

$$\hat{H} = -\frac{\hbar^2}{2} \sum_r \frac{1}{m_r} \nabla_r^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_r \sum_{s>r} \frac{Z_r Z_s e^2}{r_{rs}} - \sum_r \sum_i \frac{Z_r e^2}{r_{ir}} + \sum_{i>j} \sum_j \frac{e^2}{r_{ij}}$$

- Strategy

1. Born-Oppenheimer Approximation, leading to the concept of *potential energy surface*.
2. The method, expansion of the many-electron wave function in terms of Slater determinants.
3. The basis set, representation of Slater determinants by molecular orbitals, which are linear combinations of atomic-like-orbital functions.

Born-Oppenheimer Approximation

- The wave-function of the many-electron molecule is a function of electron and nuclear coordinates: $(E(R, r))$ (R =nuclear coords, r =electron coords).
- The motions of the electrons and nuclei are coupled.
- However, the nuclei are much heavier than the electrons $m_p \approx 2000 m_e$
- And consequently nuclei move **much** more slowly than do the electrons ($E=1/2mv^2$). To the electrons the nuclei appear fixed.
- Born-Oppenheimer Approximation: to a high degree of accuracy we can separate electron and nuclear motion: $(E(R, r)) = (E_e(r; R)) (E_N(R))$

$$\mathbb{E} = \mathbb{E}_{el}(r; R) \times \mathbb{E}_N(R)$$

- Electronic Schrödinger Equation

$$\hat{H}_{el} \mathbb{E}_{el}(r; R) = E_{el} \mathbb{E}_{el}(r; R)$$

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_r \sum_i \frac{Z_r e^2}{r_{ir}} + \sum_{j>i} \sum_{r_{ij}} \frac{e^2}{r_{ij}}$$

- Idea of Potential energy surface

$$U(R) = E_{el} + V_{NN}$$

$$V_{NN} = \sum_{r>s} \sum_{r_s} \frac{Z_r Z_s e^2}{r_{rs}}$$

- Nuclear Schrödinger Equation

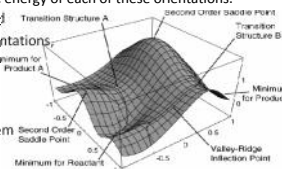
$$\hat{H}_N \mathbb{E}_N(R) = E_N \mathbb{E}_N(R)$$

$$\hat{H}_N = -\frac{\hbar^2}{2} \sum_r \frac{1}{m_r} \nabla_r^2 + U(R)$$

- Above equation can be solved by idea of Potential energy surface

What is a PES?

- The "(hyper)surface" name comes from the fact that the total energy of an atom arrangement can be represented as a curve or (multidimensional) surface, with atomic positions as variables.
- To model chemical reactions and interactions in simple chemical and physical systems.
- Must be created to take into account every possible orientation of the reactant and product molecules and the electronic energy of each of these orientations.
- Typically, the electronic energy is obtained for each of tens of thousands of possible orientations, and these energy values are then fitted numerically to a multidimensional function. The accuracy of these points depends upon the level of theory used to calculate them.



The method

- Why is it not possible to solve SWE *exactly*?

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_r \sum_i \frac{Z_r e^2}{r_{ir}} + \sum_{j>i} \sum_{r_{ij}} \frac{e^2}{r_{ij}}$$

The electron-electron interaction is the culprit!

- Approximating ψ

expansion of ψ in a basis of Slater determinants

$$\mathbb{E}_{el} = \sum_i d_i \Phi_i = d_0 \Phi_0 + d_1 \Phi_1 + d_2 \Phi_2 + \dots$$

Slater determinant

$$\Phi_0 = \frac{1}{\sqrt{N!}} \begin{vmatrix} w_1 \alpha(1) & w_1 \beta(1) & w_2 \alpha(1) \dots & w_M \alpha(1) \\ w_1 \alpha(2) & w_1 \beta(2) & w_2 \alpha(2) \dots & w_M \alpha(2) \\ \dots & \dots & \dots & \dots \\ w_1 \alpha(N) & w_1 \beta(N) & w_2 \alpha(N) \dots & w_M \alpha(N) \end{vmatrix}$$

- α/β are spin-functions (spin-up/spin-down)
- w_i are spatial functions (molecular orbitals)
- $w_i \alpha$ and $w_i \beta$ are called spin-orbitals
- Slater determinant gives proper anti-symmetry (Pauli Principle)

The basis set

- Slater determinants are built from molecular orbitals, but how do we define these orbitals?
- Linear Combination of Atomic Orbitals (LCAO) Molecular Orbitals

$$w_i = \sum_k c_{ki} t_k$$

- Molecular orbital coeffs, c_{ki} determined in SCF procedure
- The basis functions, t_i , are atom-centered functions that mimic solutions of the H-atom (s orbitals, p orbitals,...)
- The larger the expansion, the more accurate and expensive the calculations become.