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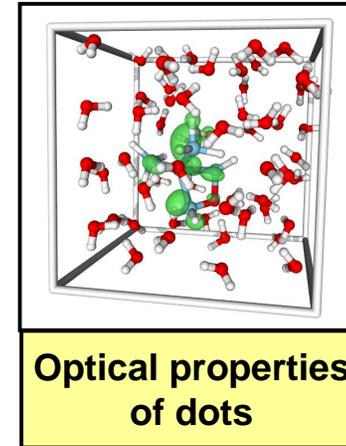
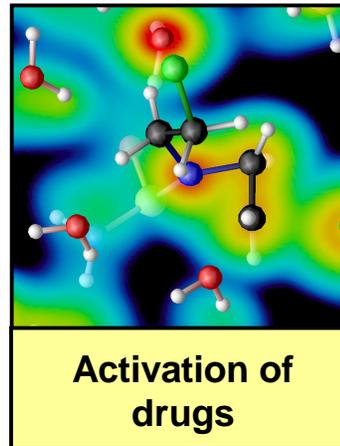
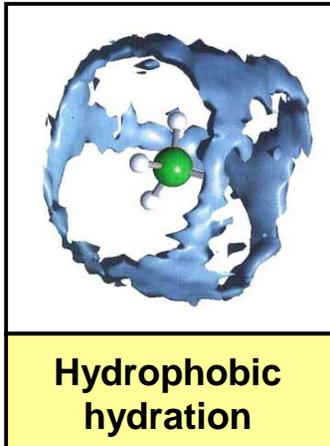
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Accuracy of density functional theory for first- principles simulations of water

**Eric Schwegler, Jeffrey C. Grossman, Erik W. Draeger,
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Liquid water: Accurate simulations at ambient conditions are challenging



We are addressing two questions:

- Can we accurately simulate the structural and dynamical properties of water from first principles using Density Functional Theory ?
- What is the “role” of proton quantum effects?

We have used classical and *ab-initio* MD simulations of water to address various technical issues



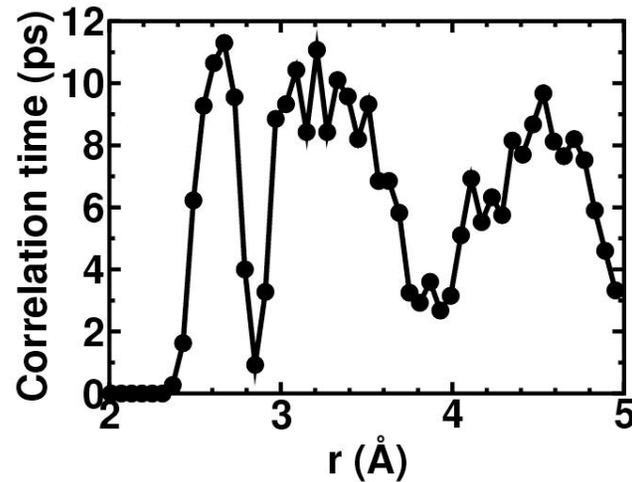
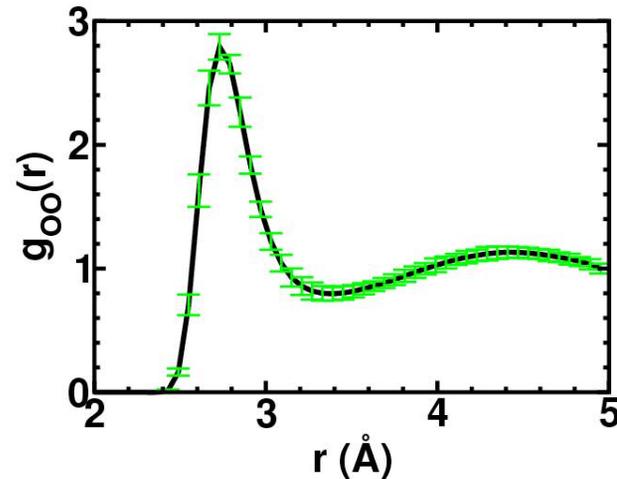
Goal: Assess the impact of approximations involved in *ab initio* molecular dynamics simulations of water by systematically varying technical simulation parameters

- **Timescales needed to accurately determine structural and dynamical properties:**
 - Correlation times determined from long classical simulations
- **Impact of finite system sizes:**
 - 32, 54, 64 and 512 water molecule cells
- **Choice of exchange-correlation potentials:**
 - PBE versus BLYP (the most widely used gradient corrected functionals)
- ***Ab-initio* molecular dynamics scheme:**
 - Car-Parrinello versus Born-Oppenheimer dynamics

How long do we need to simulate to converge structural and dynamical properties?



- We have used 2 ns simulations with well-tested **classical** potentials to examine convergence as a function of simulation time
- Data correlation times of radial distribution function bins found to be as long as 10 ps



Meaningful comparisons between different simulations and with experiment requires at least 10 ps simulations

***Ab-initio* MD simulations (CP and BO) have been carried out in the micro-canonical ensemble**



- **Norm conserving pseudopotentials:**

- Hamann (1989) pseudopotential and Hamann (1989) with Vanderbilt's smoothing scheme (1984) for hydrogen; Giannozzi's pseudopotential for hydrogen
- Hamann (1989) for oxygen with (s,p) and (s,p,d) non locality
- $E_{\text{cut}} = 85 \text{ Ry}$

- **Integration time steps:**

- CP: 0.07 fs; BO: 0.24 fs

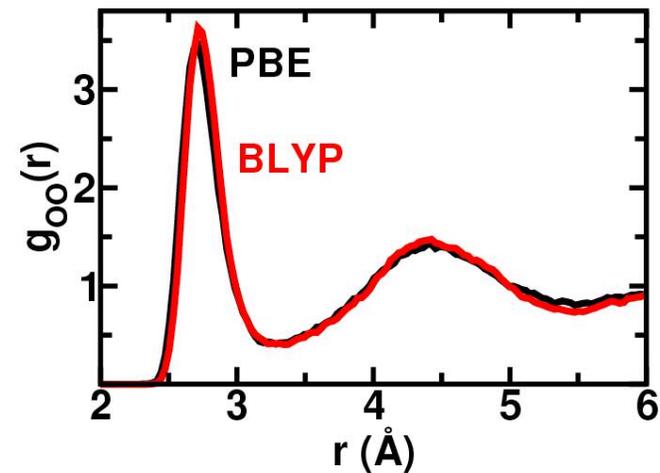
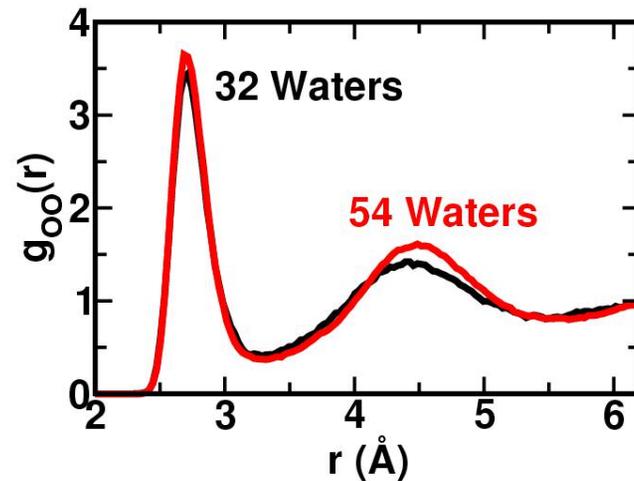
- **Simulation time (for time averages): 20 ps**

- **NVE ensemble:** no thermostats; achieving same T for oxygen and hydrogen requires accurate thermalization before collecting statistics

We have examined the impact of system size and the choice of exchange-correlation functionals

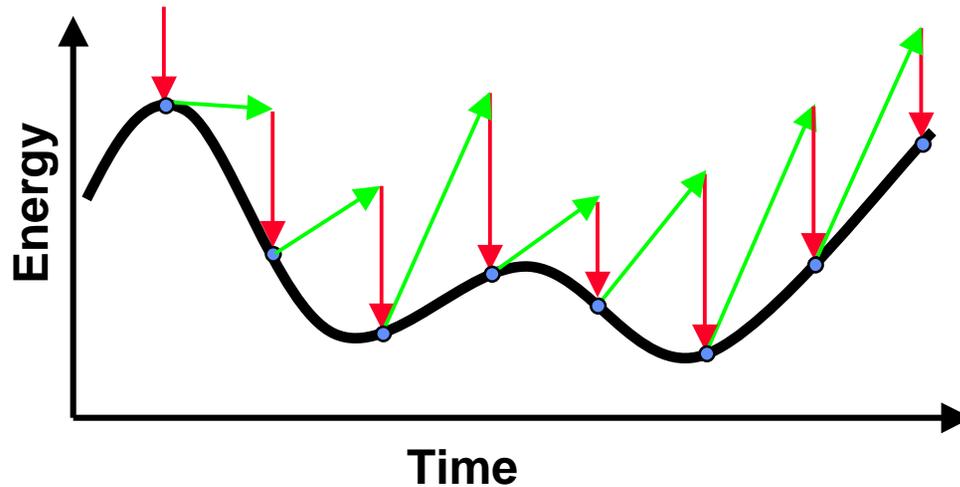


- Size effects:
 - small for structural properties (32 to 54 molecule simulations)
 - negligible on energies and forces (64 to 512 molecule snapshots)
- PBE and BLYP are two of the most accurate and widely used GGA density functionals
- With all other parameters fixed, the difference between PBE and BLYP is very small



Bin size for $g(r)$: 0.03 Å

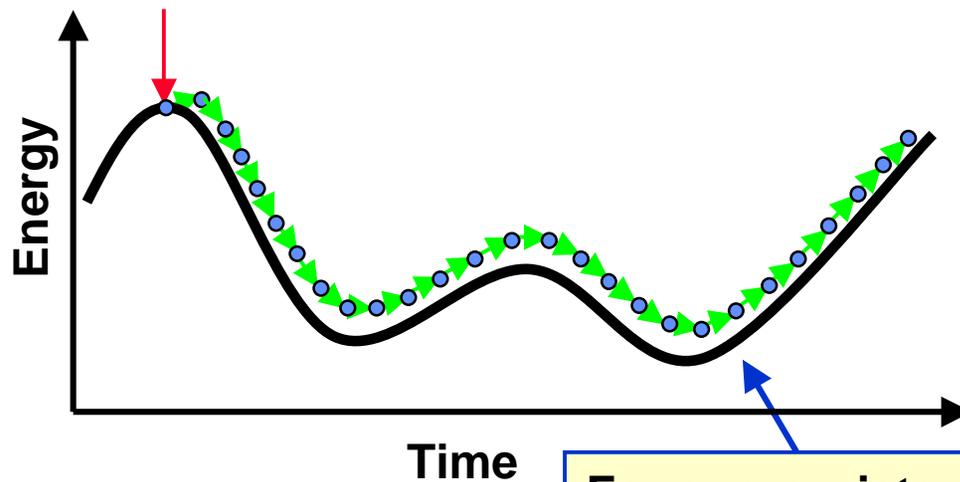
Technical details of *ab-initio* simulations



In Born-Oppenheimer (BO) dynamics, at each point on the trajectory:

$$\Phi = \min[E_{KS}]$$

$$M_I \ddot{R}_I = -\nabla_I \Phi$$



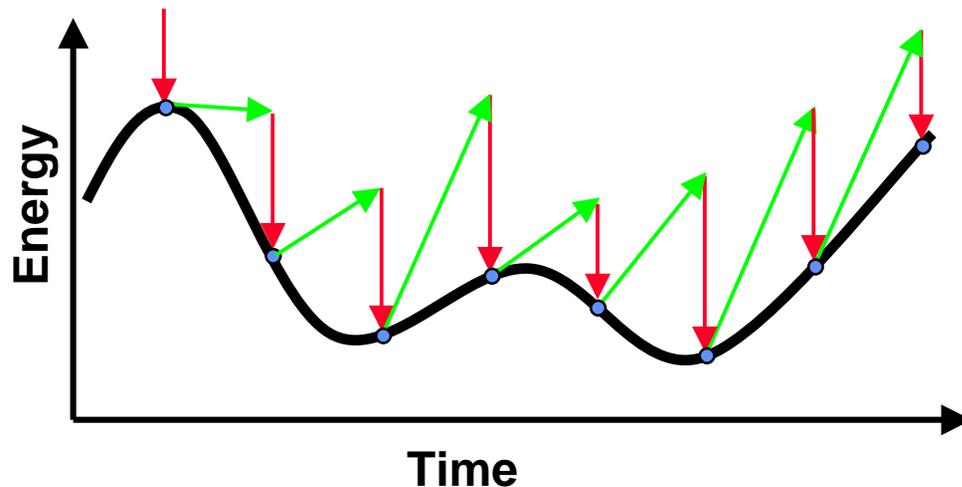
In Car-Parrinello dynamics:

$$\mu \ddot{\Psi}_i = -\frac{\partial E_{KS}[\Psi, R]}{\partial \Psi_i} - \sum \Lambda_{ij} \Psi_j$$

$$M_I \ddot{R}_I = -\frac{\partial E_{KS}[\Psi, R]}{\partial R_I}$$

For appropriate μ , electrons “stay close” to BO surface

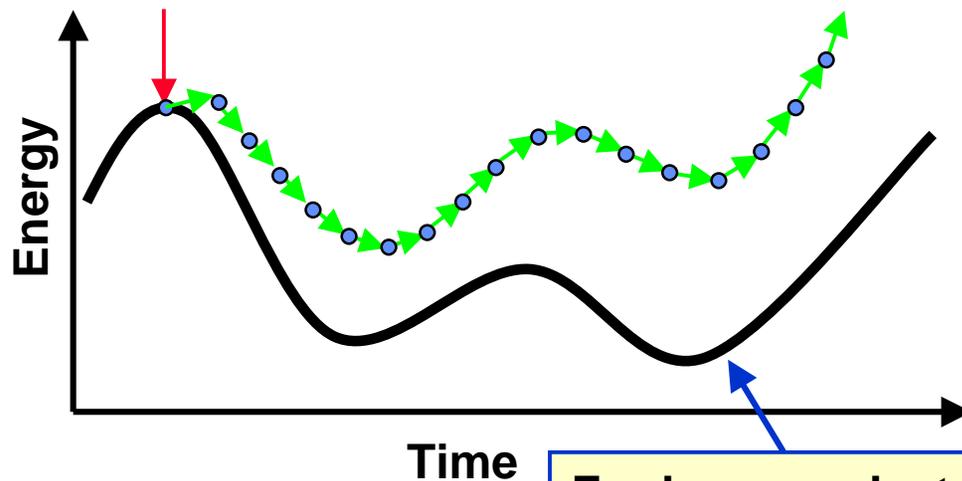
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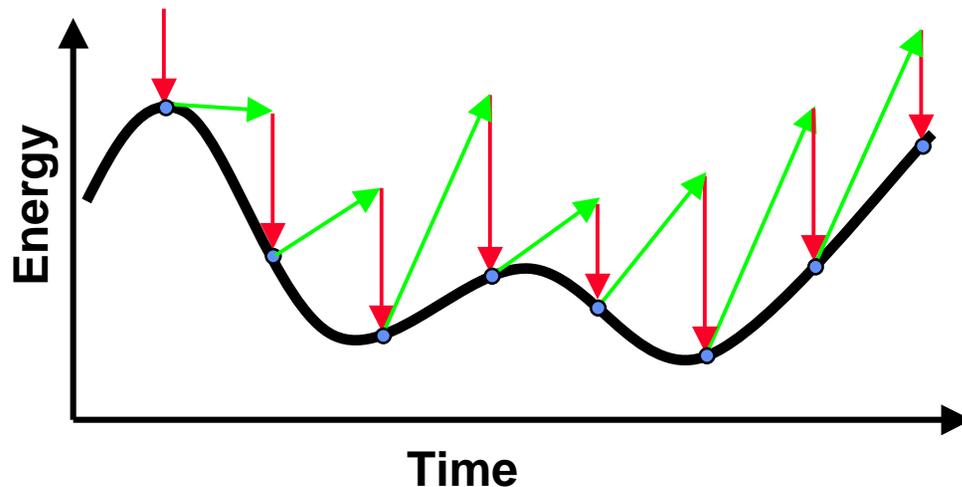
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For large μ , electrons can “drift away” from BO surface

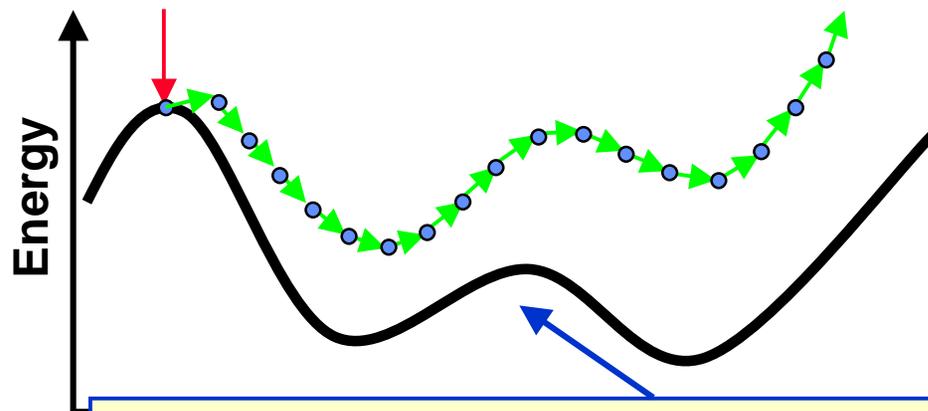
Technical details of *ab-initio* simulations



In Born-Oppenheimer (BO) dynamics, at each point on the trajectory:

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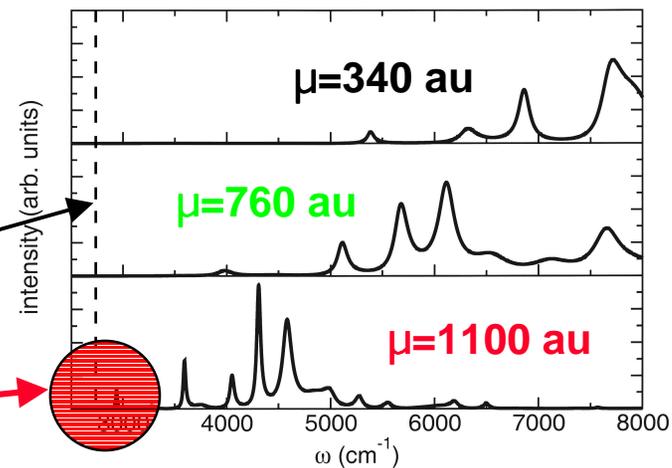
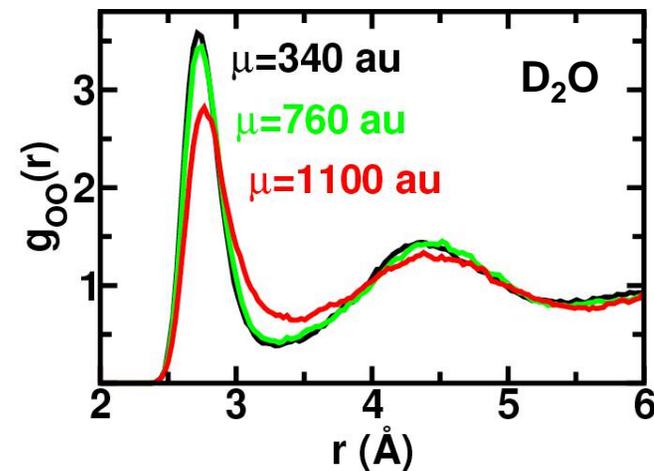
$$M_I \ddot{R}_I = -\frac{\partial E_{KS}[\Psi, R]}{\partial R_I}$$

What are the simulation conditions (choice of μ , integration time step, statistical ensemble) which insure adiabatic dynamics (i.e. accurate calculation of electronic structure at each MD step)?

Effect of the fictitious mass, μ , in simulations of D₂O



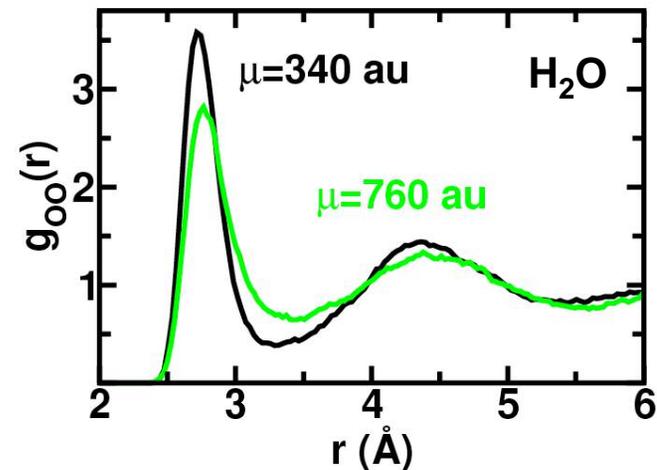
- Choosing different values of μ leads to the same thermodynamic averages, if $\mu / M \leq 1/5$ (M =Deuterium mass)
- Large values of μ result in a qualitatively different liquid structure
 - Differences can be seen in as little as 2-3 ps of simulation
- Power spectra for D₂O ionic and fictitious electronic degrees of freedom
- Highest O-D stretch mode
- For $\mu = 1100$ au, electronic and ionic modes begin to overlap



Effect of the fictitious mass, μ , in simulations of H₂O

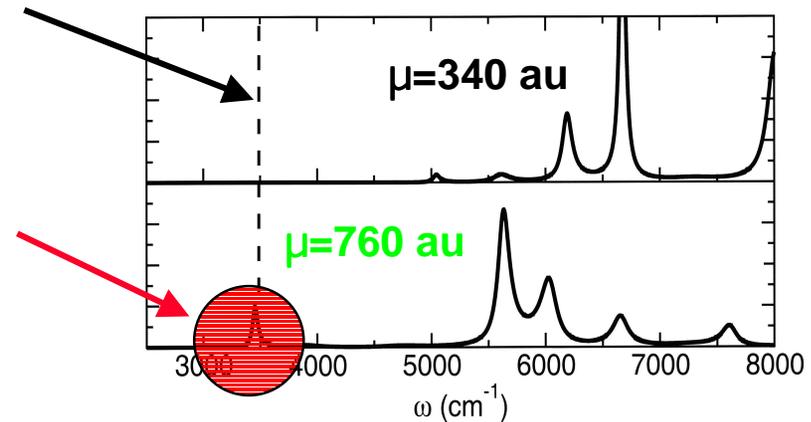


- For simulations of H₂O, the same softening in $g_{OO}(r)$ occurs when μ is too large



- O-H stretch mode is shifted to higher frequencies

- For $\mu = 760$ au, fictitious electronic and ionic modes begin to overlap

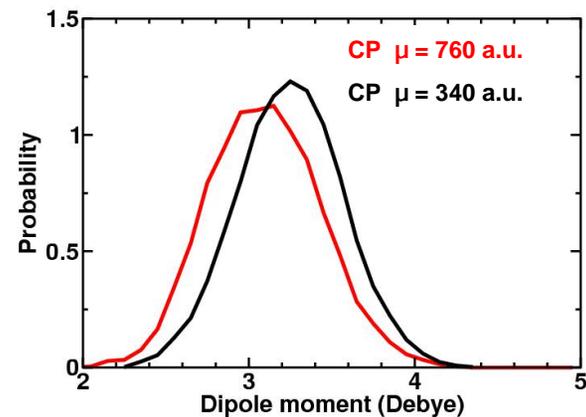


Dipole moments and diffusion coefficients



Dipole moments

- Our computed average values vary from 3.09 to 3.24 D when using different values of μ



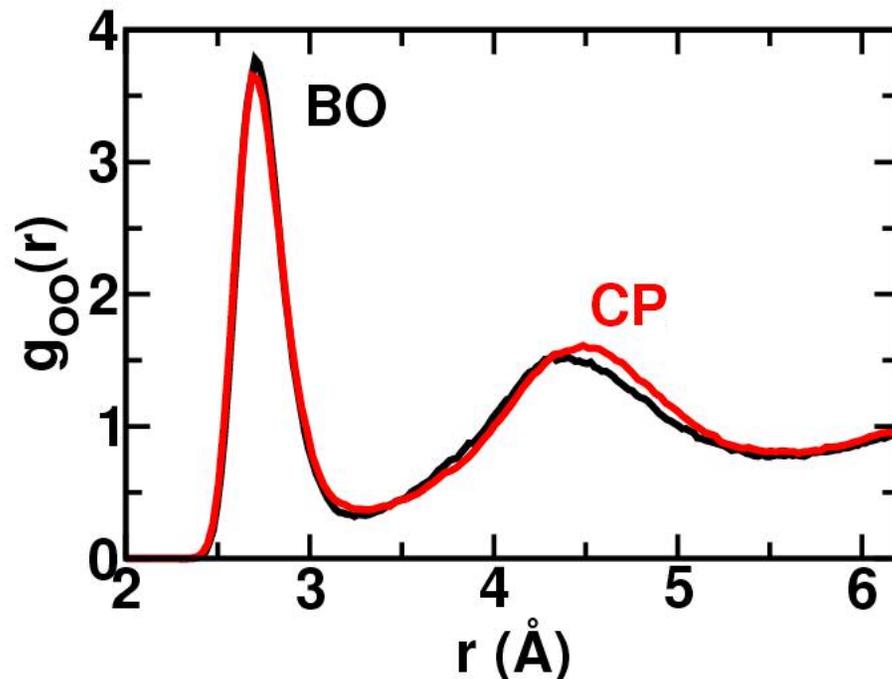
Diffusion coefficient

- Our computed values appear to vary by \sim one order of magnitude when using different values of μ

Comparison between Car-Parrinello and Born-Oppenheimer molecular dynamics



In order to fully understand the effect of the CP fictitious mass on computed properties, we have performed Born-Oppenheimer (BO) and Car-Parrinello (CP) simulations of 64 water molecules at 300 K (Qbox code, F. Gygi, LLNL 2003-2004)



- Good agreement between CP and BO dynamics if appropriate value of μ is used ($\mu/M \leq 1/5$)
- Note: choice of appropriate μ (to avoid overlap between ionic and fictitious electronic degrees of freedom) depends on phonon spectrum and electronic energy gap.

Our BO results are in agreement with L. Pratt, *et al.* PRE 6, 041505 (2003); results consistent with those of A. Pasquarello *et al.* Science 2002 and Marzari's group (2004)

Details of BO simulations



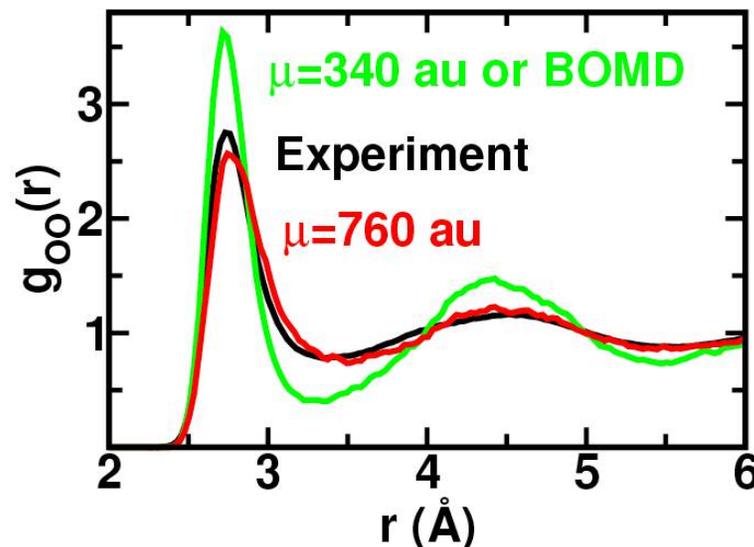
- Time step
 - 0.24 fs
 - 12 electronic iterations (Preconditioned Steepest Descent) /MD step
- Energy conservation:
 - 10^{-9} a.u. at each ionic step
 - Drift in total energy: 0.27 K/ps

Comparison with experiment



Radial distribution functions

- Experiments from neutron diffraction (A.K. Soper, 2000)
- Converged DFT simulations find a $g_{OO}(r)$ that is **overstructured** compared to experiment
- For large μ , $g_{OO}(r)$ is in **fortuitous** agreement with exp.



Diffusion coefficients

- For converged DFT simulations, $D \sim 10^{-6} \text{ cm}^2/\text{s}$
 - about 10-20 times slower than experiment
- For large μ , $D \sim 2 \times 10^{-5} \text{ cm}^2/\text{s}$

Why is there a discrepancy between theory and experiment?

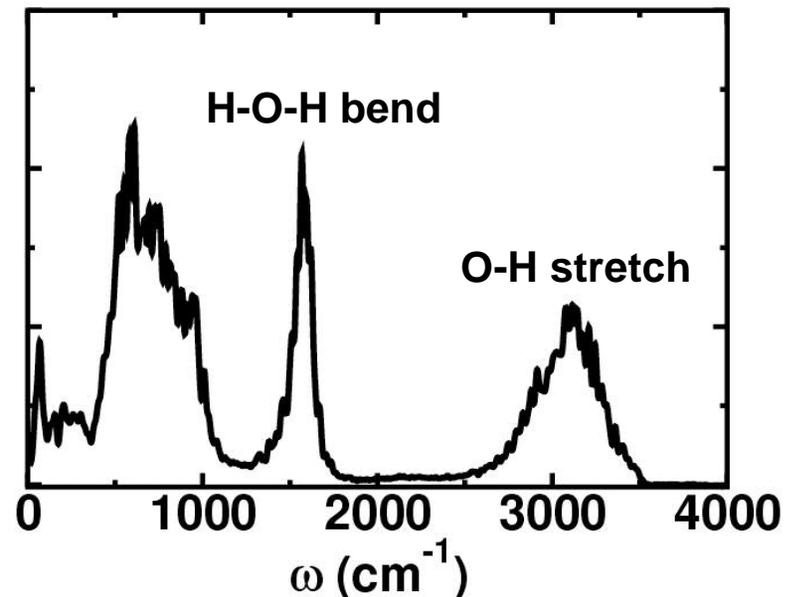
- Neglect of proton quantum effect?
- Accuracy of DFT/GGA functionals?

How important are proton quantum effects in water?



- O-H stretch and H-O-H bend are in the range of 1000 to 3500 cm^{-1}
- At a temperature of 300 K, $k_B T \sim 300 \text{ cm}^{-1}$

$$k_B T \ll (h/2\pi) \omega$$



- Intramolecular vibrations are dominated by proton quantum effects
- At $T=300 \text{ K}$, only the ground state is populated
- Quantum and classical models have very different energy distributions

Can proton quantum effects account for the large over-structure and slow diffusion observed in *ab-initio* MD?

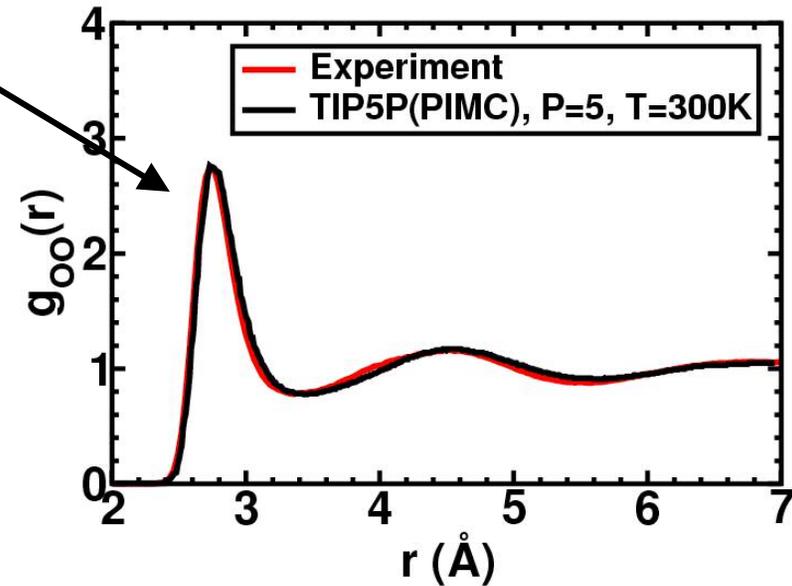
- Proton quantum effects can be directly accounted for with path integral sampling (PIMC)
- All path integral studies of water using empirical potentials have found that proton quantum effects decrease the structure of the liquid
- Consistent comparisons are difficult
 - The amount of softening in $g_{OO}(r)$ is different for each potential
 - Most empirical potentials already include quantum effects implicitly through parameterization
- Some notable exceptions:
 - TIP5P(PIMC) potential was parameterized to reproduce experimental data when used *with* path integral sampling*

*M.W. Mahoney and W.L. Jorgensen, J. Chem. Phys. 115, 10758 (2001)

Analysis of quantum effects using classical potentials



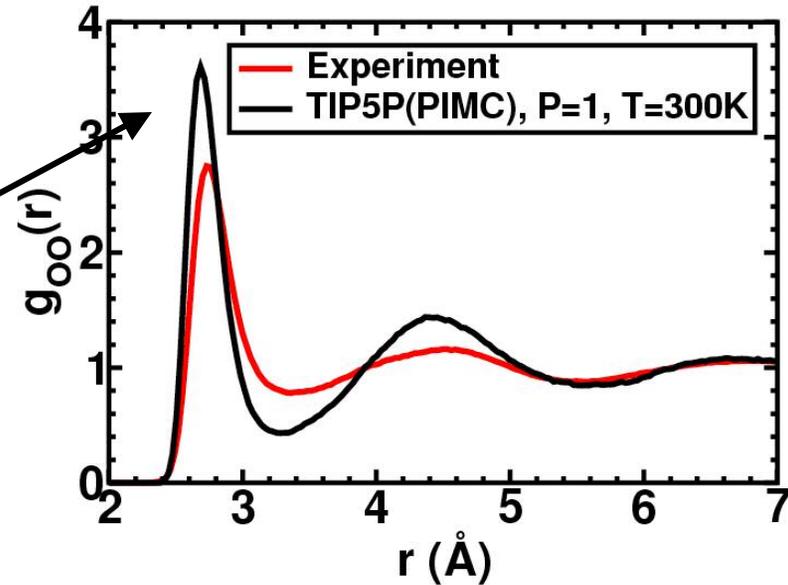
- The TIP5P(PIMC) is in excellent agreement with experiment at 300K **when** path integral sampling is used



Analysis of quantum effects using classical potentials



- The TIP5P(PIMC) is in excellent agreement with experiment at 300K **when** path integral sampling is used
- **Without** PI sampling TIP5P(PIMC) becomes overstructured at 300 K

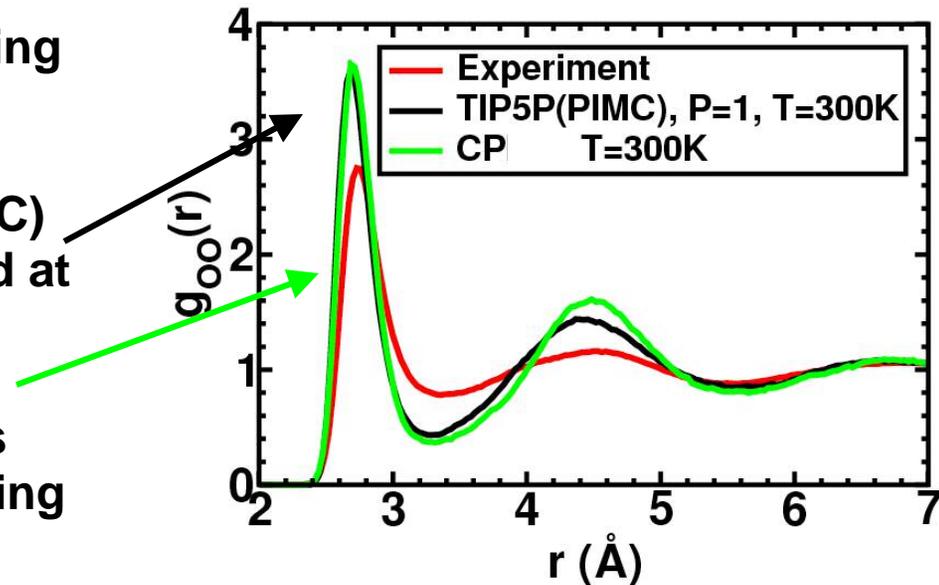


Diffusion ~10x slower than exp.

Analysis of quantum effects using classical potentials



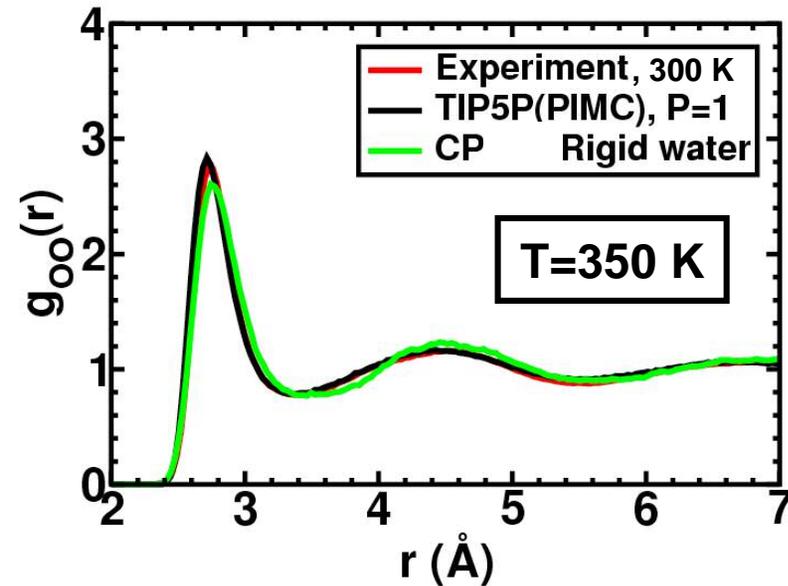
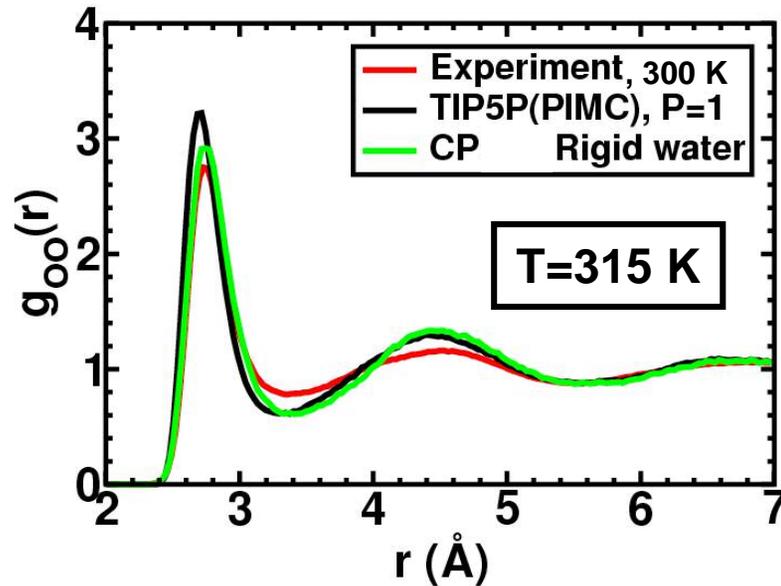
- The TIP5P(PIMC) is in excellent agreement with experiment at 300K **when** path integral sampling is used
- **Without** PI sampling TIP5P(PIMC) model becomes over-structured at 300 K
- The amount of over-structure is very similar to that obtained using DFT/GGA



However: TIP5P(PIMC) simulations use a rigid water model.

Diffusion ~10x slower than exp.

DFT simulations with rigid water molecules as a function of temperature



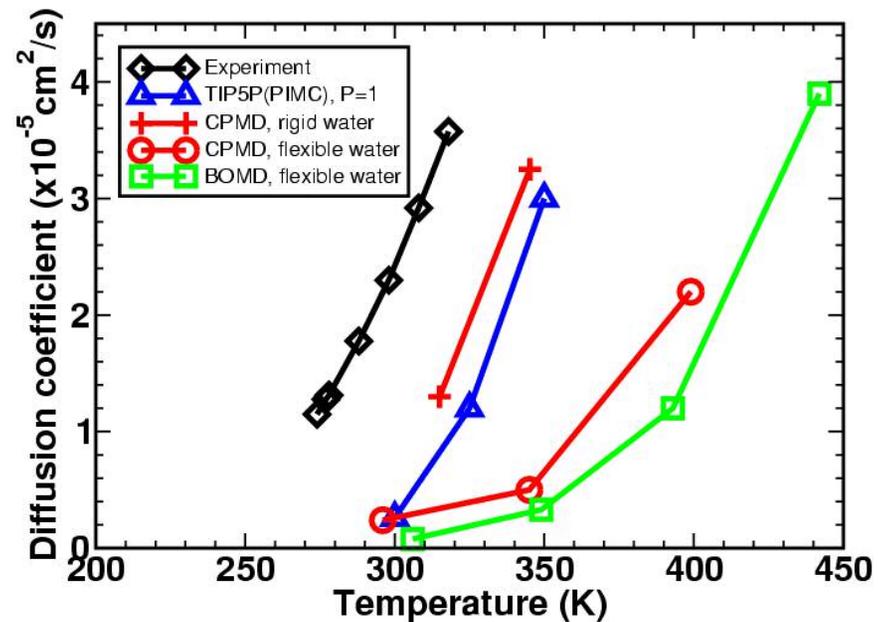
- Results of rigid water simulations within DFT are very similar to those with TIP5P(PIMC) without path integral sampling

Comparison between experiment, and classical and DFT simulations of rigid water, indicates that the effect of proton quantum motion on structure and diffusion can be reproduced by increasing T by ~ 50 K (~ 0.0043 eV)

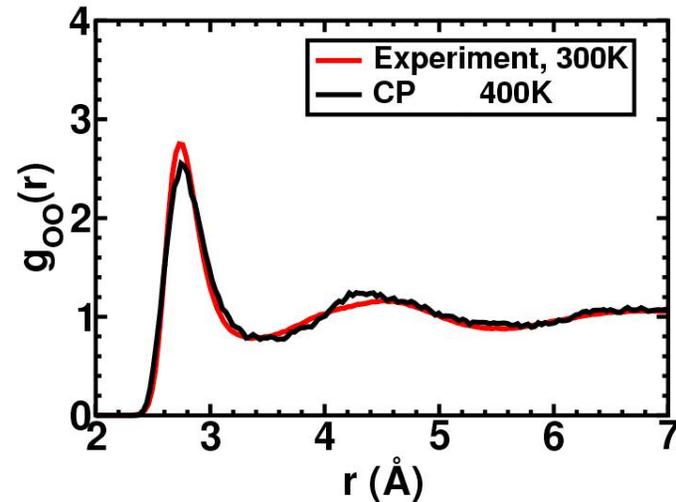
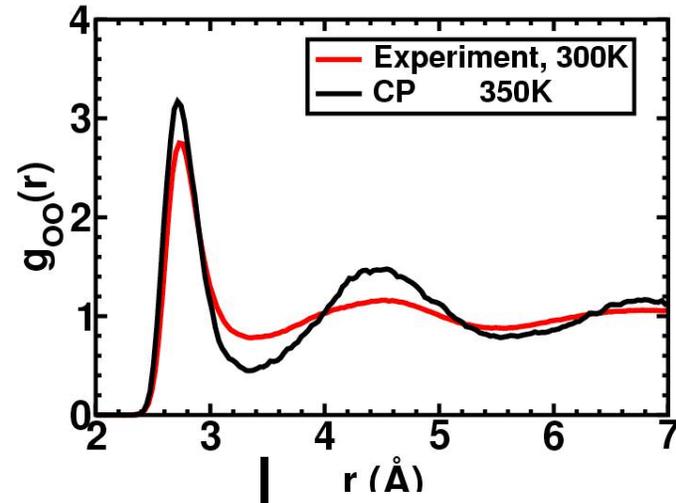
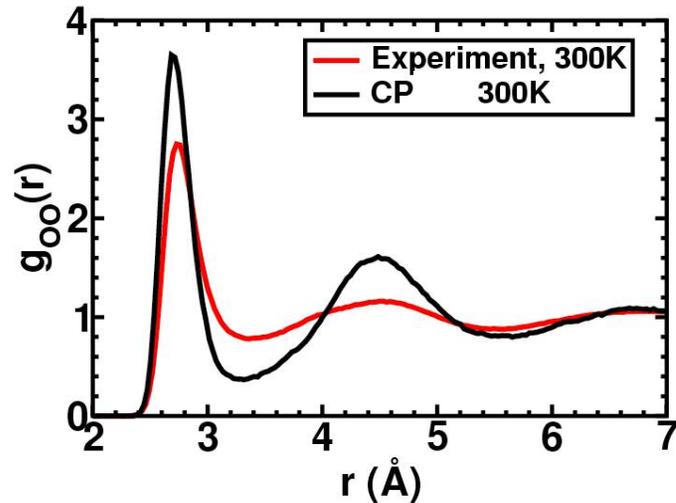
DFT simulations with flexible water molecules as a function of temperature



- Diffusion coefficients for DFT/PBE flexible water increase slowly with temperature
- Simulation temperatures of 390 to 400 K needed to obtain the 300 K experimental diffusion coefficient
- At 400 K we find a difference of a factor of 2 between BO and CP results for the diffusion coefficient.

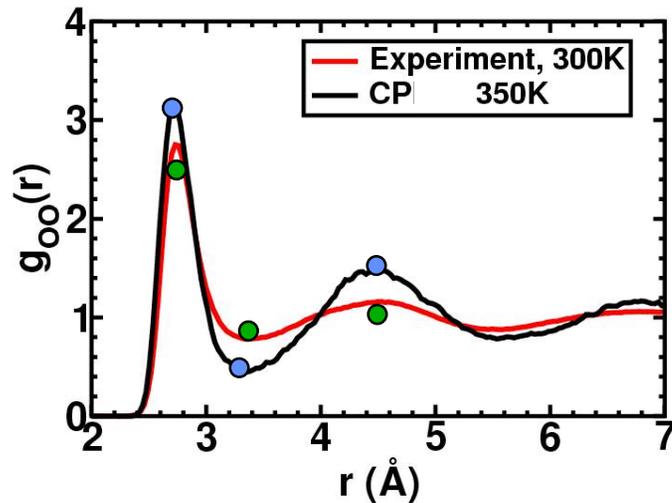


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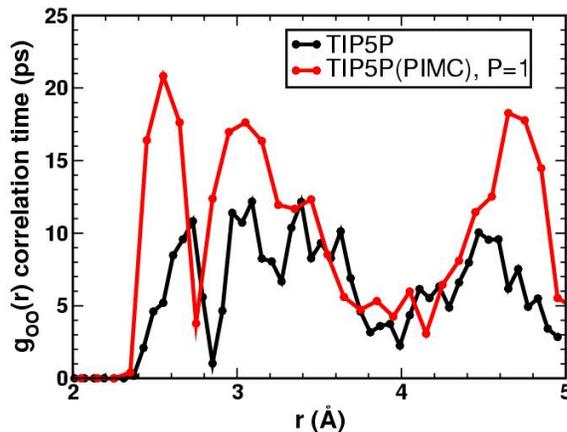
- DFT simulations of flexible water give structural results in **agreement with experiment if the temperature is increased to ~400 K**
- Work in progress to determine proton quantum effects directly for flexible water

Comparison with other *ab-initio* MD simulations



● CP and BO simulations (*) in the microcanonical ensemble at $T=315$ K; 64 molecules, normconserving, TM pseudopotentials; BLYP functional, 10 ps D in the range 10^{-5} to $3 \cdot 10^{-6}$ cm^2/s

● CP simulations in the canonical ensemble at $T=350$ K; ultrasoft pseudopotentials, PBE functional, 5ps (+)

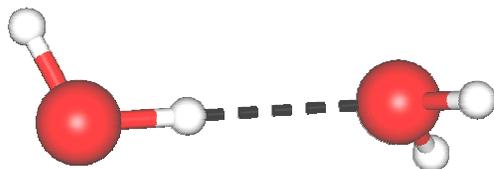


Meaningful comparisons between different simulations with $D \sim 10^{-6}$ cm^2/s require ~ 20 ps runs

(*) I.-Feng W.Kuo, C.J.Mundy, M.J.McGrath, J.I.Siepmann, J.VandeVondele, M.Spriik, J.Hutter, B.Chen, M.L.Klein, F.Mohamed, M.Krack and M.Parrinello (preprint, May 2004).

(+) B.Hetyenyi et al. et al. JCP 2004

A variety of DFT/GGA functionals work well for the water dimer



	$r_{oo}(\text{\AA})$	$D_e(\text{kcal/mol})$	$\alpha_{iso}(\text{\AA}^3)$	
PBE	2.90	-5.11	1.59	} GGA
BLYP	2.95	-4.18	1.58	
PBE1	2.90	-4.98	1.41	} Hybrid
B3LYP	2.93	-4.57	1.45	
Exp.	2.95	-5.44	1.43	

- Geometry and binding energy are accurately reproduced within DFT/GGA
- Improvements in calculated polarizability when going from simple GGAs to hybrid functionals that include Hartree-Fock exchange

Summary



- **Series of *ab-initio* simulations to examine the impact of technical details**
 - **Timescales: correlation time ~10-20 ps**
 - **System size: 32 versus 64 molecules**
 - **Choice of GGA: PBE versus BLYP**
 - **Fictitious mass in CP scheme**
- **Overstructure and slow diffusion in DFT/GGA water is most likely caused by:**
 - **Neglect of quantum effects**
 - ***Tendency of GGA to overestimate polarizabilities***
- **Convergence of path integral/DFT simulations and use of hybrid functionals are currently being explored**

Conclusions



- By systematically varying simulation parameters, we have analyzed the accuracy of DFT/PBE for water structure and diffusion at 300 K:
 - CP in agreement with BO if $\mu/M \leq 1/5$, for radial distribution functions; differences in the diffusion coefficient
 - Inaccuracies in the technique can give misleading results on theory performance and fortuitous agreement with experiment
 - Recent results from other groups in satisfactory agreement with ours, however small differences persist
 - Our ongoing study on proton quantum effects indicates they may play a critical role in determining the dynamical properties of the liquid

