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On the Definition of the Atomic Charge in a Molecule

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Atomic charges calculated by various methods for model two-center molecules have been compared with corresponding electron-count functions. Varying the overlap and polarity conditions in the model system, it could be found out under what conditions the individual definitions fail to predict physically reasonable values of atomic charges.

Key words: Charge of the atom in a molecule – Electron-count function

1. Introduction

The theoretical electron density distribution derived from molecular wave functions is an important means for studying various facets of the character of the chemical bond. Besides density contour maps it has proven to be very useful to represent the density distributions in a condensed form as certain numerical quantities, called atomic charges in a molecule. In this way it was possible to assign quantitative meaning to such concepts as reactive sites and charge redistribution within a species composed of electrons and atomic nuclei. Because of the somewhat obscure meaning of the charge assigned to an atom in a molecule, sundry definitions of this quantity have emerged, differing in their quantitative and even qualitative reliability.

This contribution examines some of the aspects of defining the charge on an atom in a molecule. Since general aspects are most transparent in simple cases, we investigate a single-electron two-center model system which allows to compare the calculated atomic charges with electron-count functions. In this way we are able to accomplish a quantitatively meaningful analysis of different approaches to the given problem. Such an analysis seems to be more appropriate than to investigate complex molecules, since in the latter case the interpretation of numerical results

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is less lucid. Namely, in applications to molecules a breakdown of the given approach rather than the order of appropriateness of all possible approaches can be observed because of lack of proper comparison with the true solution.

2. Model

We consider a system consisting of two nuclei a and b located on the z-axis, and one electron. The nuclear charge Z_b on nucleus b be equal to the proton charge and the nuclear charge Z_a on center a and the internuclear distance R be variable quantities. To this end, we shall analyze the wave functions that are variationally calculated for this system with the usual one-electron Hamiltonian and functions of the LCAO form

$$\phi = c_a A + c_b B = \sqrt{q}\,[A + pB] \tag{1}$$

where A and B are Slater-type atomic orbitals associated with centers a and b, respectively, i.e.,

$$I = \sqrt{\frac{Z_I^3}{\pi}} \exp(-Z_I r_I), \quad \text{for } I = A, B \tag{2}$$

S is the corresponding overlap integral and $q = 1/(1 + p^2 + 2pS)$. Thus, we have a sufficiently flexible model allowing to treat the influence of bond polarity and overlap effects upon the atomic charge values.

3. Atomic Charge Definitions Explored

All definitions will be given with reference to wave function (1). Because the measures of electronic charge corresponding to both centers complement each other to give a charge of one electron (with one exception, as will be seen), only the expression Q_a for electronic charge associated with center a will be given. The electronic charge will be given in multiples of e throughout the paper (e denoting the elementary charge of the electron). Accordingly, the charge of the atom in a molecule (in atomic units) is then given as $q_a = Z_a - Q_a$.

3.1. The Mulliken and Mulliken-Type Approaches

Mulliken [1] proposed that Q_a be defined as (definition M)

$$Q_a = c_a^2 + c_a c_b S = q(1 + pS) \equiv Q_a^M \tag{3}$$

Several modifications of the Mulliken scheme exist; they are attempts to improve the charge definition by a different partitioning of the overlap charge between both centers.

One idea, originally suggested by Löwdin [2] for approximate evaluation of many-center integrals, is to partition the overlap charge in such a way as to preserve the dipole moment of the orbital [3, 4]. This condition yields (definition L)

$$Q_a = q\left[1 + pS\left(1 - \frac{2\bar{z}}{RS}\right)\right], \tag{4}$$

where $\bar{z} = \int zAB\,d\tau$ and the coordinate z is measured from the midpoint between both centers.

Another possibility is to divide the overlap charge according to the ratio of the pertinent atomic orbital coefficients in each molecular orbital [5–7]. The scheme proposed by Christoffersen and Baker [7] leads to the expression (definition C)

$$Q_a = c_a^2 + \frac{c_a^2}{c_a^2 + c_b^2}(2c_a c_b S) = \frac{1}{1+p^2} \tag{5}$$

3.2. *Orthogonalization Approach*

The simplest way to circumvent the problem of partitioning the overlap charge is to work with a basis of orthogonalized atomic orbitals. Among all possibilities, the Löwdin symmetrical orthogonalization [8] is the most suitable, because it preserves the maximum similarity to the original basis set. This procedure furnishes (definition OB)

$$Q_a = Q_a^M + \frac{q(1-p^2)}{2}\left[(1+S)^{1/2}(1-S)^{1/2} - 1\right] \tag{6}$$

3.3. *Projection-Density Approach*

Roby's formulation [9] relies on Gleason's theorem [10] according to which the probability of occupancy of the molecular subspace $\mathcal{O}$ represented by the projector $\boldsymbol{P}_{\mathcal{O}}$ is $\mathrm{Tr}\,\rho\boldsymbol{P}_{\mathcal{O}}$, where ρ is the appropriate first-order density operator. We thence obtain for the subspace defined by orbital A (definition P)

$$Q_a = Q_a^M + qpS(pS+1), \tag{7a}$$

$$Q_b = (1 - Q_a^M) + qS(S+p), \tag{7b}$$

where even the expression for center b is given, because the sum of both electron populations does not equal 1 (i.e. the total electronic charge in the molecule). It is possible to arrive at the expressions (7a) and (7b) on grounds of different argumentations [11, 12].

As extensively discussed in former papers [9, 13], the values obtained by the projection-density approach have not that simple interpretation as those obtained by other methods, because the "shared" electron density is – instead of being partitioned – equally assigned to all atoms which participate in the sharing. However, in our simple two-center system we can assume that the "shared" density contributes to both centers in an equal way, so that we obtain for the "corrected" atomic charge density (definition *PC*)

$$Q'_a = \tfrac{1}{2}(Q_a - Q_b + 1) \tag{8}$$

where Q_a and Q_b are given by Eqs. (7a) and (7b), respectively.

3.4. Geometric Space Partitioning Approach

Dividing the three-dimensional space of the molecule into regions associated with the individual atoms and integrating the pertinent electron density function over each region, we obtain the physically most meaningful measure of electronic charge on atoms in a molecule [14–18]. However, the problem arises as to how to determine the borderline between the regions which can hardly be done without a portion of arbitrariness.

For our system we can express the electron density distribution function ρ as depending on one variable z; this function $\rho(z)$ we call "electron count" [14]. Thus, the task of determining the regions belonging to subsystems a and b reduces to finding a plane $z = z_0$ separating them. For calculating z_0 we used the modified criterion of Politzer and Harris [14], according to which the "electron-count" function $\rho_0(z)$ for the system consisting of hypothetically non-interacting subsystems satisfies the condition $\rho_0(z_0) = \frac{1}{2}$. We speak here about a modified criterion, because we had to attribute charges to non-interacting subsystems in a system which carries a charge. Of course, our somewhat formalistic definition of the value of $\rho_0(z_0)$ is arbitrary, nevertheless ex post justified by the form of the electron-count functions, as will be seen later.

4. Results and Discussion

All definitions of atomic charges depend on some model assumptions or preconceptions. If we want to compare the merits of one definition with those of another, we must try to extract in some way information about the degree of adequacy of the charge definition with respect to the electron density function which represents the physical quantity of closest relevance to the problem. An examination of the electron-count functions for the model corresponding to various values of Z_a and R, and the confrontation of the functions with the effective atomic charges calculated according to the main definitions given above provide a way to visualize the degree of physical reliability of the individual definitions. The graphical representation of various atomic charge definitions in terms of the electron-count function is to be understood in such a way that the amount of electronic charge to the left of the plane perpendicular to the bond axis and passing through the pertinent point is interpreted as the charge assigned to center a. Figs. 1 and 2 represent a selection of these results for two values of Z_a (1.2, 3.0) and R (1.0, 2.5).

Because of the limited quantitative meaning of the atomic charge in a molecule, there seem to be reasonable only approaches working in a proper comparative

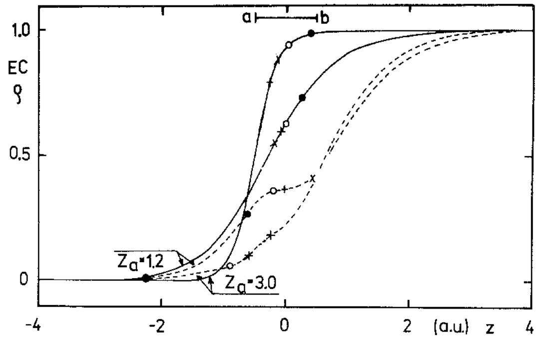

Fig. 1. Electron-count functions for ground (full curves) and virtual states (dashed curves) corresponding to $R=1$ a.u. Electronic charge values depicted on the curves are calculated according to definitions: *M* ●, *OB* ○, *PC* × and the approach *D* +

manner. From the point of view of chemical bonding the most interesting electron-transfer phenomenon occurs in the course of forming a molecule from atoms which genuinely justifies the free atom concept in this context. In regard to these arguments, one would expect the atomic charges to lie on the electron-count functions at the same value of z for both the ground and virtual states. However, it is seen from Figs. 1 and 2 that for some charge definitions the deviation from this property is considerable, the most pronounced one being for the Mulliken population analysis approach. Moreover, the position of the charge on the electron-count functions comes out in some cases far out of the line segments defined by the location of centers a and b.

It appears that among the definitions explored the geometric space partitioning approach leads to physically most meaningful values: first, this approach is directly related to the electron density function and does not depend on the special form of the wave function. Further, concerning its particular application, besides the correct relationship between the ground and virtual state charge values with respect to their position on the electron-count functions (this holds by definition), it is to be noted that the charges corresponding to virtual states are placed at the plausibly expected point, i.e. where $d\rho(z)/dz$ reaches minimum on the rising part of the curve. This means that we arrived at a model which satisfies automatically the borderline criterion suggested by Schuster *et al.* [18] in cases where the shape of the electron-count function allows the application of the criterion.

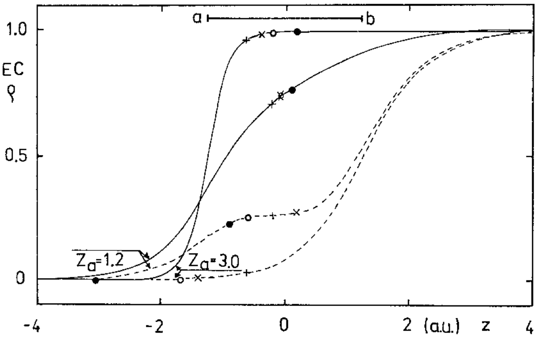

Fig. 2. Electron-count functions for ground and virtual states corresponding to $R=2.5$ a.u. All other symbols have the same meaning as in Fig. 1

These properties as well as the large amount of chemical and physical evidence which has been gathered in support of the validity of the approach [14, 19–21] make it reasonable to define the values obtained by means of space partitioning as a standard (Fig. 3) and express all other results relative to that, i.e. $\Delta Q_a = Q_a - Q_a^S$ (Figs. 4 and 5). The index S stands for "standard".

However, we neither claim superiority for this approach, nor attach any unique value to its results. We only believe in its soundest physical foundation. Therefore, the results are presented in such a way, that either absolute values of the corresponding quantities, or relative quantities of any kind of standard can be computed by elementary arithmetic. In addition it should be also mentioned that – in spite of all appealing features of the geometric space partitioning approach in application to linear molecules – it cannot be considered as a uniform and generally applicable procedure for calculating atomic charges. The reason lies in the difficulty of defining "atomic regions" within the molecule in such a way as to preserve normalization of the density in constructing the molecule from "atomic regions" [22].

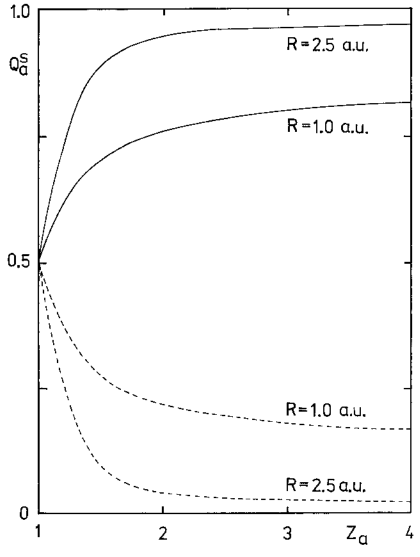

Fig. 3. Electronic charge on center a calculated according to approach D as a function of Z_a. Cases corresponding to ground and virtual states are distinguished by full and dashed curves

Figs. 4 and 5 seem to reflect a general pattern according to which the charge definitions based on the partitioning of the function space exaggerate the electronic charge redistribution due to interactions between atoms in a molecule. This finding is in accord with charge distribution calculations for a selection of linear molecules [14] and a study of charge transfer in molecular complexes [18]. The only exception of the above given conclusion represents the definition C applied to the virtual state within a certain interval of Z_a, and the definition PC at smaller polarity conditions.

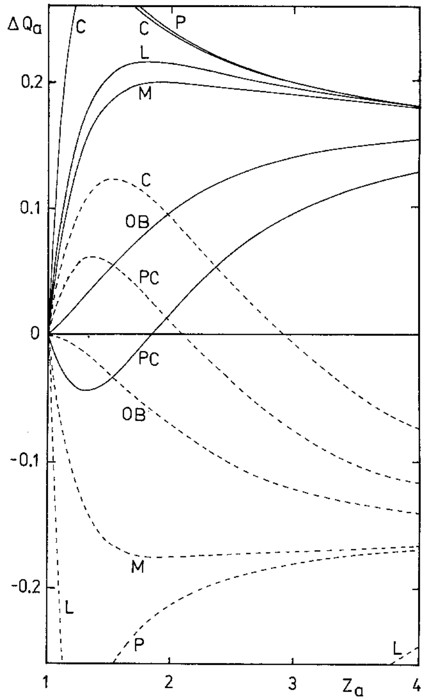

Fig. 4. Charge differences corresponding to various definitions relative to the value obtained through approach D as a function of Z_a. $R=1$ a.u. Cases corresponding to ground and virtual states are distinguished by full and dashed curves

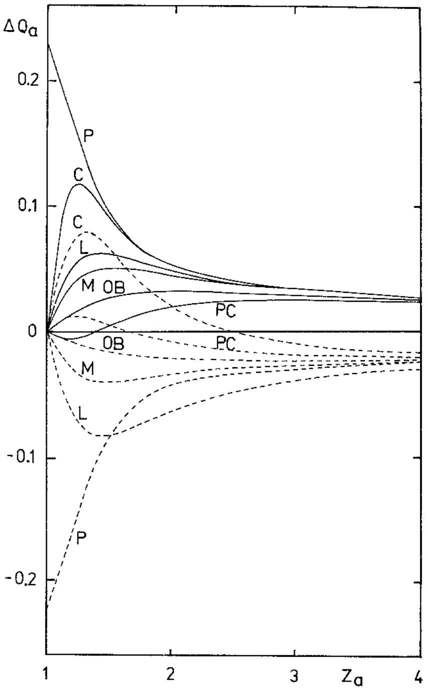

Fig. 5. Charge differences corresponding to various definitions relative to the value obtained through approach D as a function of Z_a. $R=2.5$ a.u. Cases corresponding to ground and virtual states are distinguished by full and dashed curves

It appears from Figs. 1, 2, 4 and 5 that the definition *PC* is, on the whole, the closest to the definition taken as standard. Unfortunately, the extension of this kind of approach to the case of a complex molecule is not straightforward, because the arbitrariness in dividing the "shared" electron density becomes even more distressful. Particularly it should be mentioned that the pairwise equipartitioning of "shared" electron densities, as tentatively suggested by Heinzmann and Ahlrichs [13], does not necessarily lead to restoring the "closure" relation concerning the sum of all electron populations. In regard to this difficulty it is advisable to keep this kind of wave function analysis in terms of well defined occupation numbers [9, 11–13, 23, 24] rather than to create concepts forced artificially into the problem. On grounds of our results one can tentatively conclude that the method yields reliable results concerning predictions of polarity conditions in molecules, if applied in a comparative manner.

The next "closest" results, as it is seen from Figs. 1, 2, 4 and 5, are those calculated using an orthogonalized basis set. It is gratifying that similar results concerning the favourable properties of charges calculated by means of orthogonalized AO's were found by other authors [25, 26]. However, the fact that the atomic basis functions become polycentric reduces the value of this approach. The Mulliken type approaches form the last category of results. Surprisingly enough we note in Figs. 4 and 5 that definitions *L* and *C* are inferior to the Mulliken definition with respect to the proximity to the standard. The exception already mentioned concerns the application of definition *C* to the virtual state wave function. In this case the corresponding plot follows the pattern of the curve related to the ground state. While the definition *L* seems to give for the ground state a better estimate of the charge than the definition *C*, the former fails completely if applied to the virtual state. Namely, when Z_a becomes greater than a critical value (about 1.22 and 1.60 a.u. for R equal to 1.0 and 2.5 a.u., respectively), the calculated charge on center a becomes negative (whereas the charge on center b exceeds the number of electrons considered). We see that dipole moment conservation in our case was followed by a disasterous consequence. These results justify us in claiming that, if preservation of multipole characteristics is required, only extension of the basis set for the wave function expansion can improve the charges calculated within a scheme of type *A* [27].

Finally, in Fig. 6 dependencies of the electronic charge on polarity (specifically on parameter p of Eq. (1)) and overlap conditions (for the values of S equal to 1.0, 0.7, 0.4 and 0.0) in the model system are visualized. Varying p in the interval $(-1, 1)$ and considering positive values of S, we cover all possible situations. With the Mulliken definition (Fig. 6a) we notice that the breakdown of the approach takes place in the interval of p $(-S, 0)$. Namely, Q_a becomes greater than 1 (and, consequently, Q_b negative). The effect of basis orthogonalization on the charge values is seen from Fig. 6b. Because there is no overlap dependency in the scheme corresponding to definition *C* (cf. Eq. (5)), the electronic charge is given in Fig. 6a (or Fig. 6b) by the curves pertinent to $S=0$. Fig. 6c shows the behavior of charges on both centers obtained by the projection-density approach. This figure presents in an illuminating way the fact that the "shared" electron density can assume

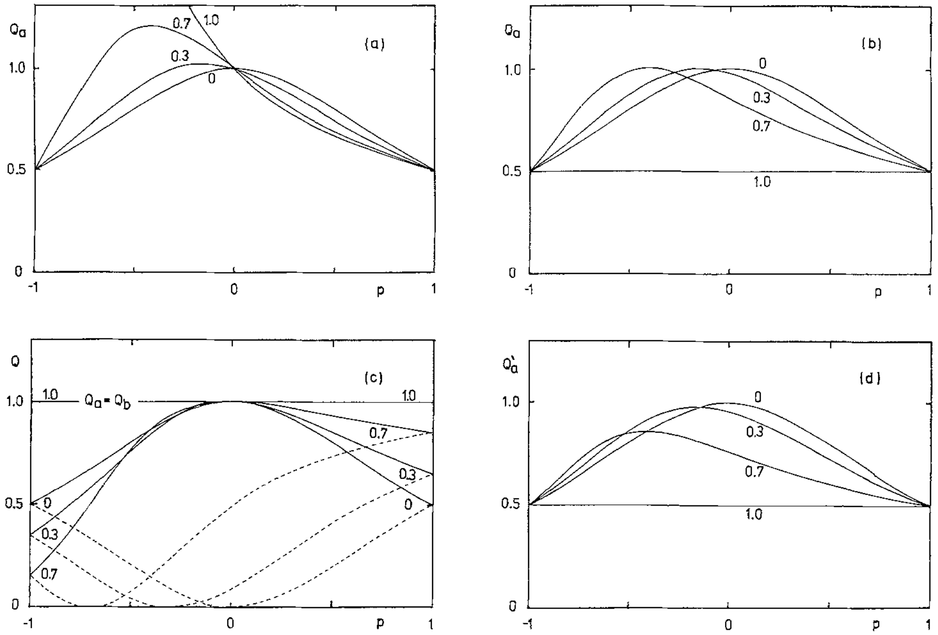

Fig. 6. Electronic charge on center *a* (full curves) and center *b* (dashed curves, in case of definition *P*) as a function of the polarity parameter *p* for four values of overlap (indicated inside the figure) (a) definition *M*, (b) definition *OB*, (c) definition *P*, (d) definition *PC*

either positive or negative values: for $p > 1/S[-1+\sqrt{1-S^2}]$, the sum of Q_a and Q_b exceeds the sum of electrons considered (i.e. 1.0), while for $p < 1/S[-1+\sqrt{1-S^2}]$ the opposite is true. For our plots corresponding to $S=0.3$ and $S=0.7$, the critical values of p are -0.154 and -0.408, respectively. In fact, the physical background of the division of the plots into two regions according to the value of p is in differentiating between ground and virtual states. The "corrected" projection density approach is the only one (cf. Fig. 6d) which in the case of non-zero overlap reaches a maximum of Q_a at a lower value than 1. This means that only at $S=0$ it is possible to attribute the total electronic charge to one center.

In concluding, we wish to express our hope that the preceding results and discussion brought a portion of insight into the concept of the charge on an atom in the molecule, and some understanding of various factors which contribute to the realistic features of the concept. Of course, many of our observations have a restricted meaning because of simplified conditions used in this work. Nevertheless one point seems to be clear. Namely, that no definition of atomic charge is without some weakness and that a mechanical interpretation of results of any method should be avoided.

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