QUANTUM MECHANICAL EFFECTS FROM RING POLYMER MOLECULAR DYNAMICS

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Outline

1. Ring polymer molecular dynamics

2. Ring polymer reaction rate theory
   - Chemical reactions:
     - $A + BC \ (H + H_2, Cl + HCl, F + H_2, Mu + H_2)$
     - $H + CH_4$

3. RPMMDrate code
1. Ring polymer molecular dynamics

Based on the classical isomorphism:\(^a\)

map each quantum particle onto an effective classical system of \(N\) beads coupled via harmonic springs and each under external potential \(V\)

Single quantum particle

QM partition function:

\[
Z = \text{tr}[e^{-\beta \hat{H}}]
\]

where

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

Classical partition function:

\[
Z = \frac{1}{(2\pi \hbar)^n} \int dp_n \int dq_n e^{-\beta_n H_n(p_n, q_n)}
\]

where

\[
H_n(p_n, q_n) = \sum_{j=1}^{n} \left[ \frac{p_j^2}{2m} + \frac{1}{2} m \omega_n^2 (q_j - q_{j-1})^2 + V(q_j) \right]
\]

with \(\beta_n = \beta / n\) and \(\omega_n = 1 / \beta_n \hbar\).

\(^a\) D. Chandler and P. G. Wolynes, JCP 74, 4078 (1981).
1. Ring polymer molecular dynamics

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\]

Classical \( n \)-bead ring polymer

\[
\Lambda(T) = \frac{h}{\sqrt{2\pi mkT}}
\]

where

\[
\langle R_G \rangle = \frac{\Lambda(T)}{\sqrt{8\pi}}
\]

Classical partition function:

\[
Z = \frac{1}{(2\pi\hbar)^n} \int dp_n \int dq_n e^{-\beta_n H_n(p_n, q_n)}
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with \( \beta_n = \beta / n \) and \( \omega_n = 1 / \beta_n \hbar \).

\[ a \] D. Chandler and P. G. Wolynes, JCP 74, 4078 (1981).
(Proof)

\[ Z = \text{tr} \left[ e^{-\beta H} \right] = \text{tr} \left[ (e^{-\beta_n H})^n \right], \quad \text{where } \beta_n = \beta / n. \]

So

\[ Z = \int dq_1 \ldots \int dq_n \langle q_1 | e^{-\beta_n H} | q_2 \rangle \ldots \langle q_n | e^{-\beta_n H} | q_1 \rangle, \]

where

\[ \langle q_{j-1} | e^{-\beta_n H} | q_j \rangle \approx \langle q_{j-1} | e^{-\beta_n T} e^{-\beta_n V} | q_j \rangle \]

\[ = \frac{1}{2\pi\hbar} \int dp e^{-\beta_n p^2 / 2m - ip(q_j - q_{j-1})/\hbar - \beta_n V(q_j)} \]

\[ = \frac{1}{2\pi\hbar} \left( \frac{2\pi m}{\beta_n} \right)^{1/2} e^{-\beta_n \left[ m\omega_n^2 (q_j - q_{j-1})^2 / 2 + V(q_j) \right]} \]

\[ \equiv \frac{1}{2\pi\hbar} \int dp_j e^{-\beta_n \left[ p_j^2 / 2m + m\omega_n^2 (q_j - q_{j-1})^2 / 2 + V(q_j) \right]}, \quad \text{with } \omega_n = 1 / \beta_n \hbar. ^a \]

Path Integral Molecular Dynamics (PIMD) $ho_n$

- The ring polymer trajectories

\[
\dot{q} = + \frac{\partial H_n(p, q)}{\partial p}, \quad \dot{p} = - \frac{\partial H_n(p, q)}{\partial q}
\]

as a sampling tool to calculate \textit{exact} values of static equilibrium properties such as

\[
\langle A \rangle = \frac{1}{Z} \text{tr}[e^{-\beta H} A]
\]

Examples:
- thermodynamic energy
- heat capacity
- Helmholtz free energy

\[
\langle E \rangle = - \frac{\partial \ln Z(\beta)}{\partial \beta} \\
C_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{1}{k_B T^2} \frac{\partial^2 \ln Z}{\partial \beta^2} \\
F = -k_B T \ln Z
\]

Note:
- any classical method (MC, MD) can be used to sample multidimensional configuration integrals: PIMD - \textbf{Molecular Dynamics}
- **PIMD**: Time is only a parameter for the exploration of phase space (considered as \textit{unphysical dynamics}).
Ring Polymer Molecular Dynamics (RPMD) $p_n$

- The same ring polymer trajectories to calculate approximate Kubo-transformed correlation functions of the form

$$\tilde{c}_{AB}(t) = \frac{1}{\beta Z} \int_0^\beta d\lambda \text{tr}\left\{ e^{-(\beta-\lambda)H} A(0) e^{-\lambda H} B(t) \right\}$$

The RPMD approximation is simply:

$$\tilde{c}_{AB}(t) \approx \frac{1}{(2\pi\hbar)^n Z} \int dp_0 \int dq_0 e^{-\beta_n H_n(p_0,q_0)} A_n(q_0) B_n(q_t),$$

where

$$A_n(q) = \frac{1}{n} \sum_{j=1}^n A(q_j) \quad \text{and} \quad B_n(q) = \frac{1}{n} \sum_{j=1}^n B(q_j).$$

(Classical molecular dynamics in an extended phase space)
Examples:

- **Chemical reaction rates**
  \[ k(T) = \frac{1}{Q_r(T)} \lim_{t \to \infty} c_{\text{flux-side}}(t), \]
  Step operator: \( h(t) = e^{+iHt/\hbar} h_1 e^{-iHt/\hbar} \),
  \( h = h(q - q^{TS}) \).
  \[
  c(t) = \frac{1}{\beta} \int_0^\beta d\lambda \text{tr} \left\{ F(-i\lambda \hbar) h(t) \right\}.
  \]
  Flux operator: \( F(-i\lambda \hbar) \equiv e^{-(\beta - \lambda)H} Fe^{-\lambda H}, \)
  \( F = \frac{i}{\hbar}[H, h]. \)

- **Diffusion coefficients**
  \[
  D(T) = \frac{1}{d} \int_0^\infty c_{\text{velocity-velocity}}(t) dt,
  \]
  \[
  c(t) = \frac{1}{\beta} \int_0^\beta d\lambda \text{tr} \left\{ \frac{p}{m} (-i\lambda \hbar) \frac{p}{m} (t) \right\}.
  \]

- **Neutron scattering**
  \[
  S_{\text{incoherent}}(k, w) = \frac{1}{2\pi} \int_{-\infty}^\infty \text{d}w \ z_{\text{intermediate}}(k, t) dt,
  \]
  \[
  S_{\text{intermediate}}(k, t) \equiv \int d\lambda \sum_{j=1}^{N_{\text{particle}}} \left\langle e^{ik \cdot r_j(t)} e^{-i\lambda \hbar} \right\rangle,
  \]
  \( \hbar w \) - energy transfer (from neutron to liquid)
  \( \hbar k \) - momentum transfer
  \( e^{-i\mathbf{k} \cdot \mathbf{r}_j} \) and \( e^{+i\mathbf{k} \cdot \mathbf{r}_j}\) - correlated density operators

- **Dipole absorption spectroscopy**
  Golden rule of TDPT:
  \[
  n(w) \alpha(w) = \frac{\pi \beta w^2}{3c \text{Volume} \varepsilon_0} I(w),
  \]
  \[
  I(w) = \frac{(1 - e^{-\beta \hbar w})}{2\pi \beta \hbar w} \int_{-\infty}^{+\infty} dt e^{-iwt} C_{\text{dipole-dipole}}(t),
  \]
  \( \alpha(w) \) - Beer-Lambert absorption coefficient
  \( n(w) \) - frequency-dependent refraction index
  \[
  C(t) = \frac{1}{\beta} \int_0^\beta d\lambda \left\langle \mu(-i\lambda \hbar) \mu(t) \right\rangle,
  \]
Properties of RPMD:

1. Exact in the limit as $t \to 0$.\textsuperscript{a}
2. Exact in the classical (high temperature) limit.\textsuperscript{b}
3. Exact in the harmonic limit (for linear $A$ and/or $B$).\textsuperscript{b}
4. Exact when $A = 1$ (the unit operator).\textsuperscript{c}
5. Consistent with the QM equilibrium distribution.

\textsuperscript{a} B. J. Braams and D. E. Manolopoulos, JCP 125, 124105 (2006).
\textsuperscript{b} I. R. Craig and D. E. Manolopoulos, JCP 121, 3368 (2004).
\textsuperscript{c} S. Habershon and D. E. Manolopoulos, JCP 131, 244518 (2009).
RPMD:

(exact QM rate coefficient for a parabolic barrier)

(exact QM $Z = e^{-\beta E_0}$ in the low T limit)
RPMD:

(exact QM rate coefficient for a parabolic barrier)

But it neglects QM interference effects in the real-time dynamics (no $e^{\pm iHT/\hbar}$)

(exact QM $Z = e^{-\beta E_0}$ in the low T limit)
Example applications:

Example applications:

2. Ring polymer reaction rate theory

Consider an atom-diatom reaction in the gas phase

\[ A + BC \rightarrow AB + C \]

The exact QM rate coefficient is

\[ k(T) = \frac{1}{Q_r(T)} \lim_{t \to \infty} \tilde{c}_{fs}(t, s) \]

where

\[ \tilde{c}_{fs}(t, s) = \frac{1}{\beta} \int_{0}^{\beta} d\lambda tr \left[ e^{-(\beta - \lambda)H} F(0) e^{-\lambda H} h(t) \right] \]

with

\[ F = \frac{i}{\hbar} [H, h] \quad \text{and} \quad h \equiv h(s) = \begin{cases} 0, & s < 0 \\ 1, & s > 0 \end{cases} \]

(Flux) \hspace{1cm} (Side)

NB:
1. \( k(T) \) is independent of \( s \)
2. \( c_{fs}(t \to 0^+) \sim 0 \)
2. Ring polymer reaction rate theory

The classical limit rate coefficient is

$$k^{cl}(T) = \frac{1}{Q_r(T)} \lim_{t \to \infty} c^{cl}_{fs}(t, s)$$

where

$$c^{cl}_{fs}(t; s) = \frac{1}{(2\pi\hbar)^f} \int d^f p_0 \int d^f q_0 e^{-\beta H(p_0, q_0)}$$

$$\times \delta[s(q_0)] \left[ \frac{ds(q_0)}{dt} \right] \times h[s(q_t)]$$

Flux ($t = 0$) Side ($t > 0$)

NB:

1. $k^{cl}(T)$ is independent of $s$
2. $c_{fs}(t \to 0) \neq 0$ $\rightarrow$ classical TST
2. Ring polymer reaction rate theory

The RPDM rate coefficient is

\[ k_{\text{RPMD}}(T) = \frac{1}{Q_r(T)} \lim_{t \to \infty} \bar{c}_{fs}(t; s) \]

where

\[ \bar{c}_{fs}(t; s) = \frac{1}{(2\pi\hbar)^{nf}} \int d^{nf}p_0 \int d^{nf}q_0 e^{-\beta_n H_n(p_0, q_0)} \]

\[ \times \delta[s(\bar{q}_0)] \frac{ds(\bar{q}_0)}{dt} \times h[s(\bar{q}_t)] \]

Flux \((t = 0)\) Side \((t > 0)\)

\[ H_n(p, q) = \sum_{j=1}^{n} \left[ \frac{p_j^2}{2m} + \frac{1}{2} m \omega_n^2 (q_j - q_{j-1})^2 + V(q_j) \right], \text{ with } \beta_n = \beta / n, \omega_n = 1 / \beta_n \hbar \]

and

\[ \bar{q} = \frac{1}{n} \sum_{j=1}^{n} q_j, \quad \bar{p} = \frac{1}{n} \sum_{j=1}^{n} p_j \]

NB:

1. \(k_{\text{RPMD}}(T)\) is independent of \(s\)
2. \(c_{fs}(t \to 0+)\neq 0 \rightarrow \) “quantum” TST (centroid density)
Computational strategy

\[ s_0(\overrightarrow{q}) = 0 \quad - \text{dividing surface in the asymptotic reactant valley} \]

\[ s_1(\overrightarrow{q}) = 0 \quad - \text{dividing surface in the region of the reaction barrier} \]
Computational strategy

\[ s_0(\overline{q}) = 0 \quad - \text{dividing surface in the asymptotic reactant valley} \]

\[ s_1(\overline{q}) = 0 \quad - \text{dividing surface in the region of the reaction barrier} \]

\[
k^{\text{RPMD}}(T) = \frac{\bar{c}_{fs}(t \to \infty; s_1)}{\bar{c}_{fs}(t \to 0^+_1; s_1)} \times \frac{\bar{c}_{fs}(t \to 0^+_1; s_1)}{\bar{c}_{fs}(t \to 0^+_0; s_0)} \times \frac{\bar{c}_{fs}(t \to 0^+_0; s_0)}{Q_r(T)} \times k^{\text{QTST}}(s_0)
\]
Computational strategy

\[ s_0(q) = 0 \quad - \text{dividing surface in the asymptotic reactant valley} \]
\[ s_1(q) = 0 \quad - \text{dividing surface in the region of the reaction barrier} \]

\[ k_{\text{RPMD}}(T) = \frac{c_{fs}(t \to \infty; s_1)}{c_{fs}(t \to 0_+; s_1)} \times \frac{c_{fs}(t \to 0_+; s_1)}{c_{fs}(t \to 0_+; s_0)} \times \frac{Q_r(T)}{k_{\text{QTST}}(s_0)} \]

- transmission coefficient for \( s_1 \)
- ratio of ring polymer averages on two different dividing surfaces
- \( k_{\text{QTST}}(s_0) \)
Computational strategy

\[ s_0(\vec{q}) = 0 \] - dividing surface in the asymptotic reactant valley

\[ s_1(\vec{q}) = 0 \] - dividing surface in the region of the reaction barrier

\[ k^{RPMD}(T) = \frac{\bar{c}_{fs}(t \to \infty; s_1)}{\bar{c}_{fs}(t \to 0^+; s_1)} \times \frac{\bar{c}_{fs}(t \to 0^+; s_1)}{\bar{c}_{fs}(t \to 0^+; s_0)} \times \frac{Q_r(T)}{k^{QTST}(s_0)} \]

Consider the following dividing surface \( s_0 \)

\[ s_0(\vec{q}) = R_\infty - |\vec{R}| \]

\[ k^{QTST}(s_0) = 4\pi R_\infty^2 \left( \frac{1}{2\pi\beta\mu_R} \right)^{1/2} \]

\[ A + BC \to AB + C \]

\[ \vec{R} = \frac{m_B \vec{r}_B + m_C \vec{r}_C}{m_B + m_C} - \vec{r}_A, \]

\[ \mu_R = \frac{m_A (m_B + m_C)}{m_A + m_B + m_C} \]
Computational strategy

\[ s_0(\mathbf{q}) = 0 \]  - dividing surface in the asymptotic reactant valley

\[ s_1(\mathbf{q}) = 0 \]  - dividing surface in the region of the reaction barrier

\[
k^{RPMD}(T) = \frac{\bar{c}_{fs}(t \rightarrow \infty; s_1)}{\bar{c}_{fs}(t \rightarrow 0_+; s_1)} \times \frac{\bar{c}_{fs}(t \rightarrow 0_+; s_1)}{\bar{c}_{fs}(t \rightarrow 0_+; s_0)} \times 4\pi R^2 \left( \frac{1}{2\pi \beta \mu_R} \right)^{1/2}
\]

Two separate stages:

1. Calculate \( \kappa(s_1) \) (dynamical)
2. Calculate \( p(s_1, s_0) \) (static)
Computational strategy

\[ s_0(\mathbf{q}) = 0 \quad \text{- dividing surface in the asymptotic reactant valley} \]

\[ s_1(\mathbf{q}) = 0 \quad \text{- dividing surface in the region of the reaction barrier} \]

\[
k^{RPMĐ}(T) = \frac{\overline{c}_{fs}(t \to \infty; s_1)}{\overline{c}_{fs}(t \to 0_+; s_1)} \times \frac{\overline{c}_{fs}(t \to 0_+; s_1)}{\overline{c}_{fs}(t \to 0_+; s_0)} \times 4\pi R_{\infty}^2 \left( \frac{1}{2\pi \beta \mu_R} \right)^{1/2}
\]

Advantages:

1. Practical way to compute \( k(T) \) when the probability that a spontaneous thermal fluctuation will bring the system to the TS is very small

2. No need to calculate \( Q_r(T) \)
Computational strategy

\[ s_0(\mathbf{q}) = 0 \quad \text{- dividing surface in the asymptotic reactant valley} \]

\[ s_1(\mathbf{q}) = 0 \quad \text{- dividing surface in the region of the reaction barrier} \]

\[ \frac{\bar{c}_{fs}(t \to \infty; s_1)}{\bar{c}_{fs}(t \to 0_+; s_1)} = \lim_{t \to \infty} \left\langle f_{s_1}(\mathbf{q}_0)^{-1} \frac{ds_1(\mathbf{q}_0)}{dt} h[s_1(\mathbf{q}_t)] \right\rangle_{s_1} \]

where

\[ f_s(\mathbf{q}) = \left\{ \sum_{i=1}^{3N-6} \frac{1}{2\pi\beta\mu_i} \left[ \frac{\partial s(\mathbf{q})}{\partial q_i} \right]^2 \right\}^{1/2} \]
Computational strategy

\[ s_0(\bar{q}) = 0 \quad - \text{dividing surface in the asymptotic reactant valley} \]

\[ s_1(\bar{q}) = 0 \quad - \text{dividing surface in the region of the reaction barrier} \]

\[
\frac{c_{fs}(t \rightarrow 0_+ ; s_1)}{c_{fs}(t \rightarrow 0_+ ; s_0)} = \frac{e^{-\beta[W(1)-W(0)]}}{p(s_1,s_0)}
\]

\( W(\xi) \) is the centroid potential of mean force along the reaction coordinate.

\[
\xi = \frac{s_0(\bar{q})}{s_0(\bar{q}) - s_1(\bar{q})}
\]

\[
\begin{cases}
1, & s_1(\bar{q}) = 0 \\
0, & s_0(\bar{q}) = 0
\end{cases}
\]

Umbrella integration along the reaction coordinate:
Chemical Reaction Rates from Ring Polymer Molecular Dynamics: Zero Point Energy Conservation in $\text{Mu} + \text{H}_2 \rightarrow \text{MuH} + \text{H}$

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2Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom

ABSTRACT: A fundamental issue in the field of reaction dynamics is the inclusion of the quantum mechanical (QM) effects such as zero point energy (ZPE) and tunneling in molecular dynamics simulations, and in particular in the calculation of chemical reaction rates. In this work we study the chemical reaction between a muonium atom and a hydrogen molecule. The recently developed ring polymer molecular dynamics (RPMD) technique is used for the reaction, and the results are compared with those of other methods. For this reaction, the thermal rate coefficients calculated with RPMD are found to be in excellent agreement with the results of an accurate QM calculation. The very minor discrepancies are within the accuracy limits even at very low temperatures. This exceptionally good agreement can be attributed to the dominant role of ZPE in the reaction, which is accounted for extremely well by RPMD. Tunneling only plays a minor role in the reaction.

SECTION: Dynamics, Clusters, Excited States

A ring polymer molecular dynamics study of the isotopeologues of the $\text{H} + \text{H}_2$ reaction

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The inclusion of Quantum Mechanical (QM) effects such as zero point energy (ZPE) and tunneling in molecular dynamics simulations, especially in the case of light molecules such as hydrogen, requires an accurate treatment of electronic dynamics. In the RPMD technique, the QM calculations are done using a path integral approach. In the ZPE approximation, the QM wave function is represented by the sum of all basis functions, and the tunneling probabilities are calculated from the ZPE wave function. The ZPE effects are then included in the classical molecular dynamics (CMD). In this work, we have performed a detailed RPMD study for the $\text{H} + \text{H}_2$ reaction and its isotopeologues $\text{Mu} + \text{H}_2$ and $\text{D} + \text{H}_2$, with a wide range of temperature ranging from 600 to 1500 K.

Thermal rate coefficients and tunneling effects have been computed and compared with exact QM calculations as well as with approximate theoretical predictions and experiments. The agreement with the QM results is good for the zero temperature, with discrepancies increasing with temperature.

The ZPE has a significant effect on the reaction dynamics, with the ZPE being zero for the $\text{H} + \text{H}_2$ reaction and non-zero for the $\text{Mu} + \text{H}_2$ and $\text{D} + \text{H}_2$ reactions. The ZPE effect is very accurate, although only a small fraction of the ZPE is accurately accounted for, and the ZPE is not very accurate for the $\text{Mu} + \text{H}_2$ reaction.

SECTION: Kinetics and Dynamics
RESULTS: H+H₂

Classical and RPMD potentials of mean force for the H+H₂ reaction at 1000 and 300 K.

Classical (dashed) and RPMD (solid) transmission coefficients for the H+H₂ reaction at 1000 and 300 K.

RESULTS: H+H₂

Arrhenius plot of quantum, RPMD, and classical rate coefficients for the distinguishable atom H+H₂ reaction between 200 and 1500 K (quantum results stopping at 1000 K).

Deep quantum tunnelling

- RPMD gives $k(T)$ within a factor of 2 of the exact QM result when the classical rate is out by 3 orders of magnitude

Symmetric barrier. $T_c = 345$ K.

RESULTS: Cl+HCl

Classical and RPMD potentials of mean force for the Cl+HCl reaction at 1000 and 300 K

Classical (dashed) and RPMD (solid) transmission coefficients for the Cl+HCl reaction at 1000 and 300 K.

RESULTS: Cl+HCl

Arrhenius plot of quantum, RPMD, and classical rate coefficients for the Cl+HCl reaction between 200 and 1500 K (quantum results stopping at 1000 K).

Symmetric barrier. $T_c = 320$ K.

Results: F+H₂

Classical and RPMD potentials of mean force for the F+H₂ reaction at 1000 and 300 K

Classical (dashed) and RPMD (solid) transmission coefficients for the F+H₂ reaction at 1000 and 300 K.

RESULTS: F+H$_2$

Arrhenius plot of quantum, RPMD, and classical rate coefficients for the distinguishable atom H+H$_2$ reaction between 200 and 1500 K (quantum results stopping at 1000 K).

Asymmetric barrier. T$_c$ = 264 K.

RESULTS: F+H$_2$

Asymmetric barrier. $T_c = 264$ K.

<table>
<thead>
<tr>
<th>T/K</th>
<th>$k^{QTST}$</th>
<th>%error$^a$</th>
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$^a (k^{QTST} - k^{QM})/k^{QM} \times 100.$

$^b (k^{RPMD} - k^{QM})/k^{QM} \times 100.$

$k^{RPMD}(T) = k^{QTST}(T, s(q)) \cdot \kappa(t_p, s(q))$

RESULTS: F+H₂

Asymmetric barrier. \( T_c = 264 \) K.

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\(^a\left( k^{\text{QTST}} - k^{\text{QM}} \right)/k^{\text{QM}} \times 100.

\(^b\left( k^{\text{RPMD}} - k^{\text{QM}} \right)/k^{\text{QM}} \times 100.

\[ k^{\text{RPMD}}(T) = k^{\text{QTST}}(T, s(q)) \cdot \kappa(t_p, s(q)) \]

The deep tunnelling regime

\[ F.T. \]

\[ i \omega_b \]

\[ \omega_{\pm 3} = \sqrt{\left(\frac{6\pi}{\beta\hbar}\right)^2 - \omega_b^2} \]

\[ \omega_{\pm 2} = \sqrt{\left(\frac{4\pi}{\beta\hbar}\right)^2 - \omega_b^2} \]

\[ \omega_{\pm 1} = \sqrt{\left(\frac{2\pi}{\beta\hbar}\right)^2 - \omega_b^2} \]

\[ \omega_0 = i\omega_b \]

Qualitative change in behaviour for

\[ \beta > \beta_c = \frac{2\pi}{\hbar \omega_b} \]

\[ T < T_c = \frac{\hbar \omega_b}{2\pi k_B} \]
RESULTS: \( \text{F+H}_2 \)

Asymmetric barrier. \( T_c = 264 \text{ K.} \)

**TABLE 1.** Low temperature rate coefficients for the distinguishable atom \( \text{F + H}_2 \) reaction in cm\(^3\) molecule\(^{-1}\) s\(^{-1}\).

<table>
<thead>
<tr>
<th>T/K</th>
<th>( k^{\text{QTST}} )</th>
<th>%error(^a)</th>
<th>( k^{\text{RPMD}} )</th>
<th>%error(^b)</th>
<th>( k^{\text{QM}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.17(-10)</td>
<td>584</td>
<td>2.33(-11)</td>
<td>37</td>
<td>1.71(-11)</td>
</tr>
<tr>
<td>300</td>
<td>7.02(-11)</td>
<td>138</td>
<td>3.25(-11)</td>
<td>10</td>
<td>2.95(-11)</td>
</tr>
<tr>
<td>400</td>
<td>9.23(-11)</td>
<td>122</td>
<td>4.35(-11)</td>
<td>4</td>
<td>4.17(-11)</td>
</tr>
<tr>
<td>500</td>
<td>1.16(-10)</td>
<td>119</td>
<td>5.51(-11)</td>
<td>4</td>
<td>5.28(-11)</td>
</tr>
</tbody>
</table>

\(^a\)(\( k^{\text{QTST}} - k^{\text{QM}} \)/\( k^{\text{QM}} \) \times 100.\)

\(^b\)(\( k^{\text{RPMD}} - k^{\text{QM}} \)/\( k^{\text{QM}} \) \times 100.\)

**centroid formalism**

\[
k^{\text{RPMD}}(T) = k^{\text{QTST}}(T, s(q)) \cdot \kappa(t_p, s(q))
\]

Ring-polymer molecular dynamics rate-theory in the deep-tunneling regime: Connection with semiclassical instanton theory

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(Received 14 October 2009; accepted 4 November 2009; published online 3 December 2009)

We demonstrate that the ring-polymer molecular dynamics (RPMD) method is equivalent to an automated and approximate implementation of the “Im F” version of semiclassical instanton theory when used to calculate reaction rates in the deep-tunneling regime. This explains why the RPMD method is often reliable in this regime and also shows how it can be systematically improved. The geometry of the beads at the transition state on the ring-polymer potential surface describes a finite-difference approximation to the “instanton” trajectory (a periodic orbit in imaginary time \( \beta \hbar \) on the inverted potential surface). The deep-tunneling RPMD rate is an approximation to the rate obtained by applying classical transition-state theory (TST) in ring-polymer phase-space using the optimal dividing surface; this TST rate is in turn an approximation to a free-energy version of the Im F instanton rate. The optimal dividing surface is in general a function of several modes of the ring polymer, which explains why centroid-based quantum-TSTs break down at low temperatures for asymmetric reaction barriers. Numerical tests on one-dimensional models show that the RPMD rate tends to overestimate deep-tunneling rates for asymmetric barriers and underestimate them for symmetric barriers, and we explain that this is likely to be a general trend. The ability of the RPMD method to give a dividing-surface-independent rate in the deep-tunneling regime is shown to be a consequence of setting the bead-masses equal to the physical mass. © 2009 American Institute of Physics. [doi:10.1063/1.3267318]
Ring-polymer molecular dynamics rate-theory in the deep-tunneling regime: Connection with semiclassical instanton theory

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We demonstrate that the ring-polymer automated and approximate imple when used to calculate reaction rates method is often reliable in this reas; geometry of the beads at the tra finite-difference approximation to on the inverted potential surface) optimal dividing surface; this TS'... Im F instanton rate. The optimal ring polymer, which explains why for asymmetric reaction barriers, rate tends to overestimate deep-tunnel symmetric barriers, and we explai... consequence of setting the bead-r

\[ k_{\text{RPMD}}^{\text{oTST}}(T') = \frac{1}{\alpha(T)} k_{\text{inst}}(T') \]
RESULTS: Mu+H₂

Classical minimum energy path (blue solid line) and vibrationally adiabatic curve for the (00⁰) state (red dashed line) for the Mu+H₂ reaction vs. the natural reaction coordinate.

Classical minimum energy path (blue solid line) and vibrationally adiabatic curve for the (00⁰) state (red dashed line) for the Mu+H₂ reaction vs. the natural reaction coordinate.

RESULTS: Mu+H$_2$

Classical minimum energy path (blue solid line) and vibrationally adiabatic curve for the (00$^0$) state (red dashed line) for the Mu+H$_2$ reaction vs. the natural reaction coordinate.

Classical minimum energy path (blue solid line) and vibrationally adiabatic curve for the (00$^0$) state (red dashed line) for the Mu+H$_2$ reaction vs. the natural reaction coordinate.

RESULTS: Mu+H$_2$

Classical (dashed red line) and RPMD (blue solid line) potentials of mean force for the Mu+H$_2$ reaction at 1000 and 200 K.

Classical (red dashed line) and RPMD (blue solid line) transmission coefficients for the Mu+H$_2$ reaction at 1000 and 200 K.

RESULTS: Mu+H$_2$

Arrhenius plot of QM, RPMD, classical and QCT rate coefficients for the Mu+H$_2$ reaction between 200 and 1000 K.

RESULTS: Mu+H₂

Table 1: Summary of classical and RPMD results for the Mu+H₂ reaction. \( \xi^\dagger \) is the position of the maximum of the potential of mean force along the reaction coordinate \( \xi \). \( \kappa \) is the transmission coefficient, and the \( k' \)s are various rate coefficients in \( \text{cm}^3/\text{s} \). The percentage deviations of the RPMD rates from these exact rates are shown in the last two columns.

<table>
<thead>
<tr>
<th>( T/K )</th>
<th>( \xi^\dagger )</th>
<th>( \xi^\dagger )</th>
<th>( \kappa )</th>
<th>( k_{TST} )</th>
<th>( k_{cl} )</th>
<th>( \xi^\dagger )</th>
<th>( \xi^\dagger )</th>
<th>( \kappa )</th>
<th>( k_{QTST} )</th>
<th>( k_{RPMD} )</th>
<th>% dev</th>
<th>QM</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.000</td>
<td>0.753</td>
<td>3.80(-22)</td>
<td>2.86(-22)</td>
<td>1.044</td>
<td>0.328</td>
<td>2.70(-23)</td>
<td>8.87(-24)</td>
<td>15</td>
<td>7.71(-24)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>1.000</td>
<td>0.743</td>
<td>2.44(-18)</td>
<td>1.82(-18)</td>
<td>1.031</td>
<td>0.489</td>
<td>1.79(-19)</td>
<td>8.75(-20)</td>
<td>6</td>
<td>8.24(-20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>1.000</td>
<td>0.733</td>
<td>1.95(-16)</td>
<td>1.43(-16)</td>
<td>1.026</td>
<td>0.513</td>
<td>3.02(-17)</td>
<td>1.55(-17)</td>
<td>1</td>
<td>1.53(-17)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>1.000</td>
<td>0.725</td>
<td>3.20(-16)</td>
<td>2.32(-15)</td>
<td>1.023</td>
<td>0.519</td>
<td>7.85(-16)</td>
<td>4.07(-16)</td>
<td>-2</td>
<td>4.17(-16)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>1.000</td>
<td>0.717</td>
<td>1.98(-15)</td>
<td>1.42(-15)</td>
<td>1.021</td>
<td>0.530</td>
<td>7.29(-15)</td>
<td>3.86(-15)</td>
<td>-4</td>
<td>4.02(-15)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>1.000</td>
<td>0.712</td>
<td>7.77(-14)</td>
<td>5.53(-14)</td>
<td>1.019</td>
<td>0.529</td>
<td>3.76(-14)</td>
<td>1.99(-14)</td>
<td>-5</td>
<td>2.09(-14)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>1.000</td>
<td>0.705</td>
<td>2.23(-13)</td>
<td>1.57(-13)</td>
<td>1.018</td>
<td>0.528</td>
<td>1.30(-13)</td>
<td>6.86(-14)</td>
<td>-6</td>
<td>7.34(-14)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>1.000</td>
<td>0.699</td>
<td>5.14(-13)</td>
<td>3.59(-13)</td>
<td>1.016</td>
<td>0.534</td>
<td>3.49(-13)</td>
<td>1.86(-13)</td>
<td>-6</td>
<td>1.98(-13)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>1.000</td>
<td>0.698</td>
<td>1.08(-12)</td>
<td>7.50(-13)</td>
<td>1.015</td>
<td>0.537</td>
<td>8.07(-13)</td>
<td>4.34(-13)</td>
<td>-2</td>
<td>4.41(-13)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$k_{\text{RPMD}}(T)$ is:

- simple to compute
- equal to $k_{\text{QTST}}(T)$ in the limit as $t \to 0^+$
- bounded from above by $k_{\text{QTST}}(T)$ in the limit as $t \to \infty$
- independent of $s(q)$ in the limit as $t \to \infty$
- reliable at high temperatures
- captures the zero-point energy effect
- within a factor of 2-3 of the exact QM results in the deep quantum tunneling regime

→ complex chemical reactions!
RESULTS: H+CH₄

\[ s_0(q) = 0 \]
\[ s_1(q) = 0 \]
\[ s_0(q) = R_{\infty} - |R|; \quad s_1(q) = \max \left\{ s_\alpha(r), s_\beta(r), s_\gamma(r), s_\delta(r) \right\} \]
\[ s_x(r) = r(C - H_x) - r(H_x - H) - \left[ r^*(C - H_x) - r^*(H_x - H) \right] \]

RESULTS: H+CH$_4$

Classical (dashed) and RPMD (solid) potentials of mean force for the H+CH$_4$ reaction at 1000 and 200 K.

Classical (dashed) and RPMD (solid) transmission coefficients for the H+CH$_4$ reaction at 1000 and 200 K.

RESULTS: H+CH$_4$

Arrhenius plot of various approximate quantum mechanical rate coefficients for the H+CH$_4$ reaction between 200 and 2000 K.

Asymmetric barrier. $T_c = 296$ K.

RESULTS: H+CH₄

A+BC % error:
- QI: ~10%
- QTST: ~50%
- CVT: ~10-15%

Percentage deviation of the QI, centroid QTST, CVT/μOMT, and RPMD rate coefficients from the more accurate MCTDH results in the temperature range from 225 to 400 K.

$k^{RPMD}(T)$ is:

- simple to compute
- equal to $k^{QTST}(T)$ in the limit as $t \to 0_+$
- bounded from above by $k^{QTST}(T)$ in the limit as $t \to \infty$
- independent of $s(q)$ in the limit as $t \to \infty$
- reliable at high temperatures
- captures the zero-point energy effect
- within a factor of 2-3 of the exact QM results in the deep quantum tunneling regime

→ complex chemical reactions!
3. RPMDRate

RPMDRATE: Bimolecular chemical reaction rates from ring polymer molecular dynamics

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b Department of Mechanical and Aerospace Engineering, Combustion Energy Frontier Research Center, Princeton University, Princeton, NJ 08544, United States

Abstract

We present RPMDRATE, a computer program for the calculation of gas phase bimolecular reaction rate coefficients using the ring polymer molecular dynamics (RPMD) method. The RPMD rate coefficient is calculated using the Bennett–Chandler method as a product of a static (centroid density quantum transition state theory (QTST) rate) and a dynamic (ring polymer transmission coefficient) factor. The computational procedure is general and can be used to treat bimolecular polyatomic reactions of any complexity in their full dimensionality. The program has been tested for the H + H2, H + CH4, OH + CH4 and H + C2H6 reactions.

Program summary

Program title: RPMDrate
Catalogue identifier: AENW_v1.0
Program summary URL: http://cpc.cs.qub.ac.uk/summaries/AENW_v1.0.html
Program obtainable from: CPC Program Library, Queen's University, Belfast, N. Ireland
Licensing provisions: MIT license
Incorporated algorithms

**Bennett-Chandler factorization of the rate coefficient.**

**Umbrella integration along the reaction coordinate.**

**RATTLE algorithm for constrained molecular dynamics simulations.**

**Andersen thermostat.**

**Colored-Noise, generalized Langevin equation thermostats.**
3. RPMDrate


```python
#!/usr/bin/env python
# encoding: utf-8

##### Step 1. Define the potential energy surface ################################
from PES import get_potential

##### Step 2. Define the bimolecular reactants ################################
label = 'H + H2 -> HH + H'
reactants(
    atoms = ['H', 'H', 'H'],
    reactant1Atoms = [1,2],
    reactant2Atoms = [3],
    Rinf = (30 * 0.52918, "angstrom"),
)

transitionState(
    geometry = (  
        [[ 0.000000, 0.000000, -1.7570],  
          [ 0.000000, 0.000000,  0.000000],  
          [ 0.000000, 0.000000,  1.7570]],
        "bohr"),
        formingBonds = [(2,3)],
        breakingBonds = [(1,2)],
)
equivalentTransitionState(
    formingBonds=[(1,3)],
    breakingBonds=[(2,1)],
)

##### Step 3. Define the thermostat ################################
thermostat('Andersen')

##### Step 4. Initial umbrella configurations ################################
xi_list = numpy.arange(-0.05, 1.05, 0.01)
generateUmbrellaConfigurations(
    dt = (0.0001, "ps"),
    evolutionTime = (5, "ps"),
    xi_list = xi_list,
    kforce = 0.1 * T,
)

##### Step 5. Biased sampling ################################
```
3. RPMD率为

Classical (solid) and centroid (dashed) potentials of mean force for the $H + H_2$, $H + CH_4$, $OH + CH_4$, $H + C_2H_6$ reactions at 300 K.

3. RPMDrate

Classical (solid) and RPMD (dashed) time-dependent transmission coefficients for the H + H₂, H + CH₄, OH + CH₄, H + C₂H₆ reactions at 300 K.

3. RPMDrate

Classical (solid) and RPMD (dashed) time-dependent transmission coefficients for the $H + H_2$, $H + CH_4$, $OH + CH_4$, $H + C_2H_6$ reactions at 300 K.

RPMDrate

Yu. V. Suleimanov et al. CPC, 2013

http://ysuleyma-scripts.mit.edu/

Dr. Yohann Scribano
Universite de Montpellier
• Ion-molecule reactions
  (D+ + H₂…)

Prof. F. Javier Aoiz Group
Universidad Complutense de Madrid
• Mu + H₂
• H + H₂
• D + H₂
• Heµ + H₂
• Cl + O₃
• ...

Prof. Hua Guo Group
University of New Mexico
• Mu + CH₄
• H + CH₄
• O + CH₄
• Cl + CH₄
• OH + CO
• ...

Dr. Albert F. Wagner
Argonne National Laboratory
• OH + HO₂
• RPMDrate v2.0
• ...

THE UNIVERSITY OF NEW MEXICO
New Mexico's Flagship University
RPMDrate

Yu. V. Suleimanov et al. CPC, 2013

http://ysuleyma.scripts.mit.edu/

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• William H. Green

• Stephen Klippenstein
• Albert Wagner

• David Manolopoulos
• Rosana Collepardo-Guevara

• Javier Aoiz
• Ricardo Perez de Tudela

• Hua Guo