Theoret. Chim. Acta (Berl.) 58, 131–136 (1981)

THEORETICA CHIMICA ACTA

Electronegativity and the Bonding Character of Molecular Orbitals

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The density-functional approach to Molecular Orbital theory shows that the chemical bonding potential is better described by orbital electronegativities than by ionization energies. This results from the fact that the electronic relaxation connected with ionization is not significant for the homolytic breaking of chemical bonds. Electronegativity, on the other hand, is an eigenvalue corresponding to the average potential seen by an electron as a molecular orbital changes into monocentric (atomic) orbitals.

1. Introduction

The concept of orbital electronegativity [1] is the subject of renewed interest due to its connections, firstly pointed out by Slater [2], with the potential function approaches ($MS-X\alpha$, X_M, etc.) to molecular SCF theory [2–6]. Quite recently Johnson [7] has emphasized the important role of molecular orbital electronegativities in chemical kinetics. Johnson has also recalled that electronegativities should not be identified with the orbital energies defined in the Hartree–Fock method, namely:

$$\varepsilon_i^{\mathrm{SCF}}=\langle E^{\mathrm{SCF}}(n_i=1)\rangle-\langle E^{\mathrm{SCF}}(n_i=0)\rangle. \tag{1}$$

This mistake has been made before [8], but it should not belittle the significance of orbital electronegativity in Chemistry. Thus, it is claimed that Klopman's approach [9] remains "the most successful theoretical rationale for acid-base interactions" [10]. In Klopman's model orbital electronegativity plays a central

0040-5744/81/0058/0131/$01.20

role, inasmuch as *softness*, defined by Eq. (13) of Ref. [9], is the electronegativity of the species in solution.

In this paper we will show that electronegativities are more significant than ionization energies for our understanding of the bonding properties of molecular orbitals. Of course, parameters such as electronegativity remain useful only at a conceptual level in which chemical species are described by single-determinantal wave functions, and electronic excitations, including those occurring in reactive collisions, are amenable to perturbation techniques. We will proceed on the assumption that there is still need for such constructs in Chemistry.

2. Electronegativity, Ionization Energy, and Bond Energy

The expression giving the average energy of the multiplets arising from a given configuration of an atom is [2–4]:

$$\langle E\rangle = \sum_{\nu} \{-n_\nu I(\nu) + \tfrac{1}{2} n_\nu (n_\nu - 1) J_{\nu\nu}\} + \sum_{\mu>\nu} \sum_{\nu} n_\nu n_\mu (\phi_\nu, \phi_\mu) \tag{2}$$

where the subscripts ν and μ refer to orbitals, $I(\nu)$ represents the one-electron terms, $J_{\nu\nu}$ is the Coulomb integral between the electrons in orbital ϕ_ν, and the round-bracket integrals, (ϕ_ν, ϕ_μ), represent the Coulomb and the exchange interactions of an electron in orbital ϕ_ν with the electrons in all occupied ϕ_μ orbitals, averaged over all possible pairs of quantum numbers m_l and m_s. Within the Born–Oppenheimer approximation, expression (2) is valid for molecules; it is only necessary to include the internuclear repulsion terms, $\sum_{\alpha>\beta} \sum_{\alpha} Z_\alpha Z_\beta (R_{\alpha\beta})^{-1}$, and to write the electronic eigenfunctions as dependent parametrically on the nuclear coordinates, $\phi_\nu = \phi_\nu(q_i; q_\alpha)$.

It follows from (2) that the difference:

$$\langle E^+(n_\nu = 1)\rangle - \langle E(n_\nu = 2)\rangle = -\varepsilon_\nu^{\mathrm{SCF}} = A(\phi_\nu) = I(\nu) - J_{\nu\nu} - \sum_{\mu} n_\nu (\phi_\nu, \phi_\mu) \tag{3}$$

represents the ionization energy of a *doubly occupied* orbital. It is easily shown [3–6] that:

$$-\varepsilon_\nu^{\mathrm{SCF}} = A(\phi_\nu) = -\left[\frac{\partial \langle E\rangle}{\partial n_\nu}\right]_{n_\nu = 3/2}. \tag{4}$$

In the same way, for singly occupied orbitals:

$$\begin{aligned} &\langle E^+(n_\nu = 0)\rangle - \langle E(n_\nu = 1)\rangle \\ &\qquad = -\varepsilon_\nu^{\mathrm{SCF}} = I(\phi_\nu) = I_\nu - \sum_{\mu} n_\nu (\phi_\nu, \phi_\mu) = -\left[\frac{\partial \langle E\rangle}{\partial n_\nu}\right]_{n_\nu = 1/2}. \end{aligned} \tag{5}$$

By taking the derivatives of $\langle E\rangle$ at points $n_\nu = \frac{3}{2}$ and $\frac{1}{2}$ one includes some orbital relaxation connected with the ionization process. The potential corresponding to Eq. (4) (or (5)) is that seen by an electron as it is removed from the orbital ϕ_ν, which changes its population from $n_\nu = 2$ to $n_\nu = 1$ (or, $n_\nu = 1$ to $n_\nu = 0$). This is the meaningful potential for the electron ionization energies. But, one may ask, is it equally significant for the dissociation of a molecule into atoms? In the latter case the pertinent potential is that which an electron sees in a molecular orbital as the MO transforms into separated atomic orbitals, as described in a correlation diagram. According to Eq. (2) this potential is:

$$-\left(\frac{\partial\langle E\rangle}{\partial n_\nu}\right)_{n_\nu=1}=I(\nu)-\tfrac{1}{2}J_{\nu\nu}-\sum_\mu n_\mu(\phi_\nu,\phi_\mu)=X(\phi_\nu). \tag{6}$$

But from (4) and (5) we can rewrite (6) as:

$$X(\phi_\nu)=\tfrac{1}{2}[A(\phi_\nu)+I(\phi_\nu)]. \tag{7}$$

Hence,

$$X(\phi_\nu)=-\left(\frac{\partial\langle E\rangle}{\partial n_\nu}\right)_{n_\nu=1}$$

is exactly Mulliken's electronegativity [11]. It corresponds to the eigenvalue of an orbital which remains half-occupied as it transforms its character from multicentric to monocentric. Since $X(\phi_\nu)$ includes only half of the interelectronic repulsion integral $J_{\nu\nu}$, $\varepsilon_\nu^{\mathrm{SCF}'}=-X(\phi_\nu)$ is more negative than $\varepsilon_\nu^{\mathrm{SCF}}=A(\phi_\nu)$. In a sense the neglect of $\tfrac{1}{2}J_{\nu\nu}$ corresponds to introducing correlation in the motion of the two electrons in ϕ_ν. This is the most important correlation effect as far as bond-breaking is concerned.

As pointed out by Jørgensen [1d] electronegativities may be considered as one-electron eigenvalues which add to the total electronic energy; for closed-shell molecules:

$$\langle E_{\mathrm{el}}\rangle=-2\sum_{\substack{\mathrm{occ}\\ \nu}}\tfrac{1}{2}[A(\phi_\nu)+I(\phi_\nu)]+\sum_{\alpha>\beta}\sum_{\alpha}Z_\alpha Z_\beta(R_{\alpha\beta})^{-1}. \tag{8}$$

The bond energy (atomization energy if the molecule is poly-atomic) is given by:

$$D_e=2\sum_{\substack{\mathrm{occ}\\ \nu}}X(\phi_\nu)-\sum_{\alpha>\beta}\sum_{\alpha}\frac{Z_\alpha Z_\beta}{R_{\alpha\beta}}+\sum\langle E\rangle_\alpha \tag{9}$$

where $\langle E\rangle_\alpha$ are the electronic energies of the atoms, given by Eq. (2) ($\langle E\rangle_\alpha<0$). For the inner MOs the $X(\phi_\nu)$s are cancelled out by terms in the various $\langle E\rangle_\alpha$. Within these limitations one should expect D_e to be a function of $X(\phi_\mu)$, where μ is the highest occupied MO. We conclude that the molecular orbital electronegativity is a measure of the bonding power of the MO.

3. Bonding Properties of Molecular Orbitals

For fifty years now, starting with the work of Hund [13] Mulliken [13] and Herzberg [14], bonding properties of molecular orbitals have been discussed in terms of three empirical criteria involving the changes of D_e, R_e and $\tilde{\nu}_e$ upon ionization: if $\Delta D_e=D_e^+-D_e<0$, $\Delta R_e=R_e^+-R_e>0$, and $\Delta\tilde{\nu}_e=\tilde{\nu}_e^+-\tilde{\nu}_e<0$, the orbital is classified as *bonding*: if $\Delta D_e > 0$, $\Delta R_e < 0$, and $\Delta\tilde{\nu}_e > 0$, the orbital is *antibonding*[1]. The experimental evidence for a great number of diatomics verify the consistency of these criteria. This is in agreement with the many known empirical relations between D_e, R_e and $\tilde{\nu}_e$, starting with Morse's potential curve [15]. However, as Mulliken has pointed out [16], there are some molecules for which the three criteria are not consistent, the best known cases being those of the alkali metal molecules, $M_2(^1\Sigma_g^+)$.

Barrow, Travis and Wright [17], and Lee and Mahan [18], have independently shown that the vertical ionization energies, A_{M_2}, of the molecules Li_2, Na_2, K_2, Rb_2 and Cs_2 are *lower* than the ionization energies of the corresponding atoms. If we neglect the second-order differences $|(D_e - D_0) - (D_e^+ - D_0^+)|$ we can write:

$$D_e^+ = D_e + I_M - A_{M_2}\,(\text{ad}). \tag{10}$$

Since $A_{M_2}\,(\text{ad}) < A_{M_2}\,(\text{vert})$, and $A_{M_2}\,(\text{vert}) < I_M$, it follows that $D_e^+ > D_e$ for these molecules, and according to the ΔD_e criterion the corresponding $n\sigma_g$ orbitals are *antibonding*. On the other hand existing evidence shows that $\Delta R_e > 0$ and $\Delta\tilde{\nu}_e < 0$, indicating that the $n\sigma_g$ orbitals are *bonding*. We have collected in Table 1 the more recent data on the Li_2/Li_2^+ and Na_2/Na_2^+ cases [19–21]. The paradoxical situation of the $2\sigma_g$ orbital of Li_2 and the $3\sigma_g$ orbital of Na_2 is seen when one compares the Li_2/Li_2^+ and Na_2/Na_2^+ pairs with typical examples such as the H_2/H_2^+ and the $F_2(^1\Sigma_g^+)/F_2^+(^2\Pi)$ cases, also included in Table 1. Clearly the $1\sigma_g$ orbital of $H_2(^1\Sigma_g^+)$ is a bonding orbital under all criteria cited above and the $1\pi_g$ orbital of $F_2(^1\Sigma_g^+)$ is antibonding under the same criteria.

According to Eq. (10), ΔD_e equals the difference $I_M - A_{M_2}$. But we have seen that the significant potential in molecular dissociation is the orbital electronegativity, not the ionization energy. Clearly the ΔD_e criterion of bonding power is not reliable. Recently Tal and Katriel [24] arrived at similar conclusion, i.e., that the ΔR_e and $\Delta\tilde{\nu}_e$ criteria have a sounder physical basis than the ΔD_e criterion.

Table 1. Bonding properties of molecular orbitals

Molecular species	A_{M_2} (eV)	I_M (eV)	D_0 (eV)	$\tilde{\nu}_e$ (cm^{-1})	R_e (Å)	Ref.
$Li_2(^1\Sigma_g^+)$	5.174	5.39	1.03	351	2.672	[19, 20]
$Li_2^+(^2\Sigma_g^+)$	—	—	1.274	235	3.432	[21, 22]
$Na_2(^1\Sigma_g^+)$	4.90	5.14	0.73	159	3.072	[21]
$Na_2^+(^2\Sigma_g^+)$	—	—	1.01	117	(3.18)[a]	[21]
$H_2(^1\Sigma_g^+)$	16.50	13.6	4.70	4395	0.742	[22]
$H_2(^2\Sigma_g^+)$	—	—	2.7	2297	1.03	[22]
$F_2(^1\Sigma_g)$	15.60	17.4	1.63	892	1.435	[23]
$F_2^+(^2\Pi_g)$	—		3.34	1055	1.326	[23]

[a] Calculated from Badger's rule, J. Chem. Phys. **2**, 128 (1934)

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[1] Ionization of *non-bonding* orbitals has a negligible effect on D_e, R_e and $\tilde{\nu}_e$.

Table 2. Electronegativity criterion of bonding power[a]

Molecule	Mol. orbital	Atomic orbital	A_{M_2}	X_{M_2}	I_M	X_M	Conclusion
Li_2	$2\sigma_g^2$	$2s^1$(Li)	5.17	7.32	5.39	—	B[b]
F_2	$1\pi_g^2$	$2p^2$(F)	15.60	21.64	—	24.36	AB[c]
Na_2	$3\sigma_g^2$	$3s^1$(Na)	4.90	6.97	5.14	—	B[b]
K_2	$4\sigma_g^2$	$4s^1$(K)	4.12	5.74	4.34	—	B[b]
Cl_2	$2\pi_g^2$	$3p^2$(Cl)	11.63	15.77	—	18.75	AB[c]
Br_2	$3\pi_g^2$	$4p^2$(Br)	10.69	14.42	—	17.02	AB[c]
N_2	$1\pi_u^2$	$2p^1$(N)	15.58	22.99	14.54	—	B[b]

[a] Energies in eV.
[b] B = bonding.
[c] AB = antibonding.

From this analysis we conclude that the bonding or antibonding character of a molecular orbital can be determined by comparing its $X(\phi_v)$ value with the eigenvalues of the atomic orbitals indicated by the correlation diagram.

Under this criterion there is no paradoxical situation in the alkali metal molecules. For example, we have calculated the $J(2\sigma_g, 2\sigma_g)$ repulsion integral in Li_2; its value is 4.30 eV [25]. Hence the electronegativity of the $2\sigma_g$ orbital of Li_2 is $X(2\sigma_g) = 5.17 + \frac{1}{2}(4.30) = 7.30$ eV. This is larger than $I(2s)$ of atomic lithium, 5.39 eV, which means that the 2σ orbital of Li_2 is a bonding orbital. Consider now the $1\pi_g$ orbital of $F_2(^1\Sigma_g^+)$. The electron–electron repulsion integral for this orbital is 12.08 eV [25]. The electronegativity of the $1\pi_g$ orbital of F_2 is $15.60 + \frac{1}{2}(12.08) = 21.64$ eV. Now the $1\pi_g$ orbital of F_2 correlates, in the separated atoms, with the doubly occupied $2p_x$ or $2p_y$ orbitals. The one-center Coulomb integral in the fluorine atom equals 13.92 eV, hence the π-electronegativity of the fluorine $2p$ orbitals is $17.4 + 1/2(13.92) = 24.36$ eV. We conclude that the $1\pi_g$ orbital of F_2 is antibonding.

We have collected in Table 2 the results of such calculations for a number of homeo-atomic molecules [25]. They support our expectation that the electronegativity criterion is consistent with the ΔR_e and $\Delta\tilde{\nu}_e$ criteria.

Finally we wish to point out that the usefulness of electronegativities encompasses solid-state properties. Ref. [26] being out-of-the-way for most solid-state physicists we might be allowed to recall that the electronegativity of metallic phases corresponds to the Fermi energy, E_F. This comes directly from the Fermi–Dirac distribution function, $n = |1 + e^{(E-E_F)/k_BT}|^{-1}$; half occupation of the conduction band occurs at $E = E_F$. This fact has been used, for example, in the calculation of photo-electric thresholds [27].

Acknowledgements. Our thanks are due to Mr. Fernando R. Ornellas for programming the electron repulsion integrals, and Dr. Milan Trsic for valuable comments. This work was supported in part by CNPq (Brazilian Government) and FAPESP (State of São Paulo).

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Received March 14, 1980