Corrected Mulliken Charges for Small Molecules

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A quantum mechanical correction is applied to the Mulliken atomic charges in order to fit them to the calculated dipole moment. This correction is obtained from the Charge — Charge flux — Overlap model (CCFO) for the interpretation of infrared intensities. Values of corrected Mulliken charges are calculated using different basis sets for the HF, H_2O, NH_3, CH_4, LiF, LiCl and NaCl molecules. The corrected charges are compared with atomic charges obtained from other partitioning schemes. Our results reveal that the corrected Mulliken charge shows an excellent numerical stability when the basis set becomes more extended. It also gives a better description of the charge separation in predominantly ionic molecules. Finally, the Mulliken charge seems to reflect more adequately intramolecular interactions when corrected as above.

INTRODUCTION

In the recent years various partitioning schemes of molecular charge have been employed to define atomic charges in molecules[1-8]. However, the definition of atomic charge has always a certain degree of arbitrariness[9] and the use of different partitioning schemes can lead to quite different atomic charges. Of these, the Mulliken partitioning scheme[1] is the one most often used to study chemical reactivity in molecules, in spite of some generally recognized limitations, such as underestimation of charge separation in ionic molecules and large dependence on the basis set. Furthermore, the Mulliken charges often fail to reproduce the calculated dipole moment.

In order to fit the Mulliken atomic charges ζ_α^M to the calculated molecular dipole moment, we have recently proposed[10] a quantum-mechanical correction deduced from the Charge — Charge flux — Overlap (CCFO) model elaborated by King and Mast[11] for the interpretation of infrared intensities. In this paper we compare the corrected Mulliken charges ζ_α^{corr} with atomic charges deduced from other partitioning schemes, and report their variations with the basis set. We also show with some examples that ζ_α^{corr} may allow a

better description of intramolecular interactions in molecules and of the dependence of atomic charges on the surroundings.

RESULTS AND DISCUSSION

The CCFO model[11] allows an element $P_\alpha^{\sigma\nu}$ of the atomic polar tensor[12], obtained from a molecular orbital calculation, to be divided into three contributions: (i) Equilibrium Mulliken charge (ζ_α^M), (ii) charge fluxes ($\Sigma_\beta \partial\zeta_\beta / \sigma_\alpha \nu_\beta^\circ$, and (iii) overlap term ($\Delta_{ov,\alpha}^{\sigma\nu}$). This model has suggested to us[10] a more consistent way of defining Mulliken atomic charges by considering the $\Delta_{ov,\alpha}^{\sigma\sigma}$ element of the overlap tensor. Here σ is the cartesian axis perpendicular to the local symmetry plane containing atom α: this term, when added to Mulliken charge, makes it fit the calculated dipole moment. The corrected Mulliken charges are then represented as:

$$\zeta_\alpha^{corr} = \zeta_\alpha^M + \Delta_{ov,\alpha}^{\sigma\sigma} \tag{1}$$

Table I shows the values of ζ_α^M and ζ_α^{corr} calculated using the 6-31G** basis set for the HF, H_2O, NH_3 and CH_4 molecules. For comparison, atomic

TABLE I

*Comparison of ζ_H^M, ζ_H^{corr}, ζ_H^L, ζ_H^{EP} and ζ_H^B (for definitions see text) calculated with a 6-31G** basis set in various molecules. Units of electrons, (e).[a]*

Molecule	ζ_H^M	ζ_H^{corr}	ζ_H^{EP}	ζ_H^L	ζ_H^B
HF	0.40	0.45	0.46	0.21	—
H_2O	0.34	0.39	0.40	0.17	—
NH_3	0.26	0.30	0.34	0.13	0.41
CH_4	0.12	0.09	0.12	—0.02	—0.06

[a] ζ_H^{EP}, ζ_H^L and ζ_H^B are taken from references 3, 15 and 5, respectively.

charges obtained from other partitioning schemes are also given. We can observe that the $\Delta_{ov,\alpha}^{\sigma\sigma}$ correction tends to make ζ_H^{corr} very similar to the atomic charges derived from electrostatic potentials[4,3] (ζ_H^{EP}). We have recently shown this similarity in a large number of molecules[13]. On the other hand, atomic charges derived from the Löwdin partitioning scheme[2] (ζ_H^L) are lower than the others; the value of ζ_H^L for CH_4 is very similar to that proposed by the Bader partitioning scheme[5] (ζ_H^B). Both ζ_H^L and ζ_H^B lead to assignment C^+H^-, in constrast to ζ_H^{corr}, ζ_H^M and ζ_H^{EP}, which lead to assignment C^-H^+, in agreement with experimental charges deduced from the observed dipole moments and infrared intensities[14].

It is interesting to analyze the dependence on the basis set of these different partitioning schemes: in Table II we give values of ζ_H^{corr}, ζ_H^M, ζ_H^L and ζ_H^{EP} for the molecule HF using the STO-3G, 6-31G, 6-31G* and 6-31G** basis sets. To our knowledge, no Bader atomic charges (ζ_H^B) of HF have so far appeared in the literature. Variations of the atomic charges with the basis set can be better visualized by looking at Figure 1. There are two distinct groups: one composed of ζ_H^{corr} and ζ_H^{EP}, and the other of ζ_H^M and ζ_H^L. The main differences between the two groups are: (i) ζ_H^{corr} and ζ_H^{EP} exhibit excellent numerical stability when the basis set becomes more

TABLE II

Comparison of ζ_H^M, ζ_H^L, ζ_H^{corr} and ζ_H^{EP} calculated for HF using various basis sets. Units of electrons, (e).[a]

Atomic charge	STO-3G	6-31G	6-31G*	6-31G**
ζ_H^M	0.21	0.48	0.54	0.41
ζ_H^L	0.15	0.37	0.41	0.21
ζ_H^{corr}	0.29	0.52	0.45	0.45
ζ_H^{EP}	0.30	0.53	0.64	0.46

[a] Values of ζ_H^L and ζ_H^{EP} are taken from references 15 and 3—4, respectively.

extended, in contrast to ζ_H^M and ζ_H^L; (ii) even if ζ_H^M and ζ_H^L show the same variation with the basis set, values of ζ_H^L are always much lower than the corresponding values of ζ_H^M. Also NH_3 and H_2O follow the same trend of Figure 1, when results from References 13 and 15 are used.
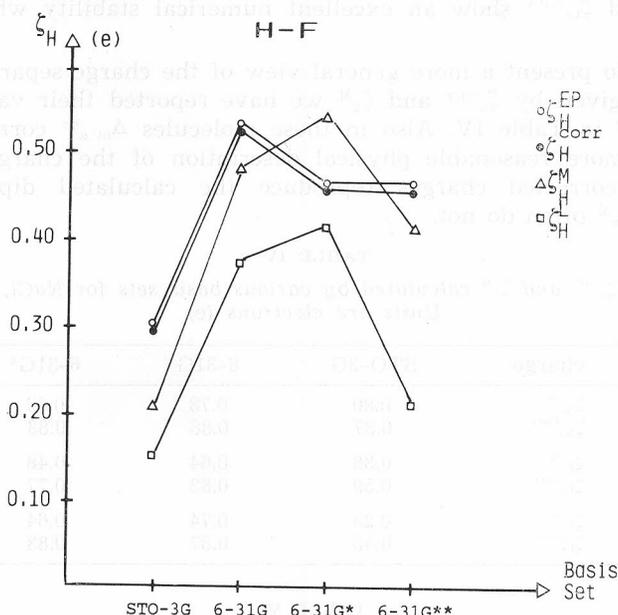
Figure 1. Variation of the Hydrogen atomic charge in HF with the extention of the basis set. The following atomic charges are reported: △, ζ_H^M (Mulliken charges; ●, ζ_H^{corr} (Mulliken charges corrected to fit the dipole moment); ○, ζ_H^{EP} (charges from Electrostatic Potentials); □, ζ_H^L (from Lowdin partitioning scheme).

Let us now consider the case of predominantly ionic molecules. Initially we take the LiF molecule as an example. In Table III we report the values of ζ_{Li}^M, ζ_{Li}^{corr}, ζ_{Li}^L, ζ_{Li}^{DI} and ζ_{Li}^{NPA} using the STO-3G, 4-31G and 6-31G* basis sets. Here ζ_{Li}^{DI} and ζ_{Li}^{NPA} are atomic charges of lithium obtained by the density integration (DI) method of Collins and Stretwieser[6] and by the natural population analysis (NPA) proposed by Reed *et al.*[7], respectively. From this Table we can observe that the values of ζ_{Li}^{corr}, ζ_{Li}^{DI} and ζ_{Li}^{NPA} are substantially

TABLE III

Comparison of ζ_{Li}^M, ζ_{Li}^L, ζ_{Li}^{DI}, ζ_{Li}^{NPA}, ζ_{Li}^{corr} calculated for LiF using various basis sets. Units of electrons, (e).[a]

atomic charge	STO-3G	4-31G	6-31G*	6-31G**
ζ_{Li}^M	0.23	0.72	0.64	0.66
ζ_{Li}^L	0.09	0.58	0.35	—
ζ_{Li}^{DI}	0.62	0.86	0.87	—
ζ_{Li}^{corr}	0.48	0.86	0.83	0.83
ζ_{Li}^{NPA}	0.53	0.92	0.93	—

[a] ζ_{Li}^L, ζ_{Li}^{DI} and ζ_{Li}^{NPA} from reference 15, 6 and 7, respectively.

congruent for any basis set, while ζ_{Li}^M and ζ_{Li}^L are appreciably lower than the others. The value which better describes the degree of ionicity is the one which better fits the molecular dipole moment; therefore, more adequate values are provided by ζ_{Li}^{corr}; ζ_{Li}^M and ζ_{Li}^L seem to give a poor estimation of the polarity in LiF, as already noticed by Kar and Sannigrahi[15]. Moreover, ζ_{Li}^{corr} ζ_{Li}^{DI} and ζ_{Li}^{NPA} show an excellent numerical stability when the basis set changes.

In order to present a more general view of the charge separation in ionic molecules as given by ζ_α^{corr} and ζ_α^M we have reported their values for LiF, LiCl and NaF in Table IV. Also in these molecules $\Delta_{ov,\alpha}^{\sigma\sigma}$ correction makes ζ_α^{corr} give a more reasonable physical description of the charge separation, because the corrected charges reproduce the calculated dipole moment, whereas the ζ_α^M often do not.

TABLE IV

Comparison of ζ_α^{corr} and ζ_α^M calculated by various basis sets for NaCl, LiCl and LiF. Units are electrons (e)

Molecule	charge	STO-3G	6-31G	6-31G*	6-31G**
NaCl	ζ_{Na}^M	0.80	0.78	0.66	0.66
	ζ_{Na}^{corr}	0.87	0.88	0.83	0.83
LiCl	ζ_{Li}^M	0.38	0.64	0.48	0.48
	ζ_{Li}^{corr}	0.59	0.82	0.77	0.77
LiF	ζ_{Li}^M	0.23	0.74	0.64	0.66
	ζ_{Li}^{corr}	0.48	0.87	0.83	0.83

TABLE V

Comparison of the calculated hydrogen charges and CH bond properties[a]

Molecule	ν_{CH} (cm^{-1})	r_{CH}° (A)	A_{CH} (darks)	ζ_H^{corr} (e)	ζ_H^M (e)
	EXP			6-31G**	
C_2H_4	3060	1.085	960	0.147	0.127
HCOF	2981	1.093	1750	0.088	0.146
HCOH	2813	1.111	8155	0.073	0.099

[a] The values of ν_{CH} and r_{CH}° are from reference 16; ν_{CH} is the CH bond stretching frequency measured in the deuterated derivative where only one CH appears. A_{CH} is the contribution to the total CH stretching intensity by each CH bond, in the infrared spectra.

The fact that the application of the $\Delta_{ov,\alpha}^{\sigma\sigma}$ correction to ζ_α^M leads to a better description of intramolecular interactions has been largely commented elsewhere[10]. We add here another example: the decrease of CH bond strength from ethylene to formaldehyde is well known[16], as shown by an increase in bond length and decrease in CH stretching frequency.
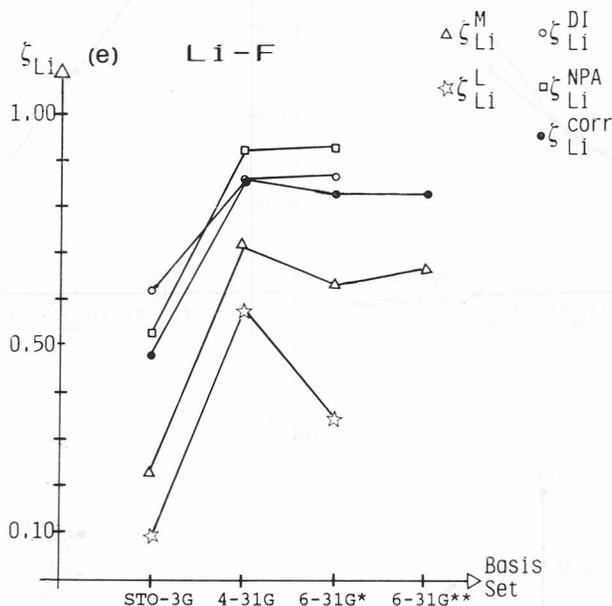
Figure 2. Variations of the Lithium atomic charge in LiF with the extention of the basis set. The following atomic charges are reported: $\triangle$, ζ_{Li}^M (Mulliken charges); $\bullet$, ζ_{Li}^{corr} (Mulliken charges corrected to fit the dipole moment); $*$, ζ_{Li}^L (from Löwdin partitioning scheme); $\bigcirc$, ζ_{Li}^{DI} (charges from density integration); $\square$, ζ_{Li}^{NPA} (charges from natural population analysis).

This is due to backdonation of electronic charge from the lone-pair of Oxygen to σ^*_{CH}. The consequence should be a decrease of atomic charge on Hydrogen[17], as revealed both by ζ_H^M and ζ_H^{corr} and a consequent increase in the CH stretching infrared intensity (which, indeed, has an increment of one order of magnitude). However, when also HCOF is considered, where the effect of backdonation is in part compensated by the inductive effect of Fluorine, ζ_H^{corr} gives correctly an account of this, while ζ_H^M wouldn't.

Another example of the superiority of ζ_α^{corr} on ζ_α^M in revealing intramolecular interactions is reported in Table VI. Hydrogen charges in the CH bonds are expected to be different according to the hybridization of Carbon: sp^3, sp^2, sp Carbon atoms show different electronegativities. However, ζ_H^M does not distinguish in a clear way sp^3 from sp^2 hybridization, while ζ_H^{corr} gives a much clearer pattern. Notice that both ν_{CH} and r_{CH}° show the same trend of ζ_H^{corr}, as expected. As shown in Figure 3, the trend of ζ_X^{corr} vs. hybridization is linear not only for the hydrocarbons (X=H) but also for their halogenated derivatives (X=F, Cl). Instead, ζ_X^M, also for X=F, Cl does not stress as clearly as ζ_X^{corr}, the difference in carbon electronegativity.
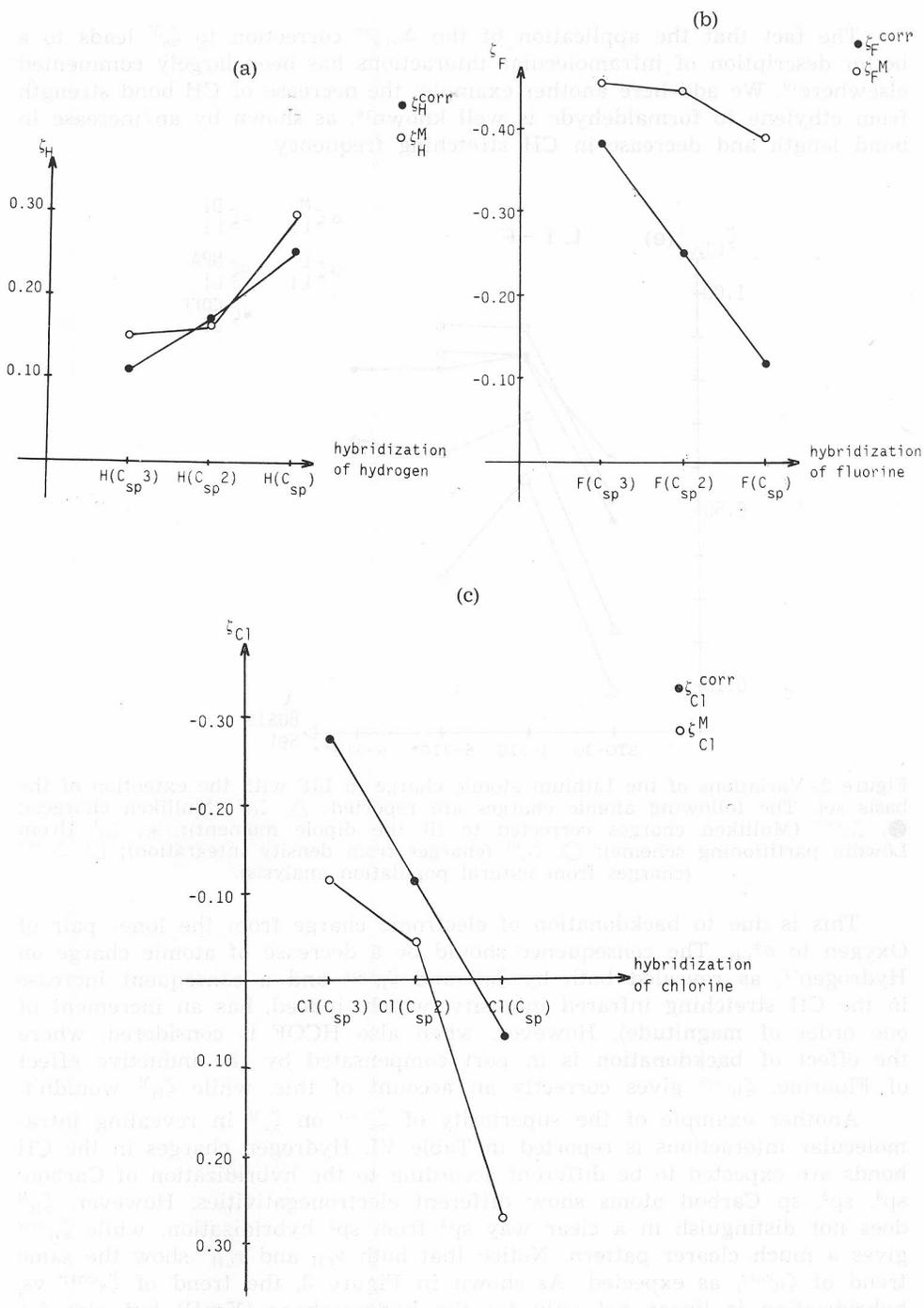
Figure 3. ○, ζ_X^M (Mulliken atomic charges) and ●, ζ_X^{corr} (Mulliken atomic charges corrected to fit the dipole moment) for: (a) X = H; (b) X = F; (c) X = Cl bonded to C (sp³), C (sp²) and C (sp).

Unfortunately, the $\Delta_{ov,\alpha}{}^{\sigma\sigma}$ is not univocally defined for non planar molecules containing atoms with lone-pairs: for example $\Delta_{ov,\alpha}{}^{\sigma\sigma}$ is not univocally defined in CH_3F. In these cases $\Delta_{ov,\alpha}{}^{\sigma\sigma}$ contains a dynamical contribution which changes with the orientation of the lone-pair with respect to the reference system. For instance, we can define two local planes containing the hydrogen atom in CH_3F: the CHH and the CHF planes. This leads to different values of $\Delta_{ov,H}{}^{\sigma\sigma}$ because the relevant charge fluxes due to the presence of lone-pairs have different projections on different reference systems. However, the variation of $\Delta_{ov,H}{}^{\sigma\sigma}$ with the variation of the reference system is relatively small and tends to decrease with the size of the basis set (se Table VII). In this Table we report values of $\zeta_H{}^M$ and $\Delta_{ov,H}{}^{\sigma\sigma}$ calculated with the 4-31G and 6-31G** basis sets in two different orientations of the reference system for CH_3F, CH_3Cl, CH_2F_2 and CH_3CH_3 Of course $\Delta_{ov,H}{}^{\sigma\sigma}$ for CH_3CH_3 is invariant with the orientation of the reference system because of the absence of atoms with lone-pairs.

TABLE VI

Comparison of the calculated charges of hydrogen atoms bonded to carbon atoms in different hybridization states (sp^3, sp^2 and sp) and other CH bond properties

Molecule	ν_{CH} (cm^{-1})	$r_{CH}{}^\circ$ (A)	$\zeta_H{}^{corr}$ (e)	$\zeta_H{}^M$ (e)
C_2H_6	2950	1.096	0.109	0.150
C_2H_4	3050	1.085	0.172	0.164
C_2H_2	3300	1.060	0.253	0.299

TABLE VII

*Values of $\Delta_{ov,H}^{XX}$ in CH_3F, CH_2F_2 and CH_3Cl calculated with the 4-31G and 6-31G** basis sets in two different orientations of the reference system. Values of $\zeta_H{}^M$ are given for comparison. Units of electrons, e.*

Molecule	$\zeta_H{}^M$	$(\Delta_{ov,H}^{XX})$ a	6-31G** (4-31G) $(\Delta_{ov,H}^{XX})$ b	a—b
CH_3F	0.11	—0.03	—0.02	—0.01
	(0.16)	(—0.04)	(—0.02)	(—0.02)
CH_3Cl	0.17	—0.06	—0.04	—0.02
	(0.22)	(—0.10)	(—0.07)	(—0.03)
CH_3CH_3	0.11	—0.02	—0.02	0.00
	(0.15)	(—0.04)	(—0.04)	(0.00)
CH_2F_2	0.10	—0.03	—0.03	0.00
	(0.18)	(—0.09)	(—0.08)	(—0.01)

a = yz in the CHH plane.
b = yz in the CHX plane with X = F, Cl and CH₃.

The variation of $\Delta_{ov,}{}^{\sigma\sigma}$ with the orientation is small also for $\alpha \neq H$ atoms (Table VIII). Notice that in the case of fluorine the difference in $\Delta_{ov,F}{}^{\sigma\sigma}$ for different orientations is about 19% $\Delta_{ov,F}{}^{\sigma\sigma}$; in the case of Chlorine about 3% $\Delta_{ov,Cl}{}^{\sigma\sigma}$. However, the $\Delta_{ov,\alpha}{}^{\sigma\sigma}$ itself is not negligible, both for Fluorine and for Chlorine.

TABLE VIII

Values of $\Delta_{ov,d}^{xx}$ with $\alpha = F$ and Cl calculated with a basis set 4-31G basis set in two different orientations of the reference system for several molecules. Values of ζ_α^M are given for comparison. Units of electrons, e.

Molecule	ζ_α^M	$(\Delta_{ov,\alpha}^{xx})_a$	$(\Delta_{ov,\alpha}^{xx})_b$	a—b
$\alpha = F$				
CH_2F_2	—0.43	0.07	0.06	0.01
CHF_3	—0.40	0.06	0.06	0.00
$CFClH_2$	—0.40	0.07	0.03	0.04
$\alpha = Cl$				
CH_2Cl_2	—0.03	—0.17	—0.18	0.01
$CHCl_3$	0.08	—0.22	—0.24	0.02
$CClFH_2$	—0.09	—0.16	—0.15	—0.01

a = yz in the CXY plane with X and Y = F and/or Cl.
b = yz in the CXH plane with X = F or Cl.

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SAŽETAK

Korigirani Mullikenovi naboji (atoma) u nekim malim molekulama

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Predložena je korekcija Mullikenovih atomskih naboja tako da reproduciraju izračunate dipolne momente. Korekcija je izvedena u okviru modela koji se koristi za interpretaciju infracrvenih intenziteta. Vrlo dobri rezultati dobiveni su za proširene skupove osnovnih funkcija.