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Semiclassical Real-Time Tunneling by Multiple Spawning of Classical Trajectories

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We systematically extend semiclassical real-time propagation methods based on Gaussian wave packets by using the composition property of the time-dependent quantum-mechanical Green function. For the first time, in an application to the problem of barrier tunneling, a semiclassical time-domain calculation of the transmission probability exhibits good agreement with exact quantum mechanical values at energies below the barrier top. Only two insertions of unity are needed for these results in a benchmark model of reactive scattering.

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The problem of tunneling has been a fascinating one ever since the advent of quantum theory because there seems to be no straightforward explanation of the phenomenon in terms of real-valued classical trajectories evolving in real time in general. While successful approaches to understand parabolic barrier tunneling by using real trajectories in the Wigner picture do exist [1], the question if incoherent and coherent tunneling in physically realistic systems can be accounted for properly by real-time classical trajectories has received considerable attention recently. Initiated by semiclassical investigations of barrier tunneling using modified plane waves [2], several authors have employed Gaussian initial states with energetic components above the barrier to study if the corresponding classical trajectories, which can connect positions on opposite sides of the barrier, give reasonable results for the transmission probability at energies below the barrier [3,4]. A mathematically satisfactory semiclassical procedure has not emerged yet, however. In an investigation of the semiclassical propagator across a barrier it has, e.g., been stated that classically allowed real-time trajectories are not, in general, sufficient to explain tunneling amplitudes in the energy domain [5]. Also for the coherent tunneling in a double well potential, which has its origin in the splitting between the lowest two energy levels, the question is still unanswered if the doublet structure can be extracted from a *single* semiclassical wave packet propagation. It has been shown that by propagating a large number of initial wave packets, one can extract tunnel splittings from the semiclassical dynamics but single wave packet results showed no sign of the corresponding quantum beats [6].

The time-dependent semiclassical methods used in the articles mentioned above have ranged from the van Vleck propagator [7] to the initial value representation (IVR) of the semiclassical propagator of Herman and Kluk [8]. This last, Gaussian wave packet based methodology avoids the classical root search problem indigenous to the van Vleck propagator and has shown the greatest potential recently in different applications in atomic, molecular, and chemical physics [9,10]. It is known, however, that for the problem of incoherent tunneling in an Eckart potential the same kind of nonconvergence as reported in [3], using the van Vleck propagator, has to be dealt with also in calculations using the Herman-Kluk (HK) propagator [4]. In order to remove these shortcomings, in the following we will present an extension of the method of Herman and Kluk, which is in the same spirit as the original (i.e., only using classical initial value trajectories) but allows for a systematic improvement towards the correct quantum result, in which tunneling is contained by definition. It has been a long-standing challenge to include hard quantum effects, like diffraction or tunneling, in semiclassical theories. In order to deal with these phenomena, semiclassical work in the energy domain uses so-called bounces and instantons, i.e., imaginary time trajectories [11], or diffractive orbits [12]. In this Letter, however, we focus on a time-dependent semiclassical viewpoint of the tunneling process [13] which has

conceptual advantages, e.g., for driven systems. Furthermore, the numerical implementation of the uniform semiclassical IVR propagator of Herman and Kluk leads to a black box method which can be applied for any kind of system dynamics and complexity. This feature of the standard HK methodology is shared by the extended one to be laid out subsequently.

The picture of diffraction at an obstacle is very helpful for understanding the physical content of the formalism presented in the following. In a geometrical optics context light and shadow regions of an obstacle are created by a light source. Using real-time trajectories starting at the source, how would these be able to penetrate into the shadow region? This can, e.g., happen if a trajectory reaching the edge of the obstacle is then allowed to spawn new trajectories in all different directions in the spirit of Huygens' principle of wave optics. The same kind of argument also holds true for tunneling processes. If a trajectory representing a particle approaches a barrier with energy less than the barrier height, it cannot overcome this barrier. By spawning off new trajectories with all kinds of different energies, however, the particle can (at least partially) overcome the barrier. The question is how to allow for such a spawning procedure in a consistent way. To reach this goal, in the following we will present a systematic extension of the semiclassical HK approach based on the multiple insertion of unity into the propagator followed by suitable semiclassical approximations.

The methodology rests on the well known composition property of the nonrelativistic quantum mechanical propagator (time-dependent Green function)

$$\begin{aligned} K(\mathbf{x},t;\mathbf{x}',0) &\equiv \langle \mathbf{x}|\exp\{-i\hat{H}t/\hbar\}|\mathbf{x}'\rangle \\ &= \int d\mathbf{x}''\langle \mathbf{x}|\exp\{-i\hat{H}t/(2\hbar)\}|\mathbf{x}''\rangle \\ &\quad\times\langle \mathbf{x}''|\exp\{-i\hat{H}t/(2\hbar)\}|\mathbf{x}'\rangle, \end{aligned} \tag{1}$$

in the position representation for a system with an N-component coordinate space vector $\mathbf{x}$. Here the propagation over the time interval $[0,t]$ has been "sliced" into two steps over intervals of length $t/2$ by using $\exp\{-i\hat{H}t/\hbar\} = \exp\{-i\hat{H}t/(2\hbar)\}\exp\{-i\hat{H}t/(2\hbar)\}$ together with an insertion of unity using the position space basis. The decisive progress now is to invoke the semiclassical Herman-Kluk approximation

$$\begin{aligned} K(\mathbf{x},t;\mathbf{x}',0) = \int \frac{d\mathbf{p}'\,d\mathbf{q}'}{(2\pi\hbar)^N}\langle \mathbf{x}|g_\gamma(\mathbf{p}_t',\mathbf{q}_t')\rangle R(\mathbf{p}',\mathbf{q}',t) \\ \times\exp\{iS(\mathbf{p}',\mathbf{q}',t)/\hbar\}\langle g_\gamma(\mathbf{p}',\mathbf{q}')\,|\,\mathbf{x}'\rangle \end{aligned} \tag{2}$$

for the successive propagators. In this expression

$$\begin{aligned} \langle \mathbf{x}|g_\gamma(\mathbf{p}',\mathbf{q}')\rangle = \left\{\frac{\gamma}{\pi}\right\}^{N/4}\exp\Big\{-\frac{\gamma}{2}(\mathbf{x}-\mathbf{q}')^2 \\ + \frac{i}{\hbar}\,\mathbf{p}'\cdot(\mathbf{x}-\mathbf{q}')\Big\} \end{aligned} \tag{3}$$

represents a Gaussian wave packet with width parameter γ, which is centered around the initial phase space point $(\mathbf{p}',\mathbf{q}')$. $S(\mathbf{p}',\mathbf{q}',t)$ denotes the classical action functional, being the time integral of the Lagrangian, and the preexponential factor $R(\mathbf{p}',\mathbf{q}',t)$ contains a determinant of submatrices of the classical stability matrix [8].

The next step after insertion of the semiclassical propagators is to perform the $\mathbf{x}''$ integration in Eq. (1) analytically. This leads to the emergence of a Gaussian factor

$$\begin{aligned} \langle g_\gamma''\,|\,g_\gamma'(t/2)\rangle = \exp\Big\{-\frac{\gamma}{4}(\mathbf{q}''-\mathbf{q}_{t/2}')^2 \\ + \frac{i}{2\hbar}(\mathbf{q}''-\mathbf{q}_{t/2}')\cdot(\mathbf{p}''+\mathbf{p}_{t/2}') \\ - \frac{1}{4\gamma\hbar^2}(\mathbf{p}''-\mathbf{p}_{t/2}')^2\Big\}. \end{aligned} \tag{4}$$

Two integrations stemming from twice inserting Eq. (2) into Eq. (1) are then left over, one over initial (indicated by a single prime), the other over intermediate phase space (double primes). The final expression is

$$\begin{aligned} K(\mathbf{x},t;\mathbf{x}',0) = \int \frac{d\mathbf{p}'d\mathbf{q}'}{(2\pi\hbar)^N}\int \frac{d\mathbf{p}''d\mathbf{q}''}{(2\pi\hbar)^N}\langle \mathbf{x}\,|\,g_\gamma(\mathbf{p}_{t/2}'',\mathbf{q}_{t/2}'')\rangle R\Big(\mathbf{p}'',\mathbf{q}'',\frac{t}{2}\Big)\exp\Big\{iS\Big(\mathbf{p}'',\mathbf{q}'',\frac{t}{2}\Big)\Big/\hbar\Big\} \\ \times\langle g_\gamma''|g_\gamma'(t/2)\rangle R\Big(\mathbf{p}',\mathbf{q}',\frac{t}{2}\Big)\exp\Big\{iS\Big(\mathbf{p}',\mathbf{q}',\frac{t}{2}\Big)\Big/\hbar\Big\}\langle g_\gamma(\mathbf{p}',\mathbf{q}')\,|\,\mathbf{x}'\rangle. \end{aligned} \tag{5}$$

If the integrations over initial and intermediate phase space are performed by a Monte Carlo procedure, the physical content of Eq. (5) is that every trajectory of the swarm starting out from an initial phase space point $(\mathbf{p}',\mathbf{q}')$, when it reaches the intermediate time $t/2$ spawns off a new swarm of trajectories with initial phase space coordinates $(\mathbf{p}'',\mathbf{q}'')$ and not necessarily the same energy. The phase space volume from which the new trajectories are drawn is centered around the point $(\mathbf{p}_{t/2}',\mathbf{q}_{t/2}')$ the initial trajectory has reached at $t/2$ and is smoothly cut off by the Gaussian weight factor in Eq. (4). This semiclassical time slicing scheme can be used several times and for arbitrarily long divisions of the time interval. We want to mention that, with respect to energy nonconservation, the modified semiclassical methodology resembles the stochastic energetic jumps of trajectories in a classical trajectory Monte Carlo study of proton hydrogen collisions [14].

Furthermore, we want to emphasize that by performing the intermediate phase space integration in Eq. (5) numerically exactly and *not* by the stationary phase method, an improvement of the semiclassical results is to be

expected. This is because stationary phase leads back to the standard semiclassical result, while the procedure proposed above could in principle be carried through *ad infinitum* and would then lead to the exact quantum mechanical propagator in an analogous way as the (Riemann) integral representation of the Feynman path integral [15], which uses free particle short time propagators. It is not the intention of this Letter to converge the numerics to the full path integral result by using semiclassical propagators for the short time steps [16], however. We want to improve time-dependent semiclassics by using very few time slices and will show in the following that a realistic description of tunneling dynamics can be achieved by using the proposed spawning procedure resting on the HK propagator.

The problem to be studied in the remainder of this Letter is the incoherent tunneling of a particle through a symmetric Eckart barrier, centered around the coordinate origin. In contrast to parabolic barrier scattering, this potential has physical boundary conditions (reaching a constant value at $x \rightarrow \pm\infty$) and is widely used in different branches of physics as a benchmark problem. For realistic parameters we choose the barrier to represent a one-dimensional (1D) model of the H + H_2 exchange reaction studied previously in the same context [2–4,17]. A wave packet correlation function formulation is then used for the calculation of the $S(E)$ matrix element for transmission through the barrier [18].

In Fig. 1 full quantum results from a numerical wave packet propagation based on the split operator formalism are shown. We have depicted the correlation function

$$c_{\beta\alpha}(t) = \langle \Psi_\beta | \exp\{-i\hat{H}t/\hbar\} | \Psi_\alpha \rangle \qquad (6)$$

between a Gaussian wave packet $\langle \mathbf{x} \,|\, \Psi_\beta \rangle$ centered to the right [with $\gamma = 12$ and ($\mathbf{p}_\beta = 6, \mathbf{q}_\beta = 3$) for the dimensionless wave packet parameters [3]] and a propagated Gaussian wave packet $\langle \mathbf{x} \,|\, \Psi_\alpha \rangle$ initially to the left of the barrier ($\mathbf{q}_\alpha = -\mathbf{q}_\beta$) as a function of time (in units of 25.6 fs). The quantum results are compared to semiclassical HK results without time slicing. For short times there is very good agreement, whereas for longer times the results (which need exceedingly many trajectories to be converged) deviate more and more from the quantum ones by lagging behind in time. At first sight it seems as if this should not have a big effect on physically observable quantities. However, in Ref. [3] it has been shown that the opposite is the case already in the moderate tunneling regime. Extracting the transmission probability by exactly numerically Fourier transforming the time series and normalizing the outcome to calculate $S_{\beta\alpha}(E)$ [18], the slowly oscillating behavior at long times becomes dominant for energies below the barrier top (which is here at 0.425 eV). Therefore the observed deviations in the time signal are decisive for the incapability of standard time-dependent semiclassical methods to describe tunneling probabilities correctly. In previous studies, e.g., a nonconvergence of the transmission probability with respect to the initial center of the propagated wave packets has been observed [3,4]. The standard semiclassical time-domain methodology does not only perform much poorer than uniform semiclassical WKB or energy domain IVR techniques [17], but it is of limited use for the tunneling problem from a mathematical point of view.

The time-dependent semiclassical results thus need to be improved, and we will investigate if this goal can be reached by successive application of the extended semiclassical procedure introduced above. In Fig. 2 the kind of improvement is shown that can be achieved by applying the spawning procedure once or twice in the course

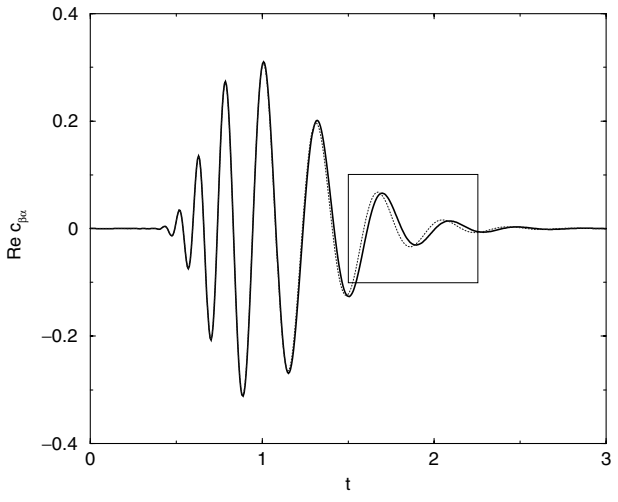

FIG. 1. Real part of the correlation function $c_{\beta\alpha}$ versus time. Solid line: full quantum result; dotted line: standard semiclassical result *without* time slicing. The box indicates the region depicted in Fig. 2.

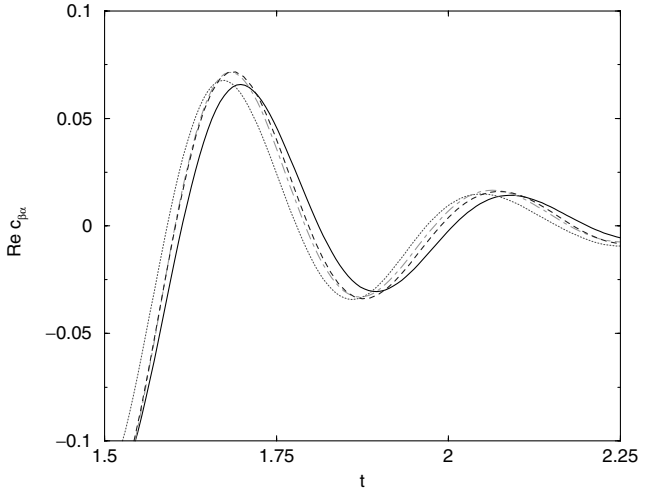

FIG. 2. Real part of the correlation function. Solid line: full quantum result; dotted line: standard semiclassical result; dash-dotted line: semiclassical result with one additional spawning of trajectories; dashed line: semiclassical result with the spawning procedure applied twice.

of time. The initial parameters of the propagated wave packets are the same as for the standard semiclassical calculation, and we have just shown the long time behavior (indicated by the box in Fig. 1) because only there has a significant discrepancy between semiclassics and quantum mechanics been observed. The slicing times were chosen well before the significant deviations in Fig. 1 occur. Although an optimization procedure for the choice of slicing parameters has not been applied and still needs to be devised (slicing at half time $T/2$ is best suited for the result at a fixed time T but here we need the result over a whole range of time), a remarkable gradual improvement (dash-dotted and dashed line) towards the exact quantum result (full line) can be achieved by this procedure. How does this affect the energy dependent transmission probabilities, however?

In order to answer this question, we have extracted the quantities $P(E) = |S_{\beta\alpha}(E)|^2$ numerically from the quantum and different semiclassical correlation functions and have plotted the results versus energy in Fig. 3 together with the uniform WKB result. The big discrepancy in the logarithmic plot between the quantum and the time-dependent semiclassical result *without* time slicing is striking. Well in the tunneling regime, at $E = 0.3$ eV (the energy of the barrier top is indicated by the arrow in Fig. 3), the standard semiclassical result (dotted line) is smaller by more than a factor of 2.4 than the quantum one (solid line). In contrast, the result for the transmission probability extracted from the time signal with two additional spawning procedures (dashed line) is much closer to the full quantum one and exhibits only a deviation by less than 20% at $E = 0.3$ eV. This is even better than the agreement that can be achieved by the application of the energy-dependent uniform WKB approximation (long dashed line in Fig. 3). The overshooting of the improved semiclassical result for energies around the barrier top is reminiscent of similar behavior of the standard HK solution (occurring at slightly higher energies [4]) which could be removed by additional time slicing.

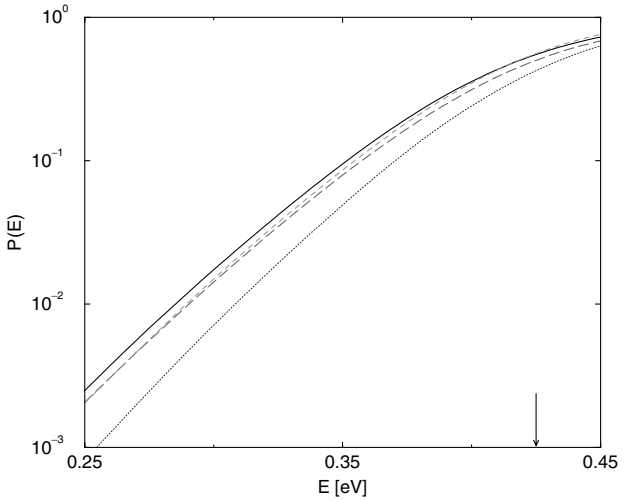

FIG. 3. Logarithmic plot of the transmission probability as a function of energy (in units of eV). Solid line: full quantum result; dotted line: standard semiclassical result; dashed line: semiclassical result with two spawnings; long dashed line: uniform WKB result. The arrow indicates the barrier height in the 1D model of the $H + H_2$ reaction.

We have proposed an extension of semiclassical real-time propagation methods which rests on enabling the classical trajectories to send out swarms of new trajectories at certain points in time. Using this methodology, we have shown that, by applying a very small number of time slicings accompanied by the spawning procedure, the shortcomings with respect to tunneling dynamics of previous time-dependent semiclassical calculations can be successively removed. This is the first time that for a so-called hard quantum effect, like the incoherent tunneling through an Eckart barrier, semiclassical time-domain results as good as or better than uniform WKB results have been reported. Thus, we have reached the goal to demonstrate that real-time classical trajectories *do* account for quantum-mechanical tunneling if they are allowed to spawn off new ones in the course of time. Obviously, the number of trajectories to be propagated increases with every additional time slicing procedure. The calculations can be started with a relatively small number of trajectories in the beginning, however. Every insertion of unity then increases the number of trajectories to be propagated by about 3 orders of magnitude. It would be worthwhile to explore how well this procedure works in other circumstances. In this respect, we want to emphasize that the proposed time-dependent methodology is not restricted to one-dimensional, autonomous problems and can in principle be improved step by step through additional insertions of unity. It is therefore much more flexible than standard semiclassical methods.

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