

## Studies in Electronegativity

### I. An Overlap Corrected Electronegativity Equalization Method

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The possibilities for preserving the principle of electronegativity equalization are analysed within a localized molecular orbital scheme, using a set of approximations centred around the Mulliken approximation. The necessity of including molecular terms in the definition of the orbital electronegativity is demonstrated. However, even with this modification the principle cannot be straightforwardly maintained, due to corrections from overlap distributions taking the form of overlap electronegativities.

#### 1. INTRODUCTION

It has been known for some time that in order to obtain reasonable results from the principle of electronegativity equalization<sup>1</sup> (EE), it is necessary to express the electronegativity of an orbital on a polyvalent atom as a function of the ionic characters of *all* bonds involving the atom.<sup>2-4</sup> This, in fact, constitutes the first step towards the use of effective electronegativities of orbitals *in situ*. However, a complete definition of the concept requires inclusion of additional molecular terms. Some of these have already been considered by various authors,<sup>5-7</sup> but the theories developed so far have not been able to account for all molecular corrections in a satisfactory way.

In the present paper we analyse a localized molecular orbital scheme, in which the molecular energy is expanded as a power series in the polarities of the bonds. The key approximations used in the theory are the Mulliken approximation<sup>8</sup> and generalizations thereof.<sup>9,10</sup>

Within this set of well-defined approximations it is demonstrated that the principle of EE can be preserved in a straightforward way only in the crudest description, in which quadratic and higher order terms in the bond polarities are neglected in the energy expression. Beyond this point non-trivial corrections due to overlap distributions appear.

Theories similar in nature to the one presented here have been called Differential Ionization Energy methods.<sup>11,7</sup> It is, however, our feeling that the

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term Overlap Corrected Electronegativity Equalization (OCEE) is a more appropriate one, considering the conceptual foundation of the theory.

Some attention has recently been devoted to the problem of left-right correlation within a two-electron bond.<sup>13,7</sup> It is shown here that attempts to include this effect weaken the electronegativity concept.

## 2. BASIC THEORY AND APPROXIMATIONS

We consider the ground state of a given molecule and approximate the electronic wavefunction,  $\Phi$ , by a single Slater determinant, built from doubly occupied, localized molecular orbitals (LMO's;  $\psi$ ). Only valence electrons are treated explicitly. For the interactions with inner shell electrons and nuclei we adopt the Goepfert-Mayer-Sklar-approximation<sup>15</sup> by introducing a core potential  $U$ .

Thus for a molecule with  $2N$  valence electrons and  $M$  nuclei we get the wavefunction and the electronic Hamiltonian (a.u.):

$$\Phi = |\psi_1^+ \psi_1^- \psi_2^+ \psi_2^- \cdots \psi_N^+ \psi_N^-| \quad (1)$$

$$\hat{H} = \sum_{i=1}^{2N} \hat{h}(i) + \sum_{i=1}^{2N} \sum_{j>i}^{2N} \frac{1}{r_{ij}} \quad (2)$$

$$\hat{h}(i) = \hat{T}_i + \sum_{A=1}^M U_A(i), \quad \hat{T}_i = -\frac{1}{2} \nabla_i^2 \quad (3)$$

The LMO's representing the bonds and lone pairs in the molecule are constructed from normalized atomic hybrid orbitals (AHO's;  $\phi$ ). Bond LMO's are made up of two AHO's and contain one variational parameter each after the normalization. As parameter we choose the bond polarity  $\gamma$ , a real quantity defined by the following form of the LMO:

$$\psi_i = C_i [(1 + \gamma_i)\phi_{i1} + (1 - \gamma_i)\phi_{i2}] \quad (4)$$

$$C_i \equiv \frac{1}{\sqrt{2}} [1 + S_i + (1 - S_i)\gamma_i^2]^{-\frac{1}{2}} = C_i^\circ [1 - \frac{1}{2}q_i(1 - S_i)\gamma_i^2 + O(\gamma_i^4)] \quad (5)$$

$$S_i = \text{Re} \langle \phi_{i1} | \phi_{i2} \rangle \equiv \text{Re} \int \phi_{i1}^* \phi_{i2} \, d\tau \quad (6)$$

$$C_i^\circ \equiv (2 + 2S_i)^{-\frac{1}{2}}, \quad q_i \equiv 2|C_i^\circ|^2 = (1 + S_i)^{-1} \quad (7)$$

As lone pair LMO's we use single AHO's, these orbitals being completely determined by the hybridization scheme. It is easily seen that the form (4) can be employed even for lone pairs provided that we put  $\phi_{i1} = \phi_{i2} (= \psi_i)$ . We need therefore not make any distinction between the two types of LMO's in the following.

The LMO's are assumed to be mutually orthogonal. This approximation is permissible, since hybridization maintains the orthogonality of AHO's on the same center. The overlaps neglected are thus either between orbitals two bond distances or more apart, or between orbitals on neighbouring atoms but

pointing away from each other.

From (1) and (2) we get the total electronic energy

$$E = 2 \sum_{i=1}^N (H_{ii} + \frac{1}{2}J_{ii}) + \sum_{i=1}^N \sum_{j \neq i}^N (2J_{ij} - K_{ij}) \quad (8)$$

with

$$H_{ii} \equiv \langle \psi_i | \hat{h} | \psi_i \rangle \equiv \int \psi_i^* \hat{h} \psi_i \, d\tau \quad (9)$$

$$J_{ij} \equiv [\psi_i \psi_j | \psi_j \psi_i] \equiv \iint \psi_i^*(1) \psi_i(1) \frac{1}{r_{12}} \psi_j^*(2) \psi_j(2) \, d\tau_1 d\tau_2 \quad (10)$$

$$K_{ij} \equiv [\psi_i \psi_j | \psi_j \psi_i] \equiv \iint \psi_i^*(1) \psi_j(1) \frac{1}{r_{12}} \psi_j^*(2) \psi_i(2) \, d\tau_1 d\tau_2 \quad (11)$$

The integrals in (9)–(11) are over LMO's. For AHO's we use the following notation:

$$J(l, k) \equiv [\phi_l \phi_l | \phi_k \phi_k] \equiv [U|kk] \quad (12)$$

$$K(l, k) \equiv [\phi_l \phi_k | \phi_k \phi_l] \equiv [U|kl] \quad (13)$$

The symbols  $[U|..]$  and  $[..|l.]$  to be used later on denote operators with matrix elements

$$\langle \phi_k | [U|..] | \phi_m \rangle \equiv [U|km] \quad (14)$$

$$\langle \phi_k | [..|l.] | \phi_m \rangle \equiv [kl|lm] \quad (15)$$

Defining the bond energy

$$E_i \equiv 2[H_{ii} + \frac{1}{2}J_{ii} + \sum_{j \neq i}^N (2J_{ij} - K_{ij})] \quad (16)$$

allow us to write the total energy in the form

$$E = \sum_{i=1}^N E_i - \sum_{i=1}^N \sum_{j \neq i}^N (2J_{ij} - K_{ij}) \quad (17)$$

It is readily shown that

$$\sum_{i \neq k} \frac{\partial E_i}{\partial \gamma_k} = \frac{\partial}{\partial \gamma_k} \left[ \sum_{i=1}^N \sum_{j \neq i}^N (2J_{ij} - K_{ij}) \right] \quad (18)$$

and thus we obtain the following condition for  $E$  to be stationary with respect to the bond polarities:

$$\frac{\partial E}{\partial \gamma_k} = \frac{\partial E_k}{\partial \gamma_k} = 0, \quad k = 1, 2, \dots, N \quad (19)$$

or, by inserting (16) and dividing by  $2q_k$ :

$$\frac{1}{q_k} \left[ \frac{\partial H_{kk}}{\partial \gamma_k} + \frac{1}{2} \frac{\partial J_{kk}}{\partial \gamma_k} + \sum_{j \neq k}^N \left( 2 \frac{\partial J_{kj}}{\partial \gamma_k} - \frac{\partial K_{kj}}{\partial \gamma_k} \right) \right] = 0 \quad (20)$$

In order to simplify (20) we introduce the Mulliken approximation<sup>8</sup>

$$\phi_{i1}^*(1)\phi_{i2}(1) + \phi_{i2}^*(1)\phi_{i1}(1) \cong S_i[\phi_{i1}^*(1)\phi_{i1}(1) + \phi_{i2}^*(1)\phi_{i2}(1)] \quad (21)$$

in  $J_{kk}$  and  $J_{kj}$ , and a generalized version of (21) first proposed by Ruedenberg<sup>9</sup>

$$\phi_{i1}^*(1)\phi_{i2}(2) + \phi_{i2}^*(1)\phi_{i1}(2) \cong S_i[\phi_{i1}^*(1)\phi_{i1}(2) + \phi_{i2}^*(1)\phi_{i2}(2)] \quad (22)$$

in  $K_{kj}$ . The latter approximation does not have a numerical justification like the one that has been established for the Mulliken approximation.<sup>16</sup> However, since  $J_{kj}$  is an order of magnitude greater than  $K_{kj}$ , and the two approximations are employed simultaneously, the inaccuracy in the evaluation of  $2J_{kj} - K_{kj}$  is probably still dominated by errors stemming from the use of (21).

Using (4)–(7) we obtain directly ( $m=1$  or  $2$ ):

$$\begin{aligned} \frac{1}{q_k} \frac{\partial}{\partial \gamma_k} \{ \psi_k^*(1)\psi_k(m) \} &= \phi_{k1}^*(1)\phi_{k1}(m) - \phi_{k2}^*(1)\phi_{k2}(m) \\ &+ 2S_k q_k \gamma_k \{ \phi_{k1}^*(1)\phi_{k1}(m) + \phi_{k2}^*(1)\phi_{k2}(m) - \frac{1}{S_k} [\phi_{k1}^*(1)\phi_{k2}(m) + \phi_{k2}^*(1)\phi_{k1}(m)] \} \\ &- 3(1 - S_k) q_k \gamma_k^2 [ \phi_{k1}^*(1)\phi_{k1}(m) - \phi_{k2}^*(1)\phi_{k2}(m) ] + O(\gamma_k^3) \end{aligned} \quad (23)$$

and with (21) and (22) in the terms independent of and proportional with the square of  $\gamma_i$ :

$$\begin{aligned} \psi_i^*(1)\psi_i(m) &\cong \frac{1}{2} [\phi_{i1}^*(1)\phi_{i1}(m) + \phi_{i2}^*(1)\phi_{i2}(m)] \\ &+ q_i \gamma_i [\phi_{i1}^*(1)\phi_{i1}(m) - \phi_{i2}^*(1)\phi_{i2}(m)] + O(\gamma_i^3) \end{aligned} \quad (24)$$

It is seen that the use of (21) and (22) would eliminate the first order term in (23). However, whereas this is acceptable in the  $J$ - and  $K$ -integrals (precisely the justification for applying the approximations in (24)) it is certainly not so in  $H_{kk}$  because of the presence of the operator  $\hat{T}$  in  $\hat{h}$ . Since we cannot do away with the term completely, we prefer to keep it everywhere as it stands.

We notice from (24) that the assumption of orthogonality of the LMO's together with (21) and (22) allow us to approximate the charge distribution in the molecule by one arising from a collection of fractionally charged atoms in suitable valence states. The fact that (24) is applicable to both Coulomb and exchange interactions implies that the charges left in the hybrids must be regarded as made up of equal amounts from the two bonding electrons with opposed spins.<sup>17</sup>

### 3. ELECTRONEGATIVITY EQUALIZATION

The preceding section contains the general framework for the discussions to follow. The remaining part of the paper will be concerned with the explicit evaluation of (20) and the interpretation of this equation in terms of Electronegativity Equalization (EE). This is most conveniently done in steps, successively including energy terms of increasing order in the bond polarities.

*3.1. First order theory.* The first order theory is of course of limited practical use since (20) to this order does not involve the bond polarities. This simple

case, however, will provide us with some useful definitions appropriate to the point of reference, *i.e.* the situation where all bonds are homopolar.

In the following it is assumed that  $\phi_{k1}$  and  $\phi_{k2}$  are centred on atoms A and B, respectively. Upon insertion of the zeroth order terms from (23) and (24) into (20) this equation now reduces to

$$X_M(k1) + \sum_{C \neq A}^M PE_C(k1) = X_M(k2) + \sum_{C \neq B}^M PE_C(k2) \quad (25)$$

$PE_C$  denotes the penetration energy of the orbital in question into the neutral atom C.  $X_M$  is the Mulliken electronegativity<sup>18</sup> defined in terms of the ionization potential  $I_V$  and the electron affinity  $A_V$  for the orbital in the appropriate valence state V of the atom. Using the definition

$$\hat{\epsilon}_C \equiv U_C + \sum_l \{[ll..] - \frac{1}{2}[.ll.]\} \quad (26)$$

where the summation runs over all AHO's on C counting lone pair AHO's twice, we have

$$PE_C(k1) \equiv -\langle \phi_{k1} | \hat{\epsilon}_C | \phi_{k1} \rangle \quad (27)$$

$$X_M(k1) \equiv \frac{1}{2} \{ I_V(k1) + A_V(k1) \} = -\langle \phi_{k1} | \hat{T} + \hat{\epsilon}_A | \phi_{k1} \rangle \quad (28)$$

and corresponding expressions for  $\phi_{k2}$ .

The term

$$\langle \phi_{k1} | [k1k1..] - \frac{1}{2}[.k1k1.] | \phi_{k1} \rangle = \frac{1}{2}[k1k1|k1k1] \quad (29)$$

entering the definition (28) of the Mulliken electronegativity, expresses the fact that a charge element transferred to  $\phi_{k1}$  through the bond can interact with half the charge already present, *i.e.* the portion due to the other electron.

Introduction of left-right correlation between the two electrons in the bond can be considered equivalent to allowing the charges in the orbitals forming the bond to be made up of different amounts from the bonding electrons. This explicit correlation effect is clearly incompatible with the general features of simple MO-theory and cannot be included *via* a consistent approximation scheme in a theory of this nature. Furthermore, if the effect is introduced by some (necessarily inconsistent) means, it will require additional assumption to maintain the concept of electronegativity in the Mulliken sense. The term (29), which is part of the definition, can namely only be justified if the test charge element added to  $\phi_{k1}$  contains equal amounts from the two electrons. It follows, as an immediate consequence of the preceding remark, that the electronegativity concept cannot be derived from the quantum mechanics of isolated atoms.<sup>12,14</sup>

Eqn. (25) is the EE-equation for the trivial case of perfect homopolarity of all bonds. We take this as the basis for the definition of the generalized homopolar electronegativity,  $X_C^\circ$ , of the orbital in the molecular environments. However, arguments similar to the one given in connection with (29) force us to remove part of the interaction between  $\phi_{k1}$  and  $\phi_{k2}$  in order to avoid self-interaction of the electron. We thus write

$$X_G^\circ(k1) \equiv X_M(k1) + \sum_{C \neq A}^M PE_C(k1) + \frac{1}{2}[J(k1,k2) - K(k1,k2)] \quad (30)$$

and similarly for  $\phi_{k2}$ .

Introducing the homopolar Fock-operator  $\hat{F}^\circ$  (actually derived from the valence state atoms) and the self-interaction correction operator  $\hat{\beta}_k$

$$\hat{F}^\circ \equiv \hat{T} + \sum_{C=1}^M \hat{\epsilon}_C \quad (31)$$

$$\hat{\beta}_k \equiv \frac{1}{2}\{[k1k1|..] + [k2k2|..] - [k1|k1.] - [k2|k2.]\} \quad (32)$$

$$\langle \phi_{k1} | \hat{\beta}_k | \phi_{k1} \rangle = \langle \phi_{k2} | \hat{\beta}_k | \phi_{k2} \rangle = \frac{1}{2}[J(k1,k2) - K(k1,k2)] \quad (33)$$

$$\langle \phi_{k1} | \hat{\beta}_k | \phi_{k2} \rangle = 0 \quad (34)$$

allow us to write (30) in the form

$$X_G^\circ(k1) \equiv -\langle \phi_{k1} | \hat{F}^\circ - \hat{\beta}_k | \phi_{k1} \rangle \quad (35)$$

$X_G^\circ(k2)$  is given as the negative expectation value of the same operator with respect to  $\phi_{k2}$ .

*3.2. Second order theory.* In order to obtain equations from (20) which can be solved for the bond polarities, and which can therefore be used in calculations of these important quantities, we have to evaluate the energy to at least 2. order in the  $\gamma$ 's.

If this is done, while the LMO's are normalized only to 1. order, *i.e.* when the 1. order term in (23) is neglected, we get from (20):

$$\begin{aligned} X_G^\circ(k1) - \sum_{j \neq k}^N 2q_j \gamma_j \{ [J(k1,j1) - \frac{1}{2}K(k1,j1)] - [J(k1,j2) - \frac{1}{2}K(k1,j2)] \} \\ - q_k \gamma_k [J(k1,k1) - J(k1,k2)] = X_G^\circ(k2) - q_k \gamma_k [J(k2,k1) - (J(k2,k2))] \\ - \sum_{j \neq k}^N 2q_j \gamma_j \{ [J(k2,j1) - \frac{1}{2}K(k2,j1)] - [J(k2,j2) - \frac{1}{2}K(k2,j2)] \} \end{aligned} \quad (36)$$

The  $\gamma$ -dependent (inductive) terms in (36) are recognized as being corrections to the  $X_M$ - and PE-terms stemming from the deviations from homopolarity of the bonds. The quantity  $2q_j \gamma_j$  is the charge transferred from  $\phi_{j2}$  to  $\phi_{j1}$ .

Defining the general Fock-operator  $\hat{F}$ :

$$\hat{F}(\boldsymbol{\gamma}) = \hat{F}^\circ + \Delta \hat{F}(\boldsymbol{\gamma}) \quad (37)$$

$$\Delta \hat{F}(\boldsymbol{\gamma}) = \sum_{j=1}^N 2q_j \gamma_j \{ ([j1j1|..] - \frac{1}{2}[j1|j1.]) - ([j2j2|..] - \frac{1}{2}[j2|j2.]) \} \quad (38)$$

enables us to rewrite (36)

$$\begin{aligned} X_G(k1) &\equiv - \langle \phi_{k1} | \hat{F} - (1 - 2q_k \gamma_k) \hat{\beta}_k | \phi_{k1} \rangle \\ &= - \langle \phi_{k2} | \hat{F} - (1 + 2q_k \gamma_k) \hat{\beta}_k | \phi_{k2} \rangle \equiv X_G(k2) \end{aligned} \quad (39)$$

The coefficient of  $\hat{\beta}_k$  in (39) is the charge in the partner orbital in the bond. This term will thus remove the self-interaction connected with that part of the charge distribution.

The reason for including the inconsistent 2. order treatment giving rise to (39) is that this seems to be the best we can do if we want (20) to come out as an EE-equation. The complete 2. order theory, including the 1. order term in (23), gives the equation

$$X_G(k1) - X_G(k2) + 2q_k S_k \gamma_k \{X_G^\circ(k1) + X_G^\circ(k2) - 2X_G^\circ(kS)\} = 0 \quad (40)$$

where we have used (39) and (35) plus a definition of the homopolar overlap electronegativity analogous to (35):

$$X_G^\circ(kS) \equiv - \text{Re} \langle \phi_{k1} | \hat{F}^\circ - \hat{\beta}_k | \phi_{k2} \rangle / S_k = - \text{Re} \langle \phi_{k1} | \hat{F}^\circ | \phi_{k2} \rangle / S_k \quad (41)$$

Eqn. (40) can be cast into a form similar to (39) if we are willing to accept another generalization of the Mulliken approximation (21), namely the Wolfsberg-Helmholz approximation<sup>10</sup> for  $\hat{F}^\circ$ :

$$\text{Re} \langle \phi_{k1} | \hat{F}^\circ | \phi_{k2} \rangle \cong G \frac{S_k}{2} \{ \langle \phi_{k1} | \hat{F}^\circ | \phi_{k1} \rangle + \langle \phi_{k2} | \hat{F}^\circ | \phi_{k2} \rangle \} \quad (42)$$

$G$  is here an empirical parameter greater than 1. In that case (40) takes the form

$$\begin{aligned} & - \langle \phi_{k1} | \hat{F} - (1 - 2q_k \gamma_k) \hat{\beta}_k - 2q_k S_k \gamma_k [\hat{\beta}_k + (G - 1) \hat{F}^\circ] | \phi_{k1} \rangle = \\ & = - \langle \phi_{k2} | \hat{F} - (1 + 2q_k \gamma_k) \hat{\beta}_k + 2q_k S_k \gamma_k [\hat{\beta}_k + (G - 1) \hat{F}^\circ] | \phi_{k2} \rangle \end{aligned} \quad (43)$$

It may be argued that the Wolfsberg-Helmholz approximation ought to be applied to  $\hat{F}^\circ - \hat{\beta}_k$  rather than to  $\hat{F}$ ; so that the equation would reduce to (39) for  $G=1$ . However, the Wolfsberg-Helmholz approximation does not in general, as the Mulliken approximation, conserve the total charge involved in the interactions. Since the justification for the approximation therefore is purely numerical, and no direct physical interpretation can be given for the resulting terms, it was found rational to leave out the diagonal operator  $\hat{\beta}_k$  (see eqn. 34). From the computational point of view the two approaches give very similar results although of course different  $G$ -values.

*3.3. Third order theory.* Preliminary calculations seem to indicate that most molecules in which the bonding is commonly considered as covalent, are adequately described by the 2. order theory. Only in comparatively few cases will bonds of sufficient polarity be present as to warrant inclusion of terms in the energy involving the bond polarities to 3. order.

With the energy evaluated to this order eqn. (20) becomes a second order equation. It will, however, still be relatively simple since the only further term in (22) and (23) which contributes is the 2. order term in (23). By analogy to the derivation of (25) it is seen, that this term will give an additional

$$- 3(1 - S_k)q_k\gamma_k^2[X_G^\circ(k1) - X_G^\circ(k2)] \quad (44)$$

on the left-hand side of (40). The remaining 2. order terms arising from the derivatives of  $J_{kk}$ ,  $J_{kj}$ , and  $K_{kj}$  can be eliminated by applying (21) and (22) in (23). Thus writing out (43) with inclusion of (44) and collecting all 1. order terms [see (37), (38), and (39)] on one side of the equation we have

$$\begin{aligned} & 2q_k\gamma_k\{S_k(G - 1)[X_G^\circ(k1) + X_G^\circ(k2)] - S_kG[J(k1,k2) - K(k1,k2)] \\ & + \frac{1}{2}[J(k1,k1) + J(k2,k2)] - J(k1,k2)\} + \sum_{j \neq k}^N 2q_j\gamma_j A_{kj} \\ & = [1 - 3(1 - S_k)q_k\gamma_k^2] [X_G^\circ(k1) - X_G^\circ(k2)] \end{aligned} \quad (45)$$

where

$$\begin{aligned} A_{kj} & \equiv J(k1,j1) - J(k1,j2) - J(k2,j1) + J(k2,j2) \\ & - \frac{1}{2}[K(k1,j1) - K(k1,j2) - K(k2,j1) + K(k2,j2)] \end{aligned} \quad (46)$$

*3.4. Further remarks.* In order to make the connection between the three orders treated, let us consider the charge distribution in the  $k$ 'th bond

$$2|\gamma_k|^2 = Q_{k1}|\phi_{k1}|^2 + Q_{k2}|\phi_{k2}|^2 + Q_{ks}(\phi_{k1}\phi_{k2}^* + \phi_{k1}^*\phi_{k2})/2S_k \quad (47)$$

$$Q_{k1} = q_k\{1 + 2\gamma_k + 2S_kq_k\gamma_k^2 - 2(1 - S_k)q_k\gamma_k^3\} + O(\gamma_k^4) \quad (48)$$

$$Q_{k2} = q_k\{1 - 2\gamma_k + 2S_kq_k\gamma_k^2 + 2(1 - S_k)q_k\gamma_k^3\} + O(\gamma_k^4) \quad (49)$$

$$Q_{ks} = 2q_kS_k\{1 - 2q_k\gamma_k^2\} + O(\gamma_k^4) \quad (50)$$

Eqn. (19) can be written

$$\begin{aligned} - \frac{\partial E}{\partial \gamma_k} & = \left(- \frac{\partial E}{\partial Q_{k1}}\right) \frac{\partial Q_{k1}}{\partial \gamma_k} + \left(- \frac{\partial E}{\partial Q_{k2}}\right) \frac{\partial Q_{k2}}{\partial \gamma_k} + \left(- \frac{\partial E}{\partial Q_{ks}}\right) \frac{\partial Q_{ks}}{\partial \gamma_k} \\ & \equiv X_G(k1) \frac{\partial Q_{k1}}{\partial \gamma_k} + X_G(k2) \frac{\partial Q_{k2}}{\partial \gamma_k} + X_G(ks) \frac{\partial Q_{ks}}{\partial \gamma_k} = 0 \end{aligned} \quad (51)$$

where we have adopted the now generally accepted definition of the electronegativity<sup>14</sup> as being the derivative of the energy with respect to the charge (properly signed). Eqns. (25), (40), and (45) are seen to be (51) calculated to various orders and as such telling us what to include in the  $X_G$ 's.

The bond term added in going from (39) to (40) originates from the 2. order contributions to (48)–(50), which describes a migration of charge from the overlap distribution to the bonding orbitals. Since the overlap is the main factor responsible for the bonding, this term represents the inherent inertia towards weakening of the bond. No equalizing effect on the electronegativities can be attributed to the bond term, and (40) and (45) can consequently not be regarded as EE-equations in a simple sense.

In attempts to establish the validity of the principle of EE within LMO-theories Baird, Sichel and Whitehead<sup>13</sup> included resonance terms similar to our overlap electronegativities in their orbital electronegativity definition. It is, however, difficult to visualize these quantities as potentials for charges



in any of the two orbitals involved. Not even the Wolfsberg-Helmholz approximation will solve this problem, since this, as previously mentioned, is no more than a convenient but unphysical way out of computational difficulties.

#### 4. CONCLUSION

The principle of electronegativity equalization constitutes an intuitively appealing and, as shown above, theoretically justifiable framework for molecular orbital calculations on molecules reasonably well described by localized orbitals. It is, however, absolutely necessary that molecular corrections be taken into account in applications of the principle. Preliminary calculations demonstrate very clearly that both neutral penetration energies and terms originating from changes in overlap distributions are extremely important corrections without which the theory would be seriously unbalanced.

In the near future a full report on calculations according to the present theory will be published.

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