Electronic properties of water\textsuperscript{1} DAVID PRENDERGAST, JEFFREY GROSSMAN, GIULIA GALLI, Lawrence Livermore National Laboratory — Recent experiments to analyze the structure of liquid water have been carried out using x-ray absorption and photo-emission. To interpret the resulting spectra requires accurate theoretical models. To this end, we investigate the electronic properties of water at ambient conditions using \textit{ab initio} density functional theory (DFT). We generate long (250 ps) classical trajectories for large supercells (up to 256 molecules), from which uncorrelated conformations of water molecules are extracted for use in DFT calculations of the electronic structure. We find that the density of occupied states of this molecular liquid is well described with 32 molecule supercells. However the description of the density of unoccupied states (u-EDOS) is sensitive to finite size effects. Small supercell, Γ-point calculations (32 molecules) yield a spuriously isolated state above the Fermi level. Nevertheless, the more accurate u-EDOS of large supercells may be reproduced using small supercells and increased \textit{k}-point sampling. Exploiting this improved understanding of the electronic properties of liquid water, we outline efficient approaches to increasing the accuracy of calculated spectra associated with optical absorption, near-edge x-ray absorption, and x-ray photo-emission.

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