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Nearly real trajectories in complex semiclassical dynamics

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We introduce a very general approximation to the quantum propagator that is based on the assumption that the most important contributions to the complex semiclassical propagator evolve from real classical trajectories that *almost* satisfy the desired boundary conditions. Our results for two systems — the autocorrelation function for the quartic anharmonic oscillator and the photodissociation spectrum of CO_2 — show that these nearly real contributions yield an excellent approximation to the quantum propagator for quite long times. The approach taken here is applicable to problems with many (e.g., several hundred) degrees of freedom, and hence promises to provide an accurate and useful representation of the quantum dynamics for a wide variety of physically interesting systems.

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Coherent states are an extremely useful tool for the description of quantum phenomena [1]. In the position representation, they take the form

$$\langle x|q_0,p_0\rangle=\left(\frac{\gamma}{\pi}\right)^{1/4}\exp\left[-\frac{\gamma(x-q_0)^2}{2}-ip_0\left(x-\frac{q_0}{2}\right)\right], \tag{1}$$

where q_0 and p_0 are the *average* position and momentum of the state and γ controls the width of the coherent state in position space. These coherent states admit an elegant semiclassical interpretation, where each wave packet is associated with a point (q_0,p_0) in phase space [2]. For example, the matrix elements of the propagator,

$$\langle q_f,p_f|e^{-i\hat{H}t/\hbar}|q_i,p_i\rangle, \tag{2}$$

are very well represented by the *classical* dynamics of a trajectory with initial conditions (q_i,p_i) [3–5].

A more rigorous semiclassical approximation to these amplitudes [i.e., one that only involves the stationary path approximation (SPA)] has been presented by several authors [6–8]. The central object in this formalism is the *complex* classical path $\{q(t),p(t)\}$ that connects (q_i,p_i) to (q_f,p_f) in real time. However strange they may appear at first sight, complex classical trajectories have shown great promise in describing quantum-dynamics and spectra [9–11], scattering [12], tunneling [13–17], and the quantum-classical transition in chaotic systems [14–18]. Unfortunately, at present the applications of complex semiclassical approximations to Eq. (2) are limited to "special cases" where, for example, the phase space can be inspected visually or the periodic orbits can be explicitly enumerated. Treating more realistic systems has not been possible because the number of complex trajectories proliferates very rapidly as a function of time and it is not, in general, understood how many such trajectories one needs to consider or how to locate these trajectories in a many dimensional system. No acceptable solution to these two difficulties has as yet been proposed.

The importance of nearly real complex trajectories has already been observed in several situations [9,10,14,16,18,19]. For coherent states, this observation is physically supported by the interpretation of Eq. (2) in terms of a single real classical trajectory [3–5]. The complexification simply diverts the real path by a small amount so that, instead of barely missing, it satisfies the boundary conditions exactly. Thus, while it is not entirely clear to what extent subdominant contributions (usually associated with tunneling [14,16]) must be included in order to obtain satisfactory results, it is still conventional wisdom that the dominant complex paths tend to be associated with real classical trajectories that very nearly connect the initial and final points in phase space.

In this paper, we examine the possibility that the dominant contributions by themselves may give a faithful representation of the true result. We present calculations of the autocorrelation function of the quartic anharmonic oscillator and the photodissociation of CO_2, which show that including only the nearly real trajectories (and discarding all subdominant contributions) can give excellent results for realistic potentials. The use of only nearly real paths is particularly appealing because it allows one to overcome both of the major obstacles that have heretofore limited complex semiclassical approaches. First, because the imaginary part is by assumption small, it should be very easy to find the desired trajectories — they should reside in a thin shell in phase space around the real trajectory. Second, the number of trajectories one must consider will be significantly reduced, because most paths will have large imaginary components [14]. Our methodology takes maximum advantage of these simplifications, so that the approach presented here is transparently applicable to systems with up to several hundred degrees of freedom. As a result of these developments, the nearly real semiclassical formalism appears very promising for the description of the quantum dynamics of large systems.

The SPA to Eq. (2) can be written in the standard semiclassical form [6–8] (choosing units so that $\hbar=1$)

$$\langle q_f,p_f|e^{-i\hat{H}t}|q_i,p_i\rangle\approx\sum_{paths}A(p,q,t)e^{iS(p,q,t)}. \tag{3}$$

The complex classical action is given by

$$S(p,q,t)=\int_0^t \frac{p\dot{q}-q\dot{p}}{2}-H(p,q)dt$$
$$-i\,\frac{\gamma^2 q(0)^2+p(0)^2-|\gamma q(0)+ip(0)|^2}{2\gamma}$$
$$-i\,\frac{\gamma^2 q(t)^2+p(t)^2-|\gamma q(t)-ip(t)|^2}{2\gamma}. \qquad (4)$$

The second and third terms in Eq. (4) arise from the fact that the coherent states are not eigenfunctions of an Hermitian operator and, therefore, the standard classical action (i.e., the first term) is not by itself appropriate [6]. The sum in Eq. (3) runs over all complex classical trajectories that satisfy Hamilton's equations

$$\dot{q}=\frac{\partial H}{\partial p}, \quad \dot{p}=-\frac{\partial H}{\partial q}, \qquad (5)$$

and the boundary conditions

$$\gamma q(0)+ip(0)=\gamma q_i+ip_i, \qquad (6)$$

$$\gamma q(t)-ip(t)=\gamma q_f-ip_f. \qquad (7)$$

The above conditions are easily understood when one realizes that if Eq. (6) is satisfied, the coherent state $|q(0),p(0)\rangle$ is the same physical wave function (i.e., it has the same $\langle\hat{q}\rangle$, $\langle\hat{p}\rangle$ and width) as the state $|q_i,p_i\rangle$. Likewise, if Eq. (7) is satisfied, the bra states $\langle q(t),p(t)|$ and $\langle q_f,p_f|$ are also the same. Hence, the boundary conditions do, indeed, encapsulate our intuitive assumption that the complex trajectory should "connect" the initial and final points.

The prefactor in Eq. (3) is given by

$$A(p,q,t)=\left[\frac{1}{2}\left(\frac{\partial q(t)}{\partial q(0)}+\frac{\partial p(t)}{\partial p(0)}-\frac{i}{\gamma}\frac{\partial p(t)}{\partial q(0)}+i\gamma\frac{\partial q(t)}{\partial p(0)}\right)\right]^{-1/2}. \qquad (8)$$

The derivatives $\partial q(t)/\partial q(0)$, etc., are the elements of the complex stability matrix, which can be obtained by integrating the matrix equation

$$\begin{pmatrix} \frac{\partial \dot{q}(t)}{\partial q(0)} & \frac{\partial \dot{q}(t)}{\partial p(0)} \\ \frac{\partial \dot{p}(t)}{\partial q(0)} & \frac{\partial \dot{p}(t)}{\partial p(0)} \end{pmatrix}=\begin{pmatrix} \frac{\partial^2 H}{\partial q\partial p} & \frac{\partial^2 H}{\partial p\partial p} \\ -\frac{\partial^2 H}{\partial q\partial q} & -\frac{\partial^2 H}{\partial p\partial q} \end{pmatrix}\times\begin{pmatrix} \frac{\partial q(t)}{\partial q(0)} & \frac{\partial q(t)}{\partial p(0)} \\ \frac{\partial p(t)}{\partial q(0)} & \frac{\partial p(t)}{\partial p(0)} \end{pmatrix} \qquad (9)$$

along the classical trajectory.

The central obstacle to applying Eq. (3) is *finding* the complex trajectories that connect the initial and final points in phase space. This task is strictly analogous to the standard problem of trying to find a real trajectory that connects a given pair of points in position space. One simple approach to this problem is to use Newton-Raphson (NR) [20] iterations to locate solutions of the boundary conditions [Eqs. (6) and (7)]. The NR iterations converge quadratically, provided the initial guess is sufficiently close to the desired solution. In general, predicting the location of solutions of Eqs. (6) and (7) is impossible, and so one must make use of physical insight to obtain an initial guess that is "near" the physical solution. In the present context, we are interested only in the nearly real solutions, and hence it is reasonable to use the purely real trajectory as a guess. As a result, *by design*, our search will only find trajectories that are in some sense "near" the real trajectory.

Usually, we will be considering the propagator as a function of some continuous label (e.g., the final time). Given a nearly real trajectory at a particular time, we can trace out an entire curve of analogous solutions by taking a series of small steps forward and backward in time, using NR to adjust the initial conditions at each step. Along this curve, the complex trajectory will change continuously as a function of time, and we call this set of trajectories a "branch" [9]. Of course, a trajectory that is nearly real at one particular time may obtain a significant complex part as it evolves along its branch. But one cannot discard this branch after it has wandered some distance from the real solution, or the resulting semiclassical amplitude would be a discontinuous function of time. Thus, our approximation to the propagator will be constructed as the sum of contributions from branches that are *at some time* nearly real.

A simple one-dimensional example is illustrative. Consider the quartic anharmonic potential $V(x)=\frac{1}{2}x^2+\frac{1}{8}x^4$. For short times, a discussion of the complex phase space for potentials of this type has been presented elsewhere [19,21]. We will consider the autocorrelation function, setting $q_i=q_f=1.5$ and $p_i=p_f=0$. The underlying trajectory is periodic, as is every other trajectory in this potential, and so the "nearly" real solutions for this case are just the recurrences of this orbit and they are, in fact, exactly real. We have used the NR search to locate all of the branches associated with these recurrences. It turns out that each return lies on its own branch, and we present the results for the first four such branches in Fig. 1. As one would expect, the contribution from each branch is maximal near the real trajectory, and each contribution is fairly localized in time. However, the "tails" of different contributions overlap strongly, which will lead to the interference effects characteristic of semiclassical approaches. The frequency chirp evident in each contribution results from the fact that higher energies give higher frequencies in this potential. Thus, the trajectories that return first are those that have higher energy and hence a more oscillatory phase. The broadening along each branch reflects the spreading of the coherent state in the anharmonic potential.

In Fig. 2, we show the autocorrelation function for this case, which is just the sum of the individual branches. The agreement between the semiclassical result and the quantum result is excellent, with the semiclassics reproducing the features of the quantum autocorrelation function even after

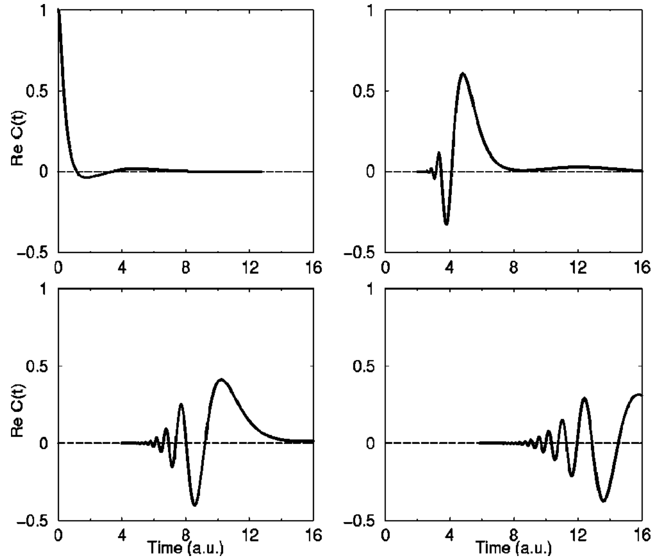

FIG. 1. The first several nearly real branches of the quartic anharmonic oscillator. Each branch is exactly real after successively 0,1,2,3, . . . periods of classical oscillation ($T_{cl}=4.64$).

many periods of oscillation. This may be compared to the amplitude obtained using only the real trajectory — the ''thawed Gaussian'' approximation [3] — which is not qualitatively correct even for the first recurrence. Hence, for this problem, the nearly real complex branches encode the quantum interference structure, while a purely real method essentially misses this structure entirely.

We next turn our attention to the photodissociation of CO_2 as an example of a well-characterized multidimensional problem. Using the two-dimensional empirical potential of Kulander and Light [22], the photodissociation of CO_2 has been studied using both quantum [23,24] and semiclassical [25] methods. The photodissociation involves the promotion of an initial wave packet from near the minimum of the ground electronic state (R[C—O$_a$]=R[C—O$_b$] $\approx$2.2 bohr) to an excited state, which is unstable relative to the dissociation $CO_2 \rightarrow O + CO$. Contour plots of this surface are shown in Fig. 3. The photodissociation absorption spec-

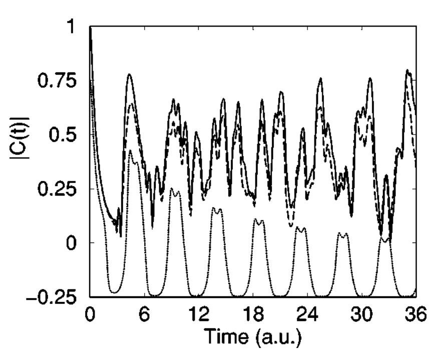

FIG. 2. The quantum (solid) and semiclassical (dashed) autocorrelation functions for the quartic anharmonic oscillator. The semiclassical result is obtained by summing the first 16 branches such as those in Fig. 1. Also shown is the result obtained using only the real trajectory (dotted). For clarity, it has been shifted by 0.25 units relative to the others.

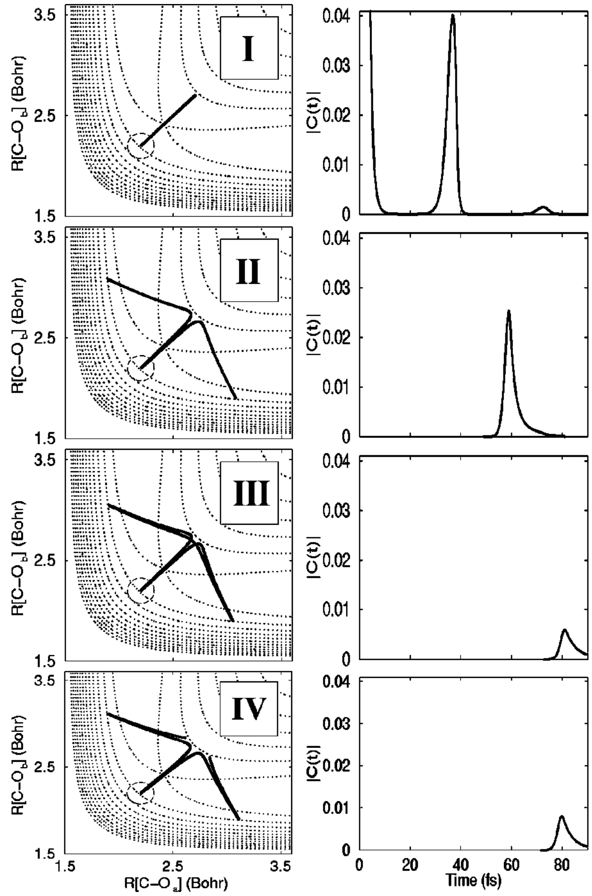

FIG. 3. On the left, four periodic orbits for CO_2 are shown superimposed on the excited potential surface. The periods of these orbits are 36.7 fs, 118.3 fs, 82.2 fs, and 161.9 fs, respectively. A circle represents the initial wave packet. The branches that arise from each orbit are shown to the right of the orbit. Orbit I gives rise to 2 branches in this time interval, and orbits II and IV give rise to early peaks because they return to the Franck-Condon region twice per period. The real trajectory omits all but the contributions from orbit I.

trum is the Fourier transform of the autocorrelation function of the initial wave packet on the excited surface. The structure of the autocorrelation function has been semiquantitatively explained in terms of several periodic orbits [25], shown in Fig. 3. Within the complex semiclassical approximation, one expects that the important branches should arise from these nearby periodic orbits. We have located the nearly real solutions for this problem and we find that this is precisely the case; each orbit gives rise to its own set of nearly real branches. The branches that appear in the first 90 fs are shown in Fig. 3, next to the relevant orbit.

The sum of the nearly real branches for CO_2 is shown in Fig. 4 and the agreement between the semiclassical and quantum results is once again excellent, as one would expect for a system with such massive nuclei. The corresponding absorption spectra are shown in the inset of Fig. 4. The envelope of the spectrum is determined by the rapid initial decay of $C(t)$ and the oscillations are due to the recurrences at later time. The quantum and semiclassical results are almost indistinguishable.

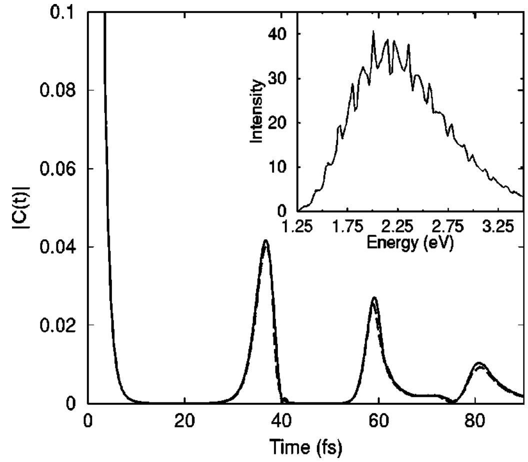

FIG. 4. Quantum (solid) and semiclassical (dotted) autocorrelation functions for CO_2. The inset shows the corresponding absorption spectra, which are essentially identical.

Previously, the major obstacle to applying complex semiclassical mechanics has been determining the solutions of Eqs. (6) and (7). However, our results show that the nearly real contributions can be quite easily determined — even for a system like CO_2, which has multiple unstable periodic orbits. Further, the results obtained from the nearly real trajectories are in excellent agreement with the quantum results, making the nearly real semiclassical formalism a very promising technique. The most difficult step for large systems is expected to be the evaluation of the stability matrix elements [Eq. (9)], which only requires one matrix multiplication per time step. Hence, we anticipate the present approach should be feasible for at least several hundred degrees of freedom. This should be contrasted with current ''integral expressions'' for the semiclassical propagator [26,27] that have shown great promise in chemical dynamics [28–30], but are typically limited by an integration over all phase space. Since the integral formulations are typically introduced to *circumvent* the boundary conditions, the present method can be thought of as a ''back to basics'' alternative. Applications to larger systems and generalization to systems that exhibit more exotic effects such as tunneling and chaos — where Stokes phenomenon [14] and trajectories that are homoclinic to real orbits [16] must be considered — are in progress.

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