Chapter 10
On the Method of the Determination of the Global Hardness of Atoms and Molecules

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ABSTRACT

In this chapter, the authors have discussed the time evolution of the concepts and various scales for the determination of the global hardness of atoms and molecules. The chapter also attempts to understand the physical basis and operational significance of the concept—global hardness. The physical hardness was introduced and theorized by condensed matter physicists. The chemical hardness was introduced by chemists to generalize and rationalize the HSAB principle. We have tried to establish that the physical hardness and the chemical hardness with evolution of time have converged to one and the same general principle—the hardness.

Since, the hardness is a conceptual hypothesis only and not observable; there is no possibility of its quantum mechanical evaluation. Any attempt of modeling this abstract semiotic representation for the purpose of developing some mathematical algorithms and to convert it into theoretical quantities of cognitive representations, it is required that the hardness should be reified in terms of the physico-chemical behavior of such conundrums goaded by the quantum mechanical principles. Some scales of measurement of hardness are introduced with the evolution of time.

DOI: 10.4018/978-1-4666-1607-3.ch010
INTRODUCTION

The hardness is an important conceptual constructs of chemistry and physics. It has equal rank and status with other two very important conceptual constructs viz. atomic radius and the electronegativity. The importance of the hypothetical constructs is self evident from the statement that, without the concept and operational significance of radius, hardness and electronegativity, chemistry and many aspects of condensed matter physics, become chaotic and the long established unique order in chemico-physical world would be disturbed. The notion of hardness was first introduced by Mulliken (1952) when he pointed out that the ‘Hard’ and ‘Soft’ behavior of various atoms, molecules and ions can be conceived during acid-base chemical interaction. Soon after Mulliken’s classification, the terms “hardness” and “softness” were in the glossary of conceptual chemistry and implicitly signified the resistance towards the deformability of atoms, molecules and ions under small perturbation usually developed during the event of chemical reaction. Thereafter, Pearson (1963) and Klopman (1964) tried to systematize and rationalize this intrinsic property of atoms and molecules. Pearson (1963) qualitatively classified molecules, atoms and ions in three classes, hard, soft and borderline- known as the HSAB principle and Klopman (1964) had drawn a link to Hard –Soft behavior with the HOMO-LUMO gap of the frontier orbital theory.

It is unequivocal that the hardness as conceived in chemistry fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation generated during the process of the chemical reaction. Thus, the general operational significance of the hard-soft behavior of a chemical species may be understood in the following statement. If the electron cloud is strongly held by the nucleus, the chemical species is ‘hard’ but if the electron cloud is loosely held by the nucleus, the system is ‘soft’(Klopman, 1964; Pearson, 1963).

The quest for the theoretical basis of the hardness and softness of atoms and molecules has created such a surge of fundamental research in chemistry that it gave birth of a new branch of density functional based theoretical science known as ‘Conceptual Density Functional Theory, CDFT’ (Geerlings, Proft, & Langenaeker 2003).


It is important to mention here some outstanding fundamental works of Putz and his coworkers (Putz et al 2003,2005,2006,2007,2008,2009,2010) on electronegativity and hardness and their usefulness for the theoretical prediction of several physicochemical properties-like the fundamentals of chemical bonding and aromaticity. It is shown that the aromaticity of peripheral topological path may be well described by superior finite difference schemes of electronegativity and chemical hardness indices in certain calibrating conditions.

THE PHYSICAL HARDNESS

The materials engineers have used for centuries the legend “hardness” to describe mechanical stability (Gilman 1997). In solid mechanics, hardness means the resistance to deformation, both elastic and plastic. The particular properties are the bulk modulus which measures the resistance to elastic volume changes, the shear modulus which