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Covalent Interaction and Semiempirical Modeling of Small Molecules

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The use of sophisticated methods for modeling complex systems is gaining ever more importance recently because they allow the design of material with properties tailored to specific applications. However, problems may arise from conflicts between different reaction pathways inherent in the wide variety of chemical elements used. This is reflected by the impossibility of exactly solving the Schroedinger equation or of exactly describing the exchange interaction in density functional theory when the system complexity increases. An alternative is offered by the application of semiempirical methods because they strongly reduce system complexity. Normally, this is accomplished by increasing the degree of the approximations to the detriment of the formalism generality. This work is aimed to improve the semiempirical electronegativity equalization method. This is accomplished by modifying the point charge Madelung potential with the introduction of covalent interaction to better describe the chemical bonds.

1. Introduction

The dream of creating high-technology materials with peculiar properties for specific purposes is intimately linked to the ability to model and predict their characteristics. Among these, electron distribution is one of the most important factors in determining the physical and chemical properties of the materials. Since the beginning of the 1960s, this has led to increased interest in developing reliable ab initio methods to obtain detailed information about charge densities. In this respect, an alternative framework to the traditional quantum-mechanical methods based on molecular orbitals (MOs) is the density functional theory (DFT). Its popularity in the past few decades has grown dramatically because DFT-based approaches can be used in a variety of disciplines ranging from condensed matter to chemistry, biophysics and material science. It is the tight relation between DFT and thermodynamics[1−4] that allows DFT to be a suitable formalism for a wide range of time and length scales involved in system modeling.

However, increased system complexity results in severe increases in the difficulty of formulating a correct description and represents a significant computational load. For this reason, other frameworks were developed in parallel to MO and DFT formalisms in an attempt to simplify the modeling without loss of information. At the base of the alternative semiempirical approaches is the equalization of electronegativity as in the Pauling model.[5] Among other popular semiempirical methods, we can mention one based on the *principle of equalization of the electronegativity* developed by Sanderson[6] and one based on the *hard−soft acid−base* principle developed by Pearson.[7] As described in ref 8, all of these techniques suffer from problems. In the present work we discuss the application of the *electronegativity equalization method* (EEM) developed by Mortier.[9,10] With respect to the other methods, here the system energy is better described through an additional term that represents the external potential generated by the surrounding atoms. However, the EEM needs to be trained to a specific class of compounds. In particular, atom electronegativities χ and the hardnesses η must be calibrated to a set of known charges for some model molecules.[11]

Apart from the heavy work required for a good calibration (refer to the example application of the EEM to a set of neuroleptic pharmaceutical molecules[12]), the need for calibrated values means a loss of generality in the EEM formalism.

In this paper we will demonstrate that, by modifying the original EEM, it is possible to avoid calibrations. Following the Mulliken[13] and Parr[14] definitions, the values of $\chi°$ and $\eta°$ for isolated atoms are easily estimated from the ionization potential and electron affinity. These parameters can be obtained from high-precision experimental data reported in the literature.[15,16] In sections 2 and 3, the semiempirical EEM approach is illustrated and a new term describing the covalent interaction aimed to improve the predictive power of the EEM is introduced. In section 4, we describe how these relations were applied in the modified EEM (MEEM). Some experimental results are presented in section 5. Finally, section 6 includes the discussion and the conclusion.

2. Energy of an Atom in a Chemical Environment

As a starting point, we refer to the electronegativity equalization method because it is thoroughly derived from DFT concepts.[9] In particular, the authors were able to write an expression for the energy of an atom in a complex system. Following this expression, the total molecular energy assumes the general form[9]

$$E^{\text{mol}} = \underbrace{E^* + \mu^*\Delta N_\alpha + \eta^*\,\Delta N_\alpha^{2}}_{(a)} + \underbrace{\Sigma_{\beta\neq\alpha} Z_\beta/R_{\alpha\beta}}_{(b)} \qquad (1)$$

where term (a) describes the energy E^{intra} representing the contribution of the interactions inside the atom, while term (b) describes E^{inter}, namely, the atom−atom interactions (see ref 10 for more details). Here $\mu^* = -\chi^* = -(\chi°_\alpha + \Delta\chi_\alpha)$, and $\eta^* = \eta°_\alpha + \Delta\eta_\alpha$ represent the energy, the chemical potential, and the hardness of the atom in a non-neutral state. The parameters $\Delta\chi_\alpha$ and $\Delta\eta_\alpha$ portray the changes in the size (charge density)

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and shape with respect to $\chi^\circ{}_\alpha$ and $\eta^\circ{}_\alpha$ of the isolated atom that result from the presence of the molecular environment. Performing the calibration means determining the value of $\Delta\chi_\alpha$ and $\Delta\eta_\alpha$. If we derive eq 1 with respect to the electron charge N_α, we obtain the EEM equation for electronegativity:

$$\chi_\alpha = (\chi^\circ{}_\alpha + \Delta\chi_\alpha) + 2(\eta^\circ{}_\alpha + \Delta\eta_\alpha)q_\alpha + \sum\nolimits_{\beta\neq\alpha}(q_\beta/R_{\alpha\beta}) \tag{2}$$

(see refs 9 and 10 for more details). To compute the charge distribution in a generic material, a set of equations of type 2 may be written for each atom α, β, γ, ... of the molecule. If we force the electronegativities χ_α, χ_β, χ_γ, ... to be equalized, we obtain the values of the charge distribution on the material atoms (see for an example ref 9).

One annotation concerns the simple form of eq 2. In DFT, a system of N interacting particles of density $\rho(r)$ is mapped to another system of N fictitious noninteracting particles of the same density but moving in an effective potential $V_{\text{eff}}(r,\rho(r))$. The explicit form of $V_{\text{eff}}(r,\rho(r))$ is not known, and in this respect the description of the exchange interaction E_{exc} is crucial. The use of calibrated χ^* and η^* parameters is an elegant way to solve this problem.

A second annotation is related to the applicability of EEM eq 2. Redistribution of electric charge among atoms depends on differences in the values of χ^* and η^* and on gradients of the external potential $V(r) = \sum_{\beta\neq\alpha}(q_\beta/R_{\alpha\beta})$. In the case of a homonuclear molecule such as H_2, O_2, N_2, ..., there are no gradients between the atoms' electronegativities or hardnesses or in the external potential that can force the electrons from the atomic orbital into the molecular one. Thus, following the EEM approach, we cannot describe the formation of homonuclear molecules.

3. Energy and Covalent Interaction

EEM eq 2 was obtained assuming a spherical symmetry for the atomic electron densities. Moreover, it was assumed that the extension of the atomic orbitals is low compared to the bond length. As a consequence, the expression of the Madelung potential (term b in eq 1) assumes the simple form of a Coulomb-like potential of a point charge distribution. This description can be suitable in the case of ionic materials where the electric charge is located mainly on nuclei. However, this does not hold in the case of covalent compounds, where the valence electrons are placed mainly between the nuclei. In the EEM, this effect is taken into account by calibrating the electronegativities and hardnesses on a set of molecules with similar chemical bonds.

Here we want to investigate the possibility of introducing a new term to EEM eq 2 to estimate covalent interaction. There are two reasons for this: (i) to avoid the calibration of χ and η; (ii) to better describe the covalent composites. Parr and Bartolotti[17] found that a geometric mean law for electronegativity equalization implies an exponential decay of the atoms' energies with their charges. Following Mortier,[11] charge rearrangements, i.e., electronegativity equalizations, during the aggregation of an atom into a molecule lead to energy lowering. This does not hold for homonuclear molecules where the energy lowering stems from electron pairing. We hypothesized that the covalent interaction is described by a quadratic function of the charge q. If this is true from eq 1, the corrective term to the electronegativity is a linear function of q. We will prove this assertion in the next section. Concerning the estimation of electronegativity and hardness, we adopt the view of Sanderson[18] and Huheey,[19] who describe the electronegativity as the summation of an ionic and a covalent contribution:

$$\chi = \chi_{\text{ionic}} + \chi_{\text{covalent}} \tag{3}$$

A similar expression may also be written for hardness:

$$\eta = \eta_{\text{ionic}} + \eta_{\text{covalent}} \tag{4}$$

Computationally, similar terms may be introduced in an iterative loop which updates the values of χ and η until the electronegativity is equalized.

In DFT, the charge distribution in covalent bonds is described through an electron reorganization in selected regions, namely, the atomic and bond sites. Consequently, the contribution to covalent energy is ascribed to two terms: the charge accumulation in the bond region and the interaction between unpaired electrons. Here an index is added to the electron density to indicate the up- and down-spin components $\rho_\alpha(r)$ and $\rho_\beta(r)$, which integrate to the respective number of electrons N_α and N_β. For generic electron distribution under a perturbing potential $\delta V(r)$, we may describe the corresponding change in the chemical potential as[20]

$$\mu_\alpha(r) = \mu^\circ{}_\alpha(r) + \delta V(r) + \sum\nolimits_\gamma \int \eta_{\alpha\gamma}(r,r')\, \delta\rho_\gamma(r')\, \mathrm{d}r' \tag{5}$$

where the charge density vanishes outside region r of the rth atom site. $\mu^\circ{}_\alpha(r)$ and $\eta^\circ{}_{\alpha\alpha}(r,r')$ and the cross terms $\eta^\circ{}_{\alpha\beta}(r,r')$ of the unperturbed system as well as $\mu_\alpha(r)$ and $\eta_{\alpha\alpha}(r,r')$ and $\eta_{\alpha\beta}(r,r')$ may be estimated by using the spin-polarized DFT formalism. Nonetheless, for bonded sites, it is possible to estimate $\eta_{\alpha\beta}(r,r')$ using the simple Mataga−Nishimoto formula[26]

$$\eta_{\alpha\beta}(r,r') = 1/[R + \gamma(r,r')] \tag{6}$$

$$R = r - r' \quad \text{and} \quad \gamma(r,r') = 2/[\eta^\circ(r) + \eta^\circ(r')] \tag{7}$$

where only spin-averaged entities are used. We observe that eq 6 gives the off-diagonal elements representing the perturbed Madelung potential due to the rearrangement of the charge in the molecular covalent bond. When the charge rearrangement takes place, the values of χ and η are modified depending on the exchanged charge. Equation 1 may be rewritten as

$$\mu(r) = -\chi(r) = \mu^\circ(r) + \delta V(r) + \sum\nolimits_r[\eta(r,r)\, q(r,r)] + \sum\nolimits_{r'\neq r}[\eta(r,r')\, q(r,r')] \tag{8}$$

where $N(r,r') = q(r,r')$ is the fraction of covalent electron charge accumulated on the bond between the atom in r and the atom in r'. As stated in section 2 and as observed in expression 8, the covalent contribution to the electronegativity, namely, $\sum_{r'\neq r}[\eta(r,r')\, q(r, r')]$, linearly depends on the charge accumulated on the bond while the ionic contribution is described by an exponential decay as hypothesized by Parr.[15]

Now let us focus on hardness. From the definition of η[27]

$$\eta(r) = 2\eta^\circ(r)\, f(r) + \sum\nolimits_{r'\neq r}[f(r')/R] \tag{9a}$$

where $f(r) = \partial\rho(r)/\partial N$ is the Fukui function relative to the atom in r and $R = r - r'$. We may rewrite eq 9a as

$$\eta(r) = \eta_{\text{atom}}(r) + \eta_{\text{env}}(r) \tag{9b}$$

This better describes the contribution to hardness due to changes in the electron density of atom r and that due to changes of the electron densities of the environmental atoms. Considering that

$$\eta(r) = \int \eta(r,r') [\partial\rho(r')/\partial N] \, dr' = (1/N)\int \eta(r,r') \rho(r') \, dr'$$

we can rewrite eq 9a using atomic equivalents for the Fukui function $f(r) = -\partial q(r)/\partial N(r)$ and substituting integrals with summations. Taking into account the covalent interaction described by eq 6 and that $\eta(r) = \eta°(r)$ when $q(r) = 0$, we obtain

$$\eta(r) = 2\eta°(r) [1/2 + q(r)/N] + (1/N)\sum_{r'\neq r}[q(r')/(R + \gamma(r,r'))] \quad (10)$$

We observe that $q(r')$ has the opposite sign with respect to $q(r)$, and thus, the second term of eq 10 tends to lower the value of $\eta(r)$ in agreement with the rule of thumb (see ref 27), an “inverse relation exists between the softness of an atom in a molecule and the softness of its environment”.

The computation of the ionic and covalent contributions to χ and η requires the amount of charge partitioned in the ionic and covalent fractions. There are some works published in the literature describing the change in system energy during the formation of a molecular system.[28−32] On the other hand, the empirical nature of the equation obtained (Drago’s equation) or the difficulties to directly describe the covalent fraction of the chemical bond in terms of μ and η made their use quite complex. We preferred to follow a different approach based on the following considerations: (i) Covalent bonds are generally very stable, and this is in agreement with the principle of maximum hardness of Pearson.[21] (ii) Following Gao et al.,[22] the bond covalency is proportional to the HOMO−LUMO gap. (iii) In the pseudopotential theory of a covalent bond relative to homopolar semiconductors,[23] the author found that the optical gap is approximately equal to twice the [111] matrix element of the pseudopotential. This last term also represents the covalent energy in the hypothesis that the energy gap scales inversely with the square of the bond length, a hypothesis which is consistent with the bond orbital theory. (iv) There is experimental evidence that the HOMO−LUMO gap accounts for the hardness of the covalent compound.[24] (v) In some selected chemical reactions Gasquez et al.[25] showed that the change in the system energy may be expressed as $\Delta E = N \, \Delta\mu - (1/2)N^2 \, \Delta\eta$, where the first term may be associated with a covalent interaction while the second, dependent on the variation of the system hardness, resembles a Coulomb-like energy which may be associated with the ionic fraction.[25] (vi) Finally it is known that the covalence is linked to high valence states (see ref 22 and references therein and ref 38). On the basis of these arguments, we hypothesize that the covalent fraction associated with a given chemical is proportional to the bond hardness:

$$f_{\mathrm{cov}}(r,r') = 0.5[\upsilon(r) + \upsilon(r')] \, \eta_{\mathrm{hm}}(r,r') \quad (11)$$

where $\eta_{\mathrm{hm}}(r,r')$ is the bond hardness defined by Ghanty et al.[34] (the harmonic mean of the hardnesses of isolated atoms r and r') while $\upsilon(r)$ and $\upsilon(r')$ indicate the valences of atoms r and r'.

Let us focus on the ionic fraction. In this case we know the following: (i) Atoms characterized by highly different electronegativities lead to ionic compounds. This is reflected by the definitions of the ionicity given by Pauling and Phillip[39] and by the Moser−Pearson plot.[40] (ii) The polarizability of a given material is tightly bonded to its ionicity. After Nagle,[41] the polarizability may be interpreted in terms of the electrostatic force exerted by a nucleus on its valence electrons, i.e., Z_{eff}/R, where Z_{eff} is the effective nuclear charge and R is the atomic radius.

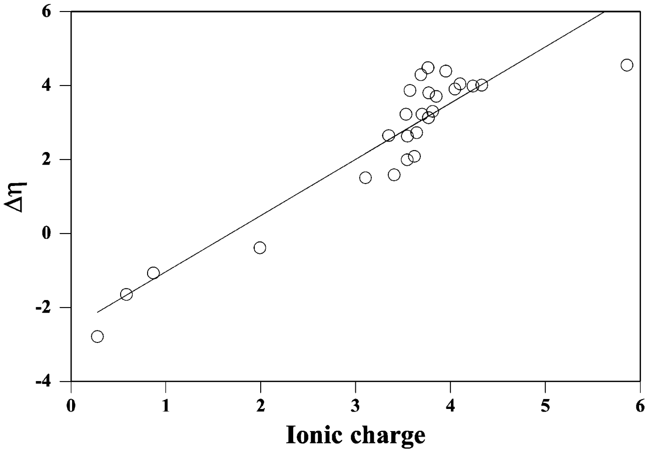

Figure 1. Trend of the difference $\Delta\eta = \eta(r) - \eta(r')$ as a function of the atomic charge computed from the dipole moments of ionic diatomic molecules.

On the other hand, simple differences in electronegativity cannot be taken as a general index for ionicity[42] due to the stabilization effect of the Madelung potential of the material. It is known that the hardest elements are strong electron acceptors while the atoms with a high donor character are softer. On this basis it is realistic to assume the difference $\eta°(r) - \eta°(r')$ is related to the amount of charge transferred from atom r' to atom r, i.e., the ionicity. This is shown in Figure 1 for ionic bonds in some diatomic molecules obtained by combining elements belonging to the I and VII and II and VI groups of the periodic table. On the basis of these considerations we hypothesize the ionic fraction to be expressed as

$$f_{\mathrm{ionic}}(r) = [Z_{\mathrm{eff}}(r)/R(r) - Z_{\mathrm{eff}}(r')/R(r')][\eta(r) - \eta(r')] \quad (12)$$

In consideration that the ionic component of the hardness is an exponential function of the charge, eq 12 resembles the Phillip expression of ionicity obtained for crystalline salts. On the other hand, when the covalent component of the hardness is non-negligible, eq 12 should describe the ionic fraction in the case of intermediate or strongly covalent compounds. Here $R(r)$ and $R(r')$ represent the atomic radii of atoms placed in r and r', respectively. The values obtained using formulas 11 and 12 are not normalized in the range 0−1. With this goal, the following fractions were introduced:

$$F_{\mathrm{cov}}(r) = f_{\mathrm{cov}}(r)/[f_{\mathrm{cov}}(r) + f_{\mathrm{ionic}}(r)] \quad (13a)$$

$$F_{\mathrm{ionic}}(r) = f_{\mathrm{ionic}}(r)/[f_{\mathrm{cov}}(r) + f_{\mathrm{ionic}}(r)] \quad (13b)$$

4. Iterative MEEM Program

In this section, we give some details concerning the iterative procedure used to compute the ECD. We will follow the program flow chart shown in Figure 2. Using the initial values of atom electronegativities and hardnesses, the program works out an initial estimation for the ECD. It then verifies whether the atoms’ electronegativities are equalized. If not, the following loop starts.

(i) Calculation of the covalent and ionic fractions of the chemical bond using eqs 11, 12, and 13a,b.

(ii) Modification of the Madelung potential. While in the EEM, the environment potential is a summation of point charges. Following Nalewajski,[36] we may rewrite the Madelung potential as $\eta(r,r') = \sum_{r'\neq r}[1/[R + \gamma(r,r')]]$. The corrective term $\gamma(r,r')$ changes at each iteration since the initial diagonal elements η-

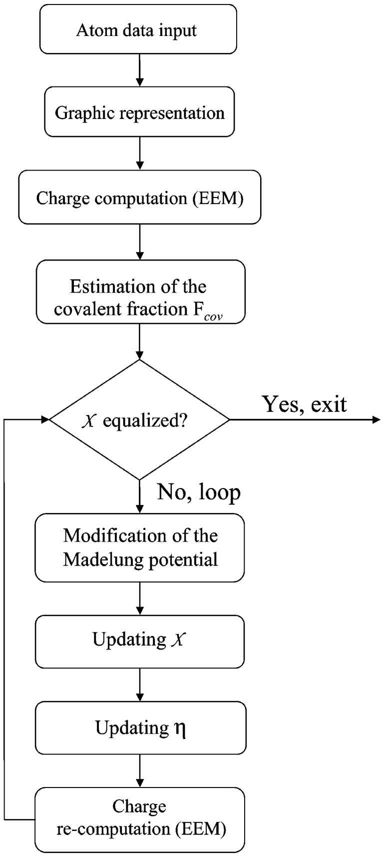

Figure 2. Flow chart of the MEEM program.

(r,r) and $\eta(r',r')$ are modified. $1/\gamma$ represents an average potential generated by the electron distribution generated by an electric charge arranged between atoms r and r', i.e., on the molecular orbital.

(iii) Updating the atom electronegativity. This task is accomplished by applying eq 3. Here the ionic contribution is equal to the conventional expression of electronegativity $\partial E/\partial q$, assuming an exponential decay for $E(q)$: $\chi_{\text{ionic}} = A\exp(kq_{\text{ionic}})$, where $q_{\text{ionic}} = (1 - F_{\text{cov}})q$. Regarding the second term of eq 3, the covalent contribution corresponds to the covalent part of the Madelung potential. Then the expression for the electronegativity as a function of the electric charge is

$$\chi = A\exp(kq_{\text{ionic}}) + \sum_{r'\neq r}[q_{\text{cov}}/[R + \gamma(r,r')]] \qquad (14)$$

(iv) Updating atom hardness by using eq 10. Here $q(r)$ and $q(r')$ are the total atomic charges without distinguishing between ionic and covalent. In fact, hardness is linked to the total atom charge.

Once the Madelung potential, the atomic electronegativities, and the hardnesses are updated, the ECD is re-estimated by solving the modified EEM system of equations. This can be performed easily by inverting the EEM-modified matrix as described in ref 11. With the new ECD, atom electronegativities can be updated and their equalization checked.

TABLE 2: Values of Atom Charges Obtained for Fluorinated Molecules via the MEEM, Hartree−Fock 6-31G and Density Functional 6-31G** BLYP ab Initio Methods, and Semiempirical PM3 Methods**

molecule	atom	MEEM	HF	BLYP	PM3
CH_4	C	−0.301	−0.473	−0.431	−0.361
	H	0.075	0.118	0.108	0.09
CH_3F	C	0.05	0.087	0.013	−0.149
	H	0.192	0.107	0.093	−0.101
	F	−0.630	−0.407	−0.292	0.153
CH_2F_2	C	0.282	0.561	0.360	0.059
	H	0.338	0.100	0.081	0.122
	F	−0.479	−0.380	−0.261	−0.151
CHF_3	C	0.538	0.943	0.616	0.265
	H	0.513	0.106	0.077	0.170
	F	−0.350	−0.350	−0.213	−0.145
CF_4	C	1.012	1.313	0.853	0.492
	F	−0.253	−0.328	−0.213	−0.123

As an example, Table 1 summarizes the input data needed for estimating the ECD of the CHOOH molecule (data from refs 16 and 43−45). Similar "cards" were composed for all the molecules studied.

5. Results

To verify the reliability of the MEEM, we used a list of simple molecules with known structure and charges characterized by bonds having different ionic/covalent fractions. What follows is an examination of the results compared with data from the Computational Chemistry Comparison and Benchmark DataBase.[45]

Fluorinated Molecules. CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4 is a set molecules in which the oxidation state of carbon increases linearly as expected from XPS data[46] with the number of fluorine atoms in the molecule. On the contrary, the charge on fluorine atoms should decrease linearly on going from CH_3F to CF_4. This enables an easy test of the correctness of the charge estimation. The results are summarized in Table 2 together with the charge values computed with some ab initio methods. Figure 3 shows the trend of the individual carbon, hydrogen, and fluorine atom charges. In contrast to those calculated with ab initio methods, the hydrogen charges increase with an increase in fluorine atoms. This is consistent with the NMR shifts for hydrogen obtained on this set of molecules[47] as shown in Figure 3. Finally, the charge on fluorine atoms follows a perfect linear trend characterized by a low slope, as expected.

Ionic Compounds: NaCl, NaF. For NaCl, the values of electric charge obtained using the MEEM correlate well with the values obtained through ab initio methods, as reported in Table 3. In contrast the semiempirical PM3 method gives the same values of charge for Na in NaCl and NaF.

Hydrides: HCl, HF, H_2S, SiH_4, PH_3, AlH_3. Again, the agreement with the other ab initio methods is very good as can

TABLE 1: Physical and Chemical Parameters for the Chemical Elements of the Modeled Molecules[a]

	χ	η	A	k	Z_{eff}	x	y	z	N_a	N_e	V	R_a
C	4.954	5.112	4.801	1.032	3.14	0.000	0.416	0.000	6	4	4	0.7
O	7.711	6.738	8.825	0.874	4.45	−1.012	−0.434	0.000	8	6	2	0.6
O	7.711	6.738	8.825	0.874	4.45	1.141	0.107	0.000	8	6	2	0.6
H	3.660	7.444	1.800	2.034	1.0	−0.363	1.439	0.000	1	1	1	0.25
H	3.660	7.444	1.800	2.034	1.0	−0.669	−1.319	0.000	1	1	1	0.25

[a] x, y, and z are the spatial coordinates of the component atoms, N_a is the atomic number, N_e is the number of electrons belonging to the most external orbital, V is the valence assumed by a specific atom in reference to the number of chemical bonds formed in the chemical site of the molecule, and R_a is the atomic radius. The other symbols are defined in the text.

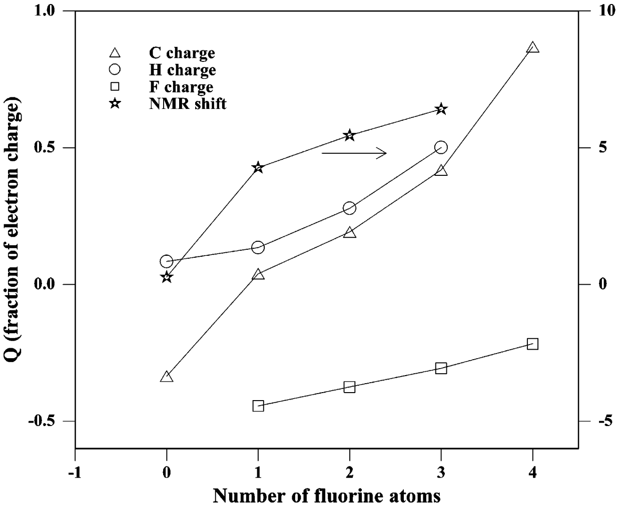

Figure 3. Trend of carbon, hydrogen, and fluorine atomic charges for the set of fluorinated molecules examined. NMR shifts of hydrogen atoms are also shown (white symbols, left scale; black symbols, right scale).

TABLE 3: Values of Atom Charges Obtained for Ionic Molecules via the MEEM, Hartree−Fock 6-31G and Density Functional 6-31G** BLYP ab Initio Methods, and Semiempirical PM3 Methods**

molecule	atom	MEEM	HF	BLYP	PM3
NaCl	Na	0.576	0.668	0.524	1.000
	Cl	−0.576	−0.668	−0.524	−1.000
NaF	Na	0.624	0.704	0.485	1.000
	F	−0.624	−0.704	−0.485	−1.000

TABLE 4: Values of Atom Charges Obtained for Some Hydride Molecules via the MEEM, Hartree−Fock 6-31G and Density Functional 6-31G** BLYP ab Initio Methods, and Semiempirical PM3 Methods**

molecule	atom	MEEM	HF	BLYP	PM3
HCl	Cl	−0.280	−0.192	−0.178	−0.174
	H	0.280	0.192	0.178	0.174
HF	F	−0.380	−0.387	−0.344	−0.180
	H	0.380	0.387	0.344	−0.180
H_2S	S	−0.074	−0.134	−0.160	−0.071
	H	0.037	0.067	0.080	0.035
NH_3	N	−0.578	−0.792	−0.671	−0.081
	H	0.193	0.264	0.224	0.027
PH_3	P	0.241	0.160	−0.011	0.623
	H	−0.080	−0.053	0.004	−0.209
SiH_4	Si	0.153	0.666	0.263	0.661
	H	−0.038	−0.167	−0.066	−0.165
AlH_3	Al	0.228	0.601	0.328	0.824
	H	−0.076	−0.200	−0.109	−0.275

be seen in Table 4. Only in the case of H_2S are the MEEM charge values lower with respect to those of the other methods.

Oxygen-Containing Molecules: H_2O, HCOOH, CH_3OH. In this case, values of $\chi(q)$ and $\eta(q)$ obtained from exponential decay are always meaningful, leading to $\chi_H < \chi_C < \chi_O$. As a consequence, the program converges in correspondence to a charge distribution that is in substantial agreement with those worked out by the ab initio methods. The results are summarized in Table 5.

TABLE 5: Values of Atom Charges Obtained for Oxygen-Containing Molecules via the MEEM, Hartree−Fock 6-31G and Density Functional 6-31G** BLYP ab Initio Methods, and Semiempirical PM3 Methods**

molecule	atom	MEEM	HF	BLYP	PM3
H_2O	H	0.272	0.335	0.289	0.263
	O	−0.543	−0.671	−0.579	−0.526
HCOOH	H	0.266	0.135	0.094	0.192
	C	0.185	0.591	0.386	0.315
	O	−0.374	−0.521	−0.382	−0.413
	O	−0.365	−0.567	−0.403	−0.345
	H	0.288	0.362	0.309	0.251
CH_3OH	C	−0.018	−0.013	−0.063	−0.129
	H	0.143	0.093	0.079	0.070
	H	0.143	0.093	0.079	0.070
	H	0.143	0.126	0.110	0.104
	O	−0.585	−0.634	−0.497	−0.321
	H	0.175	0.335	0.219	0.207

TABLE 6: Values of Bond Ionicity for Some Chemical Compounds As Obtained by Applying the Pauling Formula with Pauling Values of χ (Column 2) and the Pauling Formula with χ Values from the Exponential Fit (Column 3)[a]

bond	Pauling	exp fit χ	eq 19b
Na−F	0.9022	0.9995	0.9425
Na−Cl	0.7115	0.9983	0.7225
H−F	0.5471	0.9949	0.3992
H−Cl	0.2058	0.9852	0.7344
C−F	0.4002	0.9724	0.5998
H−O	0.3191	0.3635	0.3126
Si−O	0.4473	0.114	0.3732
C−O	0.1796	0.0709	0.3533
C−H	0.0301	0.1486	0.1300
Si−H	0.0225	0.5789	0.0279
Si−Cl	0.3275	0.9489	0.3200
Si−F	0.6609	0.9794	0.6034
S−O	0.1688	0.0654	0.0089
S−H	0.0354	0.5789	0.1709

[a] Column four gives values of bond ionicities from eq 19b.

6. Discussion and Conclusion

χ and η need to be calibrated to apply the EEM, whereas it would be advantageous to estimate charge distribution relying only on experimental data. To avoid calibration of χ and η, this paper aims to refine electronegativity and hardness as introduced by Mortier.[9,10] Currently, researchers rely on the spin-polarized version of DFT to model the rearrangement of electric charge on molecular orbitals. Nonetheless, DFT-based semiempirical approaches based on traditional formalism offer an easier method for modeling these charges. In agreement with refs 33−35, we introduced contributions to the system energy that derive from ionic and covalent interactions. Bond formation is modeled using charge flow from an atom to its counterpart. This process may be implemented in an iterative loop in which χ and η are

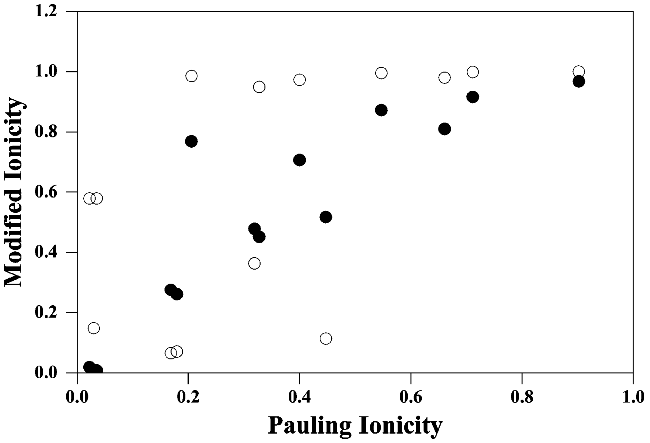

Figure 4. Bond ionicity obtained from the Pauling equation using χ values from the exponential fit (white circles) and those obtained by applying eq 14 (black circles) versus Pauling ionicity (data from Table 1).

modified on the basis of the actual atomic charge distribution. Parr[14] demonstrated that changes in electronegativity cannot be computed directly using exponential decay because of its poor predictive value. We modified this function, which represents the pure ionic contribution to the electronegativity, in consideration of a covalent term represented by eq 8. Equations 11, 12, and 13a,b describe the covalent and ionic fractions of the charge distributed on the molecular orbital. An absolute scale for bond ionicity is still not defined, and thus, it is not possible to directly check the correctness of our relations. Ionicity, as computed by some authors,[5,39,48] is mainly related to crystalline systems. More recent works done on similar materials[49] are also related to crystalline systems. The applicability of these scales is neither immediate nor general, as pointed out by Catlow et al.[50] We need a more general expression for the covalent/ionic fraction of a generic chemical bond which might range from ionic to covalent in both organic and inorganic compounds. Further, we need expressions based on the general parameters used to describe the system, namely, η and q. For these reasons, starting from the chemical and physical properties of atoms A and B, a new definition for the covalent and ionic fractions of a generic chemical bond A−B were written. To get a qualitative estimate, we compared the ionic fraction as defined in eq 13b (fourth column) with that of Pauling (second column) for the set of compounds listed in Table 6. Column three lists the Pauling ionicities obtained with the usual Pauling formula. In Figure 4, data from the third and fourth columns are plotted against the corresponding original Pauling ionicities. The correlation is absent if the Pauling ionicities are computed using χ values from the simple exponential fit, while it is present when ionicities are computed with the new relation (eq 14).

Equation 8 describes how electronegativity changes as a function of charge. $\chi°(r) + \delta V(r)$ represents the change of electronegativity due to modifications of $q(r)$ at the r atomic site, $\sum_{r'}[\eta(r,r')\ q(r,r')]$ and those due to modifications of the electron charge density of the environment. In other words, the first term may be modeled through exponential decay,[14] while the second can be modeled through a simplified empirical Mataga−Nishimoto expression of the hardness kernel (in traditional DFT formalism).[36] It is worth considering whether the exponential decay is the better function to describe the dependence of electronegativity on charge. On the basis of the principle of the geometric mean electronegativity equalization principle, Parr concluded that exponentially decaying energy $E(q)$ is more reasonable than a simple quadratic dependence of E on charge.[14] This also agrees with Pearson's principle of maximum hardness which states that "a system at a given temperature will evolve to a configuration of maximum hardness, provided the nuclear and the chemical potential remain constant". This implies that, to satisfy this principle, the hardnesses of the component atoms will change with the charge transfer during formation of a given compound. On the other hand, a simple quadratic function for energy leads to a constant value of $\eta(r)$.

It is important to observe that the iterative process describes the system evolution toward the condition of minimum system energy, i.e., maximum hardness for constant T and μ. We iteratively apply the EEM to obtain an estimation of charge distribution which, on its turn, allows the atom's electronegativity and the hardness to be updated. During the iterative process, μ and η assume a local character: μ is not equalized through the system, and the hardness is still not maximized.

Finally, the expression of hardness was also modified. Again, eq 9a—which represents $\partial^2 E/\partial N^2$, the hardness definition—is the summation of two terms representing the atom and the environmental contributions. Modifications of the Madelung potential are introduced through the Mataga−Nishimoto formula as pointed out above. Concerning the atomic contribution, we observe that, for $q(r) = 0$, hardness should approach that of an isolated atom. This is accounted for through the empirical term $2\eta°(r)[1 - q(r)/N]$. During iterations, the hardness defined by eq 9a maintains a local character. In other words, we do not get a global value for hardness when electronegativity is equalized. This is consistent with the natural configuration of chemical systems. The minimization of the system energy determines how given atoms bond together. This leads to an equalization of the chemical potential. Nonetheless, the compound formed may show different chemical reactivities in different sites.

All these corrective terms can be easily introduced in the traditional EEM equation with a low computational cost. In the MEEM, the initial values of $\chi°$ and $\eta°$ obtained from experimental values of I, $\Delta H°_f$, and A are modified in relation to electric charge through an iterative procedure. The use of an iterative process to obtain the ECD is not new.[5,37] This procedure follows the intuitive consideration that electrons move from the less to the more electronegative atom. Here we followed an approach similar to that proposed by Mendez and Gazquez[32] where the formation of the chemical bond is described in two steps, the first describing the simple charge exchange between atoms and the second related to the atomic charge reshuffling. In the same way we follow the formation of the chemical bond through a *discretization* of the charge flow between atoms. The amount of charge exchanged is used to determine the variations in the atoms' electronegativities and then in their hardnesses. The iterative loop can describe this process once we describe how the system reacts to this charge flow. In other words, we need to describe the dependencies of electronegativity, hardness, and the Madelung potential on the charge. As a matter of fact, these terms account respectively for changes in the effective nuclear electric field, the reshaping of the electron clouds during bond formation, and the modification of the environment potential. All these factors are taken into account and updated, step-by-step, up to the convergence of the electronegativities to the equalized value. The application of the MEEM to an ensemble of simple molecules gives estimates of the ECD in substantial agreement with the traditional ab initio methods shown in Tables 1−5.

In conclusion, our work is aimed to simplify and possibly improve the predictive power of the semiempirical EEM to estimate the atomic charge in generic chemical systems. Essential points achieved in this work are the following.

(i) We verified the possibility of calculating the charge distribution on atoms relying only on chemical parameters of isolated atoms obtained from the literature without the need for calibration.

(ii) The iterative procedure implemented permits recovery from possible inaccuracies in the initial parameters.

(iii) The MEEM enabled us to estimate the charge distribution in simple molecules independently from the ionic/covalent character of their chemical bonds.

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