The Importance of the External Potential on Group Electronegativity

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

Laboratoire de Chimie Quantique, Bâtiment Lavoisier, Université catholique de Louvain, 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

Received: June 8, 2005; In Final Form: August 30, 2005

The electronegativity of groups placed in a molecular environment is obtained using CCSD calculations of the electron affinity and ionization energy. A point charge model is used as an approximation of the molecular environment. The electronegativity values obtained in the presence of a point charge model are compared to the isolated group property to estimate the importance of the external potential on the group's electronegativity. The validity of the "group in molecule" electronegativities is verified by comparing EEM (electronegativity equalization method) charge transfer values to the explicitly calculated natural population analysis (NPA) ones, as well as by comparing the variation in electronegativity between the isolated functional group and the functional group in the presence of a modeled environment with the variation based on a perturbation expansion of the chemical potential.

1. Introduction

The electronegativity concept was defined in the 1930s by Pauling[1] as "the power of an atom in a molecule to attract electrons to itself". It quickly became one of the most popular and useful chemical concepts. Following the ideas of Pauling, various atomic electronegativity scales have been introduced (for reviews, see refs 2 and 3). One of the most interesting definitions of this property was given by Mulliken in a 1934 paper.[4] In this paper, he defined the atom's electronegativity as the arithmetic mean of the ionization potential (I) and electron affinity (A). By taking the valence state corrected values of these latter two properties, the "atom in molecule" aspect was taken into account. Three decades later Iczkowski and Margrave[5] were the first to describe the electronegativity as a derivative of energy with respect to charge. Quickly thereafter Hinze and Jaffé refined these ideas by introducing orbital electronegativity.[6,7] Their findings lead to defining group electronegativities.[8]

However, it was not until 1978 that a milestone in the search for a sharp definition of electronegativity was reached by Parr et al.[9] 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.[10] For the first time, a rigorous and precise definition of electronegativity for all species, atoms as well as groups, was given. Mulliken's electronegativity can be seen as an approximation of this definition. In the vortex of these ideas, the electronegativity equalization theorem for atoms and orbitals was also proven to be valid.[11]

Despite the abundance of papers concerning the electronegativity of elements and groups (for references, see ref 12), little attention has been paid to the importance of the environment on the electronegativity of atoms or groups. Nevertheless, the external potential determined among others by this environment is directly implied in the chemical potential's definition. Nalewajski[13,14] and Mortier et al.[15−17] were the first to consider the importance of this factor. They introduced an approximate external potential into an electronegativity equalization scheme to obtain charge distributions in molecules. De Proft and Geerlings[18] also promoted the use of nonempirically calculated, external potential corrected atomic electronegativity and hardness values in the framework of electronegativity equalization. The problems arising in the atomic approach used in these papers are mostly due to the approximations made such as a spherical electron density distribution or an isotropic Fukui function. This latter should in fact be heavily corrected for the size and shape effects of the electron density when passing from an isolated atom to an atom in molecule[19] situation. These problems can be partially avoided by looking at functional groups instead of atoms. Because the atoms in a functional group show already much more resemblance to the atoms in the entire molecular environment, perturbations can be expected to be smaller. This paper, in contrast to the above-mentioned papers,[13−18] will therefore no longer approach the molecule as being composed of individual atoms but as being composed of different functional groups.

Whereas the main goal of the previously mentioned papers is to obtain a strategy to calculate atomic charges, our aim is to quantify the importance of the external potential on the electronegativity of a functional group as well as to provide a computational strategy that allows one to obtain this property for a given group in a molecule. The paper is therefore organized as follows:

The first part of the paper gives a short theoretical reminder. Starting from the definition of the chemical potential (electronegativity), we identify the factors that will influence its value. We show how a variation of these factors will change the chemical potential and how for a given situation (fixed external potential), one can use Mulliken's definition to obtain an electronegativity value.

In the second part of the paper, we vary the external potential by introducing a perturbation. This can be done in a simple

---

* 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 (VUB).

10.1021/jp053068f CCC: $30.25

way by placing a point charge in the proximity of the functional group. By varying the magnitude of this point charge, one can evaluate the importance of a change in external potential on the group electronegativity value.

If the environment influences the group electronegativity value, one might expect the electronegativity of an isolated functional group to be different from the electronegativity of this group in a molecular environment. In the third part of the paper, we therefore try to obtain a representative value of group electronegativity in a molecular environment by also taking into account all atoms belonging to the molecule but not to the functional group. A simple but physically meaningful model is introduced to approximate this molecular environment. To the best of our knowledge, group electronegativity calculations in the presence of a perturbation due to the molecular environment have not yet been performed. (Studies of solvent effects on group properties were carried out on the basis of continuum models.[20−22])

In the fourth and final part of this paper, the correctness of the electronegativity values obtained using our model are verified in two distinct ways. First, one can apply an electronegativity equalization scheme between two functional groups composing a molecule. Second, one can compare the difference in electronegativity between an isolated functional group and a functional group in the presence of the modeled environment with the variation obtained using a perturbation expansion of the chemical potential.

Because this paper is mainly methodological, we shall limit the applications to only a few species of the A_2 and AB type with A,B = CH_3, NH_2 and also PH_2 to cover our recent interests in phosphorus-containing compounds.[23−25]

2. Computational Details

All structures were optimized at the coupled cluster level of theory with single and double substitutions. The introduction of a triples correction confirms the CCSD results. The CCSD(T) energy of some of the negative ions shows anomalies resulting from the approximation introduced by the numerical triples correction, and therefore CCSD results are used throughout this paper. Calculations were performed using the Gaussian series of programs.[26] cc-pVTZ and aug-cc-pVTZ basis sets showed identical behavior as the 6-31++G(d,p) basis set; the latter, being computationally less demanding, is therefore considered to be sufficiently accurate for our purpose. Charges have been obtained using a natural population analysis (NPA) at the CCD level of theory (considering that the generalized CCSD first-order density is not available in the Gaussian series of programs, the NPA analysis has been performed at the CCD level of theory). Unlike Mulliken populations, the natural populations seem to exhibit excellent numerical stability with respect to changes in basis set and methodology.[27] Nevertheless, for the model compounds considered in this paper, the results obtained using a Mulliken population analysis showed similar behavior to those using a NPA analysis.

The model molecules involving the NH_2, PH_2, and CH_3 functional groups (C_2H_6, P_2H_4, N_2H_4, CH_3PH_2, CH_3NH_2,) were chosen so as to include atoms of the second as well as the third period.

3. Results and Discussion

3.1. Factors Influencing the Chemical Potential. To identify the factors influencing the electronegativity value, we start with the well-known expression relating the energy variation with a change in number of electrons N and a change in external potential $\nu(\mathbf{r})$ (representing the molecular structure and the environment).

$$\mathrm{d}E = \left(\frac{\partial E}{\partial N}\right)_{\nu(\mathbf{r})} \mathrm{d}N + \int \left(\frac{\delta E}{\delta \nu(\mathbf{r})}\right)_N \delta\nu(\mathbf{r})\, \mathrm{d}(\mathbf{r}) = \mu\, \mathrm{d}N + \int \rho(\mathbf{r})\, \delta\nu(\mathbf{r})\, \mathrm{d}(\mathbf{r}) \quad (1)$$

with $\mu = (\partial E/\partial N)_{\nu(\mathbf{r})}$, representing the electronic chemical potential, originally introduced as a Lagrangian multiplier.[9] The latter can be identified with the negative of the electronegativity.

Like the energy functional, all concepts that are first or higher order derivatives of this functional are also unique functionals of the number of electrons N and the external potential $\nu(\mathbf{r})$. Consequently, the electronegativity of a group will also be influenced by these two factors. Because $\nu(\mathbf{r})$ depends on the environment, so will the electronegativity value.

Equation 2, in analogy with eq 1, shows how the chemical potential $\mu = \mu[N,\nu(\mathbf{r})]$ responds to a perturbation in the number of particles dN and to a perturbation in external potential $\delta\nu(\mathbf{r})$.

$$\mathrm{d}\mu = 2\eta\, \mathrm{d}N + \int f(\mathbf{r})\, \delta\nu(\mathbf{r})\, \mathrm{d}(\mathbf{r}) \quad (2)$$

Here

$$\eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{\nu(\mathbf{r})} = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu(\mathbf{r})} \quad \text{and} \quad f(\mathbf{r}) = \left[\frac{\delta \mu}{\delta \nu(\mathbf{r})}\right]_N = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{\nu(\mathbf{r})} \quad (3)$$

are the hardness[28] and the Fukui function[29] of the system.

One can obtain an electronegativity value by considering a situation with a fixed external potential. In this case, eqs 1 and 2 become

$$\mathrm{d}E = \mu\, \mathrm{d}N \quad (4)$$

$$\mathrm{d}\mu = 2\eta\, \mathrm{d}N \quad (5)$$

Considering a second-order Taylor expansion of the energy in the number of electrons, one obtains

$$E = E^0 + \mu(N - N^0) + \eta(N - N^0)^2 \quad (6)$$

with μ and η being the electronegativity and hardness of the molecule having N^0 electrons. Equation 6 leads in a finite difference approach to the well-known expressions for the electronegativity and hardness of a species:

$$-\mu = \chi = \frac{I_v + A_v}{2} \quad (7)$$

$$\eta = \frac{I_v - A_v}{2} \quad (8)$$

where I_v and A_v are the vertical ionization energy and electron affinity (cf. the demand of constant external potential). Equation 7 shows how Mulliken's electronegativity expression is recovered within a conceptual DFT context.

Equation 7 was used in earlier work by De Proft et al.[30,31] on isolated, nonperturbed functional groups. However, eq 7 can be used in any situation. It can therefore also be applied when one considers a functional group in the presence of a perturbed environment, as long as this environment is held constant during the determination of the ionization energy and electron affinity.

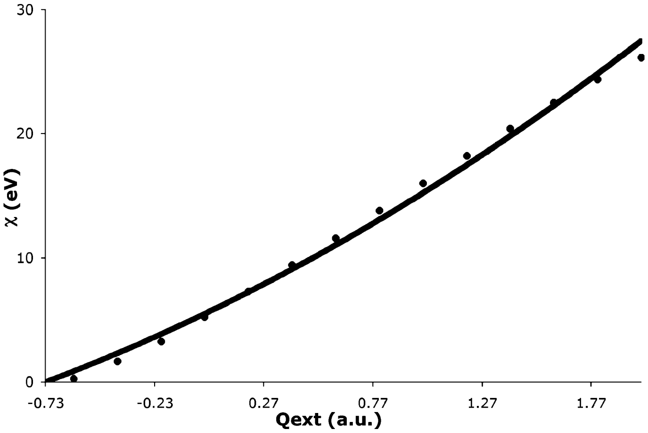

Figure 1. Variation of electronegativity (eV) of the CH_3 group (in CH_3NH_2) with respect to an external point charge placed at the N position. The best quadratic curve is drawn; correlation coefficient $r^2 > 0.99$).

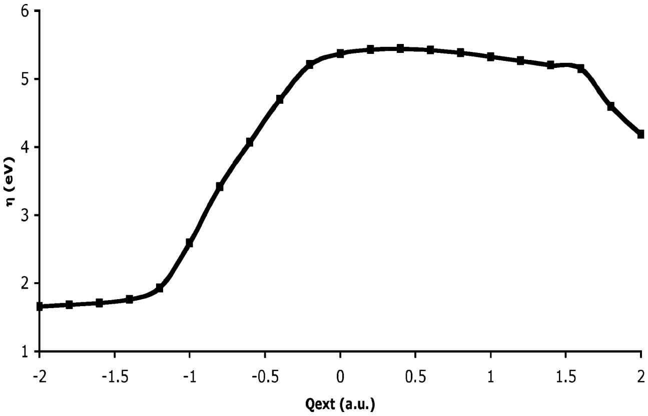

Figure 2. Variation of the hardness (eV) of the CH_3 group (in CH_3NH_2) with respect to an external point charge placed at the N position.

3.2. The Importance of an External Perturbation on Group Electronegativity. One of the easiest ways to model external perturbations is to place a single point charge close to the functional group. This was done for the CH_3, NH_2, and PH_2 functional groups, which compose the model molecules. These functional groups are given the structure they have in the CH_3PH_2 and CH_3NH_2 molecules. The point charge is placed at the carbon position for the NH_2/PH_2 and at the nitrogen/phosphorus position for the CH_3 functional group. The electronegativity is calculated using eq 7 for values of the external charge varying between -2 and $+2$. Parallel to the electronegativity, one obtains the hardness of a species (eq 8), which will therefore also be briefly discussed.

Figures 1 and 2 (some of the values presented in these figures are based on a negative electron affinity value; for a discussion on the use of these values in the context of conceptual DFT, see ref 12 and references therein) show the variation of the electronegativity and hardness of the CH_3 group in the structure it has in the CH_3NH_2 molecule. The curves of the other cases are similar. The value at $q = 0$ corresponds to the intrinsic group electronegativity and hardness of the unperturbed group. These intrinsic values were already obtained by De Proft et al.[30] The values found by these authors (4.41, 5.33, and 4.71 for the electronegativity and 5.64, 6.45, and 4.61 for the hardness of the CH_3, NH_2, and PH_2 radicals, respectively) can be compared to those given in Table 1. The slight differences are due to the difference in structure of the functional groups, as well as the difference in level of theory used (De Proft et al. used a CISD technique). The older electronegativity values obtained by Huheey,[8] using an EEM scheme and empirically determined atomic electronegativities seem to strongly overestimate this property (7.37, 8.39, and 6.95, respectively).

TABLE 1: The Isolated Group and Group in Molecule (GIM) Electronegativity and Hardness for the CH_3, PH_2, and NH_2 Groups[a] in C_2H_6, P_2H_4, and N_2H_4, Respectively

	χ (eV)			η (eV)		
	CH_3	NH_2	PH_2	CH_3	NH_2	PH_2
isolated	5.24	6.16	5.05	5.37	6.03	4.39
GIM	3.67	4.55	5.18	4.89	5.77	4.40

[a] The CH_3, NH_2, and PH_2 functional groups are given the structure that they have in the C_2H_6, N_2H_4, and P_2H_4 molecules, respectively.

The electronegativity versus external charge curve shows a regular, slightly quadratic behavior, as shown in Figure 1. Although the curve continues smoothly for values of q under -0.73, we choose not to represent this part, because the electronegativity would become negative, which would represent a physically unrealistic situation. A quadratic approximation of this curve will give a correlation coefficient superior to 0.99, meaning that a second-order development of μ with respect to $\nu(\mathbf{r})$ is sufficient. As in Figure 1, we are only changing the magnitude of the point charge and not the number of electrons; approaching in this case a variation in chemical potential by a second-order Taylor expansion in $\nu(\mathbf{r})$ gives

$$\Delta\mu = \int\left(\frac{\delta\mu}{\delta\nu(\mathbf{r})}\right)_N \Delta\nu(\mathbf{r})\,d\mathbf{r} + \frac{1}{2}\int\int\left(\frac{\delta^2\mu}{\delta\nu(\mathbf{r})\,\delta\nu(\mathbf{r}')}\right)_N \Delta\nu(\mathbf{r})\Delta\nu(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}' \tag{9}$$

with $(\delta\mu/\delta\nu(\mathbf{r}))_N = f(\mathbf{r})$, the Fukui function of the group in the absence of an external perturbation, and $(\delta^2\mu/(\delta\nu(\mathbf{r})\delta\nu(\mathbf{r}')))_N = (\delta f(\mathbf{r})/\delta\nu(\mathbf{r}'))_N$. The latter expression shows the variation of the Fukui function with respect to the external potential. This function can also be expressed as a third-order derivative of the energy functional $(\delta f(\mathbf{r})/\delta\nu(\mathbf{r}'))_N = (\delta^3E/(\delta\nu(\mathbf{r})\delta\nu(\mathbf{r}')\partial N))$ and can also be written as the N-derivative $(\partial\chi(\mathbf{r},\mathbf{r}')/\partial N)_{\nu(\mathbf{r})}$ of the two-variable linear response function $\chi(\mathbf{r},\mathbf{r}')$.[12,32] Because we have a single point charge model with the only variable being the magnitude of the charge, $\Delta\nu(\mathbf{r})$ can be approximated by$\Delta\nu(\mathbf{r}) = -q/(|\mathbf{R}-\mathbf{r}|)$, $|\mathbf{R}-\mathbf{r}|$ being the distance between $\mathbf{r}$ and the position of the point charge. Equation 9 can then be written as

$$\Delta\mu = -q\int f(\mathbf{r})\frac{1}{|\mathbf{R}-\mathbf{r}|}\,d\mathbf{r} + \frac{1}{2}q^2\int\int\left(\frac{\delta f(\mathbf{r})}{\delta\nu(\mathbf{r}')}\right)\frac{1}{|\mathbf{R}-\mathbf{r}|}\,\frac{1}{|\mathbf{R}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' \tag{10}$$

which accounts for the quadratic behavior of Figure 1. Nevertheless, the quadratic correction is small indicating a less important influence of the external potential on the variations of the Fukui function, as expected for third-order energy derivatives.[33] In this paper, we will therefore limit ourselves to a second-order development of the energy functional (first-order of chemical potential), in which case eq 9 reduces to

$$\Delta\mu = -q\int f(\mathbf{r})\frac{1}{|\mathbf{R}-\mathbf{r}|}\,d\mathbf{r} \tag{11}$$

Figure 1 clearly shows the important variation in electronegativity induced by a change in external potential. The intervals of [2.07, 9.38], [1.77, 10.18], [1.76, 8.77], and [2.66, 10.49] for a point charge lying in the range [−0.5, +0.5] for the CH_3 (in the CH_3PH_2 and CH_3NH_2 case), PH_2, and NH_2 functional groups respectively, show how important this variation can be. The interval for the methyl radical being more important in the second case can be explained by smaller $|\mathbf{R} - \mathbf{r}|$ distances (the PC and NC bond lengths are 1.86 and 1.47 Å, respectively). The magnitude of these intervals indicates that the external potential cannot be neglected when an electronegativity value is calculated.

The vertical ionization energy and electron affinity can also be used to obtain the hardness of a species. Figure 2 shows how the hardness of a species stays relatively constant when in the presence of a positive point charge but drops significantly once a negative point charge is put in the neighborhood of the functional group, finally flattening out again for the larger negative values. The S-like graph shows a clear asymmetric behavior for the hardness of the molecule in the presence of positive point charge on one hand and a negative one on the other.

As shown above, the electronegativity of a molecule changes when we change the external potential. One might wonder what happens inside the molecule to make this change in electronegativity possible? How does the electron density rearrange and how does it interact with the external perturbation? Although the Fukui function has a predictive power being able to describe how the electronegativity value of a molecule will change when one adds an external perturbation, it is, because of its single variable nature, unable to describe in such detail what goes on inside the molecule. To do so, we would need another reactivity descriptor that describes how the electronic density rearranges when the external potential is changed, $(\delta\rho(\mathbf{r})/\delta\nu(\mathbf{r}'))_N$. The latter is the two variable linear response function $\chi(\mathbf{r},\mathbf{r}')$,[32] which is unfortunately very difficult to obtain. Therefore an alternative approach based on an energy decomposition scheme is presented in the appendix.

3.3. Group Electronegativity in a Molecular Environment. As shown above, a perturbation of the environment can have a substantial influence on the group electronegativity value. The environment of a functional group in a molecule is different from that of the isolated functional group due to the presence of the atoms belonging to the molecule but not to the functional group. The electronegativity of an isolated functional group is thus likely to be different from that of the group in a molecular environment. An attempt to evaluate this difference has been undertaken by Cioslowski[34,35] circumventing the problem creating this environment by considering the entire molecule for group electronegativity calculations. He hereby obtained $\Delta\chi$ values, expressing the difference in electronegativity between two parts of a specific molecule. We will work on isolated groups and introduce the molecular environment as a perturbation by using an appropriate model. This model of the molecular environment has to take all atoms not belonging to the functional group into account. Considering that the environment is made up of the nuclei as well as the electron clouds of these atoms,[13−17] the easiest way of modeling the environment to account for both contributions will be by replacing these atoms by point charges, which are given the value of the charge the atoms bear in the entire molecule (Figure 3). This will allow us to have a very simple but physically meaningful model of the functional group's molecular environment, which accounts for the classical part of the variation in external potential taking place when an isolated functional group is transferred into a molecule. The use of a point charge model not only keeps the model simple but also avoids the problem of the dependency of electronic structure calculations with point charges on the use of the basis functions centered on these charges. Atomic electronegativity values in the presence of point charges were already calculated by Toufar et al.[36] These authors however, limited themselves to symmetrically placed negative charges around a central atom.

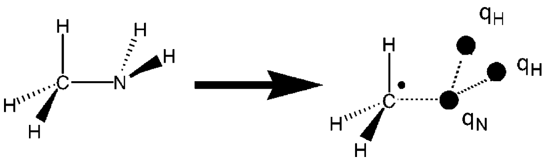

Figure 3. For the CH_3 functional group in a CH_3NH_2 molecule, the environment is created by replacing the atoms of the NH_2 group by the respective charge that they carry in the CH_3NH_2 molecule. The electronegativity of CH_3 is then calculated in the presence of this approximated environment.

Table 1 gives the isolated CH_3, PH_2, and NH_2 electronegativity values as well as the electronegativity values of these functional groups in the C_2H_6, P_2H_4, and N_2H_4 molecules, respectively. As shown in this table, there is a strong variation of the group's electronegativity when the group is placed in a molecular environment. The fact that electronegativity and hardness values of the different functional groups do not vary by the same amount is due to the difference in environment (the proximity and magnitude of the neighboring charges is different in all cases) as well as to the nature of the functional group itself. Considering that the electronegativity will depend on the nature of the entire molecule, the term of a "group in molecule" electronegativity becomes adequate.

3.4. Verification of the Significance of the Obtained Values. As a final step, the correctness of the electronegativity values obtained in the previous point has to be verified so as to validate our point charge model used to estimate electronegativities in a molecular environment. By using two different independent types of verification, we ensure ourselves of the correctness of these values and avoid the problem of a fortuitous agreement that can arise when using only a single method of verification.

Electronegativity Equalization. A first verification will be based on an electronegativity equalization scheme. In this case, we will use the electronegativity values to estimate a third property, the charge transfer between two functional groups. This charge transfer can then in turn be compared to the explicitly calculated NPA charge carried by the functional group in the molecule.

The group in molecule electronegativities are determined in an appropriate molecular external potential $\nu(\mathbf{r})$. In a first approximation, we will neglect the differences between the modeled external potential and the effective external potential created by the real molecular environment. When two fragments are put together to form a molecule, their change in electronegativity will then no longer be due to a change in $\nu(\mathbf{r})$ but only due to a change in N. Equation 5 can then be expanded as

$$\mu_A = \mu_A^* + 2\eta_A^*\Delta N \tag{12}$$

with μ_A^* and η_A^* representing the "group in molecule" (GIM) electronegativity and hardness obtained in the presence of our point charge model. According to Sanderson's electronegativity equalization principle,[37] the electronegativities of group A and

TABLE 2: The Group in Molecule (GIM) Electronegativity and Hardness for the CH_3, PH_2, and NH_2 Groups in CH_3NH_2 and CH_3PH_2, Charge Transfer ΔN (Eq 13), and NPA Charge of the CH_3 Group

	CH_3NH_2			
	CH_3	NH_2	ΔN	NPA
χ	2.17	6.24	0.20	0.16
η	4.35	5.90		
	CH_3PH_2			
	CH_3	PH_2	ΔN	NPA
χ	7.62	2.07	−0.30	−0.25
η	5.33	3.96		

B composing the AB molecule will equalize and the charge transfer ΔN is given by eq 13, with $\mu_A^* \geq \mu_B^*$.

$$\Delta N = \frac{\mu_A^* - \mu_B^*}{2(\eta_A^* + \eta_B^*)} \tag{13}$$

If our values of group electronegativity are physically meaningful, the value of ΔN obtained this way should approximately (taking into consideration the approximations made during our development) be equal to the charge carried by part A of the molecule. These values can be directly compared to the explicitly calculated NPA group charge of group A in the AB molecule. Table 2 gives the GIM electronegativity and hardness for the CH_3, NH_2, and PH_2 groups in the presence of the approximate environment that they experience in the CH_3PH_2 and CH_3NH_2 molecules. These values are used to compute the charge of the CH_3 group in the CH_3PH_2 and CH_3NH_2 molecules using eq 13. They are further compared with the NPA charge of the CH_3 group in these molecules. The NPA values correspond well with those calculated using eq 13. The differences are reasonably small considering the approximations that we made: first-order perturbation of chemical potential; errors in estimation of ionization energy and electron affinity; approximating the external potential by point charges (and thus neglecting nonclassical terms); using NPA charges obtained at CCD level; etc.

Considering the close agreement between ΔN and the explicitly calculated NPA charge, we can assume that the electronegativity values obtained are representative for the functional groups in their molecular environment.

Verification Based on a Perturbation Expression of the Chemical Potential. A second verification uses the definition of the chemical potential and the associated perturbation expansion up to the first order. Adding a modeled molecular environment by placing point charges in the presence of the functional group can be seen as a perturbation to the functional group. If this perturbation is relatively small, the variation in chemical potential (electronegativity) can be predicted using the first-order perturbation expansion given by eq 11 for a single external point charge. In the presence of multiple point charges, this equation can be generalized to

$$\Delta\mu = -\sum_B q_B \int f(\mathbf{r}) \frac{1}{|\mathbf{R} - \mathbf{r}|}\, d\mathbf{r} \tag{14}$$

with B running over all point charges. One can furthermore replace the integration of eq 11 by a finite sum using a condensed Fukui function,[38] in which case eq 14 reduces to

TABLE 3: Comparison of the Electronegativity Variation ($\Delta\chi$) Based on Eq 7 with the variation obtained using Eq 15

molecule	radical	$\Delta\chi_{eq7}$	$\Delta\chi_{eq15}$
C_2H_6	CH_3	−1.57	−1.62
N_2H_4	NH_2	−1.62	−2.00
P_2H_4	PH_2	0.12	0.11
CH_3NH_2	CH_3	−3.04	−3.36
	NH_2	0.07	−0.13
CH_3PH_2	CH_3	2.42	2.06
	PH_2	−2.98	−3.14

$$\Delta\mu = -\sum_A f_A \left(\sum_B \frac{q_B}{\mathbf{R}_{AB}} \right) \tag{15}$$

with $-\sum_B (q_B/\mathbf{R}_{AB})$ now being the difference in external potential at position A between the isolated group and the group in the presence of point charges (A runs over all atoms). The difference in chemical potential predicted in eq 15 should now coincide with the difference predicted by applying eq 7, respectively, on the isolated functional group and on the group in the presence of the modeled environment.

The condensed Fukui function used (eq 16c) is an average of the right- (eq 16a) and left-hand side (eq 16b) condensed Fukui function as usually adopted in radical systems and is obtained by a finite difference approach. Considering that f_A is positive except in some pathological cases,[39,40] $-\sum_B (q_B/\mathbf{R}_{AB})$ will determine the sign of $\Delta\mu$.

$$f(\mathbf{r}) = \left[\frac{\partial(\rho(\mathbf{r}))}{\partial N} \right]_{\nu(\mathbf{r})} \tag{16}$$

$$f_A^- = q_A^+ - q_A^0 \tag{16a}$$

$$f_A^+ = q_A^0 - q_A^- \tag{16b}$$

$$f_A^* = \frac{1}{2}[f_A^+ + f_A^-] \tag{16c}$$

Table 3 compares this $\Delta\mu$ value to the difference in electronegativity obtained using eq 7 both on the isolated functional group and on the group in the presence of point charges. We notice an excellent agreement for most cases, once more confirming the validity of the method used to obtain group electronegativity. The NH_2 values show slightly more deviation compared to the other cases. This could partially be due to some of the approximations made in the way of obtaining the $\Delta\chi$ ($= -\Delta\mu$) via eq 15. In fact, using a condensed Fukui function implies that the noncondensed Fukui function is symmetric around the atom, which is not always the case, especially when lone pairs are present. An integration as presented in eq 14, instead of the finite sum approximation used in eq 15, should presumably give better correspondence between the two methods. Nevertheless, the similarity between both values confirms once more the validity of the "group in molecule" electronegativity values obtained using a point charge model to approximate the molecular environment.

4. Conclusion

In this paper, we tried to obtain group electronegativity values that take into account the influence of the molecular environment. The external potential representing the position of the nuclei and the environment is one of the factors influencing the electronegativity. To have a first idea of the importance of

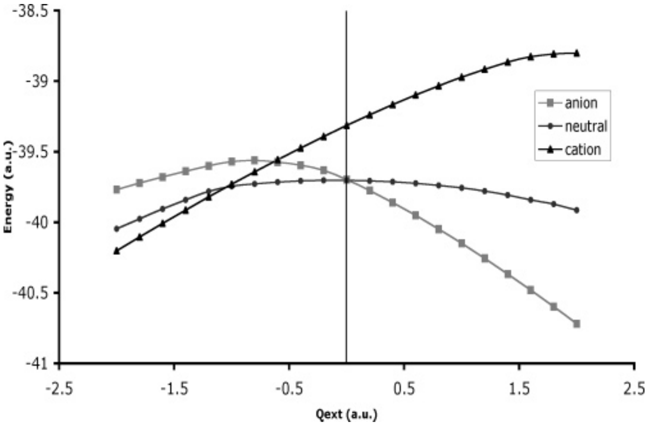

Figure 4. Variation of the energy CCSD of the CH_3 group (in CH_3-NH_2) with respect to a variation in external point charge for the anionic, radical, and cationic species.

a change in environment on the variation of the electronegativity value, we changed the external potential by placing a point charge in the surroundings of the functional group. As shown in this paper, this gives variations in electronegativity that cannot be neglected.

In a molecule, a functional group is surrounded by other functional groups. The environment of a functional group in a molecule is therefore clearly different from that of an isolated functional group. This environment has to be taken into account when the electronegativity of a functional group is calculated. The easiest way of modeling this environment is by using point charges, which mimic the nuclei not belonging to the functional group and their respective electron clouds. The electronegativity values obtained using this simple model were verified using an electronegativity equalization scheme, as well as by a method based on a perturbation expansion of the chemical potential. The results are found to be very satisfactory and encourage the use of a simple point charge model to model the environment of a functional group.

Acknowledgment. The authors are indebted to the Belgian National Fund for Scientific Research (F.N.R.S.) for its financial support to this research (Tom Leyssens is Research Fellow, Grant FC 64894). They would like also to thank the F.N.R.S. for its support to access computational facilities (FRFC Project No. 2.4556.99 “Simulations numériques et traitement des données”).

Appendix: The Electronegativity Changes Driven by an Electronic Reorganization.

As mentioned in section 3.2, the Fukui function is able to predict how the electronegativity will change with respect to an external perturbation but unable to tell us what happens locally inside the molecule. The linear response function $\chi(\mathbf{r},\mathbf{r}')$, the descriptor able to describe these changes, is very hard to obtain. So, we turned to an energy decomposition scheme to answer this question, starting from a description of how the energy of the three species involved in the determination of the electronegativity and hardness varies with respect to a changing point charge.

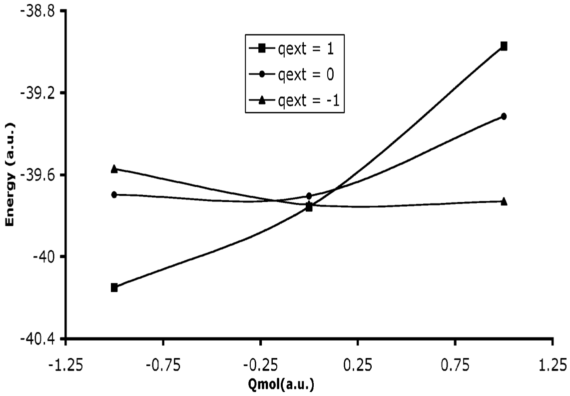

Figure 5. Variation of the energy CCSD of the CH_3 group (in CH_3-NH_2) with respect to the molecule’s charge, q_{mol} (for different external point charges).

TABLE 4: Energy (hartree) Decomposition[a] (Eq 17) for the CH_3 Group (in CH_3NH_2)

	cation		radical		anion	
q_{ext}	−1	1	−1	1	−1	1
E	−39.848	−39.091	−39.881	−39.892	−39.712	−40.300
$E°$	−39.432	−39.432	−39.834	−39.834	−39.847	−39.847
E_{def}	0.030	0.048	0.091	0.052	0.227	0.071
$E_{q_{ext}/nuclei}$	−2.915	2.915	−2.915	2.915	−2.915	2.915
$E_{q_{ext}/dens}$	2.469	−2.622	2.777	−3.025	2.823	−3.439
$E_{q_{ext}}$[b]	−0.446	0.293	−0.138	−0.110	−0.092	−0.524

[a] Energy values obtained at B3LYP//CCSD level. [b] $E_{q_{ext}} = E_{q_{ext}/dens} + E_{q_{ext}/nuclei}$.

Figure 4 shows how the energy of the cationic, neutral, and anionic CH_3 group changes with respect to an increasing point charge. This figure shows that the cationic, neutral, and anionic species come closer in energy when they are in the presence of a negative point charge. Vertical cuts on this graph yield the energy of the three species needed to construct the Mulliken−Jaffé curve for a certain point charge. Figure 5 shows these curves for a point charge value of −1, 0, and +1. As would be expected from the curves in Figure 4, the closeness in energy for the three species in the presence of a negative point charge will lead to a flattening of the Mulliken−Jaffé curves. This flattening of the curves is the reason we have a lowering of the hardness and electronegativity for the negative point charges as shown in Figures 1 and 2.

An energy decomposition scheme can help us to get deeper insight in the evolution of the energy of the three species in the presence of point charges. The scheme used decomposes the energy into different contributions:

$$E = E° + E_{def} + E_{q_{ext}/nuclei} + E_{q_{ext}/dens} \tag{17}$$

$E°$ = energy of the molecule in the absence of external perturbation (no point charge). E_{def} = contribution to the energy provoked by the deformation of the electronic cloud due to the presence of a point charge. This contribution is obtained by calculating the energy of the unperturbed group with the wave function of the perturbed situation. In accordance with the variational principle, the energy so obtained, E', will always be higher than $E°$. The quantity $E' - E° = E_{def}$ is therefore always positive and can be seen as due to the deformation of the density cloud. $E_{q_{ext}/nuclei}$ = energy due to the electrostatic interaction between the external charge and the nuclei. $E_{q_{ext}/dens}$ = the remaining energy difference contribution between E and $E°$, which can be seen as the energy due to the electrostatic interaction between the external charge and the electron density of the deformed charge cloud. This value is obtained by simple subtraction.

Table 4 shows these terms for the cationic, neutral, and anionic CH_3 group in the presence of a positive and negative point charge. As mentioned above, the deformation energy is always positive and more important for the anion, which is due

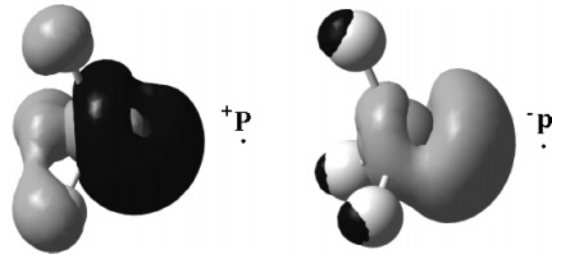

Figure 6. The polarization of the methyl functional group in the presence of a positive ($^+$p) and negative ($^-$p) point charge, given by the density difference of the radical with and without this point charge. The dark surfaces (+0.008 bohr^{-3}) indicate an increase in electron density and the brighter surfaces (−0.008 bohr^{-3}) a decrease.

to the increased number of electrons. This contribution stays relatively small compared to the other terms. The third and fourth terms of eq 17, which are electrostatic in nature, are always of approximately the same magnitude but opposite sign. The fourth term depends only on the nuclei and the value of the point charge and is constant. The E_{def} and $E_{q_{\mathrm{ext}}/\mathrm{dens}}$ terms will therefore be the two terms deciding whether a molecule will be stabilized or destabilized in the presence of a point charge.

The absolute value of the $E_{q_{\mathrm{ext}}/\mathrm{dens}}$ term for each species is bigger in the presence of a positive point charge compared to a negative point charge. This term being electrostatic in nature will depend on the polarization of the electron density. A polarization of the electron cloud away from the negative point charge leads to a smaller absolute value of this term, while a polarization toward the positive point charge will increase this term. Figure 6 confirms this polarization by showing how the CH_3 radical polarizes in the presence of a unitary positive and negative point charge. The distance between the center of the electronic distribution and the point charge furthermore confirms this polarization. This distance is shortest for the radical in the presence of a positive point charge, followed by the radical without any point charge, and longest for the radical in the presence of a negative point charge (0.76, 1.58, and 1.67 Å for $q = -1$, 0, and +1, respectively). It will be this polarization that will play a leading role in the stabilization or destabilization of a molecule in the presence of a point charge.

In presence of a positive point charge, the anionic energy is strongly stabilized with respect to the situation without a point charge. The main reason for this stabilization is the polarization of the electron density toward the point charge as mentioned above, which will lead to an important stabilizing $E_{q_{\mathrm{ext}}/\mathrm{dens}}$ term. Due to a smaller number of electrons, this term becomes smaller for the cation and is no longer sufficient to overcome the important destabilization due to the $E_{q_{\mathrm{ext}}/\mathrm{nuclei}}$ and E_{def} terms. The cationic energy therefore is destabilized. This will lead to an increasing energy difference between cation and anion in the presence of a positive point charge, which will give higher electronegativity and hardness values as shown by the Mulliken−Jaffé curve. In the presence of a negative point charge, the anionic energy is slightly destabilized with respect to the situation without a point charge. Although the destabilizing $E_{q_{\mathrm{ext}}/\mathrm{dens}}$term is not as important due to the polarization away from the point charge, this polarization creates too much of a distortion of the electronic cloud, giving a higher value of E_{def}. This will lead to a small total destabilization. For the cationic molecule, this deformation energy will be much less important due to a smaller number of electrons, which also explains the less important $E_{q_{\mathrm{ext}}/\mathrm{dens}}$term. Considering that both destabilizing terms are less important, this leads to a total stabilization of the cation. The stabilization of the cation and destabilization of the anion will lead to a flatter Mulliken−Jaffé curve, as observed in Figure 5. As a consequence, the electronegativity and the hardness will also be smaller in this case.

As shown by the discussion above, the sense and importance of the electron cloud's polarization is the main factor explaining the energy and, consequently, electronegativity (and hardness) changes of a species in the presence of a point charge.

References and Notes

(1) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1939.

(2) Pritchard, H. O.; Skinner, H. A. *Chem. Rev.* **1955**, *55*, 745−786.

(3) Mullay, J. In *Electronegativity*; Sen, K. D., Jørgenson, C. K., Eds.; Structure and Bonding 66; Springer-Verlag: Berlin, Heidelberg, 1987; p 1.

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

(5) Iczkowski, R. P.; Margrave, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 3547.

(6) Hinze, J.; Jaffé, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540−546.

(7) Hinze, J.; Jaffé, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 148−154.

(8) Huheey, J. E. *J. Phys. Chem.* **1965**, *69*, 3284−3291.

(9) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801−3807.

(10) Parr, R. G.; Yang, W. In *Density-functional Theory of Atoms and Molecules*; Oxford University Press: New York and Clarendon Press: Oxford, U.K., 1989.

(11) Donnelly, R. A.; Parr, R. G. *J. Chem. Phys.* **1978**, *69*, 4431.

(12) Geerlings, P.; De Proft, F.; Langenaeker, W. *Chem. Rev.* **2003**, *103*, 1793−1873.

(13) Nalewajski, R. F. *J. Am. Chem. Soc.* **1984**, *106*, 944−945.

(14) Nalewajski, R. F. *J. Phys. Chem.* **1985**, *89*, 2831−2837.

(15) Mortier, W. J.; Van Genechten, K.; Gasteiger, J. *J. Am. Chem. Soc.* **1985**, *107*, 829−835.

(16) Mortier, W. J.; Ghosh, S. K.; Shankar, S. *J. Am. Chem. Soc.* **1986**, *108*, 4315−4320.

(17) Van Genechten, K. A.; Mortier, W. J.; Geerlings, P. *J. Chem. Phys.* **1987**, *86*, 5063.

(18) De Proft, F.; Langenaeker, W.; Geerlings, P. *J. Mol. Struct. (THEOCHEM)* **1995**, *339*, 45−55.

(19) Bader, R. F. W. *Atoms in Molecules: a Quantum Theory*; Clarendon Press: Oxford, U.K., 1990.

(20) Safi, B.; Choho, K.; De Proft, F.; Geerlings, P. *J. Phys. Chem. A* **1998**, *102*, 5253.

(21) Safi, B.; Choho, K.; De Proft, F.; Geerlings, P. *Chem. Phys. Lett.* **1999**, *300*, 85.

(22) Safi, B.; Choho, K.; Geerlings, P. *J. Phys. Chem. A* **2001**, *105*, 591.

(23) Leyssens, T.; Peeters, D. *J. Mol. Struct. (THEOCHEM)* **2004**, *673*, 79−86.

(24) Leyssens, T.; Peeters, D. *J. Mol. Struct. (THEOCHEM)* **2004**, *686*, 71−82.

(25) Leyssens, T.; Peeters, D.; Orpen, A. G.; Harvey, J. N. *New J. Chem.*, in press.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(27) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735−746.

(28) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

(29) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.

(30) De Proft, F.; Langenaeker, W.; Geerlings, P. *J. Phys. Chem.* **1993**, *97*, 1826−1831.

(31) Vivas-Reyes, R.; De Proft, F.; Biesemans, M.; Willem, R.; Geerlings, P. *J. Phys. Chem. A* **2002**, *106*, 2753.

(32) Fuentealba, P. *J. Mol. Struct. (THEOCHEM)* **1998**, *433*, 1113−1118.

(33) Fuentealba, P.; Parr, R. G. *J. Chem. Phys.* **1991**, *94*, 5559−5564.

(34) Cioslowski, J.; Mixton, S. T. *J. Am. Chem. Soc*. **1993**, *115*, 1084.

(35) Cioslowski, J.; Stefanov, B. B.; *J. Chem. Phys*. **1993**, *99*, 5151.

(36) Toufar, H.; Nulens, K., Janssens, G. O. A.; Mortier, W. J.; Schoonheydt, R. A.; De Proft, F.; Geerlings, P. *J. Phys. Chem.* **1996**, *100*, 15383−15387.

(37) Sanderson, R. T. *J. Chem. Educ*. **1945**, *31*, 2.

(38) Yang, W.; Mortier, W. *J. Am. Chem. Soc.* **1986**, *108*, 5708.

(39) Ayers, P. W.; Morrison, R. C.; Roy, R. K. *J. Chem. Phys.* **2002**, *116*, 8731−8744.

(40) Roy, R. K.; De Proft, F.; Geerlings, P. *J. Phys. Chem. A* **1998**, *102*, 7035−7040.