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Electronegativity: Atomic Charge and Core Ionization Energies

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The atomic charges derived from the extended electronegativity function, which includes the influence of bonding, were examined. These atomic charges were found to conform to an intuitive notion of atomic charge at the intermolecular, interatomic, and electronic levels. In addition, a new model for the core ionization energy has been developed. This new model for the core ionization energy explicitly considers the various relaxation processes, and relates the core ionization energy to the electronegativity function and the atomic charges.

Introduction

A great deal has been written about electronegativity, since Pauling proposed the first modern definition nearly seventy years ago.[1] The continued importance of electronegativity arises from the fact that it is an atomic property which determines the integrated electron density (atomic charge) in a molecule. The continuing interest in electronegativity is a result of its intrinsic importance and of the difficulty in devising an adequate formulation in the form of an electronegativity function.[2,3] In addition to its intrinsic importance as an atomic property, a proper electronegativity and electronegativity function, even with the ready availability of semiempirical and ab initio molecular orbital results, remains of practical importance.[3−6]

Pauling's original definition ties electronegativity intimately to atomic charge.[1] According to this definition, essential to a proper electronegativity is that it be an actual atomic property(s), and that it be sufficient to determine atomic charges in a molecule. Reasoning that a proper electronegativity function should be embedded within the Hartee−Fock model, an extended electronegativity function (χ_i) has been formulated.[7−9] For an atom, *i*, the absolute electronegativity (a_i) and chemical hardness (b_i), which are part of the Ickowski−Margrave formulation, are major components of this extended electronegativity function (eq 1).[10]

$$\chi_i = a_i + \frac{1}{2}r_i + b_i q_i \tag{1}$$

In addition, the extended electronegativity function contains a connectivity potential (r_i), which incorporates the influence of bond formation on the electronegativity. The Sanderson Principle requires that upon the formation of a stable molecule all of the electronegativities equalize to a single global electronegativity, χ^*.[11] This being the case, rearranging eq 1 and solving for the atomic charge yields

$$q_i = \frac{\chi^* - a_i - \frac{1}{2}r_i}{b_i} \tag{2}$$

The global electronegativity derives from the global absolute electronegativity, a^*, and the global absolute hardness, b^*, and is a function of the molecular charge. These can be evaluated from the absolute electronegativities and the absolute hardnesses of the constituent atoms. The details are provided in previous communications.[2,7−9]

The concept of an atomic charge is artificial in the sense that the atomic charge itself is not an experimentally measurable quantity. This notwithstanding the influence of atomic charge on the chemical and physical properties of molecules is pervasive. Electronegativity methods aside, atomic charges may be extracted from the molecular wave functions via a number of techniques.[12−14] In addition, there have been a variety of indirect experimental measures or indicators of atomic charge.

It is well-known that atomic charges obtained using these methodologies agree poorly among themselves, and may differ even in sign and by as much as an order of magnitude. Yet in a sense these are all valid atomic charges. This notwithstanding, there should exist a set of atomic charges which corresponds to a simple intuitive notion of a molecule composed of identifiable atoms, each of which carries a charge. This communication is concerned with such a set of atomic charges.

Background

The derivation and utilization of the extended electronegativity function have been discussed in detail elsewhere.[7−9] A few special topics relevant to this communication are discussed in more detail below.

Connectivity Potentials. The persistence in the derivation of the extended electronegativity function of terms derived from the bonds in the molecule point to the shortcomings of the earlier formulations. These bonding terms in the electronegativity function have the form $H_{\mathrm{kl}}/S_{\mathrm{kl}}$ where H_{kl} and S_{kl} are, respectively, the resonance and overlap integrals between orbitals k and l. These give rise to the atomic connectivity potentials, r_i[8]:

$$r_i = \frac{1}{Q_i}\sum_{j}^{B_i} r_{ij} = \frac{1}{Q_i}\sum_{l}^{O_i}\frac{H_{\mathrm{kl}}}{S_{kl}} \tag{3}$$

Here Q_i is the number of orbitals utilized by atom *i*, B_i is number of bonds to atom *i*, and O_i is the number of orbitals used to form bonds to *i*. In the second summation k is the orbital on *i* interacting with l. When the resonance integral is approximated by the Wolfberg−Helmholtz approximation,[15] the atomic con-

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nectivity potential becomes

$$r_i = \frac{-k}{2Q_i}\sum_j^{B_i}(a_i + a_j) \tag{4}$$

where k is an adjustable parameter. The use of the absolute electronegativity in the Wolfberg–Helmholtz equation has been discussed previously.[15]

Charging Energies. The atomic charging energy of an atom in a molecule, E^C, is the energy required to bring the atom to the charge that it carries in the molecule. To a very good approximation this is given by the quadratic energy charge relationship. This is given for atom i below:

$$E_i^C(q) = a_i q_i + \frac{1}{2}b_i q_i^2 \tag{5}$$

During a chemical or physical change which involves the transfer of charge, each atom in the molecule must undergo a change in its atomic charge. For each atom there is associated with the change in the atomic charge a change in its energy. This change in energy is its change in atomic charging energy, ΔE^C.[8,9] In a molecule the change in charging energy is the sum of the changes in atomic charging energy for each atom.

Core Binding Energies of Atoms. Among the most successful and widely investigated experimental measures or indicators of atomic charge has been the 1s core binding energies. Several models have been developed which establish the relationship between the core binding energies and the atomic charges on atoms in molecules.[16–18] None of these has seemed to be entirely satisfactory, however. An alternative model for the relationship between core binding energies and atomic charges can be developed from Slater's model for the one-electron energies.[20]

In the Slater model the dependence of the 1s core ionization energy on atomic charge resides in the electronic relaxation of each of the remaining electrons. This relaxation is simply the decrease in their one-electron energies resulting from being deshielded during the ionization. In this model the 1s core ionization energy for an atom, A, is thus

$$\mathrm{IE}_{1s} = E(\mathrm{A}^{+}*) - E(\mathrm{A}) = -\epsilon_{1s} + \Delta E^{\mathrm{core}*} + n_s\,\Delta\epsilon_s + n_p\,\Delta\epsilon_p \tag{6}$$

where the * indicates that a 1s electron has been ionized, $\Delta E^{\mathrm{core}*}$ is the relaxation energy for the core electrons (less the ionized electron), and the $\Delta\epsilon$'s are the relaxation energies of individual valence electrons. The number of s and p valence electrons are n_s and n_p, respectively. The one-electron energies, ϵ_i, are determined from the effective nuclear charges experienced by each electron, Z_i*:

$$\epsilon_i = -1312\ \mathrm{kJ/mol}\,\frac{(Z - C_i)^2}{n_i^2} = -1312\ \mathrm{kJ/mol}\,\frac{Z_i{*}^2}{n_i^2} \tag{7}$$

where C is the sum of the shielding constants for each of the remaining electrons. The total electronic energy is then the sum of these one-electron energies.

What is particularly important is that for a given element ϵ_{1s}, $\Delta E^{\mathrm{core}*}$, $\Delta\epsilon_s$, and $\Delta\epsilon_p$ are independent of the atomic charge, and can be readily evaluated using eq 7 for the core ionized and nonionized atoms using a very simple procedure.[22] If the core ionization energies relative to the neutral atom, $\Delta\mathrm{IE}_{1s}$, are of interest, then eq 6 becomes

$$\Delta\mathrm{IE}_{1s} = n_s\,\Delta\epsilon_s + n_p\,\Delta\epsilon_p \tag{8}$$

because ϵ_{1s} and $\Delta E^{\mathrm{core}*}$ are equal for the neutral and core ionized atom.

Molecular Relaxation Energy. If an isolated atom were being ionized eqs 6 and 8 would be sufficient. However, when a core ionization occurs on an atom which is part of a molecule, the process is complicated by the response of the remaining atoms to the ionization. In a core ionization the deshielding of the ionizing atom's electrons increases the effective nuclear charge experienced by its valence electrons, which in turn increases the atom's electronegativity and its hardness. Because the electronegativity of the core ionized atom now exceeds the global electronegativity, there must be a redistribution of the electron density in order to restore electronegativity equalization. The associated change in energy is part of the 1s core ionization energy, and is called the molecular relaxation energy. Because this relaxation process results in little change in bonding, this relaxation energy can be approximated quite well as the change in charging energy for the redistribution of the molecule's electron density.

Equation 5 may be used provided that the atomic charge of each atom is known for both the core ionized and un-ionized molecules. These may be obtained using eq 2. Whereas the absolute electronegativities and absolute hardnesses have been determined for most elements,[23,24] they are not available for core ionized atoms. The equivalent core approximation may be used. In the equivalent core approximation,[25] the nucleus and K shell of the core ionized atom is approximated as the nucleus and K shell of the next heaviest element. Thus if there are A atoms in the molecule, the molecular relaxation energy, $\Delta E^{\mathrm{molec}}$, is thus

$$\Delta E^{\mathrm{molec}} = E^C(\mathrm{M}^{+}*) - E^C(\mathrm{M}) = \sum_i^A E^C{}_i(\mathrm{M}^{+}*) - \sum_i^A E^C{}_i(\mathrm{M}) \tag{9}$$

where the summation is over all of the atoms in the molecule.

Computations

The energies arising from the Coulombic interactions between a metal ion and its octahedrally coordinated water molecules are computed from Coulomb's law. The nuclear coordinates are generated using a SYBYL molecular mechanics force field,[25] which yielded a bonded hydrogen–oxygen distance of 1.07 angstroms. The metal ion–oxygen distances were set at the literature vaules[26] (Table 1). The charge of the metal ion was taken to be unity, and that of the hydrogen and oxygen were 0.263 and −0.526, respectively. These were obtained from the extended electronegativity function.

The revised rules for the computation of the effective nuclear charges experienced by an atom's electrons may be found elsewhere.[16,21] The shielding constants were optimized using the simplex method[32] to determine the shielding constants which yielded the best least-squares fit between the computed and experimental core ionization energies for the elements beryllium through argon. The experimental core ionization energies were taken from the literature.[27–31] The core ionization energy optimized shielding constants may be found in Table 2. Only three shielding constants are required to compute the core ionization energies for all of these elements, and only two are required for the relative core ionization energies. The relaxation energy for an individual electron, $\Delta\epsilon$ (eq 8), was computed by taking the difference in its one-electron energy in the atom and

TABLE 1: Metal−Water Interaction Energies

ion	metal−oxygen distance[a,c]	experimental interaction enthalpy[b,d]	computed Coulombic energies[b]	solvation enthalpy[b,e]
lithium(+1)	2.08	−514	−435	−459
sodium(+1)	2.35	−403	−364	−444
potassium(+1)	2.79	−333	−278	−360

[a] Metal−oxygen distances in angstroms. [b] Energies in kJ/mol. [c] Taken from ref 25. [d] Taken from ref 32. [e] Taken from ref 33.

TABLE 2: Slater's Shielding Constants Optimized for the Computation of 1s Core Ionization Energies

description	shielding constant
shielding of two electrons in same shell	0.3926
shielding of s electron by an electron in next inner shell	0.6356
shielding of p electron by an electron in next inner shell	0.9418

its core ionized cation. The reference molecules for carbon, nitrogen, and oxygen are, respectively, methane, dinitrogen, and dioxygen.

The details for the computation of charging energies and atomic charges have been reported previously.[8,9] The molecular relaxation energy was taken to be the difference between the charging energy of the molecule and its core ionized cation (eq 9). The charging energies for a core ionized molecule was that of its cation, where the absolute electronegativity and the absolute hardness of the core ionized atom were replaced by those of the next heaviest element. The absolute electronegativities and absolute hardnesses are those developed by Hinze and Jaffe.[23,24]

Results and Discussion

Because electronegativity is the property of atoms which determines the electron distribution in a molecule, it has a profound influence on the chemical and physical properties of molecules. The extended electronegativity function (eqs 1 and 2) is quite satisfactory in its simplicity and its ability to provide atomic charges. These atomic charges, however, differ considerably from those obtained via various more sophisticated and more complex quantum mechanical computations. The validity of each of these types of atomic charges notwithstanding, a unique set of atomic charges corresponding to the intuitive charges suggested by Pauling's definition should exist. These unique atomic charges would be the charges carried by identifiable atoms in a molecule, and would manifest themselves via the various properties of these atoms. Previous work suggests that the charges yielded by the extended electronegativity function are such atomic charges.

Charging Energies. One of the key presuppositions inherent in an intuitive atomic charge is the persistence of atoms in molecules. This being the case, the atom in the molecule would in many ways behave very much as the isolated atom would, if it carried a charge equal to the atomic charge. It is well-known that the energy of an isolated atom can be approximated quite well as a quadratic function of its charge. Thus the intuitive atomic charges should yield this energy for each atom in the molecule. That portion of the molecule's electronic energy arising from the charges that its atoms carry has been called its charging energy (approximated by eq 5). There are a variety of physical and chemical processes for which the change in charging energy dominates the energetics or the relative energetics of the process. A number of these have been explored in detail in previous communications.[2,7−9] The results suggest that for processes in which the charging energy is expected to dominate, the atomic charges extracted from the extended electronegativity function yield charging energies in excellent agreement with experimental results. Thus it would appear that the atomic charges extracted from the extended electronegativity function are able to yield excellent electronic energies for each atom in the molecule, and are thus excellent candidates for the intuitive atomic charges.

Solvation Energies. Like ions, partially charged atoms in molecules interact electrostatically with partially charged atoms in nearby molecules. The correlation of atomic charges extracted from the extended electronegativity function with the acid and base properties of molecules has been discussed previously.[8] In the case of the intermolecular Coulombic interactions between molecules, the interaction can be reasonably modeled as the electrostatic interactions of point charges located at the nuclei of the participating atoms. The intuitive atomic charges should correspond to these point charges. The solvation of ions of very low electronegativity, such as lithium, sodium and potassium, should be dominated by such Coulombic interactions. One way to model such interactions is as the electrostatic interactions of the atomic charges on the ion and on each of the atoms of the solvent. These consist of the attractions and repulsions among the atoms of the ligand and the metal. For an ion which has six water molecules arranged octahedrally about it, there are 154 nonbonded, noncovalent, solute−solvent, solvent−solvent electrostatic interactions. The experimental enthalpies for binding six water molecules,[33] the corresponding computed Coulombic energies, and the solvation enthalpies[34] for lithium, sodium, and potassium may be found in Table 1.

In that the Coulombic interactions between a solvent and an ion can only account for a portion of the total interaction,[34] the computed Coulombic energies are expected to be less than the experimental interaction energies. This is, in fact, the case. The computed energies are 83−90% of the total interaction energies for binding six water molecules. The actual solvation energies derive from many additional interactions, and are thus significantly larger. Although the Coulombic model is very simplistic, the agreement with experiment is quite good. What is most significant, however, is that the charges extracted from the extended electronegativity function are quite appropriate for the nonbonded electrostatic interactions between atoms and ions.

Core Electron Ionization Energy. Of the experimental techniques which indicate atomic charge, core−electron photoelectron spectroscopy would seem to be the most direct and least ambiguous indicator of atomic charge. What has been lacking is an entirely suitable model which would permit the extraction of atomic charges from the core photoelectron spectra.

A number of models have been proposed which seek to establish a relationship between the core ionization energies of atoms and various atomic properties including atomic charge. The models include ab initio and semiempirical molecular orbital models, charge and valence potential models, and thermochemically based models. These have been reviewed and evaluated by a number of investigators. The model which has been developed here partitions the core ionization energy into the energy acquired by the ionized electron, the relaxation energy of the remaining nonvalence electrons of the ionized atom, the relaxation energy of the valence electrons of the ionized atom, and the relaxation energy of the valence electrons of all of the other atoms in the molecule. In the Slater model the one-electron energy of a 1s electron and the relaxation energy of the core electrons are independent of the number of valence electrons, and hence the atomic charge. Thus, for the relative core ionization energies (relative to the neutral atom) the first two partitionings cancel. As a result the relative core ionization energies are derived from only the valence electron and molecular relaxation energies. Combining eqs 8 and 9, yields

$$\Delta \mathrm{IE}_{1\mathrm{s}}^{\mathrm{rel}} = n_\mathrm{s}\,\Delta\epsilon_\mathrm{s} + n_p\,\Delta\epsilon_\mathrm{p} + \sum_i^A E^\mathrm{C}{}_i(\mathrm{M}^+*) - \sum_i^A E^\mathrm{c}{}_i(\mathrm{M}) - \Delta \mathrm{IE}_{1\mathrm{s}}(\mathrm{ref}) \quad (10)$$

Here the computed core ionization energy of the reference molecule for the element of interest has been subtracted. The charging energies are implicit functions of the atomic charges of all of the atoms and of the electronegativity function. It will turn out that its contribution is quite small. However, n_s and n_p are very much explicit functions of the charge on the core ionized atom. This constitutes the functional relationship between atomic charge and the core ionization energy.

To evaluate $\Delta\epsilon_\mathrm{s}$ and $\Delta\epsilon_\mathrm{p}$ (for eq 7), effective nuclear charges are required for the valence electrons. Recently Slater's shielding constants have been expanded and reevaluated to yield four shielding constants for the light elements (through argon) and four additional constants are needed to include the elements through xenon.[16,21] In this form Slater's model sucessfully estimates the energies for the first, second and third valence electron ionizations. It reproduces the energies for sequential ionizations of the same atom. It provides very viable estimates of promotion energies and estimates of the energies for electronic optical excitations. Thus the model appears to be both versatile and reliable.

Of particular interest here is that using only three of these parameters, the 1s core ionization energies for atoms of the elements lithium through argon can be estimated with an average absolute error of only 2.3%. Although this ability to yield 1s core ionization energies is impressive, these shielding constants were optimized for the first ionization of the valence electrons.[16,21] However, when these constants are optimized for the 1s core ionizations, the average absolute error drops to only 0.27% for the elements beryllium through argon (Lithium yields an exceptionally large error). The model thus provides a viable means for the computation of the core ionization energies for the isolated atoms of elements through argon (eqs 7 and 8). The core ionization optimized shielding constants may be found in Table 2.

Using the shielding constants which were optimized for the core ionization of isolated atoms and the absolute electronegativities and hardnesses, the relative core ionization energies were computed for fifty core ionizations of carbon, nitrogen, and oxygen. The Wolfsberg Helmholtz k was set to 1.75 which is the value set by Wolfsberg based on spectroscopic data. The molecular relaxation makes only a small contribution to the core ionization energy. For example when the 1s electron of the α carbon of acetic acid is ionized, the ionized electron acquires 427.62 eV, the valence electrons lose −81.15 eV as a result of the concomitant deshielding and the molecular relaxation energy is −0.30 eV. Thus, the relative core ionization energy is dominated by the valence electron relaxation energy.

TABLE 3: The Relative Experimental 1s Core Ionization Energies for a Series of Simple Molecules[a]

molecule	relative core ionization energy (eV)				
molecule	exptl	computed ($k = 1.89$)	error[e]	computed ($k = 1.75$)	source
$\mathit{C}H_3CH_3$	−0.2	0.21	−0.41	0.21	*b*
$\mathit{C}H_2CH_2$	0.1	0.28	−0.17	0.26	*b*
CH_4	0.0	0.0	0.00	0.0	*b*
$\mathit{C}H_3CH_2OH$	0.2	0.41	−0.21	0.42	*b*
$\mathit{C}HCH$	0.4	0.38	0.02	0.37	*b*
$\mathit{C}H_3COCH_3$	0.5	0.76	−0.26	0.73	*c*
$\mathit{C}H_3CHO$	0.6	0.88	−0.28	0.87	*b*
$\mathit{C}H_3CO_2H$	0.7	1.03	−0.3	1.05	*b*
$CH_3\mathit{C}H_2OH$	1.6	1.02	0.58	0.98	*b*
$\mathit{C}H_3OH$	1.6	0.93	0.67	0.93	*b*
$\mathit{C}H_3CN$	2.6	0.55	2.05	0.56	*b*
$H\mathit{C}N$	2.6	1.92	0.68	1.91	*b*
$\mathit{C}H_3F$	2.8	2.17	0.63	2.08	*b*
$CH_3\mathit{C}N$	2.9	1.64	1.26	1.56	*b*
$CH_3\mathit{C}OCH_3$	3.1	1.93	1.17	1.82	*c*
$H_2\mathit{C}O$	3.2	2.50	0.7	2.42	*b*
$CH_3\mathit{C}HO$	3.2	2.11	1.09	2.00	*b*
$CH_3\mathit{C}O_2H$	4.7	2.97	1.73	2.85	*b*
$H\mathit{C}O_2H$	5.0	3.50	1.50	3.42	*b*
$\mathit{C}O$	5.2	3.39	1.81	3.39	*b*
$\mathit{C}H_2F_2$	5.6	4.69	0.91	4.52	*b*
$\mathit{C}O_2$	6.8	6.83	−0.03	6.67	*b*
$\mathit{C}F_4$	11.0	11.44	−0.44	11.07	*b*
$(\mathit{C}H_3)_3N$	−5.2	−3.27	−1.93	−3.27	*b*
$(\mathit{C}H_3)_2NH$	−5.0	−3.31	−1.69	−3.14	*d*
$\mathit{C}H_3NH_2$	−4.8	−3.15	−1.49	−3.16	*d*
$\mathit{N}H_3$	−4.3	−3.69	−0.69	−3.63	*b*
$\mathit{N}H_2NH_2$	−3.8	−3.05	−0.75	−3.02	*d*
$CH_3C\mathit{N}$	−3.8	−2.91	−0.89	−2.91	*b*
$HC\mathit{N}$	−3.4	−2.56	−0.84	−2.54	*d*
$\mathit{N}NO$	−1.4	−0.60	−0.80	−0.51	*b*
N_2	0.0	0.0	0	0.0	*b*
$\mathit{N}O$	0.8	1.42	−0.62	1.42	*b,d*
$N\mathit{N}O$	2.6	3.27	−0.67	3.10	*b*
$\mathit{N}O_2$	3.0	3.74	−0.74	3.62	*b,d*
$O\mathit{N}F_3$	7.1	7.85	−0.75	7.52	*d*
$CH_3CH\mathit{O}$	−5.5	−5.66	0.16	−5.62	*b*
$H_2C\mathit{O}$	−5.5	−5.28	−0.22	−5.23	*b*
$CH_3C(\mathit{O})OH$	−4.9	−4.98	0.08	−4.99	*b*
$CH_3CH_2\mathit{O}H$	−4.5	−5.51	1.01	−5.52	*b*
$HC(O)\mathit{O}H$	−4.3	−4.62	0.32	−4.91	*b*
$CH_3\mathit{O}H$	−4.2	−5.48	1.28	−5.47	*b*
$CH_3C\mathit{O}CH_3$	−4.1	−5.80	1.7	−5.76	*c*
$H_2\mathit{O}$	−3.4	−5.94	2.54	−5.84	*b*
$CH_3C(O)\mathit{O}H$	−3.1	−5.42	2.32	−5.40	*b*
$HC(\mathit{O})OH$	−2.7	−4.98	2.28	−4.59	*b*
$C\mathit{O}_2$	−2.3	−3.14	0.84	−3.09	*b*
$NN\mathit{O}$	−1.9	−2.57	0.67	−2.54	*b*
$C\mathit{O}$	−1.0	−3.00	2.00	−3.00	*b*
O_2	0.0	0.0	0.00	0.0	*b*

[a] The core ionization energies are relative to CH_4 for carbon, N_2 for nitrogen, and O_2 for oxygen. The core ionized atoms are underlined. [b] Experimental values taken from ref 27. [c] Experimental values taken from ref 28. [d] Experimental values taken from ref 29. [e] The difference between the experimental and computed (k = 1.89) relative core ionization energies.

The experimental relative core ionization energies have been plotted against the computed relative core ionization energies in figure one. In Table 3 may be found the experimental relative core ionization energies and the relative core ionization energies computed using the literature value for k (1.75) and the optimized values for k (1.89). The correlation coefficient for both plots is 0.963 which is quite reasonable. All of the points are clustered about a line of unit slope and zero intercept. The slope of the least-squares line is 0.928 and the intercept is −0.292. The experimental ionization energies would seem to have an uncertainty on the order of tenths of an electronvolt which cannot completely account for the scatter indicated in Figure 1 and Table 3. Part of the scatter certainly arises from the limitations of eq 2. This notwithstanding, the atomic charges extracted from the extended electronegativity function are able to yield quite reasonable estimates of core ionization energies. Although the correlations are not completely satisfactory, the new core ionization model does represent an improvement over previous models. It considers each interaction in more explicit

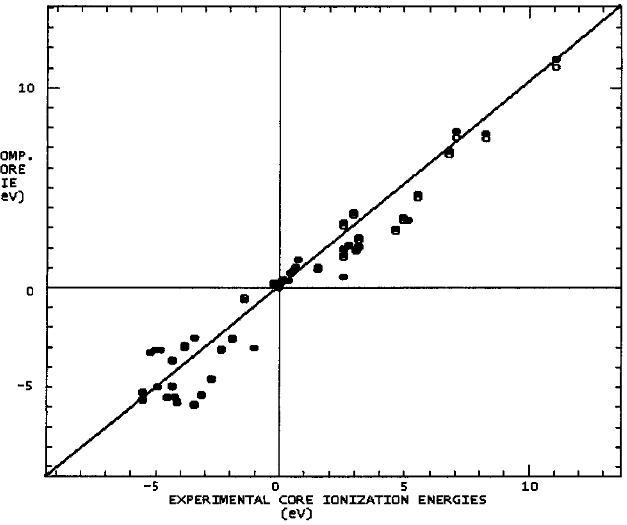

Figure 1. Plot of the experimental versus the computed relative 1s core ionization energies for the core ionizations of carbon, nitrogen, and oxygen. The value of the Wolfsberg−Helmholtz *k* was 1.75 (●) and 1.89 (○).

detail, and this model has not been parametrized to fit the atomic charges to the core ionization data for molecules.

The value assigned to *k* has an influence on both the absolute and relative values of the atomic charges. When *k* is allowed to vary from 0 to 3.0 there is a single minimum in the plot of *k* against the sum of the square error of the experimental and computed core ionization energies. The minimum was quite shallow, and occurs at 1.89. In Figure 1 the open circles indicate the points derived from setting *k* equal to 1.89. With few exceptions these points coincide or overlap with the points derived from setting *k* equal to 1.75. The correlation coefficient resulting from both values of *k* is 0.963, but the slope increases slightly to 0.952 and the intercept increases slightly to −0.252 for $k = 1.89$. Changing *k* from 1.75 to 1.89 appears not to significantly improve the correlation, and changes in the atomic charges would be within the level of confidence for these atomic charges. It would thus seem reasonable to retain the more general value of *k* established by Wolfsberg and Helmholtz.

In Closing

The simplest and most intuitive concept of an atomic charge would require that it be a property of an atom which persists in a molecule, and that atom behaves as if the atomic charge were the charge on that atom. This being the case, a set of atomic charges which satisfies this criterion must do so over the full range of situations in which the atom's charge influences its behavior. The influence of the atomic charge extracted from the extended electronegativity function has been examined for the influence of atomic charges on the intermolecular interactions among atoms and ions, the influence of atomic charges on the energetics of charge transfer in molecules, and the influence of an atom's charge on its own electrons. The atomic charges which have been extracted from the extended electronegativity function are quite successful in each of these domains. In addition, a new model has been developed which relates the atomic charge to the 1s core ionization energy of atoms in molecules. The extended electronegativity function is a very simple model from which quite reasonable atomic charges and energy information can be obtained.

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