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Development of a First-Principles Hydrogen Vibrational Spectrum in Liquid H_2O

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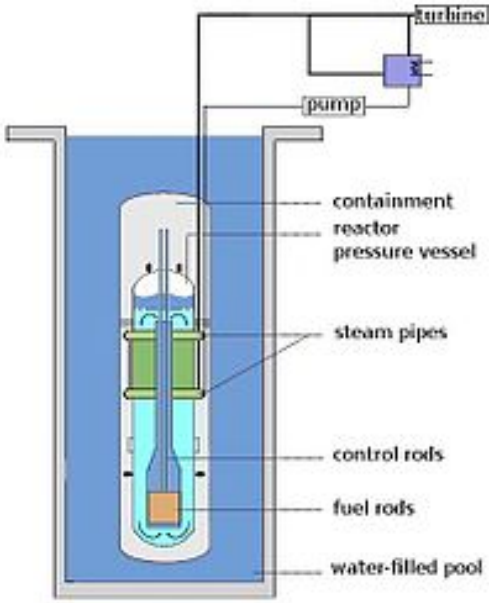
Outline

- Motivation and applications
- *Ab-initio* Molecular Dynamics (AIMD)
- Structural properties of H_2O from AIMD
- Dynamical properties of liquid H_2O
- Generation of vibrational density of states (VDOS) from AIMD simulations

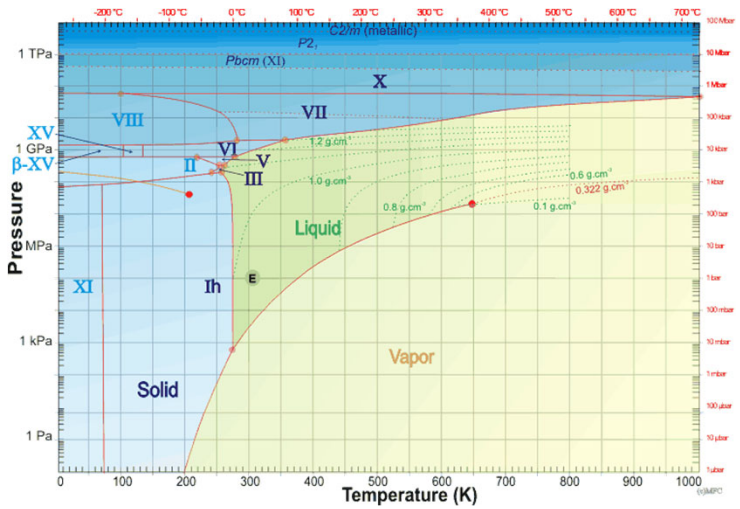
Liquid H_2O in Nuclear Applications

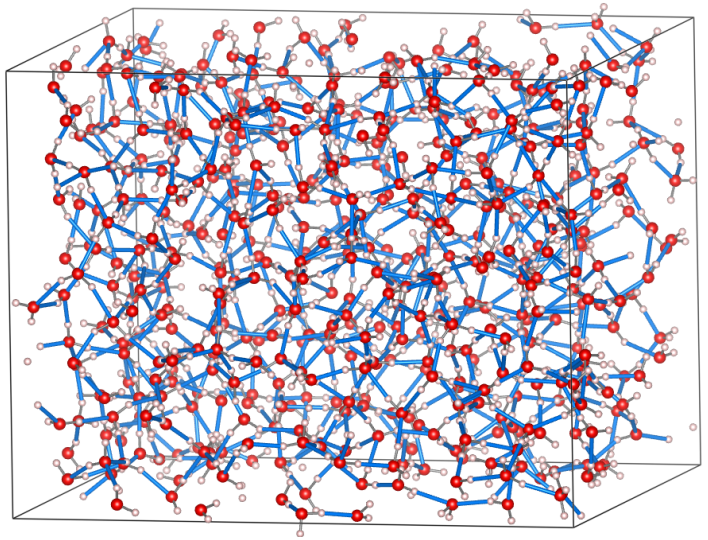


- **Light water is present in many critical systems**
- Nuclear fuel coolant
- Natural shield against radioactive material

- Discrepancies in Thermal Scattering Law (TSL) libraries can be addressed with computational molecular models
- Molecular simulations are the precursor to cross-section calculations and TSL calculations needed for nuclear criticality safety measures

Macroscale → Nanoscale Liquid H_2O



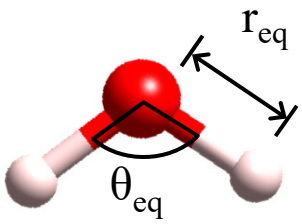


Density (ρ)	0.997 g/cm^3
Diffusivity (D_{self})	2.30 × 10^{-5} cm^2/s

- Atomic and molecular properties from computational models are used to generate thermal neutron scattering cross-sections
- Cross-sections define reaction rates in materials and are needed to assess and inform design & utilization

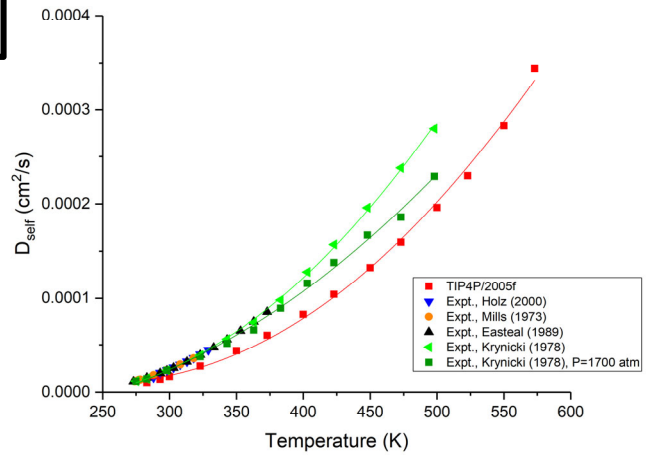
Molecular properties of H_2O: Current Scientific Understanding

Molecular geometry

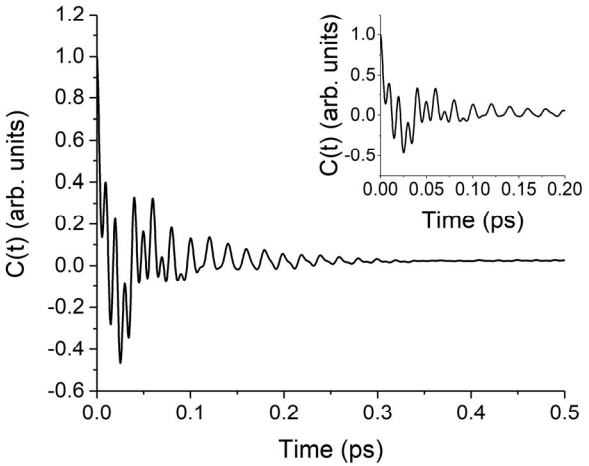


$r_{eq} \approx 0.94 - 1.0$ Å

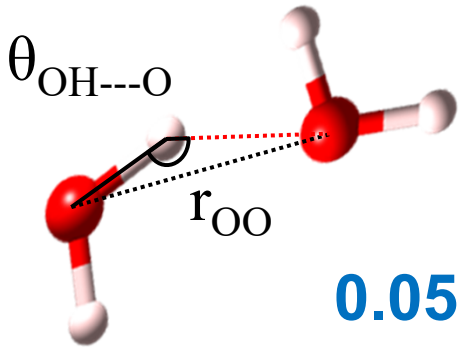
$\theta_{eq} \approx 100 - 110^\circ$



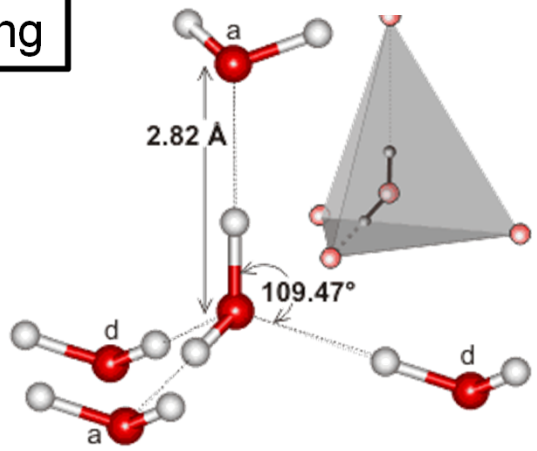
Dynamical properties



Hydrogen bonding



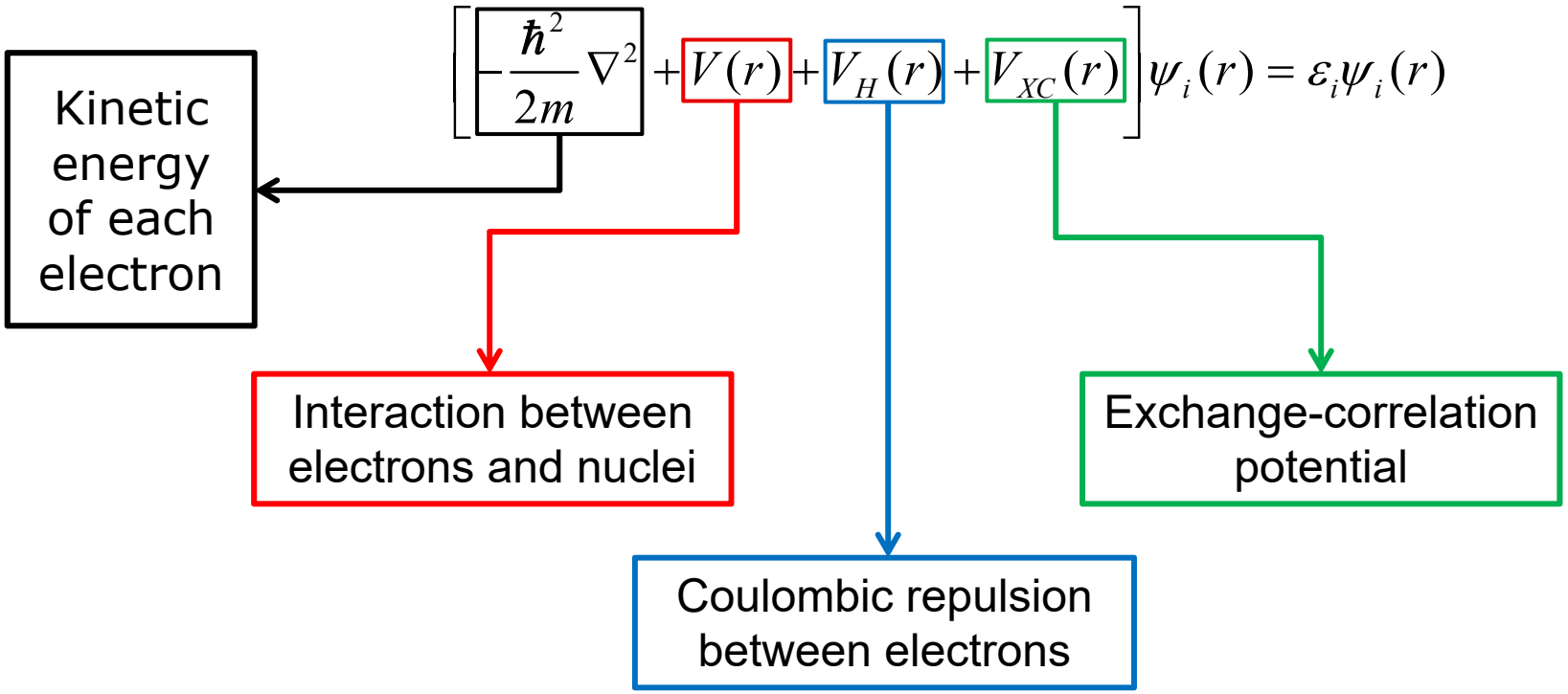
0.05 - 0.2 eV



Tetrahedral H-bonds in hexagonal ice (ice-Ih)

Density Functional Theory (DFT)

Finding the right electron density can be expressed in a way that involves solving a set of single electron Schrodinger equations:



All ***V*** terms are analogous to a classical interatomic potential energy

Pseudopotentials in DFT

- Core electrons not necessarily important in defining chemical bonding and other physical characteristics – these properties are dominated by less tightly bound valence electrons

- Pseudopotentials reduce the computational burden of computing wave functions of the core electrons
  - Frozen core approximation

DFT-MD approach for liquid H_2O

- Vienna *Ab initio* Software Package (VASP)

- Initial models use PBE functional
- Physically correct starting structure is necessary for accurate and well-converged DFT calculations
- 32 H_2O molecules (96 atoms)
- 9.8Å × 9.8Å × 9.8Å simulation cell
- Timestep = 0.5 fs
- NVT ensemble
- Revised PBE with ***dispersion corrections*** (rPBE+D3)

Dispersion corrections in DFT

- Empirical corrections
- Implemented to capture van der Waals (**long-range**) forces that are not included in exchange-repulsion and electrostatic interactions

$$E_{MF-D} = E_{MF} + E_{disp}$$

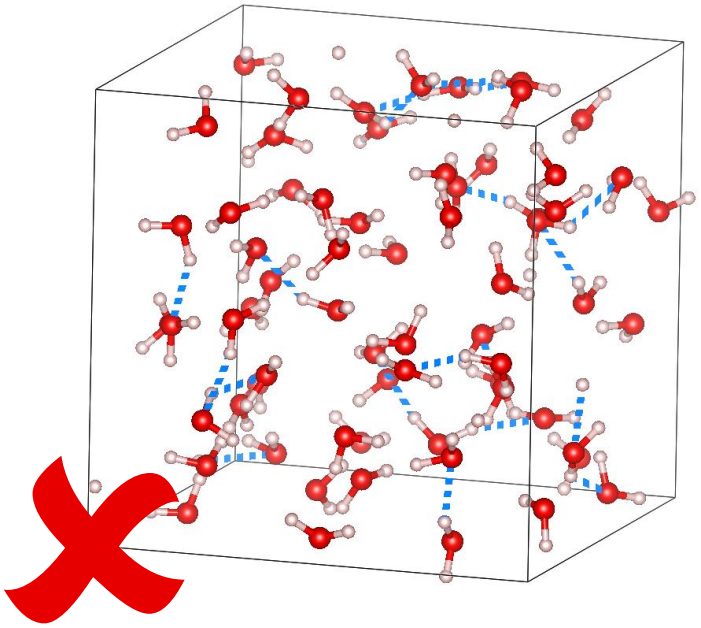
$$E_{disp} = -s_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} \left[\frac{1}{1+e^{-\alpha(R_{ij}/R_0-1)}} \right] (R_{ij})$$

$$C_6^{ij} = 2\frac{C_6^i C_6^j}{C_6^i + C_6^j}$$

Grimme, Stefan, *Journal of computational chemistry* (2004): 1463-1473.

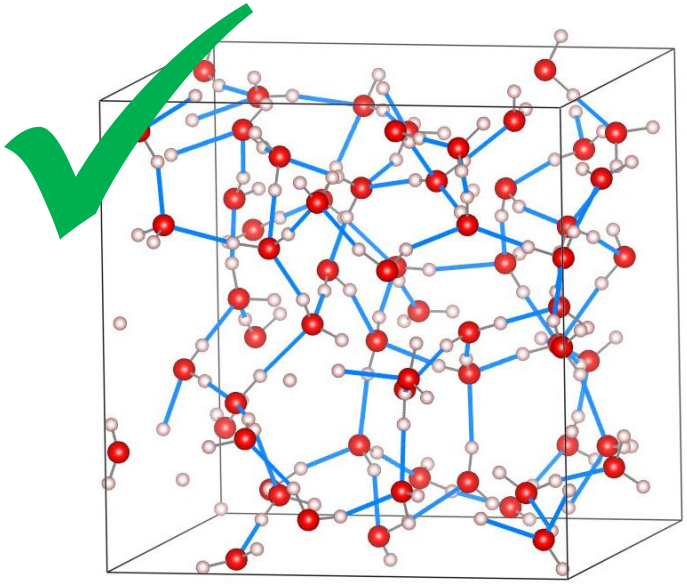
Liquid H_2O Structure Generation

Structure built using "Amorphous Builder" module in MedeA ©



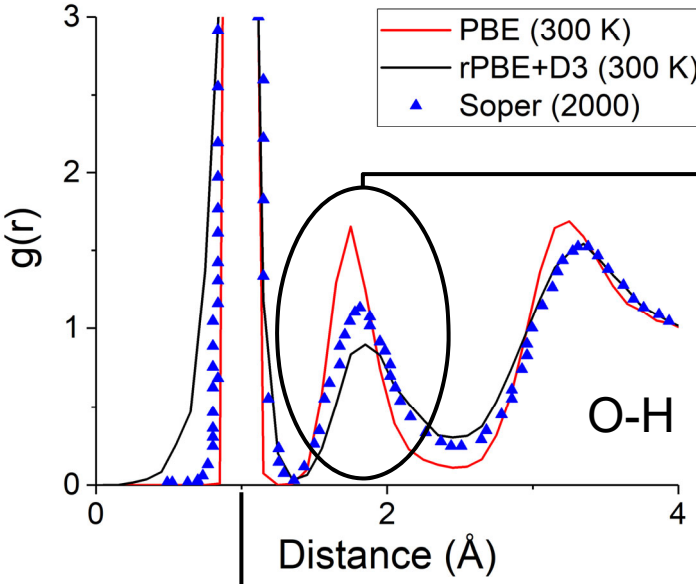
Too few H-bonds per molecule

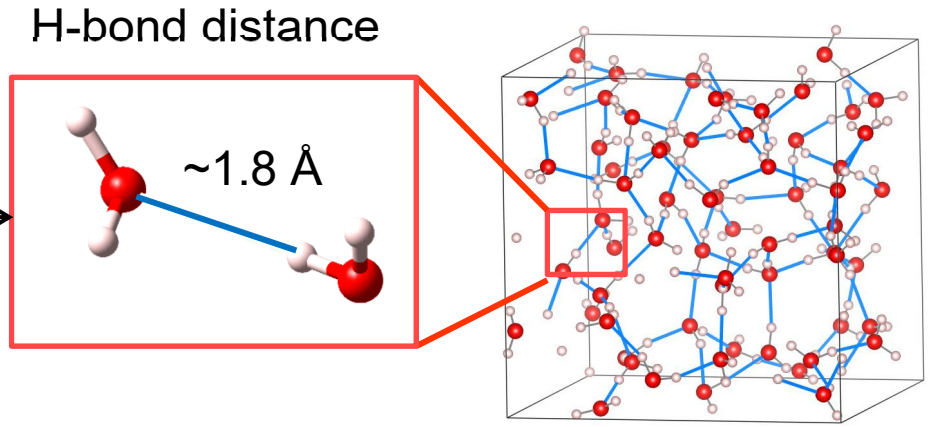
3-4 H-bonds per molecule

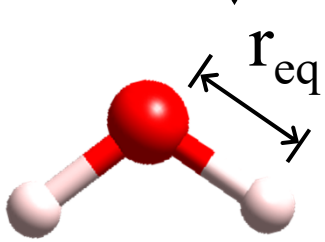


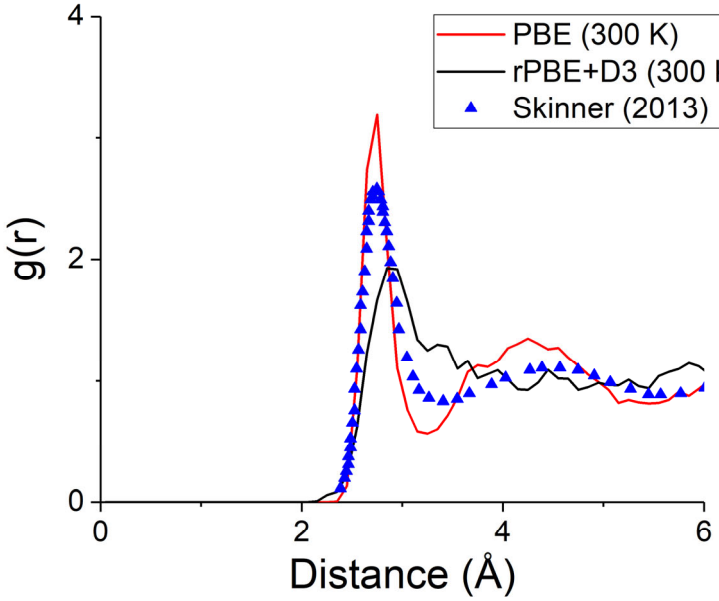
Structure generated from TIP4P classical MD simulation

Structural information from radial distribution functions

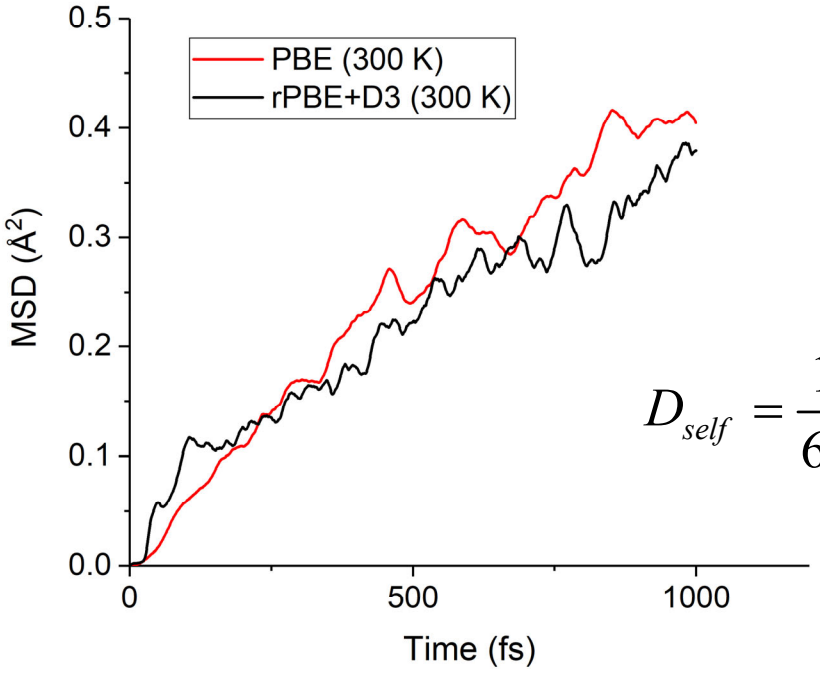








Dynamical properties of liquid H_2O predicted by DFT-MD



$$D_{self} = \frac{1}{6t} \lim_{t \to \infty} \left\langle \left| r_i(t) - r_i(0) \right| \right\rangle^2$$

	D_{self} (Å²/ps)	D_{self} (cm²/s)
Experiment	0.230	2.30×10^{-5}
PBE	0.053	0.53×10^{-5}
rPBE + D3	0.055	0.55×10^{-5}

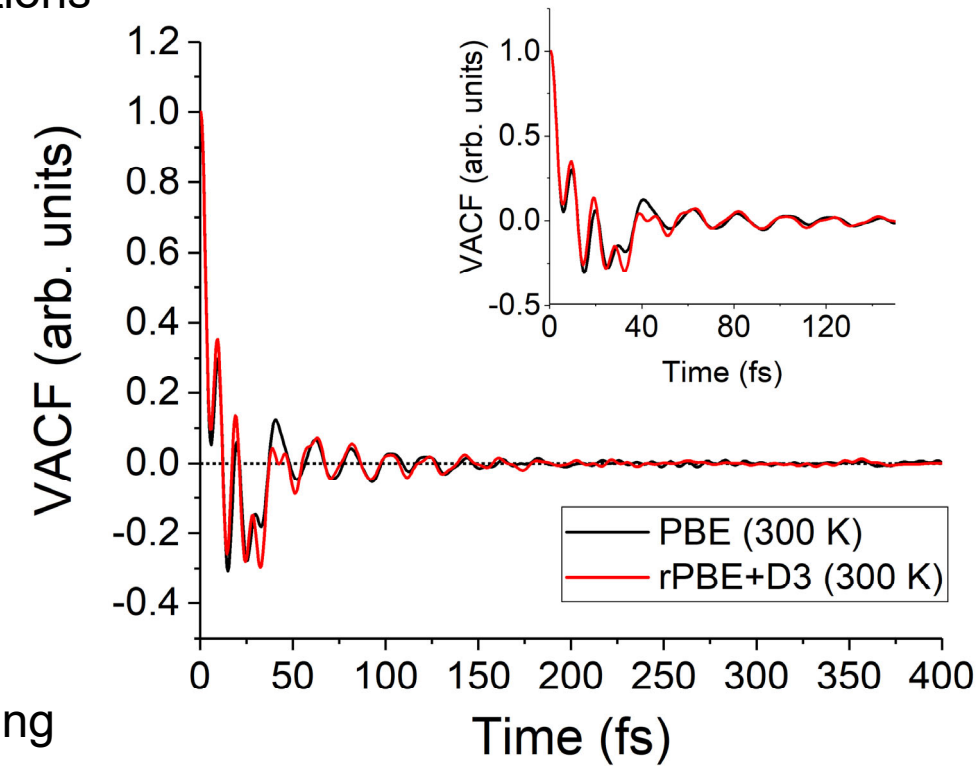
Velocity autocorrelation function

- Calculated from atomic trajectories generated using DFT-MD simulations

Atomic velocity at time origin

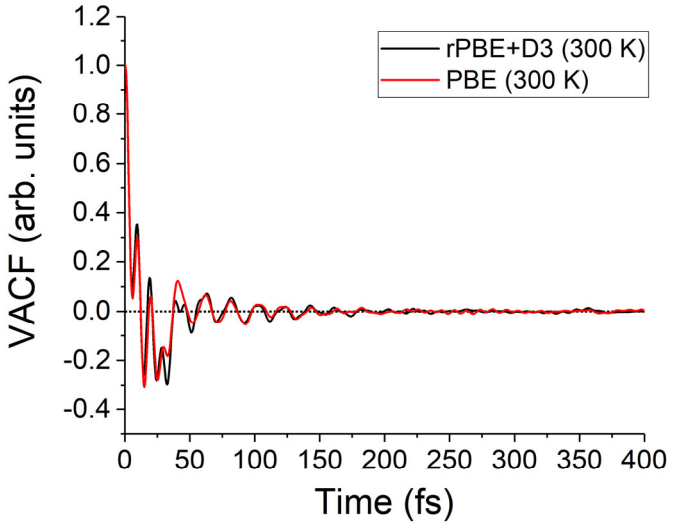
$$C(t) = \frac{\langle v(0)v(t)\rangle}{\langle v(0)^2\rangle}$$

"VACF"



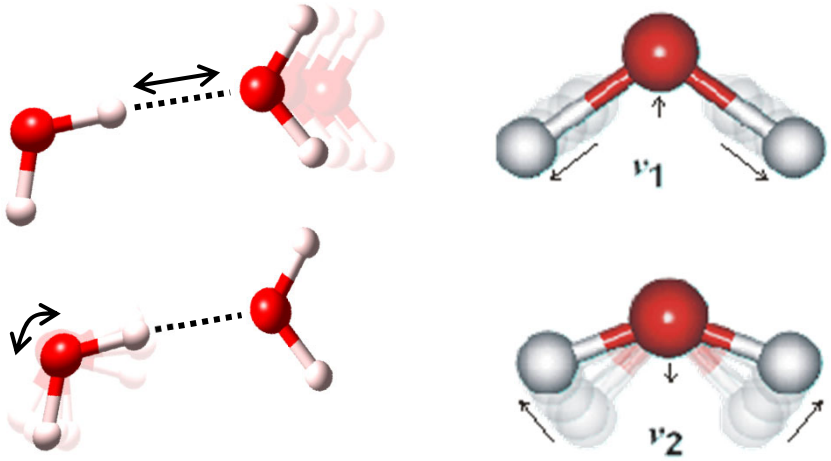
- Better sampling achieved by using multiple time origins

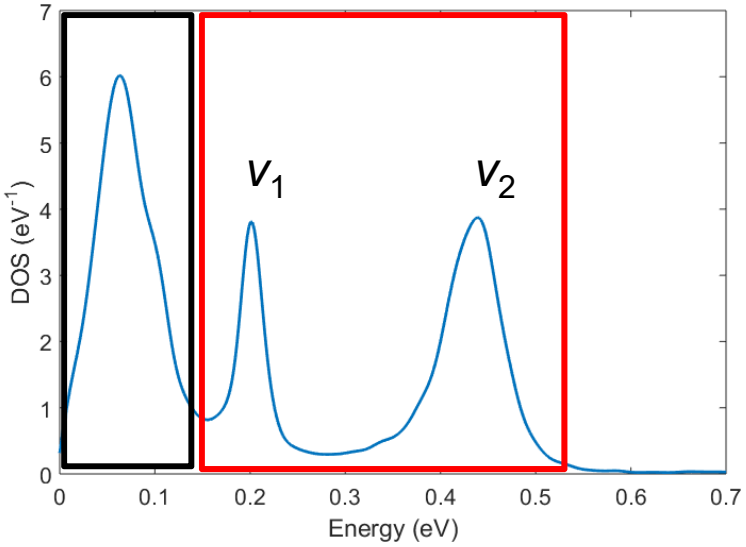
Vibrational Spectrum from VACF



$$\rho_t(\omega) = \int_0^\infty \exp(-i\omega t) C(t) dt$$

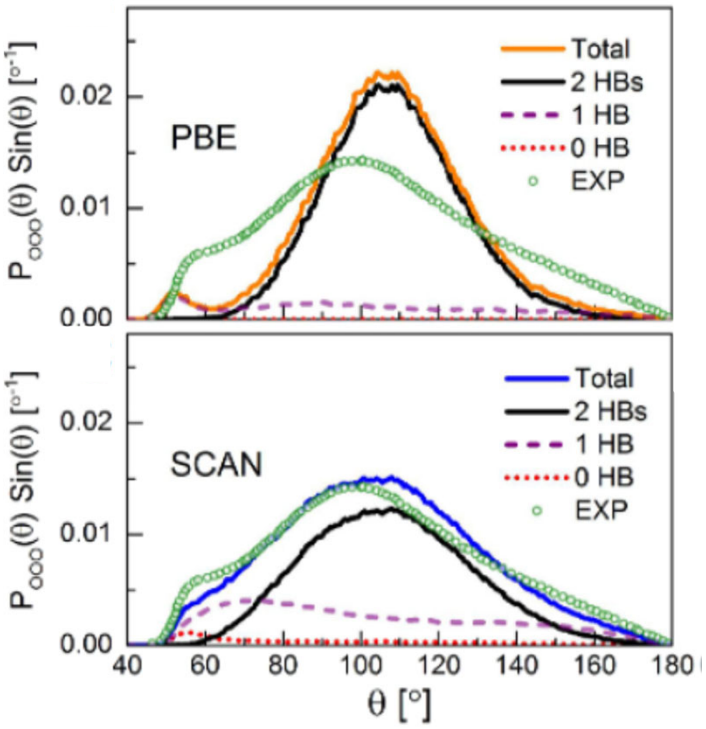
Fourier transform of VACF





Improved functionals show promise for new liquid H_2O models

- SCAN functional (Temple U.)
- Computationally more expensive
- Not currently supported by the GPU version of VASP



	D_{self} (Å^2/ps)	D_{self} (cm^2/s)
Experiment	0.230	2.30×10^{-5}
PBE	0.053	0.53×10^{-5}
SCAN	0.190	1.90×10^{-5}

M. Chen et al., *PNAS*, (2017)

Summary

- Accurate cross-sections are needed to inform nuclear criticality safety analysis
- Molecular modeling techniques are used to generate VDOS which is the input to thermal neutron scattering cross-section calculations
- AIMD techniques explored for H_2O simulations
  - Aim is to avoid empirical or semi-empirical potentials that can be tedious to use
- Further development to optimize computational implementation will allow new AIMD simulations to be used in generation of thermal scattering law (TSL) libraries for H_2O and other materials in the future

Acknowledgements

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- Naval Nuclear Propulsion Program (NNPP)