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

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Where are nuclear quantum effects important?

- Relation between thermal De Broglie wavelength $\Lambda$ and interparticle spacing $l$

\[ \Lambda = \frac{h}{\sqrt{2\pi mk_BT}} \]

$\Lambda \gg l$

- Low temperature, low mass
- $\Rightarrow$ nuclear quantum effects important

$\Lambda \ll l$

- High temperature, high mass
- $\Rightarrow$ classical Boltzmann statistics are fine

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- How far from equipartition of energy? ($k_BT/2$ for each vibrational mode)

$$\text{Systems approximately harmonic} \Rightarrow \frac{\hbar\omega}{k_BT} \gg 1 \Rightarrow \text{quantum (vibration dominated by ZPE)}$$

$T=300K$ corresponds to $\omega \approx 208\text{cm}^{-1}$ $\Rightarrow$ anything above is ZPE dominated
Where are nuclear quantum effects important?

- Classically the average value of the kinetic energy follows equipartition (Boltzmann operator factorizes) and is given by

\[ \langle K \rangle = \frac{3N k_B T}{2} \]
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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_{q,m}^{\text{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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1. Parametrize the full Born-Oppenheimer surface and solve the Schrödinger equation for the nuclei
   - Impossible Impractical for high-dimensional systems
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2. Restore quantum nuclear fluctuations by “fudging” classical nuclear velocities: Generalized Langevin equation (GLE) based colored noise thermostats [Ceriotti, Bussi, Parrinello, JCTC 6, 1170 (2010)]
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The time-dependent Schrödinger Equation

Time dependent Schrödinger equation:

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

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

Time evolution propagator
The time-dependent Schrödinger Equation

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Project into position space:

\[ \langle q' | \Psi(t) \rangle = \langle q' | \exp(-i\hat{H}t/\hbar) |\Psi(0)\rangle \]

\[ = \int dq \langle q' | \exp(-i\hat{H}t/\hbar) q \rangle \langle q | \Psi(0) \rangle \]

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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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Must evaluate matrix elements of this form
Rotating to imaginary time

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

\[ \hat{U}(t) = \exp(-i\hat{H}t/\hbar) = \exp(-\beta\hat{H}) = \hat{\rho}(\beta) \]

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?

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

\( \hat{K} \) and \( \hat{V} \) do not commute
Computing the quantum canonical density matrix

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  \[ \text{K and V do not commute} \]

- Trotter theorem:
  \[ e^{\hat{A} + \hat{B}} = \lim_{n \to \infty} \left[ e^{\hat{A}/2n} e^{\hat{B}/n} e^{\hat{A}/2n} \right]^n \]
**Computing the quantum canonical density matrix**

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  e^{\hat{A}+\hat{B}} = \lim_{n \to \infty} [e^{\hat{A}/2n} e^{\hat{B}/n} e^{\hat{A}/2n}]^n
  \]

- Using the theorem we get:
  \[
  \rho(q, q', \beta) = \lim_{n \to \infty} \langle q' | [e^{-\beta_n \hat{K}(p)/2} e^{-\beta_n \hat{V}(q)} e^{-\beta_n \hat{K}(p)/2}] n | q \rangle
  \]

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

  with \(\beta_n = \beta / n\)

  \(\beta \hbar\) (imaginary time)

  has been divided in \(n\) slices
Computing the quantum canonical density matrix

- Now we can introduce $n$ identities (position eigenstates) in $\rho$:

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

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

$$\hat{I} = \int dq |q\rangle \langle q|$$
Computing the quantum canonical density matrix

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

- Each matrix element can be evaluated:

$$\langle q_{k-1} | e^{-\beta_n \hat{V}(q)/2} e^{-\beta_n \hat{K}(p)} e^{-\beta_n \hat{V}(q)/2} | q_k \rangle =$$

$$= \frac{1}{\sqrt{2\pi}} e^{ipq/h}$$

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

complete the square

⇒ Gaussian integral

We got rid of the operators!
Computing the quantum canonical density matrix

- So, the final result is:

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

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

\[ \omega_n = 1/(\beta_n \hbar) \]

harmonic interaction between neighboring points of a path

with \( q_0 = q \quad q_n = q' \)
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\(q, q_1, q_2, \ldots, q'\) constitute a path \(q(\tau)\), where \(\tau \in [0, \beta \hbar]\)

\[
\rho(q, q') = \int D[q(\tau)] e^{\Phi[q(\tau)]} \quad q(0)=q, \ q(\beta \hbar)=q'
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Integral over paths

harmonic interaction between neighboring points of a path

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

- The partition function \( Z \) is:

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

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

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harmonic interaction between neighboring points of a path

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Integral over paths

\( q_n = q_0 = q \)
Sampling the partition function

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

\[ Z_n = \frac{1}{2\pi \hbar} \left( \frac{2\pi m}{\beta_n} \right)^{1/2} \int dq_1 \ldots dq_n e^{-\beta_n \sum_k [V(q_k) + \frac{m\omega_n^2}{2} (q_k - q_{k-1})^2]} \]

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Can be sampled by Monte Carlo
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- Reintroduce momenta

\[ 1 = \left( \frac{\beta_n}{2\pi m} \right)^{1/2} \int dp_k e^{-\beta_n p_k^2/2m} \]

\[ Z_n = \frac{1}{(2\pi \hbar)^n} \int dp \int dq e^{-\beta_n \sum_k \frac{p_k^2}{2m} + \frac{m\omega_n^2}{2}(q_k - q_{k-1})^2 + V(q_k)} = \frac{1}{(2\pi \hbar)^n} \int dp \int dq e^{-\beta_n H_n} \]

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

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\[ Z = \lim_{n \to \infty} Z_n \]

\[ q_{n+1} = q_1 \]

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

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

Can be sampled by Molecular Dynamics
Properties and estimators

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

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- Each bead evolves at temperature \( nT \)
- \( n \) determined by how “quantum” the problem is
- \( n \gg \beta \hbar \omega_{max} \)
  (typically between 10 and 100)
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\[ \langle r^2 \rangle^{1/2} = \Lambda / \sqrt{8\pi} \quad \Lambda = \frac{h}{\sqrt{2\pi mk_B T}} \]
Properties and estimators

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- Ensemble averages of operators

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

If: \( \hat{A} = \hat{A}(q) \) Then: \( \langle A \rangle = \frac{1}{Z} \int dp \int dq \frac{1}{n} \sum_k A(q_k) e^{-\beta n H_n} \)

Else: complicated — open paths, etc.

(e.g. Lin, Morrone, Car PRL 105, 110602)

Some examples:

\[ \langle V \rangle = \frac{1}{n} \sum_{i=1}^n \langle V(q_i) \rangle \]

\[ \langle K_{cv} \rangle = \frac{3Nk_B T}{2} + \frac{1}{2n} \sum_{j=1}^N \sum_{i=1}^n (\nabla V(q_i^1, ..., q_i^N) \cdot (q_i^j - q_i)) \]

(From thermodynamic relation)
For a system of $N$ distinguishable particles:

$$H_n = \sum_{k=1}^{n} \sum_{j=1}^{N} \left[ \frac{(p_k^j)^2}{2m_j} + \frac{1}{2} m_j \omega_n^2 (q_k^j - q_{k-1}^j)^2 \right] + \sum_{k=1}^{n} V(q_k^1, q_k^2, \ldots q_k^N)$$

The problem is exactly like \textit{(ab initio)} molecular dynamics, but involving several replicas of the system.
• For a system of $N$ distinguishable particles:

$$H_0 \text{ (free ring polymer Hamiltonian)}$$

$$H_n = \sum_{k=1}^{n} \sum_{j=1}^{N} - \left[ \frac{(p_k^j)^2}{2m_j} + \frac{1}{2} m_j \omega_n^2 (q_k^j - q_{k-1}^j)^2 \right] + \sum_{k=1}^{n} V(q_k^1, q_k^2, \ldots q_k^N)$$

• $H_0$ can be solved analytically by transforming it into normal modes

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

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

$$\tilde{p}_s^j = \sum_{k=1}^{n} p_k^j C_{ks} \quad \tilde{q}_s^j = \sum_{k=1}^{n} q_k^j C_{ks}$$
The Nuts and Bolts of the PIMD simulation

- For a system of N distinguishable particles:

\[ H_0 \text{ (free ring polymer Hamiltonian)} \]

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

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

- 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?

\[
H_n = \sum_{k=1}^{n} \sum_{j=1}^{N} \left[ \frac{(p_k^j)^2}{2m_j} + \frac{1}{2} m \omega_n^2 (q_k^j - q_{k-1}^j)^2 \right] + \sum_{k=1}^{n} V(q_k^1, q_k^2, \ldots q_k^N)
\]

\[
H_n = H_0 + H_V
\]
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- How to integrate the PIMD equations of motion efficiently?

\[
H_n = \sum_{k=1}^{n} \sum_{j=1}^{N} \left[ \frac{(p_k^j)^2}{2m_j} + \frac{1}{2}m\omega_n^2(q_k^j - q_{k-1}^j)^2 \right] + \sum_{k=1}^{n} V(q_k^1, q_k^2, \ldots q_k^N)
\]

\[H_n = H_0 + H_V\]

- Small digression about the Liouville operator

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

\[
\frac{d}{dt} a = \frac{d}{dq} \dot{q} + \frac{d}{dp} \dot{p}
\]

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

One can define the Liouville operator \( L \):

\[
iL = \frac{\partial H}{\partial p} \frac{d}{dq} - \frac{\partial H}{\partial q} \frac{d}{dp}
\]
Integrating PIMD Equations of Motion

• How to integrate the PIMD equations of motion efficiently?

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\[ H_n = H_0 + H_V \]

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

\[ \frac{d a}{d t} = \frac{d a}{d q} \dot{q} + \frac{d a}{d p} \dot{p} \]

\[ \frac{d a}{d t} = \frac{d a}{d q} \frac{\partial H}{\partial p} - \frac{d a}{d p} \frac{\partial H}{\partial q} \]

One can define the Liouville operator \( L \):

\[ iL = \partial H \frac{d}{d q} - \frac{\partial H}{\partial q} \frac{d}{d p} \]

Such that:

\[ \frac{d a}{d t} = iLa \rightarrow a(t) = e^{iL} a(0) \]

We can also split the operator

\[ iL = iL_1 + iL_2 \]

\[ L_1 = \frac{\partial H}{\partial p} \frac{d}{d q} \quad L_2 = -\frac{\partial H}{\partial q} \frac{d}{d p} \]

And the pieces do not commute

\[ a(t) = e^{iL_1+iL_2} a(0) \]

\[ [iL_1, iL_2] \neq 0 \]
**Integrating PIMD Equations of Motion**

- How to integrate the PIMD equations of motion efficiently?

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

\[
H_n = H_0 + H_V
\]

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We can also split the operator

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iL = iL_1 + iL_2
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\[
L_1 = \frac{\partial H}{\partial \dot{p}} \frac{d}{dq} \quad L_2 = -\frac{\partial H}{\partial \dot{q}} \frac{d}{dp}
\]

And the pieces do not commute

\[
a(t) = e^{iL_1+iL_2}a(0) = e^{[iL_1,iL_2]}a(0)
\]

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

For microcanonical 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?

\[
H_n = \sum_{k=1}^{n} \sum_{j=1}^{N} \left[ \frac{(p_k^j)^2}{2m_j} + \frac{1}{2} m_j \omega_n^2 (q_k^j - q_{k-1}^j)^2 \right] + \sum_{k=1}^{n} V(q_k^1, q_k^2, \ldots q_k^N)
\]

\[H_n = H_0 + H_V\]

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

\[e^{iL \Delta t} \approx e^{iL_V \Delta t/2} e^{iL_0 \Delta t} e^{iL_V \Delta t/2}\]

Involves \(H_V\) \hspace{1cm} Involves \(H_0\) \hspace{1cm} Involves \(H_V\)

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

The middle step can be computed analytically (especially easy in the normal mode representation).

\[\Rightarrow\] 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:

\[
p^j_k \leftarrow p^j_k - \frac{\Delta t}{2} \frac{\partial V(q^1_k, \ldots, q^N_k)}{\partial q^j}
\]

\[
\tilde{p}^j_s = \sum_{k=1}^n p^j_k C_{ks} \quad \tilde{q}^j_s = \sum_{k=1}^n q^j_k C_{ks}
\]

\[
\left( \begin{array}{c} \tilde{p}^j_s \\ \tilde{q}^j_s \end{array} \right) \leftarrow \left( \begin{array}{cc} \cos(\omega_s \Delta t) & -m_j \omega_s \sin(\omega_s \Delta t) \\ \frac{1}{m_j \omega_s} \sin(\omega_s \Delta t) & \cos(\omega_s \Delta t) \end{array} \right) \left( \begin{array}{c} \tilde{p}^j_s \\ \tilde{q}^j_s \end{array} \right)
\]

\[
p^j_k = \sum_{s=0}^{n-1} C_{ks} \tilde{p}^j_s 
\]

\[
q^j_k = \sum_{s=0}^{n-1} C_{ks} \tilde{q}^j_s
\]

\[
p^j_k \leftarrow p^j_k - \frac{\Delta t}{2} \frac{\partial V(q^1_k, \ldots, q^N_k)}{\partial q^j}
\]

Textbook time evolution for set of uncoupled harmonic oscillators
The actual scheme for integrating then becomes:

\[
p_k^j \leftarrow \text{thermostat \((\Delta t/2)\)}
\]

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

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

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

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

\[
p_k^j \leftarrow \text{thermostat \((\Delta t/2)\)}
\]
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)*
The nature of the hydrated excess proton in water

Dominik Marx*, Mark E. Tuckerman†, Jürg Hutter* & Michele Parrinello*
clear effects, which can result in either weakening or strengthening intermolecular bond bending and intramolecular bond stretching. Hydrogen bonds are weak, generally intermolecular bonds, which can be important for the rattling of the proton in the hydrogen bond. It has a number of important implications, such as explaining the contrasting influence QNEs have on a wide range of H-bonded interactions from the electronic structure. We find that the quantum nature of the hydrogen bond can consequently be considered part of a `low-barrier hydrogen bond' complex in which the proton becomes equally shared between two water molecules (Fig. 1a). In water, the proton can consequently be considered part of a `low-barrier hydrogen bond' complex in which this proton becomes equally shared between two water molecules (Fig. 1a). In liquid hydrogen fluoride (HF), for example, density-functional theory (DFT) calculations reveal that the strength of the hydrogen bond is about 12% weaker than the empirical value. This suggests that the quantum nature of the proton must be taken into account when calculating the strength of hydrogen bonds.
Quantum nature of the hydrogen bond
Xin-Zheng Li, Brent Walker, and Angelos Michaelides

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Dominik Marx*, Mark E. Tuckerman†, Jürg Hutter* & Michele Parrinello*

PNAS | April 19, 2011 | vol. 108 | no. 16 | 6369–6373

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Nuclear Quantum Effects in Water
Joseph A. Morrone
Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA

Roberto Car*
Department of Chemistry and Department of Physics, Princeton University, Princeton, New Jersey 08544, USA
of the hydrogen bonds, and the corresponding structures, across a
intermolecular bond bending and intramolecular bond stretching.

Edited by Michael L. Klein, Temple University, Philadelphia, PA, and approved February 23, 2011 (received for review November 9, 2010)

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PRL 101, 017801 (2008)

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A Channel

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A few applications

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Surface Science 605 (2011) 689–694

Quantum nuclear effects on the location of hydrogen above and below the palladium (100) surface

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Biophysical Journal Volume 71 July 1996 19–39

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Physical Review Letters

PRL 101, 078101 (2008)

7988–7991 | PNAS | May 22, 2012 | Vol. 109 | No. 21

Many many more!!
Dynamical Observables
PIMD uses ring polymer trajectories to calculate exact (static) averages of the form

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

- PIMD uses ring polymer trajectories to calculate exact (static) averages of the form
  \[ \langle A \rangle = \frac{1}{Z} \text{Tr}[e^{-\beta \hat{H}} \hat{A}] \]

- But many important quantities are actually given by time dynamic (time dependent) averages:
  Time correlation function
  \[ c_{AB}(t) = \text{Tr}[e^{-\beta \hat{H}} \hat{A}(0) \hat{B}(t)] \]

  Diffusion coefficient
  \[ D(T) = \frac{1}{3} \int_0^\infty c_{v \cdot v}(t) \, dt \]

  IR spectrum (dipole adsorption cross section)
  \[ n(\omega) \alpha(\omega) = \frac{\pi \omega}{3hcV\epsilon_0} (1 - e^{-\beta \hbar \omega}) C_{\mu \cdot \mu}(\omega) \]
  \[ C_{\mu \cdot \mu}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} c_{\mu \cdot \mu}(t) \, dt \]
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  \[ n(\omega) \alpha(\omega) = \frac{\pi \omega}{3hcV \epsilon_0} (1 - e^{-\beta h \omega}) C_{\mu\cdot\mu}(\omega) \]
  \[ C_{\mu\cdot\mu}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} c_{\mu\cdot\mu}(t) \, dt \]

- PIMD does not give access to real time (propagation is in imaginary time)
  Approximate these quantities - easier to approximate Kubo transforms
  \[ \tilde{c}_{AB}(t) = \frac{1}{\beta} \int_0^\beta c^\lambda_{AB}(t) \]
  \[ c^\lambda_{AB}(t) = \text{Tr}[e^{-(\beta-\lambda) \hat{H}} \hat{A}(0) e^{-\lambda \hat{H}} \hat{B}(t)] \]
Path integral approximations for real time dynamics

- Normal mode transformation of free ring polymer Hamiltonian:

\[
H_0 = \sum_j \sum_{s=0}^{N-1} \left[ \frac{\tilde{p}_s}{2(m_j)^{\frac{1}{2}}} + \frac{1}{2} m_j \omega_s^2 (\tilde{q}_s)^2 \right] \omega_s = 2\omega_n \sin(s\pi/n) \\
\omega_n = nk_bT/\hbar
\]

\( s=0 \) \( \Rightarrow \) centroid mode; \( s\neq 0 \) \( \Rightarrow \) internal modes

Path integral approximations for real time dynamics

- Normal mode transformation of free ring polymer Hamiltonian:

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- Ring polymer molecular dynamics (RPMD)[1]
  - \( m' = m \), Newtonian dynamics, no thermostat
  - Issue: beads resonate with physical frequencies

Path integral approximations for real time dynamics

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\(s=0\) ⇒ centroid mode; \(s\neq 0\) ⇒ internal modes

- Ring polymer molecular dynamics (RPMD)\(^1\)
  - \(m' = m\), Newtonian dynamics, no thermostat
  - Issue: beads resonate with physical frequencies

- Centroid molecular dynamics (CMD)\(^2\)
  - \(m' = \sigma m\) (\(\sigma < 1\) 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.

---

\(^1\) Craig and Manolopoulos, JCP 121, 3368 (2004)

\(^2\) Cao and Voth, JCP 100, 5093 (1994)
Model Application: IR spectrum of OH molecule


- Model OH molecule with interatomic interactions given by:

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

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

  \[
  \phi = D_0 \left[ 1 - e^{-\alpha(r-r_0)} \right]^2
  \]

  Morse (parameters from real molecule)
**Model Application: IR spectrum of OH molecule**


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Path integral approximations for real time dynamics

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\[
H_0 = \sum_{j} \sum_{s=0}^{n-1} \left[ \frac{\tilde{p}_s^j}{2(m_j)^{\frac{1}{2}}} + \frac{1}{2} m_j \omega_s^2 (\tilde{q}_s^j)^2 \right] \omega_s = 2\omega_n \sin(s\pi/n) \\
\omega_n = nk_BT/\hbar
\]

\(s=0 \Rightarrow \text{centroid mode}; s \neq 0 \Rightarrow \text{internal modes}\)


- Thermostatted Ring Polymer Molecular Dynamics (TRPMD)
  - \(m'=m\), white noise Langevin thermostat applied to \textit{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:

\[
\frac{d}{dt} \tilde{p}_i^{(k)} = -m_i \omega_k^2 \tilde{q}_i^{(k)} - \gamma^{(k)} \tilde{p}_i^{(k)} + \sqrt{\frac{2m_i}{\beta_n}} \xi_i^{(k)} \\
\frac{d}{dt} \tilde{q}_i^{(k)} = \tilde{p}_i^{(k)}/m_i
\]

- 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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  \[ \phi = \frac{k_b}{2}(r - r_0)^2 \]
  Harmonic (parameters from JCP 130, 194510 (2009))

  \[ \phi = D_0 \left[ 1 - e^{-\alpha(r-r_0)} \right]^2 \]
  Morse (parameters from real molecule)

![Graphs showing IR spectra for different temperatures and methods: CMD, TRPMD, RPMD.](image-url)
Model Application: IR spectrum of OH molecule


- Model OH molecule with interatomic interactions given by:

\[
\phi = D_0 \left[1 - e^{-\alpha(r-r_0)}\right]^2
\]

Morse (parameters from real molecule)

![Graph showing FWHM, wavenumber, and temperature relations for TRPMD, CMD, and Classical models.](image)

![Graphs comparing TRPMD and CMD results for different wavenumbers and temperatures.](image)
IR Spectrum of the Zundel Ion

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

![Graphs showing IR spectra at 100K and 300K](image)
IR Spectrum of Liquid Water

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

![Graphs showing IR spectrum for experimental and simulated data.](image)

J. E. Bertie and Z. Lan, Appl. Spectrosc. 50, 1047 (1996)
IR Spectrum of Liquid Water

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

![Graph showing IR spectrum of liquid water with various simulations and experimental data]

**Diffusion Coefficients**

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

<table>
<thead>
<tr>
<th>Simulation</th>
<th>( D )</th>
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<tbody>
<tr>
<td>Classical</td>
<td>0.194(5)</td>
</tr>
<tr>
<td>RPMD</td>
<td>0.218(3)</td>
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<tr>
<td>CMD</td>
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<tr>
<td>Expt.</td>
<td>0.230</td>
</tr>
</tbody>
</table>

*Price, Ide, Arata, JPCA 103, 448 (1999)
The End

References

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Quantum Mechanics and Path Integrals
*R. P. Feynman, A. R. Hibbs*

How to do it?

[aims.fhi-berlin.mpg.de](http://aims.fhi-berlin.mpg.de)

[i-PI](http://imx-cosmo.github.io/gle4md/index.html?page=ipi)
References

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