

# Comment on “Electron flow and electronegativity equalization in the process of bond formation” [J. Chem. Phys. 99, 5151 (1993)]

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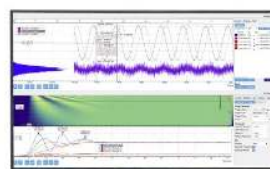
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Comment on "Electron flow and electronegativity equalization in the process of bond formation" [J. Chem. Phys. 99, 5151 (1993)]

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In a recent article<sup>1</sup> the results of charge-constrained electronic structure calculations have been presented and discussed as a means of analyzing electron flow and electronegativity equalization during bond formation. Here, the further implications of these results for crossing potential energy surfaces<sup>2</sup> are pointed out.

Cioslowski *et al.* have defined a quantity called the bond hardness<sup>3</sup>  $\kappa_{AB}(Q_{CT})$ , being the second derivative of the total molecular energy (in a charge-constrained calculation) with respect to the charge transferred between the constituent atoms *A* and *B*, at fixed external potential. By carrying out a perturbative expansion of the total molecular energy, through second order in the quantity of charge transferred ( $Q_{CT}$ ), Cioslowski and Stefanov obtain the exact result

$$\kappa_{AB}(Q_{CT}^0) = -(1/2) \left[ \sum_i' |\langle 0|q|i\rangle|^2 / (E_0 - E_i) \right]^{-1} \quad (1)$$

[Eq. 34 of Ref. 1], where  $E_0$  and  $E_i$  are the ground state electronic energy and energy of the *i*th excited state, respectively, and *q* is a one-electron operator whose expectation value gives the number of electrons in the molecular fragment *A*. The authors have discussed the increase of bond hardness with increasing distance between the fragments *A* and *B*, as also the lower bond hardness in systems with lower excitation energies.

An extreme example of the latter situation is when there is a crossing between molecular potential energy surfaces, as for example occurs in a Jahn–Teller molecule. In this situation the bond hardness disappears entirely and the electronic charge is capable of unhindered oscillation between the constituent atoms.<sup>4</sup>

In practice, however, the Jahn–Teller degeneracy is split by molecular distortions. In an extended system with periodic symmetry, this results in a finite band gap (in the clamped nuclei picture) and in finite resistance to electron flow along the lattice.

In conclusion I would like to point out the relevance of these considerations to a recently proposed density functional theory of superconductivity,<sup>5</sup> wherein Fritsche has argued that in a first-principles theory, there is no room for a mechanism of superconductivity that is not related to electron–phonon interaction, and that the Born–Oppenheimer approximation leads only to normal conductivity or to an insulating state.

In the nonadiabatic Born–Huang formalism,<sup>6</sup> the nonadiabaticity arises from the action of the nuclear derivative operator upon the electronic wavefunctions, which leads to additional terms in the molecular Hamiltonian, the first of which is

$$\mathbf{A}_{i0}^\alpha(\mathbf{R}) \cdot \mathbf{p}_\alpha \quad (2)$$

where  $\mathbf{p}_\alpha$  is the nuclear momentum and

$$\mathbf{A}_{i0}^\alpha(\mathbf{R}) = -i\hbar \langle i(\mathbf{R}) | \nabla_\alpha | 0(\mathbf{R}) \rangle \quad (3)$$

is the so-called Born coupling.<sup>7</sup> The nonadiabatic Hamiltonian with the Born coupling term (2) can then result in a new (superconducting) ground state of lower energy than the adiabatic ground state, due to the large magnitudes of the Born couplings associated with the Jahn–Teller intersection.

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