

# 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<sup>1</sup> or induced dipoles.<sup>2</sup> There have also been attempts to unify these approaches allowing for both charge rearrangements and induced dipoles.<sup>3</sup>

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 heterogeneous 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 structure with an  $E$ .

Our approach builds on the density overlap hypothesis<sup>4-7</sup> 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<sup>8,9</sup> based on iterated stockholder atoms which can be used to define Slater-like densities

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

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

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

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,  $S_{\rho}^{ij}$ , has a more complicated form, but it has been shown that setting  $b_{ij} = \sqrt{b_i b_j}$  allows the expression for  $S_{ii}^{\rho}$  to be used for different atom types with negligible approximation.<sup>7</sup> The polynomial prefactor in the overlap is,

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

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.<sup>5,10,11</sup> In this work, we employ two different models for Pauli repulsion, both inspired by the work of Van Vleet *et al.*<sup>7,12</sup> 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 essentially for ion-ion interactions at shorter-than-equilibrium distances,

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

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.<sup>12</sup> First, the anisotropy is introduced by multiplying the isotropic term with a spherical harmonic expansion. The spherical harmonics used here are given by,

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

where  $\theta$  and  $\phi$  are the polar and azimuthal angles calculated between two local axis systems for each atom.<sup>13</sup> That is,  $\theta_i$  is the angle of the vector between two axis systems,  $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ , and the z-axis of axis system  $i$ .  $\phi_i$  is the azimuthal angle, which is the angle of  $\mathbf{r}_{ij}$  in the range  $[0, 2\pi]$  from the x-axis of axis system  $i$ .

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

## 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<sup>14,15</sup> out to hexadecapoles on all atoms.

$$E^{CP} = E_{EDA}^{elec} - E_{DMA}^{elec} \quad (6)$$

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.<sup>16</sup>

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

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

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

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

$$\begin{pmatrix} \mathbf{T}_{qq} & \mathbf{1}_{\lambda} & \mathbf{T}_{q\mu} \\ \mathbf{1}_{\lambda}^{\dagger} & 0 & 0 \\ \mathbf{T}_{q\mu}^{\dagger} & 0 & \mathbf{T}_{\mu\mu} \end{pmatrix} \begin{pmatrix} \delta q \\ \lambda \\ \mu \end{pmatrix} = \begin{pmatrix} -\mathbf{V} \\ \mathbf{Q} \\ \mathbf{E} \end{pmatrix} \quad (8)$$

## 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<sup>8</sup> available in CamCASP<sup>17</sup> to obtain these parameters from monomer electron densities.

## Results and discussion

## Acknowledgement

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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		

## Supporting Information Available

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