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Dipole-Renormalized Reservoirs for Adaptive Open-QM/MM Simulations of Liquid Water

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Open-boundary QM/MM simulations allow a quantum subsystem to exchange molecules and energy with a surrounding classical reservoir. This provides a natural framework for studying condensed-phase systems, but it also raises a central question: how physically compatible must the classical reservoir be with the quantum region, especially when the QM subsystem is small and interface effects become important?
Here, we address this question for liquid water by constructing a dipole-renormalized molecular reservoir for adaptive open-QM/MM simulations. Starting from a flexible Amber-compatible three-site water model, we optimize the reservoir against a full ab initio liquid-water trajectory. The key target is the molecular dipole distribution extracted from maximally localized Wannier centers, which transfers low-order quantum electronic information into the classical model. The optimization adjusts atomic charges, bonded parameters, and Lennard-Jones interactions while preserving the simple three-site Amber functional form.
The optimized reservoir is tested in CP2K open-QM/MM simulations for different QM-region sizes. For a large QM region containing approximately 440 water molecules, the energy-ratio diagnostic confirms that the boundary contribution is small and the system satisfies the Grand Canonical condition. In this regime, the dipole-renormalized reservoir reproduces the particle-number distribution, structural radial distribution functions, Wannier-resolved RDFs, and molecular dipole distribution of the corresponding ab initio subsystem. For a smaller QM region containing approximately 190 water molecules, where the surface-to-volume ratio is less favorable and the interface becomes more influential, the optimized reservoir still maintains substantially improved molecular consistency compared with a non-renormalized flexible TIP3P reservoir. An additional extreme test with approximately 50 QM water molecules defines the qualitative compatibility limit of the present dipole-matched three-site model.