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MOLECULAR HARDNESS AND ROOTHAAN ENERGY EQUATIONS

by

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ABSTRACT

Using the dependence of the electronic energy on MO occupation numbers, it is shown that for an N-electron species hardness depends on whether N is even or odd. For odd N, we find that the usual (I-A) expression is appropriate. For even N, hardness is given by the interaction between electrons in the HOMO and the LUMO. We show the results of calculations for this last case and compare with other authors' results.

Key-words: Hardness-softness-frontier orbitals.

1. Introduction

The problem of non-integral occupation numbers has troubled many authors [1,2]. Actually, the energy of a system had already been considered as a continuous, differentiable function of N in current electronegativity theory [3,4]. Fully aware of the conceptual dilemma, in a previous paper we have also dealt with the occupation number dependence of the electronic energy [5].

In Ref. [6] it is mentioned that hardness and softness may be determined by the energies of the frontier orbitals. Pearson [7] has formulated this idea in terms of MO's. According to him, hardness is twice the gap between the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO). It seems worthwhile to develop these ideas. This is what we do in the present note, taking into account Ref. [5]; we arrive here at conclusions similar to Pearson's for odd N, and related ones, but different, for even N.

We have proposed elsewhere a statistical approach to the hardness/softness of an atom <u>within</u> a molecule [8]. The atomic softnesses arising from this prescription may be geometrically averaged in order to obtain reasonable molecular softnesses [9]. The statistical approach is related to the differential softness/hardness. Here. however, we shall not enter into the distinction between chemical and differential electronegativity or hardness appointed by Komorowski [10].

We shall assume that energy is a differentiable function of the occupation numbers and we shall not use the finite difference approximation [11,12].

2. A definition for molecular hardness

The Roothaan equation [13] for the electronic energy of a closed-shell system, introducing the MO occupation numbers, is

$$E = \sum_i n_i H_{ii} + (1/4) \sum_{ij} n_i n_j (2J_{ij} - K_{ij}) \qquad (1)$$

We have [5]

$$\partial^2 E / \partial n_i \partial n_j = (2J_{ij} - K_{ij})/2 \qquad (2)$$

In (2) we have neglected relaxation effects. At the time of Ref. [5], the second derivative of the energy with respect to the number of electrons N had not yet received the name of hardness; its physical meaning could not be fully disclosed. The term for this derivative was coined by Parr and Pearson [11] and thereafter an abundant literature flourished. Let us retake the above formulation in order to propose an operational approach to molecular hardness.

If we denote a closed-shell N-electron species by S^0, in the process $S^+ \rightarrow S^0 \rightarrow S^-$ (or viceversa) the number of electrons changes through the variation of the occupation numbers of the i-th and (i+1)-th levels (see Fig. 1a). Hence, instead of writing hardness η as defined by Parr and Pearson [11,14]

$$\eta = \partial^2 E/\partial N^2 \tag{3}$$

we shall do it under the slightly different form

$$\eta = \partial(\partial E/\partial n_j)/\partial n_i = \partial(\partial E/\partial n_i)/\partial n_j = \partial^2 E/\partial n_i \partial n_j \tag{4}$$

By (2), we arrive then at the expression

$$\eta = (2J_{i,i+1} - K_{i,i+1})/2 \tag{5}$$

which states that, in a closed-shell species, hardness is given by the interaction between electrons in the HOMO and the LUMO.

Now, let us suppose that the situation corresponds to Fig. 1b, i.e. N is odd. In this case, it is convenient to distinguish α and β spins in the occupation numbers

$$n_i = n_i^\alpha + n_i^\beta \tag{6}$$

and Eq.(1) may be written as [5]

$$E = \sum_i [(n_i^\alpha+n_i^\beta)H_{ii} + n_i^\alpha n_i^\beta J_{ii} + (1/4) \sum_{j\neq i} (n_i^\alpha+n_i^\beta)(n_j^\alpha+n_j^\beta)(2J_{ij}-K_{ij})] \tag{7}$$

We propose for η in this case the expression

$$\eta = \partial^2 E/\partial n_i^\alpha \partial n_i^\beta \tag{8}$$

Hence

$$\eta = J_{ii} \tag{9}$$

That is, the hardness of a chemical N-electron species depends on whether N is even or odd. <u>In the odd case</u>, with the assumption that the one-center Coulomb integral is given by the Pariser estimation [15], <u>we obtain the already classical I-A</u>

result (I, ionization potential; A, electron affinity). Pearson reports this last result from a differnt MO approach [7].

3. Results and discussion

In this note we intend to give an alternative to other operational approaches to hardness with no pretense of an exhaustive quantitative analysis. Perhaps the simplest option which arises for the calculations in Eq. (5) is the CNDO method and the results shown in the Tables have been obtained by applying it.

Table 1 reports our results for cases of even N, obtained through equation (5), together with those of other authors. In Ref. [16], $1/\eta$ is calculated as the arithmetic average of the experimental $1/(I-A)$ for the atoms in the molecule. Let us recall that the experimental estimatives of $(I-A)$ are not so direct as they appear [7,17]; a consistent quantitative approach to the hardness concept of the HSAB theory is still lacking [10,12].

If we pick up from the Table the neutral basic species appearing in the Parr-Pearson table [11], the following ordering is obtained for our η:

$$H_2O > NH_3 > CO > SH_2 > PH_3 \qquad (10)$$

which coincides with their ordering. Doing the same thing for the neutral Lewis acids, it is found

$$CO_2 > SO_2 > C\ell_2 > A\ell C\ell_3 \quad (11)$$

for us, while Parr and Pearson have

$$CO_2 > A\ell C\ell_3 > SO_2 > C\ell_2 \quad (12)$$

That is, we agree in predicting that CO_2 is a harder acid than SO_2, as it should, but we disagree as to the position of $A\ell C\ell_3$. Now, this last substance is considered a hard acid [6], although the addition of three chlorine ions is supposed to decrease the high hardness of $A\ell^{3+}$ [11] and it is known to be softer than other acids [17]. It is seen that, as happens with the Parr-Pearson scale, the sequences (10) and (11) for bases and acids do not span the same range. The anion OH^- is known to be a hard base and SH^- a soft one. Our results reproduce well this behaviour; the results of Ref. [11] too, although they refer to neutral species.

Some results, apparently, do not correspond to the experience available [6]. For example, SO_3 belongs to the group of hard acids and SO_2 is placed among the borderline ones. We have $\eta(SO_2)>\eta(SO_3)$, as the experimental (I-A).

The results for Eq.(5) depend strongly on the approximations used when calculating the J and K integrals. This is most evident for NH, where the HOMO and LUMO are π and π' orbitals and thus η reduces to the N one-center Coulomb integral. Despite CNDO is considered the all-valence-electron generalization of the PPP method, the theoretical CNDO/2 formula for this integral differs considerably from the Pa-

riser-Parr approximation, which is the widely known (I-A) formula [15]. Hence, perhaps the CNDO/2 values for η are somewhat high. The STO-3G approximation gives, with the N one-center Coulomb and exchange integrals for π and π' functions, a similarly high value of 17.96 eV compared with $(I-A)_N$=14.52 eV[11].

Tables 2 and 3 underline a systematic ordering in certain groups of molecules. Table 2 refers to X_2 and Table 3 to XH_n, where X is a first-row or a second-row atom.

Through Table 2, hardness of the X_2 diatomic homonuclear molecules is seen to be a monotonic increasing function of electronegativity within each row. For the sake of completeness, $\eta(H_2)$=19.72 eV. Instead, the values of (I-A) for X are not monotonic, having a maximum at the V A group, i.e. at N and P; it is usually supposed that species with high electronegativity are hard and those with low electronegativity are soft [6]. For each group, hardness of Table 2 appears higher when X belongs to the first row of the periodic table than when it belongs to the second row. This is also found, more generally, for $(I-A)_X$ of alkali metals, of the VI A group, of halogens and of acid and basic ions [11,12].

In Table 3, accordingly, it seems reasonable that hardness of the hydrides XH_n should follow the electronegativity of X along the period. It is a known experimental fact that NH_3 is harder than PH_3 and H_2O harder than SH_2 [18]. Also, the beha-

viour of the hydrides SiH_4, PH_3, SH_2 - compared with that of their first-row electronic analogues - is in agreement with electron transmission spectroscopy results: the first-row hydrides for C, N and O are expected to be poor electron acceptors [19]. Chemical periodicity in families of compounds has been recently appointed for hardness-electronegativity plots [20], so we may expect to meet features such as those above mentioned in other sequences; we have, for example, $\eta(CO)=14.84$ eV and $\eta(SiO)=9.60$ eV.

Nevertheless, let us recall that electronegativity is only one of the factors accounting for hardness. For instance, in the pair (CO_2, SO_2) C and S have the same electronegativity; as we have mentioned, CO_2 is a harder acid than SO_2, in agreement with the η values of Table 1.

4. Conclusions

- The hardness definition proposed here, given by the HOMO-LUMO interaction between electrons for even N and by J_{ii} of the HOMO for odd N, may be satisfactorily applied in different series of compounds.

- A qualitative comparison gives reasonable agreement with other definitions relying on the finite difference approximation.

- For X_2 and XH_n molecules, where X is a first-row or a second-row element, η increases monotonically with electronegativity within each row of the periodic table.

Figure caption

Fig. 1. Ionization of the N-electron species S^0. a) N even, $i=N/2$; b) N odd.

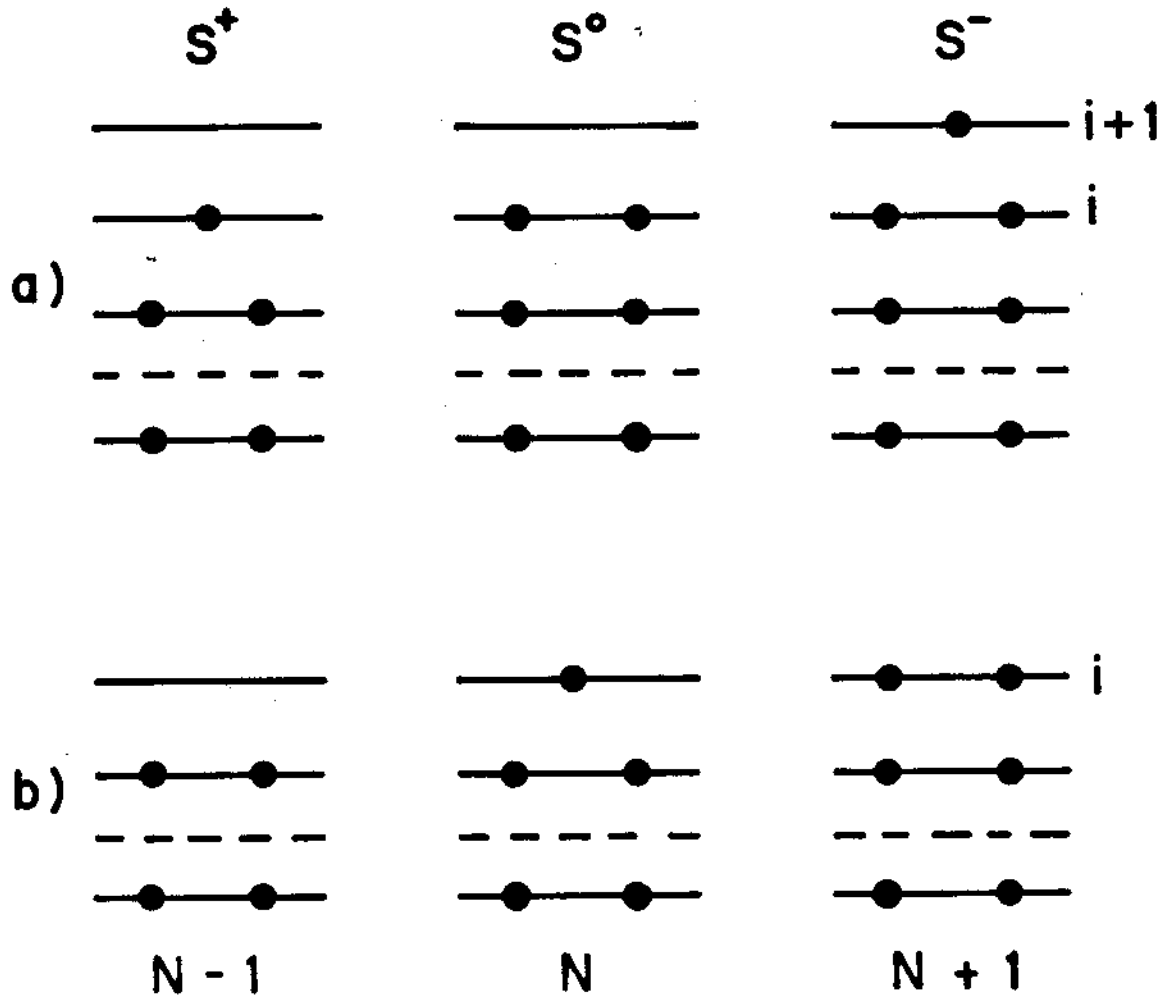

fig. 1

Table 1
Hardness (η, in eV) for cases of even N.

	η eq(5)	η ref[16]	$(I-A)^{a}_{exp}$
Diatomic molecules			
P_2	9.17	9.74	8.95
S_2	10.65	8.28	7.74
Cl_2	10.72	9.40	9.08
SO	12.94	9.85	8.87
CLB	12.96		12.70[c]
C_2	13.13	9.99	9.06
CO	14.84		12.0[b];15.8[c]
N_2	15.74		17.2[c]
O_2	17.03	12.15	11.62
F_2	17.92	14.02	12.62
NE	19.28	13.63	12.72
H_2	19.72		17.4[c]
Triatomic molecules			
COS	7.12	9.90	10.72
S_2C	9.05	8.78	9.08
SO_2	11.34	10.51	11.29
SH_2	12.11		10.6[b]
N_2O	12.26	13.64	11.42
CO_2	12.89		13.8[b]
O_3	13.44	12.15	10.85
CH_2	15.57		9.4[c]
H_2O	17.46		14.0[b];12.6[c]
Polyatomic molecules			
$AlCl_3$	6.62		11.8[b]
PCl_3	7.41	9.48	9.11
SF_6	9.34	12.76	14.60
PH_3	10.62		10.0[b]
SO_3	10.63	10.88	9.30
C_2H_2	14.23	11.24	10.98
NH_3	16.21		13.8[b]
Anions			
SH^-	12.05		8.2[b]
ClO^-	12.92		9.0[b]
CH_3^-	13.89		8.0[b];9.8[c]
CN^-	14.30		10.6[b]
OH^-	14.60		11.2[b]
NH_2^-	16.47		10.6[b]

[a] Data from ref.[16], except as noted; [b] Ref.[11]; [c] Ref.[17].

Table 2

Hardness (η, in eV) of X_2, where X belongs to the first and second periods.

Molecule	Li_2	B_2	C_2	N_2	O_2	F_2
η	5.53	10.59	13.13	15.74	17.03	17.92
Molecule	Na_2		Si_2	P_2	S_2	$C\ell_2$
η	4.53		7.89	9.17	10.65	10.70

Table 3

Hardness (η, in eV) of XH_n, where X belongs to the first and second periods.

Molecule	LiH	BeH_2	BH_3	CH_4	NH_3	OH_2	FH
η	7.23	9.38	11.73	12.74	16.21	17.46	18.65
Molecule	NaH	MgH_2	$A\ell H_3$	SiH_4	PH_3	SH_2	$C\ell H$
η	5.93	7.53	8.77	9.27	10.62	12.11	12.96

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