A Group Electronegativity Equalization Scheme Including External Potential Effects

Tom Leyssens,*,† Paul Geerlings,‡ and Daniel Peeters†

Laboratoire de Chimie Quantique, Bâtiment Lavoisier, Université Catholique de Louvain (UCL), place Louis Pasteur 1, B-1348 Louvain-la-Neuve, Belgium, and Eenheid Algemene Chemie (ALGC), Faculteit Wetenschappen, Vrije Universiteit Brussel (VUB), Pleinlaan 2, 1050 Brussels, Belgium

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By calculating the electron affinity and ionization energy of different functional groups, CCSD electronegativity values are obtained, which implicitly account for the effect of the molecular environment. This latter is approximated using a chemically justified point charge model. On the basis of Sanderson's electronegativity equalization principle, this approach is shown to lead to reliable "group in molecule" electronegativities. Using a slight adjustment of the modeled environment and first-order principles, an electronegativity equalization scheme is obtained, which implicitly accounts for the major part of the external potential effect. This scheme can be applied in a predictive manner to estimate the charge transfer between two functional groups, without having to rely on cumbersome calibrations. A very satisfactory correlation is obtained between these charge transfers and those obtained from an ab initio calculation of the entire molecule.

1. Introduction

In 1978, Parr et al.[1] were the first to give a rigorous, theoretical definition of electronegativity.[2−4] They identified this property with the negative of the chemical potential ($\mu = -\chi$), the Lagrange multiplier introduced in the variational procedure for the energy-density functional following the Hohenberg−Kohn theorems in density functional theory.[5] The chemical potential is given by $\mu = (\partial E/\partial N)_{v(r)}$, the derivative of the energy with respect to the number of electrons N at constant external potential (owing among others to the position of the nuclei). Later on, this derivative took a firm place in the broader context of response functions in conceptual DFT.[6]

Not always adequately appreciated by the chemical community is the fact that electronegativity should be considered as an atom in molecule[7] property, meaning that the electronegativity of an isolated atom differs from that of the atom in a molecule. In earlier years this variability was thought to be fully accounted for by considering the valence-state corrected electronegativity values.[8−10] Considering this correction to be sufficient is however a common myth.[11] We[12] and others[13−16] have shown that the introduction of an environment has a substantial influence on the electronegativity values.

Any property extracted from these latter can therefore only be expected to be accurate if the effect of the environment is taken into account. One such property is the charge transfer between two fragments composing a molecule, which according to Sanderson's equalization principle,[17,18] should be such that the electronegativities of both fragments become equal. The use of atomic valence-state corrected electronegativities to determine charge transfers[19,20] as well as group electronegativities,[21−24] hereby neglecting the influence of the molecular environment, leads to doubtful results.

Nalewajski et al.[25,26] were the first to correct the charge-transfer expression for the effect of the external potential (the molecular environment), basing themselves on external potential corrected electronegativities. In line with these ideas, Mortier et al.[27−30] developed the electronegativity equalization method (EEM), which explicitly accounts for the external potential and allows a fast estimation of atomic charges.[31−34] Other advances lead to the formulation of different electronegativity equalization formalisms, the most important ones being the charge equilibration method (Qeq) by Rappé and Goddard,[35] the atom-bond electronegativity equalization method (ABEEM) by Yang and Wang,[36,37] the chemical potential equalization method by York and Yang,[38,39] and the fluctuating charge model by Berne et al.,[40,41] all in some manner *explicitly* accounting for the effect of the external potential.

In this paper, we are introducing a different approach, aiming to *implicitly* account for the effect of the external potential by incorporating this effect into the electronegativity value. Such an approach can substantially simplify the above-mentioned electronegativity equalization formalisms, such as the EEM method. In this latter, the effective atomic electronegativity is approximated as the sum of the isolated atomic electronegativity, a charge correction, calibrated correction terms accounting for the difference in size and shape effects between the isolated atom and the atom inside a molecule,[42] and an explicitly calculated term accounting for the change in external potential owing to the molecular environment. The problems associated with this method lie not only in the calibration of the correction parameters, depending among others on the size and nature of the calibration set, but also in the approximation of the external potential effect by a coulomb term. At the atomic level this represents quite a substantial approximation. The authors agree that an implicit incorporation of the external potential effect in the electronegativity parameter would be more valuable from a practical point of view.[43]

In a previous paper,[12] we obtained such parameters by directly estimating group electronegativity in a molecular environment using a crude, yet effective technique based on the approximation of this latter by a point charge model. The advantage of working with functional groups is that they already contain part

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* E-mail: t.leyssens@chim.ucl.ac.be. Phone: 32 10 47 28 19. Fax: 32 10 47 27 07.

† Université Catholique de Louvain.

‡ Vrije Universiteit Brussel.

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of the molecular geometry and have electronic structures closer to that of the resulting molecule. This means that the size and shape effects of the atoms constituting the functional group are comparable to those of the atoms in the molecule and therefore no longer have to be corrected for.[44]

The thus obtained group electronegativities implicitly account for the molecular environment and are therefore referred to as "group in molecule" (GIM) electronegativities. These can be directly inserted in an electronegativity equalization scheme to estimate the charge transfer between two functional groups in an effective yet simple manner. Note, however, that the approximated environment is created by replacing the atoms not belonging to the functional group by the respective charges these atoms bear in the entire molecule,[12] therefore requiring an a priori knowledge of the ab initio charge distribution in the molecule. Constructing an electronegativity equalization scheme (EES), which demands an a priori knowledge of the charge distribution in the entire molecule would be pointless and unfeasible when the procedure is used for evaluating properties of large series of large molecules as typical EES strategies aim at.[45]

The goal of the present paper is to show that by starting from the correct definition of the chemical potential and by using a similar type of modeled environment, one can estimate the charge transfer between two functional groups A and B forming the AB molecule by implicitly including the major part of the external potential effect. This no longer requires an a priori knowledge of the charge distribution in the entire molecule, nor calibration of multiple parameters. The paper is organized as follows:

The first part gives a short theoretical reminder. Starting from the definition of the chemical potential (electronegativity), we highlight the factors that influence the latter and show how to obtain an electronegativity value for a given external potential. In a second part, we will verify the reliability of the GIM electronegativity values by comparing the estimated charge transfer with the ab initio values. In a third and final part, we show that it is not necessary to rely on an a priori knowledge of the charge distribution of the entire molecule to construct the major part of the molecular environment. Using a slightly different environment, we are able to include the major part of the external potential effect implicitly and come to a predictive charge-transfer scheme.

2. Computational Details

All structures were optimized at the coupled cluster level of theory with single and double substitutions,[46] using a 6-31++G-(d,p) basis set.[47] This basis set has been shown to perform well for the estimation of group electronegativity, hardness, and softness.[12,43,48] Calculations were performed using the Gaussian series of programs.[49] Charges have been obtained using a natural population analysis (NPA)[50−53] at the CCD level of theory (considering that the generalized CCSD first-order density is not available in the Gaussian series of programs). Unlike Mulliken populations, the natural populations seem to exhibit excellent numerical stability with respect to changes in basis set and methodology.[52] In this paper we study compounds of the form CH_3X with X = $-C_2H_3$, $-C_2H$, $-CH_2F$, $-CH_2Cl$, $-CHO$, $-COOH$, $-NH_2$, $-NO_2$, $-OH$, $-OCl$, $-OCH_3$, $-SiH_3$, $-PH_2$, and $-SH$ covering thereby second as well as third row functional groups. For the electronic structure of the functional groups to resemble the electronic structure of the resulting molecule as much as possible, singlet state cations are considered for the NH_2, OH, OCl, OCH_3, PH_2, and SH groups, instead of the often more stable triplet states. This formally corresponds to ionization from the orbital involved in chemical bonding.

3. Results and Discussion

3.1. The Chemical Potential (Electronegativity): A Theoretical Reminder.

Like the energy functional, the chemical potential ($(\mu = \partial E/\partial N)_{\upsilon(r)}$) depends on the number of electrons N and the external potential $\nu(r)$ (representing the molecular structure and the environment).

$$d\mu = 2\eta\, dN + \int f(r)\, \delta\upsilon(r)\, dr \qquad (1)$$

with η and $f(r)$ respectively being the hardness[54] and the Fukui function[55] of the system. In this paper, we will limit ourselves to second-order developments of the energy functional (first order of μ), considering the third-order energy derivatives to be small,[56] although they might be implicitly included in some of our values as will be mentioned later on.

The use of a quadratic energy expansion is accurate enough in the context of this paper, where functional groups are at covalent distance from one another. For larger distances this approximation is no longer sufficient,[57,58] leading to artificial intermolecular charge transfer. This problem can be solved by going beyond the quadratic expression[58] or by constraining the charge transfer to a specific ensemble of molecules.[39,59]

To estimate the electronegativity of a species in a given external potential (a given environment), two different approaches are possible. The first of these requires the knowledge of an initial chemical potential (μ_1), which is often chosen to be that of the isolated species ($\mu°$). The chemical potential in a second situation (μ_2) can than be obtained directly using a first-order Taylor expansion of the chemical potential variation:

$$\mu_2 = \mu_1 + 2\eta\Delta N + \int f(r)\, \Delta\upsilon(r)\, dr \qquad (2)$$

This nevertheless requires an expression for the variation in external potential ($\Delta\upsilon(r)$) as well as the knowledge of the Fukui function. Mortier et al.[27−30] used this technique to estimate the electronegativity of an atom in a molecular environment starting from the isolated atom properties ($\mu°$ and $\eta°$). They approximated the change in external potential ($\Delta\upsilon(r)$) by a coulomb potential considering the other atoms as point charges and replaced the spatial Fukui function $f(r)$ by its condensed counterpart.[60] They were forced to correct the chemical potential expression by introducing additional correction terms, which account not only for the errors due to the important approximations mentioned above, but also for some of the higher order energy derivative corrections, as well as for the change in size and shape of the atom in a molecule with respect to the isolated atom. These correction terms were acquired by calibration, which requires among others an appropriate choice of the calibration set.

A second approach, so far not used in electronegativity equalization schemes, estimates the electronegativity directly in the presence of the external potential. The thus obtained electronegativity values will then implicitly account for the external potential effect. In this approach, eq 2 reduces to

$$\mu_2 = \mu_1^{\#} + 2\eta^{\#}\Delta N \qquad (3)$$

with $\mu^{\#}$ and $\eta^{\#}$ being respectively the chemical potential and hardness of a $N°$ electron species in the given environment (fixed external potential). On the basis of a second-order Taylor

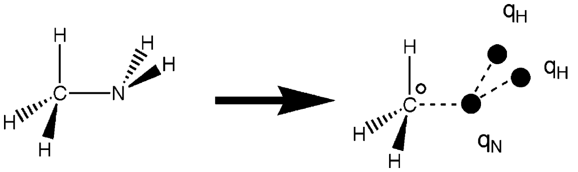

Figure 1. For the CH_3 functional group in a CH_3NH_2 molecule, the GIM environment is created by replacing the atoms of the NH_2 group by the respective charge they carry in the CH_3NH_2 molecule. The electronegativity of CH_3 is then calculated in the presence of this molecular environment.

expansion of the energy, these properties[61] are obtained in a finite difference approach by

$$-\mu^{\#} = \chi^{\#} = \frac{I_v^{\#} + A_v^{\#}}{2} \tag{4}$$

$$\eta^{\#} = \frac{I_v^{\#} - A_v^{\#}}{2} \tag{5}$$

with $I_v^{\#}$ and $A_v^{\#}$ respectively the vertical ionization energy and electron affinity in the given environment, and therefore different from the isolated species properties I_v^0 and A_v^0. The value $\chi^{\#}$ implicitly accounts for the effect of the external potential, meaning that an explicit estimation of the $\int f(r)\, \Delta v(r)\, \mathrm{d}r$ term is no longer needed. The presence of a given environment will furthermore provoke changes in size and shape effects of the atoms and implicitly introduce higher order terms (the hardness is estimated in a given environment so terms such as $(\delta\eta/\delta v(r))_N$ are implicit).

As can be seen from the discussion above, this second approach is straightforward, demands less effort, and does not require any form of calibration considering the external potential effects to be implicitly accounted for. The only difficulty encountered is the need to estimate the vertical ionization energy and electron affinity in a given environment. Obtaining the group electronegativity of A in the AB molecule, would therefore require the estimation of these properties in the molecular environment created by B. No exact physical description of such a molecular environment exists, and one therefore has to turn to a chemically motivated approximation of the molecular environment, in which the vertical properties can then be estimated. In the next section we will suggest one such approximation of the molecular environment and furthermore verify its reliability.

3.2. A Point Charge Model of the Molecular Environment. We will now construct a chemically motivated model of the molecular environment and consequently estimate the electronegativity of some functional groups in their respective molecular environment, thus obtaining the group in molecule (GIM) electronegativity values.[12]

The environment experienced by a functional group in a molecule is created by the presence of all atoms not belonging to the functional group. A chemically justified model of the molecular environment therefore has to account for the nuclei as well as the electron density of these atoms. The most crude and simple way of doing so, is by replacing these atoms by point charges, which are given the values of the charges the atoms bear in the entire molecule (Figure 1). Considering that for short distances such as the covalent distance considered in this work, the charge distribution between groups A and B overlap, a simple coulomb model might be insufficient. Basis functions centered on the point charges can be introduced to account for the shielding between overlapping charge clouds,[35,41,62−66] which could increase the accuracy of the obtained results. However, our objective is to show how to implicitly include the external potential effect in the electronegativity value, and we prefer doing so by keeping the model as simple as possible, even if this requires a partial loss in accuracy. Toufar et al.[43] already calculated the hardness and electronegativity of atoms in the presence of point charges. They nevertheless limited themselves to charges, which were placed symmetrically around the central atom and which did not account for the presence of the other atoms surrounding the central atom.

To obtain the electronegativity and hardness of a functional group in the modeled molecular environment, the vertical ionization energy and electron affinity of the functional group have to be computed in the presence of the point charge modeled environment and then inserted into eqs 4 and 5, respectively.

Although the model of the molecular environment presented above has a sound chemical basis, we still need to check the reliability of the obtained GIM electronegativity values. As presented previously,[12] one way of doing so is to consider the electronegativity equalization principle, under the assumption that the difference between the modeled external potential (molecular environment) and the effective external potential can be neglected ($\delta v(r) \approx 0$). In this case, the difference between the GIM electronegativity and the effective electronegativity of the functional group in the actual molecule is only due to the charge carried by the functional group in the molecule ($q = -\Delta N$). Equation 3 can then be written for a functional group A in the molecule AB as

$$\chi_A = \chi_A^* + 2\eta_A^* q_A \tag{6}$$

with χ_A^* and η_A^* being the GIM electronegativity and hardness calculated within the presented point charge model and χ_A being the effective electronegativity of the functional group A in the AB molecule.

According to Sanderson's principle, the effective electronegativities of A and B are equal in the AB molecule:

$$\chi_A = \chi_B \tag{7}$$

Inserting eq 6 for A and B into eq 7, and knowing that $q_A = -q_B$, leads to

$$q_A = \frac{\chi_B^* - \chi_A^*}{2(\eta_A^* + \eta_B^*)} \tag{8}$$

The presence of the GIM parameters χ^* and η^*, which implicitly account for the external potential effects, make eq 8 different from the earlier expression[44] based on the isolated group parameters $\chi°$ and $\eta°$:

$$q_A = \frac{\chi_B^0 - \chi_A^0}{2(\eta_A^0 + \eta_B^0)} \tag{9}$$

If the GIM electronegativities and consequently the point charge model of the environment are meaningful, the charge of A estimated by eq 8 should coincide with the ab initio computed charge of A in the AB molecule.

Table 1 gives the NPA ab initio charge (CCD) of the CH_3 group in the studied CH_3X molecules and the charge estimated using eqs 8 and 9, as well as the difference between the ab initio charge and the latter two.

The most important differences between the ab initio charge and the charge estimated by eq 8 are obtained for X = −CHO,

TABLE 1: NPA ab Initio (CCD) Charge of the CH_3 Group in the CH_3X Molecules (q_{AI}), the Charge Estimated by Equation 8 Using the GIM Parameters (q_{GIM}), and the Charge Estimated by Equation 9 Using the Isolated Group Parameters (q_{isol}), as Well as the Difference between the AI Charge and These Latter Two[a]

X	q_{AI}	q_{GIM}	q_{isol}	$q_{AI} - q_{GIM}$	$q_{AI} - q_{isol}$
C_2H_3	0.00	−0.02	0.00	0.02	0.00
C_2H	0.03	0.09	0.14	−0.06	−0.11
CH_2F	0.00	−0.09	0.01	0.09	−0.01
CH_2Cl	0.03	0.00	0.00	0.03	0.03
CHO	−0.02	−0.20	−0.03	0.18	0.01
COOH	0.01	−0.15	0.03	0.16	−0.02
NH_2	0.16	0.20	0.04	−0.04	0.12
NO_2	0.27	0.13	0.10	0.14	0.17
OH	0.29	0.36	0.13	−0.07	0.16
OCl	0.34	0.39	0.10	−0.05	0.24
OCH_3	0.31	0.35	0.07	−0.04	0.24
SiH_3	−0.39	−0.60	−0.03	0.21	−0.36
PH_2	−0.25	−0.30	−0.01	0.05	−0.24
SH	−0.09	−0.05	0.07	−0.04	−0.16

[a] The GIM as well as isolated group parameters needed to obtain these results can be found in the Supporting Information.

−COOH, and $-NO_2$. These variations are due to the finite difference approximation used to obtain electronegativity parameters and not to the use of a modeled environment. In the finite difference approximation, one estimates the electronegativity of a functional group as the arithmetic mean of the ionization potential and electron affinity, under the assumption that electronic structures of the cationic, neutral, and anionic functional groups resemble that of the functional group in the molecule. This is however not the case for species that are characterized by strong delocalization effects such as the cationic CHO, COOH, and NO_2 molecules for which multiple resonance structures can be written. The electronic structure of these cationic groups therefore does not resemble the localized electronic structure the functional group has in the CH_3X molecule, which is clearly in contradiction with the assumption made earlier. A hypothetically less delocalized description of the electronic structure would imply a higher energy for the cationic molecules, leading to an increased ionization potential and consequently an increased electronegativity value. As an effect, the CH_3 group would become more positively charged and thus be in better agreement with the ab initio charge.

The problem encountered for CHO, COOH, and NO_2 groups is thus clearly inherent to the finite difference approach and not due to our model of the molecular environment. It can be avoided if the electronegativity is estimated by small increments of N (cf. $\mu = (\partial E/\partial N)_{v(r)}$), which would imply a noninteger number of electrons and is presently not feasible. A finite difference approach should therefore be limited to species that are not characterized by strong electronic reorganization, in other words for which multiple resonance forms cannot be written.

To check the correctness of the GIM parameters and thus of the point charge model, we therefore have to exclude the species for which the finite difference approach cannot be used (X= −CHO, −COOH, and $-NO_2$) from the analysis. As shown by Table 1, the ab initio CH_3 charge and the charge estimated using GIM parameters are always similar for the remaining 11 CH_3X molecules, with an average absolute difference of 0.06. The charges of the CH_3 group estimated using eq 8, vary between −0.60 and 0.39 covering hereby the complete span of the ab initio charges ([−0.40; 0.34]). Figure 2 shows a least-squares linear regression curve between both the ab initio charges and the charges obtained from eq 8. The excellent correlation between both values ($r^2 = 0.97$), as well as the slope of the curve, which is close to 1, confirms the reliability of the GIM parameters.

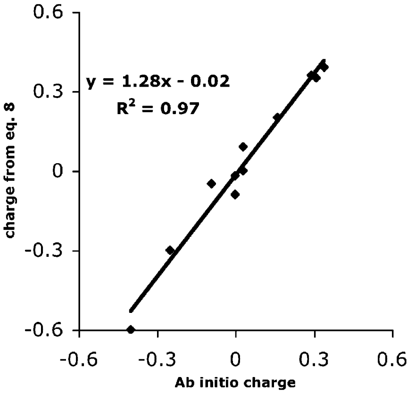

Figure 2. Ab initio charge of the CH_3 group in the CH_3X molecules compared to the charge estimated via eq 8, using "group in molecule" electronegativities and hardnesses.

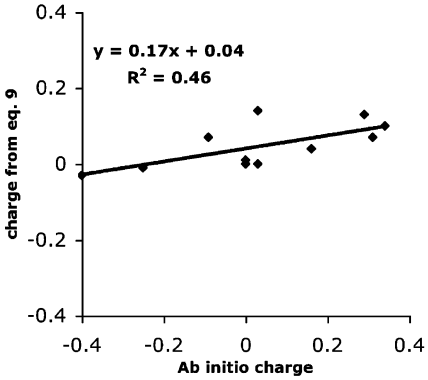

Figure 3. Ab initio charge of the CH_3 group in the CH_3X molecules, compared to the charge estimated via eq 9 using isolated group electronegativities and hardnesses.

Although we have shown that the GIM approach leads to reliable group electronegativity values, the need to include the molecular environment might be questioned.[44] This can easily be answered by considering the CH_3 charges estimated using the isolated group electronegativities (eq 9). The charges estimated from these isolated properties show a more important average absolute difference with respect to the ab initio results (0.15), indicating that they are less accurate than the GIM results. The estimated CH_3 charges for the different CH_3X molecules are furthermore all close to 0 and vary between −0.03 and 0.14, an interval which is not even spanning half of the ab initio charge interval ([−0.40; 0.34]). Figure 3 confirms this graphically and furthermore shows vary bad correlation ($r^2 = 0.46$) between the ab initio charges and those obtained using eq 9. These results confirm the earlier statement[12] that the influence of the molecular environment on the chemical potential cannot be neglected and doing so could lead to inaccurate results.

We have now shown that one needs to take the effect of the external potential into account in order to obtain reasonable charge transfer values between functional groups. This can be done implicitly using a chemically justified model of the molecular environment. The approach suggested however requires the a priori knowledge of the charge distribution in the entire molecule to create the modeled molecular environment. So, it is pointless to implement this procedure in an electronegativity equalization scheme, aiming to estimate the charge transfer between two functional groups at covalent distance from one another. In the next point, we will therefore

SCHEME 1: Scheme Leading to Self-Consistent Polarizations of the CH_3 and PH_2 Functional Groups When Placed in the Presence of One Another and to the Charge Transfer between Functional Groups

0. Calculate the isolated group electronegativities χ^0 and hardness η^0.
1. Compute the charge distribution of the isolated functional group PH_2.
2. Use the charge distribution of PH_2 ($\sum_A q_A = 0$) to construct an environment for CH_3.
3. Compute the charge distribution of CH_3 in the presence of this environment.
4. Use the charge distribution of CH_3 ($\sum_B q_B = 0$) to construct an environment for PH_2.
5. Compute a new charge distribution for PH_2 in the presence of this environment.
6. Inject this new charge distribution of PH_2 ($\sum_A q_A = 0$) in step 2, and continue until convergence of the charge distributions for PH_2 and CH_3 is reached.
7. Use these charge distributions to create the unconnected environment for PH_2 and CH_3 and calculate the unconnected properties χ', η', and $f^{0\prime}$.
8. Insert the values for these unconnected properties into equation 19 and set a value for λ (e.g. 0.65) to obtain q_{CH_3}.

TABLE 2: The Charge Distribution in the Functional Groups CH_3 and PH_2 Following the Iterative Procedure Presented in Scheme 1, and the Unconnected (χ'), as Well as Isolated (χ^0) Group Electronegativity Values of the CH_3 and PH_2 Groups

	CH_3		PH_2		χ(eV)	
	q_C	$\bar{q}_H$	q_P	$\bar{q}_H$	CH_3	PH_2
0					5.198 (χ^0)	5.047 (χ^0)
1			0.182	−0.091		
2 + 3	−0.468	0.156				
4 + 5			0.206	−0.103		
2′ + 3′	−0.470	0.157				
4′ + 5′			0.207	−0.103		
2″ + 3″	−0.471	0.157				
4″ + 5″			0.207	−0.103		
6	−0.471	0.157	0.207	−0.103		
7					5.677 (χ')	4.190 (χ')
8					$\Longrightarrow$	$q_{CH_3} = -0.15$

show that it is possible to construct an alternatively modeled environment, which contains most of the information included in the approximated molecular environment described above, but with the advantage that we do not have to rely on an a priori knowledge of the charge distribution in the entire molecule. The small differences between both models can be accounted for by slightly adjusting the electronegativity expression given in eq 8. This latter can then be used to simplify the EEM scheme, by implicitly accounting for the major part of the external potential effect.

3.3. An Electronegativity Equalization Scheme. We start by considering the functional group A. In a next step, a functional group B is placed in the environment of A without creating a chemical bond between the two functional groups. This is opposite to what we did for the GIM environment, which was created by considering the charge distribution of the entire molecule, implying that A and B were chemically connected. Once more we model the effect of B by point charges. These point charges have to represent the effect of the nuclei and electron density of the atoms of B. They can therefore be given the value of the charges the atoms bear in the isolated functional group B and consequently have to sum up to 0. In a similar manner, the charge distribution of the isolated group A could serve to create an environment for the functional group B.

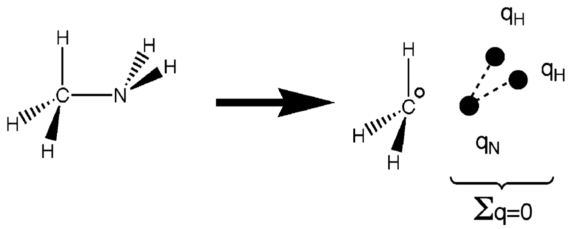

Figure 4. For the unconnected CH_3 functional group in a CH_3NH_2 molecule, the environment is created by replacing the atoms of the NH_2 group by the self-consistent charges of the NH_2 functional group. The electronegativity (χ') of CH_3 is then calculated in the presence of this approximated environment. (During the entire procedure all atoms are held fixed at the position they have in the complete molecule).

Although still remaining chemically unconnected, group A can be allowed to polarize because of the environment created by B. This new charge distribution of A can be calculated and serve to create a new environment for B, which can then in turn be allowed to polarize, leading to a new charge distribution for B. This latter can once more be used to create a new environment for A, and so forth. Clearly an iterative scheme is installed, which is described in Scheme 1 and Table 2 for the CH_3 and PH_2 functional groups forming the CH_3PH_2 molecule.

Upon convergence, A and B can be considered fully polarized because of each other's presence, while remaining unconnected. The thus created environment is therefore named the "unconnected" environment (Figure 4). As can be seen from Table 2, convergence is reached rapidly.

By computing the ionization energy and electron affinity of A and B in their respective unconnected environments and by inserting these values in eq 4, the unconnected electronegativity χ' of A and B can be obtained. This unconnected electronegativity is situated somewhere between the isolated and the GIM electronegativity and implicitly accounts for a major part of the external potential effect.

The unconnected electronegativity χ' can be related to the earlier obtained GIM electronegativity χ^* by explicitly accounting for the difference in external potential between the two modeled environments ($\Delta\nu(r)$).

$$\chi^* = \chi' - \int f(r)\, \Delta\nu(r)\, \mathrm{d}r \qquad (10)$$

The difference in external potential $\Delta\nu(r)$ between the GIM model and the unconnected model is due to the fact that we did not chemically connect groups A and B for the latter. In other words, the only difference between the GIM model and the unconnected model is that the charge transfer is included to create the model environment in the former case. The $\int f(r)\, \Delta\nu(r)\, \mathrm{d}r$ term in eq 10 can therefore be related to the charge transfer q.

The classical part of $\Delta\nu(r)$ for a group A in the presence of a group B can be approximated using a Coulomb model:

$$\Delta\nu(r) = -\lambda \sum_S \Delta q_S / |R_S - r| \qquad (11)$$

with Δq_S being the variation of a point charge in the unconnected environment created by B because of the charge transfer ($\sum_S \Delta q_S = q$). The term $|R_S - r|$ represents the distance between r and a point charge, and the summation runs over all point charges of the unconnected environment created by B. Including the entire charge transfer (q) in the environment might be quite a substantial approximation. The parameter λ allows us to adjust the part of the charge transfer that we want to include to correct the unconnected environment and thus varies between 0 and 1 with $\lambda = 0$ corresponding to the unconnected environment. This parameter will furthermore allow us to account for the nonclassical terms omitted in the approximation of $\Delta\nu(r)$ (eq 11) as well as for the errors introduced in further approximations.

The function telling us how a transferred charge will distribute over the point charges (atoms) of B, is by its definition the condensed Fukui function[60] of B. The condensed Fukui function used (12) is an average of the right (12a) and left-hand-side (12b) condensed Fukui function as usually adopted in radical systems and is obtained by a finite difference approach. The condensed Fukui function $f_s^{0\prime}$ is computed in the same environment as χ', to implicitly account for the correction of this function with respect to the external potential $(\delta f(r)/\delta\nu(r'))$.[67]

$$f_S^- = q_S^+ - q_S^0 \tag{12a}$$

$$f_S^+ = q_S^0 - q_S^- \tag{12b}$$

$$f_S^0 = \frac{1}{2}[f_S^+ + f_S^-] \tag{12}$$

Using this function Δq_S can be approximated as

$$\Delta q_S = f_S^{0\prime} q_B \tag{13}$$

with q_B $(= -q_A)$ being the total transferred charge. Inserting eq 13 into eq 11 leads to

$$\Delta\nu(r) = \lambda \sum_S \frac{f_S^{0\prime} q_A}{|R_S - r|} \tag{14}$$

Using eq 14, the GIM electronegativity (eq 10) can be written for a functional group A as

$$\chi_A^* = \chi_A' - \lambda q_A \sum_S \int f(r) \frac{f_S^{0\prime}}{|R_S - r|}\,dr \tag{15}$$

By replacing the integration in eq 15 by a finite sum using this time the condensed Fukui function of A, one can further reduce eq 15 to

$$\chi_A^* = \chi_A' - \lambda q_A \sum_R \sum_S \frac{f_R^{0\prime} f_S^{0\prime}}{R_{RS}} \tag{16}$$

with R running over all atoms of A and R_{RS} being the distance between an atom R and a point charge S. As already mentioned above, for distances where the charge distributions of A and B overlap, a simple Coulomb law (eqs 11, 14−16) might be insufficient. A shielding correction can be included by introducing Slater type functions.[35,41,62−6] Although this would probably increase the accuracy of our results it will complicate our model and go beyond the objective of this work, which concentrates on showing how using basic chemical concepts and a correct theoretical definition of electronegativity, one can come to a reasonable charge transfer scheme by implicitly accounting for the major part of the external potential effect. The λ factor introduced above can furthermore partially correct for the lacking shielding correction.

We have shown above that the GIM χ^* electronegativities lead to excellent charge transfers, when they are used in an electronegativity equalization scheme. We therefore insert eq 16 into eq 6, which when using η_A' instead of η_A^* (differences are expected to be small, and can furthermore be partially corrected by λ), gives

$$\chi_A = \chi_A' + 2\eta_A' q_A - \lambda q_A \sum_R \sum_S \frac{f_R^{0\prime} f_S^{0\prime}}{R_{RS}} \tag{17}$$

as an expression for the effective electronegativity of A in the AB molecule. A similar expression can be given for the effective electronegativity of B.

$$\chi_B = \chi_B' + 2\eta_B' q_B - \lambda q_B \sum_R \sum_S \frac{f_R^{0\prime} f_S^{0\prime}}{R_{RS}} \tag{18}$$

Inserting both equations into eq 7, and knowing $q_A = -q_B$, leads to

$$q_A = \frac{\chi_B' - \chi_A'}{2(\eta_A' + \eta_B') - 2\lambda \sum_R \sum_S \frac{f_R^{0\prime} f_S^{0\prime}}{R_{RS}}} \tag{19}$$

which gives a practical charge-transfer scheme with predictive power considering that all properties on the right-hand-side of eq 19 are obtained without having to do any calculation on the entire molecule. By changing the parameter λ we are able to correct for part of the errors introduced by the approximations made.

Equation 19 was used to estimate the CH_3 group charge in the same 11 CH_3X compounds studied above. The results are given in Table 3 for $\lambda = 1$ and $\lambda = 0.65$. The correlation between the ab initio NPA charges and those obtained using the electronegativity equalization scheme does not vary much with the size of λ ($r^2 = 0.80$, 0.79, and 0.78 for $\lambda = 0$, 0.65, and 1, respectively). This shows that most of the external potential effects are already implicitly accounted for by the unconnected χ' electronegativity values. The correction of the effective electronegativity due to the contribution of the charge transfer to the external potential (the $\lambda\Sigma_R\Sigma_S f_R^{0\prime} f_S^{0\prime}/R_{RS}$ term in eq 19) should therefore be seen as relatively small. The obtained correlation is very satisfactory especially compared to the lack of correlation when using the isolated $\chi°$ values, and is furthermore comparable to that obtained by the earlier electronegativity equalization method for atoms.[27−34] The advantage of the charge-transfer equation proposed in this paper (eq 19) is that it does not require cumbersome calibrations for every element introduced, the only variable being λ.

Table 3 shows the results to be overestimated for $\lambda = 1$, which is to say that including the total of the transferred charge into the external potential leads to an overestimation of the external potential effect, and hence a too small value for the denominator in eq 19 (The condensed Fukui function is positive except in some pathological cases,[68−70] so $\lambda\Sigma_R\Sigma_S f_R^{0\prime} f_S^{0\prime}/R_{RS}$ is also positive). Although, as mentioned above, a change in λ does not change the correlation, it nevertheless allows us to adjust the size of the charge transfers. A value of $\lambda = 0.65$ gives charge values closest to the ab initio obtained charges, as can be seen from the almost unitary slope of the least-squares regression curve in Figure 5.

The differences between the ab initio charges and those estimated using eq 19 are small, showing an average absolute difference of 0.09, which is once more comparable to the results found in the earlier electronegativity equalization scheme on atoms.[27−34] The stronger variation for X = $-CH_2F$ can partially be due to the fact that we are approaching the limit of our finite difference approach. Indeed, the cation needed to obtain the

TABLE 3: NPA ab Initio (CCD) Charge of the CH_3 Group in the CH_3X Molecules (q_{AI}), the Charge Estimated by Equation 19 Using Unconnected Parameters (q_{unc}) with $\lambda = 1$ and $\lambda = 0.65$, as Well as the Difference between the AI Charge and This Latter[a]

X	q_{AI}	q_{unc} ($\lambda = 1$)	q_{unc} ($\lambda = 0.65$)	$q_{AI} - q_{unc}$ ($\lambda = 0.65$)
C_2H_3	0.00	−0.15	−0.08	0.08
C_2H	0.03	0.12	0.07	−0.04
CH_2F	0.00	−0.45	−0.21	0.21
CH_2Cl	0.03	−0.14	−0.07	0.10
NH_2	0.16	0.41	0.14	0.02
OH	0.29	0.67	0.28	0.01
OCl	0.34	0.42	0.22	0.12
OCH_3	0.31	0.40	0.20	0.11
SiH_3	−0.39	−0.83	−0.39	0.00
PH_2	−0.25	−0.33	−0.15	−0.10
SH	−0.09	0.13	0.07	−0.16

[a] The unconnected χ' and η' properties needed to obtain these results can be found in the Supporting Information.

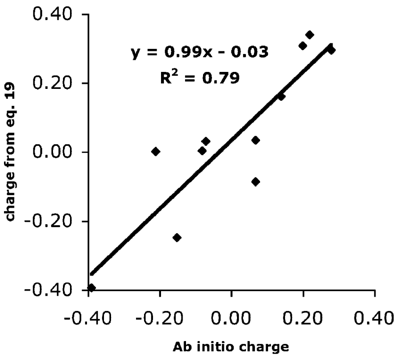

Figure 5. Ab initio charge of the CH_3 group in the CH_3X molecules, compared to the charge estimated via eq 19 ($\lambda = 0.65$), using unconnected group electronegativities, hardnesses, and condensed Fukui functions.

vertical ionization energy shows fluorine lone pairs, which are strongly polarized toward the carbon atom, showing therefore an electronic structure quite different from that of the functional group in the molecule.

4. Conclusion

On the basis of the correct definition of electronegativity and using basic chemical concepts, we have developed a first principle electronegativity equalization scheme, which implicitly accounts for a major part of the external potential effect and leads to satisfactory charge-transfer results.

External potential effects are shown to have quite a substantial influence on group electronegativity values. The molecular environment effects can be implicitly included in the electronegativity value by estimating this latter in a chemically justified model of the molecular environment. This model is created by replacing all of the atoms not belonging to the functional group by point charges given the values the atoms bear in the entire molecule.

An electronegativity equalization scheme developed in order to predict charge transfers can however not depend on an a priori knowledge of the charge distribution in the entire molecule. By slightly adjusting the above-mentioned model and explicitly accounting for the difference between both models, an electronegativity equalization scheme is developed that does not require an a priori knowledge of the charge distribution in the entire molecule. This latter can therefore be used as a predictive tool to estimate the charge transfer between two functional groups. The results are shown to be quite accurate and encourage the use of external potential corrected electronegativity values.

As this paper is mainly methodological in nature, we have limited ourselves to the applications on molecules composed of two functional groups. For an extension of this method to large molecules such as biomolecules composed of a multitude of functional groups, it might be desirable to improve the model by including some shielding correction, as well as a factor preventing an artificial charge transfer at large distances because of the quadratic approximation used. By decomposing the biomolecules in fragments, which are not characterized by strong delocalization effects, and equalizing their electronegativities, one could, combined with the knowledge of the total molecular charge, calculate the charge carried by each of these fragments.

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Supporting Information Available: Electronegativity and hardness values of the different species treated in the present paper used to estimate the charges in Tables 1 and 3 in pdf format. This material is available free of charge via the Internet at http://pubs.acs.org.

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