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Preface: Special Topic: From Quantum Mechanics to Force Fields

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This Special Topic issue entitled "From Quantum Mechanics to Force Fields" is dedicated to the ongoing efforts of the theoretical chemistry community to develop a new generation of accurate force fields based on data from high-level electronic structure calculations and to develop faster electronic structure methods for testing and designing force fields as well as for carrying out simulations. This issue includes a collection of 35 original research articles that illustrate recent theoretical advances in the field. It provides a timely snapshot of recent developments in the generation of approaches to enable more accurate molecular simulations of processes important in chemistry, physics, biophysics, and materials science. *Published by AIP Publishing.* https://doi.org/10.1063/1.5008887

This special issue grew out of a series of Telluride Science Research Center (TSRC) workshops focused on the interface between electronic structure theory and accurate force fields that we have organized over the past eight years. In comparing the presentations at the first of these workshops in 2010 with that held last year (2016), it is clear that much progress has been made in this area over the past few years. This issue of JCP includes 35 manuscripts dealing with new developments in the force field design, the force-field based simulations, and the development of electronic structure methods that are computationally fast enough to tackle problems restricted to force fields in the past. The manuscripts in this issue can be characterized as falling into the following areas: (1) potential energy surfaces from *ab initio* data, (2) faster electronic structure based simulation methods, (3) new approaches for including many-body polarization, (4) ion solvation, and (5) novel force field methods. Obviously, some of the papers could be placed in more than one of these categories.

(1) PESs from *ab initio* data

The contribution of Wang and Bowman[1] describes the development of an accurate two-body force field for the CO_2–H_2O dimer system based on CCSD(T)-F12[2] (Explicity Correlated Coupled-Cluster Singles Doubles and Noniterative Triples Correction) calculations. The dimer force field was combined with the many-body force field for water from the Paesani group[3] and used to study CO_2 encapsulated in an $(H_2O)_{20}$ dodecahedral cluster. Wheatley and co-workers[4] describe the use of machine learning methods to develop potential energy surfaces from limited *ab initio* data, and Liu and Herbert[5] present a detailed analysis of the *N*-body expansion and treatment of the basis set superposition error (BSSE) in such expansions. Paesani and co-workers[6] present many-body potentials determined from CCSD(T)-F12 calculations for

alkali ions interacting with water. Steffen and Hartke[7] use an empirical valence bond extension of a quantum-mechanically derived force field to generate reliable potential energy surfaces that are used to compute reaction rate data for three representative systems.

(2) Faster electronic structure methods

David Sherrill and co-workers[8] demonstrate that the CCSD(T)-F12 method gives interaction energies close to those from complete-basis-set-limit CCSD(T) calculations but at a greatly reduced computational cost. Shaw and co-workers[9] introduce a neural network scheme for reweighting the various contributions to MP2[10] energies, demonstrating a 6-7 fold improvement in accuracy over traditional MP2 calculations. Song and Martínez[11] report an implementation of analytical MP2 gradients using the tensor hyper-contraction scheme, demonstrating that with this approach MP2 gradients can be calculated with a quartic scaling with system size. Grimme and co-workers[12] report a procedure for generating accurate intermolecular potential energy functions using data from their recently introduced tight-binding scheme.[13] Wu, Shen, and Yang[14] describe an internal force correction (determined using a machine-learning approach) for semi-empirical quantum mechanical/molecular mechanics (QM/MM) molecular dynamics (MD) simulations. Cui and co-workers[15] introduce a method combining coupled cluster and density-functional theory (DFT) methods to calculate the binding molecular energies of dimers in solution.

(3) Models for polarization

Several articles analyze and present new approaches for describing many-body polarization. Brooks and co-workers[16] compare force fields that use atom-centered multipoles and point-inducible dipoles to those that use point-charges (including off-atom-centered sites) and Drude oscillators[17] to describe polarization. It is demonstrated that one can transfer parameters between the two types of force fields.

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Head-Gordon and co-workers[18] find that the AMOEBA force field[19] overestimates polarization, with the overestimation being traced to the Thole damping model.[20] Misquitta and Price[21] introduce an anisotropic polarizable atom-atom force field for pyridine which they use to model polymorphs of crystalline pyridine. Piquemal and co-workers[22] introduce an efficient scheme for calculating analytical gradients in the truncated conjugate gradient scheme. The resulting method enables long-time MD simulations with polarizable force fields. The article of Choi, Vazhappilly, and Jordan[23] describes a mixed real space/momentum space discrete variable representation (DVR) approach[24] for solving for the eigenvalues and eigenvectors of a model Hamiltonian approach for treating non-valence correlation bound anions of fullerenes and other systems.

(4) Ion solvation

Schenter and Mundy[25] use MD simulations with DFT energies/forces to calculate solvation-free energies of single ions in water. They conclude that real ions are much more complex than simple charged hard spheres. Wick[26] develops and applies a multi-state empirical valence-bond model to characterize HCl, HBr, and HI at the air/water interface. Spezia *et al.*[27] describe the development of new polarizable and non-polarizable force fields for calculating the hydration properties of ions. Chang and Dang[28] use polarizable force fields to study ethylene carbonate exchange between the first and second solvation shells around Li^+ and the dissociation kinetics of $Li^+\left[BF_4^-\right]$ and $Li^+\left[PF_6^-\right]$ in ethylene carbonate. Masella and co-workers[29] report MD simulations using polarizable force fields of carboxylate/methylated ammonium pairs in bulk water and in salt solutions. Pollard and Beck[30] and Andrés Cisneros and co-workers[31] present simulations modeling processes in Li^+ ion batteries. Whereas, Beck and co-workers use DFT simulations to study Li^+ ions in ethylene and propylene carbonates and conclude that polarization is important, Cisneros and co-workers use polarizable force fields in simulations of spirocyclic pyrrolidinium with BF_4^- and Li^+. Chaudhari, Rempe, and Pratt[32] use *ab initio* molecular dynamics (AIMD) simulations in combination with quasi-chemical theory[33] to study the shell structure of $F^-(aq)$. Ahlstrand, Zukerman Schpector, and Friedman[34] carry out simulations of alkali ion-acetate systems to better understand the interaction of these ions in aqueous solutions, with the goal of understanding protein solvation in electrolyte solutions. Ren and co-workers[35] use AMOEBA-type polarizable force fields to study Mg^{2+} and Ca^{2+} ions interacting with model compounds for amino acids.

(5) Novel force field methods

Several papers in the special issue deal with accurate modeling of molecular charge distributions. Meuwly and co-workers[36] present a novel minimal distributed charge model based on off-centered point charges and compare it to the results of electrostatic potentials obtained from distributed multipoles and atom-centered point charge approaches. Laboda and Millot[37] study the geometry dependence of the charge distribution of water as a function of OH bond lengths and HOH angle in order to design flexible electrostatic models ranging from point charge to distributed multipole models.

Dharmawardhana and Ichiye[38] examine the influence of the shape of the molecular charge distribution on liquid state properties by correlating multipoles of non-polarizable water models with their liquid state properties in computer simulations. Chong and co-workers[39] study an alternative to the fixed charge ff15ipq protein force field, first, deriving bonded parameters in the context of the ff15ipq solution phase charge set and, second, taking bonded parameters and running simulations with the vacuum phase charge set used to derive those parameters. Ryan Rogers and Wang[40] describe the determination of atomic Millikan-Thomson charges by computationally determined atomic forces. Such charges provide information about charge-transfer phenomena. Other articles in the special issue deal with force field generation strategies. For example, Kent and co-workers[41] combine information from configurational energies and forces generated in molecular dynamics simulations and use this information to optimize a force field by minimizing the statistical distance similarity metric. Voth and co-workers[42] propose novel multiscale reactive molecular dynamics (MS-RMD) force fields whose design utilizes relative entropy minimization. Finally, two papers describe new force fields. Salanne and co-workers[43] develop a polarizable model for sodium borosilicate glasses which is validated against neutron diffraction and nuclear magnetic resonance experiments, and Coupry, Addicoat, and Heine[44] include an explicit treatment of hydrogen bonds in the Universal Force Field[45] for metal-organic frameworks, hydrates, and host-guest complex applications.

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