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377

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Average Local Ionization Energies as a Route to Intrinsic Atomic Electronegativities

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Abstract: Historically, two important approaches to the concept of electronegativity have been in terms of: (a) an atom in a molecule (e.g., Pauling) and (b) the chemical potential. An approximate form of the latter is now widely used for this purpose, although it includes a number of deviations from chemical experience. More recently, Allen introduced an atomic electronegativity scale based upon the spectroscopic average ionization energies of the valence electrons. This has gained considerable acceptance. However it does not take into account the interpenetration of valence and low-lying subshells, and it also involves some ambiguity in enumerating d valence electrons. In this paper, we analyze and characterize a formulation of relative atomic electronegativities that is conceptually the same as Allen's but avoids the aforementioned problems. It involves the property known as the average local ionization energy, $\bar{I}(\mathbf{r})$, defined as $\bar{I}(\mathbf{r}) = \sum \rho_i(\mathbf{r})|\varepsilon_i| / \rho(\mathbf{r})$, where $\rho_i(\mathbf{r})$ is the electronic density of the ith orbital, having energy ε_i, and $\rho(\mathbf{r})$ is the total electronic density. $\bar{I}(\mathbf{r})$ is interpreted as the average energy required to remove an electron at the point $\mathbf{r}$. When $\bar{I}(\mathbf{r})$ is averaged over the outer surfaces of atoms, taken to be the 0.001 au contours of their electronic densities, a chemically meaningful scale of relative atomic electronegativities is obtained. Since the summation giving $\bar{I}(\mathbf{r})$ is over all occupied orbitals, the issues of subshell interpenetration and enumeration of valence electrons do not arise. The procedure is purely computational, and all of the atoms are treated in the same straightforward manner. The results of several different Hartree−Fock and density functional methods are compared and evaluated; those produced by the Perdew−Burke−Ernzerhof functional are chemically the most realistic.

Electronegativity

The concept of electronegativity is an old one, dating back at least to Berzelius in 1835,[1,2] and it is an extremely important one. It has been used to rationalize and predict a great deal of chemical behavior. However electronegativity is not a physical observable and cannot be determined experimentally. It is an arbitrarily defined property and therefore can be—and has been—formulated in many different ways. In this paper, after briefly examining some of these approaches, we shall focus upon ionizaton energy as a pathway to electronegativity.

Pauling assigned relative electronegativities to the elements on the basis of the estimated degrees of ionic character in the heteronuclear covalent bonds that they form.[3,4] His scale remains, in updated form,[5] a standard against which others are measured. Pauling viewed electronegativity as "the power of an atom in a molecule to attract electrons to itself".[6] His focus upon polarity and upon the atom in a molecular environment is reflected in many of the treatments of electronegativity that followed, different as they might be in detail. For example, Mulliken defined the electronegativity

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χ in terms of the energetics of the atom in a molecule gaining or losing an electron:[7,8]

$$\chi = 0.5(I_{vs} + A_{vs}) \tag{1}$$

I_{vs} and A_{vs} are the valence-state ionization energy and electron affinity of the atom.

Allred and Rochow represented electronegativity as the electrostatic force exerted by the atom's effective nuclear charge upon an electron at its covalent radius.[9] Iczkowski and Margrave,[10] following earlier work by Pritchard and Sumner,[11] expressed electronegativity as $(\partial E/\partial Q)_{Q=0}$, where E and Q are the energy and the net charge of the atom *in a molecule*.

Already in 1961, the number and the diversity of electronegativity definitions was such that Iczkowski and Margrave were led to remark that "... there is some confusion as to what physical picture corresponds to the term electronegativity".[10] They pointed out that there was not even agreement as to its units, which had included energy, energy$^{1/2}$, force, force/distance, and potential. Numerous comparisons and critiques of the various formulations of electronegativity have appeared over the years.[2,12–19]

A new chapter in the electronegativity saga began in 1978. In the density functional treatment of a ground-state N-electron system having electronic density $\rho(\mathbf{r})$, the term "chemical potential" is applied to the Lagrangian multiplier μ used in minimizing the energy functional $E[\rho(\mathbf{r})]$ subject to the constraint of constant N, $N = \int \rho(\mathbf{r})d\mathbf{r}$.[16] The chemical potential can be expressed as

$$\mu = \left(\frac{\partial E[\rho]}{\partial \rho}\right)_{v(\mathbf{r})} \tag{2}$$

in which $v(\mathbf{r})$ is the external potential, which usually refers to the nuclei of the system. Parr et al. rewrote eq 2 as

$$\mu = \left(\frac{\partial E[N]}{\partial N}\right)_{v(\mathbf{r}),N_0} \tag{3}$$

where N_0 is the number of electrons in the ground state. The quantity μ was interpreted as the negative of the electronegativity χ:[20]

$$\mu = -\chi \tag{4}$$

The μ (and χ) defined by eqs 3 and 4 have been described as measuring the escaping tendency of an electron within the system.[16] This is significantly different from the conception of electronegativity held by Pauling (see above) and by many chemists.

Several points can be mentioned in support of eqs 3 and 4:

(a) It has been shown that μ must be uniform throughout a system at equilibrium.[20,21] This is consistent with Sanderson's postulate of electronegativity equalization.[22,23]

(b) Eq 2 can readily be converted (although not rigorously) to the easily evaluated form:

$$\mu = -0.5(I + A) = -\chi \tag{5}$$

where I and A are the system's ionization potential and electron affinity. This can be done by: (a) assuming that E is a quadratic function of N, (b) applying a finite-difference approximation to the derivative $(\partial E/\partial N)_{v(\mathbf{r}),N_0}$, or (c) expanding $E(N)$ in a Taylor series around N_0 and truncating after the second-order term.[24–26] The point is that eq 5 has the same form as the electronegativity expression introduced by Mulliken, eq 1.[7,8] However Mulliken's equation pertains to the valence state of the atom, and eq 5 pertains to the ground state.

(c) The electronic chemical potential as given by eq 3 is clearly analogous to the chemical potential of a component i of a macroscopic system in classical thermodynamics, which must also be uniform at equilibrium.

As was already mentioned, the approach to electronegativity represented by eqs 3 and 4 differs fundamentally from that of Pauling. The latter focuses upon the degree of ionic character of the atom in a molecule, while eqs 3 and 4 are for the ground state and can refer to a molecule as well as an atom. The differences are sufficiently important that both Pearson[27] and Allen[28,29] have suggested that Pauling's electronegativity and the chemical potential be regarded as two separate and distinct properties.

Eqs 3 and 4 have also been criticized on various grounds,[2,29,30] such as the validity of taking E to be a differentiable function of N given that N is restricted to having integral values. This issue has been discussed on a number of occasions.[16,31–33] Note that this problem does not arise with the thermodynamic chemical potential, which involves differentiating with respect to the number of moles of component i; this can certainly have nonintegral values.

If one accepts the differentiability of $E(N)$ and subsequently arrives at the approximation represented by eq 5, then it should be recognized that eq 3, and therefore eq 5, requires a constant nuclear potential. Thus the I and A in eq 5 should be the vertical values, not the adiabatic. For atoms this is of course trivial, but for molecules the effect can be significant, especially for A.[34] Furthermore, the vertical electron affinity is often negative for closed-shell molecules.[35] Then $E(N)$ must have a minimum for N in the vicinity of N_0; by eq 3, such molecules have zero or near-zero chemical potentials (as is predicted for any molecule by Thomas–Fermi theory).[16]

In practice, the requirement of constant $v(\mathbf{r})$ is frequently ignored, and I and A are taken to be the ground-state adiabatic values rather than the vertical. Thus, we are confronted with three similar formulas for χ:

$$\chi = 0.5(I_{vs} + A_{vs})_{N_0} \tag{1a}$$

$$\chi = 0.5(I_{vert} + A_{vert})_{N_0} \tag{6}$$

$$\chi = 0.5(I_{adiab} + A_{adiab})_{N_0} \tag{7}$$

Eq 1 is due to Mulliken and pertains to the atom in its valence state in the molecule. Eq 6 is based approximately upon eqs 3 and 4 and obeys the restriction that $v(\mathbf{r})$ must be constant. Eq 7 is also based approximately upon eqs 3 and

Table 1. Some Literature Electronegativity Values. Note that Pauling's are in Arbitrary Units

Atom
Eq. (7); eV[a]
Pauling; arbitrary units[b]
Configuration energies; eV[c]

Main group elements

H	Be	B	C	N	O	F	He
7.18							---
2.20							---
13.61							24.59

Li	Be	B	C	N	O	F	Ne
3.01	4.9	4.29	6.27	7.30	7.54	10.41	---
0.98	1.57	2.04	2.55	3.04	3.44	3.98	---
5.392	9.323	12.13	15.05	18.13	21.36	24.80	28.31

Na	Mg	Al	Si	P	S	Cl	Ar
2.85	3.75	3.23	4.77	5.62	6.22	8.30	---
0.93	1.31	1.61	1.90	2.19	2.58	3.16	---
5.140	7.646	9.539	11.33	13.33	15.31	16.97	19.17

K	Ca	Ga	Ge	As	Se	Br	Kr
2.42	2.2	3.2	4.6	5.3	5.89	7.59	---
0.82	1.00	1.81	2.01	2.18	2.55	2.96	---
4.340	6.113	10.39	11.80	13.08	14.34	15.88	17.54

First transition series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3.34	3.45	3.6	3.72	3.72	4.06	4.3	4.40	4.48	4.45
1.36	1.54	1.63	1.66	1.55	1.83	1.88	1.91	1.90	1.65
7.042	8.170	9.063	9.77	10.34	10.64	10.86	11.13	10.96	9.395

[a] Taken from ref 16. [b] Taken from ref 36. Note that Pauling's are in arbitrary units. [c] Taken from refs 41 and 42.

4 but disregards the limitation upon $v(\mathbf{r})$. Eqs 6 and 7 are intended to apply to molecules as well as to atoms; for the latter, they are equivalent.

Eq 7, despite the problems mentioned above, is now widely used to calculate atomic and molecular electronegativities. How meaningful are they, from a chemical standpoint? In Table 1 are the results obtained with eq 7 for the elements H−Kr, using experimental ground-state I and A.[16] In general, they follow the expected trends in the periodic table, increasing from left to right in the horizontal rows and decreasing from top to bottom in the vertical columns. However there are a number of deviations from chemical experience (and from Pauling's electronegativities,[36] also in Table 1); some of the more striking ones are Cl > O, Cl > N, Br ~ O, Br > N, H > C, H > S, H ~ N. Thus, for example, amines would not be predicted to form hydrogen bonds!

These unrealistic relative values can usually be avoided by utilizing eq 1, with valence-state ionization energies and electron affinities.[10,18,37−39] However this produces a different χ for each valence state of an atom, of which there can be several; for instance, Hinze and Jaffé list seven possible valence states for triply coordinated nitrogen.[37] There can be serious ambiguity in specifying the valence state.[38,39] An analogous problem is actually inherent in any electronegativity treatment that focuses upon the atom in a molecule, including Pauling's, since a given atom differs somewhat from one molecular environment to another. (In this context, see Allen.)[29] It can be argued that there is a need for an electronegativity definition that is intrinsic to an atom and yet serves as a realistic guide to its interactions with others.

Electronegativity and Ionization Energy

The ionization energies of ground-state atoms are considerably larger than their electron affinities, often by factors of

5−10.[36] In eq 7, it is therefore I_{adiab} that primarily governs the magnitude of χ. Sacher and Currie used a double linear regression to determine the combination of I_{adiab} and A_{adiab} that best correlates with the Allred−Rochow electronegativities and concluded that the contribution of A_{adiab} is insignificant.[40] However using I_{adiab} alone to represent χ, i.e.,

$$\chi = I_{adiab} \tag{8}$$

is also beset with problems O < N, H ~ O, H > Cl, H > Br, H > C, etc.[36]

Allen et al. have introduced an electronegativity scale that is within the context of ionization energy but does not lead to the chemically unrealistic predictions that result from eqs 7 and 8.[1,15,29,41,42] They proposed that electronegativity be defined as the "configuration energy" (CE) of the ground-state free atom. By configuration energy, they mean the average ionization energy of its valence electrons. Thus, for the main group (nontransition) elements:

$$\chi = CE = \frac{n_s \varepsilon_s + n_p \varepsilon_p}{n_s + n_p} \tag{9}$$

In eq 9, n_s and n_p are the numbers of s and p valence electrons, and ε_s and ε_p are the multiplet-averaged differences in total energy between the ground-state neutral atom and its monopositive ion resulting from the loss of a s or p electron. Spectroscopic data are used to obtain ε_s and ε_p insofar as possible; indeed Allen originally referred to the CE as "spectroscopic electronegativities."[15] The quantities ε_s and ε_p can also be approximated computationally, using the appropriate orbital energies.[15]

The configuration energy concept has been quite effective in producing chemically meaningful electronegativities (Table 1), as discussed in detail by Allen.[1,15,29] It has gained considerable acceptance over the past 20 years.[41]

The approach has also been extended to the transition series, but for these it is not as straightforward as for the main group elements.[15,42] For example, there is some arbitrariness in deciding the numbers of d electrons to be used in calculating the configuration energies.

For both the main group and the transition elements, there is furthermore the issue that interpenetration between the valence shell and lower-lying subshells is not being taken into account. This can be quite significant, even for main group elements and certainly for those in the transition series. A quantitative measure of this can be obtained by computing the exchange/repulsion interaction energy between a valence electron and one in an inner subshell and by comparing this to the expected value in the absence of interpenetration.[43] For the bromine 4p−3s, 3p combination, the ratio (actual/no penetration) is about 0.91; for the sulfur 3p−2s, 2p, it is 0.92. The effect is much greater for 3d electrons; for 3d−3s, 3p interactions, the ratio is only 0.7 to 0.8!

In an earlier preliminary study,[44] we proposed a variation of Allen's approach that is conceptually the same but that avoids the problems associated with subshell interpenetration and enumeration of d valence electrons. We now present a

detailed characterization of this procedure. It involves the average local ionization energies of the atoms.

Average Local Ionization Energy

The property known as the average local ionization energy, $\bar{I}(\mathbf{r})$, was introduced in 1990 as a measure of the energy required to remove an electron from a specific point $\mathbf{r}$ in an atom or molecule.[45] The focus is upon the point in space, not a particular orbital. $\bar{I}(\mathbf{r})$ is given by

$$\bar{I}(\mathbf{r}) = \frac{\sum_i \rho_i(\mathbf{r})|\varepsilon_i|}{\rho(\mathbf{r})} \tag{10}$$

in which $\rho_i(\mathbf{r})$ is the electronic density of orbital $\varphi_i(\mathbf{r})$, having energy ε_i, and $\rho(\mathbf{r})$ is the total electronic density. The summation is over all occupied orbitals.

The interpretation of $\bar{I}(\mathbf{r})$ as a local ionization energy is formally justifiable in Hartree−Fock theory if it is assumed that the loss of an electron from one orbital does not affect the others; some support for this is provided by Koopmans' theorem.[46,47] $\bar{I}(\mathbf{r})$ as defined by eq 10 has also been shown to be effective within the framework of Kohn−Sham density functional methodology.[48,49] The magnitudes are different from the Hartree−Fock but the relative values and trends are generally the same, which is the key point. This will be addressed again in the next section.

The lowest values of $\bar{I}(\mathbf{r})$ indicate the locations of the least tightly held, most reactive electrons. $\bar{I}(\mathbf{r})$ has indeed been found to be quite successful in predicting and ranking sites for electrophilic attack as well as pK_a values.[45,48−52] In these studies, $\bar{I}(\mathbf{r})$ is typically computed on the molecular "surface", which is usually taken to be the 0.001 au (electrons/bohr^3) contour of the electronic density $\rho(\mathbf{r})$, as proposed by Bader et al.[53]

The significance of $\bar{I}(\mathbf{r})$ is not limited to reactive behavior. It has been shown to be linked to local kinetic energy density, atomic shell structure, and local polarizability/hardness. It can be used to identify radical sites and strained C−C bonds. The various aspects of $\bar{I}(\mathbf{r})$ are discussed in detail elsewhere.[54,55]

Average Local Ionization Energy and Electronegativity

It has been demonstrated that the 0.001 au surfaces of the atoms lie within their valence shells.[56,57] Thus if we compute the average value of $\bar{I}(\mathbf{r})$ on these surfaces, we are in fact obtaining primarily the average ionization energies of their valence electrons—the same concept as Allen's configuration energies![41,42] However if an inner orbital $\varphi_i(\mathbf{r})$ has a significant presence in the valence shell, then this will be reflected in its $\rho_i(\mathbf{r})$ on the 0.001 au surface, and its contribution to $\bar{I}(\mathbf{r})$ will be included. Thus the problem of accounting for subshell interpenetration does not arise, because the summation in eq 10 is over all of the atom's electrons. Similarly, the need to enumerate d valence electrons is eliminated, again because of summing over all electrons. These two issues that are associated with Allen's approach are accordingly resolved.

We shall use $\bar{I}_{\text{S,ave}}$ to designate the average value of $\bar{I}(\mathbf{r})$ on the 0.001 au surface of an atom. In our earlier study,[44] we computed $\bar{I}_{\text{S,ave}}$ for the atoms H−Kr. Clementi's Hartree−Fock wave functions, written in terms of extended basis sets of Slater-type orbitals, were used for He−Kr;[58] hydrogen was treated exactly. The resulting $\bar{I}_{\text{S,ave}}$ correlated well with Allen's configuration energies and showed the relative values and trends expected for electronegativity, with two exceptions:[44] $\bar{I}_{\text{S,ave}}$ for hydrogen was larger than for sulfur, 13.61 vs 13.26 eV, and sulfur in turn was less than carbon, 14.30 eV. These are contrary to chemical experience, e.g., the known formation of −S−H···X hydrogen bonds.[59]

Clementi's wave functions were at the Hartree−Fock level and therefore did not include electronic correlation. Furthermore, the p and d subshells were treated as spherically symmetrical. In order to assess the effects of these factors, and to more fully characterize the $\bar{I}_{\text{S,ave}}$ approach to electronegativity, we now present the $\bar{I}_{\text{S,ave}}$ for the atoms H−Kr as computed by several different approaches:

(a) Hartree−Fock, STO: Extended basis sets of Slater-type orbitals, p and d subshells spherically symmetrical.[58] The resulting $\bar{I}_{\text{S,ave}}$ are the ones given in our earlier paper.[44]

(b) Optimized Potential Method (OPM): Exchange-only, spherically symmetrical Kohn−Sham. Formally the same energy functional as Hartree−Fock, OPM is used to obtain Kohn−Sham exchange potentials.[60,61]

(c) Hartree−Fock, 6-311G(3d, 2p).

(d) PBEPBE/6-311G(3d, 2p): Pure density functional,[62] no Hartree−Fock exchange.

(e) B3LYP/6-311G(3d, 2p): Three-parameter hybrid functional,[63,64] 20% Hartree−Fock exchange.

(f) MO62X/6-311G(3d, 2p): Hybrid meta density functional,[65,66] 54% Hartree−Fock exchange.

Procedures (d−f) are Kohn−Sham, with local exchange and correlation plus various amounts of Hartree−Fock exchange. In (c−f), the p and d subshells are not necessarily spherically symmetrical; the orbitals have the occupancies corresponding to the ground-state configurations. The wave functions for (c−f) were obtained with Gaussian 09,[67] while the $\bar{I}_{\text{S,ave}}$ were computed using the WFA surface analysis suite.[68] For the PBEPBE functional, we also investigated the addition of diffuse functions to the basis set but found these to have no significant effect.

The results, for procedures (a−f), are in Table 2. To facilitate comparisons, Table 3 lists their relative values, based upon fluorine being assigned a value of 4.00 in each case. (This was its original Pauling electronegativity.)[3,4]

Discussion

Tables 2 and 3 show that the overall variation of $\bar{I}_{\text{S,ave}}$ is as expected of electronegativity: it increases from left to right in the horizontal rows and decreases from top to bottom in the vertical columns. This is depicted graphically in Figure 1.

Looking first at the absolute values of $\bar{I}_{\text{S,ave}}$, in Table 2, it is evident that they fall into two groups: The Hartree−Fock and the OPM (exchange-only Kohn−Sham) $\bar{I}_{\text{S,ave}}$ have the larger magnitudes, the exchange plus correlation Kohn−Sham

Table 2. Unscaled $\bar{I}_{S,ave}$ Values, in eV, for Main Group Elements and First Transition Series

The six values in each cell correspond, top to bottom, to:

Atom
HF-STO, from ref. 44
OPM
HF/6-311G(3d,2p)
PBEPBE/6-311G(3d,2p)
B3LYP/6-311G(3d,2p)
M06-2X/6-311G(3d,2p)

Method	H							He
HF-STO	13.61							24.98
OPM	13.60							24.94
HF	13.60							24.95
PBEPBE	7.55							15.63
B3LYP	8.75							17.91
M06-2X	10.31							20.57

Method	Li	Be	B	C	N	O	F	Ne
HF-STO	5.34	8.42	11.12	14.30	17.87	19.48	21.89	24.97
OPM	5.34	8.40	11.33	13.45	15.94	18.57	21.45	24.56
HF	5.34	8.41	11.47	14.38	17.44	19.27	21.84	25.25
PBEPBE	3.22	5.60	6.99	8.39	9.98	10.91	12.37	14.42
B3LYP	3.65	6.31	8.07	9.79	11.63	12.84	14.59	16.94
M06-2X	4.20	7.26	9.31	11.50	13.89	15.29	17.42	20.27

Method	Na	Mg	Al	Si	P	S	Cl	Ar
HF-STO	5.01	6.89	7.98	9.75	12.12	13.26	15.05	17.30
OPM	5.01	6.87	7.88	9.08	10.71	12.59	14.66	16.89
HF	5.03	6.88	8.47	10.11	12.21	13.54	15.08	17.23
PBEPBE	3.15	4.70	5.41	6.21	7.52	8.45	9.52	11.00
B3LYP	3.60	5.29	6.08	7.02	8.48	9.57	10.80	12.46
M06-2X	4.28	6.18	7.06	8.23	9.99	11.18	12.58	14.47

Method	K	Ca	Ga	Ge	As	Se	Br	Kr
HF-STO	5.20	5.34	8.12	9.47	11.40	12.18	13.53	15.31
OPM	5.12	5.34	8.01	8.77	10.03	11.56	13.11	14.84
HF	5.12	5.34	8.94	9.88	11.40	12.32	13.67	15.34
PBEPBE	3.31	3.78	5.84	6.07	6.93	7.67	8.69	9.94
B3LYP	3.71	4.22	6.60	6.89	7.83	8.70	9.84	11.21
M06-2X	4.22	4.98	7.41	8.10	9.29	10.25	11.51	13.00

Method	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
HF-STO	5.82	6.19	6.49	6.79	6.96	7.26	7.51	7.77	7.98	8.17
OPM	5.78	6.08	6.42	6.73	7.00	7.26	7.51	7.73	7.01	8.17
HF	5.70	5.96	6.20	5.65	5.67	5.76	5.84	5.93	7.58	7.77
PBEPBE	3.99	4.22	4.38	3.56	4.66	4.76	3.77	3.83	5.33	5.45
B3LYP	4.52	4.75	4.95	4.07	5.29	4.27	4.36	5.90	5.43	6.22
M06-2X	5.25	5.48	5.67	4.88	6.00	6.13	6.26	6.40	6.57	6.72

have the smaller. This is fully consistent with earlier work.[55] The two sets of Hartree−Fock results are in general quite similar for the main group elements but differ by more than 1.0 eV for the transition atoms Cr−Ni. This suggests that symmetry, or lack thereof, is more important in the d subshell than in the p.

The fact that the OPM $\bar{I}_{S,ave}$ is overall quite close to the Hartree−Fock provides significant support for the validity of extending the definition of $\bar{I}(\mathbf{r})$, eq 10, to the Kohn−Sham framework. The OPM energy functional is formally the same as the Hartree−Fock; the two methods differ only in the exchange potential that enters the single-particle Hartree−Fock or Kohn−Sham equations. In the latter, this potential is constrained to be local (and multiplicative), whereas in the former it is nonlocal. In Hartree−Fock theory, the interpretation of $\bar{I}(\mathbf{r})$ as an average local ionization energy is partially justified by Koopmans' theorem,[46,47] but the Kohn−Sham counterpart, Janak's theorem,[69] holds only for the highest-occupied and lowest-unoccupied orbitals. The OPM and Hartree−Fock results in Table 2 show that when the energy functionals are formally identical, the $\bar{I}_{S,ave}$ obtained with the local and nonlocal potentials not only show the same trends but also have quite similar values.

It was mentioned earlier in this paper that the widely used electronegativity expression, eq 7, produces a number of chemically unrealistic results, including Cl > O, Cl > N, Br ∼ O, Br > N, H > C, H > S, and H ∼ N. (See Table 1.) Do any of these persist in the $\bar{I}_{S,ave}$ in Table 2? The Hartree−Fock procedures as well as the OPM do show H > S; the OPM also yields H > C (Table 2). Furthermore, the Hartree−Fock and OPM methods encounter a problem with C, S, and Br, predicting that C > S and C > Br. The exchange plus correlation approaches fare better, but only the PBEPBE functional is really satisfactory with respect to the relative C, S, and Br values. In particular, it is the only one of the six methods tested that shows bromine to be distinctly more electronegative than carbon.

Is it the complete absence of Hartree−Fock exchange that makes the PBEPBE functional more effective than the B3LYP and the M06-2X for present purposes? To test this possibility, we computed $\bar{I}_{S,ave}$ for a series of atoms (H, C, N, O, S, Cl, Br) using the M06-L functional,[65,66] which also involves no Hartree−Fock exchange, and the 6-311G(3d,2p) basis set. The results for this group of atoms are overall realistic, and $\bar{I}_{S,ave}$ is indeed larger for bromine than for carbon, although by relatively little, 8.99 vs 8.82 eV.

Table 3. Scaled $\bar{I}_{S,ave}$ Values for Main Group Elements and First Transition Series[a]

Atom
HF-STO
OPM
HF/6-311G(3d,2p)
PBEPBE/6-311G(3d,2p)
B3LYP/6-311G(3d,2p)
M06-2X/6-311G(3d,2p)

H							He
2.49							4.57
2.54							4.65
2.49							4.57
2.44							5.06
2.40							4.91
2.37							4.72

Li	Be	B	C	N	O	F	Ne
0.98	1.54	2.03	2.61	3.27	3.56	4.00	4.56
1.00	1.57	2.11	2.51	2.97	3.46	4.00	4.58
0.98	1.54	2.10	2.64	3.20	3.53	4.00	4.63
1.04	1.81	2.26	2.71	3.23	3.53	4.00	4.66
1.00	1.73	2.21	2.68	3.19	3.52	4.00	4.65
0.97	1.67	2.14	2.64	3.19	3.51	4.00	4.65

Na	Mg	Al	Si	P	S	Cl	Ar
0.92	1.26	1.46	1.78	2.22	2.42	2.75	3.16
0.94	1.28	1.47	1.69	2.00	2.35	2.73	3.15
0.92	1.26	1.55	1.85	2.24	2.48	2.76	3.16
1.02	1.52	1.75	2.01	2.43	2.73	3.08	3.56
0.99	1.45	1.67	1.93	2.32	2.63	2.96	3.42
0.98	1.42	1.62	1.89	2.29	2.57	2.89	3.32

K	Ca	Ga	Ge	As	Se	Br	Kr
0.95	0.98	1.48	1.73	2.08	2.23	2.47	2.80
0.96	1.00	1.50	1.64	1.87	2.16	2.45	2.77
0.94	0.98	1.64	1.81	2.09	2.26	2.51	2.81
1.07	1.22	1.89	1.96	2.24	2.48	2.81	3.22
1.02	1.16	1.81	1.89	2.15	2.39	2.70	3.07
0.97	1.14	1.70	1.86	2.13	2.35	2.64	2.98

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1.06	1.13	1.19	1.24	1.27	1.33	1.37	1.42	1.46	1.49
1.08	1.13	1.20	1.26	1.31	1.35	1.40	1.44	1.31	1.52
1.05	1.09	1.14	1.04	1.04	1.06	1.07	1.09	1.39	1.42
1.29	1.37	1.42	1.15	1.51	1.54	1.22	1.24	1.72	1.76
1.24	1.30	1.36	1.12	1.45	1.17	1.20	1.62	1.49	1.71
1.21	1.26	1.30	1.12	1.38	1.41	1.44	1.47	1.51	1.54

[a] Fluorine is assigned 4.00.
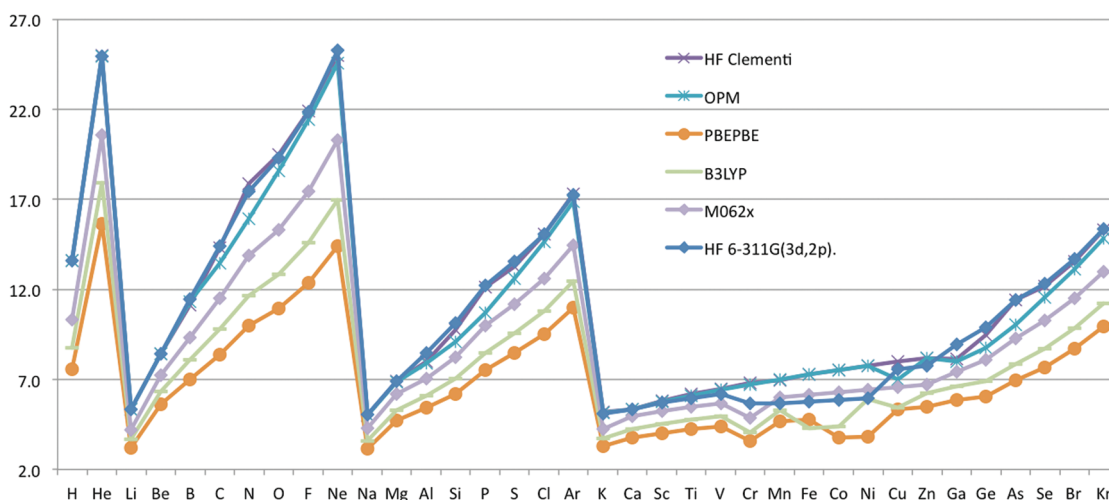
Figure 1. Computed unscaled $\bar{I}_{S,ave}$ values, in eV, for main group elements and first transition series.

Scaling the $\bar{I}_{S,ave}$ so that the value for fluorine is exactly 4.00 by each method considerably diminishes the differences between the six sets of results (Table 3). The scaled PBEPBE, B3LYP, and M06-2X $\bar{I}_{S,ave}$ of the main group atoms usually differ very little. The method dependence is greater for the first transition series, but it is not really clear what should be expected. Perhaps the key points for the transition elements are that the magnitudes tend to be rather small and to vary relatively little over the whole series (about 0.4), for each of the three procedures.

The PBEPBE functional gives the lowest results of all of the methods, followed by the B3LYP, and the M06-2X. This

reflects the amount of Hartree−Fock nonlocal exchange in each of these functionals: 0% for PBEPBE, 20% for B3LYP, and 54% for M06-2X.

Summary

The average local ionization energies on the 0.001 au surfaces of the ground-state atoms, as computed with the PBEPBE exchange plus correlation density functional, provide an effective measure of their relative electronegativities. This is an alternative means of implementing the concept introduced by Allen et al.[1,15,29,41,42] This approach is purely computational and treats all atoms in exactly the same straightforward manner. The problem of accounting for interpenetration between valence and lower-lying subshells does not arise nor does the need to enumerate d valence electrons.

It should be noted that we are addressing electronegativity, not the chemical potential. We do not necessarily assume the validity of eq 4, $\mu = -\chi$. As mentioned earlier, Pearson[27] and Allen[28,29] questioned this already some years ago. We agree with Allen that electronegativity should be an intrinsic property of a ground-state atom[29] as opposed to an atom in a molecule or in some valence state, given the ambiguity that these entail.

If we do not require that $\mu = -\chi$, then the evidence[20,21] that μ must be uniform throughout a system at equilibrium is not relevant for χ. While the notion of electronegativity equalization may be appealing, it also seems counter to chemical experience, as pointed out by Allen[29] and by Hinze.[2] Atoms do retain much of their identities in molecules; this can be confirmed by looking at plots of molecular electronic densities.[70,71] The rearrangements of electrons that accompany the formation of a molecule are very subtle, as can be seen in density difference plots.[70−72] The free atom electronegativities provide us with some initial qualitative guidelines concerning these rearrangements.

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