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Comment on "Ruling out Any Electrophilicity Equalization Principle" and Hardness Equalization Principle

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In the literature, popular electronic structure principles regarding electronegativity, chemical hardness and electrophilicity concepts are available. It is undeniable that the equalization principles related to reactivity indexes such as electronegativity, hardness, and electrophilicity have been widely used to calculate the partial charges of atoms in a molecule. It is apparent that all such equalization process about reactivity properties are described with the help of the relationship between said chemical property and charge.

Chattaraj et al. [1] suggested a method of computing equalized electrophilicity at the event of molecule formation. Recently Szentpaly [2], has ruled out the possibility of such a physical process of electrophilicity equalization during the event of molecule formation. Szentpaly [2] has also investigated the efficacy and justifiability of geometric mean method of computing of equalized electrophilicity of molecules in terms of the values of atomic electrophilicities as proposed by Chattaraj et al. [1] and argued that there is no reason for suggesting a principle of electrophilicity equalization by arithmetic, geometric, or harmonic averaging of atomic values.

After the publication of the paper of Szentpaly [2], Chattaraj et al. [3] seems to argue on the possibility of existence of electrophilicity equalization principle and have tried to justify the electrophilicity equalization principle in terms of their suggested ansatz. In the next communication Szentpaly [2] further criticized the electrophilicity equalization principle. He has firmly ruled out, on the basis of his findings, the existence of electrophilicity equalization.

In difference to Szentpaly [2,3], we [4-9] believe that the equalization process does exit and work in the formation of hetero nuclear molecule. But in deference to him, we agree to the idea that the geometric as well as other mean principles are not that successful in studying the chemical interactions and hence to study the equalization of the structural descriptors like electronegativity, hardness and electrophilicity.

After going though the papers of Chattaraj et al. [1,3] and Szentpaly [2] it transpires that the physical process of electrophilicity equalization was conceived by Chattaraj et al. [1] for the first time and he is first detractor. But, in fact, electrophilicity equalization is a prevailing idea of conceptual density functional theory (CDFT) sporadically segregated in chemical literature [10-17].

The electrophilicity is a property of atoms which signifies the energy lowering process on soaking electrons from the environment, donors. In fact Chaquin [12] has drawn an analogy between electrophilicity and electrical power which has the classical equation as $P=U^2/R$, where P is the electrical power or the amount of power that is dissipated (in Amperes), R is the electrical resistance (in ohm) and U is the voltage (in volt). In this sense the electrophilicity index is a kind of power.

Although the ansatz of Parr et al. [18], $\omega = \dfrac{\mu^2}{2\eta}$ (Where ω is the electrophilicity index, μ is the electronic chemical potential and η is

the chemical hardness of atoms, ions or molecules), for electrophilicity physically means that it simultaneously encompasses both the properties of the electrophile to acquire an additional electronic charge driven by μ^2 and the resistance of the system to exchange electronic charge with the environment described by η, effectively it is conceived as representing the stabilization energy of the system when it gets saturated by electrons coming from the surroundings.

We have already mentioned above that the electrophilicity equalization principle, similar to electronegativity equalization and hardness equalization is implicit and sporadically segregated in the literature of CDFT. However, there are adherents and detractors of the principle; adherents are many and detractor is only one. Survey of literature shows that several workers [10,11] have studied the variation of electrophilicity during molecular vibrations and internal rotations and it is found [12] that under constant chemical potential V(r), there would be a minimum electrophilicity principle along a reaction path. Chaquin [12], by an analogy with classical electrostatics, suggests an interpretation of the Parr's 'electrophilicity index' as a 'global energy index' leading to the 'minimum electrophilicity principle'. It is expected to decrease during an exothermal process and as compared with the principle of maximum hardness; the 'principle of minimum electrophilicity' seems to be more often obeyed [13-15].

Ayers and Parr [16-17] opined that since electronegativity and hardness are both equalized, the electrophilicity (being their ratio) must be also equalized. The electrophilicity equalization principle is also implicit in the work of Chaquin [12] and Noorizadeh and Shakerzadeh [13-14]. Therefore, it is quite probable that there should be, similar to the physical process of electronegativity equalization [19,20] and the hardness equalization [4-9,16-17,21-23], an analogous process of equalization of electrophilicity during the event of molecule formation. Looking at the ansatz of Parr et al, for the definition of electrophilicity, it is given that electrophilicity is the result of conjoint action of two global quantities of CDFT, the electronegativity and the chemical hardness. Thus the strongest argument in favour of the electrophilicity equalization follows from the fact that, since the electronegativity equalization is unequivocal and widely accepted and the hardness equalization is also now established [4-9], and since if electronegativity

and hardness are both equalized, then electrophilicity (being their ratio) must be also inevitably equalized. Thus, the present analysis logistically establishes that it is unequivocal that electrophilicity equalization exits and is manifest during the chemical events of molecule formation. In a recent communication we have tried to establish logistically that it is unequivocal that electrophilicity equalization exits and is manifest during the chemical events of molecule formation [24]. We have also pointed out the theoretical discrepancies distinct in the method suggested by Chattaraj et al. [1] is invoking the mean principle.

On critical survey it transpires that Szentpaly [2] considered the possibility of occurrence of electrophilicity equalization in some homo nuclear molecules such as fullerene and metal clusters. He applied some empirical method to calculate I and A of such systems and also invoked the geometric mean principle to calculate the equalized electrophilicity from their atomic values. On analyzing critically it seems to us that he erred in conceiving proper domain of the equalization phenomenon. The charge transfer is initiated by the chemical potential difference, $\Delta\mu$ hardness difference, $\Delta\eta$ etc in case of the formation of hetero nuclear molecules only. This paradigm is totally absent in case of the formation of homo nuclear molecules because there is no whisper of charge transfer and generation of dipoles in such molecules Thus for obvious reason equalization principle cannot be applied for such homonuclear systems.

Regarding his comment on hardness equalization we are to state that we suggested formulae for hardness equalization for some hetero nuclear di atomic systems [4] and poly atomic systems [9] which is assumed to be a cluster of atoms. We have applied our suggested scheme of hardness equalization in the study of acid-base double exchange reactions [5,9], computation of hetero nuclear bond lengths [7], computation of dipole charges and dipole moments of hetero nuclear molecules [6]. In our study, we have discovered the commonality of the operational significance, origin and development of electronegativity and hardness.

These detail study would contradict unequivocally the statement of Szentpaly [2] that "there is no support for any hardness equalization process".

Gázquez et al. [25] studied the local hardness equalization and supported the principle of maximum hardness. In a recent work Chattaraj and et al. [3] also proved the applicability of electrophilicity equalization principle.

At the end we think that the hardness equalization is a law of nature like the well established electronegativity equalization process. This is our quest whether there is any electrophilicity equalization principle, like the electronegativity equalization and hardness equalization principle, does occur during event of chemical reactions.

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