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Equalized Electronegativity Based on the Valence Electrons and Its Application

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We take the contribution of all valence electrons into consideration and propose a new valence electrons equilibration method to calculate the equalized electronegativity including molecular electronegativity, group electronegativity, and atomic charge. The ionization potential of alkanes and mono-substituted alkanes, the chemical shift of ¹H NMR, and the gas phase proton affinity of aliphatic amines, alcohols, and ethers were estimated. All the expressions have good correlations. Moreover, the Sanderson method and Bratsch method were modified on the basis of the valence electrons equilibration theory. The modified Sanderson method and modified Bratsch method are more effective than their original methods to estimate these properties.

Key words: Electronegativity equalization, Valence electrons equilibration method, Molecular electronegativity, Group electronegativity, Atomic charge

I. INTRODUCTION

The principle of electronegativity equalization was first enunciated by Sanderson [1]. It has gained wide acceptance and been applied to the calculation of molecular electronegativity, group electronegativity, atomic charge, and so on [2–10]. At present, there are several different methods of calculating equalized molecular electronegativity, such as quantum chemistry methods [11–13] and empirical methods [8–10]. The empirical method still gains more attention due to its fast and simple calculation and specific physical meaning. In this field, the most well-known methods are Sanderson's geometric mean method [6–8], Bratsch's harmonic mean method [9], and Smith's weighted mean method [10]. All the three methods the equalized molecular electronegativity were calculated based on the atomic electronegativity and the number of atoms.

It is worth further investigating whether the atomic electronegativity and the number of atoms are sufficient to quantify the molecular electronegativity. As we all know, in the process of molecule formation, electrons flow must lead to the energy equalization for all the valence electrons of the component atoms, which results in the molecular valence electronic energy different from those of atoms. In fact, Allen defined the av-

erage one-electron energy (the multiplet-averaged total energy differences between a ground-state neutral and a singly ionized atom) as the elemental electronegativity [14]. Cao agreed that the atomic electronegativity was related to all the valence electrons [15]. Known from the above analysis, the molecular electronegativity is not only related to the number of component atoms, but also depends on the number of valence electrons of the component atoms. That is to say, all the valence electrons of the component atoms should contribute to the equalized molecular electronegativity. In this work, the electronegativity equilibration method based on valence electrons was proposed.

II. PRINCIPLE CONCEPTS AND METHODS

A. The valence electrons equilibration method

Cao has calculated the sum of valence electronic energy (SVEE) for atoms or molecules [16] with

$$\text{SVEE} = -\chi N_{\text{ve}} = \frac{\sum n_i E_i}{\sum n_i} N_{\text{ve}} \quad (1)$$

$$\text{SVEE}_X = \left[\frac{\sum n_i E_i}{\sum n_i} \right]_X N_{\text{ve},X} \quad (2)$$

$$\text{SVEE}_M = \left[\frac{\sum n_i E_i}{\sum n_i} \right]_M N_{\text{ve},M} \quad (3)$$

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where χ is the electronegativity for atoms or molecules, E_i is the energy of the i th valence electron and n_i is the number of the valence electron with E_i , $SVEE_X$ and $SVEE_M$ are the sum of valence electronic energy of the isolated atom X and the molecule M, respectively, N_{ve} is the number of valence electrons, $N_{ve,X}$ for the isolated atom X, and $N_{ve,M}$ for the molecule M. According to Eq.(1)–Eq.(3), we obtain the following expressions,

$$\chi_X = -\frac{SVEE_X}{N_{ve,X}} = -E_{av,X} \quad (4)$$

$$\chi_M = -\frac{SVEE_M}{N_{ve,M}} = -E_{av,M} \quad (5)$$

where χ_X is the electronegativity of an isolated atom X, χ_M is the electronegativity of a molecule M. $E_{av,X}$ and $E_{av,M}$ are the average valence electronic energies of isolated atom X and molecule M, respectively.

According to quantum chemical molecular orbital theory, the atomic inner electrons are close to the nucleus and tied strongly, they almost stay in its original atomic orbitals in the formation of a molecule. Whereas the valence electrons are far from the nucleus and have higher energy, they will interact with each other and form the molecular orbitals in the formation of molecules. Once the molecule achieves electronegativity equilibration, the chemical potential of each part in the molecule is equal. Then, we think, all the valence electronic energy of the component atoms in a molecule should be equal, that is, molecular electronegativity equilibration should be the energy equilibration of molecular valence electrons.

How to quantify the average valence electronic energy $E_{av,M}$ in a molecule? To begin with, we use the flowing process of water in a connector as a model to illustrate the valence electronic flowing process. As shown in Fig.1(a), the height of the liquid level in part A is h_A , and the height of the liquid level in part B is h_B . After turning on the switch at the bottom, because of the difference of potential energy, the water will flow from part B to part A until the two parts have the same height (see Fig.1(b)).

Conforming to the principle of volume conservation, it can be easily deduced that

$$h_A S_A + h_B S_B = h_{AB}(S_A + S_B) \quad (6)$$

$$h_{AB} = \frac{h_A S_A + h_B S_B}{S_A + S_B} \quad (7)$$

Seen from Eq.(7), the height of the liquid level after connecting (h_{AB}) is not simply equal to $1/2(h_A + h_B)$ or $(h_A h_B)^{1/2}$, but is related to S_A and S_B .

Similarly, in the formation of molecule AB, because of the difference of extranuclear electronic chemical potential between atom A and atom B, the valence electrons will flow from a region of higher chemical potential to that of lower chemical potential, finally all the valence electrons in the molecule have the same chemical potential (see Fig.2).

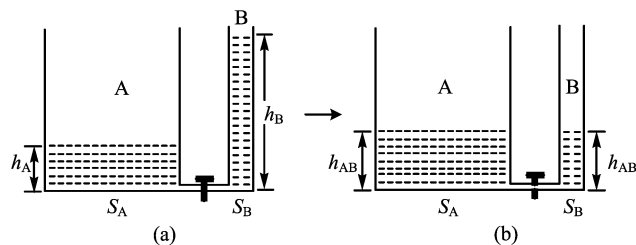


FIG. 1 Schematic diagram of potential energy equilibration for water in a connector ((a) before connecting, (b) after connecting).

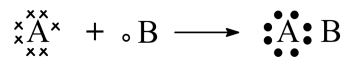


FIG. 2 Schematic diagram of valence electronic energy equilibration (dots denote the valence electrons being in the same chemical potential in molecule AB).

We analogize the valence electronic energy equilibration process of molecule formation from the flowing process of water (Fig.1). That is, the height of the liquid level h is equivalent to E_{av} . The basal area S is equivalent to N_{ve} . Then $E_{av,AB}$ can be calculated with Eq.(8).

$$E_{av,AB} = \frac{E_{av,A} N_{ve,A} + E_{av,B} N_{ve,B}}{N_{ve,A} + N_{ve,B}} \quad (8)$$

Further, Eq.(8) can be deduced in another way. Compound AB is formed from the isolated atoms A and B, as shown in Eq.(9):



The heat of formation ΔH_f^\ominus for compound AB can be approximately evaluated with Eq.(10), ignoring the inner-shell electronic energy [16].

$$\Delta H_f^\ominus = SVEE_{AB} - (SVEE_A + SVEE_B) \quad (10)$$

Combining Eq.(1)–Eq.(3) with Eq.(10), we can obtain Eq.(11) and Eq.(12):

$$\Delta H_f^\ominus = -E_{av,AB}(N_{ve,A} + N_{ve,B}) - [-E_{av,A} N_{ve,A} + (-E_{av,B} N_{ve,B})] \quad (11)$$

$$E_{av,AB} = \frac{E_{av,A} N_{ve,A} + E_{av,B} N_{ve,B} - \Delta H_f^\ominus}{N_{ve,A} + N_{ve,B}} \quad (12)$$

The $\sum SVEE_X$ and ΔH_f^\ominus values of 147 alkanes, haloalkanes, amines, alcohols, ethers, thiols, and thioethers have been studied. In this work, we calculated the $\Delta H_f^\ominus / \sum SVEE_X$ values and found that they are all less than 1% (see Tables I, II and III in the supplementary materials). It implies that the ΔH_f^\ominus can be neglected in the calculation of valence electronic energy. Therefore, if we remove the item ΔH_f^\ominus in Eq.(12), the obtained $E_{av,AB}$ will have no obvious error. That is to

TABLE I The ionization potential (Ip) (in eV), $\chi_{\text{ve(M)}}$, and GMPEI values of some alkanes.

Alkane ^a	Ip _{exp.} [21]	$\chi_{\text{ve(M)}}$	GMPEI	Ip _{calc.} ^b	Δ^c
1	12.61	2.38	—	12.75	0.14
2	11.56	2.40	1.0000	11.32	-0.24
3	10.95	2.41	1.3753	10.84	-0.11
4	10.53	2.42	1.5951	10.52	-0.01
2m3	10.57	2.42	1.5847	10.55	-0.02
5	10.28	2.42	1.7423	10.28	0.00
2m4	10.32	2.42	1.7334	10.31	-0.01
22mm3	10.20	2.42	1.7484	10.26	0.06
6	10.13	2.42	1.8486	10.10	-0.03
2m5	10.12	2.42	1.8419	10.12	0.00
3m5	10.08	2.42	1.8302	10.16	0.08
22mm4	10.06	2.42	1.8562	10.07	0.01
23mm4	10.02	2.42	1.8394	10.13	0.11
7	9.93	2.42	1.9292	9.96	0.03
8	9.80	2.42	1.9926	9.84	0.04
2m7	9.84	2.42	1.9884	9.85	0.01
224mmm5	9.86	2.42	2.0011	9.81	-0.05
2233mmmm4	9.80	2.42	2.0299	9.71	-0.09
9	9.71	2.43	2.0438	9.74	0.03
10	9.65	2.43	2.0862	9.66	0.01
11	9.56	2.43	2.1218	9.59	0.03

^a m=methyl, for example, 3m5 represents 3-methylpentane.

^b Calculated with Eq.(18).

^c $\Delta = \text{Ip}_{\text{calc.}} - \text{Ip}_{\text{exp.}}$

say, we can employ Eq.(8) to describe molecular valence electronic energy approximately.

As stated previously, Eq.(8) can be used to calculate $E_{\text{av,M}}$. Then combining Eq.(4) and Eq.(5) with Eq.(8), we obtain the expression of the electronegativity for diatomic molecule AB.

$$\chi_{\text{ve(AB)}} = \frac{\chi_{\text{A}}N_{\text{ve,A}} + \chi_{\text{B}}N_{\text{ve,B}}}{N_{\text{ve,A}} + N_{\text{ve,B}}} \quad (13)$$

For the molecule A_nB_m , which consist of n atoms A and m atoms B, its molecular electronegativity of A_nB_m can be represented by Eq.(14).

$$\chi_{\text{ve(A}_n\text{B}_m)} = \frac{n\chi_{\text{A}}N_{\text{ve,A}} + m\chi_{\text{B}}N_{\text{ve,B}}}{nN_{\text{ve,A}} + mN_{\text{ve,B}}} \quad (14)$$

Further, for the molecule M composed of different atoms i , the valence electron equalized electronegativity $\chi_{\text{ve(M)}}$ can be calculated with Eq.(15),

$$\chi_{\text{ve(M or G)}} = \frac{\sum n_i \chi_i N_{\text{ve},i}}{\sum n_i N_{\text{ve},i}} \quad (15)$$

where χ_i is the initial, pre-bonded electronegativity of a particular atom i ; $N_{\text{ve},i}$ is the number of valence elec-

TABLE II The χ_{Pauling} and P values of some atoms [22].

Atom	χ_{Pauling}	P	Atom	χ_{Pauling}	P
H	2.20	0.6668	Br	2.96	3.05
C	2.55	1.76	I	2.66	4.7
F	3.98	0.557	O	3.44	0.802
Cl	3.16	2.18	N	3.04	1.1

trons of atom i , n_i is the atom number of element i in the molecule.

Take the calculation of $\chi_{\text{ve(M)}}$ of 2-methylbutane ((CH_3)₂CHCH₂CH₃) as example. Using Pauling electronegativity scale, the numbers N_{ve} of valence electrons of C and H are 4 and 1, the electronegativities of C and H are 2.55 and 2.20, the atom numbers χ of C and H are 5 and 12, respectively.

$$\chi_{\text{ve(2-m-butane)}} = \frac{5\chi_{\text{C}}N_{\text{ve,C}} + 12\chi_{\text{H}}N_{\text{ve,H}}}{5N_{\text{ve,C}} + 12N_{\text{ve,H}}} = 2.42$$

B. Group electronegativity

According to the valence electrons equilibration method, the group electronegativity is given by Eq.(15). Take group $-\text{CH}_3$ as an example to elucidate the calculation of valence electrons equilibration electronegativity (using Pauling scale),

$$\chi_{\text{ve(-CH}_3)} = \frac{4\chi_{\text{C}} + 3\chi_{\text{H}}}{7} = 2.40$$

We note that Eq.(15) can not distinguish isomers. For example, $-\text{CH}_2\text{CH}_2\text{CH}_3$ and $-\text{CH}(\text{CH}_3)_2$ have the same electronegativity 2.42 based on Eq.(15) (using Pauling scale). To overcome this difficulty, the group can be staged for processing [17]. Firstly, we calculate the electronegativity of simple group. Secondly, take the simple group as a quasi-atom, and calculate the electronegativity of the comparatively complex group. Then, repeat this process again and again. Finally, the electronegativity of target group is obtained. It should be explained that, when the group is taken as quasi-atom, the pre-bonded electron of the radical atom (for instance, the radical atom of $-\text{OH}$ is oxygen atom) is regarded as the valence electron. For example, the valence electrons equilibration electronegativity for $-\text{CH}_2\text{OCH}_3$ is expressed as follows (using Pauling scale),

$$\chi_{\text{ve(-OCH}_3)} = \frac{6\chi_{\text{O}} + \chi_{\text{ve(-CH}_3)}}{6 + 1} = 3.29$$

the number of valence electrons of $-\text{OCH}_3$ is 1.

$$\chi_{\text{ve(-CH}_2\text{OCH}_3)} = \frac{4\chi_{\text{C}} + 2\chi_{\text{H}} + 5\chi_{\text{ve(-OCH}_3)}}{4 + 2 + 5} = 2.82$$

the number of valence electrons of $-\text{OCH}_3$ is 5.

TABLE III The Ip (in eV), $\chi_{ve(M)}$, \sum PEI and P values of some haloalkanes, amines, alcohols, and ethers.

Comp.	$\chi_{ve(M)}$	\sum PEI	P^a	$Ip_{exp.}^a$	$Ip_{calc.}^b$	Δ^c	Comp.	$\chi_{ve(M)}$	\sum PEI	P^a	$Ip_{exp.}^a$	$Ip_{calc.}^b$	Δ^c
MeF	3.39	1.0000	0.557	12.850	12.853	0.003	<i>n</i> -AmI	2.50	1.2260	4.7	9.190	9.254	0.064
MeCl	2.79	1.0000	2.18	11.300	11.214	-0.086	MeOH	2.86	1.6243	0.802	10.84	10.874	0.034
EtCl	2.70	1.1405	2.18	10.970	10.844	-0.126	EtOH	2.75	1.7648	0.802	10.49	10.473	-0.017
<i>n</i> -PrCl	2.65	1.1887	2.18	10.820	10.692	-0.128	PrOH	2.69	1.8130	0.802	10.10	10.304	0.204
<i>i</i> -PrCl	2.65	1.2810	2.18	10.780	10.533	-0.247	<i>i</i> -PrOH	2.69	1.9053	0.802	10.15	10.145	-0.005
<i>n</i> -BuCl	2.62	1.2122	2.18	10.670	10.609	-0.061	BuOH	2.66	1.8365	0.802	10.04	10.210	0.170
<i>s</i> -BuCl	2.62	1.3292	2.18	10.650	10.407	-0.243	MeOMe	2.75	2.0000	0.802	9.98	10.068	0.088
<i>i</i> -BuCl	2.62	1.2368	2.18	10.660	10.566	-0.094	EtOEt	2.66	2.2810	0.802	9.60	9.445	-0.155
<i>t</i> -BuCl	2.62	1.4216	2.18	10.610	10.248	-0.362	PrOPr	2.61	2.3774	0.802	9.27	9.215	-0.055
MeBr	2.69	1.0000	3.05	10.530	10.676	0.146	(<i>i</i> -Pr) ₂ O	2.61	2.5620	0.802	9.20	8.897	-0.303
EtBr	2.63	1.1405	3.05	10.290	10.348	0.058	MeNH ₂	2.65	2.2486	1.1	8.97	9.356	0.386
<i>n</i> -PrBr	2.60	1.1887	3.05	10.180	10.219	0.039	EtNH ₂	2.60	2.3891	1.1	8.86	9.047	0.187
<i>i</i> -PrBr	2.60	1.2810	3.05	10.075	10.060	-0.015	PrNH ₂	2.58	2.4373	1.1	8.78	8.928	0.148
<i>n</i> -BuBr	2.58	1.2122	3.05	10.125	10.149	0.024	<i>i</i> -PrNH ₂	2.58	2.5296	1.1	8.72	8.769	0.049
<i>s</i> -BuBr	2.58	1.3292	3.05	9.980	9.948	-0.032	BuNH ₂	2.56	2.4608	1.1	8.71	8.865	0.155
<i>i</i> -BuBr	2.58	1.2368	3.05	10.090	10.107	0.017	<i>s</i> -BuNH ₂	2.56	2.5778	1.1	8.70	8.663	-0.037
<i>t</i> -BuBr	2.58	1.4216	3.05	9.890	9.789	-0.101	<i>i</i> -BuNH ₂	2.56	2.4854	1.1	8.70	8.822	0.122
<i>n</i> -AmBr	2.57	1.2260	3.05	10.100	10.106	0.006	<i>t</i> -BuNH ₂	2.56	2.6702	1.1	8.64	8.504	-0.136
MeI	2.51	1.0000	4.7	9.540	9.657	0.117	Me ₂ NH	2.60	2.6243	1.1	8.24	8.642	0.402
EtI	2.51	1.1405	4.7	9.330	9.408	0.078	Et ₂ NH	2.56	2.9053	1.1	8.01	8.099	0.089
<i>n</i> -PrI	2.51	1.1887	4.7	9.260	9.322	0.062	Pr ₂ NH	2.55	3.0017	1.1	7.84	7.906	0.066
<i>i</i> -PrI	2.51	1.2810	4.7	9.170	9.163	-0.007	(<i>i</i> -Pr) ₂ NH	2.55	3.1863	1.1	7.73	7.588	-0.142
<i>n</i> -BuI	2.51	1.2122	4.7	9.210	9.279	0.069	Bu ₂ NH	2.54	3.0487	1.1	7.69	7.810	0.120
<i>s</i> -BuI	2.51	1.3292	4.7	9.090	9.077	-0.013	Me ₃ N	2.58	3.0000	1.1	7.82	7.959	0.139
<i>i</i> -BuI	2.51	1.2368	4.7	9.180	9.237	0.057	Et ₃ N	2.55	3.4215	1.1	7.50	7.183	-0.317
<i>t</i> -BuI	2.51	1.4216	4.7	9.020	8.918	-0.102	Pr ₃ N	2.53	3.5660	1.1	7.23	6.914	-0.316

^a Taken from Ref.[22].^b Calculated with Eq.(19).^c $\Delta=Ip_{calc.}-Ip_{exp.}$

C. Atomic partial charge

Based on the valence electrons equilibration method of this work, the partial charge $\Delta N_{ve,i}$ on any particular atom i can be calculated by Eq.(16),

$$\Delta N_{ve,i} = n_{ve,i} \frac{\chi_{ve(M)} - \chi_i}{\chi_{ve(M)}} \quad (16)$$

For all the neutral molecules, there is

$$\sum \Delta N_{ve,i} = q = 0 \quad (17)$$

q is the sum of all the partial charge $\Delta N_{ve,i}$.

III. APPLICATION OF THE VALENCE ELECTRONS EQUILIBRATION METHOD

The ionization potential is an important physico-chemical property of compounds and closely related to

the energy of the highest occupied molecular orbital (HOMO), thus it has attracted much attention [18, 19]. The ionization potential values from experimental method can be used to study the valence electronic energy, predict molecular physical and chemical activity, and is often applied to test whether a theoretical calculation approach is correct or not. To verify the rationality of the valence electrons equilibration method, we use $\chi_{ve(M)}$ to predict the ionization potential of alkanes and mono-substituted alkanes.

A. Predicting the ionization potential of alkanes

Our previous work indicated that the Ip mainly depends on “the initial state effect” (*i.e.* molecular electronegativity) and “the final state effect” (*i.e.* geometric mean polarizability effect index, GMPEI) [20]. Taking the ionization potential values of 21 alkanes as data set, we make a regression analysis with GMPEI and

TABLE IV Regression results comparison for Bratsch method, Sanderson method, modified Bratsch (M-Bratsch) method, modified Sanderson (M-Sanderson) method and valence electrons equilibration method of this work.

Property	Method	Scale	Regression results			
			Regression equation	<i>R</i>	<i>S</i>	<i>n</i>
Ip ^a	This work	χ_{Pauling}	$-185.2321 + 83.3606\chi_{\text{ve(M)}} - 3.5104\text{GMPEI}$	0.9936	0.08	21
	Bratsch	χ_{Pauling}	$402.5567 - 172.3293\chi_{\text{B(M)}} + 1.5742\text{GMPEI}$	0.9945	0.08	21
	Sanderson	$\chi_{\text{Sanderson}}$	$919.5975 - 345.8489\chi_{\text{S(M)}} + 1.3854\text{GMPEI}$	0.9938	0.08	21
	M-Bratsch	χ_{Pauling}	$-623.6133 + 277.8862\chi_{\text{MB(M)}} - 3.3101\text{GMPEI}$	0.9959	0.07	21
	M-Sanderson	$\chi_{\text{Sanderson}}$	$-1556.9357 + 595.6606\chi_{\text{MS(M)}} - 3.2944\text{GMPEI}$	0.9960	0.07	21
Ip ^b	This work	χ_{Pauling}	$9.0828 + 1.7517\chi_{\text{ve(M)}} - 1.6799\sum\text{PEI} - 0.4505P$	0.9895	0.17	52
	Bratsch	χ_{Pauling}	$-1.1302 + 6.3284\chi_{\text{B(M)}} - 1.6927\sum\text{PEI} - 0.4807P$	0.9893	0.17	52
	Sanderson	$\chi_{\text{Sanderson}}$	$-1.4330 + 5.5757\chi_{\text{S(M)}} - 1.6640\sum\text{PEI} - 0.4398P$	0.9892	0.17	52
	M-Bratsch	χ_{Pauling}	$7.9181 + 2.2466\chi_{\text{MB(M)}} - 1.6780\sum\text{PEI} - 0.4607P$	0.9892	0.17	52
	M-Sanderson	$\chi_{\text{Sanderson}}$	$6.4460 + 2.4448\chi_{\text{MS(M)}} - 1.5969\sum\text{PEI} - 0.4007P$	0.9899	0.16	52
$\delta_{\text{H}}^{\text{c}}$	This work	χ_{Pauling}	$-5.2569 + 2.9583\chi_{\text{ve(G)}}$	0.9785	0.15	12
	Bratsch	χ_{Pauling}	$-7.6456 + 4.2541\chi_{\text{B(G)}}$	0.5271	0.62	12
	Sanderson	$\chi_{\text{Sanderson}}$	$-10.0433 + 4.5904\chi_{\text{S(G)}}$	0.5939	0.58	12
	M-Bratsch	χ_{Pauling}	$-4.6851 + 2.7460\chi_{\text{MB(G)}}$	0.7221	0.50	12
	M-Sanderson	$\chi_{\text{Sanderson}}$	$-5.4506 + 2.7389\chi_{\text{MS(G)}}$	0.7268	0.50	12
PA ^d	This work	χ_{Pauling}	$2028.7676 - 44.5056\Delta N_{\text{ve}} + 57.1678\sum\text{PEI} - 81.6328E_{\text{X}}(\text{sp}^3)$	0.9981	4.06	64
	Bratsch	χ_{Pauling}	$2232.2566 - 877.9369\Delta N_{\text{B}} + 61.1380\sum\text{PEI} - 105.1439E_{\text{X}}(\text{sp}^3)$	0.9969	5.22	64
	Sanderson	$\chi_{\text{Sanderson}}$	$2822.2159 - 897.8271\Delta N_{\text{S}} + 58.4207\sum\text{PEI} - 139.2493E_{\text{X}}(\text{sp}^3)$	0.9976	4.62	64
	M-Bratsch	χ_{Pauling}	$2172.8226 - 84.4983\Delta N_{\text{MB}} + 57.6107\sum\text{PEI} - 92.6716E_{\text{X}}(\text{sp}^3)$	0.9979	4.36	64
	M-Sanderson	$\chi_{\text{Sanderson}}$	$2267.0065 - 70.7629\Delta N_{\text{MS}} + 57.2539\sum\text{PEI} - 97.0784E_{\text{X}}(\text{sp}^3)$	0.9981	4.13	64

^a Ip of alkanes in Table I.

^b Ip of mono-substituted alkanes in Table III.

^c δ_{H} of H-CH₂Y in Table V.

^d PA of RZ in Table VI.

$\chi_{\text{ve(M)}}$ (using Pauling scale), and obtain the regression Eq.(18):

$$\text{Ip} = -185.2321 + 83.3606\chi_{\text{ve(M)}} - 3.5104\text{GMPEI}$$

$$R = 0.9936, S = 0.08 \text{ eV}, n = 21,$$

$$F = 698.81, R_{\text{cv}} = 0.9791, S_{\text{cv}} = 0.15 \text{ eV}$$

where $\chi_{\text{ve(M)}}$ is the molecular electronegativity calculated by valence electrons equilibration method. The detailed introduction for GMPEI has been given [20]. R_{cv} and S_{cv} are the correlation coefficient and standard deviation calculated by leave-one-out (LOO) method. Eq.(18) has a good correlation. The average absolute error between the experimental values and the calculated values is only 0.05 eV, within the experimental uncertainties of 0.1 eV. In Eq.(18), the positive coefficient in front of $\chi_{\text{ve(M)}}$ indicates that the molecule with larger molecular electronegativity has larger ionization potential. The negative coefficient in front of GMPEI indicates that the molecular with larger polarizability effect has lower ionization potential. The results conform to the basic theory of organic chemistry. Furthermore, the results of LOO method ($R_{\text{cv}}=0.9791$,

$S_{\text{cv}}=0.15 \text{ eV}$) confirm the stability of Eq.(18).

If the molecular electronegativity of Eq.(18) is replaced by that of Bratsch method ($\chi_{\text{B(M)}}$) and that of Sanderson method ($\chi_{\text{S(M)}}$), we get the correlation equations as good as Eq.(18). However, the coefficients in front of $\chi_{\text{B(M)}}$ and $\chi_{\text{S(M)}}$ are negative, and the coefficient in front of GMPEI is positive (see Table IV). This result contradicts the existing chemical theory, and can not be explained reasonably.

B. Predicting the ionization potential of mono-substituted alkanes

For compounds that can be expressed as RXH_{*n*} (X=F, Cl, Br, I, O, N; *n*=0, 1, 2), all have nonbonded electron pairs on halogen, nitrogen or oxygen atom. Therefore, it is generally believed that the first ionization takes place on X atom of the mono-substituted alkane molecule RXH_{*n*} [19]. The effect of molecular polarizability on the Ip could be divided into two parts: the polarizability of the X atom itself (see Table II); the polarizability of the alkyl group (R) and hydro-

TABLE V The Chemical shift δ_{H} (in ppm), $\chi_{\text{ve(G)}}$ values for some organic compounds.

Compound	$\delta_{\text{H,exp}}$ [23]	$\chi_{\text{ve(G)}}$	$\delta_{\text{H,calc.}}^{\text{a}}$	Δ^{b}	Compound	$\delta_{\text{H,exp}}$ [23]	$\chi_{\text{ve(G)}}$	$\delta_{\text{H,calc.}}^{\text{a}}$	Δ^{b}
H-CH ₂ F	4.27	3.27	4.41	0.14	H-CH ₂ NH ₂	2.47	2.56	2.30	-0.17
H-CH ₂ Cl	3.06	2.82	3.10	0.04	H-CH ₂ C(O)H	2.2	2.51	2.18	-0.02
H-CH ₂ Br	2.69	2.72	2.78	0.09	H-CH ₂ C(O)OH	2.1	2.53	2.22	0.12
H-CH ₂ I	2.16	2.56	2.30	0.14	H-CH ₂ OCH ₃	3.21	2.82	3.10	-0.11
H-CH ₂ OH	3.39	2.81	3.06	-0.33	H-CH ₂ SCH ₃	2.12	2.49	2.10	-0.02
H-CH ₂ SH	2	2.48	2.07	0.07	H-CH ₂ N(CH ₃) ₂	2.31	2.57	2.36	0.05

^a Calculated with Eq.(20).

^b $\Delta = \delta_{\text{H,calc.}} - \delta_{\text{H,exp.}}$.

TABLE VI The PA (in kJ/mol), ΔN_{ve} , $\sum \text{PEI}$ and $E_{\text{X}}(\text{sp}^3)$ (in eV) values of some aliphatic amine, alcohol and ether.

Compound	ΔN_{ve}	$\sum \text{PEI}$	$E_{\text{X}}(\text{sp}^3)$	PA _{exp.} [25, 26]	PA _{calc.} ^a	Δ^{b}
MeOH	-1.29	1.6243	17.325	763.58	764.73	1.15
EtOH	-1.61	1.7648	17.325	785.75	787.05	1.30
PrOH	-1.80	1.8130	17.325	793.29	798.03	4.74
BuOH	-1.92	1.8365	17.325	795.80	804.72	8.92
<i>i</i> -PrOH	-1.80	1.9053	17.325	803.33	803.31	-0.02
<i>t</i> -BuOH	-1.92	2.0459	17.325	809.19	816.69	7.50
MeOMe	-1.61	2.0000	17.325	799.56	800.50	0.94
EtOMe	-1.80	2.1405	17.325	816.72	816.75	0.03
PrOMe	-1.92	2.1887	17.325	820.48	824.86	4.38
BuOMe	-2.00	2.2122	17.325	825.50	829.96	4.46
<i>i</i> -PrOMe	-1.92	2.2810	17.325	830.94	830.13	-0.81
<i>t</i> -BuOMe	-2.00	2.4216	17.325	841.40	841.93	0.53
EtOEt	-1.92	2.2810	17.325	830.52	830.13	-0.39
<i>i</i> -PrOEt	-2.00	2.4216	17.325	846.42	841.93	-4.49
<i>t</i> -BuOEt	-2.06	2.5621	17.325	858.14	852.74	-5.40
PrOPr	-2.06	2.3774	17.325	841.40	842.18	0.78
<i>i</i> -PrOi-Pr	-2.06	2.5620	17.325	856.88	852.74	-4.14
<i>t</i> -BuOt-Bu	-2.15	2.8432	17.325	887.01	872.66	-14.35
cyclic(CH ₂) ₂ O	-1.45	1.6667	17.325	779.90	774.48	-5.42
cyclic(CH ₂) ₃ O	-1.69	2.0937	17.325	808.35	809.26	0.91
cyclic(CH ₂) ₄ O	-1.83	2.2342	17.325	826.76	823.83	-2.93
cyclic(CH ₂) ₅ O	-1.94	2.3131	17.325	830.52	832.83	2.31
MeNH ₂	-0.85	2.2486	15.95	896.00	892.93	-3.07
Me ₂ NH	-0.96	2.6243	15.95	923.00	919.51	-3.49
EtNH ₂	-0.96	2.3891	15.95	908.00	906.06	-1.94
Me ₃ N	-1.02	3.0000	15.95	942.00	943.82	1.82
EtMeNH	-1.02	2.7648	15.95	932.00	930.37	-1.63
<i>i</i> -PrNH ₂	-1.02	2.5296	15.95	915.00	916.93	1.93
PrNH ₂	-1.02	2.4373	15.95	912.00	911.65	-0.35
EtMe ₂ N	-1.06	3.1405	15.95	952.00	953.65	1.65
EtNH	-1.06	2.9053	15.95	945.00	940.20	-4.80
Et ₃ N	-1.11	3.4215	15.95	972.00	971.87	-0.13
<i>t</i> -BuMe ₂ N	-1.11	3.4215	15.95	971.00	971.87	0.87
<i>i</i> -Pr ₂ NH	-1.11	3.1863	15.95	963.00	958.43	-4.57
Pr ₂ NH	-1.11	3.0017	15.95	952.00	947.87	-4.13
C ₆ H ₁₃ NH ₂	-1.11	2.4836	15.95	916.00	918.26	2.26

To be continued.

Table VI continued.

Compound	ΔN_{ve}	$\sum PEI$	$E_X(sp^3)$	PA _{exp.} [25, 26]	PA _{calc.} ^a	Δ^b
Me ₂ NCH ₂ <i>t</i> -Bu	-1.13	3.2849	15.95	962.00	964.76	2.76
C ₇ H ₁₅ NH ₂	-1.13	2.4900	15.95	916.00	919.32	3.32
<i>i</i> -Pr ₂ EtN	-1.14	3.7025	15.95	984.00	989.19	5.19
<i>t</i> -BuNH ₂	-1.06	2.6720	15.95	924.00	926.76	2.76
<i>t</i> -BuNH ₂	-1.06	2.5778	15.95	922.00	921.48	-0.52
<i>i</i> -BuNH ₂	-1.06	2.4854	15.95	915.00	916.20	1.20
BuNH ₂	-1.06	2.4608	15.95	914.00	914.79	0.79
Et ₂ MeN	-1.09	3.2810	15.95	962.00	962.93	0.93
<i>i</i> -PrMe ₂ N	-1.09	3.2810	15.95	961.00	962.93	1.93
<i>i</i> -PrEtNH	-1.09	3.0458	15.95	951.00	949.48	-1.52
<i>t</i> -BuCH ₂ NH ₂	-1.09	2.5335	15.95	917.50	920.20	2.70
EtMe ₂ CNH ₂	-1.09	2.7183	15.95	930.00	930.76	0.76
C ₅ H ₁₁ NH ₂	-1.09	2.4746	15.95	916.00	916.83	0.83
<i>t</i> -Bu ₂ NH	-1.14	3.4675	15.95	976.00	975.75	-0.25
<i>s</i> -Bu ₂ NH	-1.14	3.2827	15.95	970.00	965.19	-4.81
<i>t</i> -BuCH ₂ CH ₂ NMe ₂	-1.14	3.2592	15.95	964.00	963.84	-0.16
<i>i</i> -Bu ₂ NH	-1.14	3.0979	15.95	956.00	954.62	-1.38
Bu ₂ NH	-1.14	3.0487	15.95	956.00	951.81	-4.19
<i>t</i> -BuMe ₂ CNMe ₂	-1.15	3.5660	15.95	984.00	981.83	-2.17
Pr ₃ N	-1.15	3.5660	15.95	979.00	981.83	2.83
Bu ₃ N	-1.17	3.6366	15.95	982.00	986.81	4.81
Aziridine	-0.87	2.2910	15.95	902.00	896.47	-5.53
Pyrrolidine	-1.02	2.8585	15.95	942.00	935.35	-6.65
Piperidine	-1.05	2.9374	15.95	947.00	941.52	-5.48
Cyclic-C ₆ H ₁₁ NH ₂	-1.08	2.6415	15.95	925.50	925.80	0.30
2,2,6,6-Tetramethylpiperidine	-1.13	3.4994	15.95	969.00	977.02	8.02
N-isobutylpiperidine	-1.13	3.5499	15.95	974.00	979.91	5.91
1-Methylpiperidine	-1.08	3.3131	15.95	961.00	964.19	3.19

^a Calculated with Eq.(21).^b $\Delta = PA_{calc.} - PA_{exp.}$

gen atom attached to the X atom [19]. The former is measured by atomic polarizability P , the latter is described by the parameter $\sum PEI$ (the sum of the polarizability effect index of R and hydrogen atom, *i.e.* $\sum PEI = PEI(R) + PEI(H)$). Taking $\chi_{ve(M)}$, $\sum PEI$, and P as variables to correlate with the experimental I_p values of 52 haloalkanes, amines, alcohols, and ethers (see Table III), three-parameter model is shown

$$I_p = 9.0828 + 1.7517\chi_{ve(M)} - 1.6799 \sum PEI - 0.4505P \quad (18)$$

$$R = 0.9895, S = 0.17 \text{ eV}, n = 52,$$

$$F = 749.99, R_{cv} = 0.9871, S_{cv} = 0.18 \text{ eV}$$

where $\sum PEI$ shows the polarizability effect for the R and hydrogen atom attached to the X atom. The atomic polarizability P scales the polarizability effect of X atom. Eq.(19) shows good correlation between I_p ,

$\chi_{ve(M)}$, $\sum PEI$, and P . The average absolute error between the experimental values and the calculated values is 0.11 eV, which is close to the experimental uncertainties. The positive coefficient in front of $\chi_{ve(M)}$ and the negative coefficient in front of $\sum PEI$ and P conform to the basic theory in organic chemistry, and indicate that $\chi_{ve(M)}$ is reasonable and effective.

C. Predicting the chemical shift of ¹H NMR

¹H is the most common hydrogen isotope with an abundance of more than 99.98%. Because it is sensitive to the chemical environment and convenient for detection, ¹H NMR has been widely used in spectrometric identification for organic compounds. For molecules H-CH₂Y (Y=F, Cl, Br, I, OH, and so on), different shielding effects from -CH₂Y (G) result in different chemical shifts of H (δ_H). If G is not too complex, the

δ_{H} of ^1H NMR in H–G is closely related to the electronegativity of G. Thus the δ_{H} can be used to validate the rationality of the calculation of group electronegativity.

We use δ_{H} of ^1H NMR of molecule H–G to correlate with the group electronegativity $\chi_{\text{ve(G)}}$ of G, and obtain,

$$\begin{aligned} \delta_{\text{H}} &= -5.2569 + 2.9583\chi_{\text{ve(G)}} & (19) \\ R &= 0.9785, S = 0.15 \text{ ppm}, n = 12, \\ F &= 225.62, R_{\text{cv}} = 0.9637, S_{\text{cv}} = 0.19 \text{ ppm} \end{aligned}$$

Eq.(20) has good regression results, the correlation coefficient is 0.9785, and the average absolute error between the experimental values and the calculated values is 0.11 ppm. The positive coefficient in front of $\chi_{\text{ve,G}}$ indicates that, the larger the group electronegativity of G, the higher the corresponding shielding effect, and the larger the δ_{H} of ^1H NMR. If $\chi_{\text{ve(G)}}$ is replaced by $\chi_{\text{B(G)}}$ and $\chi_{\text{S(G)}}$, we get the correlation equations with bad results, in which the correlation coefficients are 0.5271 and 0.5939, respectively (see Table IV).

D. Predicting the gas phase proton affinity of aliphatic amines, alcohols, and ethers

Taking RZ (Z=N, O) as aliphatic amines, alcohols and ethers, Cao proposed that the gas phase proton affinity of RZ depends on three dominating factors: the atomic charge of Z, the polarizability effect of alkyl group, and the characteristic of Z atom [24]. Cao used the atomic charge ΔN [23] calculated with Bratsch method [9], the polarizability effect index $\sum \text{PEI}$ and the hybrid sp^3 orbital energy $E_{\text{X}}(\text{sp}^3)$ to correlate with the gas phase proton affinity (PA) of RZ, and obtained a satisfying result. Here we calculated atomic charge ΔN_{ve} . Then ΔN_{ve} , $\sum \text{PEI}$, and $E_{\text{X}}(\text{sp}^3)$ were correlated to PA and the results were shown as,

$$\begin{aligned} \text{PA} &= 2028.7676 - 44.5056\Delta N_{\text{ve}} + 57.1678 \cdot \\ &\quad \sum \text{PEI} 81.6328 E_{\text{X}}(\text{sp}^3) & (20) \\ R &= 0.9981, S = 4.06 \text{ kJ/mol}, n = 64, \\ F &= 5360.54, R_{\text{cv}} = 0.9978, S_{\text{cv}} = 4.40 \text{ kJ/mol} \end{aligned}$$

where ΔN_{ve} is calculated by valence electrons equilibration method. $E_{\text{X}}(\text{sp}^3)$ is the hybrid orbital energy of neutral atom. Eq.(21) has a good linear correlation. The correlation coefficient is 0.9981, and the average absolute error between the experimental and the calculated values is 2.96 kJ/mol.

Further, we calculate ΔN with Bratsch method (ΔN_{B}) and Sanderson method (ΔN_{S}) (see Table IV in supplementary material), and use them to estimate PA as shown in Eq.(22) and Eq.(23). Their correlations all

were less than that of Eq.(21).

$$\begin{aligned} \text{PA} &= 2232.2566 - 877.9369\Delta N_{\text{B}} + 61.1380 \cdot \\ &\quad \sum \text{PEI} - 105.1439 E_{\text{X}}(\text{sp}^3) & (21) \end{aligned}$$

$$\begin{aligned} R &= 0.9969, S = 5.22 \text{ kJ/mol}, n = 64, F = 3235.86 \\ \text{PA} &= 2822.2159 - 897.8271\Delta N_{\text{S}} + 58.4207 \cdot \\ &\quad \sum \text{PEI} - 139.2493 E_{\text{X}}(\text{sp}^3) & (22) \\ R &= 0.9976, S = 4.62 \text{ kJ/mol}, n = 64, F = 4133.86 \end{aligned}$$

IV. RESULTS AND DISCUSSION

Based on the principle of electronegativity equalization, we considered the energy contribution of all the valence electrons, and developed the methods for calculating molecular electronegativity, group electronegativity, and atomic charge. The descriptors based on the valence electrons equilibration method were correlated to a series of physico-chemical properties, and the obtained results were better than those with Bratsch and Sanderson methods. If we modified the Sanderson method and Bratsch method basing on the valence electrons equilibration theory, that is, use the valence electron number to replace the atomic number for calculating molecular electronegativity $\chi_{\text{MB(M)}}$ and $\chi_{\text{MS(M)}}$, the related parameters (see Tables V and VI in supporting information), the correlation results of predicting the ionization potential of alkanes and mono-substituted alkanes, the chemical shift of ^1H NMR, and the gas phase proton affinity of aliphatic amines, alcohols, and ethers have some improvements. It means that the valence electrons equilibration method is more reasonable and effective than atomic number equilibration method. The best results are those based on molecular electronegativity. Moreover, the electronegativity can be simple calculated and has specific physical and chemical meaning, thus it is expected to have wide applications.

Supplementary materials: Supplementary materials are available at the CJCP website alongside the main article.

V. ACKNOWLEDGMENTS

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