Construction of Accurate Force Fields from Energy Decomposition Analysis: Water and Monovalent Ions

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Abstract

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Introduction

Historically, there have been two main approaches to including polarization in force fields: fluctuating charges[1] or induced dipoles.[2] There have also been attempts to unify these approaches allowing for both charge rearrangements and induced dipoles.[3]

Our goal in this paper is to develop a new class of polarizable force field which is able to quantitatively reproduce all of the terms from energy decomposition analysis (EDA). The

reason to do this is that by reproducing the EDA term-by-term, we can ensure that the force field will be transferable across the phase diagram of a homogeneous system and to new heterogenous systems. Additionally, by reproducing the EDA term-by-term, the force field is able to provide insights which many other models simply cannot because they do not include particular terms. For instance, many force fields do not include charge transfer or charge penetrations terms. Many force fields also use terms which package the Pauli repulsion and dispersion energies together. We will discuss this further in the results section, but by neglecting these terms, one limits the interpretability of the energies and forces predicted by a force field. Even worse, one can only exclude charge transfer and charge penetration from force fields because these energies are strongly correlated to the Pauli repulsion (see Fig. 1). This correlation is not guaranteed to be consistent between systems, however, which may explain part of the difficulty in producing water models which generalize to heterogeneous systems.

Theory

EDA splits the interaction energy into five components: Pauli repulsion, electrostatics, dispersion, polarization, and charge transfer. The force field described in this work will model each of these term by term, resulting in two different models, which we will call the dipole model (DM) and anisotropic model (AM). Note we will use a convention of referring to all energy terms in the force field with a V and all energy terms from electronic structre with an E.

Our approach builds on the density overlap hypothesis[4–7] which states that the short-range contributions to intermolecular interactions is proportional to the electron density overlap. In order for this idea to be amenable to force fields, one must use atom-centered density overlaps. One way of doing this was developed thoroughly by Misquitta and others[8,9] based on iterated stockholder atoms which can be used to define Slater-like densities

for atoms in molecules. Since this approach has been discussed extensivly, we will only summarize the salient points.

One can show that the overlap, S_ρ^{ii}, of two identical Slater-like atomic densities at different locations, $\rho_i(\boldsymbol{r}_i)$ and $\rho_i(\boldsymbol{r}_j)$, is,

$$S_{ii}^\rho = \frac{\pi D^2}{b_{ii}^3} P(b_{ii} r_{ij}) \exp(-b_{ii} r_{ij}) \tag{1}$$

The above overlap expression is only strictly true for the exponential tail of the Slater density and for identical atoms. The overlap between atoms with different densities, S_ρ^{ij}, has a more complicated form, but it has been shown that setting $b_{ij} = \sqrt{b_i b_j}$ allows the expression for S_{ii}^ρ to be used for different atom types with negligible approximation.[7] The polynomial prefactor in the overlap is,

$$P(b_{ij} r_{ij}) = \frac{1}{3}(b_{ij} r_{ij})^2 + b_{ij} r_{ij} + 1 \tag{2}$$

where, again, we will use the combination rule $b_{ij} = \sqrt{b_i b_j}$.

Pauli Repulsion

The original aim of the density overlap model was to model the Pauli repulsion energy.[5,10,11] In this work, we employ two different models for Pauli repsulison, both inspired by the work of Van Vleet *et al.*[7,12] The first is a simple isotropic model of Pauli repulsion where the energy is proportional to the density overlap with a quadratic term that we found essentialy for ion-ion interactions at shorter-than-equilibrium distances,

$$V^{exch} = \sum_{i<j} a_{ij}^{(1),exch} S_{ij}^\rho + a_{ij}^{(2),exch}(S_{ij}^\rho)^2 \tag{3}$$

In Eq. 7, $a_{ij}^{exch} = a_i^{exch} a_j^{exch}$ where a_i^{exch} is a free parameter for atom i. This isotropic sum is the approach we use for the DM model. In the anisotropic model (AM), we, unsurprisingly,

put anisotropy into the atom-specific parameters. We do this similarly to the approach of Van Vleet, but with some minor modifications.[12] First, the anisotropy is introduced by multiplying the isotropic term with a spherical harmonic expansion. The spherical harmonics used here are given by,

$$C_{lm}(\theta, \phi) = \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\theta, \phi) \tag{4}$$

where θ and ϕ are the polar and azimuthal angles calculated between two local axis systems for each atom.[13] That is, θ_i is the angle of the vector between two axis systems, $\boldsymbol{r}_{ij} = \boldsymbol{r}_j - \boldsymbol{r}_i$, and the z-axis of axis system i. ϕ_i is the azimuthal angle, which is the angle of $\boldsymbol{r}_{ij}$ in the range $[0, 2\pi]$ from the x-axis of axis system i.

$$a_i^{exch} = a_{i,iso}^{exch} \left(1 + \sum_{l>0,k} a_{i,lk}^{exch} C_{lk}(\theta_i, \phi_i) \right) \tag{5}$$

Electrostatics

Our description of electrostatics comes from a traditional point multipole approach and a charge penetration contribution. We will refer to these contributions as the DMA energy and CP energy, respectively. Our working definition of charge penetration comes by taking the classical electrostatic energy from EDA minus the interaction energy when using Stone's distributed multipole analysis[14,15] out to hexadecapoles on all atoms.

$$E^{CP} = E_{EDA}^{elec} - E_{DMA}^{elec} \tag{6}$$

The advantage of this approach is it allows us to ensure that our multipoles are not biased to compensate for error in the description of charge penetration, which is essential to reproduce the classical electrostatic energy in EDA. All distributed multipole calculations were carried out in Stone's Orient program.[16]

Our description of charge penetration in the models is essentially the same as for Pauli repulsion. Namely, the DM model uses only isotropic terms and includes a quadratic overlap

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term which, again, is immensely helpful for the short range description of ion-ion interactions:

$$V^{CP} = \sum_{i<j} a_{ij}^{(1),CP} S_{ij}^{\rho} + a_{ij}^{(2),CP} (S_{ij}^{\rho})^2 \tag{7}$$

For the AM model, we include anisotropy in the first order charge penetration parameter, $a_{ij}^{(1),CP}$, in the same way as for exchange in Eq. (5).

The permanent point electrostatics aim to reproduce the distributed multipole energies used in defining the charge penetration, E_{DMA}^{elec}. The electrostatic energy is expressed as,

PUT EXPRESSIONS IN HERE FOR MULTIPOLES AND DAMPING AND ALL THAT.

Polarization

We introduce a combined fluctuating charge (FQ) and induced dipole model of electronic polarization. There are two reasons we have pursued this combined polarization approach. The first is quite simple. We want to reproduce all terms from EDA, one of which is charge transfer. If charges are not allowed to vary, then one cannot model the explicit transfer of charge between molecules. The second reason is that atomic polarizabilities naturally contain both charge-flow and induced dipole contributions.[17] Typically, the charge-flow contributions are localized away,[18] but our approach does not require nonlocal charge flow polarizabilities.

The FQ contribution to our polarization model is a modification of the electronegativity equalization model (EEM) of polarization.[19] In EEM, the energy of a molecule is expanded to second-order as a function of charge, then, these charges are allowed to interact. Mathematically, this takes the following form,

$$V(\boldsymbol{q}) = \sum_i \chi_i q_i + \frac{1}{2} \sum_i \eta_i q_i^2 + \sum_{i<j} \frac{q_i q_j}{r_{ij}} \tag{8}$$

In Eq. 8, χ_i represents the electronegativity of atom i and η_i is the atomic hardness

of atom i. The principle of electronegativity equalization states that at equilibrium, the electronegativity of all atoms will become equal. This allows the charges in an atom to be determined by solving a system of linear equations. There are several known shortcomings of EEM. The first is the long-range transfer of charge between molecules, even at infinite distance, which is unrealistic for the dielectric systems studied here.[20,21] Our solution to this problem is to only allow charge rearrangements within a molecule and not between molecules. This constraint can be introduced using Lagrange multipliers. A second limitation of EEM is that the approach in Eq. 8 gives back the total charge of atoms in a molecule. This is somewhat awkward because we want to separate the multipolar electrostatics, which depends on the total charge, from the polarization contribution which should only depend on the external potential experienced by each atom. Hence, we drop the linear term and focus only on the fluctuation of charges around the reference charge used for permanent electrostatics. Another way of viewing this is that we are equalizing electronegativity around an "already equalized" state. The change in electronegativity at each atom due to an environment is simply the electric potential at that atom. We can then write the FQ contribution in our model as,

$$V(\delta \boldsymbol{q}) = \frac{1}{2} \sum_i \eta_i \delta q_i^2 + \sum_i \delta q_i V_i + \sum_{i<j} \frac{\delta q_i \delta q_j}{r_{ij}} + \sum_\alpha \lambda_\alpha \sum_{i \in \alpha} \delta q_i \tag{9}$$

To summarize, Eq. 9 allows charges to rearrange, δq_i in response to an external potential, V_i, with a quadratic penalty determined by the atomic hardness, η_i. The charge rearrangements are constrained to only occur between atoms such that rearranged charges in a molecule sum to the total charge of a molecule. Therefore, the model has N lagrange multipliers, λ_α, where N is the number of molecules in the system. These molecules could be water or an ion in this work. Note that all fluctuating charges (and induced dipoles) are allowed to interact whether they are in the same molecule or not.

We also allow electric fields due to the environment to induce dipoles on all atoms. The

energy of an induced dipole in an electric field, $\boldsymbol{E}$, including mutual polarization is,

$$V(\boldsymbol{\mu}^{ind}) = -\frac{1}{2} \sum_i \boldsymbol{\mu}_i^{ind} \cdot \boldsymbol{E}_i + \sum_{i<j} \boldsymbol{\mu}_i^{ind} \boldsymbol{T}_{ij}^{\mu\mu} \boldsymbol{\mu}_j^{ind} \qquad (10)$$

In Eq. 10, the induced dipoles at each polarizable site, $\boldsymbol{\mu}_i^{ind}$, interact with an external electric field, $\boldsymbol{E}_i$, and with each other via the dipole interaction tensor. We will have more to say about this tensor in the next section when we discuss the short-range damping of polarization.

What now remains is to determine the values of $\delta\boldsymbol{q}$ and $\boldsymbol{\mu}^{ind}$ which minimize the total energy of the system. In order to do this, we take the derivative with respect to each δq_i and each component of each $\boldsymbol{\mu}_i^{ind}$ and set them all equal to zero. This results in a system of linear equations which can be written succintly as follows:

$$\begin{pmatrix} \boldsymbol{T}^{qq} & \mathbf{1}_\lambda & \boldsymbol{T}^{q\mu} \\ \mathbf{1}_\lambda^\dagger & 0 & 0 \\ -\boldsymbol{T}^{\mu q} & 0 & \boldsymbol{T}^{\mu\mu} \end{pmatrix} \begin{pmatrix} \delta\boldsymbol{q} \\ \boldsymbol{\lambda} \\ \boldsymbol{\mu} \end{pmatrix} = \begin{pmatrix} -\boldsymbol{V} \\ \boldsymbol{Q} \\ \boldsymbol{E} \end{pmatrix} \qquad (11)$$

The solution vector in Eq. 11 contains the electric potential, $\boldsymbol{V}$, the total charges of each molecule, $\boldsymbol{Q}$, and the electric field on each atom $\boldsymbol{E}$. The matrix has several blocks containing the charge-charge ($\boldsymbol{T}^{qq}$), charge-dipole ($\boldsymbol{T}^{q\mu}$), dipole-charge ($\boldsymbol{T}^{\mu q}$), and dipole-dipole interaction tensors ($\boldsymbol{T}^{\mu\mu}$). Note that the diagonal elements of $\boldsymbol{T}^{qq}$ are the atomic hardness η and the 3×3 diagonal blocks of $\boldsymbol{T}^{\mu\mu}$ are the inverse polarizability tensor $\boldsymbol{\alpha}_i^{-1}$. The block $\mathbf{1}_\lambda$ has a column for each molecule in the system. An entry in that column is 1 if the ith atom is in that molecule and zero otherwise. These blocks enforce the charge-conservation constraints for each molecule. Finally, $\delta\boldsymbol{q}$ contains the optimally rearranged charges, $\boldsymbol{\lambda}$ contains the Lagrange multipliers which enforce charge conservation, and $\boldsymbol{\mu}$ are the induced dipoles.

The form of the ij entries of the multipole interaction tensors are as follows:

$$T_{ij}^{qq} = f_2(x_{ij}) \frac{1}{r_{ij}} \tag{12}$$

$$\boldsymbol{T}_{ij}^{q\mu} = f_4(x_{ij}) \frac{-\boldsymbol{r}_{ij}}{r_{ij}^3} \tag{13}$$

$$\boldsymbol{T}_{ij}^{\mu\mu} = f_6(x_{ij}) \left(\frac{\boldsymbol{r}_{ij} \otimes \boldsymbol{r}_{ij}}{r_{ij}^5} - \frac{\boldsymbol{1}}{r_{ij}^3} \right) \tag{14}$$

The interaction tensors in Eq. 14 are the usual cartesian multipole interaction tensors, generated by successive gradients of $1/r_{ij}$ where r_{ij} is the distance between two atoms. These tensors are multiplied by a damping function, which we will discuss in more detail now.

Damping

The interaction tensors in Eq. 11 are often damped to prevent over-polarization. One common approach is to use Thole damping,[22] which takes a model electron density and computes the appropriate damping function. This approach is a bit awkward both because it requires an arbitrary parameter which controls the extent of damping, but also because the model electron densities chosen have no apparent physical meaning. For those reasons, we take a different approach in damping all terms related to polarization and utilize the Tang-Toennies (TT) damping functions.[23]

$$f_n(x_{ij}) = 1 - e^{-x_{ij}} \sum_{k=0}^{n} \frac{x_{ij}^k}{k!} \tag{15}$$

The appropriate form of x for the tail of a Slater electron density has been derived before[7] and takes the form,

$$x_{ij} = b_{ij} r_{ij} - \frac{2b_{ij}^2 r_{ij}^2 + 3b_{ij} r_{ij}}{b_{ij}^2 r_{ij}^2 + 3b_{ij} r_{ij} + 3} \tag{16}$$

The TT damping functions were originally derived to describe the short-range damping of dispersion interactions. These damping functions have been very successful in modifying

the short-range contribution to dispersion. Considering that dispersion is simply another form of polarization, we apply the TT damping functions to all polarization interactions in this force field.

There are two big advantages to TT damping functions worth discussing. First, as shown in Eq. 16, the scale over which damping is relevant is related to the Slater exponent for each pair of atoms, b_{ij}. This is convenient because it means the damping between each pair of atoms will better reflect the size of each atom. Additionally, by reusing these Slater exponents, we eliminate the need for the global parameter used to control the damping strength in Thole damping. Note that the TT damping functions depend parametrically on the choice of integer n. Generally, higher n means damping occurs more rapidly. This brings us to the second advantage. TT damping allows us to apply different damping scales to different types of interactions just by modifying the value of n.

In the original work by Tang and Toennies, they show that the appropriate choice of n for dispersion is $n = 6$. This makes sense because the damping function will then have an exponential multiplied by a sixth order polynomial. This polynomial is able to control the r^{-6} scaling of dispersion, while the exponential ensures no damping at long distances.

Inspired by this, we choose to damp mutual polarization with $n = 2, 4, 6$ for charge-charge, charge-dipole, and dipole-dipole interactions, respectively. The reason we choose $n = 2, 4, 6$ rather than $n = 1, 2, 3$ is because mutual polarization roughly decays as the square of permanent interactions of the same type. Just how dispersion, which can be thought of as describing interacting instantaneous dipoles, decays as r^{-6}, the interaction of two induced dipoles decays as roughly r^{-6} because the field which induces the interaction also decays rapidly. Notice that this interaction would actually decay at different lengths if the polarizing field comes from a charge, dipole, or quadrupole. One might instead choose to damp with f_5 or f_7. In our experience the more aggressive damping is slightly better and also ensures greater stability of the system of equations.

In fact, the typical Thole damping functions also take the form of a polynomial multiplied

by an exponential. The polynomial for damping induced dipoles would be third-order in Thole damping, which, as just discussed, is insufficient to control the polarization energy at short-range. Therefore, we consider our more aggressive damping to be well-justified especially since we are interested in ions where polarization catastrophes have motivated the use of diminished polarizabilities.[24]

Charge Transfer

Charge transfer is the most difficult of the terms in EDA to model. This is because there is no classical analogue for charge transfer. One common approach to capturing charge transfer is to use a simple exponential dependent on the distance between atoms.[25] This captures the main effect which is the short-range exponential stabilization due to charge delocalization. Unfortunately, many-body charge transfer is non-negligible and this effect will be completely missed when using just exponentials. Another attempt is to essentially treat charge transfer the same way as polarization and solve a set of induced dipole equations.[26,27] This has the benefit that it can capture many-body charge transfer. One drawback of this approach is that it does not actually allow for charge to flow between molecules and therefore misses some of the salient physics. It is also ambiguous if the induced dipoles relevant to CT should be treated as real dipoles and allowed to interact with permanent and induced multipoles. Perhaps a bigger problem is that charge transfer can be an even larger contribution than polarization, especially at short range. This means the charge transfer energy would be even more susceptible to polarization catastrophes than ordinary polarization.

For all of these reasons, we introduce a new approach to describing charge transfer which is enabled by the fact we allow for explicit charge rearrangements in our description of polarization. Our charge transfer model includes both direct and indirect energy contributions. The direct contributions allow for energetic stabilization associated with both forward and

backward charge transfer.

$$V_{i \to j}^{CT} = a_{i \to j}^{CT} S_{ij}^{\rho} \tag{17}$$

$$V_{j \to i}^{CT} = a_{j \to i}^{CT} S_{ij}^{\rho} \tag{18}$$

$$V_{direct}^{CT} = \sum_{i<j} V_{i \to j}^{CT} + V_{j \to i}^{CT} \tag{19}$$

As shown in Eq. 19, the forward and backward contributions to charge transfer are directly proportional to the density overlap. We take inspiration from perturbation theory which shows, roughly, that the amount of charge transferred between two molecules is proportional to the energy associated with forward and backward charge transfer.[28–30] Therefore, we define the amount of charge transferred from i to j, $\Delta Q_{i \to j}^{CT}$, and from j to i, $\Delta Q_{j \to i}^{CT}$, as

$$\Delta Q_{i \to j}^{CT} = \frac{V_{i \to j}^{CT}}{\epsilon_{i \to j}} \tag{20}$$

$$\Delta Q_{j \to i}^{CT} = \frac{V_{j \to i}^{CT}}{\epsilon_{j \to i}} \tag{21}$$

The proportionality constant between direct charge transfer energy and the amount of transferred charge is written as $\epsilon_{i \to j}$ to emphasize that this proportionality is related to the difference in energy of an occupied orbital on i and an unoccupied orbital on j.[28]

The novel thing about this approach is that we can explictly move charge between fragments by modifying the molecular charge constraints used in Eq. 11. The charge constraint for a fragment A will then take the form,

$$Q_A^{CT} = Q_A + \sum_{i \in A} \sum_{j \notin A} \Delta Q_{j \to i}^{CT} - \Delta Q_{i \to j}^{CT} \tag{22}$$

The charge constraint including charge transfer, Q_A^{CT}, is simply the difference in charge transferred to atom i (in A) and charge transferred from atom i, summed over all atoms in

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molecule A. These charges may not be optimally distributed, so they will be allowed to relax during the polarization process. This allows us to capture the so-called "re-polarization"[28] effect in which orbitals relax after allowing for occupied-virtual mixing. For example, when charge is transferred from oxygen to hydrogen in a water dimer, the final excess charge will mostly come to rest on the oxygen in the water with net-negative charge.

The main effect, however, of allowing charge to move between fragments comes from the energy penalty associated with any atoms having nonzero values of δq. This is consistent with two known effects about the stability of water clusters. First, homodromic rings have particularly large non-additivities.[31] In our model, this type of ring benefits from many-body charge transfer since each molecule can pass its excess charge along to the next molecule, resulting in a minor excess charge penalty. Similarly, this model makes it clear why water molecules which accept two hydrogen bonds without donating any hydrogen bonds are particularly unstable. That is, charge gets transferred out of the double acceptor molecule and every molecule gets stuck with nonzero total charges.

Make a figure illustrating these two scenarios. Charge getting trapped on an AA molecule and charge getting passed along in a ring.

There is one technical point worth noting about this model. Because the charge transferred between fragments is proportional to the direct CT contributions, the charge constraints depend on the distance between atoms. This means there is a gradient contribution which multiplies the lagrange multipliers with the gradient of $\Delta Q_{i \to j}^{CT}$ and $\Delta Q_{j \to i}^{CT}$. This is not difficult or expensive to evaluate, but because it is a rather unusual gradient term, we wanted to point this out clearly.

Parameterization

The last important point in this model concerns the determination of the atomic width, b_i. We utilize the implementation of the ISA model of Misquitta[8] available in CamCASP[32] to

obtain these parameters from monomer electron densities.

Results and discussion

Table 1: *Comparison of the MAE of all terms in the EDA for both the dipole and anisotropic models. The first line for each term is the MAE over all dimers used in the parameterization. The second line is the MAE over all gathered data which includes dimers through pentamers. See text for explanation of each of the energy terms.*

MAE of EDA Terms (kcal/mol)		
Term	Dip. Model	Aniso. Model
Pauli		
Disp.		
DMA Elec.		
CP Elec.		
Elec.		
Pol.		
CT		
Total		

Acknowledgement

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Supporting Information Available

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