Molecular Electronic Excitation and Minimum Electrophilicity Principle

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ABSTRACT

The rationality of the minimum electrophilicity principle (MElP) as a companion of minimum polarizability principle (MPP) and maximum hardness principle (MHP) is studied for simple molecules. Two types of excitations, namely vertical and adiabatic, are considered. Processes involving conservation and change in spin multiplicity are included during excitation. The general trend is that the molecules are less electrophilic in the ground state than those in the corresponding excited states. It is found that adiabatic excitation validates the principle even for the triplet ground state molecules undergoing an excitation where spin multiplicity gets altered.

Keywords: CDFT; electrophilicity; hardness; excited state

1. Introduction

In chemistry bonds are formed and cleaved due to redistribution of electron density. Various reactivity parameters have been introduced to understand the redistribution of electron density in a molecule during the reaction.[1–4] Linus Pauling initiated the concept of electronegativity and defined it as "the power of an atom in a molecule to attract electrons to itself."[5] In the electronegativity equalization principle, Sanderson[6] states that "the electronegativities of all the constituent atoms in a molecule have the same value and that can be expressed as the geometric mean of the electronegativity values of the associated isolated atoms." The notion of hardness was first propounded by Pearson. Subsequently two principles related to hardness, viz., hard-soft-acid-base (HSAB) principle[7–10] and the maximum hardness principle (MHP) wereintroduced .[11,12] The HSAB principle states that "hard acids prefer to coordinate with hard bases and soft acids with soft bases for both thermodynamic and kinetic considerations." The statement of MHP is, "there seems to be a rule of nature that molecules arrange themselves to be as hard as possible."

The wavefunction of an N-electron system is governed by N and external potential, $v(\vec{r})$ which are sufficient to define the Hamiltonian of the system. The hardness and electronegativity can be obtained from the response of the system when N is varied at a fixed $v(\vec{r})$. Within conceptual density functional theory (CDFT) the first-order[13] derivative provides electronegativity, χ (chemical potential, μ) and second-order[14] derivative gives hardness, η:

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

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

The chemical potential appears as normalization constraint, and it is negative of the electronegativity. Interchangeably the hardness can be expressed as[15,16]:

$$\eta = \frac{1}{N}\iint \eta(\mathbf{r}, \mathbf{r'})f(\mathbf{r'})\rho(\mathbf{r})\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r'} \tag{3}$$

where the Fukui function[17][18] is denoted as $f(\mathbf{r})$, and the expression for hardness kernel[15,16] is

$$\eta(\mathbf{r}, \mathbf{r'}) = \frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r'})} \tag{4}$$

where $F[\rho]$ is the universal functional of DFT as defined by Hohenberg and Kohn [19,20]. Averaging over $\eta(\mathbf{r}, \mathbf{r'})$ provides the local hardness and that can be expressed as[15,16,21,22]

$$\eta(\mathbf{r}) = \frac{1}{N}\int \eta(\mathbf{r}, \mathbf{r'})\rho(\mathbf{r'})d\mathbf{r'} = \frac{1}{N}\frac{\rho(\mathbf{r})}{s(\mathbf{r})} \tag{5}$$

where the local softness, $s(\mathbf{r})$ may be integrated to the global softness related to [20,22] the inverse of the hardness. The polarizability (α) measures the change in energy with change in $v(\vec{r})$ at fixed N.[23] The minimum polarizability principle (MPP)[21,24–27] states that, "the natural direction of evolution of any system is toward a state of minimum polarizability." This is a natural consequence[24] of MHP and the reciprocal behaviour of η and α.

Another related term is the electrophilicity, which also describes the electron acceptor property, and the electrophilicity index (ω)[28] which is defined as:

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \qquad (6)$$

According to the minimum electrophilicity principle (MElP), chemical the spontaneous direction of a reaction or the most stable configuration of a system is often connected with minimum electrophilicity values.[29] Molecules are less polarizable and harder in the ground state than that of the corresponding excited states as molecules are more reactive in the excited states.[25,26] This is also considered as the essential ramification of MPP and MHP. The prognosis was supported by actual numerical calculations of the isoelectronic helium structures, namely, He, Li$^+$, Be^{2+}, B^{3+}, and C^{4+}.[23] The linearity of S vs $\alpha^{1/3}$ was verified in the excited states. The MHP and MPP in the ground and excited states were further justified from the calculations of twelve diatomic molecules.[30] Chattaraj and co-workers[29] have studied 101 exothermic reactions and shown that MElP and MHP are followed by 69.3% and 61.4% of the reactions, respectively. For the reactants and products, the hardnesses were calculated as the respective geometric means.

A chemical reaction is a dynamic process, and hence time evolution of the reactivity parameter is a vital aspect to consider. In this regard, the protonation CO (CO + H$^+$ → COH$^+$)[27] was studied, and the time-dependent electrophilicity of CO in the ground state was found to be less than the corresponding excited state, which validates the MElP. By the application of an external magnetic field of amplitude β_{max} = 1, 2, and 100, the electrophilicity in the excited state (n = 15) is shown to be larger than that of the ground state (n = 1) of H, and He atoms.[31] The electrophilicity decreases with increasing confinement in the presence and absence of external field in the ground and excited states validating the MElP.[31] The principle was further studied in the process of internal rotations and molecular vibrations.[32] It was further extended to a finite temperature grand canonical ensemble study[33], varying the absolute hardness and chemical potential[34], Paternò–Büchi reactions[35] as well as some acid base reactions[36]. Miranda-Quintana et al. have proved

the MHP and MElP mathematically where electrostatic and entropic effects were neglected.[33]

Unlike the MHP and MPP, the MElP has not been studied for simple molecules in the excited states. In this letter, we numerically calculated the hardness and electrophilicity in the ground and excited states of simple diatomic, triatomic and tetratomic molecules. The results validate the MElP as an essential ramification of the MPP and MHP.

2. Computational details

All the conceptual density functional theory based calculations (optimization, frequency and single point energy) were performed using Gaussian09 suite of the program[37]. Widely accepted and reliable hybrid functional (exchange-correlation) , B3LYP developed by Becke and Lee, Yang, and Parr respectively [38,39] has been employed in all cases. 6-311+G(d,p) basis set was used. CIS method was employed in the calculation of excited states. GaussView5.0 was used to draw the input geometries. The definition of hardness and electronegativity as obtained from the method of finite difference[40] is

$$\eta \cong I - A \qquad (7)$$

$$\chi = I + A \qquad (8)$$

In the gas phase of a species the minimum amount of energy required to transfer the outermost electron to infinity is defined as the first ionization energy (I). Conversely, the amount of energy released by a species in the gas phase when an extra electron is added to the outermost orbital is termed as electron affinity (A). Applying Koopmans' approximation [41], through the energies of the frontier orbitals the ionization energy (I) and electron affinity (A) can be expressed as:

$$I = -\varepsilon_{HOMO}; A = -\varepsilon_{LUMO} \qquad (9)$$

where the energies of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are represented as ε_{HOMO} and ε_{LUMO}, respectively. The I and A can also be calculated through ΔSCF method[40] utilizing the energy of the N-electron system in concurrence with the single-point energies of corresponding cation and anion obtained at the neutral molecule geometry. In this method, the I and A are defined as

$$I = E(N\text{-}1) - E(N) \qquad (10)$$

$$A = E(N) - E(N\text{+}1) \qquad (11)$$

One should be careful in the application of Koopmans' theorem for calculation of the I and A as it is less accurate than the ΔSCF method.[40] Thus, in the calculations of I and A, the ΔSCF is used in the current work.

3. Results and discussion

The optimized bond lengths, energy, hardness, and electrophilicity of the studied molecules are presented in Table 1. For the molecules H_2, Li_2, N_2, F_2, HF, BF, LiF, H_2O, and NH_3, the ground state is $^1\sum$, and for O_2, OS, S_2, NH, and LiN, the ground state is $^3\sum$. All the geometries are optimized in the ground state. Two types of excitations are considered: i) vertical excitation where no relaxation has been permitted after excitation, ii) adiabatic excitation where a change in geometry is permitted after excitation. For the ground singlet state, the excitation is performed to the corresponding singlet and triplet excited states. In the same way, for triplet ground state molecules, the excitation is carried out to the corresponding triplet and singlet excited states. In the singlet $\rightarrow$ singlet vertical excitation of H_2, Li_2, N_2, BF, LiH, H_2O, and NH_3, the MHP and MElP are followed. Also, triplet $\rightarrow$ triplet vertical excitation of O_2, OS, S_2, NH, and LiN obeys the MHP and MElP. F_2 and HF show anomalous behaviour; although MHP is followed in F_2 and LiN, the difference in electrophilicity is minimal. LiH does not follow MHP, and the difference in electrophilicity is negligible. The singlet $\rightarrow$ triplet vertical excitation of most molecules does not follow the MHP except H_2, N_2, HF, H_2O, and NH_3. In the same way, MElP is only maintained in H_2, Li_2, N_2, BF, H_2O, and NH_3. In the case of the triplet ground state molecules (O_2, OS, S_2, NH, and LiN) the vertical excitation to the singlet state does not follow the MHP and MElP. It is important to note that during the vertical transition with a change in spin, the triplet ground state molecules show ambiguity.

Next, the hardness and electrophilicity of the molecules are calculated for adiabatic excitation considering conservation and change in spin multiplicity. In the singlet $\rightarrow$ singlet transition, the MHP is followed in all the molecules except LiH. Also, all molecules follow the MElP except HF. In the case of the singlet $\rightarrow$ triplet transition Li_2, LiH, and BF do not follow the MHP whereas MElP is followed by all singlet ground state molecules except HF and LiH. The MHP is followed for the triplet ground state molecules in the electronic excitation with a change in spin state, i.e., triplet $\rightarrow$ singlet. The MElP is also followed in these molecules when spin is changed during the transition, with the exception of O_2 and NH. Interestingly in the case of adiabatic excitation, most of the molecules follow the MHP and MElP principles irrespective of conservation and change in spin state. This is

because, during the adiabatic transition, geometric relaxation is allowed; as a result, the molecules in the excited states are more stable compared to their vertical counterpart.

It is known that MHP implies MElP in case the electronegativity remains more or less constant, the variation in χ^2 is less dominant than that of η, or an increase in η is accompanied by a decrease in χ^2. Fortunately, the calculated electronegativity values follow the favorable trends in most cases.

The anomalous behavior of F_2 and HF is observed in this study. In addition, when the spin state is changed in the excited state, the atomic distance is surprisingly high (7.074 Å), as if there is no bond. The ionization potential of F obeys the periodic trend; however, the electron affinity of F along group 17 is not the maximum. Thus, in the process of accepting an extra electron via a covalent bond formation or anion generation, an extra amount of energy has to be added to the system.[42] In the same way, H-F bond formation in HF and C-F bond formation in alkyl fluoride also require some energy. Thus, there is an anomalous behaviour associated with F. Although speculative, the results containing the F atom may be the manifestation of this fact.

Table 1 Bond Lengths (Å), Energies (au), Hardness and electrophilicity values (eV) of diatomic, triatomic, and tetratomic molecules for vertical excitation.

Species	Electronic Configuration (State)	Bond Length (Å)	Energy (au)	Electronegativity (eV)	Hardness (eV)	Electrophilicity index (eV)
H_2	$\sigma_g^2(^1\Sigma_g^+)$	0.600	-1.179	6.380	20.305	1.002
	$\sigma_g^1\sigma_u^1(^1\Sigma_u^+)$	0.600	-0.631	12.623	14.536	5.480
	$\sigma_g^1\sigma_u^1(^3\Sigma_u^+)$	0.600	-0.614	12.623	13.611	5.853
Li_2	$\sigma_g^2(^1\Sigma_g^+)$	2.705	-15.015	2.858	4.926	0.829
	$\sigma_g^1\sigma_u^1(^1\Sigma_u^+)$	2.705	-14.789	3.501	3.476	1.763
	$\sigma_g^1\sigma_u^1(^3\Sigma_u^+)$	2.705	-14.842	3.501	6.358	0.964
N_2	$\sigma_g^2(^1\Sigma_g^+)$	1.095	-109.559	6.944	17.866	1.349
	$\sigma_g^1\pi_g^1(^1\Pi_g)$	1.095	-108.658	6.420	1.737	11.858
	$\sigma_g^1\pi_g^1(^3\Pi_g)$	1.095	-108.713	6.420	4.687	4.396
F_2	$\pi_u^4\pi_g^4(^1\Sigma_g^+)$	1.408	-199.571	8.440	15.290	2.329
	$\pi_u^4\pi_g^3\sigma_u^1(^1\Pi_u)$	1.408	-198.547	5.503	12.073	1.254
	$\pi_u^4\pi_g^3\sigma_u^1(^3\Pi_u)$	1.408	-198.617	5.503	15.887	0.953
HF	$\sigma^2\pi^4(^1\Sigma^+)$	0.922	-100.482	7.000	18.689	1.310
	$\sigma^2\pi^3\sigma^1(^1\Pi)$	0.922	-99.615	3.153	-0.905	-5.490
	$\sigma^2\pi^3\sigma^1(^3\Pi)$	0.922	-99.723	3.153	4.926	1.009
BF	$\pi^4\sigma^2(^1\Sigma^+)$	1.270	-124.677	5.258	10.516	1.314
	$\pi^4\sigma^1\pi^1(^1\Pi)$	1.270	-123.897	7.584	4.744	6.062
	$\pi^4\sigma^1\pi^1(^3\Pi)$	1.270	-124.041	7.584	12.564	2.289
LiH	$\sigma^2(^1\Sigma)$	1.592	-8.086	4.351	7.875	3.801
	$\sigma^1\sigma^1(^1\Sigma)$	1.592	-7.835	9.305	11.303	3.830
	$\sigma^1\sigma^1(^3\Sigma)$	1.592	-7.861	9.305	12.719	3.403
O_2	$\pi_g^1\pi_g^1(^3\Sigma_g^-)$	1.206	-150.370	6.587	13.081	1.658
	$\pi_g^1\pi_u^1(^3\Sigma_g^-)$	1.206	-149.486	6.314	5.719	3.485
	$\pi_g^2(^1\Sigma_u^+)$	1.206	-149.643	6.314	14.266	1.397
OS	$\pi^1\pi^1(^3\Sigma)$	1.510	-473.406	5.953	9.710	1.636
	$\pi^1\pi^1(^3\Sigma)$	1.510	-472.238	5.605	4.060	3.869
	$\pi^2(^1\Sigma)$	1.510	-472.358	5.605	10.619	1.479
S_2	$\pi_g^1\pi_g^1(^3\Sigma_g^-)$	1.927	-796.416	5.707	8.176	1.992
	$\pi_g^1\pi_u^1(^3\Sigma_g^-)$	1.927	-794.973	5.411	4.564	3.207
	$\pi_g^2(^1\Sigma_u^+)$	1.927	-795.054	5.411	8.961	1.633
NH	$\sigma^2\pi^1\pi^1(^3\Sigma)$	1.043	-55.241	7.057	13.304	1.872
	$\sigma^2\pi^1\pi^1(^3\Sigma)$	1.043	-54.824	5.694	6.349	2.553
	$\sigma^1\pi^2\pi^1(^1\Sigma^+)$	1.043	-54.972	5.694	14.416	1.124
LiN	$\pi^1\pi^1(^3\Sigma^-)$	1.867	-62.161	5.036	9.380	1.351
	$\pi^1\pi^1(^3\Sigma^-)$	1.867	-61.810	3.316	4.750	1.157
	$\pi^2(^1\Sigma^+)$	1.867	-61.826	3.316	5.648	0.973
H_2O	$1b_1^2$	0.969	-76.458	4.991	15.585	0.799
	$1b_1^13a_1^1(S)$	0.969	-75.715	4.012	0.668	12.034
	$1b_1^13a_1^1(T)$	0.969	-75.734	4.012	1.671	4.815
NH_3	$2a_1^2$	1.018	-56.582	4.263	12.879	1.768
	$2a_1^13a_1^1(S)$	1.018	-55.928	5.694	4.739	3.515
	$2a_1^13a_1^1(T)$	1.018	-56.347	5.694	0.107	6.723

Table 2 Bond Lengths (Å), Energies (au), Hardness and electrophilicity Values (eV) of Diatomic, triatomic, and tetratomic Molecules for adiabatic excitation.

Species	Electronic Configuration (State)	Bond Length (Å)	Energy (au)	Electronegativity (eV)	Hardness (eV)	Electrophilicity index (eV)
H_2	$\sigma_g^2(^1\Sigma_g^+)$	0.600	-1.179	6.380	20.305	1.002
	$\sigma_g^1\sigma_u^1(^1\Sigma_u^+)$	1.330	-0.693	6.765	8.201	2.790
	$\sigma_g^1\sigma_u^1(^3\Sigma_u^+)$	0.865	-0.623	10.681	10.681	5.096
Li_2	$\sigma_g^2(^1\Sigma_g^+)$	2.705	-15.015	2.858	4.926	0.829
	$\sigma_g^1\sigma_u^1(^1\Sigma_u^+)$	3.083	-14.792	3.426	3.426	1.664
	$\sigma_g^1\sigma_u^1(^3\Sigma_u^+)$	2.623	-14.842	3.511	6.430	0.958
N_2	$\sigma_g^2(^1\Sigma_g^+)$	1.095	-109.559	6.944	17.866	1.349
	$\sigma_g^1\pi_g^1(^1\Pi_g)$	1.231	-108.702	6.381	4.805	4.616
	$\sigma_g^1\pi_g^1(^3\Pi_g)$	1.236	-108.754	6.660	7.032	2.895
F_2	$\pi_u^4\pi_g^4(^1\Sigma_g^+)$	1.408	-199.571	8.440	15.290	2.329
	$\pi_u^4\pi_g^3\sigma_u^1(^1\Pi_u)$	1.652	-198.588	7.400	8.901	3.076
	$\pi_u^4\pi_g^3\sigma_u^1(^3\Pi_u)$	7.074	-198.780	9.716	15.653	3.015
HF	$\sigma^2\pi^4(^1\Sigma^+)$	0.922	-100.482	7.000	18.689	1.310
	$\sigma^2\pi^3\sigma^1(^1\Pi)$	1.609	-99.718	7.400	7.884	0.792
	$\sigma^2\pi^3\sigma^1(^3\Pi)$	0.937	-99.527	9.716	-5.723	-0.846
BF	$\pi^4\sigma^2(^1\Sigma^+)$	1.270	-124.677	5.258	10.516	1.314
	$\pi^4\sigma^1\pi^1(^1\Pi)$	1.297	-123.898	7.602	4.776	6.050
	$\pi^4\sigma^1\pi^1(^3\Pi)$	1.306	-124.042	7.610	12.642	2.290
LiH	$\sigma^2(^1\Sigma)$	1.592	-8.086	4.351	7.875	3.801
	$\sigma^1\sigma^1(^1\Sigma)$	1.936	-7.841	8.408	10.366	3.409
	$\sigma^1\sigma^1(^3\Sigma)$	2.062	-7.868	8.081	11.531	2.831
O_2	$\pi_g^1\pi_g^1(^3\Sigma_g^-)$	1.206	-150.370	6.587	13.081	1.658
	$\pi_g^1\pi_u^1(^3\Sigma_g^-)$	1.408	-149.534	7.039	10.162	2.438
	$\pi_g^2(^1\Sigma_u^+)$	1.152	-149.597	5.687	11.470	1.410
OS	$\pi^1\pi^1(^3\Sigma)$	1.510	-473.406	5.953	9.710	1.636
	$\pi^1\pi^1(^3\Sigma)$	1.455	-472.275	5.301	5.907	2.379
	$\pi^2(^1\Sigma)$	1.454	-472.321	5.301	8.393	1.674
S_2	$\pi_g^1\pi_g^1(^3\Sigma_g^-)$	1.927	-796.416	5.707	8.176	1.992
	$\pi_g^1\pi_u^1(^3\Sigma_g^-)$	2.153	-794.995	5.621	6.447	2.450
	$\pi_g^2(^1\Sigma_u^+)$	1.878	-795.022	5.224	7.913	1.996
NH	$\sigma^2\pi^1\pi^1(^3\Sigma)$	1.043	-55.241	7.057	13.304	1.872
	$\sigma^2\pi^1\pi^1(^3\Sigma)$	1.015	-54.824	5.708	6.404	2.543
	$\sigma^1\pi^2\pi^1(^1\Sigma^+)$	1.019	-54.903	5.706	10.696	1.522
LiN	$\pi^1\pi^1(^3\Sigma^-)$	1.867	-62.161	5.036	9.380	1.351
	$\pi^1\pi^1(^3\Sigma^-)$	1.736	-61.812	3.373	5.263	1.081
	$\pi^2(^1\Sigma^+)$	1.835	-61.767	3.332	2.475	2.242
H_2O	$1b_1^2$	1.867	-76.458	4.991	15.585	0.799
	$1b_1^13a_1^1(S)$	1.088	-75.730	3.760	1.669	4.235
	$1b_1^13a_1^1(T)$	1.177	-75.764	4.508	5.561	1.827
NH_3	$2a_1^2$	1.018	-56.582	4.263	12.879	1.768

$2a_1^13a_1^1(S)$	1.029	-55.948	5.972	6.347	2.809
$2a_1^13a_1^1(T)$	1.010	-55.964	5.966	6.786	2.623

4. Conclusion

Molecules in the ground state are less reactive than in their excited states. The reactivity increases due to decreased hardness and increased electrophilicity. Thus, during molecular excitation, hardness should decrease, and electrophilicity should increase. That means the maximum hardness principle (MHP) and minimum electrophilicity principle (MElP) should be valid during molecular excitation. In this study, twelve diatomic, one triatomic, and one tetratomic molecules are studied. Most of the singlet state molecules obey these principles when the vertical excitation with conserved spin state is considered. However, triplet ground-state molecules are off the trend in the spin changed excitation. On the other hand, the validity of these principles broadened when adiabatic excitations are considered. It is found that some triplet ground state molecules also obey the rules in the spin changed transition.

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