The Importance of Exact Exchange and van der Waals Interactions in Modeling X-Ray Absorption / Emission and Photon-Emission Spectra of Water and Aqueous Solution

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Introduction

Both advanced *ab initio* molecular dynamics (AIMD) [1] method by including exact exchange (PBE0) and van der Waals (vdW) interaction, and the GW-based electronic excitation theories are essential in accurately predicting the structural and spectroscopic properties of liquid water and aqueous ionic solutions. Focusing on the above physics, we are carrying out research on the following topics:

- The importance of water structures predicted by PBE0+vdW-AIMD on the theoretical calculations of X-ray absorption spectra (XAS) based on GW-based electron excitation theory.
- To theoretically understand the X-ray emission spectra (XES) and its signatures from H-bond network by advanced AIMD and GW-based electron excitation theory.
- To improve the prediction of ionization potentials (IPs) of solvated Cl^- in water by AIMD method including both PBE0 and vdW functionals.

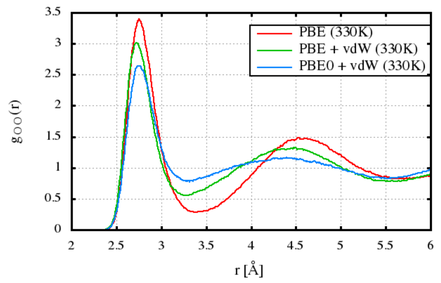
AIMD simulation details

- Car-Parrinello molecular dynamics
- Simulation cells include 64 H_2O molecules or one Cl^- ion surrounded by 63 H_2O molecules
- Structures based on AIMD by including both PBE0 and Tkatchenko and Scheffler (TS)-vdW interactions [2] in modeling XAS of liquid water and IPs of hydrated Cl^-
- Structures by PBE+TS-vdW based AIMD used in modeling XES spectra of liquid water
- Ecut = 71 Ry, dt = 2.5 a.u.
- Well equilibrated over 15 ps
- Linear scaling exact exchange is used to speed up the PBE0 computations

GW-based electron excitation theory

- Static Coulomb hole plus screened exchange (COHSEX) approximations
- Homogeneous screening model
- Inhomogeneous screening model based on the local density ansatz of Hybertsen and Louie exchange [6]

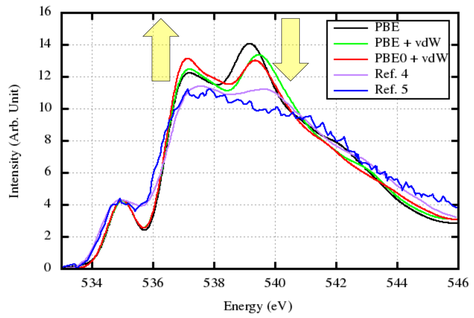
Radial Distribution Function (RDF)



	Water Density (g/cm³)
PBE	0.868
PBE + vdW	1.007
PBE0 + vdW	1.014

AIMD with constant pressure (Biswajit Santra et al.)

XAS spectra of liquid water



- Averaged spectra considering thermal fluctuations will be performed
- Theoretical results from Ref. 4 is based on BLYP-Path Integral AIMD

Reference

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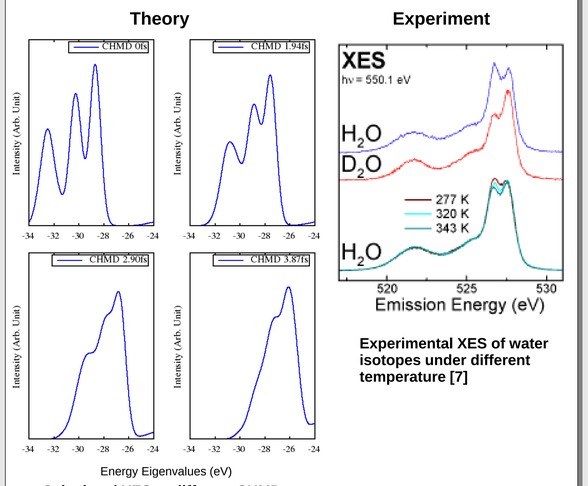
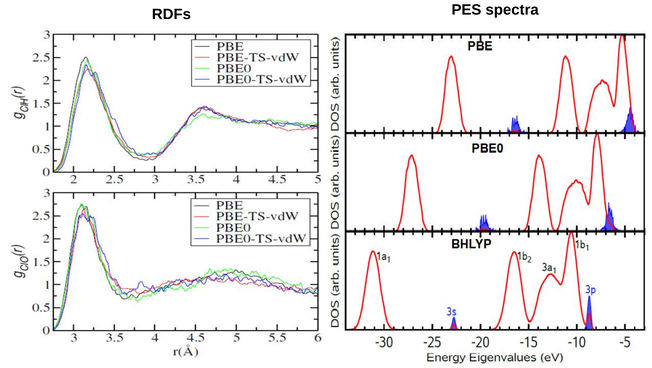
XES spectra as functions of core-hole molecular dynamics (CHMD) time



Calculated XES at different CHMD instances

Experimental XES of water isotopes under different temperature [7]

Cl^- ion solutions

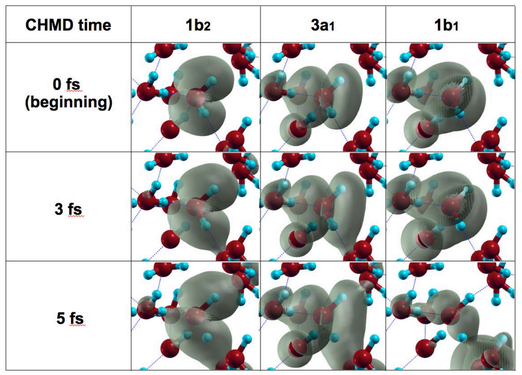


	PBE	PBE -TS-vdW	PBE0	PBE0 -TS-vdW
r_{ClH}^{max}	2.15	2.18	2.16	2.16
n_{ClH}	5.22	5.21	5.18	5.19
r_{ClO}^{max}	3.10	3.12	3.10	3.12
n_{ClO}	5.36	6.33	6.21	5.84

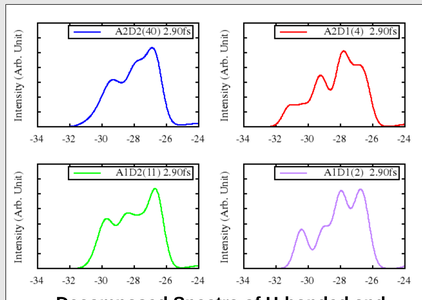
δE(ev) = HOMO of Cl^- - Highest VBE of Water

MD / δE(ev)	PBE	PBE -TS-vdW	PBE0	PBE0 -TS-vdW
PBE	-0.27	-0.11	-0.07	-0.07
PBE0	0.14	0.29	0.36	0.34
BHLYP	0.72	0.88	0.95	0.92

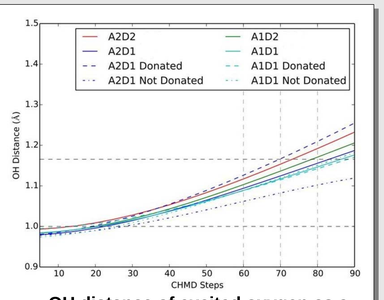
Orbital distortion of excited oxygen during CHMD



- In XES experiments, OH bond is elongating within the excited water molecule resulting in the distorted $1b_2$, $3a_1$, and $1b_1$ orbitals within the life-time of core-hole as shown
- Sharp $1b_1$ peak in XES spectra



Decomposed Spectra of H-bonded and non H-bonded water molecules



OH distance of excited oxygen as a function of CHMD time

Conclusions

XAS

- XAS of liquid water based on structures from classical GGA-AIMD simulations gives qualitatively incorrect spectra.
- Structures by path-integral AIMD by considering nuclear quantum effect of H atoms largely corrected the above error.
- PBE0+TS-vdW has an effect to bring the theory further close to experiments by additional softening the H-bond structure.

XES

- The modeling of core-hole dynamics related to fast disassociation of OH covalent bond due to the excited O is essential.
- Strongly dependent on the H-bond structure of liquid, H-bonded and non H-bonded water molecules will have distinct XES features.
- Water structures from AIMD by including PBE0+TS-vdW and quantum nuclei effect are required in the future to predict the double splitting feature of XES.

Ionization energy of solvated Cl^-

- The PES study shows only the hybrid functional (PBE0 and BHLYP) can qualitatively predict the electronic properties in solutions and be consistent with photoelectron detachment measurements.

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