

Ab Initio Path Integral Molecular Dynamics Study of Liquid Water via van der Waals Inclusive Hybrid Density Functional Theory

Robert A. DiStasio Jr.¹, Biswajit Santra¹, Michele Ceriotti², and Roberto Car¹

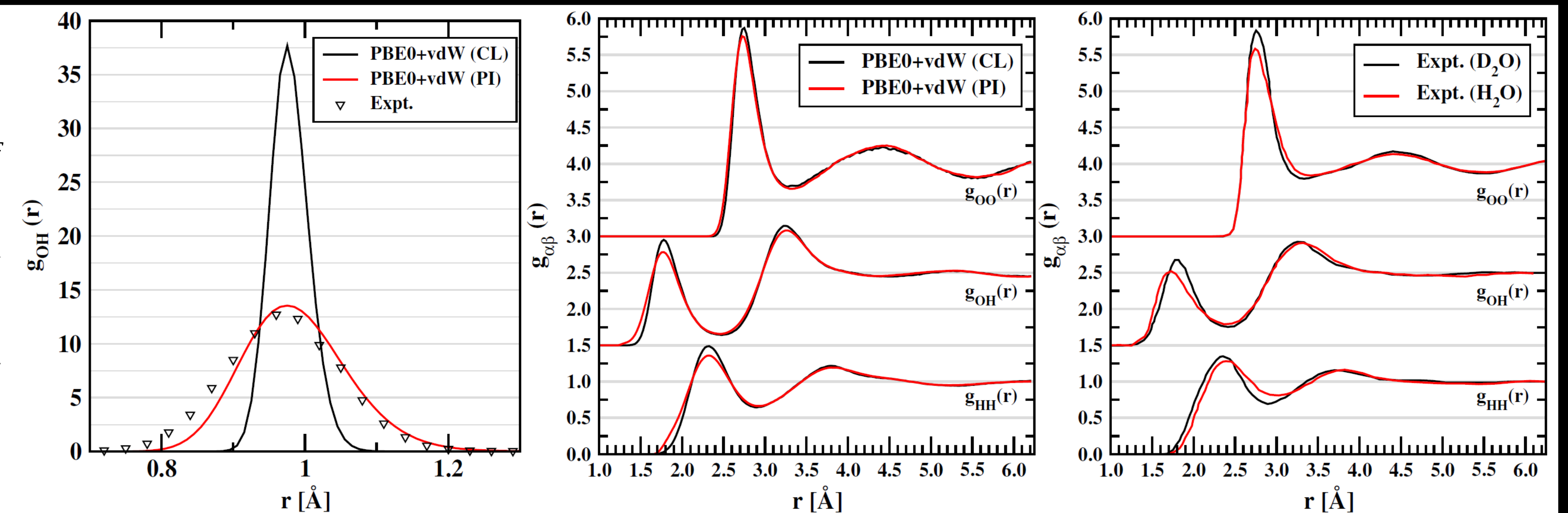
¹Department of Chemistry, Princeton University, Princeton, NJ. ²Laboratory of Computational Science and Modeling, EPFL, Lausanne, Switzerland.

PROJECT SCOPE

- To develop a theoretical and algorithmic framework for accurate modeling of the microscopic structure and dynamics of water and aqueous solutions, using density functional theory (DFT) based *ab initio* molecular dynamics (AIMD).
- Liquid water generated using classical AIMD and the generalized gradient approximation (GGA) is substantially overstructured with respect to experiment—due to the limitations of the underlying exchange-correlation (XC) potential and the use of classical nuclei.
- To address these limitations, we have utilized improved XC functionals that reduce self-interaction error via exact exchange (Exx) and account for non-local van der Waals/dispersion (vdW) interactions in conjunction with the Feynman discretized path integral (PI) approach to capture nuclear quantum effects (NQE).

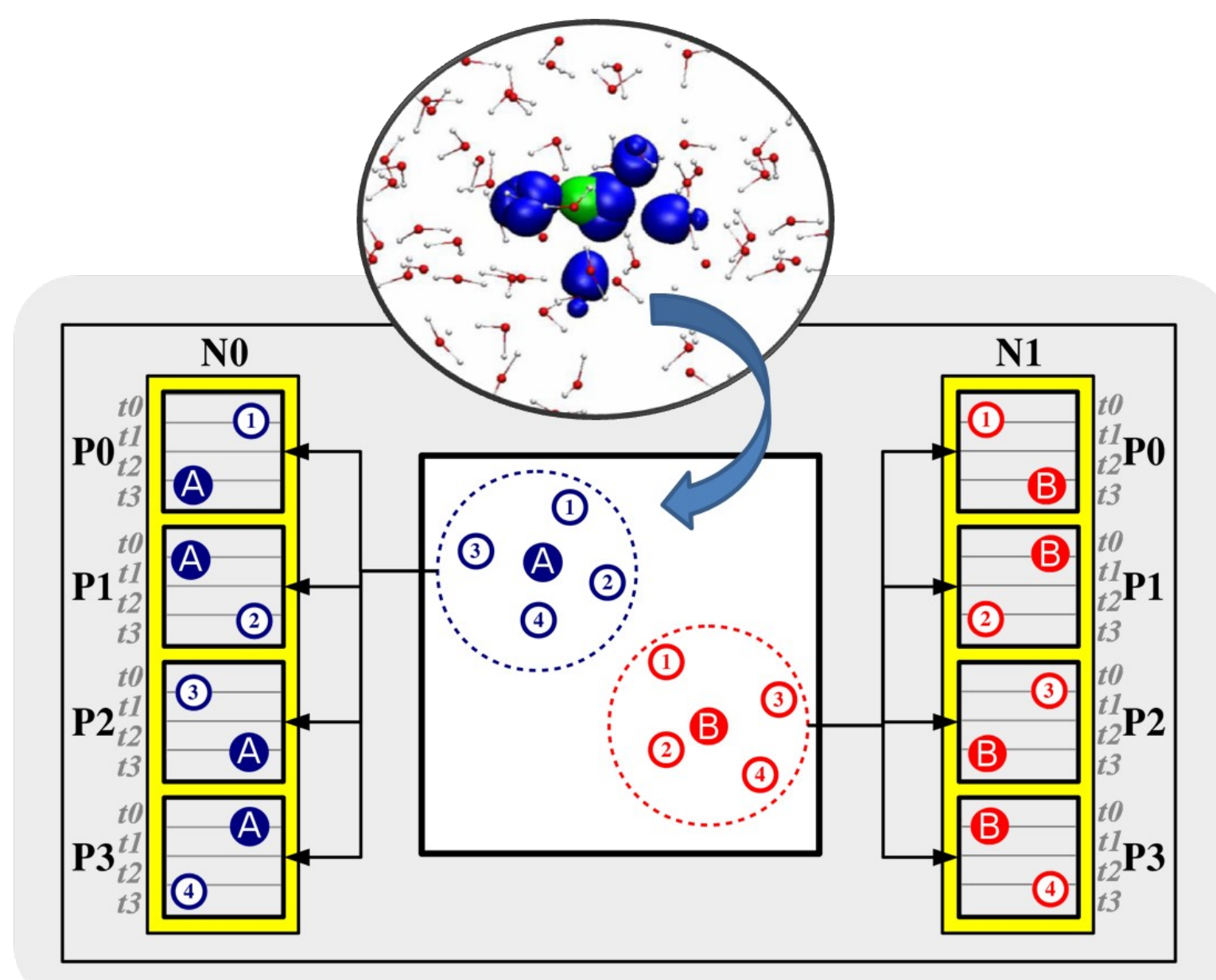
AMBIENT LIQUID WATER: A PI-AIMD STUDY

Plots of the oxygen-oxygen, $g_{OO}(r)$, oxygen-hydrogen, $g_{OH}(r)$, and hydrogen-hydrogen, $g_{HH}(r)$, radial distribution functions of liquid water obtained from theory (via classical (CL) and path integral (PI) AIMD simulations at the PBE0+vdW level at 330 K) and experiment (via empirical potential structure refinement based on joint X-ray/neutron scattering data at 298 K) [7].



THEORETICAL AND ALGORITHMIC DEVELOPMENTS

Linear Scaling Exact Exchange



Schematic of the MPI-OpenMP algorithm used to compute the Exx energy in hybrid DFT calculations. This algorithm was implemented in the open-source Quantum ESPRESSO (QE) [1] software package.

- For each overlapping pair of maximally localized Wannier functions [2], the Exx potential is efficiently obtained via solution of the Poisson equation in real-space with order(N) computational effort [3].
- Enables large-scale hybrid DFT calculations to utilize 10-100K processors on the BG/Q (Mira) super-computer architecture with a computational cost only 2-3 times more expensive than GGA-DFT.

BOMD via Damped Dynamics

EXTRAPOLATION

$$\tilde{\psi}(t + \Delta t) = 2\psi(t) - \psi(t - \Delta t) + \left(\frac{\Delta t^2}{\mu_{BO}}\right) F_{\psi}(t)$$

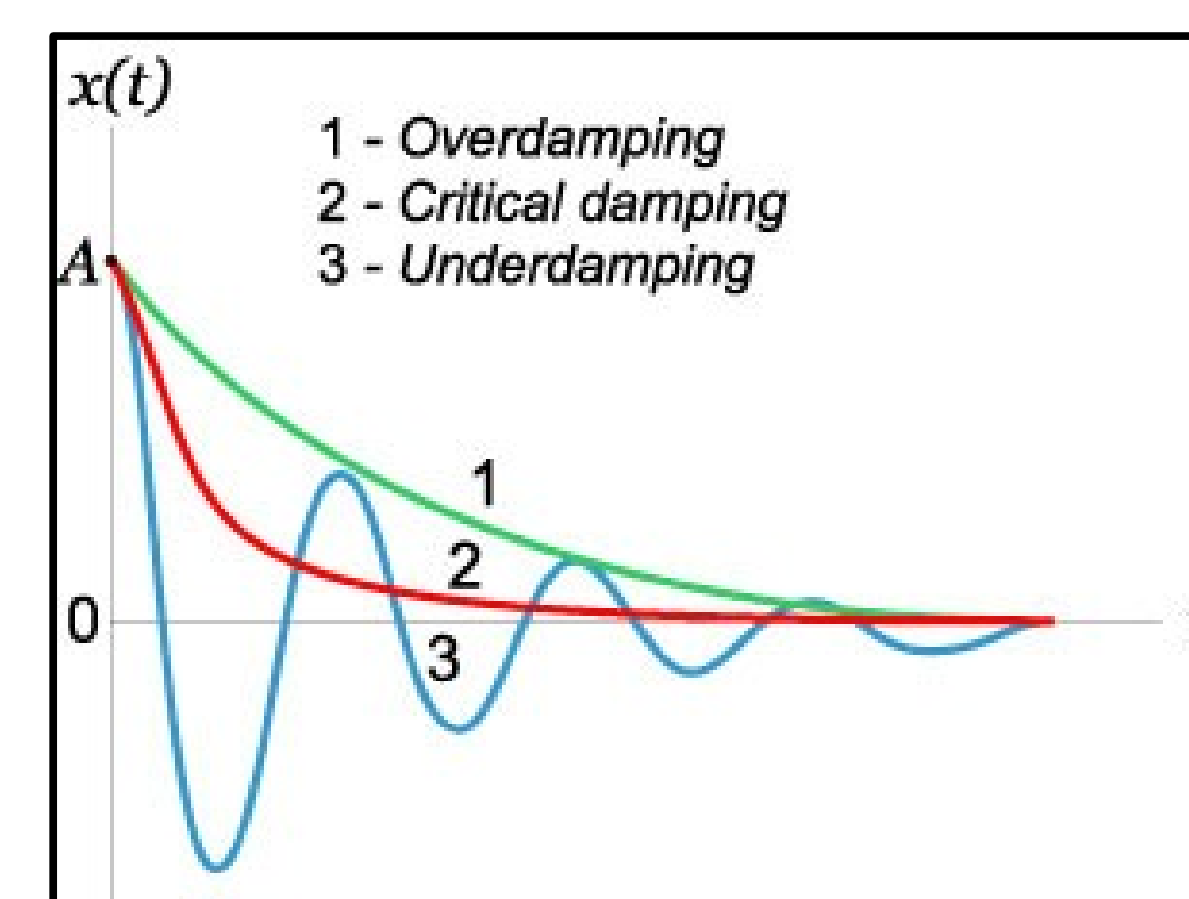
BO time scale

MINIMIZATION

$$\phi(\tau + \Delta\tau) = \left(\frac{1}{1 + \gamma}\right) \left(2\phi(\tau) - (1 - \gamma)\phi(\tau - \Delta\tau) + \left(\frac{\Delta\tau^2}{\mu}\right) F_{\phi}(\tau)\right)$$

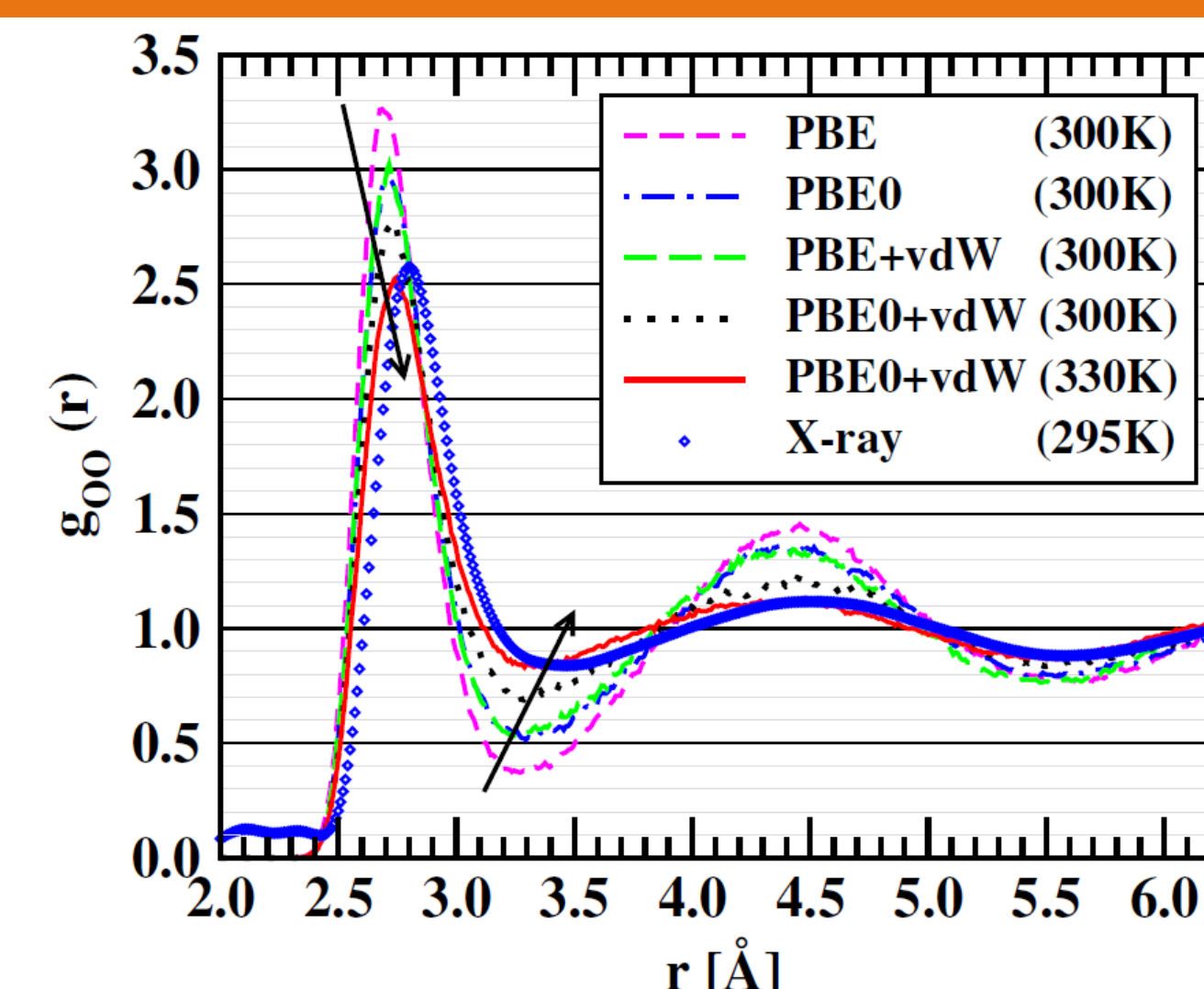
Damping parameter

CP time scale

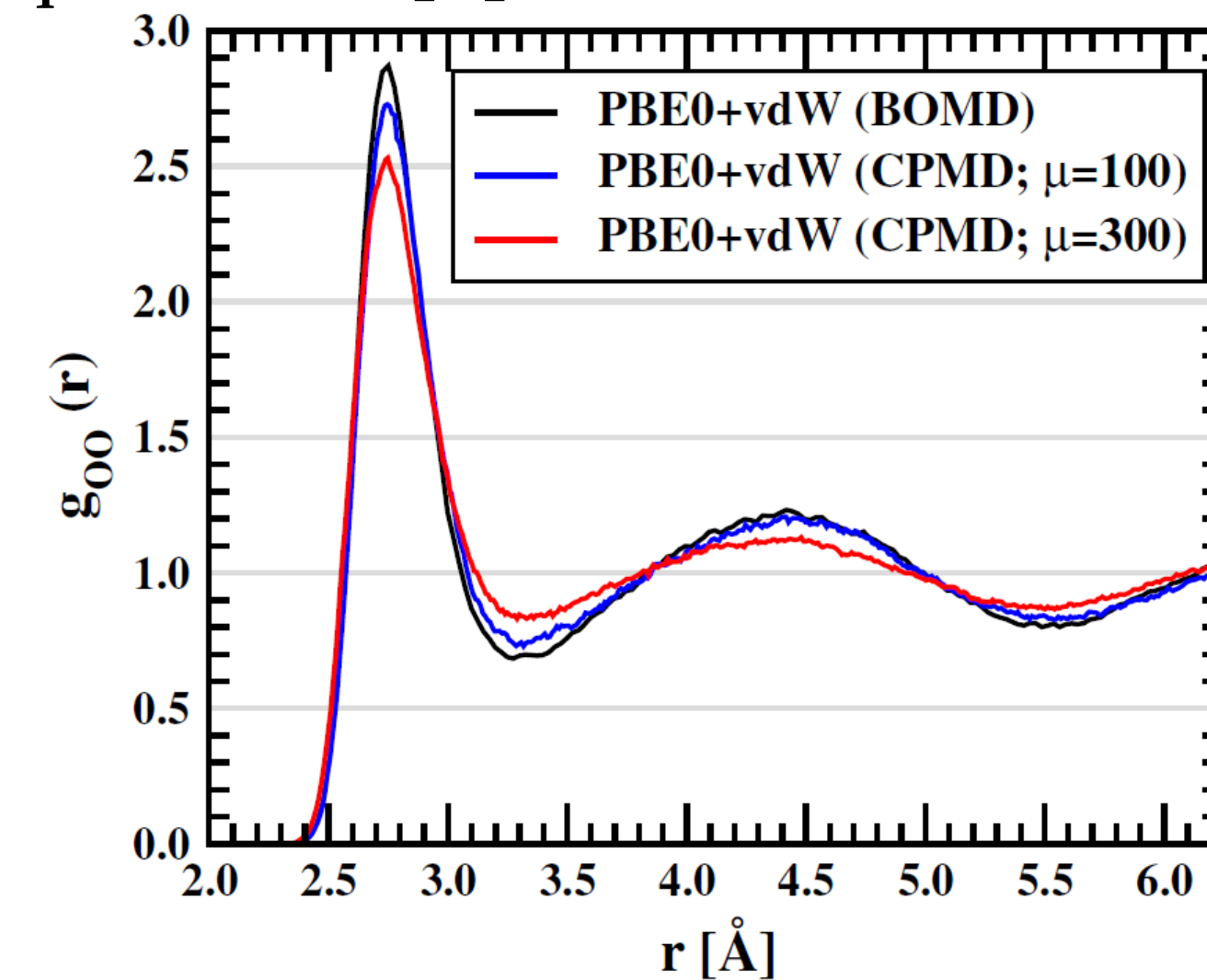


- Born-Oppenheimer (BOMD) simulations require minimization of the electronic wavefunctions at each step—the need for localized orbitals to evaluate Exx makes diagonalization approaches prohibitive.
- Second-order damped dynamics can be used to perform the electron minimization, resulting in a robust and computationally competitive Car-Parrinello [4] approach to BOMD.

vdW Inclusive Hybrids



- The collective inclusion of Exx and vdW [5] in the underlying XC potential is essential for increasing the fluidity and reducing the overstructuring in GGA-DFT liquid water [6].



- We have observed that the typical fictitious mass ($\mu \approx 300$) values used in CPMD simulations of liquid water yield a less structured $g_{OO}(r)$ with respect to fully converged BOMD.

- PI-AIMD simulations [8] at the PBE0+vdW level are capturing the main experimental isotope effects in the $g_{OO}(r)$, $g_{OH}(r)$, and $g_{HH}(r)$ and the zero-point effects in the covalent O-H bond.

- However, slight disagreement still remains between PI-AIMD PBE0+vdW simulations at 330K and experiment at 298K that cannot be attributed to the difference in temperature.

- It is likely that these discrepancies originate from the remaining deficiencies in the XC potential.

FUTURE WORK

- Performing PI-AIMD simulations in the isobaric-isothermal (NpT) ensemble to investigate the anomalous density difference between liquid water and crystalline ice at the PBE0+vdW level.
- We will also seek to improve the underlying XC potential (by further reducing the self-interaction error and increasing the level of electron correlation) with the goal of providing a benchmark microscopic description of the structure of liquid water and aqueous solutions.

[1] P. Giannozzi et al., *J. Phys.: Condens. Matter* **21**, 395502 (2009). [2] N. Marzari and D. Vanderbilt, *Phys. Rev. B* **56**, 12847 (1997). [3] X. Wu, A. Selloni, and R. Car, *Phys. Rev. B* **79**, 085102 (2009). [4] R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985). [5] A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.* **102**, 073005 (2009). [6] R. A. DiStasio Jr., B. Santra, Z. Li, X. Wu, and R. Car, *J. Chem. Phys.* (accepted). [7] A. K. Soper and C. J. Benmore, *Phys. Rev. Lett.* **101**, 065502 (2008); A. K. Soper, *Chem. Phys.* **258**, 121 (2000). [8] M. Ceriotti, D. Manolopoulos, and M. Parrinello, *J. Chem. Phys.* **134**, 084104 (2011); M. Ceriotti and D. Manolopoulos, *Phys. Rev. Lett.* **109**, 100604 (2012); M. Ceriotti, J. More, and D. Manolopoulos, *Comput. Phys. Commun.* **185**, 1019 (2014).

