PHYSICAL REVIEW
LETTERS

VOLUME 71 27 SEPTEMBER 1993 NUMBER 13

Semiclassical Theory of Quantum Propagation: The Coulomb Potential

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(Received 11 March 1993)

A semiclassical method is discussed for propagating wave packets that incorporates nonlinear classical dynamical information through the use of multiple reference trajectories. We apply the theory to obtain an *analytic* approximation for the autocorrelation function in the Coulomb potential which is extremely accurate in many circumstances in spite of the Coulomb singularity. All the detailed quantum behavior is reproduced including the long time revivals and the spectrum. The evolving phase space structure of the classical analog reveals how well a particular case will be approximated.

PACS numbers: 03.65.Sq, 03.65.Ge, 32.30.−r

The semiclassical theory of quantum wave function propagation has for many years formally existed in the form of the stationary phase approximation known as time-dependent WKB theory [1]. It explains, in principle, how to evolve a quantum state approximately in terms of a predetermined set of classical trajectories. One important aspect of building approximate quantum solutions out of classical trajectories is the deep insight it provides into a system's behavior, but actual implementations in nontrivial circumstances are rare. Recently new efficient methods for propagating wave packets have been developed [2,3] which have shown that semiclassical propagation can be surprisingly accurate even in fully developed chaotic situations. These methods go beyond the linearized approximations known as linear wave packet dynamics [4] to incorporate nonlinear dynamics through the use of a time-dependent semiclassical Green's function approach and multiple reference trajectories.

The purpose of this Letter is twofold. First, we simplify this nonlinear dynamical theory [2] by placing it in the same framework as earlier derivations of linear wave packet dynamics [4]. Second, we treat explicitly wave packet propagation in the Coulomb potential which is of direct interest to experiments. We shall address a number of crucial questions for this case. Does the Coulomb singularity pose any special difficulties to semiclassical propagation that might destroy the validity of this new approximation? Can coherent, long-time-scale quantum effects such as the theoretically predicted and experimentally observed wave packet revivals and fractional revivals [5–9] be understood directly from a semiclassical *time-dependent* point of view, without reference to the spectrum or WKB quantization of classical trajectories? How well are line intensities and spectra reproduced? What are the circumstances under which the approximation is expected to work?

The short-time-scale quantum behavior does not distinguish between regular and chaotic motion as is also true of the classical behavior. As long as the natural wavelength of a problem is sufficiently small and a wave packet is well localized in position and momentum, only the local behavior of the potential in the neighborhood of the wave packet's moving center is relevant to its evolution. The trajectory of the wave packet's center represents the local classical motion to within small, linear deviations, and all the neighboring trajectories needed to construct the wave packet are taken into account by a linear stability analysis of the central trajectory. This is how linear wave packet dynamics works—a single classical reference trajectory represents a group of trajectories that collectively fully support the construction of the evolving wave packet [4]. As nonlinearities in the dynamics begin to emerge, the wave packet is no longer described in this way, because the purely classical dynamics is no longer being treated properly in this approximation. This is well

0031-9007/93/71(13)/1961(4)$06.00

illustrated by comparing the evolution of a Gaussian wave packet in a Coulomb potential with a corresponding Gaussian ensemble of classical particles. Although the quantum wave packet spreads rapidly into a non-Gaussian shape within a fraction of a Kepler period, a very close correspondence is maintained between the quantum and classical distributions [10]. The key to going beyond linear wave packet dynamics, as pointed out in [2], begins by restoring a proper treatment of the classical dynamics. This task is simplified by focusing on correlation functions in which initially localized wave packets or coherent states are propagated and overlapped with some localized final state. For exposition, the autocorrelation function

$$C_\beta(t) = \langle \beta | \beta(t) \rangle = \int dq\, \psi_\beta^*(q,0)\psi_\beta(q,t) \qquad (1)$$

suffices, where the subscript β stands for the parameters that specify the initial and final states.

A nonlinear dynamical method with the same form as linear wave packet dynamics is possible once a few crucial points are recognized. To start, even if nonlinear motion has developed and the linearized solution is incorrect globally, it may still be valid *locally* in the neighborhood of a reference trajectory. It is important to recognize that local in this context refers to phase space. Thus it is only the features of the wave function which reside simultaneously in a certain range of position and wavelength that is expected to be approximated properly. Next, it is possible to choose reference trajectories whose motion does not coincide with the mean position of the wave packet. The key idea is to apply this flexibility to approximate different local regions of the solution as required. In other words, if one is interested in how a portion of the tail of the wave packet evolved, the best reference trajectory originates from that tail. As a result of this flexibility it is possible to ensure that the reference trajectories are chosen such that the valid domain of the wave function is in the zone of the final state whatever the time of propagation considered. The initial conditions of the reference trajectories are therefore strongly time dependent, and the theory describes the choice of these trajectories as a function of time.

Finally, with nonlinear dynamics, the need for multiple reference trajectories quickly develops whether the system is integrable or chaotic. Quite generically, in the short wavelength approximation, $\hbar \to 0$, the set of trajectories contributing to $C_\beta(t)$ is uniquely divided into subgroups which appear as thin branches in the corresponding classical phase space. Within each subgroup the trajectories are all very similar in their properties such as actions and stabilities. However, each branch is topologically separate from the others. For example, with the Coulomb potential it will be seen that the number of collisions with the Coulomb singularity will uniquely label the branches; see Fig. 1 and discussion ahead. Each such branch supports a local portion of a wave packet constructed as though it were part of an independent, linearized wave packet whose reference trajectory falls well within the part of the branch overlapping the final state. Correlation functions are therefore written as a coherent sum of overlaps with locally good solutions, one for each reference trajectory.

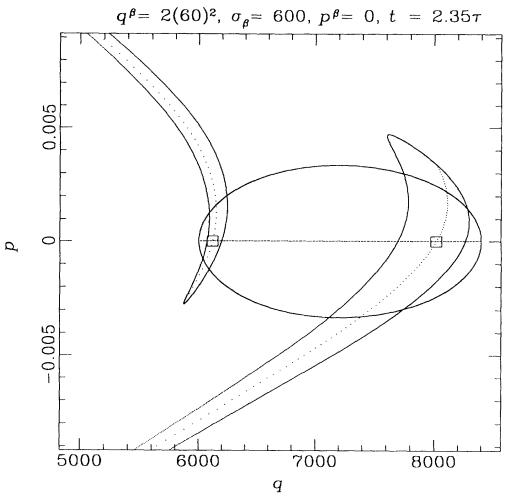

FIG. 1. An ellipse in phase space representing the initial Gaussian with parameters $q^\beta, p^\beta, \sigma_\beta$ is propagated classically. The inner branch is formed by trajectories on their third return, and the outer branch are those on their second return. The initial manifold ($p=0$ line inside ellipse) is likewise propagated to give the final manifold (dotted line), and the intersections correspond to the initial and final points (denoted by □) of the reference trajectories used to calculate the autocorrelation function.

To investigate the questions posed earlier about the Coulomb problem, the orbital angular momentum is not relevant. In fact, zero angular momentum presents the most serious difficulty because all the trajectories collide with the singularity. We will therefore restrict ourselves to the case $L=0$, or equivalently to the Coulomb potential with dynamics in one dimension. We develop the method in a one-dimensional notation though it should be clear that the multidimensional extension is straightforward. The Schrödinger equation in 1 degree of freedom is

$$i\frac{\partial \psi(q,t)}{\partial t} = -\frac{1}{2}\frac{\partial^2 \psi(q,t)}{\partial q^2} + V(q)\psi(q,t)\,, \qquad (2)$$

where for the Coulomb potential $V(q) = -1/q$ in atomic units ($\hbar = m = e^2 = 1$). Let us assume that we are interested in a local semiclassical approximation associated with one particular reference trajectory which is specified by its position and momentum for all times and denoted $\{q_t, p_t\}$. This trajectory satisfies the equations of motion for the corresponding classical Hamiltonian, $H = p^2/2 + V(q)$, and can be solved in parametric form for the Coulomb potential.

A solution of Eq. (2) best suited to the neighborhood of such a trajectory starts by expanding the potential $V(q)$ up to the quadratic form

$$V(q) \approx V(q_t) + V'(q_t)(q-q_t) + \tfrac{1}{2} V''(q_t)(q-q_t)^2 . \quad (3)$$

Since q_t is evolving, the expansion is continuously changing with time. In the Coulomb case, on each pass of the trajectory through $q=0$ the expansion fails. Nevertheless, we will see that this causes no problems once the trajectory reemerges from the origin.

Equations (2) and (3) govern the motion of a quantum harmonic oscillator with a time varying frequency and center. Hence, any initial state with a Gaussian or wave packet form will retain this form albeit distorted under time evolution, and we may therefore express the solution as

$$\psi_\beta(q,t) = A \exp\{i[\xi_t(q-q_t) + \alpha_t(q-q_t)^2 + \gamma_t]\} . \quad (4)$$

The variables ξ_t, α_t, and γ_t are *complex* functions of time which satisfy ordinary nonlinear differential equations [11] obtained by substituting Eq. (4) in the Schrödinger equation (2) with $V(q)$ approximated by Eq. (3). Their initial conditions are determined by the parameters β of the initial Gaussian wave packet and the specific reference trajectory (A is a time-independent normalization constant). For example, a normalized initial Gaussian wave packet of variance σ_β^2, centered at q^β and with average momentum of p^β, has the form

$$\psi_\beta(q,0) = (\pi\sigma_\beta^2)^{-1/4} \exp\left[ip^\beta(q-q^\beta) - \frac{(q-q^\beta)^2}{2\sigma_\beta^2}\right] . \quad (5)$$

Comparing with the notation of Eq. (4), we obtain at $t=0$

$$\begin{aligned} &\alpha_0 = i/2\sigma_\beta^2, \quad \xi_0 = p^\beta + 2\alpha_0(q_0 - q^\beta) , \\ &\gamma_0 = (q_0-q^\beta)[\alpha_0(q_0-q^\beta) + p^\beta] , \end{aligned} \quad (6)$$

where q_0 denotes the reference trajectory's initial position and $A = (\pi\sigma_\beta^2)^{-1/4}$.

We now evaluate the autocorrelation function $C_\beta(t)$, Eq. (1), by constructing the time-dependent state as a superposition of wave functions, Eq. (4), corresponding to different reference trajectories, with relative phase equal to unity [12]. For the special case that $q_t = q_0$, which will be used in our calculations, we obtain

$$C_\beta(t) = \sum_j \left\{ \left[\frac{2\alpha_0}{\alpha_t + \alpha_0}\right]^{1/2} \exp\left[i(\gamma_t - \gamma_0^*) - \frac{i(\xi_t - \xi_0^*)^2}{4(\alpha_t + \alpha_0)}\right] \right\}_j , \quad (7)$$

where the subscript j refers to a given trajectory. We simplify our calculations by choosing the initial wave packet at the classical turning point ($q^\beta = 1/E$, $p^\beta = 0$).

A suitable set of reference trajectories must be chosen [12]. This is illustrated in Fig. 1, where the ellipse denotes the region of initial conditions in phase space most relevant to a wave packet that is used as an example. After about 2.35 times the Kepler period of the center trajectory, the trajectories that have returned fall into one of two branches which correspond to 2 or 3 collisions with the origin. Good reference trajectories in the central portion of the branches are found at the intersection of the $p=0$ line with the curve resulting from propagating the same line 2.35 Kepler periods. It can be verified that at all times (beyond the initial decay), one and only one trajectory is selected and is centrally located with each branch. In our units each reference trajectory has the initial conditions $p_0 = 0$, $q_0 = 2(t/2\pi j)^{2/3}$ where j is the number of Kepler periods of the orbit, and we obtain [12]

$$\begin{aligned} &\xi_t = \xi_0^* + 4\alpha_0(q_0 - q^\beta) , \\ &\alpha_t = \alpha_0 + 3t/4q_0^3 , \\ &\gamma_t = \gamma_0^* + 3t/q_0 + 2\alpha_0(q_0 - q^\beta)^2 , \end{aligned} \quad (8)$$

where the dependence on the index j has been suppressed. Substituting this result in Eq. (7), we obtain an *analytic* expression for the semiclassical autocorrelation function $C_\beta(t)$. The absolute value is compared with the exact quantum result in Fig. 2 for the first 22 Kepler periods. Our semiclassical approximation agrees accurately with the exact solution to extremely long time and shows the quantum revivals of the wave packet [5–9]. Setting

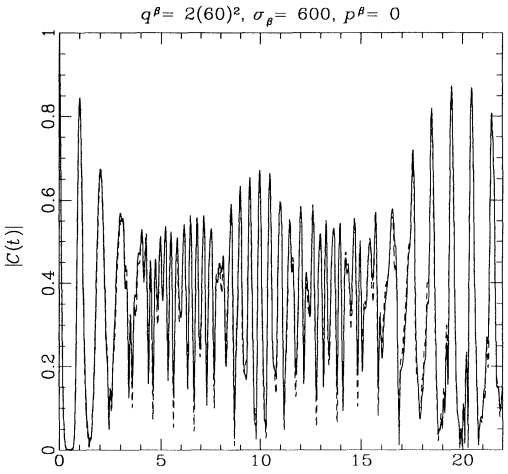

FIG. 2. Comparison of the absolute value of the semiclassical (solid line) and the exact quantum (dashed line) autocorrelation function $C_\beta(t)$. Time is in units of the Kepler period of the initial Gaussian center. Notice that the quantum revivals of the wave packet, particularly at approximately $n/3 = 20$, are accurately described.

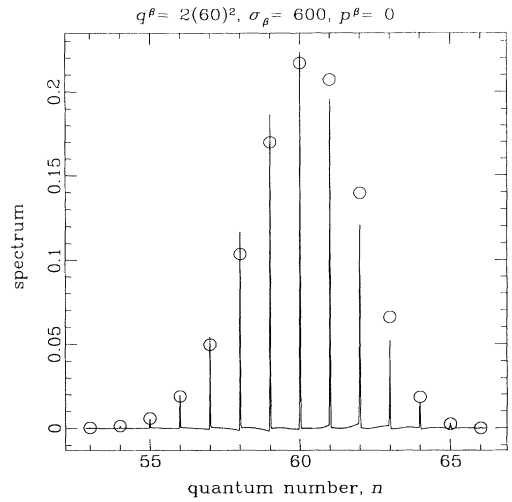

FIG. 3. A comparison between the semiclassical (solid line) and quantum (circles) spectra for the case of $q^\beta = 7200$ and $\sigma_\beta = 600$.

$t = N + \delta$, where N is an integer, and expanding the phase factors in each term of Eq. (7) to second order in $j - N$, these terms then add constructively when $N = n_\beta/3$, and $\delta = \pm \frac{1}{2}$, where $q_\beta = 2n_\beta^2$.

The Fourier transform of $C_\beta(t)$, Eq. (7), gives the intensity weighted spectrum and Fig. 3 shows the comparison with the exact spectrum. Plotting the spectrum computed with a finite time resolution of 50 Kepler periods vs the "quantum number" $n = 1/\sqrt{2E}$ shows that the peaks occur very accurately at integer values of n as expected for the Coulomb potential, and the intensities are within $\pm 5\%$ of the exact values. It is remarkable that the familiar quantum Coulomb spectrum is obtained here directly from a continuous energy range of classical trajectories without imposing any quantization conditions on their actions. Indeed, standard WKB quantization is not valid here due to the singularity of the Coulomb potential at the origin, and it gives a wrong spectrum [13].

By incorporating the nonlinear classical dynamics correctly, we have demonstrated that the semiclassical approximation for the Coulomb potential is accurate to long times far beyond the breakdown of ordinary linear wave packet dynamics. By varying the parameters we have verified that the accuracy in the present scheme fails if the β parameters chosen lead to branches of classical trajectories that are curved too sharply within the overlap region [11]. Thus, with a phase space plot similar to Fig. 1, the accuracy of the approximation can be determined in advance.

In conclusion, we have simplified the derivation of a semiclassical theory [2] which incorporates nonlinear dynamics by placing it in the same framework as earlier derivations of linear wave packet dynamics thereby avoiding the use of Green's function techniques. We applied this semiclassical method to one of the most physically interesting potentials. The example given here demonstrates the simplicity of the method and the excellent accuracy obtained which holds also for long times. We found that the singularity of the Coulomb potential did not present difficulties outside the vicinity of the origin, giving encouragement to applications of this semiclassical approximation to other problems of experimental interest in atomic and molecular physics.

This work was supported by ONR Grant No. N00014-90-J1015. One of us (S.T.) was also supported by National Science Foundation Grants No. CHE-9014555 and No. DMR-89-16052.

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