

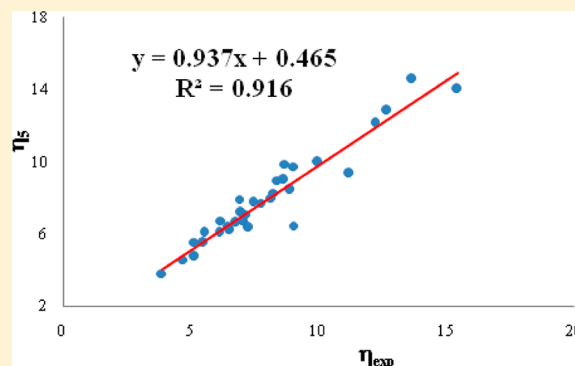
# Evaluation of Absolute Hardness: A New Approach

Siamak Noorizadeh\* and Hadi Parsa

Chemistry Department, College of Science, Shahid Chamran University, Ahvaz, 61357-43169, Iran

## S Supporting Information

**ABSTRACT:** By taking the energy to be a Morse-like function of the number of electrons,  $E(N) = \alpha\{1 - e^{-\beta(N-\delta)}\}^2 - \kappa$ , the electronic chemical potential and global hardness values for a set of atoms and some molecules are calculated from the accurate definitions of these two concepts and using the hybrid B3LYP functional and 6-311++G\*\* basis set. By a comparison between the obtained hardnesses and the corresponding *experimental* values, it is found that the proposed model yields better values for hardnesses with respect to those that are obtained from the other frequently used methods. It is claimed that the difference between the calculated and experimental hardness values may arise from the approximate equation used for the evaluation of experimental hardnesses. Both of the calculated and experimental molecular hardnesses are used to investigate the change of hardness during the course of some exothermic reactions according to the maximum hardness principle (MHP). It is shown that the obtained hardnesses of reactions from the calculated hardnesses ( $\Delta\eta_{\text{calc}}$ ) are more successful in predicting the directions of these reactions than those that are evaluated from the experimental hardnesses ( $\Delta\eta_{\text{exp}}$ ).



## INTRODUCTION

The understanding and prediction of molecular reactivity have been a challenging area in chemistry. The past few decades have seen several attempts for this purpose using quantum mechanical methods as well as density-functional-based descriptors. Several of these functions, such as electronegativity ( $\chi$ ), chemical potential ( $\mu$ ), hardness ( $\eta$ ), and molecular electrostatic potential, have become increasingly more important within the context of conceptual density functional theory (DFT).<sup>1–7</sup> Undoubtedly, the chemical potential<sup>8</sup> and hardness<sup>9</sup> are among the most commonly and widely used concepts. In fact, any chemical system (atom, molecule, ion, or radical) is characterized by these two keys, which are defined as the first- and second-order partial derivatives of the total electronic energy ( $E$ ) with respect to the number of electrons ( $N$ ) at a fixed external potential,  $\nu(r)$ , respectively. Hence the *exact* definitions of these two quantities in the framework of the conceptual DFT are

$$\mu = \left[ \frac{\partial E}{\partial N} \right]_{\nu(r)} \quad (1)$$

and

$$\eta = \left[ \frac{\partial^2 E}{\partial N^2} \right]_{\nu(r)} = \left[ \frac{\partial \mu}{\partial N} \right]_{\nu(r)} \quad (2)$$

It seems that the chemical potential is the tendency of a system to accept an electron, whereas the chemical hardness is a measure of chemical species' resistance to change its electronic configuration and is a quality that determines or

controls the chemical reactivity. It should be mentioned that the accurate values for these concepts should be evaluated from eqs 1 and 2; and according to these equations, for a given system  $\mu$  and  $\eta$  are simply the instantaneous slope and curvature of the plot of  $E$  versus  $N$ , respectively. But there is no simple function for  $E(N)$  and the exact function is to be piecewise linear,<sup>10,11</sup> which gives a delta-function-like hardness.<sup>12</sup> Therefore, many attempts have been made to calculate the hardnesses of different systems using approximation methods;<sup>13–21</sup> for example, it is demonstrated that the absolute hardness of an electronic system could be determined from the electrostatic potentials.<sup>22</sup> It is also suggested that the obtained absolute hardness from DFT is identified with the chemical hardness of Pearson principle of hard and soft acids and bases.<sup>23–31</sup> Torrent-Sucarrat and Geerlings<sup>32</sup> evaluated the weights of the energetic components (electronic kinetic, electron–nucleus, electron–electron Coulombic and correlation energies) of the global hardness for some systems. A hardness-based similarity index for studying the quantum similarity of atoms is also analyzed by Borgoo and co-workers.<sup>33</sup> A critical account on the local hardness is given by Chattaraj et al.,<sup>34</sup> and this concept is analyzed and calculated for some different systems.<sup>35–39</sup>

As mentioned, a problem associated with eqs 1 and 2 is that the number of electrons in isolated atoms and molecules can change only by integer amounts, and hence  $E$  is not a continuous function of  $N$ . To solve this difficulty, a three-point

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**Table 1.** Calculated Three-Point, Five-Point, and Experimental Values for the Hardnesses and Chemical Potentials of the Selected Atoms Together with the Reported Hardnesses (in electronvolts)

atom	$\eta_3$	$\eta_5$	$\eta_{\text{exp}}^a$	$\mu_3$	$\mu_5$	$\mu_{\text{exp}}^a$	$I - A$	$(I + A)/2$	$\eta_{\text{C}}^b$	$\eta_{\text{GC}}^b$	$\eta_{\text{I}}^b$	$\eta_{\text{GI}}^b$
H	12.67	12.67	12.84	−6.43	−6.21	−7.18	12.80	−7.27	21.65	21.68	34.37	32.87
Li	4.81	5.13	4.77	−2.39	−2.48	−3.01	5.06	−3.09	6.23	6.27	5.03	5.22
Be	9.05	8.62	9.03	−3.40	−3.49	−4.81	9.34	−4.44	8.86	8.99	11.59	11.62
B	8.02	8.14	8.02	−3.58	−3.73	−4.29	9.09	−4.19	9.83	10.06	2.90	5.20
C	10.00	9.96	10.00	−5.57	−5.74	−6.26	10.19	−6.45	12.04	12.47	5.07	8.11
N	14.37	13.64	14.61	−6.38	−6.40	−7.23	14.55	−7.41	13.99	14.70	7.81	11.42
O	12.16	12.20	12.16	−6.53	−7.71	−7.54	12.52	−7.87	15.51	16.54	10.85	14.73
F	14.03	15.44	14.02	−9.43	−9.64	−10.41	14.28	−10.63	16.89	18.26	14.17	18.14
Na	4.73	4.69	4.59	−2.56	−2.55	−2.84	4.84	−3.00	4.14	4.21	2.26	2.84
Mg	7.80	7.15	7.10	−3.04	−2.95	−4.09	7.95	−3.75	5.37	5.49	5.20	5.47
Al	5.52	5.47	5.55	−2.69	−2.94	−3.21	5.63	−3.20	5.03	5.16	1.38	2.07
Si	6.71	7.07	6.76	−4.25	−4.26	−4.77	6.78	−4.72	6.22	6.40	2.29	3.26
P	9.40	9.04	9.74	−5.11	−5.01	−5.62	9.48	−5.65	7.27	7.53	3.32	4.55
S	8.26	8.24	8.28	−5.92	−6.22	−6.22	8.31	−6.35	8.14	8.49	4.44	5.86
Cl	9.30	11.20	9.36	−7.92	−7.59	−8.30	9.35	−8.40	9.00	9.44	5.69	7.28
K	3.84	3.86	3.84	−2.11	−2.14	−2.42	3.97	−2.51				
Ca	6.04	5.51	6.09	−2.57	−2.40	−3.07	6.14	−3.08				
Sc	7.38	7.25	6.37	−2.92	−3.45	−3.37	8.27	−3.98				
Ti	6.46	6.17	6.75	−3.48	−3.63	−3.45	6.55	−3.96				
V	6.35	6.51	6.22	−3.77	−3.71	−3.64	6.68	−4.23				
Cr	6.16	6.10	6.10	−3.56	−3.74	−3.72	6.39	−3.84				
Mn	8.09	6.89	7.93	−3.01	−3.28	−3.47	8.12	−3.46				
Fe	7.44	7.43	7.75	−3.76	−3.89	−4.03	7.59	−4.20				
Co	7.20	6.97	7.22	−4.11	−4.58	−4.27	7.44	−4.75				
Ni	7.06	9.00	6.48	−4.33	−3.85	−4.40	8.00	−5.15				
Cu	6.49	6.47	6.49	−4.31	−4.39	−4.48	6.82	−4.62				
Zn	9.88	8.69	9.88	−3.34	−3.72	−4.45	10.46	−4.20				
Ga	5.42	5.15	5.57	−3.02	−2.86	−3.21	5.59	−3.24				
Ge	6.51	6.77	6.67	−4.31	−4.15	−4.57	6.58	−4.61				
As	8.65	8.39	8.98	−4.96	−4.83	−5.30	8.89	−5.42				
Se	7.56	7.73	7.73	−5.60	−5.75	−5.89	7.61	−6.02				
Br	8.21	8.87	8.45	−7.31	−7.05	−7.59	8.37	−7.78				
	Mean Absolute Deviation (eV)											
	0.121	0.443							1.822	1.923	4.631	3.847
	(0.171)	(0.496)		(0.481)	(0.441)		(0.328)	(0.207)				
						$R^2$						
	0.995	0.951		0.762	0.791		0.356	0.519				
	(0.988)	(0.916)		(0.964)	(0.956)		(0.966)	(0.982)				

<sup>a</sup>From ref 83. <sup>b</sup>From ref 56.

finite difference approximation and valence state parabola model<sup>40–42</sup> are considered, which lead to the following most popular operational definitions of these quantities:

$$\mu \approx -\frac{1}{2}(I + A) \quad (3)$$

$$\eta \approx (I - A) \quad (4)$$

where  $I$  and  $A$  are the first vertical ionization and electron affinity energies, respectively. Many authors used these formulas to calculate the chemical potential and hardness values for different chemical systems. It is proper to mention that the use of the finite difference approximation is only appropriate if the value of the derivative  $(\partial\mu/\partial N)_{v(r)}$  does not vary appreciably over the interval  $N$ , which is valid in the frozen orbital approximation.<sup>35,43</sup> Thus, the invocation of this approximation requires that the absolute hardness be essentially independent of charge over an interval of two units of charge  $N(\Delta N=2)$ . This does not appear to be the case for absolute

hardnesses of atoms, which are to some extent dependent on charge.

Using Janak theorem,<sup>44</sup>  $\mu$  and  $\eta$  can be possibly approximated in terms of the energies of HOMO and LUMO ( $\epsilon_{\text{H}}$  and  $\epsilon_{\text{L}}$ ) as

$$\mu \approx \frac{1}{2}(\epsilon_{\text{L}} + \epsilon_{\text{H}}) \quad (5)$$

and

$$\eta \approx (\epsilon_{\text{L}} - \epsilon_{\text{H}}) \quad (6)$$

It is shown that the most stable structure has the largest HOMO–LUMO energy gap;<sup>45–51</sup> and therefore an electronic system with a large HOMO–LUMO gap should be less reactive than those having small gaps. It is the base of the maximum hardness principle (MHP),<sup>47,52–58</sup> whose validity is verified in different systems;<sup>59–63</sup> but in some cases it somewhat breaks down.<sup>18,64–67</sup> Therefore, conditions under

which MHP is valid have been the subject of extensive investigations.

Assuming a differentiable curve for  $E(N)$  of a chemical system, and writing it as a Taylor series expansion around  $N_0$  (the number of electrons in the considered system), leads to the following relation

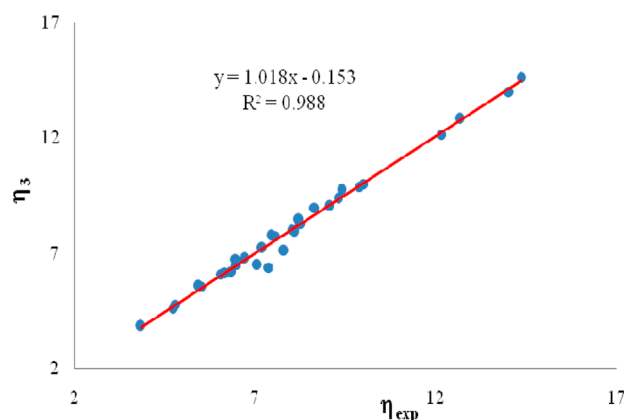
$$E(N) = E(N_0) + (N - N_0)\mu + \frac{1}{2}(N - N_0)^2\eta + \frac{1}{6}(N - N_0)^3\gamma + \dots \quad (7)$$

where  $\mu$  and  $\eta$  are inserted in accordance with eqs 1 and 2. It is shown that the above expansion may not converge for some atoms if the series is truncated after the second-order term; and therefore the change in  $\mu$  and  $\eta$  that result from taking the Taylor series past second order would generally be very small or even zero if  $I_n = n(I_1)$ , in which  $I_n$  is the  $n$ th successive atomic ionization energy. March<sup>68</sup> extended the series through the fifth order to obtain a modified  $\mu$  in terms of the first four ionization energies and electron affinities. Parr and Bartolotti<sup>69</sup> used nonparabolic and nonpower series model for  $E$  versus  $N$  model. Putz and co-workers<sup>70</sup> used alternative finite difference schemes, named “compact finite difference schemes with spectral-like resolution (SLR)”, for a less rough estimate of the analytical hardness definition as the second-order derivative of the energy with respect the electron number. They also plotted the energy of some bases with respect to the electron number,  $E(N)$ , in the range of  $M^{3+}-M^{3-}$ , and they concluded that the energy behavior is parabolic and hardness correctly represents the curvature of the plot. It is noteworthy that the exact definitions for  $\mu$  and  $\eta$  are eqs 1 and 2, and all other operational equations that provide these values (in particular eqs 3–6) are approximate. The lack of a rigorous definition has the consequence that different approximations can yield different and even sometimes contradictory conclusions.

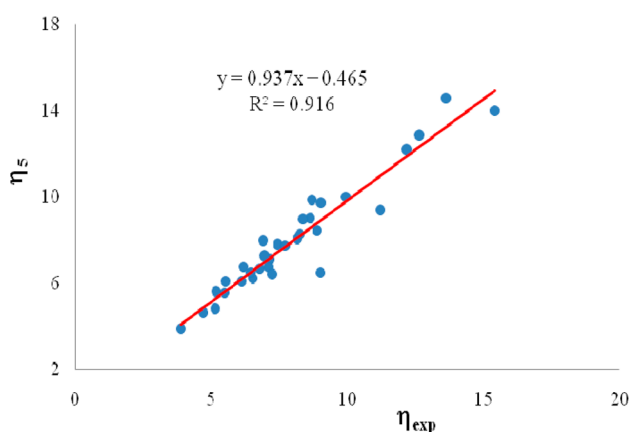
In many articles, the reported *experimental* chemical potential/hardness values are not derived from the exact eqs 1 and 2, but from the approximate eqs 3 and 4 and using the available experimental values of  $I$  and  $A$ . Calculation of *experimental* hardness ( $\eta_{\text{exp}}$ ) from eq 4 is subject to several error sources, the most important being the fact that the finite difference approximation, which has been used in this approximation, just can be strictly applied using an integer number of electrons.<sup>71</sup> There is the same problem for calculating the experimental chemical potential ( $\mu_{\text{exp}}$ ). Therefore, exploring new ways to compute more accurate values for these quantities is very important. The present article attempts to give a simple method for evaluation of accurate values for chemical potentials and hardnesses of atomic and molecular systems by considering a Morse-like function for  $E(N)$  instead of using a truncated Taylor series expansion. The calculated values are compared with those that were obtained from experimental data or other theoretical methods.

## RESULTS AND DISCUSSION

To calculate the chemical potential and hardness values using the accurate equations, i.e., eqs 1 and 2, total electronic energy of a chemical system (atom, molecule, ion, or radical) is considered as a function of the total number of electrons,  $N$ , and the external potential,  $\nu(r)$ , which is consistent with the description of an electronic system in DFT. Although it is not established that  $E$  is concave in  $\nu(r)$  and convex in  $N$ ,<sup>72</sup> it is



**Figure 1.** Calculated atomic hardnesses using three-points curve fitting vs experimental values for 32 selected atoms.



**Figure 2.** Calculated atomic hardnesses using five-point curve fitting vs experimental values for 32 selected atoms.

assumed here that  $E(N)$  function should be nearly similar to the potential energy function of a diatomic molecule,  $E(r)$ . A simple function, which is frequently used for  $E(r)$  curve, is the Morse function.<sup>73</sup> Therefore, it seems that the same function could be also considered for the  $E(N)$  curve. This model for the energy curve was used successfully for calculation of electrophilicities of atoms and molecules to introduce a new scale of electronegativity<sup>74</sup> and investigating the aromaticity of fulvene molecules.<sup>75</sup> Therefore, the following simple form is assumed for the electronic energy as a function of the number of electrons

$$E(N) = \alpha\{1 - e^{-\beta(N-\delta)}\}^2 - \kappa \quad (8)$$

where  $\alpha$ ,  $\beta$ ,  $\delta$ , and  $\kappa$  are adjustable parameters, which have physical meanings<sup>74</sup> and could be easily determined using a simple fitting procedure. Note that using a Morse-like function for  $E(N)$  is similar to considering nearly all terms in the Taylor series expansion of energy, i.e., eq 7, and therefore the obtained quantities from this function should be more accurate than those calculated from the approximate expressions. First- and second-order derivatives of eq 8 with respect to  $N$ , which are related to chemical potential and hardness, respectively, are

$$\left[\frac{\partial E}{\partial N}\right]_{\nu(r)} = \mu = 2\alpha\beta e^{-\beta(N_0-\delta)}\{1 - e^{-\beta(N_0-\delta)}\} \quad (9)$$

Table 2. Calculated Five-Point and Available Experimental Values for the Hardnesses and the Chemical Potentials of the Selected Molecules Together with the Corresponding Experimental Electron Affinities (in electronvolts)

molecules	$\eta_s$	$\eta_{\text{exp}}^a$	$\mu_s$	$\mu_{\text{exp}}^a$	$\Delta\eta_s$	$A_{\text{exp}}^a$	$I - A$	$(I - A)/2$
BF <sub>3</sub>	14.20	19.4	-5.43	-6.20	-5.20	-3.50	16.12	-7.23
SO <sub>3</sub>	10.99	11.0	-6.04	-7.20	-0.01	1.70	11.90	-6.85
Cl <sub>2</sub>	9.88	9.20	-6.02	-7.00	0.68	2.40	10.24	-6.57
H <sub>2</sub>	15.79	17.4	-5.34	-6.70	-1.61	-2.00	18.01	-7.53
SO <sub>2</sub>	11.25	11.2	-5.89	-6.70	0.05	1.10	11.21	-6.89
N <sub>2</sub>	17.0	17.8	-4.50	-6.70	-0.73	-2.20	17.87	-6.94
Br <sub>2</sub>	8.36	8.00	-5.85	-6.60	0.36	2.60	8.85	-6.26
O <sub>2</sub>	11.14	11.8	-5.98	-6.30	-0.65	0.44	9.74	-6.58
CO	14.17	15.8	-4.63	-6.10	-1.63	-1.80	15.55	-6.44
CS	11.38	11.52	-4.56	-5.96	-0.13	0.20	11.47	-5.82
HNO <sub>3</sub>	11.62	10.46	-5.02	-5.80	1.16	0.57	12.76	-6.19
CH <sub>3</sub> NO <sub>2</sub>	11.06	10.68	-4.08	-5.79	0.38	0.45	11.64	-5.72
PF <sub>3</sub>	12.18	13.4	-4.30	-5.70	-1.22	-1.00	13.42	-5.87
HCN	13.01	16.0	-5.17	-5.70	-2.99	-2.30	14.83	-6.70
BBr <sub>3</sub>	9.56	9.70	-4.22	-5.67	-0.14	0.82	9.74	-5.40
PBr <sub>3</sub>	8.57	8.40	-4.80	-5.60	0.17	1.60	8.82	-5.56
S <sub>2</sub>	7.26	7.70	-5.33	-5.51	-0.44	1.66	6.21	-5.71
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	8.92	8.80	-4.34	-5.50	0.12	1.10	9.16	-5.47
PCl <sub>3</sub>	9.85	9.40	-4.32	-5.50	0.45	0.80	10.62	-5.34
CS <sub>2</sub>	9.74	9.46	-4.07	-5.35	0.28	0.62	10.03	-5.10
CO <sub>2</sub>	13.01	17.6	-5.09	-5.00	-4.59	-3.80	14.68	-6.47
HF	13.93	22.0	-7.35	-5.00	-8.07	-6.00	17.10	-7.80
HCl	11.64	16.0	-5.21	-4.70	-4.36	-3.30	13.38	-6.10
CH <sub>3</sub> CN	11.91	15.0	-4.96	-4.70	-3.09	-2.80	13.59	-6.37
CH <sub>2</sub> O	10.33	12.4	-4.13	-4.70	-2.07	-1.50	11.58	-5.13
HCO <sub>2</sub> CH <sub>3</sub>	10.34	12.8	-3.88	-4.60	-2.46	-1.80	11.73	-5.22
C <sub>2</sub> H <sub>4</sub>	10.18	12.4	-3.68	-4.40	-2.22	-1.80	11.49	-4.85
C <sub>5</sub> H <sub>5</sub> N	9.04	10.0	-3.31	-4.40	-0.96	-0.60	10.13	-4.52
H <sub>2</sub> S	9.69	12.4	-4.13	-4.20	-2.71	-2.10	11.00	-4.92
C <sub>2</sub> H <sub>2</sub>	10.71	14.0	-3.88	-4.40	-3.29	-2.60	12.18	-5.31
HCONH <sub>2</sub>	9.74	12.4	-3.94	-4.20	-2.66	-2.00	10.89	-4.93
PH <sub>3</sub>	9.75	12.0	-4.15	-4.10	-2.25	-1.90	11.22	-4.95
C <sub>6</sub> H <sub>6</sub>	8.75	10.6	-3.27	-4.10	-1.85	-1.20	9.88	-4.34
C <sub>6</sub> H <sub>5</sub> OH	8.10	9.60	-3.01	-3.80	-1.50	-1.00	9.02	-4.02
C <sub>6</sub> H <sub>5</sub> SH	7.70	9.20	-3.06	-3.80	-1.50	-0.80	8.66	-3.90
CH <sub>3</sub> Cl	10.51	15.0	-4.29	-3.80	-4.49	-3.70	11.94	-5.38
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	7.49	8.80	-2.83	-3.30	-1.31	-1.10	8.34	-3.67
CH <sub>3</sub> F	12.06	18.8	-4.78	-3.20	-6.73	-6.20	13.81	-6.21
H <sub>2</sub> O	12.03	19.0	-4.82	-3.10	-6.97	-6.40	13.49	-6.03
NH <sub>3</sub>	10.34	16.4	-4.08	-2.60	-6.06	-5.60	11.60	-5.07
CH <sub>4</sub>	12.94	20.6	-5.07	-2.50	-7.66	-7.80	14.93	-6.71
C(CH <sub>3</sub> ) <sub>4</sub>	10.06	16.6	-3.93	-2.20	-6.54	-6.10	11.53	-5.20
O(CH <sub>3</sub> ) <sub>2</sub>	9.41	16.0	-3.57	-2.00	-6.59	-6.00	10.65	-4.66
N(CH <sub>3</sub> ) <sub>3</sub>	7.92	12.6	-3.11	-1.50	-4.68	-4.80	8.96	-3.88
CH <sub>3</sub> OH	10.19	17.0	-4.06	-2.34	-6.81	-6.16	11.57	-5.16
LiH	7.25	8.16 <sup>b</sup>	-3.37	-4.12	-0.91	0.34	7.87	-4.35
LiCl	8.63	9.50 <sup>b</sup>	-4.11	-5.30	-0.87	0.59	9.46	-5.41
LiBr	8.32	8.66	-3.84	-4.99	-0.34	0.66	8.82	-5.14
CCl <sub>4</sub>	10.08	11.2	-4.90	-5.90	-1.12	0.30	10.91	-5.81
LiF	10.42	11.74 <sup>b</sup>	-4.49		-1.32		11.74	-6.36
SiH <sub>4</sub>	11.74	13.6 <sup>b</sup>	-4.56		-1.86		13.51	-5.89
CH <sub>3</sub> OCH <sub>3</sub>	9.40	16.0 <sup>c</sup>	-3.57		-6.60		10.65	-4.67
CH <sub>3</sub> NH <sub>2</sub>	9.04	14.4 <sup>c</sup>	-3.61		-5.36		10.26	-4.47
CH <sub>3</sub> SCH <sub>3</sub>	8.48	12.0 <sup>b</sup>	-2.99		-3.52		9.50	-3.95
HBr	10.85	13.66 <sup>d</sup>	-4.66				12.37	-5.63
SiF <sub>3</sub> H	13.68	12.14 <sup>d</sup>	-4.52				15.47	-6.59
CH <sub>2</sub> F <sub>2</sub>	12.13	15.68 <sup>d</sup>	-4.87				13.84	-6.23
CH <sub>2</sub> (OH) <sub>2</sub>	10.28	15.16 <sup>d</sup>	-4.08				11.69	-5.23
CF <sub>4</sub>	14.94	18.04 <sup>d</sup>	-5.19				17.09	-7.09
SiF <sub>4</sub>	14.31	13.62 <sup>d</sup>	-5.54				16.12	-7.51

Table 2. continued

molecules	$\eta_s$	$\eta_{\text{exp}}^a$	$\mu_s$	$\mu_{\text{exp}}^a$	$\Delta\eta_s$	$A_{\text{exp}}^a$	$I - A$	$(I - A)/2$
CF <sub>3</sub> H	13.43	15.84 <sup>d</sup>	−5.32				15.37	−6.87
SiH <sub>3</sub> F	11.91	11.92 <sup>d</sup>	−4.40				13.43	−5.89
FCH <sub>2</sub> OH	11.23	15.10 <sup>d</sup>	−4.42				12.71	−5.77
HOCH <sub>2</sub> NH <sub>2</sub>	9.28	14.16 <sup>d</sup>	−3.74				10.51	−4.68
CH <sub>2</sub> (NH <sub>2</sub> ) <sub>2</sub>	8.70	12.94 <sup>d</sup>	−3.53				9.86	−4.37
FCH <sub>2</sub> NH <sub>2</sub>	9.78	13.98 <sup>d</sup>	−4.14				11.03	−5.11
SiF <sub>2</sub> H <sub>2</sub>	12.40	11.42 <sup>d</sup>	−4.19				13.86	−5.92
CF <sub>2</sub> Cl <sub>2</sub>	11.38	11.14 <sup>d</sup>	−4.45				12.55	−5.69
C(OCH <sub>3</sub> ) <sub>4</sub>	8.85	13.56 <sup>d</sup>	−3.38				10.08	−4.54
CF <sub>3</sub> Cl	12.54	12.54 <sup>d</sup>	−4.51				14.14	−5.97
CH <sub>3</sub> CH <sub>3</sub>	11.42	16.46 <sup>d</sup>	−4.27				13.02	−5.76
Si(OCH <sub>3</sub> ) <sub>4</sub>	8.96	9.92 <sup>d</sup>	−3.32				10.23	−4.57
HOI	12.13	15.64 <sup>d</sup>	−5.40				13.53	−6.37
CH <sub>3</sub> SH	8.95	11.84 <sup>d</sup>	−3.53				10.03	−4.43

<sup>a</sup>From ref 81, except the ones which indicated. <sup>b</sup>From ref 84. <sup>c</sup>From ref 85. <sup>d</sup>These values are calculated hardness from refs 84 and 85.

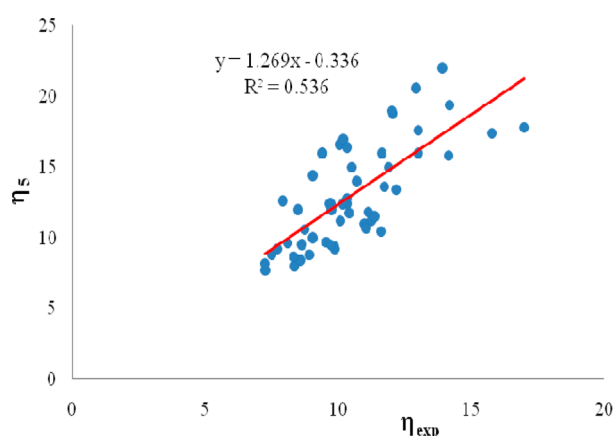


Figure 3. Calculated molecular hardnesses using five-point curve fitting vs experimental values for selected molecules.

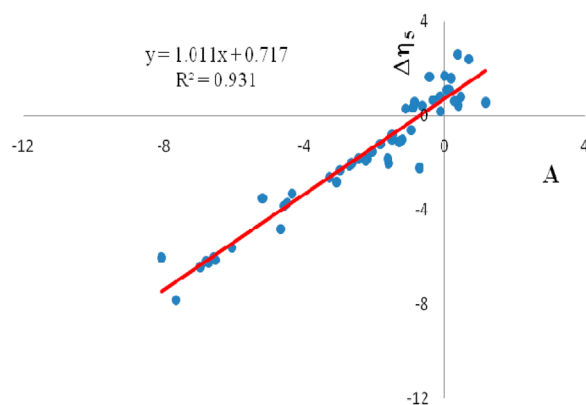


Figure 4. Correlation between hardness differences  $\Delta\eta_s$  and the electron affinities for the selected molecules.

$$\left[ \frac{\partial^2 E}{\partial N^2} \right]_{v(r)} = \eta = 2\alpha\beta^2 e^{-\beta(N_0-\delta)} \{ 2e^{-\beta(N_0-\delta)} - 1 \} \quad (10)$$

where  $N_0$  is the number of electrons in the proposed system. Therefore, by evaluating the adjustable parameters for a given chemical species using fitting procedure,  $\mu$  and  $\eta$  values can be easily calculated for this system from these equations. The proposed method could be performed for both atomic and molecular systems in neutral or ionic forms.

Different set of points (included  $M^{3+}-M^{3-}$ ,  $M^{2+}-M^{2-}$ ,  $M^+-M^-$ ,  $M$ , etc.) are considered to find the adjustable parameters of an atom. It is found that the less standard deviation and best regression are obtained when the least cationic forms ( $M^+-M^{3-}$ ) are considered in fitting procedure. This may be due to this fact that the Morse potential function nearly properly describes the attractive part of the curve, but is not so successful in predicting the repulsive part of the potential curve. Therefore, to find the adjustable parameters in an atomic case, the energies of neutral and five different ionic forms ( $M^+$ ,  $M$ ,  $M^-$ ,  $M^{2-}$ , and  $M^{3-}$ ) of a given atom are calculated using the hybrid B3LYP functional<sup>76-78</sup> and 6-311++G\*\* basis set using the Gaussian 98W program.<sup>79</sup> It should be mentioned that the considered multiplicity for each atom in neutral or ionic forms are in accordance with the Pauli exclusion principle. The obtained  $E(N)$  curves are then fitted to the Morse-like function using a mathematical software to find the adjustable parameters. This method is applied to the first three row elements of the periodic table, except for noble gases. One of these fitting curves (for C atom) is brought as an example in the Supporting Information (Figure S1). The obtained values for the adjustable parameters are given in Table S1 of the Supporting Information; and the calculated atomic chemical potential and hardness values atoms from eqs 9 and 10 are collected in Table 1. The experimental hardnesses ( $\eta_{\text{exp}}$ ) and chemical potentials ( $\mu_{\text{exp}}$ ) for these atoms, which are computed from the reported ionization energy and electron affinity values<sup>80</sup> by using eq 4, are also gathered in this table for comparison. Note that two kinds of calculated chemical potentials and hardnesses are reported in this table: those values calculated using a three-points curve ( $M^+$ ,  $M$ , and  $M^-$ ) and denoted as  $\mu_3$  and  $\eta_3$ ; and those values which are evaluated from a five-points curve ( $M^+$ ,  $M$ ,  $M^-$ ,  $M^{2-}$ , and  $M^{3-}$ ) and shown by  $\mu_s$  and  $\eta_s$ . It is clear that, although  $\eta_3$  and  $\eta_{\text{exp}}$  values are nearly the same (see Figure 1), there is a significant difference between the calculated hardness from the five-point curve fitting ( $\eta_s$ ) and the corresponding experimental value for each atom (mean absolute deviation is 0.496). Figure 2 shows that there is no a good linear correlation between the obtained  $\eta_s$  and experimental values ( $R^2 = 0.916$ ). The closeness of  $\eta_3$  and  $\eta_{\text{exp}}$  values may arise from this fact that considering a three-point curve fitting for calculating the hardness values is similar to using a probable model (finite difference approximation). Surprisingly, the most deviations of  $\eta_s$  from  $\eta_{\text{exp}}$  are observed for those elements which have the



Table 3. Evaluated Hardness of Reactions Using Calculated and Experimental Hardness Values (in electronvolts) and  $\Delta H^\circ$  Values (in kcal/mol) for the Selected Reactions<sup>a</sup>

	reaction	$\Delta\eta_{\text{exp}}$	$\Delta\eta_{\text{calc}}$	$\Delta H^\circ$
(1)	$2\text{CH}_3\text{OH} \rightarrow \text{CH}_4 + \text{CH}_2(\text{OH})_2$	1.76	2.85	$-15^b$
(2)	$\text{CH}_3\text{NH}_2 + \text{CH}_3\text{OH} \rightarrow \text{CH}_4 + \text{HOCH}_2\text{NH}_2$	3.36	2.99	$-12.7^c$
(3)	$2\text{CH}_3\text{NH}_2 \rightarrow \text{CH}_4 + \text{CH}_2(\text{NH})_2$	4.74	3.57	$-10.6^c$
(4)	$\text{CH}_3\text{NH}_2 + \text{CH}_3\text{F} \rightarrow \text{CH}_4 + \text{FCH}_2\text{NH}_2$	1.38	1.62	$-17.6^c$
(5)	$2\text{SiH}_3\text{F} \rightarrow \text{SiH}_2\text{F}_2 + \text{SiH}_4$	1.18	0.31	$-8^b$
(6)	$2\text{CF}_2\text{Cl}_2 \rightarrow \text{CF}_4 + \text{CCl}_4$	6.96	2.25	$-16.3^b$
(7)	$3\text{CH}_3\text{F} \rightarrow 2\text{CH}_4 + \text{CHF}_3$	0.64	3.12	$-31.4^b$
(8)	$4\text{CHF}_3 \rightarrow \text{CH}_4 + 3\text{CF}_4$	11.36	4.02	$-22.9^b$
(9)	$4\text{CH}_3\text{F} \rightarrow 3\text{CH}_4 + \text{CF}_4$	4.64	5.50	$-63^b$
(10)	$4\text{CH}_3\text{Cl} \rightarrow 3\text{CH}_4 + \text{CCl}_4$	13	6.85	$-6^b$
(11)	$4\text{CH}_3\text{OCH}_3 \rightarrow 3\text{CH}_4 + \text{C}(\text{OCH}_3)_4$	11.36	10.07	$-52^b$
(12)	$4\text{CF}_3\text{Cl} \rightarrow 3\text{CF}_4 + \text{CCl}_4$	15.16	4.75	$-27.1^b$
(13)	$4\text{CH}_3\text{CH}_3 \rightarrow 3\text{CH}_4 + \text{C}(\text{CH}_3)_4$	12.56	3.22	$-13^b$
(14)	$4\text{SiH}_3\text{F} \rightarrow 3\text{SiH}_4 + \text{SiF}_4$	6.74	1.88	$-23^b$
(15)	$\text{C}(\text{OCH}_3)_4 + \text{SiH}_4 \rightarrow \text{CH}_4 + \text{Si}(\text{OCH}_3)_4$	3.36	1.30	$144^b$
(16)	$\text{HCl} + \text{LiH} \rightarrow \text{LiCl} + \text{H}_2$	2.74	5.53	$-56.1^d$
(17)	$\text{HOF} + \text{LiH} \rightarrow \text{LiF} + \text{H}_2\text{O}$	6.94	3.07	$-144.1^d$
(18)	$\text{CH}_3\text{F} + \text{CH}_3\text{SH} \rightarrow \text{CH}_3\text{SCH}_3 + \text{HF}$	3.36	1.40	$-12.9^d$
(19)	$\text{LiF} + \text{HBr} \rightarrow \text{LiBr} + \text{HF}$	5.26	0.99	$-10.8^d$
(20)	$2\text{CH}_3\text{F} \rightarrow \text{CH}_4 + \text{CH}_2\text{F}_2$	<b>-1.32</b>	0.94	$-14^b$
(21)	$\text{LiH} + \text{HF} \rightarrow \text{LiF} + \text{H}_2$	<b>-1.02</b>	5.03	$-49.0^d$
(22)	$\text{HF} + \text{SiH}_4 \rightarrow \text{SiH}_3\text{F} + \text{H}_2$	<b>-6.28</b>	2.03	$-26.2^d$
(23)	$\text{CH}_3\text{F} + \text{CH}_3\text{OH} \rightarrow \text{CH}_4 + \text{FCH}_2\text{OH}$	<b>-0.1</b>	1.92	$-16.2^c$
(24)	$\text{SiF}_3\text{H} + \text{CF}_4 \rightarrow \text{SiF}_4 + \text{CF}_3\text{H}$	<b>-0.72</b>	<b>-0.88</b>	$-37^b$

<sup>a</sup>The obtained  $\Delta\eta$ 's are bolded for those cases in which the MHP failed. <sup>b</sup>Reference 85. <sup>c</sup>Reference 87. <sup>d</sup>Reference 84.

half or full closed-shell electronic structures, i.e., the elements of IIA, IIB and VA groups. It is recalled that for these elements the second ionization energies ( $I_2$ ) have significant differences with  $2I_1$  values and therefore the finite difference approximation is not a proper assumption for computing the hardnesses of these atoms. Hence, although the experimental values of electron affinities and ionization potentials are used in eq 4, this relation is just an approximation for hardness and cannot give the accurate value for this quantity. Therefore, it is claimed that the reported *experimental* hardnesses ( $\eta_{\text{exp}}$ ) are not *accurate* and the observed differences between the hardnesses obtained from eq 10 and  $\eta_{\text{exp}}$  may arise from this problem.

The calculated values from the proposed method for some atoms are compared with those obtained from the method of energy expansion which is introduced by Liu and Parr.<sup>56</sup> In this approach, the total energy of an atomic system is expanded in terms of its chemical potential, hardness and response function up to the second order. Expansions are given within the four basic canonical ( $\eta_C$ ), grand canonical ( $\eta_{GC}$ ), isomorphic ( $\eta_I$ ), and grand isomorphic ( $\eta_{GI}$ ) ensembles. The reported hardnesses from these ensembles are gathered in Table 1. It is clear that the hardnesses obtained using canonical ensemble ( $\eta_C$ ) show a better agreement with the experimental data (mean absolute deviation is 1.822 for 15 atoms). It also appears that the calculated hardness values in the present work ( $\eta_s$ ) have the least mean absolute deviation (0.443 for 15 atoms)

than the other considered methods. The linearity between each set of evaluated hardnesses and the  $\eta_{\text{exp}}$  is also examined, and the obtained regression coefficients are given in Table 1. A comparison between the obtained  $R^2$  values indicates that the reported values from the introduced method show a better correlation with the experimental hardnesses.

To check the ability of the proposed method in predicting better values for the hardnesses of molecular systems, the same procedure is applied to some simple molecular species (see Table 2). The molecules are chosen so that both closed and open shell electronic structures are included in this series. The geometries of the considered molecules are optimized using the same level of theory which is used for the atomic systems; i.e. B3LYP/6-311++G\*\*. The frequency values are also calculated mainly to check the number of imaginary frequencies. The energies of ionic states for each molecule are calculated at the same optimized geometry of the neutral molecule to ensure that no change in the external potential is occurred during the variation of the number of electrons. Then the chemical potential and hardness values are evaluated using eqs 9 and 10, respectively. The obtained adjustable parameters are gathered in Table S2 of Supporting Information and the calculated values for  $\eta_s$  and  $\mu_s$  are shown in Table 2. The difference between the calculated and experimental hardnesses ( $\Delta\eta_s$ ) together with the corresponding experimental electron affinity for each molecule<sup>81</sup> is also given in this table. Comparison

between the experimental hardnesses and calculated values shows that in most cases the calculated values are to some extent lower than the experimental ones. This may be due to the presence of extra negative terms in the electronic energy expansion, which are neglected in eq 4 for the evaluating of experimental hardnesses but are considered in eq 10. Figure 3 shows that there is no a good correlation between the calculated and experimental hardnesses ( $R^2 = 0.536$ ); and these differences are more considerable for the molecules than the atoms (compare Figure 2 with Figure 3).

Surprisingly, there is a satisfactory linear relation with a positive slope between the obtained  $\Delta\eta_5$  and the corresponding electron affinities for the selected molecules (see Figure 4). It seems that the experimental hardnesses of molecules with large electron affinities show considerable differences with the calculated ones. This implies the fact that eqs 3 and 4 are not reliable for calculating the chemical potential and hardness values in systems with large negative electron affinities.<sup>82,83</sup> It is worth mentioning that  $\Delta\eta_5$  values could be used for predicting the electron affinities of different molecular systems, which nowadays is a challenging task in DFT.

To check the reliability of the proposed method and the accuracy of the obtained  $\eta_5$ , we attempted to test the validity of the maximum hardness principle (MHP) in some selected hypothetical reactions<sup>84–86</sup> using both the calculated and experimental hardness values for the reactants and products of these reactions. The considered reactions are shown in Table 3, and the obtained values for the changes in the calculated and experimental hardnesses during each reaction ( $\Delta\eta_{\text{calc}}$  and  $\Delta\eta_{\text{exp}}$ ) are also gathered in Table 3.  $\Delta\eta$  for each reaction, called the hardness of reaction, is defined as the difference between the hardnesses of products and reactants of the reaction ( $\Delta\eta_{\text{calc}} = (\sum_P(\eta_{\text{calc}}^P) - \sum_R(\eta_{\text{calc}}^R))$  and  $\Delta\eta_{\text{exp}} = (\sum_P(\eta_{\text{exp}}^P) - \sum_R(\eta_{\text{exp}}^R))$ ). Note that all of the selected reactions are exothermic and therefore the products of these reactions should be thermodynamically more stable than the reactants. Hence according to the MHP, a positive sign for  $\Delta\eta$  is expected for all of these reactions. Table 3 shows that, if the experimental hardnesses are used for the calculation of  $\Delta\eta_{\text{exp}}$ , there are at least five cases (reactions 20–24) in which MHP has failed. But when the values obtained from the proposed method are used to calculate the hardness of reactions ( $\Delta\eta_{\text{calc}}$ ), nearly in all cases (with one exception, reaction 24) the MHP successfully predicts the directions of these reactions. Therefore, it seems that the reported values for the hardnesses from the introduced method are more accurate and reliable than those that are obtained from eq 4 and using the experimental  $I$  and  $A$ .

## CONCLUSION

It is claimed that none of the previously reported experimental hardnesses and chemical potentials are accurate, and it may be due to this fact that these values are evaluated using approximate formulas for these concepts. It is shown that, using a Morse-like function for  $E(N)$ , it is possible to calculate the hardness and chemical potential more accurately for a given chemical system. The obtained hardness from five-point curve fitting ( $\eta_5$ ) using this procedure shows more deviation from the experimental values for the systems with considerable negative electron affinities. Therefore, these values are more accurate than those hardnesses which are evaluated from three-point curve fittings ( $\eta_3$ ). The accuracy of the obtained values is checked in some reactions through the maximum hardness principle.

## ASSOCIATED CONTENT

### Supporting Information

Calculated adjustable parameters for the considered atoms and molecules together with the  $E(N)$  five-point curve for carbon atom as an example. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*Email: noorizadeh\_s@scu.ac.ir.

### Notes

The authors declare no competing financial interest.

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#### ■ NOTE ADDED IN PROOF

While this paper was in review, the nonparabolic and nonpower series models for  $E$  versus  $N$  were extended by Carlos Cardenas and Patricio Fuentealba in an accepted paper (in *J. Mol. Model.*).