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Estimating and modeling charge transfer from the SAPT induction energy

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Abstract

Recent studies using quantum mechanics energy decomposition methods, e.g. SAPT and ALMO, have revealed that the charge transfer energy may play an important role in short ranged inter-molecular interactions, and have a different distance dependence comparing with the polarization energy. However, the charge transfer energy component has been ignored in most current polarizable or non-polarizable force fields. In this work, firstly, we proposed an empirical decomposition of SAPT induction energy into charge transfer and polarization energy that mimics the regularized SAPT method (ED-SAPT). This empirical decomposition is free of the divergence issue, hence providing a good reference for force field development. Then, we further extended this concept in the context of AMOEBA polarizable force field, proposed a consistent approach to treat the charge transfer phenomenon. Current results show a promising application of this charge transfer model in future force field development.

Graphical abstract

The charge transfer energy component has been one of the missing components in most current force fields. We report an approach to estimate the charge transfer energy from the SAPT induction energy and to model it using an atomic multipole moment model. The SAPT induction energy of water clusters were well reported using the new model.

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Supporting Information

Additional Supporting Information may be found in the online version of this article.

Keywords

charge transfer; polarization; induction; SAPT; energy decomposition; AMOEBA; polarizable force field

Introduction

Non-covalent intermolecular forces control the interactions and dynamics of the molecules in chemical and biological processes, from small ions and drug molecules to large biomolecules, such as proteins and nucleic acids. The importance of electrostatic, exchange-repulsion, dispersion and polarization interactions have been widely recognized and implemented in current force fields. The charge transfer contribution, however, are less discussed in force field development. Earlier attempts to add charge transfer in force field were made in the SIBFA force field¹, which uses an integration based method to account the charge transfer energy².

The limited implementation of charge transfer in force fields may partly because there is no unified and widely accepted quantitative definition of this phenomenon. As a result, the charge transfer contribution is absent in most widely used force fields, including AMOEBA polarizable force field^{3–7}, currently. Hence, there are demands in the force field community to have a reliable quantum mechanical energy decomposition method in model development. The recently developed symmetry adapted perturbation theory (SAPT)^{8–10}, absolutely localized molecular orbital (ALMO)^{11–12}, block-localized wavefunction (BLW)^{13–14} and other DFT-based decomposition methods^{15–17} have been used to understand the molecular interactions and be compared with force field results. Among which, SAPT might be one of the most widely used quantum mechanical energy decomposition analysis tools. It provides almost all intermolecular interaction energy components, e.g., electrostatic, induction, dispersion and exchange-repulsion energy and has comparable accuracy with CCSD(T) interaction energy^{18–21}. However, one challenge of the current SAPT method is that it does not separate polarization and charge transfer (CT) from the induction energy component.

Some other methods, which do separate polarization and charge transfer, however, they do not provide some other energy components, for example, dispersion energy.

As an early attempt in SAPT, Stone and Misquitta suggested that the charge transfer energy can be estimated as the difference between the second order induction energies calculated using the dimer and monomer basis sets (CT-SM09)²². However, like many other CT energy decomposition methods, CT-SM09 has two problems. One is that it is not basis set independent, i.e., the calculated CT energy is depend on the basis set used and approaches zero toward the basis set limit^{16, 23–24}. The other problem is that it tends to overestimate the polarization energy and underestimate the CT energy at shorter intermolecular distances²⁴. To address these problems, Misquitta²⁴ recently proposed a regularized SAPT(DFT) method to suppress the charge delocalization to the neighboring molecular orbitals, which was suggested to be the source of the charge transfer energy. In this way, the CT contribution could be removed in the SAPT induction energy, leaving out the polarization energy only. Then, subtracting the polarization energy from the induction energy gives the CT energy.

Although Misquitta's regularized SAPT(DFT) method solved the basis set convergence problem, it works for the second order energy only. More recently, Misquitta and Stone³⁰ reported an approach to estimate the infinite order charge transfer energy using the second order induction energy and a polarization model by assuming that non-iterative classical polarization model best matches the regularized second order polarization energy. This is an interesting work. However, it might not be applicable to broader spectrum. As the higher order polarization and charge transfer energy contribute considerably to the intermolecular interaction energy, in attempts to address these challenges, we propose an empirical decomposition of SAPT induction energy (ED-SAPT) into polarization and charge transfer energy that mimics the regularized SAPT approach. Then, we further extended this concept in the context of AMOEBA polarizable force field, developed a consistent treatment of charge transfer and polarization energy. We hope this study can facilitate the development of next generation polarizable force fields.

Methods

Charge transfer in SAPT induction energy

In the regularized SAPT(DFT) method introduced by Misquitta²⁴, the concept of regularization was revisited, which was initially introduced to address the divergence issue of the polarization expansion at higher orders caused by the Pauli-forbidden continuum¹⁰. This can be viewed as the electrons initially assigned to one monomer are not prevented by the Pauli principle from falling onto the core of the other monomer, causing an unphysical energy lowering. Therefore, to prevent the system converging to the unphysical Pauli-forbidden states, a regularized (or screened) Coulomb potential can be used in the perturbation operator, so that the electrons on one monomer do not see the singular Coulomb potential ($1/r$) of the other monomer, hence breaking the symmetry. In this way, the Coulomb potential can be split into the regular part (v_p) and the singular part (v_t), i.e., $1/r = v_p(r) + v_t(r)$, where the subscripts p and t indicate that the potential are responsible for the polarization and tunneling phenomenon, respectively. Following this idea, Misquitta argued that the charge transfer phenomenon could be considered as a tunneling effect. By

introducing the split Coulomb potential above with a Gaussian-based regularization function (Equation 1) in SAPT, the polarization and charge transfer energy could be obtained. When calculating the second order SAPT induction energy, instead of using the singular $1/r$ potential for electron-nuclear interactions, a well-behaved long-ranged part (v_p , Equation 1) was used to calculate the second order regularized polarization energy. The charge transfer energy was then obtained by subtracting the regularized polarization energy from the normal induction energy. To obtain the proper amount of regularization, a value of 3.0 au for η was empirically derived by Misquitta. The polarization and charge transfer energy obtained using this method had a good convergence towards the basis set limit.

$$\begin{aligned} v_t(r) &= \frac{1}{r} e^{-\eta r^2} \\ v_p(r) &= \frac{1}{r} \left(1 - e^{-\eta r^2} \right) \end{aligned} \quad (1)$$

Inspired by Misquitta's approach, we propose an empirical decomposition of SAPT induction energy (ED-SAPT) into charge transfer and polarization energy that mimics the regularized SAPT use Equation 2:

$$\begin{aligned} E_{CT} &= E_{ind} \exp \left[-\lambda \left(\frac{R}{R_m} \right)^n \right] \\ E_{pol} &= E_{ind} \left(1 - \exp \left[-\lambda \left(\frac{R}{R_m} \right)^n \right] \right) \end{aligned} \quad (2)$$

where R is intermolecular distances, R_m is the equilibrium intermolecular distance, n is a constant that equals to 3 and λ is defined as the ratio between the distances of the closest non-hydrogen atoms and the closest atoms involving hydrogen. The value of n was determined by comparing the mean unsigned error (MUE) and mean signed error (MSE) of the charge transfer energy using Equation 2 against the regularized SAPT(DFT)/aTZ energy of the S16 $\times$ 7 dataset. When n equals 2, 3 and 4, the MUE/MSE were 0.46/0.40, 0.25/−0.04, and 0.57/−0.44 kcal/mol, respectively. As a result, $n = 3$ yielded the smallest error, thus were used in subsequent calculations. In practice, λ can be set to either 1.6 when this ratio is greater than one or 1.0 if such ratio is equal or less than one for simplicity. For instance, for a hydrogen-bonded water dimer, λ is 1.6, and for a noble gas pair or a BH₃-CO pair, it is 1.0. Physically, this could be interpreted as when two heavier (non-hydrogen) atoms directly facing each other, there would be more electrons on one atom tunneling to the other; however, when a proton was placed in between, such tunneling or delocalization might be hindered slightly. In this study λ equals to 1.6 were used in all calculations if not otherwise mentioned.

Data set

A data set with 16 $\times$ 7 molecule pairs (S16 $\times$ 7) were selected from our previously developed S101 $\times$ 7 database¹⁸, including pairs 01 (Water-Water), 08 (MeOH-Water), 12 (MeNH₂-Water), 20 (AcOH-AcOH), 21 (AcNH₂-AcNH₂), 24 (Benzene-Benzene π - π), 30 (Benzene-Ethene), 51 (Ethyne-Ethyne T-shaped), 73 (PO₄H-Water), 74 (PO₄H₂-Water), 75 (PO₄H₃-Water), 80 (MeCl-Water), 90 (CH₂Cl₂-CH₂Cl₂), 92 (MeNH₃-Water), 93

(Imidazole⁺–Water), and 95 (AcOH[–]–Water). Among which, 01, 08, 12, 20, 21 and 75 are polar or hydrogen-bonded pairs; 24, 30, 51, 80 and 90 are nonpolar or non-hydrogen-bonded pairs; 92 and 93 are positively charge pairs while 73, 74 and 95 are negatively charged pairs. Hence, this 16×7 data set is a reasonably comprehensive set that covers the majority of the intermolecular interactions that are common in biologically interested systems in different orientations and distances. The geometries of the pairs were optimized using MP2/cc-pVTZ level of theory with counterpoise correction applied. Then each pair was pulled or compressed along a defined vector axis at separations of 0.70, 0.80, 0.90, 0.95, 1.00, 1.05 and 1.10 fold of their optimal geometry. The S16×7 data set along with seven Ar...Ar pairs at different separations from previous study²⁴ were served as the training set to determine n and λ in Equation 2. In addition, a number of typical charge transfer dimers reported in previous studies^{24–25} were also prepared as an additional test set.

For all pairs, the regularized second order SAPT(DFT) polarization and charge transfer energy, the second order SAPT2+ induction energy, higher order HF contribution were calculated using aug-cc-pVTZ basis set if not otherwise mentioned. SAPT(DFT) calculations were performed using CamCASP^{9, 24, 26} and NWChem²⁷, while SAPT2+ calculations were performed using PSI4²⁸. Abbreviations aXZ have been used in the context for aug-cc-pVXZ, where X were D, T, Q or 5.

Results

Converged SAPT induction energy

As discussed above, the SAPT charge transfer and polarization energy predicted by many energy decomposition methods suffer from the basis set convergence issue. Because our ED-SAPT method is based on the SAPT induction energy, the first question we were interested was whether SAPT induction energy had the same problem. From our previous work on S101×7 database¹⁸, we found that the total induction energy calculated using the SAPT2+ method²⁰ converges well to the basis set limit. The results obtained using aug-cc-pVTZ basis set were already very close to the complete basis set limit for the examined molecule pairs at equilibrium distances. Here, we further examined the basis set convergence for shorter intermolecular separations and reached the same conclusion (Table 1). Therefore, it is reasonable to assume that the induction energy obtained from SAPT2+ calculation can well approximate the complete basis set (CBS) limit. However, if we follow CT-SM09 approach to separate the polarization and charge transfer energy, we will face an issue, i.e., the charge energy approaches to zero toward the CBS limit. The charge transfer energy approaches zero as the basis size increases. Consequently, the polarization energy will be overestimated²⁴. Similar problem has also been reported for ALMO, where the polarization energy tends to be overestimated, especially at shorter intermolecular separations²³. This is also demonstrated in Figure 1. Such problem prevents a quantitative definition of the charge transfer and polarization energy, hence motives the development of new approaches.

Empirical decomposition of the second order SAPT(DFT) induction energy into polarization and charge transfer energy

As the regularized SAPT(DFT) method provides stable charge transfer and polarization energy that were free of the basis set convergence issue, we first trained our ED-SAPT method (Eq. 2) using the regularized SAPT(DFT) results of the S16×7 data set (Table 2 and Figure 2) and seven Ar pairs at different separations (Supporting Information). The ED-SAPT results based on SAPT(DFT) induction energy will be referred as ED-SAPT(DFT). Likewise, ED-SAPT2+ refers to results based on SAPT2+ induction energy. As a result, the second order ED-SAPT(DFT) charge transfer and polarization energy of S16×7 data set correlates well with the second order regularized SAPT(DFT) results, given the r^2 correlation coefficients of 0.99 for both energy components (Table 2 and Figure 2). The calculated mean unsigned errors (MUE) of the ED-SAPT(DFT) polarization and charge transfer energy are both 0.25 kcal/mol, while the mean signed error (MSE) are 0.04 and -0.04 kcal/mol respectively.

We then further tested the second order ED-SAPT(DFT) polarization and charge transfer energy on additional molecule dimers, including some “charge transfer molecules”. This includes some pairs from Misquitta²⁴ and Hobza’s work²⁵. In generally, the MUE of these pairs is slightly greater than the error of S16×7 data set, this is mainly because of some pairs have large charge transfer energy, hence the larger magnitude of errors (Table 3). For instance, the H₃B-CO pair taken from Misquitta’s work has the charge transfer energy of -44.38 and -33.22 kcal/mol for the regularized SAPT(DFT) and ED-SAPT(DFT) methods respectively. Their absolute error may look large, however, the relatively errors are still within an acceptable range (25%). Nonetheless, if these pairs with large energy were excluded, the MUE of these pairs were also well below 0.5 kcal/mol, hence in a similar level of our training S16×7 data set. On the other hand, the mean relative error of the ED-SAPT(DFT) charge transfer energy is considerably larger for Misquitta and Hobza’s pairs than that for the S16×7 pairs. This is because most these pairs have very small CT energy, of which the magnitude is often less than 0.3 kcal/mol.

Empirical decomposition of the second order SAPT2+ induction energy into polarization and charge transfer energy

While the second order ED-SAPT(DFT) polarization and charge transfer energy agree well with the regularized SAPT(DFT) counterparts, we then examined whether or not this estimation method is transferable to *ab initio* based SAPT method, e.g., SAPT2+. The SAPT2+ induction energy²⁰ was defined as

$$E_{Ind}^{SAPT2+} = E_{ind,resp}^{20} + E_{exch-ind,resp}^{20} + {}^tE_{ind}^{22} + {}^tE_{exch-ind}^{22} + \Delta HF, \text{ where as the second order}$$

SAPT2+ induction energy was defined as $E_{Ind}^{SAPT2+} - \Delta HF$. Comparing the second order SAPT2+ induction energy against the second order SAPT(DFT) induction energy of all the pairs in S16×7 data set gives a MUE of 0.75 kcal/mol. In contrast, the MUE of the second order ED-SAPT2+ charge transfer and polarization energy are 0.39 and 0.48 kcal/mol, respectively (Table 4 and Figure 3). The sum of the MUEs of the charge transfer and polarization energy is quite close to the MUE of the induction energy, so are the MSEs of the respective energy terms. Similar trends can also be found in the subgroups of $R/R_m =$

0.7~0.9 and 0.9~1.1. This, may not be a direct evidence of the transferability of the ED-SAPT method, but at least suggested that the ED-SAPT2+ results have a plausible accuracy comparing to the regularized SAPT(DFT) polarization and CT energy.

The higher order contribution included ED-SAPT2+ polarization and charge transfer energy

So far, our discussions about the ED-SAPT polarization and charge transfer energy are limited at second order only, the higher order contributions are ignored, which, however, are significant in many cases. For example, the HF term, which is used to account the higher order induction energy contribution in the SAPT2+ method, contributes -4.0 kcal/mol to the total interaction energy for the S16 $\times$ 7 data set on average. Therefore, if it is ignored, the MUE of the induction energy would be 4 kcal/mol larger, which is not negligible indeed. So how can we split it into the polarization and charge transfer energy? Naively, the simplest way to do this may be just follow the way to split the second order energy using Equation 2.

As regularized SAPT(DFT) is limited to second order energy only, to determine how well this assumption (Equation 2) is, we will compare the higher order included ED-SAPT results with the ALMO/HF results. To make a fair comparison, we used the SAPT0 induction energy²⁰, which was $E_{Ind}^{SAPT0} = E_{ind,resp}^{20} + E_{exch-ind,resp}^{20} + \Delta HF$. In this way, the SAPT and ALMO polarization and charge transfer energy are all limited at the HF level of theory.

As expected, when the molecule pairs are around the equilibrium distances ($R/R_m = 0.9\sim 1.1$ in S16 $\times$ 7 data set), the induction energy calculated using SAPT and ALMO are very close given their very similar physical definitions. As a result, the mean unsigned and mean signed differences (MUD and MSD) of the total induction energy are only 0.21 and 0.20 kcal/mol for these pairs, respectively (Table 5). In terms of the polarization and charge transfer energy, the MUD/MSD of ED-SAPT0 against ALMO/HF are slight larger for the pairs in the same distance range, of 0.55/ -0.51 and 0.71/0.71 kcal/mol, respectively. The much larger relative difference between the two methods for polarization and CT energy around the equilibrium distances may partly because of the smaller magnitude of the polarization and CT energy, which could amplify the error when calculating the relative differences. For the pairs at shorter intermolecular separations ($R/R_m = 0.7\sim 0.8$), the results are not comparable, since it is known that ALMO suffers from the divergence issue. By plotting the ED-SAPT0 polarization and CT energy against the ALMO/HF results (Figure 4), it is clear that ALMO tends to have stronger polarization but weaker charge transfer energy than ED-SAPT0 at shorter separations. Since previous study suggested that ALMO tends to overestimate polarization energy and underestimate charge transfer energy at shorter intermolecular separations²³, it is possible that the ED-SAPT0 energy may be closer to the “correct” values than ALMO/HF.

Consistent classical models for charge transfer and polarization

The results in previous sections demonstrated that based on a simple exponential function (Equation 2), it is possible to extrapolate the charge transfer and polarization energy from the SAPT induction energy with a reasonable accuracy. This inspired our development of a consistent model to treat charge transfer and polarization in the context of a molecular

mechanics (MM) force field. In previous studies, we have systematically demonstrated that the SAPT2+ electrostatic, dispersion and exchange-repulsion energy can be reproduced based on the framework of AMOEBA force field^{18, 29}. Here, we attempted to build a consistent charge transfer and polarization model that can reasonably reproduce the ED-SAPT2+ counterparts, hence the total SAPT2+ induction energy, within the frame of AMOEBA. In the following discussion, if not otherwise mentioned, the SAPT2+ energy are all HF inclusive, and SAPT2+ and ED-SAPT2+ are used interchangeably when referring to the charge transfer and polarization energy.

First, we compared the polarization energy of the S16×7 data set calculated using AMOEBA polarizable model with the ED-SAPT2+ polarization energy. Not surprisingly, it is found that the AMOEBA polarization model has a reasonable agreement with the SAPT2+ polarization energy, given a MUE of 1.40 and 2.27 kcal/mol for pairs around the equilibrium distance ($R/R_m = 0.9\sim 1.1$) and all distances ($R/R_m = 0.7\sim 1.1$), respectively (Table 6). The agreement is even better when the AMOEBA polarization are compared with the second order polarization energy (regularized SAPT(DFT)), where the higher order contribution is not included. The above MUEs drop to 1.08 and 1.34 kcal/mol, respectively. The value of r^2 correlation coefficient also increased from 0.82 to 0.93. However, due to the lack of charge transfer treatment in the AMOEBA force field, the MUE between the AMOEBA polarization energy and SAPT2+ induction energy is much larger, resulting a MUE of 2.81 and 6.92 kcal/mol for the subgroups of S16×7 data set at $R/R_m = 0.9\sim 1.1$ and $0.7\sim 1.1$, respectively.

Therefore, to fill the gap in the current AMOEBA force field, we proposed a charge transfer model that is consistent with the polarizable dipole model. Inspired by the split electron-nuclear potentials in regularization concept (Equation 1) and the exponential relationship shown in Equation 2, we hypothesized that it might be possible to use an exponential-function-scaled induced dipole model to mimic the charge transfer energy. In addition to the induced dipole of the polarization model, we created an “induced charge transfer dipole” to model the charge transfer energy. The AMOEBA polarizable model was also modified slightly to fit the higher order contribution included ED-SAPT2+ polarization energy. The new model can be written as:

$$\begin{aligned}
 E_{pol}^{new} &= \frac{1}{2} \sum_i \sum_{j \neq i} \mu_i^{pol} \mathbf{T}^{new} \mathbf{M}_j \\
 E_{ct} &= \frac{1}{2} \sum_i \sum_{j \neq i} \mu_i^{ct} \mathbf{T}^{ct} \mathbf{M}_j \\
 \mu_i^{pol} &= \alpha_i \left(\sum_{j \neq i} \mathbf{T}^{new} \mathbf{M}_j + \sum_{j \neq i} \mathbf{T} \mu_j^{pol} \right) \\
 \mu_i^{ct} &= \alpha_i \left(\sum_{j \neq i} \mathbf{T}^{ct} \mathbf{M}_j \right)
 \end{aligned} \quad (3)$$

where the superscript *new* indicates that the new polarization instead of the AMOEBA polarization energy, is the induced dipole for the polarization part, is the charge transfer dipole for the charge transfer part, $\mathbf{T}$ is the multipole interaction matrix, and $\mathbf{M}$ is the

permanent multipole moments. In AMOEBA polarizable force field, the **T** matrix elements are damped to avoid polarization “catastrophe”. For instance, the first order **T** element that has f_3 damping function is shown in Equation 4. The damping functions, e.g. f_5 , f_7 and f_9 , in higher order elements can be easily derived³, thus are not shown here. The parameters a , b , c and d used in the damping functions are universal for all atoms, where a equals 0.39 is same as the AMOEBA model, b is 0.7, c is 0.1 and d is 1.0. The damping functions in first order **T** matrix element can be written as:

$$\begin{aligned} \mathbf{T}_\zeta &= -f_3 \frac{R_\zeta}{R^3}, \zeta=x, y, z \\ f_3 &= 1 - \exp(-au^3) \\ f_3^{new} &= 1 - b \exp(-au^3) \\ f_3^{ct} &= \exp(-cu^3) \end{aligned} \quad (4)$$

where $u=R_{ij}/(\alpha_i\alpha_j)^{1/6}$, α is the atomic polarizability at sites i and j .

In this model (Equations 3 and 4), charge transfer and polarization are all considered as a result of the distorted charge density due to the external field, except that one is short-ranged and the other is long-ranged (Figure 5).

To keep the calculations simple and fast, we currently limited the charge transfer dipoles to include the direct field only. For the polarization energy part, we modified the **T** matrix for the direct induction part as shown in Equation 3. However, the mutual induction part remains to be the same as the AMOEBA model, given the fact that the current AMOEBA model is reasonably well in reproducing the many-body effects of the water clusters³, which will also be discussed in later sections.

In general, the new charge transfer model agrees well with the ED-SAPT2+ charge transfer energy for pairs near the equilibrium distances ($R/R_m = 0.9\sim 1.1$) in S16 $\times$ 7 data set, given the MUE and MSE of 0.45 and 0.24 kcal/mol, and r^2 correlation of 0.90, respectively (Table 6 and Figure 6). However, for molecule pairs at compressed intermolecular separations, the error is notably greater, resulting a larger MUE and MSE of 1.42 and 0.91 kcal/mol, but similar r^2 correlation of 0.91 for all pairs ($R/R_m = 0.7\sim 1.1$).

After adding the charge transfer energy, the new model greatly reduces the error of the total induction energy. The MUE/MSE are reduced from 2.81/2.81 and 6.92/6.92 kcal/mol of AMOEBA to 1.39/1.23 and 2.68/2.11 kcal/mol of the new model for near equilibrium pairs and for all pairs, respectively. The r^2 correlation of the induction with the SAPT2+ values are also increased from 0.61 to 0.93 for all the pairs in the S16 $\times$ 7 data set.

It is worth to mention that although the polarization in the new model slightly reduced the MUE of AMOEBA from 2.27 kcal/mol to 1.68 kcal/mol for all pairs in the S16 $\times$ 7 data set. It is likely a result of an artificial improvement on parameterization. In other words, such improvement is a result of a purposed over-fitting of the polarizable dipole model to reproduce the physics beyond its scope, i.e., the missing higher order polarizable multipole moments in the polarizable dipole model. For instance, the r^2 correlation of the new

polarization energy with the higher order included SAPT2+ and the second order only regularized SAPT(DFT) polarization energy are 0.87 and 0.93 respectively for the S16 $\times$ 7 data set. Respectively, correlation coefficients of 0.75 and 0.83 are obtained for AMOEBA polarization energy. We also found that it would be very hard, if not impossible, to further improve the agreement of the current polarizable model with SAPT2+ results. For example, we were able to further reduce the polarization energy error for the S16 $\times$ 7 data set, but the error of the water clusters will be even larger (Figure 7). The more the water molecules, the larger the error is. As we just mentioned, this might be due to the limitation of the polarizable dipole model.

Conclusion

In this work, we first discussed the possibility to estimate the charge transfer and polarization energy from the SAPT induction energy using our ED-SAPT method. Our results showed that the proposed empirical approach inspired by the regularization concept is effective and reasonably accurate for the purpose of examining and developing classical force fields. As the SAPT induction energy is free of the distance and basis set dependent issues, the ED-SAPT charge transfer and polarization energy are also free of such issues, which are the notable problems of other popular energy decompose methods like CT-SM09 and ALMO.

Following this idea, we further proposed a new approach to model the charge transfer energy in the context of AMOEBA polarizable force field. In this new model, charge transfer and polarization are all considered as a consequence of the distorted charge density induced by the external field, except that one is short-ranged and the other is long-ranged, respectively. Our results demonstrated that this model is capable of reproducing the SAPT energy components reasonably. The advantage of this charge transfer model is that it is consistent with the current polarizable dipole model, and can also be easily implemented in the current code. Nonetheless, further studies are necessary to fully assess the performance of the model. In addition, by comparing the polarizable dipole model with the second order regularized SAPT(DFT) polarization energy and with the higher order contribution included ED-SAPT2+ polarization energy, the current polarization model may still have some room for future improvement. Either by adding the polarizable quadrupoles to the model or by replacing the functional form in the current polarizable dipole model with an improved one so that the higher order contribution could be better approximated.

In general, such consistent treatment of charge transfer and polarization effect in the context of a polarizable force field may open up new ways for future force field developments. We anticipate that with further effort in parameterization and implementation, the new charge transfer and polarization models along with our previous work in electrostatic¹⁸ and vdW interaction²⁹ would reproduce not only the total QM interaction energy, but also all the SAPT energy components.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Abbreviations

CT	charge transfer
ED-SAPT	empirical decomposition of SAPT induction energy
ED-SAPT0	empirical decomposition of SAPT0 induction energy
ED-SAPT(DFT)	empirical decomposition of SAPT(DFT) induction energy
ED-SAPT2+	empirical decomposition of SAPT2+ induction energy

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Figure 1.

The second order charge transfer energy approaches to zero toward the complete basis set limit for water dimers at the equilibrium distance (upper) and at distances of 0.8 fold of the equilibrium distance (lower). The charge transfer and polarization energy were calculated using CT-SM09 scheme at the level of SAPT2+/aug-cc-pVTZ.

Figure 2.

Plots of the second order ED-SAPT(DFT) polarization and charge transfer energy against the reference second order regularized SAPT(DFT)/aug-cc-pVTZ counterparts for the S16 $\times$ 7 data set.

Figure 3. Plots of the second order ED-SAPT2+ polarization and charge transfer energy against the second order regularized SAPT(DFT)/aug-cc-pVTZ counterparts for the S16×7 data set.

Figure 4. Plots of the higher order contribution included ED-SAPT0 polarization and charge transfer energy against the ALMO/HF/aug-cc-pVTZ counterparts for the S16 $\times$ 7 data set.

Figure 5.
Plots of the polarization and charge transfer energy against intermolecular distances.

Figure 6.

Plots of AMOEBA and the new model against the SAPT2+/aug-cc-pVTZ induction energy and the ED-SAPT2+ polarization and charge transfer energy for near equilibrium (i.e. $R/R_m = 0.9 \sim 1.1$) pairs in the S16 $\times$ 7 data set. Polarization energy compared with the second order regularized SAPT(DFT) results (without HF contribution) are also plotted.

Figure 7.

Comparison of AMOEBA and the new model with the SAPT2+/aug-cc-pVTZ induction energy and the ED-SAPT2+ polarization and charge transfer energy for water clusters ($n = 2, 3, 4, 5, 6$). The SAPT2+ energy of the water cluster was obtained by dividing the sum of the SAPT2+ energy of each water molecule with the rest $n - 1$ water molecules by two, i.e.,

$$\frac{1}{2} \sum_{i \in n} E_{i,n-1}^{SAPT2+}, \text{ where } n \text{ is the number of water molecules in the cluster.}$$

Table 1

Convergence of the induction energy (kcal/mol) calculated using SAPT2+ method. R is intermolecular distances, and R_m is the equilibrium intermolecular distance.

R/R_m	aDZ	aTZ	aQZ	a5Z
Water-Water				
0.7	-14.368	-14.504	-14.427	-14.384
0.8	-7.237	-7.300	-7.265	-7.246
1.0	-2.004	-2.002	-1.998	-1.994
Water-MeNH ₂				
0.7	-22.145	-21.952	-21.900	-21.809
0.8	-11.989	-11.944	-11.895	-11.881
1.0	-3.778	-3.760	-3.751	-3.738
Ethyne-Ethyne TS				
0.7	-5.826	-5.925	-5.919	-5.889
0.8	-2.507	-2.568	-2.561	-2.554
1.0	-0.506	-0.514	-0.514	-0.511

Table 2

Error of the second order ED-SAPT(DFT) polarization and charge transfer energy (kcal/mol) against the reference second order regularized SAPT(DFT)/aug-cc-pVTZ results for the S16×7 data set.

S16×7 set ($R/R_m = 0.7\sim 1.1$)	2nd ED-SAPT(DFT)	
	E_{pol}	E_{ct}
MUE (MSE)	0.25 (0.04)	0.25 (−0.04)
% Error	7%	18% [*]
r^2	0.99	0.99

^{*} Some pairs at longer separations have rather weak charge transfer energy, thus pairs with $|E_{ct}| < 0.01$ kcal/mol were ignored, as even very small errors with such small denominators would introduce huge noises in the calculated percentages.

Table 3

Comparison of the second order ED-SAPT(DFT) polarization and charge transfer energy (kcal/mol) with the reference second order regularized SAPT(DFT)/aug-cc-pVTZ results. The empirical parameter λ used in the ED-SAPT calculation (Eq. 2) is also given. Results of HF-HF and Water-Water pairs at different distances can be found in Supporting Information.

Molecules	λ	2 nd Regularized SAPT(DFT)		2 nd ED-SAPT(DFT)	
		E_{pol}	E_{ct}	E_{pol}	E_{ct}
Misquitta2013 ^[a]					
HF-HF	1.6	-1.16	-0.33	-1.19	-0.30
Water-Water	1.6	-1.03	-0.42	-1.16	-0.29
FH-CO	1.6	-1.22	-0.36	-1.26	-0.32
FH-OC	1.6	-0.64	-0.10	-0.59	-0.15
Pyridine-Pyridine	1.6	-0.70	-0.10	-0.64	-0.16
H ₃ B-CO	1.0	-45.91	-44.38	-57.08	-33.22
H ₃ B-NH ₃	1.0	-26.43	-17.77	-27.94	-16.26
MUE				1.85 (9%)	1.85 (28%)
Max UE				11.16 (24%)	11.16 (25%)
Hobza 2011 ^[b]					
H ₃ B-NH ₃	1.0	-29.22	-21.57	-32.10	-18.68
H ₃ B-NMe ₃	1.0	-32.19	-24.47	-35.81	-20.84
C ₂ H ₂ -ClF	1.0	-0.95	-0.18	-0.72	-0.42
C ₂ H ₄ -F ₂	1.0	0.00	0.03	0.02	0.01
H ₂ O-ClF	1.0	-1.28	-0.23	-0.96	-0.56
HCN-ClF	1.0	-1.21	-0.18	-0.88	-0.51
H ₃ N-Cl ₂	1.0	-1.57	-0.56	-1.35	-0.78
H ₃ N-ClF	1.0	-4.57	-3.53	-5.12	-2.98
H ₃ N-F ₂	1.0	-0.21	0.04	-0.10	-0.06
H ₃ N-SO ₂	1.0	-1.54	-0.35	-1.20	-0.70
SO ₂ -NMe ₃	1.0	-6.98	-5.50	-7.89	-4.59

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Molecules	λ	2 nd Regularized SAPT(DFT)		2 nd ED-SAPT(DFT)	
		E_{pol}	E_{ct}	E_{pol}	E_{ct}
MUE				0.87 (21%)	0.87 (71%) [c]
Max UE				3.63 (11%)	3.63 (15%)

[a] structures were taken from the reference24;

[b] structures were minimized using MP2/cc-pVTZ, same as that used in the reference25 and in the S16×7 data set;

[c] when calculating the percentage of error for charge transfer energy, pairs with positive energy contributions were ignore.

Table 4

Mean unsigned error, mean signed error (in parenthesis) and mean relative error of the second order SAPT2+/aug-cc-pVTZ induction energy and its second order ED-SAPT2+ polarization and charge transfer energy against the second order regularized SAPT(DFT)/aug-cc-pVTZ results for the S16×7 data set. Units in kcal/mol.

Distance (R/R_m)	2 nd SAPT2+ E_{ind} ($E_{pol} + E_{ct}$)	2 nd ED-SAPT2+	
		E_{pol}	E_{ct}
0.7~0.8	1.33 (−1.32)	0.61 (−0.41)	0.91 (−0.91)
%Error	10%	12%	16%
0.9~1.1	0.51 (−0.51)	0.43 (−0.43)	0.18 (−0.08)
%Error	14%	14%	27%
All	0.75 (−0.74)	0.48 (−0.42)	0.39 (−0.32)
%Error	13%	14%	23% ^[a]

^[a] Some pairs at longer separations have rather weak charge transfer energy, thus pairs with $|E_{ct}| < 0.01$ kcal/mol were ignored, as even very small errors with such small denominators would introduce huge noises in the calculated percentages.

Table 5

Mean unsigned differences, mean signed differences (in parenthesis) and relative differences of SAPT0/aug-cc-pVTZ induction, polarization and charge transfer energy compared with ALMO/HF/aug-cc-pVTZ results for the S16×7 data set. Units in kcal/mol.

Distance (R/R_m)	MUD (MSD) of SAPT0 vs ALMO/HF		
	E_{ind}	E_{pol}	E_{ct}
0.7~0.8	3.29 (3.29)	5.11 (5.02)	2.88 (-1.73)
% Difference	14%	27%	25%
0.9~1.1	0.21 (0.20)	0.55 (-0.51)	0.71 (0.71)
% Difference	3%	29%	44%
All	1.09 (1.08)	1.85 (1.07)	1.33 (0.01)
% Difference	6%	29%	38%

Table 6

Mean unsigned error (mean signed error in parenthesis, kcal/mol) of AMOEBA and the new model against the higher order contribution included SAPT2+/aug-cc-pVTZ induction energy and ED-SAPT2+ polarization and charge transfer energy for the S16×7 data set.

Distance (R/R_m)	AMOEBA vs SAPT2+				New vs SAPT2+			
	E_{ind}	E_{pol}	E_{pol}^*	E_{ct}	E_{ind}	E_{pol}	E_{pol}^*	E_{ct}
0.7-0.8	17.18 (17.18)	4.45 (4.26)	2.01 (-0.33)	/	5.91 (4.30)	2.78 (1.71)	3.46 (-2.88)	3.84 (2.59)
0.9-1.1	2.81 (2.81)	1.40 (1.23)	1.08 (-1.06)	/	1.39 (1.23)	1.24 (0.99)	1.31 (-1.30)	0.45 (0.24)
r^2	0.80	0.82	0.93	/	0.93	0.86	0.95	0.90
All	6.92 (6.92)	2.27 (2.10)	1.34 (-0.86)	/	2.68 (2.11)	1.68 (1.20)	1.93 (-1.76)	1.42 (0.91)
r^2	0.61	0.75	0.83	/	0.93	0.87	0.93	0.91

* error was calculated against the second order regularized SAPT(DFT) polarization energy (without the higher order HF contribution).