ACCOUNTS
of chemical research

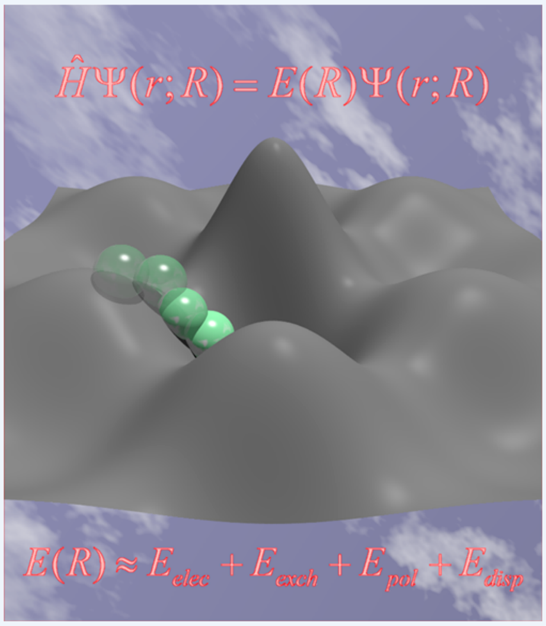
Article

pubs.acs.org/accounts

Transferable Next-Generation Force Fields from Simple Liquids to Complex Materials

J. R. Schmidt,* Kuang Yu,[†] and Jesse G. McDaniel

Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin−Madison, Madison, Wisconsin 53706, United States



CONSPECTUS: Molecular simulations have had a transformative impact on chemists' understanding of the structure and dynamics of molecular systems. Simulations can both explain and predict chemical phenomena, and they provide a unique bridge between the microscopic and macroscopic regimes. The input for such simulations is the intermolecular interactions, which then determine the forces on the constituent atoms and therefore the time evolution and equilibrium properties of the system. However, in practice, accuracy and reliability are often limited by the fidelity of the description of those very same interactions, most typically embodied approximately in mathematical form in what are known as force fields.

Force fields most often utilize conceptually simple functional forms that have been parametrized to reproduce existing experimental gas phase or bulk data. Yet, reliance on empirical parametrization can sometimes introduce limitations with respect to novel chemical systems or uncontrolled errors when moving to temperatures, pressures, or environments that differ from those for which they were developed. Alternatively, it is possible to develop force fields entirely from first principles, using accurate electronic structure calculations to determine the intermolecular interactions. This introduces a new set of challenges, including the transferability of the resulting force field to related chemical systems.

In response, we recently developed an alternative approach to develop force fields entirely from first-principles electronic structure calculations based on intermolecular perturbation theory. Making use of an energy decomposition analysis ensures, by construction, that the resulting force fields contain the correct balance of the various components of intermolecular interaction (exchange repulsion, electrostatics, induction, and dispersion), each treated by a functional form that reflects the underlying physics. We therefore refer to the resulting force fields as physically motivated. We find that these physically motivated force fields exhibit both high accuracy and transferability, with the latter deriving from the universality of the fundamental physical laws governing intermolecular interactions.

This basic methodology has been applied to a diverse set of systems, ranging from simple liquids to nanoporous metal−organic framework materials. A key conclusion is that, in many cases, it is feasible to account for nearly all of the relevant physics of intermolecular interactions within the context of the force field. In such cases, the structural, thermodynamic, and dynamic properties of the system become naturally emergent, even in the absence of explicit parameterization to bulk properties. We also find that, quite generally, the three-body contributions to the dispersion and exchange energies in bulk liquids are crucial for quantitative accuracy in a first-principles force field, although these contributions are almost universally neglected in existing empirical force fields.

■ INTRODUCTION AND BACKGROUND

Molecular dynamics simulations have progressed immensely in the nearly 60 years since Alder and Wainwright first modeled a condensed-phase system of hard spheres.[1] Since then, simulations have revolutionized chemists' understanding of the structure and dynamics of molecular systems by providing a microscopic, atomistic perspective from which to interpret, analyze, and predict corresponding macroscopic phenomena. Standard molecular dynamics and Monte Carlo techniques are now routinely used to model systems consisting of many thousands of atoms on microsecond time scales. In principle, the time evolution of both the nuclei and electrons in these simulations is governed by the time-dependent Schrödinger equation. In practice, however, the quantum effects associated with nuclear motion and non-Born−Oppenheimer effects can often (but certainly not always!) be neglected, with the nuclei

Received: July 30, 2014
Published: February 17, 2015

DOI: 10.1021/ar500272n
Acc. Chem. Res. 2015, 48, 548−556

treated instead as classical marbles rolling on a curved potential energy surface (PES) determined by the electrons.

The fundamental challenge of molecular simulation thus reduces largely to describing accurately the 3N-dimensional PES for chemical system of interest (while also striving to simulate ever-larger systems for longer time scales). However, even this goal remains intractable for all but the most trivial examples. In terms of practical molecular simulations, one is left with few viable options: calculate the PES on-the-fly using so-called ab initio molecular dynamics (AIMD) simulations, which solve the electronic Schrödinger equation at each nuclear configuration, or, alternatively, develop a simple classical mathematical approximation to the PES, known as a force field.[2] While AIMD and its variants are becoming increasingly common, force fields presently dominate the field of molecular simulation.

It is interesting to note that the vast majority of the popular and successful force fields were parametrized not via their fidelity in directly reproducing the PES (as determined by experiment or calculations) but indirectly, matching to experimental structural, thermodynamic (e.g., equation of state), or dynamic data. From a pragmatic viewpoint, the focus on bulk properties makes a great deal of sense, as given appropriate experimental data and a sufficiently flexible functional form, such empirical force fields can offer essentially quantitative accuracy, at least in the domain over which they were parametrized. There are thus a huge variety of well-tested empirical force fields spanning many chemical systems of interest.

Alternatively, it is possible to take a bottom-up approach and parametrize directly to the PES as determined by electronic structure calculations. While this approach is philosophically appealing and opens the door to examining systems where experimental data are sparse, it poses a number of additional challenges. Of course, one is limited by the intrinsic accuracy of the underlying electronic structure methodology, but significant advances in both computer power and algorithms have greatly expanded the types of systems that can be examined with high accuracy. Nonetheless, all first-principles-based force fields face two primary challenges. First, many-body effects in condensed-phase systems necessitate inclusion of intermolecular interaction terms beyond pairwise (i.e., beyond sum of interacting dimers).[3,4] In contrast, empirical force fields often hide these many-body effects in terms of an effective two-body interaction potential. Second, ab initio force fields are typically parametrized on the basis of calculations involving specific interacting molecular pairs, which potentially limits transferability.

We recently developed a novel approach to generate first-principles force fields that largely overcomes these challenges, yielding accurate force fields that exhibit transferability over wide ranges of temperatures, pressures, and chemical environments.[5] Building on work of Stone and Misquitta,[6] our methodology uses symmetry-adapted perturbation theory calculations and exploits the inherent energy decomposition to parametrize a force field. Thus, in contrast to common ab initio force fields, it is fit on a term-by-term basis (rather than to the total interaction energy), with explicit terms representing various fundamental components of intermolecular interaction: exchange repulsion, electrostatics, polarization, and dispersion. This physically motivated, term-by-term approach ensures, by construction, the correct balance of all fundamental interaction types and enables the use of corresponding functional forms that reflect the underlying physics.

Neither the basic idea of employing energy decomposition analysis in force field development nor the use of SAPT to develop force fields is entirely novel in and of itself. There is a long history of SAPT-based intermolecular potential development because it is both accurate and free from basis set superposition error.[7−10] Yet, in almost all cases, those potentials did not exploit the energy decomposition and were fit only to the total energy. One notable exception is ref 8, where the full SAPT decomposition was used to generate a force field for interactions between antibiotics and small peptide ligands. Furthermore, many of these early potentials were not intended to be atom−atom potentials for use in bulk simulations, but rather they were described by dimer interactions in terms of a series expansion in the 6 rigid-body coordinates.

Similarly, several groups of authors have previously employed energy decomposition analysis for the construction of force fields.[6,11,12] In particular, the SIBFA (sum of interactions between fragments ab initio computed) approach of Gresh, Piquemal, and co-workers uses a related energy decomposition (electrostatic, repulsion, polarization, charge transfer, and dispersion).[11] As in our approach, many of the resulting force field parameters can be derived on the basis of monomer properties. An important point of contrast lies in that SIBFA employs a relatively complex functional form (accounting for orbital-dependent repulsion, anisotropy, ...), giving significant flexibility but also making it incompatible with standard simulation packages. A similar comparison can also be drawn with the effective fragment potential (EFP) approach of Gordon and co-workers.[12] Although originally developed for use in QM/MM-type applications, EFP employs a similar energy decomposition, with many terms derived from monomer properties. However, due to the computational complexity of EFP, the potentials are not particularly suitable for standard molecular simulation. In contrast, our emphases lies on generating transferable next-generation atom-atom force field, employing physically motivated functional forms, which are largely compatible with existing simulation packages.

In the remainder of this Account, we provide a brief technical overview of the methodology and recount a variety of applications ranging from simple liquids to complex materials. We place a particular emphasis on the importance of many-body dispersion effects in the condensed phase, a contribution that is particularly notable in that this effect is excluded in nearly all existing force fields. Finally, we end with a short outlook on the future evolution of next-generation force fields.

■ OVERVIEW OF METHODOLOGY

Our force field development approach is based upon intermolecular interaction energies calculated using symmetry-adapted perturbation theory (SAPT).[7] SAPT is formally based on a triple perturbation theory, including two intramolecular (electron correlation, similar to MP2) and one intermolecular perturbation. Symmetry-adapted refers to the fact that standard Rayleigh−Schrödinger perturbation theory expressions have been modified to enforce the proper antisymmetry so as to enforce the Pauli principle and capture the resulting short-range exchange repulsion. SAPT is useful in that it yields both accurate intermolecular energies and a chemically intuitive energy decomposition. The latter can be exploited to ensure the correct balance of the various fundamental intermolecular interactions: exchange repulsion,

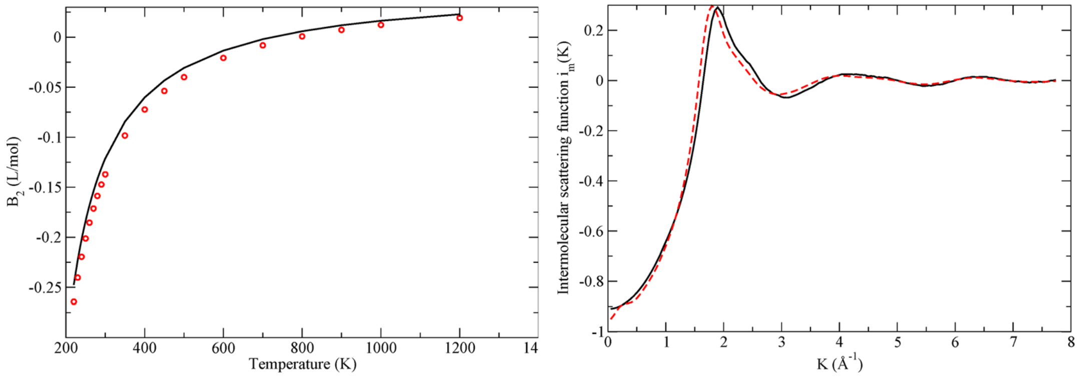


Figure 1. Second virial coefficient of CO_2 (left) and intermolecular scattering function (right); simulation (red) is compared to experiment (black). Adapted from ref 16. Copyright 2011 American Chemical Society.

electrostatics, polarization, and dispersion. Although our basic methodology could, in principle, be used with any SAPT variant, essentially all of our prior work uses SAPT(DFT),[9] which offers an excellent computational efficiency and accuracy comparable to the gold standard quantum chemistry, CCSD(T) at the complete basis set limit, particularly for dispersion-dominated complexes.[13]

To construct our force fields, we use SAPT to calculate intermolecular interaction energies for a wide variety of intermolecular geometries. This yields both the total interaction energy and the energy decomposition for each configuration

$$E_{\text{int}} = E_{\text{elec}} + E_{\text{exch}} + E_{\text{pol}} + E_{\text{disp}} + E_{\partial\text{hf}} \tag{1}$$

where the terms represent the electrostatic, exchange, polarization, dispersion, and delta Hartree−Fock (i.e., higher-order polarization) contributions, respectively. (We have grouped the cross-terms resulting from antisymmetry [e.g., exchange-polarization, exchange-dispersion] with the corresponding polarization/dispersion. This has been shown to cancel unphysical divergences in the separate terms.)

The energy decomposition is fit to functional forms that are motivated by the underlying physics governing the associated interaction, accounting for electron density overlap/charge penetration and enforcing asymptotic correctness. The particular functional form of each term can be found elsewhere,[5] but the sum of these terms (i.e., the total intermolecular energy) has the following form

$$E_{\text{tot}} = \sum_{i,j} f_1(B_{ij}, r_{ij}) \frac{q_i q_j}{r_{ij}} + \sum_{i,j} \left(A_{ij}^{\text{tot}} \exp(-B_{ij} r_{ij}) - \sum_{n=6,8,10,12} f_n(B_{ij}, r_{ij}) \frac{C_n^{ij}}{r_{ij}^n} \right) + E_{\text{pol}}^{\text{Drude}} + E_{\text{disp}}^{\text{3b}} \tag{2}$$

Note that similar functional forms for the total energy have been used before.[6,8,10] Here, $f_n(\lambda,r) = 1 - e^{-\lambda r} \sum_{m=0}^{n} ((\lambda r)^m/m!)$ is the Tang−Toennies damping function[14] and is used to damp both the electrostatic and dispersion multipole expansions, $A_{ij}^{\text{tot}} = A_{ij}^{\text{elec}} + A_{ij}^{\text{exch}} + A_{ij}^{\text{pol}} + A_{ij}^{\partial\text{hf}}$ are the coefficients governing the strength of the interactions, and $E_{\text{pol}}^{\text{Drude}}$ is the many-body polarization energy, evaluated using a standard Drude oscillator (i.e., charge-on-spring) model. These terms are largely compatible with those used in many standard simulation packages. As discussed below, non-additive three-body contributions to dispersion and/or exchange can sometimes make important contributions in the condensed phase; when applicable, these are treated in a separate term, $E_{\text{disp}}^{\text{3b}}$.

Monomer properties are used to determine the vast majority of the parameters,[6] relying on SAPT only to determine those parameters influenced by electron density overlap (e.g., charge penetration or exchange-related terms, A_{ij}). If the monomer properties are calculated at a level consistent with the SAPT monomer treatment, then the resulting parameters will yield exact asymptotic agreement with corresponding SAPT calculations while also ensuring both accuracy and transferability. In particular, the atomic ionization potentials determine the asymptotic density decay, B_{ii}, whereas the polarizability ($E_{\text{pol}}^{\text{Drude}}$) and dispersion ($C_{ii}$) parameters are derived from the static and imaginary frequency molecular response, respectively; in these cases, atomic parameters are obtained from the molecular response via a self-consistent, iterative extension of the approach of Williams and Stone.[15] Charges (q_i) are determined via an analytic distributed multipole analysis, subsequently reduced to point charges. A more detailed technical overview can be found in ref 5.

■ APPLICATIONS: SIMPLE LIQUIDS

Our work is motivated largely by the following hypothesis: If it is possible to construct a force field that contains the right balance (and magnitude) of all of the fundamental physics of intermolecular interactions, then all relevant bulk properties of interest should be naturally emergent, even in the absence of explicit parameterization to those properties. It is thus useful to start by examining a relatively simple and weakly interacting molecular system where an essentially complete accounting of these physics is feasible. In ref 16, we examined carbon dioxide as an ideal candidate system.

Using several hundred of SAPT calculations on representative CO_2 dimers yields a two-body force field. The resulting model includes many-body polarization, but it omits other many-body effects. In principle, nuclear quantum effects should also be included when comparing to experiments, but these effects are extremely small for CO_2 at even the lowest temperatures studied.[17] For light molecules (e.g., H_2) at low temperatures, inclusion of these effects (e.g., via path integral simulation) is crucial since quantum effects have not been parameterized into the model.[18] Zero-point energy makes an important contribution to some properties (heat capacity, absolute internal energy) and must be accounted for when comparing with experiment,[16] but it can often be neglected in

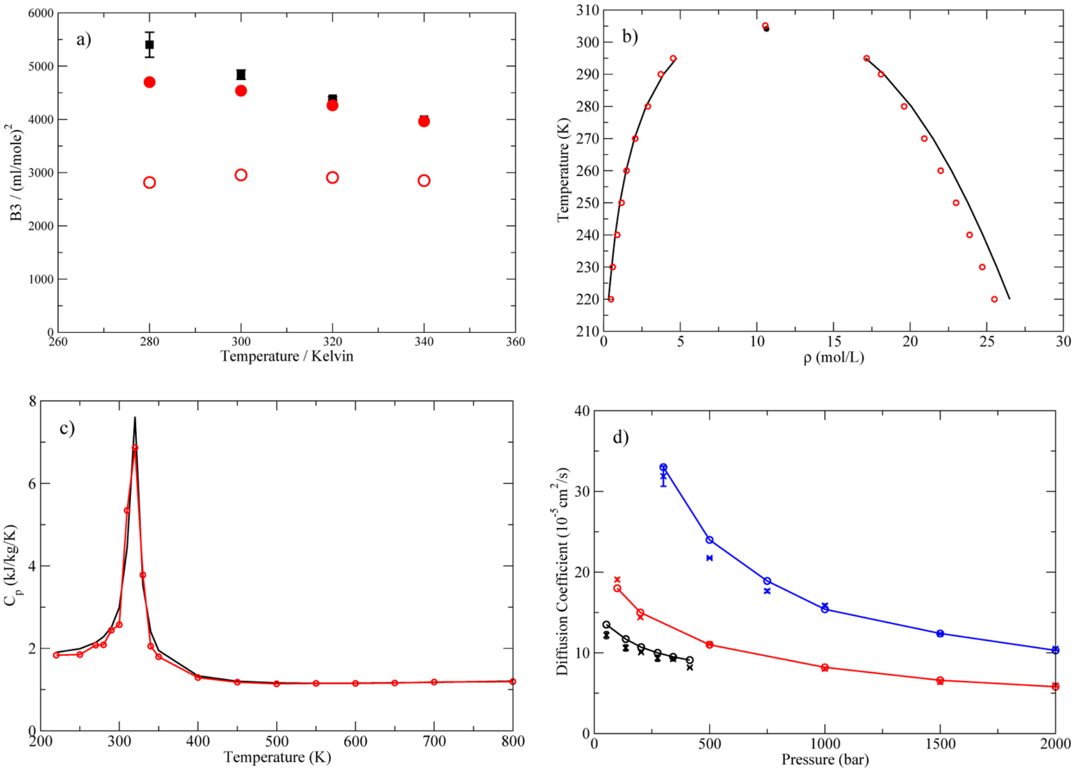


Figure 2. CO_2 properties. (a) Third virial coefficient; simulation results from full three-body force field (closed red circles) and two-body plus polarization (open red circles) are compared to experiment (black squares). (b) Vapor−liquid coexistence (circles) as compared to experiment (solid); the critical point is shown at the apex. (c) Heat capacity; simulation results (red circles) compared to experiment (black line). (d) Diffusion coefficients at 273 K (black), 298 K (red), 373 K (blue); simulation results (crosses) compared to experiment (circles). Adapted from ref 16. Copyright 2011 American Chemical Society.

the potential as long its magnitude is not a strong function of conformation.

As might be expected, this model also accurately reproduces the experimentally measured second virial coefficient (see Figure 1). However, also perhaps unsurprisingly, the resulting bulk properties are not faithfully recovered, with (in particular) significant errors in the predicted density. This result suggests that important physics have been omitted from the model.

The source of the discrepancy is, of course, many-body effects. Although the above model accounts for many-body electrostatic interactions (via polarizability), it omits many-body interactions in exchange and dispersion. Accordingly, in ref 3, we used three-body SAPT(DFT)[19] to quantify the nonadditive three-body dispersion and exchange interactions in a set of CO_2 trimers. On the basis of the results of these three-body SAPT calculations, we fit parameters for the three-body exchange and dispersion interactions for inclusion in the CO_2 model. The resulting model thus includes true many-body electrostatic interactions and dispersion/exchange interactions up to the three-body level; in general, the three-body dispersion interactions dominate over their exchange counterpart.

The key results from this model are shown in Figure 2. In particular, as hypothesized, the bulk properties of the system now emerge naturally. Using our explicit many-body model (or a computationally more efficient mean-field variant derived thereof), we find that the structural, thermodynamic, and dynamic properties are reproduced to high accuracy, even in the absence of explicit parametrization to these bulk properties. We find similar or better agreement in the case of N_2.

Although there are certainly other empirically parametrized models for CO_2 and N_2 that exhibit comparable accuracy in terms of their bulk properties,[20,21] we believe that our physically motivated models offer some unique advantages. Specifically, we anticipate that these models should exhibit superior transferability to different chemical or physical environments, based on the underlying universality of the physical laws governing the various components of intermolecular interaction to which they were fit. As a simple example, we developed a simple ansatz for the CO_2/N_2 heterodimer interactions based on the homodimer exchange, electrostatic, and dispersion interactions, in the similar spirit to common (empirical) combining rules. Comparison against explicit heterodimer SAPT and bulk mixture calculations validates the ansatz.[16] This inherent transferability (at least for atoms within similar chemical environments) is a key result, and it is one that we have exploited in a wide variety of subsequent applications.

■ APPLICATIONS: BULK ORGANIC LIQUIDS

Applying these same ideas to typical condensed-phase organic systems presents two specific challenges. First, three-body exchange and dispersion contributions play a nontrivial role, quite generally, in the bulk, beyond the specific example of CO_2. These contributions must be accounted for in a computationally tractable and transferable manner. Second, in the spirit of popular existing empirical condensed-phase potentials (such as OPLS-AA,[22] DREIDING,[23] TraPPE,[24] ...), we desire a model based upon transferable parameters for atoms within their chemical environment (e.g., alkane carbon, amide nitrogen, ...) so as to generate a parameter library that can be exploited for a wide range of chemical systems, without additional parametrization.

In ref 5, using the basic methodology outlined above, we derived atomic exchange, electrostatic, polarization, and dispersion parameters on the basis of monomer and dimer calculations. The monomers consisted of a set of representative small molecules spanning a wide variety of functional groups and chemical environments, and the atomic parameters were fit in a self-consistent manner. An important result from that work is shown in Figure 3, where the resulting parameter library is validated against a wide variety of small molecule second virial coefficients. Since no system-specific parameters were included in these results, the excellent agreement suggests these parameters should be quite transferable to a wide variety of chemical systems; use of system-specific parameters would likely yield even higher quantative accuracy, but with potential loss of transferability.

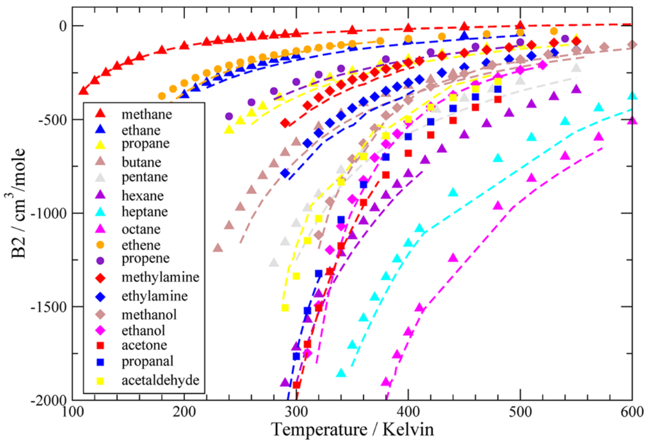


Figure 3. Second virial coefficients of small organic molecules. Simulation results (symbols) are compared to corresponding experimental data (dashed lines). Adapted from ref 5. Copyright 2013 American Chemical Society.

Applying the above force fields to the bulk once again leads to small but systematic errors in the bulk density. In particular, neglect of the dominant (repulsive) three-body dispersion contribution leads to systematic positive deviations in density and an enthalpy of vaporization that is too large in magnitude. A particular challenge thus arises to account for these three-body effects in an accurate, transferable, and computationally tractable manner. In ref 4, we show that the dominant three-body effects can be included using an Axilrod–Teller–Muto form,[25] reflecting the leading order dipole–dipole–dipole interaction

$$E_{\text{disp}}^{3b} = \sum_{i',j',k'} f_{\text{damp}} C_9^{ijk} \frac{1 + 3\cos\phi_{ijk}\cos\phi_{jik}\cos\phi_{ikj}}{R_{ij}^3 R_{ik}^3 R_{kj}^3}$$

where the sum is restricted to atoms on three separate molecules, the damping function, f_{damp}, approaches 1 asymptotically, and the remaining terms depend on the distances and angles between the three atoms. Even more appealing, the C_9 coefficient can be written in terms of the same quantities used to calculate the two-body dispersion; no additional calculations or parametrization are required.

Introduction of the explicit three-body contributions yields substantial improvements to the bulk density and enthalpy of vaporization for a wide variety of organic liquids and (generally) brings these properties into good agreement with the corresponding experimental values, across the phase diagram. See, for example, results for ethane shown in Figure 4. Note in particular the substantial improvement in the predicted liquid-phase densities upon inclusion of the three-body contributions. Although these three-body contributions are not large, typically 3–4% of the internal energy of the bulk under liquid-like conditions, the effect is systematic and density-dependent (vanishing in the low-density limit). The three-body contributions thus contribute an effective internal pressure of ~100 bar to the liquid; neglect of this pressure (e.g., by omitting three-body terms) yields significant errors at constant pressure, although the structure and dynamics of the liquid are affected only minimally at constant density. Interestingly, the importance of three-body dispersion extends to even polar systems (e.g., methanol) where many-body electrostatics dominate; neglect of the former nonetheless leads to systematic errors (unless otherwise parameterized away).[4]

■ APPLICATIONS: GAS ADSORPTION IN METAL–ORGANIC FRAMEWORKS

We have also explored a variety of applications to more complex systems, including metal–organic framework (MOF)

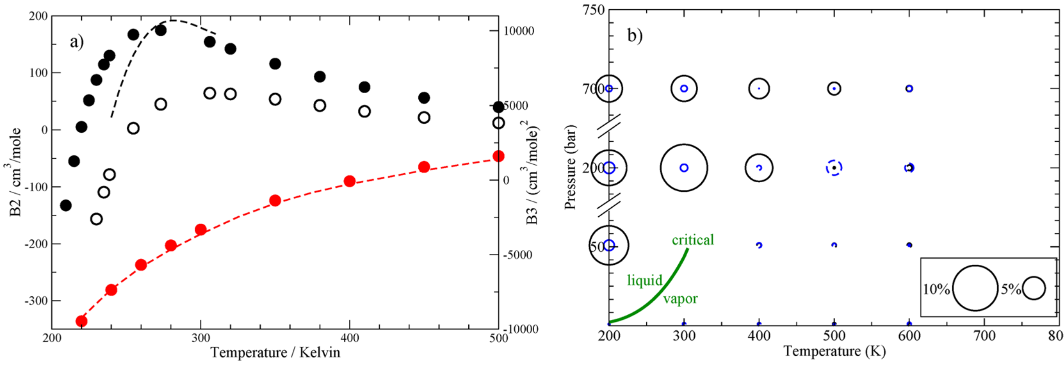


Figure 4. (a) Second (red) and third (black) virial coefficients for ethane. Simulation results (symbols) are compared to experimental results (dashed lines). For the third virial coefficient, simulations with (closed circles) and without (open) explicit three-body terms. (b) Error in density of ethane at different temperatures and pressures. Adapted from ref 4. Copyright 2014 American Chemical Society. The magnitude of error is depicted by symbol size, with positive (solid) and negative (dashed) errors. Blue (black) circles depict simulation results including (excluding) three-body force field terms.

materials.[5,15,18,26] MOFs are nanoporous crystalline organometallic materials built from small metal clusters linked by organic bridging groups.[27] MOFs exhibit extremely high surface areas as a result of their nanoporosity and permeability to small adsorbates, and they have received a tremendous amount of attention due to their applications in diverse fields ranging from catalysis to gas adsorption and separation. In the latter cases, both the gas adsorption capacity and gas selectivity are tunable by functionalization of the organic bridging groups, leading to the possibility of the design and optimization of MOFs for targeted applications.[28] We have focused extensively on CO_2 adsorption and separation, motivated by applications for CO_2/N_2 flue gas separation at coal-fired power plants.

It has been estimated that there are millions of potentially synthesizable MOFs, only a tiny fraction of which have ever been synthesized and fewer still have been characterized. There is, therefore, considerable interest in predictive computational approaches capable of identifying promising candidates for particular separations.[28] Although the performance of a separation material is multifaceted, gas adsorption isotherms, measuring gas uptake as a function of pressure, are a key performance metric. These isotherms are straightforward to calculate using standard simulation techniques, but the quantitative accuracy of the predicted isotherm is sensitive to the accuracy of the underlying force field.

Motivated by these applications, many groups have used molecular simulations to examine gas uptake and separation in MOFs (including some with unsaturated open metal sites[29]), as well as efforts toward high-throughput computational screening of candidate materials. Although the volume of this work is too vast to be reviewed here, it has been concisely summarized in several recent reviews.[30−32] Briefly, almost all of these works have used existing standard empirical force fields that have not been specifically parametrized for MOFs. The reliance on standard force fields has allowed rapid initial progress, but, unfortunately, it may also limit the accuracy and reliability of the resulting simulations. In response, we have developed transferable force fields for a wide variety of functionalized metal−organic frameworks, spanning a number of the most common metal centers and bridging ligands. We used the same basic methodology outlined above to extract atomic exchange, electrostatic, induction, and dispersion parameters for several common metal clusters and bridging linkers.

We combined these results with our previously calculated library of organic substituents to develop a unified force field capable of describing nearly arbitrary MOF functionalization. In conjunction with our existing transferable CO_2 model, the resulting force field is sufficient to describe many popular functionalized MOFs in the literature. Representative isotherms for a number of functionalized MOFs are shown in Figure 5. In general, agreement with comparable experimentally measured quantities is very good, typically within ∼10% (and comparable to variations seen within reported experimental uptakes). Note that in this case our models are rigid and exclude the possibility of MOF flexibility. Such contributions can be included via the introduction of intramolecular force field terms[33] and are particularly important for MOFs that exhibit pressure-induced structural transformations or when examining transport properties.

Our ability to describe these gas adsorption problems with high accuracy and confidence opens the door to new and exciting fundamental science, including the origins of enhanced gas uptake in mixed metal−organic frameworks made with admixtures of several types of organic linking groups.[18] We were able to attribute this enhancement to the formation of especially favorable linker arrangements that yield particularly favorable adsorption and thus dominate the adsorption isotherm at equilibrium. To the extent that such ligand ordering is synthetically controllable (either via thermodynamics or kinetics, potentially exploiting the ligand−ligand interaction), these results suggest that ligand ordering may complement composition and topology as an additional, design axis for exploration.

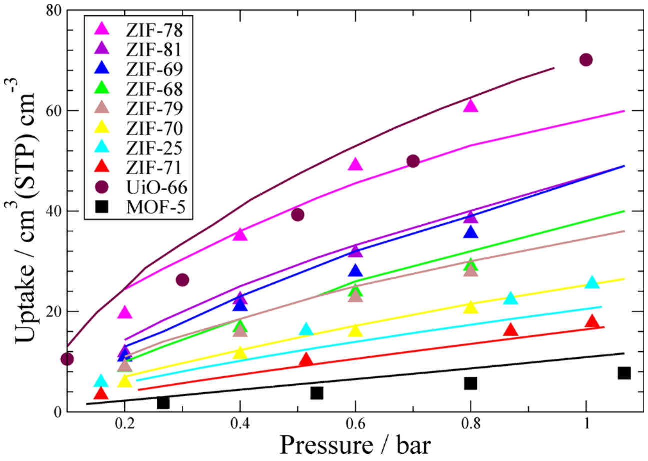


Figure 5. CO_2 gas adsorption isotherms at 298 K for selected MOFs. Simulation results (symbols) are compared with corresponding experimental values (lines). Adapted from refs 5, 15, and 18. Copyright 2013, 2012, and 2013 American Chemical Society, respectively. Our simulation data for UiO-66 is previously unpublished, and the corresponding experimental data is taken from ref 34. Copyright 2013 American Chemical Society.

■ APPLICATIONS: IONIC LIQUIDS

Ionic liquids (ILs) are intriguing due to their diverse applications as nonvolatile electrolytes and solvents. These applications have driven a corresponding interest in force field development, including models derived (at least in part) based on ab initio calculations, those accounting for polarizability[35,36] and/or charge transfer (either explicitly or implicitly), and even coarse grained or united atom models; much of this abundant literature is summarized in several recent reviews.[37,38] In essentially all cases, the resulting force fields required empirical tuning to reproduce accurately the bulk structural, thermodynamic, and dynamic properties of interest.

An entirely first-principles model would facilitate design of novel, tailored ILs and increase confidence when examining more complex systems (IL mixtures, electrochemical interfaces, ...). In the same spirit as our prior work, we focused initially on the ubiquitous [BMIM][BF_4] ionic liquid and derived a set of physically motivated force field parameters for both the cation and anion.[39]

Perturbation theory remains quantitatively accurate for these strongly interacting systems since the energy is electrostatically dominated and therefore is exceptionally well-described by even low-order perturbation theory. All intermolecular terms were derived entirely from ab initio data, whereas intramolecular contributions (accounting for monomer flexibility) are taken from the standard OPLS-AA[22] force field. In collaboration with Yethiraj and co-workers,[39] we showed the bulk properties of the resulting model are in excellent agreement with experiment, even in the absence of any empirical parametrization or refinement. In particular, the enthalpy of vaporization (for the ion pair) is in nearly quantitative agreement with experimental values, and the cation/anion diffusion and conductivity are within ~10% of the respective measured quantities.

It is particularly interesting to note that our model uses full (unscaled) formal charges on the cation and anion. In contrast, several previous simulations have found that scaled charges are required to simultaneously capture the correct enthalpy of vaporization and reasonable dynamic properties.[40,41] Such scaling has been motivated on the basis of charge transfer between cations and anions. Interestingly, our calculations and model provide no evidence for substantial charge transfer. In particular, the polarization energy calculated by SAPT (i.e., the second-order electrostatic interaction, which formally encompasses both induction and charge transfer) is quantitatively reproduced by a classical Drude oscillator model of intermolecular polarization, without the need to resort to charge transfer; a similar conclusion can be drawn from the electron density differences (Figure 6). It is important to note that charge transfer may certainly play a role in other IL systems, particularly those with smaller cations/anions (e.g., [BMIM][Cl]) or in ionic melts.

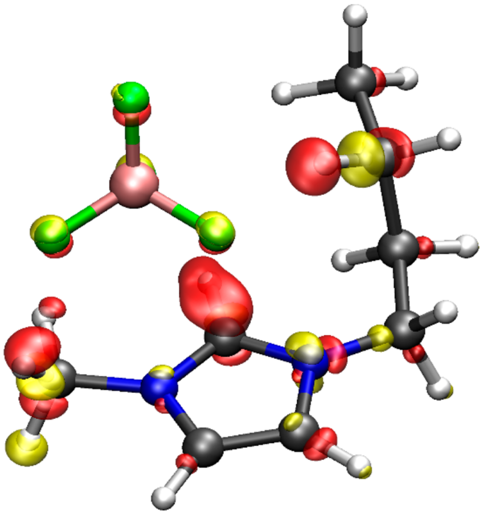


Figure 6. [BMIM][BF_4] minimum energy ion complex. Figure depicts difference in electron density of ion complex relative to isolated ions. Isosurfaces of +0.003 and −0.003 au, are shown in yellow and red, respectively. Reproduced from ref 39. Copyright 2014 American Chemical Society.

Within the context of such a polarizable full-charge model, we are able to accurately and simultaneously reproduce the bulk enthalpy of vaporization, dynamical properties, and the cohesive energy of the ion pair (in that case, compared to electronic structure calculations). The latter observation is particularly significant since a scaled charge model necessarily dramatically underestimates the total cohesive energy of the liquid. Although the bulk properties of such a scaled charge model could be (and, in many cases, are!) very accurate, the use of scaled charges is perhaps more concerning when considering the interaction of the IL with absorbed solutes or within heterogeneous mixtures. We are currently working on generalizing these results to a wide variety of common IL motifs.

FUTURE DIRECTIONS

The holy grail of next-generation field development would be an approach that yields both high accuracy and transferability for a wide variety of chemical systems, entirely from first principles. In practice, perfection in both arenas is extremely difficult to achieve for at least two reasons. The inherent accuracy of the underlying electronic structure method is one modest bottleneck, although theoretical and computational advances have, in many cases, mitigated this limitation. However, it is also important to note the somewhat conflicting goals of accuracy and transferability. It is, therefore, interesting to consider the limits to which the approach we have outlined above could be pushed.

A logical extension would be to increase the complexity of the force field functional form (whose expression for the total energy is given in eq 2). In particular, it is well-known that more accurate models for exchange repulsion can be written in terms of explicit monomer electron density overlap.[42] The downside of this (and other) extensions is the loss of compatibility with many existing molecular simulation packages (in the absence of rather extensive modifications). More practically, one could imagine supplementing our purely ab initio approach with experimental data to refine the transferable atomic parameters for particular targeted properties and systems of interest. By definition, such experimental data captures the relevant physics and should not be neglected, if available. This hybrid approach would harness a key advantage of traditional empirical force fields (quantitative accuracy for parametrized target(s) of interest) while largely preserving the proper balance of exchange, electrostatics, polarization, and dispersion and thus much of the force field's transferability.

What about water? Given the success of prior SAPT-based water models,[43] there is some reason for optimism regarding application of our approach to water and aqueous solutions. Alternatively, it is possible to employ a hybrid approach, using an existing empirically optimized water model in conjunction with SAPT-based force fields for the solute−solute and solute−water interactions. This would, even in the short term, open up a whole new world of exciting applications, including those in biomolecular simulation.

AUTHOR INFORMATION

Corresponding Author

*E-mail: schmidt@chem.wisc.edu.

Present Address

†(K.Y.) Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544-5263, United States.

Notes

The authors declare no competing financial interest.

Biographies

J. R. Schmidt is an Assistant Professor of Chemistry at the University of Wisconsin−Madison. He earned his B.S. from Hope College in 2001 and a Ph.D. in Physical Chemistry from the University of Wisconsin (with Prof. Jim Skinner) in 2006. After postdoctoral work at Yale (with Prof. John Tully), he returned to UW in 2008. His research interests span force field development approaches, nanoporous materials, and computational heterogeneous catalysis.

Kuang Yu earned his B.S. in chemistry in 2008 from Peking University, China. In 2013, he earned his Ph.D. degree in theoretical chemistry (with Prof. J.R. Schmidt) at the University of Wisconsin—Madison. Currently, he is undertaking postdoctoral research at Princeton University (with Prof. Emily Carter). His current research interests includes first-principles studies on thin-film solar cell systems and developing embedded correlated wavefunction methods for solid-state materials.

Jesse G. McDaniel earned his B.A. in chemistry in 2008 from Washington University in St. Louis. He is currently a Ph.D. student under the supervision of Prof. J. R. Schmidt, at the University of Wisconsin—Madison. His research interests include the development of ab initio force fields for use in molecular simulation, with particular focus on the study of gas adsorption in metal organic frameworks.

■ ACKNOWLEDGMENTS

This work was supported by Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, under award DE-FG02-09ER16059. J.R.S. is an Alfred P. Sloan Research Fellow and a Camille Dreyfus Teacher—Scholar.

■ REFERENCES

(1) Alder, B. J.; Wainwright, T. E. Studies in molecular dynamics. I. General method. *J. Chem. Phys.* **1959**, *31*, 459—466.

(2) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*; Academic Press: San Diego, CA, 2002.

(3) Yu, K.; Schmidt, J. R. Many-body effects are essential in a physically motivated CO_2 force field. *J. Chem. Phys.* **2012**, *136*, 034503-1—034503-7.

(4) McDaniel, J.; Schmidt, J. R. First-principles many-body force fields from the gas-phase to the liquid: a "universal" approach. *J. Phys. Chem. B* **2014**, *118*, 8042—8053.

(5) McDaniel, J. G.; Schmidt, J. R. Physically-motivated force fields from symmetry-adapted perturbation theory. *J. Phys. Chem. A* **2013**, *117*, 2053—2066.

(6) Stone, A. J.; Misquitta, A. J. Atom—atom potentials from ab initio calculations. *Int. Rev. Phys. Chem.* **2007**, *26*, 193—222.

(7) Jeziorski, B.; Moszynski, R.; Szalewicz, K. Perturbation theory approach to intermolecular potential energy surfaces of van der Waals complexes. *Chem. Rev.* **1994**, *94*, 1887—1930.

(8) Li, X.; Volkov, A. V.; Szalewicz, K.; Coppens, P. Interaction energies between glycopeptide antibiotics and substrates in complexes determined by X-ray crystallography: application of a theoretical databank of aspherical atoms and a symmetry-adapted perturbation theory-based set of interatomic potentials. *Acta Crystallogr., Sect. D: Biol. Crystallogr.* **2006**, *62*, 639—647.

(9) Misquitta, A. J.; Podeszwa, R.; Jeziorski, B.; Szalewicz, K. Intermolecular potentials based on symmetry-adapted perturbation theory with dispersion energies from time-dependent density-functional calculations. *J. Chem. Phys.* **2005**, *123*, 214103-1—214103-14.

(10) Podeszwa, R.; Bukowski, R.; Rice, B. M.; Szalewicz, K. Potential energy surface for cyclotrimethylene trinitramine dimer from symmetry-adapted perturbation theory. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5561—5569.

(11) Gresh, N.; Cisneros, G. A.; Darden, T. A.; Piquemal, J.-P. Anisotropic, polarizable molecular mechanics studies of inter- and intramolecular interactions and ligand—macromolecule complexes. A bottom-up strategy. *J. Chem. Theory Comput.* **2007**, *3*, 1960—1986.

(12) Gordon, M. S.; Freitag, M. A.; Bandyopadhyay, P.; Jensen, J. H.; Kairys, V.; Stevens, W. J. The effective fragment potential method: a QM-based MM approach to modeling environmental effects in chemistry. *J. Phys. Chem. A* **2000**, *105*, 293—307.

(13) Parker, T. M.; Burns, L. A.; Parrish, R. M.; Ryno, A. G.; Sherrill, C. D. Levels of symmetry adapted perturbation theory (SAPT). I. Efficiency and performance for interaction energies. *J. Chem. Phys.* **2014**, *140*, 094106-1—094106-16.

(14) Tang, K. T.; Toennies, J. P. An improved simple model for the van der Waals potential based on universal damping functions for the dispersion coefficients. *J. Chem. Phys.* **1984**, *80*, 3726—3741.

(15) McDaniel, J. G.; Schmidt, J. R. Robust, transferable, and physically-motivated force fields for gas adsorption in functionalized zeolitic imidazolate frameworks. *J. Phys. Chem. C* **2012**, *116*, 14031—14039.

(16) Yu, K.; McDaniel, J.; Schmidt, J. R. Physically-motivated, robust, ab inito force fields for CO_2 and N_2. *J. Phys. Chem. B* **2011**, *115*, 10054—10063.

(17) Bock, S.; Bich, E.; Vogel, E. A new intermolecular potential energy surface for carbon dioxide from ab initio calculations. *Chem. Phys.* **2000**, *257*, 147—156.

(18) McDaniel, J. G.; Yu, K.; Schmidt, J. R. Microscopic origins of enhanced gas adsorption and selectivity in mixed-linker metal—organic frameworks. *J. Phys. Chem. C* **2013**, *117*, 17131—17142.

(19) Podeszwa, R.; Szalewicz, K. Three-body symmetry-adapted perturbation theory based on Kohn—Sham description of the monomers. *J. Chem. Phys.* **2007**, *126*, 194101-1—194101-14.

(20) Potoff, J. J.; Siepmann, J. I. Vapor—liquid equilibria of mixtures containing alkanes, carbon dioxide, and nitrogen. *AIChE J.* **2001**, *47*, 1676—1682.

(21) Harris, J. G.; Yung, K. H. Carbon dioxide's liquid—vapor coexistence curve and critical properties as predicted by a simple molecular model. *J. .Phys. Chem.* **1995**, *99*, 12021—12024.

(22) Jorgensen, W. L.; Maxwell, D. S.; TiradoRives, J. Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. *J. Am. Chem. Soc.* **1996**, *118*, 11225—11236.

(23) Mayo, S. L.; Olafson, B. D.; Goddard, W. A. DREIDING: a generic force-field for molecular simulations. *J. Phys. Chem.* **1990**, *94*, 8897—8909.

(24) Chen, B.; Siepmann, J. I. Transferable potentials for phase equilibria. 3. Explicit-hydrogen description of normal alkanes. *J. Phys. Chem. B* **1999**, *103*, 5370—5379.

(25) Axilrod, B. M.; Teller, E. Interaction of the van der Waals type between three atoms. *J. Chem. Phys.* **1943**, *11*, 299—300.

(26) McDaniel, J. G.; Yu, K.; Schmidt, J. R. Ab initio, physically motivated force fields for CO_2 adsorption in zeolitic imidazolate frameworks. *J. Phys. Chem. C* **2012**, *116*, 1892—1903.

(27) Eddaoudi, M.; Moler, D. B.; Li, H. L.; Chen, B. L.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. Modular chemistry: secondary building units as a basis for the design of highly porous and robust metal—organic carboxylate frameworks. *Acc. Chem. Res.* **2001**, *34*, 319—330.

(28) Wilmer, C. E.; Leaf, M.; Lee, C. Y.; Farha, O. K.; Hauser, B. G.; Hupp, J. T.; Snurr, R. Q. Large-scale screening of hypothetical metal—organic frameworks. *Nat. Chem.* **2012**, *4*, 83—89.

(29) Dzubak, A. L.; Lin, L.-C.; Kim, J.; Swisher, J. A.; Poloni, R.; Maximoff, S. N.; Smit, B.; Gagliardi, L. Ab initio carbon capture in open-site metal—organic frameworks. *Nat. Chem.* **2012**, *4*, 810—816.

(30) Colon, Y. J.; Snurr, R. Q. High-throughput computational screening of metal—organic frameworks. *Chem. Soc. Rev.* **2014**, *43*, 5735—5749.

(31) Yang, Q.; Liu, D.; Zhong, C.; Li, J.-R. Development of computational methodologies for metal—organic frameworks and their application in gas separations. *Chem. Rev.* **2013**, *113*, 8261—8323.

(32) Jiang, J. Molecular simulations in metal—organic frameworks for diverse potential applications. *Mol. Simul.* **2014**, *40*, 516—536.

(33) Bureekaew, S.; Amirjalayer, S.; Tafipolsky, M.; Spickermann, C.; Roy, T. K.; Schmid, R. MOF-FF—a flexible first-principles derived force field for metal—organic frameworks. *Phys. Status Solidi B* **2013**, *250*, 1128—1141.

(34) Wu, H.; Chua, Y. S.; Krungleviciute, V.; Tyagi, M.; Chen, P.; Yildirim, T.; Zhou, W. Unusual and highly tunable missing-linker defects in zirconium metal—organic framework UiO-66 and their important effects on gas adsorption. *J. Am. Chem. Soc.* **2013**, *135*, 10525—10532.

(35) Borodin, O. Polarizable force field development and molecular dynamics simulations of ionic liquids. *J. Phys. Chem. B* **2009**, *113*, 11463−11478.

(36) Salanne, M.; Rotenberg, B.; Jahn, S.; Vuilleumier, R.; Simon, C.; Madden, P. A. Including many-body effects in models for ionic liquids. *Theor. Chem. Acc.* **2012**, *131*, 16-1−16-19.

(37) Dommert, F.; Wendler, K.; Berger, R.; Delle Site, L.; Holm, C. Force fields for studying the structure and dynamics of ionic liquids: a critical review of recent developments. *ChemPhysChem* **2012**, *13*, 1625−1637.

(38) Maginn, E. J. Molecular simulation of ionic liquids: current status and future opportunities. *J. Phys.: Condens. Matter* **2009**, *21*, 373101.

(39) Choi, E.; McDaniel, J.; Schmidt, J. R.; Yethiraj, A. First-principles, physically motivated force field for the ionic liquid [BMIM][BF_4]. *J. Phys. Chem. Lett.* **2014**, *5*, 2670−2674.

(40) Chaban, V. V.; Voroshylova, I. V.; Kalugin, O. N. A new force field model for the simulation of transport properties of imidazolium-based ionic liquids. *Phys. Chem. Chem. Phys.* **2011**, *13*, 7910−7920.

(41) Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J. Why is CO_2 so soluble in imidazolium-based ionic liquids? *J. Am. Chem. Soc.* **2004**, *126*, 5300−5308.

(42) Söderhjelm, P.; Karlström, G.; Ryde, U. Comparison of overlap-based models for approximating the exchange-repulsion energy. *J. Chem. Phys.* **2006**, *124*, 244101-1−244101-10.

(43) Mas, E. M.; Bukowski, R.; Szalewicz, K. Ab initio three-body interactions for water. II. Effects on structure and energetics of liquid. *J. Chem. Phys.* **2003**, *118*, 4404−4413.