

*Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth*

## CHEMICAL HARDNESS: QUANTUM OBSERVABLE?

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**ABSTRACT.** The question whether chemical hardness may be regarded as ordinary quantum observable is responded in negative employing the second quantification within fermionic Fock space.

**Keywords:** *annihilation and creation particle operators, valence energy, electronic density, ionization and affinity energies*

### INTRODUCTION

In modern quantum chemistry the chemical reactivity is conceptualized throughout specific indices, among which the chemical hardness stands a pre-eminent one, often seen as a companion of the electronegativity [1,2]. However, the phenomenological and analytical definitions of chemical hardness together with its principles, i.e. hard and soft-acids and bases HSAB and maximum hardness principles MHP, are systematically presented within the density functional theory framework and applied on paradigmatic atomic and molecular systems [3-6]. Despite this, the recent proof on the two decades question about the quantum nature of the electronegativity [7] opens the natural similar question about chemical hardness; this communication likes to offer an analytical answer in this regard.

### INTRODUCING QUANTUM CHEMICAL HARDNESS

The fermionic Fock space is build by the aid of the creation and annihilation particle operators

$$\mathbf{a}^+ = |1\rangle\langle 0|, \mathbf{a} = |0\rangle\langle 1|, \quad (1)$$

such that the vacuum and uni-particle sectors cover the entire particle projection space:

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$$\mathbf{1} = |0\rangle\langle 0| + |1\rangle\langle 1| = \mathbf{a}\mathbf{a}^+ + \mathbf{a}^+\mathbf{a} = \{\mathbf{a}, \mathbf{a}^+\}, \quad (2)$$

that allows for the equivalent density normalization relationships

$$\begin{aligned} 1 &= \langle \psi_0 | \psi_0 \rangle = \langle \psi_0 | \mathbf{1} | \psi_0 \rangle = \langle \psi_0 | (\mathbf{a}\mathbf{a}^+ + \mathbf{a}^+\mathbf{a}) | \psi_0 \rangle = \langle \psi_0 | \mathbf{a}\mathbf{a}^+ | \psi_0 \rangle + \langle \psi_0 | \mathbf{a}^+\mathbf{a} | \psi_0 \rangle \\ &= |\langle 0 | \psi_0 \rangle|^2 + |\langle 1 | \psi_0 \rangle|^2 = (1 - \rho_0) + \rho_0, \quad \rho_0 \in [0, 1], \end{aligned} \quad (3)$$

for unperturbed state  $|\psi_0\rangle$  with associated eigen-energy  $E_0$  for a given atomic or molecular valence system.

In these conditions, the chemical processes of electronic exchange with environment (releasing by ionization or accepting through affinity) are modelled by the associate ionization and affinity second quantized wave-functions

$$|\psi_\lambda^I\rangle = (1 + \lambda\mathbf{a}\mathbf{a}^+)|\psi_0\rangle = |\psi_0\rangle + \lambda|0\rangle\langle 1|1\rangle\langle 0|\psi_0\rangle = |\psi_0\rangle + \lambda\sqrt{1 - \rho_0}|0\rangle, \quad (4a)$$

$$|\psi_\lambda^A\rangle = (1 + \lambda\mathbf{a}^+\mathbf{a})|\psi_0\rangle = |\psi_0\rangle + \lambda|1\rangle\langle 0|0\rangle\langle 1|\psi_0\rangle = |\psi_0\rangle + \lambda\sqrt{\rho_0}|1\rangle \quad (4b)$$

by means of the perturbation factor  $\lambda$ ; they enter in calculation of the perturbed energy

$$\langle E_{\lambda \in \mathbb{R}}^{I \leftrightarrow A} \rangle = \frac{\langle \psi_\lambda^I | H | \psi_\lambda^A \rangle}{\langle \psi_\lambda^I | \psi_\lambda^A \rangle} \quad (5)$$

and electronic density

$$\rho_{\lambda \in \mathbb{R}}^{I \leftrightarrow A} = \frac{\langle \psi_\lambda^I | \mathbf{a}^+\mathbf{a} | \psi_\lambda^A \rangle}{\langle \psi_\lambda^I | \psi_\lambda^A \rangle} \quad (6)$$

that finally provide the chemical hardness realization as

$$\eta_\lambda = \frac{1}{2} \frac{\partial^2 \langle E_\lambda \rangle}{\partial \rho_\lambda^2} \quad (7)$$

By considering the basic chain-derivation rule

$$\frac{\partial \bullet}{\partial \rho_\lambda} = \frac{\partial \bullet}{\partial \lambda} \cdot \frac{\partial \lambda}{\partial \rho_\lambda} \quad (8)$$

chemical hardness of Eq. (7) unfolds as

$$\eta_\lambda = \frac{1}{2} \left\{ \left[ \frac{\partial}{\partial \lambda} \left( \frac{\partial \langle E_\lambda \rangle}{\partial \lambda} \right) \right] \frac{\partial \lambda}{\partial \rho_\lambda} + \frac{\partial \langle E_\lambda \rangle}{\partial \lambda} \left[ \frac{\partial}{\partial \lambda} \left( \frac{\partial \lambda}{\partial \rho_\lambda} \right) \right] \right\} \frac{\partial \lambda}{\partial \rho_\lambda} \quad (9)$$

to be in next evaluated.

### QUANTUM VALUES OF CHEMICAL HARDNESS

Equation (9) may be further expressed by employing the inverse density and energy gradients respecting the chemical perturbation factor  $\lambda$ , see Ref. [7]:

$$\frac{\partial \lambda}{\partial \rho_\lambda} = \frac{(1 + \lambda \rho_0)^2}{\rho_0 (1 - \rho_0)}, \quad (10a)$$

$$\frac{\partial \langle E_\lambda \rangle}{\partial \lambda} = E_0 \frac{1 - \rho_0}{(1 + \lambda \rho_0)^2} \quad (10b)$$

toward the second order perturbation terms

$$\frac{\partial}{\partial \lambda} \left( \frac{\partial \lambda}{\partial \rho_\lambda} \right) = 2 \frac{1 + \lambda \rho_0}{1 - \rho_0}, \quad (11a)$$

$$\frac{\partial}{\partial \lambda} \left( \frac{\partial \langle E_\lambda \rangle}{\partial \lambda} \right) = -2 E_0 \rho_0 \frac{1 - \rho_0}{(1 + \lambda \rho_0)^3} \quad (11b)$$

leading with the chemical hardness limits

$$\eta_\lambda = 0 \cdot E_0 \frac{1 + \lambda \rho_0}{\rho_0 (1 - \rho_0)} = \begin{cases} 0, & \rho_0 \in (0,1) \\ 0 \cdot \infty = ?, & \rho_0 \rightarrow 0 \\ 0 \cdot \infty = ?, & \rho_0 \rightarrow 1 \end{cases} \quad (12)$$

The results of Eq. (12) give the answer that the chemical hardness is *not* an observable, having neither a *non-zero* nor a *definite* value for any electronic density realization or limit, respectively. Such a behavior is somehow explained by the energetic nature of chemical hardness usually associated with the HOMO-LUMO gap for a molecular system, i.e. with an energy interval (or energy difference) rather than with an eigen-energy (or an energy level) of a spectrum.

However, the result (12) does not exclude the “real”, even as “hidden” or dispersed, values of chemical hardness: for the fractional occupied states – the first upper branch of Eq. (12) – are assessed to the open states of

chemical bonding, while the empty or fully occupied valence states – the middle and lower branches of Eq. (12) – are described by the not definite (in eigen-value sense) of chemical hardness, since is uncertain it will allow fully engagement or inert chemical response in reactivity and bonding, respectively.

## CONCLUSIONS

In modeling of chemical reactivity by means of electronegativity and chemical hardness, there was proofed that while electronegativity may be assumed as a quantum observable with an eigen-value equating the chemical potential [7], the chemical hardness, although as driving the chemical force in bonding through the electronegativity change with engaged charge change of a given (valence) system [2], cannot be associated with a non-zero or a definite energetic value for fractional or fully empty/filled electronic states in interacting states. However, the hidden quantum nature of chemical hardness may be appropriately fitted with the non-locality electronic measures of chemical bond accompanying any localized charge in bonding, being thus susceptible to be further considered in elucidation of aromaticity chemical concept, for instance. Yet, related studies in the second quantization framework are expected to be very fruitful in elucidating quantum aspects of chemical reactivity and bonding and will be addressed in the years to come and in subsequent communications.

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