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Short Communication

Electronegativities and the Bonding Character of Molecular Orbitals: A Remark

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From the density functional theory of Hohenberg–Kohn it is possible to prove that a molecular orbital is bonding (antibonding) if its electronegativity is larger (smaller) than the electronegativities of the corresponding atomic orbitals.

Key words: Electronegativity – Bonding MO – Antibonding MO.

Introduction

We have recently proposed [1] that the bonding or antibonding character of a molecular orbital [2–4] depends on the difference in the electronegativities of the MO (χ_M) and of the atomic orbital (χ_{at}) which correlates with the molecular orbital[1]: if $\chi_M - \chi_{at} > 0$ the MO is bonding; if $\chi_M - \chi_{at} < 0$, it is antibonding. In the present communication we give a direct proof of this proposal, starting from the density functional theory of Hohenberg–Kohn [5].

According to this very general theory the electronic chemical potential is given by:

$$\mu = \nu(1) + \left.\frac{\delta F[\rho']}{\delta \rho'(1)}\right|_{\rho'=\rho} \tag{1}$$

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1 In heteroatomic molecules χ_{at} refers to the most electronegative AO

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where $\nu(1)$ is the one-electron potential, $\nu(1)=-\sum_\alpha E_\alpha/r_{\alpha 1}$, and $F[\rho']$ is a functional given by the sum of the kinetic and the inter-electronic potential energies:

$$F[\rho']=T[\rho']+V[\rho'], \tag{2}$$

$\rho'(1)$ is a variational approximation to the exact electron density,

$$\rho(1)=N\int |\psi(1,2,\dots N)|^2\, d\sigma_1\, d\tau_2\, d\tau_3 \dots d\tau_n$$

($d\tau_i=d\sigma_i\, dx_i$; $d\sigma_i$ are spin coordinates and dx_i are space coordinates). The ground-state electronic energy of a system being given by $E[\rho]=\int \rho(1)\nu(1)\, dx_1+F[\rho]$, it is possible to show [6] that $\mu=[dE/dN]_\nu=-\chi$, that is, to identify the orbital electronegativity with the negative of the electronic chemical potential. This result can also be reached independently of the density functional theory [7–9]. The difference of the chemical potentials of an electron in a molecule and in an atom is:

$$\mu_{\mathrm{M}}-\mu_{\mathrm{at}}=\nu_{\mathrm{M}}(1)-\nu_{\mathrm{at}}(1)+\frac{\delta F[\rho_{\mathrm{M}}]}{\delta\rho_{\mathrm{M}}}-\frac{\delta F[\rho_{\mathrm{at}}]}{\delta\rho_{\mathrm{at}}}. \tag{3}$$

The Virial theorem, applied to atoms and molecules, respectively, is:

$$T[\rho_{\mathrm{at}}]=-E[\rho_{\mathrm{at}}] \tag{4}$$

$$T[\rho_{\mathrm{M}}]=-E[\rho_{\mathrm{M}}]-R\frac{dE[\rho_{\mathrm{M}}]}{dR}. \tag{5}$$

Hence:

$$F[\rho_{\mathrm{at}}]=-\int \nu_{\mathrm{at}}(1)\rho_{\mathrm{at}}(1)\, d\tau_1-T[\rho_{\mathrm{at}}] \tag{6}$$

$$F[\rho_{\mathrm{M}}]=-\int \nu_{\mathrm{M}}(1)\rho_{\mathrm{M}}(1)\, d\tau_1-T[\rho_{\mathrm{M}}]-R\frac{dE[\rho_{\mathrm{M}}]}{dR}. \tag{7}$$

Substituting (6) and (7) in (3), and recalling that $\partial/\partial\rho(1)\int \nu(1)\rho(1)\, d\tau_1=\nu(1)$, one obtains:

$$\mu_{\mathrm{M}}-\mu_{\mathrm{at}}=-\frac{\delta T[\rho_{\mathrm{M}}]}{\delta\rho_{\mathrm{M}}}+\frac{\delta T[\rho_{\mathrm{at}}]}{\delta\rho_{\mathrm{at}}}-\frac{\delta}{\delta\rho_{\mathrm{M}}}\left(R\frac{dE[\rho_{\mathrm{M}}]}{dR}\right). \tag{8}$$

From the electrostatic Hellmann–Feynman theorem [10, 11] the force which the electrons exert on the nuclei is $F_{\mathrm{e}}=-dE[\rho_{\mathrm{M}}]/dR$. Therefore:

$$\mu_{\mathrm{M}}-\mu_{\mathrm{at}}=-\frac{\delta T[\rho_{\mathrm{M}}]}{\delta\rho_{\mathrm{M}}}+\frac{\delta T[\rho_{\mathrm{at}}]}{\delta\rho_{\mathrm{at}}}+\frac{\delta(R\cdot F_{\mathrm{e}})}{\delta\rho_{\mathrm{M}}}. \tag{9}$$

Eq. (9) is exact; following Parr et al. [6] we will assume that $T[\rho]$ is a functional of the *local* electron density of the form $T_{\mathrm{L}}[\rho]\sim\int \rho^{5/3}\, d\tau$. This permits us to write (9) as:

$$\mu_{\mathrm{M}}-\mu_{\mathrm{at}}=A[\rho_{\mathrm{at}}^{2/3}-\rho_{\mathrm{M}}^{2/3}]+\frac{\delta(R\cdot F_{\mathrm{e}})}{\delta\rho_{\mathrm{M}}} \tag{10}$$

or

$$\chi_M - \chi_{at} = A[\rho_M^{2/3} - \rho_{at}^{2/3}] - \frac{\delta(R \cdot F_e)}{\delta \rho_M}. \tag{11}$$

Suppose an electron moves from an atomic orbital to a *bonding* MO. Its energy becomes more negative and, from the Virial theorem, its kinetic energy increases. Therefore, $\rho_M^{2/3} - \rho_{at}^{2/3} > 0$. The product $(R \cdot F_e)$ is the energy term caused by the nuclei moving as $\rho_{at} \rightarrow \rho_M$. Since the MO is bonding, the energy term is stabilizing, that is $(R \cdot F_e) < 0$; besides, $(R \cdot F_e)$ becomes more negative as ρ_M increases, which means that $\delta(R \cdot F_e / \delta\rho_M < 0$. From Eq. (11) we conclude that if a MO is bonding, $\chi_M > \chi_{at}$. By the same argument we can show that a MO is antibonding if $\chi_M < \chi_{at}$ (in heteroatomic molecules χ_{at} should refer to the more electronegative atom) [12].

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12. Starting with the separate AOs, the energy of each bonding (antibonding) MO lowers (increases) monotonically as R decreases, the MOs transforming into united-atom orbitals. Hence $R \cdot F_e < 0$ $(R \cdot F_e > 0)$ as an electron moves from an isolated atomic orbital to a bonding (antibonding) MO. For the equilibrium molecular geometry, $R_e \cdot F_e = 0$; this energy minimum at R_e is the result of a sum over the bonding and antibonding electrons (plus the internuclear repulsion). We wish to thank the referee for calling our attention to this problem.

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