1   Introduction

There is currently an urgent need to develop high fidelity and transferable molecular models in the energy industry to accurately model the high pressure, high temperature and heterogeneous conditions associated with petroleum and petrochemical environments, where current generation force fields are inadequate. Force fields were developed for the C2 hydrocarbons (ethane, ethylene and acetylene), as they serve as a relatively simple set of molecules, to robustly test the new potentials and fitting procedures as well as being among the most ubiquitous petrochemical compounds found in industrial applications. Ethane is the second most prevalent component of natural gas and has been used as both an energy source and feedstock for other chemical processes. Ethylene is currently the most produced organic compound in the world with global production exceeding 200 million tonnes per year.[4] Acetylene is a delirious byproduct of the ethane-propane cracking process so it is essential to remove from ethylene streams. These force fields enabled development of a larger set of 82 representative small molecules that are suitable for a much wider variety of chemical compositions related to petroleum applications. These force fields are designed to be transferable and allow easy extension to new molecules that might be relevant as novel petroleum compositions are simulated.

2   Progress

Two different families of models are being pursued in this project, differing in the choice of the repulsion and dispersion potentials. The PHAST models, including those previously published on small gas molecules[1, 2], are based on the Lennard-Jones equation, extended to the current petrochemicals for backwards compatibility with existing force fields. Concurrently, a new generation of potentials, PHAST-TT, is being developed based on a combination of the three leading asymptotically correct dispersion coefficients damped by an incomplete gamma function as first described by Tang and Toennies and exponential repulsion of the form suggested by Stone as to make the parameters more tractable.[6, 5] This form of the potential was decided upon after analyzing symmetry adapted perturbation theory results that demonstrated the necessity of including more than just the leading dispersion coefficient in the intermediate region of interaction as well as the extremely exponential behavior of the exchange/repulsion energy in the same region. The asymptotically correct dispersion coefficients are able to be accurately calculated via the polarizabilities at imaginary frequencies allowing them to be constrained in the fitting process, thereby reducing the dimensionality of the parameter space. Additionally, both families of models incorporate explicit polarization which is necessary to describe many-body effects especially important in heterogeneous interactions. A point polarizability model of the Thole-Applequist type is adopted due to its numerical stability and the ease with which parameters may be obtained as part of the dispersion coefficient fitting process.

Force fields for the C2 hydrocarbons have been developed with the previous considerations in mind. Atom-centered point polarizabilities at static and imaginary frequencies were calculated using the default procedure by the CamCASP program. The three leading asymptotically correct dispersion coefficients were then obtained via the Casimir-Polder formula and Gauss-Legendre quadrature. The Lennard-Jones parameters in the case of the PHAST family of models or the exponential repulsion parameters in the case of the PHAST-TT family of models were then fit to reproduce the *ab initio* single point energies of 2,000 randomly generated trimer configurations calculated with the quantum chemistry program ORCA at the DLPNO-CCSD(T) level of theory as shown in figure 1. These models have already been successfully applied to petrochemical separations.[3] Comparison with bulk thermodynamic and crystallographic data is ongoing.

Tentative force fields for the representative set of small molecules have been developed in a similar manner to the C2 hydrocarbons. A generic set of atomic parameters for atom "types" based upon the local environs are being pursued to facilitate transferability and easy extension to novel compositions. Polarizabilities and, through extension, dispersion coefficients are averaged over the entire set in a self consistent manner. This naturally allows for distinguishing of potential atom "types" based on their similarity. Final verification of force field accuracy is currently ongoing and will include *ab initio* interaction energies with the C2 hydrocarbon models already developed as well as simulation of thermophysical properties of petroleum mixtures.
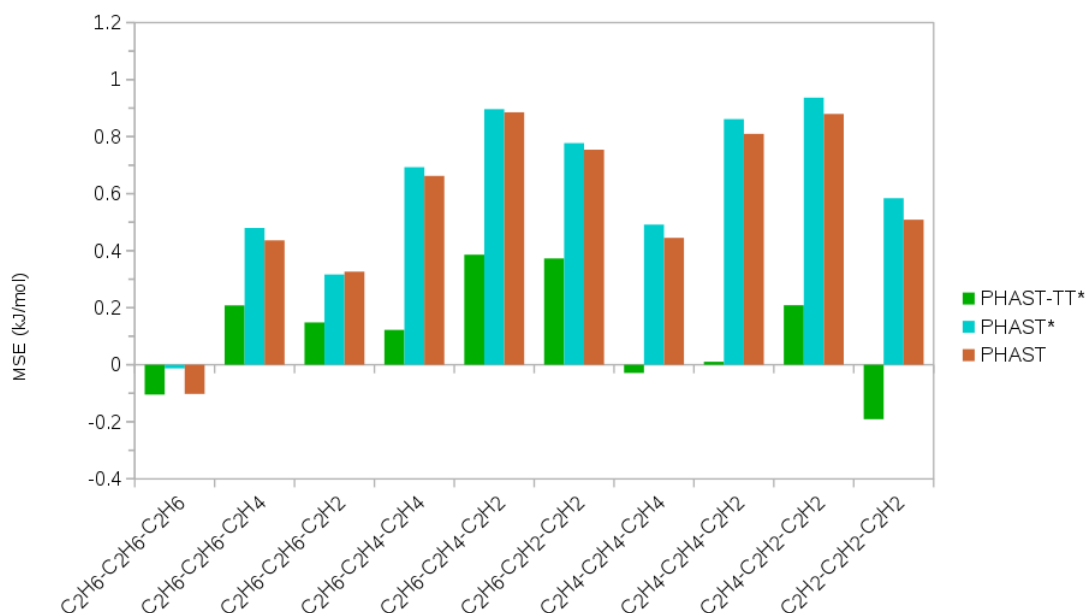
Figure 1: The mean signed error (MSE) of the fits of the C2 hydrocarbons to DLPNO-CCSD(T) in kJ/mol for both families of models. An asterisk (*) indicates explicit polarization is included in the model.

3 Impact

A new direction of research has been created for Professor Space relating to the development and testing of force fields for petroleum applications. This grant has also supported one graduate student, Adam Hogan, who is currently in his final year of graduate school and has two manuscripts resulting from this project currently in preparation.

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