Quasiperiodic orbit analysis of nonadiabatic cis–trans photoisomerization dynamics

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Adopting a multidimensional model of nonadiabatic cis–trans photoisomerization, quantum-mechanical and classical simulations of the ultrafast wave-packet dynamics associated with this photoreaction are presented. The quantum calculations demonstrate that nonadiabatic photoisomerization typically leads to a largely delocalized and diffuse wave function, which hampers an intuitive understanding of the dynamics in terms of specific nuclear motion. To facilitate a classical description, a recently proposed theoretical formulation is employed that affords an exact mapping of discrete electronic states onto continuous degrees of freedom and therefore provides a well-defined classical limit of a nonadiabatically coupled system. It is shown that a simple quasiclassical implementation of the mapping formulation is able to reproduce at least qualitatively the complex quantum dynamics of the system. In addition, the classical description allows us to characterize the nonadiabatic photoisomerization dynamics in terms of a few “quasiperiodic orbits.” These orbits are close to a true unstable periodic orbit but are exactly periodic only with respect to the slow reaction coordinate of the system. Various types of quasiperiodic orbits of nonadiabatic photoisomerization are identified and analyzed. It is shown that the diffuse appearance of the quantum-mechanical wave function can be directly connected to irregular classical orbits propagating on vibronically coupled potential-energy surfaces. The chaotic behavior of the system is mainly caused by the relatively high energy corresponding to photoexcitation, the large anharmonicity of the isomerization potentials, and the reflection of the trajectory at surface crossings. The results demonstrate that quasiperiodic orbits represent a concept well suited to analyze the quantum dynamics of complex systems in terms of classical trajectories without the cumbersome search for periodic orbits. © 2003 American Institute of Physics.

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I. INTRODUCTION

In many areas of chemical physics, the application of classical mechanics has proven to be a powerful tool to describe the dynamics of polyatomic systems. While this approach is well established for systems with an obvious classical analog, it is a priori not clear how to incorporate discrete quantum-mechanical states and nonadiabatic transitions between these states into a classical formulation. As a remedy, a number of mixed quantum-classical models have been proposed, including, most notably, the surface-hopping and the mean-field trajectory method.1–3 Since electronic and nuclear dynamics are treated on a different dynamical footing, however, quantum-classical models may not necessarily provide a satisfying classical picture of nonadiabatic dynamics. For example, it is not clear how to define vibronic surfaces-of-section or vibronic periodic orbits.

Employing quantum-mechanical bosonization techniques, recently a “mapping” formulation has been proposed, which bypasses the problem of a classical treatment of discrete quantum degrees of freedom by transforming the discrete quantum variables to continuous variables.4,5 The method consists of two steps: A quantum-mechanical exact mapping of discrete onto continuous degrees of freedom and a standard classical or semiclassical treatment of the resulting dynamical problem. The relation of the mapping approach to other formulations has been discussed,4–6 including the mean-field trajectory method,1–3 the classical electron analog model of Meyer and Miller,7–9 and the spin coherent state formulation.10–12 Furthermore, the method has recently been applied to a variety of systems with nonadiabatic dynamics.4–6,13–18

Since the mapping representation of a vibronically coupled molecular system has a well-defined classical limit, the approach allows us to employ usual methods of nonlinear
dynamics to study nonadiabatic quantum phenomena. With this end in mind, we have recently investigated the classical phase space of a nonadiabatically coupled system and also introduced the classical periodic orbits of such a system.\(^\text{19–21}\) Periodic orbits, i.e., solutions of the classical equation of motion that return to their initial conditions, are of particular interest, because they can be directly linked to spectral response functions via semiclassical trace formulas.\(^\text{22}\) Because periodic-orbit theory allows us to express quantum observables in terms of classical trajectories, it represents an appealing tool to analyze complicated or elusive quantum phenomena with the aid of intuitively clear classical concepts.\(^\text{22–29}\) Adopting a simple model of intramolecular electron transfer, we have identified the shortest periodic orbits of the system and used them to analyze the nonadiabatic quantum dynamics.\(^\text{19}\) In particular, it has been demonstrated that transient oscillations observed in electron-transfer femtosecond experiments may be explained in terms of a few classical trajectories.\(^\text{21}\)

So far, we have restricted our studies to a highly idealized spin-boson-type model, i.e., to an electronic two-state system with constant interstate coupling and a single linearly shifted harmonic vibrational mode. As a first attempt to extend our investigations to multidimensional and anharmonic vibronic-coupling systems, in this work we are concerned with cis–trans photoisomerization dynamics. In the course of this photoreaction, the perpendicularly twisted configuration leads to a degeneracy of the adiabatic potential-energy surfaces—a so-called conical intersection—which triggers an ultrafast internal-conversion process from the photoexcited singlet state back to the ground state.\(^\text{30–33}\)

In our studies, we adopt a multidimensional model of nonadiabatic cis–trans photoisomerization proposed by Domcke and co-workers.\(^\text{32–34}\) The model comprises two coupled electronic states \(|\psi_0\rangle,|\psi_1\rangle\) and three nuclear degrees of freedom: A large-amplitude coordinate along which the molecule undergoes isomerization (the “reaction mode” \(x_r\)), a vibronically active mode which may couple the two electronic states (the “coupling mode” \(x_c\)), and a Condon-active mode along which the energy gap between the two electronic states is tuned (the “tuning mode” \(x_t\)). Adopting a diabatic electronic representation, the model Hamiltonian can be written as \((\hbar = 1)\)

\[
H = \hbar_0 \mathbf{1} + \sum_{n,m=0,1} |\psi_n\rangle V_{nm} (|\psi_m\rangle),
\]

\[
\hbar_0 = -\frac{1}{2I} \frac{\partial^2}{\partial \varphi^2} + \frac{\sum_{j=c,t} \omega_j^2}{2} \left( x_j^2 - \frac{\partial^2}{\partial x_j^2} \right),
\]

\[
V_{nn} = E_n + \frac{1}{2} W_n (1 - \cos \varphi) + \delta_{1,n} k x_t,
\]

\[
V_{01} = V_{10} = \lambda x_c,
\]

where \(\hbar_0\) contains the vibrational kinetic energy and the state-independent part of the vibrational potential energy, while \(V_{nm}\) represents the elements of the diabolic potential matrix. The tuning and coupling modes are described by dimensionless positions \(x_t\) and \(x_c\), the frequencies \(\omega_t\) and \(\omega_c\), and the coupling constants \(k\) and \(\lambda\), respectively. The dynamics along the reaction coordinate \(\varphi\) is determined by the moment of inertia \(I\) and the energies \(E_n\) and \(W_n\). Similar to Ref. 34, the parameters of the model are in \(\text{eV}\): \(\omega_t = 0.1, \omega_c = 0.085, \lambda = 0.17, I^{-1} = 5.5 \times 10^{-4}, E_0 = -2.5, W_0 = 2.25, E_1 = 0,\) and \(W_1 = -2.25\).

To study the photoinduced reaction dynamics of the system we consider initial states of the form

\[
|\Psi(0)\rangle = |\phi_t\rangle |\phi_r\rangle |0_c\rangle.
\]

Here, \(|0_c\rangle\) and \(|0_r\rangle\) denote the vibrational ground state of the tuning and coupling mode, respectively. The initial state of the reaction mode \(|\phi_r\rangle\) is assumed to be a Gaussian wave-
complete basis set. The normalization factor is given by

$$\phi_n(\varphi) = \frac{1}{\varphi_0} \sqrt{\varphi_0} e^{-\alpha^2 (\varphi - \varphi_0)^2}$$

where

$$\langle \varphi | \varphi_0 \rangle = \frac{1}{\pi^{1/4}} \sum_{n = -\infty}^{\infty} \sum_{m = -\infty}^{\infty} e^{-\alpha^2 (\varphi - \varphi_0 - 2 \pi n)^2 + i n (\varphi - \varphi_0 - 2 \pi m)}$$

are coherent states on the circle.\(^{40-43}\) The sum in Eq. (7) ensures the correct periodicity of the wave function. The coherent states (7) are not normalized but form a (over)complete basis set. The normalization factor is given by

$$\langle \varphi_0 | \varphi_0 \rangle = \frac{1}{\pi^{1/4}} \sum_{n = -\infty}^{\infty} \sum_{m = -\infty}^{\infty} e^{-\alpha^2 n^2} e^{2 \pi n \varphi_0}$$

If the width parameter $\alpha$ is sufficiently large (i.e., $\alpha \ll 1$), 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. 40 and 42. For $\varphi_0 = 0$, $p_0 = 0$, the initial state (5) corresponds to photoexcitation from the electronic and vibrational ground state. Initial states with nonzero values for $\varphi_0$ and $p_0$ can be prepared experimentally—at least in principle—by using pulse-shaping techniques.\(^{44}\)

As an illustration of the photoisomerization reaction described by the model, Fig. 1 shows the diabatic potential-energy curves $V_{00}$ and $V_{11}$ along the reaction coordinate $\varphi$. We note that the excited-state potential $V_{11}$ is inverted, i.e., the upper diabatic electronic state for $\varphi = 0$ (cis configuration) becomes the lower one for $\varphi = \pi$ (trans configuration).

Furthermore, the initial state $|\Psi(0)\rangle$ of the system is indicated by a Gaussian envelope on the upper potential-energy curve, assuming that at $t = 0$ the system has been excited from its electronic and vibrational ground state in the cis configuration by an ultrashort laser pulse\(^{45}\) [i.e., $\varphi_0 = 0$, $p_0 = 0$ in Eq. (5)]. Following the excitation, the wave packet bifurcates in two parts, which—to due to the periodicity of the potential—subsequently meet each other around $\varphi = \pm \pi$. As a consequence, already a simple one-dimensional periodic problem may reveal a wealth of coherent quantum phenomena such as interferences and tunneling.\(^{56}\) Considering a vibronically coupled system, however, matters may become much more complicated. This is because the corresponding adiabatic potential-energy surfaces

$$V_{01}^{\text{ad}} = \frac{1}{2} (V_{00} + V_{11}) \mp \frac{1}{2} \sqrt{(V_{11} - V_{00})^2 + 4V_{01}^2}$$

exhibit two conical intersections at $x = 0$ and $\varphi = \pm \pi/2$, which again may affect a splitting of the wave packet.

To characterize the time evolution of the nonadiabatic photoisomerization process, it is helpful to introduce various time-dependent observables.\(^{32,44}\) Let us first consider the electronic dynamics of the system, which may be described via the time-dependent population probability of a given electronic state. Projecting the time-dependent state vector $|\Psi(t)\rangle$ on the diabatic state $|\psi_k\rangle$, we obtain the diabatic population probability

$$P_{k}^{\text{ad}}(t) = |\langle \Psi(t) | \psi_k \rangle |^2$$

which represents a key quantity in the discussion of intracconversion processes.\(^{32}\) For interpretational purposes, it is often advantageous to change to the adiabatic representation with basis states $|\psi_k^{\text{ad}}\rangle = \sum_{m} S_{km} |\psi_m\rangle$, where $S_{km}$ denotes the adiabatic to diabatic transformation matrix.\(^{33}\) and consider the corresponding adiabatic population probability

$$P_{k}^{\text{ad}}(t) = |\langle \Psi(t) | \psi_k^{\text{ad}} \rangle |^2$$

The isomerization dynamics of the system may be described via the probability of finding the system in either the cis or trans configuration. These probabilities are given as the expectation value of the projectors

$$\hat{P}_{\text{trans}} = \Theta(|\varphi| - \pi/2)$$

$$\hat{P}_{\text{cis}} = 1 - \hat{P}_{\text{trans}}$$

where $\Theta$ denotes the Heaviside step function and $\varphi$ is restricted to $-\pi/2 \leq \varphi \leq 3 \pi/2$. To visualize both electronic and isomerization dynamics of the system, one may consider the probability density

$$P_{k}^{\text{ad}}(\varphi, t) = |\langle \Psi(t) | \psi_k^{\text{ad}} \rangle |^2$$

which is obtained by projecting the state vector $|\Psi(t)\rangle$ on the adiabatic state $|\psi_k^{\text{ad}}\rangle$ and on the reaction coordinate $\varphi$.

B. Quantum wave-packet dynamics

To obtain a first impression of the cis–trans photoisomerization dynamics of the above-introduced three-mode model, Fig. 2 shows the quantum-mechanical probability density $|\langle \Psi(t) | \psi_k^{\text{ad}} \rangle|^2$ of the system, plotted as a function of time $t$ and the isomerization coordinate $\varphi$. To clearly show the
S\textsubscript{1}→S\textsubscript{0} internal-conversion process, the wave function has been projected on the S\textsubscript{1} (upper panel) and S\textsubscript{0} (lower panel) diabatic electronic state, respectively.

While the initial excited-state dynamics of the system is described by a localized wave packet, the subsequent time evolution in the electronic ground state is much harder to characterize. Reaching the lower adiabatic electronic state via the “photochemical funnel” represented by the intersection, the wave function rapidly spreads out over the entire PES and remains completely delocalized for larger times. Obviously, the diffuseness of the vibrational wave function hampers a simple intuitive understanding of the dynamics in terms of specific nuclear motion. We thus have the curious situation that, even though the complete quantum-mechanical wave function of the system is available, it is far from obvious how to characterize the nuclear motion on coupled PESs in simple physical terms.

In an attempt to obtain additional information on the dynamics exhibited by our model, we have also considered further time-dependent observables of the system. As an example, Fig. 3 shows the population probabilities $P^{\text{ad}}(t)$ and $P^{\text{di}}(t)$ pertaining to the initially excited adiabatic and diabatic electronic states, respectively, as well as the probability $P_{\text{cis}}(t)$ to remain in the cis configuration. Besides reconfirming the overall findings described earlier, the data highlight various features of the nonadiabatic photoisomerization process. For example, it is found that the coherent motion along the tuning and coupling modes shows up as a high-frequency beating of the diabatic population probability. Moreover, the probability $P_{\text{cis}}(t)$ as well as the diabatic population $P^{\text{di}}(t)$ are seen to fluctuate for large times around $\sim 0.5$, thus reflecting the symmetry of the diabatic isomerization potentials $V_0$ and $V_1$. We have also studied additional quantities such as the autocorrelation function and various expectation values of the nuclear degrees of freedom (data not shown). However, none of the quantum-mechanical observables considered was suited to disentangle the complex nuclear motion on coupled PESs shown in Fig. 2.

From general experience with wave-packet motion in periodic potentials,\textsuperscript{46} it may be expected that the complexity of the dynamics is partially caused by the symmetric excitation of the system (i.e., at $\varphi_0=0$ and zero initial momentum), which results in a bifurcation of the wave function right from the beginning. To simplify the analysis, it is therefore helpful to invoke an initial preparation which results in a preferred direction of motion of the system. With this end in mind, we have considered various initial states, the energy distributions of which are shown at the left-hand side of Fig. 1.\textsuperscript{47} The distribution labeled by “$E>0$” represents a wave packet initially centered at $\varphi_0=0$ with a dimensionless average momentum of $p_0=23.24$, corresponding to an additional kinetic energy of $T\approx 0.15$ eV, “$E<0$” represents a wave packet starting at $\varphi_0=0.4\pi$ with momentum $p_0=23.24$, corresponding to a kinetic energy of $T\approx 0.15$ eV, while “$E=0$” refers to the symmetric preparation of the system at $\varphi_0=0$ and $p_0=0$, i.e., without initial kinetic energy.

Figure 4 shows the time-dependent probability densities $P^{\text{ad}}(\varphi,t)$ and $P^{\text{di}}(\varphi,t)$ for the case $E>0$. As a consequence of the initial momentum, the wave packet is seen to move in one direction only, that is, toward increasing values of $\varphi$. 

**FIG. 2.** Quantum-mechanical probability densities [Eq. (14)] of the nonadiabatic cis–trans photoisomerization model for the case $E=0$, plotted as a function of time $t$ and the isomerization coordinate $\varphi$. To clearly show the $S_1\rightarrow S_0$ internal-conversion process, the wave function has been projected on the $S_1$ (upper panel) and $S_0$ (lower panel) diabatic electronic state, respectively.

**FIG. 3.** Comparison of quantum (solid lines) and classical (dashed lines) results obtained for the adiabatic population $P^{\text{ad}}(t)$, the diabatic population $P^{\text{di}}(t)$, and the probability $P_{\text{cis}}(t)$ to remain in the cis configuration. Shown are the cases $E<0$ (left), $E=0$ (middle), and $E>0$ (right).
Within \( \approx 100 \) fs, the system reaches the conical intersection at \( \phi = \pi/2 \) and decays almost completely into the electronic ground state. The next two encounters with conical intersections at \( \phi = 3/2 \pi \) and \( 5/2 \pi \) only mildly affect the wave packet, hence its unidirectional motion on the lower adiabatic PES is continued for almost two periods. For larger times, however, smaller parts of the population recur via the intersections to the upper PES, thus rendering the overall appearance of the wave function again rather diffuse. Nevertheless, for \( E > 0 \) the splitting of the wave packet at conical intersections is much clearer to see than in the symmetric case discussed earlier, although the effect is expected there as well.

Let us finally consider the case \( E < 0 \), where the wave packet starts at \( \phi = 0.4 \pi \) with a kinetic energy of \( \approx 0.15 \) eV. As shown in Fig. 5, this case provides the most detailed description of the nuclear motion on vibronically coupled PESs. Following the initial decay, it is seen that at every encounter of a conical intersection the wave packet splits up in several parts: (i) the main ground-state component, which continues in the initial direction on the lower potential-energy surface, (ii) a reflected ground-state component which, following the reflection at a surface-crossing, propagates in the opposite direction on the lower PES, and (iii) an excited-state component, which is localized in the vicinity of the conical intersection and seems to oscillate on the upper adiabatic PES.

The latter example suggests that, at least in principle, it should be possible to explain complex nuclear motion on vibronically coupled PESs in terms of several interfering but localized wave trains. However, as shown in the above-given examples, in most cases it is not clear how to extract these wave trains from a standard quantum-mechanical calculation, because the various components rapidly become too delocalized to be separated. In Sec. III, it is shown that a classical description of nonadiabatic photoisomerization dynamics may yield a simple physical picture of the nuclear motion on coupled PESs.

III. CLASSICAL DESCRIPTION

A. Mapping formulation

The mapping formulation has been described in detail in Refs. 3–6 and is only briefly reviewed here. The basic idea is to represent a discrete \( N \)-state system quantum-mechanically exactly by a system of \( N \) oscillators and subsequently treat the mapped system by standard classical methods. The mapping relations for the operators and basis states read

\[
|\psi_n\rangle|\psi_m\rangle \rightarrow |X_n - iP_n |X_m + iP_m\rangle, \quad (15)
\]

\[
|\psi_n\rangle \rightarrow |0_1,...,1_n,...,0_N\rangle, \quad (16)
\]

where \( X_n, P_n \) are position and momentum operators of the \( n \)th oscillator with commutation relations \([X_n, P_m] = i\delta_{nm}\), and \(|0_1,...,1_n,...,0_N\rangle\) denotes a harmonic-oscillator eigenstate with a single quantum excitation in the \( n \)th mode. Note that the image of the \( N \)-level Hilbert space is the subspace of the \( N \)-oscillator Hilbert space with a single quantum excitation. This “physical” subspace is invariant under the action of any operator which results by the mapping (15) from an arbitrary \( N \)-level system operator. It is easy to show that the mapping of the operators (15) preserves the commutation relations and leads to the exact identity of the electronic matrix elements of the propagator.

According to Eq. (15), the oscillator representation of the Hamiltonian (1) is given by

\[
H = h_0 + \frac{1}{2} \sum_{n,m=0,1} V_{nm}(X_nX_m + P_nP_m - \delta_{nm}), \quad (17)
\]

which obviously has a well-defined classical limit. The transition to classical mechanics is simply performed by changing from the Heisenberg operators \( X_n, P_n \) obeying Heisenberg’s equations of motion to the corresponding classical equations

\[
\dot{X}_n = \frac{P_n}{\hbar}, \quad \dot{P}_n = -\frac{\partial}{\partial X_n} H, \quad (18)
\]

\[
\dot{P}_n = \frac{\partial}{\partial X_n} H, \quad (19)
\]
functions obeying Hamilton’s equations. As has been discussed in detail elsewhere, this classical limit of the mapping formulation is equivalent to the classical electron analog model of Meyer and Miller and also closely related to the mean-field trajectory method. The latter model can be formed for the classical approximation is performed for the complete system.

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

\[
A^C(t) = \int dq dp \rho(q,p) A(q(t),p(t)).
\]

(18)

Here the quantity \( A \) is considered as a function of the classical trajectory \( \{q(t),p(t)\} \) with initial conditions \( \{q,p\} \) 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 diabatic electronic population probability (10), we calculate the expectation value of the corresponding diabatic projection operator (15), thus yielding

\[
P_k^C(t) = \int dx dp \int dX dP \rho_{el}(X,P) \rho_{nuc}(x,p) \frac{1}{2}(X_k^2 + P_k^2 - 1).
\]

(19)

To sample the electronic and the nuclear initial distributions \( \rho_{el} \) and \( \rho_{nuc} \), we have introduced classical action-angle variables \( \{n,\phi\} \) via the transformation \( p_j + i q_j = \sqrt{(2n_j + 1)} e^{i \phi_j} \) and performed an average over the initial angles \( \phi_j \) while keeping the initial actions \( n_j \) constant. For example, the initial action

\[
j = \frac{1}{2} \int dq dp \rho_{el}(q,p) dq dp
\]

is considered as a function of the classical trajectory \( \{q(t),p(t)\} \) with initial conditions \( \{q,p\} \) 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 diabatic electronic population probability (10), we calculate the expectation value of the corresponding diabatic projection operator (15), thus yielding

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Although it is clear from the derivation of the mapping formulation that an appropriate theory should include the zero-point energy excitation of the electronic oscillators, it has been found to possibly lead to artifacts in quasiclassical calculations because of the so-called zero-point energy problem of classical mechanics. As a remedy, it has been proposed to invoke quantum corrections, which at the simplest level of the theory correspond to including only a fraction \( \gamma \) \( (0 \leq \gamma \leq 1) \) of the full zero-point energy into the classical calculation. That is, \( \gamma = 1 \) corresponds to the original mapping formulation which takes into account the full amount of zero-point energy, while for \( \gamma = 0 \) all electronic zero-point energy is neglected and the mapping approach becomes equivalent to the mean-field trajectory method.

In the mapping description, the electronic zero-point energy appears in (i) the quasiclassical description of the initial electronic state \( \rho_{el} = \delta(n_0 - \gamma/2) \delta(n_1 - (1 + \gamma/2)) \), (ii) in the electronic projectors \( \frac{1}{2}(P_n^2 + X_n^2 - \gamma) \), and (iii) in the Hamiltonian (17) where \( \delta_{nm} \) is replaced by \( \gamma \delta_{nm} \). A number of ways have been discussed to determine the value of the correction \( \gamma \) for a given problem, which are all based on the idea that an appropriate classical theory should correctly reproduce long-time limits of the electronic population. In particular, it was demonstrated that if the long-time limit of an observable is known a priori, the value of the correction \( \gamma \) can be determined without quantum mechanical reference calculation. For the example considered in this work, we adopt the value of \( \gamma = 0.5 \), which has been determined this way in Ref. 3 for a photoisomerization model very similar to the reaction considered in the present work.

FIG. 6. Classical probability densities \( P_{1ad} \) (upper panels) and \( P_{0ad} \) (lower panels) for the case \( E=0 \), plotted as a function of time \( t \) and the isomerization coordinate \( \varphi \). (A) The complete quasiclassical average, (B) the results for rotating orbits only (i.e., no turns), and (C) the results for orbits with one and more turns.
B. Classical wave-packet dynamics

Let us first investigate to what extent the quasiclassical mapping approach is able to reproduce the quantum results obtained in Sec. II B. To this end, we consider Fig. 6, which shows the quasiclassical probability densities $P_{k}^{ad}(\varphi, t)$ for the case $E=0$. The classical calculation is seen to accurately match the initial decay of the quantum-mechanical wave packet (cf. Fig. 2) as well as the appearance of the wave function on the lower PES. Although the classical ground-state probability density does not include the finer details of the quantum calculation, it nevertheless reproduces the overall structure of the wave function remarkably well. Since we use a simple quasiclassical approach that does not account for possible quantum effects such as interference and tunneling, this finding indicates that—within the mapping formulation—the dynamics underlying the nonadiabatic photoisomerization is essentially of classical nature.

It is interesting to note that, in contrast to this result, recent classical and semiclassical studies of a one-dimensional photoisomerization problem have revealed a wealth of coherent quantum phenomena, which were quite difficult to catch by a classical description. As discussed in Refs. 39, 53, and 54, it is the strong vibrational and electronic relaxation of the multidimensional system that affects a rapid randomization of the quantum phases and makes the dynamics amenable to a classical description.

The above-presented discussion has focused on the case without initial kinetic energy ($E=0$), which reveals the strongest distortion of the wave function. Let us next consider the other two cases including kinetic energy, i.e.,

![Diagram](Image)

**FIG. 7.** Same as in Fig. 6, but for the case $E>0$.

![Diagram](Image)

**FIG. 8.** Same as in Fig. 6, but for the case $E<0$. 
For $E>0$ and $E<0$ shown in Figs. 7(A) and 8(A), respectively. For $E>0$, the quasiclassical calculation is almost in quantitative agreement with the quantum result, with the exception that the quantum calculation shows some minor recurrences of the population to the excited state also for larger times. For $E<0$, interestingly, the agreement between classical and quantum results is not that satisfying. As discussed earlier, at every encounter of a conical intersection the quantum calculation predicts a splitting of the wave packet into a main ground-state component continuing in the initial direction, a reflected ground-state component with reversed direction of motion, and an oscillatory excited-state component. While the classical calculation clearly describes the main ground-state component, it shows only weak indications of the other two features. As discussed in the following, the splitting of a wave packet at a conical intersection includes quantum-mechanical interference phenomena, which get lost in the quasiclassical averaging. This problem appears to be particularly severe in the case $E<0$, where due to the relatively low excitation energy vibrational and electronic relaxation effects are less effective than in the other two cases and, therefore, quantum phases are more important. Furthermore, it is interesting to note that computational studies employing a semiclassical initial-value representation have shown that this splitting is also quite difficult to get in a truly semiclassical calculation.

To obtain a more quantitative comparison of classical and quantum results, one may consider the time-dependent observables $P_{\text{ad}}(t)$, $P_{\text{th}}(t)$, and $P_{\text{cis}}(t)$ shown in Fig. 3. Again, it is seen that the mapping calculations are at least in qualitative agreement with the exact quantum data, although the decay of the recurrences is somewhat exaggerated by the classical description. The latter is particularly evident in the case $E<0$, which is in accordance with the results shown in Fig. 8.

To summarize, it has been demonstrated that the quasiclassical mapping description is able to reproduce various time-dependent quantities characterizing the nonadiabatic photoisomerization dynamics. Thereby, the overall agreement between quasiclassical and quantum mechanical results was found to be better for higher energies of the initial state (i.e., in the cases $E>0$, $E=0$), where vibrational and electronic relaxation effects cause a rapid randomization of the quantum phases and thus make the dynamics more amenable to a classical description. In what follows, we wish to identify and analyze the classical trajectories underlying these observables, in the hope that the trajectories may facilitate an intuitively clear understanding of the complex wave-packet dynamics.

C. Quasiperiodic orbits

Applying the mapping formalism to a one-dimensional spin-boson model, we have recently analyzed the classical phase space of a vibronically coupled molecular system. Except for very low or very high energies, the system was found to exhibit mixed classical dynamics: Most of the area of the energetically available phase space belongs to chaotic motion, but there are also some islands of integrability, which contain fixed points associated with the periodic orbits of the system. We have identified the shortest of these periodic orbits, which were also found to be most important for the interpretation of nonadiabatic quantum dynamics. Adopting the adiabatic electronic representation, these vibronic periodic orbits could be characterized in a simple and physically appealing way. First, there are periodic orbits that evolve predominantly on a single (either the lower or the upper) Born–Oppenheimer surface. Furthermore, we have identified numerous periodic orbits that propagate “in-between” adiabatic PESs or perform Rabi-type oscillations between the two coupled potentials. Finally, a number of periodic orbits were found that combine several of these features in a single periodic orbit.

For the photoisomerization problem defined by Eq. (1), however, the situation is much more complicated. First of all, this is because the mapping Hamiltonian (17) of the system comprises two electronic and three nuclear degrees of freedom, thus resulting in a ten-dimensional phase space. Although several methods have been proposed to find periodic orbits in a many-dimensional phase space, so far the vast
The majority of studies has been restricted to systems with two nuclear degrees of freedom. A second complication arises from the fact that the molecular system contains several time scales: The observed period of $\approx 150$ fs of the torsional mode $\varphi$ corresponds to the slowest motion of the system, the two vibrational modes with frequencies $\omega_1=0.1$ eV and $\omega_2=0.085$ eV oscillate with periods around 40 fs, and the fastest time scale of $\approx 2$ fs corresponds to the energy gap $W_0=2.5$ eV between the two electronic states. Since a vibronic periodic orbit by definition describes both vibrational and electronic motions, the shortest possible periodic orbit with a single period in the torsional mode therefore contains almost one hundred oscillations of the electronic oscillators. Last, but not least, a straightforward search for vibronic periodic orbits is hampered by the fact that the phase space of the vibronically coupled molecular system in Eq. (17) is largely irregular. Employing Poincaré surfaces-of-section and Liapunov-exponent analyses, we have studied several types of vibronically coupled isomerization problems under various conditions. Only for energies below the surface crossing, stable orbits could be found. For energies corresponding to photoexcitation, however, most trajectories were found to sample phase space in an ergodic manner and lose the memory of their initial conditions within a few picoseconds. For example, the system may “spontaneously” reverse the direction of torsional motion, even if it starts with a momentum in a specific direction.

As a representative example, Fig. 9(A) shows the time evolution of the torsional coordinate $\varphi$ of such a trajectory, obtained for the case $E=0$. For further reference, the various types of motion exhibited by the trajectory have been color-coded. Starting out to propagate along the torsional potentials in positive direction (green line), the trajectory is trapped in the trans potential for $0.5$ ps $\leq t \leq 1.5$ ps (red line), before it continues to propagate back towards the potentials in negative direction. Apart from a few oscillations in the cis potential (blue line), this direction of motion is kept up to $t \approx 3$ ps. The next two picoseconds the trajectory exhibits a somewhat irregular behavior (various colors, see the following), which is followed by a quite regular oscillation in the cis potential.

Although the phase space of the nonadiabatic photoisomerization system is largely irregular, Fig. 9(A) demonstrates that the time evolution of a long trajectory can be characterized by a sequence of a few types of “quasiperiodic” orbits. The term quasiperiodic refers here to orbits that are close to an unstable periodic orbit and are, over a certain time scale, exactly periodic in the slow torsional mode and approximately periodic in the high-frequency vibrational and electronic degrees of freedom. In Fig. 9(B), these orbits are schematically drawn as colored lines in the adiabatic potential-energy curves $V_0^d$ and $V_2^d$. The first class of quasiperiodic orbits we wish to consider are orbits that predominantly propagate along the ground-state torsional potential in a single direction [green line in Fig. 9(B)]. As this motion corresponds to an internal rotation of the molecule, these orbits will be referred to as “rotating orbits.” The next class of quasiperiodic orbits to consider are orbits that predominantly propagate on the excited-state potential-energy surface. The most common kind here is an orbit that oscillates in the excited-state potential well between the cis and trans configuration [magenta line in Fig. 9(B)]. Interestingly, we hardly found rotating orbits on the upper PES for the model system and energies considered. The last class of quasiperiodic orbits consists of various “mixed orbits,” i.e., trajectories that propagate “in between” two potentials, that is, on a superposition of the adiabatic PESs. Although mixed orbits typically perform rotating motion, they may exhibit quite irregular behavior. As an example of this case, the time evolution of the trajectory between $t_1=2.7$ ps and $t_2=3.9$ ps is shown in more detail in Fig. 9(C) (see the following discussion).

To obtain a more quantitative description of these orbits, one may consider the diabatic electronic population variable $N_{ad}=(X_1^d+P_1^d)/4$, which by construction varies between 0 (system is in $|\psi_0\rangle$) and 1 (system is in $|\psi_1\rangle$). Alternatively, we may introduce the adiabatic population variable $N_{aa}=(\bar{X}_1+\bar{P}_1)/4$, where $\bar{X}_k,\bar{P}_k$ represent adiabatic electronic variables which are obtained from the corresponding diabatic

![FIG. 10. (Color) Distribution of rotating orbits (green) as well as of cis (blue), trans (red), and excited state (magenta) oscillating orbits. The data are drawn as a function of the period and the average (A) adiabatic and (B) diabatic electronic population probability $N_{ad}$ and $N_{aa}$, respectively.](image-url)
variables $X_k, P_k$ via the standard adiabatic–diabatic transformation.\footnote{Employing these definitions, a quasiperiodic orbit may be characterized by its type (e.g., oscillating or rotating), its period, and by its average adiabatic and diabatic population probabilities.}

With this end in mind, we have performed a statistical analysis of a trajectory of 1 ns duration for the case $E=0$. Plotted as a function of the period and the average electronic population probability, Fig. 10 shows the distribution of rotating orbits (green) as well as of cis (blue), trans (red), and excited-state (magenta) oscillating orbits. We first consider panel (A), which displays the average adiabatic population probability of the orbits. In accordance with the above-presented qualitative discussion, it is found that most oscillating orbits evolve on the lower adiabatic PES, that is, $N_{\text{ad}}\lessapprox 0.2$. There is a clear correlation between the mean adiabatic population and the period of these orbits, i.e., the orbits with the lowest adiabatic population $N_{\text{ad}}=0$ have the largest kinetic energy and therefore the shortest periods of $\sim 120$ fs, while orbits with $N_{\text{ad}}=0.2$ may exhibit periods up to 250 fs.

A large part of the rotating orbits is also located on the lower adiabatic PES and exhibits periods of typically 80–150 fs. However, there are numerous mixed rotating orbits with $N_{\text{ad}}\sim 0.3$–0.8 and periods up to 300 fs. Finally, at $N_{\text{ad}}\sim 0.8$ we find a small contribution of orbits that oscillate in the excited-state potential well.

The diabatic representation shown in panel (B) highlights further properties of the quasiperiodic orbits. First, the cis and trans oscillating orbits are readily distinguished, since in the electronic ground state the cis and trans configurations correspond to the $|\psi_0\rangle$ and $|\psi_1\rangle$ diabatic state, respectively. On the other hand, the rotating orbits exhibit an average diabatic population probability $N_{\text{dia}}=0.5$, which reflects the fact that they propagate to equal parts in both configurations. Finally, Fig. 10(B) gives an impression about the relative contribution of the various types of orbits. In the present case, there are 45% rotating orbits, 16% cis oscillations, 10% trans oscillations, and about 1% excited-state oscillations. During the remaining 28% of the time, the trajectory could not easily be assigned to an oscillatory motion with a well-defined period. This is the case, for example, for highly irregular motion associated with spontaneous turns and electronic transitions of the trajectory.

As an example of the latter case, Fig. 9(C) shows the vibronic time evolution of the sample trajectory during the time $t_1=2.7$ ps $< t < t_2=3.9$ ps. To provide an intuitive picture of the vibronic trajectory, the orbit is represented as a curve $N_{\text{ad}}V_{\text{ad}}^0 + (1-N_{\text{ad}})V_{\text{dia}}^0$ between the coupled potentials, i.e., for $N_{\text{ad}}=0$ the orbit moves along the lower adiabatic PES $V_{\text{ad}}^0$ and for $N_{\text{ad}}=1$ the orbit moves along the upper adiabatic PES $V_{\text{dia}}^0$. Starting at $\varphi/2\pi=-6$ as a ground-state rotating orbit (green line), the system exhibits at $\varphi/2\pi \approx -8.2$ a rapid nonadiabatic transition to the upper PES and continues as a mixed rotating orbit. This mixed orbit (i) propagates to the left (blue line), (ii) is reflected at $\varphi/2\pi \approx -10$ and propagates back to the right (orange line), and (iii) is reflected at $\varphi/2\pi \approx -6$ and again propagates to the left (blue line). It is interesting to note that reflections of the trajectory always occur at a surface crossing. In particular, at $\varphi/2\pi = -8.75$ the system is briefly trapped around the conical intersection in the excited-state potential well between the cis and trans configuration (magenta line).

To summarize, we have identified several types of quasiperiodic orbits that describe nonadiabatic photoisomerization dynamics. Similar to previous studies of a one-dimensional electron-transfer system,\footnote{There are various orbits that predominantly evolve on a single adiabatic PES: Rotating orbits and cis and trans oscillating orbits in the electronic ground state, as well as orbits oscillating in the excited-state potential well between the cis and trans configuration. Furthermore, we have discussed various orbits that propagate in between adiabatic PESs. These are mostly rotating orbits and various irregular orbits. It is noted that no orbits along the upper adiabatic PES or along the two diabatic PESs could be observed. Extending the studies to energies $E>0$ and $E<0$, the general picture remains the same (i.e., we find the same types of orbits), while the details (such as periods, average electronic populations, and relative contribution of the orbit types) change to some extent.}

IV. CLASSICAL ANALYSIS OF NONADIABATIC PHOTOISOMERIZATION

In the last two sections, we have presented a quantum and a classical description of nonadiabatic photoisomerization dynamics. On the one hand, we have found the somewhat curious situation that, even though the complete quantum-mechanical wave function of the system is available, it is far from obvious how to characterize the diffuse and largely delocalized nuclear motion on coupled PESs in simple physical terms. On the other hand, it has been shown that the quasiclassical mapping formulation is able to reproduce at least qualitatively the nonadiabatic photoisomerization process. Furthermore, the classical description has facilitated the identification of the quasiperiodic orbits underlying this dynamics. Hence, we are now in a position to analyze the quantum wave-packet dynamics presented in Sec. II in terms of the quasiperiodic orbits introduced in Sec. III.

With this end in mind, we consider again the time evolution of classical trajectories following the three initial preparations $E=0$, $E>0$, and $E<0$ shown in Figs. 6–8. The simplest way to characterize the trajectories in terms of the quasiperiodic orbits is to count the number of turning points in $\varphi$. For example, there are no turns for a rotating orbit, and two turns during a single period of an oscillating orbit. In contrast to Sec. III, where the analysis was based on a single long trajectory, here we consider all trajectories that contribute in the quasiclassical sampling procedure over a timescale of 600 fs. Let us begin with the case $E>0$ shown in Fig. 7. Due to the finite initial momentum, the classical motion is clearly dominated by rotating orbits. Indeed, the analysis reveals that a large part (46%) of the trajectories perform continuous rotating motion (i.e., no turns) during the first 600 fs.

About 30% of the trajectories exhibit a single turn, 14% two turns, and only 10% three and more turns. To elucidate the effect of the turns on the classical wave-packet motion, Fig. 7 shows the results for rotating orbits only [no turns, panel (B)] and for orbits with one and more turns [panel (C)]. As is expected from the above-presented discussion, the rotating...
orbits show up as diagonally moving wave trains with a recurrence time of \( \approx 100 \) fs. As a consequence of the broad distribution of periods shown in Fig. 10, the width of the wave trains becomes larger in the course of time. Considering the trajectories with one and more turns, the excited-state distribution indicates a reflection of the orbits at the conical intersections at \( \varphi = 0.5\pi \) and \( 1.5\pi \), occurring at times \( \approx 100 \) and \( 150 \) fs. At larger times, the system predominately evolves on the lower PES. Again, the turning points of the orbits at the conical intersections can be seen clearly. Furthermore, it is noted that these “turning orbits” result in quite diffuse structures, which may explain the increasing diffuseness of the quantum-mechanical wave function at larger times.

In the case \( E < 0 \), the quantum calculation shown in Fig. 5 has exhibited prominent oscillatory wave-packet motion on both adiabatic PESs. In agreement with this finding, the analysis of the underlying trajectories reveals that during the first 600 fs only 22% of the trajectories perform continuous rotating motion, 24% exhibit a single turn, and 18%, 12%, 7%, and 17% perform two, three, four, and more turns, respectively. Considering first the orbits without turns shown in Fig. 8(B), the traversing motion of the rotating orbits on the ground-state PES is again seen clearly. There is also a weak signature of rotating motion on the upper adiabatic PES which, however, is most likely an artifact due to the averaged potential energy in the classical description. The turning orbits are shown in panel (C). On the excited-state PES, only the first oscillation and a weak feature at \( \approx 500 \) fs is reproduced by the classical description. Similarly, there is only a weak indication of the counter-motion of the reflected orbits on the lower PES. Nevertheless, the classical calculations indicate the origin of these effects. To correctly reproduce these coherent phenomena in a classical framework, one would need to invoke a semiclassical approach which includes quantum interferences and affords a correct weighting of the various orbits.

In the case \( E = 0 \), the quantum-mechanical wave function shown in Fig. 2 was found to be quite delocalized and diffuse. To explain this result, Fig. 6 displays the corresponding classical distributions, again obtained for trajectories with and without turns. Since there are no classical recurrences of the population to the upper PES, this classification cannot be used to explain the excited-state dynamics. Considering the electronic ground state, however, it is seen that the prominent broad appearance of the quantum-mechanical wave function is already caused by continuously rotating orbits (32% relative contribution). In other words, the clear signature of the rotating motion, which was found for the preparations \( E > 0 \) and \( E < 0 \) is hardly visible in this case. This somewhat surprising effect arises because the energy \( E = 0 \) corresponds to a preparation of the system right at the turning point, i.e., on top of the torsional barrier. As a consequence, we obtain a large contribution of irregular orbits, in particular mixed rotating orbits. The latter exhibit a broad distribution of periods (see Fig. 10), and thus lead to a rapid delocalization of the resulting wave trains. Adding the orbits containing one and more turns, moreover, yields the quite structureless appearance of the total distribution. Again, the turns mostly occur in the vicinity of the conical intersections at \( \varphi = 0.5\pi \) and \( 1.5\pi \).

We note in passing that we have hardly found oscillating orbits during the first 600 fs of the photoisomerization reaction. This is because these orbits have only very little phase-space overlap with the initial states considered, and therefore hardly contribute to the short-time dynamics of the system.

V. CONCLUSIONS

In this paper we have presented a quantum-mechanical and a classical description of the ultrafast nonadiabatic wave-packet dynamics associated with a cis–trans photoisomerization reaction. Employing quantum wave-packet dynamics, it has been demonstrated that, even though the complete quantum-mechanical wave function of the system is available, it is far from obvious how to characterize the diffuse and largely delocalized nuclear motion on coupled PESs in simple physical terms. The quantum-mechanical analysis may be simplified by considering various initial states, which affect a preferred direction of motion of the system. In this way, characteristic elements of the short-time quantum dynamics, such as the initial wave-packet motion along the gradient of the PES toward the conical intersection and the splitting of the wave-packet into different ground- and excited-state components, could be identified. For longer times, however, the diffuse and delocalized nature of the wave function hampers an intuitive physical understanding.

We have made some effort to understand the largely delocalized wave functions of this process in terms of the classical nuclear motion on coupled PESs. Employing a quasiclassical implementation of the mapping formulation, we were able to reproduce at least qualitatively the exact quantum-mechanical reference data. In addition, the mapping approach allows us to characterize the nonadiabatic photoisomerization dynamics in terms of a few quasiperiodic orbits. These orbits are close to an unstable periodic orbit but are exactly periodic only with respect to the slow reaction coordinate of the system and only over a certain time scale. Although the phase space of the nonadiabatic photoisomerization system was found to be largely irregular, only a few types of quasiperiodic orbits were shown to be of importance for the time evolution of the system. There are various orbits that predominantly evolve on a single adiabatic PES: Rotating orbits, orbits that oscillate in the cis or trans configuration of the electronic ground state, as well as orbits oscillating in the excited-state potential well between the cis and trans configuration. Furthermore, there are numerous, mostly irregular, orbits that propagate in between the adiabatic PESs. Interestingly, these findings are quite similar to previous periodic-orbit studies of an electron-transfer system, thus indicating that this classification may be quite generic.

Analyzing the contribution of the various types of orbits, we have shown that rotating orbits represent the most important type of vibronic motion of the system. The signature of these orbits can be found in the time-dependent quantum probability distributions of all three cases considered. While the majority of rotating orbits evolve on the lower adiabatic PES, there are also mixed rotating orbits, which evolve in between the coupled PESs. Since the latter are mostly irregu-
lar orbits that exhibit a broad distribution of periods, mixed orbits lead to a rapid delocalization of the resulting wave trains. The wave-packet dynamics associated with a nonadiabatic photo reaction therefore represents a beautiful example of the well-known correspondence of diffuse quantum-mechanical wave functions and irregular classical trajectories.\textsuperscript{22–29} In the case of nonadiabatic photoisomerization, the chaotic behavior is mainly caused by (i) the relatively high energies corresponding to photoexcitation, (ii) the large anharmonicity of the isomerization potentials, and (iii) the reflection of the trajectory at surface crossings. We note that in the presence of a conical intersection, the latter effect is particularly prominent because of the divergence of the nonadiabatic couplings at the seam of the intersection.

Finally, it should be noted that the present work can only be regarded as a first attempt to employ the ideas of periodic-orbit theory to nonadiabatic photodynamics in complex molecular systems. Since the majority of these systems is presumably irregular, quasiperiodic orbits may present a suitable concept to analyze the complex quantum dynamics in terms of classical trajectories without explicitly going through the cumbersome search of unstable periodic orbits.

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3 G. Stock and M. Thoss, in Ref. 33.


