An Investigation of Definitions
of the Charge on an Atom in a Molecule

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A study has been made of three different procedures used to define the charge on an atom in a molecule. It was found that none of the three is completely satisfactory, although that proposed by Löwdin seemed to give the best results. The effect of certain other factors, such as the nature of the basis set and the inclusion of the Madelung potential, was also investigated.

Drei verschiedene Methoden zur Bestimmung der Ladung eines Atoms in einem Molekül werden untersucht. Keine der drei Methoden kann als völlig zufriedenstellend bezeichnet werden. Die besten Ergebnisse scheint die von Löwdin vorgeschlagene Methode zu liefern. Der Einfluß verschiedener Faktoren wie Art der Basis und Berücksichtigung des Madelung-Potentials werden untersucht.

Etude de trois procédés différents pour la définition de la charge sur un atome dans une molécule. Aucun des trois procédés n'est complètement satisfaisant, celui proposé par Löwdin semblant donner cependant les meilleurs résultats. L'effet de certains autres facteurs: nature de la base, introduction du potentiel de Madelung a aussi été étudié.

Introduction

It has recently been pointed out that there exists a definite problem with regard to defining a measure of the charge on an atom in a molecule [1, 2]. Semi-empirical LCAO-MO wave functions were computed for diborane by the procedure of iteration to self-consistency in the charges on the atoms, using first the Mulliken definition of charge [3], and then the definition which has been proposed by Löwdin [4]. It was found that distinctly different wave functions were obtained in the two cases, differing both in electronic density distributions and also with respect to the energies of the molecular orbitals. Furthermore, for any given wave function, the computed "charges" on the atoms differed quite considerably when one or the other definition was used. It appears to be necessary, therefore, to seek some means of deciding which definition of charge, whether it be one of these two or some other, is the most useful and physically the most meaningful. The present study was undertaken as a first step toward reaching such a decision.

Procedure

Semi-empirical LCAO-MO wave functions were computed for three different diatomic molecules: carbon monoxide, boron monofluoride, and lithium fluoride. These were chosen in order to have a gradation in polarity, from the essentially non-polar CO to the very highly polar LiF. The molecular orbitals were built

up from 2s and 2p orbitals on the two atoms involved (only valence electrons were included in these calculations). The diagonal Hamiltonian matrix elements were taken to be functions of the charges on the atoms, using the formulae derived by Basch, Viste and Gray from atomic spectral data [5], and the final form of the wave function was determined by iteration to self-consistency over these charges. The off-diagonal elements were approximated by means of the formula which has been proposed by Cusachs [6].

Three different definitions of charge were used to compute the charges on the atoms, so that three somewhat different versions were obtained of each molecular wave function. These definitions shall be briefly summarized. Mulliken suggested that the electronic charge on an atom r be defined as

$$Q_r = \sum_k N_k \left[\sum_m (C_{km}^2 + \sum_{s,n} C_{km} C_{kn} S_{mn}) \right]$$

where the kth molecular orbital is

$$\Psi_k = \sum_{r,m} C_{km} \psi_m .$$

The subscripts m and n refer to atomic orbitals on atoms r and s, respectively, S_{mn} is the overlap integral between orbitals m and n, and N_k is the number of electrons in the kth molecular orbital.

By the Mulliken definition, the overlap charge is apportioned equally between the two atoms, which would in general be realistic only for a homonuclear molecule. There has therefore been proposed a modification of the Mulliken scheme; instead of dividing the overlap charge equally, it is apportioned between the two atoms in a weighted fashion which will hopefully take at least partial account of the difference in the extents of the contributions from the atoms [7]. Thus the charge on atom r would be

$$Q_r = \sum_k N_k \left[\sum_m (C_{km}^2 + \sum_{s,n} 2F_{mn} C_{km} C_{kn} S_{mn}) \right] .$$

For the factor F_{mn} was suggested the ratio $C_{km}^2/(C_{km}^2 + C_{kn}^2)$. It was pointed out by Cusachs [8a] that for this particular F_{mn} this expression for Q_r reduces to

$$Q_r = \sum_k N_k \left(\sum_m C_{km}^2 \right) \bigg/ \left(\sum_m C_{km}^2 + \sum_n C_{kn}^2 \right)$$

which is identical with a charge definition suggested by Ros and Schuit [8b].

Finally, the Löwdin definition is based on a molecular wave function written in terms of a basis set of orthogonalized atomic orbitals,

$$\Psi_k = \sum_{r,m} K_{km} \phi_m \qquad S_{mn} = \int \phi_m^* \phi_n \, d\tau = 0 .$$

Then,

$$Q_r = \sum_k N_k \left(\sum_m K_{km}^2 \right) .$$

The semi-empirical wave functions being computed here will depend upon other factors, in addition to the manner in which the charge is defined. One such factor is the choice of atomic orbital basis set. In order to see its effect more clearly, three different ones were used in this work: the single-zeta atomic orbitals

of Clementi and Raimondi [9], the double-zeta orbitals of Clementi [10], and finally his accurate, extended-zeta, Roothaan-Hartree-Fock atomic orbitals [10]. All three of these basis sets were used for CO and BF. For LiF, only the calculation in terms of single-zeta orbitals could be carried out, because the double- and extended-zeta orbitals do not include lithium atom $2p$ functions.

Finally, the so-called Madelung potential was also considered [11]. This refers to the effect upon the valence orbital ionization potentials of atom A (which are being used for the diagonal elements of the Hamiltonian matrix) of the charge which has built up around atom B. In the present work, this build-up was approximated as a point charge at B, and its Coulomb potential at A was added to the valence orbital ionization potentials of A. The wave function computations were carried out both with and without inclusion of the Madelung potential.

Results

The results are listed in Tables 1 and 2. For each computed wave function, there is stated the charge definition in terms of which it was balanced, and the value at which this balance occurred. There are also indicated, for the given function, the charges in terms of the other two definitions, so that the degree of variation between the three values can be seen. It is quite significant. As an indication of the electronic density distribution associated with each wave function, the corresponding dipole moment was calculated. This was done both rigorously, evaluating the electronic moment as $\langle \Psi | z | \Psi \rangle$, and approximately, taking the dipole moment to be the product of the bond length and the atomic charge at which the particular wave function was balanced. Finally, the sum of the molecular orbital energies (excluding core electrons) is listed for each function.

In order to permit an assessment of these calculated results, Table 3 presents the experimentally-determined dipole moments of these molecules and the sums of orbital energies obtained from SCF molecular wave functions of near Hartree-Fock accuracy.

Discussion

It should be noted first of all that the situation encountered in the case of diborane [1] is found to occur once again: First, for any given molecular wave function, the charges calculated by the three different definitions are quite far apart, and second, a comparison of the three wave functions obtained in any particular case by using successively each of the definitions of charge shows that these functions differ quite considerably, in terms of such properties as dipole moments and orbital energies. It is certainly necessary, therefore, to arrive at some decision as to which charge definition is to be preferred.

In regard to these variations among the charges, there is one general pattern which may be noted: For any given single wave function, the Löwdin charge is always the lowest (or the most negative) and the modified Mulliken is the highest (or the most positive); likewise, considering the three different functions corresponding to each particular molecule and basis set, the charge at which balance is

Table 1. Results of wave function computations – not including Madelung correction

Molecule	Basis set	Charge definition used to balance	Charges at which balanced[a]	Dipole moment accurate calc.[b]	Dipole moment approx. calc.	Sum of orbital energies (eV)
CO	single-zeta	Löwdin	0.08 (M: 0.30 M–M: 0.65	0.145 (C⁻O⁻)	0.178 (C⁺O⁻)	−94.57
		Mulliken	0.11 (L: −0.09 M–M: 0.43	0.502 (C⁻O⁺)	0.226 (C⁺O⁻)	−94.10
		Modified-Mulliken	0.12 (L: −0.34 M: −0.16	1.01 (C⁻O⁺)	0.258 (C⁺O⁻)	−93.60
CO	double-zeta	Löwdin	0.07 (M: 0.29 M–M: 0.69	0.304 (C⁻O⁺)	0.146 (C⁺O⁻)	−94.50
		Mulliken	0.09 (L: −0.11 M–M: 0.45	0.671 (C⁻O⁺)	0.202 (C⁺O⁻)	−93.97
		Modified-Mulliken	0.11 (L: −0.35 M: −0.18	1.19 (C⁻O⁺)	0.232 (C⁺O⁻)	−93.41
CO	extended-zeta	Löwdin	0.06 (M: 0.29 M–M: 0.68	0.306 (C⁻O⁺)	0.138 (C⁺O⁻)	−94.45
		Mulliken	0.10 (L: −0.10 M–M: 0.46	0.656 (C⁻O⁺)	0.212 (C⁺O⁻)	−93.95
		Modified-Mulliken	0.11 (L: −0.35 M: −0.18	1.19 (C⁻O⁺)	0.235 (C⁺O⁻)	−93.37
BF	single-zeta	Löwdin	0.15 (M: 0.38 M–M: 0.64	0.704 (B⁻F⁺)	0.346 (B⁺F⁻)	−98.60
		Mulliken	0.20 (L: −0.03 M–M: 0.45	1.05 (B⁻F⁺)	0.470 (B⁺F⁻)	−96.83
		Modified-Mulliken	0.23 (L: −0.24 M: −0.03	1.49 (B⁻F⁺)	0.518 (B⁺F⁻)	−95.39
BF	double-zeta	Löwdin	0.13 (M: 0.40 M–M: 0.74	0.894 (B⁻F⁺)	0.308 (B⁺F⁻)	−100.4
		Mulliken	0.17 (L: −0.08 M–M: 0.52	1.32 (B⁻F⁺)	0.401 (B⁺F⁻)	−97.90
		Modified-Mulliken	0.21 (L: −0.35 M: −0.12	1.89 (B⁻F⁺)	0.489 (B⁺F⁻)	−95.92
BF	extended-zeta	Löwdin	0.12 (M: 0.39 M–M: 0.75	0.438 (B⁻F⁺)	0.291 (B⁺F⁻)	−100.5
		Mulliken	0.16 (L: −0.09 M–M: 0.53	0.778 (B⁻F⁺)	0.391 (B⁺F⁻)	−97.97
		Modified-Mulliken	0.21 (L: −0.36 M: −0.13	1.27 (B⁻F⁺)	0.489 (B⁺F⁻)	−95.94
LiF	single-zeta	Löwdin	0.43 (M: 0.56 M–M: 0.70	1.84 (Li⁺F⁻)	1.22 (Li⁺F⁻)	−61.94
		Mulliken	0.44 (L: 0.31 M–M: 0.59	1.47 (Li⁺F⁻)	1.25 (Li⁺F⁻)	−61.12
		Modified-Mulliken	0.46 (L: 0.17 M: 0.30	0.984 (Li⁺F⁻)	1.30 (Li⁺F⁻)	−60.52

[a] Definition of symbols: L = Löwdin, M = Mulliken, $M – M$ = Modified-Mulliken. – [b] Values are in atomic units.

Table 2. Results of wave function computations – Madelung correction included

Molecule	Basis set	Charge definition used to balance	Charges at which balanced			Dipole moment accurate calc.	Dipole moment approx. calc.	Sum of orbital energies (eV)
CO	single-zeta	Löwdin	0.26 (M:	0.49 M – M:	0.86)	0.252 (C⁺O⁻)	0.563 (C⁺O⁻)	−93.93
		Mulliken	0.33 (L:	0.12 M – M:	0.69)	0.023 (C⁻O⁻)	0.701 (C⁺O⁻)	−93.54
		Modified-Mulliken	0.41 (L:	−0.09 M:	0.08)	0.462 (C⁻O⁺)	0.883 (C⁺O⁻)	−93.30
CO	double-zeta	Löwdin	0.24 (M:	0.47 M – M:	0.90)	0.071 (C⁺O⁻)	0.507 (C⁺O⁻)	−93.89
		Mulliken	0.31 (L:	0.09 M – M:	0.71)	0.224 (C⁻O⁺)	0.650 (C⁺O⁻)	−93.36
		Modified-Mulliken	0.40 (L:	−0.14 M:	0.04)	0.696 (C⁻O⁺)	0.844 (C⁺O⁻)	−93.01
CO	extended-zeta	Löwdin	0.23 (M:	0.47 M – M:	0.90)	0.072 (C⁺O⁻)	0.499 (C⁺O⁻)	−93.84
		Mulliken	0.31 (L:	0.09 M – M:	0.71)	0.213 (C⁻O⁺)	0.650 (C⁺O⁻)	−93.32
		Modified-Mulliken	0.40 (L:	−0.14 M:	0.04)	0.682 (C⁻O⁺)	0.851 (C⁺O⁻)	−92.96
BF	single-zeta	Löwdin	0.34 (M:	0.60 M – M:	0.83)	0.296 (B⁻F⁺)	0.818 (B⁺F⁻)	−97.98
		Mulliken	0.46 (L:	0.22 M – M:	0.70)	0.515 (B⁻F⁺)	1.09 (B⁺F⁻)	−95.34
		Modified-Mulliken	0.56 (L:	0.08 M:	0.31)	0.774 (B⁻F⁺)	1.33 (B⁺F⁻)	−93.70
BF	double-zeta	Löwdin	0.28 (M:	0.56 M – M:	0.87)	0.582 (B⁻F⁺)	0.661 (B⁺F⁻)	−99.48
		Mulliken	0.40 (L:	0.14 M – M:	0.74)	0.835 (B⁻F⁺)	0.964 (B⁺F⁻)	−96.29
		Modified-Mulliken	0.52 (L:	−0.06 M:	0.19)	1.22 (B⁻F⁺)	1.25 (B⁺F⁻)	−93.90
BF	extended-zeta	Löwdin	0.26 (M:	0.54 M – M:	0.88)	0.223 (B⁻F⁺)	0.627 (B⁺F⁻)	−99.42
		Mulliken	0.39 (L:	0.13 M – M:	0.74)	0.402 (B⁺F⁻)	0.936 (B⁺F⁻)	−96.31
		Modified-Mulliken	0.52 (L:	−0.07 M:	0.17)	0.705 (B⁻F⁺)	1.24 (B⁺F⁻)	−93.89
LiF	single-zeta	Löwdin	0.82 (M:	0.96 M – M:	0.98)	2.74 (Li⁺F⁻)	2.34 (Li⁺F⁻)	−65.39
		Mulliken	0.93 (L:	0.79 M – M:	0.96)	2.69 (Li⁺F⁻)	2.64 (Li⁺F⁻)	−62.71
		Modified-Mulliken	0.96 (L:	0.78 M:	0.91)	2.67 (Li⁺F⁻)	2.73 (Li⁺F⁻)	−62.05

E. W. Stout, Jr., and P. Politzer:

achieved in terms of the Löwdin definition is again invariably the lowest, while the modified Mulliken once more gives the highest[1].

The effect of using the Madelung potential is basically the same for all three molecules. It increases considerably the charges at which balance was attained; in each case, the positively-charged atom (carbon, boron, or lithium) becomes more positive, the negatively-charged atom more negative. The magnitudes of these changes are 0.2 to 0.3 electronic units for CO and BF, and 0.4 to 0.5 electronic units for LiF.

The accurately-calculated dipole moments are almost invariably greatly improved by inclusion of the Madelung potential. The polarities (C^-O^+ [12], B^-F^+, and Li^+F^-) were correct even before, but the dipoles were too positive in the direction of the electronegative elements (oxygen and fluorine), and too negative in the direction of the less electronegative elements (carbon, boron,

Table 3

Molecule	Dipole moment	Sum of SCF orbital energies[a]
CO	0.0441 au (C^-O^+)[b]	− 113.1 eV
BF	0.380 au (B^-F^+)[c]	− 120.9 eV
LiF	2.49 au (Li^+F^-)[b]	− 77.37 eV

[a] Ref. [14]. − [b] Experimental values; Ref. [15]. − [c] Theoretical value; Ref. [16].

and lithium). The effect of the Madelung potential, in general, was to greatly improve this situation, and bring the magnitudes of the dipole moments much closer to the correct values.

One of the most striking features of the data presented in Tables 1 and 2 is the relationship between the computed charges and the accurately-calculated dipole moments for CO and BF. For every CO wave function, balance was attained with the carbon atom being positively-charged, and the oxygen being negative. Yet the accurately-calculated dipole moments corresponding to these wave functions have, in all cases but three, polarities of C^-O^+. This same lack of consistency between the polarities of the dipole moments and the calculated charges is encountered with BF, but now it is even more pronounced. For every single BF wave function, the charges at which it was balanced indicate a polarity of B^+F^-, while the dipole moment corresponding to that wave function is B^-F^+. This is clearly an unfortunate situation; its implications shall be further discussed later in this paper.

A second factor whose importance this study is examining is the size of the basis set. In general, for any given molecule and charge definition, there is seen to be a decrease in the charge at which balance occurs in going from the single-zeta to the double-zeta basis set. However there is little further change in the charge in going on to the extended-zeta basis. As far as the accurately-calculated dipole moment and the orbital energies are concerned, increasing the basis set, whether from single- to double-zeta or from double- to extended-zeta, does not

[1] In comparing and discussing the various "charges", the convention is used of speaking always of the charge on the atom which comes first in the formula of the molecule, for example C in CO.

seem to be of any clearcut benefit; it improves the results in some cases, worsens them in others. This observation may not be valid, of course, under conditions different from those which were in effect in this work, as, for instance, if the basis set included d orbitals.

It is not really surprising that increasing the basis is not universally advantageous. The nature of the basis set enters into the computation of the wave function only through the magnitudes of the overlap integrals; in calculations of such a high degree of approximation, these must be viewed, at least to some extent, as semi-empirical parameters. It does not follow, therefore, that numbers which most accurately reflect the actual degree of overlap (being based on the most refined atomic orbitals), will best fulfill the various functions which may be required of these parameters.

Finally, the third factor which is being investigated, and the one which is of greatest interest in this study, is the means used to define the charge on an atom in a molecule. The original purpose of this work was to compare the wave functions resulting from iteration over charges defined by one or another of these methods and to try to decide which would be the most physically meaningful. Such a comparison can be made, on the basis of the results presented in Tables 1 and 2. In general, the functions computed in terms of Löwdin charges seem to be the most satisfactory, in both orbital energies and dipole moments; this is particularly true when the Madelung potential has not been included. Also, since these functions are balanced at lower charges than is the case when one of the other definitions is used, they present the smallest discrepancies between the polarities of the charges and those of the dipole moments[2].

But for most of the carbon monoxide functions and for all of the boron monofluoride functions, the charges at which balance was attained — whether these be Löwdin, Mulliken, or modified-Mulliken — predict a polarity opposite to the accurately-calculated dipole. This is a very important point. For any given wave function, if the computed charges on the atoms have a polarity opposite to the accurately-calculated dipole moment corresponding to that same wave function, then the charge definition must be considered to be faulty. It may be very useful in many other situations, and it may also conceivably have some other significance, but it is not completely satisfactory — it does not satisfy, in at least two cases, the simple intuitive requirement that the computed "charges" on the atoms indicate the polarity of the molecule. In this respect, then, all three definitions fall short.

It may be, however, that no definition of charge will be without some weakness of this sort. The charge on an atom in a molecule is, after all, a *defined* quantity rather than an actual physical property. It represents an attempt to assign a property to an entity (an atom) which has to some extent lost its identity, which means that there is bound to be present an element of artificiality. It may be unrealistic, therefore, to demand that this defined quantity correlate consistently with some true physical property, such as the dipole moment. An $s - p$ hybrid orbital, for instance, can have a high degree of polarity — yet by any one of the

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[2] Further favoring the Löwdin definition is the fact that in computing XeF_2, XeF_4 and XeF_6 wave functions, Harris [13] found that the Löwdin charges came very close to matching those estimated from NMR data, while the other definitions gave results which differed significantly.

definitions discussed in this paper its charge would be assigned entirely to its parent nucleus, just as if the orbital were perfectly symmetrical about that nucleus.

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