The Influence of Electric Field on the Global and Local Reactivity Descriptors: Reactivity and Stability of Weakly Bonded Complexes

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The response of the global and local reactivity density-based descriptors (chemical potential, hardness, softness, Fukui function, and local softness) in the presence of external electric field has been studied for some of the simple prototype molecular systems. In addition to the analysis on the reactivity of these systems, the influence of the electric field on the interaction energy of the complexes formed by these systems has also been studied using the recently proposed semiquantitative model based on the local hard−soft acid−base principle. By using the inverse relationship between the global hardness and softness parameters, a simple relationship is obtained for the variation of hardness in terms of the Fukui function under the external electric field. It is shown that the increase in the hardness values for a particular system in the presence of external field does not necessarily imply that the reactivity of the system would be deactivated or vice versa.

1. Introduction

The prediction of the changes in reactivity and selectivity of the atom centers within a molecule and the interaction between the molecular systems, in general, can be described by energy-density response functions.[1−4] A study on the behavior of electron density and its variation with respect to the small perturbations can thus reveal many interesting aspects concerning the reactivity pattern of the atomic and molecular systems.[5−8] The electron density of the interacting systems will be redistributed due to small perturbations, which can lead to some specific strong, weak, or van der Waals bond type interactions. These perturbations can be introduced in many ways. More importantly, the medium in which the reaction is taking place has a profound impact in determining many aspects of the reactions.[9] Owing to the importance of the solvent effects, many theoretical efforts have been devoted to study these effects. In addition to the explicit solvent effects, one can also have these effects by introducing homogeneous and inhomogeneous electric fields. An inhomogeneous electric field can be produced by placing fictitious point charges around the systems. These effects are generally known as environmental effects.[10,11] These external fields can affect the physical properties and reactivity of the molecular systems. These effects are especially important in ordered crystalline environments such as solid oxides (e.g., zeolites and other metal oxides) and biological macromolecules.[12−15] These local electrostatic fields play an important role in catalytic functions and in governing the stabilization of many biomolecular systems.[16−18] The environmental effects cause dramatic changes in the reactivity, which can be different from the gas phase. As a result, the stability of the complexes can become weaker or stronger depending on such effects. Hence, the prediction of the reactivity and stability of molecular systems in the presence of such environmental factors (solvent, electric field, or point charges) becomes an important issue.

Our interest in the present paper is to study these environmental effects on the reactivity of simple molecular systems as well as the stability of their complexes in terms of the density-based descriptors,[19] namely Fukui function, local softness, hardness, and chemical potential. These descriptors have been found to be very useful in rationalizing the reactivity patterns of the molecular systems.[23−30] Geerlings et al. have recently reviewed the theoretical basis for these descriptors and their applications.[31] Because most of these descriptors are the derivatives of energy and electron density variables, it is expected that they will provide the modified reactivity information of the molecular systems in the presence of such external effects. A semiquantitative model based on the energy density perturbation theory has also been proposed to calculate the interaction energy between the molecular systems and demonstrated its applicability in detail.[32−34] This model also forms the theoretical basis for the local version of the hard−soft acid−base (HSAB) principle. This model has been critically examined for the general types of molecular interactions,[36,28] and its reliability has been systematically analyzed with respect to several theoretical factors, such as basis set, electron correlation, and different electron population methodologies.[37]

The previous studies have dealt with the interactions in vacuum (or in the gas phase), where the system is completely independent of its surroundings.[33,34,36,37] However, if one is interested in the features of the chemical process in condensed media such as aqueous solution or in the presence of other external fields, it is important to include such external effects. Such studies, in particular, the change in the reactivity and stability of different complexes due to the applied electric field in terms of the reactivity descriptors, are very scarce in the literature. By using energy-density perturbation methods, Fuentealba and Cedillo have derived an expression for the variation of Kohn−Sham Fukui function under the external fields involving the Unsöld approximation.[38] Senet has recently generalized the higher-order derivatives of global and local reactivity descriptors in terms of different perturbation variables

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and included the linear and nonlinear response functions within the framework of DFT.[39] Apart from these few works, there have been other studies considering the solvent effect explicitly to investigate the reactivity of molecular systems by the reactivity descriptors using the continuum dielectric model, Born−Onsager approach, and effective fragment potential approach.[40−44]

Accordingly, in this paper, we will study how the global and local reactivity descriptors (hardness and Fukui function) response in the presence of an external perturbation. In addition, an attempt has also been made to study the stability of the model systems using these descriptors. By using a simple relationship between the hardness and softness parameters, the variation of these descriptors in the presence of external field has also been explained.

The present paper is organized as follows: In Section II, we give a brief theoretical background of the global and local reactivity descriptors and describe the local HSAB principle for the single-site interactions. In Section III, the methodology and computational details are presented. In Section IV, we will present our results for the systematic description of the reactivity and stability of the molecular systems in the presence of external field in terms of these reactivity descriptors.

2. Theoretical Background

2.1. Global and Local Reactivity Descriptors. The ground-state energy of an atom or a molecule, in density functional theory, can be expressed in terms of electron density, $\rho(r)$ as[35]

$$E[\rho] = F_{\mathrm{HK}}[\rho] + \int v(r)\rho(r)\,\mathrm{d}r \tag{1}$$

where, $v(r)$ is the external potential and $F_{\mathrm{HK}}[\rho]$ is the universal Hohenberg−Kohn functional expressed as

$$F_{\mathrm{HK}}[\rho] = T[\rho] + V_{\mathrm{ee}}[\rho] \tag{2}$$

is the sum of electronic kinetic energy ($T[\rho]$) and electron−electron interaction energy ($V_{\mathrm{ee}}[\rho]$)

The first and second partial derivative of $E[\rho]$ with respect to the number of electrons N under constant external potential $v(r)$ are defined as chemical potential, μ, and the hardness, η, for a system[21]

$$\mu = \left(\frac{\partial E[\rho]}{\partial N}\right)_{v(r)} \tag{3}$$

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E[\rho]}{\partial N^2}\right)_{v(r)} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \tag{4}$$

Global softness, S, defined as the inverse of hardness, can be written as

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} \tag{5}$$

It has been customary to use the finite difference approximation to compute μ and η as[19]

$$\mu \approx \frac{-I - A}{2} \tag{6}$$

$$\eta \approx \frac{I - A}{2} \tag{7}$$

where I and A are ionization potential and electron affinity of a chemical species, respectively.

The principle of maximum hardness was proposed by Pearson,[45] relating the hardness and stability of a system at constant chemical potential and later proved by Parr and Chattaraj.[46] The global hardness reflects the overall stability of a system. However, the site selectivity and reactivity can only be studied using the local reactivity descriptors, such as local softness,[20b] $s(r)$, which is defined as

$$s(r) = \left(\frac{\partial \rho(r)}{\partial \mu}\right)_{v(r)} = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)}\left(\frac{\partial N}{\partial \mu}\right)_{v(r)} = f(r)S \tag{8}$$

and

$$\int s(r)\,\mathrm{d}r = S \tag{9}$$

where $f(r)$ is the Fukui function (FF),[20a]

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} = \left(\frac{\delta \mu}{\delta v(r)}\right)_N \tag{10}$$

Thus, Fukui function can be interpreted either as the change of electron density at point r when the total number of electrons is changed or as the sensitivity of chemical potential of a system to an external perturbation at a particular point r.

The N discontinuity problem of atoms and molecules[47] in eq 10 leads to the introduction[20a] of both right- and left-hand-side derivatives at a given number of electrons, $N_0 (= N)$

$$f^{+}(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^{+}_{v(r)} \quad \text{for nucleophilic attack, and} \tag{11a}$$

$$f^{-}(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^{-}_{v(r)} \quad \text{for electrophilic attack} \tag{11b}$$

By the finite difference method using the electron densities of N_0, $N_0 + 1$, and $N_0 - 1$ electron systems, Fukui functions for the nucleophilic and electrophilic attack can be defined respectively as

$$f^{+}(r) \approx \rho_{N_o+1}(r) - \rho_{N_o}(r) \tag{12a}$$

$$f^{-}(r) \approx \rho_{N_o}(r) - \rho_{N_o-1}(r) \tag{12b}$$

and for radical attack,

$$f^{o}(r) \approx \frac{1}{2}(\rho_{N_o+1}(r) - \rho_{N_o-1}(r)) \tag{12c}$$

To describe the site reactivity or site selectivity, Yang et al.[22] proposed an atom-condensed Fukui function based on the idea of electronic population around an atom in a molecule, similar to the procedure followed in population analysis technique.[49] The condensed Fukui function for an atom k undergoing nucleophilic, electrophilic, or radical attack can be defined respectively as

$$f_k^{+} \approx q_k^{N_o+1} - q_k^{N_o} \tag{13a}$$

$$f_k^{-} \approx q_k^{N_o} - q_k^{N_o-1} \tag{13b}$$

$$f_k^{o} \approx \frac{1}{2}(q_k^{N_o+1} - q_k^{N_o-1}) \tag{13c}$$

where q_k's are electronic population of the kth atom of a particular species. The condensed local softness, s_k^{+} and s_k^{-}, are defined accordingly for nucleophilic and electrophilic attack, respectively.

2.2. Local HSAB Principle for the Single Interacting Site. Using energy as a functional of number of electrons (N) and the external potential (v), the interaction energy of the two interacting model systems A and B is given as[32,48]

$$\Delta E_{\mathrm{int}} = \frac{-1}{2}\left(\frac{(\mu_{\mathrm{A}} - \mu_{\mathrm{B}})^2}{\eta_{\mathrm{A}} + \eta_{\mathrm{B}}}\right)_{\nu} - \frac{1}{2} N_{\mathrm{AB}}{}^2(\nu_{\mathrm{AB}} - \eta^*_{\mathrm{AB}})_{\mu} \quad (14)$$

where η_{AB} and η^*_{AB} are the hardness of the complex at the equilibrium and at the isolated state, respectively. For the details of the mathematical part of the derivation for eq 11, one can refer to the work of Gazquez and Mendez[32,48] and our work.[33,34] In this model, the interaction between the system A and B is assumed to take place in two steps, ΔE_{v} and ΔE_{μ}. In the first step, the interaction takes place at constant external potential through the equalization of chemical potential, which is referred as ΔE_{v}.[32] In the second step, A and B evolve toward the equilibrium state through changes in the electron density of the global system produced at constant chemical potential, which is referred ΔE_{μ}.[48] The second step is a manifestation of principle of maximum hardness.[45,46] One can relate the difference in the hardness terms present in the second term of the above eq 14 to the softness of system A and B with a proportionality constant (K).[33] Thus, we have shown that, by introducing λ as the product of $2N_{\mathrm{AB}}{}^2$ and the proportionality constant K, ΔE_{μ} can be rewritten in terms of the softness of the systems A and B as

$$\Delta E_{\mu} = -\frac{1}{2} N_{\mathrm{AB}}{}^2 K\left(\frac{1}{(S_{\mathrm{A}} + S_{\mathrm{B}})}\right)_{\mu} = -\lambda[1/4(S_{\mathrm{A}} + S_{\mathrm{B}})]_{\mu} \quad (15)$$

This parameter λ can be computed rigorously only through the softness of the molecular complexes. On substituting the expression (eq 15) in eq 14, one can get the global model in terms of the softness parameter of the systems A and B.

$$\Delta E_{\mathrm{int}} \approx \frac{-(\mu_{\mathrm{A}} - \mu_{\mathrm{B}})^2}{2}\left(\frac{S_{\mathrm{A}}S_{\mathrm{B}}}{S_{\mathrm{A}} + S_{\mathrm{B}}}\right)_{\nu} - \frac{1}{4}\left(\frac{\lambda}{S_{\mathrm{A}} + S_{\mathrm{B}}}\right)_{\mu} \quad (16)$$

If the interaction between the systems occur through the atom x of A with the atom k of the molecular system B, one can express the total interaction energy from the local point of view as[32,33]

$$(\Delta E_{\mathrm{int}})_{\mathrm{A}x-\mathrm{B}k} = \frac{-(\mu_{\mathrm{A}} - \mu_{\mathrm{B}})^2}{2}\left(\frac{S_{\mathrm{A}} f_{\mathrm{A}x} S_{\mathrm{B}} f_{\mathrm{B}k}}{S_{\mathrm{A}}\, f_{\mathrm{A}x} + S_{\mathrm{B}}\, f_{\mathrm{B}k}}\right)_{\nu} - \frac{1}{4}\left(\frac{\lambda}{S_{\mathrm{A}}\, f_{\mathrm{A}x} + S_{\mathrm{B}}\, f_{\mathrm{B}k}}\right)_{\mu} \quad (17)$$

where S_{A},S_{B}, and $f_{\mathrm{A}x}$, $f_{\mathrm{B}k}$ are the global softness and condensed FF of the atoms x and k in systems A and B, respectively. We have used the local softness and FF of isolated systems, and this approximation is justified for weak to moderately weak interactions. We have related the parameter λ as the change in the electron densities at the interacting site before and after the interaction process.[33] This change will give the effective number of valence electrons that have participated in the interaction process. Thus, an expression for the term λ can be written as the difference in the sum of the atomic charges of the system A before and after the interaction,

$$\lambda_{\mathrm{A}} = \sum_{i=1}^{p} Q^{\mathrm{eq}}_{\mathrm{A}_i} - \sum_{i=1}^{p} Q^{\mathrm{o}}_{\mathrm{A}_i} \quad (18)$$

Alternately, the term λ can also be defined for the system B as

$$\lambda_{\mathrm{B}} = \sum_{i=1}^{q} Q^{\mathrm{eq}}_{\mathrm{B}_i} - \sum_{i=1}^{q} Q^{\mathrm{o}}_{\mathrm{B}_i} \quad (19)$$

The indices p and q are the number of atoms of systems A and B respectively, and Q^{eq} refers to the condensed electron population of the respective atoms in equilibrium and Q° refers to the condensed electron population of the respective atoms of the isolated systems.

The other details of the above expression and its extension to different types of interactions have been explained in our recent work.[34]

3. Methodology and Computational Details

In this study, we have chosen some of the prototype systems HCCH, HF, HCN, and CO and the weakly bonded complexes, namely HCC**H**—**C**O, HCC**H**—**O**C, F**H**—**C**O, F**H**—**O**C, NC**H**—**C**O, NC**H**—**O**C, HCC**H**—**N**CH, and F**H**—**N**CH (bold atoms are the reactive atoms). All of the systems are aligned along the Z-axis of the coordinate system, and hence the principle bond axis is the Z-axis. All individual monomers and their complexes were completely optimized at the HF level with zero field using the 6-31G (d,p) basis set, and these geometries have been considered for further study. The minima of all these systems and their complexes have been confirmed by frequency analysis. The electric fields were varied from 0.000 au to 0.012 au in steps of 0.002 au to calculate the energy of neutral, cationic, and anionic species at the DFT level with the B3LYP hybrid functional. The electric field has been applied parallel and perpendicular to the principal axis (bond axis) of all of the molecular systems. The chemical potential, hardness, and condensed FF were calculated from eqs 6, 7, and 13, respectively. The effect of change in the orientation of the electric field along the principal axis for all of the molecular systems has also been studied. All of the calculations were performed using the GAMESS system of programs.[50] The expression (eq 17) is used for the computation of interaction energy of the complexes interacting through single sites. The parameter λ has been calculated using eqs 18 or 19 through the Lowdin population scheme.[51] In conventional methods, the interaction energy is evaluated by the difference between the energy of the complex AB and sum of the energy of the monomer A and B, $\Delta E = E_{\mathrm{AB}} - (E_{\mathrm{A}} + E_{\mathrm{B}})$.

4. Results and Discussions

4.1. The Effect of Electric Field on Global and Local Reactivity Descriptors. In this section, we will first discuss the effect of the electric field on the global reactivity descriptors (GRD) and local reactivity descriptors(LRD) for some of the systems, namely, HF, CO, HCN, and C_2H_2, and later make an attempt to provide a possible explanation for the observations. The subsequent discussion on the stability of the weakly bonded complexes will be made in the next section. The changes in GRD and LRD (chemical potential, hardness, and Fukui functions) with respect to zero field for all the monomers against the electric field are presented graphically in Figures 1−4. When

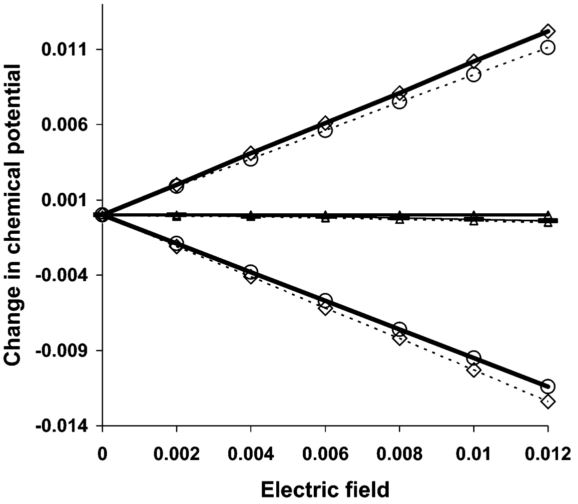

Figure 1. Plot of change in chemical potential with respect to zero field against electric field for the molecular systems, HF (◊), CO (○), HCN (△), and HCCH (−). Dashed line represents the values of the parameter when the field is applied toward the electronegative atom, while the solid line represents the value of that parameter when the field is applied in the opposite direction.

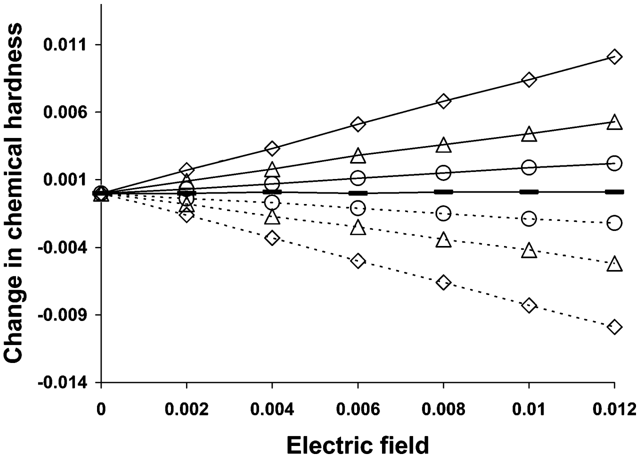

Figure 2. Plot of change in chemical hardness with respect to zero field against electric field for the molecular systems, HF (◊), CO (○), HCN (△), and HCCH (−). Dashed line represents the values of the parameter when the field is applied toward the more electronegative atom, while the solid line represents the value of that parameter when the field is applied in the opposite direction

the electric field is applied along the more electronegative atom of HF, CO, and HCN, it has been observed that the hardness values for all the molecular systems decrease with the increase of electric field strength from 0.000 au to 0.012 au (Figure 2). In case of C_2H_2, due to the symmetrical nature of the molecule, we observe that the hardness is constant in this field range. Further, the global chemical potential is found to decrease as the electric field is applied along the more electronegative atom for all of these systems, except in CO, where it follows a reverse trend (Figure 1). It is interesting to note that the change in the values of chemical potential change is more significant than the variation of hardness under the application of external field.

The influence of the electric field on the condensed Fukui function of the reactive atoms is observed to be similar to the case of the global descriptors. It is also evident from Figures 3 and 4 that a small amount of electric field is sufficient to distort the electron density distribution, and hence it will have a great impact on the reactivity of the systems as well.

Now, from Figures 3 and 4, we observe that if the electric field is applied toward the more electronegative atom of the systems HF and HCN, the value of its condensed Fukui function for electrophilic attack (nucleophilicity) decreases with increasing field strength. For instance, when the field is applied toward the N and F atoms in HCN and HF, respectively, the nucleophilicity of these atoms decreases. This is also supported by the fact that the induced dipole moment of these systems decreases when the field is applied along the more electronegative atom (Table 1a,c). It is interesting to note the exceptional behavior of CO. When the field is applied toward the C atom, its nucleophilicity increases marginally. However, the induced dipole moment of $C^{-}O^{+}$ decreases as the field is applied toward the C atom (Table 1b). Hence, although the pattern of induced dipole moment of CO is the same as that of HF and HCN, the behavior of the nucleophilicity of the C atom is quite different. It is well-known that CO exhibits a small dipole moment and

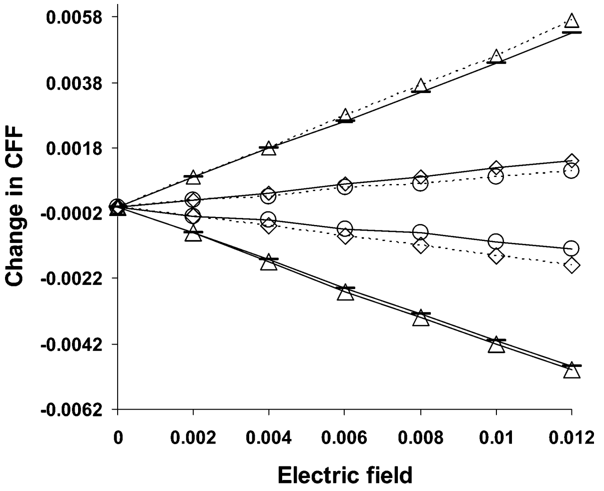

Figure 3. Plot of change in condensed Fukui function (CFF) for nucleophilic attack with respect to zero field for the reactive atoms (bolded) **H**F (◊), **C**O (○), **H**CN (△), and **H**CCH (−). Dashed line represents the values of the parameter when the field is applied toward the more electronegative atom, while the solid line represents the value of that parameter when the field is applied in the opposite direction.

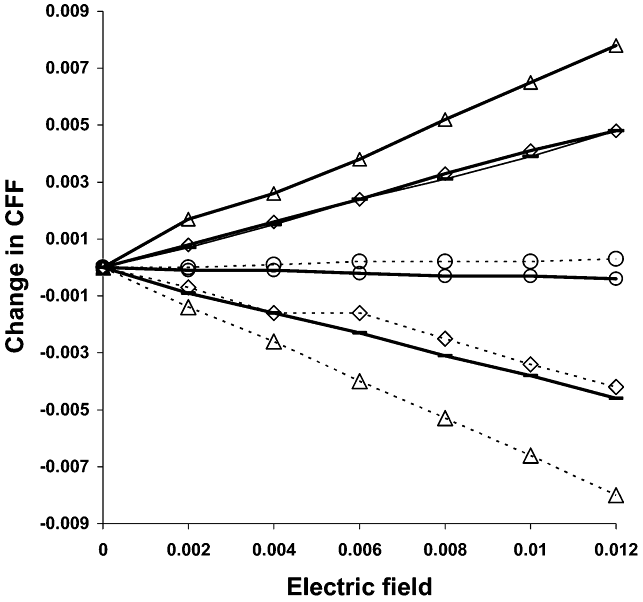

Figure 4. Plot of change in condensed Fukui function (CFF) for electrophilic attack with respect to zero field against electric field for the reactive atoms (bolded) H**F** (◊), **C**O (○), HC**N** (△), and **H**CCH (−). Dashed line represents the values of the parameter when the field is applied toward the electronegative atom, while the solid line represents the value of that parameter when the field is applied in the opposite direction

TABLE 1: Variation of Chemical Potential, Hardness, and Condensed Fukui Function (all Values Are in au) and Dipole Moment (in Debye) with Electric Field for HF, CO, HCN, and C_2H_2 Molecules

(a) HF

electric field[a] (au)	chemical potential	hardness	f_H^+	f_H^-	f_F^+	f_F^-	dipole moment
0.000	−0.1911	0.3865	0.8149	0.1293	0.1851	0.8707	1.7972
0.002 (H)	−0.1891	0.3882	0.8151	0.1285	0.1849	0.8715	1.8194
0.004 (H)	−0.1870	0.3898	0.8153	0.1277	0.1847	0.8723	1.8414
0.006 (H)	−0.1850	0.3916	0.8156	0.1269	0.1844	0.8731	1.8634
0.008 (H)	−0.1830	0.3933	0.8158	0.1260	0.1842	0.8740	1.8851
0.010 (H)	−0.1809	0.3949	0.8161	0.1252	0.1839	0.8748	1.9068
0.012 (H)	−0.1789	0.3966	0.8163	0.1245	0.1837	0.8755	1.9282
0.002 (F)	−0.1932	0.3849	0.8146	0.1300	0.1854	0.8700	1.7748
0.004 (F)	−0.1952	0.3832	0.8143	0.1309	0.1857	0.8691	1.7523
0.006 (F)	−0.1973	0.3815	0.8140	0.1318	0.1860	0.8682	1.7297
0.008 (F)	−0.1993	0.3799	0.8137	0.1327	0.1863	0.8673	1.7068
0.010 (F)	−0.2014	0.3782	0.8134	0.1335	0.1866	0.8665	1.6839
0.012 (F)	−0.2035	0.3766	0.8131	0.1345	0.1869	0.8655	1.6607

(b) CO

electric field (au)	chemical potential	hardness	f_C^+	f_C^-	f_O^+	f_O^-	dipole moment
0.000	−0.1927	0.3183	0.6865	0.6886	0.3135	0.3114	0.1412
0.002 (C)	−0.1908	0.3179	0.6863	0.6886	0.3137	0.3114	0.0793
0.004 (C)	−0.1890	0.3176	0.6862	0.6887	0.3138	0.3113	0.0176
0.006 (C)	−0.1871	0.3172	0.6859	0.6888	0.3141	0.3112	−0.0440
0.008 (C)	−0.1852	0.3168	0.6858	0.6888	0.3142	0.3112	−0.1054
0.010 (C)	−0.1834	0.3164	0.6856	0.6888	0.3144	0.3112	−0.1667
0.012 (C)	−0.1816	0.3161	0.6854	0.6889	0.3146	0.3111	−0.2278
0.002 (O)	−0.1946	0.3186	0.6868	0.6885	0.3132	0.3115	0.2033
0.004 (O)	−0.1965	0.3190	0.6869	0.6885	0.3131	0.3115	0.2655
0.006 (O)	−0.1984	0.3194	0.6872	0.6884	0.3128	0.3116	0.3279
0.008 (O)	−0.2003	0.3198	0.6873	0.6883	0.3127	0.3117	0.3905
0.010 (O)	−0.2022	0.3202	0.6876	0.6883	0.3124	0.3117	0.4532
0.012 (O)	−0.2041	0.3205	0.6878	0.6882	0.3122	0.3118	0.5161

(c) HCN

electric field (au)	chemical potential	hardness	f_N^-	f_N^+	f_C^-	f_C^+	f_H^-	f_H^+	dipole moment
0.000	−0.1774	0.3305	0.4791	0.3958	0.4059	0.5011	0.1151	0.1030	2.8794
0.002 (H)	−0.1774	0.3314	0.4804	0.3966	0.4050	0.5012	0.1146	0.1022	2.9773
0.004 (H)	−0.1774	0.3323	0.4817	0.3974	0.4041	0.5013	0.1142	0.1013	3.0750
0.006 (H)	−0.1774	0.3333	0.4829	0.3982	0.4033	0.5014	0.1138	0.1004	3.1724
0.008 (H)	−0.1774	0.3341	0.4843	0.3989	0.4023	0.5015	0.1134	0.0996	3.2696
0.010 (H)	−0.1774	0.3349	0.4856	0.3996	0.4014	0.5016	0.1131	0.0988	3.3666
0.012 (H)	−0.1774	0.3358	0.4869	0.4004	0.4005	0.5016	0.1128	0.0980	3.4633
0.002 (N)	−0.1775	0.3297	0.4777	0.3951	0.4067	0.5010	0.1156	0.1039	2.7812
0.004 (N)	−0.1775	0.3288	0.4765	0.3943	0.4075	0.5009	0.1160	0.1048	2.6827
0.006 (N)	−0.1776	0.3280	0.4751	0.3936	0.4083	0.5007	0.1165	0.1058	2.5840
0.008 (N)	−0.1777	0.3271	0.4738	0.3927	0.4091	0.5005	0.1171	0.1067	2.4851
0.010 (N)	−0.1778	0.3263	0.4725	0.3920	0.4098	0.5004	0.1177	0.1076	2.3858
0.012 (N)	−0.1779	0.3253	0.4711	0.3912	0.4105	0.5002	0.1182	0.1087	2.2863

(d) C_2H_2

electric field (au)[b]	chemical potential	hardness	$f_{C_1}^-$	$f_{C_1}^+$	$f_{C_2}^-$	$f_{C_2}^+$	$f_{H_3}^-$	$f_{H_3}^+$	$f_{H_4}^-$	$f_{H_4}^+$
0.000	−0.1194	0.2893	0.4118	0.4104	0.4118	0.4104	0.0882	0.0896	0.0882	0.0896
0.002 (C_2−H_3)	−0.1194	0.2893	0.4139	0.4105	0.4098	0.4103	0.0873	0.0888	0.0873	0.0905
0.004 (C_2−H_3	−0.1195	0.2894	0.4160	0.4106	0.4077	0.4102	0.0866	0.0880	0.0866	0.0914
0.006 (C_2−H_3)	−0.1195	0.2893	0.4180	0.4106	0.4056	0.4100	0.0859	0.0871	0.0859	0.0922
0.008 (C_2−H_3)	−0.1196	0.2894	0.4201	0.4107	0.4035	0.4100	0.0851	0.0863	0.0851	0.0931
0.010 (C_2−H_3)	−0.1197	0.2894	0.4221	0.4107	0.4014	0.4098	0.0844	0.0855	0.0844	0.0940
0.012 (C_2−H_3)	−0.1198	0.2894	0.4241	0.4108	0.3993	0.4096	0.0836	0.0847	0.0836	0.0949

[a] Atom(s) along which the electric field has been applied is shown in the parenthesis. [b] Variation when the field is applied along one of the C−H bonds are given, as the other values will be the same due to the symmetric nature.

the value is quite sensitive to the calculation. This probably explains the anomaly. On the other hand, the electrophilicity of the electropositive atom in HF increases when the field is applied toward that atom (Table 1a). However, when the field is applied toward the H and O atoms in the case of HCN and CO, respectively, its electrophilicity decreases. This behavior of CO is anomalous with the behavior of induced dipole moment. However, in either case, it is interesting to note the marginal change in electrophilicity as well as the nucleophilicity of the C and O atoms in CO. This is again expected due to its small dipole moment. The symmetrical molecule C_2H_2 has a different behavior. When the field is applied toward one of the

TABLE 2: Variation of the Parameter λ (in au) with Electric Field for the Molecular Complexes

	values of the parameter λ for the complex							
	FH—CO when field is toward		FH—OC when field is toward		HCCH—CO when field is toward		HCCH—OC when field is toward	
electric field (au)	FH	CO	FH	OC	HCCH	CO	HCCH	OC
0.000	0.0453	0.0453	0.0253	0.0253	0.0128	0.0128	0.0084	0.0084
0.002	0.0435	0.0472	0.0244	0.0262	0.0120	0.0136	0.0080	0.0088
0.004	0.0417	0.0491	0.0236	0.0272	0.0113	0.0145	0.0076	0.0093
0.006	0.0399	0.0510	0.0227	0.0281	0.0105	0.0153	0.0071	0.0098
0.008	0.0383	0.0530	0.0219	0.0291	0.0098	0.0163	0.0068	0.0103
0.010	0.0366	0.0551	0.0211	0.0301	0.0091	0.0173	0.0065	0.0107
0.012	0.0349	0.0572	0.0203	0.0311	0.0084	0.0183	0.0060	0.0113

	values of the parameter λ for the complex							
	NCH—CO when field is toward		NCH—OC when field is toward		HCN—HCCH when field is toward		HCN—HF when field is toward	
electric field (au)	NCH	CO	NCH	OC	HCN	HCCH	HCN	HF
0.000	0.0202	0.0202	0.0142	0.0142	0.0180	0.0180	0.0564	0.0564
0.002	0.0191	0.0212	0.0136	0.0148	0.0190	0.0171	0.0584	0.0544
0.004	0.0181	0.0223	0.0129	0.0154	0.0200	0.0162	0.0604	0.0526
0.006	0.0172	0.0236	0.0124	0.0161	0.0212	0.0153	0.0625	0.0507
0.008	0.0162	0.0248	0.0119	0.0168	0.0223	0.0143	0.0645	0.0489
0.010	0.0153	0.0261	0.0113	0.0174	0.0235	0.0135	0.0667	0.0470
0.012	0.0145	0.0274	0.0108	0.0182	0.0246	0.0126	0.0689	0.0453

C—H bond, the nucleophilicity as well as the electrophilicity of those atoms decreases, but the decrease in the electrophilicity of the C atom is marginal (Table 1d). Moreover, on comparing across the different systems like HF and HCN, the electrophilicity of the H atom in the former is found to be more than that of the latter at all of the field values. In case of CO, the value of the Fukui function for C (f_C^-) is observed to be more than that of O (f_O^-). These results reveal that the nucleophilicity of the C atom is more than that of the O atom.

It is also pertinent to note that the variation of the GRD and LRD is observed to be almost linear and uniform with respect to the applied electric field except for the case of C_2H_2. In the case of C_2H_2, the chemical potential and hardness almost remain constant at the chosen field values.

As can be seen from Figures 1−4, as the field direction is reversed, the variation of GRD and LRD are reversed. This important observation reveals that the direction of the external perturbation on the molecular systems will have an important role in defining the reactivity of a particular atom.

Another interesting observation is that there is no significant change in the value of the global and local reactivity descriptors when the external field is applied perpendicular to the molecular axis of these linear systems. It also means that the polarization induced by the electric field in the perpendicular direction is almost negligible for these systems and hence one cannot expect any change in the reactivity of the descriptors. It should, however, be noted that the change in the reactivity and stability trend for the polyatomic and nonlinear systems can be significant and this is rather difficult to explain.

Earlier, we discussed the change in the hardness and condensed Fukui function parameters due to the external perturbation on the molecular system. It is of particular interest to establish a relation for the variation of these two parameters under the external field. In a recent paper, Fuentealba and Cedillo have shown that the variation of the Kohn−Sham Fukui function with respect to the external perturbation depends on the knowledge on the HOMO density and a mean energy difference of all of the occupied and unoccupied orbitals.[38] Here, the quantity, mean energy difference, has been approximately interpreted as hardness. Under this approximation, it has been stated that the greater the hardness, the smaller the variation of the Fukui function will be under the external perturbation. This statement signifies that the system will become less reactive as the hardness of the systems increases due to the external perturbation.

Contrary to the above statement, in the present study, we have observed that both the hardness and Fukui function decreases when the field is applied along the more electronegative atom of the HF and HCN systems. At the same time, it has also been noticed that the f_k^- value of C in CO increases marginally with the increase of field values and the global hardness value decreases. A similar effect has also been observed for other systems also. These results may probably imply that the decrease of hardness parameters does not necessarily mean that reactivity of the systems increases or vice versa. In what follows, we explain the above using a simple relationship for the variation of the hardness parameters and FF with respect to the electric field. Considering the inverse relationship of hardness with global softness, one can express the variation of hardness with respect to the field (F) as ($\partial\eta/\partial F$)[52]

$$\partial\eta/\partial F = -1/{S_0}^2\ \partial S/\partial F \tag{20}$$

where S_0 is the global softness. The above expression has been used earlier to explain a relation between the polarizability and dipole moment as well as to explain the change in hardness values with respect to the external field.[52]

At this stage, two comments are pertinent. First, the change in hardness with respect to the electric field is inversely proportional to the square of global softness calculated at the zero fields with a negative sign. The second important point is that the variation of hardness with respect to the external field is directly proportional to the first-order variation of softness of the system.

It can be noticed from the above expression (eq 20) that the change in hardness parameter with respect to the electric field is actually dependent on the variation of FF of all of the atoms present in the molecule. The values of the condensed Fukui function for some of the atoms in a molecule in the presence of the field can become more (or less) than the value of the FF calculated in the isolated state or vice versa. In any case, it

TABLE 3: Values of Interaction Energy (kcal/mol) Calculated by Both Local HSAB and Quantum Chemical Methods With Electric Field for FH—CO and FH—OC, HCCH—CO and HCCH—OC, NCH—CO and NCH—OC, and HCCH—NCH Complexes

(a) F**H**—**C**O and F**H**—**O**C complexes

	interaction energy (kcal/mol)							
	F**H**—**C**O complex when field is toward				F**H**—**O**C complex when field is toward			
	FH		CO		FH		OC	
electric field (au)	local HSAB	quantum[a] chemical	local HSAB	quantum chemical	local HSAB	quantum chemical	local HSAB	quantum chemical
0.000	−3.3277	−4.3499	−3.3277	−4.3499	−2.5715	−2.3513	−2.5715	−2.3513
0.002	−3.1884	−4.0757	−3.4808	−4.6323	−2.4743	−2.1367	−2.6694	−2.5715
0.004	−3.0535	−3.8102	−3.6396	−4.9228	−2.3877	−1.9271	−2.7786	−2.7974
0.006	−2.9255	−3.5517	−3.8058	−5.2221	−2.2904	−1.7225	−2.8784	−3.0290
0.008	−2.8181	−3.3013	−3.9841	−5.5302	−2.2051	−1.5230	−2.9876	−3.2656
0.010	−2.7083	−3.0591	−4.1755	−5.8478	−2.1191	−1.3284	−3.0968	−3.5084
0.012	−2.6054	−2.8238	−4.3719	−6.1741	−2.0338	−1.1389	−3.2078	−3.7575

(b) HCC**H**—**C**O and HCC**H**—**O**C complexes

	interaction energy(kcal/mol)							
	HCC**H**—**C**O complex when field is toward				HCC**H**—**O**C complex when field is toward			
	HCCH		CO		HCCH		OC	
electric field (au)	local HSAB	quantum chemical	local HSAB	quantum chemical	local HSAB	quantum chemical	local HSAB	quantum chemical
0.000	−1.8524	−1.5995	−1.8524	−1.5995	−2.2446	−1.0210	−2.2446	−1.0210
0.002	−1.7376	−1.4458	−1.9672	−1.7633	−2.1549	−0.9080	−2.3331	−1.1414
0.004	−1.6359	−1.3021	−2.0953	−1.9378	−2.0676	−0.8032	−2.4479	−1.2701
0.006	−1.5217	−1.1672	−2.2126	−2.1229	−1.9559	−0.7059	−2.5634	−1.4075
0.008	−1.4213	−1.0423	−2.3350	−2.3193	−1.8932	−0.6166	−2.6782	−1.5525
0.010	−1.3215	−0.9268	−2.4975	−2.5264	−1.8311	−0.5350	−2.7698	−1.7062
0.012	−1.2218	−0.8208	−2.6406	−2.7460	−1.7206	−0.4608	−2.9116	−1.8681

(c) NC**H**—**C**O and NC**H**—**O**C complexes

	interaction energy(kcal/mol)							
	NC**H**—**C**O complex when field is toward				NC**H**—**O**C complex when field is toward			
	NCH		CO		NCH		OC	
electric field (au)	local HSAB	quantum chemical	local HSAB	quantum chemical	local HSAB	quantum chemical	local HSAB	quantum chemical
0.000	−2.5709	−2.5546	−2.5709	−2.5546	−3.4632	−1.6955	−3.4632	−1.6955
0.002	−2.4228	−2.3312	−2.7065	−2.7887	−3.3107	−1.5123	−3.6119	−1.8869
0.004	−2.2892	−2.1172	−2.8558	−3.0334	−3.1388	−1.3366	−3.7651	−2.0858
0.006	−2.1674	−1.9127	−3.0328	−3.2888	−3.0133	−1.1684	−3.9426	−2.2935
0.008	−2.0350	−1.7175	−3.1965	−3.5548	−2.8897	−1.0078	−4.1177	−2.5088
0.010	−1.9164	−1.5318	−3.3747	−3.8335	−2.7435	−0.8547	−4.2708	−2.7328
0.012	−1.8104	−1.3548	−3.5536	−4.1234	−2.6199	−0.7091	−4.4760	−2.9650

(d) HCC**H**—**N**CH complex

	interaction energy (kcal/mol)			
	HCC**H**—**N**CH complex when field is toward			
	HCCH		NCH	
electric field (au)	local HSAB	quantum chemical	local HSAB	quantum chemical
0.000	−3.3446	−2.5929	−3.3446	−2.5929
0.002	−3.1821	−2.3042	−3.5272	−2.8953
0.004	−3.0164	−2.0287	−3.7111	−3.2116
0.006	−2.8545	−1.7671	−3.9326	−3.5423
0.008	−2.6738	−1.5179	−4.1328	−3.8881
0.010	−2.5301	−1.2826	−4.3524	−4.2489
0.012	−2.3670	−1.0599	−4.5557	−4.6247

[a] $\Delta E_{\mathrm{int}} = E_{\mathrm{AB}} - E_{\mathrm{A}} - E_{\mathrm{B}}$

should be noted that the net effect would be proportional to $d\eta/dF$. It also signifies that the decrease or increase of hardness of a molecule under the external field does not necessarily imply that the reactivity of a specific site or atom present in the molecule would be enhanced or deactivated due to the variation in the hardness parameter. The variation of the hardness parameter in the presence of external perturbation is actually dependent on the net cooperative effect exhibited by the collection of all of the atoms present in the molecule. This is well supported by our earlier discussions. Although the present analysis is not very rigorous, it can, however, explain the present observation in the variation of condensed FF as well as the

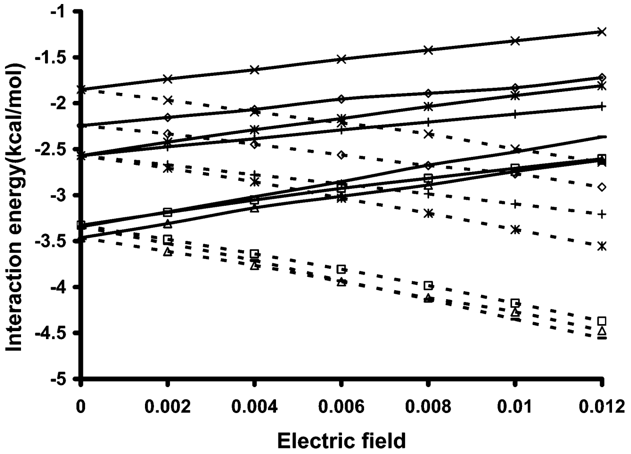

Figure 5. Effect of electric field on the interaction energy (kcal/mol) for F**H**—**C**O (□), F**H**—**O**C (|), NC**H**—**C**O (*), NC**H**—**O**C (△), and HCC**H**—**C**O (×), HCC**H**—**O**C (◊), and HCC**H**—**N**CH (−) complexes. Dashed lines signify that the field is applied along CO while solid lines represent the interaction energy values when the field direction is reversed. For interactions occurring through the N atom, dashed lines signify that the field is applied along NCH, while solid lines represent the interaction energy values when the field direction is reversed.

hardness parameters. A further detailed study should be made in this direction.

4.2. Stability of Complexes under External Field. In Section 4.1, the influence of electric field on the determination of global and local parameters has been explained qualitatively. Because the external field influences significantly on both the charge-transfer term (λ) and the global and local reactivity descriptors, it would be, therefore, interesting to study the stability of the complexes formed by the above systems in the presence of the external field. The stability of the complexes will therefore primarily depend on these two parameters.

Although different complexes can be formed from the above-mentioned systems, we have considered only selected complexes formed by the interaction of CO with C_2H_2, HCN, and HF as well as the interaction of HCN with C_2H_2 through the N atom in the presence of the electric field. As both of the atoms C and O in CO can interact with other systems, we have also considered the other possible modes of interaction, CHCH—OC, NCH—OC, and FH—OC. The effects of increasing the magnitude of electric field strength on the value of the charge-transfer term λ for the above complexes are reported in Table 2 and the interaction energies are reported in Table 3a,b,c,d for the F**H**—**C**O, F**H**—**O**C, HCC**H**—**C**O, HCC**H**—**O**C, NC**H**—**C**O, NC**H**—**O**C, and HCC**H**—**N**CH complexes, respectively.

It can be seen from Table 2 that, when the field is applied toward C_2H_2 for all the above-mentioned interactions, the value of the intermolecular charge-transfer term λ decreases linearly upon increase in the strength of the electric field. It also shows that the direction of the external field is important for the intermolecular charge transfer, which will eventually affect the mutual interaction between the monomer systems and, hence, the stability of the complexes also. This field effect is very important in studying the primary electron-transfer processes, especially for the case of electron donor—acceptor systems.

Moreover, when the field direction is toward CO and whether the interaction occurs through the C or O atoms, the intermolecular charge-transfer term λ always increases, but HCN has a dual behavior. When the field direction is toward HCN and the interaction occurs through the H atom with CO or OC, the intermolecular charge-transfer term λ decreases, but for the interaction occurring through the N atom with C_2H_2 or HF, there is an increase in the λ value with the increase in field strength.

Because the resulting effects in the Fukui function and the term λ are increasing or decreasing linearly at all of the field values depending on the field direction, the interaction energy of NC**H**—**C**O, NC**H**—**O**C, HCC**H**—**C**O, HCC**H**—**O**C, F**H**—**C**O, F**H**—**O**C, and HCC**H**—**N**CH complexes also increases and decreases approximately linearly with increasing or decreasing the field strength (Figure 5). It can also be observed that the stability of the above complexes, formed with CO, increases when the field is applied along the CO direction irrespective of the fact that the interaction may occur either through the C or the O atom. Because the nucleophilicity of C is stronger than O in CO, the interaction energy of HF with the former is much stronger than that of the later. The actual quantum chemical calculations also show this similar trend, but the local HSAB interaction energy of C_2H_2 and HCN with C in CO is less than that of the O atom. This anomaly can be attributed to the combined effect of both of the values of the charge-transfer term and the FF of the reactive atoms. But for the complex HCC**H**—**N**CH, interacting through the N atom of HCN gets stabilized when the field is applied toward HCN, whereas the interaction decreases when the field direction is reversed. The actual quantum chemical calculation for all of these complexes also shows this similar trend. Now, if we compare the stability of the above complexes (Figure 5), we can conclude that the complexes F**H**—**C**O, NC**H**—**O**C, and HCC**H**—**N**CH are more stabilized than the others and their stability increases with the increase in field strength at a particular direction.

It is also evident from Figure 5 that the effect of changing the external field direction on the interaction energy of these complexes is observed to be very significant and these trends show some similarities with the change in the value of global and local reactivity descriptors due to the external field.

In general, the calculated interaction energy for the above complexes shows that these complexes are stabilized more in the presence of an external field, in a particular direction, compared to the zero field. It is interesting to observe that, although the value of global hardness parameter increases or decreases for all of the systems in presence of the electric field, there is a further enhancement or decrease of the bond strength of these complexes at the higher field values. This interesting feature can be attributed to the increase or decrease in the value of the FF indices and the parameter λ due to the applied electric field in a particular direction.

Despite the fact of using the Lowdin-based method of population analysis and medium level basis set, the present model gives an insight about the stability of the complexes in the external field. Thus this model can be useful for studying other types of complexes in terms of these reactivity descriptors. However, a further study is required to clarify many issues on the variation of the global and local reactivity descriptors due to the external perturbation and its relation with the reactivity of the molecular systems.

5. Conclusions

The present work is focused on the study of the influence of the applied electric field (environmental effects) on the reactivity of some simple prototype systems as well as their complexes using the global and local reactivity descriptors. It is observed that the increase or decrease in the global hardness and the FF of the systems that are considered in the present work depends on the direction in which the electric field is applied along the principle bond axis. Whenever the direction of the field is changed, the descriptors show the opposite trend. This unusual trend has been explained by a simple inverse relationship between hardness and Fukui function parameters in the presence of the field. We have also demonstrated that the increase in the value of global hardness in the presence of the electric field does not necessarily imply that the reactivity of the molecular systems would be lowered or vice versa. The variation of the hardness parameter in such cases is actually dependent on the net cooperative effect exhibited by the collection of all of the atoms present in the molecule. It is also observed that complexes formed by the above simple prototype systems are more stabilized at the higher field applied in a specified direction than at the zero fields.

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