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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[1] 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[2] are pointed out.

Cioslowski *et al.* have defined a quantity called the bond hardness[3] $\kappa_{AB}(Q_{CT})$, 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

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

[Eq. 34 of Ref. 1], where E_0 and E_i are the ground state electronic energy and energy of the ith 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.[4]

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,[5] 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,[6] 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

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

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

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

is the so-called Born coupling.[7] 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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