Electric binding energies of hydrated OH^- and H_3O^+: ab initio molecular dynamics combined with GW quasiparticle theory

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Motivation and Summary:

Understanding the proton transfer mechanism for hydrated H_3O^+ and OH^- ions in liquid water is an important prerequisite in describing pH-related processes. Recent Photoemission Spectroscopy experiments[1] have accurately determined the electron binding energies for these ions. However, an accurate model has yet to be introduced to describe, and numerically recreate, these binding energies.

This project aims to apply recent developments in electronic structure analysis to accurately generated solvation structures in order to simulate these experimental results. Further more, it is hoped that the combination of accurate solvation and electronic structures will lead to an improved description of the proton transfer mechanism for hydrated H_3O^+ and OH^- ions.

The following research is broken down into two major parts:

1) 64-molecule ab initio molecular dynamics simulations of the relevant defect (Ion) systems in water. Systems are brought to equilibrium and then solvation structures are collected for approximately 20 ps.
2) Static GW Local Field and GW Homogeneous Field calculations are performed on the above structures (see below for details). Averages of the total density of states and the local density of states (those related to the defects) are produced over a 10 ps interval.

GW Static Local Field Method:

Expanding on the previously introduced GW Homogeneous Field method[3], the GW Local Field method has been numerically implemented[2] to statically analyze the electronic structure:

- Based on the **G**reen's function approach to the Kohn-Sham self-consistent Density Functional Theory calculations and screened Coulomb interactions (**W**). The GW approximation was designed for the self-energy of the excited electron in presence of a static core hole.
- Uses the static Coulomb-hole and screened exchange (COHSEX) approximation[3] for the self-energy operator Σ.
- Includes local fields, due to the inhomogeneity of the medium, within the screened Coulomb interactions in accordance with the Hybertsen-Louie ansatz[7].
- Effects of the screened Coulomb interaction on the self-energy are included by use of the convolution theorem for the bare interaction[2].

For Information on the GW Local Field Method: Please See Ref 2. and Ref 3.

References/Acknowledgments:

1) Bernd Winter, et al., J. Am. Chem. Soc., 2006, 128 (12), pp 3864–3865.
2) Lingzhu Kong, Xifan Wu, Roberto Car, arXiv:1204.0268v1 [physics.chem-ph].
3) Wei Chen, Xifan Wu, and Roberto Car, Phys. Rev. Lett. 100, 027801 (2008).
4) Tuckerman et al., J. Chem. Phys., Vol 103, No. 1, 1 July 1995.
5) Tuckerman et al., Acc. Chem. Res. 2006, 39, 151-158.
6) P. Giannozzi et al., http://www.quantum-espresso.org.
7) M. S. Hybertsen and S. G. Louie, Phys. Rev. B 37, 2733 (1988).

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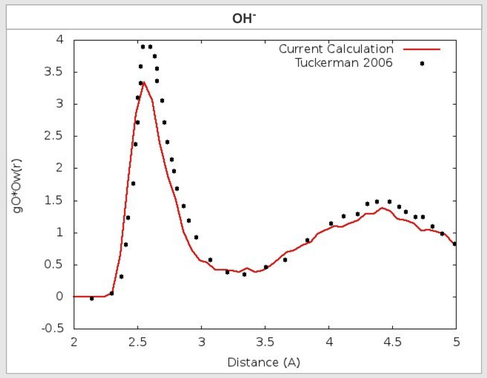
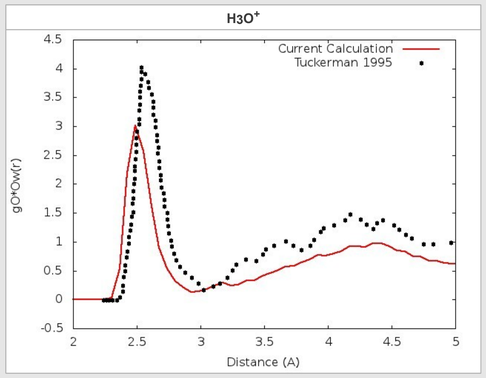
Comparison of radial distribution functions with previous calculations





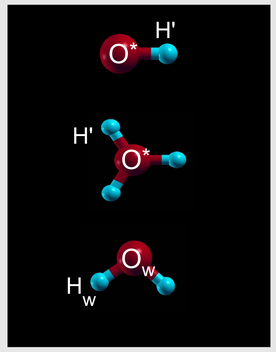
MD Simulation Details:

All simulations were performed using a modified version of the QUANTUM-ESPRESSO[6] code package. Three different simulations were carried out:

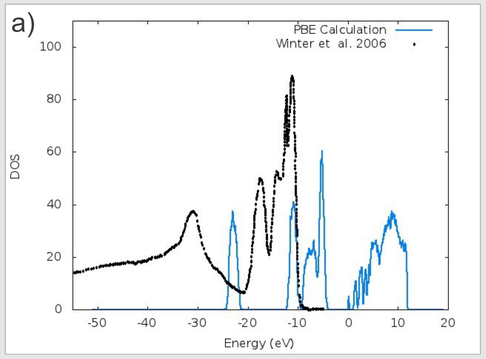
1) OH^- (63 H_2O molecules, 1 OH^- molecule)
2) H_3O^+ (63 H_2O molecules, 1 H^+ ion)
3) H_2O (64 H_2O molecules)

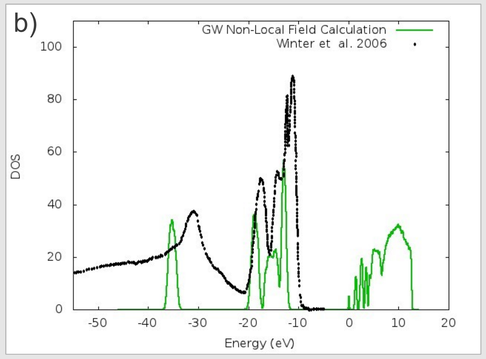
Simulation details are as follows:

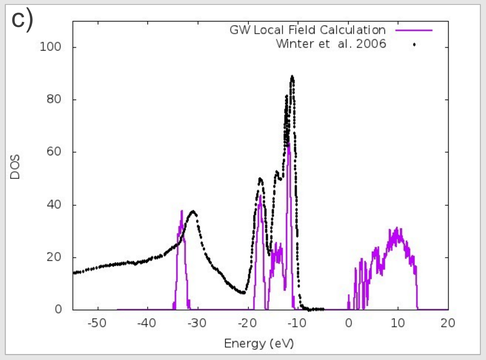
- CP dynamics with a time step = 0.09675 fs (each for over 20 ps) and a box size = 12.446 Å.
- Nosé-Hoover thermostats at 330 K to simulate Nuclear Quantum effects.
- PBE Pseudopotentials (Future work will be performed with the PBE0 Hybrid Functional to create a more accurate solvation structure).



Comparison of different electronic structure methods with experiment







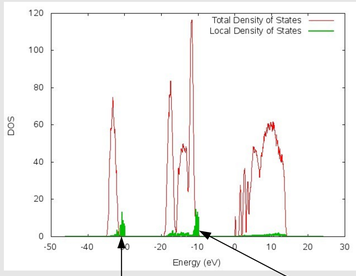
Electronic structure methods were performed, statically, on the solvation structures generated from the above CPMD simulations.

The following calculations were performed:

- a) PWscf PBE Electronic Minimization
- b) GW Homogeneous Field Calculation[3]
- c) GW Local Field Calculation[2]

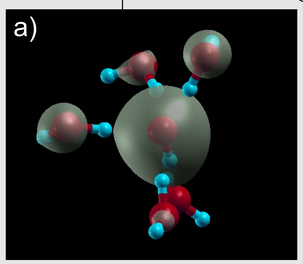
Both the GW Homogenous Field and, even more so, the GW Local Field greatly improve the description of the of the electron binding energies as compared to experiments; most notably the band gap.

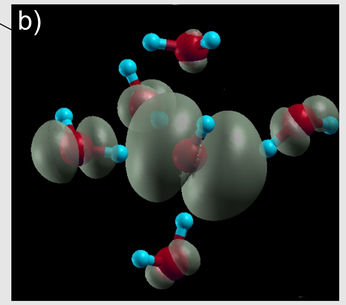
OH^- Defect Orbital Analysis



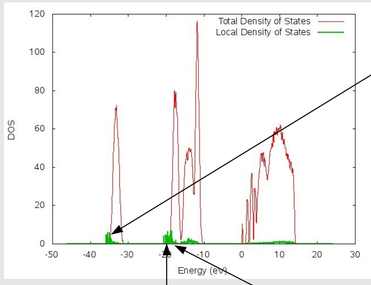
Two defect states consistent with experiment (both in position and spread):

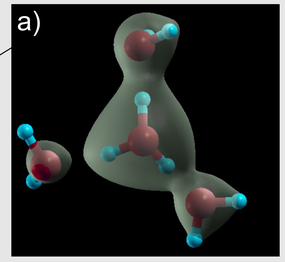
a) Defect state around the $2a_1$ orbitals. Note the distorted s-orbitals of the surrounding water molecules.
b) Lone pair ($1b_1$) defect state. Surrounding water molecules have slightly rotated $1b_1$ in, perhaps, competition for a proton transfer.

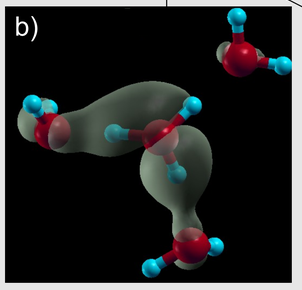


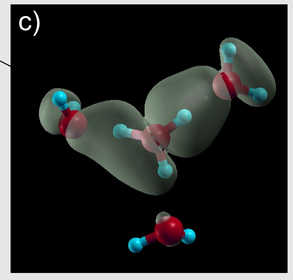


H_3O^+ Defect Orbital Analysis









The local density of states reveals 3 different defect states associated with H_3O^+ (spread and position also consistent with experiment):

a) $2a_1$ orbital defect state
b) and c) Similar to degenerate orbitals in a single (gas-pase) H_3O^+ simulation positioned around the $1b_2$ H_2O orbitals. However, due to the broad spread of the local DOS further investigation is needed to determine if these states simply have a wide range of energies or the degeneracy can actually be split.