ELECTRONEGATIVITY AND AVERAGE LOCAL IONIZATION ENERGY

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We appreciate the opportunity to participate in this tribute to Josef Paldus, a fine theoretician and a good friend.

A variation of an earlier formulation of electronegativity by Allen, as the average valence electron ionization energy of a ground-state atom, is proposed. It is shown that the calculated average local ionization energies on the 0.001 a.u. electronic density contours of atoms correlate very well with Allen's values. Our procedure makes it unnecessary to enumerate valence electrons, which can be a problem due to interpenetration of shells.

Keywords: Electron affinity; Ionization potential; Valence electrons; Configuration energy; Atomic surfaces; Electronegativity.

The concept of electronegativity is qualitatively of great importance in chemistry, in rationalizing and predicting molecular properties and reactive behavior. Historically it is probably associated most with Pauling[1–3], although he did not claim to originate it; Allen[4] and Hinze[5] have pointed out that it can be traced at least to Berzelius, in the mid-nineteenth century.

Pauling established a scale of relative electronegativities[1,2], based upon the ionic characters of heteronuclear bonds, as measured by the differences between their bond energies and those of the corresponding homonuclear bonds. In updated form, his scale is still widely cited, and is one of the standards against which the numerous subsequent ones are assessed. Many of these, especially the earlier ones, have been based upon his famous definition of electronegativity as "the power of an atom in a molecule to attract electrons to itself"[3].

Pauling's words "in a molecule" are significant because they serve to conceptually differentiate his and some of the subsequent approaches from a more recent formulation of electronegativity. In 1978, Parr et al.[6] identified

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it with the negative of the chemical potential, μ; for a system of N electrons in an external potential $\nu(\mathbf{r})$ and total energy E, this is given by

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{\nu(\mathbf{r})} . \qquad (1)$$

Within the framework of density functional theory, μ appears as the Lagrangian multiplier in minimizing the energy[6] subject to the constraint that the electronic density $\rho(\mathbf{r})$ integrate to N. Parr et al. proposed that

$$\chi = -\mu \qquad (2)$$

χ being electronegativity. In terms of Eqs (*1*) and (*2*), it has proven possible to justify the postulate that the electronegativity (or chemical potential) is uniform throughout a molecule at equilibrium[6–8], as originally asserted by Sanderson[9,10].

Equations (*1*) and (*2*) are commonly implemented by means of a three-point finite-difference approximation[6,11], which leads to

$$\chi = \frac{I + A}{2} . \qquad (3)$$

I and A are the ground-state ionization potential and the electron affinity of the system, respectively. While Eq. (*3*) is widely invoked, it has some significant weaknesses[4,12]; for example, it predicts chlorine to be more electronegative than oxygen, and hydrogen to be more so than carbon and sulfur and nearly the same as nitrogen.

In contrast to Pauling's and other earlier views of electronegativity as a property of an atom in an interactive situation, the chemical potential approach applies to molecules as well as atoms, and it refers to their ground states. For example, while Eqs (*1*) and (*3*) are very similar to those proposed some time ago by Iczkowski and Margrave[13] and by Mulliken[14], these latter are specifically for valence states of atoms. This allows Mulliken's version of Eq. (*3*) to avoid some of the problems encountered in the ground state[15,16]. Pearson[17,18] and Allen[19] have in fact suggested that μ and χ represent two distinct properties, and should not be equated. Thus, despite the significant efforts that have been made to establish a rigorous basis for electronegativity, there remains some validity to the observation by Iczkowski and Margrave, in 1961, that "there is some confusion as to what physical picture corresponds to the term electronegativity"[13]. Numerous overviews and critiques of its various formulations have appeared over the years[4,5,12,17–25].

ELECTRONEGATIVITY AND IONIZATION ENERGY

It has been argued on several occasions that the primary determinant of the chemical potential of a free atom is its ionization potential[26–28]. The feasibility of equating electronegativity to the ionization potential was in fact examined by Sacher and Currie[29]. However, there are difficulties with this analogous to those that arise for Eq. (*3*). For instance, both oxygen and sulfur would then have electronegativities lower than the atoms that precede them in their rows of the periodic table, nitrogen and phosphorus.

Allen has argued strongly[4,12,30,31] that electronegativity should be defined as the average ionization energy of the valence electrons of a free atom in its ground state. He originally referred to this as the "spectroscopic electronegativity" χ_{spec}[12], but later as the "configuration energy" CE[4,30,31]. For the main-group (i.e. non-transition) elements, it is taken to be

$$\mathrm{CE} = \frac{n_{\mathrm{s}}\varepsilon_{\mathrm{s}} + n_{\mathrm{p}}\varepsilon_{\mathrm{p}}}{n_{\mathrm{s}} + n_{\mathrm{p}}} , \qquad (4)$$

where n_{s} and n_{p} are the numbers of *s* and *p* valence electrons and ε_{s} and ε_{p} are the multiplet-averaged total energy differences between the ground-state atom and its monopositive ion. These energies are to be obtained spectroscopically; however, some use of computed data has been necessary[30,31].

Allen et al. have presented extensive comparisons of his and other electronegativity scales, and of its relationship to a variety of chemical and physical properties, particularly within the context of the periodic table[4,12,30,31]. Overall, the CE approach to electronegativity appears to be quite effective, and it has been included in a number of textbooks, as cited by Mann et al.[30]

Allen et al. recognized that extending Eq. (*4*) to transition elements encounters the problem that the number and type of valence electrons are often ambiguous. They circumvent this by means of a computational procedure that produces fractional s and d occupancies, which are then combined with spectroscopic data[31]. However this neglects the possible role of interpenetration involving lower-lying subshells[32,33]. For the same reason, the difficulty in identifying and quantifying valence electrons is not limited to transition elements; it can be significant for main-group ones as well, although to a lesser extent.

In this paper, we shall present a variation of Allen's formulation that is fully in the spirit of the latter, but avoids the need to identify and count valence electrons. It is purely computational, requiring no data from any other source, and each atom is treated in exactly the same straightforward manner.

AVERAGE LOCAL IONIZATION ENERGY

Our version of Allen's approach is based upon a property that we introduced in 1990 [34], the average local ionization energy $\bar{I}(\mathbf{r})$. It is defined by

$$\bar{I}(\mathbf{r}) = \sum_i \frac{\rho_i(\mathbf{r})|\varepsilon_i|}{\rho(\mathbf{r})} \qquad (5)$$

in which $\rho_i(\mathbf{r})$ is the electronic density of the *i*th occupied atomic or molecular orbital, having energy ε_i, and

$$\rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r})\ . \qquad (6)$$

In Hartree–Fock theory, the ε_i can be viewed as reasonable approximations to the respective electronic ionization energies, some support for this being provided by Koopmans' theorem[35,36]. Accordingly, we interpret $\bar{I}(\mathbf{r})$ as the average energy needed to remove an electron at the point **r**. Our focus with Eq. (*5*) is upon the point in space, not upon a specific orbital.

It follows that the lowest values of $\bar{I}(\mathbf{r})$ indicate the locations of the least tightly bound, most reactive electrons. $\bar{I}(\mathbf{r})$ has indeed been found to be effective in predicting and correlating sites for electrophilic attack[34,37–40], as well as pK_a values[37,38,41,42]. In these applications, $\bar{I}(\mathbf{r})$ is generally computed on an outer surface of the molecule, which is taken to be (following Bader et al.[43]) an outer contour of the molecular electronic density, usually $\rho(\mathbf{r})$ = 0.001 a.u. (electrons/bohr^3). It has been shown that this contour typically encloses at least 98% of the electronic charge[43]. We have confirmed that the same trends are obtained using other outer contours, such as $\rho(\mathbf{r})$ = 0.002 a.u.[42]

In addition to being a guide to sites most reactive toward electrophiles, $\bar{I}(\mathbf{r})$ has some other interesting properties. Its radial variation in atoms delineates their shell structures[44], and it is related to local temperature[45,46], provides a means for characterizing covalent bonds[47], and is a measure of local polarizability[44,48]. A more extensive discussion of $\bar{I}(\mathbf{r})$ has been given by Murray and Politzer[49].

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For an atom, taking it to be spherically-symmetrical[50], $\bar{I}(\mathbf{r}) = \bar{I}(r)$. When it is computed on an outer surface of the atom, e.g. $\rho(r) = 0.001$ a.u., then $\bar{I}(r)$ is conceptually consistent with Allen's average ionization energy of the valence electrons, which is his definition of electronegativity[4,12,30,31].

In Table I are the $\bar{I}(r)$ on the $\rho(r) = 0.001$ a.u. surfaces of the atoms H–Kr, which we will label $\bar{I}_S(\rho = 0.001)$. They were calculated with Clementi's extended-basis-set Hartree–Fock wave functions[51], except for hydrogen, for which the exact ε_i and $\rho_i(r)$ were used. In general, the $\bar{I}_S(\rho = 0.001)$ in Table I show the trends traditionally associated with electronegativity; they in-

TABLE I
Calculated $\bar{I}(r)$, in eV, on atomic surfaces corresponding to $\rho(r) = 0.001$ a.u.[a], designated as $\bar{I}_S(\rho = 0.001)$. The radii of the surfaces, in Å, are given in parentheses

Main-group elements

H							He
13.61 (1.525)							24.98 (1.323)
Li	Be	B	C	N	O	F	Ne
5.34 (2.206)	8.42 (2.207)	11.12 (2.065)	14.30 (1.911)	17.87 (1.774)	19.48 (1.688)	21.89 (1.604)	24.97 (1.526)
Na	Mg	Al	Si	P	S	Cl	Ar
5.01 (2.251)	6.89 (2.427)	7.98 (2.437)	9.75 (2.356)	12.12 (2.239)	13.26 (2.154)	15.05 (2.062)	17.30 (1.970)
K	Ca	Ga	Ge	As	Se	Br	Kr
5.20 (2.292)	5.34 (2.728)	8.12 (2.396)	9.47 (2.383)	11.40 (2.315)	12.18 (2.269)	13.53 (2.203)	15.31 (2.133)

First transition series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
5.82 (2.668)	6.19 (2.611)	6.49 (2.562)	6.79 (2.519)	6.96 (2.479)	7.26 (2.439)	7.51 (2.398)	7.77 (2.364)	7.98 (2.330)	8.17 (2.304)

[a] Ref.[51]

crease horizontally from left to right, and decrease vertically from top to bottom. The only minor deviations from this pattern involve Ga, just after the end of the transition elements. The various problems encountered by Eq. (*3*), mentioned earlier, do not arise.

With the exception of the special case of hydrogen, the $\bar{I}_S(\rho = 0.001)$ are invariably larger in magnitude than the ε_i for the highest occupied orbital of the atom. This reflects the contributions of orbitals below the highest occupied one, that do have some electronic density at the $\rho(r) = 0.001$ a.u. surface. Thus, $\bar{I}_S(\rho = 0.001)$ by its nature, takes into account any interpenetration of shells, which can be an important problem in identifying and counting valence electrons. We have verified, however, that the innermost shell makes essentially no contribution to $\bar{I}_S(\rho = 0.001)$[44,52].

For the main-group elements through Kr, our $\bar{I}_S(\rho = 0.001)$ correlate with Allen's CE (i.e., his electronegativity), with $R^2 = 0.976$ (Fig. 1). With Pauling's and the Eq. (*3*) results (as cited by Allen[12]), $R^2 = 0.939$ and 0.921, respectively. When the first transition series is included, R^2 with Allen is 0.959 (Fig. 2), with Pauling it is 0.913, and 0.936 with Eq. (*3*). Thus our $\bar{I}_S(\rho = 0.001)$ reproduce Allen's CE very well on a relative basis – which is what is important for electronegativity. The largest discrepancy between our $\bar{I}_S(\rho = 0.001)$ and Allen's CE is for Zn, which we predict to be more electronegative than do Allen et al.; for example, our value for Zn is 2% greater than for Cu, while theirs is 14% smaller. Allen et al. assumed that

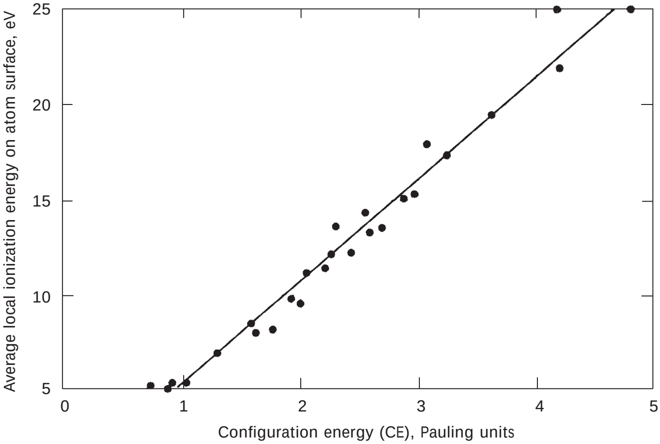

FIG. 1
Average local ionization energies on atom surfaces, $\bar{I}_S(\rho = 0.001)$, plotted against Allen's configuration energies, CE (electronegativities), for the main-group elements H–Kr. $R^2 = 0.976$

the valence shell of Zn consists of only the 4s electrons[31]. However $\bar{I}_S(\rho = 0.001)$ for Zn, 8.17 eV, is significantly higher than $|\varepsilon_i|$ for the 4s electrons, 7.96 eV, indicating a substantial contribution from the next highest subshell, the 3d.

DISCUSSION AND SUMMARY

We have proposed an alternative means of implementing Allen's definition of electronegativity. Our approach is entirely computational and quite straightforward, treating all atoms in the same prescribed manner, without the necessity of enumerating valence electrons.

The choice of atomic surface is somewhat arbitrary; however, we have shown some time ago[44] that $\bar{I}(r)$ is relatively constant within atomic shells, suggesting that other outer contours, such as $\rho(r) = 0.0015$ or 0.002 a.u., would produce the same trends. (As already mentioned, this has in fact been found to be true in the molecular context, for other properties[42].) The radii of our $\rho(r) = 0.001$ a.u. surfaces, given in Table I, confirm that all except that of K are within the outermost shells of the atoms[44].

Our Hartree–Fock results neglect relativistic factors (which are expected to become significant only considerably lower in the periodic table) and electronic correlation. However, the very good R^2 with Allen's purely spectroscopically-based values for the main-group elements suggests that inclusion of correlation would not greatly affect the patterns observed.

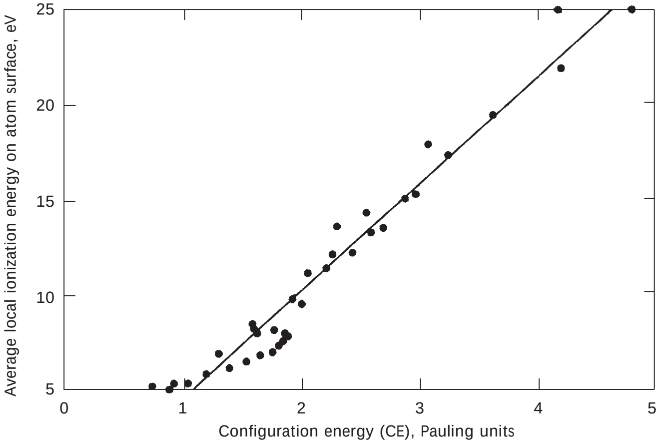

FIG. 2
Average local ionization energies on atom surfaces, $\bar{I}_S(\rho = 0.001)$, plotted against Allen's configuration energies, CE (electronegativities), for all of the elements H–Kr. $R^2 = 0.959$

In conclusion, we will digress from Allen's and our treatments of electronegativity to return to the discussion of Eq. (*3*). We wish to point out another difficulty that arises with it as a formulation of electronegativity. Conceptually, one can think in terms of a local electron affinity $\bar{A}(\mathbf{r})$ as well as a local ionization energy $\bar{I}(\mathbf{r})$, whatever may be their definitions. Indeed, Ehresmann et al. have already introduced an $\bar{A}(\mathbf{r})$ [53]. If the chemical potential is equal in magnitude to the electronegativity, and if the former is uniform throughout a molecule at equilibrium[6–8], then Eq. (*3*) implies that the sum $\bar{I}(\mathbf{r}) + \bar{A}(\mathbf{r})$ must be constant for a given molecule. Physically, however, it appears reasonable to anticipate that low $\bar{I}(\mathbf{r})$, indicating facile loss of an electron, should be associated with low $\bar{A}(\mathbf{r})$, and vice versa. This precludes their sum being constant. Thus there is a problem.

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