

Chapter 1

Introduction

Representing a multitude of apparently disjoint phenomena in terms of a few parameters has been a widely – shared goal for all scientists. Two such key parameters in the chemical literature are electronegativity and hardness. Pauling [1] was the first person to introduce the concept of electronegativity in chemistry. His definition of electronegativity, viz. “the power of an atom in a molecule to attract electrons to itself”, has been proved useful in correlating various fields of chemical knowledge and experience [2]. Not many chemists paid attention to the concept of electronegativity because of its empirical nature as is discernible from several definitions [3-29] of electronegativity until very recently Parr et al. [54] provided with a rigorous theoretical definition, within the density functional theory, through its correlation with chemical potential. A quantum – thermodynamic definition had also been proposed earlier by Gyftopoulos and Hatsopoulos [15].

Among various electronegativity scales, Pauling [1] and Mulliken [3] scales have been popular for a very wide cross – section of chemists. It is apparent from Pauling’s definition of electronegativity that it is not the property of the isolated atom but it depends on the molecular environment in which the atom is in. Pauling had given his relative electronegativity scale based on the thermochemical data. He argued that any heteronuclear species would be more stable than their homonuclear counterparts owing to the fact that the corresponding electronegativity difference would stabilise the molecule by ionic – covalent resonance energy. Unlike Pauling scale, Mulliken scale is the absolute one because it depends on fundamental energy values for isolated atoms. Mulliken defined the electronegativity as the average of ionisation potential and electron affinity of the isolated atom. This definition is important because it has a bearing in the modern density functional definition [54] of electronegativity. Other methods consider

electronegativity to be some function, e.g. energy, force, etc., of size and charge. Allred and Rochow [5] defined the electronegativity as the electrostatic force exerted by the valence electrons while Sanderson [12] defined it in terms of relative electron density.

A promising new scale has been suggested by Allen [25] who considers the electronegativity to be the third dimension (energy) in the periodic table, the other two being the atomic number and the number of shells respectively. In this spectroscopic scale, the electronegativity is defined as average one - electron energy of the valence - shell electrons for the isolated atoms in their ground states. These values match very well with Pauling [1] and Allred - Rochow [5,6] values and have provided chemically meaningful bond polarity values [30] between atoms in a molecule. Considering these aspects this scale is considered [25,30] to be "the first quantitative quantum mechanical realisation of Pauling electronegativity scale".

So far we have been considering the electronegativity of atoms either in the free state or in a molecular environment. The electronegativity of the molecule from the constituent atoms is generally obtained by taking the geometric mean. The genesis of this calculation is based on Sanderson's principle [31] which states that when a molecule is formed from atoms the electronegativities get equalised and the final value of the molecular electronegativity is given by the geometric average of the electronegativities of the individual atoms [32]. Sanderson's principle has been endorsed by other workers [33,34] and has also been modified to include external potential effects [35]. The importance of electrostatic interaction between atoms and their influence on atoms in a molecule has also been studied by others [36-38]. An important outcome of these studies is the idea of electronegativity equalisation in terms of the harmonic mean [35] of the valence state atom's electronegativities in a molecule.

In studying a variety of acid - base chemical reactions, Pearson [39-44] understood the necessity of a second parameter apart from the electronegativity. He [39] introduced the concepts of hardness and softness for this purpose and categorized different acids and bases based on their properties as follows. (i) Acids, the acceptors of electrons, are termed as hard if they do not have easily - excited outer electrons and have small sizes and high positive charges; otherwise they are soft acids. (ii) Bases, the donors of electrons, are called hard if they have low polarizabilities, high electronegativity

values, are hard to oxidize and associated with empty orbitals of high energy; other bases are soft.

The importance of this nomenclature is in the hard and soft acids and bases principle, popularly known as HSAB principle [39]. It states that “Hard acids prefer to react with hard bases and soft acids prefer to react with soft bases”. This principle is based on both thermodynamic and kinetic stability and accordingly helped classifying a wide variety of chemical facts.

In this thesis we try to present the physical basis of concepts like chemical hardness and electronegativity within density functional theory. In this chapter we discuss density functional theory as well as the concepts of chemical potential, global and local hardness, Fukui function etc.

An introduction to density functional theory (DFT)

Formulation of the many - particle problem in the single – particle framework demands the replacement of the many – particle wavefunction by a suitable quantity of at most three variables. Single – particle density $\rho(\vec{r})$ is a candidate [45] for the same and for a normalised $|\psi\rangle$ of an N – electron system it is defined as

$$\rho(\vec{r}) = N \sum_s \int \psi^*(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) d\vec{r}_2 \dots d\vec{r}_N \quad (1.1)$$

where \vec{x}_i stands for both space and spin coordinates for the i – th electron. Density functional theory [46-48] attempts to use $\rho(\vec{r})$ as the fundamental variable of an electronic structure theory for different many – electron systems encompassing atoms, molecules and solids. The single – particle density $\rho(\vec{r})$ may get the status similar to that of the many – particle wave – function $\psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)$ only if the former contains almost all the informations obtainable from the latter. At least for the ground state or the lowest state of a given symmetry, this has been proved to be true by Hohenberg and Kohn [48] in terms of their following important theorems:

(i) The nondegenerate ground state of an N - electron system moving under the influence of their mutual coulomb repulsion and a static external single – particle

potential $v(\vec{r})$, arising, say, from a set of nuclei is completely characterised by $\rho(\vec{r})$, i.e. $v(\vec{r})$, ψ and hence all ground – state properties of the system are unique functionals of the density. For studying time – dependent situations [50,51] and excited states [52,55], one needs to know the current density $\vec{j}(\vec{r},t)$ which is obtainable from the continuity equation,

$$\frac{\partial \rho(\vec{r},t)}{\partial t} + \nabla \cdot \vec{j}(\vec{r},t) = 0. \quad (1.2)$$

(ii) For a given external potential, the energy functional assumes a minimum value for the true density. Therefore, the variational minimisation of the energy functional $E[\rho]$ (first theorem allows one to write E in terms of ρ alone) with respect to the trial density, conserving the total number of particles, may be regarded as an alternative to the usual Rayleigh – Ritz variational scheme in wavefunction – based quantum mechanics. In other words, the ground state density (and hence all other quantities including the energy) is obtainable through minimisation of $E[\rho]$ with respect to ρ subject to the following normalisation condition,

$$\int \rho(\vec{r}) d\vec{r} = N \quad (1.3)$$

as a constraint, i.e. using the stationary condition,

$$\delta \{E[\rho] - \mu \int \rho(\vec{r}) d\vec{r}\} = 0 \quad (1.4)$$

or equivalently, in terms of the familiar Euler – Lagrange equation,

$$\frac{\delta E[\rho]}{\delta \rho} - \mu = 0 \quad (1.5)$$

where μ is a Lagrange multiplier and has been interpreted as chemical potential [21] or the electronegativity which measures the escaping tendency of an electron cloud. Therefore, density functional theory is an electronic structure theory of ground (equilibrium) electronic states in which the electronegativity of chemistry plays the similar role in density – based variational principle as being played by energy in usual variational scheme in wavefunction based quantum mechanics. This clearly indicates that the density functional theory can describe the chemistry well.

Problem comes in implementing the variational technique, starting from the Euler eq. (1.5), because the Hohenberg – Kohn theorem being merely an existence theorem

suggests nothing regarding the functional form for $E[\rho]$ and one tries to decompose it and to characterize the components whose forms are known. Writing $E[\rho]$ as [54]

$$E[\rho] = F[\rho] + \int v(\vec{r})\rho(\vec{r})d\vec{r} \quad (1.6)$$

where $F[\rho]$ is a universal functional comprising kinetic and electron – electron interaction energies and, thus, can again be decomposed as

$$F[\rho] = G[\rho] + \frac{1}{2} \iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}'. \quad (1.7)$$

In eq. (1.7) the functional $G[\rho]$ consists of kinetic and exchange – correlation energy functionals. Therefore, the total energy functional can be written as

$$E[\rho] = \int v(\vec{r})\rho(\vec{r})d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' + T[\rho] + E_{xc}[\rho]. \quad (1.8)$$

Exact forms for $T[\rho]$ and $E_{xc}[\rho]$ are not known. Since $T[\rho]$ dominates over $E_{xc}[\rho]$, both locally and globally, the construction of a proper kinetic energy functional with acceptable local and global behaviour as well as the correct functional derivative has been considered [54] and the exchange – correlation energy functional and their subsequent refinement provide better forms for $E[\rho]$ and hence better densities from the solution of the Euler eq. (1.5).

There is another approach where in the spirit of Hartree theory, one considers a system of N non – interacting fermions moving under a static effective self – consistence one – body potential $v_{eff}(\vec{r})$ and accordingly the Euler – Lagrange equation becomes

$$\frac{\delta T[\rho]}{\delta \rho} + v_{eff}(\vec{r}) = \mu \quad (1.9)$$

where,

$$v_{eff}(\vec{r}) = v(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \frac{\delta E_{xc}[\rho]}{\delta \rho}. \quad (1.10)$$

Eq. (1.9) transforms into a set of one – particle Hartree – like equations,

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(\vec{r}) \right] \phi_i = \epsilon_i \phi_i \quad (1.11)$$