QTPIE: Charge transfer with polarization current equalization. A fluctuating charge model with correct asymptotics

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Abstract

Polarization and charge transfer are important effects which are difficult to describe using conventional force fields. Charge equilibration models can include both of these effects in large-scale molecular simulations. However, these models behave incorrectly when bonds are broken, making it difficult to use them in the context of reactive force fields. We develop a new method for describing charge flow in molecules – QTPIE. The QTPIE method is based on charge transfer variables (as opposed to atomic charges) and correctly treats asymptotic behavior near dissociation. It is also able to provide a realistic description of in-plane polarizabilities.
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1. Introduction

Polarization and charge transfer are important molecular interactions which are difficult to model correctly with the empirical force fields used in large-scale simulations. Polarization is popularly modeled using Drude oscillators, also called 'charge-on-spring' or 'shell' models, where each atom has a charge attached to it through a harmonic spring [1–3]. While promising, these models cannot describe charge transfer. Other approaches that employ atom-centered multipole expansions truncated at the dipole term also suffer the same restriction to polarization in practice [4,5].

Since charge transfer is an extreme manifestation of polarization, models that make no artificial distinctions between these two phenomena are highly desirable. The most promising such models are the 'fluctuating charge' (also called charge equilibration or chemical potential equalization) models [6,7], which are based on the chemical concepts of electronegativity and hardness. This concept of electronegativity equalization dates back to Pauling and

Yost [8], and inspired several highly parameterized models [9–11] and the minimally-parameterized QEq [6] and *fluc-q* [7,12] methods. However, there are difficulties [13,14] in reconciling electronegativity concepts with the known discontinuities of the derivative of the electronic energy with respect to the number of electrons [15]. In previous work, we have analyzed charge equilibration methods from a wavefunction viewpoint to elucidate the important issues [16,17]. First, we identified charge transfer as more fundamental than atomic charges. Second, we pointed out that electronegativities should depend on molecular geometries. We use these ideas here to develop a new charge equilibration method.

We briefly review charge equilibration methods using QEq as an example. The electrostatic energy of a molecular system is given by pairwise Coulomb interactions plus an internal energy term expanded to second order in the partial charges

$$E(\mathbf{q}) = \sum_{i=1}^{n} \left(\chi_i^0 q_i + \frac{1}{2} \eta_i q_i^2 \right) + \sum_{i<j} q_i q_j J_{ij} \qquad (1)$$

where i indexes the n atomic sites. The screened Coulomb interaction J_{ij} is described by an integral over single ns-type Slater orbitals (STOs)

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$$J_{ij}(\mathbf{R}_{ij}) = \left\langle \phi_i \phi_j \left| \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \phi_i \phi_j \right\rangle;$$

$$\phi_i(\mathbf{r}_i; \mathbf{R}_i) = N_i |\mathbf{r}_i - \mathbf{R}_i|^{n-1} e^{-\zeta_i |\mathbf{r}_i - \mathbf{R}_i|} \quad (2)$$

where $\mathbf{r}_i$ and $\mathbf{R}_i$ refer to the positions of electrons and nuclei, respectively, and $\mathbf{R}_{ij}$ is the distance between the ith and jth atoms. The coefficients in the first two terms of the expansion are identified as Mulliken electronegativities [18], χ_i^0, and Parr–Pearson hardnesses [19,20], η_i

$$\chi_i^0 = \frac{1}{2}(\mathrm{IP}_i + \mathrm{EA}_i) = -\mu_i$$

$$\eta_i = \frac{1}{2}(\mathrm{IP}_i - \mathrm{EA}_i) \quad (3)$$

where IP_i and EA_i are the ionization potential and electron affinity of the ith atom, respectively. The electronegativity χ_i^0 is trivially related to an atomic chemical potential μ_i. The atomic charges q_i are obtained by minimizing the energy of Eq. (1) under the constraint of fixed total number of electrons. This produces a linear system of n equations, which can be solved by standard matrix algebraic methods.

The QEq model works well for chemically reasonable structures near equilibrium [6]. However, it has fundamental problems that cause unreasonable charge distributions predicted for geometries far from equilibrium; this restricts its use in reactive molecular dynamics simulations involving bond dissociation [14,16,17]. For example, the QEq solution for a neutral diatomic molecule is

$$q_2 = -q_1 = \frac{\chi_2^0 - \chi_1^0}{J_{11} - 2J_{12} + J_{22}}$$

$$\Rightarrow \lim_{R_{12} \to \infty} q_2 = \frac{\chi_1^0 - \chi_2^0}{J_{11} + J_{22}} \neq 0 \quad (4)$$

The partial charges do not vanish in the asymptotic limit $R_{12} = |\mathbf{R}_1 - \mathbf{R}_2| \to \infty$ and are in general some non-integral value, which is unphysical. QEq and similar models generally overestimate the propensity for charge flow in polyatomic molecules, giving rise to inflated values of molecular electrostatic properties such as dipole moments and polarizabilities, especially for geometries far from equilibrium [21]. We therefore desire a fluctuating-charge model that can predict partial charges in such geometries with at least qualitative accuracy.

2. Theory

We have previously analyzed the behavior of charge equilibration methods and have addressed their shortcomings in an improved model [16,17], which was constructed and tested numerically on a diatomic molecule. Here, we generalize to polyatomic molecules and test the method's numerical accuracy. The fundamental variables of our new method are not atomic partial charges $\mathbf{q}$, but charge transfer variables $\mathbf{p}$ that describe a polarization current, i.e. a tendency for electronic density to migrate from one atom onto another. The method is thus named QTPIE, for charge transfer with polarization current equilibration.

The charge transfer variables are related to the atomic charges by continuity

$$q_i = \sum_j p_{ji} \quad (5)$$

where p_{ji} describes the amount of charge transferred from the ith atom to the jth atom. By symmetry, the charge transfer variables must form an antisymmetric matrix, i.e. $p_{ij} = -p_{ji}$. A similar variable transformation was used previously to simplify the numerical solution of charge equilibration models [22]. In terms of these transformed charge transfer variables, the QEq energy expression has the form

$$E(\mathbf{p}) = \sum_{ij} \chi_i^0 p_{ji} + \frac{1}{2} \sum_{ijkl} p_{ki} p_{lj} J_{ij} \quad (6)$$

where we have defined $J_{ii} = \eta_i$. The transformed variables allow us to introduce a distance-dependent function $f_{ji} = f_{ji}(\mathbf{R})$ which penalizes long-range charge transfer. This modified energy function is the central equation of QTPIE

$$E(\mathbf{p}) = \sum_{ij} \chi_i^0 f_{ji} p_{ji} + \frac{1}{2} \sum_{ijkl} p_{ki} p_{lj} J_{ij}$$

$$= \sum_{i<j} p_{ji} \left[\left(\chi_j^0 - \chi_i^0 \right) f_{ji} + \frac{1}{2} \sum_{k<l} p_{lk} (J_{ik} - J_{jk} - J_{il} + J_{jl}) \right] \quad (7)$$

In the second line of Eq. (7), we exploited the antisymmetry of the charge transfer variables and the symmetry of f_{ij} to write the equation in skew-symmetric form.

As shown previously [16], the function f_{ji} should decay with distance on a length scale related to the orbitals involved on atoms i and j. Also, detailed balance requires f_{ji} to be invariant under index exchange, i.e. $f_{ij} = f_{ji}$. The simplest choice of f_{ij} is therefore an overlap integral between orbitals on the ith and jth atoms. In the present work, we take this function to be a scaled overlap integral of the ns-type orbitals which are used to represent the screened Coulomb interaction, i.e.

$$f_{ji} = k_{ji} S_{ji} = k_{ji} \langle \phi_j | \phi_i \rangle \quad (8)$$

The scaling factors k_{ji} could be optimized, even for different bond types; however, here we simply choose k_{ji} to be unity for all atom pairs unless otherwise stated. The sum in Eq. (7) is *not* limited to bonded atom pairs – all information about molecular connectivity is embedded in the screened Coulomb interaction and the attenuation factor f_{ij} – so bonding need not be specified a priori. We use the QEq parameters for electronegativities, hardnesses, and orbital radii without modification. Explicit reparameterization can thus be expected to improve all of the results reported here.

Minimizing the energy of Eq. (7) with respect to all charge transfer variables leads to the system of linear simultaneous equations

$$\forall i, j : 0 = \frac{\partial E}{\partial p_{ji}}$$

$$= \left(\chi_j^0 - \chi_i^0 \right) k_{ji} S_{ji} + \sum_{k<l} p_{lk} (J_{ik} - J_{jk} - J_{il} + J_{jl}) \quad (9)$$

The QTPIE solution for a diatomic molecule is thus

$$q_2 = p_{21} = \frac{\chi_2^0 - \chi_1^0}{J_{11} - 2J_{12} + J_{22}} k_{12} S_{12} \Rightarrow \lim_{R_{12} \to \infty} q_2 = 0 \qquad (10)$$

In contrast to the QEq solution of Eq. (4), QTPIE correctly predicts vanishing charge transfer in the dissociation limit and should therefore provide a more accurate description of fluctuating charges for non-equilibrium geometries.

3. Results and discussion

The QEq and QTPIE methods were implemented in Scilab and solved in a linear algebraic representation in the space of unique atomic pairs. We did not implement the charge-dependent atomic radius for hydrogen atom described in the original QEq method [6], but instead use the equations as embodied in Eqs. (1)–(3). Thus, the results presented here are denoted QEq(-H), indicating that the hydrogen correction is not employed.

The QTPIE method as formulated contains $\sim n^2$ charge transfer variables but charge transfer around closed loops does not influence the energy expression of Eq. (7). Both methods therefore only have $(n - 1)$ independent variables. The linear system of Eq. (9) is therefore rank-deficient and hence singular. The system was solved by constructing the pseudoinverse from singular value decomposition [23].

We performed calculations on three representative small molecules: sodium chloride, water and phenol. For each molecule, we compared the predictions of QEq(-H) and QTPIE with the results of ab initio calculations. Since atomic charges are not well-defined quantum-mechanical observables, we chose two distinct definitions for comparison, namely Mulliken population [24] and distributed multipole [25] analysis (DMA). The DMA calculation was restricted to monopoles on the atomic centers. The electronic structure calculations for these charge analyses were in general performed using multi-reference ab initio methods with small basis sets. We chose well-localized basis sets to facilitate comparisons between the ab initio and QTPIE/QEq methods, which implicitly use minimal basis sets.

For illustrative purposes, we present results of the QEq(-H) and QTPIE models applied to an isolated sodium chloride molecule at different internuclear distances. Ab initio results are obtained from a complete active space (CAS) calculation [26] using eight electrons in five orbitals, i.e. CAS(8,5), with a 3-21G basis set [27]. This full valence active space wavefunction describes both ionic and covalent characters. Because of the weakly avoided crossing between the covalent and ionic diabatic states, the transition from ionic to covalent character on the ground electronic state is quite rapid, as seen in both the Mulliken and DMA charges shown in Fig. 1. The Mulliken and DMA definitions of the atomic charges give similar values throughout, indicating the robustness of the ab initio partial charges we are using for comparison with the QTPIE and QEq(-H) results. Fig. 1 shows that, as expected from Eq. (4), the QEq(-H) method exhibits a dissociation catas-
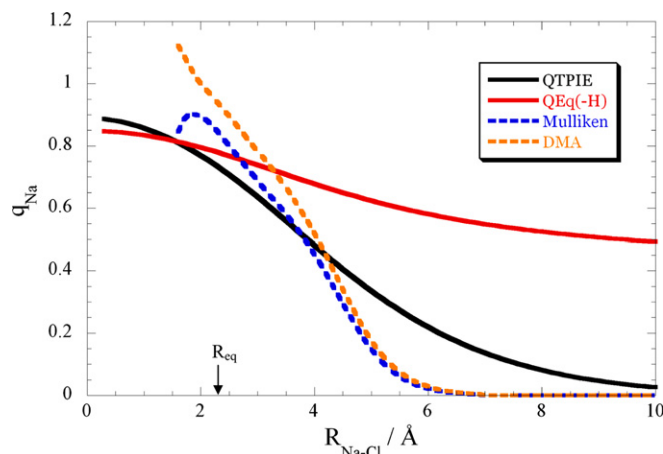

Fig. 1. Partial charges (in atomic units) on dissociating NaCl as computed using QEq(-H) and QTPIE. CAS(8,5)/3-21G calculations were also analyzed using Mulliken population and distributed monopole analysis (DMA). At infinity, QEq(-H) predicts significant charge transfer while QTPIE predicts uncharged fragments in this limit, in agreement with the ab initio results. The experimentally-determined equilibrium bond length of NaCl is indicated on the graph ($R_{eq} = 2.361$ Å).

trophe, i.e. it predicts finite charge transfer at infinite separation: asymptotically $q_{Na} = -q_{Cl} = 0.394$. However, QTPIE correctly predicts no charge transfer here. The QTPIE charges are not in quantitative agreement with the ab initio charges. This is expected, since only a fully quantum mechanical method is expected to capture the weakly avoided crossing (at large internuclear distance) between the covalent and ionic states.

We also calculated partial charges for asymmetrically dissociated water molecules. In this hypothetical reaction, the H–O–H internal bond angle was set to $\theta = 104.5°$ and one of the O–H bonds was kept fixed at 0.97 Å while the other O–H bond length was varied. The ab initio data were computed at the CAS(10,7)/STO-3G level of theory. In Fig. 2, we show the atomic charges on the dissociating hydrogen and oxygen atom computed from ab initio, QEq(-H), and QTPIE methods. The atomic charge on the remaining hydrogen atom can be deduced by considering overall charge neutrality. Similar to the NaCl example, the QTPIE charges are asymptotically correct, unlike the QEq(-H) values. The QTPIE partial charge on the oxygen atom in the OH fragment is closer to the ab initio result than that predicted by QEq(-H). However, it is still too large, indicating an overestimation of the dipole moment of OH. Thus, we attempt the simplest reparameterization possible, namely varying k_{OH} of Eq. (8), while demanding that $k_{OH} = k_{HH}$. We chose the value for k_{OH} which led to agreement of the partial charge on oxygen atom at the equilibrium geometry of the water molecule ($k_{OH} = k_{HH} = 0.4072$). With this modification, the QTPIE charges are in good agreement with the ab initio values across the whole range of O–H distances, as shown in Fig. 3.

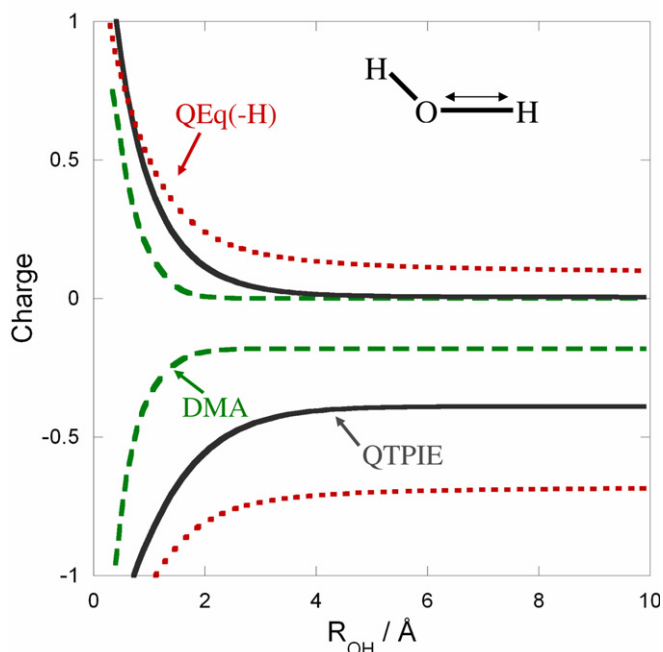In order to explore the adequacy of a single set of QTPIE parameters for other molecular geometries, we

Fig. 2. Partial charges (in atomic units) for a dissociating water molecule. Positive values are charges on the dissociating hydrogen, and negative values are charges on the oxygen. Distributed multipole analysis (DMA) charges were obtained from a CAS(10/7) wavefunction in a STO-3G basis set. QTPIE without reparameterization reproduces the vanishing charge on the dissociating hydrogen atom at infinite separation predicted by the ab initio method.

computed similar dissociation curves with varying $\angle HOH$ in the range 60–150°. The results (using $k_{OH} = k_{HH} = 0.4072$, as discussed above) are compared with ab initio
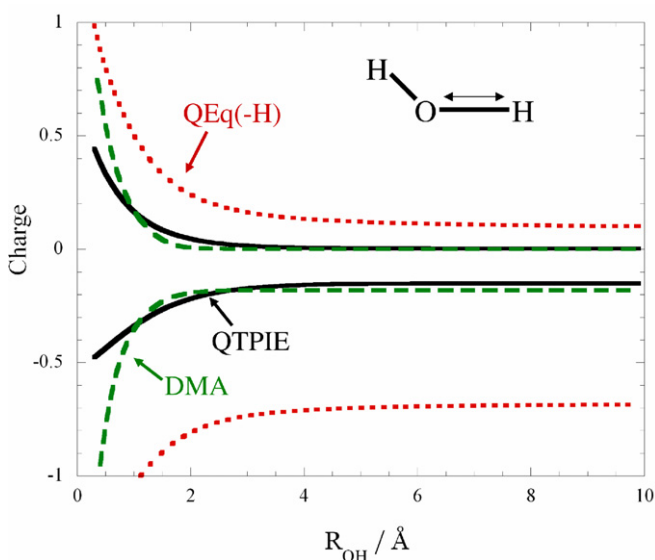

Fig. 3. As in Fig. 2, but using $k_{OH} = k_{HH} = k$ of Eq. (8) which is optimized ($k = 0.4072$) to give agreement of QTPIE and DMA charges at the equilibrium geometry of the water molecule. With minimal reparameterization, the QTPIE method agrees well with ab initio charges throughout (except for very short bond distances, where the concept of partial charge breaks down).

charges from Mulliken analysis on CASPT2(10,7)/STO-3G data in Fig. 4. The results from QTPIE remain in similarly good agreement with the ab initio calculations for all of these geometries, particularly in the dissociation limit. In Fig. 5, we show that this good agreement between ab initio and QTPIE charges persists for larger molecules such as phenol.

It is important that a fluctuating charge model be able to accurately model the change in atomic charges with response to an external electric field. Thus, we have also computed the molecular polarizability tensor using QEq and QTPIE. These results are again compared with ab initio calculations.

The QEq model has two shortcomings when computing molecular polarizabilities. The first is a tendency to overestimate the in-plane components, which is related to the overestimation of charges for weakly interacting (i.e. widely separated) atoms. The second is its inability to calculate the out-of-plane component of the molecular polarizability tensor for planar molecules. This latter deficiency arises because the model considers only atomic charges and not atomic dipoles or charge centers apart from the locations of the atoms. This makes it impossible to have charge fluctuations along any direction other than in directions directly leading to another point charge. In terms of molecular graphs, charge flow is restricted only to edges and therefore cannot flow out of the plane of the molecule. Similar restrictions apply in the QTPIE method as described here, and thus one might expect that QTPIE will also fail to describe the out-of-plane polarizabilities for planar molecules. Dummy atoms specified in the molecular geometry could conceivably improve matters, but only at the expense of additional parameters. Charge equilibration methods with expanded basis sets, which describe the charge fluctuations using both s- and p-type functions on each atomic site, are a more promising route to solve this problem [28]. We plan to investigate the application of similar ideas to QTPIE in future work.

The QTPIE energy expression in an external electrostatic field $\vec{\varepsilon}$ is given by

$$E(\mathbf{p}; \vec{\varepsilon}) = \sum_{ij} \chi_i^0 f_{ji} p_{ji} + \frac{1}{2} \sum_{ijkl} p_{ki} p_{lj} J_{ij} + \sum_{ij} p_{ij} \vec{x}_i \cdot \vec{\varepsilon} \qquad (11)$$

We compute the QTPIE polarizability numerically by the method of finite fields, being the fluctuation in the dipole moment with respect to changes in $\vec{\varepsilon}$. The dipole moment was recalculated with re-optimized charge transfer variables in Eq. (11) at each value of $\vec{\varepsilon}$. The scaling factor for the overlap, k_{ij}, was taken to be unity in all of these QTPIE calculations. Table 1 summarizes the results for sodium chloride, water and phenol. The ab initio polarizabilities were calculated as second derivatives of the second-order Møller–Plesset perturbation theory (MP2) energy, also using the method of finite fields. The ab initio calculations use an aug-cc-pVDZ basis set [29,30] which includes the diffuse functions necessary for accurate calculations of polarizabilities. Ground state equilibrium geometries were
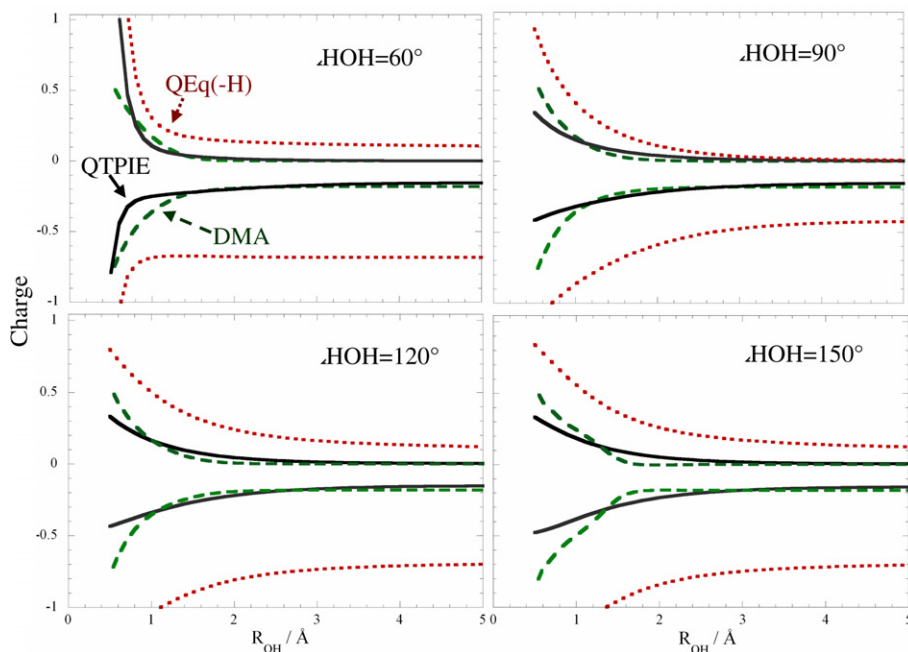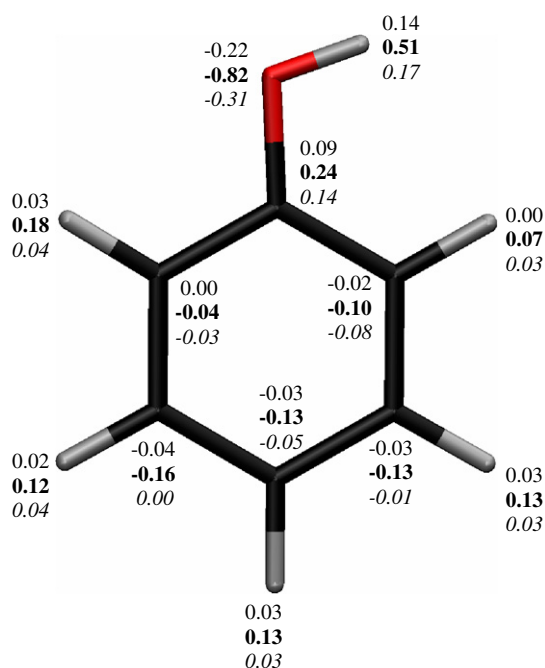
Fig. 4. As in Fig. 3, but for varying internal angles θ.

Fig. 5. Atomic partial charges for phenol in the equilibrium geometry computed with MP2/cc-pVDZ. Charges from QTPIE, QEq(-H) (bold), and Mulliken population analysis (italics) are shown for each atom.

Table 1
Eigenvalues (sorted by descending magnitude) of the dipole polarizability tensor (in units of $\mathring{A}^3$) for three molecules

	QEq(-H)	QTPIE	MP2/aug-cc-pVDZ
NaCl	13.9474	6.2171	4.5042
	0.0000	0.0000	3.6932
	0.0000	0.0000	3.6931
H_2O	3.4653	1.8338	1.4502
	1.2317	0.6516	1.3678
	0.0000	0.0000	1.2883
Phenol	24.6244	13.0298	13.6758
	20.3270	10.7566	12.3621
	0.0000	0.000	6.9981

ability for these planar molecules. The eigenvalues of the polarizability tensor in QTPIE are smaller than those from QEq(-H), generally by a factor of approximately two. The in-plane components of the polarizability predicted by QTPIE are in good agreement with the ab initio values.

4. Conclusions

We have defined a new fluctuating charge model, QTPIE, which defines atomic charges as sums over charge-transfer variables. This construction allowed us to create a simple fluctuating-charge model that exhibits correct asymptotic behaviors for weakly-interacting atoms, i.e. near dissociation. We showed that the QTPIE model also describes molecular polarizabilities more accurately than previous fluctuating charge models. We did not make any significant attempt to optimize the parameters for QTPIE, but instead used parameters (electronegativities, hardnesses, and orbital radii for the shielded Coulomb

optimized using MP2/aug-cc-pVDZ; the same geometries were used for all polarizability calculations.

Molecular polarizabilities calculated using the three methods above were found to be stable with respect to small perturbations in the nuclear geometries, so discrepancies in the eigenvalues due to geometric effects can be ruled out. As expected, both QEq(-H) and QTPIE incorrectly predict a vanishing out-of-plane component of the polariz-

interaction) optimized for the QEq method. We are currently investigating our expectation of improved results with parameters reoptimized for QTPIE. We hope that the successes and limitations of QTPIE will motivate the development of even more accurate fluctuating-charge models and improve our understanding of the chemically useful concepts of electronegativity and hardness.

Acknowledgement

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