On the Charges of Atoms in Molecules

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(Z. Naturforsch. **29 a**, 1927–1928 [1974];
received October 25, 1974)

Recently deduced values for the partial charges of atoms in molecules are compared with those predicted by Wilmshurst's expression for the bond polarity. The assumption that atoms in molecules can have fractional charges seems to lead to an ionic approximation to chemical bonding in the first place.

In a recent paper, Evans and Huheey[1] commented on the meaning and definition of "charge" in molecules. It was shown therein that the values of the partial charges of atoms in molecules, computed by Politzer et al.[2], are similar to the ones obtained from the empirical bonding theory, advanced by Evans and Huheey[3].

It may well be asked whether or not these relatively complicated methods for obtaining partial charges of atoms in molecules throw a new light on the meaning of charges in molecules. Indeed, a very simple calculation of charge separation with Pauling-electronegativities, based upon the Wilmshurst approximation[4] for the polarity I of an heteronuclear bon AB, i. e.

$$I = (\chi_B - \chi_A)/(\chi_A + \chi_B) \tag{1}$$

yields values which compare will – even quantitatively – with those obtained by Evans and Huheey and by Politzer et al., as to be seen from the data collected in Table 1.

Table 1. Charges of atoms in molecules calculated by different methods.

Molecule	Atom	Charges calculated		
		From eqn (1)	by Evans and Huheey[a]	by Politzer et al.[b]
HF	H	+0.31	+0.29	+0.26, 0.27
	F	−0.31	−0.29	−0.26, 0.27
HCl	H	+0.18	+0.16	+0.17
	Cl	−0.18	−0.16	−0.17
LiF	Li	+0.60	+0.62	+0.52
	F	−0.60	−0.62	−0.52
LiH	Li	+0.35	+0.48	+0.37
	H	−0.35	−0.48	−0.37
NaF	Na	+0.63	+0.63	+0.62
	F	−0.63	−0.63	−0.62
NaCl	Na	+0.54	+0.72	+0.60
	Cl	−0.54	−0.72	−0.60
HCCH	H	+0.22[c]	+0.14	+0.14
	C	−0.22[c]	−0.14	−0.14
HCCF	F	−0.10[c]	−0.07	−0.05
HCCCl	Cl	+0.05[c]	+0.04	+0.03

[a] taken from Ref. 1.

[b] taken from Ref. 2 as collected in Ref. 1.

[c] tentative values only, obtained with a constant $\chi_{\mathrm{Csp}} = 3.29$[9], since it is difficult to find a convenient formalism to compute groupelectronegativities in such a way, that the Wilmshurst charge definition can unambiguously be applied to polyatomic molecules. This question is however considered as irrelevant for the present discussion.

Evans and Huheey further paid attention to the charge coefficient b appearing in the expression for the electronegativity

$$\chi_X(I) = a + b\,I = \chi_X(0) + b\,I \tag{2}$$

and argued that b, which can be considered as an inverse measure for charge capacity, is as important as the neutral electronegativity $a = \chi_X(0)$ in determining charge separations. It was even concluded that the neglect of charge capacity is a serious oversight in any simple application of electronegativity.

Now, a simple transformation of Eq. (1) leads to

$$\chi_A(1+I) = \chi_B(1-I) \tag{3}$$

or, in terms of Eq. (2):

$$\chi_X(I) = \chi_X(0)\,(1 \pm I)\,. \tag{4}$$

Hence, the Wilmshurst approximation is obtained from Eq. (2) by putting $a = b$ or by assuming that the "inverse measure of charge capacity" is nothing but the neutral electronegativity itself. This however has rather serious consequences for the absolute χ-values of both methods but the formal gain in simplicity would be considerable, if Eq. (4) would be generally valid for expressing electronegativities in function of the charge separation. The results of Table 1 are in favour of this latter supposition and other consequences of Eqs. (3) and (4), illustrating the Sanderson-concept of electronegativity-equalization[5], have already been discussed elsewhere[6].

However, Wilmshurst's derivation of Eq. (1) is even more descriptive for the concept of charges in molecules. Wilmshurst indeed inferred that, in a two-centre two-electron heteronuclear bond AB, the probability of finding the valence electron pair near A or B will be equal to

$$\chi_A/(\chi_A + \chi_B) = a^2$$

$$\text{and} \qquad \chi_B/(\chi_A + \chi_B) = b^2 \tag{5}$$

respectively, whereby $a^2 + b^2 = 1$ and $b^2 - a^2 = I$.

If the partial charges of atoms in molecules are now consistently interpreted in terms of the probabilities (5) as indicated by Wilmshurst, several important consequences immediately follow from this concept, which, unfortunately, are usually overlooked.

Indeed, when $a^2 = 1$ (or $b^2 = 1$), the energy of the valence electrons is given by $IE_A + EA_A$ (or $IE_B +$

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EA_B), where IE_X and EA_X are the valence-state-ionization energy and -electron-affinity of X respectively.

A rigourous application of the Wilmshurst definition of partial charges then implies that at least one contribution to the valence electron energy of a bond AB, ε_{AB}, is known:

$$\varepsilon_{AB} = a^2 (IE_A + EA_A) + b^2 (IE_B + EA_B) + x_{AB} \quad (6)$$

where the equilibrium probabilities (5) have been used and wherein the term x_{AB} represents yet unknown bonding contributions.

However, a consideration of ionic structures A^-B^+ and A^+B^- as in Eq. (6) calls for a Coulomb attraction term. Since $a^2 + b^2 = 1$, one readily obtains:

$$\varepsilon_{AB} = a^2 (IE_A + EA_A) + b^2 (IE_B + EA_B) + e^2/r_{AB} \quad (7)$$

if r_{AB} is the equilibrium separation and if, for the sake of simplicity, Born-repulsion is not explicitly considered.

This leads to a bond energy E_{AB}:

$$E_{AB} = \varepsilon_{AB} - (IE_A + IE_B) \quad (8)$$

$$= a^2\, EA_A + b^2\, EA_B + e^2/r_{AB} - a^2\, IE_B - b^2\, IE_A\,. \quad (9)$$

For an homonuclear bond AA, this expression reduces to

$$E_{AA} = EA_A - IE_A + e^2/r_{AA} \quad (10)$$

and hence, the Wilmshurst definition of charges of atoms in molecules directly leads to an ionic approximation to chemical bonding, a question we recently discussed extensively [7].

Furthermore, it is clear from the above that Mulliken's electronegativity-definition [8] and generalizations thereof [9] are incompatible with the requirement $a = b$ in Eq. (2), as imposed by the Wilmshurst definition of polarity, although, in principle, both approaches assume the electronegativity to vary linearly with charge.

A particular solution, corresponding with $\chi_X = EA_X = E_{XX}$, has been advanced elsewhere [10], which seems to meet these conditions. Moreover, the following equilibrium values are then obtained

$$E_{AB} = a^2\, EA_A + b^2\, EA_B \quad (11)$$

$$= (1/2)\,(E_{AA} + E_{BB})\,(1 + I^2) \quad (12)$$

and

$$r_{BA} = b^2\, IE_A + a^2\, IE_B \quad (13)$$

which may be considered as a further elaboration of Eq. (9) conform with the Wilmshurst definition of partial charges of atoms in molecules. These expressions are consistent with a completely ionic approximation to chemical bonding but, nevertheless, can easily be transformed to yield the more commonly accepted ionic-covalent resonance formalism. In particular, the completely ionic approximation (9) is then still consistent with the empirical Pauling bond energy equation, as to be seen from Eq. (12).

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