Popular Electronic Structure Principles in a Dynamical Context

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To understand the implications of the electronegativity equalization principle, the maximum hardness principle, the minimum polarizability principle, and the maximum entropy principle in a time dependent situation, a charge transfer process from a Be atom to an α-particle is studied within a quantum fluid density functional framework. It is observed that in general a system tries to evolve to a state associated with maximum hardness, maximum entropy, and minimum polarizability values.

I. Introduction

Rationalization of a large body of scattered information often demands the enunciation of qualitative principles. In chemical literature the popular electronic structure principles include the electronegativity equalization principle,[1] the hard−soft acid−base (HSAB) principle,[2] and the maximum hardness principle.[3] The electronegativity equalization principle states that "the electronegativities of all the constituent atoms in a molecule have the same value, which can be expressed as the geometric mean of the electronegativity values of the associated isolated atoms". While the HSAB principle[2] states that "hard likes hard and soft likes soft", the maximum hardness principle[2] can be stated[3] as "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible". Two other principles are the maximum entropy principle[4] and the minimum polarizability principle. The former states that "the most probable distribution is associated with the maximum value of the Shannon entropy".[5] There is no formal statement of the latter. However, as a consequence of the maximum hardness principle[3] and an inverse relationship[6] between hardness and polarizability, it may be stated that "the natural direction of evolution of any system is towards a state of minimum polarizability". To our knowledge, the explicit statement of the minimum polarizability principle is given here for the first time especially in a dynamical context. The constraints associated with this principle may be legitimately assumed to be the same as those with the maximum hardness principle,[3] and the former may as well be extended to all cases where the latter is operative.[3]

Density functional theory[7] has been found to be highly successful in rationalizing various qualitative electronic structure principles as discussed above. For an N-electron system with external potential $v(\mathbf{r})$, electronic chemical potential μ, and total electronic energy E, electronegativity (χ)[8] and hardness (η)[9] are respectively defined as follows:

$$\chi = -\mu = -(\partial E/\partial N)_v \tag{1}$$

and

$$\eta = (\partial^2 E/\partial N^2)_v = (\partial \mu/\partial N)_v \tag{2}$$

Hardness can alternatively be written in its integral form[10] as

$$\eta = \int \eta(\mathbf{r})\, f(\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{3}$$

where $\eta(\mathbf{r})$ is the local hardness[10a,b] and $f(\mathbf{r})$ is the Fukui function.[11]

The above formulation of density functional theory[12] in terms of only single-particle density $\rho(\mathbf{r})$ as the basic variable is essentially restricted to ground state quantum mechanics and is not easily applicable to time dependent situations. Fortunately a time dependent version of it is already available,[13] where it has been shown that the mapping between the time dependent potential and density is invertible and the quantum dynamics of many-electron systems can be studied in terms of single-particle density, $\rho(\mathbf{r})$ and current density, $j(\mathbf{r})$. It also provides a justification for the quantum fluid dynamics (qfd)[14] of a many-electron system where the time evolution of a quantum system is governed by two hydrodynamical equations, viz., an equation of continunity and a Euler type equation of motion.

An amalgamation of these two theories, viz., time dependent density functional theory and quantum fluid dynamics, gives rise to quantum fluid density functional theory,[15] which has already been applied in studying various dynamical phenomena. In the present paper we try to analyze the electronegativity equalization principle, the maximum hardness principle, the HSAB principle, the maximum entropy principle, and the minimum polarizability principle in a dynamical context. For this purpose we apply quantum fluid density functional theory to study a charge transfer process during atomic collisions. In section II we discuss the theoretical background, while in section III we provide the numerical details. Section IV presents the results and discussion, which is followed by concluding remarks in section V.

II. Theoretical Background

In quantum fluid density functional theory[15] an N-electron system is mapped onto a system of N noninteracting particles moving under the influence of a nonlinear one-body effective potential, $v_{\mathrm{eff}}(\mathbf{r},t)$. In this paper we study the dynamics of charge transfer through collision between a beryllium atom and an α-particle. The associated time dependent electron density $\rho(\mathbf{r},t)$ and current density $\mathbf{j}(\mathbf{r},t)$ can be obtained from the solution of the following generalized nonlinear Schrödinger equation,[15]

$$[(-1/2)\nabla^2 + v_{\mathrm{eff}}(\mathbf{r},t)]\phi(\mathbf{r},t) = \mathrm{i}\partial\phi(\mathbf{r},t)/\partial t \tag{4a}$$

$$\rho(\mathbf{r},t) = |\phi(\mathbf{r},t)|^2 \tag{4b}$$

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$$\mathbf{j}(\mathbf{r},t) = [\phi_{re}\nabla\phi_{im} - \phi_{im}\nabla\phi_{re}] \quad (4c)$$

$$v_{eff}(\mathbf{r},t) = \delta T_{NW}/\delta\rho + \delta E_{XC}/\delta\rho + \int[\rho(\mathbf{r}',t)/|\mathbf{r}-\mathbf{r}'|]d\mathbf{r}' - Z_1/|\mathbf{R}_1(t)-\mathbf{r}| + v_{ext}(\mathbf{r},t) \quad (4d)$$

where T_{NW} and E_{XC} denote the non-Weizsäcker part of the kinetic energy and exchange-correlation energy functionals, respectively, whose explicit forms are given elsewhere.[15] Although the existence of these functionals is guaranteed by Hohenberg−Kohn theorems,[12] their exact explicit forms are as yet unknown even for ground states, let alone excited states and time dependent situations. The external potential, $v_{ext}(\mathbf{r},t)$, in eq 4d has been taken as

$$v_{ext}(\mathbf{r},t) = -Z_2/|\mathbf{R}_2(t)-\mathbf{r}| \quad (4e)$$

In eqs 4d and 4e Z_1, Z_2 and $\mathbf{R}_1$, $\mathbf{R}_2$ are atomic numbers and radius vectors of the target (Be) and the projectile (He^{2+}) nuclei, respectively. The position of the target nucleus is chosen as the origin of the coordinate system, and that of the projectile is given by a Coulomb trajectory as prescribed by Kulander et al.[16] The nuclear motion involved in ion−atom collisions studied so far[15] within quantum fluid density functional theory has been approximated by a standard straight line trajectory.

According to the time dependent density functional theory,[13] the mappings between external potential and charge and current densities are uniquely invertible and accordingly $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ uniquely determine all time dependent properties of the system. For example, the time dependent energy $E(t)$ can be written as the following density functional,

$$E(t) = (1/2)\int[|\mathbf{j}(\mathbf{r},t)|^2/\rho(\mathbf{r},t)]\,d\mathbf{r} + T[\rho] + (1/2)\int\int[\rho(\mathbf{r},t)\,\rho(\mathbf{r}',t)/|\mathbf{r}-\mathbf{r}'|]\,d\mathbf{r}\,d\mathbf{r}' - Z_1\int[\rho(\mathbf{r},t)/|\mathbf{R}_1-\mathbf{r}|]d\mathbf{r} - Z_2\int[\rho(\mathbf{r},t)/|\mathbf{R}_2-\mathbf{r}|]\,d\mathbf{r} + E_{XC}[\rho] \quad (5)$$

where the first and second terms are the macroscopic kinetic energy and intrinsic kinetic energy, respectively. To monitor the time evolution of the chemical potential (negative of electronegativity), we define it as[15d,e]

$$\mu(t) = -\chi(t) = \delta E(t)/\delta\rho = (1/2)\,[|\mathbf{j}(\mathbf{r},t)|/\rho(\mathbf{r},t)] + \delta T/\delta\rho + \int[\rho(\mathbf{r}',t)/|\mathbf{r}-\mathbf{r}'|]\,d\mathbf{r}' - Z_1/|\mathbf{R}_1-\mathbf{r}| - Z_2/|\mathbf{R}_2-\mathbf{r}| + \delta E_{XC}/\delta\rho \quad (6)$$

In case there exists a point where the sum of functional derivatives of exchange-correlation and total kinetic energies is zero, we have

$$\mu(t) = \int[\rho(\mathbf{r}',t)/|\mathbf{r}_c-\mathbf{r}'|]\,d\mathbf{r}' - Z_1/|\mathbf{R}_1-\mathbf{r}_c| - Z_2/|\mathbf{R}_2-\mathbf{r}_c| \quad (7)$$

where $\mathbf{r}_c$ is the radial distance for which

$$(1/2)[|\mathbf{j}(\mathbf{r},t)|/\rho(\mathbf{r},t)] + \delta T/\delta\rho + \delta E_{XC}/\delta\rho = 0 \quad (8)$$

Since $\mathbf{j}(\mathbf{r},\mathbf{o}) = 0$, the above condition becomes identical to that of the ground state density functional theory suggested by Politzer et al.[17] to calculate the covalent radius of an atom. At every time step, r_c can be found as the solution of eq 8. Required $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ at that time step can be obtained by solving eq 4a. Once r_c is obtained, $\mu(\mathbf{r},t)$ is calculated from eq 7. Under the influence of the time dependent external potential, the electron density gets redistributed at every time step and the electronegativity changes until it attains the molecular electronegativity value; a chemical reaction dynamics can be envisaged in terms of the electronegativity of an atom in an external field created by all other atoms taking part in the molecule formation.[15d,e]

Time evolution of hardness can be studied by writing it as the following integral,[10]

$$\eta(t) = \int\eta(\mathbf{r},t)\,f(\mathbf{r},t)\,d\mathbf{r} \quad (3)$$

where $\eta(\mathbf{r},t)$ is local hardness at time t given by[10a,b]

$$\eta(\mathbf{r},t) = (1/2N)\int[\delta^2F[\rho(\mathbf{r},t)]/\delta\rho(\mathbf{r},t)\,\delta\rho(\mathbf{r}',t)]\,\rho(\mathbf{r}')\,d\mathbf{r}' \quad (9)$$

In eq 9 $F[\rho]$ is the Hohenberg−Kohn functional, whose explicit approximate form is given elsewhere.[15] The integral formula for η, eq 3, can be a density functional if the Fukui function can be expressed as a density functional. Recently a variational method has been prescribed[18] for determination of f and, in turn, η. Implementation of this technique, however, is not straightfoward in a time dependent situation. The homogeneous electron gas formula for f is[15g,h,19,20]

$$f = \rho(\mathbf{r})/N \quad (10)$$

A gradient correction to this local density approximation formula for f has been proposed[20] recently for systems with spherical symmetry. Since that formula would be valid only when the target and the projectile are very close to each other such that external potential can be considered to be central in nature, we refrain from using that in the present situation.

It may be noted that eqs 3 and 9 provide the zero hardness value for the hydrogen atom because being a single electron system it does not have electron−electron repulsion and exchange-correlation terms in $F[\rho]$ and the Weizsäcker functional is the exact kinetic energy functional for this atom.

It is also interesting to note that because of the ambiguity in local hardness,[10e] one may write η as[10c−e]

$$\eta = \eta(\mathbf{r}) = \int f(\mathbf{r}')\,\eta(\mathbf{r},\mathbf{r}')\,d\mathbf{r}' \quad (11)$$

and reach the natural conclusion,[10e] "Necessary conditions for the ground state are that both the chemical potential and hardness are constant throughout the system". This hardness equalization process[10e] associated with the movement of any system from one ground state to another deserves a thorough treatment. Implications of this equalization have already been analyzed within an atom-in-a-molecule framework[21] as well as for a geometric mean principle for hardness.[22]

The high projectile velocity used in the present work allows us to legitimately assume the cylindrical symmetry of the charge density about an axis ($-\infty \le \tilde{z} \le \infty$, say) passing through the target nucleus.[15a−h,16] Polarizability dynamics is studied in terms of the time evolution of the diagonal component of the polarizability tensor along the $\tilde{z}$ axis, designated as $\alpha(t)$. The definition of $\alpha(t)$ used here is as follows,[15c]

$$\alpha(t) = |D^{\tilde{z}}_{ind}(t)|/|E_{\tilde{z}}(t)| \quad (12)$$

where $D^{\tilde{z}}_{ind}(t)$ is the electronic part of the induced dipole moment and $E_{\tilde{z}}(t)$ is the $\tilde{z}$ component of the external Coulomb field.

To follow the time evolution of entropy, the N-electron system is mapped onto a system of N noninteracting particles moving under the influence of $v_{eff}(\mathbf{r},t)$, whose entropy can be defined as[15a,b,g,h]

$$S(t) = \int \{(5/2)k - k \ln \rho(\mathbf{r},t) + (3/2)k \ln(k\vartheta(\mathbf{r},t)/2\pi)\}\rho(\mathbf{r},t)\, d\mathbf{r} \quad (13)$$

where k is the Boltzmann constant and ϑ is a space−time dependent temperature defined in terms of kinetic energy density as

$$t_s(\mathbf{r};\rho(\mathbf{r},t)) = (3/2)\, \rho(\mathbf{r},t)k\, \vartheta(\mathbf{r},t) + \left(\frac{|j(\mathbf{r},t)|^2}{2\rho(\mathbf{r},t)}\right) \quad (14)$$

It is important to note that the solution of eqs 4 provides the time evolution of $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$, which in turn would allow us to monitor the dynamics of all the quantities discussed in this section.

III. Numerical Solution

The generalized nonlinear Schrödinger equation takes the following form in the cylindrical polar coordinates $(\tilde{\rho},\tilde{\phi},\tilde{z})$ by making use of the following transformations,

$$y = \tilde{\rho}\phi \quad (15a)$$

and

$$\tilde{\rho} = x^2 \quad (15b)$$

and also an analytical integration over $0 \le \tilde{\phi} \le 2\pi$,

$$\{(3/4x^3)\, \partial y/\partial x - (1/4x^2)\, \partial^2 y/\partial x^2 - \partial^2 y/\partial \tilde{z}^2\} - (1/x^4 - 2v_{\mathrm{eff}})y = 2\mathrm{i}(\partial y/\partial t) \quad (16)$$

The above equation is numerically solved using a leap-frog-type finite difference scheme.[15c−i] The origin of the coordinate system is taken on the Be nucleus, and the α-particle follows a Coulomb trajectory.[16] The method being described here is very general and can be applied to study a chemical reaction dynamics for a very low energy collision and/or a collision in the presence of a third collisional partner to take away the excess collisional energy. The numerical solution is launched with a near Hartree−Fock density[23] of a Be atom in a ^{1}S state and an α-particle with initial velocity 1 au approaching it on a Coulomb trajectory. Note that for a low-energy collision leading to a chemical reaction a classical equation of motion involving electron density obtained from eq 4a should be solved to fix the nuclear trajectory, which in turn would provide the external potential for the electron distribution. The numerical method is discussed at length elsewhere.[15c−i] The electronic repulsion potential is calculated as the Green function of the Laplacian operator. The impact parameter and the scattering angle have been chosen as[16] 0.1 au and 5.25°, respectively. At $t = 0$, the α-particle was taken at a distance of 10 au from the Be nucleus, and the integration is carried out until it goes to a similar distance away. The spatial and temporal grids are taken as follows: $\Delta x = \Delta z = 0.05$ au and $\Delta t = 0.025$ au.

IV. Results and Discussion

Figure 1 depicts the time dependence of the electronic chemical potential (negative of electronegativity). The whole collision process is divided into three regimes: approach, encounter, and departure. Variation of difference density and induced dipole moment made this division transparent in an earlier study of ion−atom collisions within quantum fluid density functional theory.[15c] In the encounter regime the actual charge exchange process takes place. After the initial transients die out a steady value of μ is obtained in the approach regime.

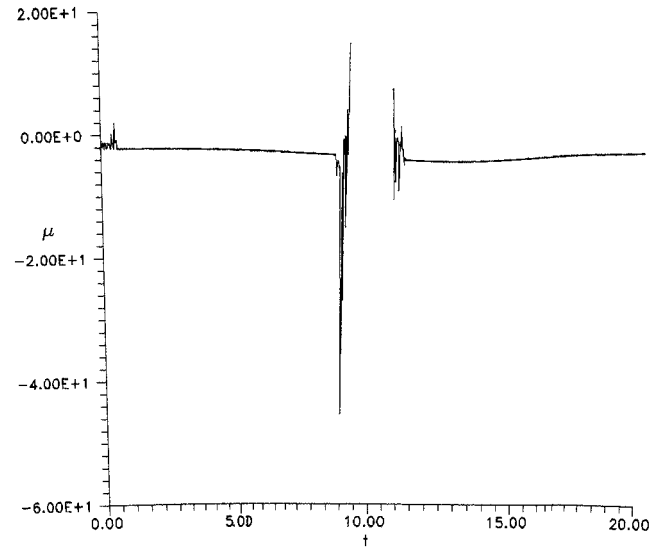

Figure 1. Time evolution of chemical potential (μ) during charge transfer between a Be atom and an α-particle.

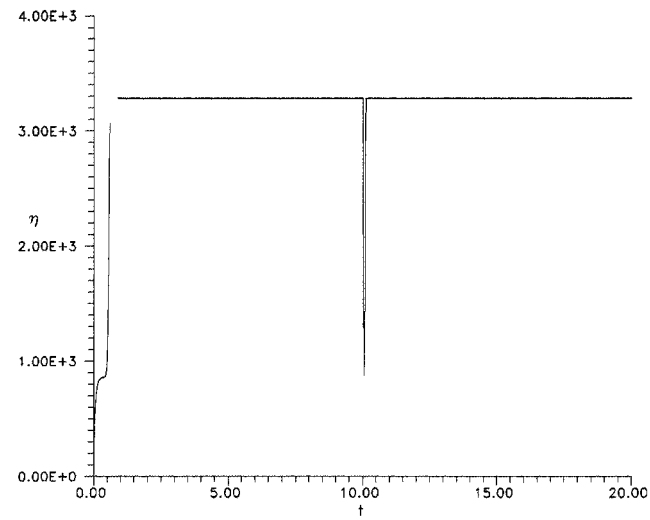

Figure 2. Time evolution of hardness (η) during charge transfer between a Be atom and an α-particle.

Electron density at these time steps is starting to be shared by both the nuclei, reflecting a charge exchange. Neither r_c nor μ can be calculated at the encounter regime because nowhere in space is the condition eq 8 met. At the beginning of the departure regime again we see fluctuations in μ, which ultimately stabilize when the α-particle goes a reasonable distance away from the Be atom.

Temporal evolution of hardness is presented in Figure 2. It increases with time to eventually reach a high value. The hardness does not change appreciably thereafter. Since the charge and current densities also do not alter significantly after certain time steps (not shown here), one may think it as some sort of "dynamic equilibrium" of the whole scattering system. The maximization of η in a time dependent situation may be considered as a dynamical variant of the maximum hardness principle. There is a sudden drop in η at a single temporal mesh point corresponding to the closest approach of the two nuclei due to the singularity associated with the Coulomb potential. We ignore this behavior because a larger temporal step size does show a more or less constant hardness value for all times after the largest hardness value is reached and there is no sudden reduction in η value anywhere in between. The lack of a clear-cut maximum in the η profile may stem from several reasons: (a) use of ground state functional forms for $T[\rho]$,

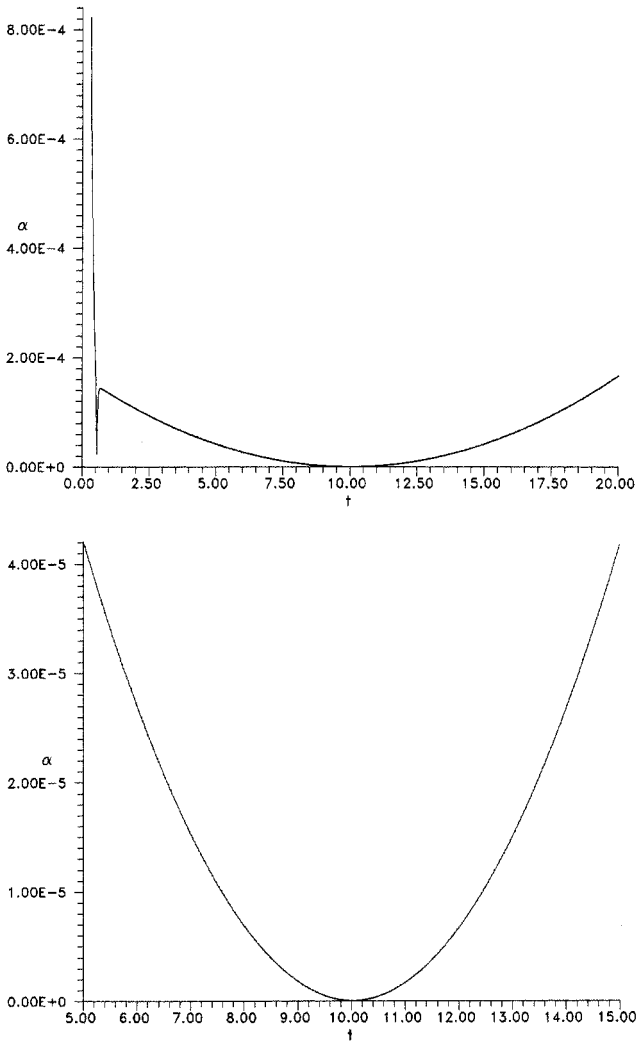

Figure 3. (a, top) Time evolution of polarizability (α) during charge transfer between a Be atom and an α-particle. (b, bottom) Magnified plot of α for $5 \leq t \leq 15$.

$E_{XC}[\rho]$, and $\eta(\mathbf{r})$ when mixing of excited states with the ground state is conspicuous through nonvanishing current density values (not shown here); (b) use of an approximate form for $f(\mathbf{r})$; (c) use of Coulomb trajectory for the nuclear motion. It may be noted that all quantities calculated here are not sensitive to these restrictions.

Figures 3 illustrate the variation of polarizability with time. It is heartening to note that except for initial transients α gradually decreases and passes through a minimum at $t = 10$ au. This fact clearly reflects that the charge exchange process considered here is a favorable one and a dynamical variant of the minimum polarizability principle is operative.

Time dependent entropy is plotted in Figure 4. Once initial undulations die off, entropy attains a steady value. At the encounter regime S suddenly starts increasing and attains a maximum value. This maximization of entropy in the encounter regime is a consequence of the maximum entropy principle in a dynamical situation, and it reflects that the charge exchange between Be and He^{2+} is a favorable process. The entropy value then comes down and in the departure regime attains the same steady value as that in the approach regime. Unlike η and μ, α and S do not strongly feel the effect of the two nuclei coming closer.

V. Concluding Remarks

A quantum fluid density functional technique is adopted in order to understand the implications of various popular electronic structure principles in connection with a typical time dependent process of charge transfer in atomic collisions. An electronegativity profile helps monitor the whole collision process in terms of approach, encounter, and departure of the projectile relative to the target. Hardness attains a very high value and remains more or less constant thereafter. Polarizability minimizes while entropy maximizes during the actual charge exchange in the encounter regime. These results are in conformity with the principles of electronegativity equalization, maximum hardness, minimum polarizability, and maximum entropy in a dynamical situation.

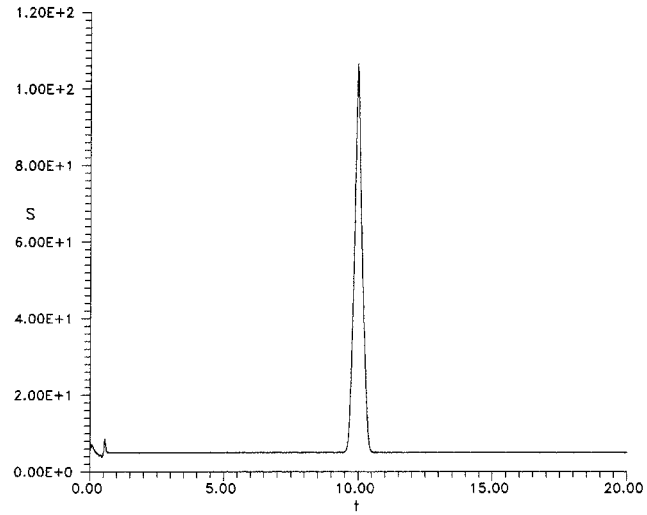

Figure 4. Time evolution of entropy (S) during charge transfer between a Be atom and an α-particle.

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