Electronegativity and hardness profiles of a chemical process: Comparison between quantum fluid density functional theory and *ab initio* SCF method

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Abstract. Temporal evolution of electronegativity and hardness associated with a collision process between a Be atom and a proton has been studied within a quantum fluid density functional framework. In the presence of a third collisional partner to take away excess energy, this collision may lead to a chemical reaction producing a BeH^+ molecule. For comparison *ab initio* SCF level calculation (with 6–31G** basis set) on BeH^+ molecule with different geometries have been performed. Electronegativity equalization and maximum hardness principles are analyzed.

Chemical concepts like electronegativity [1–4] and hardness [5–9] have been found to be important in understanding various physico-chemical processes. Electronegativity was first defined by Pauling [1] as the power of an atom in a molecule to attract electrons to itself and was shown to be related to chemical potential (μ) in density functional theory (DFT) as [3, 4]

$$-\chi = \mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)} \tag{1}$$

where E, N, $v(r)$ are electronic energy, number of electrons and external potential respectively. The concept of hardness which was introduced by Pearson [5] has been defined, within DFT, as [6–9]

$$\eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)}. \tag{2}$$

Using finite difference approximations and assuming Koopmans' theorem to be valid, μ and η become [7–10]

$$\mu \simeq -(I + A)/2 \simeq (\varepsilon_{LUMO} + \varepsilon_{HOMO})/2 \tag{3}$$

$$\eta \simeq (I - A)/2 \simeq (\varepsilon_{LUMO} - \varepsilon_{HOMO})/2. \tag{4}$$

Here I and A are ionization potential and electron affinity respectively and ε_{HOMO} and ε_{LUMO} are energies of highest occupied and lowest unoccupied molecular orbitals respectively.

In a chemical reaction, difference of electronegativity drives the electron transfer from a species of lower electronegativity to one with higher electronegativity until their electronegativity values become equal. According to Sanderson's electronegativity equalization (EE) principle [3, 11–15] this molecular electronegativity is equal to the geometric mean of isolated atoms' electronegativities. An important principle of molecular electronic structure theory associated with hardness concept is hard-soft-acid-base (HSAB) principle [5, 16] which states that hard acids will prefer to react with hard bases and soft acids with soft bases to form a stable molecule. This principle is closely related to maximum hardness principle (MHP) [17–19] which states that "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible". Pearson [17] postulated MHP on the basis of his vast experience on chemical reactions. The first formal proof of it for a class of states (cf. eq. (14) of ref. 18) has been provided by Parr and Chattaraj [18]. Thus during molecule formation or in general in a chemical reaction, electronegativity of an atom changes until it attains the molecular electronegativity value and its hardness gets maximized which is the consequence of MHP. Therefore a chemical reaction dynamics can be envisaged in terms of temporal evolution of electronegativity and hardness during a chemical reaction. Several systems and processes have been studied in order to understand the implications of EE [13–15, 20, 21], MH [22–33] and HSAB [23, 25–27] principles. In this letter we study a collision process between a Be atom and a proton and study the temporal evolution of χ and η during the process within a quantum fluid density functional (QFDF) framework [37–40]. Since, in the presence of a third partner to take away the excess energy, this collision may lead to the formation of BeH$^+$, which is a stable closed shell molecule with $D_0 = 3.14$ eV and $R_e = 1.3122$ Å [34–36] we also supplement this calculation by *ab initio* SCF calculations [41]. In both the cases χ and η have been expressed as functions of internuclear distance (R) and hence have implicit temporal dependence. *Ab initio* calculations have been carried out at SCF level with 6–13 G** basis set for different internuclear distances of BeH$^+$. It should be noted here that the former calculation is within a dynamical context and hence the excited states get mixed during temporal evolution whereas the latter calculation refers to movement from one ground state to another.

In QFDF formalism [37–40] which is an amalgamation of quantum fluid dynamics (QFD) and time-dependent density functional theory (TDDFT), time-evolution of electron density (ρ) and current density (j) can be found by solving a generalized nonlinear Schrödinger equation (GNLSE). The electron density and current density in turn uniquely determine all other properties of the system [42, 43]. The GNLSE is given by [37–40],

$$[-\tfrac{1}{2}\nabla^2 + v_{\text{eff}}(r, t)]\phi(r, t) = i\frac{\partial\phi(r, t)}{\partial t} \tag{5}$$

with

$$\phi = \rho^{1/2}\exp(i\xi) \quad \text{and} \quad j = [\phi_{\text{re}}\nabla\phi_{\text{im}} - \phi_{\text{im}}\nabla\phi_{\text{re}}] = \rho\nabla\xi$$

where ξ is the velocity potential. In eq. (5) the effective potential v_{eff} is given by [20, 37–39]

$$v_{\text{eff}} = \frac{\delta T_{\text{NW}}}{\delta\rho} + \frac{\delta E_{\text{XC}}}{\delta\rho} + \int\frac{\rho(r', t)}{|r - r'|}dr' - \frac{Z}{r} + v_{\text{ext}}(r, t) \tag{6}$$

where T_{NW} and E_{XC} denote non-Weizsäcker part in kinetic energy (KE) and exchange correlation energy functionals respectively, explicit forms of which have been given earlier [20, 37, 38]. Although Hohenberg–Kohn theorems [44] assert the existence of these functionals, their exact forms are still not known even for the ground state and various approximations with respective merits and demerits have been proposed [45]. The external potential denoted by $v_{ext}(r, t)$ is as given below,

$$v_{ext}(r, t) = -\frac{1}{|R(t) - r|} \tag{7}$$

where $R(t)$ refers to the classical trajectory of two nuclei and has been calculated by standard straightline approximation [37]. Since $v_{ext}(r, t)$ vanishes at the boundary, the validity of TDDFT [42, 43] allows us to legitimately assume that the mappings $v_{ext}(r, t) \rightarrow \rho(r, t)$ and $v_{ext}(r, t) \rightarrow j(r, t)$ are uniquely invertible and accordingly the total time-dependent Hamiltonian is a unique functional of $\rho(r, t)$ and $j(r, t)$. Therefore, in this context one can define a time-dependent energy quantity, $E(t)$, as a density functional [46] and the corresponding definition for the time-dependent chemical potential can be given by [20]

$$-\chi(t) = \mu(t) = \frac{\delta E(t)}{\delta \rho} = \frac{1}{2}(\nabla \xi)^2 + \frac{\delta T}{\delta \rho} + \int \frac{\rho(r', t)}{|r - r'|} dr' - \frac{Z}{r} + \frac{\delta E_{XC}}{\delta \rho} + v_{ext}(r, t). \tag{8}$$

Since μ is constant over the whole space in a molecule, if at a distance r_μ, we get [20]

$$\frac{1}{2}(\nabla \xi)^2 + \frac{\delta T}{\delta \rho} + \frac{\delta E_{XC}}{\delta \rho} = 0, \tag{9}$$

the chemical potential becomes equal to total electrostatic potential at r_μ in that time step as

$$-\chi(t) = \mu(t) = \int \frac{\rho(r, t)}{|r_\mu - r|} dr - \frac{Z}{r_\mu} + v_{ext}(r_\mu, t). \tag{10}$$

At time $t = 0$, (9) and (10) become identical to that given by Politzer *et al* [47] considering principle of equalization of electronegativity and the distance r_μ was found to match well with the covalent radii of atoms.

Temporal evolution of η has been calculated at every time step from the following expression [48, 49]

$$\eta(t) = \int f(r, t)\eta(r, t)dr \tag{11}$$

where $\eta(r, t)$ is the local hardness at time t given by [48, 49]

$$\eta(r, t) = \frac{1}{2N} \int \frac{\delta^2 F[\rho(r, t)]}{\delta \rho(r, t)\delta \rho(r', t)} \rho(r')dr'. \tag{12}$$

Here $F[\rho]$ is the usual Hohenberg–Kohn functional explicit approximate form of which has been given elsewhere [20, 37]. The Fukui function, $f(r)$ has been given

by [50]

$$f(r) = \left(\frac{\partial \rho}{\partial N}\right)_{v(r)}. \tag{13}$$

This can be approximated [32,33] by neglecting the smaller second term in the expression of Hellmann–Feynman force [48] written as the sum of forces acting on $f(r)$ and a term involving the product of the matrix elements of perturbation caused by small changes in external potential and local hardness. Thus $f(r)$ becomes [32,33]

$$f(r,t) = \frac{\rho(r,t)}{N}. \tag{14}$$

Same approximate form of $f(r)$ has been found by Gázquez expressing density of charged species as the renormalized electron density of the neutral species [51].

It is important to note that exact forms for $T[\rho]$ and $E_{XC}[\rho]$ are not known even for the ground state [45]. As it has been done in all earlier time-dependent calculations within QFDF framework [37–40], in this paper also it has been assumed that $T[\rho]$
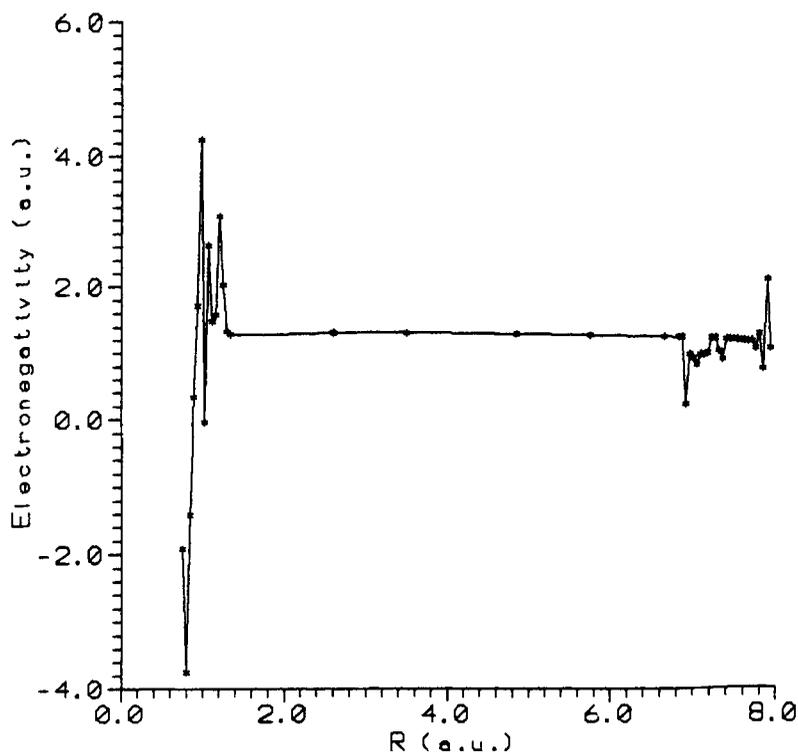

Figure 1. The plot of electronegativity (χ) versus internuclear distance (R) of BeH$^+$ (a supermolecule as in ref. 37) calculated within a quantum fluid density functional (QFDF) framework.

and $E_{xc}[\rho]$ have the same forms in ground and excited states. This assumption need not always be valid. The present state of knowledge of excited-state DFT does not leave any other alternative [38].

Time evolution of the system as well as its properties like electronegativity and hardness has been found by solving eq. (5) as an initial-boundary value problem. The numerical solution starts with a near Hartree–Fock [52] density of Be-atom in a ^1S state and a proton with a KE value of 5 keV approaching it for a head-on collision. A leap-frog finite difference scheme which is stable for quantum mechanical equations of motion due to the presence of $i(i^2 = -1)$ [53] has been adopted here to solve eq. (5). The numerical method has been reported in detail earlier [20, 38, 39]. In *ab initio* SCF calculations [41] χ and η have been calculated from (3) and (4) using energies of HOMO and LUMO obtained at different internuclear distances.

The electronegativity profiles obtained from QFDF and *ab initio* calculations have been presented in figures 1 and 2 respectively. The electronegativity profile obtained from QFDF calculation (figure 1) shows some initial transients as the electron density gets reoriented around the nucleus due to nonlinear effective potential field, v_{eff}. After elapse of certain time the electron density does not change appreciably which is akin to some sort of dynamic equilibrium. At this stage, χ attains a constant value over a range
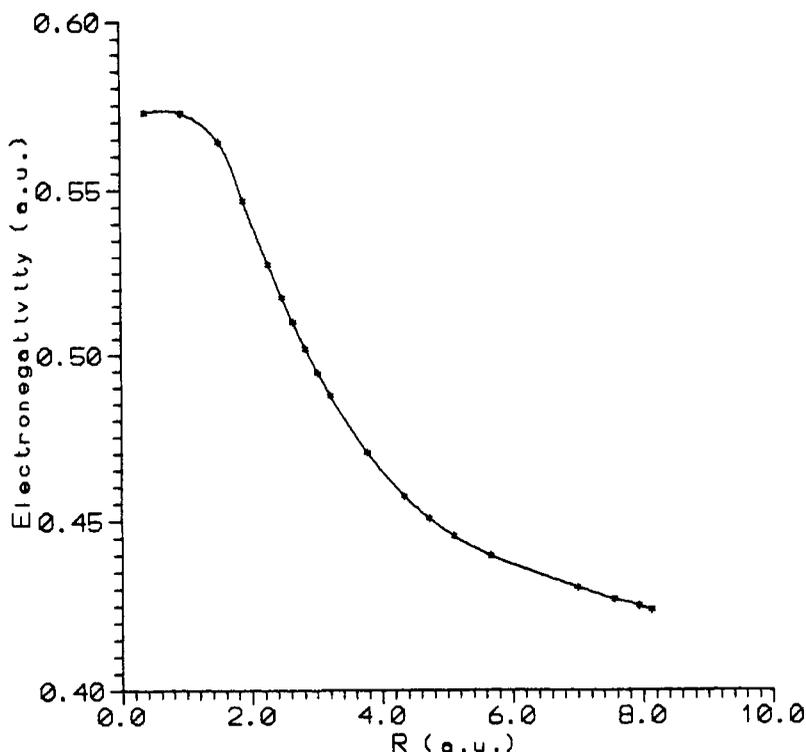

Figure 2. The plot of electronegativity (χ) versus internuclear distance (R) of BeH$^+$ obtained through an *ab initio* SCF calculation.

of internuclear distances. When two nuclei come closer and encounter each other, electronegativity shows a sharp increase. However χ does not remain constant after reaching the high value. This is because the proton is approaching with a high $KE(\simeq 5\,keV)$. Hence in the encounter regime where internuclear distance is too small, electronegativity profile shows sharp fluctuation due to rapid nonlinear charge oscillations at the vicinity of the two nuclei. On the other hand, the SCF results being associated with ground states of BeH^+ at different internuclear distances, the electronegativity profile does not show oscillations but increases monotonically in the process of molecule formation and reaches a plateau corresponding to the molecular electronegativity value (figure 2). It has been found in this SCF calculation that as the proton approaches Be atom, charge (Mulliken population) on Be atom decreases from 3·44 at $R = 4\cdot3\,\text{Å}$ to the minimum value of 3·06 at the equilibrium bond distance $(R_e = 1\cdot3122\,\text{Å})$ and it increases again as BeH^+ molecule ion is squeezed beyond its equilibrium configuration.

Figures 3 and 4 present the hardness profiles obtained from QFDF and *ab initio* SCF calculations respectively. Both figures show rise in hardness as the two nuclei approach
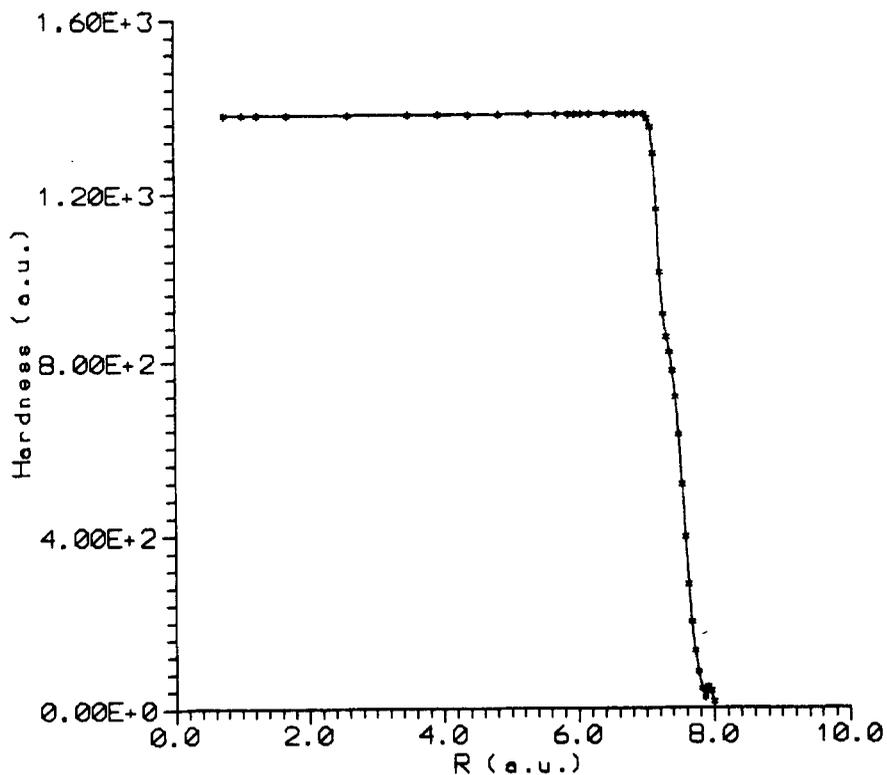

Figure 3. The plot of hardness (η) versus internuclear distance (R) of BeH^+ (a supermolecule as in ref. 37) calculated within a quantum fluid density functional (QFDF) framework.
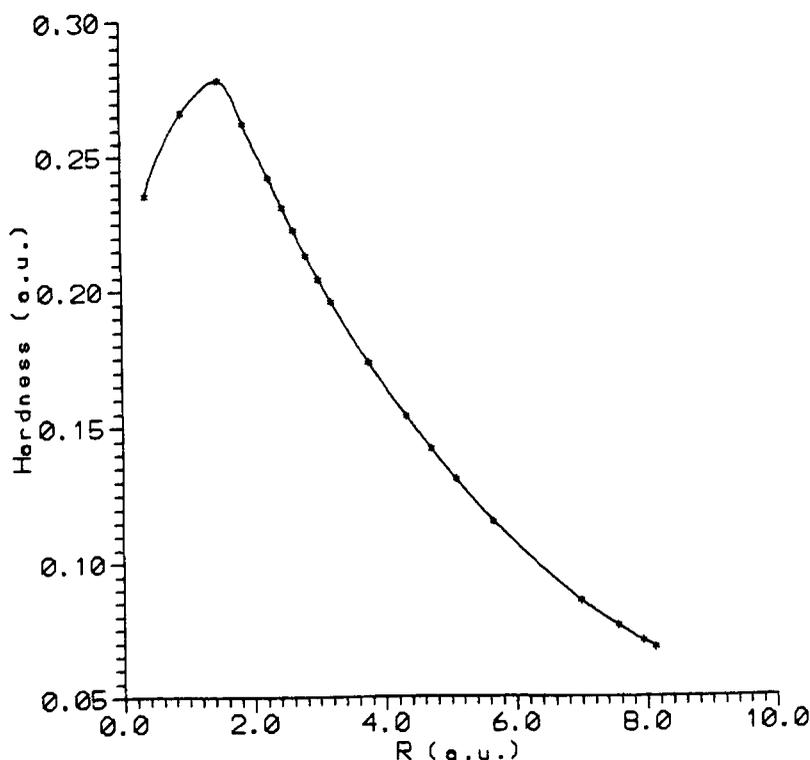
Figure 4. The plot of hardness (η) versus internuclear distance (R) of BeH^+ obtained through an *ab initio* SCF calculation.

each other. Hardness in figure 3 rises sharply as the proton approaches Be atom. In this dynamical process, as the electron density of Be atom gets accumulated near the nucleus and does not change appreciably in course of time, η becomes constant after attaining a high value which may be considered as the dynamical variant of maximum hardness principle [32, 33]. In SCF method, however, rise in η is not so sharp along the reaction path of formation of BeH^+ molecule. In this case η passes through a maximum which, however, is not at equilibrium bond distance of BeH^+ because the extrema for the electronic energy and the nuclear repulsion energy do not appear in the same point of the potential energy curve [19, 22, 31].

It may be noted that the major features in χ and η profiles obtained from structure and dynamics calculations do not match in general. The differences in numerical values as well as other features in the profiles are probably due to the following reasons. The dynamical formalism involves mixing of excited state densities with ground state density as is evidenced from nonvanishing current density, while, in *ab initio* SCF method, calculations were restricted to ground states with different internuclear geometries of BeH^+. The electron correlation has not been taken into account in *ab initio* SCF calculations. Exact forms for kinetic and exchange-correlation energy functionals of DFT are not known [45]. Hence approximate forms for these functionals

are used and their validity in excited states is tacitly assumed. It is in the spirit of Slater's transition state approach [54] where the ground state Hartree–Fock–Slater formalism is considered to be applicable to excited states as well. Straight-line approximation has been used for the calculation of classical trajectory of nuclei. Finally the expression for $f(r)$ given in (14) is an approximation which may be modified by incorporating appropriate inhomogeneity corrections.

This study compares the χ and η profiles generated through electronic structure and dynamics calculations. In SCF calculation, electronegativity increases from a small value corresponding to that of Be atom when proton is much away from it and increases monotonically as proton approaches and finally reaches an asymptote which may be identified as the electronegativity of BeH^+ molecule. This is a consequence of the electronegativity equalization principle. Hardness also increases as the inter-nuclear distance decreases and passes through a maximum in the neighbourhood of equilibrium configuration, as expected from the maximum hardness principle. In the dynamical situation rapid charge oscillation is observed in the encounter zone and excited state densities get mixed with the ground state density.

Acknowledgements

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