“Can DFT-Based Ab Initio Hydrated Electron Simulations Correctly Predict Experiment?”

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ABSTRACT: The hydrated electron is the simplest condensed-phase quantum mechanical system, consisting of an excess electron solvated by water. Most past simulation work on this system relied on mixed quantum-classical (MQC) models, where only the electron is treated quantum mechanically via pseudopotentials. In the MQC picture, the choice of pseudopotentials strongly affects the predicted solvation structure, and no model has been able to capture the experimental behavior of the hydrated electron correctly. Thus, in this work, we explore the DFT-based ab initio simulations of the hydrated electron, investigating two distinctively different models. First, we explore a minimalist model, which consists of 4 or 16 water molecules surrounded by a polarizable continuum at 0 K. We extend the model by running dynamics at room temperature, and find that the addition of kinetic energy dramatically changes the electron’s solvation structure in such a way as to destroy any agreement of the 0 K model with experiment. Our analysis shows that the polarizable continuum is not able to provide adequate confinement for the electron at room temperature when the water molecules can fluctuate, emphasizing the importance of using explicit water molecules. Second, we ran DFT-based ab initio dynamics simulations of the hydrated electron with a fully periodic system and explored both finite-size effects and temperature-dependent properties. We find that the fluctuations of the electron’s solvation structure are not converged even for system sizes up to 128 waters, which required months of calculation time. The calculations are unable to correctly predict the absorption spectrum of the hydrated electron, although they do qualitatively reproduce the experimental temperature-dependent red-shift. We conclude that DFT-based ab initio simulations are not adequate for understanding the nature of the hydrated electron.

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