

**ELECTRONEGATIVITIES OF DIATOMIC MOLECULES CALCULATED
BY THE $X\alpha$ METHOD WITH A SELF-CONSISTENT PARAMETER α
USING THE PRINCIPLE OF ELECTRONEGATIVITY EQUALIZATION**

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Dedicated to Dr R. Zahradník on the occasion of his 60th birthday.

The $X\alpha$ method with a self-consistent parameter α has been used to calculate the electronegativity of several diatomic molecules. The electronegativities have been determined on the principle of electronegativity equalization using the results of atomic calculations.

The concept of electronegativity has long been of great use in chemistry. However, its rigorous theoretical analysis has been accomplished only recently¹⁻⁵. The Euler equation of the density functional theory⁶ provides a natural way of its calculation. Balbás, Alonso and Iniguez⁷ have calculated the electronegativities of atoms within the density functional theory using the pseudopotential approach. Bartolotti, Gadre and Parr⁴ and Manoli and Whitehead⁸ have determined these electronegativities using the $X\alpha$ method. Gazquez and Ortiz⁹ have calculated the electronegativities of open shell atoms with the hyper-Hartree-Fock and $X\alpha$ methods. The authors of this paper¹⁰ have applied the $X\alpha$ method with a self-consistent parameter α to the determination of the electronegativities of atoms.

The principle of electronegativity equalization has been widely applied to calculate the electronegativity of molecules^{9,11-15}. It allows us to evaluate the electronegativities of molecules from neutral atomic calculations. On the basis of this principle the electronegativities of several diatomic molecules has been determined by the $X\alpha$ method with a self-consistent parameter α .

The $X\alpha$ Method with Self-Consistent Parameter α

The $X\alpha$ method providing self-consistent parameter α has been discussed in detail in earlier papers^{16,17}. Here, only a brief summary is presented.

In the free-electron gas model the exchange potential of an electron having spin up is given by

$$V_{X\uparrow}(1) = -8F(\eta) \left| \frac{3}{4\pi} \rho_{\uparrow}(1) \right|^{1/3}, \quad (1)$$

where

$$F(\eta) = \frac{1}{2} + \frac{1 - \eta^2}{4\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| \quad (2)$$

and $\eta = P/P_F$ is the reduced momentum of the electron in question. P_F and ϱ_{\uparrow} are the Fermi momentum and the total electron density for electrons with spin up, respectively. To get rid of the momentum dependence, it is customary to average expression (1) over the Fermi sphere. An average for the whole Fermi sphere leading to $\alpha = 1$ was proposed by Slater¹⁸. Averaging near the Fermi surface for a layer, thickness of which goes to zero, we get $\alpha = 2/3$ following Gáspár¹⁹ and Kohn and Sham²⁰. Considering a case between these two extremes, an average is done for a layer having $v_{i\uparrow} = U_i^* U_i$ electrons in the unit volume near the Fermi surface:

$$\alpha_i = \frac{\varrho_{\uparrow}}{v_{i\uparrow}} \left(1 - \frac{1}{2}\eta_i^3 - \frac{1}{2}\eta_i + \frac{1}{4}(\eta_i^2 - 1)^2 \ln \left| \frac{1 - \eta_i}{1 + \eta_i} \right| \right), \quad (3)$$

where

$$\eta_i = \left(1 - \frac{v_{i\uparrow}}{\varrho_{\uparrow}} \right)^{1/3}. \quad (4)$$

The parameters α_i given by Eq. (3) are different for the different spin orbitals U_i and depend on the position vector. The r -dependence of the parameters α of different shells has been analysed in literature²¹. The average over the shells

$$\alpha_{\uparrow}(1) = \frac{\sum_{i\uparrow} (n_i \alpha_i)}{\sum_{i\uparrow} n_i} \quad (5)$$

leads to a parameter α_{\uparrow} that only slightly depends on the position (1) (ref.¹⁷), and can be considered to be constant (n_i is the occupation number of the shell i).

The parameter α can be calculated self-consistently, so a notation α_{SCF} is used. This way of calculating the parameter of the X α method contains no fitting or adjustment, it can be considered an *ab initio* procedure.

Calculation of the Electronegativity

The electronegativity χ of an atom or a molecule has been defined¹ as the negative of the chemical potential μ

$$\chi = -\mu = -\partial E / \partial N. \quad (6)$$

The Mulliken formula²²

$$\chi_M = \frac{1}{2}(I + A) \quad (7)$$

provides an excellent approximation to the electronegativity^{1,10,23}, where I and A are the ionization potential and the electron affinity, respectively. The electronegativity χ can also be easily calculated in the $X\alpha$ method^{4,9,10} using Slater's transition-state method²⁴.

The principle of electronegativity equalization is used to calculate the electronegativity and the charge transfer in a molecule. The chemical potentials of the atoms **A** and **B** are $\chi_A = \chi(Z_A, N_A)$ and $\chi_B = \chi(Z_B, N_B)$, respectively. For neutral atoms $Z_A = N_A$ and $Z_B = N_B$. In the process of formation of a molecule **AB** a redistribution of charge takes place

$$\chi(Z_A, N_A^*) = \chi(Z_B, N_B^*), \quad (8)$$

where N_A^* and N_B^* are the number of electrons of atomic ions **A** and **B** in the molecule. The non-integral numbers N_A^* and N_B^* satisfy

$$N_A^* + N_B^* = Z_A + Z_B \quad (9)$$

as the total number of electrons remained the same. Expanding the electronegativity $\chi(Z, N^*)$ around the neutral-atom limit $N^* = Z$, we get

$$\chi(Z, N^*) = \chi(Z, Z) + \chi'(N^* - Z) + \dots, \quad (10)$$

where

$$\chi' = \left(\frac{\partial \chi(Z, N)}{\partial N} \right)_{N=Z}$$

Neglecting the second and the higher-order terms, Eqs (8)–(10) lead to

$$\chi_A + \chi'_A Q = \chi_B - \chi'_B Q, \quad (11)$$

where

$$Q = N_A^* - Z_A \quad (12)$$

is the charge transferred from **A** to **B**. From Eq. (11) the charge transfer and the electronegativity are given by

$$Q = (\chi_B - \chi_A) / (\chi'_A + \chi'_B) \quad (13)$$

and

$$\chi = \chi_A + (\chi_B - \chi_A) / (1 + \chi'_B / \chi'_A), \quad (14)$$

respectively.

To determine χ' the ionization energy I and the electron affinity A are expanded as

$$\begin{aligned}
 I &= E(Z, N - 1) - E(Z, N) = \\
 &= - \left(\frac{\partial E}{\partial N} \right)_{N=Z} + \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{N=Z} - \frac{1}{3!} \left(\frac{\partial^3 E}{\partial N^3} \right)_{N=Z} + \dots
 \end{aligned} \quad (15)$$

and

$$\begin{aligned}
 A &= E(Z, N) - E(Z, N + 1) = \\
 &= - \left(\frac{\partial E}{\partial N} \right)_{N=Z} - \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{N=Z} - \frac{1}{3!} \left(\frac{\partial^3 E}{\partial N^3} \right)_{N=Z} + \dots
 \end{aligned} \quad (16)$$

TABLE I

Charge transfer in mixed halides obtained from Eq. (13) using the $X\alpha_{\text{SCF}}$ and the experimental data¹² (electronic charge is transferred from atom A to atom B)

Molecule	Charge transfer	
	$X\alpha_{\text{SCF}}$	Exp.
FCl	0.12	0.09
ClBr	0.05	0.04
FBr	0.17	0.12

TABLE II

Electronegativities of several diatomics (in eV) obtained from Eq. (14) by the $X\alpha$ method with α_{HF} and α_{SCF} parameters taken from literature⁹ and using the experimental data^{11,12}

Molecule	$X\alpha$		Exp.
	α_{HF}	α_{SCF}	
BrF	8.49	8.62	8.74
ClF	9.18	9.32	9.22
BrCl	7.64	7.53	8.00
SO	7.42	7.54	6.78
SeO	6.94	7.05	7.18
PN	5.74	5.99	6.55
AsN	5.46	5.55	6.31

From the expressions (15) and (16) neglecting the fourth and higher-order terms we get

$$A - I = - \left(\frac{\partial^2 E}{\partial N^2} \right)_{N=Z} = \left(\frac{\partial \chi}{\partial N} \right)_{N=Z} = \chi' . \quad (17)$$

Expressions (15) and (16) lead to the Mulliken formula of the electronegativity

$$\chi = \frac{1}{2}(I + A) . \quad (18)$$

From Eq. (18) the electron affinity can be given by

$$A = 2\chi - I . \quad (19)$$

The self-consistent parameter α has been used to calculate the electronegativities and ionization energies of atoms with the $X\alpha$ method¹⁰. The electron affinity has been determined using the expression (19). Table I presents the charge transfer in mixed halides calculated from the expression (13). The $X\alpha_{\text{SCF}}$ results are compared with the values obtained by Alonso and March¹². They have used the experimental ionization energies and electron affinities in Eqs (7), (13), (14), and (17) to get the charge transfer. There is a good agreement between their and our data. Table II shows the electronegativities of several diatomics calculated with the expression (14). Table II contains the $X\alpha$ results obtained with the parameters α_{HF} and α_{SCF} taken from literature⁹. Values obtained by Ray, Samuels and Parr¹¹ and Alonso and March¹² using the experimental ionization energy and electron affinity are also included in Table II. The agreement between the $X\alpha$ and experimental values is satisfactory.

We can conclude that the $X\alpha$ method with a self-consistent parameter α is suitable to calculate the electronegativities of molecules. This method is purely theoretical, there is no fitting or adjustment in it.

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