

Are “GAPT Charges” Really Just Charges?

Wagner E. Richter, Leonardo J. Duarte, and Roy E. Bruns*



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ABSTRACT: Generalized atomic polar tensor (GAPT) has turned into a very popular charge model since it was proposed three decades ago. During this period, several works aiming to compare different partition schemes have included it among their tested models. Nonetheless, GAPT exhibits a set of unique features that prevent it from being directly comparable to “standard” partition schemes. We take this opportunity to explore some of these features, mainly related to the need of evaluating multiple geometries and the dynamic character of GAPT, and show how to obtain the static and dynamic parts of GAPT from any static charge model in the literature. We also present a conceptual evaluation of charge models that aims to explain, at least partially, why GAPT and quantum theory of atoms in molecules (QTAIM) charges are strongly correlated with one another, even though they seem to be constructed under very different frameworks. Similar to GAPT, infrared charges (also derived from atomic polar tensors of planar molecules) are also shown to provide an improved interpretation if they are described as a combination of static charges and changing atomic dipoles rather than just experimental static atomic charges.

GAPT: **static** + **dynamics**

Static: commonly used atomic charge models

QTAIM, Hirshfeld, CHELPG, ADCH, DDEC6...

Dynamics:

Changes in charges (charge transfers) and changes in atomic polarizations

INTRODUCTION

The concept of atomic charge in chemistry is ubiquitous in the same measure as it is evasive. It is promptly invoked in all kinds of discussions, from molecular properties to reaction mechanisms while at the same time its very physical significance is debatable. This endless dispute has produced dozens of different partition schemes interpreted as atomic charges^{1–10} and new models continue to be proposed. Each of them has its own pros and cons, which quite often involve feasibility, reproducibility, transferability, basis set dependency, geometry dependency, and computational cost. Another desirable criterion is the reproduction of the total electric dipole moment, even though a number of partition schemes do not fulfill this requirement. The appearance of studies presenting comparisons between such models is natural, aiming to find the most suitable one for a given purpose or the one whose results are more meaningful in terms of what is expected from chemical insight.^{11–16} On the myriad of different partition schemes, Koritsanszky and Coppens point out that “the definition of net atomic charge introduces a much larger, conceptual, variation than uncertainties in either experiment or theory. At the current state of the art, differences between experiment and theory for a given molecule appear small compared with differences between alternative definitions”.¹⁷

Among all charge definitions available in the literature, generalized atomic polar tensor (GAPT) can be completely determined from experimental data, infrared intensities and frequencies, and equilibrium dipole moments and molecular geometries. Its origin comes from the mean dipole moment derivative appearing soon after the introduction of the polar tensor formalism by Morcillo and co-workers¹⁸ and later

extended by Person and Newton.¹⁹ The mean dipole moment derivatives calculated from experimental atomic polar tensors have been studied for both diatomic²⁰ and polyatomic²¹ molecules. This parameter measures the average change in the molecular dipole moment for atomic Cartesian displacements of each atom in the molecule. Cioslowski⁸ recognized the potential use of the mean dipole moment derivative as a charge parameter owing to its advantageous mathematical properties such as relative invariance to basis set changes. Since then, GAPTs have been used in hundreds of applications. It is worth mentioning that GAPT belongs to the select group of models that are accessible by both theory and experiment, and a compilation of experimentally determined GAPTs was published just a few years ago.²²

Two recent and very interesting contributions from Cho et al.¹⁵ and Manz¹⁶ reported careful statistical analyses over more than 20 different schemes for computing atomic charges. Although aiming at different goals, they report similar results concerning the correlation between the various partition schemes. For instance, both present a correlation matrix that is blocked around some schemes under similar approaches, e.g., the group derived from electrostatic potentials (MK, CHELPG, HLY, RESP) and the group derived from deformation densities (Hirshfeld, Voronoi). They also report a quite high correlation

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between GAPT and quantum theory of atoms in molecules (QTAIM), which surprised the authors.¹⁵ Considering the profound differences between GAPT and other charge models in the literature, which were not the focus of the research by these authors, and considering this somewhat surprising correlation between GAPT and QTAIM, we aim to explore some of their features that can help demystify this correlation.

■ GAPT, IR INTENSITIES, AND POLAR TENSORS

GAPTs have their origin in experimental infrared spectroscopy, specifically infrared intensities that are proportional to the squares of the dipole moment derivatives with respect to their normal coordinates

$$\Lambda_k = \left(\frac{N_A \pi}{3c^2} \right) \left(\frac{\partial \vec{p}}{\partial Q_k} \right)^2, \quad k = 1, 2, \dots, 3N - 6 \quad (1)$$

with N_A and c representing Avogadro's constant and the speed of light.^{23,24} These derivatives can be transformed into atomic Cartesian coordinates resulting in atomic polar tensors (APTs)^{18,19}

$$\mathbf{P}_X^{(j)} = \begin{pmatrix} \left(\frac{\partial p_x}{\partial x_j} \right) & \left(\frac{\partial p_x}{\partial y_j} \right) & \left(\frac{\partial p_x}{\partial z_j} \right) \\ \left(\frac{\partial p_y}{\partial x_j} \right) & \left(\frac{\partial p_y}{\partial y_j} \right) & \left(\frac{\partial p_y}{\partial z_j} \right) \\ \left(\frac{\partial p_z}{\partial x_j} \right) & \left(\frac{\partial p_z}{\partial y_j} \right) & \left(\frac{\partial p_z}{\partial z_j} \right) \end{pmatrix}, \quad j = 1, 2, \dots, N \quad (2)$$

for an N atom molecule. Although experimental gas-phase integrated intensities for all normal modes have been measured for only about a hundred molecules, they are accurately calculated by high-quality ab initio quantum mechanical methods.^{25,26}

The mean dipole moment derivative, now popularly known as GAPT, has been defined as one-third of the trace of the atomic polar tensor⁸

$$q_j^{\text{GAPT}} = \bar{p}_j = \frac{1}{3} \left[\left(\frac{\partial p_x}{\partial x_j} \right) + \left(\frac{\partial p_y}{\partial y_j} \right) + \left(\frac{\partial p_z}{\partial z_j} \right) \right] \quad (3)$$

The reader should notice that it is the molecular dipole moment that is being perturbed by the displacement of the j th atom in eq 3, so all of the electrons are being considered. The separation is not based on electronic atomic densities but actually on atomic displacements along the Cartesian coordinates (for instance, check the labels on eq 5 of ref 8): It is a criterion based on movement rather than an electronic one that defines the atomic contribution. The key point is that GAPT shows how a given atom affects the molecular dipole moment assuming it is the only atom moving. The extent of this perturbation is, of course, primarily related to the electronic environment around the displaced atom, and more or less polarizable atoms, when displaced, will perturb the molecular dipole moment differently. We need to keep in mind that all electrons are, in principle, being perturbed, even those far away from the moving atom.

This is actually the main feature differing GAPT from nearly all of the remaining charge models available in the literature: while these deal with static (usually equilibrium, but not restricted to) geometries, the charges obtained from them are also "static charges". In contrast, GAPT parameters are "dynamic" since they take into account the dynamic nature of vibrational motion. One must stress that in nature, atoms within a molecule are never static at their equilibrium geometries; unfortunately, most of the studies comparing atomic charges from different procedures totally ignore calculations on displaced, nonequilibrium geometries. Another important difference is that GAPT is a charge assignment scheme that cannot be evaluated based only on a single-point calculation since, by its own definition, the molecular dipole moment needs to be evaluated at multiple different geometries.

Because GAPT is not static, but actually dynamic, it is desirable to find a way of relating them to the static charges available in the literature. If the molecule is not planar, all partition schemes able to reproduce the total dipole moment can, in principle, be used to obtain GAPT. Among the several models that fulfill this condition, all of them belong to one of the two following categories

$$\vec{p} = \sum_{i=1}^N \vec{p}_i \left\{ \begin{array}{l} \vec{p} = \sum_{i=1}^N (q_i \cdot \vec{r}_i) \quad (\text{charge-only models}) \\ \vec{p} = \sum_{i=1}^N (q_i \cdot \vec{r}_i + \vec{m}_i) \\ (\text{charge-and-dipole models}) \end{array} \right. \quad (4)$$

for which q_i , \vec{r}_i and \vec{m}_i stand for the atomic charge, position vector, and intraatomic dipole of the i th atom, respectively. It should be mentioned that these i indexes are related to the atomic contributions to the electronic dipole moment, whereas the j index is used for the displacements in earlier equations. The substitution of each case of eq 4 into eq 2 leads to a partition of the APT in two (if a charge-only model was used) or three (if a charge-and-dipole model is used) terms

$$\mathbf{P}_X^{(j)} = \mathbf{P}_{X,C}^{(j)} + \mathbf{P}_{X,CT}^{(j)} \quad (\text{under charge - only models}) \quad (5)$$

$$\mathbf{P}_X^{(j)} = \mathbf{P}_{X,C}^{(j)} + \mathbf{P}_{X,CT}^{(j)} + \mathbf{P}_{X,DP}^{(j)} \quad (\text{under charge - and - dipole models}) \quad (6)$$

It is easy to reach this conclusion: if charge-only models are used, the derivatives in eq 2 require the application of the chain rule on the $q_i \cdot \vec{r}_i$ product, leading to two sets of derivatives, which ultimately can be expressed as two sets of complementary polar tensors, here named charge (C) and charge transfer (CT). If atomic dipoles are also included, then the third set of derivatives will appear, expressed as a third polar tensor, named dipolar polarization (DP). In either case, the sum of the C, CT, and DP (if present) polar tensors must recover the total (experimentally determined) APT. The charge tensor is a diagonal matrix composed of the atomic charges from the equilibrium geometry, while the charge transfer tensor concerns the fluctuations, or rearrangements, of the electronic density that occurs as a response to the atomic displacements. Similar to CT, the DP tensor concerns the modifications of the intraatomic dipoles that are also caused by displacements. A more detailed derivation of

the above equations is presented in a recent report from our group,²⁷ specifically within equations 15–30.

The immediate consequence of the latter equations is that if the APT can be separated into smaller terms, GAPT, as defined from the total APT, can also be divided into equivalent terms. In fact, it can be divided into C, CT, and DP terms by taking one-third of the trace of each of the polar tensors

$$q_j^{\text{GAPT}} = q_j^{\text{C}} + q_j^{\text{CT}} \quad (\text{under charge - only models}) \quad (7)$$

$$q_j^{\text{GAPT}} = q_j^{\text{C}} + q_j^{\text{CT}} + q_j^{\text{DP}} \quad (\text{under charge - and - dipole models}) \quad (8)$$

As mentioned earlier, GAPT is not “static” but rather a dynamic parameter. Indeed, regardless of the charge model chosen for their determination, there is no way of avoiding the charge transfers and dipolar polarization, which are the dynamic corrections to the equilibrium static charge given within the charge tensor. The main aspect is that the relative magnitudes of the C, CT, and DP components of GAPT will be different for each of the charge models chosen. To exemplify this, Tables 1–5 show GAPT's calculated for all fluorochloromethanes using five

Table 1. Charge (C), Charge Transfer (CT), and Dipolar Polarization (DP) Contributions to the Total GAPT as Obtained from QTAIM Atomic Charges and Dipoles^a

	atom	C	CT	DP	GAPT
CH ₄	C	0.013	-0.354	0.362	0.021
	H	-0.003	0.089	-0.091	-0.005
CH ₃ F	C	0.650	-0.360	0.289	0.579
	F	-0.699	0.145	0.064	-0.490
CH ₂ F ₂	H	0.016	0.072	-0.119	-0.031
	C	1.314	-0.412	0.217	1.119
CHF ₃	F	-0.703	0.133	0.051	-0.518
	C	2.021	-0.557	0.135	1.598
CF ₄	H	0.046	0.073	-0.159	-0.040
	C	2.786	-0.845	0.107	2.048
CClF ₃	F	-0.696	0.211	-0.028	-0.513
	C	2.211	-0.202	-0.119	1.890
CCl ₂ F ₂	Cl	-0.135	-0.199	0.076	-0.258
	F	-0.692	0.134	0.018	-0.540
CCl ₃ F	C	1.635	0.350	-0.269	1.717
	F	-0.687	0.082	0.046	-0.559
CCl ₄	Cl	-0.131	-0.257	0.093	-0.295
	C	1.052	0.822	-0.398	1.475
CHCl ₃	F	-0.680	0.056	0.061	-0.564
	Cl	-0.124	-0.292	0.111	-0.305
CH ₂ Cl ₂	C	0.466	1.237	-0.510	1.194
	Cl	-0.117	-0.309	0.124	-0.301
CH ₃ Cl	C	0.363	0.792	-0.234	0.921
	H	0.125	-0.055	-0.103	-0.034
CH ₂ Cl ₂	Cl	-0.163	-0.246	0.114	-0.295
	C	0.255	0.357	0.002	0.614
CH ₃ Cl	Cl	-0.214	-0.174	0.099	-0.289
	H	0.087	-0.004	-0.101	-0.019
CH ₃ Cl	C	0.140	-0.039	0.198	0.299
	Cl	-0.271	-0.092	0.087	-0.276
	H	0.044	0.044	-0.095	-0.008

^aAll terms are in units of electrons, e.

Table 2. Charge (C), Charge Transfer (CT), and Dipolar Polarization (DP) Contributions to the Total GAPT as Obtained from Hirshfeld Atomic Charges and Dipoles^a

	atom	C	CT	DP	GAPT
CH ₄	C	-0.112	0.036	0.097	0.021
	H	0.028	-0.009	-0.024	-0.005
CH ₃ F	C	0.051	0.294	0.235	0.579
	F	-0.160	-0.201	-0.125	-0.486
CH ₂ F ₂	H	0.037	-0.031	-0.037	-0.031
	C	0.185	0.591	0.341	1.117
CHF ₃	F	-0.137	-0.253	-0.127	-0.517
	H	0.044	-0.043	-0.043	-0.042
CF ₄	C	0.300	0.906	0.397	1.604
	H	0.055	-0.041	-0.045	-0.030
CClF ₃	F	-0.119	-0.288	-0.117	-0.524
	C	0.410	1.230	0.415	2.055
CCl ₂ F ₂	F	-0.103	-0.307	-0.104	-0.514
	C	0.355	1.300	0.251	1.906
CCl ₃ F	Cl	-0.058	-0.221	0.014	-0.265
	F	-0.099	-0.360	-0.088	-0.547
CCl ₄	C	0.301	1.311	0.105	1.717
	F	-0.094	-0.397	-0.072	-0.563
CHCl ₃	Cl	-0.056	-0.258	0.019	-0.295
	C	0.248	1.259	-0.023	1.484
CH ₂ Cl ₂	F	-0.091	-0.422	-0.053	-0.566
	Cl	-0.052	-0.279	0.026	-0.306
CH ₃ Cl	C	0.194	1.147	-0.129	1.212
	Cl	-0.048	-0.287	0.032	-0.303
CH ₂ Cl ₂	C	0.135	0.813	-0.023	0.925
	H	0.059	-0.060	-0.036	-0.038
CH ₃ Cl	Cl	-0.065	-0.251	0.020	-0.296
	C	0.073	0.490	0.051	0.614
CH ₂ Cl ₂	Cl	-0.090	-0.205	0.006	-0.289
	H	0.054	-0.040	-0.032	-0.018
CH ₃ Cl	C	-0.005	0.215	0.091	0.301
	Cl	-0.128	-0.140	-0.007	-0.276
	H	0.044	-0.025	-0.028	-0.008

^aAll terms are in units of electrons, e.

different partition schemes: four of them using atomic charges and atomic dipoles (QTAIM, Hirshfeld, DDEC6, and CHELPG with intraatomic dipoles, labeled CHELPG-qm) and a fifth one composed only of point charges (CHELPG-q). Computational details are given in the final section of this manuscript.

Inspection of Tables 1–5 confirms that the total GAPT values are absolutely equal within numerical accuracy. This is not a surprise as among these four partition schemes, two of them naturally reproduce the total dipole moment and the remaining two were constrained to do so; in other words, the intensities and polar tensors will be calculated to be the same within numerical error. On the other hand, it is easily seen that the individual C, CT, and DP terms (only C and CT for CHELPG-q) are indeed very different for each model. These differences are better visualized in Figure 1.

As can be seen, there the five models show striking differences for the C, CT, and DP parcels in all cases. First, analyzing the GAPT for carbon in methane (+0.021e), if obtained using QTAIM parameters, the equilibrium (static) charge is nearly zero (it barely appears in the figure) and the CT and DP components are larger but have opposite signs. This is expected from chemical insight because the IR intensities in hydrocarbons are expected to be described almost solely by dynamic terms, as

Table 3. Charge (C), Charge Transfer (CT), and Dipolar Polarization (DP) Contributions to the Total GAPT as Obtained from CHELPG Atomic Charges and Dipoles^a

	atom	C	CT	DP	GAPT
CH ₄	C	1.050	0.555	-1.584	0.021
	H	-0.263	-0.134	0.392	-0.005
CH ₃ F	C	1.596	0.471	-1.488	0.579
	F	-0.471	-0.346	0.328	-0.489
	H	-0.375	0.054	0.289	-0.032
CH ₂ F ₂	C	1.759	0.560	-1.202	1.117
	F	-0.559	-0.224	0.264	-0.520
	H	-0.320	-0.058	0.338	-0.040
CHF ₃	C	1.996	0.747	-1.140	1.604
	H	-0.288	-0.054	0.314	-0.028
	F	-0.570	-0.241	0.287	-0.524
CF ₄	C	2.341	1.019	-1.305	2.055
	F	-0.585	-0.271	0.342	-0.515
CClF ₃	C	2.499	1.060	-1.653	1.906
	Cl	-0.594	-0.041	0.369	-0.266
	F	-0.635	-0.411	0.501	-0.546
CCl ₂ F ₂	C	2.694	0.989	-1.965	1.718
	F	-0.705	-0.395	0.541	-0.559
	Cl	-0.642	-0.077	0.424	-0.295
CCl ₃ F	C	2.731	0.880	-2.128	1.484
	F	-0.721	-0.846	1.009	-0.558
	Cl	-0.670	0.328	0.040	-0.302
CCl ₄	C	2.904	0.658	-2.350	1.212
	Cl	-0.726	-0.208	0.630	-0.304
CHCl ₃	C	2.735	0.408	-2.218	0.925
	H	-0.664	0.325	0.303	-0.035
	Cl	-0.690	-0.213	0.609	-0.294
CH ₂ Cl ₂	C	2.481	0.339	-2.206	0.614
	Cl	-0.670	-0.367	0.747	-0.290
	H	-0.571	-0.063	0.614	-0.020
CH ₃ Cl	C	2.072	0.408	-2.180	0.301
	Cl	-0.620	0.026	0.317	-0.277
	H	-0.484	-0.191	0.666	-0.009

^aAll terms are in units of electrons, e.**Table 4. Charge (C) and Charge Transfer (CT) Contributions to the Total GAPT as Obtained from CHELPG Atomic Charges (No Dipoles)^a**

	atom	C	CT	DP	GAPT
CH ₄	C	-0.360	0.381	0.000	0.021
	H	0.090	-0.095	0.000	-0.005
CH ₃ F	C	0.144	0.435	0.000	0.579
	F	-0.247	-0.239	0.000	-0.487
	H	0.035	-0.065	0.000	-0.031
CH ₂ F ₂	C	0.389	0.728	0.000	1.117
	F	-0.227	-0.291	0.000	-0.518
	H	0.032	-0.074	0.000	-0.042
CHF ₃	C	0.540	1.064	0.000	1.604
	H	0.052	-0.082	0.000	-0.030
	F	-0.197	-0.327	0.000	-0.524
CF ₄	C	0.682	1.373	0.000	2.055
	F	-0.170	-0.343	0.000	-0.514
CClF ₃	C	0.334	1.572	0.000	1.906
	Cl	-0.033	-0.232	0.000	-0.265
	F	-0.100	-0.447	0.000	-0.547
CCl ₂ F ₂	C	0.072	1.646	0.000	1.717
	F	-0.045	-0.517	0.000	-0.562
	Cl	0.009	-0.303	0.000	-0.294
CCl ₃ F	C	-0.088	1.571	0.000	1.484
	F	-0.016	-0.550	0.000	-0.566
	Cl	0.035	-0.341	0.000	-0.306
CCl ₄	C	-0.270	1.481	0.000	1.212
	Cl	0.067	-0.370	0.000	-0.303
CHCl ₃	C	-0.135	1.059	0.000	0.925
	H	0.186	-0.224	0.000	-0.038
	Cl	-0.017	-0.280	0.000	-0.297
CH ₂ Cl ₂	C	-0.111	0.725	0.000	0.614
	Cl	-0.087	-0.203	0.000	-0.290
	H	0.143	-0.162	0.000	-0.019
CH ₃ Cl	C	-0.157	0.458	0.000	0.301
	Cl	-0.161	-0.114	0.000	-0.276
	H	0.106	-0.115	0.000	-0.008

^aAll terms are in units of electrons, e.

the atomic charges in these molecules are expected to be nearly zero.²⁸ If obtained using Hirshfeld parameters, a static charge is still small, though a bit larger than QTAIM in magnitude; however, the most important difference is that now the CT and DP terms no longer have opposite signs but reinforce one another. One can see that the interpretations of GAPT's by the different models are not necessarily equivalent.

The CHELPG results for methane deserve a more careful evaluation. As the same total GAPT must be reproduced by all models, the C and CT terms for CHELPG-q combined have only a single degree of freedom. The charge term is determined directly from the equilibrium, static charges, and so CT must be such that, summed to C, it will reproduce the total GAPT. As the GAPT values for methane are almost zero, the C and CT terms from CHELPG-q must necessarily cancel each other almost perfectly, which is indeed observed. By adding an additional degree of freedom (the intraatomic dipoles from CHELPG-qm), one could expect a much better description for these atoms, but this is not the case. In fact, CHELPG-qm indicates that the static atomic charge for carbon is greater than 1.00e and for hydrogen is lower, i.e., more negative, than -0.2e, clearly contrary to the archetype of a nonpolar bond.

CHELPG-qm interpretations are even stranger for the polar CF₄ and CCl₄ molecules. First, notice that static charges from CHELPG-qm are larger for carbon in CCl₄ than in CF₄, opposite to expectations based on the electronegativity order. The same problems occur for the terminal atoms, with chlorine (in CCl₄) being described as more negatively charged than fluorine (in CF₄). CHELPG-q, on the other hand, shows a slightly negative carbon and slightly positive chlorine, again contrary to the electronegativity trends. CHELPG-qm also shows problems when handling CHCl₃ and CH₂Cl₂, resulting in quite similar static charges for hydrogen and chlorine.

Similar problems occur for DDEC6 results as the carbon atom in methane is the most negatively charged atom in the entire set, even more, negative than any of the halogens. Moreover, when looking at fluoromethane, DDEC6 suggests both carbon and fluorine as negatively charged, the only model to do so, and for chloromethane, the carbon atom is more negatively charged than chlorine. This could suggest that the carbon's electronegativity is greater than the chlorine, but in CCl₄ the expected trend (negative halogen, positive carbon) is observed instead. Also, the DDEC6 results do indicate that the charge transfer and polarization contributions have opposite signs in all but one GAPT estimation.

Table 5. Charge (C), Charge Transfer (CT), and Dipolar Polarization (DP) Contributions to the Total GAPT as Obtained from DDEC6 Atomic Charges and Dipoles^a

	atom	C	CT	DP	GAPT
CH ₄	C	-0.568	0.709	-0.119	0.023
	H	0.142	-0.176	0.029	-0.005
CH ₃ F	C	-0.052	0.829	-0.197	0.579
	F	-0.189	-0.235	-0.066	-0.490
CH ₂ F ₂	C	0.363	0.939	-0.184	1.117
	F	-0.218	-0.341	0.042	-0.517
CHF ₃	C	0.733	1.090	-0.220	1.603
	H	-0.008	-0.076	0.052	-0.032
CF ₄	C	1.123	1.411	-0.477	2.057
	F	-0.280	-0.319	0.087	-0.513
CClF ₃	C	0.912	1.376	-0.383	1.905
	Cl	-0.188	-0.215	0.138	-0.265
CCl ₂ F ₂	C	0.723	1.446	-0.451	1.718
	F	-0.205	-0.461	0.103	-0.563
CCl ₃ F	C	0.536	1.418	-0.469	1.484
	F	-0.172	-0.500	0.106	-0.566
CCl ₄	C	0.370	1.430	-0.588	1.211
	Cl	-0.092	-0.371	0.161	-0.302
CHCl ₃	C	0.225	1.046	-0.347	0.924
	H	0.092	-0.102	-0.028	-0.038
CH ₂ Cl ₂	C	0.040	0.731	-0.154	0.616
	Cl	-0.127	-0.277	0.116	-0.288
CH ₃ Cl	C	-0.238	0.710	-0.173	0.299
	Cl	-0.146	-0.219	0.090	-0.275
	H	0.128	-0.205	0.069	-0.008

^aAll terms are in units of electrons, e.

For polar molecules, QTAIM and Hirshfeld result in more reasonable interpretations. First of all, they both follow electronegativity expectations for static charges and show a larger dynamic character for CCl₄ than for CF₄, which nicely agrees with their relative polarizabilities. However, QTAIM and Hirshfeld are by no means equivalent to each other as the Hirshfeld has all C, CT, and DP terms having the same sign in CF₄ (positive for the carbon atom, negative for fluorine), whereas QTAIM has CT and DP terms with opposite signs for each atom, canceling one another. QTAIM also has a greater DP term for the atoms in CCl₄, which seems to agree with the smaller positive charge for carbon and the greater polarizability of chlorine, but Hirshfeld indicates the opposite: fluorine having larger intraatomic dipole changes than chlorine.

Similar analyses could be carried out for all of the molecules in Tables 1–4 and using other alternative partition schemes that reproduce the dipole moment derivatives, like ADCH, DDEC6, and others; this is not the aim here, however. One can expect that each charge model will result in different interpretations for the static and dynamic parts of GAPT. GAPT is intrinsically dynamic, but how dynamic depends on the partition scheme chosen?

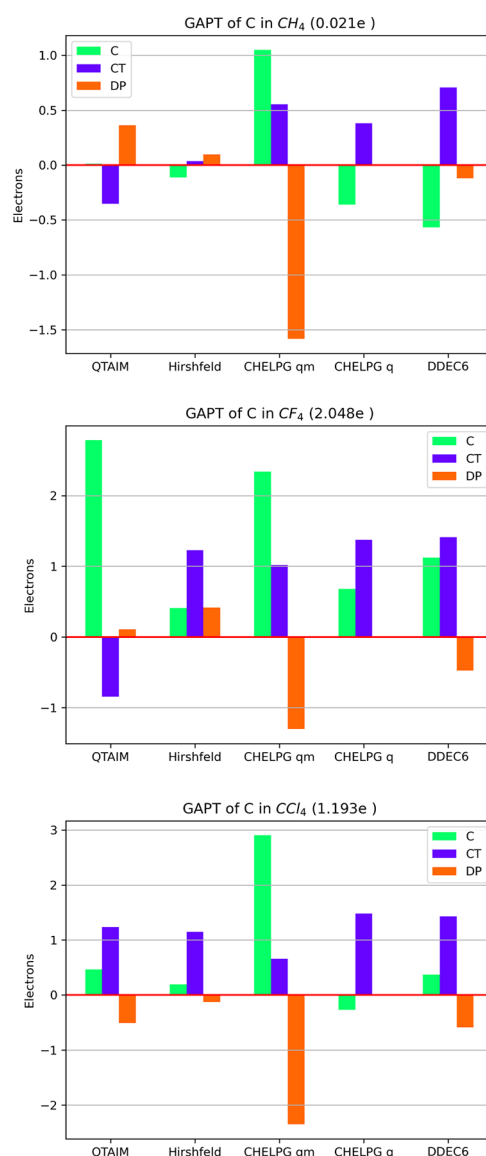


Figure 1. C, CT, and DP contributions from QTAIM, Hirshfeld, and CHELPG with charges-and-dipoles (CHELPG-qm), CHELPG with only point-charges (CHELPG-q), and DDEC6 to GAPT for carbon in CX₄ molecules. All quantities are in electrons.

Planar Molecules and Infrared Charges. The previous discussion made no distinction between the different classes of molecules that can have their GAPTs evaluated and divided into C + CT or C + CT + DP terms. However, in the case of planar molecules, special features arise and these have important implications on the equations and their interpretations.

In 1989, Dinur and Hagler²⁹ have shown that due to the symmetry of the positive and negative atomic displacements, the out-of-plane bending vibrations in planar molecules should have zero charge transfer (charge flux, in the original). This is a general result for any planar molecule and immediately implies that if a charge-only model is being considered (i.e., the dipole is described as $p_z = \sum_{i=1}^N (q_i z_i)$, the dipole moment derivative would be reduced to simply a static, equilibrium charge. If this is correct, then the reverse approach could be used as a path toward experimental atomic charges: considering a planar molecule within the *xy* plane, the APT element concerning the out-of-plane vibration ($p_{zz} = \frac{\partial p_z}{\partial z_i}$) could be interpreted as a

Table 6. C, CT, DP, and GAPT = C + CT + DP Terms for Carbon and Hydrogen in Ethene, Calculated at m06-2X/aug-cc-pVTZ^a

ethene model	carbon				hydrogen			
	C	CT	DP	GAPT	C	CT	DP	GAPT
QTAIM	-0.031	-0.082	0.035	-0.078	0.016	0.042	-0.019	0.039
Hirshfeld	-0.078	0.005	-0.004	-0.077	0.039	-0.003	0.002	0.039
DDEC6	-0.256	0.278	-0.100	-0.078	0.128	-0.109	0.020	0.039
CHELPG-qm	-0.294	-1.254	1.470	-0.078	0.147	0.622	-0.732	0.037
CHELPG-q ¹	-0.256	0.192	0.000	-0.065	0.128	-0.096	0.000	0.032
CHELPG-q ²	-0.255	0.207	0.000	-0.048	0.128	-0.104	0.000	0.023
ADCH	-0.250	0.187	0.000	-0.063	0.125	-0.093	0.000	0.031
VDD	-0.062	0.108	0.000	0.046	0.031	-0.054	0.000	-0.023
Gaussian				-0.080				0.040

^aAll values are in units of electrons. CHELPG-q¹ with only atomic charges, constrained to reproduce the molecular dipole moment and CHELPG-q² with only atomic charges, not constrained to reproduce the molecular dipole moment.

Table 7. Diagonal Elements for the Atomic Polar Tensors of Carbon and Hydrogen in Ethene, Calculated at m06-2X/aug-cc-pVTZ^a

ethene	carbon			hydrogen		
	p_{xx}	p_{yy}	p_{zz}	p_{xx}	p_{yy}	p_{zz}
QTAIM	0.092	-0.029	-0.297	-0.046	0.015	0.148
Hirshfeld	0.092	-0.030	-0.294	-0.046	0.015	0.147
DDEC6	0.091	-0.031	-0.294	-0.046	0.015	0.147
CHELPG-qm	0.092	-0.031	-0.294	-0.049	0.012	0.147
CHELPG-q ¹	0.092	-0.030	-0.256	-0.046	0.015	0.128
CHELPG-q ²	0.112	-0.001	-0.255	-0.057	-0.001	0.128
ADCH	0.093	-0.031	-0.250	-0.046	0.016	0.125
VDD	0.105	0.096	-0.062	-0.052	-0.048	0.031
Gaussian	0.090	-0.036	-0.295	-0.045	0.018	0.147

^aAll values are in units of electrons. CHELPG-q¹ with only atomic charges, constrained to reproduce the molecular dipole moment and CHELPG-q² with only atomic charges, not constrained to reproduce the molecular dipole moment.

static atomic charge derived directly from the experiment, free of ambiguities and fully satisfying the molecular dipole moment. This approach was widely used in several papers in attempts to assign atomic charges based on APT elements related to the out-of-plane vibrations in planar molecules,^{30–34} and the charges obtained by these procedures were called infrared charges.

On the other hand, Dinur and Hagler²⁹ also considered a situation where the dipole moment is not properly described from point charges, but actually as a sum of atomic charges and dipoles ($p_z = \sum_{i=1}^N (q_i z_i + m_{z,i})$). Equation 17 in their paper is exactly equal to the second case in eq 4 here. The charge transfer constraint is zero but the dipolar polarization term, DP, is not. Therefore, in the case of charge-and-dipole models, the dipole moment derivative of the out-of-plane distortion will be reduced to the sum of the static charges and the derivatives of the atomic dipoles, which is precisely the case of equation 19 in their paper.²⁹ To evaluate the differences from charge-only to charge-and-dipole models for planar molecules, GAPT parameters were calculated for ethene under eight different charge models, as shown in Table 6. For CHELPG-q, the indexes 1 and 2 indicate (1) constraints to reproduce the molecular dipole moment or (2) their absence.

It can be seen that the first four models agree very nicely with the GAPT reported directly by Gaussian (last line); the small differences are due to numerical errors from the Placzek program, used for their calculation. As we will see, it is not a mere coincidence that all of the models that are in agreement with Gaussian values contemplate atomic dipoles. VDD and CHELPG-q², which do not reproduce the molecular dipole moment, fail in this task, again as expected. The surprise is that

ADCH and CHELPG-q¹, which do reproduce the molecular dipole moment (either naturally or because of constraints to do so), also fail (though to a smaller extent). The reason for this can only be understood by looking at the individual APT elements, shown in Table 7.

On comparing the values obtained directly from Gaussian (last line) with those obtained from the different models, only two of them do not reproduce the molecular dipole moment (VDD and CHELPG-q²). These also fail to correctly determine all of the APT elements (p_{xx} , p_{yy} , and p_{zz}). On the other hand, all models that do reproduce the molecular dipole moment succeed in predicting the p_{xx} and p_{yy} values (which are related to in-plane vibrations), and only the models having atomic dipoles also succeed in predicting p_{zz} . The failure in predicting p_{zz} by the charge-only models is because of the Dinur's CT = 0 condition,²⁹ which makes p_{zz} for ADCH and CHELPG-q¹ simply the equilibrium charges for the atoms. Therefore, interpretation of spectroscopic p_{zz} values requires either static charges (for charge-only models) or static charges with changes in atomic dipoles (for charge-and-dipole schemes). However, employing only charges results in wrong predictions for p_{zz} whereas charges and dipoles successfully provide precise estimates. We then conclude that the experimental measurements of p_{zz} for planar molecules cannot be interpreted simply as charges and the only manner to link theory and experiment, in this case, is to employ both charges and changes in the dipoles (as stated in equation 19 of Dinur²⁹). Therefore, similar to GAPT, infrared charges are also not true static charges. This is consistent with previous evidence of the importance of atomic dipoles in describing out-of-plane vibrations.^{35,36} Its correct

interpretation will lead to successful applications in future research endeavors.

■ HIDDEN CORRELATION BETWEEN QTAIM AND GAPT

We have seen that any partition scheme giving atomic charges (or charges and dipoles) that satisfactorily reproduces the total molecular dipole moment can be used to obtain partitioned GAPT's with the same total value; if the molecule is planar, then the additional condition of featuring atomic dipoles is also required. However, both Cho et al.¹⁵ and Manz¹⁶ reported quite high (and somewhat unexpected¹⁵) correlations between QTAIM and GAPT, which are not observed with any of the more than 20 charge models investigated (the i-ACP case will be discussed later). We shall discuss this GAPT-QTAIM correlation now.

Investigations of the charge, charge transfer, and dipolar polarization contributions to mean dipole moment derivatives, often referred to as GAPT charges, employing QTAIM atomic charges and dipoles were first published in a series of papers by our group between 2005 and 2007 for most molecules for which experimental absolute intensities have been measured for all active normal modes. Intensities and CCTDP contributions were calculated at the MP2/6-311G++(3d,3p) level with the agreement between the theoretical and experimental intensities commensurate with experimental error. High negative correlations were found between the charge transfer and dipolar polarization contributions. The following sets of molecules, number of vibrations, and correlation coefficients are as follows: AB₃ (A = N, P; B = H, F),³⁷ 16, -0.82; fluorochloromethanes,³⁸ 34, -0.92; difluoro- and dichloroethylenes,³⁹ 42, -0.91; and X₂CY (X = H, F, Cl; Y = O, S),⁴⁰ 36, -0.83. These correlations arise owing to the opposite signs for the charge transfer and dipolar polarization contributions resulting in cancellation leaving a predominant charge contribution to GAPT. Examination of the values in Table 1 also indicates a strong negative correlation between the charge transfer and polarization contributions for the polar tensor elements from which the dipole moment contributions for normal modes are calculated. This can be explained by a relaxation effect. As the net charge transfer between atoms occurs in one direction, atomic dipoles are polarized in the opposite direction. This phenomenon has been used before to explain the small permanent dipole moment of carbon monoxide and its unexpected polarity based on the electronegativity considerations.⁴¹ As the neutral carbon and oxygen atoms approach each other from infinity to form a chemical bond, the electronic charge is transferred from carbon to oxygen with the polarization of both the carbon and oxygen dipoles occurring with opposite polarity. Our group has also found opposite signs for the charge and atomic dipole contributions to the permanent dipole moments of HX (X = F, Cl, Br), LiH, NaH, and other small molecules.⁴²

We will now consider eq 4. If we choose a charge-only model, the total dipole moment will be completely determined from the distribution of the charges. In other words, 100% of the dipole is accounted for by the charges. For charge-and-dipole models, however, the total dipole is a sum of two parcels, one arising from the charges and another arising from the intrinsic atomic polarization. One could write then $\vec{p}_{\text{tot}} = \vec{p}_{\text{ch}} + \vec{p}_{\text{ad}}$, for which ch stands for "charges" and ad for "atomic dipoles". To exemplify this, Table 8 shows these quantities for fluoromethane (CH₃F), from QCISD/aug-cc-pVTZ wavefunctions.

Table 8. Dipole Values from Charges, from Atomic Dipoles, and Total Dipole Moment for Fluoromethane (CH₃F) Calculated from QTAIM, Hirshfeld, DDEC6, CHELPG-q, and CHELPG-qm Parameters Calculated at the QCISD/aug-cc-pVTZ Level^a

model	\vec{p}_{ch}	\vec{p}_{ad}	\vec{p}_{tot}
QTAIM	-4.7106	2.8942	-1.8165
Hirshfeld	-1.2499	-0.5657	-1.8156
DDEC6	-1.6673	-0.1483	-1.8156
CHELPG-qm	-1.1873	-0.6283	-1.8156
CHELPG-q	-1.8156	0.0000	-1.8156
Gaussian			-1.8156

^aAll values are in Debye (D).

Those familiar with comparisons between charge models may recall two common statements concerning QTAIM and Hirshfeld charges: while QTAIM charges are usually claimed to be too high, Hirshfeld charges are claimed as being too low. These biased arguments were widely explored by Bader and his colleagues^{41,43,44} as they are pointless unless the atomic charges and atomic dipoles are compared together. For example, QTAIM charges are high but the atomic polarization is directed in the opposite way; the two parcels compensate one another, resulting in the correct dipole moment. Conversely, Hirshfeld charges are low but the dipole owing to the atomic polarization is aligned with the one arising from the charges; the two parcels reinforce each other and also sum to the correct dipole moment. As for QTAIM, these parcels have different signs, and the substitution of eq 4 in eq 1 will lead to terms with opposing signs (CT and DP, for instance), and this cancellation results in intensities (and GAPT's) dominated by the charge (C) term; this is the origin of high correlation. The same does not occur for Hirshfeld and other models because their contributions to the static dipole moment usually have the same sign. Therefore, they do not cancel one another. The dynamic terms are still large in magnitude and the correlation between GAPT and the static charge (C) will, of course, be much lower for these models.

Apart from these mathematical features, GAPT and QTAIM share conceptual similarities as well. The first one concerns the potential for observability; these are among the very few models for which the input data required makes no distinction between theory or experiment. GAPT is defined in such a way that requires either an experimental or theoretical atomic polar tensor as input to be computed. The same is true for QTAIM: it requires the molecular electronic density, but the theorems therein make no distinction between experimental or theoretical densities. This feature links QTAIM and GAPT to one another and distinguishes them from most of the remaining models. The concept of atomic charge as being "experimentally observable" is at the core of a long-term discussion in the literature (see, for example, the discussion in refs 41, 45–47 and references therein), but this is not the point here. We state that within each definition, QTAIM and GAPT are two of the very few models that can have both theoretical and experimental values. Moreover, while several partition schemes are designed to satisfy specific goals (to reproduce the electrostatic potential, or to reproduce the dipole moment, etc.), QTAIM and GAPT are consequences of simple criteria (the division of the molecular density into disjoint spaces separated by zero-flux surfaces or the response of the molecular dipole to an individual atomic displacement): no fitting, no parametrization, and no database.

We have stated earlier in this text that “unfortunately, most of the studies comparing atomic charges from different procedures totally ignore calculations on displaced, nonequilibrium geometries”. We demonstrated how important this is for drawing the correct picture given by GAPT. Concerning this, Bader and co-workers⁴³ stated that “the dipole moment is given by a sum over the net charge and first moment of every atom in a molecule. The first term leads to a charge transfer contribution p_c (the \vec{p}_{ch} in Table 8) and the second to an atomic polarization contribution p_a (the \vec{p}_{ad} in Table 8). It is shown that both terms are, in general, of equal importance in determining both the static molecular dipole moment and the moment induced by a nuclear displacement. Models that employ only point charges and corresponding bond moments, which follow rigidly the nuclear framework, i.e., models that approximate p_c and ignore p_a are shown to lead to results that are incompatible with the changes that are found to occur in a molecular charge distribution during a nuclear vibration”. Further ahead they are even more incisive: “Any use of the spherical atom-charge transfer model in the description of changes in dipole moment accompanying nuclear vibrations, even when modified to include changes in the atomic charges, the so-called atomic fluxes, is still less acceptable as it cannot adequately describe the relaxations in the charge density induced by the nuclear motions”.

Even though QTAIM was not designed to reproduce the changes in the dipole moments during nuclear vibrations, they satisfy this condition. This was a concern of Bader and co-workers that were fully confirmed when we demonstrated that coherent infrared intensity modeling can only be reached by including atomic polarization.⁴⁸ We just demonstrated that the inclusion of atomic dipoles is not enough to achieve a chemically meaningful description of these parameters. For example, CCTDP values from CHELPG with atomic charges and dipoles fail in following elementary electronegativity trends,⁴⁹ as seen in the aforementioned CF_4/CCl_4 discussion.

Atomic charges determined from polar tensors evaluated using infrared intensities can be very useful. Core electron ionization energies obtained from X-ray photoelectron spectroscopy are expected to be related to atomic charges by Siegbahn's simple potential model.⁵⁰ Experimental ionization energies have been found to have very high correlations with mean dipole moment derivatives obtained from experimental spectroscopic data of halomethanes, saturated and unsaturated hydrocarbons, and carbonyl and cyano molecules.⁵¹ For sp^3 , sp^2 , and sp , the correlations were 0.996, 0.994, and 0.995 and if only the halomethanes are considered a correlation of 0.9996 is found. It is important to stress that only experimental data were used for both the GAPT charges and 1s core ionization energies. These correlations were found to be significantly higher than those found using CHELPG, Mulliken, and QTAIM charges.⁵²

It should be noted that both Cho et al.¹⁵ and Manz¹⁶ reported another model with a high correlation to GAPT, namely i-ACP.⁵³ Its actual implementation as a charge-only model does not reproduce the molecular dipole moment from the wavefunctions, and therefore, it could not be used to obtain an accurate expression of GAPT as a C + CT sum. However, one of the reviewers pointed out that although this was not implemented yet, i-ACP's framework could admit atomic dipoles to be calculated. It would be certainly very interesting to see how the CCTDP parameters of GAPT would appear if modeled from i-ACP atomic charges and dipoles and infer about their correlation as well as made for QTAIM here. The same can

be said about other charge models, which were not tested by our group yet, like ISA charges and dipoles.⁵⁴ Nonetheless, this is out of the scope of the present manuscript.

CONCLUSIONS

It has been demonstrated that the generalized atomic polar tensor, while called a charge, is actually a measure of the extent of the fluctuations in the electronic density accompanying atomic displacements. Apart from the static term, C, the dynamic part of GAPT can be described by a charge transfer term, CT, or by a sum of charge transfer and polarizations arising from atomic dipoles, CT + DP. Several models can be used to obtain the CT or CT + DP terms and each of them will result in different values for these contributions. Particularly for the case of QTAIM, CT and DP tend to cancel each other, which can make the total C + CT + DP dominated by the static charge term, C. Since the C + CT + DP sum is equivalent to GAPT, this explains why QTAIM and GAPT values have a strong correlation.

Similar to GAPT, infrared charges (also derived from atomic polar tensors) also have important dynamical parts as it is impossible to obtain correct APT terms for out-of-plane vibrations without considering atomic dipoles, and by including them the static character of IR charges is definitely removed. In short, obtaining direct information about static atomic charges from experimental measurements (IR intensities, core-binding electron energies, polarizabilities, etc.) seems unattainable as molecules in nature are never completely static. These observations also suggest that models featuring both atomic charges and atomic dipoles seem to be more closely related to real, measurable, and unambiguous molecular properties derived from electronic densities.

We then conclude that discussions concerning charge models would be far more fruitful if atomic dipoles were also included in the analysis rather than only atomic charges. Atomic dipoles seem to be a source of information as rich as the charges themselves.

DATA AND SOFTWARE AVAILABILITY

All geometries were optimized using Gaussian09 (rev. B.01),⁵⁵ for the fluorochloromethanes at the QCISD/aug-cc-pVTZ level, whereas for ethene at m06-2X/aug-cc-pVTZ. G09 also delivered the full vibrational analysis, Hessian matrix, and raw GAPT values at the same level of theory. The protocol, however, is not restricted to Gaussian since these tasks can be performed by a number of codes, some of them being open-source. The C, CT, and DP components from GAPT were calculated by the Placzek program using the equilibrium and additional 6N (for an N-atom molecule) distorted geometries (± 0.01 Å on each Cartesian direction) by means of a well-known protocol described in detail elsewhere.^{27,49,56} Hirshfeld atomic charges and dipoles, as well as CHELPG charges, were obtained by Gaussian's default routines, with additional constraint for CHELPG to reproduce the correct molecular dipole moment given by the wavefunction (pop = (hirshfeld, chelpg, dipole)); this constraint applies only to CHELPG as Hirshfeld charges and atomic dipoles combined will naturally reproduce the dipole moment. CHELPG charges with additional intraatomic dipoles were obtained by means of the (pop = (chelpg, dipole, atomdip)) setup. QTAIM charges and dipoles were calculated by AIMAll;⁵⁷ DDEC6 charges and dipoles were calculated by Chargemol,¹⁰ and CHELPG-q², ADCH, and VDD charges were calculated by Multiwfn.⁵⁸ The atomic polar tensors and also

their C, CT, and DP inner tensors are then calculated by Placzek using two-point numerical derivatives^{49,56}

$$\frac{\partial q_i}{\partial x_j} = \frac{q_i^{(+)} - q_i^{(-)}}{2\Delta x} \quad \text{and} \quad \frac{\partial m_{i,x}}{\partial x_j} = \frac{m_{i,x}^{(+)} - m_{i,x}^{(-)}}{2\Delta x} \quad (9)$$

for which the (+) and (−) superscripts denote the positive and negative displaced geometries within a given Cartesian direction, and similar relations hold for y and z components.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jcim.1c00165>.

All input and output files; Placzek's main output, PLACZEK.OUT, contains the C, CT, DP, and (TOTAL = C + CT + DP) polar tensor ready to be interpreted, as well as total and partitioned GAPTs; Placzek program is distributed by its developer free of charge, SI contains a link to it; please contact the author (WER) for further details (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Roy E. Bruns – Institute of Chemistry, State University of Campinas, Campinas 13083-861 SP, Brazil; orcid.org/0000-0002-8234-1129; Email: bruns@iqm.unicamp.br

Authors

Wagner E. Richter – Department of Chemical Engineering, Federal University of Technology—Paraná, Ponta Grossa 84017-220 PR, Brazil; orcid.org/0000-0002-2019-774X

Leonardo J. Duarte – Institute of Chemistry, State University of Campinas, Campinas 13083-861 SP, Brazil; orcid.org/0000-0002-1955-6872

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.jcim.1c00165>

Notes

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