Ab initio calculations of water and ice: structural, electronic, and optical properties

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Abstract

Extended aqueous systems, crystalline ice and liquid water, are studied computationally to investigate their ground state and excited state properties. Methods from solid state physics and quantum chemistry are combined to shed light on some of the unusual properties of water and ice.

For the ground state of crystalline ice, density functional theory (DFT) calculations are compared to an *ab initio* incremental ansatz that utilizes periodic Hartree-Fock together with localized electron correlation calculations. It is shown that the many-body decomposition of the electron correlation converges very fast, allowing the achievement of excellent agreement with experimental data even when limiting correlation energy contributions to two-body terms only. The incremental method is utilized by a computer program that combines the periodic and localized calculations, and allows for structural optimization of the system of interest.

The adsorption of water molecules on the surface of ice is studied using DFT. Adsorption is found to be favoured on non-crystallographic adsorption sites, and a slight tendency towards the formation of rough surfaces is reported. The localization of excess electrons at the surface of ice is facilitated by co-adsorbed water molecules. For a correct theoretical description of the latter, a self-interaction correction scheme for the excess electron has to be used. However, it is sufficient to limit the self-interaction correction to the excess electron only, since the neutral ice surface itself is well described within conventional DFT. The self-interaction correction scheme is incorporated into a commonly used DFT program package.

Optical excitations of crystalline ice are calculated using many-body perturbation theory. Solving the two-particle Bethe-Salpeter equation yields optical spectra in excellent agreement with experimental data. Based on this agreement, an embedding model is developed that reduces the hydrogen bond network to its most important contribution. The model is applied to crystalline ice, where it reproduces the experimental spectral features, and to microscopic liquid water structures obtained from molecular dynamics simulations, where it reproduces the energy shift of the first absorption peak and gives overall good agreement with experiment. The driving force of water's anomalous optical behaviour is identified.

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