THE SOFTNESS OF AN ATOM IN A MOLECULE AND A FUNCTIONAL GROUP SOFTNESS DEFINITION; AN LCAO SCALE

by

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ABSTRACT

We introduce a scale for the softness of an atom in different molecules and we similarly define a functional group softness. These definitions, unlike previous ones, are not tied to the finite difference approximation neither, hence, to valence state ionization potentials and electron affinities; they result from the LCAO calculation itself. We conclude that a) the softness of an atom in a molecule shows wide variations; b) the geometric average of the softnesses of the atoms in the molecule gives the most consistent results for the molecular softnesses; c) the functional group softness is transferable within a homologous series.

Key words: LCAO softness scale - Self-charge - Functional group softness.

1. Introduction

In a recent work, the softness of a molecule has been related to the softness of the constituent atoms [1]; this in turn led to a connection with the concept of the geometric mean principle of hardness equalization [2]. The first reference and related works are formulated within the framework of density functional theory which, indeed, has given rigorous foundations to the otherwise elusive notion of hardness and softness [3-6].

We have proposed a quite different approach for the softness of an atom in a molecule [7]. We shall show here that, although we refer to the same concept, we are led to a softness scale which is not comparable in a clear-cut way with the other known scales. The other definitions are all founded upon valence state ionization potentials and electron affinities, while our expressions stem from the self-charge of an atom within a molecule. We could refer to other scales as semiempirical and to the present one as non-empirical.

As an extension of the above mentioned definition, we introduce here the softness of a functional group and we discuss the results for homologous series. This procedure may be systematized for any functional group. It seems worthwhile to be able to deal quantitatively with the softness of a functional group within a molecule.

2. Atomic, molecular and functional group softness

In the same way as the Mulliken atomic charge q_A is the invariant associated to the first-order density matrix 2π [8], the bond index I_{AB} arises quite naturally as the scalar associated to the second-order density matrix [9].

In the tensor notation [9] for closed shells,

$$2\pi_a^c = 2 \sum_i' x_{ia} x^{ic} \tag{1}$$

where x_{ia} (x^{ia}) are the covariant (contravariant) coefficients of orbital $\underline{a}$ in the $\underline{i}$-th MO of a doubly occupied level.

I_{AB} is then [10,11]

$$I_{AB} = 4 \sum_{\substack{a \in A \\ b \in B}} \pi_a^b \pi_b^a \tag{2}$$

The valence of atom A is [8]

$$V_A = \sum_{B \neq A}' I_{AB} \tag{3}$$

and

$$q_A = (1/2)(I_{AA} + \sum_{B \neq A}' I_{AB}) = (1/2)(I_{AA} + V_A) \tag{4}$$

$$-\sum_A' q_A = N \tag{4a}$$

where N is the number of electrons in a molecule.

Plenty of efforts have been devoted to estimating I_{AB}. The implications of the I_{AA} definition have deserved much less attention. We have shown [7] that I_{AA} — which, as I_{AB}, is an invariant deriving from the second-order density matrix — is

related to the softness (s_A) or hardness (η_A) of atom A in a molecule:

$$s_A = 1/\eta_A = -\beta I_{AA} \quad ; \quad \beta = 1/kT \tag{5}$$

Following the definition of the softness of A in a molecule with L atoms [7] in terms of fluctuations in a grand ensemble [6]

$$s_A = \beta(\langle\hat{q}_A^2\rangle - \langle\hat{q}_A\rangle^2) = -\beta I_{AA} \tag{6}$$

where $\hat{q}$ is the electronic density operator ($\langle\hat{q}_A\rangle = q_A$) and I_{AA} is twice the self-charge, we shall similarly define the molecular softness S as

$$S = \beta(\langle N^2\rangle - \langle N\rangle^2) \tag{7}$$

Recalling that [7,9]

$$\langle\hat{q}_A\hat{q}_B\rangle - \langle\hat{q}_A\rangle\langle\hat{q}_B\rangle = -I_{AB} \tag{8}$$

and taking into account (4) we have, by (6),(7) and (8), that

$$-kTS = I_{AA} + I_{BB} + \ldots + I_{LL} + 2I_{AB} + \ldots + 2I_{AL} + \ldots + 2I_{L-1,L} \tag{9}$$

and in turn, by (3) and (5)

$$kTS = kT(s_A + s_B + \ldots + s_L) - (V_A + V_B + \ldots + V_L) \tag{10}$$

This estimation of the softness of a molecule is neither the sum of the atomic softnesses nor their average as predicted by Yang, Lee and Ghosh [1]. The sum of our atomic softnesses would lead to the molecular softness in eq.(10) only if the fluctuations of any two q's from their average values were not correlated [7,9], i.e. in the absence of chemical bonds. Chemical bonds are seen to decrease the molecular softness.

On the other hand, introducing (4a) in (9),

$$kTS = -2 \sum_{A} q_A = 2N$$

$$S = \beta(<N^2> - <N>^2) = 2\beta N \qquad (11)$$

The lone pairs and core electrons should be subtracted from N in eq.(11) (see further in this section). Thus, the fluctuation of the total number of electrons in a molecule is twice the number of valence electrons in the strict sense.

S does not seem to be an appropriate expression for the molecular softness, for it does not fulfil the expected requirements; while s_A is associated to the second-order density matrix [7,9], S in eq.(10) is related to the first-order density matrix and this could be a source of discordance. For example, molecules such as (H_2O, H_2S) which, having the same number of valence electrons are known to have quite different softness, are levelled by eq.(11) which is not satisfactory. Hence we divert our attention to another alternative, starting from the softness of an atom in a molecule given by eq.(5). We shall see in the next section that the geometric average prescription ($\bar{S}$) for molecular softness [2] leads to results in qualitative agreement with expectations.

Let us underline that the present definitions are quite different from previous estimations for softness. While the other definitions are all founded upon valence state ionization potentials and electron affinities, our expressions are based

on the self-charge of an atom within a molecule in the equi-
librium condition, that is when the chemical potentials (elec-
tronegativities) of the atoms are all equal.

From eq.(6), as core and lone pairs are additive constants
C, they should be subtracted when estimating the self-charge,
for they do not contribute to the charge fluctuation. In order
to eliminate the lone pair contribution from I_{AA}, the follow-
ing MO prescription is given, for they are often not so evident
as they are, for example, in the NH_3 case:

If we pick the intra-atomic elements of the first-order
density matrix, a matrix $(2\Pi_A)$ is built

$$2\Pi_A = \| 2\Pi_a^{a'} \| \qquad (a,a' \epsilon A) \qquad (12)$$

Obviously,

$$Tr(2\Pi_A) = <\bar{q}_A> = q_A \qquad (13)$$

On diagonalizing $2\Pi_A$, core electrons (in <u>ab initio</u>) and
valence lone pairs (both in <u>ab initio</u> and semiempirical ap-
proaches) are neatly displayed in typical sample molecules.
In Ref. [12], a similar diagonalization is performed for a
symmetrical density operator, but aiming at eigenfunctions
rather than at eigenvalues.

In molecules where lone pairs are not fully isolated, we
write

$$\hat{q}_A = \bar{q}_A' + C + \bar{\epsilon} \qquad (14)$$

where $\hat{\epsilon}$ is a perturbation operator (i.e. $\langle\hat{\epsilon}\rangle$ is a small number) which depends on the other $\hat{q}$'s. It is easily seen that, to first order in $\hat{\epsilon}$

$$\langle\hat{q}_A^2\rangle - \langle\hat{q}_A\rangle^2 = \langle\hat{q}_A'^2\rangle - \langle\hat{q}_A'\rangle^2 + [\langle\hat{\epsilon}\hat{q}_A'\rangle + \langle\hat{q}_A'\hat{\epsilon}\rangle - 2\langle\hat{\epsilon}\rangle\langle\hat{q}_A'\rangle] \quad (15)$$

We choose as a limit $\langle\hat{\epsilon}\rangle = 0.13$ (see next section). In other words, a lone pair is considered as such up to 6%. The different calculation methods used here generally lead to results closer to 2 than this limit.

Let us explore what kind of softness should be ascribed to a functional group within a molecule. By extension of the s_A expression, we shall include the internal active charge in the self-charge of the group. Group softness s_G is thus

$$s_G = -\beta \sum_{A,A' \in G} (I_{AA} + I_{AA'}) \quad (A' \neq A) \quad (16)$$

The regional component of hardness defined by Berkowitz, Ghosh and Parr [5] is additive, while $1/s_G$ is not; hence we are dealing with different quantities.

Let us remark that, even if we calculate the molecular softness as the geometric average of the softnesses of each atom in the molecule, nothing forces us to use the same recipe for the group softness. It is seen at once, for example, that the molecular softness would not be then the geometric average of the group softnesses, except for some particular cases.

3. Results and discussion

Our definitions of softness (hardness) are not tied to the usual finite difference approximation. We have proposed a "thermodynamic" approach, through the Gibbs free energy [7], which does not have recourse to the finite difference approximation: our s_A results from the LCAO calculation itself.

It is the finite difference approximation which in turn sets the link with experimental ionization potentials and electron affinities; for this reason, we shall not compare with "experimental" softnesses intrinsically entangled to the above approximation [1-3]. The fascinating simplification of the original Parr-Pearson treatment [3] is appropriate for isolated atoms (which we are not in a position to calculate), neutral or ionized. Parr and Pearson themselves have, however, introduced a working assumption for bases, suffering from a disturbing asymmetry compared with that for acids [3]. For molecules, Orsky and Whitehead [13] have proposed new self-consistent definitions for acids and for bases. These too rely on the finite difference approximation, as well as the calculations for atoms based on the Kohn-Sham formalism reported in Ref. [14]. We prefer then to propose the softness scale of Table II with no reference to "experimental" values.

As an example of the lone pair identification through the diagonalization of $2\Pi_A$ in eq. (12) we report in Table I the

results of the approximations IEH, CNDO and STO-nG with 4 and 6 Gaussian functions applied to ozone. The three methods exhibit very similar features; they coincide in ascribing one lone pair to the central oxygen and two valence lone pairs to the lateral atoms, which are not fully evident from the classical VB structures [15]. The secondary bond O_1-O_3 has a high I_{AB} value [11], which may perhaps be related to an interaction between lone pairs. The STO-6G basis does not alter the information furnished by the STO-4G basis.

Table II shows that the softness of an atom in a molecule varies over a wide range. Part of this behaviour may be ascribed to the different number of lone pair electrons, for instance in oxygen. However, the argument certainly does not apply to hydrogen, an example which we had briefly mentioned elsewhere [7]; it exhibits three groups of softnesses: a "band" around $1(\pm0.1)$, and those decidedly higher and lower than these. For H_2, $s_H=1$; for other diatomic homonuclear molecules, s_X values are $s_O\approx2$, $s_N\approx3$, $s_F\approx1$.

Nalejawski found an approximate proportionality between the values of μ^0 and η^0 for isolated atoms [16]. In his model, the changes in hardness of the atoms in molecules are ignored, for the corresponding perturbation is supposed to be slight. He therefore concludes that the mentioned proportionality remains valid within molecules. In Ref. [1] it is further sup-

posed that the proportionality constant is the same as that for isolated atoms.

In view of our results, the assumption that the hardness of an atom in a molecule is nearly equal to that of the isolated atom [16] (whichever way the latter is estimated) is not valid. The conclusions stemming from it are likewise open to objections. In particular, we forcedly disagree with the corollary according to which an equalization of the electronegativities of the atoms constituting a molecule amounts to the equalization of their hardnesses [2]. Tables II enlightens instead the qualitative assertion of Ref. [5] that "each atom has its own effective hardness in a molecule".

As we have said, the molecular softness S is seen to be unsatisfactory; pairs of molecules of known different softnesses, such as (NH_3, PH_3) or (H_2O, H_2S) [17] cannot be distinguished. Even so, this gross estimate fulfils the expectation that $(OH)^-$ is harder than H_2O [3], or that O_2 and O_3 should have different hardnesses. In this last case, if the molecular softness is supposed to be any kind of mean value of the isolated atom values, they are automatically equal, unlike our prediction either from S or from $\bar{S}$.

The values for the above mentioned pairs (NH_3, PH_3) and (H_2O, H_2S) persuade us to favour the geometric mean instead of the arithmetic average of the atomic softnesses proposed in Ref. [1]. The latter leads to the wrong result that NH_3 is

softer than PH_3 and H_2O softer than H_2S. Although the $\bar{S}$ va-
lues are perhaps still too close to each other, as Kharabaev
et al. [17] object to the Parr-Pearson scale [3], they are
nevertheless in the correct direction.

Despite the wide variation in the values of s_X, these re-
main close to each other for related compounds. It is seen,
for instance, for s_H in the series HM, where M is an alkali
metal, and in the isologous series (CH_2, CH_4) and (C_2H_2, C_2H_4,
C_2H_6). Carbon, instead, has a completely different value in
CH_2 and CH_4, due to its lone pair in the former molecule. In
the isologous series (C_2H_2, C_2H_4, C_2H_6), $\bar{S}$ decreases smooth-
ly with the amount of π bonding; the opposite happens with S.

While CNDO and STO-4G may more or less differ as to their
prediction for s_X, they agree fairly well for $\bar{S}$. The value
of S is independent of the calculating method.

Table III shows s_G of alcohol, aldehyde and acid function-
al groups in homologous series.

Here also the three approximations (IEH, CNDO, STO-4G) are
alike, except for the acid group. IEH would rule out alter-
native a), while CNDO would discard b). The IEH eigenvalues
in question lie in the range 1.70-1.80 for the lone pair of
the oxygen linked to hydrogen in the corresponding hydroxyl
group; the difference to 2 is practically the I_{OO} value of
the secondary bond, which is perhaps overestimated and leads

thus to a less isolated lone pair. CNDO, instead, adheres more to the classical lone pair model (the value for the same oxygen is 1.90). In STO-4G results, the lone pair diagnosis depends on the allowed limit for the value of $<\hat{\varepsilon}>$ in eq.(14). For the oxygen in question, the second lone pair is close to the mentioned limit of 1.87 so that, in this somewhat doubtful case, we have reported both a) and b).

If we choose alternative b), the s_G/β value of the acid functional group in the homologous series would be approximately 21. However, we prefer to be more flexible with the value of $<\hat{\varepsilon}>$ because we have the feeling that s_G of alcohol, aldehyde and acid should not vary as much as predicted in b). The conclusions are not affected by either choice.

The main inference that we can draw from Table III is that s_G obeys the transferability property for functional groups in homologous series. The Gauss results are the most unfavourable regarding this constancy, obeyed within 1.5% for each functional group. CNDO and IEH results are even more constant. The radical seems therefore to have small influence on the active and self-charges of the elements constituting a functional group. Actually not everything runs exactly in this way; on exploring a secondary and a tertiary alcohol, we found $s_G/\beta = 11.14$ for propanol-2 and 10.98 for methylpropanol-2 (STO-4G).

We are tempted to associate our conclusion with the precise

comments about topological groups made by Bader [18]. Quoting him, "when two atoms or two functional groupings of atoms 'look the same', i.e. when they have the same spatial distribution of charge, they have the same properties..."; that is, in our case, the same softness.

We can follow the variations in s_G starting from the group considered as an isolated molecule and participating of various types of compounds. For example, let us consider some IEH results for CO. In carbon monoxide, $S/\beta = 12$. When becoming a group, its s_G/β shall depend on the kind of compounds it enters. In cetones, it seems to obey the above mentioned transferability, being 10.31 in acetone and 10.32 in butanone. In the complexes $Fe(CO)_5$, $Ni(CO)_4$ and $HCo(CO)_4$ [11], the values of s_G/β for CO range from 13.50 up to 14.53. In formamide [19] it is 9.95, while in uracyl [20] it is 9.69 for (C_2-O) and 9.72 for (C_4-O).

In short, in the same way that it is important to give a quantitative meaning to the hardness of an isolated atom or molecule [3], we think that it is worthwhile to "measure" the softness of a functional group.

4. Conclusions

- The softness of an atom in a molecule is subject to a wide range of variation in different compounds, even for hydrogen, devoid of the valence lone pairs which must be eli-

minated in other atoms.

- The molecular softness shows the most consistent results for the geometric average of the softnesses of the atoms in the molecule.

- The softness of a functional group fulfils the transferability requirement in homologous series.

Table I

Eigenvalues of the $2\Pi_A$ matrix (eq.(12)) for ozone (O_1-O_2-O_3), calculated from different methods.

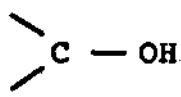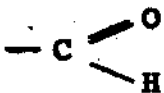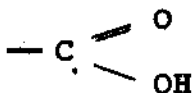|	IEH	CNDO	STO-4G	STO-6G
O_1			2.0000	2.0000
	1.9999	2.0000	2.0000	2.0000
	1.9873	1.9910	1.9779	1.9780
	1.2143	1.4514	1.3473	1.3475
	0.8544	0.7109	0.7458	0.7453
O_2			2.0000	2.0000
	2.0000	2.0000	1.9992	2.0000
	1.5716	1.3313	1.4114	1.4118
	1.3450	1.2649	1.3054	1.3050
	0.9713	1.0971	1.1411	1.1417

Table II

Softness s_X of some first period atoms in different molecules, calculated in the IEH approximation. S results from eq. (11). $\bar{S}$ is the geometric average of the softness of the atoms in the molecule. * t = terminal; b = bridge

Molecule	s_H/β	s_B/β	s_C/β	s_N/β	s_O/β	s_F/β	$S/4\beta$	$\bar{S}/\beta$
HLi	1.516						1	0.946
HN$_a$	1.504						1	0.949
HK	1.632						1	0.909
BH	1.090	0.913					4	1.398
(OH)$^-$	1.344				0.707		1	0.975
HF	0.604					1.495	1	0.950
HCl	0.826						.1	0.992
H$_2$O	0.763				2.539		2	1.168
H$_2$O$_2$	0.714				2.539		3	1.346
H$_2$S	0.956						2	1.240
CH$_2$	0.930		2.145				2	1.229
CH$_4$	0.957		4.174				4	1.285
C$_2$H$_2$	0.911		4.132				5	1.940
C$_2$H$_4$	0.947		4.130				6	1.547
C$_2$H$_6$	0.959		4.144				7	1.383
HCN	0.827		3.818	3.438			4	2.214
NH$_3$	0.822			3.591			3	1.188
PH$_3$	1.022						3	1.331
S$_i$H$_4$	1.098						4	1.398
*B$_2$H$_6$	t)1.097 b)0.954	2.329					6	1.373
BN		2.380		7.197			4	4.139
FB		0.226				8.979	3	1.423
BF$_3$		1.735				5.054	6	3.869
CO			1.231		5.549		3	2.614
CO$_2$			3.669		5.706		6	4.251
N$_1$-N$_2$-O				1)3.119 2)6.072	5.688		6	4.798
O$_1$-O$_2$-O$_3$					1)2.154 2)5.222		4	2.894
F$_2$O					1.705	1.134	2	1.299

Table III

STO-G4 results for the softness s_G/β of some functional groups in homologous series. a) two valence lone pairs in hydroxyl oxygen; b) one valence lone pair in hydroxyl oxygen.

Functional Group / Derivative of	$\diagup C - OH$	$-C \diagup^O_{\diagdown H}$	$-C \diagup^O_{\diagdown OH}$	
			a)	b)
methane	11.47	13.29	17.61	21.36
ethane	11.30	13.13	17.54	21.29
propane	11.31	13.11	17.54	21.28
butane	11.32	13.14	17.45	21.20

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