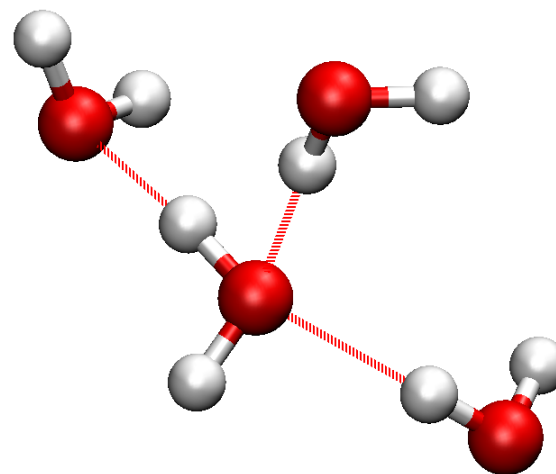


Quantum effects in condensed-phase systems

Scott Habershon

Department of chemistry, University of Warwick



THE UNIVERSITY OF
WARWICK



The Leverhulme Trust

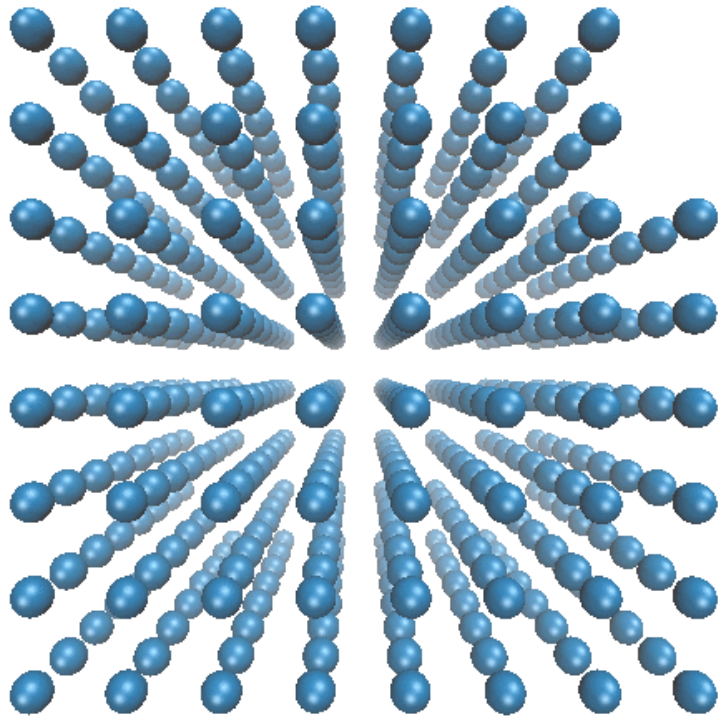
EPSRC

Engineering and Physical Sciences
Research Council

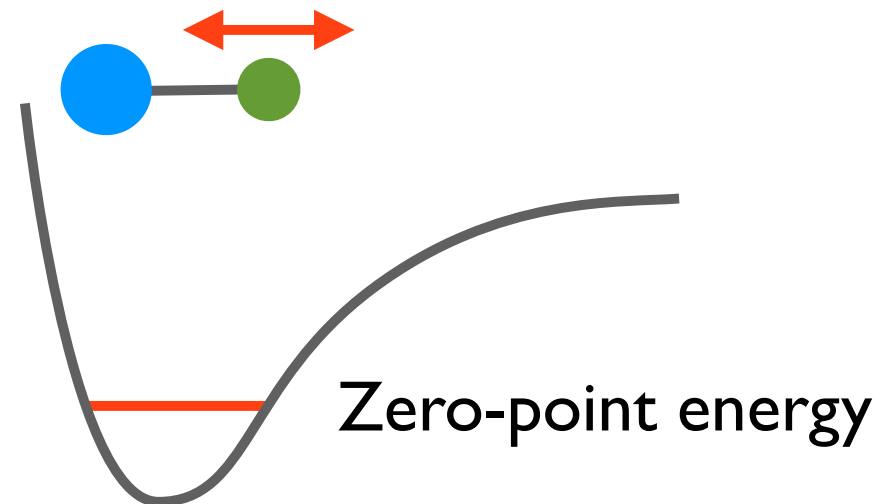
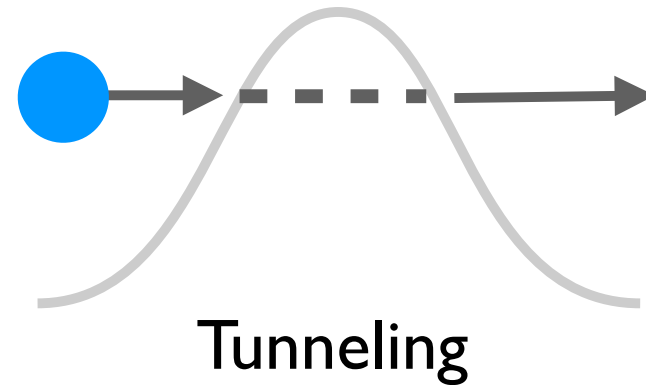
3rd December 2012

Classical vs. quantum simulations

Classical molecular dynamics gives us *microscopic* insights into *macroscopic* properties....



....but what about **quantum effects**!?!



Quantum effects in water

	H₂O	D₂O	
Melting point / °C	0	4	
Molar volume / cm ³	18.069	18.133	
	↑	↑	
	<i>Classically identical</i>		
Diffusion coefficient (25 °C) / Å ps ⁻²	0.23	0.18	Ratio: 1.28

Classical ratio is **1.05**
(Boltzmann RMS speed)

$$\mathbf{ZPE_{H_2O} > ZPE_{D_2O}}$$

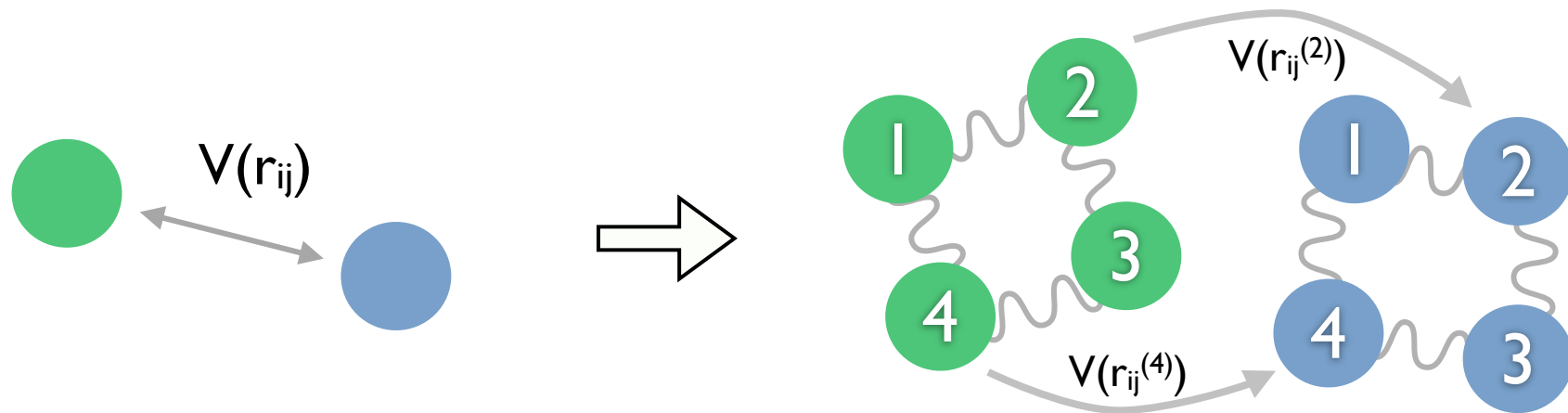
Path integral molecular dynamics

$$\langle A \rangle = \frac{1}{Z} \text{Tr} \left[e^{-\beta \hat{H}} \hat{A} \right] \xrightarrow{\text{Path integral}} \langle A \rangle = \frac{1}{2\pi\hbar Z_n} \int d\mathbf{p}^n d\mathbf{q}^n e^{-\frac{\beta}{n} H_n(\mathbf{p}, \mathbf{q})} A_n(\mathbf{q})$$

3Nn-dimensional integral

$$A_n = \frac{1}{n} \sum_{j=1}^n A(q_j)$$

$$H_n(\mathbf{p}, \mathbf{q}) = \sum_{j=1}^n \left[\frac{p_j^2}{2m_j} + V(q_j) + \frac{m_j (nk_B T)^2}{2\hbar^2} (q_j - q_{j-1})^2 \right]$$

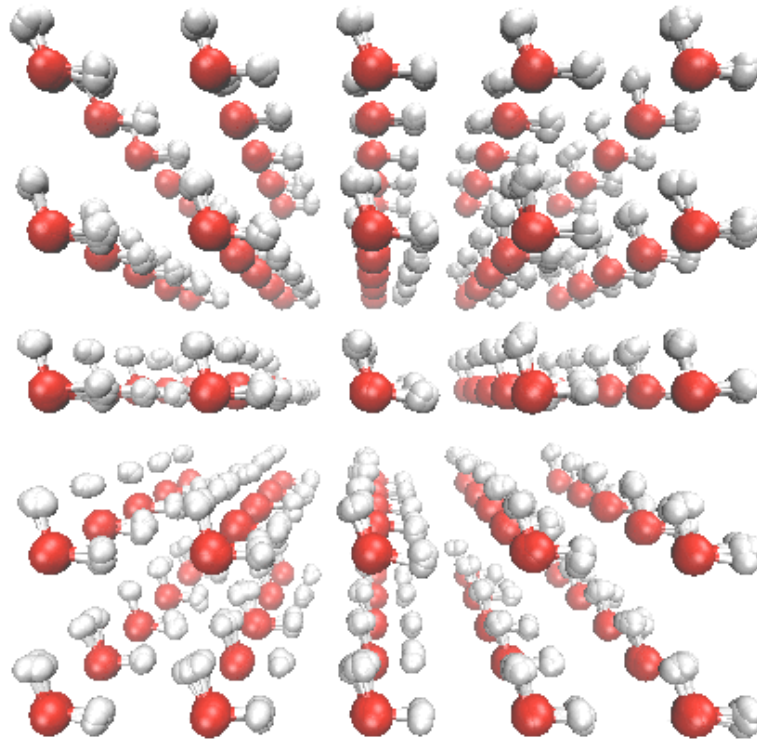


Exact quantum properties from n classical simulations

Path integral molecular dynamics

$$H_n(\mathbf{p}, \mathbf{q}) = \sum_{j=1}^n \left[\frac{p_j^2}{2m_j} + V(q_j) + \frac{m_j(nk_B T)^2}{2\hbar^2} (q_j - q_{j-1})^2 \right]$$

PIMD is just classical MD in an extended phase-space

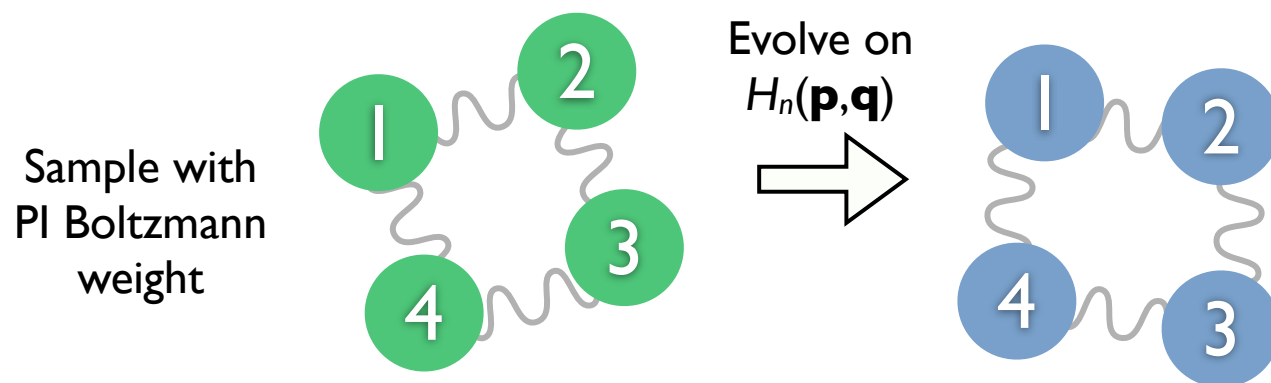


Ring polymer molecular dynamics (RPMD)*

$$\tilde{C}_{AB}(t) = \frac{1}{\beta Z} \int_0^\beta d\lambda \text{Tr} \left[e^{-(\beta-\lambda)\hat{H}} \hat{A} e^{-\lambda\hat{H}} e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} \right] \Rightarrow D = \frac{1}{3} \int_0^\infty \tilde{C}_{\mathbf{v}\cdot\mathbf{v}}(t) dt$$

$$\tilde{C}_{AB} \approx \frac{1}{2\pi\hbar Z_n} \int d\mathbf{p}^n d\mathbf{q}^n e^{-\frac{\beta}{n} H_n(\mathbf{p}, \mathbf{q})} A_n(0) B_n(t)$$

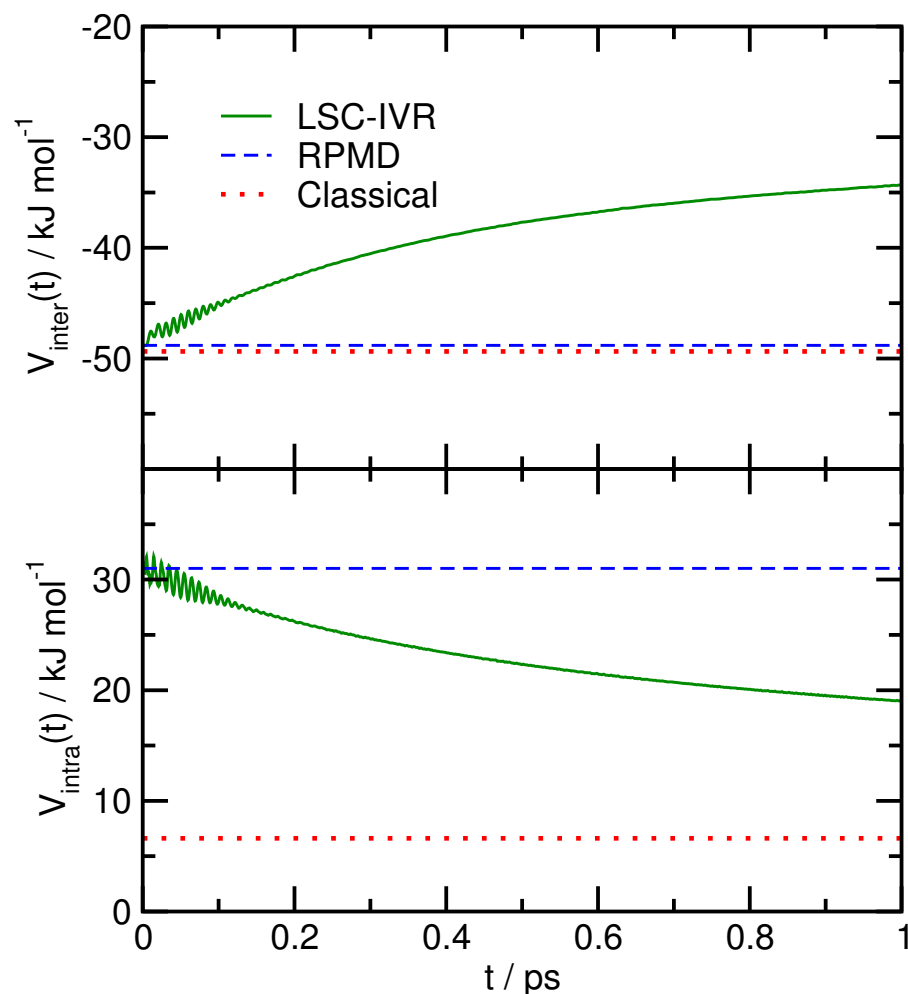
$$A_n = \frac{1}{n} \sum_{j=1}^n A(q_j)$$



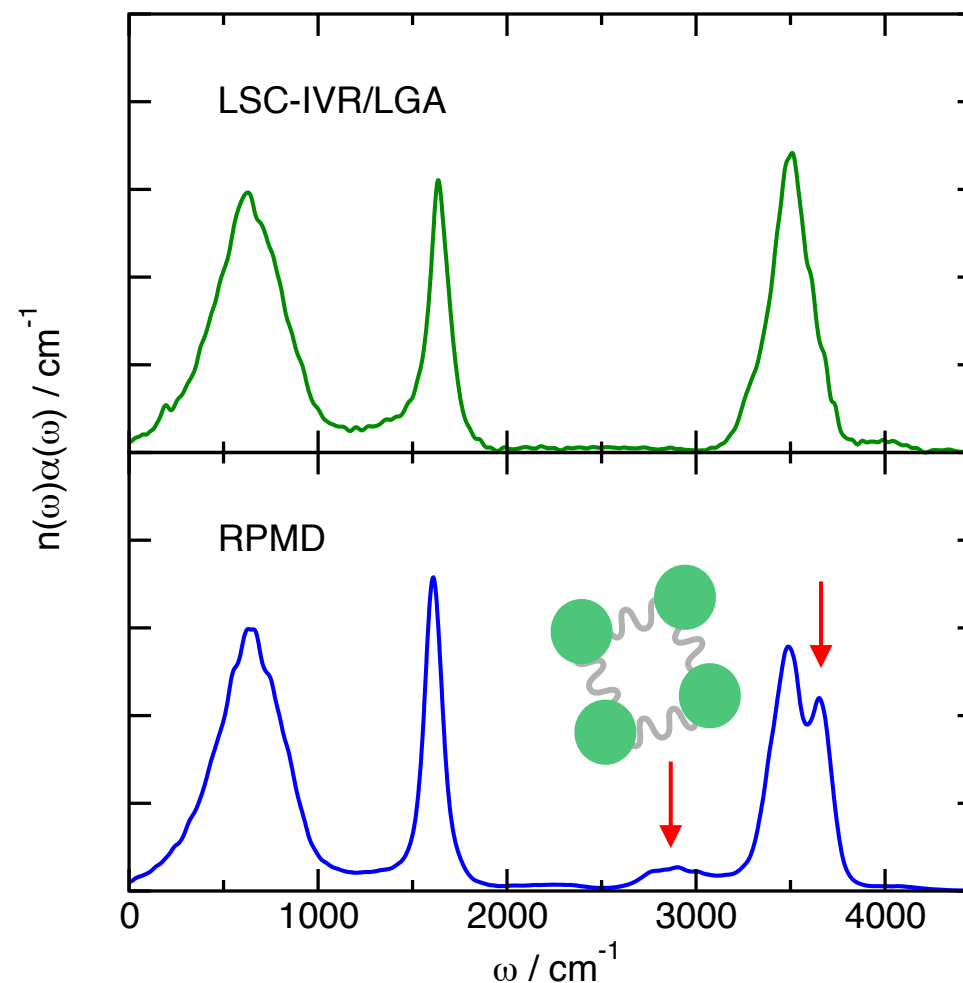
- *Exact* for SHO for linear A and/or B
- *Exact* at $t = 0$ and high-T limits
- Same symmetries as exact quantum TCF

Zero-point energy leakage*

Quantum simulations of simple flexible water model



RPMD conserves quantum
Boltzmann distribution *at all times*



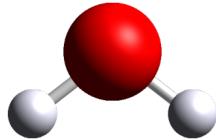
RPMD exhibits spurious Matsubara
frequencies in vibrational spectra

Quantum simulations of water

Model	Quantum method	Classical diffusion	Quantum diffusion	D_{qm} / D_{cl}
SPC/E	RPMD	0.242	0.343	1.42
TIP4P	CMD	0.358	0.548	1.53
SPC/F	RPMD	0.279	0.400	1.43
SPC/F	CMD	0.30	0.42	1.40
SPC/RW	LSC-IVR	0.25	0.47	1.88

On average, $D_{qm} / D_{cl} \sim 1.5$

Empirical water models

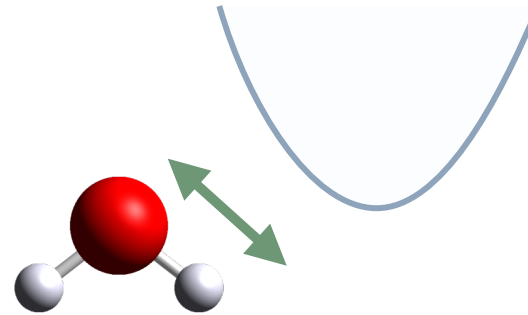


Rigid models

Intramolecular ZPE ignored

SPC/E

TIP4P



Harmonic models

Non-physical vibration

SPC/F

SPC/RW

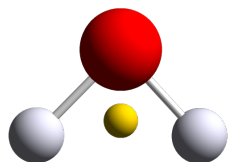
Parameterization again experimental data

“double-counts” quantum effects

**Flexible, anharmonic model
parameterized for quantum simulations: q-TIP4P/F**

q-TIP4P/F water model*

4-site flexible *anharmonic* water model

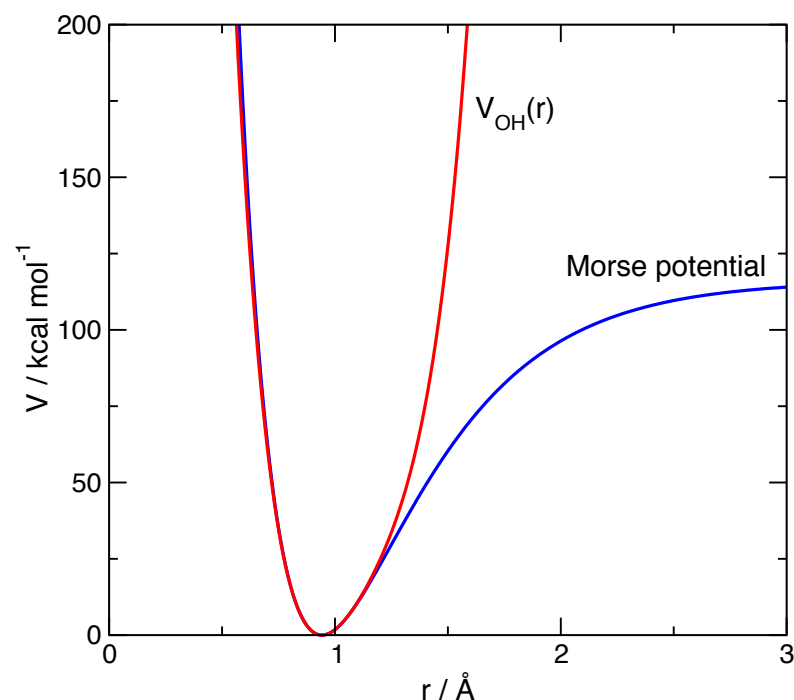


$$\mathbf{r}_M = \gamma \mathbf{r}_O + (1 - \gamma)[\mathbf{r}_{H1} + \mathbf{r}_{H2}]/2$$

$$V = V_{inter} + V_{intra}$$

$$V_{inter} = \sum_i \sum_{j>i} \left\{ 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \sum_{m \in i} \sum_{n \in j} \frac{q_m q_n}{r_{mn}} \right\}$$

Parameters from Vega's TIP4P/2005 (rigid)



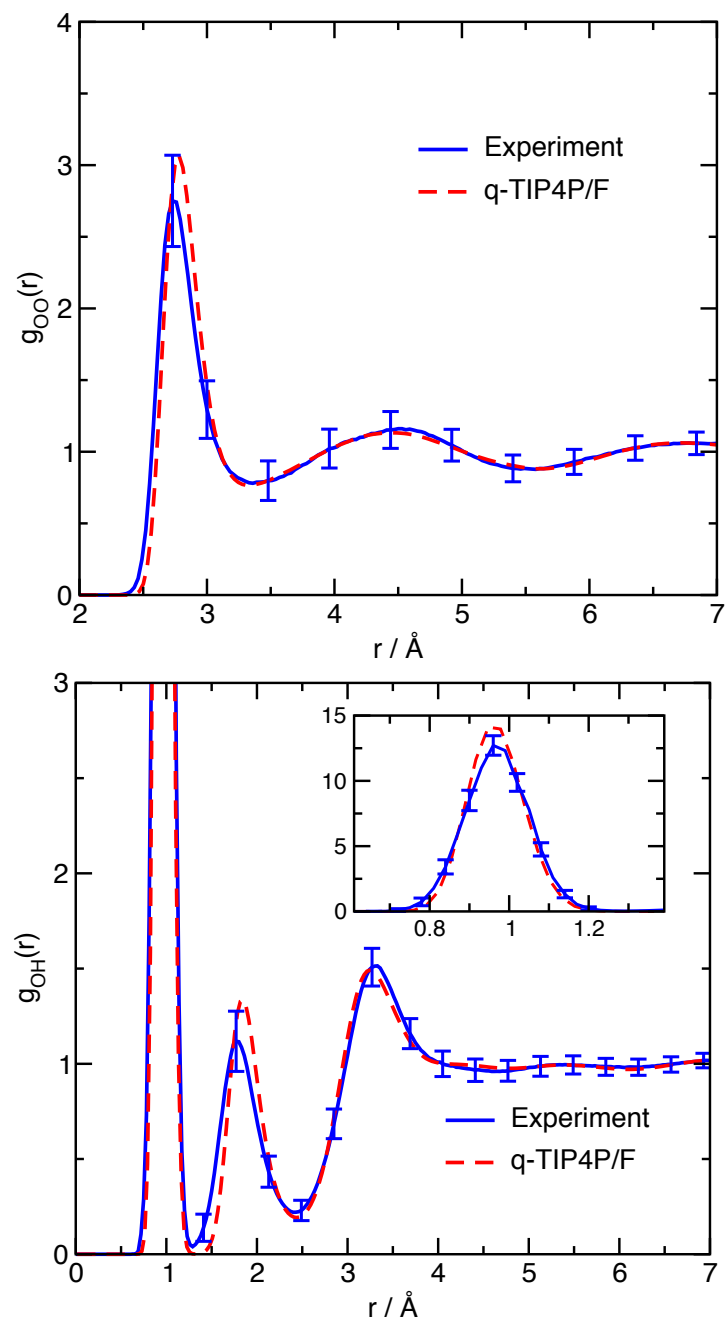
$$V_{intra} = \sum_i \left[V_{OH}(r_{i1}) + V_{OH}(r_{i2}) + \frac{1}{2} k_\theta (\theta_i - \theta_{eq})^2 \right]$$

$$V_{OH}(r) = D_r \left[\alpha_r^2 (r - r_{eq})^2 - \alpha_r^3 (r - r_{eq})^3 + \frac{7}{12} \alpha_r^4 (r - r_{eq})^4 \right]$$

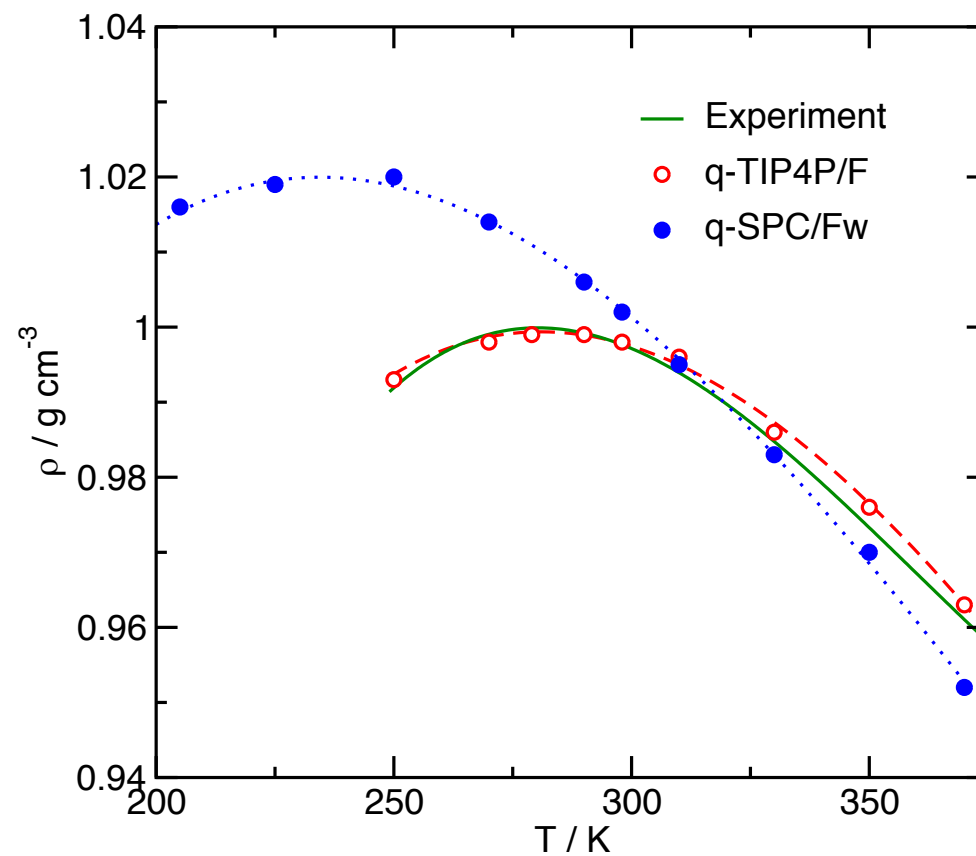
Parameterize using **quantum** simulations of:

- Experimental RDFs
- Experimental diffusion coefficient
- Experimental liquid vibrational frequencies

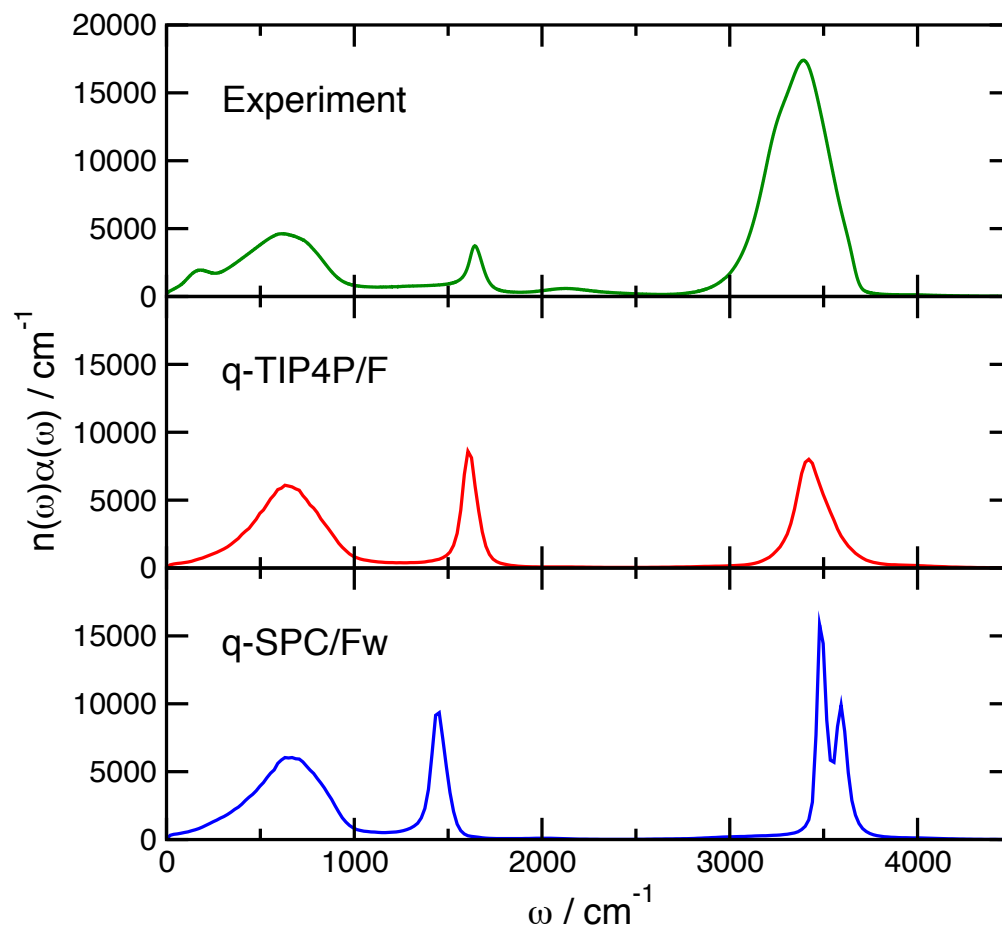
q-TIP4P/F water: statics



PIMD densities at 1 bar pressure



q-TIP4P/F water: dynamics



	q-TIP4P/F	Expt.
$D_{\text{H}_2\text{O}} / \text{\AA ps}^{-2}$	0.221	0.23
$D_{\text{D}_2\text{O}} / \text{\AA ps}^{-2}$	0.172	0.177
$D_{\text{H}_2\text{O}} / D_{\text{D}_2\text{O}}$	1.28	1.30
$\tau_2^{\text{HH}} / \text{ps}$	2.22	1.6 - 2.5
$\tau_2^{\text{OH}} / \text{ps}$	1.90	1.95
τ_2^{μ} / ps	1.52	1.90



Quantum results from
ring-polymer molecular dynamics (RPMD)

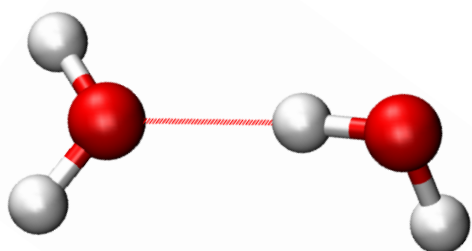
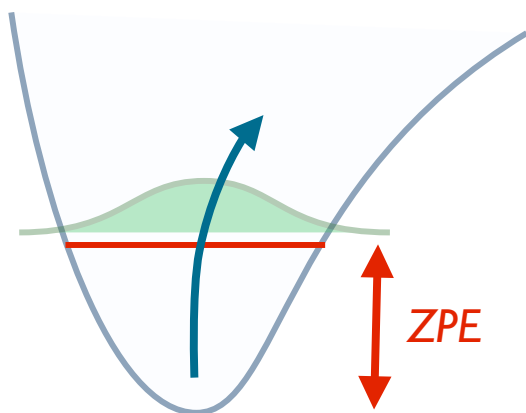
I. R. Craig and D. E. Manolopoulos, *J. Chem. Phys.*, **121**, 3368 (2004)

An interesting observation...

Model	Quantum method	Classical diffusion	Quantum diffusion	D_{qm} / D_{cl}
SPC/E	RPMD	0.242	0.343	1.42
TIP4P	CMD	0.358	0.548	1.53
SPC/F	RPMD	0.279	0.400	1.43
SPC/F	CMD	0.30	0.42	1.40
SPC/RW	LSC-IVR	0.25	0.47	1.88
q-TIP4P/F	RPMD	0.192	0.221	1.15

Why is the quantum effect so small in q-TIP4P/F?

Competing quantum effects

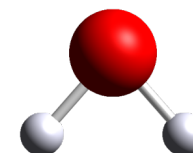


Intermolecular interactions

ZPE weakens hydrogen-bonding network

Expect quantum dynamics *faster* than classical dynamics

	Classical	Quantum
$r_{\text{OH}} / \text{\AA}$	0.963	0.978
$\theta / ^\circ$	104.8	104.7



μ / D	2.311	2.348
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Intramolecular interactions

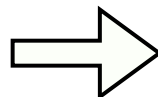
Geometry changes increase dipole moment

Expect quantum dynamics *slower* than classical dynamics

Competition between quantum effects results in cancellation

Further verification

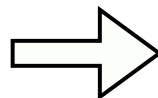
Turning off flexibility results in a large QM effect again



Rigid q-TIP4P/F simulations

Classical D / $\text{\AA ps}^{-2}$	0.308
Quantum D / $\text{\AA ps}^{-2}$	0.440
$D_{\text{qm}} / D_{\text{cl}}$	1.43

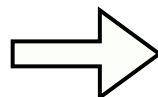
**Not specific to q-TIP4P/F:
ab initio simulations
demonstrate similar results**



PIMD simulations of BLYP water*

Classical $\mu = 3.04$ D
Quantum $\mu = 3.18$ D

Experimental support



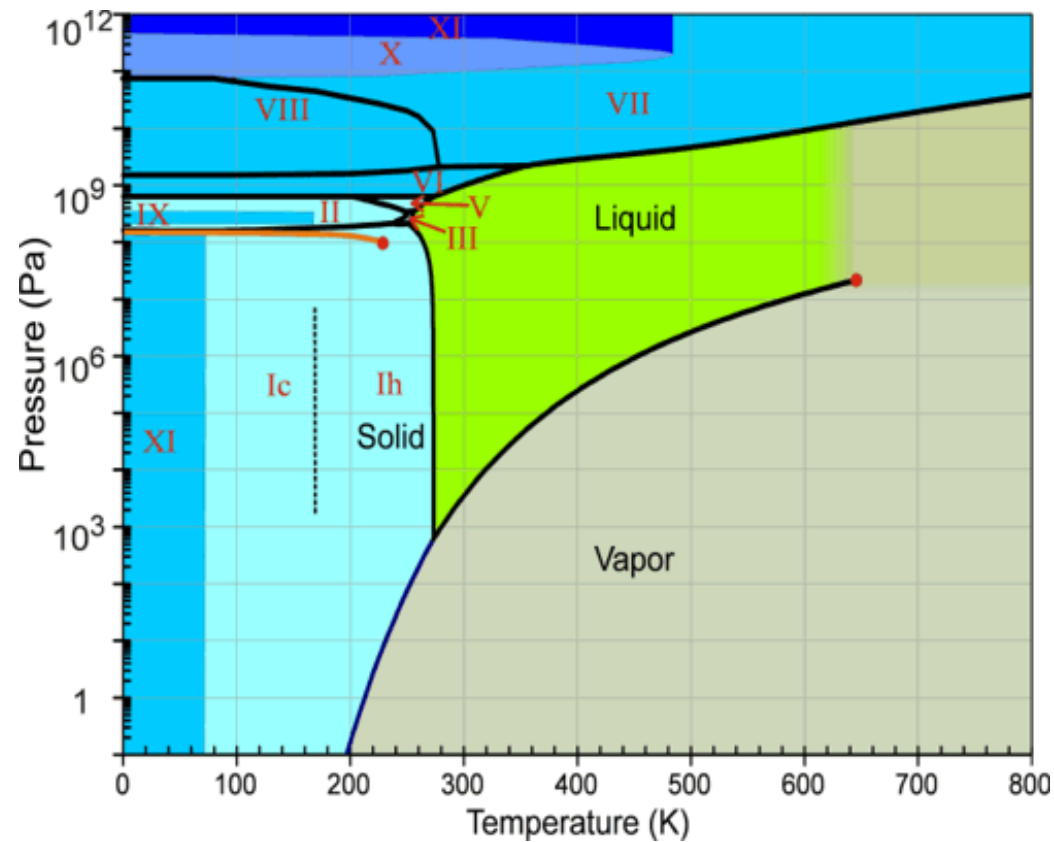
X-ray / neutron diffraction studies**

O-H bond length in H_2O ~3% longer
than O-D bond length in D_2O

*M. Parrinello et. al, *Phys. Rev. Letters*, **91**, 215503 (2003)

A. K. Soper et. al, *Phys. Rev. Letters*, **101, 065502 (2008)

Quantum phase diagrams*



$$F_q = F_c + \Delta F_{qc}$$

Free energy
of quantization

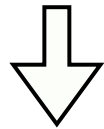
Free energy calculations for a flexible water model,
S. Habershon and D. E. Manolopoulos, *Phys. Chem. Chem. Phys.*, **13**, 19714 (2011)

Quantum Free Energies

$$F_q = F_c + \Delta F_{qc} \longrightarrow \text{Free energy of quantization}$$

Introduce a path variable to the Hamiltonian.....

$$H(\mathbf{p}, \mathbf{q}; \lambda)$$



$$F(\lambda) = -\frac{1}{\beta} \ln [Z(\lambda)] \Longrightarrow \Delta F = F(\lambda = 1) - F(\lambda = 0) = \int_0^1 \left(\frac{\partial F}{\partial \lambda} \right) d\lambda$$

Quantum

Classical

Thermodynamic integration from classical to quantum mechanics

Integral easy to evaluate by quadrature

$$\Longrightarrow \frac{\partial F(\lambda)}{\partial \lambda} = \left\langle \frac{\partial H(\mathbf{p}, \mathbf{q}; \lambda)}{\partial \lambda} \right\rangle_{\lambda}^{NVT, NPT}$$

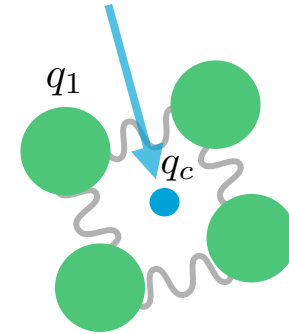
Morales-Singer (MS) method*

$$H_n(\mathbf{p}, \mathbf{q}) = \sum_{j=1}^n \left[\frac{p_j^2}{2m_j} + \mathbf{V}(\mathbf{q}_j) + \frac{1}{2} m_j \omega_j^2 (q_j - q_{j-1})^2 \right]$$



$$H_n^{\text{MS}}(\mathbf{p}, \mathbf{q}; \lambda) = \sum_{j=1}^n \left[\frac{p_j^2}{2m_j} + \lambda \mathbf{V}(\mathbf{q}_j) + (1 - \lambda) \mathbf{V}(\mathbf{q}_c) + \frac{1}{2} m_j \omega_j^2 (q_j - q_{j-1})^2 \right]$$

Ring-polymer centroid



$\lambda = 1 \longrightarrow$ QUANTUM PI Hamiltonian recovered

$\lambda = 0?$

Potential evaluated at centroid only, RP normal modes integrate out to give....

$$Z_n^{\text{MS}}(\lambda = 0) = \frac{1}{(2\pi\hbar)} \left(\frac{2\pi m}{\beta} \right)^{1/2} \int dq_c e^{-\beta V(q_c)}$$

...which is just the CLASSICAL partition function!

$$\Delta F = F(\lambda = 1) - F(\lambda = 0) = \int_0^1 \left(\frac{\partial F}{\partial \lambda} \right) d\lambda$$

$$\left(\frac{\partial F(\lambda)}{\partial \lambda} \right) = \left\langle \frac{1}{n} \sum_{j=1}^n [V(q_j) - V(q_c)] \right\rangle_{\lambda}^{\text{MS}}$$

Evaluate in PI simulation with
MS Hamiltonian

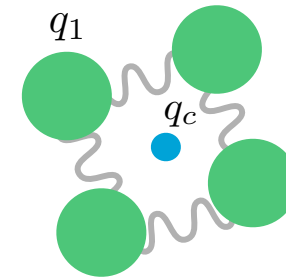
*J. J. Morales and K. Singer, *Mol. Phys.*, **73**, 873 (1991)

MS method fails for strongly quantum systems

$$\left(\frac{\partial F(\lambda)}{\partial \lambda} \right) = \left\langle \frac{1}{n} \sum_{j=1}^n [V(q_j) - V(q_c)] \right\rangle_{\lambda}^{\text{MS}}$$

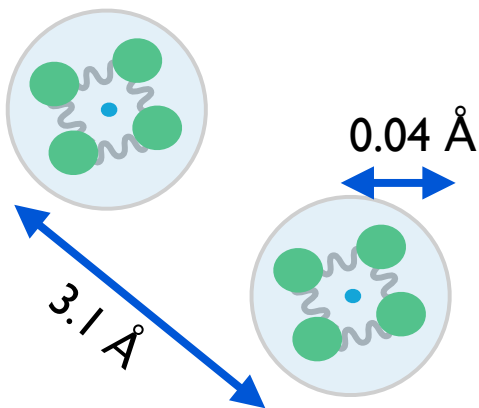
Potential on *beads*

Potential on *centroid*

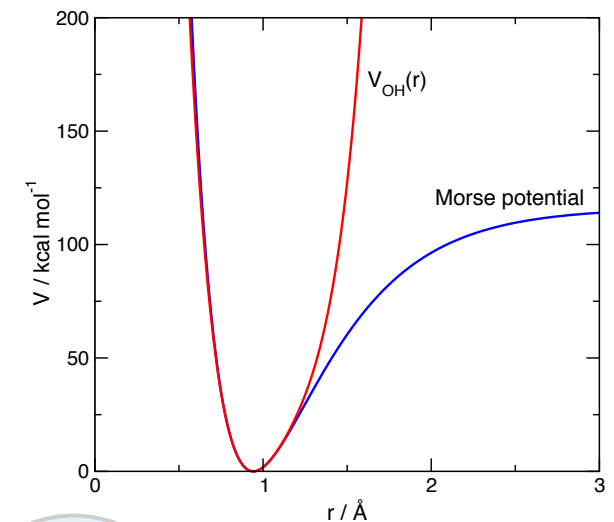
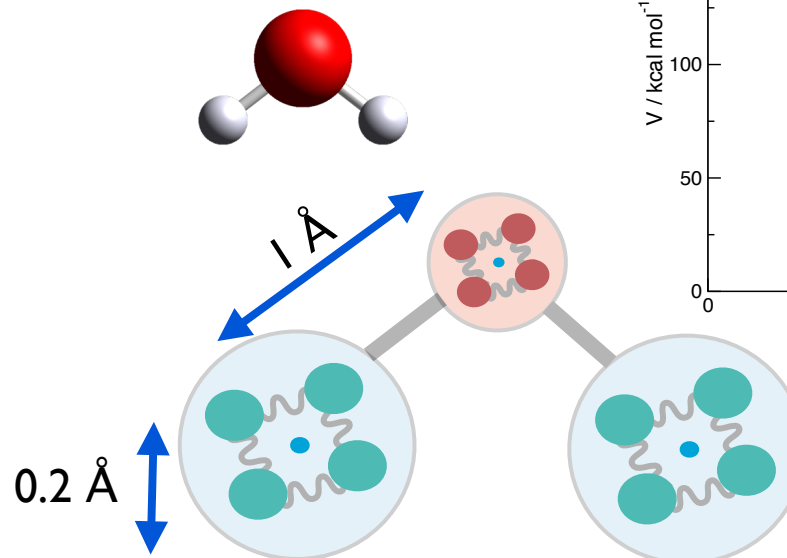


For small λ , bead positions sampled from *free ring-polymer distribution*

Liquid neon, $T = 25 \text{ K}$



Liquid water, $T = 298 \text{ K}$

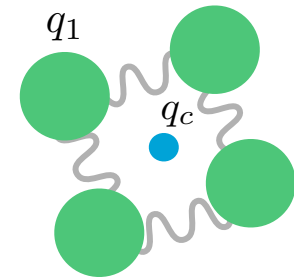


Scaled coordinate (SC) method

$$H_n(\mathbf{p}, \mathbf{q}) = \sum_{j=1}^n \left[\frac{p_j^2}{2m_j} + \mathbf{V}(\mathbf{q}_j) + \frac{1}{2}m_j\omega_j^2(q_j - q_{j-1})^2 \right]$$



$$H_n(\lambda; \mathbf{p}, \mathbf{q}) = \sum_{j=1}^n \left[\frac{p_j^2}{2m_j} + \mathbf{V}(\lambda\mathbf{q}_j + (1-\lambda)\mathbf{q}_c) + \frac{1}{2}m_j\omega_j^2(q_j - q_{j-1})^2 \right]$$



$$u_j^\lambda = \lambda q_j + (1-\lambda)q_c$$

$\lambda = 1 \longrightarrow$ QUANTUM PI Hamiltonian and partition function recovered

$\lambda = 0 \longrightarrow$ CLASSICAL Hamiltonian and partition function as before

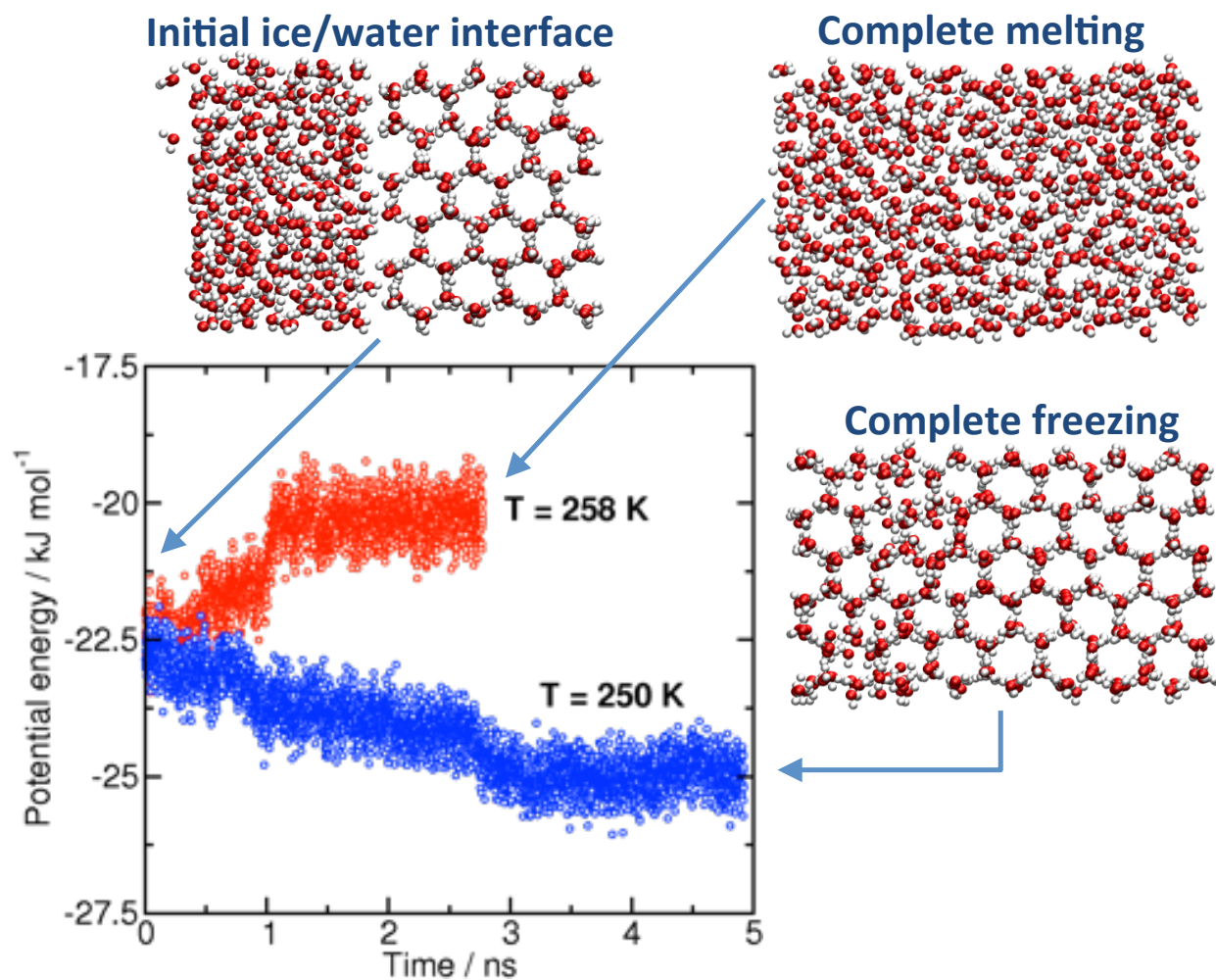
$$\Delta F = F(\lambda = 1) - F(\lambda = 0) = \int_0^1 \left(\frac{\partial F}{\partial \lambda} \right) d\lambda$$

$$\left(\frac{\partial F(\lambda)}{\partial \lambda} \right) = \left\langle \frac{1}{n} \sum_{j=1}^n (q_j - q_c) \frac{\partial V(u_j^\lambda)}{\partial u_j^\lambda} \right\rangle_\lambda^{\text{SC}}$$

Evaluated in *NPT* simulations

Stable estimator for **all** values of λ
No problems with strong delocalization like MS

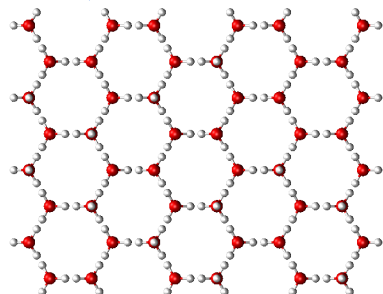
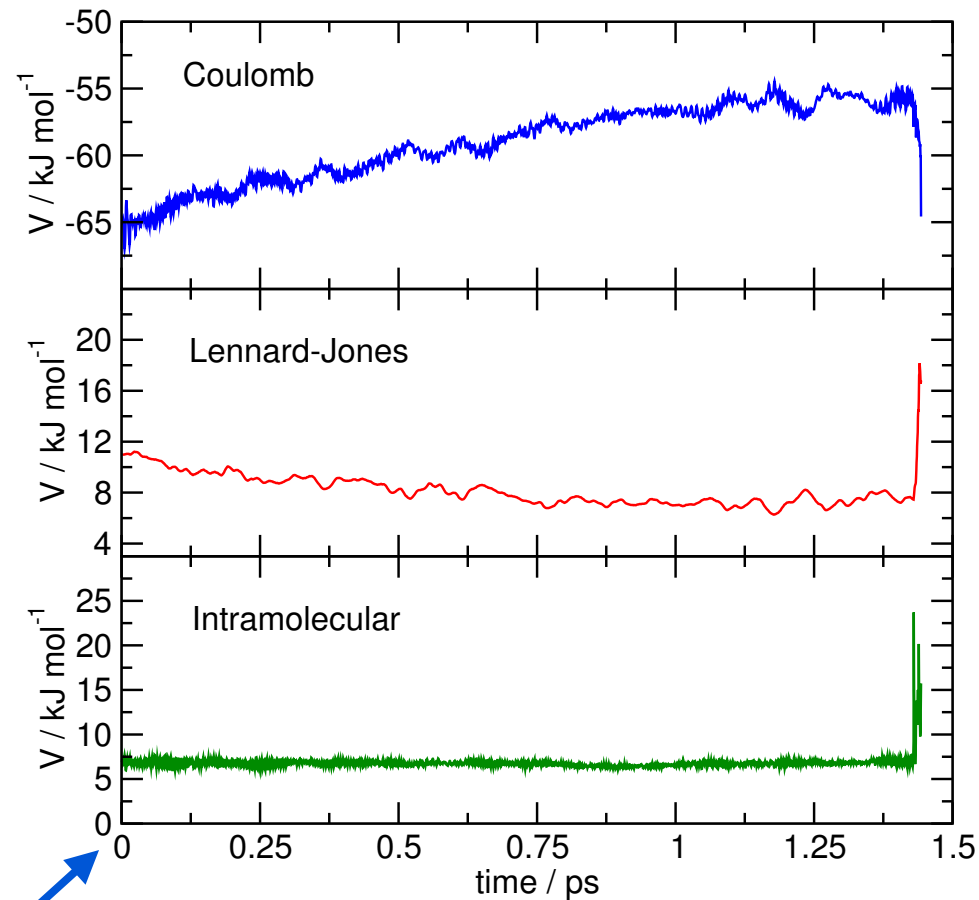
Application: q-TIP4P/F water melting point



	q-TIP4P/F (classical)	q-TIP4P/F (quantum)	q-SPC/FW (quantum)	TIP3P (classical)
Melting point / K	259	251	195	146

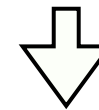
Instability in the MS method

q-TIP4P/F water simulation at $T = 298$ K, $p = 1$ bar, MS method with $\lambda = 0.01$

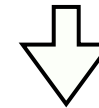


Energies shown for melting of
initial ice system at 298 K

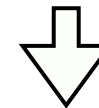
Large RP radius of hydrogen ($0.2 \text{ \AA}$)



H can closely approach O atoms



Strong attractive Coulomb interactions

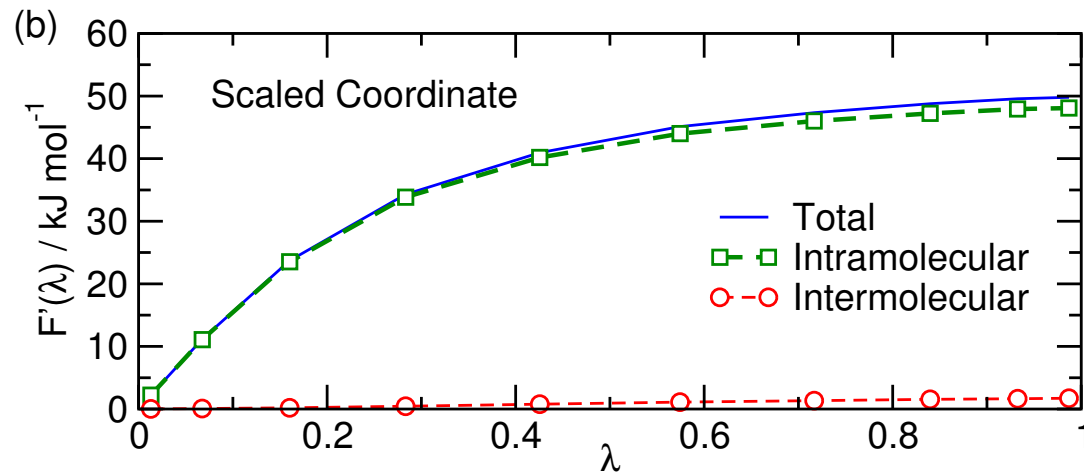
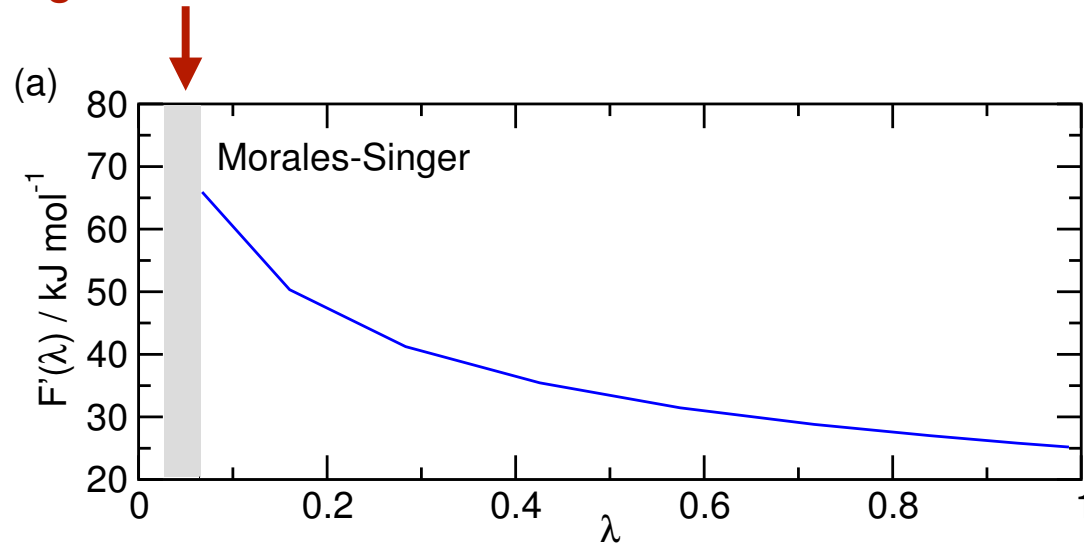


O-O interactions hit LJ wall...
difficult to integrate equations-of-motion

MS vs. SC methods

q-TIP4P/F water simulation at $T = 250$ K, $p = 1$ bar

Impossible to calculate
integrands for small λ



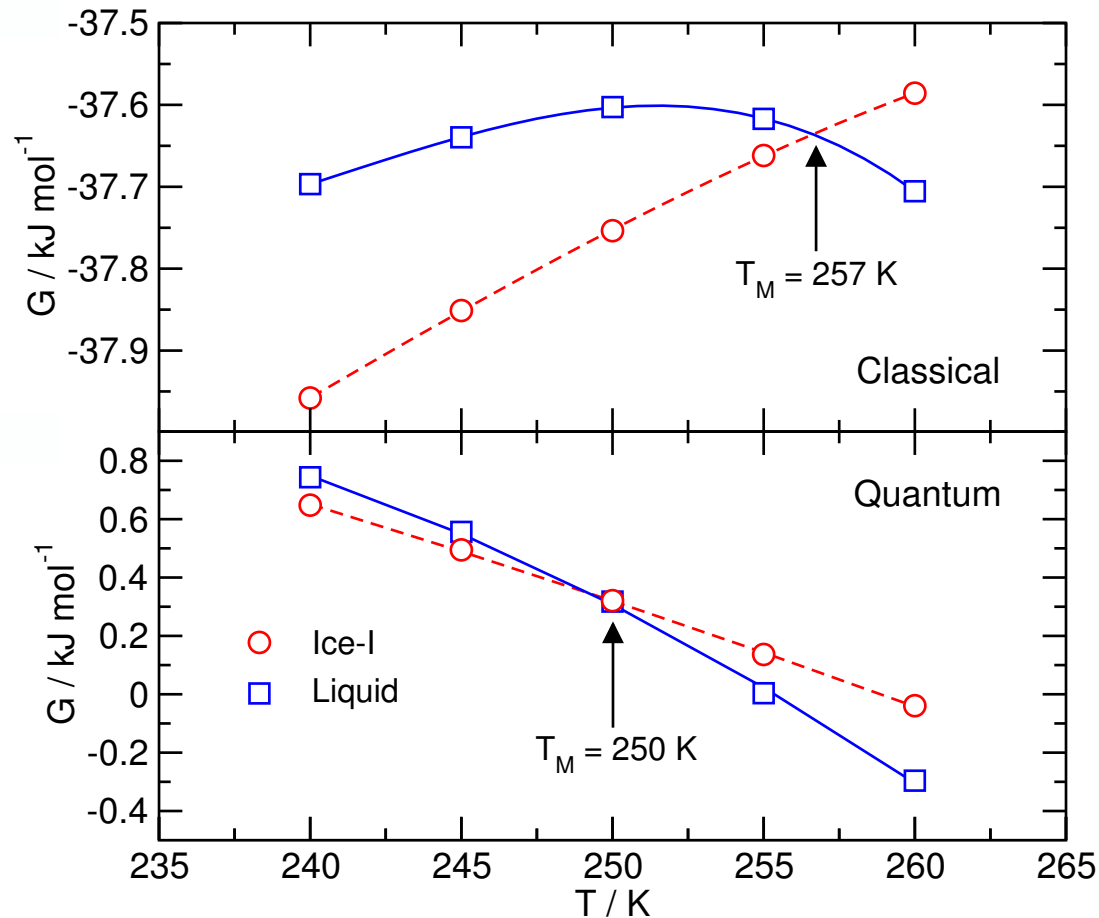
Major contribution from
intramolecular modes

Classical



Quantum

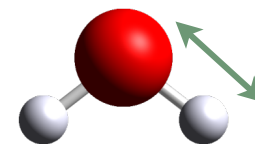
Quantum melting point of q-TIP4P/F



$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$S_{cl} = k_B [1 - \ln(\beta \hbar \omega)]$$

$$\hbar \omega > 2.72 k_B T$$



$$\hbar \omega \simeq 18 k_B T$$

From direct coexistence simulation, quantum $T_M = 251 \text{ K}$

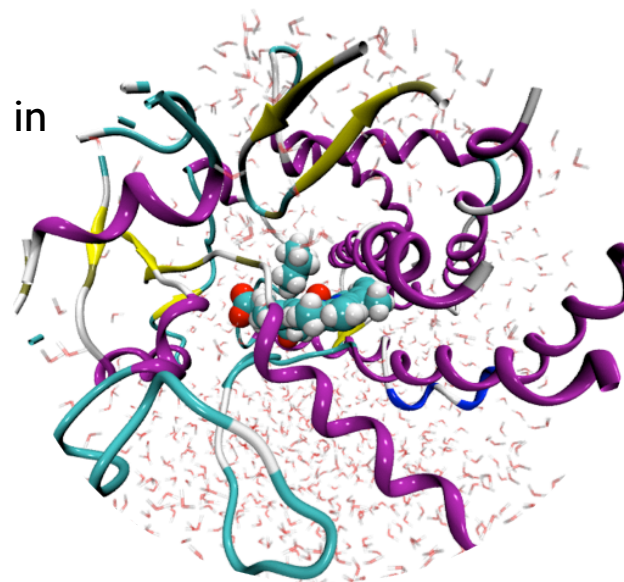
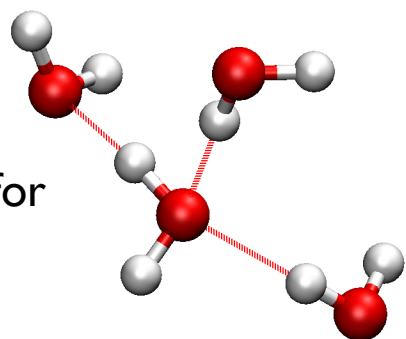
Current work

RPMD quantum dynamics

Quantum free energies

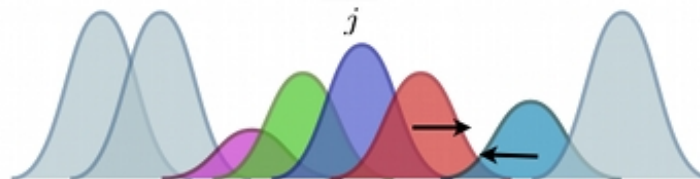
Kinetic isotope effects in
enzyme-catalysis

Quantum phase diagrams for
accurate water models



Quantum dynamics with wavefunctions

$$\Psi(\mathbf{q}; t) = \sum_j^m c_j(t) \phi_j(\mathbf{q}; t)$$



Trajectory-guided configuration interaction simulations of multidimensional quantum dynamics,
S. Habershon, *J. Chem. Phys.*, 136, 054109 (2012)

Linear dependence and energy conservation in Gaussian wavepacket basis sets,
S. Habershon, *J. Chem. Phys.*, 136, 014109 (2012)

Summary

Thermodynamic integration from classical to quantum mechanics,

S. Habershon and D. E. Manolopoulos, *J. Chem. Phys.*, **135**, 224111 (2011)

Competing quantum effects in liquid water,

S. Habershon, T. E. Markland and D. E. Manolopoulos, *J. Chem. Phys.*, **131**, 024501 (2009)

Free energy calculations for a flexible water model,

S. Habershon and D. E. Manolopoulos, *Phys. Chem. Chem. Phys.*, **13**, 19714 (2011)

Research support



The Leverhulme Trust

