In many areas of chemical physics the application of classical methods and concepts has proven to be a powerful tool to describe and analyze the dynamics of complex molecular systems. Molecular dynamics simulations, for example, are now routinely applied to large molecular systems. Such purely classical methods cannot be employed, however, if the process under consideration or the observables of interest exhibit significant quantum effects. A typical example are processes that involve the motion of electrons or protons or observables that require phase information such as time-resolved nonlinear spectra. The development of methods that are based on classical trajectories but incorporate quantum effects, therefore, continuous to be a central issue in chemical reaction dynamics.1–3 Quasiclassical and semiclassical methods are of particular interest in this respect.

Quasiclassical methods, such as for example the classical Wigner approach,4–6 differ from purely classical methods in that the correct, quantum mechanical initial state is taken into account. Since the classical Wigner approach, however, incorporates phase information only within the harmonic approximation, the description of quantum effects such as interference is limited to very short time. Semiclassical approximation, the description of quantum effects such as interference, zero-point energy conservation and tunneling. In particular semiclassical methods based on the initial-value representation7–10 (which circumvent the cumbersome root search problem in boundary-value based semiclassical methods) have been applied successfully to a variety of different problems in molecular dynamics in recent years (for a recent review, see Ref. 11). Due to the oscillatory nature of the integrand involved in these semiclassical methods, the numerical effort is, however, much larger than in quasiclassical methods.

In a recent study,12 we have investigated the capability of quasiclassical methods to describe photoinduced isomerization dynamics at conically intersecting surfaces. Adopting a multidimensional model of nonadiabatic cis–trans photoisomerization,13,14 we have shown that the quasiclassical implementation of the mapping approach15–17 is able to reproduce at least qualitatively the complex quantum dynamics of this system. Furthermore, we have introduced the concept of “quasiperiodic orbits” to facilitate the physical interpretation of the dynamics which on the quantum mechanical level is hampered by the largely delocalized and diffuse nature of the wave function. Our studies have also revealed that these type of systems represent a particular challenge to classical methods because the periodicity in the torsional degree of freedom results in strong quantum interference effects. Moreover, the photoexcitation may result in an initial preparation of the wave function that is coherent, but in which the wave-function distribution is not conserved. The semiclassical method, on the other hand, provides an excellent description of the dynamics of such systems. Moreover, the semiclassical method has been shown to be particularly useful for a variety of problems in chemical reaction dynamics.1–3 Quasiclassical methods, such as for example the classical Wigner approach,4–6 differ from purely classical methods in that the correct, quantum mechanical initial state is taken into account. Since the classical Wigner approach, however, incorporates phase information only within the harmonic approximation, the description of quantum effects such as interference is limited to very short time. Semiclassical approximation, the description of quantum effects such as interference, zero-point energy conservation and tunneling. In particular semiclassical methods based on the initial-value representation7–10 (which circumvent the cumbersome root search problem in boundary-value based semiclassical methods) have been applied successfully to a variety of different problems in molecular dynamics in recent years (for a recent review, see Ref. 11). Due to the oscillatory nature of the integrand involved in these semiclassical methods, the numerical effort is, however, much larger than in quasiclassical methods.

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ratiation of the system close to the torsional barrier, where tunneling effects become important.

In the system studied in Ref. 12, a detailed analysis of these two interrelated problems of the classical approximation was rather difficult due to the multidimensional nature of the problem and the involvement of two interacting electronic states. In the present paper, we consider, therefore, a simpler one-dimensional isomerization model problem, represented by a hindered rotor. This will allow us to investigate in detail the capability of the quasiclassical method to describe quantum dynamics in systems with periodic degrees of freedom. In addition, we investigate how the dynamical description can be improved by employing semiclassical instead of quasiclassical approaches.

The remainder of this paper is organized as follows: The model and the observables of interest are introduced in Sec. II. In Secs. III and IV, respectively, the semiclassical and quasiclassical methods employed in the study are outlined. In particular, we discuss some peculiarities of the semiclassical description of systems with periodic degrees of freedom. The advantages and shortcomings of the quasiclassical and semiclassical methods are studied in detail in Sec. V based on a comparison with quantum mechanical results. To obtain a comprehensive picture, we study the dynamics for different initial states, corresponding to different parts of the phase space of the hindered rotor, as well as for different observables. Section VI summarizes and concludes.

II. MODEL AND OBSERVABLES OF INTEREST

To investigate the capability of semiclassical and quasiclassical methods to describe quantum dynamics in a periodic potential, we consider a hindered rotor as a simple model for an isomerization reaction. The Hamiltonian of the hindered rotor is given by

\[ H = \frac{\hbar^2}{2I} \left( \frac{d^2}{dt^2} - \cos \varphi \right). \]  

(2.1)

Here, \( \varphi \) denotes the torsional angle (the physical range of which is restricted to \( -\pi/2 \leq \varphi \leq 3\pi/2 \)), \( p \) is the corresponding dimensionless momentum, and \( I \) is the moment of inertia. A torsional angle of \( \varphi = 0 \) is in the following referred to as cis configuration, while \( \varphi = \pi \) corresponds to the trans configuration of the isomerization reaction. The parameters of the model have been chosen similar to our previous study in Ref. 12, i.e., \( I^{-1} = 5.5 \times 10^{-4} \) eV and \( W = 2.25 \) eV.

The dynamics of the hindered rotor can be characterized by different observables. The most detailed dynamical information is embodied in the time-dependent probability density (\( \hbar = 1 \) hereafter)

\[ P(\varphi, t) = \langle \varphi | e^{-iHt} | \varphi \rangle^2. \]  

(2.2)

Here, \( | \varphi \rangle \) denotes the initially prepared state (see below). The isomerization dynamics of the system, on the other hand, may be described via the probability of finding the system in either the cis or trans conformation. These probabilities are given by

\[ P_{cis}(t) = \frac{\pi^2}{2} \int_{-\pi/2}^{\pi/2} d\varphi P(\varphi, t), \]  

(2.3a)

\[ P_{trans}(t) = 1 - P_{cis}(t). \]  

(2.3b)

Another observable of interest is the autocorrelation function of the initially prepared state

\[ J(t) = \langle \Psi_0 | e^{-iHt} | \Psi_0 \rangle. \]  

(2.4)

If one considers the hindered rotor as a model for isomerization in an electronically excited state, then the Fourier transform of \( J(t) \) gives the absorption spectrum.

In the numerical studies reported below, we consider initial states \( | \Psi_0 \rangle \) which are Gaussian wave packets centered around the angle \( \varphi_i \), with average momentum \( p_i \), and width \( \gamma \), i.e.,

\[ \Psi_i(\varphi) = \frac{\langle \varphi | \varphi, p_i \rangle}{\sqrt{\langle \varphi, p_i | \varphi, p_i \rangle}}, \]  

(2.5)

where

\[ \langle \varphi | \varphi, p_i \rangle = \left( \frac{\gamma}{\pi} \right)^{1/4} \sum_{n=-\infty}^{\infty} e^{-\gamma/2[(\varphi - \varphi_n + 2\pi n)^2 + ip_i(\varphi - \varphi_n - 2\pi n)]}. \]  

(2.6)

are coherent states on the circle.\(^{18-21}\) The sum in Eq. (2.6) ensures the correct periodicity of the wave function. The coherent states (2.6) are not normalized but form a (over)complete basis set. The normalization factor is given by

\[ \langle \varphi, p_i | \varphi, p_i \rangle = \int_{-\pi/2}^{\pi/2} d\varphi |\langle \varphi | \varphi, p_i \rangle|^2 = \sum_{n=-\infty}^{\infty} e^{-\gamma/2 \pi^2 n^2} \cos(2\pi np_i). \]  

(2.7)

If the width parameter \( \gamma \) is sufficiently large (i.e., \( \gamma \gg 1 \)), the different images of the Gaussian do not overlap and the normalization factor is close to unity. For a detailed discussion of the properties of these states we refer to Refs. 18 and 20.

\[ \langle \varphi, p_i | \varphi, p_i \rangle = \int_{-\pi/2}^{\pi/2} d\varphi |\langle \varphi | \varphi, p_i \rangle|^2 = \sum_{n=-\infty}^{\infty} e^{-\gamma/2 \pi^2 n^2} \cos(2\pi np_i). \]  

(2.7)

III. SEMICLASSICAL DESCRIPTION

Most of the applications of semiclassical approaches to molecular dynamics in recent years have been based on initial-value representation methods\(^ {7-10}\) which circumvent the cumbersome root search problem in boundary-value based semiclassical approaches such as the Van-Vleck–Gutzwiller propagator.\(^ {22}\) A widely used method is the Herman–Kluk (coherent state) initial-value representation.\(^ {23}\)

For a system with Hamiltonian \( \tilde{H} \) involving a single Cartesian degree of freedom the Herman–Kluk propagator is given by

\[ e^{-i\tilde{H}t} = \int_{-\infty}^{\infty} dq_0 dp_0 \langle q_0 | \varphi(p_0) \rangle C \psi_i^{HK}(q_0 p_0), \]  

(3.1)

where

\[ \psi_i^{HK}(q_0 p_0) = \frac{\langle \varphi | \varphi, p_i \rangle}{\sqrt{\langle \varphi, p_i | \varphi, p_i \rangle}}, \]  

(3.2)
FIG. 1. Potential-energy curve of the hindered rotor. Various initial states of the problem are considered, the energy distribution of which is shown in the left panel. The case \( E = 0 \) refers to the symmetric preparation of the system at \( \varphi = 0 \) without initial kinetic energy. This case is also illustrated by a Gaussian wave packet on the upper potential-energy curve. Furthermore, the case \( E > 0 \) represents a wave packet starting at \( \varphi = 0 \) with an additional kinetic energy of \( T \approx 0.15 \) eV and the case \( E < 0 \) represents a wave packet starting at \( \varphi = 0.4 \pi \) with a kinetic energy of \( T \approx 0.15 \) eV.

where \( (p_0, q_0) \) are initial momenta and coordinates for classical trajectories, \( p_i = p_i(p_0, q_0) \) and \( q_i = q_i(p_0, q_0) \) are the classically time-evolved phase space variables and \( S_i \) is the classical action integral along the trajectory, i.e.,

\[
S_i = \int_0^t ds(p_i, \dot{q}_i - \vec{H}).
\]

The pre-exponential factor \( C_i \) is given by

\[
C_i(p_0, q_0) = \sqrt{\frac{1}{2} \left( \frac{\partial q_i}{\partial q_0} + \frac{\partial p_i}{\partial q_0} - i \gamma^{-1} \frac{\partial q_i}{\partial p_0} + i \gamma^{-1} \frac{\partial p_i}{\partial q_0} \right)}.
\]

It involves a combination of the elements of the monodromy matrix

\[
M_i = \begin{pmatrix}
\frac{\partial q_i}{\partial q_0} & \frac{\partial p_i}{\partial q_0} \\
\frac{\partial q_i}{\partial p_0} & \frac{\partial p_i}{\partial p_0}
\end{pmatrix}.
\]

In the above expression \( \gamma \) denotes the width parameter for the coherent state \( |qp \rangle \), the coordinate space representation of which is given by

\[
\langle x | qp \rangle = \left( \frac{\gamma}{\pi} \right)^{1/4} e^{-\gamma((x-q)^2 + ip(x-q))}.
\]

Within the applicability of the semiclassical approximation, the propagator (3.1) is rather insensitive to the particular value of the width parameters \( \gamma \), but this parameter can of course affect the numerical efficiency of the calculation.

As has been discussed by several authors, \(^{21,24–26}\) semiclassical initial-value representations such the Herman–Kluk propagator cannot be directly applied to systems which involve non-Cartesian coordinates such as for example the 2\( \pi \)-periodic angle \( \varphi \) in the hindered rotor. This problem is due to the fact, that boundary conditions, e.g., the periodicity of the wave function, are not fulfilled by the propagator (3.1). \(^{25}\) For the specific case of a 2\( \pi \)-periodic angular degrees of freedom (i.e., motion on a circle) several approaches to circumvent this problem have been proposed. \(^{21,24–26}\) A rather straightforward way to obtain a semiclassical initial-value representation for non-Cartesian degrees of freedom exists if the quantum dynamics of the system under consideration can be represented as the projection from a Cartesian system. This question has been investigated some time ago in the context of path-integral quantization in multiply-connected spaces\(^{27–31}\) and in systems with constrained geometries. \(^{32}\)

Specifically, for the rotor considered here it can be easily shown that the quantum propagator on the circle can be represented by the quantum propagator on the real line via

\[
\langle \varphi' | e^{-i\vec{H} t} | \varphi \rangle = \sum_{n=-\infty}^{\infty} \langle \chi' = \varphi' + 2 \pi n | e^{-i\vec{H} t} | \chi = \varphi \rangle,
\]

where \( |\chi\rangle \) are the usual position eigenstates on the real line, \( \vec{H} \) denotes the continuation of \( H \) from the circle to the real line, and the angle states \( |\varphi\rangle \) fulfill the completeness relation

\[
\int_{-\pi/2}^{3\pi/2} d\varphi |\varphi\rangle \langle \varphi | = 1.
\]

A semiclassical initial-value representation can then be obtained by replacing the quantum propagator \( e^{-i\vec{H} t} \), for example, by the Herman–Kluk propagator for the Cartesian degree of freedom, i.e.,
\[ \langle \varphi' | e^{-iHt} | \varphi \rangle_{HK} = \sum_{n=-\infty}^{\infty} \langle \varphi' = \varphi + 2\pi n | e^{-iHt} \rangle_{HK} |x = \varphi \rangle = \sum_{n=-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{dq_0 dp_0}{2\pi} \langle \varphi' = \varphi + 2\pi n | q, p \rangle \times C \, e^{iS(q, p)|x = \varphi \rangle}. \] (3.8)

Employing Eq. (3.8), the definition of the coherent states on the circle, Eq. (2.6), as well as the periodicity of the classical trajectory \( q_t \) in a periodic potential, it is readily shown that the semiclassical Herman–Kluk propagator on a circle for a transition amplitude between general (2π-periodic) states \( |\Psi_i\rangle \) and \( |\Psi_f\rangle \) is given by

\[ \langle \Psi_f | e^{-iHt} | \Psi_i \rangle_{HK} = \frac{1}{2\pi} \int_{-\pi/2}^{\pi/2} d\varphi_0 \int_{-\infty}^{\infty} dp_0 \langle \Psi_f | \varphi, p \rangle C \, e^{iS(q, p)|x = \varphi \rangle}. \] (3.9)

The propagator can also be written in the form

\[ (e^{-iHt})_{HK} = \frac{1}{2\pi} \int_{-\pi/2}^{\pi/2} d\varphi_0 \int_{-\infty}^{\infty} dp_0 \langle \Psi_f | \varphi, p \rangle C \, e^{iS(q, p)|x = \varphi \rangle}. \] (3.10)

The only differences between this propagator and the Herman–Kluk propagator in Cartesian coordinates (3.1) are, thus, the integration limits for the position and the angle, respectively, and the definition of the coherent states involved in the propagator.

The semiclassical propagator (3.10) has been obtained before by Sun and Miller,32 as well as Maitra,21 Kay25 has also analyzed other possibilities to obtain an initial-value representation for non-Cartesian coordinates, demonstrating that there exists a variety of choices that mainly differ in the way the proper boundary conditions of the wave functions are implemented. Since the mapping of the quantum dynamics on the circle onto the quantum dynamics on the real line appears to be rather unique, the derivation used here, however, singles out the initial-value representations (3.9) and (3.10). Furthermore, it is noted that in the same way as outlined here for the circle, semiclassical initial-value representations can be obtained for other geometries that allow a quantum mechanical mapping to a Cartesian system, such as, e.g., the torus30 or a particle on a half-line.32

IV. QUASICLASSICAL DESCRIPTION

To calculate the observables introduced in Sec. II within a quasiclassical trajectory approach, we consider the classical expectation value of an observable \( A \), given by

\[ A^{QC}(t) = \int dq_0 dp_0 \rho(q_0, p_0) A(q_t, p_t). \] (4.1)

Here, the observable \( A \) is considered as a function of the classical trajectory \( (q_t, p_t) \) with initial conditions \( (q_0, p_0) \) and \( \rho \) represents a phase-space distribution function describing the quantum-mechanical initial state of the system. For example, in order to obtain the quasiclassical approximation to the probability to find the system in the cis conformation, \( P_{cis}(t) \), we calculate the expectation value of the corresponding projection operator,

\[ \hat{P}_{cis} = \Theta(\pi/2 - |\varphi|), \] (4.2)

where \( \Theta \) denotes the Heaviside step function, thus yielding

\[ P_{cis}^{QC}(t) = \int_{-\infty}^{\infty} dp_0 \rho(q_0, p_0) \Theta(\pi/2 - |\varphi(t)|). \] (4.3)

Thereby, the angle \( \varphi \), in the argument of the Heaviside step function is to be understood modulo 2\( \pi \). To sample the initial distributions \( \rho \), different phase-space distributions can be applied. A particular popular choice is the Wigner function of the initial quantum state.6,35 The thus resulting quasiclassical approach is the classical Wigner method which has been applied quite successfully to a variety of different systems with Cartesian-type coordinates.4,5 It is noted that the classical Wigner approach can also be derived from a semiclassical expression for \( \langle A \rangle(t) \) using a linearization approximation.36,37

Similar to the semiclassical description discussed in Sec. III, also in the classical Wigner approach some peculiarities have to be considered if it is applied to periodic (angular) degrees of freedom. Several authors have studied the Wigner function for periodic degrees of freedom.38–40 Starting from a definition of the Wigner function which takes into account the periodicity of the angle and the discrete nature of the momentum in these systems, Bizarro has investigated in detail the dynamical equation of motion in the Wigner representation.40 Due to the discrete nature of the momentum, the resulting expressions appear to be rather complicated. In the Appendix, we pursue a different route to extend the classical Wigner approach to periodic degrees of freedom. In a similar way as for the semiclassical propagator in Sec. III, we employ the mapping of the quantum propagator from the circle to the real line, Eq. (3.6), and subsequently use the classical Wigner approximation on the real line. This way it can be shown that for all observables and initial states considered in this paper the classical Wigner approximation can be written in the form (4.1). The explicit expressions for the initial distribution \( \rho(q_0, p_0) \) and the representation of the observable \( A(q_t, p_t) \) are given in the Appendix.

V. RESULTS AND DISCUSSION

In this section we will study the capability of the semiclassical and quasiclassical method outlined above to describe the quantum dynamics of the hindered rotor. For a given dynamical system, the quality of an approximate description generally depends on the initial state and on the observable under consideration. Therefore, we will study the dynamics of the hindered rotor for various different initial preparations and observables of interest. The choice for the former is motivated by the phase-space structure of the hindered rotor. Depending on the total energy, the phase space of the hindered rotor can be separated into two parts: If the energy of the rotor is below the torsional barrier, the rotor
will perform oscillations (librations) around the equilibrium geometry which corresponds in the present convention to the \textit{trans} conformation. For an average initial energy above the barrier, on the other hand, it will perform full rotations.

To obtain a comprehensive picture of the performance of the semiclassical and quasiclassical approximation in these different dynamical regimes, we shall consider initial states \(|\varphi_i_0, p_i_0\rangle\) with three different sets of parameters for the center of the Gaussian wave packet \(\varphi_i\) and its average momentum \(p_i\):

(i) An initial state with parameters \(\varphi_i = 0, p_i = 0\) representing a Gaussian wave packet located at the top of the torsional barrier without initial kinetic energy. This situation is schematically illustrated in Fig. 1 and is in the following referred to as "\(E = 0\)".

(ii) A state which is initially also localized around \(\varphi_i = 0\) but with finite average momentum, \(p_i = 23.24\), corresponding to a kinetic energy of \(T \approx 0.15\) eV. Since the average energy of this wave packet is above the torsional barrier, it is denoted by "\(E > 0\)."

(iii) Finally, the choice \(\varphi_i = 0.4\pi, p_i = 23.24\) corresponds to a mean energy below the torsional barrier, and will be referred to as "\(E < 0\)." The width of the initial state as well as the width of coherent states in the semiclassical propagator (3.10) was chosen in all three cases as the width of the ground state in the potential well (within the harmonic approximation), i.e., \(\gamma = \sqrt{\frac{W}{2}} \approx 45\).

The wave-packet dynamics for the three cases is depicted in Fig. 2. For each case the results of the quantum mechanical description, the semiclassical, and the quasiclassical approach are shown. Let us first consider the quantum results, which are shown in the left panels. The comparison of the three cases demonstrates the qualitatively different dynamical behavior in the different regimes: For an average energy above the torsional barrier (\(E > 0\)), the initial momentum is seen to result in unidirectional rotation of a well localized wave packet for short times. For longer times (\(t > 300\) fs) the distribution becomes more and more delocalized (due to dispersion) and, furthermore, quantum interference effects become apparent in oscillatory structures. As may be expected, for energies above the torsional barrier the dynamics of the hindered rotor is quite similar to the time evolution of a free rotor. The dynamics is quite different if the average energy of the wave packet is well below the torsional barrier (\(E < 0\)). In this case the wave packet is confined to the potential well and performs periodic oscillations around the equilibrium geometry. The anharmonicity of

\[\gamma = \sqrt{\frac{W}{2}} \approx 45\]

\[\text{FIG. 2. Probability densities for the cases } E > 0 \text{ (top), } E = 0 \text{ (middle), and } E < 0 \text{ (bottom), plotted as a function of time } t \text{ and the isomerization angle } \varphi. \text{ Shown are the quantum mechanical results (QM), as well as the results of the semiclassical (SC) and quasiclassical (QC) approach.}\]
the potential results in some interference structures, but overall the wave packet stays mainly localized. The most complicated dynamics is seen in the intermediate case, where the wave packet is prepared directly at the torsional barrier without kinetic energy, $E=0$. In this case the wave packet splits into two parts moving into opposite direction. Due to the periodicity of the potential the two parts meet after half a rotational period resulting in strong interference effects and a largely delocalized density.

Let us next consider the performance of the semiclassical and quasiclassical approach on the basis of the time-dependent density. While the semiclassical description and the classical Wigner formulation are exact for the free rotor\(^4\) (due to the linearity of the equation of motion), both approaches represent an approximation in the case of the hindered rotor. The semiclassical results shown in the middle panels of Fig. 2 are seen to reproduce all the details of the quantum wave function in the cases $E>0$ and $E<0$. In particular, the interference structures present in the dynamics at $E>0$ for longer times are well described. For the situation where the wave packet is initially prepared at the top of the torsional barrier, i.e., $E=0$, the semiclassical result is also in rather good agreement with the quantum result for the first rotational period. For longer times, however, the semiclassical results deteriorate significantly. The quasiclassical approach, on the other hand, can only reproduce the overall features of the dynamics, but misses all structures that are based on quantum interference. This is particularly apparent in the case $E=0$, but can also be seen for $E>0$ at longer times.

To obtain a more quantitative comparison between the different dynamical approaches, Fig. 3 presents results for two different observables: the probability to find the system in the cis conformation, $P_{cis}(t)$, and the autocorrelation function, $J(t)$, of the initially prepared wave packet. Overall, the results shown in Fig. 3 confirm the qualitative picture obtained from the wave-packet dynamics. For the discussion of the quasiclassical method below, it is interesting to note that, depending on the initial condition, the quantum results for $P_{cis}(t)$ fluctuate at larger times around a specific value $\langle P_{cis} \rangle$, the time average of $P_{cis}(t)$. Employing von Neumann’s criterion for quantum ergodicity, this time average can be calculated as\(^4\)

$$\langle P_{cis} \rangle = \frac{E_{cis}}{E_{cis}^2} \sum_n |\langle n|\Psi_i\rangle|^2 |\langle n|P_{cis}|n\rangle|,$$  
(5.1)

where $\{|n\rangle\}$ represent the eigenstates of the system and $P_{cis}$ denotes the projector on the cis configuration. The calculation yields $\langle P_{cis} \rangle = 0.45$, 0.81, and 0.70 for the cases $E<0$, $E=0$, and $E>0$, respectively, which is in excellent agreement with the results in Fig. 3.

Let us first discuss the performance of the semiclassical method. For both observables studied, the results of the semiclassical approach can hardly be distinguished from the quantum results for the cases $E>0$ and $E<0$. In the case $E=0$, on the other hand, the semiclassical approach can only describe the short-time dynamics (i.e., the first rotational period), but fails severely for longer times. The excellent agreement between semiclassical and quantum results for $E>0$ and $E<0$ demonstrates the capability of semiclassical methods based on the initial-value representation to describe systems which exhibit strong quantum interference effects. The failure of the semiclassical approach for $E=0$, on the other hand, is related to the well known problem of semiclassical propagators, that are based on real trajectories, to describe barrier tunneling (and above barrier reflection). This problem has been studied by several authors for different model problems, such as a double-well potential\(^4\) as well as the Eckart barrier.\(^44\)–\(^47\) It was shown that the failure of semiclassical methods such as the Herman–Kluk propagator is particularly severe in case of coherent tunneling in the double-well potential.\(^4\) In contrast to the double-well potential, in the present problem tunneling (and above-barrier reflection) becomes only important close to the torsional barrier and,

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**FIG. 3.** Comparison of quantum (solid lines), quasiclassical (dashed lines), and semiclassical (dotted line) results obtained for the probability $P_{cis}(t)$ to remain in the cis configuration (left) and the modulus of the autocorrelation function, $J(t)$, of the initially prepared state (right). Shown are the cases $E>0$ (top), $E=0$ (middle), and $E<0$ (bottom).
therefore the quantum dynamics for $E<0$ and $E>0$ is excellently described by the semiclassical approach.

The breakdown of the semiclassical approximation for $E=0$ manifests itself also in a strong deviation of the norm of the wave function from unity. While in the cases $E>0$ and $E<0$ the norm of the wave function is preserved within 3% and 1%, respectively, for $E=0$ the norm falls below 0.7 for longer times. Since the norm of the wave function in semiclassical initial-value representation methods such as the Herman–Kluk propagator is only preserved within the semiclassical approximation, the deviation can be used as an independent check of the semiclassical approximation. It is noted that several schemes have been devised to improve the performance of semiclassical initial-value representation propagators for systems which exhibit tunneling effects.

Let us next consider the results of the quasiclassical method. Overall the results shown in Fig. 3 demonstrate that this method has problems to describe the dynamics of the hindered rotor for situations where quantum effects are important, i.e., for the initial preparations $E>0$ and $E=0$. In both cases, the quasiclassical result can reproduce the quantum dynamics for short times (up to about one rotational period). At longer times, however, the quasiclassical method cannot resolve the oscillations in the dynamics but decays to an average value, which in case of $P_{cis}$ is in rather good agreement with the quantum-mechanical average value $\langle P_{cis} \rangle$ [see Eq. (5.1)]. Since Eq. (5.1) directly accounts for the level densities of the cis and trans potential wells, the agreement indicates that the quantum and classical level densities are quite similar for the energies under consideration. The rapid decay of the quasiclassical data, on the other hand, reflects the well-known fact that for anharmonic systems the classical Wigner approach may only give a short-time approximation to quantum mechanics. Only in the case $E<0$, which corresponds to wave-packet motion in the potential well, the quasiclassical method is in rather good agreement with the quantum results even for longer times. In this case the wave packet stays mainly localized and performs oscillations around the equilibrium geometry of the potential well and, therefore, the dynamics of both observables studied can be rather well described by classical dynamics. Quantum interference effects in this case become only effective at longer times, resulting in high-frequency oscillations of the autocorrelation function (for $t>1400$ fs) as well as a revival of the population on a much longer time scale (at $\sim 18$ ps, data not shown).

To obtain a better understanding why the semiclassical/quasiclassical approaches work rather well for some initial preparations but fail for others, it is instructive to analyze the eigenvalue structure of the system under consideration and, in particular, which eigenstates contribute to the dynamics for the three different initial preparations. For the autocorrelation function, this is determined by the overlap matrix element between the eigenstates of the hindered rotor, $|n\rangle$, and the initially prepared state, i.e., the Franck–Condon factor $\langle n | \Psi_i \rangle$. As is illustrated in Fig. 1, the distribution of the Franck–Condon factors shows remarkable differences for the three cases $E>0$, $E=0$, and $E<0$. While for $E<0$ there are 26 eigenstates with a Franck–Condon factor larger than 0.1, in the case $E>0$ only nine eigenstates are significantly populated. Moreover, while in the former case the eigenvalues of the contributing eigenstates are almost equidistant, in the latter case the spacing between the most important states increases regularly with increasing eigenvalue. In the case $E=0$, finally, only six eigenstates have a Franck–Condon factor higher than 0.1 and there is a far bigger difference in absolute value between the Franck–Condon factors of the important states compared to the other two cases.

Figure 4 illustrates how this qualitative difference in the distribution of Franck–Condon factors manifests itself in the quantum autocorrelation function. Let us first consider the initial preparation $E<0$. In this case, the autocorrelation function is characterized by a damped oscillation with a period of $\sim 110$ fs. For longer times the phase difference between the different eigenstates results in high-frequency oscillations. It is interesting to see how many eigenstates are required to reproduce the dynamics of the autocorrelation function. Figure 4 demonstrates that the two most populated eigenstates are enough to reproduce the main period of 110 fs. Taking the 12 most important eigenstates into account cannot yet reproduce the signal completely, particularly the damping is still to weak. To reproduce the autocorrelation function on the time scale shown, 26 eigenstates are required. The reason why the semiclassical and also the quasiclassical approach are able to describe the dynamics in this case correctly is thus not only that the energy is far below the torsional barrier but also the rather large number of relevant eigenstates which have almost equidistant eigenvalues and contribute with almost equal weight. The situation is different in the $E>0$ system, where the energy of the initially prepared state is above the torsional barrier. Here, nine eigenstates are required to reproduce the autocorrelation function. In contrast to the $E<0$ case, the spacing of these eigenstates is unequal resulting in the rather irregular oscillation of the autocorrelation function for longer times. The semiclassical approach can describe this dynamics very well because it takes phase information properly into account. The quasiclassical approach, on the other hand, misses the phase information (beyond the harmonic approximation) and therefore fails for longer times. Finally, we consider the case $E=0$. Fourier transforming the signal of the autocorrelation function for the $E=0$ case yields three essential periods of 65, 115, and 133 fs. The slowest of these periods can be understood as the beating of the two most relevant eigenstates. Taking one more eigenstate into account, the autocorrelation function is already well reproduced. With as few as five eigenstates, the system is described completely. Therefore, the initial preparation at the top of the torsional barrier corresponds effectively to a few state system which cannot be described within the quasiclassical approach. While the semiclassical approach is generally able to describe systems which involve only few states, it typically fails to reproduce the correct energies close to barriers and, therefore fails in the case $E=0$. 

VI. CONCLUSIONS

In this paper we have studied the capability of semiclassical and quasiclassical methods to describe quantum dynamics in a periodic potential. To this end, we have studied various different initial preparations as well as different dynamical observables. The results of the quasiclassical calculations, which were based on the quasiclassical Wigner approach, overall show that such methods have problems to describe the dynamics in periodic potentials. Only for situations where the dynamics is confined to the potential well, and for highly averaged observables the quasiclassical method was found to work rather well.

A significantly better description of the dynamics—albeit at a higher numerical cost—can be obtained by employing semiclassical instead of quasiclassical approximations. Here, we have used the Herman–Kluk initial-value representation, generalized to properly take into account the boundary conditions of the wave function in periodic potentials. For situations where the dynamics is confined to the potential well, and for highly averaged observables the quasiclassical method was found to work rather well.

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For an initial preparation of the wave packet close to the barrier, however the semiclassical approach was found to fail after a relatively short time (of the order of one rotational period). This is related to the well known problem of semiclassical methods based on real trajectories to describe barrier tunneling.

We have, furthermore, analyzed the relation between the performance of the quasiclassical/semiclassical method and the eigenvalue structure of the participating eigenstates. This study has revealed that in the situation where the quasiclassical method works well many eigenstates with equidistant eigenvalues contribute to the dynamics with almost equal weight. On the other hand, it was found that in situations where the semiclassical approach (and also the quasiclassical method) failed, only very few eigenstates contribute to the dynamics, i.e., the system exhibits strong quantum mechanical character. Since the eigenvalues of those states are, furthermore, close to the barrier they are not correctly described by the semiclassical method.

Finally, we would like to comment on the relation between the present study and our previous investigation of the performance of quasiclassical methods for photoinduced isomerization reactions at conically intersecting surfaces. In contrast to the present results, in our previous study it was found that quasiclassical methods can at least qualitatively reproduce the quantum dynamics. The reason for this discrepancy is the different nature of the systems considered. In the present study we have focused on a simple one-dimensional isomerization model where quantum interfer-

FIG. 4. Modulus of the autocorrelation function of the initially prepared state. Top: $E>0$ with 2 (long dashed line), 6 (dashed line), 12 (dotted line), and all (solid line) eigenstates; Middle: $E=0$ with 2 (long dashed line), 3 (dashed line), 5 (dotted line), and all (solid line) eigenstates; Bottom: $E<0$ with 2 (long dashed line), 12 (dashed line), 26 (dotted line), and all (solid line) eigenstates.
ence effects are particularly strong. In the more complex system studied in Ref. 12, on the other hand, the multidimensionality of the problem and the conical intersection result in ultrafast dephasing processes which quench interference effects, thereby effectively improving the performance of quasiclassical methods.

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APPENDIX: CLASSICAL WIGNER METHOD FOR PERIODIC POTENTIALS

In this Appendix we give a brief outline, how the classical Wigner method, which is well known for Cartesian coordinates, can be applied to systems with periodic coordinates such as the hindered rotor. Thereby we follow the same strategy as for the semiclassical method in Sec. III, i.e., we use the relation between the quantum dynamics on the circle and the quantum dynamics on the real line.

Let us consider the expectation value of an observable \( A \) at time \( t \) given by

\[
\langle A \rangle(t) = \langle \Psi_i | e^{i\mathcal{H}t} A e^{-i\mathcal{H}t} | \Psi_j \rangle,
\]

(A1)

where \( | \Psi_j \rangle \) denotes the initial state. Using the relation between the quantum dynamics on the circle and on the real line, Eq. (3.6), \( \langle A \rangle(t) \) can be written in the form

\[
\langle A \rangle(t) = \sum_{n,m} \int_{-\pi}^{\pi} d\varphi' d\varphi \int_{-\pi}^{\pi} d\varphi' d\varphi \Psi^*_{\varphi}(\varphi') \Psi_{\varphi'}(\varphi') \\
\times \langle \varphi' A | \varphi' \rangle \langle x_i = \varphi + 2\pi m | e^{i\mathcal{H}t} | x_f = \varphi + 2\pi m \rangle \\
\times \langle x' \varphi = \varphi' | e^{-i\mathcal{H}t} | x' \varphi = \varphi' + 2\pi m \rangle.
\]

(A2)

Here, as in Eq. (3.8), \( | \rangle \) is the usual position eigenstates on the real line and \( \mathcal{H} \) denotes the continuation of \( H \) and the requirement of localization is fulfilled if

\[
\Psi_{\varphi}(\varphi) = \sum_m g_m(\varphi + 2\pi m),
\]

(A6)

with \( g(\varphi) \) a localized function. In the applications considered in this paper the function \( g_i \) is (up to a normalization constant) given by [cf. Eq. (2.6)],

\[
g_i(\varphi) = \left( \frac{\gamma}{\pi} \right)^{1/4} e^{-\gamma/2(\varphi - \varphi_i)^2 + i\pi(\varphi - \varphi_i)},
\]

(A7)

and the requirement of localization is fulfilled if \( \gamma \gg 1 \). Furthermore, let us assume that the observable \( A \) projects on a state that is also given in the form (A6), i.e.,

\[
A = |\Psi_j \rangle \langle \Psi_j |
\]

(A8)

with

\[
\Psi_{\varphi}(\varphi) = \sum_m g_m(\varphi + 2\pi m),
\]

(A9)

and a function \( g_{ij} \) that is well localized in the angle \( \varphi \). We note in passing that all observables considered in this paper fulfill this requirement. This is obvious for the autocorrelation function, Eq. (2.4), and the torsional probability density, Eq. (2.2). In the former case the function \( g_{ij} \) is given by Eq. (A7) in the latter case it is a delta function. The third observable considered, the probability to find the system in the \( cis \) conformation, \( P_{cis}(t) \), can be obtained via Eq. (2.3a) from the density.

Taking into account the \( 2\pi \)-periodicity of the wave function \( \Psi_{\varphi}(\varphi) \) as well as the periodicity of the classical trajectory in a periodic potential, Eq. (A3) can be rewritten in the form

\[
\langle A \rangle^{QC}(t) = \frac{1}{2\pi} \sum_{n,m} \int_{-\pi}^{\pi} d\varphi_0 d\varphi_0 \int_{-\pi}^{\pi} d\varphi_0 \int_{-\pi}^{\pi} d\varphi_0 \\
\times \langle \varphi_0 + 2\pi l - s/2 | A | \varphi_0 + 2\pi l + s/2 \rangle \\
\times \Theta(\pi - | \varphi_0 + 2\pi l - s/2 |) \\
\times \Theta(\pi - | \varphi_0 + 2\pi l + s/2 |) \\
\times \int_{-\pi}^{\pi} ds' e^{i\mathcal{H}s'} \Psi_{\varphi_0}(\varphi_0 - s'/2) \Psi^*_{\varphi_0 + s'/2}.
\]

(A5)
If these requirements are fulfilled, it can be shown that the classical Wigner expression (A5) can be well approximated by the simpler formula,

$$\langle A \rangle^{QC}(t) = \int_{-\pi}^{\pi} d\varphi_0 \int_{-\infty}^{\infty} dp_0 A_W(\varphi_0, p_0) \rho_{iW}(\varphi_0, p_0),$$

(A10)

where \( \rho_{iW}(\varphi_0, p_0) \) is given by the 2\( \pi \)-periodic continuation of the Wigner function of \( g_i \), i.e.,

$$\rho_{iW}(\varphi_0, p_0) = \sum_n \frac{1}{2\pi} \int_{-\infty}^{\infty} ds e^{i\varphi_0 s} g_n(\varphi_0 + 2\pi n - s/2)$$

$$\times g_n^*(\varphi_0 + 2\pi n + s/2),$$

(A11)

and, likewise, \( A_W(\varphi_1, p_1) \) is the 2\( \pi \)-periodic continuation of the Wigner function of \( g_i \), i.e.,

$$A_W(\varphi_1, p_1) = \sum_n \int_{-\infty}^{\infty} ds e^{i\varphi_1 s} g_n(\varphi_1 + 2\pi n - s/2)$$

$$\times g_n^*(\varphi_1 + 2\pi n + s/2).$$

(A12)

For the autocorrelation function of the initial state, Eq. (2.5), we thus have

$$\rho_{iW}(\varphi_0, p_0) = A_W(\varphi_1, p_1)/(2\pi)$$

$$= \frac{1}{\pi} \sum_n \exp\{-\gamma(\varphi_0 + 2\pi n - \varphi_1)^2$$

- \( (p_0 - p_1)^2/\gamma \}.$$

(A13)

The Wigner function for the torsional probability density, \( P(\varphi, t) \), is given by

$$A_W(\varphi_1, p_1) = \sum_n \delta(\varphi - \varphi_1 - 2\pi n),$$

(A14)

and, finally, the Wigner function for the probability to find the system in the cis conformation, \( P_{cis}(t) \), reads

$$A_W(\varphi_1, p_1) = \sum_n \Theta(\pi/2 - |\varphi_1 + 2\pi n|).$$

(A15)

Since the sum over \( n \) in the last two equations effectively results in defining the angle \( \varphi_i \) modulo 2\( \pi \), this result coincides with Eq. (4.3).

1See, for example, articles in Quantum and Classical Dynamics in Condensed Phase Simulations, edited by B. J. Berne, G. Cicotti, and D. F. Coker (World Scientific, Singapore, 1998).


26M. Ovchinnikov (unpublished).


