Nuclear reactivity and nuclear stiffness in density functional theory

Piotr Ordon, Ludwik Komorowski [*]

Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, PL.-50-370 Wrocław, Poland

Abstract

The nuclear reactivity has been identified with the derivative of the chemical potential (electronegativity) versus the deformation. A similar derivative of hardness has been proposed as a novel density functional theory index, nuclear stiffness. Both quantities have been calculated for a set of diatomic molecules. They provide information on the susceptibility of the molecule to attack in a collinear reaction. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The density functional theory (DFT) of many electron systems [1,2] has been found useful in providing rigorous formulation for two important qualitative chemical concepts: electronegativity and chemical hardness. The idea of chemical hardness, first introduced by Pearson, has been in the chemical vocabulary for over three decades [3]. His HSAB (hard and soft acids and bases) principle has been proposed as a purely experimental rule of thumb; a

need to provide a theoretical framework for the concept of hardness has been recognized ever since. The expectations have been fulfilled by Pearson himself in the joint work with Parr; they proposed a definition of global hardness based on DFT [4]:

$$\eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{\nu(\mathbf{r})} = \frac{1}{2}\left(\frac{\partial^2 E(N,\nu(\mathbf{r}))}{\partial N^2}\right)_{\nu(\mathbf{r})}$$

$$\cong \frac{I-A}{2} \cong \frac{\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}}{2} \tag{1}$$

$\nu(\mathbf{r})$ is external potential, μ is chemical potential of the electronic system $\mu = (\partial E/\partial N)_{\nu(\mathbf{r})}$ identified as negative of electronegativity [5], $\chi = -\mu$. The important property of hardness is in governing charge transfer processes. When a system exchanges elec-

---

[*] Corresponding author.

trons, the change of its chemical potential is given by:

$$d\mu = 2\eta dN + \int f(\mathbf{r}) d\nu(\mathbf{r}) d\mathbf{r} \qquad (2)$$

$f(\mathbf{r})$ is Fukui function:

$$f(\mathbf{r}) = \left(\frac{\partial \mu}{\partial \nu(\mathbf{r})}\right)_N = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{\nu(\mathbf{r})} \qquad (3)$$

Thermodynamically, a big change in the chemical potential ($d\mu$) provides the driving force for the process of changing the electron density $\rho(\mathbf{r})$, thus also N and/or $\nu(\mathbf{r})$. The first term in Eq. (2) reflects the effect of changing N, hence it produces the charge transfer driven increment to the bonding energy. The second term, which does not vanish when $\eta \to 0$, contains the reminding interactions that produce a bond beyond the net charge transfer. For interacting neutral objects, this second term leads to what chemists label as covalent energy. While both are equally important, the more easily tractable charge transfer part has drawn special attention. The charge transfer energy, identified with the ionic energy of the bond, has been a source of the original notion of electronegativity by Pauling [6]. The operational formula describing the energy gain in the charge transfer process is due to Parr and Pearson [4] (many others have been proposed, see Ref. [7] for a review.):

$$\Delta E_{AB} = -\frac{(\Delta\mu)^2}{4(\eta_A + \eta_B)} \,. \qquad (4)$$

This energy vanishes when $\Delta\mu = 0$, as e.g. for the interaction of identical atoms that form a covalent bond; this justifies the identification of ΔE_{AB} with the ionic bonding energy (between originally neutral species). An interesting proof of the HSAB principle proposed by Parr et al. is also built on the analysis of the sole charge transfer energy [8]. The authors introduced the grand potential: $\Omega_i = E_i - (N_i - N_i^0)\mu$ as the natural thermodynamical potential for electrons near the equilibrium. They proved for every part (an open subsystem) of the system, $\Delta\Omega_i$ tends to be as negative as possible:

$$\Delta\Omega_i = -(\Delta\mu)^2 \frac{\eta_i}{4(\eta_i + \eta_{rest})^2} \,. \qquad (5)$$

At constant $\Delta\mu$ (also T and $\nu(\mathbf{r})$) the HSAB principle is recovered. However, this argument can hardly be applied to the atomic or molecular interactions when neither μ nor $\nu(\mathbf{r})$ are constant. As a consequence, Eq. (2), not Eq. (4) or Eq. (5), must be referred to as a primary source of information on the effect of varying hardness on the reaction.

The role of hardness in bond formation has been a subject of several studies. An early comment on the HSAB principle by Nalewajski was: hard/hard interactions produce predominantly ionic bonds, and soft/soft interactions lead to the covalent ones [9]. Berkowitz suggested that the induced electron flow is greater, the softer are the partners [10]. Parr and Yang analyzed the interaction energy to second-order (Ref. [2], Chap. 10). They found, in the limit $\eta \to 0$, the electronegativity equalization is achieved by balancing the potential rather than a net charge. The polarization energy appears as the leading term here. Since the analysis was incapable of describing directly what chemists call covalent energy, this large (and always negative) polarization term must be identified as the quantitative measure of that effect on the simplified DFT level. Another important principle involving hardness has been proposed by Pearson [11] and proved by Parr and Chattaraj [12], the maximum hardness principle: the global hardness of a system in equilibrium is at a maximum at constant $\nu(\mathbf{r})$. Pearson and Palke provided the support for that principle by proving that the global hardness is also at a maximum against any non-totally symmetric distortion of the molecule [13]. The maximum hardness principle has been supplemented by Zhou and Parr, who introduced the idea of activation hardness, the increase of hardness when going from stable substrates to the transition state on the reaction path [14]. The low hardness barrier on the reaction path (activation hardness) promotes a reaction involving the electron transfer also, they argue that the greater the absolute hardness, the more stable is a molecule.

This work extends the application of the DFT apparatus to reaction dynamics. It focuses on expectations concerning the role of molecular deformation

in changing the global hardness and chemical potential, hence, also the affinity for an intermolecular electron exchange process.

2. Hardness and the molecular deformation

To examine the dependence of hardness on molecular deformation we consider the derivative:

$$\mathbf{G}_i = \left(\frac{\partial \eta}{\partial \mathbf{Q}_i} \right)_N \qquad (6)$$

where $\mathbf{Q}_i = \mathbf{R}_i - \mathbf{R}_{i,0}$ is the displacement vector of atom i from an equilibrium position $\mathbf{R}_{i,0}$. Using the definition of hardness (Eq. (1)), $\mathbf{G}_i$ can be related to the electrostatic forces occurring upon ionization. The proof is as follows [15]:

$$\mathbf{G}_i = \left(\frac{\partial \eta}{\partial \mathbf{Q}_i} \right)_N = \left\langle \frac{\partial}{\partial \mathbf{Q}_i} \left[\frac{1}{2} \frac{\partial^2 E(N, \nu(\mathbf{r}))}{\partial N^2} \right]_{\nu(\mathbf{r})} \right\rangle_N$$

$$= \frac{1}{2} \left\langle \frac{\partial^2}{\partial N^2} \left[\frac{\partial E(N, \nu(\mathbf{r}))}{\partial \mathbf{Q}_i} \right]_N \right\rangle_{\nu(\mathbf{r})}. \qquad (7)$$

However, $\left[\dfrac{\partial E(N, \nu(\mathbf{r}))}{\partial \mathbf{Q}_i} \right]_N = -\mathbf{F}_i$ where $\mathbf{F}_i$ is the Hellman–Feynman force [16] Thus:

$$\mathbf{G}_i = \left(\frac{\partial \eta}{\partial \mathbf{Q}_i} \right)_N = -\frac{1}{2} \left(\frac{\partial^2 \mathbf{F}_i}{\partial N^2} \right)_{\nu(\mathbf{r})} \qquad (8)$$

Feynman has proven that:

$$\mathbf{F}_i = -\left(\frac{\partial E(N, \nu(\mathbf{r}))}{\partial \mathbf{Q}_i} \right)_N = \int \rho(\mathbf{r}) \boldsymbol{\varepsilon}_i(\mathbf{r}) d\mathbf{r} + \mathbf{F}_i^{n-n} \qquad (9)$$

where $\rho(\mathbf{r})$ electron density, $\boldsymbol{\varepsilon}_i(\mathbf{r})$ is the electric field due to ith nuclei and $\mathbf{F}_i^{n-n}$ is a sum of mutual forces between ith nucleus and all others. F_i^{n-n} does not depend on the number of electrons so this term will not be present in Eq. (8). Also $\boldsymbol{\varepsilon}_i(\mathbf{r})$ does not depend directly on N. Inserting Eq. (9) into Eq. (8) gives:

$$\mathbf{G}_i = \left(\frac{\partial \eta}{\partial \mathbf{Q}_i} \right)_N = -\frac{1}{2} \int \left(\frac{\partial^2 \rho(\mathbf{r})}{\partial N^2} \right)_{\nu(\mathbf{r})} \boldsymbol{\varepsilon}_i(\mathbf{r}) d\mathbf{r}$$

$$= -\frac{1}{2} \int \left(\frac{\partial f(\mathbf{r})}{\partial N} \right)_{\nu(\mathbf{r})} \boldsymbol{\varepsilon}_i(\mathbf{r}) d\mathbf{r}. \qquad (10)$$

A working approximation for $\left(\dfrac{\partial f(\mathbf{r})}{\partial N} \right)_{\nu(\mathbf{r})}$ $= \left(\dfrac{\partial^2 \rho(\mathbf{r})}{\partial N^2} \right)_{\nu(\mathbf{r})}$ is needed at this point. The finite difference approximation to the $\rho(N)$ function appears to be a reasonable starting point. Taking $\rho(N_o)$ $= \rho^o$, $\rho(N_o + 1) = \rho^+$ and $\rho(N_o - 1) = \rho^-$, the following result is readily obtained:

$$\left[\frac{\partial f(\mathbf{r})}{\partial N} \right]_{\nu(\mathbf{r})} \cong \rho(\mathbf{r})^+ + \rho(\mathbf{r})^- - 2\rho(\mathbf{r})^0 \qquad (11)$$

The final relation for $\mathbf{G}_i$ is:

$$\mathbf{G}_i \cong -\frac{1}{2} \int \left[\rho(\mathbf{r})^+ + \rho(\mathbf{r})^- - 2\rho(\mathbf{r})^o \right] \boldsymbol{\varepsilon}_i(\mathbf{r}) d\mathbf{r}$$

$$= -\frac{1}{2} (\mathbf{F}_i^+ + \mathbf{F}_i^-) + \mathbf{F}_i^o = -\frac{1}{2} (\mathbf{F}_i^+ + \mathbf{F}_i^-). \qquad (12)$$

By considering the increment from the nuclei unchanged upon ionization ($\mathbf{F}_i^{n-n}$), the balance of electronic forces has been replaced by $\mathbf{F}_i^+$ and $\mathbf{F}_i^-$, the total forces acting on the ith nucleus in a system whose nuclear positions have been kept unchanged, but the number of electrons has increased $(+)$ or decreased $(-)$, respectively. The corresponding total force $\mathbf{F}_i^o$ in the neutral, equilibrium system is identically zero, $\mathbf{F}_i^o = 0$. The non-zero forces $\mathbf{F}_i^+$ and $\mathbf{F}_i^-$ occur only because the ionized species are of the hypothetical, unrelaxed structure. Searching for the proper name of the $\mathbf{G}_i$ index, the name nuclear stiffness may be proposed, as adequately reflecting its physical context.

3. Calculation of the nuclear reactivity (Φ_i) and the $\mathbf{G}_i$ indices

The nuclear stiffness $\mathbf{G}_i$ index presents a natural extension for another quantity earlier introduced and discussed by Cohen et al. [17] and also Baekeland et al. [18] — the nuclear reactivity Φ_i. It has been defined as the derivative of the Hellmann–Feynman force versus the number of electrons:

$$\Phi_i = \left(\frac{\partial \mathbf{F}_i}{\partial N} \right)_{\nu(\mathbf{r})}. \qquad (13)$$

It is straightforward to prove, using the method applied above that $\mathbf{\Phi}_i$ is identical to the derivative of electronegativity versus atomic displacement:

$$\mathbf{\Phi}_i = \left(\frac{\partial \mathbf{F}_i}{\partial N}\right)_{\nu(\mathbf{r})} = -\left(\frac{\partial}{\partial N}\left(\frac{\partial E(N,\nu(\mathbf{r}))}{\partial \mathbf{Q}_i}\right)_N\right)_{\nu(\mathbf{r})}$$

$$= -\left(\frac{\partial}{\partial \mathbf{Q}_i}\left(\frac{\partial E(N,V)}{\partial N}\right)_{\nu(\mathbf{r})}\right)_N$$

$$= -\left(\frac{\partial \mu}{\partial \mathbf{Q}_i}\right)_N = \left(\frac{\partial \chi}{\partial \mathbf{Q}_i}\right)_N \qquad (14)$$

where χ is the electronegativity of the system. This identity hints to a potential value of the nuclear reactivity index $\mathbf{\Phi}_i$, as a source of information beyond its meaning originally proposed by Cohen. Using the same method as above, the following simplified working formula for the nuclear reactivity is obtained:

$$\mathbf{\Phi}_i \cong \tfrac{1}{2}\left(\mathbf{F}_i^+ - \mathbf{F}_i^-\right). \qquad (15)$$

Both indices $\mathbf{\Phi}_i$ and $\mathbf{G}_i$ are vectors in 3D space (as are forces $\mathbf{F}_i^+$ and $\mathbf{F}_i^-$), characteristic to each atom in the molecule. An important and useful property of these vectors is disclosed by Eqs. (12) and (15), while it is by no means evident from their definitions Eqs. (7) and (14): Φ_i and G_i are independent of the deformation $\mathbf{Q}_i$! $\mathbf{\Phi}_i$ and $\mathbf{G}_i$ reflect an intrinsic property of the molecule (of the electric force field therein) and hence are a potential source of information on how the reactivity of a molecule is modified by a deformation. The transformation of the $\mathbf{\Phi}_i$ and $\mathbf{G}_i$ vectors into meaningful indices is possible through their projection onto the direction of a chosen deformation. This is particularly simple for diatomic molecule. Let $\mathbf{q}$ be a unit vector of the bond stretching deformation of a diatomic molecule. Then the projections are simply the scalar products and are numbers whose sign indicate the orientation of the original vectors at given site (i): $\Phi_i = \mathbf{q}\mathbf{\Phi}_i$ and $G_i = \mathbf{q}\mathbf{G}_i$. For a diatomic molecules, the scalar index (Φ_i and G_i) is identical for both atoms; polyatomic molecules require more elaborate methods of mapping the pair of vector indices $\mathbf{\Phi}_i$ and $\mathbf{G}_i$.

4. Results and discussion

The $\mathbf{\Phi}_i$ and $\mathbf{G}_i$ have been calculated by means of Eqs. (12) and (15) for a set of diatomic molecules.

Table 1
Calculated projection of nuclear reactivity Φ_i and nuclear stiffness G_i on the stretching deformation of the diatomic molecules

Molecule	$\eta = \dfrac{I-A}{2}$	Φ_i	G_i	F_i^+	F_i^-
	(V/e)	(eV/Å)	(eV/Å)	(eV/Å)	(eV/Å)
LiH	3.729	0.530	−0.928	1.457	0.397
HF	9.465	0.139	−3.684	1.886	3.494
F_2	7.578	−9.169	−8.120	−1.049	17.289
Cl_2	5.332	−4.883	−2.939	−1.944	7.822
Li_2	0.046	0.042	−0.444	0.486	0.402
FCl	6.154	−6.562	−2.340	−4.223	8.902
CO	7.899	−4.054	4.393	−8.415	−0.338
LiF	5.592	−1.272	−1.920	0.646	3.189
BCl	5.063	−3.010	0.663	−3.672	2.364
BH	4.682	−0.570	0.178	−0.747	0.392
CS	5.767	−3.968	0.740	−4.707	3.228
NF	4.421	−6.524	0.149	−6.673	6.375
SO	3.552	−2.619	0.594	−3.214	2.024
HCl	7.277	−0.280	−1.445	1.164	1.726
LiCl	4.675	0.590	−1.248	1.837	0.658
BF	5.928	−2.830	0.372	−3.203	2.458
SiO	6.089	−1.058	−0.958	−0.099	2.016

The projection of the forces calculated for the increasing (F_i^+) and decreasing (F_i^-) number of electrons is also given.

The calculations were performed using the MP2 method and 6-311 + G(3df,3dp) basis set as implemented in the GAUSSIAN 94 code [19]. The geometry was optimized for the neutral molecule by a quasi Newton–Raphson procedure [20,21]. Anion and cation energies and forces were calculated in the neutral molecular geometry. These quantities were used to obtain the hardness (Eq. (1)), nuclear reactivity Φ_i and nuclear stiffness G_i given as scalar indices in Table 1. They represent a projection on the stretching deformation of the molecule, thus positive values indicate the increase of the electronegativity and hardness, respectively, upon the bond length increase. The role of the forces $\mathbf{F}_i^+$ and $\mathbf{F}_i^-$ can be observed directly through the data in Table 1, where the projection of the forces on the stretching mode is also given as scalars, F_i^+ and F_i^-. A convention introduced in Section 2 must be recalled: F_i^+ is the force occurring when an electron is added to the molecule.

The calculated Φ_i and G_i indices may be confronted with the expectation derived from the model

consideration. The simple point-charge or the spherical, non-overlapping AIM models analyzed by Nalewajski and Korchaviec [22] always produce $G_i < 0$. This follows from the general dependence of the hardness matrix elements on the internuclear distances $\eta_{ij} \approx 1/R_{ij}$. (More refined model e.g. Mataga and Nishimoto [23] or Ohno [24] also demonstrate this property.) Sample prediction for the derivative of the electronegativity (Φ_i), may be based on the original idea by Gordy [25], who identified the measure of electronegativity with the potential at the covalent boundary, $Z^* e/r$. This leads to an initial guess that Φ_i is also negative. The data in Table 1 match surprisingly well the rough estimates of the sign of the derivatives. They indicate, however, that Φ_i and G_i contain more subtle information than might be deduced from models. This information cannot be overestimated: it represents the finite difference approximation to the derivatives, thus averaging any effect of the bond deformation. A most attractive perspective for the data presented in Table 1 appears to be in enlightening the mechanism of simple reactions. For a collinear reaction:

$$\mathbf{X}\text{—}\mathbf{Y} + \mathbf{Z} \rightarrow \mathbf{X}\ldots\mathbf{Y}\ldots\mathbf{Z} \rightarrow \mathbf{X} + \mathbf{Y}\text{—}\mathbf{Z}$$

the successful attack of $\mathbf{Z}$ is conditional to two factors: (i) the energy barrier for the attack on the collinear reaction path, and (ii) the site of attack, which in this simple case may be either the $\mathbf{X}$ or $\mathbf{Y}$ atom. The first condition corresponds to what is described as *reactivity*, the second represents *selectivity*. Both properties have been the subjects of numerous studies at the DFT level (e.g. Ref. [26]). The pair of indices Φ_i and G_i introduced in this work provides a formidable, semiquantitative tool for the description of the first effect. The collinear approach of $\mathbf{Z}$ to $\mathbf{XY}$ is associated with increasing the $\mathbf{X}$—$\mathbf{Y}$ bond. If this process increases the global hardness of $\mathbf{XY}$ ($G_i > 0$) the electron exchange between $\mathbf{XY}$ and $\mathbf{Z}$ (the reaction) becomes hindred. When $G_i < 0$, approach of $\mathbf{Z}$ softens the molecule and increases the chance of electron transfer, exactly as it has been postulated by the 'harpoon mechanism'. This process is, however, subject to the selectivity condition. The role of electronegativity change due to the initial bond expansion in $\mathbf{XY}$ is described by Φ_i. When $\Phi_i > 0$ the stretched molecule becomes a better acceptor, when $\Phi_i < 0$ it changes to a better

donor of electrons. The overall effect of this change on the reaction depends on the nature of $\mathbf{Z}$ (donor or acceptor) and on the site of the attack (polarization of $\mathbf{XY}$). The selectivity factor determined by the polarization (due either to the electrostatic repulsion/attraction indicated by the atomic population, or to the suitable orbital overlap) can usually be envisaged by a chemist qualitatively; the quantitative information provided by the Φ_i and G_i indices significantly extends the power of such predictions concerning the reactivity at the site selected. Another interesting application that may be envisaged is the hypothetical metallization process suggested by Gilman as the possible first step in detonation [27]. In terms of the DFT, the metallic state is characterized by zero global hardness. Metallization might be induced by compressing the bonds due to the intermolecular collisions under pressure only when G_i is positive, which is rather exceptional for the molecules studied.

Acknowledgements

References

[1] P. Hohenberg, W. Kohn, Phys. Rev. B 136 (1964) 864.
[2] R.G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules (Oxford University Press, 1989).
[3] R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533.
[4] R.G. Parr, R.G. Pearson, J. Am. Chem. Soc. 105 (1983) 7512.
[5] R.G. Parr, R.A. Donnelly, M. Levy, W.E. Palke, J. Chem. Phys. 69 (1978) 4431.
[6] L. Pauling, J. Am. Chem. Soc. 54 (1932) 3570.
[7] L. Komorowski, Structure and Bonding, Vol. 80 (Springer, Berlin, 1993) pp. 46–70.
[8] P.K. Chattaraj, H. Lee, R.G. Parr, J. Am. Chem. Soc. 113 (1991) 1855.
[9] R.F. Nalewajski, J. Am. Chem. Soc. 106 (1984) 944.
[10] M. Berkowitz, J. Am. Chem. Soc. 109 (1987) 4823.
[11] R.G. Pearson, J. Chem. Educ. 64 (1987) 561.
[12] R.G. Parr, P.K. Chattaraj, J. Am. Chem. Soc. 113 (1991) 1854.

[13] R.G. Pearson, W.E. Palke, J. Phys. Chem. 96 (1992) 3283.

[14] Z. Zhou, R.G. Parr, J. Am. Chem. Soc. 112 (1990) 5720.

[15] P. Ordon, L. Komorowski, 7th International Conference on the Applications of the DFT in Chemistry and Physics, Vienna, September 1997.

[16] R.P. Feynman, Phys. Rev. 56 (1939) 340.

[17] M.H. Cohen, M.V. Ganduglia-Pirovano, J. Kudrnovsky, J. Chem. Phys. 101 (1994) 8988.

[18] B.G. Baekelandt, A. Cedillo, R.G. Parr, J. Chem. Phys. 103 (1995) 8548.

[19] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. DeFrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN94, Revision A.1, Gaussian, Pittsburgh, PA, 1995.

[20] J. Baker, J. Comput. Chem. 7 (1995) 385.

[21] H.B. Schlegel, J. Comput. Chem. 3 (1982) 214.

[22] R.F. Nalewajski, J. Korchowiec, Charge Sensitivity Approach to Electronic Structure and Chemical Reactivity, Advanced Series in Physical Chemistry, Vol. 8 (World Scientific Publ., Singapore, 1997).

[23] K. Nishimoto, N. Mataga, Z. Phys. Chem. 12 (1957) 335.

[24] K. Ohno, Adv. Quant. Chem. 3 (1967) 239.

[25] W. Gordy, Phys. Rev. 69 (1946) 604.

[26] Y. Li, J.N.S. Evans, J. Am. Chem. Soc. 117 (1995) 7756.

[27] J.J. Gilman, Phil. Mag. B77 (1995) 1057.