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Atomic Charges in the Multiple Scattering Molecular Orbital Method*

Sven Larsson**

Department of Quantum Chemistry,
Uppsala University, Box 518, S-751 20 Uppsala, Sweden

The concept of atomic charges in molecular orbital theory is discussed. A definition which pays special attention to the behaviour of the orbitals close to the atomic nuclei, is suggested. This new definition is particularly simple to apply in the multiple scattering method. Some transition metal complexes are considered as examples. The existence of the back donation effect is demonstrated for a series of octahedral cyanides.

Key words: Multiple scattering MO theory – Back bonding – Atomic charges in molecules

1. Introduction

The distribution of charges and spins is of essential importance for the understanding of the physical properties of a molecule, its reactive centers and the stability of its bonds. Since the quantum mechanical charge density is not easily visualized or overlooked in three dimensions one normally tries to divide up the charge and count it to the different atomic centers and bonds. Mulliken [1], Coulson and Longuet-Higgins [2] used simply the coefficients in the LCAO expansions of semi-empirical molecular orbitals for this purpose. Mulliken generalized his original method to apply to orbitals expanded in larger basis sets [3]. The Mulliken method is basis set dependent in the sense that a given wave function resolves into different "charge distributions" depending on what basis set is used for its expansion. Consequently very different Mulliken charges are often found for a given molecule [4, 5]. This arbitrariness is not removed by

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** Present address: Division of Physical Chemistry 2, Lund's Technical University Chemical Center, S-22007 Lund, Sweden.

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using larger basis sets. Davidson, Politzer and many others realized this problem and used definitions which are independent of basis sets [6–10]. Unfortunately these methods are not in common use.

In the multiple scattering molecular orbital method (MSMO) [11, 12] the charge density is routinely integrated in the atomic muffin-tin spheres. The integrated charge cannot directly be used as a measure of the electronic charge on the atom in question since it depends, of course, on the size of the sphere. In the case of well localized atomic components one may apply a renormalization procedure, and get a fair estimation of an "occupation number" [13]. For more extended atomic component orbitals it is less clear how the charge should be counted. Partitioning of the interatomic charge in one way or the other have been suggested [14, 15] but the atomic charges obtained are also dependent on sphere radii.

In the present paper an alternative definition of atomic charges in molecules is given which is related to the Davidson approach [6] and particularly well suited for the multiple scattering method. It looks on the charges from the point of view of the nuclei, in a way similar to one discussed by Mulliken in two papers from 1932 [16].

2. The Multiple Scattering Formalism

The MSMO method for molecular systems is characterized by the exact integration of the one-particle Schrödinger equations where the potentials are approximated as "muffin-tin" potentials [12]. Using local coordinates:

$$V(\boldsymbol{r}) = V_0^{(\alpha)}(\boldsymbol{r}) \quad \text{for } r < R_\alpha \tag{1}$$

where R_α is the radius of the atomic sphere α. In each sphere α the wave function may be written

$$\psi^{(\alpha)}(\boldsymbol{r}) = \sum_{l,m} C_{lm}^{(\alpha)} R_l^{(\alpha)}(r) Y_{lm}(\theta, \phi) \tag{2}$$

The radial functions $R_l^{(\alpha)}(r)$ are the solutions of the one-particle Schrödinger equations

$$\left[-\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{l(l+1)}{r^2} + V_0^{(\alpha)}(r) \right] R_l^{(\alpha)}(r) = \varepsilon R_l^{(\alpha)}(r) \tag{3}$$

in the different atomic regions.

In the region between the atomic spheres a constant potential is used which makes it possible to express the wave function in known functions. The boundary condition at the sphere boundaries requires the orbitals to be continuous and have continuous first derivatives.

The potential $V_0^{(\alpha)}(r)$ is different from corresponding atomic function only by an almost constant function since the only significant difference between the two systems is in outer shielding [17]. A constant potential does not change the form of the orbital and consequently all molecular orbitals are almost proportional

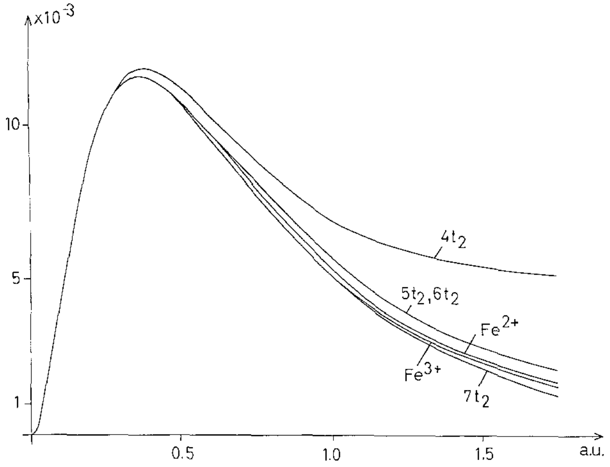

Fig. 1. $R_2^{(\mathrm{Fe})}$ for molecular orbitals of t_2 symmetry for FeCl_4^- compared to radial functions for the $3d$ orbitals of Fe^{3+} and Fe^{2+}. The values of $C_{lm}^{(\alpha)}$ for the orbitals $4t_2-7t_2$ are 7.5, 89.9, 0.19 and 130.6, resp.; for Fe^{2+} 158.5 and for Fe^{3+} 168.4

to the corresponding atomic orbitals in the core region. This is shown by an example in Fig. 1 where the functions $R_2^{(\mathrm{Fe})}$ for the molecular orbitals of t_2 symmetry for FeCl_4^- are given and compared to the $3d$ functions in a Hartree–Fock–Slater calculation on the configurations $3d^5 4s^0$ and $3d^6 4s^0$. Only $5t_2$ and $7t_2$ have large values on $|C_{2m}^{(\mathrm{Fe})}|$. $5t_2$ has bonding and $7t_2$ antibonding character.

Orbitals for other systems show a similar behaviour with an almost constant quotient between atomic and molecular orbitals in a large part of the core region. It is intuitively clear that the square of the coefficients $C_{lm}^{(\alpha)}$ may be used to define an atomic occupation. This will be further discussed in the next section.

3. Theory

The occupation number of orbital f_i was defined[1] by Davidson [6] as

$$n_{ii} = \int f_i^*(1)\gamma(1,1')f_i(1')\,d\tau d\tau' \tag{4}$$

where γ is the one-particle reduced density matrix [18]:

$$\gamma(1,1') = \int \psi(1,2,\ldots,N)\psi^*(1',2,\ldots,N)\,\mathrm{d}\tau_2\ldots d\tau_N \tag{5}$$

It can be shown that [18]:

$$0 \leqslant n_{ii} \leqslant 1 \tag{6}$$

In the case of a determinantal wave function with orbitals ϕ_μ,

$$n_{ii} = \sum_\mu \langle f_i \mid \phi_\mu \rangle^2 \tag{7}$$

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[1] Contrary to Davidson we are here using spin orbitals where 1 stands for (r_1, s_1), $d\tau_1 = dv_1\, ds_1$, where s refers symbolically to the spin coordinate. The spin is retained in γ.

In experimental determinations of atomic charges, one usually measures properties associated with the behaviour of the wave function close to the nucleus. EPR hyperfine splittings measure $\langle 1/r^3 \rangle$ and $\phi_\uparrow^2(0)-\phi_\downarrow^2(0)$, whereas X-ray photoelectron shifts (ESCA shifts) measure essentially $\langle 1/r \rangle$. Mössbauer isomer shifts measure $\phi^2(0)$ whereas quadrupole coupling constants again measure $\langle 1/r^3 \rangle$. In a theoretical definition of an electron charge on an atom one should accordingly emphasize quantities which depend on the behaviour of the orbitals close to the nucleus. We may thus choose to carry out the integration in Eq. (7) only within a certain sphere Ω_R with radius R around the atomic centre of interest:

$$\int_{\Omega_R} \phi_\mu^* f_i \, d\tau \tag{8}$$

The atomic component of the molecular orbital ϕ_μ should then be defined

$$q_R(f_i) = \left(\frac{\int_{\Omega_R} \phi_\mu^* f_i \, d\tau}{\int_{\Omega_R} f_i^* f_i \, d\tau} \right)^2 \tag{9}$$

Since this q_R according to our experience is almost independent of R as long as R is small, we may eliminate the R-dependence and use

$$q(f_i) = \lim_{R \to 0} q_R(f_i) \tag{10}$$

as a definition of the atomic charge component or population of ϕ_μ. Since we divide by the squared norm of f_i within Ω_R in Eq. (9) rather than just the norm, Eq. (6) will no longer be valid. It is intuitively clear, however, that Eq. (6) must hold to a very good approximation as long as f_i is chosen appropriately.

In the multiple scattering method it is suitable to let f_i be an atomic orbital calculated with the same exchange approximation. q will be the square of the quotient between the expansion coefficient $C_{lm}^{(\alpha)}$ and corresponding quantity for the atomic orbital. All relevant information is printed in most current versions of the multiple scattering and Hartree–Fock–Slater programs.

The electronic charges defined in this way will strongly depend on which atomic orbital is chosen as reference orbital. For instance, the expansion coefficients for Fe^{3+} and Fe^{2+} are 168.2 and 158.5, respectively. The difference of about 6% will lead to a 12% difference in electronic charges if defined in the way suggested in Eq. (10). This is a too large difference and the results may be misleading, for instance when a sub-shell is about to be filled. In a filled sub-shell we want, of course, the number of electrons, summed over all molecular orbitals, to be equal to $2 \cdot (2l+1)$.

We may improve our model by choosing the atomic comparison orbital in such a way that the number of electrons in a particular sub-shell automatically sums up to $2 \cdot (2l+1)$ when we count both the occupied and the lowest unoccupied orbitals. We may alternatively choose only one particular symmetry representation where we require the sum to be equal to the degeneracy. The atomic reference orbital does not correspond to an integer Z any longer, but this does not lead to any particular problems since only the expansion coefficient $C_l^{(\alpha)}$ is of interest, and this coefficient is determined by using the sumrule above. As we will see in the next section, $C_l^{(\alpha)}$ will take on expected values, close to the ones for the actual ions.

4. Examples

4.1. *The* H_2 *Molecule*

The occupied $1\sigma_g$ orbital for H_2 may be approximated:

$$\phi=(1s_A+1s_B)/\sqrt{(2+2S)};\qquad S=\langle 1s_A \mid 1s_B\rangle \tag{11}$$

from which we obtain by Eqs. (9) and (10):

$$q(1s_A)=[(1+e^{-R})/\sqrt{(2+2S)}]^2 \tag{12}$$

At the equilibrium distance ($R=0.74$ and $S=0.7$) $q(1s_A)=0.66$; at $R=\infty$ $q(1s_A)=0.5$ and at $R=0$ $q(1s_A)=1.0$. The Davidson occupation number for $1s_A$ will be $n(1s_A)=\frac{1}{2}(1+S)=0.85$ (for each spin) whereas the Mulliken populations will be 0.3 on each centre and 0.4 in the bond.

4.2. Fe^{2+} *and* Fe^{3+} *Complexes with* F^- *Ligands*

Tables 1 and 2 show atomic charges q defined according to Eq. (10) for octahedral FeF_6 with 89 and 90 electrons present in the systems, respectively. The reference orbital is chosen in such a way that the sum of atomic occupancies for the $e_g\uparrow$ orbital is exactly equal to unity for F2*s*, F2*p* and Fe3*d*. The values determined for C_l in this way are given and are close to the atomic values which are: 168.2 for

Table 1. Composition of occupied molecular orbitals of e_g and t_{2g} symmetry for FeF_6^{3-} (Eq. (10))

Orbital		C_l	$2e_g\uparrow$	$2e_g\downarrow$	$3e_g\uparrow$	$3e_g\downarrow$	$4e_g\uparrow$	$1t_{2g}\uparrow$	$1t_{2g}\downarrow$	$2t_{2g}\uparrow$
$R_{Fe}=2.04$Å	Fe3*d*	165.3	0.002	0.001	0.725	0.199	0.274	0.826	0.070	0.139
$R_F=1.85$Å	F2*s*	12.04	0.986	0.983	0.009	0.002	0.005	—	—	—
	F2*p*	21.11	0.000	0.000	0.173	0.672	0.827	0.079	0.741	0.793
$R_{Fe}=1.76$Å	Fe3*d*	167.3	0.002	0.001	0.778	0.204	0.221	0.871	0.062	0.105
$R_F=2.13$Å	F2*s*	12.02	0.987	0.984	0.008	0.001	0.005	—	—	—
	F2*p*	21.00	0.000	0.000	0.138	0.678	0.862	0.057	0.756	0.810

Table 2. Composition of occupied molecular orbitals of e_g and t_{2g} symmetry for FeF_6^{2-} (Eq. (10)). ($2t_{2g}$ is occupied by one electron)

Orbital		C_l	$2e_g\uparrow$	$2e_g\downarrow$	$3e_g\uparrow$	$3e_g\downarrow$	$4e_g\uparrow$	$1t_{2g}\uparrow$	$1t_{2g}\downarrow$	$2t_{2g}\uparrow$	$2t_{2g}\downarrow$
$R_{Fe}=2.04$ Å	Fe3*d*	161.2	0.001	0.000	0.282	0.064	0.717	0.122	0.016	0.831	0.862
$R_F=1.85$ Å	F2*s*	12.03	0.985	0.984	0.002	0.000	0.013	—	—	—	—
	F2*p*	20.89	0.000	0.000	0.600	0.854	0.400	0.689	0.810	0.176	0.059
$R_{Fe}=1.76$ Å	Fe3*d*	163.0	0.001	0.001	0.294	0.060	0.705	0.113	0.013	0.853	0.882
$R_F=2.13$ Å	F2*s*	12.00	0.986	0.985	0.001	0.000	0.013	—	—	—	—
	F2*p*	20.79	0.000	0.000	0.598	0.868	0.402	0.703	0.810	0.157	0.049

Fe^{3+} $3d$ and 158.5 for Fe^{2+} $3d$, 12.22 for F2*s*, and 21.51 for F2*p*. The atomic charges are given for two different choices of sphere radii.

For the Fe^{2+} complex the orbitals $4e_g$ and $2t_{2g}$ correspond to the orbitals treated in crystal field theory. In molecular orbital theory these orbitals are antibonding. Their bonding counterparts are $3e_g$ and $1t_{2g}$. As a rule the charges defined in Eq. (10) are rather similar for the two different choices of sphere radii. It may be noted that it is only the sum of charges for each irreducible representation which counts, and this sum seems to be almost independent of sphere radii. The charge distribution in orbitals whose antibonding counterparts are incompletely occupied ($3e_g\downarrow$, $1t_{2g}\downarrow$) are also very similar for the two different choices of sphere radii.

In FeF_6^{3-} $3e_g\uparrow$ and $1t_{2g}\uparrow$ are the orbitals which have the largest $3d$ character due to the greater exchange stabilization at the iron site in the d^5 case. The occurrence of a $3d$ type orbital with lower orbital energy than the ligand valence orbitals is not in disagreement with any experimental results since the ground state properties are not affected by a unitary transformation. The change of atomic character of the orbitals indicates agreement with results from X-ray photoelectron spectroscopy in the following sense. As is well-known the orbital energies have no particular meaning in a ground state calculation but if we decrease the occupancy by $\frac{1}{2}$ in $3e_g$, the orbital energy of this orbital has a certain meaning as an ionization energy [19]. Such a change leads to even larger $3d$ character in the $3e_g$ orbital. In X-ray photoelectron spectra of transition metal compounds the $3d$ orbital seems to be more strongly bound than the ligand valence orbitals [20]. This has been referred to by Jørgensen as the "Third revolution in ligand field theory" [21]. The "effect" is not contradictory to the small nephelauxetic effect observed since the latter should be obtained in a different transition state calculation in which the orbitals will be different.

In Table 3 atomic charges are given for some iron complexes. The same values have been used for $C_{00}^{(\mathrm{Fe})}$ and $C_{2m}^{(\mathrm{Fe})}$. The difference between the Fe^{2+} and Fe^{3+} complexes is now smaller than in Tables 1 and 2 since we are expressing the charges with the help of the same atomic orbital f_i.

Table 3. Fe $3d$, $4s$ and $4p$ charges in different octahedral and tetrahedral clusters with $R_{\mathrm{Fe}} = 1.76$ a.u. The normalization constant is 165 for $3d$, 10 for $4s$, and 60 for $4p$

Cluster	FeF_6^{3-}	FeF_6^{4-}	$FeCl_4^-$	$FeCl_4^{2-}$
Interatomic distance (Å)	1.91	2.06	2.19	2.31
$3d_\sigma$	2.47	2.07	—	—
$3d_\pi$	3.18	3.73	—	—
$3d_\sigma + 3d_\pi$	5.55	5.80	5.83	5.90
$4s$	0.38	0.24	0.36	0.26
$4p$	0.90	0.58	0.65	0.47

4.3. 4s and 4p Charges

The value used for $C_0^{(\mathrm{Fe})}$ in Table 3 corresponds to a 4*s* orbital for the neutral iron atom. Since the 4*s* and 3*s* orbitals have the same behaviour in the nuclear region we could in principle have expressed the atomic charges in terms of a reference 3*s* orbital. Since $\phi_{3s}^2(0)$ is about 15 times larger than $\phi_{4s}^2(0)$ the charges will be a factor 15 smaller if we use 3*s*.

In interpreting ESCA shifts [22] in terms of atomic charge distributions the 3*d* and 4*s* charges should not just be added since the atomic 4*s* and 3*s* orbitals have very different values of $\langle 1/r \rangle$. The best way to treat the 4*s* charges in this case would be to redefine them in terms of 3*s* charges by dividing approximately by a factor 15 and use $\langle 1/r \rangle$ referring to 3*s*. $\langle 3s|1/r|3s \rangle$ is only a little larger than $\langle 3d|1/r|3d \rangle$. The net result is thus that the 4*s* charge should be divided by a factor of about 10 before being added to the 3*d* charges, and consequently they may be neglected for most practical purposes when interpreting ESCA shifts.

4.4. Back-Donation

As a last example we may consider the back-donation mechanism [23]. This phenomenon occurs for a number of transition metal complexes where the ligands have low-lying unoccupied π-orbitals. The ligands donate electrons to the metal ion in the σ-orbitals whereas the metal ion donates electrons back to the ligands in the empty ligand orbitals. Theoretical calculations have not always given any clear answer as to the existence of the back-donation effect. To a large extent this is due to the lack of relevant charge estimations.

In Table 4 are given total d_σ and d_π populations for some octahedral cyanides. As a normalization constant for each complex is used (as in the case of FeF_6^{n-})

$$\sum_{i=1}^{4} C_{i\sigma}^2$$

where the summation includes the unoccupied "crystal field" orbital[2]. The π-back-donation given in Table 4 is defined as the difference between the total d_π population and the occupation number of the highest occupied t_{2g} orbital. The data in Table 4

Table 4. σ-donation to 3*d* orbital and π-back-donation (number of electrons) in a series of octahedral cyanides. The occupation number for the highest occupied molecular orbital is given

Complex	$\mathrm{Cr(CN)_6^{3-}}$	$\mathrm{Mn(CN)_6^{4-}}$	$\mathrm{Fe(CN)_6^{3-}}$	$\mathrm{Fe(CN)_6^{4-}}$	$\mathrm{Co(CN)_6^{3-}}$
Norm. const	106.42	127.88	159.65	156.83	191.63
Occ. numb.	3	5	5	6	6
$3d_\sigma$	1.12	1.16	1.42	1.27	1.66
$3d_\pi$	2.44	3.64	4.10	4.47	4.87
Back-don.	0.56	1.36	0.90	1.53	1.13

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[2] In a previous paper [24] a different normalization constant was used for e_g and t_{2g} orbitals, which is the reason for the discrepancy between the results of that paper and those in Table 4.

clearly show the existence of a σ-donation and a π-back-donation which are in good agreement with the interpretation of stretching frequencies [25]. In particular we see an increased σ-donation for the +3 ions in the series $Cr^{3+} < Fe^{3+} < Co^{3+}$. The π-donation is roughly proportional to the occupancy in the highest occupied π-orbital for each series. For the +2 ions (Mn^{2+} and Fe^{2+}) the σ-donation tends to be smaller and the π-donation larger than for corresponding +3 ions.

It should be pointed out that the results in Table 4 are obtained in the non-overlapping muffin-tin method with touching spheres. Particularly in the case of cyanides with their short bonding distance between the C and N atoms, this approach may have its shortcomings. Calculations with improved methods are in progress. It appears likely, however, that the results are qualitatively correct regarding the shift in amount of back-donation from one complex to another, but perhaps not qualitatively correct in the absolute magnitude of the back-donation.

5. Conclusion

A quantity q defined by Eqs. (9) and (10) is suggested as one possible measure of the electronic charge population in atomic orbitals. The definition bears some resemblance to the occupation numbers defined by Davidson but the behaviour of the valence orbitals in the core region is emphasized and the calculated charge should therefore correlate closely with estimations of spin and charge densities in a number of experimental methods where the charge or spin density in the core region is probed.

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