

Abstract Submitted
for the MAR05 Meeting of
The American Physical Society

Electronic properties of water¹ 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 *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 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.

¹This work was performed under the auspices of the U.S. Department of Energy at the University of California/Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

David Prendergast
Lawrence Livermore National Laboratory

Date submitted: 03 Dec 2004

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