Quantum Nuclei: Path Integral Molecular Dynamics for Static and Dynamical Observables

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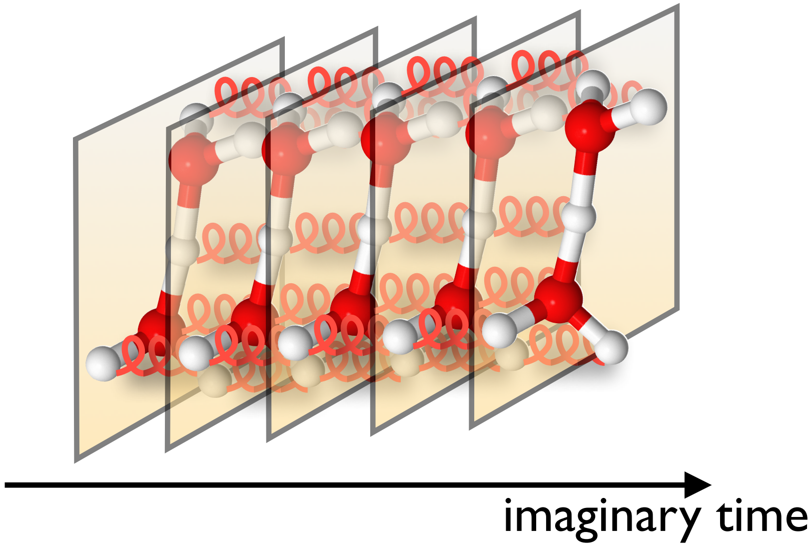

Density functional theory and beyond, IPAM, Los Angeles CA, USA

Where are nuclear quantum effects important?

- Relation between thermal De Broglie wavelength Λ and interparticle spacing l

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$\Lambda \gg l$$

Low temperature, low mass
⇒ nuclear quantum effects important

$$\Lambda \ll l$$

High temperature, high mass
⇒ classical Boltzmann statistics are fine

Species	T(K)	Λ
e	300	43.03
H	300	1.00
He	300	0.50
He	4	4.35

Species	T(K)	Λ
Li	300	0.38
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- How far from equipartition of energy? (k_BT/2 for each vibrational mode)

Systems approximately harmonic ⇒ $\frac{\hbar\omega}{k_B T} \gg 1$ ⇒ quantum (vibration dominated by ZPE)

T=300K corresponds to ω≈208cm-1 ⇒ anything above is ZPE dominated

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- In quantum mechanics, Boltzmann operator does not factorize (because momentum and position do not commute). E.g. for a system of harmonic oscillators:

$$\langle K_{qm}^{harm}\rangle = \sum_i \frac{\hbar\sqrt{k_i}}{4\sqrt{m_i}} \coth\left(\frac{\beta\hbar\sqrt{k_i}}{2\sqrt{m_i}}\right)$$

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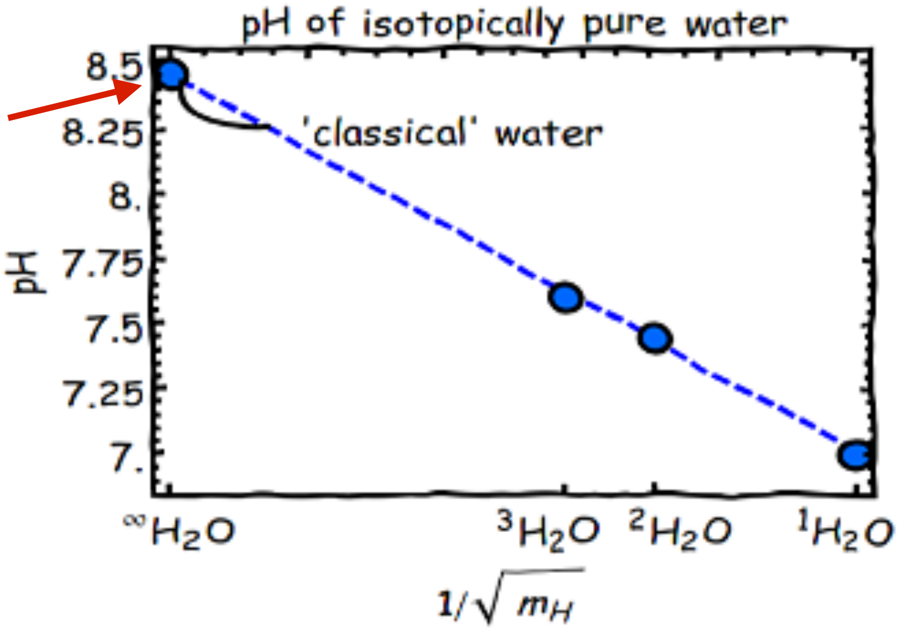

Classical water would be quite deadly!

Figure from M. Ceriotti (https://epfl-cosmo.github.io/gle4md/)

Quantum nuclear effects beyond harmonic approximation

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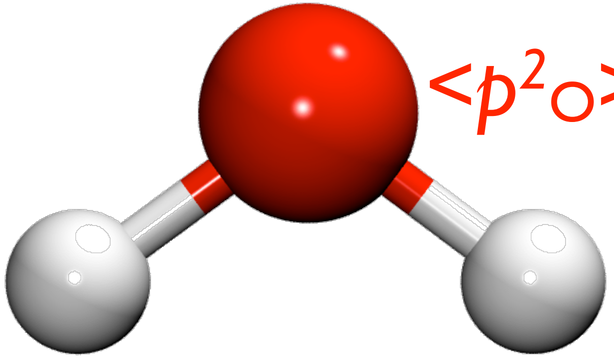

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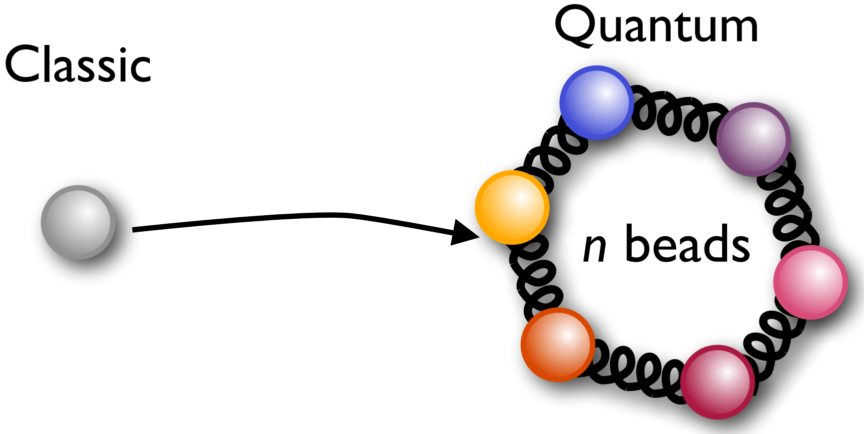

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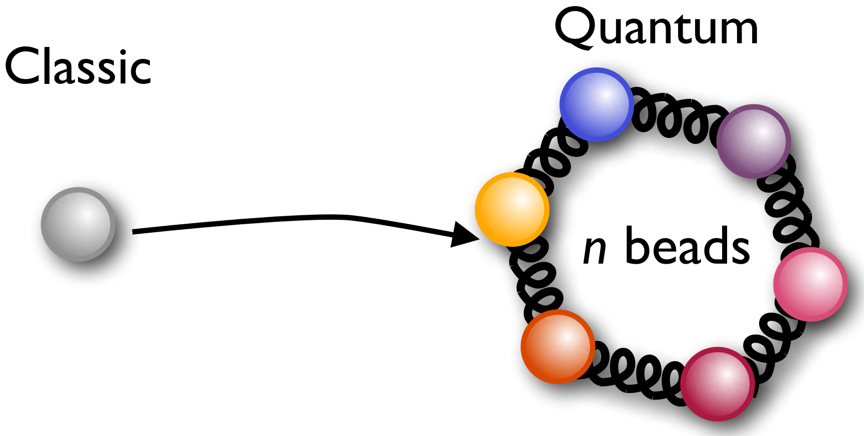

The time-dependent Schrödinger Equation

Time dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}|\Psi\rangle = \hat{H}|\Psi\rangle$$

$$|\Psi(t)\rangle = \exp(-i\hat{H}t/\hbar)|\Psi(0)\rangle = \hat{U}(t)|\Psi(0)\rangle$$

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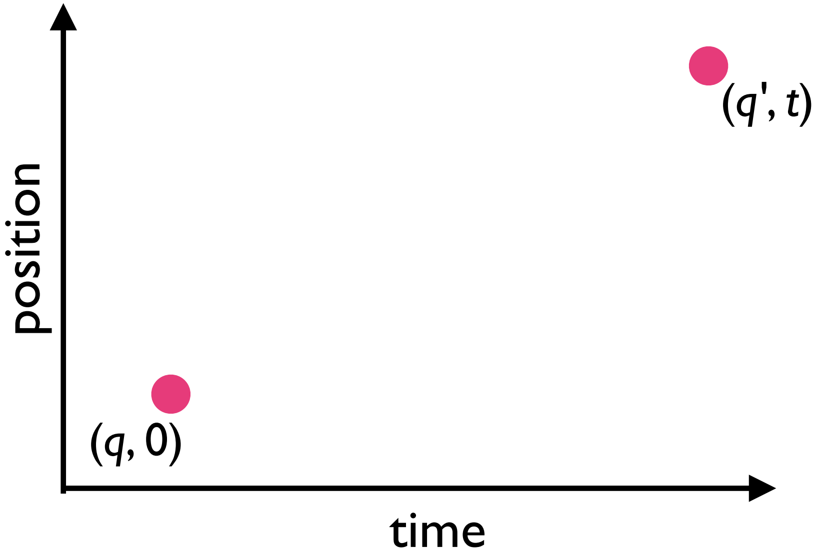
$$\begin{aligned}\langle q'|\Psi(t)\rangle &= \langle q'|\exp(-i\hat{H}t/\hbar)|\Psi(0)\rangle \\ &= \int dq\langle q'|\exp(-i\hat{H}t/\hbar)|q\rangle\langle q|\Psi(0)\rangle \\ &= \int dq\langle q'|\exp(-i\hat{H}t/\hbar)|q\rangle\Psi(q,0)\end{aligned}$$



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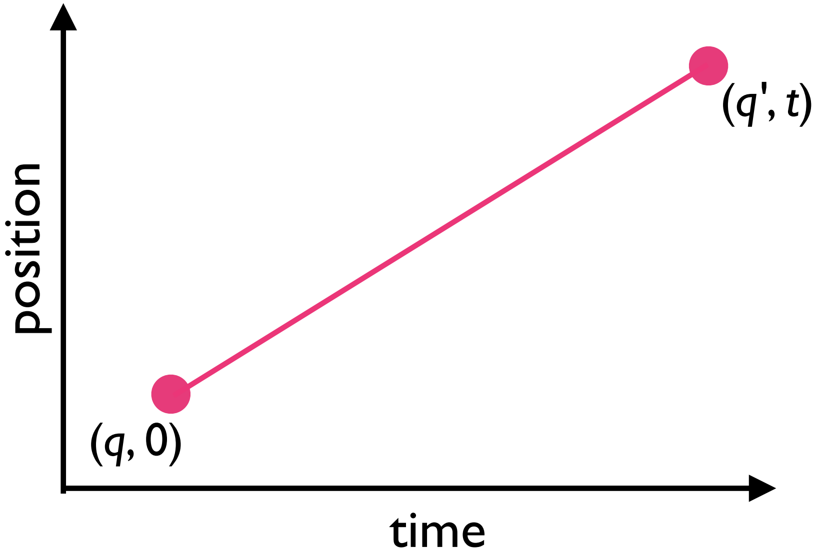

Probability of finding particle at (q’,t):

$$P(q,0;q',t) = |\langle q'|\hat{U}(t)|q\rangle|^2$$

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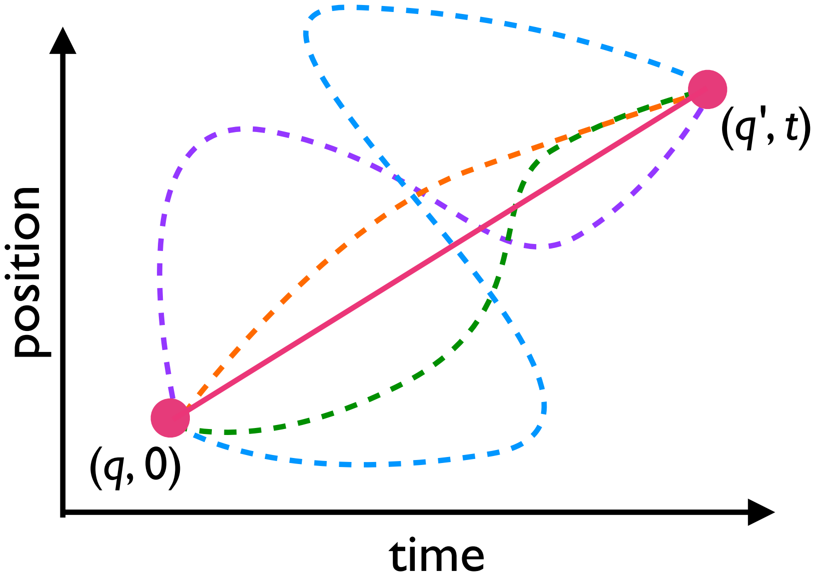

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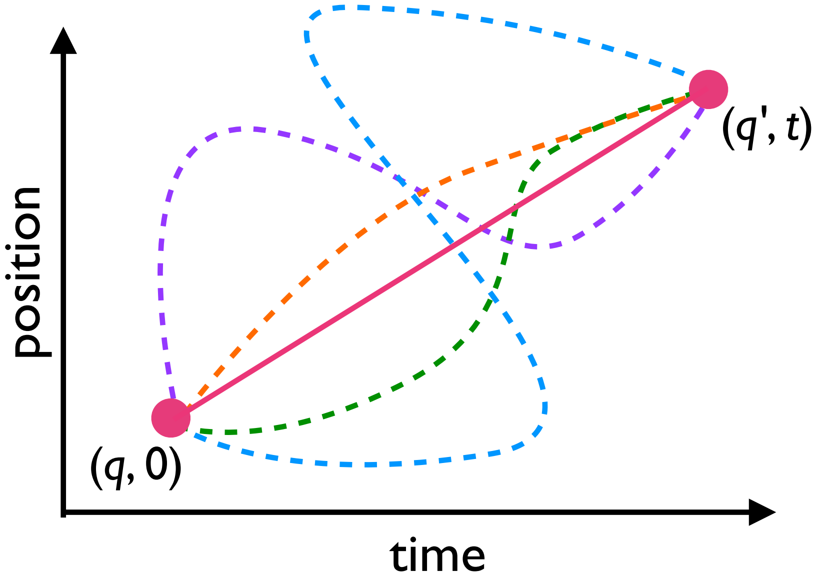

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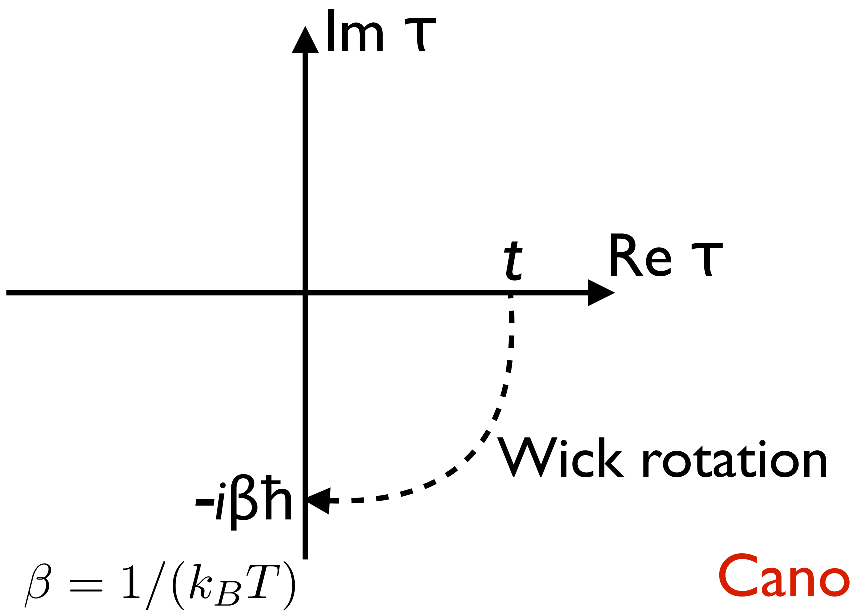
Must evaluate matrix elements of this form

Rotating to imaginary time

- How to do it? — Can we exploit some kind of isomorphism?



Canonical Density Matrix
⇒Quantum Statistical Mechanics

$$\hat{U}(t) = \exp(-i\hat{H}t/\hbar) \underset{t\,=\,-i\beta\hbar}{=} \exp(-\beta\hat{H}) = \hat{\rho}(\beta)$$

Now must evaluate the following matrix element

$$\rho(q, q', \beta) = \langle q'|\exp(-\beta\hat{H})|q\rangle = \langle q'|\hat{\rho}(\beta)|q\rangle$$

Computing the quantum canonical density matrix

- Can we compute these matrix elements without dealing with operators?

$$\exp(-\beta\hat{H}) = e^{-\beta[\hat{K}(p)+\hat{V}(q)]} \neq e^{-\beta\hat{K}(p)}e^{-\beta\hat{V}(q)}$$

K and V do not commute

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- Trotter theorem: $e^{\hat{A}+\hat{B}} = \lim_{n\to\infty} [e^{\hat{A}/2n} e^{\hat{B}/n} e^{\hat{A}/2n}]^n$

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- Using the theorem we get:

$$\rho(q,q',\beta) = \lim_{n\to\infty}\langle q'|[e^{-\beta\hat{K}(p)/2n}e^{-\beta\hat{V}(q)/n}e^{-\beta\hat{K}(p)/2n}]^n|q\rangle$$

$$= \langle q'|[e^{-\beta_n\hat{K}(p)/2}e^{-\beta_n\hat{V}(q)}e^{-\beta_n\hat{K}(p)/2}][e^{-\beta_n\hat{K}(p)/2}e^{-\beta_n\hat{V}(q)}e^{-\beta_n\hat{K}(p)/2}][e^{-\beta_n\hat{K}(p)/2}e^{-\beta_n\hat{V}(q)}e^{-\beta_n\hat{K}(p)/2}]\ldots|q\rangle$$

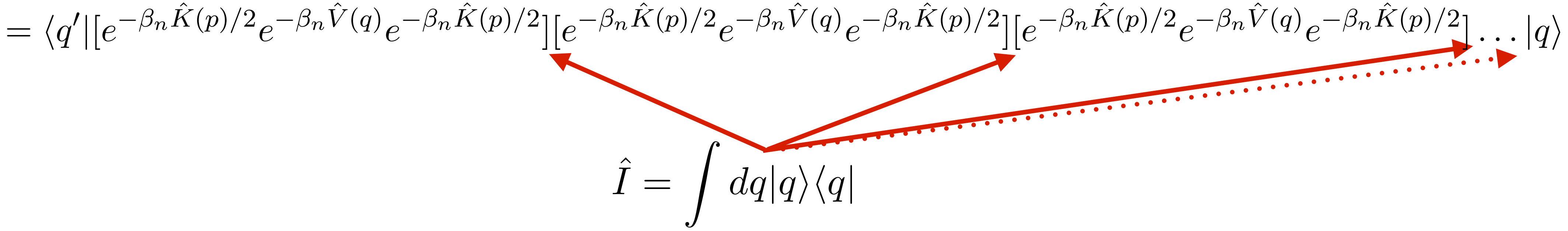
with $\beta_n = \beta/n$

βħ (imaginary time)
has been divided in n slices

Computing the quantum canonical density matrix

- Now we can introduce *n*-1 identities (position eigenstates) in ρ:

$$\rho(q,q',\beta) =$$



$$= \langle q'|[e^{-\beta_n \hat{K}(p)/2} e^{-\beta_n \hat{V}(q)} e^{-\beta_n \hat{K}(p)/2}][e^{-\beta_n \hat{K}(p)/2} e^{-\beta_n \hat{V}(q)} e^{-\beta_n \hat{K}(p)/2}][e^{-\beta_n \hat{K}(p)/2} e^{-\beta_n \hat{V}(q)} e^{-\beta_n \hat{K}(p)/2}]\dots|q\rangle$$

$$\hat{I} = \int dq|q\rangle\langle q|$$

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- Each matrix element can be evaluated:

$$\begin{aligned}
\langle q_{k-1}|[e^{-\beta_n\hat{V}(q)/2}e^{-\beta_n\hat{K}(p)}e^{-\beta_n\hat{V}(q)/2}]\ \ |q_k\rangle \ &= \\
&= e^{-\beta_n V(q_{k-1})/2}\langle q_{k-1}|e^{-\beta_n\hat{K}(p)}|q_k\rangle e^{-\beta_n V(q_k)/2} = \\
&= e^{-\beta_n[V(q_{k-1})+V(q_k)]/2}\int dp\, e^{\beta_n K(p)}\langle q_{k-1}|p\rangle\langle p|q_k\rangle = \\
&= \frac{e^{-\beta_n[V(q_{k-1})+V(q_k)]/2}}{2\pi\hbar}\int dp\, e^{\beta_n p^2/2m+i(q_{k-1}-q_k)p/\hbar} = \\
&= \boxed{\frac{1}{2\pi\hbar}\left(\frac{2\pi m}{\beta_n}\right)^{1/2} e^{-\beta_n\left\{[V(q_{k-1})+V(q_k)]/2+\frac{m}{2\beta_n^2\hbar^2}(q_k-q_{k-1})^2\right\}}}
\end{aligned}$$

$$\langle q|p\rangle = \frac{1}{\sqrt{2\pi}}e^{ipq/\hbar}$$

complete the square
⇒ Gaussian integral

We got rid of the operators!

Computing the quantum canonical density matrix

- So, the final result is:

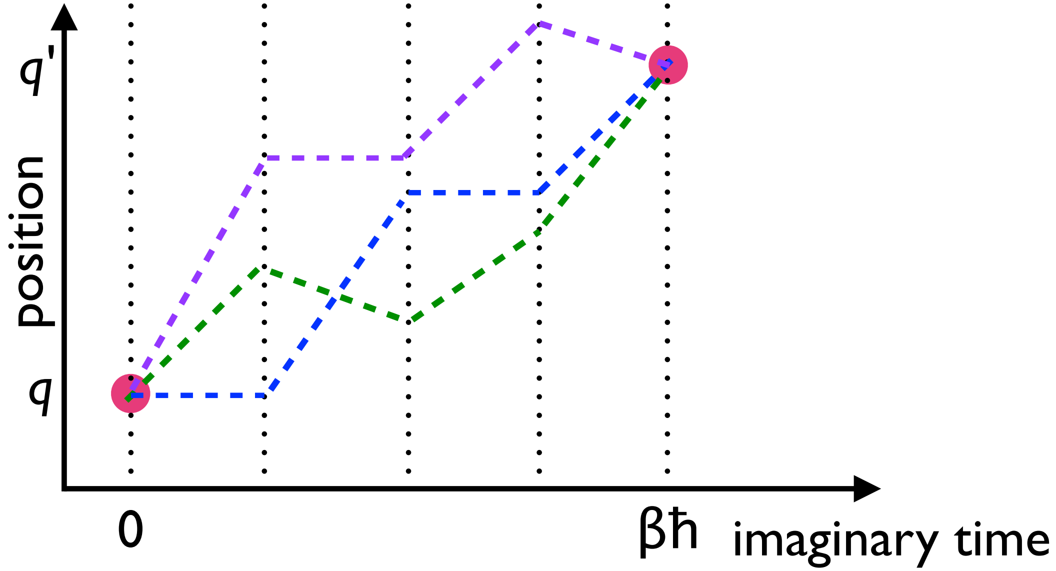
harmonic interaction between neighboring points of a path

$$\omega_n = 1/(\beta_n \hbar)$$

$$\rho_n(q,q',\beta) = \frac{1}{(2\pi\hbar)^n}\left(\frac{2\pi m}{\beta_n}\right)^{n/2}\int dq_1 \ldots dq_{n-1} e^{-\beta_n \sum_k \{[V(q_{k-1})+V(q_k)]/2 + \frac{m\omega_n^2}{2}(q_k-q_{k-1})^2\}}$$

with $q_0 = q \quad q_n = q'$

$$\rho(q,q',\beta) = \lim_{n\to\infty} \rho_n$$



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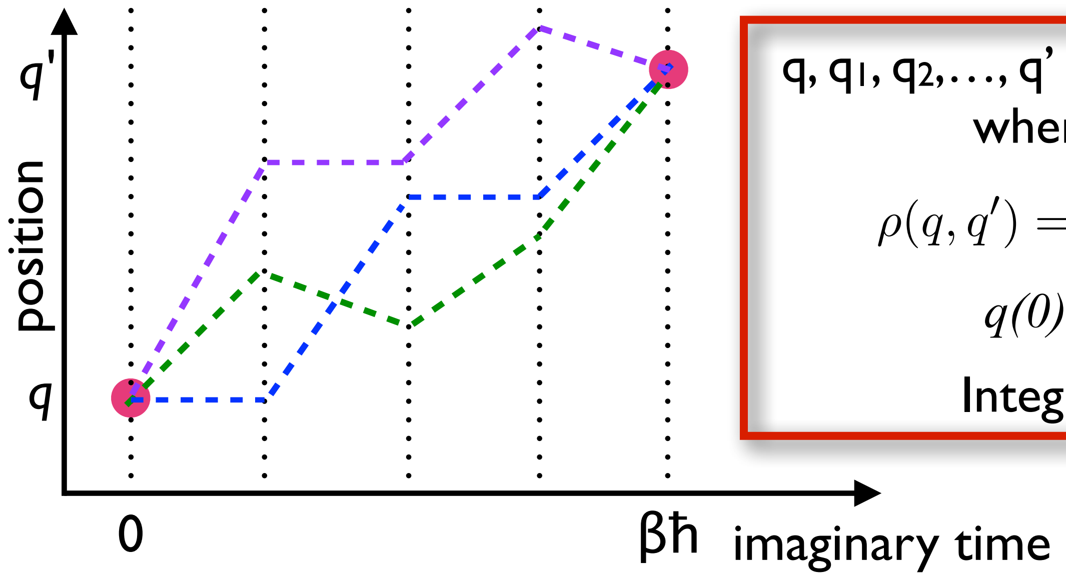

q, q₁, q₂,…, q’ consititute a path q(τ), where τ ∈ [0, βħ]

$$\rho(q,q') = \int \mathcal{D}[q(\tau)]e^{\Phi[q(\tau)]}$$

$q(0)=q,\ q(\beta\hbar)=q'$

Integral over paths

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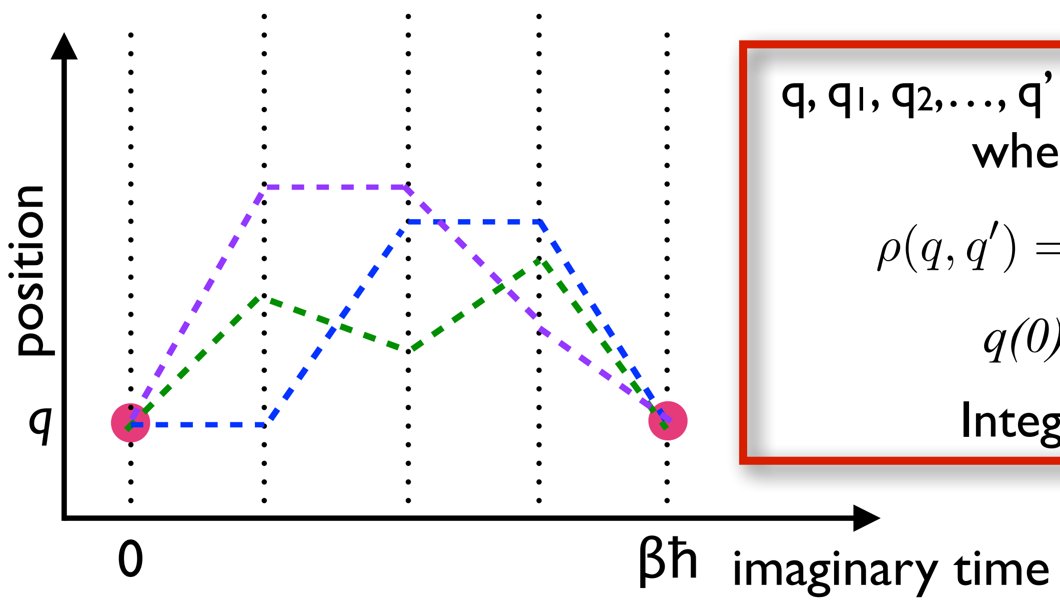

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Integral over paths

- <u>The partition function *Z* is:</u>

$$Z_n = \mathrm{Tr}[\hat{\rho}(\beta)] = \int dq \rho(q,q,\beta) = \frac{1}{(2\pi\hbar)^n}\left(\frac{2\pi m}{\beta_n}\right)^{n/2}\int dq_1 \ldots dq_n e^{-\beta_n \sum_k [V(q_k)+\frac{m\omega_n^2}{2}(q_k-q_{k-1})^2]}$$

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$$Z = \lim_{n\to\infty} Z_n$$

Sampling the partition function

- How to sample the partition function and get ensemble averages?

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- Reintroduce momenta

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Note that these are fictitious (sampling) masses
Could be set to any value!

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- Partition function of a *classical* ring polymer with Hamiltonian

$$H_n = \sum_k[\frac{p_k^2}{2m} + \frac{m\omega_n^2}{2}(q_k - q_{k-1})^2 + V(q_k)]$$

Can be sampled by Molecular Dynamics

Properties and estimators

$$H = \frac{p^2}{2m} + V(q)$$

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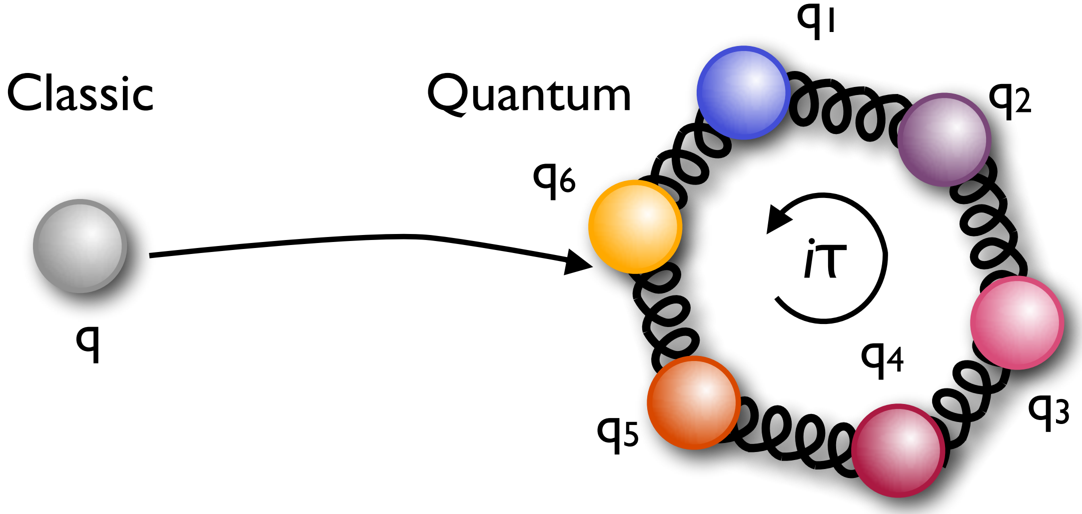

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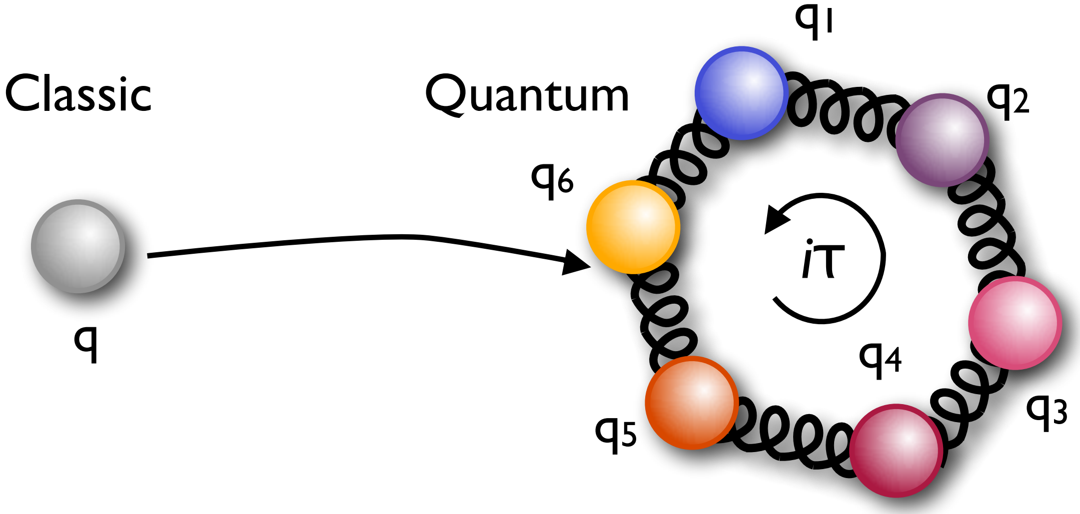

- Each bead evolves at temperature *nT*
- *n* determined by how “quantum” the problem is
- $n > \beta\hbar\omega_{max}$ (typically between 10 and 100)

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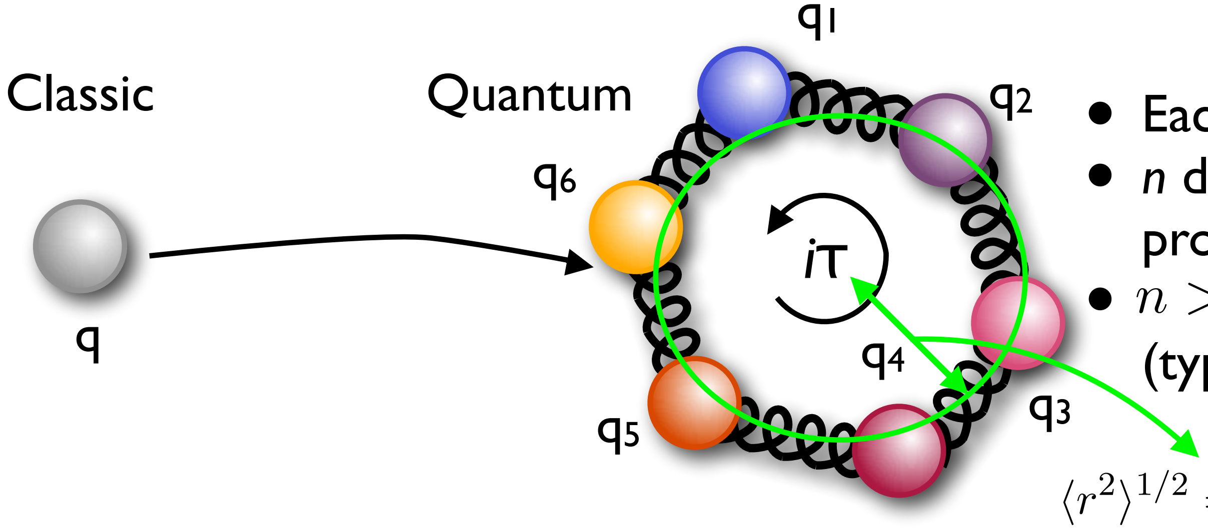

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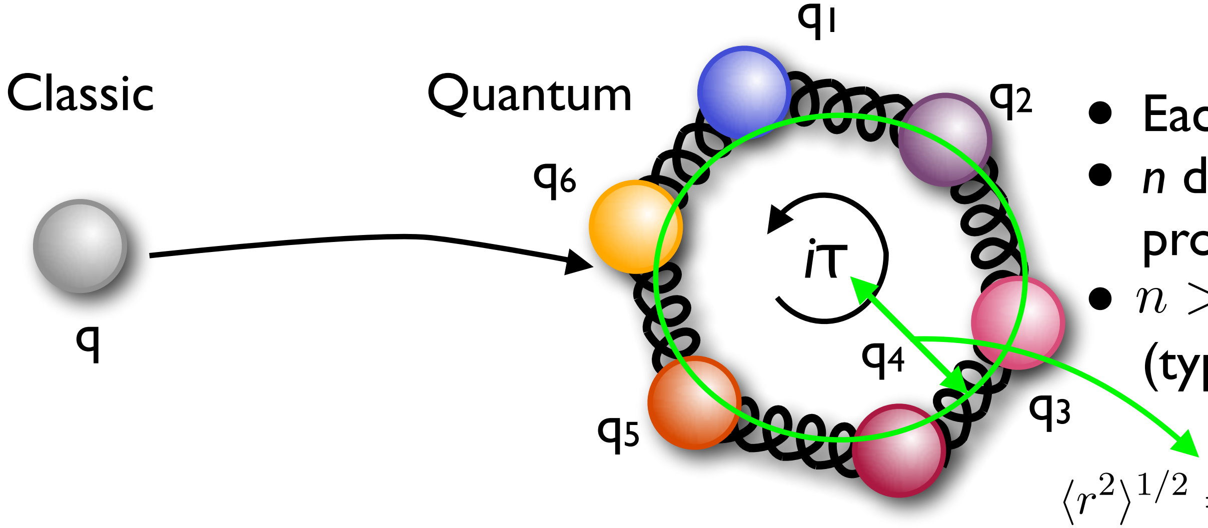
$$\langle r^2 \rangle^{1/2} = \Lambda/\sqrt{8\pi} \qquad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

Properties and estimators

$$H = \frac{p^2}{2m} + V(q) \qquad H_n = \sum_k \left[\frac{p_k^2}{2m} + \frac{m\omega_n^2}{2}(q_k - q_{k-1})^2 + V(q_k)\right]$$



- Each bead evolves at temperature *nT*
- *n* determined by how "quantum" the problem is
- $n > \beta\hbar\omega_{max}$ (typically between 10 and 100)

$$\langle r^2\rangle^{1/2} = \Lambda/\sqrt{8\pi} \qquad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

- Ensemble averages of operators

$$\langle A\rangle = \frac{1}{Z}\mathrm{Tr}[\hat\rho\hat A]$$

If: $\hat A = \hat A(q)$

Then: $\langle A\rangle = \frac{1}{Z}\int d\mathbf{p}\int d\mathbf{q}\,\frac{1}{n}\sum_k A(q_k)\; e^{-\beta_n H_n}$

Else: complicated — open paths, etc.
(e.g. Lin, Morrone, Car PRL 105, 110602)

$\bar{\mathbf{q}} = 1/n\sum_i \mathbf{q}_i$

Some examples: $\langle V\rangle = \frac{1}{n}\sum_{i=1}^{n}\langle V(\mathbf{q}_i)\rangle$

$$\langle K_{cv}\rangle = \frac{3Nk_BT}{2} + \frac{1}{2n}\sum_{j=1}^{N}\sum_{i=1}^{n}\langle(\mathbf{q}_i^j - \bar{\mathbf{q}}^j)\cdot\nabla V(\mathbf{q}_i^1,\ldots,\mathbf{q}_i^N)\rangle$$

(From thermodynamic relation)

The Nuts and Bolts of the PIMD simulation

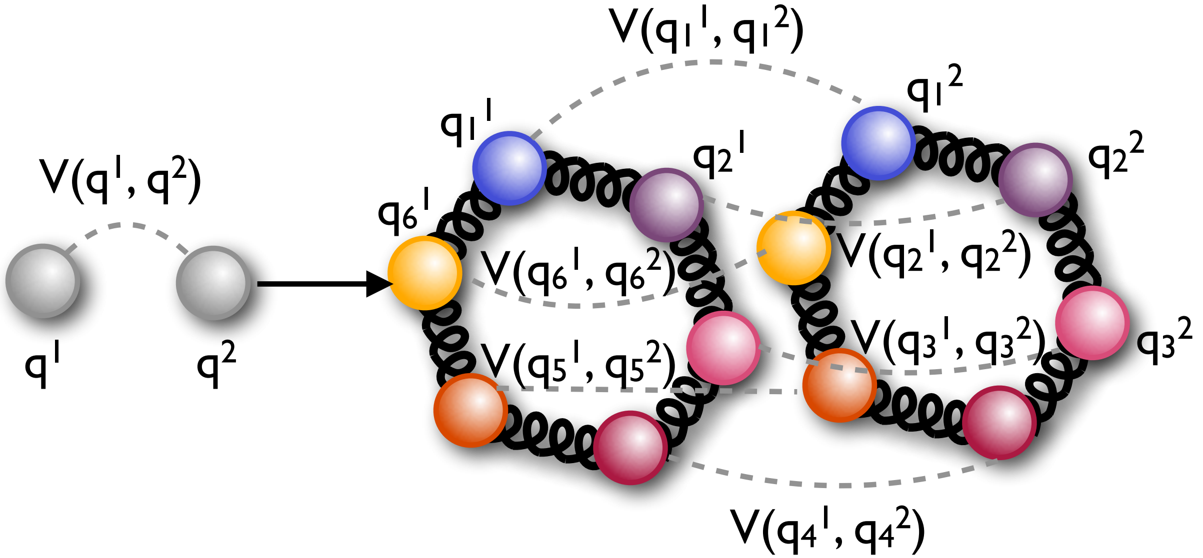
- For a system of N distinguishable particles:

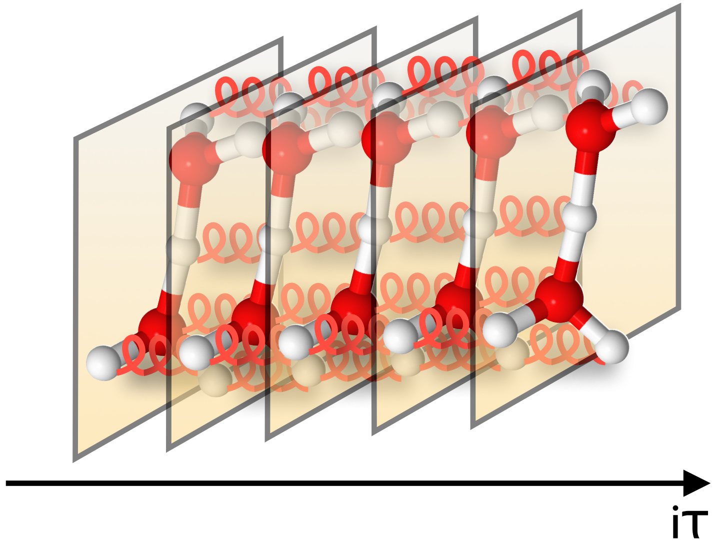
potential,
e.g. from first-principles
electronic structure

atom index

$$H_n = \sum_{k=1}^{n} \sum_{j=1}^{N} [\frac{(\mathbf{p}_k^j)^2}{2m^j} + \frac{1}{2} m^j \omega_n^2 (\mathbf{q}_k^j - \mathbf{q}_{k-1}^j)^2] + \sum_{k=1}^{n} V(\mathbf{q}_k^1, \mathbf{q}_k^2, \dots \mathbf{q}_k^N)$$

bead index





- Problem is exactly like (*ab initio*) molecular dynamics, but involving several replicas of the system

The Nuts and Bolts of the PIMD simulation

- For a system of N distinguishable particles:

$$H_n = \overbrace{\sum_{k=1}^{n}\sum_{j=1}^{N}\left[\frac{(\mathbf{p}_k^j)^2}{2m^j} + \frac{1}{2}m^j\omega_n^2(\mathbf{q}_k^j - \mathbf{q}_{k-1}^j)^2\right]}^{H_0 \text{ (free ring polymer Hamiltonian)}} + \sum_{k=1}^{n} V(\mathbf{q}_k^1, \mathbf{q}_k^2, \ldots \mathbf{q}_k^N)$$

- H_0 can be solved analytically by transforming it into normal modes

$$H_0 = \sum_{j}^{N}\sum_{s=0}^{n-1}\left[\frac{\tilde{\mathbf{p}}_s^j}{2m^j} + \frac{1}{2}m^j\omega_s^2(\tilde{\mathbf{q}}_s^j)^2\right]$$

$$\omega_s = 2\omega_n \sin(s\pi/n)$$

$$\tilde{\mathbf{p}}_s^j = \sum_{k=1}^{n}\mathbf{p}_k^j C_{ks} \qquad \tilde{\mathbf{q}}_s^j = \sum_{k=1}^{n}\mathbf{q}_k^j C_{ks}$$

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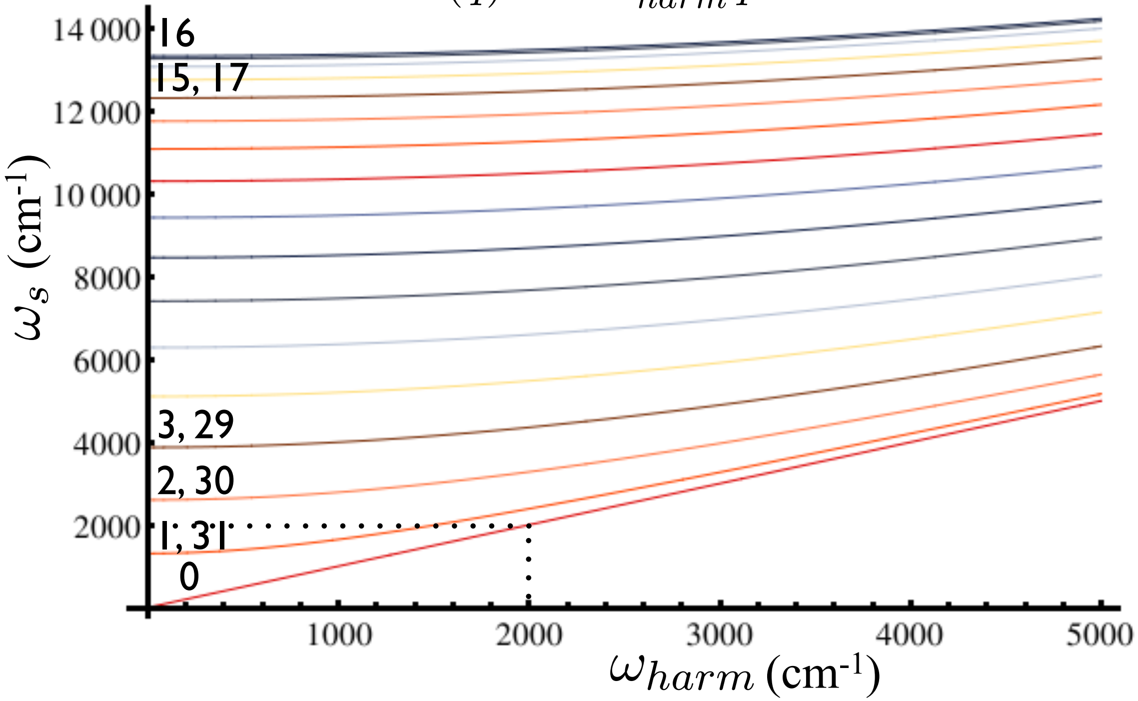
- Could be painful to integrate the high frequencies numerically (would need small time steps)

For a harmonic oscillator at 300K with 32 beads

$$V(q) = m\omega_{harm}^2 q^2$$



Integrating PIMD Equations of Motion

- How to integrate the PIMD equations of motion efficiently?

$$H_n = \sum_{k=1}^{n}\sum_{j=1}^{N}[\frac{(\mathbf{p}_k^j)^2}{2m^j} + \frac{1}{2}m\omega_n^2(\mathbf{q}_k^j - \mathbf{q}_{k-1}^j)^2] + \sum_{k=1}^{n} V(\mathbf{q}_k^1, \mathbf{q}_k^2, \ldots \mathbf{q}_k^N)$$

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- Small digression about the Liouville operator

For a quantity *a* evolving by Hamiltonian dynamics (in 1D):

$$\frac{d\,a}{dt} = \frac{d\,a}{dq}\dot{q} + \frac{d\,a}{dp}\dot{p}$$

$$\frac{d\,a}{dt} = \frac{da}{dq}\frac{\partial H}{\partial p} - \frac{da}{dp}\frac{\partial H}{\partial q}$$

One can define the Liouville operator *L:*

$$iL = \frac{\partial H}{\partial p}\frac{d}{dq} - \frac{\partial H}{\partial q}\frac{d}{dp}$$

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Such that:

$$\frac{d\,a}{dt} = iLa \rightarrow a(t) = e^{iL}a(0)$$

We can also split the operator

$$iL = iL_1 + iL_2$$

$$L_1 = \frac{\partial H}{\partial p}\frac{d}{dq} \qquad L_2 = -\frac{\partial H}{\partial q}\frac{d}{dp}$$

And the pieces *do not* commute

$$a(t) = e^{iL_1 + iL_2}a(0)$$

$$[iL_1, iL_2] \neq 0$$

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$$[iL_1, iL_2] \neq 0$$

In order to apply it piecewise, must again do a Trotter splitting

For microcanical dynamics, the (second order) Trotter splitting leads to the Verlet algorithm

Integrating PIMD Equations of Motion

- How to integrate the PIMD equations of motion efficiently?

$$H_n = \sum_{k=1}^{n}\sum_{j=1}^{N}[\frac{(\mathbf{p}_k^j)^2}{2m^j} + \frac{1}{2}m^j\omega_n^2(\mathbf{q}_k^j - \mathbf{q}_{k-1}^j)^2] + \sum_{k=1}^{n} V(\mathbf{q}_k^1, \mathbf{q}_k^2, \dots \mathbf{q}_k^N)$$

$$H_n = H_0 + H_V$$

- Hamiltonian dynamics can be evolved with the Liouville operator, which here can be factorized in the following way:

$$e^{iL\Delta t} \simeq e^{iL_V\Delta t/2} e^{iL_0\Delta t} e^{iL_V\Delta t/2}$$

Involves H_V

Involves H_0

Involves H_V

$$H_0 \quad = \quad \sum_{j}^{N}\sum_{s=0}^{n-1}\left[\frac{\tilde{\mathbf{p}}_s^j}{2m^j} + \frac{1}{2}m^j\omega_s^2(\tilde{\mathbf{q}}_s^j)^2\right]$$

The middle step can be computed analytically
(especially easy in the normal mode representation)
⇒ Resulting dynamics of a free particle would be independent of time step

Attention: In a real system modes couple (resonate) — maximum time step is constrained!

Integrating PIMD Equations of Motion

- The actual scheme for integrating then becomes:

$$p_k^j \leftarrow p_k^j - \frac{\Delta t}{2} \frac{\partial V(q_k^1, ..., q_k^N)}{\partial q^j}$$

$$\tilde{p}_s^j = \sum_{k=1}^{n} p_k^j C_{ks} \quad \tilde{q}_s^j = \sum_{k=1}^{n} q_k^j C_{ks}$$

Textbook time evolution for set of uncoupled harmonic oscillators

$$\begin{pmatrix} \tilde{p}_s^j \\ \tilde{q}_s^j \end{pmatrix} \leftarrow \begin{pmatrix} \cos(\omega_s \Delta t) & -m_j \omega_s \sin(\omega_s \Delta t) \\ \frac{1}{m_j \omega_s} \sin(\omega_s \Delta t) & \cos(\omega_s \Delta t) \end{pmatrix} \begin{pmatrix} \tilde{p}_s^j \\ \tilde{q}_s^j \end{pmatrix}$$

$$p_k^j = \sum_{s=0}^{n-1} C_{ks} \tilde{p}_s^j \quad q_k^j = \sum_{s=0}^{n-1} C_{ks} \tilde{q}_s^j$$

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$$p_k^j \leftarrow \text{thermostat}\,(\Delta t/2)$$

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$$p_k^j = \sum_{s=0}^{n-1} C_{ks}\tilde{p}_s^j \qquad q_k^j = \sum_{s=0}^{n-1} C_{ks}\tilde{q}_s^j$$

$$p_k^j \leftarrow p_k^j - \frac{\Delta t}{2}\frac{\partial V(q_k^1, ..., q_k^N)}{\partial q^j}$$

$$p_k^j \leftarrow \text{thermostat}\,(\Delta t/2)$$

To sample the
ensemble efficiently,
attach (massive)
thermostats to beads

Some last considerations: reduce computational cost

- How can we reduce the number of beads needed for computation?
  - Ring polymer contraction

    Markland, Manolopoulos, CPL 464, 256 (2008)

  - Using higher order integrators (and better estimators)

    Jang, Jang, Voth, JCP 115 , 7832 (2001)

  - Smart thermostatting of internal modes (generalized Langevin equation based colored noise thermostats)

    Ceriotti, Parinello, Markland, Manolopoulos, JCP 133, 124104 (2010)

A few applications

NATURE | VOL 397 | 18 FEBRUARY 1999 |

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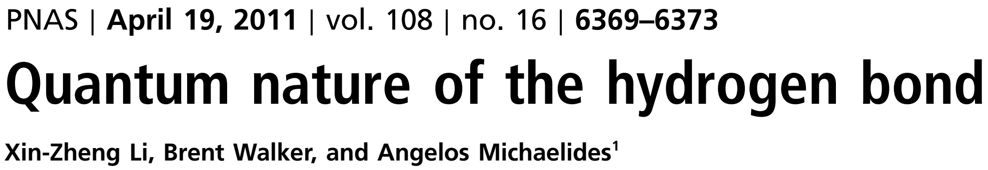

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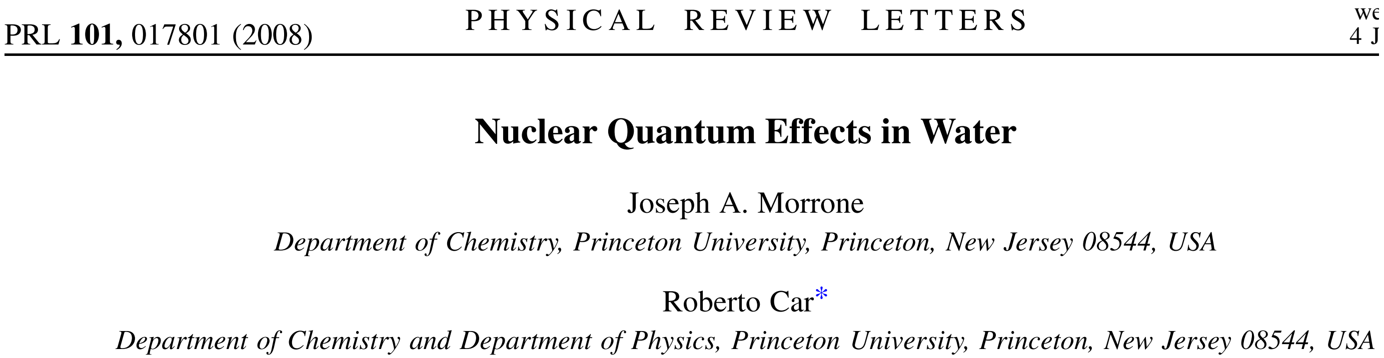

PRL **101,** 017801 (2008) PHYSICAL REVIEW LETTERS we 4 J

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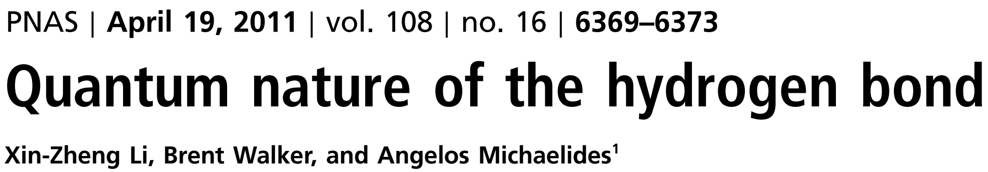
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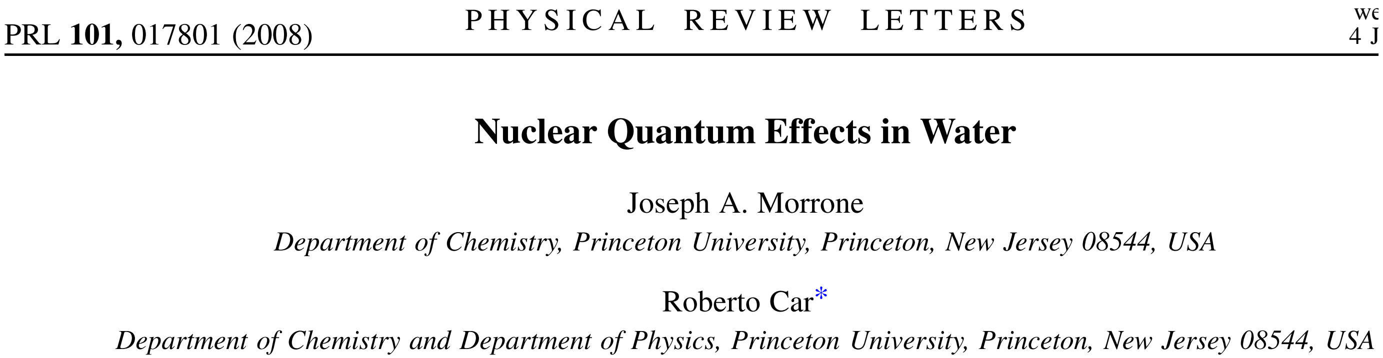
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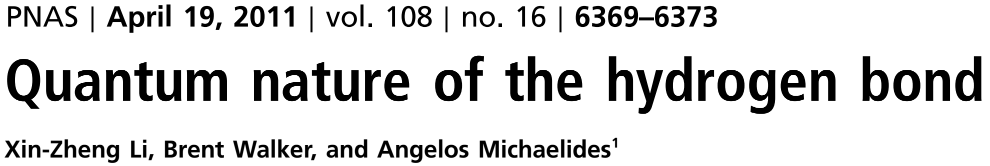

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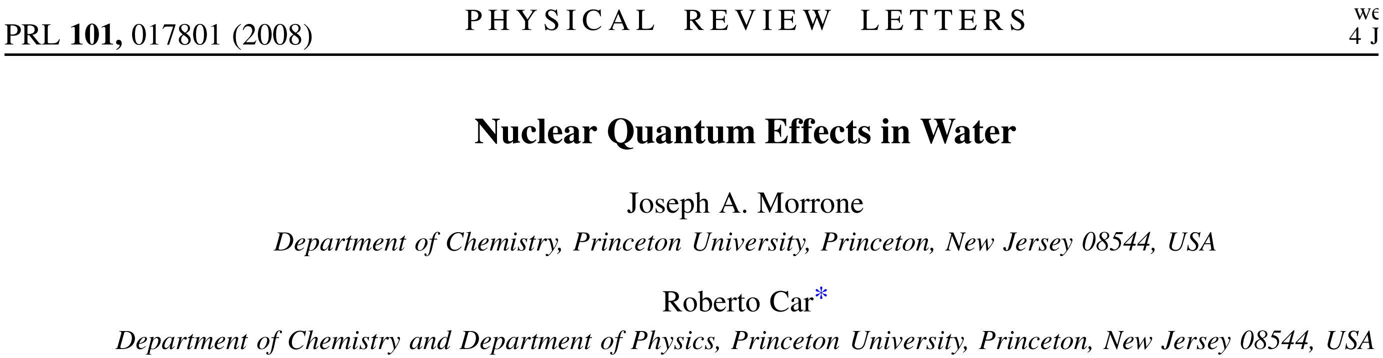

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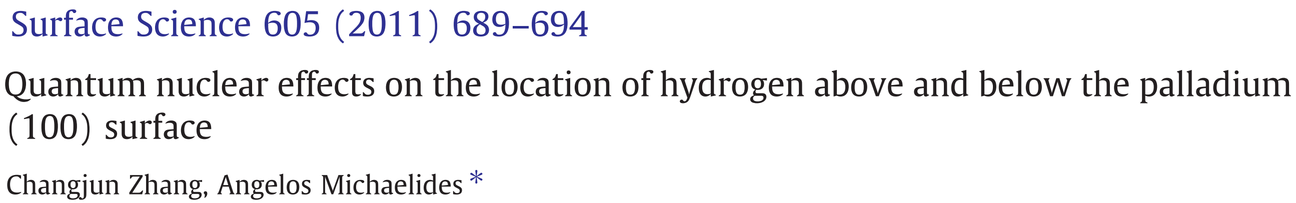

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MANY MANY MORE!!!

Dynamical Observables

Approximating dynamical observables

- PIMD uses ring polymer trajectories to calculate exact (static) averages of the form

$$\langle A \rangle = \frac{1}{Z} \mathrm{Tr}[e^{-\beta \hat{H}} \hat{A}]$$

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- But many important quantities are actually given by time dynamic (time dependent) averages:

Time correlation function

$$c_{AB}(t) = \mathrm{Tr}[e^{-\beta\hat{H}}\hat{A}(0)\hat{B}(t)]$$

Diffusion coefficient

$$D(T) = \frac{1}{3}\int_0^\infty c_{\mathbf{v}\cdot\mathbf{v}}(t)\,dt$$

↖ velocity

IR spectrum (dipole adsorption cross section)

$$n(\omega)\alpha(\omega) = \frac{\pi\omega}{3\hbar c V\epsilon_0}(1-e^{-\beta\hbar\omega})C_{\mu\cdot\mu}(\omega)$$

$$C_{\mu\cdot\mu}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}c_{\mu\cdot\mu}(t)\,dt$$

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- PIMD does not give access to real time (propagation is in imaginary time) Approximate these quantities - easier to approximate Kubo transforms

$$\tilde{c}_{AB}(t) = \frac{1}{\beta}\int_0^\beta c_{AB}^{\lambda}(t) \qquad c_{AB}^{\lambda}(t) = \mathrm{Tr}[e^{-(\beta-\lambda)\hat{H}}\hat{A}(0)e^{-\lambda\hat{H}}\hat{B}(t)]$$

Path integral approximations for real time dynamics

- Normal mode transformation of free ring polymer Hamiltonian:

$$H_0 = \sum_{j}^{N} \sum_{s=0}^{n-1} \left[\frac{\tilde{\mathbf{p}}_s^j}{2(m^j)'} + \frac{1}{2} m^j \omega_s^2 (\tilde{\mathbf{q}}_s^j)^2 \right] \quad \begin{aligned} \omega_s &= 2\omega_n \sin(s\pi/n) \\ \omega_n &= n k_b T/\hbar \end{aligned}$$

s=0 ⇒ centroid mode; *s*≠0 ⇒ internal modes

*[1] Craig and Manolopoulos, JCP **121**, 3368 (2004)*
*[2] Cao and Voth, JCP **100**, 5093 (1994)*

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$$H_0 = \sum_{j}^{N}\sum_{s=0}^{n-1}\left[\frac{\tilde{\mathbf{p}}_s^j}{2(m^j)'} + \frac{1}{2}m^j\omega_s^2(\tilde{\mathbf{q}}_s^j)^2\right] \quad \begin{aligned}\omega_s &= 2\omega_n \sin(s\pi/n)\\ \omega_n &= nk_bT/\hbar\end{aligned}$$

s=0 ⇒ centroid mode; s≠0 ⇒ internal modes

- Ring polymer molecular dynamics (RPMD)[1]
  - *m'* = *m*, Newtonian dynamics, no thermostat
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*[1] Craig and Manolopoulos, JCP **121**, 3368 (2004)*
*[2] Cao and Voth, JCP **100**, 5093 (1994)*

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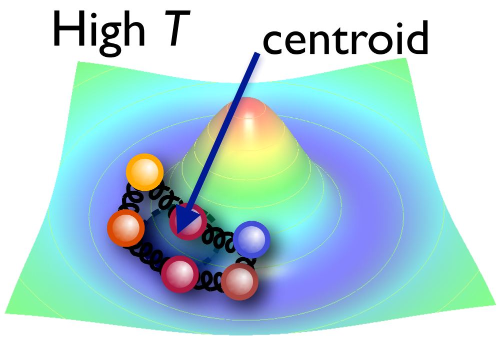
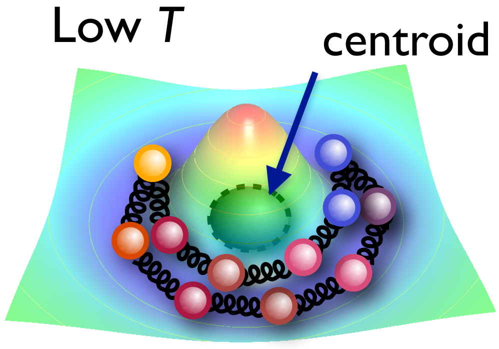
- Ring polymer molecular dynamics (RPMD)[1]
  - *m'* = *m*, Newtonian dynamics, no thermostat
  - Issue: beads resonate with physical frequencies
- Centroid molecular dynamics (CMD)[2]
  - *m'*=σ*m* (σ<1 for non-centroid modes), thermostatted
  - Centroid moves in the effective potential given by the internal modes
  - Issues: "curvature problem", and needs very small time steps.





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Model Application: IR spectrum of OH molecule

Rossi, Ceriotti, Manolopoulos, J. Chem. Phys. 140, 234116 (2014)

- Model OH molecule with interatomic interactions given by:

$$\phi = \frac{k_b}{2}(r - r_0)^2$$

Harmonic (parameters from JCP 130, 194510 (2009))

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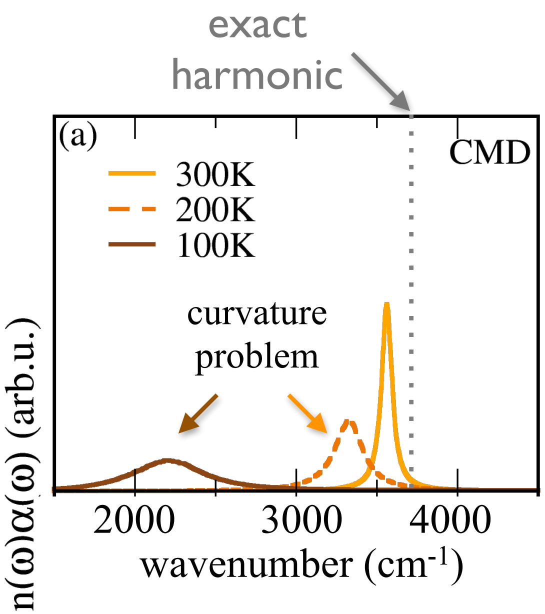

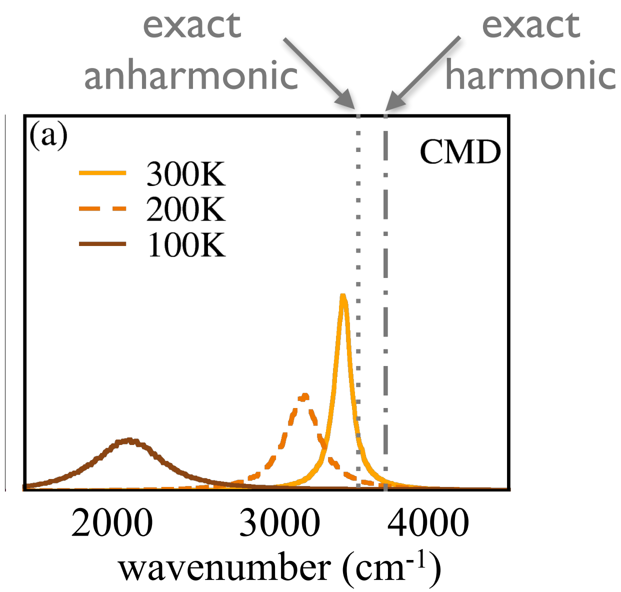

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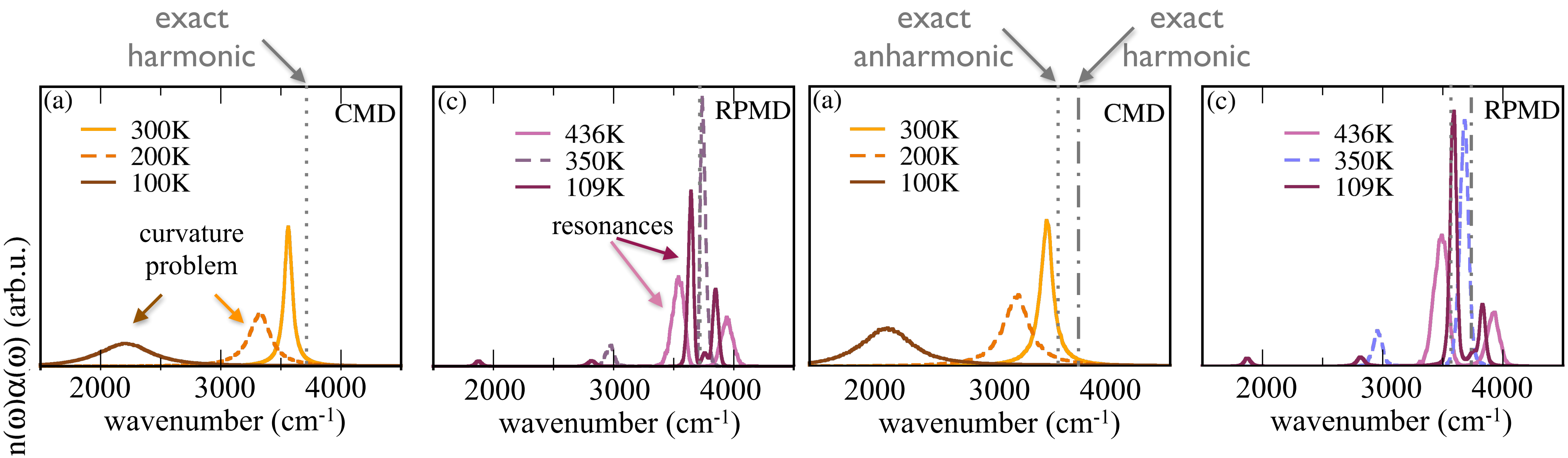

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s=0 ⇒ centroid mode; *s*≠0 ⇒ internal modes

Rossi, Ceriotti, Manolopoulos, J. Chem. Phys. 140, 234116 (2014)

- Thermostatted Ring Polymer Molecular Dynamics (TRPMD)
  - *m'*=*m*, white noise Langevin thermostat applied to *internal modes* of the ring polymer only (centroid obeys Hamiltonian dynamics)
  - Maintains *all* exact limits of RPMD (classic, harmonic, etc.)!
  - Time step needed is the same as in usual PI simulations
  - Equations of motion:

$$\frac{d}{dt}\tilde{\mathbf{p}}_i^{(k)} = -m_i \omega_k^2 \tilde{\mathbf{q}}_i^{(k)} - \gamma^{(k)} \tilde{\mathbf{p}}_i^{(k)} + \sqrt{\frac{2 m_i \gamma^{(k)}}{\beta_n}} \boldsymbol{\xi}_i^{(k)} \qquad \frac{d}{dt}\tilde{\mathbf{q}}_i^{(k)} = \tilde{\mathbf{p}}_i^{(k)}/m_i,$$

- Optimal damping (harmonic oscillator): $\gamma_c^{(k)} = \omega_k$
- Issue: no mathematical way to fix damping parameter, artificial broadening of peaks

Model Application: IR spectrum of OH molecule

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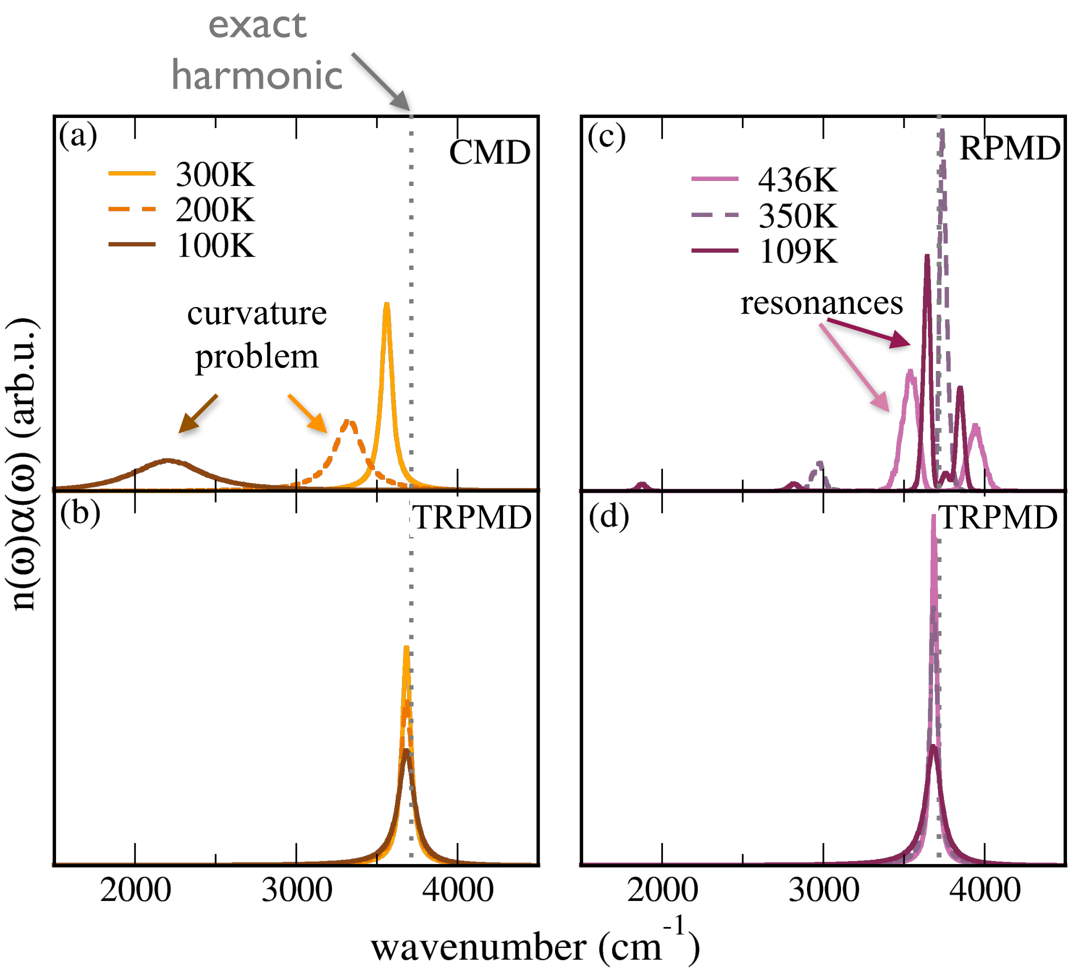

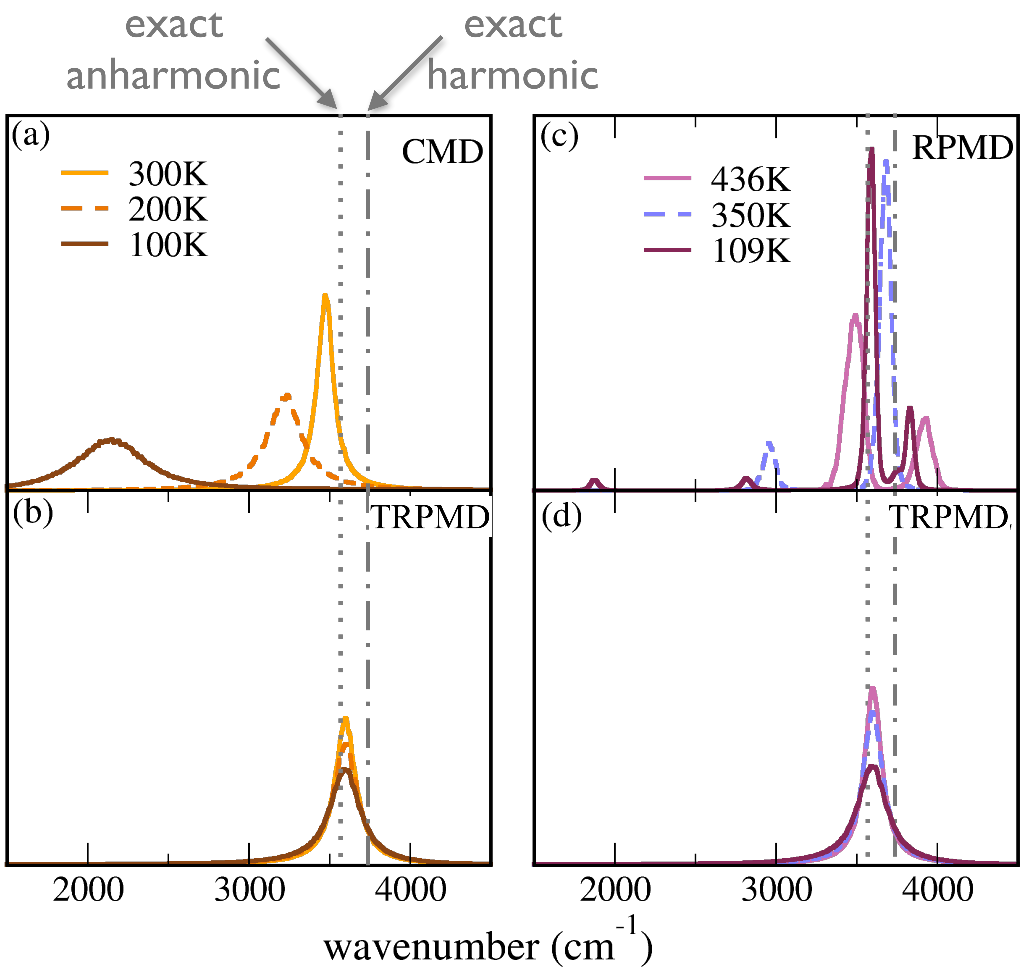

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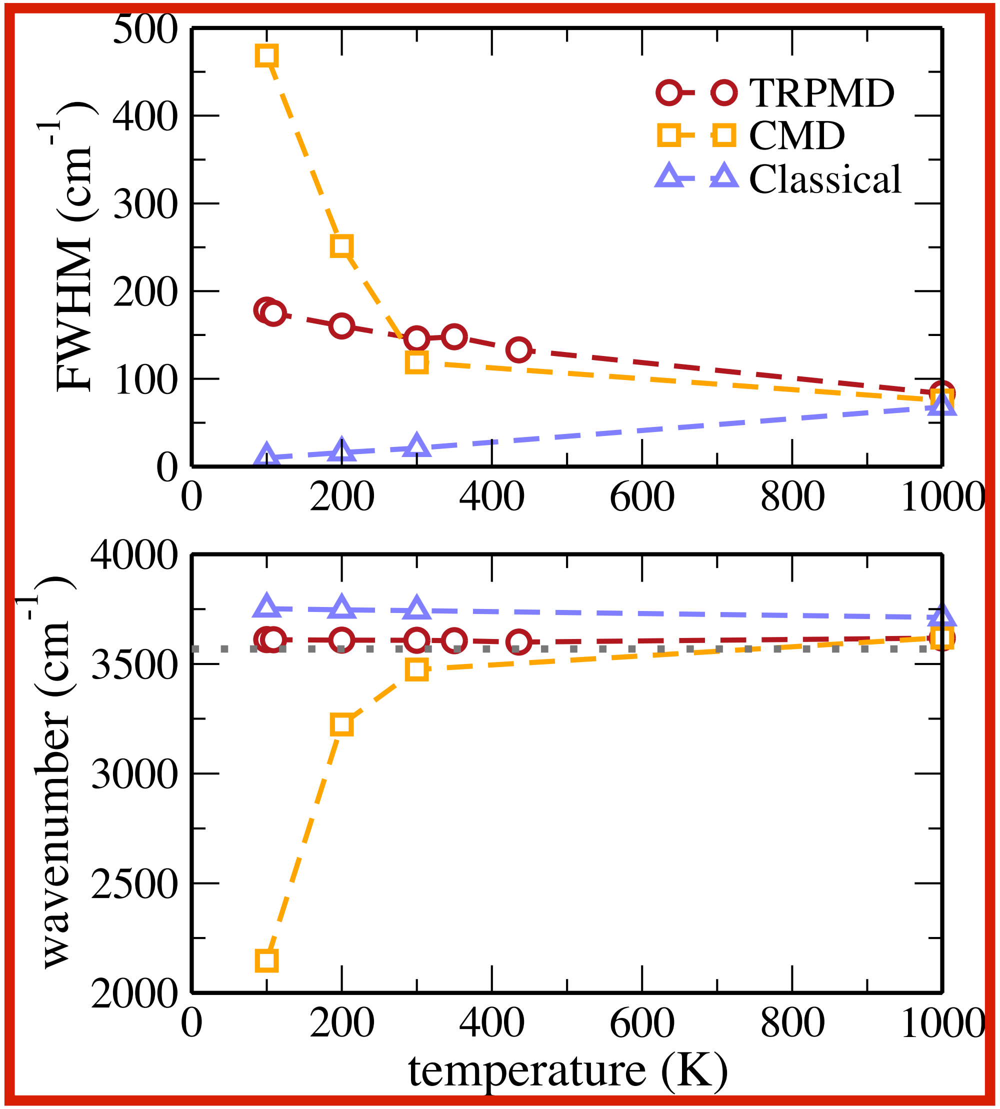
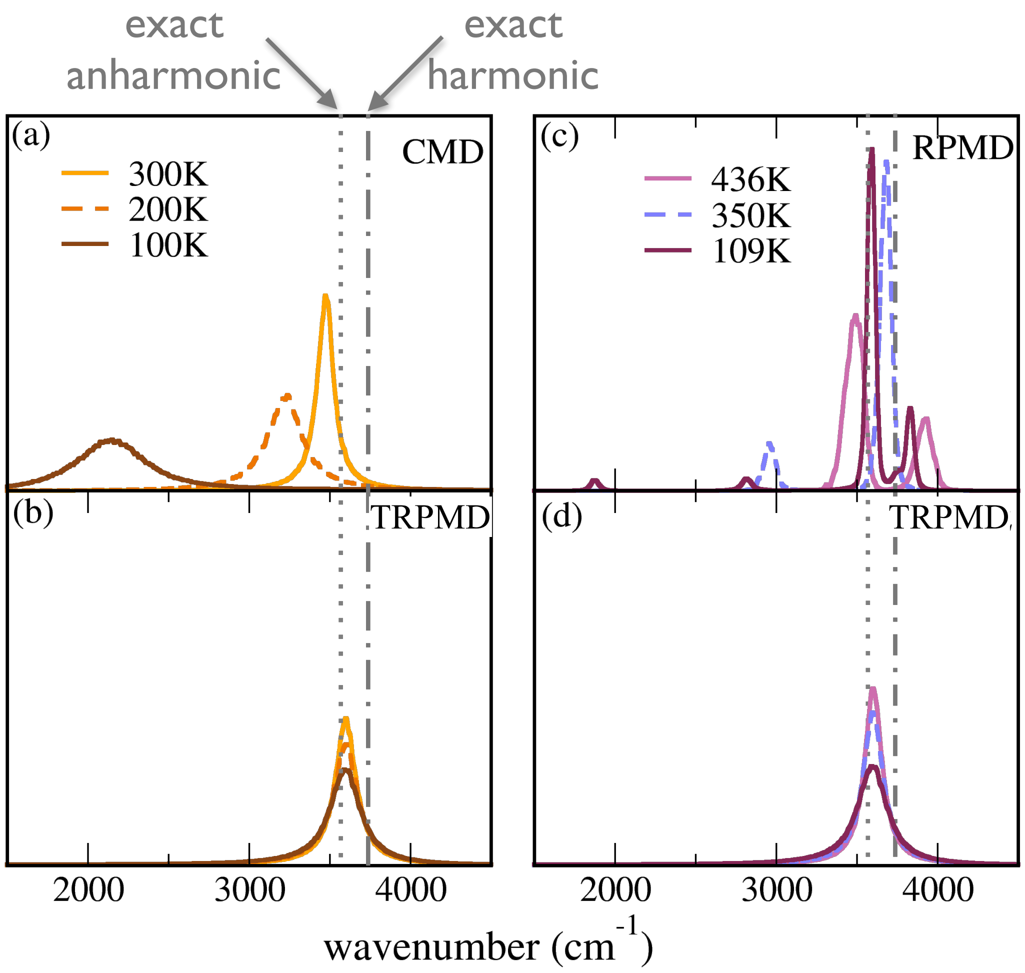
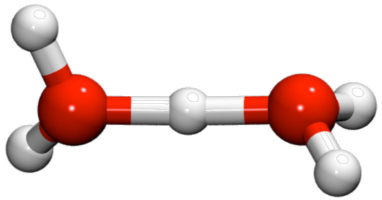


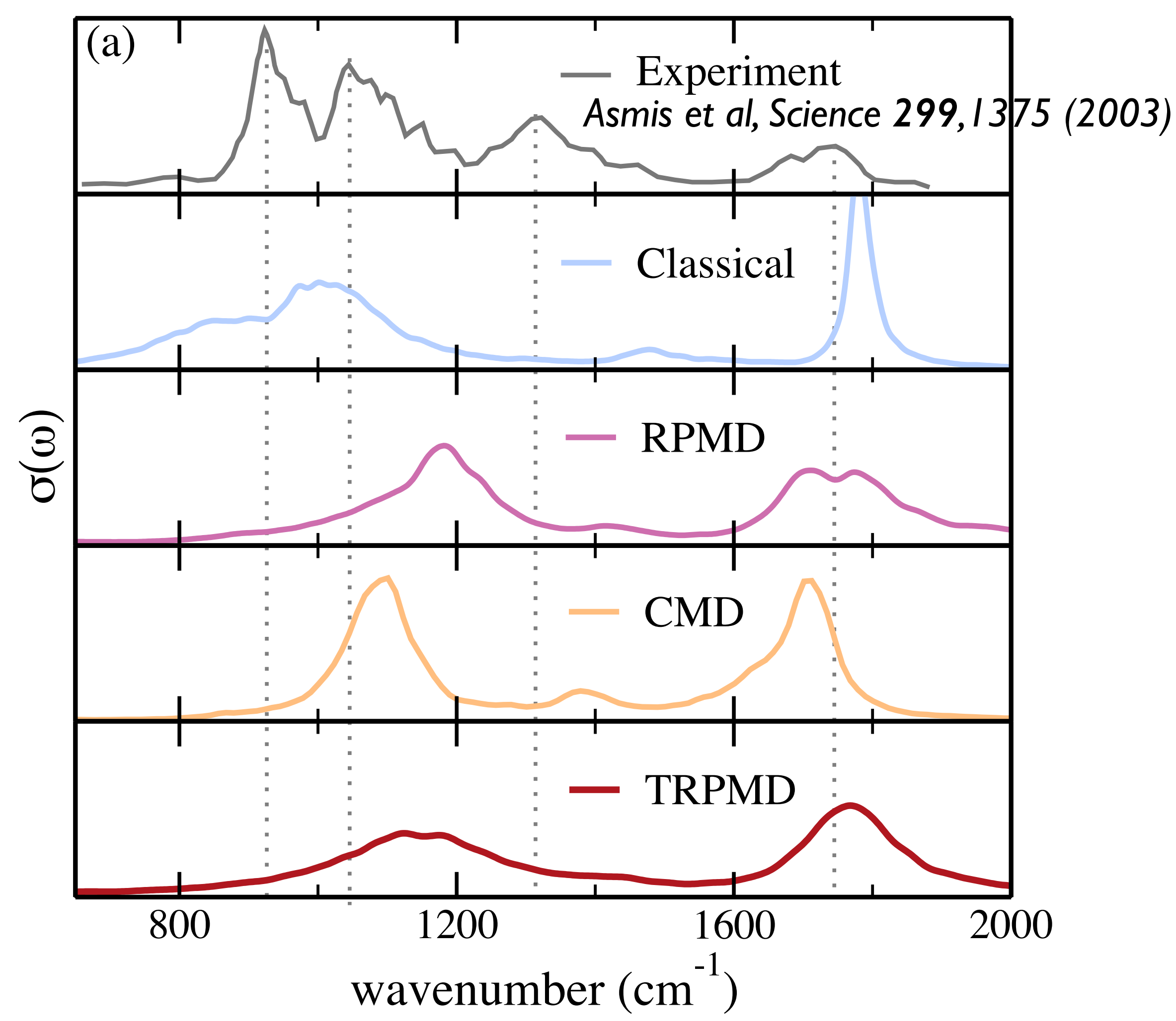


IR Spectrum of the Zundel Ion

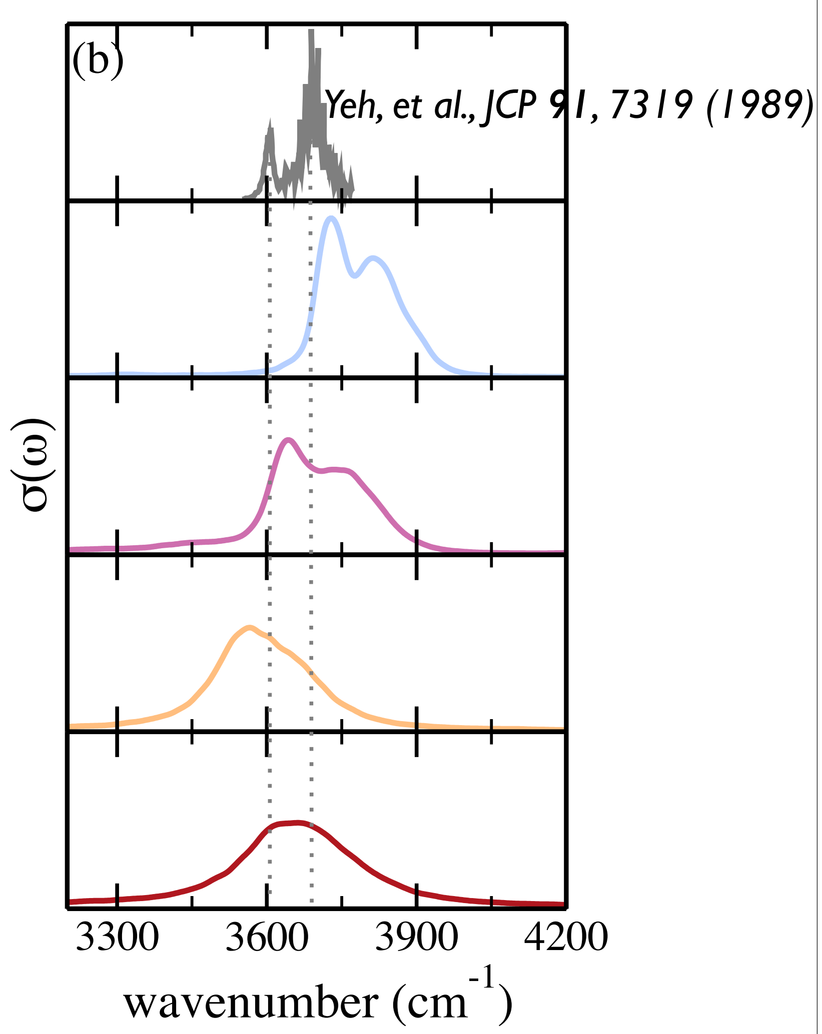
- Simulations on CCSD(T) parametrized potential of *Huang, Braams, Bowman, JCP 122, 044308 (2005)*



100K

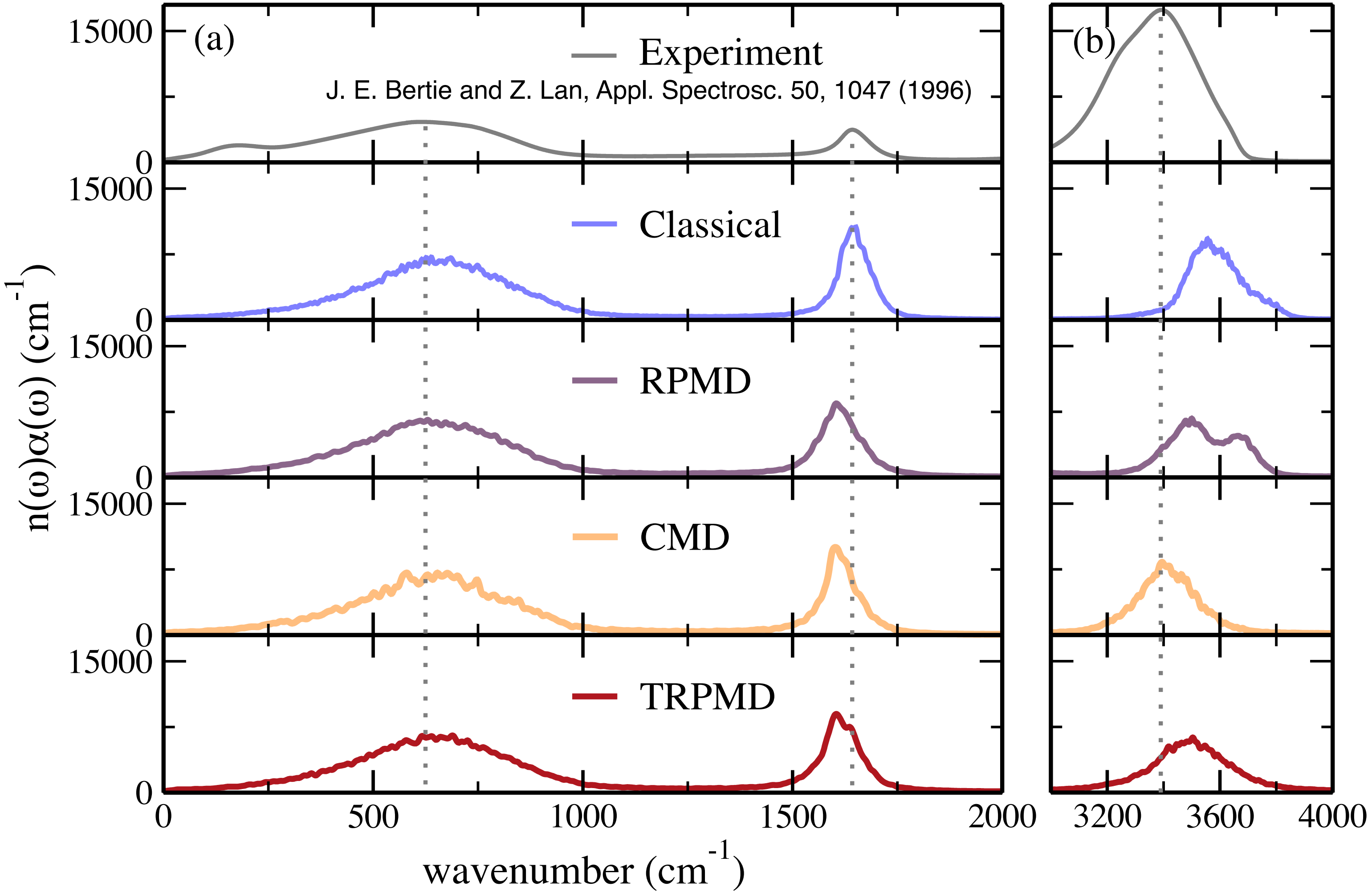


300K



IR Spectrum of Liquid Water

- Simulations on the q-TIP4Pf potential energy surface at 300K (box with 216 molecules)



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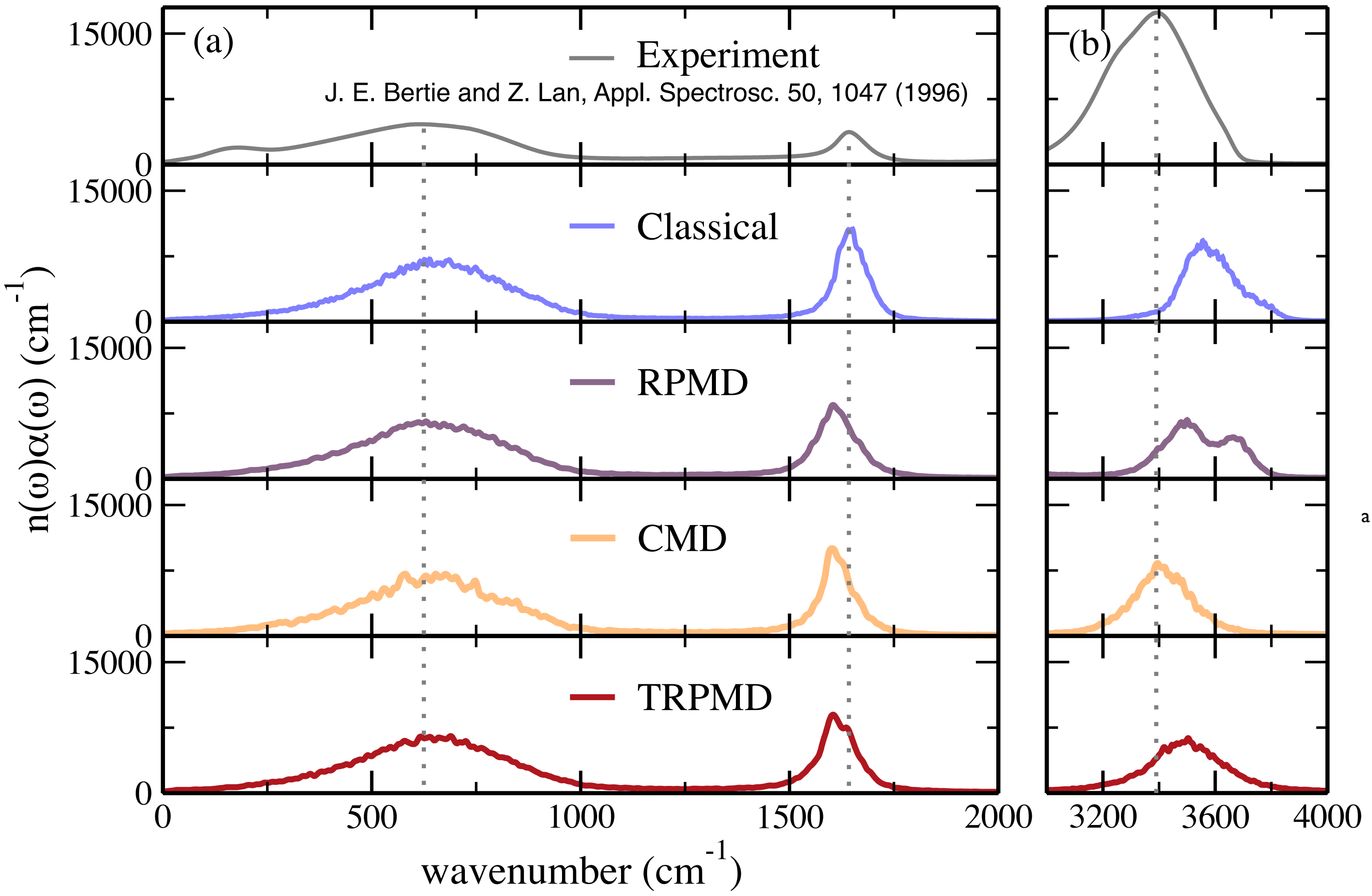

J. E. Bertie and Z. Lan, Appl. Spectrosc. 50, 1047 (1996)

Diffusion Coefficients

$$D = \frac{1}{3}\int_0^\infty \tilde{c}_{\mathbf{v}\cdot\mathbf{v}}(t)\,dt$$

	D
Class.	0.194(5)
RPMD	0.218(3)
CMD	0.219(2)
TRPMD	0.217(2)
Expt.	0.230

[a] Price, Ide, Arata, JPCA **103**, 448 (1999)

The End

References

Statistical Mechanics: Theory and Molecular Simulation
M. Tuckerman

Ab initio molecular dynamics: Theory and Implementation
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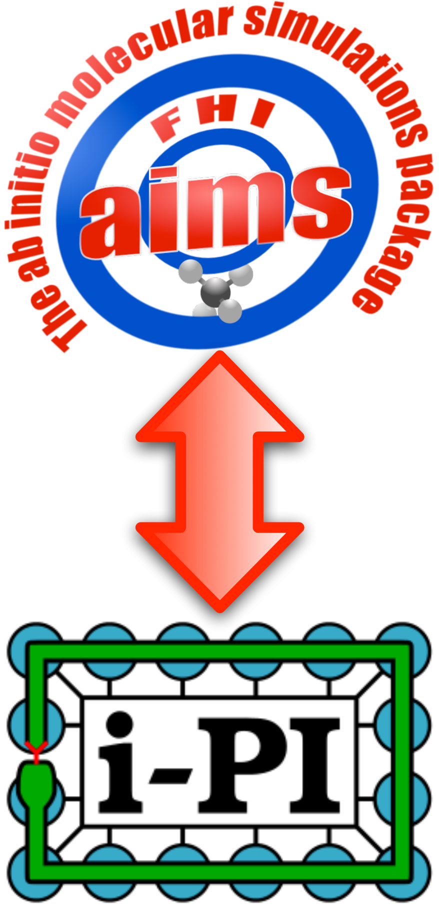
How to do it?

aims.fhi-berlin.mpg.de



imx-cosmo.github.io/gle4md/index.html?page=ipi

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Thank you!