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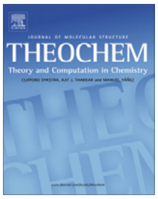

Atomic charges from atomic polar tensors: A comparison of methods

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Different definitions of atomic charge obtained by DFT computed atomic polar tensors are compared in the case of fluorine and chlorine substituted ethylenes. Based on the analytic expressions of atomic polar tensors (APTs) in terms of infrared equilibrium charges and charge fluxes (ECCF) it is shown that the GAPT charges, routinely provided with quantum chemical predictions of vibrational spectra, include a large contribution of charge fluxes that could make them unreliable for a quantitative investigation of molecular charge distribution at equilibrium and poorly transferable from one molecule to molecules sharing the same chemical groups. On the other hand, within the ECCF model, IR equilibrium charges are free from spurious contributions due to dynamical charge rearrangement and they give a description in very good agreement with other popular population schemes based on the fitting of the molecular electrostatic potentials. Furthermore, IR charges obtained from calculated APTs by DFT method give a good quantitative description of the intramolecular chemical/physical effects which take place in molecules, in agreement with the picture provided by ECCF parametrization of experimental IR intensities.

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1. Introduction

The determination of reliable atomic charges is essential for the modeling and the investigation of several physical/chemical properties of molecules and molecular materials. Since the birth of quantum chemistry different schemes were proposed (e.g. Mulliken population analysis [1], Lowdin population analysis [2]) and many others were developed later or are currently developed based on the partitioning of the wave function or of the electronic density (natural population analysis [3], atom-in-molecules charges [4], Hirshfeld partitioning [5]) or based on the fitting of the molecular electrostatic potentials (MK [6], Chelp [7], Chelpg [8]). All these charges share an intrinsic weakness, since they cannot be directly related to experimentally measurable properties and thus their suitability cannot be verified by comparison with a corresponding observable which could be experimentally determined.

Some decades ago, some models were developed for the interpretation of infrared intensities based on the molecular charge distribution and its mobility during vibrational displacements [9,10]. In this ground, models based on electro-optical parameters (EOP) [11], equilibrium charges and charge fluxes (ECCF) [12] and atomic polar tensors (APT) [13] were widely used [10,14]. Those models were initially devoted to the parametrization and interpretation of intensity data rather than to be applied as a general scheme for the description of the charge distribution in molecules and only later their importance in this context was recognized and they were applied to the discussion of chemical/physical properties [10,14,15]. The ECCF model in particular allowed to obtain a definition of atomic charges from experimental IR intensities that could give an interpretation of intramolecular effects such as inductive effects, hyperconjugation, charge backdonation; moreover these charges allow to classify molecular sites in terms of their ability to form hydrogen bonds [10]. On the other hand, some models were developed based on quantum chemically computed properties but sharing the same philosophy; in particular, the charge–charge flux-overlap (CCFO) model [16] and its modified version (CCFOM model [17]) were proposed as the theoretical counterpart of ECCF model. According to CCFOM model, atomic charges are described as corrected Mulliken charges through an overlap contribution which can be obtained on the basis of suitable terms derived from the computed APTs. On the other hand, Cioslowski proposed a straightforward definition of atomic charges based on APT invariants [18]: these charges, named generalized atomic polar tensor (GAPT) charges, can be immediately calculated by standard quantum chemical codes, they satisfy the requirement of electroneutrality of the molecule and they are directly related to experimentally measurable quantities (i.e. IR intensities). These features contributed to the success of GAPT charges as a model alternative to the most used and popular schemes.

In recent papers [19,20], analytical expressions of the APT elements in terms of ECCF parameters have been re-visited and worked out, in order to propose a way to obtain both equilibrium atomic charges (IR charges) and charge fluxes from computed APTs: this model allows a definition of atomic charges and charge

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fluxes which are equivalent to those determined by CCFOM model. On this basis, several classes of organic molecules have been analyzed, showing that a very good description of charge on H atoms in CH bonds [19] and in OH groups [20] can be obtained, in good agreement with charges obtained by other widely used methods.

In this paper, GAPT and IR charges will be compared considering both their analytical relationship and their values (obtained by DFT calculations); their reliability will be discussed through the comparison with available experimental data and with charges obtained by means of the fitting of the molecular electrostatic potentials. It will be shown that in many cases GAPT charges give a very different description from the infrared ones, since they implicitly contains relevant contributions from charge fluxes, as quantitatively proved here. This limitation can be solved (or partially solved) while adopting a definition of atomic charges borrowed from ECCF model, as in the case of IR charges.

To this aim, DFT calculations will be carried out focusing on fluorine and chlorine substituted ethylenes: the charge distribution of these systems has been indeed widely studied in the past thanks to the existence of reliable experimental data [21] and due to the peculiar intramolecular effects involved [22].

IR charges will be used also for the description of peculiar intramolecular interactions occurring in fluorine-substituted ethylenes showing different configurations and a good agreement is obtained with available experimental data, thus assessing the validity of IR charges both qualitatively and quantitatively.

2. Results and discussion

2.1. Model and calculations

GAPT [18] and IR charges [19] are defined on the basis of atomic polar tensors (APT) components: APTs are the tensors that collect the derivatives of the molecular dipole with respect to the cartesian displacements of the atoms and can be represented in form of a 3 × 3 matrix for each atom.

The general uv component of the APT associated to the β atom can be written as:

$$P^{\beta}_{uv} = \left(\frac{\partial M_u}{\partial v_\beta}\right)^0 \tag{1}$$

where the '0' apex indicates the values calculated at the minimum (equilibrium) geometry and the two indexes u and v represent respectively the x, y or z component of the dipole moment being derived and the x, y or z cartesian displacement coordinate of the β atom upon which the derivation is carried out.

IR charges relies on a basic assumption adopted by different models, such as for example the ECCF theory: atomic charges q_α are assumed to be spherically symmetric such as that the molecular dipole moment **M** can be written as:

$$\mathbf{M} = \Sigma_\alpha q_\alpha \mathbf{r}_\alpha \tag{2}$$

where $\mathbf{r}_\alpha$ is the position vector of the α atom.

By adopting this assumption, the atomic dipoles and their changes during vibrations are not considered explicitly. Polarization effects associated to atomic dipoles can be taken into account including atomic dipole fluxes derived for example in the framework of AIM theory [4], as in the Charge–Charge Flux-Dipole Flux (CCFDF) model [23]. However, as analytically shown by Dinur and Hagler [24] and discussed below, in the case of planar molecules, static atomic charges that implicitly include some information on atomic dipoles can be defined, under the assumption of Eq. (2).

On the basis of Eqs. (1) and (2) it is possible to write:

$$P^{\beta}_{uv} = q^0_\beta \delta_{uv} + \Sigma_\alpha \left(\frac{\partial q_\alpha}{\partial v_\beta}\right)^0 u^0_\alpha \tag{3}$$

This equation is general and describes any uv component of the APT; it is based on the only hypothesis that Eq. (2) holds.

On the basis of Eq. (3) and introducing the internal coordinates R^t_β involving displacements of the β atom considered, the three diagonal component of the APT of β atom are:

$$P^{\beta}_{xx} = q^0_\beta + \Sigma_\alpha \left(\frac{\partial q_\alpha}{\partial x_\beta}\right)^0 x^0_\alpha = q^0_\beta + \Sigma_\alpha \Sigma_t \left(\frac{\partial q_\alpha}{\partial R^\beta_t}\right)^0 \left(\frac{\partial R^\beta_t}{\partial x_\beta}\right)^0 x^0_\alpha \tag{4}$$

$$P^{\beta}_{yy} = q^0_\beta + \Sigma_\alpha \left(\frac{\partial q_\alpha}{\partial y_\beta}\right)^0 y^0_\alpha = q^0_\beta + \Sigma_\alpha \Sigma_t \left(\frac{\partial q_\alpha}{\partial R^\beta_t}\right)^0 \left(\frac{\partial R^\beta_t}{\partial y_\beta}\right)^0 y^0_\alpha \tag{5}$$

$$P^{\beta}_{zz} = q^0_\beta + \Sigma_\alpha \left(\frac{\partial q_\alpha}{\partial z_\beta}\right)^0 z^0_\alpha = q^0_\beta + \Sigma_\alpha \Sigma_t \left(\frac{\partial q_\alpha}{\partial R^\beta_t}\right)^0 \left(\frac{\partial R^\beta_t}{\partial z_\beta}\right)^0 z^0_\alpha \tag{6}$$

Therefore, each APT component is partitioned into two terms: the equilibrium atomic charge q^0_β of the β atom and a sum of charge fluxes $\left(\frac{\partial q_\alpha}{\partial R^\beta_t}\right)$ over all the other atoms of the molecule, induced by displacements of the whole set of internal coordinates R^β_t involving the β atom. This partitioning corresponds to the starting assumption of CCFOM model [17] allowing the definition of corrected Mulliken atomic charges and the associated charge fluxes through APT components.

According to the definition proposed by Cioslowski [18], GAPT charges are defined on the basis of the trace of the APT:

$$q^{\mathrm{GAPT}}_\beta = \frac{1}{3}\left[P^\beta_{xx} + P^\beta_{yy} + P^\beta_{zz}\right] \tag{7}$$

As already pointed out in previous papers [25], GAPT charges corresponds to the so called "mean dipole derivative" $\bar{p}_\beta$ introduced in the past by Person [26] in conjunction with the other APT invariants, namely the King effective charge χ_β [27], the APT anisotropy η_β and of the derived "undeformability parameter" $\bar{p}_\beta/\eta_\beta$. The performances of APT invariants in giving an average description of the characteristics of the electron cloud nearby an atom and a subsequent atoms classification have been widely discussed in the past [10,15,26], clearly showing that any of these parameters cannot distinguish between equilibrium properties and dynamical characteristic of the charge distribution, but in the case of very undeformable atomic charges where $\bar{p}_\beta/\eta_\beta \to 0$ and $\bar{p}_\beta = q^0_\beta$

Introducing Eqs. (4)–(6) into Eq. (7) the following expression is therefore obtained:

$$q^{\mathrm{GAPT}}_\beta = q^0_\beta + \frac{1}{3}\Sigma_\alpha \Sigma_t \left[\left(\frac{\partial q_\alpha}{\partial R^\beta_t}\right)^0 \left(\frac{\partial R^\beta_t}{\partial x_\beta}\right)^0 x^0_\alpha + \left(\frac{\partial q_\alpha}{\partial R^\beta_t}\right)^0 \left(\frac{\partial R^\beta_t}{\partial y_\beta}\right)^0 y^0_\alpha + \left(\frac{\partial q_\alpha}{\partial R^\beta_t}\right)^0 \left(\frac{\partial R^\beta_t}{\partial z_\beta}\right)^0 z^0_\alpha\right] \tag{8}$$

This definition is split in two terms: the first one is exactly the partial equilibrium atomic charge q^0_β on atom β defined according to Eq. (2) while the second terms contains all the charge fluxes induced by vibrational motions of the β atom. Therefore, a correspondence between GAPT charges and q^0_β is expected only if the molecular charge distribution is mainly undeformable during atomic motions, i.e. all the charge fluxes are small. This is indeed a special case and usually it does not happen, since charge fluxes are often very large [10,14,15,20] and usually involve atoms not directly bonded to the one (β) considered. This is the reason why GAPT charges cannot be safely used to obtain a picture of the

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