Towards an accurate treatment of many-body dispersion and polarization for chemical accuracy via a coarse grained Gaussian Electronic Structure

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Computer clock speeds are no longer increasing and increases in computational power are now limited to increases in processor number, unfamiliar territory for   computational scientists who have ridden the wave of CMOS-scaling for the past 30 years. In this brave new world, gains in computational accuracy and performance will be driven by methodological development. In this lecture, a treatment of long range forces will be described to increase chemical accuracy of atomistic simulations. There are many physical systems where the non-pairwise additive nature of polarization and dispersion interactions becomes important, in particular, the complex heterogeneous systems of interest in chemistry, biology and physics. For example, the dipole moment of water changes from 1.85 Debye in the gas phase to approximately 2.6 Debye in the bulk liquid and attains intermediate values at hydrophobic interfaces due to many-body polarization. Similarly, although the bulk properties of hydrophobic fluids can be modeled using a pair potential, this underestimates the surface tension by 30% due to many-body dispersion interactions. In order to model both the full many-body polarization and dispersion interactions in atomic and molecule systems, a system of quantized Drude oscillators is introduced and a O(N) simulation method based on quantum path integrals is described using diagramatic expansions of the propagator. Applications to the phase diagram of water and water's properties at surfaces, are given.
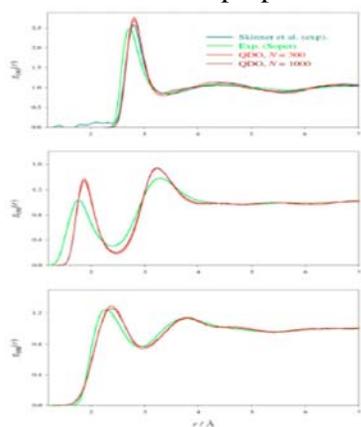

Figure 1: Comparison of the radial distribution functions of the QDO model of water to those obtained from the inversion of experimental results by Soper et al and Skinner et al.