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Atomic charges based on spherical harmonics expansion at the atomic centers

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Molecular orbitals are expanded in spherical harmonics functions around atomic centers. The expansion coefficient is a function of the distance from the nucleus and the quotient between this function and a corresponding atomic orbital is almost constant in the core region. The square of the quotient is used as a definition of an atomic charge component. The erratic dependence on the type of basis functions in the Mulliken method is thereby avoided. The relationship between the new charge and the Mulliken population is investigated and a new invariant Mulliken population is suggested.

Key words: Atomic charges — Spherical harmonics expansion — Net populations — *Ab initio* wave functions

1. Introduction

Molecular orbitals (MO), the elements of the quantum mechanical description of molecular electronic structure, are complicated mathematical functions of a three-dimensional variable. To be able to overview their extension in space they may be analysed in atomic components. In the Mulliken analysis the squares of the expansion coefficients of the orbital basis functions is used to define an atomic charge [1-4]. Originally, this was applied for the simple LCAO case when each basis function corresponds to an atomic orbital [1, 2]. If the method is extended to the case of many atomic radial functions on each center for each atomic orbital, the well-known difficulties of the Mulliken analysis begin to appear. Some basis functions on different centers will have a large overlap. If they are orthogonalized the new functions will be centered on many nuclei and the expansion coefficient squared then loses its meaning of an atomic charge component. Another problem, closely related to the first one, is that the basis may become complete, in principle, by expanding on just one center, in which case the Mulliken analysis would refer all electrons to this center. A many-center expansion is more practical, of course, since one may obtain reasonable results in a small expansion. Improving on a many-center expansion, on the other hand, quickly leads to overcompleteness problems with increasing arbitrariness in the expansion coefficients.

As a consequence of the mentioned problems, for some molecules there exist a number of accurate calculations with rather different Mulliken populations. The actual differences in the wave functions for given points in space are usually much smaller. The problem is not in the calculation of the wave function but in the interpretation of the calculation. One way to proceed would be to list the wave function in given points or to interpret it in terms of expectation values. Another way is to use integrated charges, but a difficulty is then to define a suitable region for the integration. A very elegant way of discussing the topographical features of the charge density has been worked out by Bader and co-workers [5].

There are actually a number of ways of defining atomic charges in a basis set independent way, but unfortunately they are not in common use [6-10]. The approach followed here makes use of the spherical harmonics expansion of the MO around atomic centers [11-19].

$$\phi_i(r)=\sum_{l=0}^{\infty}\sum_{m=-l}^{l} C_{lm}(r)\,Y_{lm}(\Omega) \tag{1}$$

If an MO is expressed in terms of Gaussians, each Gaussian $u_\nu=\exp(-\alpha r_A^2)$ centered at a point A with spherical coordinates (R_A, θ_A, ϕ_A) gives a contribution $C^{(\nu)}_{lm}$ to C_{lm} defined by [19]:

$$C^{(\nu)}_{lm}(r)=[4\pi\exp(-\alpha R_A^2)\,Y^*_{lm}(\theta_A, \phi_A)]\,i_l(2\alpha R_A r) \tag{2}$$

where i_l are modified spherical Bessel functions of the first kind.

The functions $C_{lm}(r)$ referring to an MO expressed in Gaussians or any other basis set are usually proportional to the orbitals of the neutral atom in the core region [11, 12]. For instance the singly occupied orbital in linear CuF_2, which is an σ_g orbital has $C_{00}(r)$, $C_{20}(r)$, $C_{40}(r)$, etc. as the only non-zero expansion "coefficients". $C_{00}(r)$ has the same nodal structure as the Cu4s orbital and the ratio $C_{00}(r)/R_{4s}(r)$ is almost constant in the core region (except in a region close to the nodes). The same applies to $C_{20}(r)$ and $R_{3d}(r)$. This feature of molecular orbitals may be used to define atomic charges in molecules [11, 12].

Due to the erratic behavior of the charges obtained by applying the Mulliken method to *ab initio* wave functions, quantum chemical methods are in some disrepute in connection with "charges". This is unnecessary since basis set independent methods can be used. It must be realized, of course, that different definitions lead to different "charges". Experimentally, atomic charges and spin distributions may be obtained in for example ESCA [20-23], NMR, ESR, NQR or Mössbauer spectra. In the first two the shift is measured by an operator which behaves like $1/r$ in the core region outside the ionized shell. In the others, except the last one the r-dependence of the relevant operator is $1/r^3$ and in the last one the charge density at the nucleus is measured. In all cases the region close to the nucleus is heavily weighted. Consequently, a charge (or spin) definition which, like the one used in this paper, is based on the behavior of the valence orbitals in this region will be in good agreement with these measured charges or spins.

2. Theory

In the core region, the orbital shape of MO ϕ_i is determined essentially by the kinetic energy and nuclear attraction terms and Coulomb repulsions from the electrons "inside" the orbital under study. All these terms are very similar in the atom and the molecule. One may therefore expect that the molecular orbital component $C_{lm}^{(i)}(r)$ and its corresponding atomic orbital α_{lm} have a nearly constant ratio in the core region.

The contribution from ϕ_i to the charge component q_{lm} at the atom center A is defined as:

$$q(\phi_i, A, l, m) = [\lim_{r\to 0} C_{lm}^{(i)}(r)/\alpha_{lm}(r)]^2 \tag{3}$$

where r is radius vector at A.

Several other definitions are possible as for instance

$$q(\phi_i, A, l, m) = \left[\lim_{R\to 0} \frac{\int_0^R \int_\Omega \alpha_{lm}^*(r)\phi_i(r)r^2\,dr\,d\Omega}{\int_0^R \int_\Omega \alpha_{lm}^*(r)\alpha_{lm}(r)r^2\,dr\,d\Omega} \right]^2 \tag{4}$$

which leads to the same result as Eq. (3). If $r^2\,dr$ is replaced by $\omega(r)r^2\,dr$ in Eq. (4) and $\omega(r)$ is an operator which strongly weighs the nuclear region (as for instance $1/r^3$) the charge may be defined as:

$$q(\phi_i, A, l, m) = \left[\frac{\int_0^R \int_\Omega \alpha_{lm}^*(r)\phi_i(r)\omega(r)r^2\,dr\,d\Omega}{\int_0^R \int_\Omega \alpha_{lm}^*(r)\alpha_{lm}(r)\omega(r)r^2\,dr\,d\Omega} \right]^2 \tag{5}$$

and will then be almost the same as in Eq. (4). Equation (5) is useful if ϕ_i has an erratic behavior very close to the nucleus, which is often the case with Gaussian orbitals.

For $R\to\infty$ in Eq. (4) we obtain:

$$n(\phi_i, A, l, m) = \int_0^\infty \int_\Omega \alpha_{lm}^*(r)\phi_i(r)r^2\,dr\,d\Omega \tag{6}$$

which is identical to the Davidson definition of the contribution of ϕ_i to the

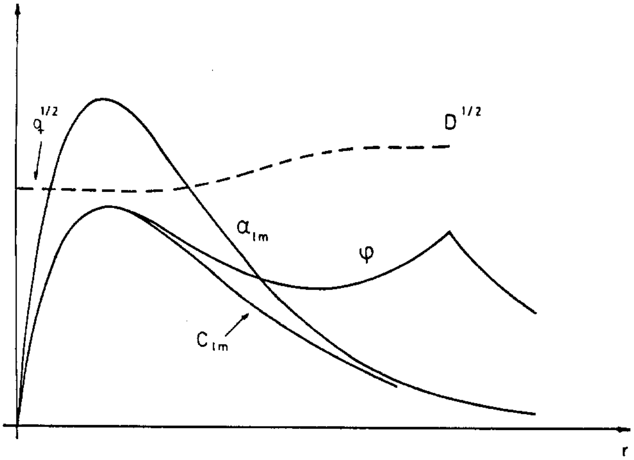

Fig. 1. Molecular orbital ϕ plotted along an interatomic axis, component C_{lm} and corresponding atomic orbital α_{lm}. The *dashed line* is the quotient $\int_0^r \int_\Omega \alpha_{lm}\phi_i / \int_0^r \int_\Omega \alpha_{lm}^2$. q is the charge defined in this paper [Eq. (3)] and D the corresponding number of Ref. [6]

occupation number of the atomic orbital α_{lm} [6]:

$$n(\phi_i, A, l, m) = \langle \phi_i | \alpha_{lm} \rangle^2 \tag{7}$$

The difference between our definitions Eqs. (3)–(5), and the one of Davidson is clarified in Fig. 1. For a bonding orbital, we should have

$$n(\phi_i, A, l, m) > q(\phi_i, A, l, m) \tag{8}$$

and the other way around for an antibonding orbital.

The charge used here, as well as the Davidson occupation number, has the property that it converges to a definite result as the wave function is improved. None of these two definitions has the property that all atomic components of a given orbital sum to unity. In both cases we are moreover missing the concept of "overlap charge" which has been found useful in the Mulliken definition. We will now show that an "overlap charge" may be obtained by comparing the Davidson approach to the one presented here.

Let us assume that the normalized molecular orbital ϕ_i may be written as a linear combination of atomic orbitals χ_A and χ_B centered on A and B, respectively:

$$\phi_i = \lambda_A \chi_A + \lambda_B \chi_B \tag{9}$$

We may assume that $\lambda_B \chi_B$ is small on center $A[\lambda_B \chi_B(A) \ll \lambda_A \chi_A(A)]$. We then obtain:

$$q(\phi_i, A) = \lambda_A^2 \tag{10}$$

where indices l, m have been discarded. This is identical to the Mulliken net population $P(\phi_i, A)$. The Davidson occupation of χ_A is:

$$n(\phi_i, A) = \langle \chi_A | \phi_i \rangle^2 = \lambda_A^2 + 2\lambda_A \lambda_B \langle \chi_A | \chi_B \rangle + \lambda_B^2 \langle \chi_A | \chi_B \rangle^2 \tag{11}$$

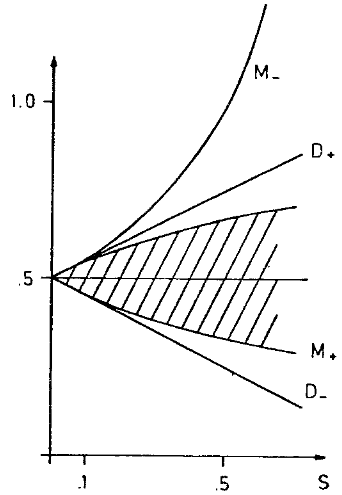

Fig. 2. Mulliken net populations (M) and Davidson occupations for bonding (+) and antibonding (−) orbital of Eq. (9). $\lambda_A = \lambda_B$. See text for explanation of *dashed area*

The third term is small if either λ_B or the overlap is small. The second term is the Mulliken overlap charge. On the basis of Eq. (11) it would be reasonable to interpret the difference between the charge component $q(i, A)$ and the Davidson occupation $n(i, A)$ as an overlap charge. This is shown in Fig. 2. The overlap charge for a bonding orbital corresponds to the hatched area. If terms to second order in S are neglected, the Davidson occupation is equal to the sum of the Mulliken net population and the overlap population. For corresponding antibonding orbital the Davidson occupation is equal to the Mulliken net population minus the overlap population. Since S is usually smaller than 0.3, the suggested overlap definition would be reasonable and we would then have "invariant" definitions of overlap as well as charge. However, we have neglected some terms which at least in some cases make $q(i, A)$ very different from $P(i, A)$.

The charge components $q(i, A, l, m)$ defined by Eq. (3) also contain a contribution arising from orthogonality to inner shells as well as $\lambda_B \chi_B(A)$ which was neglected above. To see this we write a valence orbital as:

$$\phi_i' = (1 - |\xi_A \times \xi_A| - |\xi_B \times \xi_B|)(\lambda_A \chi_A + \lambda_B \chi_B) \tag{12}$$

where ξ_A and ξ_B are core atomic orbitals on A and B, respectively (for simplicity we assume only one such function on each atom). The core functions, ξ_A and ξ_B, are orthogonal to χ_A and χ_B, respectively, and it may also be assumed that $\xi_B(A) = 0$. We obtain

$$q(i, A) = [\lambda_A + \mu(i, A)]^2 \tag{13}$$

where

$$\mu(i, A) = \lambda_B[\chi_B(A) - \xi_A(A)\langle\xi_A|\chi_B\rangle]/\chi_A(A) \tag{14}$$

The new correction term due to the core orbital ξ_A is often larger than $\chi_B(A)$. For Li_2 $\xi_A\langle\xi_A|\chi_B\rangle \approx 8 \cdot \chi_B(A)$. Clearly μ is an important correction term in all methods which only include the valence orbitals particularly in calculations of isomer shifts.

We also obtain from Eqs. (13) and (14):

$$\langle\phi_i'|\chi_A\rangle=\lambda_A+\lambda_B\langle\chi_B|\chi_A\rangle-\lambda_A\langle\xi_B|\chi_A\rangle^2 \tag{15}$$

In most cases the third term can be ignored and we then obtain no correction of the Davidson occupation compared to Eq. (11). The Mulliken net population on A due to ϕ_i' is:

$$P(i,A)=\lambda_A^2+\lambda_B^2\langle\xi_A|\chi_B\rangle^2 \tag{16}$$

Again the correction may be ignored compared to λ_A^2.

In the case of large basis sets, $q(i,A)$ is calculated from Eqs. (3), (4) or (5). The atomic orbital should be expanded in the same atomic basis set as is used in the molecular calculation. One may then hope for some error cancellation. The important thing is that $q(i,A)$ is an invariant quantity, independent of the basis set once the latter is complete. This is not so for the Mulliken population. An invariant Mulliken net population, however, may be defined on the basis of Eqs. (13) and (14):

$$P(i,A)=[\sqrt{q(i,A)}-\mu(i,A)]^2 \tag{17}$$

3. Examples

3.1. H_2

The occupied $1\sigma_g$ orbital may be approximated as

$$1\sigma_g=(1s_A+1s_B)/\sqrt{2+2S};\qquad S=\langle 1s_A|1s_B\rangle \tag{18}$$

where

$$1s_A(r)=\frac{1}{\sqrt{\pi}}\exp(-r) \tag{19}$$

Using Eqs. (3), (10) and (11) we obtain:

$$q(1\sigma_g,A,0,0)=[(1+e^{-R})/\sqrt{2+2S}]^2 \tag{20}$$
$$P(1\sigma_g,A)=(2+2S)^{-1}$$
$$n(1\sigma_g,1S_A)=(1+S)/2$$

For $R=\infty$, $q(1s_A)=0.5$ and for $R=0$, $q(1s_A)=1$. The Mulliken net populations, P, are 0.5 for $R=\infty$ and 0.25×2 for $R=0$. The Davidson occupations, n, of the orbital $1/\sqrt{\pi}\,e^{-r}$ are 0.5 for $R=\infty$ and 1.0 for $R=0$. All values given here refer to one electron. The total charges, populations and occupations are thus twice as large. At the equilibrium distance $R=1.4\,a_0$, where $S=0.753$, we obtain $q(1s_A)=0.44$, $P(1s_A)=0.29$ and $n(1s_A)=0.88$. The difference $q(1s_A)-P(1s_A)$

equal to 0.15 is due to the term $\lambda_B \chi_B(A)$, which is particularly large in the case of H_2 with a short bonding distance and large overlap. The large overlap also leads to the large Davidson occupation, which overshoots the sum of Mulliken net and overlap population $(0.29+0.42)$ by 0.17.

The low value of q at the equilibrium distance is due to the inadequate wave function. An optimized basis set of van Duijneveld [25] (9*s* contracted to 3*s* and augmented by *p* functions) gives $q(1s_A)=0.67$ at the equilibrium distance. At $R=0$ the correct value, obtained in a Hylleraas calculation for the He atom [26], is $q(1s_A)=5.69$. Apparently the simple LCAO basis, which gives $q(1s_A)=1.0$ is very inadequate for small interatomic distances.

3.2. Li_2

Ab initio MO were calculated using the basis sets of Roos and Siegbahn [27] (7*s* contracted to 3*s*) and Huzinaga (9*s*, 4*p*) [28]. (Basis sets I and II, respectively.) The result is given in Table 1. We notice, as in the previous case of H_2, that the charge component $q(2\sigma_g, A, 0, 0)$ is considerably larger than the invariant Mulliken net population. In this case, however, the main contribution to this difference is not $\lambda_B \chi_B(A)$. The latter term is small and contributes to a lowering of $q(2\sigma_g, A, 0, 0)$. The major part is the term due to orthogonality between χ_B and the 1*s* orbital on *A*. It contributes to an increase of $q(2\sigma_g, A, 0, 0)$ by about a factor of two compared to $P(2\sigma_g, A)$. Obviously in this case the Mulliken net population would not even be close to any experimentally measurable quantity.

The $q(2\sigma_g, A, 1, 0)$ charge, i.e. the $2p_z$ component is very much increased when *p* functions are added to the basis set. In a good basis set the $2p_z$ functions thus have to be included. On the other hand the $2p_z$ component is surprisingly small and indicates a very small amount of $s-p$ hybridization. The free atom 2*p* orbital is obtained from the ^2P state of Li. Since the orbital is not a strongly bound one, one may expect that core region proportionality is not very well obeyed.

Although well-known, it may be of interest to point out that the charge densities at the nucleus using Gaussian functions are rather bad. For the Li atom we obtain 12.5 by the Roos-Siegbahn basis and 13.0 by the Huzinaga basis, whereas the accurate value is 13.81 (with correlation corrections 13.83) [29]. Accurate values

Table 1. Charge components *q*, Mulliken net and gross populations, *P*, and invariant Mulliken populations *P'* for $Li_2 2\sigma_g$ orbital. I refers to the basis set of [27] and II to the basis set of [28]

AO	Basis	q	P_{net}	P_{gross}	P'
2*s*	I	0.579	0.320	0.500	0.304
2*p*	I	0.002	—	—	[a]
2*s*	II	0.540	0.282	0.461	0.284
2*p*	II	0.051	0.012	0.039	[a]

[a] not calculated

have been obtained for Li_2 and LiH by Pyykkö et al. [30] and are 13.825 and 13.790, respectively; both on the Hartree-Fock level.

The invariant Mulliken population (P') are slightly different for the four basis sets. There is thus a real difference in the two wave functions.

3.3. LiH

Results for LiH using the Huzinaga basis set [28] are given in Table 2 and Fig. 3. The most remarkable thing is that the density at the hydrogen nucleus is about the same in LiH as in the hydrogen atom [(a) and (b) are almost the same at the nucleus in Fig. 3]. The singly occupied $1s$ orbital of the hydrogen atom is larger by roughly $\sqrt{2}$ than the doubly occupied 2σ orbital of LiH at the hydrogen nucleus. The contribution from 1σ is negligible. The accurate value for the charge density at the H nucleus obtained by Pyykkö et al. [30] is 0.374, thus slightly lower than our result.

For the H nucleus as for the Li nucleus above, basis set errors for the charge density are generally larger than differences due to "environment". It may be of interest to study also accurate values for H^-. As is seen in Fig. 3, the H^-

Table 2. Charge components and Mulliken net populations for LiH 2σ orbital using basis sets of Huzinaga (Li) and van Duijneveld (H) [25, 28]

AO	q	P_{net}	P_{gross}	P'
Li2*s*	0.590	0.179	0.373	0.256
H1*s*	0.516	0.433	0.627	0.460

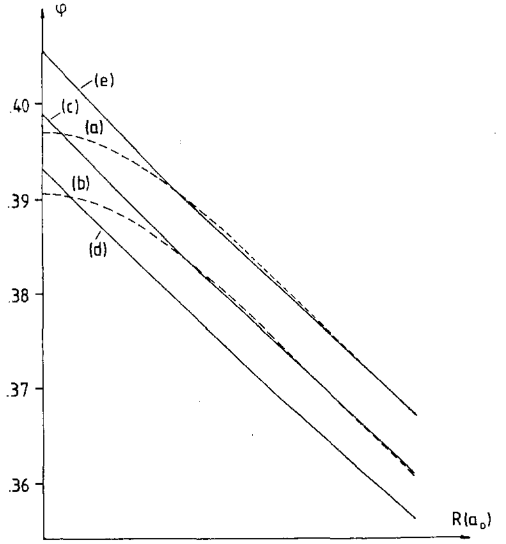

Fig. 3. Comparison of wave functions close to the hydrogen nucleus. (*a*) (*dashed*) $C_{00}(r)$ for LiH using a gaussian basis set (see text); (*b*) (*dashed*) H1*s* divided by $\sqrt{2}$ using the same basis set; (*c*) H1*s* divided by $\sqrt{2}$ $[1/\sqrt{2\pi}\exp(-r)]$; (*d*) 1*s* orbital for H^- obtained by the Hartree-Fock method; (*e*) square-root of electronic density for H^-

Hartree–Fock $1s$ orbital obtained in a very accurate Slater type basis set [26] is smaller than the H_{1s} orbital, divided by $\sqrt{2}$, close to the nucleus. However, if correlation effects are included the density at the nucleus in H^- is somewhat larger (Fig. 3 and Ref. [26]). These results show, among other things, that it is impossible to tell whether LiH is closer to $Li-H$ or to $Li^+ - H^-$. There is almost no difference in charge densities between H and H^- or Li^+ and Li close to the nucleus and far from the nuclei the charge density is deformed anyway due to MO formation.

Also in the LiH case the Mulliken net population is much different from the charges q defined here, particularly at the Li nucleus where the $1s$-orthogonality term is large. Again we have a case when the Mulliken net population (Table 2) stands no chance in being in agreement with measured "charges".

4. Discussion

The charge components $q_A^{(i)}$ are a measure of how the wave function starts out from each nucleus. It is a useful measure if the quotient is constant in most of the core region, and then the result of Eqs. (3), (4) and (5) agree very closely. The sum of the charge components defined by Eqs. (3), (4) and (5) over the various nuclei will not add up to unity as is the case with the total Mulliken populations. The same problem appears if the charges are derived experimentally by measuring expectation values of core region weighted operators. In fact our method quite clearly reveals the dangers in the experimental determinations as well as in calculations using only valence orbitals. The latter tell only about the behavior at the nucleus and cannot be used for a global partitioning of the electron charge on atoms. The reason is that the orthogonality between the core orbital ξ_A and the valence orbital (χ_B) on other centers. The problem is particularly important for isomer shifts since $\langle\xi_A|\chi_B\rangle$ is large in that case.

It is quite obvious that the core orbitals look similar in the molecule as in the free atom. To which extent the similarity is valid for the valence orbitals depends on how strongly these orbitals are bound. Weakly bound orbitals are very different already in different electronic configurations of the atom. As an example one obtains large differences in the $2p$ orbitals for the Be atom in the ^1P and ^3P states. Consequently, it is impossible to define an atomic charge component with reference to these losely bound orbitals. The full plot of the molecular component has to be given together with the different atomic orbitals.

In our procedure we will thus arrive at an answer regarding the existence of atomic components of weakly bound orbitals in molecular orbitals, as for instance a sulphur $3d$ component in molecules containing sulphur atoms [31]. There will be a d-component in those orbitals where it is allowed by symmetry, even if the basis set does not contain any d-functions. As in the case of the p component in Li_2 the $S3d$ component will be larger and better described if d functions are included in the basis set. Only by calculations is it possible to decide whether this d-component takes on a maximum in the region between the S nucleus and its neighbors, and thereby resembles an atomic orbital. The next question is whether it resembles any atomic orbital for an excited state of sulphur. If it does not, as is likely, one cannot ascribe a well-defined $S3d$ charge to the orbital in question.

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