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ABOUT COUNTERINTUITIVE ORBITAL MIXING AND BOND POPULATIONS

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ABSTRACT

It is shown that negative bond and orbital populations may be avoided by the introduction of a weight factor in a bond index definition, together with a suitable parameterization. The negative bond populations found for first-row metal complexes need not be ascribed to counterintuitive orbital mixing but rather, essentially, to the equipartition of the charge distribution. Different definitions of the bond population are compared for ferrocene and the effects of some parameterizations are discussed.

Key words: Weighted bond index - Negative electronic populations - Counterintuitive orbital mixing.

1. INTRODUCTION

In different papers about electronic structure of first-row transition metal complexes, both in semiempirical calculations and in ab-initio ones, negative values for the metal 4s and 4p orbital populations were found; the same thing happened for the metal-ligand overlap populations [1-4]. These unexpected disturbing results have troubled various researchers [5,6]. The phenomenon has been ascribed to the counterintuitive orbital mixing (COM) [4]; the circumstances under which it appears and its consequences have been thoroughly discussed [4,6].

We shall explore here if the equipartition of overlap population can play an important role in understanding the paradox. Bond charge is most commonly assumed to be equally divided between both atoms in the bond [7-10]. In this paper we introduce an appropriate weight in a previously proposed generalized bond index definition [10]; this weight depends on the binding atoms' valence orbital electronegativity. We perform an EH calculation on the ferrocene molecule, which will suffice for our purposes. We compare the results obtained using the present definition, the same one without a weight, Wiberg's and Mulliken's bond populations, and various parameterizations. The comparison supports the hypothesis that the appearance of negative bond populations may be ascribed to the equipartition of bond charge distribution and to the choice of parameters, rather than to COM.

2. ALTERNATIVE BOND POPULATION DEFINITIONS

The well-known Mulliken overlap population [8], k_μ being an orbital centered on atom μ and r_ν one centered on atom ν, is:

$$p_{\mu\nu}^{(M)} = \sum_{k_\mu} \sum_{r_\nu} p_{k_\mu r_\nu} \tag{1}$$

$$p_{k_\mu r_\nu} = 2 \sum_{i} x_{ik_\mu} x_{ir_\nu} S_{k_\mu r_\nu} \tag{2}$$

S being the overlap matrix and x_{ik_μ} the coefficient of the atomic orbital k_μ in the i-th doubly occupied wavefunction.

Wiberg's index [11], defined for orthogonal basis, is:

$$p_{\mu\nu}^{(M)} = \sum_{k_\mu} \sum_{r_\nu} p_{k_\mu r_\nu}^2 \tag{3}$$

where $p_{k_\mu r_\nu}$ is the original Coulson's bond order. This index is hence forcedly positive; the basis may always be orthogonalized through Löwdin's procedure [12].

The bond index which generalizes the Wiberg index for non-orthogonal basis [10] is:

$$I_{\mu\nu} = \sum_{k_\mu} \sum_{r_\nu} I_{k_\mu r_\nu} I_{r_\nu k_\mu} \tag{4}$$

with

$$I_{k_\mu r_\nu} = 2 \sum_{i} \sum_{t_\rho} x_{ik_\mu} x_{it_\rho} S_{t_\rho r_\nu} \tag{5}$$

In these definitions it is implicitly assumed that the centroid of the charge distribution lies at the midpoint of the internuclear distance, which is correct only in the homonuclear case [13,14] and has been extensively discussed [15]. There exist several alternatives for a weighted partition of the bond charge [5,16-19]; many suffer from the drawback of not being invariant under unitary transformations of basis orbitals.

We have chosen a weight which takes into account the orbital electronegativity, so that the centroid of the charge distribution is displaced towards the more electronegative orbital.

Formula (4) for the generalized bond index becomes

$$I_{\mu\nu} = \sum_{k_\mu} \sum_{r_\nu} I'_{k_\mu r_\nu} I'_{r_\nu k_\mu} \tag{6}$$

with

$$I'_{k_\mu r_\nu} = 4 \sum_{i} \sum_{t_\rho} x_{ik_\mu} x_{it_\rho} S_{t_\rho r_\nu} \omega_{t_\rho r_\nu} \tag{7}$$

and

$$\omega_{t_\rho r_\nu} = \chi_{t_\rho} / (\chi_{t_\rho} + \chi_{r_\nu}) \tag{8}$$

where χ_{t_ρ} is the electronegativity of the orbital t belonging to atom ρ. Any weight will verify $\omega_{t_\rho r_\nu} + \omega_{r_\nu t_\rho} = 1$ [13].

Definition (4) is rotationally invariant [10] and remains so after the introduction of the proposed weight factor. In a semimepirical calculation such as this one, it is reasonable to

use a weight which depends on empirical quantities instead of one involving results from the calculation itself.

If a weight [5,19] is introduced in the Mulliken definition (1), it will not alter the overlap population but only the atomic and hence the gross populations; it is indeed the same overlap population which is partitioned in a different way. That is, the introduction of a weight does not avoid the appearance of negative overlap populations, although it may avoid the negative atomic orbital populations, as has been verified [5,19]. In eq. (4), instead, the weight changes the bond index.

3. RESULTS AND DISCUSSION

When applying the previous formulae to ferrocene $(C_5H_5)_2Fe$, the geometry is taken from Sutton [20] for D_{5h} symmetry; the basis set exponentials are Slater's and for Fe Slater's and those of ref. [21]; ionization potentials and electronegativities are taken from Hinze and Jaffé [22] and ref. [21]. The basic IEH program is Dibout's [23].

Table 1 shows the results of EH calculations for different definitions, with the same parameterization, i. e. exponents for Fe from [21] and Wolfsberg-Helmholz's formula [24] for H_{ij}. Mulliken's overlap populations involving Fe are significantly negative. It is seen that the introduction of the weight in the generalized bond index permits overcoming the appearance of negative values in this case. Wiberg's populations are "a priori" positive.

Table 2 shows how the weight and the parameterizations influence

IEH results for atomic charges and bond populations. We report in this Table the results which we considered more interesting, after trying a variety of parameterizations. A modified expression for H_{ij} has been proposed in ref. [4], reducing COM and negative overlap populations. We have explored the effect of modifying H_{ij}, ζ_{Fe} or both, and of introducing the weight factor. We can remark at once that iteration by itself eliminates the negative Fe-C bond index found in Table 1, even without introducing a weight: -0.176 becomes 0.101.

It is seen that modifying H_{ij} changes appreciably several results when the bond index definition does not involve a weight; with weight the results are quite insensitive to H_{ij}. The exponents used for Fe change somewhat the values, but not the trends. All these parameterizations give positive bond populations with weight.

As to net charges, all the IEH calculations exhibit similar values, quite different from those obtained in the two ab-initio ones; polarity, as expected, is preserved in both kinds of approximations.

Formulae (4) or (6) give the charges [10] through:

$$q_\mu = \frac{1}{2} \left(I_{\mu\mu} + \sum_{\mu \neq \nu} I_{\mu\nu} \right) \qquad (9)$$

and it is seen that eq. (9) cannot be expressed as a sum over k_μ, due to the cross-term contributions. We have thus lost the concept of orbital charge. However, since eq. (9) reduces to the familiar Chirgwin-Coulson expression [9,10] in the closed-shell case, we may safely adopt here the Chirgwin and Coulson orbital

electronic densities.

Table 3 shows that Wolfsberg-Helmholz's H_{ij} gives negative Chirgwin-Coulson populations for the 4s and the $4p_z$ orbitals of Fe, without weight. The Table shows that the alternative expression for H_{ij} [4] eliminates the negative 4s population and lowers, but does not avoid, the $4p_z$ negative population; this verifies both for the Mulliken and the Chirgwin-Coulson definitions. With weight, Wolfsberg-Helmholz's H_{ij} works better than the one proposed in [4]. The Fe exponents of ref. [21] are preferable to Slater's, which still lead to a small negative population in the $4p_z$ orbital, even with weight.

The introduction of weight is thus seen to represent a significant step, although not capable by itself of preventing negative populations. It must be wisely combined with parameterization.

Let us now examine more closely how the use of a weight factor influences the 4s and $4p_z$ negative orbital populations of Table 3. This is shown in Table 4, which reproduces only the MO's contributing to the 4s and $4p_z$ population, with Wolfsberg-Helmholz's H_{ij}. One can see that the weight factor affects very little the energy levels and not appreciably the coefficients. However, the contribution of each MO to the orbital population may change drastically and the modification always has the desired sense. As we shall see next, there is no fundamental objection against the negative contribution of an individual MO, but of course we expect the total orbital population to be positive. Thus, the contribution of the lowest MO to the $4p_z$ or-

bital population of Fe becomes positive when using a weight factor; but the contribution of the next MO to the 4s population, although diminishing, still remains negative. The contributions of the other MO's, which are not responsible of the negative populations, are not significantly affected by the weight factor.

For a better comprehension of the above, let us consider a system of two interacting atomic orbitals ϕ_1 and ϕ_2. The contribution of one MO to the atomic population of ϕ_1 is

$$\rho(\phi_1) = 2\ (x_1^2 + x_1 x_2 S_{12}) \qquad (10)$$

In the case of antibonding orbitals $x_1 x_2 S_{12} < 0$; when this takes place in the low-lying occupied MO's, we have what has been named COM. If besides $|x_1 x_2 S_{12}| > x_1^2$, $\rho(\phi_1)$ shall be negative.

Now, if the weight (8) is introduced

$$\rho'(\phi_1) = 2\ (x_1^2 + 2\ x_1 x_2 S_{12}\ \chi_1/(\chi_1 + \chi_2)) \qquad (11)$$

If $\chi_1 < \chi_2$, then $\rho'(\phi_1) > \rho(\phi_1)$. This is what we find for ferrocene, for the electronegativities of the 4s and $4p_z$ orbitals of Fe are less than the electronegativity of the 2s orbital of the C atom, which is dominant in the first two MO's (Table 4). Thus, if COM occurs, the introduction of a weight factor leads to an increase of the orbital populations of the least electronegative atoms.

The analysis of the ferrocene MO's symmetry has shown us that their sequence is unaltered for the eight lowest lying MO's in all our calculations and coincides with that of ref. [4]. Higher

on, some alterations may occur; for example, in Table 4, orbital No.27 in (A) becomes No.29 in (B).

The COM phenomena deserves some remarks which we made long ago from another point of view [26-28]. It is not peculiar to valence or more extended basis sets, for it may appear in the π approximation when introducing overlap [26]. The expectation that the lowest energy level should correspond to a nodeless wavefunction relies upon the analogy between LCAO and "electron-in-a-box" wavefunctions [29]. Care must be taken not to follow this analogy too literally [30]. If the Hamiltonian H commutes with S, a calculation with overlap will lead to the same bond order results as one without overlap [9,10,28,31]. When the commutator $[H,S] \neq 0$, its eigenvalues move away from zero [32] and the principal directions of H and S do not coincide any more. It is [H,S] which rules the behaviour of each approximation; if it does not vanish, the difference between an LCAO calculation with overlap and a Hückel calculation may become qualitative. For instance, a nodal wavefunction for the lowest energy level may be obtained [26,28] and this needs not at all be considered anomalous.

4. Conclusions

-One of the causes giving rise to negative electronic populations is the equipartition of bond populations.

-In semiempirical calculations, the negative populations obtained following any definition can be improved through an adequate

choice of parameters.

-Even with COM persistance, the introduction of a weight such as the one proposed here, combined with an appropriate parameterization, permits avoiding negative populations.

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TABLE 1 - Comparison of EH results for the different bond population definitions, with the same parameters: Wolfsberg-Helmholz H_{ij} [24], exponents for Fe from ref. [21].

Bond Population	Mulliken	Wiberg	Bond Index	
			no weight	with weight
C-C	1.145	1.246	1.450	1.242
C-H	0.889	0.982	1.032	0.944
Fe-C	-0.391	0.387	-0.176	0.249
Fe-H	-0.065	0.010	-0.040	0.003
10(Fe-C+Fe-H)	-4.56	3.97	-2.16	2.52

TABLE 2 - Effect of parameterizations and weight on IEH atomic charges and bond populations. (*) ζ_{Fe} from [21]; (**) Slater's ζ_{Fe}. [a] Wolfsberg-Helmholz [24]; [b] ref. [4].

		Mulliken [4]	Bond Index (*)				Bond Index (**)		Ab-Initio S C F	
			no weight		with weight		no weight	with weight		
		H_{ij}^{b}	H_{ij}^{a}	H_{ij}^{b}	H_{ij}^{a}	H_{ij}^{b}	H_{ij}^{a}	H_{ij}^{a}	ref. [3]	ref. [25]
Net atomic charges	Fe	0.464	0.336	0.297	0.236	0.242	0.489	0.382	1.228	1.388
	C	-0.052	-0.047	-0.044	-0.052	-0.045	-0.061	-0.063	-0.311	-0.206
	H	0.005	0.014	0.020	0.030	0.031	0.013	0.026	0.188	0.067
Bond populations	C-C	1.081	1.351	1.314	1.237	1.245	1.312	1.204	1.090	
	C-H	0.837	1.014	0.999	0.950	0.957	1.006	0.955	0.853	
	Fe-C	0.049	0.101	0.247	0.294	0.291	0.143	0.287	-0.067	0.072
	Fe-H	-0.013	-0.018	-0.006	0.004	0.002	-0.015	0.002	-0.009	-0.008
10(Fe-H+Fe-C)		0.36	0.83	2.41	2.98	2.93	1.28	2.89	-0.76	0.64

TABLE 3 - Comparison of IEH atomic orbital populations.

(*) ζ_{Fe} from [21]; (**) Slater's ζ_{Fe}. [a] Wolfsberg-Helmholz [24]; [b] ref. [4].

			Mulliken [4]	Chirgwin and Coulson (*)				Chirgwin and Coulson (**)	
				no weight		with weight		no weight	with weight
			H_{ij}^{b}	H_{ij}^{a}	H_{ij}^{b}	H_{ij}^{a}	H_{ij}^{b}	H_{ij}^{a}	H_{ij}^{a}
Fe	3d	z^2	1.978	1.980	1.981	1.986	1.987	1.977	2.013
		xz,yz	0.847	1.190	0.968	0.898	0.897	1.206	1.027
		x^2-y^2,xy	1.901	1.908	1.883	1.872	1.871	1.817	1.763
	4s		0.013	-0.027	0.041	0.046	0.071	0.017	0.023
	4p	x,y	0.140	0.065	0.133	0.073	0.101	-0.023	0.006
		z	-0.232	-0.614	-0.252	0.047	-0.031	-0.481	-0.012
C	2s		1.195	1.235	1.173	1.276	1.269	1.210	1.274
	2p	x,y	0.918	0.937	0.923	0.867	0.855	0.891	0.869
		z	1.021	0.945	0.999	1.029	1.028	1.023	1.068
H	1s		0.995	0.986	0.980	0.971	0.970	0.985	0.974

TABLE 4 - Contribution of individual MO's to Chirgwin and Coulson atomic orbital populations.

Energy levels: ε_i. Abbreviations used for wavefunctions: iron [4s(s), 4p$_z$(z), 3d$_z$2(z^2)], carbon [2s(s); 2p$_x$, 2p$_y$(σ); 2p$_z$(π)], hydrogen (H). (A) no weight; (B) with weight.

Nº	Γ_i	ε_i(-eV)	Metal's coefficients	C and H coefficients	Fe's atomic orbital population	
					4s	4p$_z$
			(A)			
1	a_2''	29.66293	-0.3683 z	0.2652 s -0.0220 π -0.0309 σ 0.0561 H		-0.6443
2	a_1'	28.63933	0.1102 s 0.0006 z^2	-0.2245 s 0.0068 π 0.0007 σ -0.0322 H	-0.1696	
11	a_1'	16.25620	-0.0179 s 0.1340 z^2	0.0245 s 0.0034 π -0.1641 σ -0.1487 H	0.0010	
12	a_2''	15.94547	0.0164 z	-0.0194 s -0.0053 π 0.1748 σ 0.1513 H		-0.0063
13	a_1'	14.17020	0.1411 s 0.0490 z^2	-0.0164 s -0.2333 π 0.0072 σ 0.0202 H	0.1193	
18	a_2''	13.45603	0.0667 z	0.0016 s -0.2559 π 0.0099 σ -0.0007 H		0.0368
27	a_1'	11.93625	0.0989 s -0.9922 z^2	0.0104 s -0.0101 π -0.0403 σ -0.0427 H	0.0225	
				total	-0.027	-0.614
			(B)			
1	a_2''	30.06139	0.4364 z	-0.2721 s 0.0272 π 0.0371 σ -0.0656 H		0.0334
2	a_1'	28.60397	0.1423 s 0.0064 z^2	-0.2254 s 0.0094 π 0.0021 σ -0.0404 H	-0.0759	
11	a_1'	16.24953	-0.0110 s 0.0843 z^2	0.0304 s 0.0034 π -0.1632 σ -0.1543 H	0.0005	
12	a_2''	15.97059	-0.0265 z	0.0249 s -0.0054 π -0.1734 σ -0.1538 H		-0.0048
13	a_1'	13.95330	-0.1293 s -0.0315 z^2	0.0143 s 0.2347 π -0.0058 σ 0.0192 H	0.1014	
18	a_2''	13.27350	-0.0536 z	-0.0028 s 0.2568 π -0.0081 σ -0.0004 H		0.0187
29	a_1'	10.87129	0.0987 s -0.9982 z^2	0.0096 s -0.0030 π -0.0318 σ -0.0353 H	0.0197	
				total	0.046	0.047