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Stress Test for Quantum Dynamics

Approximations: Deep Tunneling in the Muonium Exchange Reaction \( D + H_{\text{Mu}} \rightarrow D_{\text{Mu}} + H \)

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Abstract

Quantum effects play a crucial role in chemical reactions involving light atoms at low temperatures, especially when a light particle is exchanged between two heavier partners. Different theoretical methodologies have been developed in the last decades attempting to describe zero-point energy and tunneling effects without abandoning a classical or semiclassical framework. In this work we have chosen the D + HMu → DMu + H reaction as a stress–test system for three well established methods: two representative versions of transition state theory (TST) – canonical variational theory and semiclassical instanton – and ring polymer molecular dynamics (RPMD). These calculations will be compared with accurate quantum mechanical results. Despite its apparent simplicity, the exchange of the extremely light Muonium atom (0.114 u) becomes a most challenging reaction for conventional methods. The main result of this work is that RPMD provides an overall better performance than TST-based methods for such a demanding reaction. RPMD might well turn out to be a useful tool beyond TST applicability.

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Ring polymer molecular dynamics (RPMD) calculations have been performed for the D + HMuDMu + H reaction. The beads (dots) from the RPMD span beyond the minimum energy path, allowing an appropriate description of multidimensional tunneling.

Keywords

Isotope effect, chemical kinetics, reaction dynamics, molecular simulations, gas phase reactions
The study of quantum effects in chemical reactivity has long been an issue in the field of computational chemistry. These effects appear in the simplest atom–diatom reactions as well as in a wide range of complex phenomena: extreme tunneling effects have been shown to be responsible for some enzymatic proton transfer mechanisms\textsuperscript{1} and also for an astounding enhancement in the reactivity of alcohols at very cold temperatures in interstellar space\textsuperscript{2,3} just to name two examples. Since the first classical formulations of transition state theory (TST)\textsuperscript{4–6} in the 1930’s, considerable efforts have been made to include zero–point energy (ZPE) and tunneling effects in the description of reactive collisions. Nowadays, a number of different TST–based and non TST–based theoretical methods are available to compute the rate coefficients using different approaches.

Isotopic substitution in the H + H\textsubscript{2} reaction provides an excellent simple benchmark system for assessing the accuracy of various theoretical approximations to calculating chemical reaction rate coefficients. In particular, it allows one to separately investigate the importance of quantum mechanical effects. The substitution of the hydrogen atom by an atypical hydrogen isotope named muonium (Mu) is of particular interest in this matter. This isotope is formed by a positive muon and an electron and has an extremely small mass of just 0.11398 u which gives rise to a dominant tunneling effect when Mu is transferred between two significantly heavier partners.

In this letter, we present a comparative study of three representative theoretical approaches using the Mu–transfer reaction D + HMu \rightarrow DMu + H as a stress–test system: canonical variational theory (CVT), semiclassical instanton (SCI) approximation and ring polymer molecular dynamics (RPMD). The first two techniques are the most representative transition-state theory (TST) methods which are based on various static approximations to the real–time correlation functions used to describe chemical reactions. For this small system exact Quantum Mechanical (QM) calculations were available,\textsuperscript{7} providing an excellent benchmark for the aforementioned methods.
CVT$^8$–$^{13}$ is a variational version of TST developed by Truhlar and coworkers in the 80’s. As for any TST, CVT employs the short–time limit of the classical real–time flux and side correlation functions. The dividing surface is variationally optimized at each temperature along the reaction coordinate which separates reactants from products to reduce the recrossing effect, $i.e.$, to minimize the difference between the long– and short–time limits. CVT is inherently a classical theory and suitable at sufficiently high temperatures, where the classical description of nuclear motions may be adequate. At low temperatures, especially for the reactions involving the motions of light atoms (e.g., the present case of muonium), however, quantum effects become quite significant. To make CVT still valid for such low temperature reactions, two main modifications have been proposed. First, to take into account the ZPE effect, the classical partition functions are replaced by their quantum counterparts. Second, tunneling is taken into account as a semiclassical correction factor. However, these approaches do not provide a unique way for quantization. The various approximations used to calculate quantum partition functions, such as assuming harmonic and separable modes, can lead to inaccurate results even at high temperatures,$^{14}$ and using separable correction factors for tunneling effects might be a limitation at low temperatures where this effect plays a dominant role. Nevertheless, due to the practical simplicity of CVT and its efficient implementation$^{15}$–$^{17}$ in available codes, it has been broadly applied to numerous reactions.

Semiclassical instanton theory$^{18,19}$ (SCI) provides an approximation to the rate in the deep–tunneling regime based on a single periodic imaginary-time trajectory. In its earliest form, such trajectories, known as instantons, were extremely difficult to locate on multidimensional potential energy surfaces and applications were limited to one– and two–dimensional models.$^{20}$ Recently a more efficient method was discovered for obtaining the instantons by locating saddle points in the extended space of ring–polymers$^{21}$ and performing integrals within the steepest–descent approximation. This method was shown to be equivalent, except for a small difference in the prefactor, to a harmonic approximation of an optimal ring–polymer transition state theory (RPTST),$^{22}$ where the instanton is identified as
the dominant ring–polymer configuration. Although SCI makes harmonic approximations in
directions perpendicular to the instanton, it incorporates anharmonicity along the pathway
and does not require a reaction coordinate chosen a priori. One can therefore expect the
method to provide results on the correct order of magnitude as long as recrossing effects are
not too important.

RPMD\textsuperscript{23–27} is an alternative full–dimensional dynamical approach developed recently by
Manolopoulos and coworkers, including one of us (YVS). RPMD differs from all TST meth-
ods in its explicit, though approximate, consideration of the real–time dynamics. RPMD
exploits the isomorphism between the statistical properties of the quantum system and those
of a classical fictitious ring polymer consisting of many copies of the original system con-
ected by harmonic springs.\textsuperscript{28} This isomorphism enables the inclusion of quantum effects via
real–time classical molecular dynamics simulations in an extended phase space, an approach
which has also been introduced in ad hoc manner and still has not been rigorously derived
from the quantum Liouville equation. However, RPMD has proved to give accurate estimates
for correlation functions approximately linear in position or momentum, especially in the case
of those used for calculating chemical reaction rate coefficients. The RPMD rate coefficient
becomes exact in the high temperature limit, where the ring polymer collapses to a single
bead. The RPMD rate coefficient has well defined short–time limits that act as upper bounds
on the RPMD rate. When the transition state dividing surface is defined in terms of the cen-
troid of the ring polymer, this short–time limit coincides with a well known (centroid density)
version of quantum TST. In the deep–tunneling regime, when the transition state dividing
surface is optimally defined as a function of several modes of the ring polymer the short–time
limit of RPMD rate coefficient, known as RPTST, is also connected with the semiclassical
(“free energy”) version of instanton theory.\textsuperscript{22} In a series of recent papers\textsuperscript{29–31} it has been
solidly established that this RPTST, and hence RPMD itself, gives the exact quantum rate
coefficient in the absence of recrossing. The long–time limit of the RPMD rate coefficient,
however, is rigorously independent of the choice of the transition state dividing surface used
to compute it, a feature that distinguishes it from TST–based methods. Recently a general code for RPMD calculations (RPMDrate) has been developed by Suleimanov and coworkers.\textsuperscript{32} Several applications to various chemical reactions\textsuperscript{14,25–27,33–42} have demonstrated that (i) RPMD provides quite reliable results at high and even intermediate temperatures; (ii) captures almost perfectly the ZPE effect;\textsuperscript{34} (iii) captures the tunneling effect and is usually within a factor of 2–3 of accurate QM results at very low temperatures in the deep quantum tunneling regime; (iv) also provides accurate estimates for barrierless–type reactions.\textsuperscript{40}

The dynamics of the \(D + \text{HMu}\) reaction has recently been studied in detail using quasi-classical trajectories (QCT) and exact QM calculations.\textsuperscript{7} As shown there, the two possible reaction routes yield significant amounts of both tunneling and ZPE due to the low mass of Muonium. However, among the two channels, the abstraction reaction \(D + \text{HMu} \rightarrow \text{DH} + \text{Mu}\) is more classical, as shown in ref. 7. The reverse of the abstraction reaction is very similar to the recently studied \(\text{Mu} + \text{H}_2\),\textsuperscript{34} where it was found that not only RPMD gave the best results to date but also that CVT worked extraordinarily well. The detailed balance principle ensures that both RPMD and TST are expected to work similarly well for \(D + \text{HMu} \rightarrow \text{DH} + \text{Mu}\), and therefore the abstraction reaction is of no interest to this work. The second exit channel, however, offers a more challenging scenario. In fact, the \(D + \text{HMu} \rightarrow \text{DMu} + \text{H}\) exchange reaction benefits from a significant enhancement of tunneling compared to that of the abstraction channel due to its thinner vibrationally adiabatic barrier.\textsuperscript{7} In addition, as already shown,\textsuperscript{7} the ZPE–corrected potential energy surface displays a quite complex structure near the transition state (TS). These two features make the \(D + \text{HMu} \rightarrow \text{DMu} + \text{H}\) reaction a perfect candidate for testing various theoretical approaches.

Here we outline the calculations performed in this work. The minimum energy path (MEP) from reactants to products as a function of the internal reaction coordinate (IRC) and the corresponding vibrationally adiabatic curve for the \((00^0)\) state were computed using the ABCRATE code.\textsuperscript{15} The vibrationally adiabatic curve is computed along the MEP as
the sum of the potential energy plus the sum of the zero-point energies of the 3 (symmetric stretching and degenerate bending) modes orthogonal to the MEP. The stretching mode was computed using the WKB approximation while the semiclassical method was employed for the bending modes. The particular version of CVT used in this work was iCVT/µOMT, where the letter “i” in iCVT\textsuperscript{43,44} stands for improved treatment of the energetic reaction threshold region and µOMT\textsuperscript{45} stands for microcanonically optimized multidimensional tunneling algorithm. iCVT/µOMT rates were computed using ABCRATE. SCI rates at various temperatures were obtained by locating saddle points on the ring-polymer surface and diagonalizing the Hessian. Results were then converged with respect to the number of beads and rotations and translations treated as if the ring-polymer was a large classical supermolecule.\textsuperscript{46} Such calculations were performed up to the crossover temperature, which in the case of the D + HMu → DMu + H reaction is $T_C \approx 860$ K, which is unusually high, and corresponds to a TS imaginary harmonic frequency of 3736 cm\textsuperscript{-1}. The equivalent method for higher temperatures is Wigner’s parabolic barrier approximation.\textsuperscript{6} The RPMD\textsuperscript{25,27} calculations were performed using the RPMDrate code,\textsuperscript{32} which computes the rate coefficients in two steps. First the potential of mean force (PMF) is computed along an appropriate dimensionless reaction coordinate.\textsuperscript{25} From this PMF, or free energy profile, the centroid version of the TST rate coefficient is obtained. The second stage implies the computation of a recrossing factor, which corrects the bias introduced by the arbitrary choice of the dividing surface as well as including dynamical recrossing effects in an approximate manner. Numerical details for the RPMD method can be found as supplementary material. All calculations were performed using the H\textsubscript{3} BKMP2 potential energy surface by Boothroyd \textit{et al.}\textsuperscript{47}
In Fig. 1 the minimum energy path and the vibrationally adiabatic curve for the (000) state are depicted for the D + HMu → DMu + H reaction, as a function of the mass–dependent internal reaction coordinate $s$. Also RPMD potentials of mean force for 200 K, 500 K and 1000 K are shown in Fig. 1. The MEP shows an almost symmetrical profile because the particles at both sides of the collinear D–Mu–H structure have similar masses compared to the extremely light central Mu atom. Should the TS be D–H–Mu, which corresponds to the H abstraction reaction, the profile adopts a much more asymmetric shape (see ref. 7). The vibrationally adiabatic curve shows a remarkable structure, displaying two almost identical barriers placed at both reactants and products sides and a well in between. The region of the well responds to the neighbourhood of the TS, where the potential orthogonal to the IRC is wider. Such intricate structure is already observed in the one–dimensional vibrationally adiabatic curve, which only considers the stretching mode. All these features undoubtedly picture the complexity of the Muonium exchange process. It is therefore mandatory for any method attempting to describe this reaction to include an accurate characterization of the ZPE effect. Although the vibrationally adiabatic curve and the potentials of mean force computed by RPMD are described in terms of different reaction coordinates, in general one is able to establish connections between the most salient features, such as the barrier at the TS or even van der Waals wells. However, in this case we do not observe any trace of complex structure in the PMF profile near the TS. It is reasonable to think that the dynamical well which appears from computing the ZPE along the one–dimensional MEP will be washed out when RPMD averages over configurations over a wide phase space region around the TS. Another notable feature of the vibrationally adiabatic curve is its near symmetry, definitely due to the fact that the zero–point energy of both MuH and MuD species are very similar. As pointed out in previous works, RPMD is expected to underestimate the exact rate coefficients, as will be shown below.
The free energy barriers computed by RPMD (see Fig. 1) are very low, roughly half of those for \( \text{Mu} + \text{H}_2 \), and in particular, for low temperatures they display a broad flattened top. This results from the fact that RPMD averages points in configurational space on both sides of the potential energy barrier, modelling the effect of the deep–tunneling. The RPMD recrossing factors give similarly low values for all the temperatures studied, ranging from 0.30 at 200 K to 0.44 at 1000 K. The heavy–light–heavy mass combination and the particularly low mass of muonium (which makes \text{Mu} atom much more delocalized than the other two and therefore its beads will be more spread in the configuration space) makes it a especially difficult task to define a dividing surface in terms of centroid variables below the crossover temperature \( T_C \), when quantum effects start to matter. As mentioned before, \( T_C \approx 860 \text{ K} \), therefore practically throughout the entire temperature range covered in this work the \( \text{D} + \text{HMu} \rightarrow \text{DMu} + \text{H} \) reaction takes place in the deep–tunneling regime. Again, any method undertaking the task of describing this reaction must incorporate a sound conception of tunneling.

The results of our calculations - classical, iCVT/\( \mu \)OMT, SCI, RPMD and QM rate coefficients for the \( \text{D} + \text{HMu} \rightarrow \text{DMu} + \text{H} \) reaction between 150 K and 1000 K - are summarized in Table 1. The general behavior of the rates is depicted in Fig. 2. For a more detailed comparison of the performance of the different methods, the ratio between the iCVT/\( \mu \)OMT, SCI and RPMD rates and the exact QM one is shown in Fig. 3.

One immediately notices that the results of the purely classical calculations (one bead) are very poor for this reaction even at the highest temperature, where the exact QM rate is underestimated by a factor of 20. At low temperatures the situation gets much worse, where the discrepancy increases up to 12 orders of magnitude. This massive disagreement is a reflection of the fact that the \( \text{D} + \text{HMu} \rightarrow \text{DMu} + \text{H} \) reaction is indeed a process where quantum effects are paramount, and in particular, the fact that the deep–tunneling regime takes place at such high temperature. The iCVT/\( \mu \)OMT method performs much better for temperatures above 600 K, giving rates within a factor 2 from QM. Below that, accuracy is
Table 1: Classical, RPMD, SCI, iCVT/$\mu$OMT and QM$^7$ thermal rate coefficients for the $D + HMu \rightarrow DMu + H$ reaction for temperatures from 150 K to 1000 K. Above the crossover temperature (860 K), Wigner’s parabolic barrier approximation has been used instead of the SCI method. The parenthesis denote powers of ten.

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>Classical</th>
<th>RPMD</th>
<th>SCI/Wigner</th>
<th>iCVT/$\mu$OMT</th>
<th>QM$^7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>2.04(-26)</td>
<td>2.70(-15)</td>
<td>1.15(-13)</td>
<td>7.28(-17)</td>
<td>1.43(-14)</td>
</tr>
<tr>
<td>200</td>
<td>2.79(-22)</td>
<td>1.10(-14)</td>
<td>1.73(-13)</td>
<td>1.39(-15)</td>
<td>4.27(-14)</td>
</tr>
<tr>
<td>300</td>
<td>1.63(-18)</td>
<td>1.15(-13)</td>
<td>8.09(-13)</td>
<td>4.78(-14)</td>
<td>3.33(-13)</td>
</tr>
<tr>
<td>400</td>
<td>1.43(-16)</td>
<td>4.85(-13)</td>
<td>3.42(-12)</td>
<td>3.30(-13)</td>
<td>1.33(-12)</td>
</tr>
<tr>
<td>500</td>
<td>1.99(-15)</td>
<td>1.28(-12)</td>
<td>1.17(-11)</td>
<td>1.09(-12)</td>
<td>3.32(-12)</td>
</tr>
<tr>
<td>600</td>
<td>1.36(-14)</td>
<td>2.54(-12)</td>
<td>3.03(-11)</td>
<td>2.47(-12)</td>
<td>6.30(-12)</td>
</tr>
<tr>
<td>700</td>
<td>6.91(-14)</td>
<td>4.25(-12)</td>
<td>5.79(-11)</td>
<td>4.44(-12)</td>
<td>1.01(-11)</td>
</tr>
<tr>
<td>800</td>
<td>2.53(-13)</td>
<td>6.27(-12)</td>
<td>8.93(-11)</td>
<td>6.92(-12)</td>
<td>1.45(-11)</td>
</tr>
<tr>
<td>900</td>
<td>5.96(-13)</td>
<td>9.17(-12)</td>
<td>3.50(-10)</td>
<td>9.78(-12)</td>
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<tr>
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<td>1.24(-12)</td>
<td>1.23(-11)</td>
<td>1.45(-10)</td>
<td>1.29(-11)</td>
<td>2.47(-11)</td>
</tr>
</tbody>
</table>

Figure 2: Classical, RPMD, iCVT/$\mu$OMT, SCI and QM$^7$ thermal rate coefficients for the $D + HMu \rightarrow DMu + H$ reaction between 150 K and 1000 K.

rapidly lost, and at 150 K iCVT/$\mu$OMT underestimates QM by almost 3 orders of magnitude. Calculations using SCI give rates that overestimate QM by factors of less than 5 in the temperature range 200–600 K. At higher temperatures near the crossover temperature (860 K), the steepest–descent approximation breaks down and the rates are incorrectly estimated too high. Below 200 K, overestimation quickly grows, as can be seen in Fig. 3. As was predicted based on the quasi symmetric vibrational adiabatic curve, RPMD underestimates the exact rate. RPMD reproduces the results from iCVT/$\mu$OMT at temperatures above 600 K, which already were within a factor 2 from the QM rates. However RPMD keeps this tendency with decreasing temperature, and at the lowest temperature studied of 150 K it gives a value for the rate only 5 times lower than the exact QM calculations.

The results from iCVT/$\mu$OMT and SCI, i. e., the two versions of TST, show the exact opposite behavior: while the former underestimates the rates, the other overestimates them. In particular, the $\mu$OMT tunneling correction method does not seem to be sufficient to prop-
erly describe the extreme tunneling at low temperatures. The difference between the rates computed with iCVT (without $\mu$OMT) and QM is of 6 orders of magnitude at the lowest temperatures. Such an amount of tunneling seems to go beyond the capabilities of the $\mu$OMT semiclassical tunneling correction. The $D + HMu \rightarrow DMu + H$ reaction has a skewing angle of $23^\circ$, therefore an appreciable part of the tunneling is likely to proceed along paths very much distorted from the MEP in a corner–cutting fashion. Although iCVT/$\mu$OMT method had been previously employed successfully for reactions with even smaller skewing angles, the particular features of the $D + HMu \rightarrow DMu + H$ reaction might overcome the possibilities of the large curvature tunneling ground–state approach, implemented in $\mu$OMT for reactions with large path curvature, which uses the straight-line path approximation in evaluating the largest tunneling probability and assumes that tunneling is initiated by vibrational motions perpendicular to the reaction coordinate rather than motion along the reaction coordinate. In contrast, the instanton in SCI theory automatically finds the best pathway around the corner and therefore describes the deep–tunneling regime considerably better than iCVT/$\mu$OMT. The main sources of error are due to the harmonic approximation perpendicular to the instanton coordinate and the no–recrossing assumption which are the cause of the systematic overestimation of the exact result. There is of course also a discontinuity at the cross-over temperature (860 K) where the steepest-descent approximation is no longer valid and where we switch to the Wigner method, which itself tends to infinity at this point. We note, however, that it has recently been shown how this cross-over regime can be treated within the SCI method by integrating explicitly over the problematic mode. The RPMD method is in many ways very similar to the SCI except that the integrals are performed by sampling over the full extended space rather than relying on a harmonic approximation. It also includes dynamical recrossing effects in an approximate manner, although as the recrossing factors are not particularly small, this does not give the dominant difference from SCI. For these reasons, RPMD has proved to give more stable results, with deviations from the exact QM results that barely change with temperature.
Figure 3: Quotient between the computed rates (classical, iCVT/µOMT, SCI and RPMD) and the exact QM rates from ref.\textsuperscript{7} for the D + HMu → DMu + H reaction between 150 K and 1000 K.

Also the overall accuracy achieved by RPMD is better than any of the TST–based methods in the whole temperature range covered in this study.

To summarize, in this work we have employed the Mu–transfer reaction D + HMu → DMu + H as a stress–test system to assess how three well-established methods for calculating chemical reaction rate coefficients handle the quantum mechanical effects of nuclear motion, particularly in the deep–tunneling regime. We found that the two TST–based methods (iCVT/µOMT and SCI) show non systematic behavior: while the former underestimates the rates and fails at low temperatures, the latter overestimates them and also its accuracy exhibits an irregular dependence with temperature. On the other hand, the alternative RPMD method shows an overall better agreement with exact QM calculations and, what is more important, the accuracy is kept practically constant throughout the whole temperature range covered in this study. Moreover, RPMD has the advantage of being free of any adjustable empirical (or semiempirical) parameters and this is likely the origin of its reliability. Recent developments over the original RPMD formalism, however, obtained by applying an internal mode thermostat have recently been proposed and demonstrated to work better for correlation functions used in the theory of vibrational spectroscopy.\textsuperscript{54} It might be the case that this new implementation could also be able to provide better performance for other applications such as chemical reaction rates, which would require reproducing RPMD calculations throughout numerous recent studies,\textsuperscript{14,25–27,34–42} including the present one. The RPMD technique is rapidly becoming a reference method, particularly in the field of gas–phase chemical reactions, and it seems that there is still room for promising improvements.
Acknowledgement

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Supporting Information Available

In the supporting information document numerical details of the QM and RPMD calculations are supplied. This material is available free of charge via the Internet at http://pubs.acs.org. This material is available free of charge via the Internet at http://pubs.acs.org/.

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