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Ab-initio Atomic Charges from Atomic Polar Tensors

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Abstract
The dipole moment derivatives with respect to the cartesian coordinates are explained in terms of charge and charge flux tensors, which are calculated for the hydrogen and fluorine atoms for a series of molecules. The 4-31G basis set is used in these calculations. An atomic charge is derived from the charge tensor which is within a narrower range of values than Mulliken's net atomic charge and in excellent agreement with the Mulliken's corrected charge for the H_2O and CH_3OH molecules.

1. INTRODUCTION

The analysis of the infrared intensities, formulated in terms of atomic polar tensors (APT)[1] has been widely used in the last fifteen years. The APT have been interpreted, in terms of quantum mechanical molecular orbital calculations, by the charge, charge-flux, overlap (CCFO) model[2,3] and by the recently proposed[4] method for the partitioning of the APT. In the present work, the calculated APT is interpreted according to the charge and charge flux contributions. Also, an atomic charge is obtained from this charge tensor.

The APT for a given atom α, $\underset{\sim}{P}_x^{(\alpha)}$, which is the gradient of the dipole moment vector $\vec{p}$, is given by

$$\underset{\sim}{P}_x^{(\alpha)} = q_\alpha \underset{\sim}{E} + \sum_A (\nabla_\alpha q_A)\vec{R}_A - \sum_A \sum_{\mu<\nu}^{A} \nabla_\alpha (2P_{\mu\nu} \vec{R}^A_{\mu\nu}) - \sum_{A<B} \sum_\mu^A \sum_\nu^B \nabla_\alpha (2P_{\mu\nu} \vec{R}^{AB}_{\mu\nu}) \quad (1)$$

where q_α is the Mulliken's net atomic charge and $\underset{\sim}{E}$, a 3 x 3 unit matrix. The second term in eq. (1) is the charge flux and the last two are the atomic and homopolar dipole flux

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contributions[4] respectivelly, where $P_{\mu\nu}$ are density matrix *elements and* $\vec{\hat{R}}_{\mu\nu}$ *the respective centers of charge. The* gradient of the product ($P_{\mu\nu}$ $\bar{R}^{\wedge *}_{\mu\nu}$) in eq. (1) yields two tensors, the bonding charge and another charge flux. So, the Mulliken's net atomic charge added to the bonding charge (from the homnopolar dipole flux) gives the total atomic *charge tensors. By the other hand, the charge flux added to* the charge fluxes from the atomic and homopolar dipole fluxes gives the total charge flux tensor. So, the APT can be explained in terms of the total charge and charge flux tensors. Most of the time, the total charge tensor is not diagonal. Nevertheless, note that the Euclidean norm and the averaged trace of the total charge tensor, unlike its elements, are invariant upon rotation of the axis. Consequently they have an intrinsic physical meaning. So, it is reasonable to define the atomic charge as follows[5]:

$$\sqrt{1/3\ T_r\ [(P_x^{(\alpha)}\text{charge})(P_x^{(\alpha)}\text{charge})^T} \qquad \text{norm of the total charge tensor} \qquad (2a)$$

or

$$1/3\ T_r\ (P_x^{(\alpha)}\text{charge}) \qquad \text{average trace of total charge tensor} \qquad (2b)$$

The total charge and charge flux tensors have been calculated for the hydrogen and fluorine atoms for a series of molecules. All calculations were made using a 4-31G basis set with the R_α bond lying on the Z axis, where R is a heavy atom and α stands for either the hydrogen or the fluorine atom.

2. RESULTS

The total charge and charge flux contributions to the hydrogen and fluorine atoms for the studied molecules are in Table I. The experimental values also shown in that Table, are in good agreement with the calculated APT. Note that the P_{xx} and P_{xy} elements of the charge tensor for the hydrogen bonded to the carbon atom have the same order of magnitude ranging from 0.113 for the CH_4 to 0.132e for the CHF_3 molecule. For the hydrogen bonded to other atoms, these values grow with the electronegativity of the heavy atom. The P_{xx} and P_{xy} elements for the fluorine charge tensor, (abount 0.4e) also does not vary among the fluoromethanes. *The numerical values of the* P_{zz} *elements of the hydrogen* charge tensors grow with the electronegativity of the heavy atom bonded to the hydrogen. For the fluoromethanes, as the CH bond is stretched, the P_{zz} element of the charge tensor decreases by approximatly 0.04e for each fluorine atom added to the molecule. Note that for the OH stretching in the H_2O, CH_3OH and H_2O_2 molecules, the P_{zz} elements are similar (0.657, 0.649 and 0.635e respectively). On the other hand, when the CF stretching is considered, the P_{zz} element of the charge tensors depends upon the fluoromethane structure. Note also the small values for the P_{xx} and P_{yy} compared to P_{zz} elements of the charge fluxes on the fluorine tensors, indicating that for deformation movements it does no occur a significant change in the charge distribution among the atoms in the molecule. So, the P_{xx} and P_{yy} elements of the fluorine polar tensors are essentially the corresponding elements of the total charge tensor. The electronegativities of the hydrogen and the carbon are similar, consequently, the CH bond is weakly polar and a reasonable charge flux is expected when the CH bond is stretched. On the other hand, the charge flux decreases when the number of fluorine atoms in the molecule increases.

Note that for the H_2O, NH_3 and CHF_3 molecules, when the OH, NH and CH is respectively stretched the charge and charge fluxes contributions for the hydrogen polar tensor are equally important but with opposite sign, cancelling each other. Numerical errors in one or both of these contributions will have a great effect in the final value of the P_{zz} element which is numerically small. That can be a source of difficulties in the theoretical prediction of the band intensities for the stretching mode. For the H_2O and NH_3 molecules, the results are shonw in Table II, suggesting a similar behavior for the CHF_3 molecule.

The calculated atomic charges, given by the norm (eq. (2a)) and by the averaged trace (eq. (2b)) of the charge tensors are in Table III. Note that for the hydrides, HF, H_2O, NH_3 and CH_4, there is an increasing of the hydrogen charge with the electronegativity of the heavy atom. The charge obtained for the hydrogen bonded to the oxygen in the H_2O, H_2O_2 and CH_3OH are nearly constant (0.460, 0.468 and 0.453e for the averaged trace and 0.481, 0.486 and 0.472e for the norm) leading to the conclusion that it is independent of the molecule. The atomic charge obtained for the hydrogen and fluorine in methane and fluoromethanes are practically insensitive to the presence of the fluorine atoms and in a narrower range of values than Mulliken's net atomic charge. Also, for those hydrogen atoms, the atomic charge decreases with increase in the number of fluorine atoms in the molecule while the opposite happens to the Mulliken's charge. The atomic charges obtained by the averaged trace on the above formulation are in excellent agreement with the Mulliken corrected charge[18], (which reproduces the dipole moment), proposed by Gussoni et all. for the hydrogen in the H_2O and CH_3OH molecules. On the other hand, there is a poor agreement for the methane and methyl fluoride although they vary in the same direction, unlike the Mulliken's charge.

Table I.
Calculated charge, charge flux and the experimental tensors. Units are (e).

molecule	charge	charge flux	total	exp.*
$\underline{H}F$	$\begin{bmatrix} 0.459 & & \\ & 0.459 & \\ & & 0.724 \end{bmatrix}$	$\begin{bmatrix} 0.060 & & \\ & 0.060 & \\ & & -0.456 \end{bmatrix}$	$\begin{bmatrix} 0.519 & & \\ & 0.519 & \\ & & 0.268 \end{bmatrix}$	$\begin{bmatrix} 0.415 & & \\ & 0.415 & \\ & & 0.317 \end{bmatrix}$
$\underline{H}_2O$	$\begin{bmatrix} 0.362 & & \\ & 0.362 & 0.005 \\ & -0.004 & 0.657 \end{bmatrix}$	$\begin{bmatrix} 0.102 & & \\ & -0.026 & -0.035 \\ & -0.094 & -0.563 \end{bmatrix}$	$\begin{bmatrix} 0.463 & & \\ & 0.336 & -0.030 \\ & -0.098 & 0.094 \end{bmatrix}$	$\begin{bmatrix} 0.329 & & \\ & 0.247 & -0.064 \\ & -0.049 & 0.132 \end{bmatrix}$
$N\underline{H}_3$	$\begin{bmatrix} 0.259 & & \\ & 0.259 & -0.013 \\ & & 0.569 \end{bmatrix}$	$\begin{bmatrix} -0.058 & & \\ & 0.080 & 0.031 \\ & -0.120 & -0.614 \end{bmatrix}$	$\begin{bmatrix} 0.201 & & \\ & 0.339 & 0.018 \\ & -0.120 & -0.045 \end{bmatrix}$	$\begin{bmatrix} 0.141 & & \\ & 0.238 & 0.037 \\ & 0.063 & 0.035 \end{bmatrix}$
$C\underline{H}_4$	$\begin{bmatrix} 0.113 & & \\ & 0.113 & \\ & & 0.447 \end{bmatrix}$	$\begin{bmatrix} -0.035 & & \\ & -0.038 & \\ & & -0.625 \end{bmatrix}$	$\begin{bmatrix} 0.078 & & \\ & 0.075 & \\ & & -0.178 \end{bmatrix}$	$\begin{bmatrix} 0.062 & & \\ & 0.062 & \\ & & -0.133 \end{bmatrix}$
$\underline{H}_2O_2$	$\begin{bmatrix} 0.392 & 0.011 & \\ & 0.365 & 0.035 \\ & 0.025 & 0.649 \end{bmatrix}$	$\begin{bmatrix} 0.082 & -0.014 & -0.006 \\ & -0.125 & -0.112 \\ -0.014 & -0.058 & -0.439 \end{bmatrix}$	$\begin{bmatrix} 0.474 & 0.003 & -0.006 \\ & 0.240 & -0.077 \\ -0.014 & -0.033 & 0.210 \end{bmatrix}$	$\begin{bmatrix} & & \\ & — & \\ & & \end{bmatrix}$
$CH_3O\underline{H}$	$\begin{bmatrix} 0.368 & & \\ & 0.356 & 0.039 \\ & 0.016 & 0.635 \end{bmatrix}$	$\begin{bmatrix} 0.087 & & \\ & -0.072 & -0.068 \\ & -0.055 & -0.484 \end{bmatrix}$	$\begin{bmatrix} 0.455 & & \\ & 0.284 & -0.029 \\ & -0.039 & 0.151 \end{bmatrix}$	$\begin{bmatrix} 0.260 & & \\ & 0.161 & 0.018 \\ & -0.070 & 0.141 \end{bmatrix}$
$C\underline{H}_3F$	$\begin{bmatrix} 0.116 & & \\ & 0.126 & -0.026 \\ & -0.022 & 0.410 \end{bmatrix}$	$\begin{bmatrix} -0.047 & & \\ & -0.140 & 0.017 \\ & 0.035 & -0.552 \end{bmatrix}$	$\begin{bmatrix} 0.069 & & \\ & -0.014 & -0.009 \\ & 0.013 & -0.142 \end{bmatrix}$	$\begin{bmatrix} 0.073 & & \\ & 0.012 & 0.021 \\ & -0.007 & -0.142 \end{bmatrix}$
$C\underline{H}_2F_2$	$\begin{bmatrix} 0.126 & & \\ & 0.131 & -0.022 \\ & -0.018 & 0.371 \end{bmatrix}$	$\begin{bmatrix} -0.142 & & \\ & -0.114 & 0.014 \\ & 0.046 & -0.480 \end{bmatrix}$	$\begin{bmatrix} -0.016 & & \\ & 0.017 & -0.008 \\ & 0.028 & -0.109 \end{bmatrix}$	$\begin{bmatrix} 0.020 & & \\ & 0.041 & 0.003 \\ & 0.038 & -0.125 \end{bmatrix}$
$C\underline{H}F_3$	$\begin{bmatrix} 0.132 & & \\ & 0.132 & \\ & & 0.341 \end{bmatrix}$	$\begin{bmatrix} -0.147 & & \\ & -0.147 & \\ & & -0.388 \end{bmatrix}$	$\begin{bmatrix} -0.015 & & \\ & -0.015 & \\ & & -0.047 \end{bmatrix}$	$\begin{bmatrix} 0.032 & & \\ & 0.032 & \\ & & -0.072 \end{bmatrix}$
$CH_3\underline{F}$	$\begin{bmatrix} 0.414 & & \\ & -0.413 & \\ & & -0.474 \end{bmatrix}$	$\begin{bmatrix} 0.034 & & \\ & 0.031 & \\ & & -0.362 \end{bmatrix}$	$\begin{bmatrix} -0.380 & & \\ & -0.382 & \\ & & -0.836 \end{bmatrix}$	$\begin{bmatrix} -0.26 & & \\ & -0.26 & \\ & & -0.93 \end{bmatrix}$
$CH_2\underline{F}_2$	$\begin{bmatrix} -0.390 & & \\ & -0.419 & 0.054 \\ & 0.011 & -0.401 \end{bmatrix}$	$\begin{bmatrix} 0.011 & & \\ & -0.021 & -0.008 \\ & -0.041 & -0.477 \end{bmatrix}$	$\begin{bmatrix} -0.378 & & \\ & -0.441 & 0.046 \\ & -0.030 & -0.878 \end{bmatrix}$	$\begin{bmatrix} -0.25 & & \\ & -0.27 & 0.22 \\ & -0.02 & -0.88 \end{bmatrix}$
$CH\underline{F}_3$	$\begin{bmatrix} -0.401 & & \\ & -0.386 & 0.067 \\ & 0.013 & -0.352 \end{bmatrix}$	$\begin{bmatrix} -0.036 & & \\ & -0.037 & -0.015 \\ & -0.062 & -0.504 \end{bmatrix}$	$\begin{bmatrix} -0.437 & & \\ & -0.423 & 0.053 \\ & -0.049 & -0.856 \end{bmatrix}$	$\begin{bmatrix} -0.29 & & \\ & -0.29 & 0.05 \\ & -0.12 & -0.95 \end{bmatrix}$
$C\underline{F}_4$	$\begin{bmatrix} -0.396 & & \\ & -0.389 & \\ & & -0.338 \end{bmatrix}$	$\begin{bmatrix} -0.040 & & \\ & -0.048 & \\ & & -0.437 \end{bmatrix}$	$\begin{bmatrix} -0.436 & & \\ & -0.437 & \\ & & -0.775 \end{bmatrix}$	$\begin{bmatrix} -0.33 & & \\ & -0.33 & \\ & & -0.92 \end{bmatrix}$

* HF, H_2O, NH_3, CH_3 OH and $C\underline{H}_3F$ from ref. [6] and properly rotated; $C\underline{H}_4$ from ref. [7]; $C\underline{H}_2F_2$ from ref.[8]; $C\underline{H}F_3$ from ref; [9]; $CH_3\underline{F}$, $CH_2\underline{F}_2$ and $C\underline{F}_4$ from ref.[10].

Table II.
Predicted intensities obtained by using the 4-31G and 6-31G**basis set and the experimental values. Units are Km/mol.

molecule	basis set	predicted*	experimental*
H_2O (ν_1)	4-31G	2.8	
	6-31G**	16	2.2
NH_3 ($\nu_1 + \nu_3$)	4-31G	28.6	
	6-31G**	1.6	11.4

* from ref. [11]

Table III.
Calculated atomic charges, Mulliken's net atomic and corrected charges. Units are (e).

molecule	calculated atomic charge* averaged trace	norm	Mulliken net atomic charge	Mulliken corrected**
$F\underline{H}$	0.547	0.561	0.479	0.518
$\underline{H}_2O$	0.460	0.481	0.393	0.464
$N\underline{H}_3$	0.362	0.391	0.298	
$C\underline{H}_4$	0.224	0.274	0.153	0.120
$\underline{H}_2O_2$	0.468	0.486	0.432	
$CH_3O\underline{H}$	0.453	0.472	0.399	0.456
$C\underline{H}_3F$	0.217	0.257	0.166	0.109
$C\underline{H}_2F_2$	0.209	0.239	0.186	
$C\underline{H}F_3$	0.202	0.224	0.217	
$CH_3\underline{F}$	-0.434	-0.435	-0.464	
$CH_2\underline{F}_2$	-0.403	-0.405	-0.438	
$CH\underline{F}_3$	-0.380	-0.382	-0.405	
$C\underline{F}_4$	-0.374	-0.375	-0.369	

* for the fluromethanes, the atomic charges are from ref. [5].
** from ref. [12]

3. ACKNOWLEDGEMENT

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