
Chapter 2

Theoretical Insight

The theoretical background for the quantification of electronic energy, charge density has been discussed. Theoretical settings for the calculation of potential energy surface of a reaction and prediction of reactivity of a molecule have been conferred here.

2.1 Introduction

The theoretical foundation for modern chemistry was laid more than 80 years ago. Today it becomes possible to use this knowledge for understanding how electrons, molecules and atoms interact. A reaction mechanism is the step by step sequence of elementary reactions by which overall chemical change occurs. The study of reaction mechanisms is important for many reasons including the understanding and controlling chemical reactions. It is the theoretical analysis which makes possible to study each step of a reaction by exact computation of electronic structure parameters such as electronic energy, charge density and potential energy surface (PES). Theory plays an important role in the development of chemical concepts. An example is the idea of a transition state for a reaction. Molecular modeling is simply an art of representing molecular structures numerically and simulating their behavior with the equations of quantum and classical physics. The density functional theory (DFT) has strongly influenced the evolution of quantum chemistry. For its development, Prof. Walter Kohn was awarded the Nobel Prize in 1998. It is presently the most successful and also the most promising approach to compute the electronic structure of matter. Its applicability ranges from atoms, molecules and solids to nuclei and quantum, classical fluids.

This chapter gives a brief introduction to density functional theory along with a special deliberation to Conceptual density functional theory. Theoretical condition for the calculation of transition state has also been conferred using Born-Oppenheimer approximation.

2.2 Overview on Hartree-Fock and Post-Hartree-Fock Methods

Before going deep into DFT it will be useful to pay a little endeavor in discussing about the wave function based methods. The fundamental equation of quantum mechanics which describes any given chemical system is the Schrödinger equation. To get a physical property of a system from Schrödinger equation we have to solve it. In 1920 Hartree and Fock gave a solution for the Schrödinger equation of many electron system based on variational principle. They assumed that the exact N-body wave function of the system can be approximated by single Slater determinant of N spin orbitals. One can get Hartree-Fock (HF) wave function and energy of the

system by solving N-coupled equations for N spin orbitals using variational principle. The main short coming of the HF method is that it assumes the electrons are moving independently; i.e. they have no correlation. That is the main reason for poor performance of HF method. Taking HF as the starting point, several post-HF methods such as configuration interaction or coupled cluster methods are introduced. These post-HF methods provide eminent ways of recovering the correlation missing from HF method. Although, Post-HF methods are more accurate, they are not so popular due to their resource intensive nature.¹

2.3 Density Functional Theory

Density functional theory (DFT) has allowed studying the physical properties and reaction energetics of compounds containing up to 100 or more heavy atoms. DFT provided a sound basis for the development of computational strategies for obtaining information about the energetic, structure, and properties of atoms and molecules at much lower computational cost than commonly used ab initio methods like Hartree-Fock. This makes DFT quite popular for calculating organic molecules. Computational efficiency and accuracy are the main benefits of DFT approaches. It is a powerful methodology for chemical simulation where the energy of the systems can be defined in terms of its electron probability density (ρ), that is, in DFT formalism the electronic energy E is treated as the functional of the electron density $E(\rho)$. Modern DFT based on two basic theorems proposed by Hohenberg and Kohn in 1964.² These are as follows:

Theorem I

For any system of interacting particles in an external potential $v_{ext}(r)$, the density is uniquely determined (in other words, the external potential is a unique functional of the density).

Theorem II

A universal functional for the energy $E[\rho]$ can be defined in terms of the density. The exact ground state is the global minimum value of this functional.

2.4 The Energy Functional

The energy functional contains three terms – the kinetic energy, the interaction with the external potential and the electron-electron interaction and can be written in the following form

$$E[\rho] = T[\rho] + V_{ext}[\rho] + V_{ee}[\rho]. \quad (2.1)$$

The interaction with the external potential is expressed as

$$V_{ext}[\rho] = \int \hat{V}_{ext} \rho(r) dr. \quad (2.2)$$

The kinetic and electron-electron functionals are unknown and they have a common form for every system. Direct minimization of the energy would be possible if good approximations to these functionals could be found.

These kinetic and electron-electron functional can be approximated by a popular approach due to Kohn and Sham.³ The Kohn-Sham system is composed of N non-interacting, thus fictitious, electrons which can be described by a single determinantal wave function in N “orbitals” ϕ_i . In this system the kinetic energy and electron density are known exactly from the orbitals;

$$T_s[\rho] = -\frac{1}{2} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle \quad (2.3)$$

Here the suffix emphasizes that this is not the true kinetic energy but is that of a system of non-interacting electrons, which reproduce the true ground state density

$$\rho(r) = \sum_i^N |\phi_i|^2 \quad (2.4)$$

The acceptance of the methodology emerges from the construction of the density explicitly from a set of orbitals. This ensures that it can be constructed from any asymmetric wave function. The electron – electron interaction term in the energy functional is distinctly composed of the classical Coulomb interaction, which is known as the Hartree energy. This can be written in terms on density as

$$V_H[\rho] = \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2. \quad (2.5)$$

Here we introduce *exchange – correlation functional*

$$E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - V_H[\rho]). \quad (2.6)$$

E_{xc} is simply the sum of the error made in using a non – interacting kinetic energy and the error made in treating the electron – electron interaction classically.

Now, the expression for the energy functional can be written as

$$E[\rho] = T_s[\rho] + V_{ext}[\rho] + V_H[\rho] + E_{xc}[\rho] \quad (2.7)$$

The non-interacting orbitals, from which the density was built in equation 2.7, satisfy the following set of equations

$$\left[-\frac{1}{2} \nabla^2 + v_{ext}(r) + \int \frac{\rho(r')}{|r - r'|} dr' + v_{xc}(r) \right] \phi_i(r) = \varepsilon_i \phi_i(r). \quad (2.8)$$

Here we have introduced a local potential which is the functional derivative of the exchange correlation energy with respect to the density,

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho}. \quad (2.9)$$

This set of non-linear equations (the Kohn-Sham equations) describes the behavior of non-interacting “electrons” in an effective local potential. For an exact local potential, the “orbitals” yield the exact ground state density via equation 2.4 and exact ground state energy via equation 2.6.

2.5 Born-Oppenheimer approximation, potential energy surface and transition state

The Schrodinger equation treats electrons and nuclei in the same way but in the Born-Oppenheimer approximation we make a compromise between classical and quantum mechanics. At this circumstance, we fairly accurate the nuclei (which are about 1000 times heavier than the electrons) as stationary classical point like particles. Thus, instead of solving the Schrodinger equation for a system of mobile electrons and nuclei, one solves the equation for the electronic motion for different fixed nuclear positions or conformations.

The Schrodinger equation for a molecule is given by

$$\hat{H}\psi(r, R) = (\hat{T}_e + \hat{T}_n + V_{en} + V_{ee} + V_{nn}) \psi(r, R) = E\psi(r, R) \quad (2.10)$$

Since the electronic and the nuclear motions are assumed to be separable we can write

$$\psi(r, R) = \psi_R(r)\varphi(R) \quad (2.11)$$

where $\psi_R(r)$ implies that the electronic wave function depends functionally on r and parametrically on R . For simplicity we shall write ψ_e for $\psi_R(r)$ and ψ_n for $\varphi(R)$. Let us define ψ_e as a function which satisfies the electronic Schrodinger equation,

$$\hat{H}_e\psi_e = (\hat{T}_e + V_{en} + V_{ee}) = E_e\psi_e \quad (2.12)$$

Substituting $\psi(r, R) = \psi_e\psi_n$ in equation 2.10 and writing the expressions for \hat{T}_e and \hat{T}_n explicitly we get

$$\left(-\sum_{\mu} \frac{\nabla_{\mu}^2}{2} - \sum_{\mu} \frac{\nabla_A^2}{2m_A} + V_{en} + V_{ee} + V_{nn}\right) \psi_e\psi_n = E\psi_e\psi_n \quad (2.13)$$

Now

$$-\sum_{\mu} \frac{\nabla_{\mu}^2}{2} (\psi_e \psi_n) = -\psi_n \sum_{\mu} \frac{\nabla_{\mu}^2}{2} \psi_e \quad (2.14)$$

$$-\sum_A \frac{\nabla_A^2}{2m_A} (\psi_e \psi_n) = -\sum_A \frac{1}{2m_A} (\psi_e \nabla_A^2 \psi_n + \psi_n \nabla_A^2 \psi_e + 2\nabla_A \psi_e \cdot \nabla_A \psi_n) \quad (2.15)$$

Using equations 2.14 and 2.15 in 2.13 gives

$$\begin{aligned} & -\psi_n \sum_{\mu} \frac{\nabla_{\mu}^2}{2} \psi_e - \left[\sum_A \frac{1}{2m_A} (\psi_n \nabla_A^2 \psi_e + 2\nabla_A \psi_e \cdot \nabla_A \psi_n) \right] - \psi_e \sum_A \frac{\nabla_A^2}{2m_A} \psi_n + \\ & (V_{en} + V_{ee} + V_{nn}) \psi_e \psi_n = E \psi_e \psi_n \end{aligned} \quad (2.16)$$

The square-bracketted terms of the above equation (2.16) describe the coupling of electronic and nuclear motion. These terms are neglected in the BO approximation. Dividing the remaining terms in this equation by ψ_n we gets

$$-\frac{\psi_e}{\psi_n} \sum_A \frac{\nabla_A^2}{2m_A} \psi_n + \left[-\sum_{\mu} \frac{\nabla_{\mu}^2}{2} + V_{ee} + V_{en} \right] \psi_e - E \psi_e + V_{nn} \psi_e = 0 \quad (2.17)$$

The second term in this equation is $\widehat{H}_e \psi_e$ (see equation 2.12). Writing $E_e \psi_e$ for this term and multiplying by $\frac{\psi_n}{\psi_e}$ one gets

$$\left(-\sum_A \frac{\nabla_A^2}{2m_A} + E_e + V_{nn} \right) \psi_n = E \psi_n \quad (2.18)$$

$$\text{or } \left(-\sum_A \frac{\nabla_A^2}{2m_A} + E(R) \right) \psi_n = E \psi_n \quad (2.19)$$

where $E(R) = E_e + V_{nn}$.

In the frame work of the BO approximation the solution of equation 2.10 consists of two steps. First, equation 2.12 is solved for various nuclear conformations to obtain E_e . Adding V_{nn}

to it we get $E(R)$ as a function of R . Then a suitable analytical expression for $E(R)$ is substituted in equation 2.19. Solution of this equation gives the total energy of the molecule. For a diatomic molecule, R is the internuclear distance and for a polyatomic molecule, R includes all possible internal coordinates (bond lengths, bond angles and dihedral angles). A plot of $E(R)$ vs R is usually called a potential energy curve (for a diatomic molecule) or a multi-dimensional potential energy surface (for a poly atomic molecule).

Since for polyatomic molecule, the potential energy E is a function of n number of internal coordinates [where n is equal to $(3N-5)$ or $(3N-6)$] so we can write

$$E = f(q_1, q_2, \dots, q_n). \quad (2.20)$$

The most interesting points on PES's are the stationary points (minima and saddle points) which occur when first partial derivative of the energy with respect to each geometric parameter is equal to zero

$$\text{i.e. } \frac{\partial E}{\partial q_1} = \frac{\partial E}{\partial q_2} = \dots = \frac{\partial E}{\partial q_n} = 0 \quad (2.21)$$

Minima and maxima can be distinguished simply by second derivatives. Local energy minima (reactants and products) correspond to

$$\frac{\partial^2 E}{\partial q^2} > 0 \quad (2.22)$$

for all q .

Transition state corresponds to

$$\frac{\partial^2 E}{\partial q^2} > 0 \quad (2.23)$$

for all q except along the reaction coordinate and

$$\frac{\partial^2 E}{\partial q^2} < 0 \quad (2.24)$$

along the reaction coordinate.

2.6 Conceptual Density Functional Theory

Conceptual DFT does not imply the other branches of DFT. It concentrates on the extraction of chemically relevant concepts and principles from DFT. Conceptual DFT provides a very convenient framework for the discussion of chemical reactivity. A series of global and local quantities, the so called reactivity descriptors or indices, have been introduced to describe the extent of the response of a molecular system toward perturbations in either its number of electrons, N , its external potential, $v(r)$, or both.⁴ An important example of these reactivity indices is the Fukui function, introduced by Parr and Yang,⁵ defined as the response of the system's electron density $\rho(r)$ due to a perturbation in its total number of electrons N at a constant external potential $v(r)$. Due to the discontinuities in slope for the $\rho(r)$ versus N curve,⁶ three different types of Fukui functions can be introduced, representing the case of a nucleophilic $f^+(r)$, electrophilic $f^-(r)$, and a neutral (radical) attack $f^0(r)$:

$$f^+(\vec{r}) = \left(\frac{\delta\rho(r)}{\delta N}\right)_{v(r)}^+ \approx \rho_{N+1}(\vec{r}) - \rho_N(\vec{r}) \approx \rho_{LUMO}(\vec{r}) \quad (2.25)$$

$$f^-(\vec{r}) = \left(\frac{\delta\rho(r)}{\delta N}\right)_{v(r)}^- \approx \rho_N(\vec{r}) - \rho_{N-1}(\vec{r}) \approx \rho_{HOMO}(\vec{r}) \quad (2.26)$$

$$f^0(\vec{r}) = \frac{1}{2}(f^+ + f^-) \approx \frac{1}{2}(\rho_{N+1}(\vec{r}) - \rho_{N-1}(\vec{r})) \quad (2.27)$$

where $\rho_{N+1}(r)$, $\rho_N(r)$, $\rho_{N-1}(r)$ are the electron densities of the $N+1$, N , $N-1$ electron system respectively, all obtained at the geometry of the N electron system, due to the fact that the derivative is taken at a constant external potential. However in chemistry it is customary to work with properties associated with atoms and functional groups in the molecule. In this context, a useful approximation to describe the site reactivity is given by the condensed to atom Fukui indices by using an atomic charge partitioning scheme.⁷

$$f_k^+ \approx N_k(N+1) - N_k(N) \quad (2.28)$$

$$f_k^- \approx N_k(N) - N_k(N-1) \quad (2.29)$$

$$f_k^0 \approx \frac{1}{2}(N_k(N+1) - N_k(N-1)) \quad (2.30)$$

where $N_k(N+1)$, $N_k(N)$ and $N_k(N-1)$ represent the electron populations on atom k in the $N+1$, N and $N-1$ electron system.

For an N -electron system with external potential $v(r)$ and total energy E , Parr et al. showed that the electronegativity⁸ could be identified as the negative of the electronic chemical potential μ :

$$\chi = -\mu = -\left(\frac{\delta E}{\delta N}\right)_{v(r)} \approx -\frac{I+A}{2} \quad (2.31)$$

Where I and A are the vertical ionization energy and electron affinity, respectively.

Chemical hardness and softness were introduced by Pearson⁹ in 1963 when he was studying and classifying Lewis acid and base interactions. He formulated the hard – soft acids bases (HSAB) principle “hard acids prefer to bond to hard bases and soft acids prefer to interact with soft bases”.⁹ In 1983, Parr and Pearson proposed a quantitative definition of this hardness:¹⁰

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \approx -\frac{I-A}{2} \quad (2.32)$$

measuring the system’s resistance toward charge transfer.

The softness S is defined as the inverse of the hardness:¹¹

$$S = \frac{1}{2\eta} \quad (2.33)$$

The local counterpart of the softness, the local softness, was introduced by Parr and Yang as^{11,12}

$$s(r) = \left(\frac{\delta \rho(r)}{\delta \mu}\right)_{v(r)} = \left(\frac{\delta \rho(r)}{\delta N}\right)_{v(r)} \left(\frac{\delta N}{\delta \mu}\right)_{v(r)} = Sf(r) \quad (2.34)$$

One can interpret the reaction ability toward soft reagents of the the different parts of the molecules with the condensed form of the local softness, written as

$$s_k^i = Sf_k^i \quad (2.35)$$

Where i equals to either +, -, or 0 depending on whether the system undergoes a nucleophilic, electrophilic, or radical attack.

2.7 References and notes

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