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# Calculation of Ionization Potential and Chemical Hardness: A Comparative Study of Different Methods

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**ABSTRACT:** The suitability of ab initio and density functional theory (DFT) methods for an accurate determination of ionization potential and chemical hardness is the subject of systematic analysis for a panel of molecules. Comparison of experimental ionization potential values with theoretical results indicates that using orbital energies obtained from the so-called statistical average of orbital potential (SAOP) model exchange correlation potential in Koopman's theorem is an efficient method to evaluate the correct ionization potentials. Experimental ionization potential and electron affinity values have been used to calculate the absolute chemical hardness. Comparative results show that the chemical hardness values calculated by using Hartree–Fock orbital energies in Koopman's theorem are sufficiently good rather than Möller–Plesset second order perturbation method and DFT-generalized gradient approximation (GGA) exchange correlation functional orbital energies. A new method given by Tozer et al. (J Phys Chem A 2005, 109, 8923) to calculate the chemical hardness works well with the orbital energies of DFT-GGA functionals together with the ionization potential values calculated from SAOP orbital energies. © 2008 Wiley Periodicals, Inc. *Int J Quantum Chem* 109: 764–771, 2009

**Key words:** electronegativity; ionization potential; chemical hardness; Koopman's theorem; statistical average of orbital potential

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## 1. Introduction

In the last two decades, density functional theory (DFT) has been increasingly employed for the prediction of molecular properties and to provide qualitative explanation for several findings in

many areas of chemistry and biology [1–5]. The success of DFT relies on its better accuracy achieved at a relatively low computational cost and due to the formulation of reactivity parameters such as Fukui function [6], chemical hardness [7–10], electronegativity [11–13], softness [14], etc. The concept of electronegativity ( $\chi$ ) was introduced by Pauling [15] as the power of an atom in a molecule to attract an electron toward it, and then the elec-

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tronegativity equalization principle was introduced by Sanderson [16]. This property was shown by Parr and Pearson [7–9] to be the negative of the Lagrange multiplier known as the chemical potential ( $\mu$ ). The chemical hardness ( $\eta$ ) is an important quantity in chemical reactivity theory and it was first put forward by Pearson [17], which is a measure of the resistance of a chemical species to change its electronic configuration. The electronegativity ( $\chi$ ) and chemical hardness ( $\eta$ ) are, respectively, defined as the first and second order derivatives of energy ( $E$ ) with respect to the number of electrons ( $N$ ) at constant external potential ( $v(r)$ ),

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)}, \quad \eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \quad (1)$$

Early applications of chemical hardness in DFT were on the basis of hard and soft acids and bases principle [15, 18–20] and the maximum hardness principle [21–26]. The relationship between chemical hardness and several physical quantities has been established and highlighted in the literature [27–29].

The practical method used to calculate chemical hardness ( $\eta$ ) and electronegativity ( $\chi$ ) was given by Parr and Pearson [7, 30] by taking the finite difference approximation for the curvature of  $E$  and  $N$  curves as

$$\eta = \frac{I - A}{2}, \quad \chi = \frac{I + A}{2} \quad (2)$$

where the ionization potential ( $I$ ) and the electron affinity ( $A$ ) are calculated through various techniques in experimental and theoretical methods. Initially, experimental ionization potential and electron affinity values have been used to calculate the absolute chemical hardness and electronegativity [31]. A familiar theoretical method to calculate the ionization potential ( $I$ ) and electron affinity ( $A$ ) is through total energies of neutral ( $E_N$ ) and ionic systems ( $E_{N+1}$ ,  $E_{N-1}$ ) of the optimized molecular configuration, i.e.,

$$I = E_{N-1} - E_N \quad (3)$$

$$A = E_N - E_{N+1}$$

In general, the above total energy based vertical method provides comparatively better results. But

the major drawback is its computation cost and possible errors in total energy values due to the approximations used in the theoretical models. Both ionization potential and electron affinity are known to be largely influenced by the incorporation of electron correlation in the calculation method and requires the use of relatively larger basis set [32].

The Koopman's theorem provides an alternate method to calculate the ionization potential ( $I$ ) and electron affinity ( $A$ ) through orbital energies of optimized neutral molecules. According to this theorem, the negative of the highest occupied molecular orbital energy ( $-E_{\text{HOMO}}$ ) and the lowest unoccupied molecular orbital energy ( $-E_{\text{LUMO}}$ ) corresponds to ionization potential and electron affinity, respectively (i.e.,  $I = -E_{\text{HOMO}}$  and  $A = -E_{\text{LUMO}}$ ). Using Koopman's theorem in Eq. (2), the chemical hardness and electronegativity are defined in terms of orbital energies:

$$\eta = \left(\frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2}\right), \quad \chi = -\frac{E_{\text{LUMO}} + E_{\text{HOMO}}}{2} \quad (4)$$

That is, the energy gap between HOMO and LUMO is equal to  $2\eta$  and  $-\chi$  is half-way between the HOMO and LUMO. Note that the Koopman's theorem assumes that the spin orbitals in the ( $N \pm 1$ ) electron states are identical with those of the  $N$ -electron state. That is, this method neglects relaxation of the spin orbitals in the ( $N \pm 1$ ) electron states which tend to produce too positive ionization potential and too negative electron affinity. However, previous studies show that the chemical hardness calculated through Koopman's approximation with orbital energies obtained from Hartree-Fock (HF) method provides sufficiently good results [33–35]. This is due to the fact that the omission of electron correlation in HF method tends to cancel the aforementioned relaxation error for ionization potential, but not for electron affinity [36]. Hence, the calculation of electron affinity is considerably more difficult than the ionization potential through Koopman's theorem [36]. When going beyond the HF method [such as Möller-Plesset second order perturbation (MP2), DFT methods] we have to be careful while using orbital energies to calculate chemical hardness, since the orbital energies are strongly dependent on the basis set and exchange correlation potential used in DFT calculations. The features and failure of Koopman's theorem are well documented in Ref. [37].

Another new method to calculate chemical hardness is based on the model proposed by Tozer and De Proft [38]. The advantage of this method is that the orbital energies obtained from DFT methods are used to calculate the chemical hardness. To use DFT-generalized gradient approximation (GGA) exchange correlation functional (such as BP, BLYP) orbital energies ( $\epsilon_{\text{LUMO}}$ ,  $\epsilon_{\text{HOMO}}$ ), Koopman's theorem requires a simple correction,

$$\eta = \frac{\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}}}{2} + I \quad (5)$$

$$\eta = -\chi + I \quad (6)$$

That is, the chemical hardness can be calculated as the difference between the exact ionization potential and the electronegativity calculated from DFT-GGA orbital energies. In this method, while calculating the chemical hardness through orbital energies of DFT-GGA functionals, the error due to the absence of asymptotic effect is cancelled. This is due to the opposite shifting of HOMO and LUMO eigenvalues from the exact values when using local exchange correlation functionals such as GGA [38]. Note that the above method requires correct ionization potential and does not depend on affinity to calculate chemical hardness. Hence, this method appears to be an attractive alternative method to compute the chemical hardness of a system with a negative LUMO eigenvalues. In this article we will compare and analyze the performance of different methods in the calculation of ionization potential and chemical hardness.

## 2. Computational Details

The ab initio calculations were performed using Gaussian 03W [39] and the DFT calculations were carried out using Amsterdam density functional theory program [40]. The geometries of the selected molecules have been optimized at HF and MP2 methods using 6-311G\* basis set. The DFT calculations have been performed with two different exchange correlation potential functionals. In the GGA type, Becke's exchange functional [41] have been used together with the correlation part of Perdew and Lee et al. [42, 43], denoted as BP and BLYP, respectively. The asymptotically corrected model exchange correlation potential, i.e., statistical average of orbital potential (SAOP), [44] has also

been used to calculate the ionization potential and chemical hardness values. It has been shown earlier that the negative of HOMO energy ( $-E_{\text{HOMO}}$ ) obtained through SAOP is equal to the vertical ionization potential for different types of molecules [44–46]. The DFT calculations have been performed with an atomic basis set of Slater-type orbitals of triple-Zeta quality including one set of polarization functions on each atom, denoted as TZP [47]. Restricted single point energy calculations have been performed for the cationic and anionic systems.

## 3. Results and Discussion

### 3.1. IONIZATION POTENTIAL

The geometry of the selected closed shell molecules (HF, N<sub>2</sub>, F<sub>2</sub>, CO, CH<sub>4</sub>, HCl, H<sub>2</sub>O, SO<sub>2</sub>, Cl<sub>2</sub>, CCl<sub>4</sub>, CH<sub>3</sub>Cl, CH<sub>2</sub>O, and CH<sub>3</sub>CHO) have been optimized at HF, MP2 of ab initio and BP, BLYP, SAOP of DFT methods using 6-311G\* and TZP basis sets, respectively. To calculate the chemical hardness using Eq. (6), the correct ionization potential is required. In this study the ionization potentials have been calculated using various methods discussed in Section 1. In Table I the calculated ionization potential values are summarized along with the experimental values taken from Refs. [38, 48, 49]. The ionization potential calculated through Koopman's theorem at HF and MP2 methods (denoted as  $I_{\text{HF(K)}}$  and  $I_{\text{MP2(K)}}$ ) are compared with the experimental values and the mean absolute error is found to be 1.2 eV. It has been observed that the vertical ionization potential calculated from the total energies (denoted as  $I_{\text{HF(V)}}$  and  $I_{\text{MP2(V)}}$  in Table I) using Eq. (3) has significantly improved from the Koopman's procedure and the mean absolute error is found to be 0.76 and 0.54 eV at HF and MP2 levels, respectively. As expected, the ionization potential calculated through orbital energies of DFT methods (using Koopman's theorem) with GGA exchange correlation functionals such as BP and BLYP has deviated much from the experimental values and the mean absolute error is found to be nearly 4.7 eV.

The vertical ionization potential calculated from the total energies obtained with GGA functionals (denoted as  $I_{\text{BP(V)}}$  and  $I_{\text{BLYP(V)}}$  in Table I) is found to agree reasonably well with the experimental values and the mean absolute error is 0.70 and 0.63 eV for BP and BLYP functionals, respectively. The ionization potential calculated from total energies of the

TABLE I

The ionization potential (in eV) calculated from different techniques of ab initio and DFT methods along with the experimental ionization potential ( $I_{\text{Expt}}$ ) values taken from Refs. [38, 48, 49].

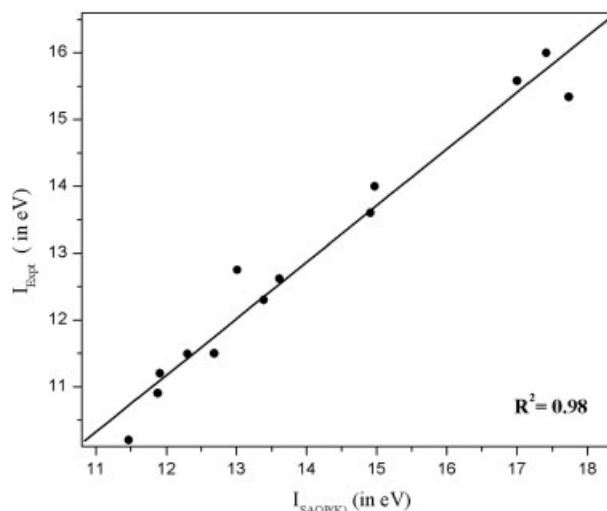
Molecules	$I_{\text{Expt}}$	$I_{\text{HF(V)}}$	$I_{\text{MP2(V)}}$	$I_{\text{BP(V)}}$	$I_{\text{BLYP(V)}}$	$I_{\text{SAOP(V)}}$	$I_{\text{HF(K)}}$	$I_{\text{MP2(K)}}$	$I_{\text{SAOP(K)}}$
HF	16.00	14.44	15.72	17.23	17.09	17.04	17.41	17.36	16.30
N <sub>2</sub>	15.58	16.03	14.76	16.03	15.87	16.30	17.00	16.41	15.50
F <sub>2</sub>	15.34	16.23	14.73	15.96	15.89	15.12	17.73	18.20	14.98
CO	14.00	13.32	13.62	14.88	14.72	14.61	14.97	15.08	13.20
CH <sub>4</sub>	13.6	13.74	14.14	14.82	12.92	14.38	14.91	14.86	14.10
HCl	12.75	11.74	12.29	13.20	14.64	13.38	13.01	13.01	12.58
H <sub>2</sub> O	12.62	13.14	14.26	13.83	13.64	14.58	13.61	13.59	13.02
SO <sub>2</sub>	12.3	12.47	11.47	12.58	12.39	12.25	13.39	13.46	12.32
Cl <sub>2</sub>	11.49	11.59	11.27	11.55	11.35	11.38	12.30	12.37	11.59
CCl <sub>4</sub>	11.5	11.87	11.48	11.01	11.41	10.55	12.68	12.69	11.71
CH <sub>3</sub> Cl	11.2	10.51	11.12	11.61	11.36	11.62	11.91	11.90	11.27
CH <sub>2</sub> O	10.9	9.67	10.93	11.42	11.77	10.97	11.88	11.98	10.51
CH <sub>3</sub> CHO	10.2	9.08	10.35	10.61	11.27	10.18	11.47	11.56	9.91
$ d $		0.756	0.535	0.702	0.631	0.721	1.207	1.222	0.430
$d$		-0.212	-0.034	0.627	0.595	0.445	1.207	1.222	0.108
$m$		0.805	0.985	0.850	0.875	0.872	0.848	0.841	0.960
$c$ (eV)		2.738	0.296	1.455	1.152	2.253	0.998	1.078	0.549
$R^2$		0.935	0.939	0.962	0.943	0.956	0.984	0.967	0.982

$|d|$  and  $d$  denote the mean absolute error and mean error (in eV), respectively, relative to experimental data.  $m$ ,  $c$ , and  $R^2$  denote the gradient, the intercept, and the correlation parameters, respectively, of the correlation plots, relative to experimental data.

neutral and cationic systems at SAOP method is slightly deviated from the experimental values and the corresponding mean absolute error is found to be 0.72 eV. It has been shown earlier that the accurate values of ionization potential, electron affinity, electronegativity, and chemical hardness were calculated using DFT methods with very large basis sets such as 6-311++G (3df, 2p), cc-pVTZ, and aug-cc-pVTZ [50], and the mean absolute deviation is  $\sim 0.15$ – $0.2$  eV. Recently, Chong et al. [44] have calculated the ionization potential for different types of molecules using orbital energies through Koopman's theorem ( $I = -E_{\text{HOMO}}$ ) with model potential SAOP as the exchange correlation functional and obtained the mean absolute error of 0.4 eV. In this study, the ionization potential calculated from the orbital energies of SAOP functional (denoted as  $I_{\text{SAOP(K)}}$  in Table I) is found to agree well with the experimental values and the mean error is found to be 0.43 eV. This improvement is due to the inclusion of asymptotic effect in the exchange correlation potential. A better linear correlation has been found between the calculated ionization potentials  $I_{\text{SAOP(K)}}$  and experimental values with the correlation coefficient of 0.98 and is shown in Figure 1.

### 3.2. CHEMICAL HARDNESS

The chemical hardness has been calculated for the selected molecules using different techniques discussed in Section 1 at HF, MP2 of ab initio and



**FIGURE 1.** Linear plot of the calculated ionization potential ( $I_{\text{SAOP(K)}}$ ) using orbital energies of SAOP functional versus experimental ionization potential ( $I_{\text{Expt}}$ ).

TABLE II

The chemical hardness (in eV) calculated by using different techniques of *ab initio* and DFT methods along with the values derived from the experimental ionization potentials and electron affinity values derived from Refs. [38, 48, 49].

Molecules	$\eta_{\text{Expt}}$	$\eta_{\text{HF(V)}}$	$\eta_{\text{BP(V)}}$	$\eta_{\text{BLYP(V)}}$	$\eta_{\text{SAOP(V)}}$	$\eta_{\text{HF(K)}}$	Method I		Method II		Method III	
							$\eta = -\chi$ + $I_{\text{(V)}}$		$\eta = -\chi$ + $I_{\text{SAOP(V)}}$		$\eta = -\chi$ + $I_{\text{SAOP(K)}}$	
							BP	BLYP	BP	BLYP	BP	BLYP
HF	11	9.15	9.42	9.39	9.57	9.69	12.01	11.77	12.71	12.62	11.07	10.99
N <sub>2</sub>	8.9	10.02	9.4	9.41	10.75	9.22	9.87	9.87	10.14	10.30	9.33	9.49
F <sub>2</sub>	7.2	9.3	7.76	7.70	8.79	7.78	7.82	7.78	7.04	7.00	6.85	6.81
CO	7.9	8.43	8.51	8.51	9.15	8.46	9.25	9.25	8.98	9.15	7.57	7.74
CH <sub>4</sub>	10.3	9.03	8.42	7.87	9.43	9.66	10.3	10.12	9.86	9.86	10.58	10.57
HCl	8	7.36	7.29	8.07	7.71	8.16	8.77	8.53	8.86	8.97	8.05	8.14
H <sub>2</sub> O	9.5	8.54	7.67	7.63	8.27	8.85	9.86	9.67	10.64	10.61	9.08	9.06
SO <sub>2</sub>	5.6	6.22	5.98	5.96	6.79	5.77	6.14	6.12	5.80	5.98	5.87	6.05
Cl <sub>2</sub>	5.2	5.7	5.32	5.23	5.55	5.3	5.23	5.35	5.26	5.35	5.47	5.56
CCl <sub>4</sub>	5.6	6.73	5.32	5.53	5.93	6.08	5.85	5.11	4.98	5.11	6.15	6.28
CH <sub>3</sub> Cl	7.5	7.07	6.59	6.53	6.9	7.11	7.43	7.77	7.69	7.77	7.34	7.43
CH <sub>2</sub> O	5.9	6.23	6.37	6.69	6.85	6.65	6.87	7.39	6.42	6.59	5.96	6.12
CH <sub>3</sub> CHO	5.7	6.09	6.18	6.93	6.25	6.48	6.56	7.41	6.14	6.32	5.86	6.04
d		0.913	0.793	0.848	0.928	0.530	0.599	0.678	0.666	0.738	0.262	0.317
<i>d</i>		0.121	−0.313	−0.322	0.316	0.070	0.588	0.603	0.478	0.564	0.068	0.152
<i>m</i>		1.096	1.199	1.154	0.979	1.234	0.927	0.930	0.789	0.804	1.004	1.045
<i>c</i> (eV)		−0.858	−1.129	−0.793	−0.152	−1.856	0.001	−0.033	1.121	1.030	−0.080	−0.501
<i>R</i> <sup>2</sup>		0.826	0.880	0.860	0.844	0.961	0.976	0.945	0.915	0.910	0.988	0.985

|d| and *d* denote the mean absolute error and mean error (in eV), respectively, relative to experimental data. *m*, *c*, and *R*<sup>2</sup> denote the gradient, the intercept, and the correlation parameters, respectively, of the correlation plots, relative to experimental data.

BP, BLYP, SAOP of DFT methods and are summarized in Table II. The ionization potential and electron affinity obtained from the experiments [38, 48, 49] have been used to calculate the chemical hardness and are compared with the present theoretical values. The electron affinity values calculated from the vertical method [Eq. (3)] are summarized along with the experimental values in Table III. The chemical hardness values calculated from the orbital energies of HF method (denoted as  $\eta_{\text{HF(K)}}$  in Table II) are found to agree quite well with the experimental values and the mean absolute error is found to be 0.53 eV. Further, a linear correlation has been plotted between the calculated chemical hardness  $\eta_{\text{HF(K)}}$  with the experimental values  $\eta_{\text{Expt}}$  and is shown in Figure 2. From the linear fit, the correlation coefficient (*R*<sup>2</sup>) is found to be 0.96. The above results again confirm the suitability of Koopman's procedure to calculate chemical hardness with HF orbital energies. The ionization potential and electron affinity calculated from total energies of HF

method have been used to calculate chemical hardness (denoted as  $\eta_{\text{HF(V)}}$  in Table II) and the values fairly agree with the experimental values and the corresponding mean absolute error is 0.91 eV. It is to be noted that the chemical hardness values calculated through the orbital energies of HF method ( $\eta_{\text{HF(K)}}$ ) has low mean absolute error. As discussed in Section 1, while calculating the chemical hardness through Koopman's theorem using orbital energies of HF method, the errors due to the omission of electron correlation and relaxation of spin state orbitals in Koopman's theorem are cancelled. But, in the vertical procedure while calculating the ionization potential and electron affinity at HF level, there is a minimal error in total energies of neutral and ionic states due to the absence of electron correlation.

The orbital energies of electron correlated MP2 method are unable to provide qualitative estimate for the chemical hardness through Koopman's theorem and the mean absolute error is found to be



TABLE III

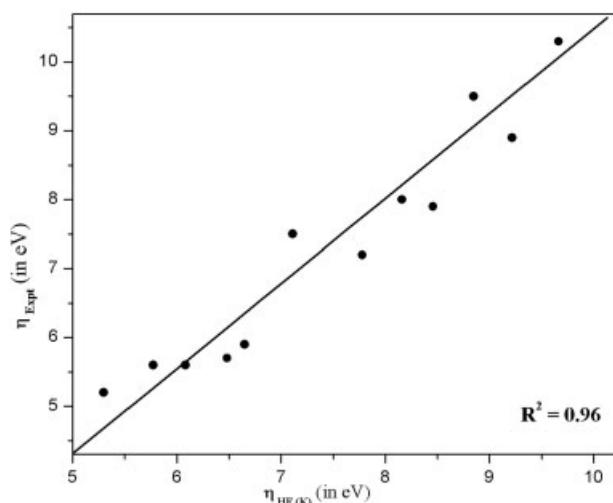
The electron affinity (EA) values (in eV) calculated by using total energies of ab initio and DFT methods (vertical procedure) along with the experimental values taken from Refs. [38, 48, 49].

Molecules	EA <sub>Expt</sub>	EA <sub>HF(V)</sub>	EA <sub>BP(V)</sub>	EA <sub>BLYP(V)</sub>	EA <sub>SAOP(V)</sub>
HF	-6.0	-3.86	-1.61	-1.69	-2.09
N <sub>2</sub>	-2.2	-4.01	-2.77	-2.95	-5.2
F <sub>2</sub>	1.24	-2.37	0.44	0.50	-2.46
CO	-1.8	-3.54	-2.14	-2.3	-3.69
CH <sub>4</sub>	-7.8	-4.32	-2.02	-2.82	-4.48
HCl	-3.3	-2.98	-1.39	-1.51	-2.04
H <sub>2</sub> O	-6.4	-3.94	-1.52	-1.62	-1.96
SO <sub>2</sub>	1.1	0.03	0.62	0.47	-1.33
Cl <sub>2</sub>	1.02	0.19	0.91	0.89	0.28
CCl <sub>4</sub>	0.3	-1.59	0.38	0.35	-1.33
CH <sub>3</sub> Cl	-3.7	-3.63	-1.57	-1.6	-2.17
CH <sub>2</sub> O	-1.5	-2.79	-1.32	-2.10	-2.74
CH <sub>3</sub> CHO	-1.2	-3.1	-1.75	-1.84	-2.31

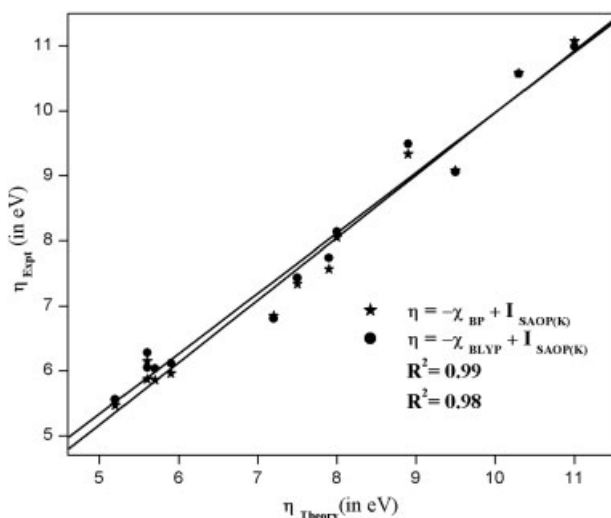
1.24 eV. This error is due to the absence of error cancellation that we have already mentioned for the HF procedure. As expected, the chemical hardness values calculated through orbital energies of DFT functionals BP and BLYP using Koopman's theorem (Eq. 4) are deviated much from the expected values, where the mean absolute error is found to be greater than 5 eV. This large error is due to the presence of negative LUMO eigenvalues, which de-

pend strongly on the basis set, and the DFT orbital energies are also dependent on exchange correlation potential used [38]. Further, the chemical hardness values calculated from the ionization potential and electron affinity obtained from total energies of DFT methods BP, BLYP, and SAOP [using Eqs. (2) and (3) denoted as  $\eta_{BP(V)}$ ,  $\eta_{BLYP(V)}$  and  $\eta_{SAOP(V)}$  in Table II] are closer to the experimental values and the corresponding mean absolute error is found to be 0.79, 0.85, and 0.93 eV, respectively, for the above functionals.

In this study, the chemical hardness values have also been calculated using Eq. (6), where the negative of electronegativity ( $-\chi$ ) obtained from the orbital energies of GGA functionals (BP and BLYP) is added with the ionization potential values obtained through the different techniques discussed above. The calculated chemical hardness values are summarized in Table II. In the first method (Method I in Table II), the ionization potential calculated through the total energies at BP and BLYP functionals is used and it has been observed that the chemical hardness values are closer to the values derived from the experimental ionization potential and electron affinity values. The mean absolute error is found to be 0.59 and 0.67 eV in BP and BLYP functionals, respectively. Note that, even though there is a small error in the ionization potential (see Table I, as  $I_{BP(V)}$  and  $I_{BLYP(V)}$ ) values obtained through total energies of GGA functionals, the results of chemical hardness values are found to be improved over the regular Koopman's



**FIGURE 2.** Linear plot of the calculated chemical hardness ( $\eta_{HF(K)}$ ) using orbital energies of Hartree-Fock of ab initio method versus chemical hardness ( $\eta_{Expt}$ ) calculated from the experimental ionization potential and electron affinity values.



**FIGURE 3.** Linear plot of the calculated chemical hardness ( $\eta_{\text{Theory}}$ ) using Tozer and De Proft model with Method III (see text) versus chemical hardness calculated from the experimental ionization potential and electron affinity values ( $\eta_{\text{Expt}}$ ).

and vertical methods. In the second method (Method II in Table II) the electronegativity values calculated using GGA functionals and the ionization potential obtained from the total energies of SAOP method ( $I_{\text{SAOP(V)}}$ ) have been used in Eq. (6). The results are found to be less accurate in comparison with Method I. The mean absolute error is found to be 0.67 and 0.74 eV in BP and BLYP functionals, respectively.

In the third method (Method III in Table II) the ionization potential obtained from the orbital energies of asymptotically corrected SAOP method (using Koopman's theorem,  $I_{\text{SAOP(K)}}$  in Table I) is used with the electronegativity obtained from the orbital energies of GGA functionals. The tabulated values show that the calculated chemical hardness is found to agree very well with the values derived from the experimental ionization potential and electron affinity values. In this method, the mean absolute error is reduced to 0.26 and 0.32 eV at BP and BLYP functionals, respectively. Further, a linear correlation between chemical hardness calculated from Eq. (6) of Method III and the chemical hardness derived from experimental ionization potential and electron affinity values is shown in Figure 3. The second order linear correlation was obtained with correlation coefficient ( $R^2$ ) closer to unity (0.99). This improvement in the evaluation of chemical hardness values show the suitability of Tozer

and De Proft model [38] to calculate chemical hardness using orbital energies of DFT methods. To check the applicability of Method III to calculate the chemical hardness of large molecules, the calculations have been performed for conjugated compounds such as ethylene, acetylene, pyrrole, and pyridine. It has been found that the results are comparable with the chemical hardness calculated by using Eq. (2) with the MP2 vertical ionization potential and electron affinity.

It is worth to mention here that using the electronegativity evaluated from the orbital energies of SAOP [using Eq. (4)] with the correct ionization potential in Eq. (6) to calculate chemical hardness is not adequate, where the mean absolute error is found to be greater than 3 eV. This discrepancy arises from the calculation of electronegativity with the orbital energies of SAOP method and is due to the absence of above mentioned (in Section 1) error cancellation. These results demonstrate that the chemical hardness can be calculated with good accuracy at an acceptable computational cost using DFT orbital energies.

## 4. Conclusion

The present work provides a comprehensive analysis on different methods used to calculate ionization potential and chemical hardness. The ionization potential and chemical hardness have been calculated for selected molecules using HF, MP2 of ab initio, and BP, BLYP, SAOP of DFT methods. The ionization potential calculated through the total energies of neutral and ionic states are comparable with the experimental values. As expected, the ionization potential calculated through the orbital energies of DFT methods with GGA exchange correlation functionals are deviated much from the experimental values. Notably, the ionization potential obtained through orbital energies of SAOP-DFT method using Koopman's theorem coincides well with the experimental values.

The chemical hardness values calculated using the orbital energies of HF method is closer to the experimental values and the mean error deviation is found to be minimum. This may be due to cancellation of errors that corresponds to omission of electron correlation in HF method and omission of relaxation of spin state orbitals in Koopman's theorem. The chemical hardness calculated through orbital energies of MP2, BP, and BLYP are deviated from the experimental values. The chemical hard-



ness calculated from the ionization potential and electron affinity obtained from vertical methods is found to be comparable with the experimental values. Among the three methods used to calculate the chemical hardness values based on Tozer and De Proft model, using electronegativity calculated from DFT-GGA functionals (BP and BLYP) with ionization potential obtained from SAOP orbital energies agree well with the values derived from experimental ionization potential and electron affinity values. From these results we can conclude that the chemical hardness can be calculated using DFT orbital energies with high accuracy and low computational cost.

## References

- Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
- Dreizler, R. M.; Gross, E. K. U. *Density Functional Theory*; Springer-Verlag: Berlin, 1990.
- Parr, R. G.; Yang, W. *Annu Rev Phys Chem* 1995, 46, 701.
- Kohn, W.; Becke, A. D.; Parr, R. G. *J Phys Chem* 1996, 100, 12974.
- Geerlings, P.; De Proft, F.; Langenaeker, W. *Chem Rev* 2003, 103, 1793.
- Parr, R. G.; Yang, W. *J Am Chem Soc* 1984, 106, 4049.
- Parr, R. G.; Pearson, R. G. *J Am Chem Soc* 1983, 105, 7512.
- Pearson, R. G. *J Am Chem Soc* 1963, 85, 3533.
- Pearson, R. G. *Chemical Hardness*; Wiley: New York, 1997.
- Pearson, R. G. *Coord Chem Rev* 1990, 100, 403.
- Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J Chem Phys* 1978, 68, 3801.
- Iczkowski, R. P.; Margrave, J. L. *J Am Chem Soc* 1961, 83, 3547.
- Sanderson, R. T. *Chemical Bonds and Bond energy*; Academic Press: New York, 1976.
- Yang, W.; Parr, R. G. *Proc Natl Acad Sci USA* 1985, 82, 6723.
- Pauling, L. *The Nature of the Chemical bond*, 3rd ed; Cornell University Press: Ithaca, NY, 1960.
- Sanderson, R. T. *Polar Covalence*; Academic Press: New York, 1983.
- Pearson, R. G. *Hard and Soft Acids and Bases*; Downen, Hutchinson and Ross: Stroudsburg, 1973.
- Chattaraj, P. K.; Lee, H.; Parr, R. G. *J Am Chem Soc* 1991, 113, 1855.
- Berkowitz, M. *J Am Chem Soc* 1987, 109, 4823.
- Li, Y.; Evans, J. N. S. *J Am Chem Soc* 1995, 117, 7756.
- Parr, R. G.; Chattaraj, P. K. *J Am Chem Soc* 1991, 113, 1854.
- Pearson, R. G. *J Chem Educ* 1987, 64, 561.
- Pearson, R. G. *Acc Chem Res* 1993, 26, 250.
- Chattaraj, P. K.; Liu, G. H.; Parr, R. G. *Chem Phys Lett* 1995, 237, 171.
- Sebastian, K. L. *Chem Phys Lett* 1994, 231, 40.
- Chattaraj, P. K.; Cedillo, A.; Parr, R. G. *Chem Phys* 1996, 204, 429.
- Chandrakumar, K. R. S.; Ghanty, T. K.; Ghosh, S. K. *J Phys Chem A* 2004, 108, 6661.
- Vijayakumar, S.; Kolandaivel, P. *J Mol Struct (Theochem)* 2006, 770, 23.
- Gomez, B.; Fuentealba, P.; Contreras, R. *Theor Chem Acc* 2003, 110, 421.
- Pearson, R. G. *J Am Chem Soc* 1988, 110, 7684.
- Zhan, C.-G.; Nichols, J. A.; Dixon, D. A. *J Phys Chem A* 2003, 107, 4184.
- Simons, J.; Jordon, K. *Chem Rev* 1987, 87, 535.
- Kolandaivel, P.; Jayakumar, N. *Int J Quantum Chem* 2000, 76, 648.
- Padmanabhan, J.; Parthasarathi, R.; Subramaniam, V.; Chattaraj, P. K. *J Phys Chem A* 2005, 109, 11043.
- Senthilkumar, K.; Kolandaivel, P. *J Mol Phys* 2002, 100, 3817.
- Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry*; Dover Publication: New York, 1996.
- Cederbaum, L. S.; Domcke, W. *Adv Chem Phys* 36, 1977, 205.
- Tozer, D. J.; De Proft, F. *J Phys Chem A* 2005, 109, 8923.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 03*; Gaussian: Pittsburgh, PA, 2001.
- Velde, G. T.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, F. C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J Comput Chem* 2001, 22, 931.
- Becke, A. D. *Phys Rev A* 1988, 38, 3098.
- Perdew, J. P. *Phys Rev B* 1986, 33, 8822.
- Lee, C.; Yang, W.; Parr, R. G. *Phys Rev B* 1988, 37, 785.
- Chong, D. P.; Gritsenko, O. V.; Baerends, E. J. *J Chem Phys* 2002, 116, 760.
- Lemierre, V.; Chrostowska, A.; Dargelos, A.; Chermette, H. *J Phys Chem A* 2005, 109, 8348.
- Takahata, Y.; Chong, D. P.; Segala, M. *J Braz Chem Soc* 2004, 15, 282.
- Snijders, J. G.; Vernooijs, P.; Baerends, E. J. *Data Nucl Data Tables* 1982, 26, 483.
- Pearson, R. G. *J Org Chem* 1989, 54, 1423.
- Pearson, R. G. *J Inorg Chem* 1988, 27, 734.
- De Proft, F.; Geerlings, P. *J Chem Phys* 1997, 106, 3270.