Properties of Atoms in Molecules. I. A Proposed Definition of the Charge on an Atom in a Molecule

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Abstract: It is suggested that the charges associated with the atoms in a molecule be evaluated by integrating the molecular electronic density over regions "belonging" to the individual atoms. Atomic charges calculated by this method for several molecules are compared to charges obtained by the "population analysis" procedure, and it is shown that in the case where the two results differ most significantly, the new value appears to be more consistent with the chemical evidence.

From a theoretical standpoint, it is somewhat ambiguous to speak of an atom in a molecule. A molecule is a new entity, different from the atoms from which it was formed; these atoms have, to a greater or lesser degree, lost their identities in the process of forming the molecule. It may be argued, therefore, that it is no longer meaningful to speak of these atoms or of their "properties."

However, it has proven to be very useful, in practice, to interpret and predict the behavior of molecules in terms of properties associated with the individual atoms. One example of this is the concept of electronegativity, a measure of the tendency of an atom *in a molecule* to attract electrons toward itself. Another example is the assigning of charges to the various atoms and using these to predict, for instance, the reactive sites in the molecule. Thus, whatever may be its theoretical basis, the concept of atoms in molecules has considerable chemical support.

In this paper will be considered the problem of obtaining, by calculation, realistic quantitative estimates of atomic charges. Subsequent papers will deal with other properties of atoms in molecules.

Some Current Definitions of Atomic Charge

Probably the most widely used method for calculating the charges associated with atoms in molecules is the "population analysis" procedure proposed by Mulliken.[1] It may be illustrated by a very simple example, in terms of a molecular orbital which is written as a linear combination of atomic orbitals on two atoms, A and B

$$\Psi = C_A\psi_A + C_B\psi_B$$

If the function Ψ is normalized, then the number of electrons, N, which occupy the molecular orbital can be written as

$$N = N(C_A{}^2 + 2C_AC_BS_{AB} + C_B{}^2)$$

where S_{AB} is the overlap integral between ψ_A and ψ_B. Mulliken suggested that the electronic charge (or "population") associated with atom A be defined as

$$Q_A = N(C_A{}^2 + C_AC_BS_{AB})$$

This definition may be generalized to

$$Q_r = \sum_i N_i[\sum_m(C_{im}{}^2 + \sum_{s,n} C_{im}C_{in}S_{mn})] \qquad (1)$$

where N_i is the number of electrons in molecular orbital Ψ_i

$$\Psi_i = \sum_{r,m} C_{im}\psi_m$$

and the subscripts m and n refer to atomic orbitals on atoms r and s, respectively.

This definition of atomic charge has been applied extensively, and has provided much useful information. It has certain weaknesses, however. First, the overlap charge, $2NC_AC_BS_{AB}$, is being divided equally between the two atoms. This is unrealistic, in general, since the overlap charge is not symmetrically distributed, except in the special case of ψ_A and ψ_B being identical. Furthermore, it can happen, depending upon the signs and magnitudes of the cross-terms, that the contribution of a given molecular orbital to the electronic population of an atom is found to be negative—or greater than two![2] Another serious weakness is that the charge $NC_A{}^2$ is assigned entirely to atom A, even though the function ψ_A may have its maximum at a significant distance from nucleus A, perhaps even in the vicinity of a neighboring nucleus.[3] For example, the charge in the hybrid orbital

$$\psi_{2s,A} + \psi_{2p,A}$$

is highly polarized, and is concentrated at some distance from nucleus A. Yet this charge is assigned solely to atom A.[4] Finally, the results obtained from a population analysis are not invariant to a transformation of the atomic orbital basis set of the molecular wave function.[5]

Several modifications of the Mulliken scheme have been proposed; many of these were attempts to find a more realistic basis for partitioning the overlap charge.[2-9] One idea, introduced by Löwdin, is to divide this in such a manner as to preserve unchanged

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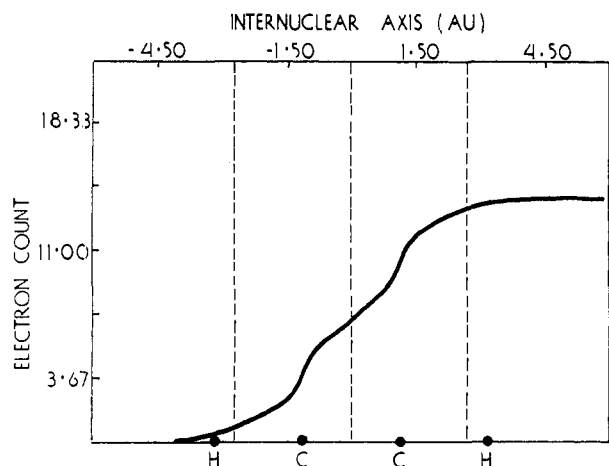
Figure 1. Electron-count function for acetylene.

the calculated electronic moment of the molecular orbital.[5,6,8,9] Another line of approach is to integrate the overlap charge up to a plane through the midpoint of the internuclear axis.[8] One can also simply eliminate the problem of partitioning the overlap charge, by orthogonalizing the atomic orbitals of the basis set;[10] all overlap terms are then equal to zero. There have been several critical discussions and comparative studies of various methods of calculating atomic charge, and it appears that at least some of them do give more satisfactory results than the population analysis approach.[2,4,5,8,11—13] All of the methods mentioned, however, retain at least some of the weaknesses of the latter.[4,5,14]

Proposed Definition of Atomic Charge

A very direct and fundamental approach to the problem of atomic charge would be in terms of the electronic density distribution

$$\rho(\mathbf{r}) = N \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \times$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) d\mathbf{r}_2 \ldots d\mathbf{r}_N \quad (2)$$

where Ψ ($\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$) is the electronic wave function for an N-electron molecule. The electronic density distribution is a physically meaningful quantity, and it has the advantage of being invariant under unitary transformations of the wave function. If the total space of the molecule could be partitioned into regions "belonging" to the individual atoms, then the electronic charge associated with a given atom could be determined by integrating the electronic density over the region of space belonging to that atom

$$Q_r = \int_r \rho(\mathbf{r}) d\mathbf{r} \quad (3)$$

(The integration in eq 3 is to be performed over the region of space belonging to atom r.)

It is necessary then to decide upon a reasonable and well-defined criterion in terms of which to partition the space of the molecule. The criterion which is being

proposed is as follows. The atomic regions will be defined such that in the limiting case of no interactions between the atoms, the electronic charge associated with each one would be the same as for the free atom. This limiting case can be represented by superposing free atom electronic densities, the atoms being placed at the same relative positions as in the molecule.

This definition of Q_r is a very direct one, since it is based upon an actual summing-up of the electronic charge associated with an atom. The problem of how to divide an overlap charge no longer arises. Furthermore, since Q_r is obtained by integrating over all variables, the analytical form of the molecular wave function is no longer important; it need not be written as a combination of atomic functions, as it must if the Mulliken definition is to be used. If one wishes to work in terms of the molecular orbital approximation, however, and to find $Q_{r,i}$ (the portion of Q_r which comes from molecular orbital Ψ_i), it is necessary only to replace Ψ and N by Ψ_i and N_i in eq 2 and 3. The region of space which belongs to atom r is unchanged. There is no possibility now of $Q_{r,i}$ being less than zero or greater than N_i.

Results

The new definition has been used to calculate the atomic charges in the acetylene molecule and in two of its derivatives, lithium acetylene and fluoroacetylene. This permits a comparison of the effects of two very different substituents upon the distribution of atomic charges. The extended-basis-set self-consistent-field molecular wave functions of McLean and Yoshimine and Veillard were used for these calculations.[15]

The basic procedure was to compute the "electron-count" functions for these molecules; the electron count is defined as[16]

$$G(z) = \int_{-\infty}^{z} dz \int_0^\infty R dR \int_0^{2\pi} \rho(R,z,\phi) d\phi \quad (4)$$

$\rho(R,z,\phi)$ is the electronic density distribution, written in cylindrical coordinates. The z axis is identical with the molecular axis, and z was taken to be increasing from left to right when the molecules are written HCCH, HCCLi, and HCCF. $z = 0$ corresponds in each case to the midpoint of the C–C axis. Thus the electron count, $G(z)$, is the number of electrons to the left of a plane passing through the molecular axis at the point z. Plots of $G(z)$ vs. z are shown for each of the three molecules in Figures 1–3.

Corresponding to each molecule, an electron-count function was also computed for the superposed free atoms. The double-ζ self-consistent-field atomic wave functions of Clementi were used,[17] in order to ensure consistency with the basis sets for the molecular wave functions.[15] The p orbitals were averaged over all spatial directions.

The regions belonging to the individual atoms were determined separately for each molecule, in terms of the electron-count function for the superposed atoms.

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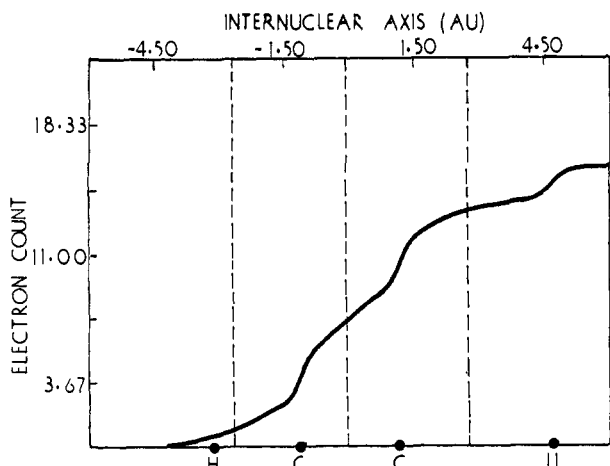
Figure 2. Electron-count function for lithium acetylene.

Figure 3. Electron-count function for fluoroacetylene.

The boundaries of the regions were established by means of hypothetical planes which perpendicularly intersect the z axis at those points for which $G(z)_{\text{atoms}} = 1, 7$, and 13. These points on the z axis then define the regions belonging to the atoms in the molecule. The number of electrons associated with each atom could subsequently be obtained from the molecular electron-count function; since the number of protons is known for each atom, the net atomic charge follows immediately. The results are presented in Table I. For the

Table I. Calculated Atomic Charges

Molecule	Atom[a]	Calculated charges This work	Population analysis[b]
HCCH	H	+0.14	+0.22
	C	−0.14	−0.22
HCCLi	H	+0.10	+0.17
	C	−0.23	−0.41
	C	−0.36	−0.47
	Li	+0.49	+0.71
HCCF	H	+0.15	+0.25
	C	−0.19	−0.17
	C	+0.09	+0.22
	F	−0.05	−0.31

[a] The atoms are listed in the same order as they appear in the molecular formula in column 1. [b] Reference 18.

purpose of comparison, charges obtained using the Mulliken definition are also listed.[18]

Discussion

It is seen from Table I that the atomic charges predicted for acetylene by the two definitions are quite similar, and are, moreover, quite reasonable from a chemical standpoint. The small positive charges on the hydrogens are consistent with the slightly acidic nature of acetylene.

In the case of lithium acetylene, the divergence between the two sets of results is somewhat greater, al-

though qualitatively they are again similar. Both indicate considerable ionic character, the negative charge being distributed to the two carbon atoms; the new definition, however, assigns a greater portion of this negative charge to the carbon next to the lithium atom. A general pattern which is emerging from the results presented in Table I is that the atomic charges obtained by the new definition, whether positive or negative, are smaller in magnitude than the corresponding Mulliken charges.

The most interesting results are those for fluoroacetylene, since here the two procedures yield significantly different atomic charges. According to the population analysis, the fluorine is distinctly negative, with a charge of −0.31 electron unit. With the new definition, however, it is found to be only very slightly negative, the calculated charge being −0.05. In view of the high electronegativity of fluorine, the idea that it has almost no charge in fluoroacetylene may appear to be questionable, and it may seem initially that the result of the population analysis is more realistic in this case. There is a considerable amount of chemical and physical evidence, however, which indicates that the −0.05 value may well be the more realistic one. It has been pointed out on a number of occasions, by various workers, that the chemical behavior of the haloacetylenes suggests that the halogen atoms in these molecules are positively charged.[19-24] Numerous examples of the chemical reactions of the molecules were cited in support of this assertion. Most of this evidence refers to the chloro, bromo, and iodo derivatives of acetylene; fluoroacetylene has been known for only a few years.[25] But if the other halogen atoms are indeed positively charged in the haloacetylenes, then it would be quite consistent and reasonable that fluorine—the most electronegative of them—would have approximately zero charge in fluoroacetylene; it would be less likely,

(18) A. Veillard, *J. Chem. Phys.*, **48**, 2012 (1968). The wave functions used to compute the Mulliken charges were also taken from ref 15, but unfortunately are not the same ones as were used in the present work; they have somewhat different basis sets. Since both groups of wave functions are close to the Hartree–Fock limit, however,[15] the charges calculated with eq 3, which involves integrating the electronic density, should be essentially the same for both groups. Thus the comparison of the two types of charges presented in Table I should be meaningful.
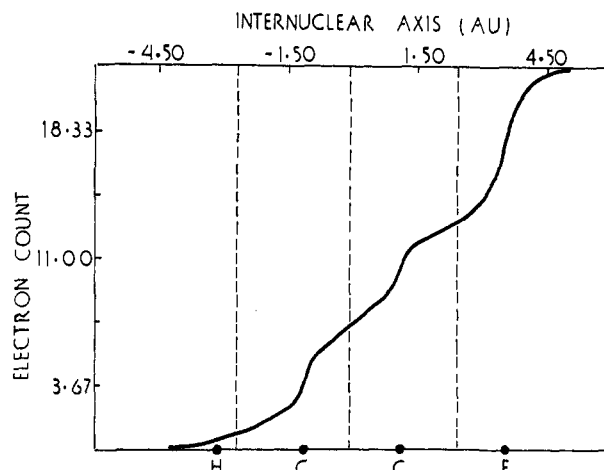
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(25) W. J. Middleton and W. H. Sharkey, *J. Amer. Chem. Soc.*, **81**, 803 (1959).

however, that the fluorine would have a negative charge as high as −0.31. Thus the charge calculated by the new definition appears to be the more realistic one.

Further evidence supporting this conclusion is found by comparing the orbital energies of the fluorine inner-shell electrons in fluoroacetylene with the corresponding values for the free fluorine atom, the F+ and F− ions, and some alkali fluoride molecules (Table II).

Table II. Orbital Energies of Fluorine Inner-Shell Electrons

Atom, ion, or molecule	Orbital	Orbital energy,[a] au
F−	1s	−25.829
NaF	2σ	−26.056
LiF	1σ	−26.096
HCCF	1σ	−26.380
F	1s	−26.383
F+	1s	−27.141

[a] These values are taken from ref 15 and 17.

If the innermost shell of an atom in a molecule is of essentially localized 1s character, then its orbital energy provides some indication of the charge associated with the atom in the molecule.[26-28] Table II shows the significant changes in the energy of the 1s orbital in going from the fluorine atom to its positive and negative ions. As anticipated, the innermost electrons are more tightly held as the atom is more positively charged. Lithium fluoride and sodium fluoride fit into this correlation very nicely, their calculated inner-shell energies being consistent with large negative charges on the fluorines. The calculated inner-shell energy for fluoroacetylene, on the other hand, is almost exactly the same as for the free *uncharged* atom.

Atomic charges obtained by the new procedure can be presented for one more molecule, lithium hydride. Using electron-count functions which have recently been computed for LiH and for the superposed lithium and hydrogen atoms, in terms of very good molecular and atomic wave functions,[16] the atomic charges in LiH are estimated to be +0.37 (Li) and −0.37 (H). Unfortunately, no comparison can be made with Mulliken charges calculated from the same molecular wave function, since it is not written in terms of atomic functions and therefore cannot be

subjected to a population analysis. This illustrates one of the drawbacks of the population analysis procedure. Mulliken charges have been computed, however, for a minimum-basis-set self-consistent-field LiH wave function, and the values which were obtained, +0.35 and −0.35, are very similar to those given above.[29] These results may appear to be surprising, in view of the large degree of ionic character which is often attributed to lithium hydride, but they are consistent with the recent conclusion that "no simple ionic or atomic model of this molecule can be acceptable."[30]

The definition of atomic charge which has been proposed admittedly contains an element of arbitrariness in that the atomic regions could be defined in terms of other criteria than the requirement that the atoms have zero charges in the limit of no interaction. For example, the boundary planes could be placed at the midpoints of the internuclear axes. This would be rather unrealistic, however, since dividing the internuclear space equally between the atoms should not, in general, be valid; it would mean, for instance, that the hydrogen atoms in acetylene would have charges of −0.44—which would be contrary to the known slightly acidic nature of acetylene.[31] Or, retaining the present criterion, it might be argued that valence-state charge distributions should be used for the atoms rather than spherically symmetrical free atom charge densities. This would mean, however, that a degree of interaction between the atoms was being included;[32] it would also introduce a certain amount of ambiguity, since it would not be clear, in many instances, which valence-state configuration should be used.

Ultimately, the validity and usefulness of any definition of atomic charge must depend upon how consistent the calculated charges are with chemical realities. On this basis, the definition which has been proposed in this paper appears to be very promising.

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(29) S. Fraga and B. J. Ransil, *J. Chem. Phys.,* 34, 727 (1961).

(30) P. Politzer and R. E. Brown, *ibid.,* 45, 451 (1966); see also ref 16.

(31) In the other molecules, the atomic charges corresponding to the boundary planes being placed at the midpoints of the internuclear axes would be: HCCLi, −0.49, + 0.33, −0.47, +0.63; HCCF, −0.42, +0.39, +0.11, −0.08.

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