

$A_u^-$  state energies relative to those of the  $B_u^+$  states and thus erroneously places each  $A_g^-$  state below the corresponding  $B_u^+$  state. We propose that in all polyenes, the semiempirical calculations similarly underestimate the  $A_g^-$  state energies relative to those of  $B_u^+$  states. But, since the energy of the  $A_g^-$  state decreases faster than that of the  $B_u^+$  state as the polyene chain increases,<sup>15,16</sup> we predict that at some point, the initially higher  $A_g^-$  state will fall below the  $B_u^+$  state. This prediction is confirmed by the experimental observations.<sup>16</sup> One should, thus, ask at what chain length does the  $A_g^-$  state fall below the  $B_u^+$  state in isolated polyenes? The only vapor phase system in which the  $A_g^-$  state is experimentally observed to lie below the  $B_u^+$  state is diphenylbutadiene.<sup>23</sup> Since the chain length equivalent of a phenyl group is estimated to be 1.5 double bonds,<sup>24</sup> the diphenylbutadiene result suggests that the  $A_g^-$  state falls below the  $B_u^+$  state in isolated polyenes containing 5 or more conjugated double bonds. Thus, we predict that for isolated molecules, decapentaene is the smallest polyene in which the  $A_g^-$  state lies below the  $B_u^+$  state. Decapentaene is thus the most propitious candidate for future investigations.

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## Conclusion

The main conclusions of this investigation are contained in Table I and Figure 3. The transition energies of the higher valence states of each multiplicity are different in *cis*- and *trans*-hexatrienes, suggesting that the photochemical properties of the two isomers should also differ. The correlation between the experimental transition energies of *trans*-hexatriene and the calculated values suggests that although we are unable to see the  $A_g^-$  valence state, it is above the  $B_u^+$  state in this molecule. In addition, our results indicate that current semiempirical calculations of polyenes underestimate the transition energies to covalent states and that the  $A_g^-$  state does not descend below the  $B_u^+$  state for polyenes of less than five double bonds.

**Note Added in Proof.** An analogous investigation of *trans*-octatetraene has recently appeared.<sup>25</sup>

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**Registry No.** *cis*-Hexatriene, 2612-46-6; *trans*-hexatriene, 821-07-8.

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## Electronegativity Equalization: Application and Parametrization

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**Abstract:** An analysis is made of three different formalisms which use electronegativity equalization principles for the calculation of partial charges of atoms in molecules. Various scales can be used with each of these formalisms provided that the variation of the (isolated-atom) electronegativity with charge can be evaluated. The Hinze and Jaffé orbital electronegativities, Sanderson's electronegativity scale, or an extension of the electronegativity concepts derived by Iczkowski and Margrave are consistent with these requirements. The geometric average of the compound electronegativity, Sanderson's formalism, may produce valuable correlations with charge-sensitive properties of atoms for homologous compounds. Two formalisms make corrections to the isolated-atom electronegativities by consideration of the effects of the electrostatic potential originating from placing an atom in a molecule. The PEOE (partial equalization of orbital electronegativity) formalism simulates this effect by considering only the connectivities of the atoms. The FEOE (full equalization of orbital electronegativity) formalism explicitly calculates the electrostatic potential, by using interatomic distances and solving a set of simultaneous equations to obtain the atomic charges in a molecular environment. The PEOE and FEOE formalism give results that are highly correlated.

The principal aim of theoretical chemistry is to develop rules to explain chemical reactions and properties of molecules, in a quantitative and predictable way. For years, efforts to attain this goal were based on quantum chemistry, but practical objections soon became apparent because of the drastic increases in computation times with the number of electrons in a system. The formulation of empirical rules based on electronegativity equalization has gained more attention from chemists in recent years. From these rules, it may be expected that, within their proper framework, they approximately predict the outcome of atomic interactions in molecules. A quantitative expression for the atomic electronegativity, and its change during bond formation, should

contain sufficient information to derive the properties of primary interest to chemists: the atomic charges. Sanderson<sup>1</sup> introduced the concept of electronegativity equalization and proposed a formalism to calculate atomic charges, based on the change in electronegativity from the isolated atom value to its value after equalization in the molecule. However, in this way, identical charges are obtained for all atoms of the same elemental type in a molecule.

Sanderson's postulate,<sup>1</sup> that when two or more different atoms combine to form a molecule, their electronegativities change to a common intermediate value, was only recently established by theoretical formulations. Parr et al.<sup>2,3</sup> investigated the electro-

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negativity concept from the point of view of the Hohenberg-Kohn density functional theory.<sup>4,5</sup> By defining electronegativity as the negative of the chemical potential, they demonstrated that not only the atomic, but also the orbital electronegativities are equal in a ground-state molecule.<sup>2,3</sup> In a beautifully simple approach, independent of any particular theoretical framework, Politzer and Weinstein<sup>6</sup> showed that in its equilibrium state, the electronegativities or chemical potentials of all arbitrary portions of the total number of electrons are the same. No theoretical framework was proposed for evaluating atomic charges in a molecule.

Sanderson<sup>1</sup> assumed that the average molecular electronegativity value is the geometric mean of the electronegativities of the individual atoms. Parr and Bartolotti<sup>7</sup> showed that the conditions sufficient for the validity of the geometric mean principle are, firstly, that the valence-state atomic energy decays exponentially with the number of electrons, and, secondly, that the decay parameter is the same for each atom. They also found that the last condition is only approximately true. Further, Parr's treatment is only valid for natural orbitals; the Hartree-Fock theory does not provide a model which easily accounts for equal electronegativity of all orbitals in a molecule. This was also pointed out by Ponec<sup>8,9</sup> who reintroduced global electronegativity values obtained within the CNDO approximation.

Reed<sup>10</sup> stressed the distinction between electronegativity as an isolated atom property and the property of an atom in a molecular environment. He could show that if isolated atom electronegativities are equalized upon bond formation, this fails to minimize the energy of the system. Whether electronegativities of free atoms can be transferred into molecular environments warrants further investigation of various electronegativity scales and equalization procedures. Balbas et al.<sup>11</sup> explicitly accounted for the electrostatic interactions between the atoms in diatomic molecules upon electronegativity equalization.

The PEOE (partial equalization of orbital electronegativity) method was introduced by Gasteiger and Marsili<sup>12</sup> for the rapid calculation of atomic charges in molecules. These were required as part of the decision strategy in the synthetic design program EROS.<sup>13</sup> The PEOE method, originally presented for  $\sigma$ -bonded and nonconjugated  $\pi$  systems, was extended to conjugated systems by Marsili and Gasteiger<sup>14</sup> and by Saller.<sup>15</sup> This formalism intends to solve two problems: (i) to take care of the electrostatic interactions of charged atoms in a molecule, and (ii) to estimate orbital electronegativities of atoms in a molecular environment from the orbital electronegativities of the free atoms. The PEOE approach does not result in a complete equalization: connectivity-dependent atomic charges and residual electronegativities for each atom in a molecule are predicted. Excellent correlations were found between the atomic charges, calculated by PEOE, and physical measurements of charge-sensitive atomic properties such as the core electron binding energies (ESCA shifts) and the resonance shift in NMR.<sup>12,14-16</sup> It was also shown that reasonably good dipole moments can be calculated from the atomic charges.<sup>17,18</sup> Further, the residual electronegativity values can be used as a quantitative measure of the inductive effect, and in conjunction with estimates of effective polarizability, for the prediction of gas-phase proton affinities of amines.<sup>19</sup>

Sanderson's geometric average electronegativity could be used to rationalize the properties of homologous compounds (where the atomic connectivity is of no importance). This becomes, e.g., evident for the variation of the gas-phase basicities of *n*-alkylamines with the average electronegativity (or the atomic charges),<sup>20</sup> or for the composition dependence of several physico-chemical properties of zeolites.<sup>20-22</sup>

The application of the above principles to the evaluation of physical and chemical properties of molecules requires an appropriate electronegativity scale (allowing the estimation of the electronegativities of charged atoms), together with a formalism for simulating the process of bond formation. Therefore, the aim of the present paper is a discussion of the two previously mentioned formalisms (Sanderson and PEOE) together with an analysis of their parametrization. A new formalism is hereby developed, which explicitly accounts for the electrostatic effects on the "effective" atomic electronegativity, arising from the insertion of an atom into a molecule. A better understanding of the concepts of electronegativity and the equalization mechanism will be the result of it. Three electronegativity scales of practical interest will be considered: (i) the atomic electronegativity scale by Sanderson,<sup>1,23-25</sup> (ii) the orbital electronegativities by Hinze et al.,<sup>26-29</sup> and (iii) the possibility of deriving an atomic electronegativity scale from the principles outlined by Iczkowski and Margrave.<sup>30</sup>

### Electronegativity Equalization Formalisms

Iczkowski and Margrave<sup>30</sup> have identified the electronegativity  $\chi$  of an atom as  $\chi = -(dE/dN)$ . Parr et al.<sup>2,3</sup> have shown that this quantity is the negative of the chemical potential in the density functional theory. It follows naturally from this that in bond formation, the chemical potential (or electronegativity) of all the participating atoms gets equalized. This, however, does not imply that there is a charge equalization of the participating species as well.

For the ground state of a many-electron system, the electronic energy can be written as a unique functional of the electron density  $\rho$  of the system:<sup>2</sup>

$$E[\rho] = F[\rho] + \int v_{ne} \rho \, d\tau \quad (1)$$

where  $v_{ne}$  is the nuclear-electron (i.e., external) potential and  $F[\rho]$  the functional containing the kinetic energy  $T[\rho]$  and electron-electron interaction terms  $V_{ee}[\rho]$ :  $F[\rho] = T[\rho] + V_{ee}[\rho]$ . The chemical potential  $\mu$ , which is obtained by placing constraints on the variation of  $\rho$  subject to  $\int \rho \, d\tau = N$ , is then given by:<sup>31,32</sup>

$$\mu = \frac{\delta E[\rho]}{\delta \rho} = v_{ne} + \frac{\delta F[\rho]}{\delta \rho} \quad (2)$$

For a variation in the ground-state energy from one state to another,  $dE[\rho] = \mu dN + \int \rho(\vec{r}) \, dv(\vec{r}) \, d\vec{r}$ . It is obvious therefore that  $\mu$  can be identified as  $\mu = (\partial E/\partial N)_v$ .

For an isolated atom,  $\mu$ , i.e., the slope of the  $E$  vs.  $N$  curve for a constant external (nuclear-electron) potential  $v_{ne}$ , is easily derived from the ionization potential, electron affinity, and the electronic transitions given in the spectroscopic tables (see, e.g., ref 30). The

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slope varies with  $N$ , and an electronegativity scale giving the variation of the electronegativity  $\chi$  with charge ( $q$ ) accounts for this ( $\chi = -\mu$  and  $q = -N$ ) (see below). For an atom placed into an external potential field, such as when inserted into a molecule, a correction to the external potential  $v_{ne}$  is required. A positive potential (such as in a matrix of positive charges) will have the effect of decreasing the "effective" chemical potential ( $\mu'$ ) of the electrons on this atom and, therefore, also the effect of increasing its electronegativity ( $\mu$ , negative for a stable atom, is decreased by  $-eq/r$  for a positive charge  $q$  at distance  $r$ ).

Atoms of the same type in different environments will therefore be associated with different effective atomic charges. This follows directly from the Hohenberg and Kohn theorem,<sup>4,5</sup> which states that the energy of a many-electron system in a given external potential is a unique functional of the density of the system. Conversely, associated with a given charge distribution, there can exist only one unique external potential. Since atoms in different environments are subject to different external potentials, their effective charge is bound to be different. We are now in a position to examine the different electronegativity equalization formalisms for the calculation of the partial charges of atoms in molecules explicitly.

**1. Sanderson's Formalism** Sanderson<sup>1</sup> postulated that the intermediate electronegativity of a compound is equal to the geometric mean of the individual electronegativities of all component atoms that make the compound formula. In his formalism, the partial charge is defined as the ratio of the change in electronegativity undergone by an atom in joining the compound to the change it would have undergone in acquiring or losing one electron. The change corresponding to the acquisition of a unit positive charge is  $k\sqrt{S}$  ( $S$  = Sanderson electronegativity;  $k$  = 2.08 for the traditional Sanderson scale,<sup>1</sup> but according to the recent revisions<sup>24,25</sup> using a scale with the electronegativity of  $F$  = 4.0,  $k$  = 1.56). The proportionality constant  $k$  was calibrated to a 75% ionicity for NaF (revised 80%). Identical charges ( $q$ ) for atoms with the same electronegativity ( $S$ ) are therefore calculated, irrespective of their connectivity as:

$$q(S) = (S_m - S) / k\sqrt{S} \quad (3)$$

where  $S_m$  = geometric mean electronegativity. Thus, e.g., in acetic acid, all four hydrogen atoms, the two carbon atoms, and the two oxygens attain the same charge, respectively. This is contrary to chemical intuition, as is the result that isomeric groups attain the same group electronegativity.<sup>33</sup> However, Sanderson uses these charges only to calculate binding energies by considering the ionicity of the bonds ( $t_i$ ), i.e., the average of the differences of the partial charges in the bonds. Moreover, the ionic blending coefficient  $t_i$  is easily derived entirely independently from the experimental bond energy ( $E$ ) and the theoretical nonpolar covalent ( $E_c$ ) and ionic energies ( $E_i$ ) as  $t_i = (E - E_c) / (E_i - E_c)$ .<sup>24,25</sup> In a discussion on standard bond energies (ref 1, p 184), Sanderson states that the energy of a given bond (and therefore also  $t_i$ ) does not vary greatly from one environment to another, unless the environmental change is rather drastic. In this way, accurate calculations of formation energies for hundreds of compounds were possible using electronegativity, covalent radii, homonuclear binding energies, and bond lengths.<sup>1,25</sup> Sanderson's scheme is internally consistent, and no such scheme has as yet been proposed for calculating energies of formation. This is also not the case in the present study.

**2. PEOE Formalism.** The PEOE method<sup>12</sup> for the calculation of the partial charges is an iterative scheme, evaluating the charge shifts in each bond separately. Only first neighbors are considered in each cycle, with the charge shift ( $dq$ ) calculated in a single bond between atoms  $i$  and  $j$  with electronegativities  $\chi_i$  and  $\chi_j$  as (first cycle):

$$dq = 0.5(\chi_i - \chi_j) / \chi_j^+ \quad (4)$$

where  $\chi_j^+$  = electronegativity of the positive ion of atom  $j$ ;  $\chi_i >$

$\chi_j$ . The influence of the second (and following) neighbors is felt only in the next cycles and attenuated by a supplementary damping factor  $(0.5)^n$ ,  $n$  being the cycle number.  $\chi_i$  and  $\chi_j$  are then the electronegativities of the partially charged atoms  $i$  and  $j$  after adjusting the atomic charges by adding the charge shifts ( $dq$ ) for all bonds. Although this approach seems quite different from Sanderson's approach, a rewriting of the preceding formula shows that there are similarities:

$$dq = (\chi_i - (\chi_i + \chi_j) / 2) / \chi_j^+ \quad (4a)$$

The charge shift is calculated here as the ratio of the change in electronegativity of an atom on bond formation to the electronegativity of the cation of one of the participating atoms in the bond. The average electronegativity is taken as the arithmetic average. The charge shifts are, relative to those calculated by Sanderson's formalism, smaller because the denominator is not the change in electronegativity from the neutral atom to the positive ion, but the electronegativity of the cation itself. However, it should be realized that the above formula (eq 4a) is used only for calculating a charge shift within one bond, and within one iteration. Sanderson uses his formula (eq 3) for equalizing the electronegativities of all atoms in a molecule in one calculation. The electronegativity equalization in formula 4a is only partial from the onset, and the supplementary damping factors further prevent complete equalization. The charge transfer is attenuated exactly in the sense as discussed in the introduction to this section. Indeed, for a bond with  $\chi_i > \chi_j$ , the positive charge at atom  $j$  will increase the "effective" electronegativity at atom  $i$ . This is realized by a smaller electron transfer from  $j$  to  $i$  than a full electronegativity equalization would require, in order to maintain a higher "free atom" electronegativity on atom  $i$ . In this way, the influence of the electrostatic environment of the atom in a molecule, and therefore also a correction to the "isolated-atom" electronegativity, is simulated.

The recent considerations on the geometric mean principle of electronegativity equalization<sup>7</sup> suggest that the use of the geometric mean  $\chi_m$  should be investigated. Our calculations indicate that the differences between both approaches in the PEOE method are small.

Another worthwhile comparison is the charge shift calculated by eq 4, with the approach by Parr and Pearson<sup>34</sup> using atomic hardness  $\eta$  ( $2\eta = [\partial\mu/\partial N]_Z$ ). Both methods calculate a charge shift proportional with the electronegativity difference of the atoms  $i$  and  $j$ , but the proportionality factor in formula 4 depends only on one atom type ( $1/2\chi_j^+$ ), while Parr and Pearson use a proportionality factor depending on both:  $1/2(\eta_i + \eta_j)$ . Again, the absolute hardness being somewhat smaller than the electronegativity, the use of the electronegativity of a positively charged atom in the PEOE formalism guarantees a smaller electron transfer than in the case of a complete equalization.

**3. FEOE Formalism.** Considering, in the density functional viewpoint, the chemical potential of an atom in a molecule, we may write  $\mu = \partial E / \partial N$ . Expressing the energy and the chemical potential of an atom in a molecule as a function of the number of electrons  $N$  and of the external potential expressed through an effective charge  $Z$ , we obtain:<sup>35</sup>

$$E(N, Z) = E^0 + \left[ \frac{\partial E}{\partial N} \Delta N + \frac{\partial E}{\partial Z} \Delta Z \right] + \frac{1}{2} \left[ \frac{\partial^2 E}{\partial N^2} (\Delta N)^2 + \frac{2\partial^2 E}{\partial N \partial Z} \Delta N \Delta Z + \frac{\partial^2 E}{\partial Z^2} (\Delta Z)^2 \right] + \dots \quad (5)$$

and

$$\mu(N, Z) = \mu^0 + \frac{\partial \mu}{\partial N} \Delta N + \frac{\partial \mu}{\partial Z} \Delta Z + \dots \quad (6)$$

The first two terms of the right-hand side of equation 6 are consistent with the variation of the chemical potential with the number of electrons for an isolated atom, i.e., with  $Z$  constant.

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**Table I.** Comparison of Atomic Charges on Carbon and C-1s Electron Binding Energy Shifts Relative to Methane

no.	compd	shift, eV	Hinze and Jaffé <sup>a</sup>			Sanderson			I & M		
			PEOE	FEOE	Sand.	PEOE	FEOE	Sand.	PEOE	FEOE	Sand.
1	CH <sub>4</sub>	0	-0.080	-0.040	-0.059	-0.050	-0.021	-0.048	-0.049	-0.026	-0.042
2	CH <sub>3</sub> -CH <sub>3</sub>	-0.2	-0.076	-0.032	-0.055	-0.046	-0.018	-0.045	-0.046	-0.021	-0.039
3	CH <sub>2</sub> =CI <sub>2</sub>	-0.1	-0.128	-0.025	-0.103	-0.037	-0.014	-0.040	-0.039	-0.017	-0.035
4	HC≡CH	0.4	-0.158	-0.015	-0.173	-0.022	-0.008	-0.030	-0.024	-0.010	-0.027
5	CH <sub>3</sub> F	2.8	0.037	0.069	0.043	0.053	0.049	0.042	0.050	0.052	0.033
6	CH <sub>2</sub> F <sub>2</sub>	5.6	0.179	0.166	0.160	0.162	0.112	0.141	0.153	0.124	0.121
7	CHF <sub>3</sub>	8.28	0.338	0.250	0.296	0.274	0.164	0.250	0.262	0.186	0.224
8	CF <sub>4</sub>	11.0	0.504	0.325	0.452	0.382	0.209	0.370	0.374	0.242	0.345
9	*CH <sub>3</sub> CH <sub>2</sub> F	0.2	-0.052	0.001		-0.024	0.003		-0.019	0.004	
10	CH <sub>3</sub> *CH <sub>2</sub> F	2.4	0.050	0.057		0.058	0.041		0.054	0.022	
11	*CH <sub>3</sub> CF <sub>3</sub>	1.1	0.013	0.047		0.022	0.029		0.038	0.040	
12	CH <sub>3</sub> *CF <sub>3</sub>	7.6	0.360	0.222		0.273	0.148		0.268	0.162	
13	CH <sub>3</sub> OH	1.6	-0.004	0.054		0.009	0.025		-0.007	0.019	
14	CH <sub>3</sub> OCH <sub>3</sub>	1.4	0.010	0.041		0.012	0.018		-0.003	0.013	
15	H <sub>2</sub> CO	3.3	0.047	0.113		0.051	0.051		0.042	0.046	
16	*CH <sub>3</sub> CHO	0.6	-0.033	0.019		-0.025	-0.003		-0.023	-0.004	
17	CH <sub>3</sub> *CHO	3.2	0.077	0.086		0.057	0.044		0.048	0.038	
18	*CH <sub>3</sub> COCH <sub>3</sub>	0.5	-0.027	0.007		-0.033	-0.007		-0.021	-0.009	
19	CH <sub>3</sub> *COCH <sub>3</sub>	3.1	0.112	0.077		0.065	0.042		0.054	0.037	
20	HCN	2.6	-0.002	0.085		0.032	0.033		0.026	0.029	
21	*CH <sub>3</sub> CN	2.1	-0.004	0.035		-0.029	-0.010		-0.027	-0.011	
22	CH <sub>3</sub> *CN	2.1	0.052	0.043		0.041	0.029		0.035	0.024	
	correlation coeff		0.976	0.990	0.979	0.986	0.983	0.997	0.980	0.978	0.995

<sup>a</sup>The PEOE values differ from those in ref 12 as instead of an arithmetic mean, a geometric mean was used (see text). For the FEOE formalism, no hybridization-dependent electronegativities were used (e.g., for C, sp<sup>3</sup> used throughout).

Referring to the electronegativity  $\chi$  ( $=-\mu$ ), this variation of the chemical potential with the charge may be estimated from an electronegativity scale (of an isolated atom) giving the variation of the electronegativity with charge. The third term in eq 6 accounts for the change of the chemical potential associated with a change in the external potential which, from a comparison with eq 2, may be directly evaluated by a correction to  $v_{ne}$ . Equation 6 can therefore be written in terms of the electronegativities as:

$$\chi'(q_i; q_j, \dots) = \chi(q_i) + k\{\sum_j q_j/r_{ij} + s_i q_i/r_i\} \quad (7)$$

The "effective" electronegativity of atom  $i$  is a function of its proper charge  $q_i$  and of the charge of all other atoms in the molecule ( $\chi'(q_i; q_j, \dots)$ ). This is equal to the sum of its charge-dependent isolated atom value  $\chi(q_i)$  and a correction for the charge variation of all the atoms, including the atom under consideration, assuming a coulombic model. The term  $s_i q_i/r_i$  is necessary to account for a change in the effective charge on the atom itself (not included in the first two terms in eq 6) by virtue of its participation in molecular bonding.  $s_i$  is an atom-dependent screening constant. It effects only the magnitude of the charges obtained; the smaller  $s_i$ , the more pronounced the charges. For  $r_i$ , the covalent radii were used. An alternative is the use of radius of the maximum density of the outermost atomic orbital ( $r \approx n^2 a_0/Z_e$ );<sup>36</sup> the quantum number  $n$  and the Bohr radius  $a_0$  are fixed, but the effective nuclear charge  $Z_e$  increases steadily with increasing positive charge. This, however, is equivalent to changing the screening constant  $s_i$ , and since only relative charges were envisaged,  $s_i$  was set equal to 1. To convert the electrostatic correction term to electronvolts,  $k = 14.399$  if the charges are expressed as unit proton charges and the interatomic distances are given in Ångströms. For a full equalization of the effective atomic electronegativities, it is then possible to calculate the  $n$  atomic charges  $q$  for the  $n$  atoms in the molecule from a set of simultaneous equations,  $n - 1$ , which have the form  $\chi'(q_i; q_j, \dots) = \chi'(q_j; q_k, \dots)$  and one equation of the form  $\sum q_i = \text{constant}$ . The application of the FEOE formalism is less straightforward than the PEOE formalism, since also the interatomic distances are required. These should be given for all atoms, although, for largely covalent compounds, it was found that the inclusion of the first and the second neighbors is sufficient.

It should be emphasized that this formalism extends the first approximations by Huheey<sup>33</sup> and Parr and Pearson.<sup>34</sup> Both methods are exactly equivalent, including their parametrization. By virtue of  $2\eta = (\partial\mu/\partial N)_Z$ , and equalizing  $\mu_A$  and  $\mu_B$  for a diatomic molecule and neglecting the third term in eq 6,  $\Delta N$  is calculated as  $\Delta N = (\mu_A^\circ - \mu_B^\circ)/2(\eta_A + \eta_B)$ .<sup>35</sup> For polyatomic molecules, this would result in connectivity-independent charges, which, of course, are lacking in physical significance. The atomic hardness will also play a role in the electrostatic correction term, since the atomic radii, and therefore also the interatomic distances, vary with the hardness of the atoms.

An electrostatic correction term was also considered by Balbas et al.<sup>11</sup> for calculating the charge transfer in diatomic molecules, which, according to the present notation, could be written as:

$$q = (\chi_A^\circ - \chi_B^\circ)/(\chi_A' + \chi_B' + 2/R)$$

where  $\chi'$  denotes  $d\chi/dq$ , and  $R$  the internuclear separation. Higher order correction terms involving  $\chi''$  were also considered. This is very similar to the FEOE formalism, except that a term  $s_i q_i/r_i$  was not considered, and which proved to be absolutely necessary for obtaining meaningful results for polyatomic molecules.

### Applications

For each of the three electronegativity equalization formalisms, three possible parametrizations were considered. The calculated atomic charges, or the average compound electronegativity, should then correlate with properties, sensitive to atomic charges. To illustrate the relative value of formalisms and parametrizations, the C-1s core electron binding energy shifts relative to methane for a series of compounds, compiled in ref 12 (Table 3), will be used. PEOE and FEOE charges, calculated using three different electronegativity scales, together with the C-1s shifts, are given in Table I (charges calculated by using the geometric mean  $\chi_m$  of the two atoms in a bond), together with the parameters of the regression analysis. For the homologous series ethane, ethene, and acetylene, and for the substituted methanes, the charges were also calculated by the Sanderson formalism ( $q(S) = (S_m - S)/\Delta S$ ),  $\Delta S$  being the electronegativity difference between the positive ion and the neutral atom. For compounds 9–12, 16–19, and 21 and 22, the Sanderson formalism is inappropriate, as it does not differentiate between carbon atoms in different molecular environments.

(36) McWeeney, R. "Coulson's Valence"; Oxford University Press: Oxford, 1979; p 44.

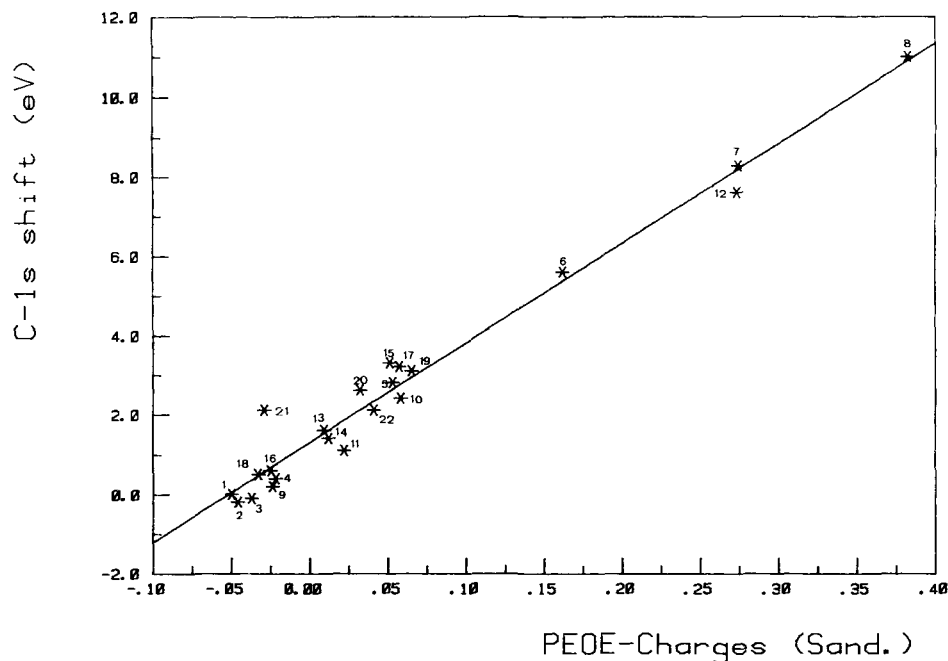


Figure 1. PEOE charges (Sanderson parametrization; geometric averaging) vs. the C-1s energy shift of carbon, relative to methane. The numbers correspond to those in Table I.

**1. Hinze and Jaffé Parametrization.** Unlike the classical atomic electronegativity scale, Hinze and Jaffé<sup>26-29</sup> developed an electronegativity, characteristic for a valence state, using Mulliken's definition<sup>37</sup> relating the electronegativity to the ionization potential ( $I_v$ ) and electron affinity ( $E_v$ ) in a specific valence state as  $(I_v + E_v)/2$ . This was the original parametrization chosen for the PEOE method as outlined in ref 12. As already mentioned, almost identical charges are calculated when using a geometric average instead of an arithmetic average in the iterative equalization. For the molecules 2, 3, and 4, with a hybridization  $sp^3$ ,  $sp^2$ , and  $sp$ , respectively, the charges vary in the opposite way than indicated by the C-1s shift (see also ref 12, Figure 2). It should, however, be noted that C-1s shifts are not only influenced by charge effects (although these are the most important), but also by reorganization effects, e.g., polarization in the ionized state. For systems containing  $\pi$  electrons, the polarization is expected to be more pronounced. The Sanderson formalism also predicts a variation of the partial charges of the carbon atoms in ethane, ethene, and acetylene opposite to the observed C-1s shifts. This must certainly be attributed to the increasing orbital electronegativity when passing from  $sp^3$  to  $sp^2$  and  $sp$ . This is not so when using atomic electronegativities (see below) or when using the Hinze and Jaffé scale, disregarding different hybridization states as for FEOE (see Table I).

Of the three parametrizations, the Hinze and Jaffé scheme produces the most pronounced charges (see Table I). It must therefore be warned that internal consistency for the calculation of binding energies in the Sanderson formalism can only be expected when using Sanderson's electronegativity scale.

**2. Sanderson Parametrization.** Unlike in the previous scale, Sanderson's scale does not enable a choice of the electronegativity of the valence state of the atoms. The use of an atomic parametrization, however, does not seem to be a drawback (see Figure 1). The changes of the carbon charges calculated with the PEOE and FEOE formalisms for ethane, ethene, and acetylene are in line with the variation indicated by the ESCA measurements. A better linearity is also observed for the substituted methanes. The correlation coefficient for the overall linear regression of the C-1s shift with the charge is also better when using Sanderson's scale. The use of an atomic parametrization has the further advantage that no previous assumption of the hybridization is required. It should be noted that there is a relation between hybridization and

Table II.  $a$ ,  $b$ , and  $c$  Parameters for the Total Energy Function of the  $p$  Electrons in the Iczkowski and Margrave Approach<sup>a</sup>

atom	hybrid.	$a$	$b$	$c$
H	$a$	-4.6660	4.9670	0.021484
Li	$(1s)^2(2p)$	-1.5084	1.8843	0.036859 <sup>c</sup>
Be	$(2p)^2$	-2.3972	3.0352	0.033947 <sup>c</sup>
B	$(2s)^2(2p)$	-3.7420	4.2752	0.031034 <sup>c</sup>
C	$(2s)^2(2p)^2$	-5.2475	5.0842	0.028466
N	$(2s)^2(2p)^3$	-6.7704	6.0945	0.024961
O	$(2s)^2(2p)^4$	-8.5079	6.9521	0.021758
F	$(2s)^2(2p)^5$	-10.4700	7.8037	0.019825
Na	$(3p)$	-0.9016	1.9077	0.025223 <sup>c</sup>
Al	$(3s)(3p)^2$	-2.4767	3.2049	0.042794 <sup>c</sup>
Si	$(3s)^2(3p)^2$	-4.5119	2.9597	0.036580
P	$(3s)^2(3p)^3$	-5.5730	4.5108	0.035797
S	$(3s)^2(3p)^4$	-6.7821	4.6331	0.014327
Cl	$(3s)^2(3p)^5$	-9.5645	6.4932	0.023168

<sup>a</sup> Mg omitted: no valence-state electron affinity for the  $3p^2$  state was given in ref 38. <sup>b</sup> Hydrogen parametrization interpolated among B, C, N, O, and F, equivalent with Sanderson. <sup>c</sup> Exponential factor extrapolated.

the number of neighbors for a given atom. Apparently, the explicit consideration of the number of atoms in a molecule in the Sanderson treatment implicitly accounts for hybridization (see also ref 1, p 186).

**3. Iczkowski and Margrave (I&M) Parametrization.** Iczkowski and Margrave<sup>30</sup> expressed the electronegativity as  $-(dE/dN)$ , i.e., the negative of the derivative of the total energy of all electrons around a nucleus, taking the neutral atom as zero and  $N$  being the number of electrons ( $n$ ) minus the atomic number  $Z$ , i.e.,  $N = n - Z$ . Zero  $N$  corresponds to the neutral atom, 1 to the negative ion, and -1 to the singly ionized ion, etc. When  $N = -1$ , the valence state ionization potential (VOIP, also abbreviated as VSIE and VSIP;  $E =$  energy,  $S =$  shell) is taken for  $E$ ; for  $N = -2$ , the sum of the first and second VOIP; and for  $N = 1$ , minus the valence-state electron affinity. Pure  $p$ -orbital electronegativities were calculated for a few atoms,<sup>30</sup> by calculating the derivative after approximation of  $E(N)$  with a polynomial.

VOIP's (the energy needed to remove an electron from a given orbital of either a specific configuration or valence configuration) are obtained as a function of the charge from compilations such as those given by Basch, Viste, and Gray,<sup>38</sup> or determined from

(37) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782.

(38) Basch, H.; Viste, A.; Gray, H. B. *Theor. Chim. Acta* **1965**, *3*, 458.

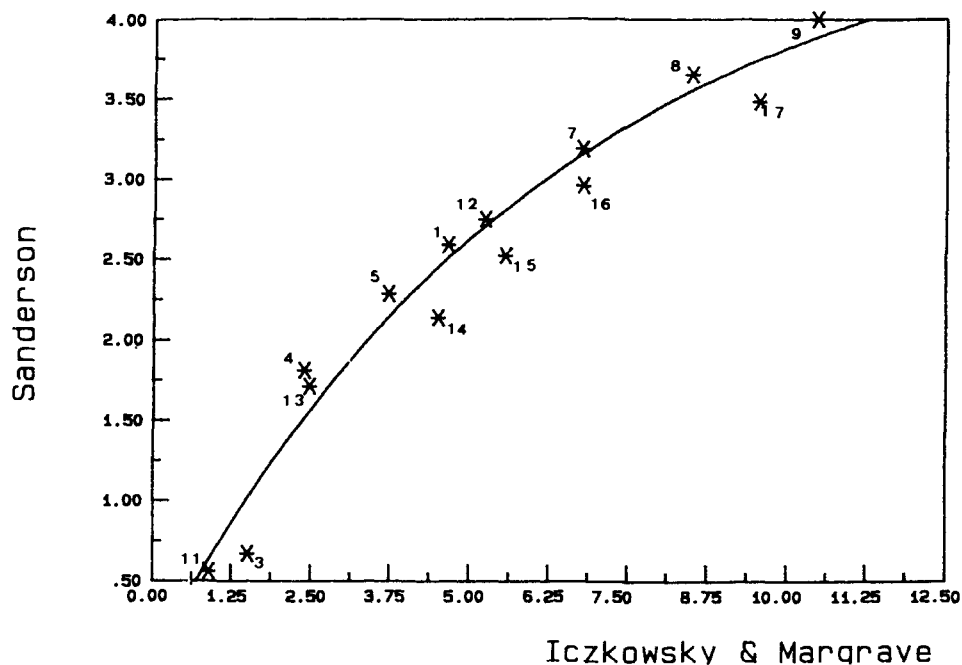


Figure 2. Correlation of the electronegativities for the neutral atoms in the I&M approximation vs. those in the Sanderson scale. The numbers correspond to atomic numbers.

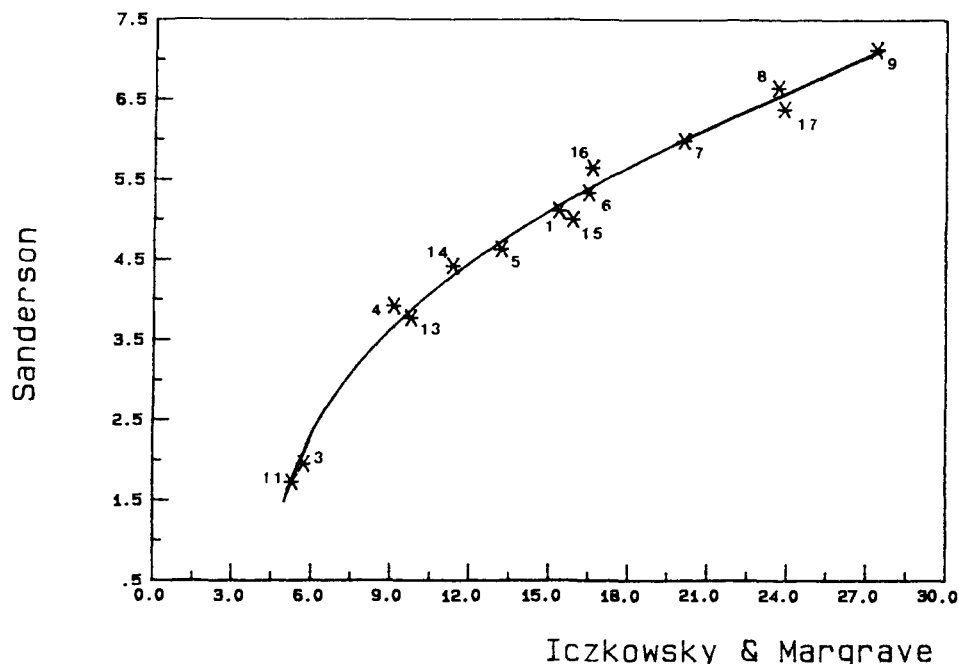


Figure 3. Correlation of the electronegativities for the +1 charged atoms in the I&M approximation vs. those in the Sanderson scale. The numbers correspond to atomic numbers.

spectroscopic tables as outlined, e.g., in ref 39. These are also commonly used in the extended Hückel calculations. In view of the fact that these are readily available or calculated, an extension of the I&M principles was further investigated. Neither a polynomial nor an exponentially decaying energy function<sup>5</sup> could be used to fit the  $E(N)$  curve for all  $N$  and for all atoms. Instead, a three-parameter equation (eq 8) gave satisfactory results.

$$E(N) = (aN + bN^2) \exp(cN^2) \quad (8)$$

Table II contains the least-squares parameters for a fit of the total energy  $E(N)$  from  $N = -2$  to  $N = 1$ , with  $E(N)$  derived from the VOIP functions determined by Basch, Viste, and Gray.<sup>38</sup> A perfect fit is possible if values up to  $N = -2$  can be calculated. For Li,

Be, B, and also for Na and Al, only  $E(-1)$ ,  $E(0)$ , and  $E(1)$  were included, and only two parameters are required for a perfect fit. It was observed that the  $c$  parameter decreases linearly with the group. The  $c$  parameter was then subsequently extrapolated within each row (for the third row omitting S). It was also found that only when using the p-orbital VOIP function for Li, Be, Na, and Al, a good, but nonlinear correlation with Sanderson's electronegativity values was possible (see Figures 2 and 3). This illustrates the importance of choosing the correct electronegativity of the atoms in a molecule, which is not consistently the ground-state electronegativity of the isolated atom.<sup>40</sup> Sanderson's values are derived from experimental data, and referring to these implicitly accounts for the choice of electronegativity values of atoms as part of a molecule. The value for hydrogen was pro-

(39) McGlinn, S. P.; Vanquickenborne, L. C.; Kinoshita, M.; Carroll, D. G. "Introduction to Applied Quantum Chemistry"; Holt, Rinehart and Winston: San Francisco, 1972; p 106.

(40) See, e.g., for a discussion on BeO, ref 36, p 215.

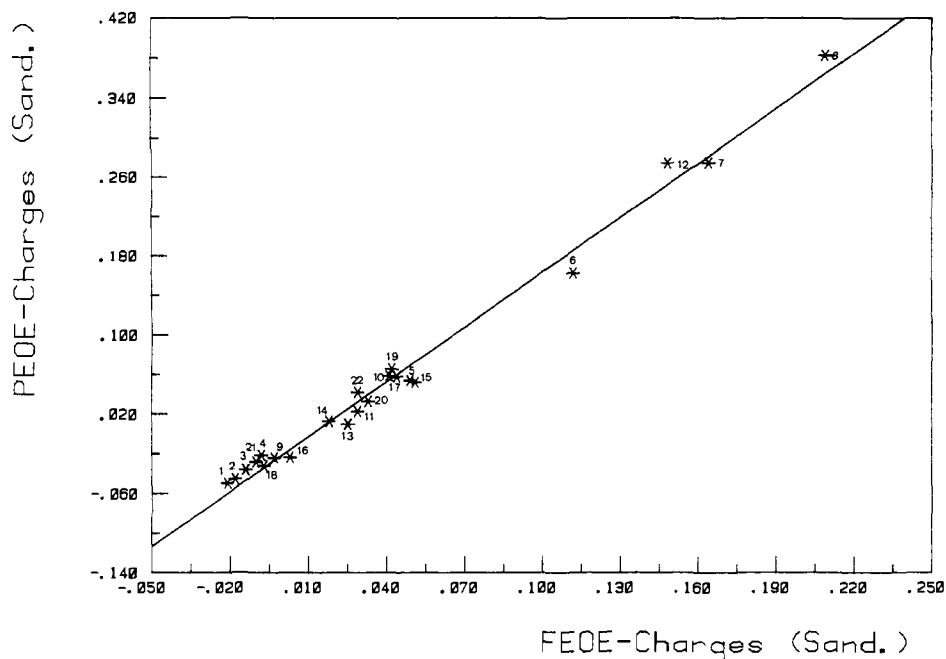


Figure 4. Correlation of the PEOE and FEOE charges, calculated using Sanderson's electronegativity scale. The numbers refer to those in Table I.

blematic. Its value was derived from a plot of the electronegativities of B, C, N, O, and F vs. Sanderson's values for the neutral and positive ions. The  $H_c$  parameter was extrapolated from  $c$  for Na and Li.

The electronegativity as a function of the charge is then calculated as in the equation:

$$\chi(q) = \exp(cq^2)(-a + 2bq - 2acq^2 + 2bcq^3) \quad (9)$$

Applying the PEOE and FEOE formalism, correlations similar to those found with the Sanderson scale are obtained. A plot of the C-1s shift vs. the charge on carbon gives a plot very similar to the one given in Figure 1, which is not surprising considering the good correlation of the Sanderson scale with the I&M scale (Figures 2 and 3).

**4. Other Electronegativity Scales.** Several electronegativity scales have been presented which, however, may not all be used in a quantitative way. A knowledge of the atomic hardness  $\eta$  should, to a first approximation, allow the estimation of the electronegativity change with the acquisition of a positive unit charge, i.e.,  $2\eta$  such that  $\chi(q) = \chi^0 + 2\eta q$ . However, there might be limitations to their use because (i) the values published refer mostly to the ground state, and (ii) some systematic errors might occur. The experimental electronegativity and hardness values of ref 34, for example, are derived from  $I$  and  $A$ , not corrected for the valence state. Furthermore defining  $\chi$  as  $(I + A)/2$  is equivalent to estimating  $(dE/dN)_{N=0}$  from the slope of a line connecting  $E(N=-1)$  with  $E(N=1)$  which might be parallel with the tangent to the  $E(N)$  curve at  $N = 0$ . This is only true if  $E(N)$  can be expressed by a simple quadratic variation:  $E(N) = aN + bN^2$ . Expressing hardness as  $\eta = (I - A)/2$  is subject to the same condition. The values reported by Parr and Pearson<sup>34</sup> for  $\chi$  and  $\eta$  are close to the values obtained from eq 8 at  $N = 0$ , i.e.,  $\chi^0 = -a$  and  $\eta^0 = b$  (Table II) only for these cases where the valence-state p-orbital electronegativity is close to its ground-state value.

#### Possibilities and Limitations

The FEOE and PEOE formalisms have the advantage that for symmetric molecules, not all atoms are required, but that the same results are obtained with the appropriate choice of boundary atoms (of which there is already an identical atom in the atoms list of the asymmetric unit). The same is true for the calculation of the atomic charges in framework moieties. The PEOE formalism is far easier to apply. Both methods give similar results, as evidenced by a plot of the PEOE vs. FEOE charges, using Sanderson's

electronegativity scale (Figure 4; data from Table I).

Conjugated  $\pi$ -bonded systems were not considered in this paper. Extensions to conjugated systems were investigated only for the PEOE formalism.<sup>14,15</sup> On the other hand, only the FEOE formalism will be able to predict charge variations for identical compounds having structurally different phases. This is, e.g., the case for the quartz homologues ( $\text{SiO}_2$ ) for which the <sup>29</sup>Si NMR shift of seven structurally different phases could be interpreted empirically in terms of interatomic distances and bonding angles.<sup>41</sup> This, of course, illustrates the importance of the coulombic correction term in the FEOE electronegativity equalization formalism. Only the FEOE formalism will yield a corrected average electronegativity value in a molecule. There is no such information in the PEOE formalism, while Sanderson's formalism yields the average value calculated from isolated-atom electronegativities.

Taking into account the above considerations, it was shown that, if an electronegativity scale can be found that enables the evaluation of electronegativity with charge, such as the Hinze and Jaffé orbital electronegativities, Sanderson's electronegativity scale, or an extension of the electronegativity concepts derived by Iczkowski and Margrave, the PEOE formalism, the FEOE formalism, and Sanderson's formalism may produce valuable correlations with charge-sensitive properties of atoms in molecules. However, when various types of the same atom exist in different bonding situations in a molecule, the Sanderson formalism is inappropriate. Only the PEOE and FEOE methods explicitly consider the constitution of a molecule and give meaningful results. Use of Sanderson's atomic electronegativity scale produces slightly better correlations of the atomic charge with the core-electron binding energy of carbon in a series of organic compounds and has the further advantage that no choice of the hybridization state has to be made before any of the formalisms is applied.

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(41) Smith, J. V.; Blackwell, C. S. *Nature (London)* **1983**, 303, 223.