Theor Chem Account (2008) 120:375–383
DOI 10.1007/s00214-008-0437-4

REGULAR ARTICLE

Electric field response of molecular reactivity descriptors: a case study

Rahul Kar · **Sourav Pal**

Received: 27 November 2007 / Accepted: 29 February 2008 / Published online: 20 March 2008

Abstract In the present article, we study the influence of external electric field on the density-based global and local reactivity descriptors using examples of some planar nonlinear polyatomic molecules with C_{2V} point group symmetry. The study mainly involves the application of weak electric field in a direction along the principal axis and along its perpendicular direction. We also discuss the strength of the electric field studied in this work in terms of the strength of the molecular interaction. The work is expected to throw light on the effect of interactions within the above range on reactivity descriptors. Results are presented for a few prototype molecules.

Keywords Reactivity descriptors · Electric field · Planar nonlinear polyatomic molecules · Molecular interaction

1 Introduction

There has been significant recent interest on the study of the behavior of the density-based reactivity descriptors in the presence of external electric field. A systematic study was done to explore the effects of electric field on reactivity descriptors for some linear molecules [1]. Analysis of the behavior of electron density and its variation with respect to the small perturbations can disclose many interesting aspects concerning the reactivity pattern of atomic and molecular systems, due to the redistribution of the electron density [2–6]. Apart from the explicit solvent effects [7], these perturbations can be introduced by the application of external electric fields. This results in the change in reactivity and physical properties of the molecular systems. Very recently, the influence of electric field on the hydrogen bond network of methanol has been studied [8]. These effects are especially important in ordered crystalline environments, such as solid oxides and biological macromolecules [9–20]. Of late, the electric field effects on the structures, energetic and transition states of water clusters have been investigated [21]. These local electrostatic fields play an important role in catalytic functions and in governing the stabilization of many bio-molecular systems [22–30]. These external effects, in the form of electric field or solvent cause dramatic changes in the reactivity. Therefore, it is of considerable interest to predict the reactivity and stability of molecular systems in the presence of such external parameters.

In the present work, we have studied the behavior of the density-based reactivity descriptors [31], such as chemical potential, hardness, Fukui function, etc., for some planar nonlinear polyatomic molecules on application of external electric field. We have also presented the strength of interactions represented by the electric field under study. These descriptors are reliable in describing the reactivity and stability patterns of several molecular systems [32–55]. In general, the descriptors are classified to refer to the whole system, called "global reactivity descriptors" (GRD) or to a local part of the system, called "local reactivity descriptors" (LRD). As most of the descriptors are related to either derivatives of energy or electron density with respect to the number of electrons, it is expected that they would provide some useful information about the reactivity of the molecular systems in the presence of such external perturbation.

The area of conceptual density functional theory (DFT) is one of the explored areas in recent times. The various

---

Contribution to the Nino Russo Special Issue.

R. Kar · S. Pal (✉)
Physical Chemistry Division, National Chemical Laboratory,
Pune 411 008, India
e-mail: s.pal@ncl.res.in

concepts involved in conceptual DFT along with their applications have been recently reviewed [56]. Most of these studies are performed in the gas phase [57–66]. Very recently, we have studied the effect of the external electric field on the reactivity descriptors for some linear molecules. Parthasarathi et al. [67] have studied the behavior of the reactivity descriptors in the presence of electric field. Our recent study of the effect of external field was restricted only to linear molecules [1]. Solvent effects on the reactivity of molecular systems have also been studied [68–75]. An expression for the variation of Kohn–Sham Fukui function under the external field, using the energy density perturbation methods, has been derived involving Unsöld approximation [76].

In this article, we will extend our previous study on the response of the GRD and LRD to some planar nonlinear polyatomic molecules with C_{2V} symmetry. In the case of linear molecules, where the electron density is mainly distributed along the molecular axis, one would easily understand the behavior of the descriptors under the application of electric field. This is not the case with nonlinear polyatomic molecules. Therefore, it is important to understand the chemistry of the reactive atoms, in these V-shaped molecules, subjected to external perturbation in the form of external electric field. It is also important to judge the strength of the applied field values in terms of energies of interaction. This allows us to define the scope of the present work in terms of the type of molecular interaction.

The present paper has been organized as follows: we give a brief theoretical background of the global and local reactivity descriptors in Sect. 2. This is followed by the methodology and computational details in Sect. 3. In Sect. 4, we present our results for the stability and reactivity of the molecular systems in the presence of external field in terms of these reactivity descriptors. The conclusions are presented in Sect. 5.

2 Theoretical background

Within the framework of DFT, the energy of an atom or molecule can be expressed in terms of electron density, $\rho(r)$ as [77]

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

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

GRD such as chemical potential, μ and hardness [78–80], η for a system can be defined as the first and second partial derivative of $E[\rho]$ with respect to the number of electron N under constant external potential $v(r)$, respectively, as

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

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E[\rho]}{\partial N^2}\right)_{v(r)} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \tag{3}$$

Inverse of hardness is the global softness, S, expressed as

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} \tag{4}$$

In order to compute μ and η, the finite difference approximation is helpful [31]

$$\mu \approx \frac{-I - A}{2} \tag{5}$$

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

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

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. One such descriptor is local softness $s(r)$ [82], which is defined as

$$\begin{aligned} s(r) &= \left(\frac{\partial \rho(r)}{\partial \mu}\right)_{v(r)} = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} \\ &= f(r)S \end{aligned} \tag{7}$$

and

$$\int s(r)\mathrm{d}r = S \tag{8}$$

where $f(r)$ is the Fukui function(FF) [81]

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} = \left(\frac{\delta \mu}{\delta v(r)}\right)_{N} \tag{9}$$

Thus, Fukui function can be restated 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 [83,84] in Eq. (9) leads to the introduction of both right- and left- hand side derivatives at a given number of electrons, $N_0(=N)$

$$f^{+}(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^{+}_{v(r)} \quad \text{for nucleophilic attack, and} \tag{10a}$$

$$f^{-}(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^{-}_{v(r)} \quad \text{for electrophilic attack} \tag{10b}$$

By finite difference method using the electron densities of N_{o}, $N_{\mathrm{o}}+1$, $N_{\mathrm{o}}-1$ electron systems, Fukui functions for the

Table 1 Variations of chemical potential, hardness and CFF with electric field applied along the principal axis for H_2O

Electric field (in au)[a]	μ (in au)	η (in au)	f_o^-	f_H^-	f_o^+	f_H^+
0.000	−0.2185	0.2459	0.8368	0.0816	0.0753	0.4623
0.001(O)	−0.2194	0.2452	0.8363	0.0818	0.0766	0.4617
0.002(O)	−0.2202	0.2445	0.8359	0.0821	0.0781	0.4609
0.003(O)	−0.2211	0.2438	0.8354	0.0823	0.0796	0.4602
0.004(O)	−0.2220	0.2430	0.8350	0.0825	0.0812	0.4594
0.005(O)	−0.2229	0.2422	0.8345	0.0828	0.0828	0.4586
0.006(O)	−0.2239	0.2415	0.8340	0.0830	0.0845	0.4577
0.001	−0.2177	0.2467	0.8372	0.0814	0.0741	0.4629
0.002	−0.2169	0.2473	0.8377	0.0812	0.0729	0.4635
0.003	−0.2161	0.2480	0.8381	0.0810	0.0719	0.4640
0.004	−0.2153	0.2486	0.8385	0.0807	0.0711	0.4644
0.005	−0.2146	0.2493	0.8390	0.0805	0.0703	0.4648
0.006	−0.2139	0.2499	0.8394	0.0803	0.0698	0.4651

[a] Field applied towards O atom is shown in parenthesis alongside the field value

nucleophilic and electrophilic attack can be defined, respectively, as

$$f^+(r) \approx \rho_{N_o+1}(r) - \rho_{N_o}(r) \tag{11a}$$

$$f^-(r) \approx \rho_{N_o}(r) - \rho_{N_o-1}(r) \tag{11b}$$

Yang et al. [85] introduced the concept of 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 [86]. The condensed Fukui function for an atom k undergoing nucleophilic and electrophilic attack can be defined, respectively, as

$$f_k^+ \approx q_k^{N_o+1} - q_k^{N_o} \tag{12a}$$

$$f_k^- \approx q_k^{N_o} - q_k^{N_o-1} \tag{12b}$$

where q_k are electronic population of the kth atom of a particular species.

3 Methodology

To study the application of electric field in case of planar nonlinear polyatomic molecules, we consider in the present paper simple molecules belonging to C_{2v} point group symmetry, such as H_2O, CH_2S, HCHO, SO_2 and O_3. The principal axis of all these molecules is the C_2 axis of symmetry which passes through the central atom(s). First, the above molecules were optimized at DFT level using 6-31++G (d, p) basis set with B3LYP hybrid functional at zero field. These minima were further confirmed by frequency calculations. Then the field was applied along the principal axis from 0.001 to 0.006 au, increasing by 0.001 au each time, to calculate the energy of the neutral, cationic and anionic systems. Hence, the global and local parameters were calculated at each field value using the Eqs. (5), (6) and (12), respectively. The local parameters such as condensed Fukui function were calculated using the Lowdin [87,88] based method of population analysis. It should, however, be noted that for higher field values sometimes is unable to converge to the correct state for ($N \pm 1$) systems. This is one of the reasons for choosing such small field values. We also analyzed whether the applied field is strong enough to really mimic the molecular interaction and reaction. To achieve this, we calculated the difference in the energy of the molecule with 0.000 and 0.006 au field. The effect of change in the orientation of the electric field for all the molecular systems has also been studied. In addition, the electric field was applied perpendicular to the molecular plane as well as in the direction perpendicular to the principal axis in the molecular plane. Similarly, all the global and local parameters were calculated at each field value. All the calculations were performed by GAMESS software [89].

4 Results and discussion

4.1 Behavior of global and local reactivity descriptors when the electric field is applied along principal axis

The behavior of the global and local reactivity descriptors for planar nonlinear polyatomic molecules, H_2O, CH_2S, HCHO, SO_2 and O_3 in presence of external electric field applied along the principal axis are presented in Tables 1, 2 and Figs. 1, 2. In order to avoid repetition, we are presenting the values of GRD and LRD for H_2O molecule in Table 1 while results for molecules with similar information, CH_2S and HCHO molecules, are presented in Figs. 1 and 2. When

Table 2 Variations of chemical potential, hardness and CFF with electric field applied along the principal axis for O_3

Electric field (in au)[a]	μ (in au)	η (in au)	f^-_{O2}	$f^-_{O1,3}$	f^+_{O2}	$f^+_{O1,3}$
0.000	−0.2803	0.1986	0.2035	0.3983	0.2553	0.3723
0.001(O2)	−0.2805	0.1987	0.2034	0.3983	0.2550	0.3725
0.002(O2)	−0.2807	0.1987	0.2032	0.3984	0.2548	0.3726
0.003(O2)	−0.2809	0.1987	0.2031	0.3984	0.2545	0.3727
0.004(O2)	−0.2811	0.1987	0.2030	0.3985	0.2543	0.3729
0.005(O2)	−0.2813	0.1987	0.2029	0.3986	0.2540	0.3730
0.006(O2)	−0.2816	0.1987	0.2028	0.3986	0.2538	0.3731
0.001	−0.2801	0.1986	0.2036	0.3982	0.2556	0.3722
0.002	−0.2799	0.1986	0.2037	0.3981	0.2559	0.3721
0.003	−0.2797	0.1986	0.2039	0.3981	0.2561	0.3719
0.004	−0.2795	0.1986	0.2040	0.3980	0.2564	0.3718
0.005	−0.2793	0.1985	0.2041	0.3979	0.2567	0.3717
0.006	−0.2791	0.1985	0.2043	0.3979	0.2570	0.3715

[a] Field applied towards central O atom (O2) is shown in parenthesis alongside the field value

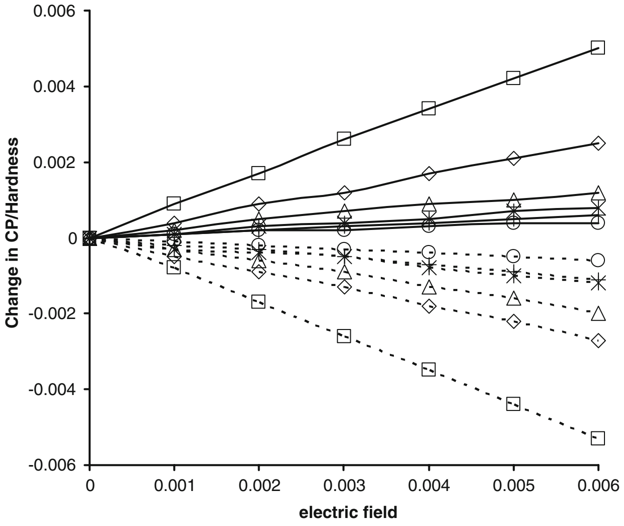

Fig. 1 Plot of change in chemical potential (CP)/hardness with respect to zero fields against electric field applied along the principal axis for the molecular systems, CH_2S, HCHO and SO_2. *Square* CP of HCHO, *triangle* CP of CH_2S, *circle* CP of SO_2, *vertical lines* Hardness of CH_2S, *diamond* Hardness of HCHO, *stars* Hardness of SO_2. *Dashed line* represents the values of the parameter when the field is applied towards more electronegative atom while the *solid line* represents the value of that parameter when the field is applied in opposite direction

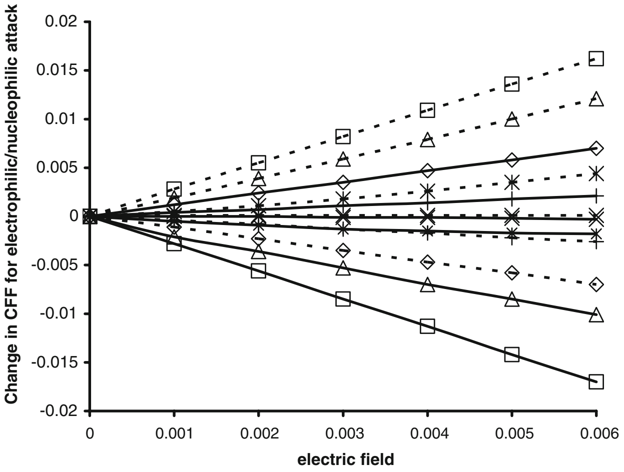

Fig. 2 Plot of Change in Condensed Fukui Function (CFF) for electrophilic/nucleophilic attack with respect to zero fields applied along the principal axis for the reactive atoms (*bold*) in CH_2S, HCHO and SO_2. *triangle* electrophilicity of CH_2S, *square* electrophilicity of HCHO, *stars* electrophilicity of SO_2, *diamonds* nucleophilicity of CH_2S, *vertical lines* nucleophilicity of HCHO, *times* nucleophilicity of SO_2. *Dashed line* represents the values of the parameter when the field is applied towards more electronegative atom while the *solid line* represents the value of that parameter when the field is applied in opposite direction

the field is applied towards the central atom (say from the line joining the two H atoms to the O atom along the principal axis, in case of H_2O) of all the species, and if the central atom is more electronegative atom the chemical potential and hardness decreases with increasing field values. For instance, when the electric field is applied towards the O and S atom in H_2O, HCHO and CH_2S, respectively, the chemical potential and hardness decreases (Table 1; Fig. 1). On the other hand, if the central atom is more electropositive and if the field is directed towards the central atom, the chemical potential and hardness increase with increasing field. In case of SO_2, the field directed towards the central atom S results in the increase in chemical potential and hardness with increasing field values (Fig. 1). Interestingly, in case of O_3, when the field is towards the central O atom, the chemical potential decreases, while the hardness remains almost constant with increasing field. But as the field direction is reversed, the chemical potential increases and hardness values decrease marginally with increasing field (Table 2). These marginal changes in O_3 may be due to its small dipole moment.

When the direction of the electric field is reversed, the trends in the chemical potential and hardness are also reversed for all the systems except O_3. This signifies that the direction of the field plays a very important role in understanding the stability and reactivity of a system.

We now turn our attention to the local reactivity descriptors. When the field is applied along the principal axis towards the central atom, the condensed Fukui function (CFF) for electrophilic attack (nucleophilicity) decreases for that atom, provided the central atom is more electronegative. As an illustration, the nucleophilicity of O in H_2O (Table 1) and HCHO and S atom in CH_2S (Fig. 2) decrease, when the electric field is applied towards those atoms. Moreover, the CFF for nucleophilic attack (electrophilicity) of H atoms in H_2O decreases (Table 1). At the same time, when the field is applied towards the central atom in CH_2O and CH_2S, the electrophilicity of C atom increases almost linearly with increasing field (Fig. 2). On the other hand, when the field is towards the electropositive central atom, the electrophilicity for that atom decreases. SO_2 provides an example for this. However, the nucleophilicity of O atoms in SO_2 decreases slowly in this field range (Fig. 2). Although ozone has a V-shaped structure, it behaves differently. When the field is directed towards the central oxygen atom, its nucleophilicity as well as its electrophilicity decreases while the nucleophilicity and electrophilicity of the other two oxygen atoms increase as the field values increase. This may be due to its resonance structure (Table 2).

When the direction of the electric field is reversed, the trends in the nucleophilicity of the reactive atoms in H_2O, CH_2S, HCHO, SO_2 and O_3 as well the electrophilicity reverses (Tables 1, 2; Fig. 2). It should, however, be noted that the global and local reactivity descriptors in case of planar nonlinear polyatomic molecules behave almost similar to those for the linear molecules. Moreover, it is important to observe from Figs. 1 and 2 that the variations of change in GRD and LRD with respect to zero fields against external electric field are almost linear and uniform. This means that the applied electric field produces small perturbation of the molecular charge distribution.

4.2 Behavior of global and local reactivity descriptors when the electric field is applied perpendicular to the principal axis

The behavior of GRD and LRD under the influence of electric field perpendicular to the principal axis for H_2O, CH_2S and SO_2 molecules are presented in Tables 3, 4 and 5 and for HCHO and O_3 molecules in Figs. 3 and 4. When the electric field is applied perpendicular to the molecular plane of the molecules H_2O, CH_2S and SO_2, the hardness and chemical potential decrease with field value increasing from 0.000 to 0.006 au (Tables 4, 6, 8) irrespective of the field being applied above or below the plane of the molecule. However, this decrease is much lower than the case in which the field is applied along the principal axis. This implies that there is an induced polarization above and below the plane of the molecule. This induced polarization perpendicular to the axis of the molecules was almost absent for linear molecules, which resulted in constant values of reactivity descriptors, when the field was applied perpendicular to the axis [1]. For O_3 molecule, on the other hand, the hardness and chemical potential remains almost constant with increasing field, regardless of the field directed above or below the molecular plane (Fig. 3).

Now, when the field is directed perpendicular to the principal axis in the molecular plane, i.e., the field is applied in a direction from, say, H_2 atom to H_1 atom in H_2O, CH_2S and HCHO and from O_1 atom to O_2 atom in SO_2. With the increase in the magnitude of field, the chemical potential and hardness for SO_2 (Table 7) decrease slowly and for CH_2S (Table 5) and HCHO (Fig. 3) these remain almost constant. It should be, however, noted that the decrease is substantial in the case of H_2O (Table 3). Although the field direction is reversed, the global parameters do not change. This is mainly due to the symmetry in the molecules.

When the field is directed perpendicular to the principal axis in the molecular plane i.e., say, from H_2 to H_1 atom in H_2O, CH_2S and HCHO, the nucleophilicity of central atoms remains almost constant throughout this field range. For instance, the nucleophilicity of O atom in H_2O, S and O atom in CH_2S and HCHO, respectively, along with C atom remains constant (Tables 3, 5; Fig. 4). Moreover, in case of in H_2O, CH_2S and HCHO, the nucleophilicity of the H atom towards which the field is applied decreases (Tables 3, 5; Fig. 4). But, in case of SO_2, the nucleophilicity of S atom decreases while the nucleophilicity of O atom towards which the field is applied increases (Table 7). This may be due to the presence of more electropositive central atom. Surprisingly, the behavior of CFF for nucleophilic attack of central atom varies as the field value is increased. It is observed that the electrophilicity of central atom in H_2O and SO_2 increases with increasing field (Tables 3, 7). On contrary, in case of HCHO, the electrophilicity of O and C atoms decreases slowly while the electrophilicity of S, in CH_2S, remains constant with increasing field (Table 5; Fig. 4). However, for H_2O, CH_2S and HCHO, the electrophilicity of atom towards which the field is assigned decreases (Tables 3, 5; Fig. 4).

When the field is assigned perpendicular to the molecular plane, the nucleophilicity of all the atoms for H_2O, CH_2S and SO_2 molecules remains almost constant with the increase in the field values (Tables 4, 6, 8). However, on the other hand, the electrophilicity behavior is quite different. The electro-

Table 3 Variation of chemical potential, Hardness and CFF for H_2O molecule when the field is applied from H_2 to H_1 atom

Electric field[a] (in au)	μ (in au)	η (in au)	f_O^-	f_{H1}^-	f_{H2}^-	f_o^+	f_{H1}^+	f_{H2}^+
0.000	−0.2185	0.2459	0.8368	0.0816	0.0816	0.0753	0.4623	0.4623
0.001	−0.2187	0.2458	0.8368	0.0813	0.0820	0.0756	0.3950	0.5294
0.002	−0.2190	0.2454	0.8368	0.0810	0.0823	0.0765	0.3309	0.5926
0.003	−0.2197	0.2448	0.8367	0.0806	0.0826	0.0780	0.2731	0.6490
0.004	−0.2205	0.2440	0.8367	0.0803	0.0829	0.0797	0.2238	0.6965
0.005	−0.2215	0.2430	0.8367	0.0800	0.0833	0.0815	0.1837	0.7348
0.006	−0.2227	0.2418	0.8367	0.0797	0.0836	0.0832	0.1521	0.7646

[a] Applying field in opposite direction will change the values CFF of H_1 to H_2

Table 4 Variation of chemical potential, hardness and CFF for H_2O molecule when the field is applied perpendicular towards the molecular plane

Electric field[a] (in au)	μ (in au)	η (in au)	f_o^-	f_H^-	f_H^+	f_o^+
0.000	−0.2185	0.2459	0.8368	0.0816	0.4623	0.0753
0.001	−0.2185	0.2460	0.8368	0.0816	0.4623	0.0754
0.002	−0.2186	0.2459	0.8368	0.0816	0.4622	0.0756
0.003	−0.2187	0.2459	0.8368	0.0816	0.4620	0.0759
0.004	−0.2187	0.2458	0.8368	0.0816	0.4618	0.0764
0.005	−0.2187	0.2458	0.8368	0.0816	0.4614	0.0771
0.006	−0.2188	0.2457	0.8368	0.0816	0.4611	0.0778

[a] Same values when the field is reversed

Table 5 Variation of chemical potential, hardness and CFF for CH_2S molecule when the field is applied from H_2 to H_1 atom

Electric field[a] (in au)	μ (in au)	η (in au)	f_S^-	f_c^-	f_{H1}^-	f_{H2}^-	f_S^+	f_c^+	f_{H1}^+	f_{H2}^+
0.000	−0.1768	0.1633	0.6610	0.1602	0.0894	0.0894	0.5122	0.3824	0.0527	0.0527
0.001	−0.1768	0.1632	0.6610	0.1602	0.0891	0.0897	0.5122	0.3824	0.0525	0.0529
0.002	−0.1769	0.1633	0.6610	0.1602	0.0889	0.0899	0.5122	0.3824	0.0523	0.0531
0.003	−0.1769	0.1633	0.6610	0.1602	0.0886	0.0902	0.5122	0.3824	0.0520	0.0533
0.004	−0.1769	0.1632	0.6610	0.1602	0.0883	0.0905	0.5122	0.3824	0.0518	0.0535
0.005	−0.1770	0.1632	0.6610	0.1602	0.0880	0.0908	0.5122	0.3824	0.0516	0.0537
0.006	−0.1770	0.1632	0.6610	0.1602	0.0878	0.0910	0.5122	0.3824	0.0514	0.0540

[a] Applying field in opposite direction will change the CFF values of H_1 to H_2

philicity of the central atom in H_2O and SO_2, i.e., O and S atom, respectively, increases while the S atom in CH_2S decreases (Tables 4, 6, 8). This may be due to the nearly equivalent electro-negativities of C and S in CH_2S. However, in case of O_3, neither the nucleophilicity nor the electrophilicity of O atoms change in this field range (Fig. 4).

As the field direction is reversed, there is no change in the behavior of the atoms in terms of their reactivity. This implies that whenever a reagent, either nucleophilic or electrophilic, attacks from above or below the molecular plane would experience similar reactivity on a particular atom.

In our earlier article [1], we inferred that the variation of the hardness parameter in the presence of external electric field is actually dependent on the net cooperative effect exhibited by the collection of all the atoms present in the molecule. The above discussions (Sects. 4.1 and 4.2) probably imply the same. Hence, the decrease or increase of hardness of a molecule under the external field does not necessarily mean that the reactivity of a specific site or atom present in the molecule would be enhanced or deactivated.

Apart from the numerical analysis discussed above, we present some of our results using the perturbative analysis. The Fukui function under the presence of electric field (F) can be written as a Taylor series expansion,

$$f(r) = f_0(r) + f'(r)F + \frac{1}{2!}f''(r)F.F + \cdots \qquad (13)$$

The first term $f_0(r)$ is the FF at zero field. The second term $f'(r) = \frac{\delta^2\rho(r)}{\delta N\delta F}$ and the third term $f''(r)$ is equal to $\frac{\delta^3\rho(r)}{\delta N\delta F\delta F}$ can be related, respectively, to the linear Fukui response and nonlinear Fukui response defined by Senet [90], who has also

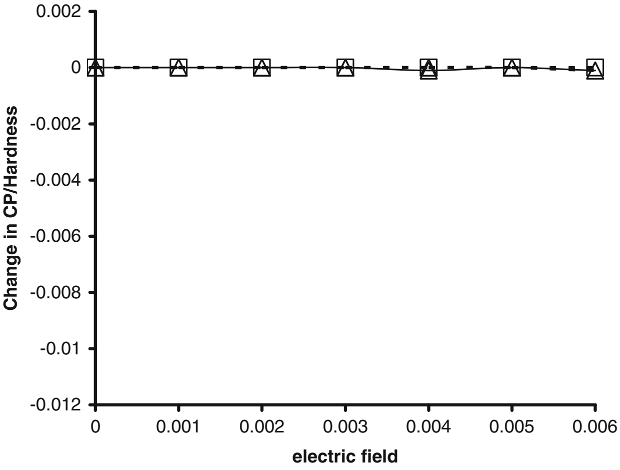

Fig. 3 Plot of change in CP/Hardness with respect to zero fields against electric field applied perpendicular to the principal axis for HCHO and O_3 molecules *square* CP/Hardness of O_3. *triangle* CP/Hardness of HCHO. *Dashed line* represents the values of Hardness while *solid line* represents the values of CP when the field is applied perpendicular to the principal axis

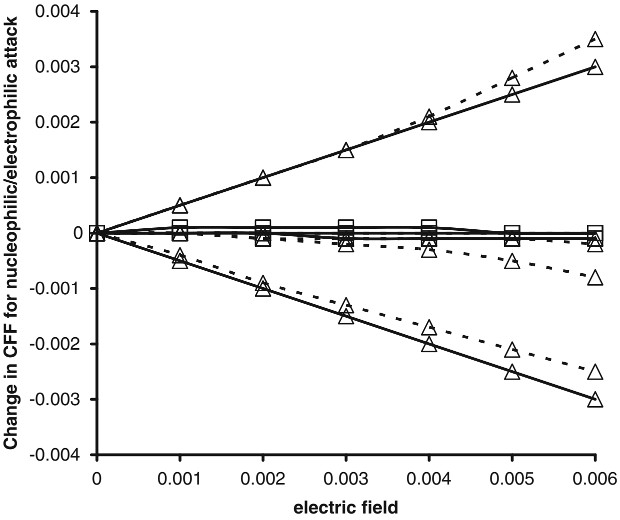

Fig. 4 Plot of change in CFF for electrophilic/nucleophilic attack with respect to zero fields against electric field applied perpendicular to the principal axis for reactive atoms in HCHO and O_3 molecules. *triangle* nucleophilicity/electrophilicity of O, C and H atoms in HCHO, *square* nucleophilicity/electrophilicity of O atoms in O_3. *Dashed line* represents the values of electrophilicity while *solid line* represents the values of nucleophilicity when the field is applied perpendicular to the principal axis

made a general perturbative analysis of electron density with respect to the number of electrons and external potential. It is clear from the above that the linear trend observed in the present numerical results will breakdown at somewhat stronger fields.

For weak fields, Figs. 1, 2, 3 and 4 show the linearity of the reactivity descriptors. To see the effect of breakdown of linearity, we extended our calculations up to larger field values. It is found that, when the field is applied along the principal axis the linearity of GRD breaks after 0.01 au of field value for CH_2S, H_2O, O_3 and SO_2. As an example, to be a linear plot the extrapolated hardness value for CH_2S should be 0.1593 au at a field value of 0.02 au along the C_2 axis, but the calculated hardness at that field is 0.1393 au. This shows a drop in hardness value which is larger than that predicted from the linear plot. Similarly, we have observed the breakdown of linearity of nucleophilicity of S in CH_2S after 0.03 au, O in HCHO after 0.015 au, O in SO_2 after 0.01 au. When the field is perpendicular to the principal axis, the variations of GRD becomes nonlinear after 0.006 au for HCHO and 0.008 au for O_3. On the other hand, the linearity in the variation of nucleophilicity is lost after 0.01 au for O in HCHO, while the variation of electrophilicity is lost after 0.006 au for central O atom in O_3. However, it should be again mentioned that it is often difficult to converge to the correct state for $(N \pm 1)$ systems for higher field values. Thus, it is difficult to demonstrate the nonlinearity at very strong field values.

Moreover, analysis of the energy difference for the above molecular systems in weak field range, applied along the principal axis and in perpendicular direction, clearly suggests that there is a weak interaction with the external electric field. It is found that the difference in the energies of the mentioned systems with and without field along the principal axis ranges from 0.8837 kcal/mol for ozone to 3.9423 kcal/mol for formaldehyde. This energy difference signifies weak interaction of the molecular systems with external electric field applied along the principal axis. The values range from 0.0757 kcal/mol for H_2O to 0.3989 kcal/mol for SO_2 in perpendicular direction. Although the present analysis is not very rigorous, it can, however, explain the present observation in the variation of CFF as well as the hardness parameters.

5 Conclusions

We have investigated the effect of electric field on reactivity of some of the C_{2V} symmetry molecules. Under such external parameter, their stability and reactivity were systematically studied using the density based reactivity descriptors. In order to understand the behavior of these descriptors in the presence of electric field for polyatomic molecules, we have studied the effect of application of external field towards the principal axis as well as to the axis perpendicular to the principal axis. In the case of application of electric field perpendicular to the principal axis, there is change in both GRD and LRD unlike linear molecules. Our results once again support that the variation of the hardness parameter is actually dependent on the net cooperative effect exhibited by

Table 6 Variation of chemical potential, hardness and CFF for CH_2S molecule when the field is applied perpendicular towards the molecular plane

Electric field[a] (in au)	μ (in au)	η (in au)	f_S^-	f_C^-	f_H^-	f_S^+	f_C^+	f_H^+
0.000	−0.1768	0.1633	0.6610	0.1602	0.0894	0.5122	0.3824	0.0527
0.001	−0.1768	0.1632	0.6610	0.1602	0.0894	0.5121	0.3824	0.0527
0.002	−0.1769	0.1632	0.6610	0.1602	0.0894	0.5118	0.3825	0.0528
0.003	−0.1769	0.1632	0.6610	0.1602	0.0894	0.5113	0.3826	0.0530
0.004	−0.1770	0.1631	0.6610	0.1602	0.0894	0.5106	0.3827	0.0533
0.005	−0.1771	0.1630	0.6610	0.1602	0.0894	0.5097	0.3829	0.0537
0.006	−0.1772	0.1629	0.6609	0.1603	0.0894	0.5086	0.3830	0.0542

[a] Same values when the field is reversed

Table 7 Variation of chemical potential, hardness and CFF for SO_2 molecule when the field is applied from O_1 to O_2 atom

Electric field[a] (in au)	μ (in au)	η (in au)	f_S^-	f_{O1}^-	f_{O2}^-	f_S^+	f_{O1}^+	f_{O2}^+
0.000	−0.2491	0.2047	0.3131	0.3434	0.3434	0.4830	0.2585	0.2585
0.001	−0.2491	0.2046	0.3130	0.3393	0.3477	0.4830	0.2584	0.2586
0.002	−0.2491	0.2046	0.3129	0.3353	0.3519	0.4831	0.2583	0.2587
0.003	−0.2491	0.2046	0.3126	0.3314	0.3560	0.4832	0.2581	0.2587
0.004	−0.2491	0.2046	0.3122	0.3278	0.3601	0.4834	0.2579	0.2587
0.005	−0.2491	0.2045	0.3117	0.3244	0.3639	0.4836	0.2577	0.2587
0.006	−0.2491	0.2045	0.3112	0.3212	0.3676	0.4839	0.2574	0.2587

[a] Applying field in opposite direction will change the values CFF of O_2 to O_1

Table 8 Variation of chemical potential, hardness and CFF for SO_2 molecule when the field is applied perpendicular towards the molecular plane

Electric field[a] (in au)	μ (in au)	η (in au)	f_S^-	f_O^-	f_S^+	f_O^+
0.000	−0.2491	0.2047	0.3131	0.3434	0.4830	0.2585
0.001	−0.2491	0.2046	0.3131	0.3434	0.4830	0.2585
0.002	−0.2491	0.2047	0.3131	0.3434	0.4832	0.2584
0.003	−0.2491	0.2046	0.3131	0.3434	0.4836	0.2582
0.004	−0.2492	0.2046	0.3132	0.3434	0.4841	0.2579
0.005	−0.2492	0.2045	0.3132	0.3434	0.4848	0.2576
0.006	−0.2493	0.2045	0.3132	0.3434	0.4857	0.2572

[a] Same values when the field is reversed

the collection of all the atoms present in the molecule. We observe from the strength of interactions that our study is applicable to effect of weak interactions on the descriptors. Moreover, we try to present some perturbative analysis to our findings and numerically show the breakdown of linearity of reactivity descriptors.

Acknowledgments R.K acknowledges the Council of Scientific and Industrial Research (CSIR), New Delhi for financial assistance.

References

1. Kar R, Chandrakumar KRS, Pal S (2007) J Phys Chem A 111:375
2. Rico JF, Lopez R, Ema I, Ramirez G (2002) J Chem Phys 116:1788
3. Dykstra CE (2001) J Mol Struct THEOCHEM 573:63
4. Buckingham AD, Fowler PW, Hutson JM (1988) Chem Rev 88:963
5. Perez P, Contreras R, Aizman A (1996) Chem Phys Lett 260:236
6. Perez P, Contreras R, Aizman A (1997) J Mol Struct THEOCHEM 290:169
7. Tomasi J, Perisco M (1994) Chem Rev 94:2027
8. Suresh SJ, Prabhu AL, Arora A (2007) J Chem Phys 126:134502
9. Kreuzer HJ, Wang LC (1990) J Chem Phys 93:6065
10. Ernst N, Drachset W, Li Y, Block JH (1986) Phys Rev Lett 57:2686
11. Bragiel P (1992) Surf Sci. 266:35
12. Cerveau G, Corriu RJP, Framery E, Ghosh S, Nobili M (2002) Angew Chem Int Ed 41:594
13. Pethica BA (1998) Langmuir 14:3115
14. Hochstrasser RM (1973) Acc Chem Res 6:263
15. Eckert M, Zundel G (1987) J Phys Chem 91:5170
16. Eckert M, Zundel G (1988) J Phys Chem 92:7016
17. Hill TL (1958) J Am Chem Soc 80:2142
18. Hobza P, Hofmann H, Zahradhik R (1983) J Phys Chem 87:573

19. Xu D, Phillips JC, Schulten K (1996) J Phys Chem 100:12108
20. Lippard S J, Berg JM (1994) Principles of bioinorganic chemistry. University Science Books. Mill Valley, CA
21. Choi YC, Pak C, Kim KS (2006) J Chem Phys 124:94308
22. Cohende Lara E, Kahn R, Seloudoux R (1985) J Chem Phys 83:2646
23. Cohende Lara E, Kahn R (1981) J Phys (Paris) 42:1029
24. Chandrakumar KRS, Pal S, Goursot A, Vetrivel R (1999) In: Murugesan V, Arabindoo B, Palanichamy M (eds) Recent trends in catalysis. Narosa Publishing House, New Delhi
25. Cohende Lara E, Kahn R (1984) J Phys Lett 45:255
26. Li P, Xiang Y, Grassian VH, Larsen SC (1999) J Phys Chem B 103:5058
27. Bordiga S, Garrone E, Lamberti C, Zecchina A, Arean C, Kazansky V, Kustov L (1994) J Phys Chem 90:3367
28. Ferrari AM, Ugliengo P, Garrone E (1996) J Chem Phys 105:4129
29. Gruver V, Fripiat JJ (1994) J Phys Chem 98:8549
30. Olivera PP, Patrito EM (1998) Electrochim Acta 44:1247
31. Parr R G, Yang W (1989) Density functional theory of atoms and molecules. Oxford University Press, New York
32. Yang W, Mortier WJ (1986) J Am Chem Soc 108:5708
33. Mineva T (2006) J Mol Struct THEOCHEM 762:79
34. Ponti A (2000) J Phys Chem A 104:8843
35. Molteni G, Ponti A (2003) Chem Eur J 9:2770
36. Mineva T, Heine T (2004) J Phys Chem A 108:11086
37. Roy RK (2003) J Phys Chem A 107:397
38. Chatterjee A, Iwasaki T, Ebina T (2000) J Phys Chem A 104:8216
39. Chandra AK, Nguyen MT (2007) Faraday Discussions 135:191
40. Nguyen HMT, Peeters J, Nguyen MT, Chandra AK (2004) J Phys Chem A 108:484
41. Melin J, Aparicio F, Subramanian V, Galvan M, Chattaraj PK (2004) J Phys Chem A 108:2487
42. Shetty S, Kar R, Kanhere DG, Pal S (2006) J Phys Chem A 110:252
43. Roy RK, Chandra AK, Pal S (1994) J Phys Chem 98:10447
44. Pal S, Chandra AK, Roy RK (1994) J Mol Struct THEOCHEM 307:99
45. Chattaraj PK, Poddar A (1998) J Phys Chem A 102:9944
46. Chattaraj PK, Poddar A (1999) 103:1274
47. Chattaraj PK, Maiti B (2001) J Phys Chem A 105:169
48. Madjarova G, Tadjer A, Cholakova T P, Dobrev A A, Mineva T (2005) J Phys Chem A 109:387
49. Santos J C, Contreras R, Chamorro E, Fuentealba P (2002) J Chem Phys 116:4311
50. Jaque P, Toro-Labbe A (2002) J Chem Phys 117:3208
51. Mineva T, Russo N, Sicila E, Toscano M (1999) Theor Chem Acc 101:388
52. Mendez F, Tamaiz J, Geerlings P (1998) J Phys Chem A 102:6292
53. Damoun S, Van de Woude, Choho K, Geerlings P (1999) J Phys Chem A 103:7861
54. Romero ML, Mendez F (2003) J Phys Chem A 107:5874
55. Mendez F, Garcýa-Garibay MA (1999) J Org Chem 64:7061
56. Geerlings P, De Proft F, Langenaeker W (2003) Chem Rev 103:1793
57. Anderson JSM, Melin J, Ayers PW (2007) J Chem Theory Comp 3:375
58. Ayers PW, Parr RG (2000) J Am Chem Soc 122:2010
59. Ayers PW, Parr RG (2001) J Am Chem Soc 123:2007
60. Pal S, Chandrakumar KRS (2000) J Am Chem Soc 122:4145
61. Mendez F, Gazquez JL (1994) J Am Chem Soc 116:9298
62. Chandrakumar KRS, Pal S (2001) J Phys Chem B 105:4541
63. Chandrakumar KRS, Pal S (2002) J Phys Chem A 106:5737
64. Chandrakumar KRS, Pal S (2002) J Phys Chem A 106:11775
65. Chandrakumar KRS, Pal S (2002) Colloids Surf A 205:127
66. Chandrakumar KRS, Pal S (2002) Int J Mol Sci 2:324
67. Parthasarathi R, Subramanian V, Chattaraj PK (2003) Chem Phys Lett 382:48
68. Lipinski J, Komorowski L (1996) Chem Phys Lett 262:449
69. Sivanesan D, Amutha R, Subramanian V, Nair BU, Ramasami T (1999) Chem Phys Lett 308:223
70. Safi B, Choho K, De Proft F, Geerlings P (1998) J Phys Chem A 102:5253
71. Fuentealba P, Perez P, Contreras R (2000) J Chem Phys 113:2544
72. Geerlings P, De Proft F (2002) Int J Mol Sci 3:276
73. Balawender R, Safi B, Geerlings P (2001) J Phys Chem A 105:6703
74. Balawender R, Safi B, Geerlings P (2001) J Phys Chem A 105:11102
75. Padmanabhan J, Parthasarathi R, Subramanian V, Chattaraj PK (2006) J Phys Chem 110:2739
76. Fuentealba P, Cedillo A (1999) J Chem Phys 110:9867
77. Hohenberg K, Kohn W (1964) Phys Rev B 136:864
78. Parr RG, Pearson RG (1983) J Am Chem Soc 105:7512
79. Pearson RG (1985) J Am Chem Soc 107:6801
80. Parr RG, Donnelly RA, Levy M, Palke WE (1978) J Chem Phys 68:3801
81. Parr RG, Yang W (1984) J Am Chem Soc 106:4049
82. Yang W, Parr RG (1985) Proc Natl Acad Sci 82:6723
83. Perdew JP, Parr RG, Levy M, Balduz JL Jr (1982) Phys Rev Lett 49:1691
84. Zhang Y, Yang W (2000) Theor Chem Acc 103:346
85. Yang W, Mortier WJ (1986) J Am Chem Soc 108:5708
86. For a review, see: Bachrach SM (1995) In: Lipkowitz KB, Boyd DB (eds) Reviews in computational chemistry. vol V. VCH, New York
87. Lowdin PO (1953) J Chem Phys 21:374
88. Lowdin PO (1950) J Chem Phys 18:365
89. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunga N, Nguyen KA, Su SJ, Windus TL, Dupuis M, Montgomery JA (1993) J Comput Chem 14:1347
90. Senet P (1996) J Chem Phys 105:6471