

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/233913023>

# The Chemical Potential of Molecules Contrasted to Averaged Atomic Electronegativities: Alarming Differences and Their Theoretical Rationalization.

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY A · DECEMBER 2013

Impact Factor: 2.69 · DOI: 10.1021/jp3103386 · Source: PubMed

CITATIONS

4

READS

67

## 3 AUTHORS:



**Dipankar Datta**

Indian Association for the Cultivation of Science

148 PUBLICATIONS 1,592 CITATIONS

SEE PROFILE



**Nirmal Shee**

Indian Association for the Cultivation of Science

14 PUBLICATIONS 18 CITATIONS

SEE PROFILE



**Laszlo von szentpaly**

Universität Stuttgart

66 PUBLICATIONS 3,302 CITATIONS

SEE PROFILE

# Chemical Potential of Molecules Contrasted to Averaged Atomic Electronegativities: Alarming Differences and Their Theoretical Rationalization

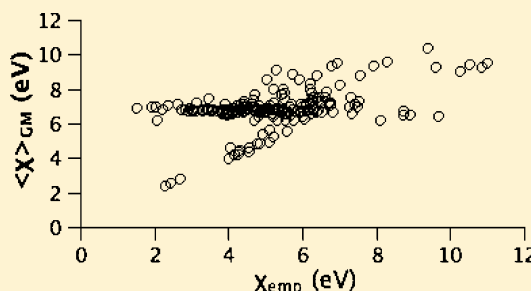
Dipankar Datta,<sup>\*,†</sup> Nirmal K. Shee,<sup>†</sup> and László von Szentpály<sup>\*,‡</sup>

<sup>†</sup>Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

<sup>‡</sup>Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70565 Stuttgart, Germany

## Supporting Information

**ABSTRACT:** We present the first large-scale empirical examination of the relation of molecular chemical potentials,  $\mu_{\text{mol}}^0 = -1/2(I_0 + A_0)_{\text{mol}}$ , to the geometric mean (GM) of atomic electronegativities,  $\langle\chi_{\text{at}}^0\rangle_{\text{GM}} = \langle 1/2(I_0 + A_0)_{\text{at}}\rangle_{\text{GM}}$ , and demonstrate that  $\mu_{\text{mol}}^0 \neq -\langle\chi_{\text{at}}^0\rangle_{\text{GM}}$ . Out of 210 molecular  $\mu_{\text{mol}}^0$  values considered more than 150 are not even in the range  $\min\{\mu_{\text{at}}^0\} < \mu_{\text{mol}}^0 < \max\{\mu_{\text{at}}^0\}$  spanned by the  $\mu_{\text{at}}^0 = -\chi_{\text{at}}^0$  of the constituent atoms. Thus the chemical potentials of the large majority of our molecules cannot be obtained by any electronegativity equalization scheme, including the “geometric mean equalization principle”,  $1/2(I_0 + A_0)_{\text{mol}} = \langle 1/2(I_0 + A_0)_{\text{at}}\rangle_{\text{GM}}$ . For this equation the root-mean-square of relative errors amounts to SE = 71%. Our results are at strong variance with Sanderson’s electronegativity equalization principle and present a challenge to some popular practice in conceptual density functional theory (DFT). The influences of the “external” potential and charge dependent covalent and ionic binding contributions are discussed and provide the theoretical rationalization for the empirical facts. Support is given to the warnings by Hinze, Bader et al., Allen, and Politzer et al. that equating the chemical potential to the negative of electronegativity may lead to misconceptions.



## 1. INTRODUCTION

In 1951 Sanderson postulated a “principle of electronegativity equalization” upon the formation of molecules and found a general relation between the effective radii of atoms-in-molecules (AiM) and their “attraction for valence electrons.”<sup>1</sup> He empirically obtained reasonable effective radii and bond lengths by postulating the “stability ratio of the molecule”, i.e., its electronegativity (EN), to be the geometric mean of the individual electronegativities of the atoms before combination.<sup>1</sup> Sanderson subsequently developed a general bonding model for molecules and solids on the basis of his particular electronegativity scale,  $S$ , and the geometric mean (GM) postulate of electronegativity equalization, ENE. This became eventually known as “Sanderson’s principle”<sup>2,3</sup>

$$S_{\text{mol}} = \langle S_{\text{at}} \rangle_{\text{GM}} = (\prod_{i=1}^n S_{\text{at},i})^{1/n} \quad (1)$$

Here  $S_{\text{mol}}$  and  $S_{\text{at}}$  are the molecular and atomic values of  $S$ , respectively, and  $j = 1 \rightarrow n$  the AiM’s. Sanderson fought a lifelong battle against Pauling’s verdict over ENE: “This idea seems to be self-contradictory inasmuch as EN is defined as the power of an atom *in a molecule* to attract electrons to itself.”<sup>4</sup> In Mulliken’s definition of the “absolute EN” of an AiM,  $X$ ,

$$\chi_{X,i}^0 = 1/2 (I_{\text{vs},X,i} + A_{\text{vs},X,i}) \quad (2)$$

$I_{\text{vs},X,i}$  and  $A_{\text{vs},X,i}$  are the valence-state ionization energy, and electron affinity of the singly occupied valence-orbital,  $i$ , respectively.<sup>5,6</sup> Mulliken strongly emphasized that in the “definition of

absolute electronegativity ... it is *essential* that  $I_X$  be taken as an appropriate *valence-state* ionization energy” because for interacting atoms the symmetries of the molecules and their dissociation products must be compatible.<sup>6</sup> Thus he efficiently included the contributions of valence-state ions-in-molecules of the proper symmetry,  $X_{\text{vs}}^+ Y_{\text{vs}}$  and  $X_{\text{vs}}^- Y_{\text{vs}}^+$ , to the energy balance needed to derive eq 2.<sup>5,6</sup>

Two active lines of research achieved an increasing discussion and acceptance of Sanderson’s postulate:

- the introduction of charge dependent EN functions,  $\chi(Q)$ , with  $Q$  as the net atomic charge,<sup>7–22</sup> and
- the identification of such EN functions with the negative of the chemical potential,  $-\mu(Q) = \chi(Q)$ , within density functional theory, DFT.<sup>23–37</sup>

## 2. EQUALIZATION MODELS OF ELECTRONEGATIVITY AND CHEMICAL POTENTIAL

Within five years after Sanderson’s first publication, Pritchard and Sumner<sup>7</sup> assumed the energy,  $E_X$ , of an AiM to be differentiable with respect to the orbital occupation number,  $n_i$ , and launched the seminal concept of a charge dependent orbital EN,  $\chi_i(n_i)$ , as an extended Mulliken EN. Mulliken originally did not take the possibility of a charge dependent EN into

**Received:** October 18, 2012

**Revised:** December 10, 2012

**Published:** December 13, 2012



consideration; however, he subsequently “reacted enthusiastically” and supported the concept as “obvious”.<sup>6c</sup> For the valence-orbital,  $i$ , of an AIM with the occupation number,  $0 \leq n_i \leq 2$ , and the net charge,  $Q = 1 - n_i$ , Pritchard and Sumner<sup>7</sup> introduced the energy polynomial

$$E_X(n_i) = -n_i I_{vs,X,i} + \frac{1}{2} (n_i - 1) n_i (I_{vs,X,i} - A_{vs,X,i}) \quad (3)$$

and defined the orbital EN as a function of either  $n_i$  or, equivalently,  $Q$

$$\begin{aligned} \chi_{X,i}(n_i) &= -\partial E_X(n_i) / \partial n_i = \frac{1}{2} (3I_{vs,X,i} - A_{vs,X,i}) \\ &\quad - n_i (I_{vs,X,i} - A_{vs,X,i}) = \chi_{X,i}^0 - (n_i - 1) \\ &\quad \times (I_{vs,X,i} - A_{vs,X,i}) = \chi_{X,i}^0 + Q(I_{vs,X,i} - A_{vs,X,i}) \\ &= \chi_{X,i}(Q) \end{aligned} \quad (4)$$

The net charge  $Q$  and the occupation numbers  $n_i$  of the AiM's were determined by self-consistent-field (SCF) calculations.<sup>7,11</sup> Expanding the charge dependent EN model, Iczkowski and Margrave noticed that the system will lower its energy by charge transfer (CT) between atoms of initially different EN,<sup>8</sup> and Hinze, Whitehead, Jaffé (HWJ), and collaborators<sup>9,10,15</sup> fine-tuned the orbital EN scale for the valence states of the main-group atoms. For the diatomic single bond with  $Q_Y = -Q_X$  and  $c_{X,i} = \frac{1}{2}(I_{vs,X,i} - A_{vs,X,i})$  HWJ<sup>9,10</sup> showed the equivalence of ENE to the minimization of the charge transfer energy,  $E_{CT}(Q_X)$ , with respect to  $Q_X$

$$\begin{aligned} E_{CT}(Q_X) &= E_X(Q_X) + E_Y(-Q_X) \\ &= \chi_{X,i}^0 Q_X + c_{X,i} Q_X^2 - \chi_{Y,j}^0 Q_X + c_{Y,j} Q_X^2 \end{aligned} \quad (5)$$

Accordingly the maximum CT energy lowering  $E_{CT,max}$  by ENE between the orbitals  $i$  of  $X$  and  $j$  of  $Y$  occurs at

$$Q_{X,HWJ} = \Delta n_{HWJ}(X \rightarrow Y) = (\chi_{Y,j}^0 - \chi_{X,i}^0) / 2(c_{Y,j} + c_{X,i}) \quad (6)$$

and amounts to

$$E_{CT,max} = -(\chi_{Y,j}^0 - \chi_{X,i}^0)^2 / 4(c_{Y,j} + c_{X,i}) \quad (7)$$

HWJ obtained an averaged orbital EN value,  $\langle \chi \rangle_{HWJ}$ , at the maximum energy lowering  $E_{CT,max}$

$$\langle \chi \rangle_{HWJ} = (\chi_{X,i}^0 c_{Y,j} + \chi_{Y,j}^0 c_{X,i}) / (c_{Y,j} + c_{X,i}) \quad (8)$$

Equation 8 provided a first independent support for Sanderson's principle, but according to a nongeometric mean formation scheme, and limited to localized two-center bonds.<sup>9,10,15</sup>

Several aspects of Sanderson's concept and ENE in general have been addressed and criticized repeatedly.<sup>10–17</sup> Pritchard,<sup>11</sup> Klopman,<sup>12</sup> and Baird, Sichel, and Whitehead<sup>10</sup> controversially discussed the SCF-MO theoretical conditions for EN equilibration in polyatomic molecules. It appeared that ENE may be a considered a good working hypothesis, only if the molecular energy can be efficiently partitioned into atomic energy terms, and the electrons are localizable in two-center bonds.<sup>10</sup> We will return to some of the criticized points in the next Section.

For polyatomic molecules the ENE in a localized electron-pair bond falls short of Sanderson's postulate of a complete and collective ENE in the whole molecule. For a general acceptance of Sanderson's principle, the occurrence of global and collective

ENE in arbitrary molecules needs to be proven theoretically and corroborated experimentally. The density functional viewpoint of EN presented by Parr et al.<sup>23–29,32</sup> has been acknowledged for achieving the rigorous deduction of Sanderson's postulate. Thereby a key importance is attributed to the chemical potential,  $\mu$ , a thermodynamic function of state, defined as the change of a characteristic function of state (e.g., internal energy, free energy, or Gibbs free energy) per change in the number of particles. Thus, the chemical potential,  $\mu = \partial E / \partial N$ , is the rate of change of the total free energy,  $E$ , with respect to a change of the average number of particles,  $N$ , in a particular component (“subsystem”) of the total system, when its other variables are kept constant. Accordingly, the electrons of a solid are at constant chemical potential, defined as the change in electronic free energy, when electrons are added or removed. In the density functional treatment of an arbitrary  $N$  electron system, the chemical potential

$$\mu = (\partial E[\rho] / \partial \rho)_{v(r)} \quad (9)$$

is introduced as a Lagrange multiplier in a constrained minimization of the energy functional,  $E[\rho]$ , of the total electronic density,  $\rho = \rho(r)$ , at constant electron number,  $N = \int \rho(r) dr$ , and constant “external” potential,  $v(r)$ , provided by the atomic nuclei of the chemical species.<sup>23–25</sup> For the  $N_0$  electrons of a neutral chemical system Parr et al.<sup>23–29</sup> formulated

$$\mu^0 = (\partial E(N, v(r)) / \partial N)_{v(r), N_0} \quad (10)$$

By the general definition of state functions,  $\mu^0$  is constant in the ground-state system, and combining several subsystems, e.g.,  $X$  and  $Y$ , of initially different  $\mu_X^0$  and  $\mu_Y^0$  values must result in a constant average value,  $\langle \mu^0 \rangle$ . An important point is that  $E$  can be treated as a function of  $N$  alone, only if  $v(r)$  is held constant, that is, by clamping the nuclei at fixed positions.<sup>23–37</sup> For such cases, a frequently used formula, dubbed the ground-state parabola model (GS),<sup>29</sup> approximates  $E(N)$  by<sup>25</sup>

$$E_{GS}(N) = E(N_0) + \mu^0(N - N_0) + \frac{1}{2} \eta (N - N_0)^2 \quad (11)$$

where  $\eta$  is defined as  $(\partial^2 E[N, v(r)] / \partial N^2)_{v(r), N_0}$ .<sup>25,33</sup> However, as the subsystem  $X$  approaches  $Y$ , the nuclei move and the external potentials  $v_X$  and  $v_Y$  change. A notable proposal accounting for the changing  $v(r)$  has been to replace the chemical potential by the apparently more appropriate electrochemical potential and assess the changes in the external potential by a Madelung–Jørgensen electrostatic potential.<sup>13b,17,18</sup> Nevertheless, the partial charge  $Q_X$  and the electronic charge flow,  $\Delta N$ , from  $X$  to  $Y$  has been very frequently presented as predominantly due to  $\mu$ -equalization, thus ignoring all changes in the external potential.<sup>23–27,29–33</sup>

$$Q_{X,GS} = \Delta N_{GS}(X \rightarrow Y) = -(\mu_Y^0 - \mu_X^0) / (\eta_X + \eta_Y) \quad (12)$$

Under such assumptions, the energy lowering by chemical potential equalization between the atoms  $X$  and  $Y$  has been expressed as

$$E_{CT,max,GS} = -(\mu_Y^0 - \mu_X^0)^2 / 2(\eta_X + \eta_Y) \quad (13)$$

Obviously eqs 12 and 13 closely resemble eqs 6 and 7. Thus, in a very far reaching generalization and modification of Mulliken's electronegativity to arbitrary electron systems, Parr et al. postulated that the chemical potential of an arbitrary system of electrons may be operationally equated at least to the first order to

$$\mu^0 = -1/2 (I_0 + A_0) \quad (14)$$

the negative of its “absolute electronegativity”.<sup>23–33</sup> In contrast to Mulliken’s emphasis of valence-state energies in eq 2, and because DFT is primarily concerned with ground-state systems,  $I_0$  is the first ionization energy and  $A_0$  the first electron affinity of the arbitrary system. Note, however, that the physical meaning of the Lagrange multiplier is affected by optionally different starting assumptions; thus  $\mu^0$  may assume rather different expressions, e.g.,  $E_{\text{GS}}(N_0)/N_0$ .<sup>15a,32,34</sup> In fact, eq 14 is a postulate, which cannot be exactly derived.<sup>15a,32,34</sup> The second derivative,  $(\partial^2 E / \partial N^2)_{v(\mathbf{r}), N_0} = \eta$ , is assumed constant and modeled by the Pearson–Parr chemical hardness<sup>33</sup>

$$\eta = (I_0 - A_0) \quad (15)$$

Following Sanderson’s example,<sup>1–3</sup> in eq 1 the empirical geometric mean rule (often denoted as principle) has been incorporated into the explicit calculation of molecular chemical potentials<sup>25,26,35,36</sup>

$$-\mu_{\text{mol}}^0 = \langle -\mu_{\text{at}}^0 \rangle_{\text{GM}} = \{ \prod_i (-\mu_{\text{at},i}^0) \}^{1/n} \quad (16)$$

Incidentally, there exists no simple linear relationship between Sanderson’s  $S_{\text{at}}$  and Parr’s  $\mu_{\text{at}}^0$  scales<sup>2,3b</sup> (see Figure S, Supporting Information). Atoms and molecules may, however, assume different  $\mu^0$  and  $\eta$  values under varying circumstances, e.g., in different valence states.<sup>9,15,19b,25b,29</sup> Because the electronegativity seemed a poorly defined concept, such density functional linked postulates have become extremely popular, met with a huge resonance, and are widely discussed and applied.<sup>25–37</sup> The generalized postulate may be called the Sanderson–Parr principle of ENE: when two or more atoms of initially different EN,  $\chi_{\text{at}}^0 = -\mu_{\text{at}}^0$ , combine chemically, their chemical potentials and EN values become equalized at an average value,  $\chi_{\text{mol}}^0 \approx \langle -\mu_{\text{at}}^0 \rangle$ .

The presentation of this principle nevertheless has been ambiguous, to say the least. On the one hand, Parr and Yang attributed a key role to EN in DFT, even comparable to the role of energy in wave mechanics,<sup>25c</sup> and maintained that “the density functional formulation of quantum theory leads rigorously to the concept of EN and the principle of ENE.”<sup>25d</sup> On the other hand, Nalewajski et al.<sup>37</sup> pointed out a major defect in the theoretical deduction that neglects important “first-order effects” due to changes in the external potential during molecule formation. Consequently, Nalewajski and Koninski<sup>37b</sup> emphasized the importance of the  $v(\mathbf{r})$  terms, which are neglected by many approximate ENE rules. Although an explicit treatment of  $v(\mathbf{r})$  would lead to complex issues, several simpler ways to model the related first-order energy contributions by reference to valence-state atoms have been reported.<sup>19–22,25,27,29,32,37</sup> Nalewajski et al.<sup>37</sup> focused on lowering the potential energy and on contractions of the electron densities of the AiM’s. Von Szentpály et al.<sup>19–22,29</sup> discussed (i) the density contraction and hybridization as affecting the molecular potential energy and (ii) the wave-mechanical sharing-interference that lowers a component of the kinetic energy according to Ruedenberg’s bond analysis.<sup>38</sup> Toro-Labbé et al.<sup>35</sup> introduced new additivity schemes for the chemical potential and hardness. Yang et al.<sup>39</sup> recently highlighted basic challenges to DFT in connection with eq 11, but without specifically discussing ENE.

### 3. TESTING THE SANDERSON–PARR PRINCIPLE

The popularity of structural principles, such as the Sanderson–Parr principle, is strongly linked to their simplicity and direct, successful applicability to a large body of structural questions. Much of their attractiveness would be called into question, and the chemical applicability seriously limited, if it became necessary to explicitly include additional first-order effects. Surprisingly, the Sanderson–Parr principle has never been tested seriously in terms of predicting experimental  $1/2(I_0 + A_0)_{\text{obsd}}$  data of molecules by averaging atomic ENs. Similarly, the chemical potential of molecules,  $\mu_{\text{mol}}^0$ , has not been systematically compared to the averaged  $\langle \mu_{\text{at}}^0 \rangle$  of atoms. Up to the early 1990s this was due to the uncertainty of experimental molecular data, as pointed out by Komorowski.<sup>18</sup> Because of the recent discussions involving one of the present authors over the validity of “empirical structural principles”,<sup>36,40–42</sup> we have decided to re-examine this important aspect of the Sanderson–Parr principle.

We are now in a better position regarding the amount and accuracy of experimental data, because updated and revised compilations are available.<sup>22,33b,36,40,42–48</sup> The detailed literature sources of experimental electron affinities of temporary radical anions are collated in ref 48. In calculating the molecular  $\chi^0 = -\mu^0$ , we use available experimental  $I_0$  and  $A_0$  data, except where indicated otherwise, e.g., theoretical results for some transition metal complexes.<sup>22,49</sup> In Table 1, we present the “absolute”, or maybe more correctly, “empirical” electronegativity values,  $1/2(I_0 + A_0)_{\text{obsd}} = \chi_{\text{emp}}^0$  for 210 molecules.<sup>22,33b,36,40,42–48</sup> (Although calculated from observed  $I_0$  and  $A_0$  data,  $\chi^0$  and  $\mu^0$  are not physical observables; thus we refrain of tagging them so.) The molecules are arranged in the order of increasing  $\chi_{\text{emp}}^0$ . We have determined averaged molecular EN values by calculating the geometrical mean,  $\langle \chi_{\text{at}}^0 \rangle_{\text{GM}}$ , using the experimental  $I_0$  and  $A_0$  values of the constituent atoms.<sup>47,50</sup> The results are given in Table 1 as  $\langle \chi_{\text{at}}^0 \rangle_{\text{GM}}$ . It is found that the mean unsigned relative error rendered by  $\langle \chi_{\text{at}}^0 \rangle_{\text{GM}}$  in reproducing  $\chi_{\text{emp}}^0$  is 49%, and the root-mean-square (rms) standard error amounts to SE = 71%. Figure 1 evidences the striking overall lack of linear correlation between  $\chi_{\text{emp}}^0$  and  $\langle \chi_{\text{at}}^0 \rangle_{\text{GM}}$ . Notable exceptions for which the Sanderson–Parr principle is reasonably obeyed are the alkali metal dimers, their halides, and a few small molecules, such as,  $\text{P}_2$ ,  $\text{SH}$ , and  $\text{O}_3$ .

Obviously, the Sanderson–Parr principle of ENE fails the numerical test performed here. We find very substantial limitations in its practical use for calculating molecular  $\chi^0$  values from  $\langle \chi_{\text{at}}^0 \rangle_{\text{GM}}$ . We are not the first ones to notice the discrepancy, but earlier reports stopped short of conclusions because of the uncertainties attributed to the  $I_0$  and  $A_0$  data.<sup>17,18</sup> Some recently examined sets of molecules have been too limited to draw general conclusions on the validity of ENE.<sup>36,40,42</sup> To highlight the problem, we point out that the relative errors in the  $\langle \chi_{\text{at}}^0 \rangle_{\text{GM}}$  values of the simple molecules  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ , and  $\text{CH}_3\text{F}$  are 135, 177, 140, and 120%, respectively (Table 1).

To generally assess the performance of different EN averaging schemes, we now divide the whole set of 210 molecules into three subsets,

- (i) molecules with  $1/2(I_0 + A_0)_{\text{obsd}} < \min\{\chi_{\text{at}}^0\}$
- (ii) molecules in the expected range of averages,  $\min\{\chi_{\text{at}}^0\} < 1/2(I_0 + A_0)_{\text{obsd}} < \max\{\chi_{\text{at}}^0\}$
- (iii) molecules with  $\max\{\chi_{\text{at}}^0\} < 1/2(I_0 + A_0)_{\text{obsd}}$

Table 1. Empirical,  $\chi^0_{\text{emp}}$ , and Atom-Averaged,  $\langle\chi^0_{\text{at}}\rangle_{\text{GM}}$ , Electronegativities of 210 Molecules<sup>a</sup>

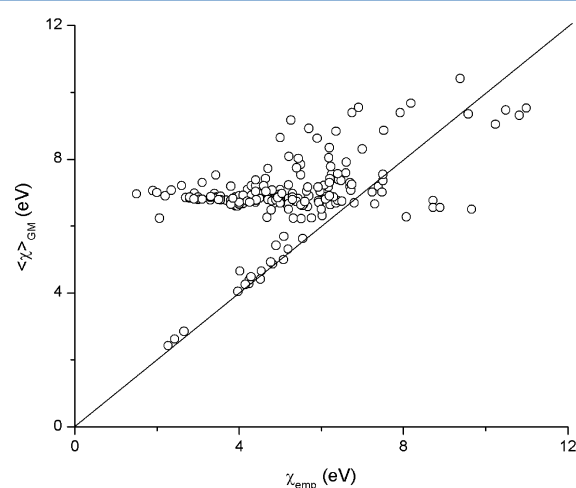
molecule	$\chi^0_{\text{emp}}$	$\langle\chi^0_{\text{at}}\rangle_{\text{GM}}$	% error <sup>b</sup>	molecule	$\chi^0_{\text{emp}}$	$\langle\chi^0_{\text{at}}\rangle_{\text{GM}}$	% error <sup>b</sup>	molecule	$\chi^0_{\text{emp}}$	$\langle\chi^0_{\text{at}}\rangle_{\text{GM}}$	% error <sup>b</sup>
(CH <sub>3</sub> ) <sub>3</sub> N	1.50	6.96	364	KCl	4.29	4.48	4	C <sub>6</sub> H <sub>5</sub> O	5.60	6.73	20
CH <sub>3</sub> NH <sub>2</sub>	1.90	7.06	271	butadiene	4.30	6.80	58	PBr <sub>3</sub>	5.64	7.04	25
(CH <sub>3</sub> ) <sub>2</sub> O	2.00	7.00	250	H <sub>2</sub> C=CHOAc	4.30	6.91	61	CH <sub>3</sub> NO <sub>2</sub>	5.67	7.16	26
Ni (NO)	2.06 <sup>49</sup>	6.23	202	<i>cis</i> -ClCH=CHCl	4.30	7.20	67	BBr <sub>3</sub>	5.67	6.58	16
(CH <sub>3</sub> ) <sub>4</sub> C	2.20	6.90	213	C <sub>2</sub> H <sub>4</sub>	4.35	6.86	58	HCN	5.70	6.90	21
K <sub>2</sub>	2.27	2.42	7	<i>trans</i> -ClCH=CHCl	4.40	7.20	64	PF <sub>3</sub>	5.70	8.92	56
CH <sub>3</sub> OH	2.35	7.07	200	H <sub>2</sub> C=CHCl	4.40	7.03	60	CS	5.76	6.24	8
KNa	2.43	2.62	7	CHCl=CCl <sub>2</sub>	4.40	7.38	68	CF <sub>3</sub> I	5.90	8.62	46
NH <sub>3</sub>	2.60	7.21	177	C <sub>2</sub> H <sub>2</sub>	4.40	6.71	52	CCl <sub>4</sub>	5.50	7.84	43
Na <sub>2</sub>	2.66	2.85	7	C <sub>5</sub> H <sub>5</sub> N	4.40	6.76	54	NO <sub>2</sub>	5.92	7.16	21
(CH <sub>3</sub> ) <sub>2</sub> S	2.70	6.85	154	4-nethylpyridine	4.42	6.78	53	<i>p</i> -benzoquinone	5.93	6.76	14
(CH <sub>3</sub> ) <sub>3</sub> P	2.80	6.83	144	CH <sub>3</sub> CHO	4.50	6.95	54	CH	5.94	6.70	13
<i>c</i> -C <sub>3</sub> H <sub>6</sub>	2.80	6.86	145	<i>p</i> -hydroquinone	4.50	6.83	52	BCl <sub>3</sub>	5.97	7.03	18
pyrrole	2.90	6.81	135	RbCl	4.52	4.41	-2	SeH	6.00	6.50	8
CH <sub>4</sub>	2.91 <sup>c</sup>	6.98	140	NaBr	4.54	4.65	2	I <sub>2</sub>	6.00	6.76	13
(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub>	3.00	6.86	129	HCO <sub>2</sub> CH <sub>3</sub>	4.60	7.02	53	BH <sub>3</sub>	6.02	6.31	5
(CH <sub>3</sub> ) <sub>3</sub> As	3.00	6.79	126	H <sub>2</sub> C=CCl <sub>2</sub>	4.60	7.20	56	NH <sub>2</sub>	6.07	7.22	19
C <sub>6</sub> H <sub>5</sub> NHCH <sub>3</sub>	3.05	6.80	123	NO	4.64	7.42	60	<i>p</i> -C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> )CN	6.10	6.80	11
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub>	3.10	6.80	119	ClCH <sub>2</sub> COCH <sub>3</sub>	4.65	7.03	51	CO	6.10	6.88	13
H <sub>2</sub> O	3.10	7.30	135	SiH <sub>2</sub>	4.68	6.26	34	IBr	6.17	7.16	16
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	3.30	6.78	105	HCHO	4.70	7.02	49	SF	6.18	8.04	30
CH <sub>3</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	3.30	6.86	108	HCl	4.70	7.72	64	maleonitrile	6.20	6.90	11
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	3.31	6.88	108	CH <sub>3</sub> CN	4.70	6.88	46	fumaronitrile	6.20	6.90	11
cyclohexene	3.40	6.86	102	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> CH <sub>3</sub>	4.70	6.79	44	BF <sub>3</sub>	6.20	8.34	34
dimethylformamide	3.40	6.97	105	PbS	4.77	4.92	3	H <sub>2</sub> C=CHF	6.20	7.30	18
CH <sub>3</sub> F	3.43 <sup>c</sup>	7.52	120	SiH <sub>3</sub>	4.78	6.48	36	HO <sub>2</sub>	6.21	7.42	19
<i>cis</i> -CH <sub>3</sub> CH=CHCH <sub>3</sub>	3.45	6.86	98	CH <sub>3</sub> Br	4.80	7.07	47	S <sub>2</sub> O	6.22	6.63	7
(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub>	3.50	6.86	96	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	4.80	6.75	41	ClO <sub>2</sub>	6.23	7.78	25
<i>trans</i> -CH <sub>3</sub> CH=CHCH <sub>3</sub>	3.50	6.86	96	NaCl	4.82	4.86	1	O <sub>2</sub>	6.25	7.54	21
furan	3.50	6.79	94	benzophenone	4.85	6.68	38	HNO <sub>3</sub>	6.26	7.41	18
C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	3.55	6.78	91	C <sub>2</sub> H <sub>3</sub>	4.85	6.80	40	SO	6.26	6.84	9
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	3.55	6.89	94	C <sub>6</sub> H <sub>5</sub> COOH	4.90	6.78	38	phthalic anhydride	6.30	6.87	9
1,2,3-trimethylbenzene	3.69	6.77	83	PbO	4.90	5.42	11	CF <sub>3</sub> Br	6.36	8.83	39
<i>p</i> -xylene	3.70	6.76	83	CH <sub>3</sub> I	4.90	6.90	41	SH	6.36	6.68	5
thiophene	3.80	6.65	75	4-chloropyridine	4.94	6.85	39	POCl <sub>3</sub>	6.38	7.53	18
cyclopentadiene	3.80	6.75	78	CH <sub>3</sub>	4.96	6.94	40	BrO	6.40	7.56	18
H <sub>2</sub> C=C=CH <sub>2</sub>	3.80	6.77	78	C <sub>6</sub> H <sub>5</sub> CHO	5.00	6.73	35	C <sub>2</sub> N <sub>2</sub>	6.40	6.76	6
C <sub>6</sub> H <sub>5</sub> OH	3.80	6.77	78	CH <sub>3</sub> S	5.00	6.79	36	N <sub>2</sub> O	6.42	7.38	15
C <sub>6</sub> H <sub>5</sub> SH	3.80	6.67	75	HF	5.00	8.64	73	C <sub>2</sub> HF	6.48	7.36	14
CH <sub>3</sub> Cl	3.80	7.19	89	CO <sub>2</sub>	5.0	7.09	42	H <sub>2</sub> C=C(CN) <sub>2</sub>	6.50	6.74	4
4-aminopyridine	3.85	6.83	77	C <sub>6</sub> H <sub>5</sub> CN	5.00	6.68	34	Br <sub>2</sub>	6.60	7.59	15
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	3.90	6.74	73	CH <sub>3</sub> COCOCH <sub>3</sub>	5.00	6.92	38	ClO	6.61	7.91	20
CH <sub>3</sub> CH=CH <sub>2</sub>	3.90	6.86	76	CHO	5.04	6.97	38	H <sub>2</sub>	6.70	7.18	7
pyrene	3.91	6.60	69	<i>o</i> -nitrotoluene	5.08	6.83	34	N <sub>2</sub>	6.70	7.30	9
chrysene	3.96	6.61	67	LiCl	5.08	4.99	-2	SO <sub>2</sub>	6.72	7.07	5
perylene	3.96	6.59	66	SnO	5.09	5.69	12	NH	6.74	7.24	7
KI	3.97	4.04	2	SiH <sub>4</sub>	5.18 <sup>c</sup>	6.61	28	SF <sub>4</sub>	6.75	9.39	39
anthracene	3.98	6.63	67	MgO	5.19	5.31	2	NCCH=C(CN) <sub>2</sub>	6.80	6.69	-2
C <sub>2</sub> H <sub>5</sub>	4.00	6.90	72	C <sub>6</sub> H <sub>5</sub>	5.20	6.67	28	SF <sub>5</sub>	6.91	9.55	38
AsH <sub>3</sub>	4.00	6.65	66	Mn(CO) <sub>5</sub>	5.20 <sup>49</sup>	6.50	25	Cl <sub>2</sub>	7.00	8.30	19
naphthalene	4.00	6.66	66	<i>p</i> -nitrotoluene	5.20	6.83	31	CNO	7.24 <sup>42</sup>	7.01	-3
biphenyl	4.00	6.71	68	SiCl <sub>3</sub>	5.20	7.23	39	O <sub>3</sub>	7.27	7.54	4
LiH	4.02	4.65	16	C <sub>6</sub> F <sub>6</sub>	5.21	8.08	55	C <sub>2</sub> (CN) <sub>4</sub>	7.30	6.66	-9
PH <sub>3</sub>	4.05	6.75	67	<i>m</i> -nitrotoluene	5.22	6.83	31	SO <sub>3</sub>	7.39	7.18	-3
azulene	4.08	6.66	63	CF <sub>3</sub>	5.26	9.17	74	OCN	7.48 <sup>42</sup>	7.01	-6
C <sub>6</sub> H <sub>5</sub> I	4.10	6.68	63	4-acetylpyridine	5.30	6.79	28	OH	7.50	7.36	-2
C <sub>6</sub> H <sub>5</sub> Br	4.10	6.74	64	H <sub>2</sub> C=CHCHO	5.30	6.86	29	FO	7.52	8.86	18
C <sub>6</sub> H <sub>5</sub> Cl	4.10	6.79	66	HI	5.30	6.97	31	PF <sub>5</sub>	7.92	9.39	19



Table 1. continued

molecule	$\chi^0_{\text{emp}}$	$\langle\chi^0_{\text{at}}\rangle_{\text{GM}}$	% error <sup>b</sup>	molecule	$\chi^0_{\text{emp}}$	$\langle\chi^0_{\text{at}}\rangle_{\text{GM}}$	% error <sup>b</sup>	molecule	$\chi^0_{\text{emp}}$	$\langle\chi^0_{\text{at}}\rangle_{\text{GM}}$	% error <sup>b</sup>
C <sub>6</sub> H <sub>5</sub> F	4.10	6.92	69	CS <sub>2</sub>	5.32	6.23	17	C <sub>2</sub>	8.07	6.27	−22
CH <sub>3</sub> COCH <sub>3</sub>	4.10	6.92	69	CCl <sub>3</sub>	5.40	7.74	43	SF <sub>6</sub>	8.18	9.67	18
phenanthrene	4.10	6.67	63	SN	5.40	6.73	25	MnO <sub>4</sub>	8.72 <sup>49</sup>	6.55	−33
benzene	4.10	6.71	64	H <sub>2</sub> C=CH−CN	5.40	6.79	26	CN	8.72	6.76	−22
styrene	4.11	6.70	63	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	5.43	6.83	26	CrO <sub>4</sub>	8.89 <sup>49</sup>	6.55	−36
CsCl	4.15	4.25	2	SiF <sub>2</sub>	5.44	8.02	47	F <sub>2</sub>	9.38	10.41	11
trans-NCCH=CHCN	4.20	6.74	60	C <sub>6</sub> H <sub>5</sub> S	5.50	6.63	20	OsF <sub>6</sub>	9.58	9.35	−2
H <sub>2</sub> S	4.20	6.84	63	PCl <sub>3</sub>	5.50	7.53	37	VO <sub>4</sub>	9.66 <sup>49</sup>	6.50	−49
HCONH <sub>2</sub>	4.20	7.09	69	S <sub>2</sub>	5.51	6.22	13	MoF <sub>6</sub>	10.24 <sup>22</sup>	9.04	−12
KBr	4.24	4.28	1	PH <sub>2</sub>	5.54	6.61	19	IrF <sub>6</sub>	10.49	9.47	−10
NaI	4.25	4.39	3	P <sub>2</sub>	5.55	5.62	1	SiF <sub>6</sub>	10.82 <sup>22</sup>	9.31	−14
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	4.26	6.71	57	COS	5.57	6.65	19	PtF <sub>6</sub>	10.99 <sup>22</sup>	9.53	−13

<sup>a</sup>The meanings of the symbols are same as in the text. The  $\chi^0_{\text{emp}}$  and/or the  $I_0$  and  $A_0$  input data are from refs 22, 33b, and 42–48, except if indicated otherwise to specify reference data. <sup>b</sup>The % error is calculated as  $100(\langle\chi^0_{\text{at}}\rangle_{\text{GM}} - \chi^0_{\text{emp}})/\chi^0_{\text{emp}}$ . <sup>c</sup>Observed vertical  $I_0$  values from: Pullen, B. P.; Carlson, T. A.; Moddeman, W. E.; Schweitzer, G. K.; Bull, W. E.; Grimm, F. A. *J. Chem. Phys.* **1970**, *53*, 768.



**Figure 1.** Lack of correlation between  $\chi^0_{\text{emp}} = 1/2(I + A)_{\text{obsd}}$  and the geometric mean  $\langle\chi^0_{\text{at}}\rangle_{\text{GM}}$  for the 210 molecules listed in Table 1. The line of slope +1 is drawn to facilitate comparison with the Sanderson–Parr principle.

The chemical potentials of the species in subsets (i) and (iii) obviously cannot result from any EN averaging scheme. However, out of 210 molecules only 56 fall into the expected range  $\min\{\chi^0_{\text{at}}\} < 1/2(I_0 + A_0)_{\text{obsd}} < \max\{\chi^0_{\text{at}}\}$ , whereas the subsets (i) and (iii) together contain 154 molecules.

It is concluded that the chemical potential of molecules  $\mu^0_{\text{mol}} \approx -1/2(I_0 + A_0)_{\text{obsd}}$  is with high probability not even in the range spanned by the atomic  $\mu^0_{\text{at}} = -\chi^0_{\text{at}}$ . The results are at strong variance with the Sanderson–Parr principle and may take many chemists by surprise as a challenge to the validity of conceptual DFT.

We now discuss reasons explaining the dramatic failure of the Sanderson–Parr principle to relate the averaged atomic EN, e.g.,  $\langle\chi^0_{\text{at}}\rangle_{\text{GM}}$ , to the molecular  $\mu^0_{\text{mol}} = -1/2(I_0 + A_0)$ . In exact DFT the chemical potential will be equalized at the energy minimum, but not necessarily in cases off-minimum. The general principle to be used in calculating molecular properties, e.g.,  $I_0$  and  $A_0$ , requires that the total energy,  $E_{\text{mol}}$ , must be at its minimum, thus the positive bonding energy,  $E_{\text{bind}}$ , at its maximum. However, long before the advent of DFT arguments supporting Sanderson’s principle, a consensus has been established that the charge transfer contribution,  $-E_{\text{CT,max}}$  of eqs 7 and 13,

is only a small part of  $E_{\text{bind}}$ .<sup>11–14,17,18</sup> Jørgensen stated in 1962 that the “principle of equilibrated EN” has to be corrected by the electrostatic Madelung energy and the covalent bond energy.<sup>17a</sup> Such corrections are accounted for by the energy minimization in self-consistent-charge (SCC) models.<sup>12–21</sup> The binding energy,  $E_{\text{bind}}$ , may be modeled as the sum of three interactions: an ionic Madelung energy,  $E_{\text{ion}}$ , a covalent bonding term,  $E_{\text{cov}}$ , and a charge transfer contribution,  $-E_{\text{CT}}$ .<sup>13–15,17–21</sup> Jørgensen,<sup>17</sup> Ferreira,<sup>13</sup> Evans and Huheey,<sup>14</sup> and von Szentpály et al.<sup>20,21</sup> assessed the weight of  $E_{\text{CT}}$  in relation to (i) the bond dissociation energy of diatoms,  $XY$ ,<sup>13,14,20b,21</sup> (ii) the lattice energies of ionic solids,  $XY_{\text{solid}}$ ,<sup>13,20c</sup> and (iii) the atomization energy of polyatomic molecules,  $XY_n$ .<sup>14,17</sup> As expected, the charge transfer energy by ENE is only a small part of the molecular binding energy, or the solid’s lattice energy. The charge transfer,  $\Delta N$ , according to eq 12 even vanishes, if the atoms forming the molecule have the same EN, notably for homonuclear clusters,  $X_n$ . For such systems, eq 13 does not even indicate any binding. However, the molecular  $I_0$  and  $A_0$  values are strongly affected by differences between the atomization energies of  $X_n^+$ ,  $X_n$ , and  $X_n^-$ . For homonuclear diatomic molecules we obtain

$$\chi^0(X_2) = \chi^0(X) + 1/2 [D_0(X_2^-) - D_0(X_2^+)] \quad (17)$$

Because the bond dissociation energies  $D_0(X_2^-)$  and  $D_0(X_2^+)$  normally do not cancel, the Sanderson–Parr principle is not valid here; cf. Table 1.

For polar molecules, Klopman,<sup>12</sup> Ferreira,<sup>13a</sup> Huheey and Evans,<sup>14</sup> and von Szentpály et al.<sup>19–21</sup> showed that the partial charges are shifted to far more polar values than those obtained by equalizing Parr’s absolute EN, and/or the HWJ electronegativity. The corresponding changes in the net atomic charge  $Q_X$  and  $E_{\text{CT}}(Q_X)$  have been calculated by different SCC models<sup>12–14,17–21</sup> and the total binding energy  $E_{\text{bind}}$  expressed as a function of  $Q_X$  at  $dE_{\text{bind}}/dQ_X = 0$ . We recall a simple SCC bond model for diatomic  $XY$ , having the net atomic charge  $Q_X$  as its variable. According to the Born–Landé model<sup>51</sup> the ionic binding energy is

$$E_{\text{ion}} = +(e^2/4\pi\epsilon_0 R_e) Q_X^2 (1 - n_{\text{BL}}^{-1}) \quad (18)$$

where  $e$  is the elementary charge,  $\epsilon_0$  is the vacuum permittivity,  $R_e$  is the equilibrium internuclear distance, and  $n_{\text{BL}}$  is the Born–Landé exponent. The covalent contribution is modeled as an

average,  $\langle D \rangle$ , of the homonuclear bond dissociation energies,  $D(X_2)$  and  $D(Y_2)$ , and is itself charge dependent as already postulated by Sanderson<sup>2,3</sup>

$$E_{\text{cov}} = \langle D \rangle (1 - Q_X^2) \quad (19)$$

The  $E_{\text{CT}}$  contribution to  $E_{\text{bind}}$  has to be expressed by its  $Q$ -dependent formulation, shown in eq 5, and taken with the opposite sign

$$-E_{\text{CT}}(Q_X) = -\{\chi_X^0 Q_X + \frac{1}{2} \eta_X Q_X^2 - \chi_Y^0 Q_X + \frac{1}{2} \eta_Y Q_X^2\} \quad (20)$$

Thus  $E_{\text{bind}}$  reaches its maximum for

$$dE_{\text{bind}}/dQ_X = d(E_{\text{ion}} + E_{\text{cov}} - E_{\text{CT}})/dQ_X = 0 \quad (21)$$

and the SCC partial charge is given by

$$Q_{X,\text{SCC}} = (\chi_Y^0 - \chi_X^0) / \{\eta_Y + \eta_X + 2\langle D \rangle - 2(e^2/4\pi\epsilon_0 R_e)(1 - n_{\text{BL}}^{-1})\} \quad (22)$$

Here the denominator differs from both eqs 6 and 12 by two additional contributions of antagonistic signs,  $2\langle D \rangle - 2(e^2/4\pi\epsilon_0 R_e)(1 - n_{\text{BL}}^{-1})$ . Depending on the reference zero energies taken for  $D(X_2)$  and  $D(Y_2)$ , i.e., by reference to separated ground-state atoms, or to specific valence states of the  $\text{AIMs}^{12-14,19-21,29}$  the sum of the additional terms will differ, but it is generally of negative sign, thus reducing the denominator and increasing  $Q_{X,\text{SCC}}$  beyond the  $Q_{X,\text{GS}}$  of eq 12. As a result, SCC models yield about twice as large bond polarities,  $Q_{\text{SCC}}$ , and electronic charge flows,  $\Delta N_{\text{SCC}}$ , than the  $Q_{\text{GS}}$  and  $\Delta N_{\text{GS}}$  obtained by Parr et al.'s ground-state parabola model, viz., by chemical potential equalization according to eq 12. A well documented comparison by Evans and Huheey<sup>14b</sup> may serve as an example

$$Q_{\text{SCC}} \approx 2.16 Q_{\text{GS}} - 0.07 \quad (23)$$

The molecular  $I_0$  and  $A_0$  are, of course, determined at the true energy minimum of the system, which, however, occurs at a rather different bond polarity. The minimization of the total energy,  $E_{\text{mol}}$ , is the decisive criterion that has to be fulfilled prior to calculating molecular properties. The partial energy minimization by ENE is, in general, not equivalent to minimizing the total energy. The above argument concerning covalent molecules, exemplified by eq 17, together with the lack of charge consistency after ENE and at equalized chemical potential are theoretical reasons against setting  $\langle \chi_{\text{at}}^0 \rangle_{\text{GM}}$  equal to  $\chi_{\text{emp}}^0$  by application of the Sanderson–Parr principle. For empirical and theoretical reasons the molecular  $\chi_{\text{emp}}^0 = 1/2(I_0 + A_0)_{\text{obsd}}$  cannot normally be represented in terms of the atomic EN's.

#### 4. CONCLUSIONS

A trend has developed to overestimate the applicability and accuracy of the “electronegativity equalization principle”. We show, however, that its basic assumptions cannot be corroborated by experimental data. In summary, there is but a highly deceptive similarity between the ENE principle and the fact of a constant chemical potential in molecules. In exact DFT, the chemical potential is equalized within a molecule at its energy minimum; however, equating the chemical potential to the negative of electronegativity is a gross operational simplification and leads to misconceptions. Our results are at strong variance

with the Sanderson–Parr principle and therefore present a serious challenge to some popular practice of conceptual DFT. We join Bergmann and Hinze,<sup>15a</sup> Bader et al.,<sup>34</sup> Allen,<sup>52</sup> and Politzer et al.<sup>53</sup> by suggesting to regard EN and the chemical potential as two separate and distinct properties. Some 22 years ago, Jørgensen and Pearson exchanged arguments, whether “Charlotte Moore’s Tables (Atomic Energy Levels<sup>50</sup>)” contain the genetic code for the Beilstein.” Jørgensen reportedly “refused to believe” such a supposition.<sup>54</sup> The present article definitely sustains Jørgensen’s conviction.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Figure on the relation between the chemical potential,  $\mu_{\text{at}}^0$  and Sanderson’s electronegativity scale,  $S$ , for elemental atoms. This information is available free of charge via the Internet at <http://pubs.acs.org>

#### ■ AUTHOR INFORMATION

##### Corresponding Author

\*E-mail: D.D., [icdd@iacs.res.in](mailto:icdd@iacs.res.in); L.S., [lszentpaly@yahoo.com](mailto:lszentpaly@yahoo.com).

##### Notes

The authors declare no competing financial interest.

#### ■ ACKNOWLEDGMENTS

L.S. thanks Prof. Hans-Joachim Werner for continued hospitality at the Institut für Theoretische Chemie and Prof. Michael C. Böhm for helpful discussions.

#### ■ REFERENCES

- (1) Sanderson, R. T. *Science* **1951**, *114*, 670–672.
- (2) (a) Sanderson, R. T. *Science* **1955**, *121*, 207–208. (b) Sanderson, R. T. *Chemical Bonds and Bond Energy*, 2nd ed.; Academic Press: New York, 1976. (c) Sanderson, R. T. *Polar Covalence*; Academic Press: New York, 1983.
- (3) (a) Sanderson, R. T. *J. Chem. Educ.* **1986**, *63*, 845–846. (b) Sanderson, R. T. *J. Chem. Educ.* **1988**, *65*, 112–118. (c) Sanderson, R. T. *J. Chem. Educ.* **1988**, *65*, 227–231.
- (4) Pauling, L.; Herman, Z. S. *Molecular Structure and Energetics*; VCH Publishers: Weinheim, Germany, 1986; Vol. 1, pp 1–15.
- (5) (a) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782–793. (b) Mulliken, R. S. *J. Chem. Phys.* **1934**, *3*, 573–585.
- (6) (a) Mulliken, R. S. *J. Chim. Phys. (France)* **1949**, *46*, 497–542. (English version: 1948/49 ONR Report on MO Theory, pp 73ff). (b) Ramsay, D. A.; Hinze, J. *Selected Papers of Robert S. Mulliken*; University of Chicago Press: Chicago, 1975; p 981. (c) Mulliken, R. S. Letter to H. O. Pritchard, May 10, 1977.
- (7) Pritchard, H. O.; Sumner, F. H. *Proc. Roy. Soc. A (London)* **1956**, *235*, 136–143.
- (8) Iczkowski, R. P.; Margrave, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 3547–3551.
- (9) (a) Hinze, J.; Jaffé, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540–546. (b) Hinze, J.; Whitehead, M. A.; Jaffé, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 148–154.
- (10) Baird, N. C.; Sichel, J. M.; Whitehead, M. A. *Theoret. Chim. Acta* **1968**, *11*, 38–50.
- (11) Pritchard, H. O. *J. Am. Chem. Soc.* **1963**, *85*, 1876–1876.
- (12) Klopman, G. *J. Am. Chem. Soc.* **1964**, *86*, 1463–1469.
- (13) (a) Ferreira, R. *J. Phys. Chem.* **1964**, *68*, 2240–2248. (b) Ferreira, R. *Adv. Chem. Phys.* **1967**, *13*, 55–84.
- (14) (a) Evans, R. S.; Huheey, J. E. *J. Inorg. Nucl. Chem.* **1970**, *102*, 373–381. (b) Evans, R. S.; Huheey, J. E. *J. Inorg. Nucl. Chem.* **1970**, *102*, 777–793.

- (15) (a) Bergmann, D.; Hinze, J. *Struct. Bonding (Berlin)* **1987**, 66, 145–190. (b) Bergmann, D.; Hinze, J. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 150–163 with earlier references quoted therein.
- (16) Edminston, C. K. *J. Chem. Educ.* **1988**, 65, 219–222.
- (17) (a) Jørgensen, C. K. *Orbitals in Atoms and Molecules*; Academic Press: New York, 1962; p 80. (b) Jørgensen, C. K. *Quim. Nova* **1988**, 11, 10–19.
- (18) (a) Komorowski, L. *Chem. Phys. Lett.* **1983**, 103, 201–204. (b) Komorowski, L. *Chem. Phys.* **1987**, 114, 55–71.
- (19) (a) von Szentpály, L. *J. Mol. Struct. (THEOCHEM)* **1991**, 233, 71–81. (b) von Szentpály, L. *Int. J. Quantum Chem.* **2000**, 76, 222–234.
- (20) (a) von Szentpály, L. *Chem. Phys. Lett.* **1995**, 245, 209–214. (b) von Szentpály, L.; Gardner, D. O. N. *J. Phys. Chem. A* **2001**, 105, 9467–9477. (c) Glasser, L.; von Szentpály, L. *J. Am. Chem. Soc.* **2006**, 128, 12314–12321 with earlier references quoted therein.
- (21) Donald, K. J.; Mulder, W. H.; von Szentpály, L. *J. Phys. Chem. A* **2004**, 108, 595–606.
- (22) von Szentpály, L. *J. Phys. Chem. A* **2010**, 114, 10891–10896 (including Supporting Information).
- (23) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, 68, 3801–3807.
- (24) Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, J. *Phys. Rev. Lett.* **1982**, 49, 1691–1694.
- (25) (a) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U.K., 1989; (b) p 93, (c) p 75, (d) p 92.
- (26) Parr, R. G.; Bartolotti, L. *J. Am. Chem. Soc.* **1982**, 104, 3801–3803.
- (27) Parr, R. G. *Int. J. Quantum Chem.* **1983**, 26, 687–692.
- (28) Fuentealba, P.; Parr, R. G. *J. Chem. Phys.* **1991**, 93, 5559–5564.
- (29) Parr, R. G.; von Szentpály, L.; Liu, S. J. *J. Am. Chem. Soc.* **1999**, 121, 1922–1924.
- (30) Chermette, H. *J. Comput. Chem.* **1999**, 20, 129–154.
- (31) Geerlings, P.; De Proft, F.; Langenacker, W. *Chem. Rev.* **2003**, 103, 1793–1874.
- (32) Katriel, J.; Parr, R. G.; Nyden, M. R. *J. Chem. Phys.* **1981**, 74, 2397–2401.
- (33) (a) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, 105, 7512–7516. (b) Pearson, R. G. *Chemical Hardness: Applications from Molecules to Solids*; Wiley-VCH: Weinheim, Germany, 1997.
- (34) (a) Nguyen-Dang, T. T.; Bader, R. F. W.; Essen, H. *Int. J. Quantum Chem.* **1982**, 22, 1049–1058. (b) Bader, R. F. W. *Can. J. Chem.* **1999**, 77, 86–93.
- (35) (a) Gutiérrez-Oliva, S.; Jaque, P.; Toro-Labbé, A. *J. Phys. Chem. A* **2000**, 104, 8955–8964. (b) Sengupta, S.; Toro-Labbé, A. *J. Phys. Chem. A* **2002**, 106, 4443–4446.
- (36) Chattaraj, P. K.; Giri, S.; Duley, S. J. *J. Phys. Chem. Lett.* **2010**, 1, 1064–1067.
- (37) (a) Nalewajski, R. F. *J. Am. Chem. Soc.* **1984**, 106, 944–945. (b) Nalewajski, R. F.; Koninski, M. *J. Phys. Chem.* **1984**, 88, 6234–6240. (c) Nalewajski, R. F. *J. Phys. Chem.* **1985**, 89, 2831–2837. (d) Nalewajski, R. F. *J. Phys. Chem.* **1989**, 93, 2658–2666.
- (38) (a) Ruedenberg, K. *Rev. Mod. Phys.* **1962**, 34, 326–376. (b) Bitter, T.; Wang, S. G.; Ruedenberg, K.; Schwarz, W. H. E. *Theor. Chem. Acc.* **2010**, 127, 237–257.
- (39) (a) Cohen, A. L.; Mori-Sánchez, P.; Yang, W. *Science* **2008**, 321, 792–794. (b) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. *Chem. Rev.* **2012**, 112, 289–320.
- (40) von Szentpály, L. *J. Phys. Chem. A* **2011**, 115, 8528–8531.
- (41) Chattaraj, P. K.; Giri, S.; Duley, S. J. *J. Phys. Chem. A* **2012**, 116, 790–791.
- (42) von Szentpály, L. *J. Phys. Chem. A* **2012**, 116, 792–795.
- (43) Yang, W.; Lee, C.; Ghosh, S. K. *J. Phys. Chem.* **1985**, 89, 5412–5414.
- (44) Pearson, R. G. *Inorg. Chem.* **1988**, 27, 734–740.
- (45) Pearson, R. G. *J. Org. Chem.* **1989**, 54, 1423–1430.
- (46) Datta, D. *Inorg. Chem.* **1992**, 13, 2797–2800.
- (47) *CRC Handbook of Chemistry and Physics*, 90th ed.; Lide, D. R., Ed.-in-Chief; CRC Press, Boca Raton, FL, 2009/2010.
- (48) (a) Puiatti, M.; Mariano, D.; Vera, A.; Pierini, A. B. *Phys. Chem. Chem. Phys.* **2009**, 11, 9013–9024. (b) Sommerfeld, T.; Weber, R. J. *J. Phys. Chem.* **2011**, 115, 6675–6682.
- (49) (a) Böhm, M. C.; Schmidt, P. C.; Sen, K. D. *J. Mol. Struct. THEOCHEM* **1982**, 87, 43–52. (b) Sen, K. D.; Böhm, M. C.; Schmidt, P. C. *Struct. Bonding (Berlin)* **1987**, 66, 99–123.
- (50) Moore, Ch. E. *Atomic Energy Levels*; National Bureau of Standards Circular 467; NBS: Washington, DC, 1949–1954.
- (51) Born, M.; Landé, A. *Ber. Preuß. Akad. Wiss. Berlin* **1918**, 45, 1048–1068.
- (52) (a) Allen, L. C. *Acc. Chem. Res.* **1990**, 23, 175–176. (b) Allen, L. C. *Int. J. Quantum Chem.* **1994**, 49, 253–277.
- (53) Politzer, P.; Shields, Z. P.-E.; Bulat, F. A.; Murray, J. S. *J. Chem. Theor. Comput.* **2011**, 7, 377–384.
- (54) Pearson, R. G. *Coord. Chem. Rev.* **1990**, 100, 403–425.