

Abstract Submitted
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Structural and Electronic Properties of the Solvated Chloride Ion from First Principles Simulations FRANCOIS GYGI, Department of Computer Science, University of California, Davis, CUI ZHANG, TUAN ANH PHAM, Department of Chemistry, University of California, Davis, GIULIA GALLI, Department of Chemistry, Department of Physics, University of California, Davis — First principles simulations of anions in aqueous solutions represent a challenging task both from a theoretical and computational standpoint, and only sporadic ab initio studies of their electronic properties have appeared in the literature. We carried out first principles molecular dynamics (MD) simulations of the chloride anion in liquid water with semi-local (PBE) and hybrid (PBE0) functionals, using the Qbox code. We found substantial differences in the orientation of the water molecules in the first anion solvation shell when using the two different levels of theory. Most importantly, the relative energies of the highest occupied level (HOMO) of the anion was found to be lower than the top of the valence band of water with PBE and the HOMO state is fairly delocalized, while it is higher with PBE0 and the corresponding state is localized on the anion. Although qualitative correct, the result obtained with PBE0 is only in fair agreement with experiment. It is only when using many body perturbation theory at the GW level and PBE0 trajectories that we could find qualitative and quantitative agreement with experiment [1]. Work supported by DOE-CMSN DE-SC0005180 and DOE-BES DE-SC0008938.

[1] P. Delahay, *Acc. Chem. Res.* 15, 40 (1982).

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