Probing the Reactivity of Different Sites within a Molecule or Solid by Direct Computation of Molecular Sensitivities via an Extension of the Electronegativity Equalization Method

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Abstract: The electronegativity equalization method, based on the equalization of the "effective electronegativity" of an atom (α) in a molecule ($\chi_\alpha = -\partial E[N,v]/\partial N_\alpha$; E = total molecular energy), allows the direct computation of the (atomic) charges q_α and the average electronegativity $\bar{\chi}$ of molecules and solids. We now demonstrate how also other local and global quantities can be calculated directly: the molecular hardness $\bar{\eta} = (\partial^2 E/\partial N^2)$, the Fukui function ($f(\vec{r}) = (\delta^2 E/\partial N \delta v)$) integrated over the atomic region f_α, and the atomic equivalent of the two-variable linear response function ($p(1,2) = (\delta^2 E/\delta v_1 v_2)$), $p(\alpha,\beta)$. It is shown how all these (fundamental) quantities depend on the environment.

Introduction

The frontier-electron theory of Fukui[1] has played a key role in developing a basic understanding of the chemical reactivity of molecules under attack of electrophilic or nucleophilic reagents. In particular, the valence-electron distribution, as it can be derived from the highest energy orbital (HOMO) electron density, is critical to identifying the reaction site for electrophilic substitution, while nucleophilic substitution is mainly determined by the characteristics of the lowest energy vacant orbitals (LUMO).

It was demonstrated by Parr and Yang[2] that most of the frontier-electron theory of chemical reactivity can be rationalized from the density functional theory of the electronic structure of molecules.[3] For a system of N electrons with ground-state energy $E[N,v]$, where v is the external potential acting on an electron due to the presence of all nuclei (and surrounding charges), several quantities of fundamental importance can be defined (see ref 3 for fundamentals and reference to the original literature): the chemical potential of the electrons μ (the negative of the electronegativity χ):

$$\mu = (\partial E/\partial N)_v = -\chi$$

the "absolute hardness" as the sensitivity of μ for a change in the number of electrons:

$$\eta = (\partial^2 E/\partial N^2)_v = (\partial \mu/\partial N)_v$$

the frontier function or Fukui function for a molecule, reflecting the reactivity of a site:

$$f(\vec{r}) = [\partial \rho(\vec{r})/\partial N]_v = [\delta \mu/\delta v(\vec{r})]_N$$

where $\rho(\vec{r})$ is the electron density function at point $\vec{r}$.

The search for an exact expression of the energy functional $E[\rho]$ still being an active research topic, the question arises of how to explicitly calculate these quantities. This is even more desired since they provide the theoretical as well as experimental chemist with clear lines of thought. The above quantities are derived from first principles such that no limits are imposed on their applicability.

The first and foremost choice is recurring to quantum chemistry, calculating the properties and the sensitivities of the electron density distribution function in an indirect way. Often, a finite-difference approach is applied, such as, e.g., for calculating the Fukui function as $-\Delta q_\alpha/\Delta N$ at atom α for a change in the number of electrons of a molecule.[4] A semiempirical approach to density functional theory, allowing the direct calculation of the average electronegativity and the atomic charges, was developed by Mortier et al.[5,6] It is based on the equalization of the effective electronegativities of all atoms in a molecule (or solid), and the method was called E(lectronegativity) E(qualization) M(ethod).[5,6] In the forthcoming paragraphs, we will demonstrate how other fundamental quantities can be calculated in a very transparent manner. Concomitant with the quantitative approach, it provides a powerful frame of thinking about the properties of molecules and solids and their interaction.

The Electronegativity Equalization Method: EEM[5,6]

Key to the method is an expression of the molecular energy as a function of the number of electrons on each atom, the nuclear charges and the molecular configuration (interatomic distances) in a way by which the electronegativity of an atom in a molecule can be explicitly calculated. The following expression meets these requirements. Using spherical atomic densities and a Taylor expansion for the intraatomic terms (of which only the first- and second-order terms are retained, ref 5), the total molecular energy is expressed as:

$$E(N_\alpha,N_\beta\ldots,Z_\alpha,Z_\beta\ldots,R_{\alpha\beta}\ldots) = \sum_\alpha (E_\alpha) = E =$$
$$\sum_\alpha \left\{ E_\alpha{}^* + \mu_\alpha{}^*(N_\alpha - N_\alpha{}^0) + \eta_\alpha{}^*(N_\alpha - N_\alpha{}^0)^2 + \ldots \qquad E^\alpha{}_{\text{intra}} \right.$$
$$\left. + \sum_{\beta \neq \alpha} \left(-\frac{N_\alpha Z_\beta}{R_{\alpha\beta}} + \frac{1}{2}\frac{N_\alpha N_\beta}{R_{\alpha\beta}} + \frac{1}{2}\frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \right) \right\} \qquad E^\alpha{}_{\text{inter}} \tag{1}$$

N_α, Z_α ($=N_\alpha{}^0$), and $R_{\alpha\beta}$ are the number of electrons on atom α, the nuclear charge (= number of electrons for the neutral atom), and the internuclear distance, respectively. $E_\alpha{}^*$, $\chi_\alpha{}^*$, ($-\mu_\alpha{}^*$), and $\eta_\alpha{}^*$ are the expansion coefficients in the expression for the intraatomic energy. Since the variables are separated, we now can define the electronegativity of an atom in a molecule as

$$\chi_\alpha = -(\partial E/\partial N_\alpha)_{R_{\alpha\beta}\ldots,N_\beta\ldots}$$

in analogy with the work of Politzer and Weinstein,[7] for which we know that (for a molecule in the ground state)

$$\chi_\alpha = \chi_\beta = \chi_\gamma = \ldots = \bar{\chi}$$

Applying this to eq 1, we readily obtain as an expression for the

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(1) Fukui, K. *Science (Washington D.C.)* **1982**, *218*, 747–754.
(2) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049–4050.
(3) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989; The Internat. Ser. Monographs. Chem. 15.
(4) Yang, W.; Mortier, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 5708–5711.
(5) Mortier, W. J.; Ghosh, S. K.; Shankar, S. *J. Am. Chem. Soc.* **1986**, *108*, 4315–4320.
(6) Van Genechten, K. A.; Mortier, W. J.; Geerlings, P. *J. Chem. Phys.* **1987**, *86*, 5063–5071.
(7) Politzer, P.; Weinstein, H. *J. Chem. Phys.* **1979**, *71*, 4218–4220.

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electronegativity of an atom in a molecule (with $q_\alpha = Z_\alpha - N_\alpha$)

$$\chi_\alpha = \chi_\alpha{}^* + 2\eta_\alpha{}^* q_\alpha + \sum_{\beta\neq\alpha}\left(\frac{q_\beta}{R_{\alpha\beta}}\right) \qquad (2)$$

which, together with the condition of conservation of the charge of the molecule $\sum q_\alpha$ = constant, allows the direct calculation of the charges and the average electronegativity by solving the set of $n + 1$ equations with $n + 1$ unknowns (n atomic charges and the average electronegativity). Expression 2 is different from the expression for the isolated-atom electronegativity ($\chi_\alpha = \chi_\alpha{}^0 + 2\eta_\alpha{}^0 q_\alpha$) in the expansion coefficients and in the presence of the external potential surrounding the atoms. The latter is crucial in applying the electronegativity equalization concepts (especially to inorganic chemistry and organic molecules containing heteroatoms).

The EEM method is easily extended to the solid state, using the Madelung potential at each site:

$$V(\vec{r}_k) = \partial E_i/\partial q_k = \sum_{j\neq k} q_j/\vec{r}_{kj}$$

where

$$E_i = \frac{1}{2}\sum_{i\neq j}\sum \frac{q_i q_j}{r_{ij}}$$

which is introduced in the EEM formalism as

$$\sum_{\beta\neq\alpha}\left(\frac{q_\beta}{R_{\alpha\beta}}\right) \equiv \sum_{\beta\neq\alpha}\left(\frac{\partial V(\vec{r}_\alpha)}{\partial q_\beta}\right)q_\beta$$

quantities which can be directly calculated.

The expansion coefficients χ^* and η^* can be calibrated and the EEM method has been successfully applied to: accurately calculate the charge distribution in large molecules;[5] calculate the charge redistribution in interacting molecules (something semiempirical quantum-chemical methods do not do so well);[5] calculate the charge distribution in silicates (solid state), whereby a new concept "intrinsic framework electronegativity" was introduced, addressing the different properties of the solids with the same composition but with a different structure;[15] investigate the interaction of molecules adsorbed on solids; and investigate the acidity and the effects of isomorphous substitution on the solid-state properties.

Several physicochemical properties of molecules and solids and their interaction could be rationalized in this way. We refer to a review paper addressing applications to catalysis.[8]

A disadvantage of the EEM method is that, in practice, only crystalline materials can be treated, since the structural information is calculated by making use of the space group symmetry (Ewald method). It should be mentioned that, although molecular charge distributions were consistently used, there is no objection to apply this method to bond charges and net atomic charges. The method, however, would then become much less general: each type of bond between atom pairs would have to be addressed separately. We now enjoy, e.g., only one calibration for carbon, independent of the hybridization state or its participation in a carboxyl group, linked to a hydroxyl or in nitrogen compounds, etc. Since its broad applicability has been demonstrated in organic as well as in inorganic systems, we are now in a position to take a closer look at the possibility of calculating other molecular quantities such as the energy and the Fukui function.

The Molecular Energy

Since E stands for the total molecular energy, it should be possible to obtain its value directly from eq 1 if the geometry is known. The parameters $\chi_\alpha{}^*$ and $\eta_\alpha{}^*$ have been calibrated earlier[9,16] for several atom types so as to reproduce ab initio (STO-3G) charges, obtained by a Mulliken population analysis of a set of molecules. These are given in Table I and can be transferred for any atom from molecule to molecule (until now only equilibrium configurations have been investigated). However, the $E_\alpha{}^*$ parameters for an atom in a molecule are not yet known. It is here demonstrated that for each atom type the $E_\alpha{}^*$ value can also be calibrated from ab initio (STO-3G) data (meanwhile keeping the $\chi_\alpha{}^*$ and $\eta_\alpha{}^*$ parameters constant), so as to reproduce the total molecular energy. $E_\alpha{}^*$ is also transferable to different chemical environments.

Table I. χ^*, η^*, and E^* Calibrated to STO-3G ab Initio Charges Relative to $\chi_O{}^* = 8.5$ (All Values in eV)

atom type	χ^*	η^*	E^*	no.[b]
H (δ+)	4.408 77	13.773 24	−15.556 01	65
H (δ−)	3.173 92	9.917 10	−15.556 01	25
C	5.680 45	9.050 58	−1018.684 33	19
N	10.599 16	13.186 23	−1492.053 22	1
O	8.5[a]	11.082 87	−2007.410 03	26
Al	−2.239 52	7.672 45	−6502.835 45	4
Si	1.331 82	6.492 59	−7771.940 43	6
P	2.905 41	6.294 15	−9163.332 03	4

[a] The $\chi_O{}^*$ value is a constant, fixed to 8.5 eV; see ref 9. [b] Number of times the atom was included to establish the correlation presented for the $E_\alpha{}^*$ parameters.

Table II. Calibration of $E_\alpha{}^*$ (STO-3G) (All Values in eV)[a]

	E(ab initio)	E(EEM)	C(EEM)
CH_3OH	−3 089.755 30	−3 088.951 66	−0.633 14
$CH_3CH_2CH_3$	−3 180.632 36	−3 180.775 63	−0.274 17
CH_3OCH_3	−4 139.760 97	−4 138.625 49	−0.510 44
CH_3NH_2	−2 588.709 30	−2 589.824 46	−1.306 37
CH_3F	−3 732.558 67	−3 733.184 57	−2.199 75
CH_2F_2	−6 384.553 81	−6 385.180 18	−4.119 46
CHF_3	−9 036.939 30	−9 037.070 31	−5.933 09
CF_4	−11 689.584 92	−11 688.855 47	−7.641 47
CH_3CH_2F	−4 782.376 55	−4 783.085 45	−2.304 72
H_3PO_2	−13 228.197 02	−13 227.585 94	−2.765 07
H_3PO_3	−15 236.776 45	−15 236.804 69	−4.573 27
$P(OH)_3$	−15 233.751 34	−15 236.419 92	−4.188 37
PH_3	−9 212.084 91	−9 210.016 60	−0.014 60
H_2CO	−3 057.293 04	−3 057.538 82	−0.332 41
CH_3CHO	−4 107.372 95	−4 107.498 05	−0.494 94
$(CH_3)_2CO$	−5 157.404 14	−5 157.457 03	−0.657 14
$HSi(OH)_3$	−13 862.430 67	−13 862.022 46	−5.627 94
$Si(OH)_4$	−15 872.100 88	−15 871.291 02	−7.485 55
SiH_4	−7 834.499 87	−7 834.739 26	−0.574 25
$H_2Si(OH)_2$	−11 852.725 84	−11 852.815 43	−3.829 91
$H_3SiOSiH_3$	−17 648.518 30	−17 648.027 34	−3.398 05
$Al(OH)_3$	−12 580.940 53	−12 579.716 80	−7.981 64
$HAl(OH)_2$	−10 570.814 77	−10 570.406 25	−6.082 14
H_2AlOH	−8 560.638 20	−8 561.110 35	−4.197 07
H_3Al	−6 550.594 79	−6 551.792 48	−2.289 00

[a] E(ab initio) = quantum-chemically calculated total energy; E(EEM) = total molecular energy using eq 1; C(EEM) = charge-dependent term of eq 1.

After calculating the charges by the EEM formalism and taking the total energy E of the molecule, the only unknowns in eq 1 are the $E_\alpha{}^*$ values of the different atom types. We can write:

$$\sum_\alpha E_\alpha{}^* = E - C$$

where C is the charge-dependent term on the right-hand side of eq 1 (see also Table II). It is then possible to obtain the values of $E_\alpha{}^*$ for the atom types involved by least-squares fitting methods. This has been done for C, H, O, N, P, Si, and Al using the 25 molecules listed in Table II. The optimized geometries were obtained from the quantum-chemical (STO-3G) calculations used in the calibration of $\chi_\alpha{}^*$ and $\eta_\alpha{}^*$.[9] The calibrated $E_\alpha{}^*$ values so obtained are compiled in column 4 of Table I. In column 5 the number of times the atom was included, to establish the correlation presented, is reported.

These $E_\alpha{}^*$ values were subsequently used for calculating the energies of the molecules in the calibration set. We indeed see that we are able to reproduce the quantum-chemical results with

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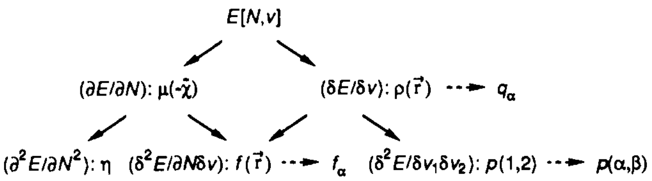
(8) Mortier, W. J. In *Emmett Series on Catalysis*; Moffat, J. B., Ed.; Van Nostrand: New York, 1990.

(9) Uytterhoeven, L.; Lievens, J.; Van Genechten, K.; Mortier, W. J.; Geerlings, P. *Preprints Conf. Eberswalde* (*GDR*) 1987.

Scheme I



a satisfactory accuracy (see Table II). The largest deviations are found for P-containing compounds. This is reasonable since only a small calibration set (of three molecules) was used for obtaining the χ_α^* and η_α^* parameters of P,[16] which can lead to deviations in the charge-dependent term.

At the same time this confirms the hypothesis that the E_α^* parameters are transferable to different chemical environments. Note that $\sum_\alpha E_\alpha^*$ can only serve as a rough estimate of E, since the other term (C) does contribute significantly to the energy. Moreover, the charge-dependent term is the only remaining one when evaluating energy differences between molecules of identical chemical composition. Optimization of the molecular geometry with the EEM formalism has at this moment not yet been explored.

The Second Derivatives

Parr and Nalewajski[10] suggested that it should be possible to express various physically important responses of a system to small perturbations in terms of an arbitrarily chosen set of independent basic derivatives of the original energy functional $E[N,v]$, for example, $(\partial E/\partial N)$, $(\partial^2 E/\partial N^2)$, $(\delta^2 E/\partial N\delta v)$, $(\delta^2 E/\delta v_1\delta v_2)$ including $(\delta^2 E/\delta v_1{}^2)$, and $(\delta E/\delta v)$, the first three being already defined in the Introduction. See Scheme I, where $p(1,2)$, is the "two-variable linear response function".[3] Using the EEM formalism, we already were able to calculate the energy, the average electronegativity ($-\mu$), and the charge distribution (finite-difference approach to $\rho(\bar{r})$). We can easily address also the second derivatives, of which $f(\bar{r})$ and $p(1,2)$ describe the change in electron density upon a perturbation of the system by changing the number of electrons or the external potential, respectively.

The Fukui Function

The derivation of eq 2 with respect to the total number of electrons gives:

$$\bar{\eta} = 2\eta_\alpha^* f_\alpha + \sum_{\beta\neq\alpha}\left(\frac{f_\beta}{R_{\alpha\beta}}\right) \qquad (3)$$

where $\bar{\eta}$ is now the global hardness of the molecule

$$\bar{\eta} = \left(\frac{\mathrm{d}\mu}{\mathrm{d}N}\right)_v = -\left(\frac{\mathrm{d}\bar{\chi}}{\mathrm{d}N}\right)_v$$

and

$$f_\alpha = \left(\frac{\mathrm{d}N_\alpha}{\mathrm{d}N}\right)_v = -\left(\frac{\mathrm{d}q_\alpha}{\mathrm{d}N}\right)_v$$

corresponds to an integration of $f(\bar{r})$ over the atomic region of atom α. The Fukui function $f(\bar{r})$ is normalized and also $\sum_\alpha f_\alpha = 1$. This follows from the normalization of the electron density distribution function:

$$\int \rho(\bar{r})\,\mathrm{d}\bar{r} = N$$

which gives after differentiation with respect to N:

$$\int \frac{\partial\rho(\bar{r})}{\partial N}\mathrm{d}\bar{r} = \frac{\partial N}{\partial N} = 1 = \int f(\bar{r})\mathrm{d}\bar{r} = \sum_\alpha f_\alpha \qquad (4)$$

Equations 3 and 4 again form a set of $n + 1$ equations with $n + 1$ unknowns: n times f_α and $\bar{\eta}$, which can be exactly solved if the molecular configuration as well as the expansion coefficients are known. The atomic Fukui function can in this way directly be calculated and immediately applies to the solid state. Some examples are given below.

A distinction has been made between f^+, f^-, and f^0 for a nucleophilic, electrophilic, and radical attack, respectively. This merely stems from the different curvature and possible discontinuity of the $E(N - Z)$ curve for a single atom at $(N - Z) = 0$. For atoms in a molecule it is highly unlikely that the perturbations we study involve a change in sign of the atomic charges. Therefore, we will constantly have two sets of atoms: negatively charged and positively charged ones. For a nucleophilic (electrophilic) attack, we need to consider the negatively (positively) charged atoms only, and those for which the Fukui function is the largest will be the most reactive.

The Two-Variable Linear Response Function

In a similar way, we can calculate $p(\alpha,\beta)$, an integration of $p(1,2)$ over the atomic regions:

$$p(\beta,\alpha) = \left(\frac{\mathrm{d}N_\beta}{\mathrm{d}v_\alpha(N_\alpha)}\right)_N = \left(\frac{-\mathrm{d}q_\beta}{-\mathrm{d}v_\alpha(q_\alpha)}\right)_N = \left(\frac{\mathrm{d}q_\beta}{\mathrm{d}v_\alpha}\right)_N$$

$$\text{and } p(\alpha,\alpha) = \left(\frac{\mathrm{d}q_\alpha}{\mathrm{d}v_\alpha}\right)_N$$

What we are looking for is the change in the electron density distribution at all atoms in the molecule, caused by a theoretical change ($\mathrm{d}v_\alpha$) in the external potential at atom α only. We therefore need to add $\mathrm{d}v_\alpha$ in the expression of the effective electronegativity (of atom α), viz.:

$$\bar{\chi} = \chi_\alpha^* + 2\eta_\alpha^* q_\alpha + \sum_{\beta\neq\alpha}\left(\frac{q_\beta}{R_{\alpha\beta}}\right) + \mathrm{d}v_\alpha \qquad (5)$$

which yields after differentiation with respect to v_α and making use of the obvious fact that we accept electronegativity equalization and that

$$\left(\frac{\mathrm{d}\mu}{\mathrm{d}v_\alpha(N_\alpha)}\right)_N = \left(\frac{-\mathrm{d}\bar{\chi}}{-\mathrm{d}v_\alpha(q_\alpha)}\right)_N = f_\alpha$$

$$f_\alpha = 2\eta_\alpha^* p(\alpha,\alpha) + \sum_{\beta\neq\alpha}\left(\frac{p(\beta,\alpha)}{R_{\alpha\beta}}\right) + 1 \qquad (6)$$

and for any atom β:

$$f_\alpha = 2\eta_\beta^* p(\beta,\alpha) + \sum_{\gamma\neq\beta}\left(\frac{p(\gamma,\alpha)}{R_{\gamma\beta}}\right) \qquad (7)$$

In this case, since

$$\frac{\mathrm{d}}{\mathrm{d}v_\alpha}\left(\sum_i \Delta q_i\right) = 0$$

we also have the constraint

$$\sum_i p(i,\alpha) = 0$$

We again can write a set of $n + 1$ equations (1 of type 6 and ($n - 1$) of type 7, together with the restrictive condition) with $n + 1$ unknowns, i.e., f_α and n $p(i,\alpha)$ ($i = \alpha,\beta,...$) values, describing the system's response to a local change in the external potential at atom α.

Numerical Example

Note that it is also possible with EEM to obtain the f_α and $p(\beta,\alpha)$ values indirectly by calculating $\Delta\bar{\chi}/\Delta v_\alpha$ or $-\Delta q_\alpha/\Delta N$ and $\Delta q_\beta/\Delta v_\alpha$, respectively. The strength of the foregoing method is that it allows a direct calculation of these quantities, and that these can also be obtained by different paths which are self-consistent. This is illustrated by the following numerical example for a water molecule.

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(10) Nalewajski, R. R.; Parr, R. G. J. Chem. Phys. **1982**, 77, 399–407.

Table III. E (eV), $\bar{\chi}$ (eV), and q for Water with and without Perturbation

	a $\Delta N = 0$ $\Delta v = 0$	b ΔN (+0.01)	c Δv_O (+0.1)	d Δv_{H_1} (+0.1)
E	−0.763 76	−0.820 56	−0.782 31	−0.754 37
q_O	−0.373 35	−0.376 67	−0.382 47	−0.368 78
q_{H_1}	+0.186 67	+0.183 33	+0.191 24	+0.181 63
q_{H_2}	+0.186 67	+0.183 33	+0.191 24	+0.187 15
$\bar{\chi}$	+5.766 93	+5.594 18	+5.800 13	+5.800 33

Table IV. Comparison of Charges, Molecular Electronegativity (eV), and Hardness (eV), and Atomic Sensitivities, Calculated Directly (a) and Obtained by a Finite Difference Approach (b) for a Water Molecule

	a	b	
q_O	−0.373 35	−0.371 00	$2[\Delta E/\Delta v_O]_N$
q_H	+0.186 67	+0.187 80	$2[\Delta E/\Delta v_H]_N$
$\bar{\chi}$	+5.766 93	+5.680 00	$-[\Delta E/\Delta N]_v$
$\bar{\eta}$	17.275 12	17.275 00	$-[\Delta\bar{\chi}/\Delta N]_v$
f_O	+0.331 97	+0.332 00	$+[\Delta\bar{\chi}/\Delta v_O]_N$
f_O	+0.331 97	+0.332 00	$-[\Delta q_O/\Delta N]_v$
f_H	+0.334 02	+0.334 00	$-[\Delta q_H/\Delta N]_v$
f_H	+0.334 02	+0.334 00	$+[\Delta\bar{\chi}/\Delta v_H]_N$
p(H,O)	+0.045 63	+0.045 70	$+[\Delta q_H/\Delta v_O]_N$
p(O,O)	−0.091 26	−0.091 20	$+[\Delta q_O/\Delta v_O]_N$
p(O,H$_1$)	+0.045 63	+0.045 70	$+[\Delta q_O/\Delta v_{H1}]_N$
p(H$_1$,H$_1$)	−0.050 40	−0.050 40	$+[\Delta q_{H_1}/\Delta v_{H_1}]_N$
p(H$_2$,H$_1$)	+0.004 77	+0.004 80	$+[\Delta q_{H_2}/\Delta v_{H_2}]_N$

In a first step the energy, the electronegativity, and the charges are calculated for the unperturbed water molecule by using eq 1 and 2 (see Table IIIa). Since E_α^* values are transferable, these were omitted in the calculations (the total energy being the sum of the values in Table III and the charge-independent term $(2E_H^* + E_O^*)$). In a second, third, and fourth step, three perturbations are imposed on the system: the total charge is set to $-\Delta N$ instead of zero for the neutral molecule (constant v); a local potential Δv_O is set on the oxygen atom, viz.:

$$\bar{\chi} = \chi_O^* + 2\eta_O^* q_O + \sum_{\beta\neq O}\left(\frac{q_\beta}{R_{O\beta}}\right) + \Delta v_O$$

the other equations (for H and for the total charge) remaining unchanged (constant N); and the same is done for a perturbation at the hydrogen atom (Δv_H).

Again, in each case the energy, the electronegativity, and the charges are calculated by using eq 1 and 2. The results for the three perturbations are represented in Table III, b, c, and d, respectively. This allow us to estimate several quantities within a finite difference approach as is illustrated in Table IV. The values are compared with those obtained by direct calculation. The small differences are obviously caused by the numerical approximation in the indirect approach. Note that

$$p(\mathrm{H,O}) = p(\mathrm{O,H}) \text{ or } \left(\frac{dq_H}{dv_O}\right)_N = \left(\frac{dq_O}{dv_H}\right)_N$$

This is a Maxwell relation describing the symmetry of polarizabilities (with respect to the indices): if a perturbation (dv) at atom α produces a charge shift dq on atom β, this perturbation at atom β will lead to the same charge shift on atom α.

The question arises further about the numerical value of the Fukui function. We may compare our results with a study by Geerlings et al.[11] who calculated f_H^+ for the bridging proton in X_2H–Si–OH–Al–HX_2, where X = H or F. The calculation was done using 3-21G as basis set, and the integrated Fukui function was evaluated as $-\Delta q_H/\Delta N$. Our calculated values for this molecule are smaller, but the trend is certainly valid (Figure 1). Remember also that our calibration of χ^* and η^* is done by

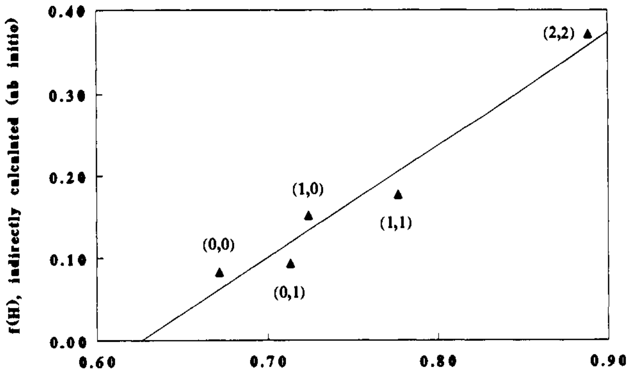

Figure 1. Comparison of f_H^+ for the bridging proton in X_2H–Si–OH–Al–HX_2 with X = H or F, calculated indirectly ($-\Delta q_H/\Delta N$) (3-21G) and f_H calculated directly (see text); (a, b) = $F_aH_{(3-a)}$–Si–OH–Al–$H_{(3-b)}F_b$.

STO-3G where the charges are much less accentuated, which may explain (in part) the numerical differences. Interesting in this respect is that it could be shown that the "probing" capacity of the Fukui function is not lost by the highly approximate integration performed when condensing it via a Mulliken population analysis.[11]

Discussion

It is interesting to concentrate on the meaning of the above equations. These allow one not only to quantitatively evaluate several partial derivatives that constitute a sensitivity analysis of the system, but they also can serve as a tool for rationalizing and predicting the outcome of molecular interactions and perturbations. As an example we focus on eq 3.

The molecular hardness ($\bar{\eta}$) is a structure- and composition-dependent global parameter such as $\bar{\chi}$. It can be associated with molecular polarizability and its value depends on the covalent/ionic character of the bonding between atoms in a molecule (or crystal).[12] By definition, the inverse of $\bar{\eta}$ is the global softness of the molecule: $S = 1/\bar{\eta}$.

At the right-hand side of eq 3, we are dealing with local properties. In a similar way as the external potential at atom α

$$v_\alpha = \sum_{\beta\neq\alpha}\left(\frac{q_\beta}{R_{\alpha\beta}}\right)$$

results from the surrounding charges,

$$F_\alpha = \sum_{\beta\neq\alpha}\left(\frac{f_\beta}{R_{\alpha\beta}}\right)$$

can be identified with the softness of the environment of atom α (a measure of the (possibility of) charge shifts around α). This is perhaps more clearly established when normalizing the hardness to one, viz.:

$$1 = 2\eta_\alpha^* s_\alpha + \sum_{\beta\neq\alpha}\left(\frac{s_\beta}{R_{\alpha\beta}}\right) = 2\eta_\alpha^*\, s_\alpha + S_\alpha \qquad (8)$$

where $s_\alpha = f_\alpha/\bar{\eta}$ is the local softness and S_α is a kind of "external softness potential". As a result we have $\sum s_\alpha = S$ which illustrates the additivity of local softnesses (to group softnesses). It is seen that there exists a linear relation between the softness of an atom (s_α) and its environment (S_α), as has already been demonstrated in the literature.[13]

It is interesting to examine the implications of eq 3 for the understanding of molecular interactions. Every interaction will cause a change in S_α which necessarily must cause shifts in the f_α's. Certain atoms of the molecule must become softer; others

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will become harder. We must therefore not only see a polarization of the interacting molecules (adjustment of the charge distribution) but also a change in the atomic polarizabilities (changes in f_α). Of course, the average global hardness will also be affected. A potential application of eq 3 lies in the linearity between s_α and S_α. We will "soften" an atom by substitution of soft for hard atoms around it.

Up to now we have dealt with the sensitivity analysis of theoretical perturbations. The question arises as to what extent these are related to real physical perturbations and whether the changes in electron density correlate with those predicted via the f's (and eventually p's). It has been established[14] that in aluminosilicates Si (Si K_β line) is more sensitive to compositional changes than Al. A study of isomorphous substitution of Si by Al in the zeolite framework revealed that the Fukui function of Si is much larger than that of Al.[12] Moreover, this sensitivity increases with increasing Si/Al ratio, i.e., with increasing covalent character of the bonds in the crystal (the global softness also increases). This further illustrates the importance of the environment (and structure) for local and global softness and hardness concepts.

It must be stressed that real perturbations, however, differ from theoretically predicted ones in that they are not infinitesimal and, for dv_α, that they are not restricted to one single atom in the molecule. It is therefore more realistic to explicitly calculate the charge shifts in interacting molecules using the original EEM equation (eq 2).

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