Population Analysis from Atomic Polar Tensors ?

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Atomic charges derived from atomic polar tensors are calculated by the *ab initio* method using a 6-31G** basis set. This charge, Q_α as defined, is invariant under rotation of the coordinate system, and their sum for all atoms in the molecule is zero. A test with water and ammonia molecules shows that it is almost invariant with respect to the basis set. A linear relationship is found between the atomic charge, Q_α, and the partical charge for the hydrogen atom which is calculated using the equalization of the electronegativity principle. Also, an excellent linear regression is obtained when Q_α is ploted against the IR experimental charge.

1. INTRODUCTION

One of the main results obtained from an *ab initio* SCF calculation is the charge density, which describes the probability of finding an electron in various regions of the space. A quantitative characterization of this charge density is obtained by calculating the molecular dipole moment (moment of charge). The partitioning of the dipole moment into atomic and bonding contributions has been explored for a long time, among others by Mulliken, Coulson and Ruedenberg [1-3]. Also, many atempts have been made in order to establish a distribution of the electronic charge among the atoms in the molecule [4-6], according to the chemical intuition. Although there is no unique way of partitioning the electronic charge, the population analysis is very useful in general for interpretative purposes and essential in molecular mechanics.

The dipole moment vector p for neutral molecules is invariant with respect to a translation of the molecule, but the magnitude of its contributions changes with the choice of the origin. Recently, we have presented a method for partitioning p, which is independent of the origin of the coordinate system [7]. The derivatives of p with respect to the cartesian coordinates of the atoms are directly connected to the infrared intensities by a method which is well known as the atomic polar tensor (APT) formalism [8,9]. In this formalism, for each atom α in the molecule there exists a (3x3) matrix $P_x^{(\alpha)}$ whose elements are $(\delta p_\tau / \delta \xi_\alpha)$, where p_τ is a

component of the dipole moment ($\tau = x, y, z$) and ξ_α a coordinate of atom α ($\xi = X, Y, Z$). Those derivatives have been interpreted in terms of atomic charges by Gussoni et al, Dinur and Cioslowski [10-12]. A partition of the APT in terms of charge and charge flux tensors has recently been proposed also by the present author [13,14]. In the latter model, the atomic charge of an atom α in the molecule, is defined as the averaged trace of the charge tensor.

$$Q_\alpha = \frac{1}{3} T_r (P_x^{(\alpha)} charge) \qquad (1)$$

This definition was motivated partially by the fact that the charge tensors are in general neither diagonal nor isotropic. The charge tensor ($P_x^{(\alpha)}$charge) is the sum of Mulliken's net atomic charge tensor and a term obtained from the homopolar dipole flux tensor [14]. The first tensor is diagonal and its elements are the Mulliken's net atomic charge q_α. The other is a tensor in which the elements are given by

$$-\sum_{B \neq \alpha} \sum_\mu^\alpha \sum_\nu^B 2 P_{\mu\nu} \nabla_\alpha \left(<\phi_\mu | r - \frac{R_\alpha + R_B}{2} | \phi_\nu > \right)$$

where $P_{\mu\nu}$ is a density matrix element. ϕ_μ and ϕ_ν are atomic orbitals belonging to atoms α and B respectively. The term between bars inside the brackets is the distance from the center of the electronic charge to the middle of the chemical bond α-B. The defined atomic charge Q_α can be interpreted as a correction to the Mulliken's charge. They are invariant under rotation and translation of

Table I. *Ab initio* and experimental atomic charges and mean dipole derivatives. Units (e)

molecule	q_α	Q_α	ξ_α^{curr}	$\overline{P}_x^{(\alpha)}$	$\overline{P}_{exp}^{(\alpha)}$ *	q^o_{exp} **
H̲F	0.387	0.460	0.449	0.420	0.382 *	0.41
H̲₂O	0.335	0.400	0.394	0.296	0.236 *	0.33
FOH̲	0.379	0.424	0.424	0.318	---	---
NH̲₃	0.264	0.326	---	0.162	0.138 *	0.27
H̲CN	0.268	0.293	0.269	0.273	0.231 *	0.22
CH̲₄	0.118	0.193	---	-0.018	-0.003 *	0.06
C₂H₂	0.233	0.276	0.218	0.215	0.19 **	0.21
LiF̲	-0.660	-0.827	-0.826	-0.837	-0.85 **	-0.84
F̲OH	-0.211	-0.187	-0.099	-0.242	---	---
HC̲N	0.118	0.151	0.069	0.004	---	---

* $\overline{P}_x^{(\alpha)} = $ mean dipole derivative $\frac{1}{3} T_r \left[P_x^{(\alpha)} \right]$, [14].

** experimental equilibrium charges from ECCF model, [10].

the molecule and their sum is zero for a neutral molecule, which are inherent properties of a physically intrinsic quantity. A test with water and ammonia molecules shows that Q_α is not as much basis set dependent as Mulliken's net charge.

2. CALCULATIONS AND RESULTS

The molecules submitted to numerical calculations and analyzed are: HF, LiF, H₂O, FOH, HCN, NH₃, CH₄ and C₂H₂. The charge and charge flux tensors have been calculated by the RHF method using the program GAMESS [15] with a 6-31G** basis set.

Table I shows the atomic charges Q_α calculated using equation (1). In this Table the first column gives the Mulliken's charges. In the third column is found the corrected atomic charges calculated according the definition of Gussoni et al [10] and Dinur [11]. The next column shows the mean dipole derivatives, corresponding to the new population analysis recently proposed by Cioslowski [12], which defines the atomic charge as 1/3 of the trace of the APT. The fifth column gives the experimental mean dipole derivatives. Finally, in the last column

is found the experimental equilibrium charges derived from infrared intensities using the equilibrium charge-charge flux model (ECCF) [10]. These infrared atomic charges as defined, reproduce the experimental dipole moment.

Except for the carbon in HCN and fluorine in FOH, our atomic charge Q_α are in good agreement with the corrected atomic charges ξ_α named this way since they are a correction on Mulliken's charge q_α so as to fit the calculated dipole moment. The agreement are specially good when the differences in the electronegativity between the atom being considered and that one bonded to it is relatively high. It is known that the Mulliken's population analysis underestimates the bond ionicity; our results clearly show the improvement over Mulliken's specially for these cases.

Table II shows the dipole moment calculated as the sum (for all atoms in the molecule) of the products between the atomic charges and the respective vector position. The results show that except for the FOH and HCN molecules, our charges are those which best reproduce the magnitude of the dipole moment.

Table II. *Ab initio* calculated dipole moments. Atomic Units (bohr.e)

molecule	$\left\| \sum_A \rho_A R_A \right\|$			
	$\rho_A = q_A$	$\rho_A = Q_A$	$\rho_A = \bar{P}_X^{(\alpha)}$	SFC
HF	0.659	0.783	0.715	0.765
H_2O	0.719	0.858	0.635	0.845
FOH	0.946	0.971	0.920	0.846
NH_3	0.544	0.672	0.334	0.723
HCN	1.363	1.537	1.139	1.261
LiF	1.939	2.430	2.459	2.428

Although the Q_H for the FOH molecule is the same as the corrected charge, the discrepancy in the calculated dipole moment is due to the fluorine charge Q_F which is overestimated, the same happening to HCN. Observe that the better agreement between the dipole moment obtained by using Mulliken's charge and the mean dipole derivative must be due to a cancellation of errors if the corrected charge is taken as the exact point charge.

Table III. Ab initio atomic charges and their basis set dependence. Units (e)

	basis set	q_H *	Q_H *	Exp **
H_2O				
	STO-3G	0.181	0.332	
	4-31G	0.392	0.460	0.33
	6-31G**	0.335	0.400	
NH_3				
	STO-3G	0.157	0.276	
	4-31G	0.298	0.362	0.27
	6-31G**	0.264	0.326	

* q_α - Mulliken's net atomic charge; Q_α - see equation (1) in the text.
** from ref. [10].

The basis set dependence was analyzed through the examples of a planar molecule, H_2O, and a non-planar molecule, NH_3. The results are shown in Table III, for three different basis set STO-3G, 4-31G and 6-31G**. From those results it can be seen that our atomic charge is rather insensitive to the choice of the basis set unlikely Mulliken's which changes substantially.

The atomic charges for hydrogen atom are shown to be linearly related to the hydrogen partial charges as show in Fig. (1). The partial charge is calculated using the equalizations of the electronegativities of the combining atoms according to the procedure proposed by Huheey [16].
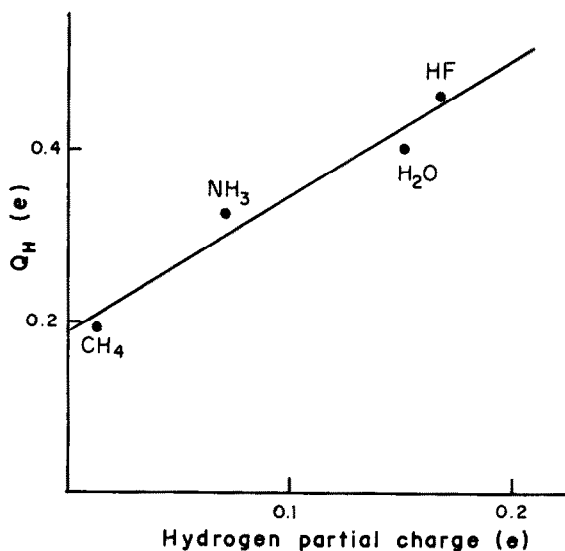

Fig. (1). Regression of hydrogen atomic charge on partial charge for the HF, H_2O, NH_3 and CH_4 molecules.

Finally, Q_H shows an excellent linear relation with the experimental hydrogen charge q_{exp}^o derived from IR intensities [10], specially when the methane (where the covalent bond CH is nearly homopolar) is not included in the linear regression, as can be seen in Fig. (2).

It is shown in this paper that the atomic charge Q_α as defined is physically meaningful. Further calculations including electron correlation

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have to be carried out in order to obtain a better insight of their behavior.
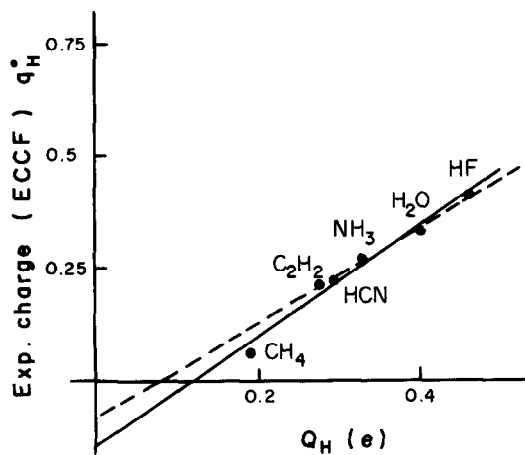

Fig.(2). Plot of the hydrogen atomic charge Q_H versus the experimental charge (ECCF), including the methane in the linear regression (——) and not including (----).

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