Progress and Issues in calculating the water absorption spectrum

Paulo Cabral do Couto[2] and Daniel M. Chipman[1]

[1] University of Notre Dame, Radiation Laboratory, Notre Dame, IN, USA

One practical approach for the theoretical study of the absorption spectrum of liquid water is the sequential QM/MD approach, where the absorption spectrum is calculated by averaging excitation energies, weighed by the oscillator strengths, over configurations appropriately sampled from liquid water molecular dynamics simulation. Usually, surface effects are minimized by embedding the sampled configurations point charges taken from also taken from simulation. Within this approach, the reliability of the theoretical method used in the calculation of excitation energies and the correction of surface effects are critical issues.

The present work reports data for benchmark EOM-CCSD calculations for the lowest valence excited states of each symmetry of the water monomer and dimer. The performance of time-dependent density functional theory within the Tamm-Damcoff approximation, using the BHandH, MPW1K and MF06-HF density functionals, is assessed. The efficacy of embedding sampled configurations in point charges as means to minimize surface effects is also assessed.