

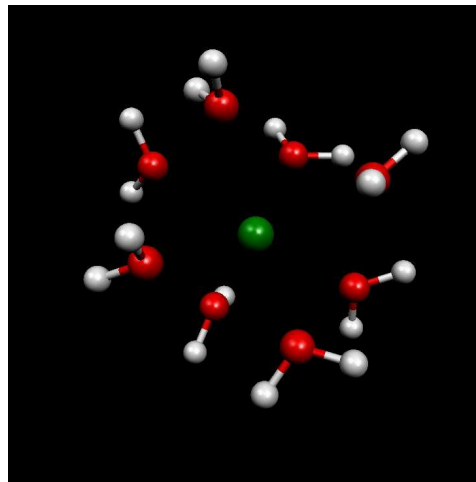
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REU Summer Presentation

Molecular simulation of Ca^{2+} hydration and the calculation of the optical response of water

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Overview

Why care: Ca^{2+} hydrates in nature.

- Biological systems.
- Physical Chemistry.

Beyond (or around) hydrates.

- Solvent interaction with surfaces.
- Bulk, cluster and gas phase characteristics of water.

Molecular mechanical dynamics.

Optical response calculations.

Overview

Why care

Molecular mechanic dynamics.

- Interaction potentials.
- MMD calculations.
- Analysis.

Optical response calculations.

Overview

Why care

Molecular mechanic dynamics.

Optical response calculations.

- TDDFT calculations.
- Dipole response, and dielectric constants.
- The loss function.

Motivation: Ca^{2+} hydration

Biological Systems

- Nerve signal transfer.
- Signal transduction.
- General structure of electrolyte solvation.
- Nutrient transport through cell walls.
- Electrolyte transport.

Physical Chemistry

- $Ca^{2+}Cl_2$, $UO_2(h_2O)_5^{2+}$ and U_2 hydration.
- Solvent interaction with MgO surfaces.

Bulk and Cluster water calculations

- Dielectric properties of bulk water.
- Cluster size dependence of dielectric properties.
- Surface effects on small water clusters.

Classical Molecular Dynamic Calculations.

Interaction Potentials

The non Coulomb interaction between atoms is given by the Lennard-Jones potential:

$$V_{ij}(r) = \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6}$$

For Coulomb interactions, a single point charge (SPC) model for water is used, with the charge parameters $Q_O = -0.82 e$ and $Q_H = 0.41 e$.

Atom-Atom interaction potential is then given as

$$V(r) = \sum_{i \neq j} \frac{Q_{ij}}{r_{ij}} + \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6}.$$

GROMACS

Groningen Machine for Chemical Simulations

The software used to do the classical molecular dynamic calculations was GROMACS(2; 3), a message passing parallel molecular dynamics package for chemical modeling.

After the system was populated with water molecules, an energy minimization calculation was performed to relax any bad Coulomb+Lennard-Jones interactions. Full molecular dynamic calculations were implemented using a positionally constrained run, followed by an unconstrained molecular dynamic calculation.

Classical Molecular Dynamic Calculations.

Analysis

Solvent behavior near the solvate ion can be understood by using two radial distribution functions (RDFs) for the water Oxygen (g_{CaO}) and Hydrogen (g_{CaH}). Where the RDFs for a given species are given by

$$g_{Ca*} = \frac{\langle \rho_{Ca*}(r) \rangle}{\langle \rho_{Ca*}(r_{local}) \rangle}$$

The coordination number can be calculated from the RDFs by

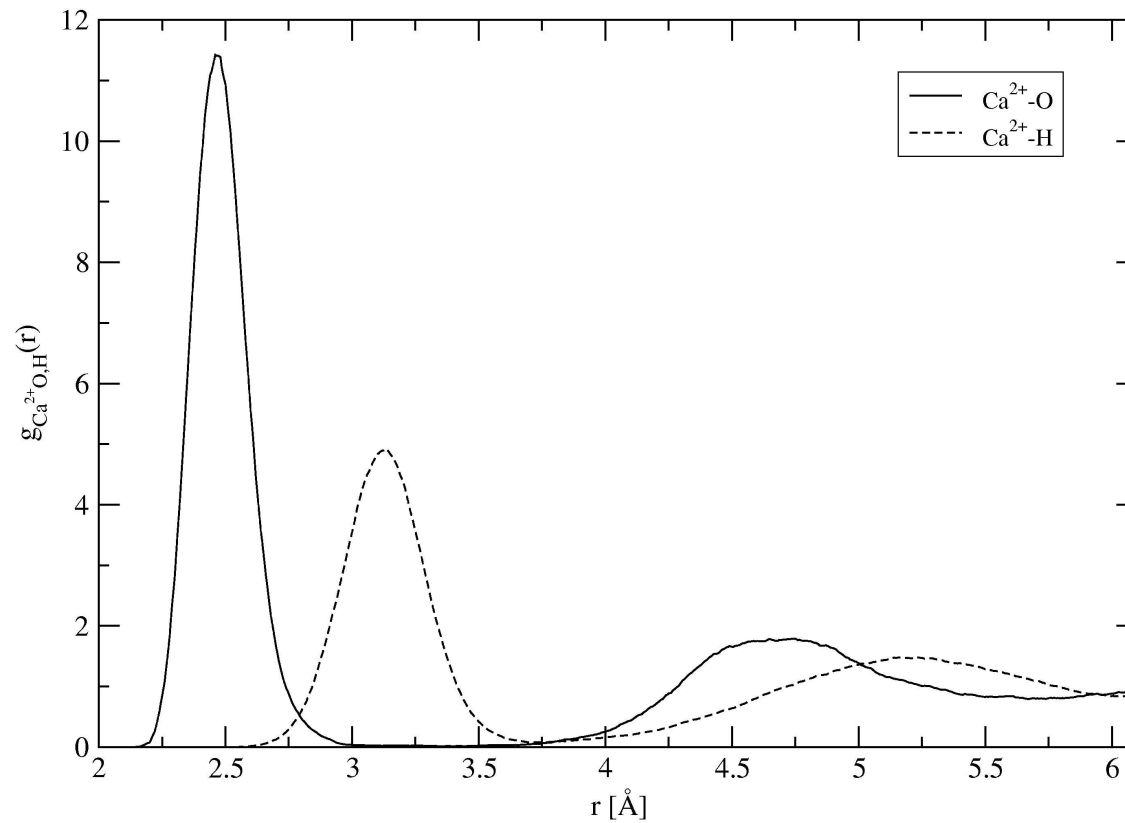
$$n_* = 4\pi \int_0^{r_{min}} dr g_{Ca*}(r) r^2$$

n_O	$r(\text{\AA})$	method
7.44	2.47	MD
6	2.397	DFT ^a (4)
8	2.46	xray(5)
7.3	2.40	N(6)
8	2.46	EXAFS(7)

^aGas phase calculation

Classical Molecular Dynamic Calculations.

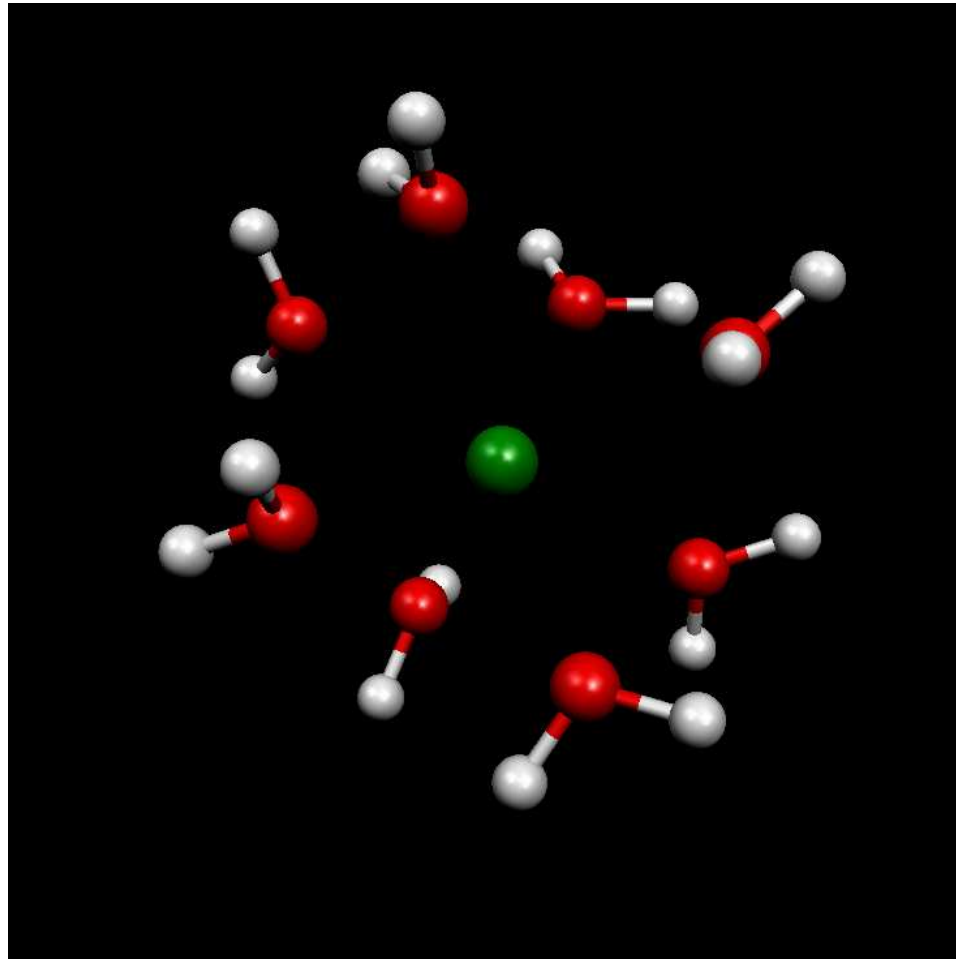
Radial Distribution Function



$\text{Ca}^{2+} - \text{O}_w$ and $\text{Ca}^{2+} - \text{H}_w$ RDF results

Classical Molecular Dynamic Calculations.

Structure of the first hydration sphere



Real Time-Time Dependant Density Functional Theory

The linear response of a system to an external electric field E is calculated by introducing a perturbation $\delta H == -x \cdot E$.

Once self consistency has been reached, the time dependence of the system is calculated using the Hamiltonian

$$H = -\frac{1}{2}\nabla^2 + V_{ext}(r, t) + \int dr' \left(\frac{\rho(r', t)}{|r - r'|} \right) + V_{xc}[\rho](r, t)$$

with

$$V_{xc}[\rho](r, t) = \frac{\delta E_{xc}^{LDA}[\rho_t]}{\delta \rho_t(r)} = V_{xc}^{LDA}[\rho_t](r, t).$$

Real Time-Time Dependant Density Functional Theory

Frequency-Dependant Response and ϵ

The dipole moment $D(t)$ can be calculated using the time dependant electron configuration, and subsequently the frequency-dependant response by Fourier transform

$$D(\omega) = \int_0^{\infty} dt e^{(i\omega - \delta)t} D(t).$$

From the frequency-dependant response, $\alpha(\omega)$ can be represented to first order as

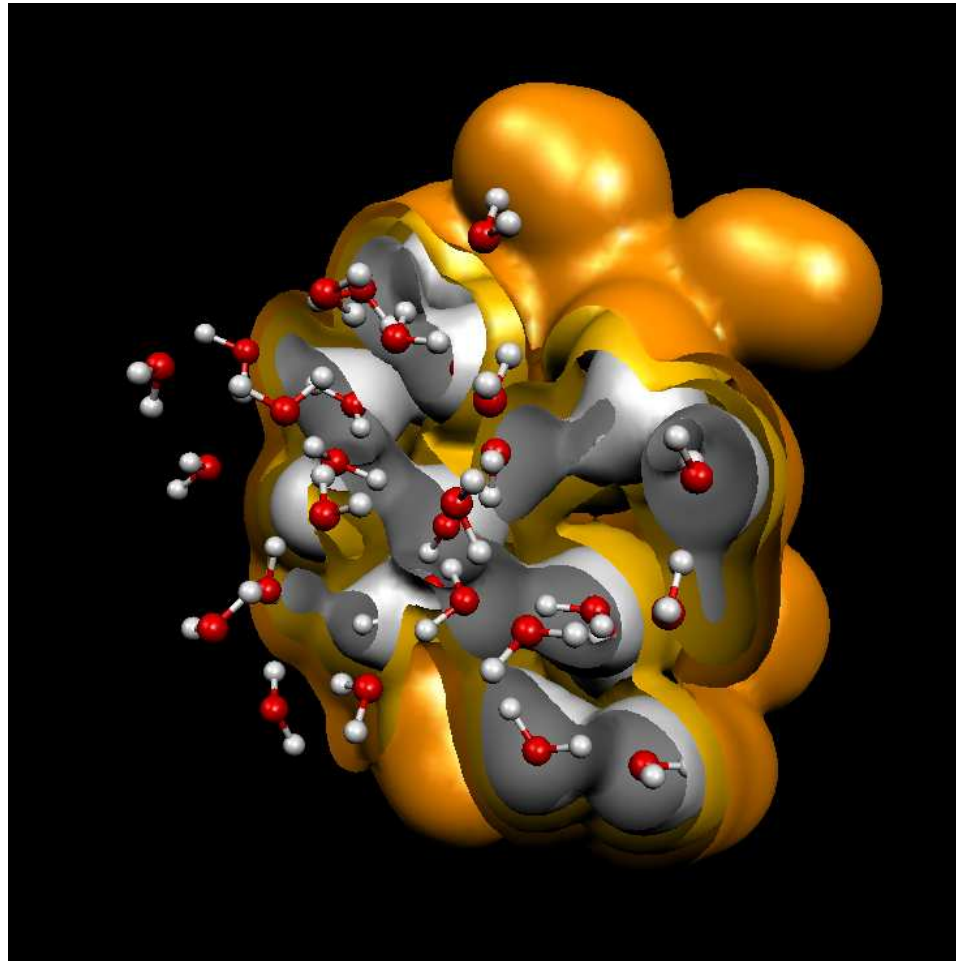
$$\alpha(\omega) = \frac{D(\omega)}{E} \Rightarrow \text{Im } \alpha(\omega) = \frac{\text{Re } D(\omega)}{E}, \quad \text{Re } \alpha(\omega) = \frac{\text{Im } D(\omega)}{E}.$$

From $\alpha(\omega)$, the dielectric constant of the system can be calculated by the relation $\epsilon = 1 + 4\pi\alpha/V_{clust}$. Using the definition $\epsilon = \epsilon_1 + i\epsilon_2$ then gives

$$\epsilon_1(\omega) = 1 + 4\pi\omega \frac{\text{Im } D(\omega)}{EV_{clust}}, \quad \epsilon_2(\omega) = 4\pi\omega \frac{i\text{Re } D(\omega)}{EV_{clust}}$$

Real Time-Time Dependant Density Functional Theory

Electronic Volume Calculation



Cut offs of 0.01, 0.001 and 0.0001.

Real Time-Time Dependant Density Functional Theory

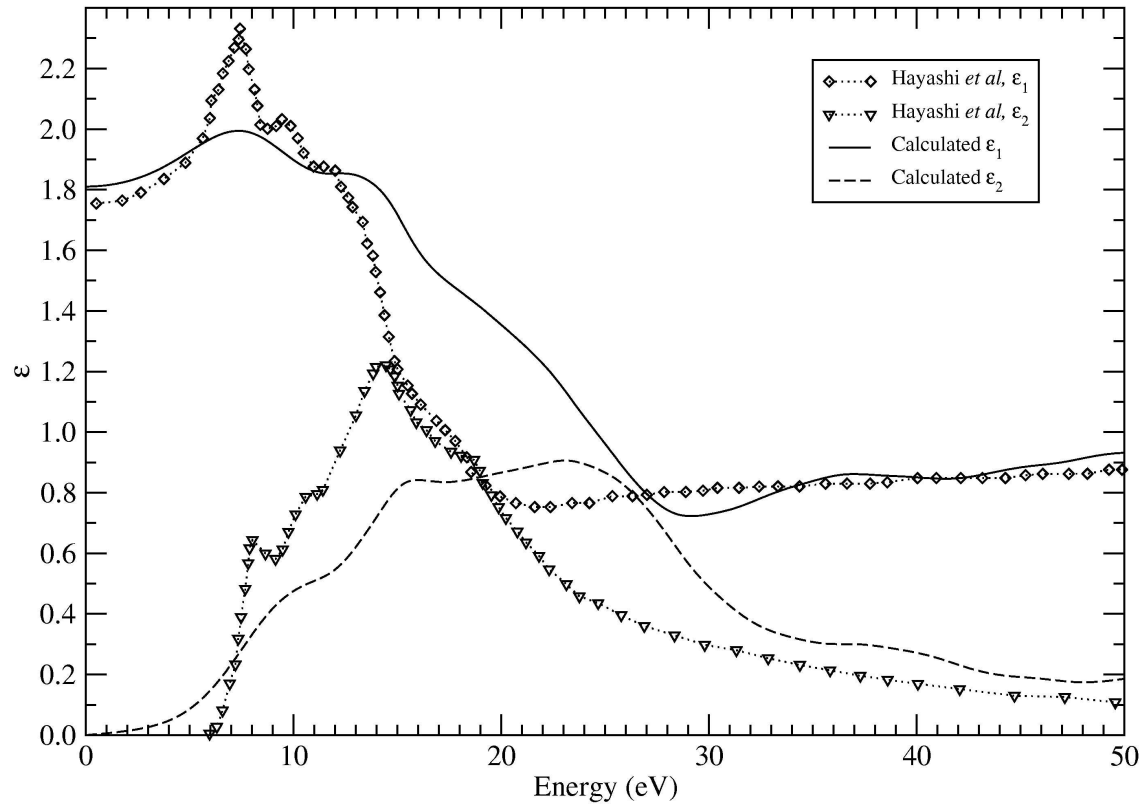
Selection of water clusters

Due to the large dipole moment of H_2O , and the finite size of clusters, the dipole moment of the system is critical to calculations.

A Monte Carlo simulation is used to sample the whole bulk system and select the most optimal configuration of molecules. Large database hash lookups are used to store and analyze the Monte Carlo data through efficient sorted table lookups.

Real Time-Time Dependant Density Functional Theory

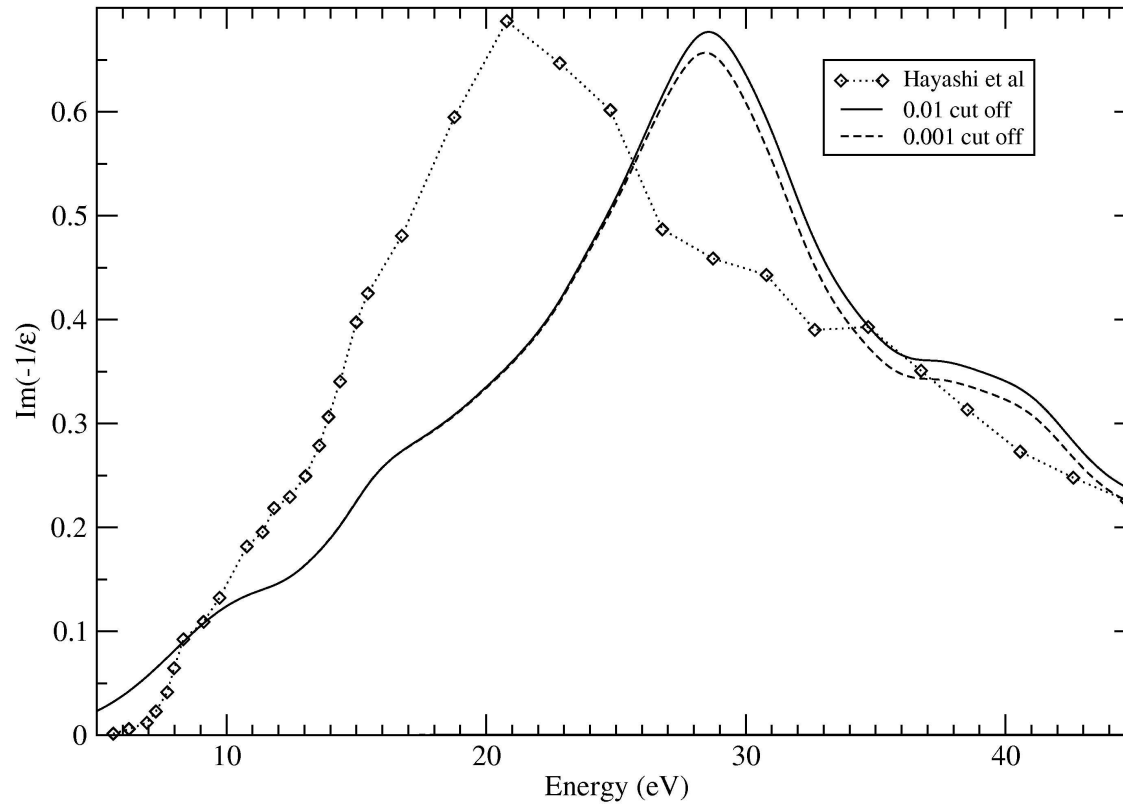
Dielectric Constant vs Energy



Dielectric constant $\epsilon(\omega)$ for liquid water.

Real Time-Time Dependant Density Functional Theory

Loss function



Calculated loss function $Im(-1/\epsilon(\omega))$ compared to experiment (9) for liquid water.

Conclusions

Theory Improvements

- Basis set improvement is needed (10), candidates are RHF/3-21+G(d) type potentials.
- Cluster size is important when surface effects are influential(4; 11).
- Run length increase for low energy resolution.

Future Work

- Investigation of near UV characteristics of water solvated systems, including UO_2 and U_2 solvated ions and MgO surface solvation behavior.
- Bulk and cluster behavior of water in the near UV spectrum.

Acknowledgments

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