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Time-dependent approach to semiclassical dynamics

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In this paper we develop a new approach to semiclassical dynamics which exploits the fact that extended wavefunctions for heavy particles (or particles in harmonic potentials) may be decomposed into time-dependent wave packets, which spread minimally and which execute classical or nearly classical trajectories. A Gaussian form for the wave packets is assumed and equations of motion are derived for the parameters characterizing the Gaussians. If the potential (which may be nonseparable in many coordinates) is expanded in a Taylor series about the instantaneous center of the (many-particle) wave packet, and up to quadratic terms are kept, we find the classical parameters of the wave packet (positions, momenta) obey Hamilton's equation of motion. Quantum parameters (wave packet spread, phase factor, correlation terms, etc.) obey similar first order quantum equations. The center of the wave packet is shown to acquire a phase equal to the action integral along the classical path. State-specific quantum information is obtained from the wave packet trajectories by use of the superposition principle and projection techniques. Successful numerical application is made to the collinear $\text{He} + \text{H}_2$ system widely used as a test case. Classically forbidden transitions are accounted for and obtained in the same manner as the classically allowed transitions; turning points present no difficulties and flux is very nearly conserved.

I. INTRODUCTION

In recent years much attention has been directed towards the investigation of the semiclassical limit of quantum mechanics. To a large extent, these recent efforts have been motivated by the fact that many aspects of molecular quantum dynamics fall into the semiclassical domain. In fact, for many systems it is only because we ask quantum questions (such as energy specific transition probabilities between two quantum states) that we need to invoke quantum mechanics at all. As Miller¹ has emphasized, suitable averages very quickly tend to wash out quantum effects. Nevertheless, with increasingly sophisticated excitation and detection techniques becoming available, it is quite possible to measure quantum state-specific properties of even very "heavy" molecular systems. For the same systems, quantitative quantum mechanical calculations may become prohibitive because of the large number of quantum states which must be coupled to describe eigenstates for heavy particles.

Current trends in the application of semiclassical techniques to molecular dynamics can be traced back to the correspondence principle and the early views of Dirac² through the Feynman path integral approach³ and up to the more recent work of Miller,⁴ Marcus,⁵ Gutzwiller,⁶ and many other important contributions. There exists by now a rather large literature on semiclassical dynamics employing the principle of expansion in \hbar (see Dirac's book,² and in this context the paper by Eu⁷) and the correspondence between stationary phase approximations to the quantum mechanical propagators and classical paths, as emphasized by Miller.

In this paper we examine an alternative avenue of approach to the semiclassical limit of quantum mechanics. The approximations involved in the theory presented below differ significantly from those of the semiclassical techniques mentioned above. It is hoped that the present theory will provide an alternative framework which may be valid in certain regimes which are complementary to existing techniques.

Most of classical mechanics deals with the time-dependent equations of motion for a system of point particles. The closest semiclassical analog to this is a corresponding system of localized quantum wave packets. The intuitive appeal of a wave packet picture is evident, but a practical scheme needs to be developed in order to exploit the wave packet picture for the purpose of obtaining specific quantum information. It is the purpose of this paper to provide such a scheme. We deal here with a single form for the wave packets, namely multivariate Gaussians. A succeeding paper will consider more general forms for semiclassical wavefunctions and a variational approach to the time dependence of these wavefunctions, allowing treatment of classes of problems (such as curve crossing) which cannot be handled with the technique presented here.

In a section of his book entitled "The Motion of Wave Packets," Dirac² has succinctly stated the point of departure for our investigation. We quote from Dirac: "For any dynamical system with a classical analogue, a state for which the classical description is valid as an approximation is represented in quantum mechanics by a wave packet, all the coordinates and momenta having approximate numerical values . . . Schrödinger's wave equation fixes how such a wave packet varies with time, so in order that the classical description may remain valid, the wave packet should remain a wave packet and should move according to the laws of classical dynamics."

Dirac then introduces the form $\psi = A \exp[(i/\hbar)S]$ and proceeds to derive equations of motion for A and S , on the assumption that \hbar is small. It is here that we adopt a different viewpoint, noting that for harmonic potentials, the above quote from Dirac is valid no matter how big or small \hbar is. In harmonic potentials, Gaussian wave packets remain Gaussian, and undergo periodic motion, and the expectation values of positions and momenta undergo the classical equations of motion. In fact, we are just stating a result of Ehrenfest's theorem,⁸ which tells us, for example,

$$\frac{d}{dt}\langle p \rangle = -\frac{\partial H(\langle p \rangle, \langle q \rangle)}{\partial \langle q \rangle} + \text{error term}, \quad (1.1)$$

$$\text{error term} \sim d^2(\partial^3 V / \partial q^3) / (\partial V / \partial q) \big|_{q=\langle q \rangle},$$

where $H = H_0 + V$ in the Hamiltonian for the system, $\langle p \rangle$, $\langle q \rangle$ are numbers representing the expectation values of the corresponding quantum operators over the wavefunction at time t , and d is the diameter of the packet. The points we are now emphasizing are that the error term is independent of \hbar and vanishes if $\partial^3 V / \partial q^3 = 0$. We also point out the fact that the error is small if d is small.⁹ This helps to motivate the approximation which we wish to introduce, in order to treat nonharmonic potentials without recourse to stationary phase and expansions in \hbar . We assert that, for sufficiently narrow wave packets and relatively smooth potentials, the wave packet is so restricted in coordinate space that it doesn't "feel" more than the first few terms in the Taylor expansion of the potential about the center of the wave packet. If we retain terms up to and including $(x - x_t)^2$ in the expansion of the potential (where x_t is the center of the wave packet), then at each instant of time the wave packet feels a harmonic potential, so initially Gaussian wavefunctions must remain Gaussian. This leads us to consider a wavefunction of the form

$$\psi = \exp[(i/\hbar)Q(x)] \\ = \exp[(i/\hbar)q_2(t)x^2 + (i/\hbar)q_1(t)x + (i/\hbar)q_0(t)], \quad (1.2)$$

which is a general time dependent Gaussian wave packet. Thus, we postulate a convenient form for ψ and determine equations of motion for its parameters. However, instead of expanding in terms of \hbar , we approximate the potential locally. We specifically wish to avoid any expansion in \hbar , since this would ultimately lead us back to the generalized WKB, classical S-matrix version of semiclassical dynamics. We are attempting to develop a procedure which rests on somewhat different assumptions than the classical S-matrix theory imposes. Accordingly, our view of the classical correspondence of quantum dynamics is not strictly the usual $\hbar \rightarrow 0$ limit. Rather, we exploit the correspondence between classical dynamics and the quantum dynamics of localized wave packets on smooth potential surfaces.

In Sec. II we derive equations of motion for the Gaussian parameters under our assumption on the expansion of the potential about the instantaneous center of the wave packet. In Sec. III, we show how nonseparable systems may be treated and how interparticle correlations can be included in the Gaussian wavefunction. Section IV discusses various techniques for obtaining the S matrix, and Sec. V contains a numerical application to the He + H₂ collinear inelastic system. Section VI discusses possible generalizations and future work. Finally, Sec. VII contains a brief conclusion and a discussion of related work dealing with wave packets.

II. ONE-DIMENSIONAL SYSTEMS

A. Quadratic potentials

As noted in the Introduction, wave packets which are initially Gaussian remain Gaussian in quadratic poten-

tials. Quadratic potentials will be taken to include harmonic, linear, and constant functions of the position variable x . The exact quantum mechanical propagator (space time Green's function) is known for such potentials,¹⁰ and it is easy to show by application of these propagators to Gaussian wave packets that the wave packets do indeed remain Gaussian, although they may spread, acquire phase factors, etc.

One of the advantages of a Gaussian function is that a very few parameters serve to specify a complete quantum wavefunction. Let us rewrite Eq. (1.2) in a more suggestive form:

$$\psi(x, t) = \exp[(i/\hbar)\alpha_t(x - x_t)^2 + (i/\hbar)p_t(x - x_t) + (i/\hbar)\gamma_t]. \quad (2.1)$$

The parameters α_t , γ_t are complex numbers and x_t , p_t are taken to be real. If γ_t has an imaginary part such that $\langle \psi | \psi \rangle = 1$, then it is easily verified that

$$\langle p \rangle (\equiv \langle \psi | p | \psi \rangle) = p_t,$$

and (2.2)

$$\langle x \rangle (\equiv \langle \psi | x | \psi \rangle) = x_t,$$

so these parameters have their classical meaning.

There are four parameters in Eq. (2.1), two complex and two real. In classical mechanics, only x_t and p_t are needed to specify the motion of the system. The classical equations of motion are

$$\frac{dp_t}{dt} = -\left. \frac{\partial H}{\partial x} \right|_{x=x_t}, \quad (2.3)$$

$$\frac{dx_t}{dt} = -\left. \frac{\partial H}{\partial p} \right|_{p=p_t}.$$

We shall try to mimic classical mechanics as closely as possible by seeking first order equations of motion for the parameters in Eq. (2.1). This is easily accomplished by inserting Eq. (2.1) into the Schrödinger equation. The Hamiltonian governing the motion is

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x), \quad (2.4)$$

where $V(x)$ is, for now, at most a quadratic function of x . We rewrite H as

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_0 + V_x(x - x_t) + \frac{1}{2} V_{xx}(x - x_t)^2, \quad (2.5)$$

where

$$V_x = \left. \frac{\partial V}{\partial x} \right|_{x=x_t},$$

etc. The parameter x_t appearing in Eq. (2.5) is just the "center of the wave packet" appearing in Eq. (2.1). No approximation to H has been made in Eq. (2.5) since the Taylor series expansion is exact for the potentials now under consideration. Inserting (2.1) and (2.5) into

$$i\hbar \frac{d\psi}{dt} = H\psi \quad (2.6)$$

yields

$$[-\dot{\alpha}_t(x - x_t)^2 + (2\alpha_t\dot{x}_t - \dot{p}_t)(x - x_t) - \dot{\gamma}_t + p_t\dot{x}_t]\psi \\ = \{[(2/m)\alpha_t^2 + \frac{1}{2}V_{xx}](x - x_t)^2 + (2\alpha_t p_t/m + V_x)(x - x_t)$$

$$+ V_0 - i\hbar\alpha_t/m + p_t^2/2m\} \psi, \quad (2.7)$$

where $\dot{\alpha}_t = d\alpha_t/dt$, etc. Comparing coefficients of like powers of $(x - x_t)$, we find that Eq. (2.7) is satisfied if

$$\dot{\alpha}_t = -(2/m)\alpha_t^2 - V_{xx}/2, \quad (2.8a)$$

$$2\alpha_t\dot{x}_t - \dot{p}_t = 2\alpha_t p_t/m + V_x, \quad (2.8b)$$

$$\dot{\gamma}_t = i\hbar\alpha_t/m + p_t\dot{x}_t - V_0 - p_t^2/2m. \quad (2.8c)$$

Equation (2.8b) makes sense if we define

$$\dot{x}_t \equiv p_t/m = \partial H/\partial p|_{p=p_t}. \quad (2.9)$$

Noting that $V_x = \partial H/\partial x|_{x=x_t}$ and that

$$H(p_t, x_t) = p_t^2/2m + V(x_t) = E, \quad (2.10)$$

our equations of motion become

$$\dot{x}_t = \partial H/\partial p_t, \quad (2.11a)$$

$$\dot{p}_t = -\partial H/\partial x_t, \quad (2.11b)$$

$$\dot{\alpha}_t = -(2/m)\alpha_t^2 - \frac{1}{2}V_{xx}, \quad (2.11c)$$

$$\dot{\gamma}_t = i\hbar\alpha_t/m + p_t\dot{x}_t - E. \quad (2.11d)$$

No approximations have been introduced, so that if Eqs. (2.11) are solved, Eq. (2.1) gives the exact result. For $V(x) \equiv 0$, we have

$$x_t = x_0 + p_0(t - t_0)/m, \quad (2.12a)$$

$$p_t = p_0, \quad (2.12b)$$

$$\alpha_t = \frac{\alpha_0}{(2/m)\alpha_0(t - t_0) + 1}, \quad (2.12c)$$

$$\gamma_t = -\frac{i\hbar}{4} \ln \left| \frac{2\alpha_0}{\pi\hbar} \right| + \frac{i\hbar}{2} \ln \left(\frac{2\alpha_0(t - t_0)}{m} + 1 \right) + E(t - t_0). \quad (2.12d)$$

Similarly, for $V(x) = \frac{1}{2}m\omega^2x^2$, x_t and p_t execute the usual harmonic motion while

$$\alpha_t = -\frac{m\omega}{2} \left(\frac{\frac{1}{2}m\omega - \alpha_0 \cot(\omega t)}{\alpha_0 + \frac{1}{2}m\omega \cot(\omega t)} \right). \quad (2.13)$$

Note that if $\alpha_0 = im\omega/2\hbar$, we have $\alpha_t = \alpha_0$ for all t . The Gaussian wave packet in this case is called a Glauber coherent state,¹¹ having useful properties which we shall employ later on.

B. Locally quadratic potentials

It is not a very large step from the results of the last section, which were exact solutions for simple potentials, to approximate solutions for more difficult potentials. As long as the potential is smoothly varying over the width of the wave packet, it is reasonable to assume that for the purpose of propagating the solution to time $t + \delta t$ a quadratic expansion of $V(x)$ about x_t is valid. Some error is inevitably incurred unless the potential is quadratic, but this error should be small for well-localized wave packets and/or smooth potentials. These are, of course, familiar semiclassical criteria.

Thus we propose to make the substitution, Eq. (2.5), in place of Eq. (2.4), for arbitrary $V(x)$. This makes the new, effective Hamiltonian time dependent, but the difference between the exact and effective Hamiltonian is smallest where the wavefunction is largest.

The derivations leading to Eqs. (2.11) are unchanged. For arbitrary $V(x)$ we must integrate the first order classical and quantum trajectories, Eqs. (2.11), numerically. This is easily accomplished with standard techniques.

It is important to note that the potential is expanded quadratically about the *instantaneous* center of the wave packet. We do not at this point envision propagating the classical parameters x_t, p_t on an approximate harmonic potential surface expanded about several fixed points. This might be a reasonable additional approximation for future examination. For now, however, x_t and p_t follow the exact classical motion on a smooth potential surface, while α_t and γ_t experience the effects of smoothly time varying linear forces.

The Fourier transform p -space counterpart of the wavefunction given by Eq. (2.1) is

$$\begin{aligned} \psi(p) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx \exp(-ipx) \psi(x) \\ &= (-2i\alpha_t)^{-1/2} \exp(-i\hbar(p - p_t)^2/4\alpha_t - ipx_t/\hbar + i\gamma_t/\hbar), \end{aligned} \quad (2.14)$$

which is a Gaussian centered about the classical momentum p_t . Thus, our wave packet approach may be interpreted as consisting of a point in phase space, representing the center of the wave packet, executing a classical trajectory; this point is "clothed" by a Gaussian function containing the information about the quantum part of the problem. The Gaussian is able to penetrate into classically forbidden territory. This property allows for a correct description of classical turning points; there are no singularity difficulties at such points. Furthermore, as we shall see in the numerical application of Sec. V, certain other classically forbidden processes, such as the dynamically inaccessible $n \rightarrow n'$ transitions in atom-diatom collinear collisions are correctly accounted for with no additional assumptions. Paradoxically, direct barrier tunneling will evidently require further work, since the center of the Gaussian wave packet always follows a completely classical trajectory in the present formulation.

C. Phase of the wave packet, eigenfunctions

The Gaussian wavefunction Eq. (2.1), at its center $x = x_t$, is simply

$$\psi(x_t) = \exp\left(i/\hbar \int_0^t \dot{\gamma}_t dt'\right). \quad (2.14')$$

Examining the three terms in the expression (2.11d) for $\dot{\gamma}_t$, we see that the first gives rise to a purely logarithmic term in the case $V \equiv 0$ [Eq. (2.12d)] and thus goes "downstairs" as a time-dependent normalization factor in ψ . On the other hand, for the coherent state of the harmonic oscillator, we have $\alpha_t = im\omega/2$, and thus the term involving α_t in Eq. (2.11d) becomes $-\hbar\omega/2$, which becomes a pure phase factor responsible for adding the correct zero point quantum energy of $1/2\hbar\omega$ onto the classical energy E appearing in Eq. (2.11d). [For example, the wave packet representing the ground vibrational state is at rest; i.e., $E = 0$ in Eq. (2.11d).]

The remaining terms in γ_t , namely

$$\begin{aligned}\phi &\equiv \int^t (p_{t'} \dot{x}_{t'} - E) dt' \\ &= \int^t [p_{t'}^2/2m - V(x_{t'})] dt' \\ &\equiv \int^t \mathcal{L} dt'\end{aligned}\quad (2.15)$$

are recognized as the action integral along the trajectory.¹² Thus, in the course of its trajectory, the wave packet acquires a phase factor

$$e^{(i/\hbar)\phi} = \exp\left[i/\hbar \int_{x_0}^{x_t} p(x) dx - iEt/\hbar\right], \quad (2.16)$$

where $p(x)$ is the classical momentum at x for total energy E .

Suppose now that we send a wave packet from large positive x_t toward $x=0$, allow it to "scatter" from $V(x)$, and wait until it again returns to large x_t . We may extract an energy eigenfunction from such a wave packet trajectory simply by a Fourier transform of $\psi(x, t)$:

$$\psi_E(x) = \lim_{\substack{t_0 \rightarrow -\infty \\ t \rightarrow \infty}} \int_{t_0}^t e^{iEt'/\hbar} \psi(x, t') dt'. \quad (2.17)$$

Figure 1(a) shows the wave packet at its turning point. It is possible to choose the initial parameters such that the turning point occurs at $t=0$ and that $\alpha_{t=0}$ is purely imaginary. Then we will have

$$x_t = x_{-t}, \quad p_t = -p_{-t}, \quad \alpha_t = -\alpha_{-t}^*, \quad \gamma_t = \gamma_{-t}^*, \quad (2.18)$$

as can easily be seen from the symmetry of the classical motion about the turning point and Eqs. (2.11).

Equations (2.18) have as a consequence

$$\psi(x, t) = \psi^*(x, -t) \quad (2.19)$$

and, as a result, Eq. (2.17) is seen to yield a purely real function of x . This is plotted schematically in Fig. 1(b). Figure 1 shows that both the wave packet and its Fourier transform behave properly at the turning point. Writing Eq. (2.17) explicitly, we have

$$\begin{aligned}\psi_E(x) &= 2 \operatorname{Re} \int_0^\infty dt' \exp[(i/\hbar)\alpha_t(x - x_{t'})^2 + (i/\hbar)p_{t'}(x - x_{t'})] \\ &\quad \times \exp\left[i/\hbar \int_0^{t'} p_{t''} \dot{x}_{t''} dt'' - \int_0^{t'} \frac{\alpha_{t''} dt''}{m} + i\gamma_0/\hbar\right].\end{aligned}\quad (2.20)$$

Since for $0 \leq t \leq \infty$ there is a unique relationship between t' and $x_{t'}$, we may take $x_{t'}$ to be the independent variable writing

$$\begin{aligned}dt' &= dx_{t'} (dt'/dx_{t'}), \\ p_{t'} &\equiv p(x_{t'}), \\ i/\hbar \int_0^{t'} p_{t''} \dot{x}_{t''} dt'' &= i/\hbar \int_{x_0}^{x_{t'}} p(x_{t''}) dx_{t''} \\ &\equiv i/\hbar \int_{x_0}^{x_{t'}} p(x) dx.\end{aligned}\quad (2.21)$$

The phase factor

$$i/\hbar \int_{x_0}^{x_{t'}} p(x) dx$$

appearing in Eqs. (2.21) and thus in Eq. (2.20) is reminiscent of a similar term in the WKB wavefunction. We may see the relationship with the WKB phase more explicitly by assuming that our time dependent wave packet $\psi(x, t)$ is propagating in free space after having interacted with $V(x)$. The *exact* wavefunction which started out Gaussian and scattered off $V(x)$ is expressible in the form

$$\psi_{\text{out}}^{\text{exact}} = \int (dp/\hbar) A(p) \exp[ipx/\hbar + 2i\delta(p) - ip^2 t/(2m\hbar)], \quad (2.22)$$

with $A(p)$ given by the p -space amplitude for the Gaussian [see Eq. (2.14)]. To find the phase shift at momentum p_0 , we project $\psi_{\text{out}}^{\text{exact}}$ onto $\exp[-ip_0 x/\hbar]$:

$$\begin{aligned}\exp[2i\delta(p_0)] &= \frac{1}{2\pi A(p_0)} \exp[ip_0^2/(2m\hbar)] \int_{-\infty}^{\infty} dx e^{-ip_0 x/\hbar} \psi_{\text{out}}^{\text{exact}}(x, t).\end{aligned}\quad (2.23)$$

An estimate of $\delta(p_0)$ can apparently be had by substituting our approximate outgoing wave packet into Eq. (2.23).

The resulting expression for $\delta(p_0)$ is

$$\delta(p_0) = -p_0 x_0/\hbar + \frac{1}{\hbar} \int_{x_0}^{\infty} dx [p(x') - p_0], \quad (2.24)$$

where we have specifically neglected any phases coming from $\int \alpha_t dt'$.¹³ Equation (2.24) is just the WKB result, minus a phase of $\pi/4$. It appears reasonable to assume that the neglected contribution to Eq. (2.24) due to α_t is something like $\pi/4$.¹³

The two techniques illustrated above, namely Fourier time transformation and asymptotic state projection, are important means of extracting state-specific information from the wave packet trajectories. Both techniques are founded on the quantum principle of superposition. That is to say, the wave packets are a linear superposition of eigenstates, and the eigenstates are superpositions of wave packets. Since our technique of expanding the potential about the center of the wave packet depends upon having well-localized wave packets, actual dynamical calculations are always carried out with such states. The superposition principle then tells us what linear combinations and projections of the individual "quantum trajectories" to take to obtain the desired state-specific results. We shall have more to say on this point in subsequent sections.

We conclude this section with a concrete and useful example of the projection-Fourier transform techniques, applied to the harmonic oscillator. We choose as an

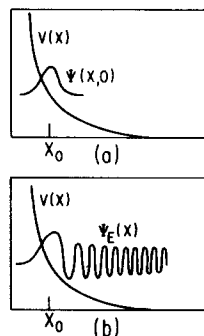


FIG. 1. (a) A Gaussian wave packet at its turning point in a one-dimension potential. (b) Fourier time transform of the wave packet appearing in (a).

initial value

$$\alpha_0 = im\omega/2,$$

and as previously noted, for this choice we have $\alpha_t = \alpha_0$ [see Eqs. (2.11c) or (2.13)]. The remaining parameters characterizing the Gaussian wave packet are (using y as the coordinate)

$$\begin{aligned} p_t &= p_0 \cos(\omega t) - m\omega y_0 \sin(\omega t), \\ y_t &= y_0 \cos(\omega t) + p_0/m\omega \sin(\omega t), \\ \gamma_t &= -\frac{1}{4}i\hbar \ln(m\omega/\pi\hbar) - \frac{1}{2}\hbar\omega t + \frac{1}{2}(p_t y_t - p_0 y_0). \end{aligned} \quad (2.25)$$

Expanding the time-dependent wave packet in terms of the eigenfunctions ψ_n of the harmonic oscillator, we have

$$\psi(y, t) = \exp[-(m\omega/2\hbar)(y - y_t)^2 + (i/\hbar)p_t(y - y_t) + (i/\hbar)\gamma_t] \quad (2.26a)$$

$$= \sum_n c_n(t) \psi_n \quad (2.26b)$$

$$= \sum_n c_n(0) \exp[-i(n + \frac{1}{2})\omega t] \psi_n. \quad (2.26c)$$

We wish to extract an eigenstate from Eq. (2.26a). In accordance with our previous discussion on obtaining eigenstates and from Eq. (2.26c), we can write

$$\psi_n(y) = \frac{\omega}{2\pi c_n(0)} \int_0^{2\pi/\omega} \exp[i(n + \frac{1}{2})\omega t] \psi(y, t) dt. \quad (2.27)$$

Having used a Fourier time transform to obtain $\psi_n(y)$, we now employ a projection onto ψ_n to obtain $c_n(0)$:

$$c_n(0) = \exp[i(n + \frac{1}{2})\omega t] \langle \psi_n | \psi(y, t) \rangle. \quad (2.28)$$

The overlap may be obtained easily by appealing to the theory of the coherent state,¹¹ which tells us

$$\psi(y, t) = \exp(-|\beta_0|^2/2 - i\omega t/2) \sum_{n=0}^{\infty} \beta_0^n / \sqrt{n!} \times \psi_n(y), \quad (2.29)$$

where

$$\beta_t = (m\omega/2\hbar)^{1/2} (y_0 + ip_0/m\omega) e^{-i\omega t},$$

thus

$$c_n(0) = \exp(-|\beta_0|^2/2) \beta_0^n / \sqrt{n!}. \quad (2.30)$$

The desired representation of $\psi_n(y)$ in terms of a superposition of wave packet states is obtained by inserting Eq. (2.30) into Eq. (2.27), giving

$$\begin{aligned} \psi_n(y) &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{\exp(-m\omega y^2/2\hbar)}{\sqrt{2^n n!}} H_n \left[\left(\frac{m\omega}{\hbar}\right)^{1/2} y \right] \\ &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp(|\beta_0|^2/2) \beta_0^{-n} \sqrt{n!} \frac{\omega}{2\pi} \int_0^{2\pi/\omega} dt \\ &\quad \times \exp \left[-\frac{m\omega}{2\hbar} (y - y_t)^2 + (i/\hbar)p_t(y - y_t) \right. \\ &\quad \left. + \frac{1}{2\hbar} (p_t y_t - p_0 y_0) + i\omega t \right], \end{aligned} \quad (2.31)$$

with p_t and y_t given by Eq. (2.25).

Equation (2.31) is an integral representation of the oscillator functions which may be approximated by an N -point quadrature in t such that the resulting inexact wavefunction has no components in the nearest $N-1$

neighboring oscillator states on either side. This is shown in the Appendix, and used in the numerical work of Sec. V.

In the oscillator case, the Fourier transform of the wave packet states results in an exact representation of the eigenfunctions. This is in contrast to the WKB wavefunctions for the harmonic oscillator, which are inexact. This emphasizes again the difference between a locally quadratic expansion of the potential and an expansion in \hbar .

III. SYSTEMS OF SEVERAL VARIABLES

A. The wavefunction and correlation terms

The techniques and results of Sec. II generalize readily to nonseparable dynamical systems of higher dimension. We illustrate the method by working out a two-dimensional system which might, for example, correspond to atom-diatom collinear inelastic and reactive scattering on a potential surface $V(x, y)$.

In direct analogy with Sec. II, we will expand the potential in a Taylor series about the center of the two-dimensional wave packet

$$\begin{aligned} V(x, y) - V_t(x_t, y_t) &\equiv V_0 + V_x(x - x_t) + V_y(y - y_t) + \frac{1}{2} V_{xx}(x - x_t)^2 \\ &\quad + \frac{1}{2} V_{yy}(y - y_t)^2 + V_{xy}(x - x_t)(y - y_t), \end{aligned} \quad (3.1)$$

where again $V_0 = V(x_t, y_t)$, etc.

The Hamiltonian is taken to be

$$H = -\frac{\hbar^2}{2m_x} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m_y} \frac{\partial^2}{\partial y^2} + V(x, y), \quad (3.2)$$

and for the purpose of propagating a given wave packet, we substitute V_t for V in the Hamiltonian. The only new twist is the correlation term $V_{xy}(x - x_t)(y - y_t)$ which makes the Hamiltonian nonseparable, since in general V_{xy} is time dependent. This term implies that we cannot expect to obtain an exact solution even to the approximate, time-dependent Hamiltonian $H_t = H_0 + V_t$ if the wavefunction is written in the form $\psi(x, t) \times \phi(y, t)$ since this form contains no x, y correlation. However, this situation is easily remedied by inclusion of the proper correlation term in the wavefunction, which takes the form

$$\exp[i/\hbar \lambda(x - x_t)(y - y_t)] \quad (3.3)$$

in the two-dimensional Gaussian $\psi(x, y, t)$:

$$\begin{aligned} \psi(x, y, t) &= \exp[i\alpha_x/\hbar(x - x_t)^2 + i\alpha_y/\hbar(y - y_t)^2 \\ &\quad + i\lambda/\hbar(x - x_t)(y - y_t) + ip_x/\hbar(x - x_t) \\ &\quad + ip_y/\hbar(y - y_t) + i\gamma]. \end{aligned} \quad (3.4)$$

We have retained the subscript t on the quantities x_t, y_t to distinguish them from the variables x, y ; otherwise, we drop the explicit time dependence, it being understood in $\alpha_x, \alpha_y, p_x, p_y, \gamma$, and λ .

The role played by the x, y correlation in the wavefunction is an interesting one. While it is true that the separable form $\psi(x, t) \times \phi(y, t)$ contains no x, y correlation, this is not true of the linear superpositions of such functions which are required to approximate quantum

eigenstates. Moreover, in the semiclassical limit, the linear terms in Eq. (3.1) will outweigh the quadratic terms for narrow wave packets. Thus the separable Hartree-like approximation may be a viable semiclassical approximation in some situations. However, explicit inclusion of x, y correlation is desirable if it can be done, since then the effective Hamiltonian H_t is closer to H . From another point of view, λ is on equal footing with α_x and α_y ; a simple rotation of coordinates shows this.

B. Equations of motion

To determine equations of motion for the parameters appearing in Eq. (3.4), we proceed as before, substituting Eq. (3.4) into the Schrödinger equation. Using $H_t = H_0 + V_t$ in place of H , we find that the resulting equations can be satisfied if the parameters obey

$$\dot{x}_t = \frac{\partial H}{\partial p_x}, \quad \dot{y}_t = \frac{\partial H}{\partial p_y}, \quad (3.5a)$$

$$\dot{p}_x = -\frac{\partial H}{\partial x_t}, \quad \dot{p}_y = -\frac{\partial H}{\partial y_t}, \quad (3.5b)$$

$$\dot{\lambda} = -2\left(\frac{\alpha_x}{m_x} + \frac{\alpha_y}{m_y}\right)\lambda - V_{xy}, \quad (3.5c)$$

$$\dot{\alpha}_x = -\frac{2}{m_x}\alpha_x^2 - \frac{1}{2}V_{xx} - \frac{1}{2m_y}\lambda^2, \quad (3.5d)$$

$$\dot{\alpha}_y = -\frac{2}{m_y}\alpha_y^2 - \frac{1}{2}V_{yy} - \frac{1}{2m_x}\lambda^2, \quad (3.5e)$$

$$\dot{\gamma} = \frac{i\hbar\alpha_x}{m_x} + \frac{i\hbar\alpha_y}{m_y} - E + p_x\dot{x}_t + p_y\dot{y}_t. \quad (3.5f)$$

Similar equations can be derived for systems of higher dimensionality. The last three terms in the expression (3.5f) for $\dot{\gamma}$ give rise again to the action integral along the classical path.

IV. APPLICATION TO COLLISIONS: OBTAINING THE S MATRIX

A. General considerations

It stands to reason that it will usually not be possible to extract quantum state specific information from a single quantum wave packet trajectory. A delocalized quantum state contains information about the dynamics over its entire extent; a single trajectory may only sample part of this dynamics. Therefore, only by performing several trajectory calculations and summing the trajectories in a coherent fashion can we hope to extract an S matrix for a system involving two or more coordinates. For two or more coordinates, there may be many dynamically distinct trajectories lying on the same energy surface, each corresponding to a different set of classical initial conditions.

The superposition principle guides us in choosing an optimum linear combination of trajectories to correspond to specific quantum transitions. However, as will be seen below, there is some flexibility in the way in which the individual trajectories are chosen. In Secs. IV. B and IV. C, we treat two methods which suggest themselves.

B. Controlled incoming state trajectories

Long before a collision has occurred between two dynamical systems, the interaction between them vanishes, and it is permissible to write the total wavefunction in the separable form

$$\Psi_{in} = \phi(y, t)\psi(x, t), \quad (4.1)$$

where now y is a collective coordinate labeling the constituents of the (initial) target system. For example, ϕ might correspond to a normalized quantum eigenstate ϕ_{n0} of the target, and ψ an incoming Gaussian wave packet. In this case, Ψ_{in} can be written

$$\Psi_{in, n0} = \phi_{n0}(y) \exp(-i/\hbar E_{n0}t)/(k_{n0})^{1/2} \times \int_{-\infty}^{\infty} dk A(k) \exp(-ikx - ik^2/2m \times t), \quad (4.2)$$

with $A(k)$ chosen to give the proper Gaussian form. Then the outgoing state Ψ_{out} can be written

$$\Psi_{out} = -\sum_{n'} \int_{-\infty}^{\infty} dk A(k) S_{n0n'}(E_{k, n0})/(k_{n'})^{1/2} \times \phi_{n'}(y) \exp(ik_{n'}x - i/\hbar E_{k, n0}t), \quad (4.3)$$

where $E_{k, n0} = E_{n0} + k^2/2m_x$, $k_{n'} = [2m_x(E_{n0} - E_{n'} + k^2/2m_x)]^{1/2}$, and $S_{n0n'}(E_{k, n0})$ is the usual scattering S matrix. Thus we can find $S_{n0n'}$ as

$$S_{n0n'}(E_{k0, n0}) = [2\pi A(k^0)]^{-1} e^{i/\hbar E_{k0, n0}t} k^0/(k_{n'})^{1/2} \times \int dx dy \phi_{n'}^*(y) e^{-ik_{n'}^0 x} \Psi_{out}(x, y), \quad (4.4)$$

where $k_{n'}^0 = [2m_x(E_{n0} - E_{n'} + k^2/2m_x)]^{1/2}$. However, Ψ_{in} of Eq. (4.1) is not, in general, an acceptable incoming state if ϕ_{n0} is an eigenstate, since then ϕ_{n0} is not a wave packet. If we know a wave packet representation for the eigenstate ϕ_{n0} , such as has already been derived for the harmonic oscillator in Sec. II. C (see also the Appendix), we can write

$$\Psi_{in, n0} \cong \sum_i a_{n0i} \Psi_{in}^{(i)} \equiv \left[\sum_i a_{n0i} g_i(y, t) \right] \psi(x, t), \quad (4.5)$$

where the sum in the brackets in Eq. (4.5) is an approximation to $\phi_{n0} \exp(-i/\hbar E_{n0}t)$ and each g_i is a Gaussian wave packet. Then each of the fully Gaussian states $\Psi_{in}^{(i)}$ is propagated individually according to our prescriptions, and we have

$$\Psi_{in}^{(i)} \rightarrow \Psi_{out}^{(i)} \quad (4.6)$$

$$\Psi_{in} \rightarrow \Psi_{out} \equiv \sum_i \Psi_{out}^{(i)}.$$

Applying this latter form for Ψ_{out} in Eq. (4.4) gives us a practical scheme for computing S matrix elements. Actually, it is possible to be more general than this; each incoming wave packet $\Psi_{in}^{(i)}$ may take the form

$$\Psi_{in}^{(i)} = g_i(y, t)\psi_i(x, t), \quad (4.7)$$

and a very similar procedure follows for finding the desired S -matrix elements.

The sense in which several trajectories are needed is

now clear from Eqs. (4.5) and (4.6). It is also clear that a single quantum trajectory $\Psi_{\text{in} \rightarrow \text{out}}$ can be used in the computation of many S -matrix elements. For example, we obtain a whole column of S , namely $S_{n0n'}$, $n' = 1, 2, \dots$ from $\Psi_{\text{in}, n0}$ in Eq. (4.5). Furthermore, we may be able to generate a different incoming state,

$$\Psi_{\text{in}, n} = \sum_i a_{ni} \Psi_{\text{in}}^{(i)}$$

from the same set of initial states, yielding more S -matrix columns.

C. Controlled collisional state trajectories

Naturally it is desirable to choose the initial parameters of the wave packet so that it remains as compact as possible for the duration of the interaction. Although simple procedures may be devised for choosing a good set of initial parameters (in particular, the "spread" parameter α), as is done in the numerical application in Sec. V, an alternative procedure is to choose the quantum parameters to have some desirable values during the most arduous part of the trajectory. Then this "collisionally controlled" state is propagated forward and backward in time:

$$\Psi_{\text{in}}^{(i)} \rightarrow \Psi_{\text{coll}}^{(i)} \rightarrow \Psi_{\text{out}}^{(i)}. \quad (4.8)$$

$\Psi_{\text{in}}^{(i)}$ will no longer be separable in x and y , but the reversibility of the equations of motion tells us that starting with $\Psi_{\text{in}}^{(i)}$ of Eq. (4.8), we have

$$\Psi_{\text{in}}^{(i)} \rightarrow \Psi_{\text{coll}}^{(i)} \rightarrow \Psi_{\text{out}}^{(i)}. \quad (4.9)$$

The different quantum trajectories (i) may all lie on a given (classical) energy surface, or they may be further restricted by requiring the target to have a certain classical energy initially.

The most rigorous treatments of scattering theory¹⁴ begin with time-dependent wave packets, since these are properly normed vectors in Hilbert space, while the energy eigenstates for a scattering system are not. The transition from time-dependent to time-independent scattering theory has typically been a device used to justify the time-independent form of the theory. Here, we can use the same formal steps to provide another viewpoint on extracting eigenstate information from our wave packet trajectories.

We further specify our asymptotic wave packets by defining $\Psi_{\text{in}}^{(i)}$ to be equal to the true wave packet for the system for large negative t (long before collision), and similarly for $\Psi_{\text{out}}^{(i)}$ for large positive t . We require that both functions propagate according to the free Hamiltonian H_0 at all times. Then, for any time t , the S operator performs the in \rightarrow out transformation¹⁴:

$$\Psi_{\text{out}}^{(i)}(t) = S \Psi_{\text{in}}^{(i)}(t). \quad (4.10)$$

S is time independent. Thus a Fourier transform of Eq. (4.10) gives

$$\Psi_{\text{out}}^{(i)}(E) = S \Psi_{\text{in}}^{(i)}(E), \quad (4.11a)$$

or

$$\sum_n B_{ni} \phi_n(y) e^{ik_n^0 x / \sqrt{k_n^0}} = S \sum_{n'} A_{n'i} \phi_{n'}(y) e^{-ik_{n'}^0 x / \sqrt{k_{n'}^0}}, \quad (4.11b)$$

where the sums in Eq. (4.11b) are over all degenerate arrangements of energy among the fragments, i.e., over all open channels. Defining

$$\frac{2\pi\hbar^2}{m_x} S_{nn'} \delta(E - E_0) = \langle \phi_n e^{ik_n^0 x / \sqrt{k_n^0}} | S | \phi_{n'} e^{-ik_{n'}^0 x / \sqrt{k_{n'}^0}} \rangle, \quad (4.12)$$

where $E = E_n + \hbar^2 k_n^2 / (2m_x)$, etc., we obtain, by projection onto the n th channel in Eq. (4.11b),

$$B_{ni} = \sum_{n'} S_{nn'} A_{n'i}, \quad (4.13)$$

or

$$S_{nn'} = (BA^{-1})_{nn'}. \quad (4.14)$$

In practice, the A 's and B 's are determined by projecting the wave packet before and after the collision onto the known asymptotic eigenfunctions

$$\phi_n(y) e^{-ik_n x / \sqrt{k_n}},$$

etc. Selecting as many distinct trajectories (or independent linear combinations of trajectories) as there are open channels, we determine the whole S matrix at once from Eq. (4.14).

V. NUMERICAL APPLICATION: COLLINEAR INELASTIC COLLISION

A. The model and details of the calculation

As the simplest nontrivial test case, we deal with collinear atom-diatomic collisions in which reaction is not allowed. The familiar model investigated quantum mechanically by Secrest and Johnson¹⁵ is used, in which the diatom is a harmonic oscillator which interacts with the projectile atom via an exponential repulsion. Transforming coordinate systems and using convenient units allows us to write the Hamiltonian as

$$H = -\frac{1}{2m_x} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + \frac{1}{2} y^2 + \exp[-a(x-y)]. \quad (5.1)$$

Corresponding to an He + H₂ collision, we have $a = 0.3$ and $m_x = 2/3$.

The over-all scheme described in the previous sections can easily be applied to this model Hamiltonian. The target oscillator eigenstates, which have the exact wave packet representation, Eq. (2.31), are approximated as finite wave packet sums. As shown in the Appendix, an N term sum can be chosen so that the approximate eigenstate has no components in any of the $N-1$ eigenstates on either side of the chosen state. We use the incoming state representation. The N -term wave packet sum corresponding to the desired initial quantum state of the oscillator is equivalent to N different initial phase angles of the classical oscillator spaced evenly on $(0, 2\pi)$. In practice, $N=4$ or 8 is more than sufficient for the work reported here.

An incoming wave packet state, where both the target and free particle are represented as Gaussians moving on asymptotic potential surfaces, has components in all

of the asymptotic quantum eigenstates of the system, including those with energies very different from the classical energy of the Gaussians. Thus, conversely, it is possible to add coherently a series of such wave packet states, all of which have classical energy E , to give a quantum incoming state of energy E' which may be much different from E . However, since we have only an approximate scheme for propagating the wave packets, it would seem best to use quantum trajectories with classical energies close to the energy of the quantum state being investigated. If this is done, we get the additional benefit that fewer quantum trajectories will be needed to define a specific eigenstate, since eigenstates far removed in energy will have very small amplitude in the wave packets and need not be specifically eliminated by the coherent sum of quantum wave packet trajectories.

Thus, in our calculations we require the oscillator to initially have classical energy n_0 or $n_0 + \frac{1}{2}$, and the free particle to have classical energy E_0 , if it desired to describe an incoming quantum state with the oscillator in the n_0 th quantum state and the projectile in the state $\exp(-ik_0x)/\sqrt{k_0}$, $k_0 = \sqrt{2E_0}$. This means that the classical energy will be within $1/2$ oscillator quantum of the eigenstate energy. For highly excited states of the oscillator, it certainly will not be necessary to match the classical initial conditions to this degree to the quantum states. However, we have not yet explored how far "off shell" a quantum trajectory may be before it gives poor information about a "distant" eigenstate.

We also have the freedom to choose α_x and α_y initially. The latter is always taken to be $1/2$, which is the value which would remain unchanged in the absence of a collision. The parameter α_x time develops, in the absence of collisions, as

$$\alpha_x = \alpha_0 / [2\alpha_0(t - T)/m_x - 1],$$

so we can choose α_0 and T to keep the wave packet as small as possible during the collision. We choose $\alpha_0 = (p_x^0)^2/M$, where $M=30, 40$, or 100 , as noted in the tables, where p_x^0 is the initial value of p_x . T was chosen from among several sample T 's to give a minimum error estimate due to the cubic part of the potential (only v_{xxx} was taken into account). The main idea is to arrange for the wave packet to "collect itself" just as it collides strongly; the results are not critically dependent on T in any case.

After the wave packet emerges again into the asymptotic region, we perform the overlaps

$$p_n^{(i)} = \int dx dy \left[\frac{e^{-y^2/2} H_n(y)}{(2^n n! \sqrt{\pi})^{1/2}} \right] e^{-ik_n^0 x / \sqrt{k_n^0}} \times \exp[i\alpha_x(x - x_t)^2 + ip_x(x - x_t) + i\alpha_y(y - y_t)^2 + ip_y(y - y_t)] \exp[i\lambda(x - x_t)(y - y_t) + i\gamma], \quad (5.2)$$

where the parameters α_x , etc. all refer to the i th trajectory. These are readily done analytically by first performing the Gaussian (dx) integration and then evaluating the (dy) integral of a Hermite polynomial with a shifted Gaussian. Such amplitudes are added coherently (with proper coefficients A_{n0i} for the i th trajectory). Finally, we obtain the inelastic transition probability

P_{n0n} :

$$P_{n0n} = \left| \sum_i A_{n0i} p_n^{(i)} \right|^2. \quad (5.3)$$

The first order equations (3.5) are solved with a fourth order Runge-Kutta routine; the time step size is typically 0.03 .

B. Results

In Fig. 2 we present results for the $\text{He} + \text{H}_2$ system for total energies of 8 and 10, comparing with Secrest and Johnson.¹⁵ Table I gives numerical values for $E_{\text{tot}} = 3, 4, 5, 6, 8$, and 10. The classical oscillator energy initially was n for trajectories used to compute $P_{n \rightarrow n'}$. Table II shows similar results, which may be compared with Table I, for the case in which $n + \frac{1}{2}$ was the classical initial oscillator energy.

The individual wave packets were found to remain unit normed to eight or nine significant figures. However, since these wave packets are added coherently, and since each different quantum trajectory is acted upon by a different effective Hamiltonian, there is no theorem guaranteeing unitarity. It is gratifying that the individual $P_{nn'}$ probabilities add up to unity to within 1% in almost all cases (see Table I).

Since in these calculations $P_{nn'}$ is computed using different trajectories than are used for $P_{n'n}$, they need not agree, and this is seen in the tables.

A few points about the trajectories are worth noting. A typical maximum value during the trajectory for $\text{Im}(\alpha_x)$, which is the parameter responsible for most of the spread of the wave packet, was 0.2 or 0.3. The typical behavior of $\text{Im}(\alpha_x)$ is to increase to a maximum, decrease, and then increase again before finally declining as the particles separated.

The results are reasonably stable against variation in the choice of incoming parameters. A very poor choice

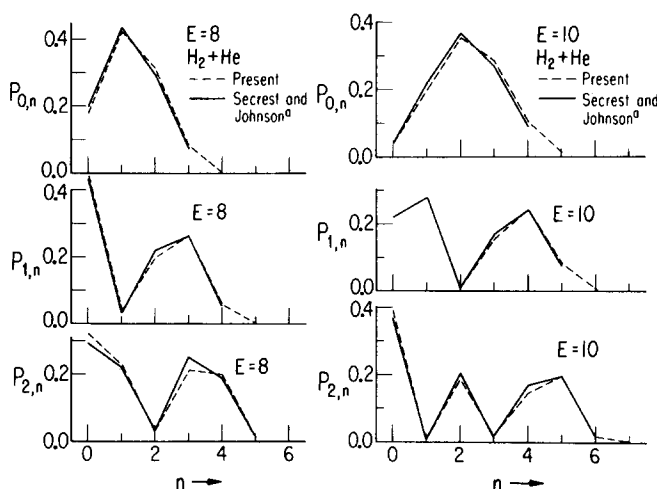


FIG. 2. The "exact" transition probabilities of Secrest and Johnson (Ref. 15) are compared to the present quantum trajectory calculations, for $E=8$ (left) and 10 (right), corresponding to an $\text{He} + \text{H}_2$ collision. Table I contains numerical values for these and other energies.

TABLE I. Transition probabilities $P_{i \rightarrow f}$ for He + H₂, $E_{\text{tot}} = 3, 4, 5, 6, 8, 10$. "QT" refers to the present result, "SJ" to Ref. 15. The values in brackets are inferred from the inelastic results of Ref. 15. Shown also are the sums $\sum_{m'} = \sum_n P_{m'}$. For energies of 3, 6, and 10, an asterisk (*) indicates a transition that is classically forbidden [Miller, Ref. 4(b)], while (**) indicates that a transition and all those below it in the table, for fixed initial state, are likewise classically forbidden. For $E_{\text{tot}} = 3$ and 4, $\alpha_0 = (p_x^0)^2/30$; for $E_{\text{tot}} = 5, 6, 8, 10$, $\alpha_0 = (p_x^0)^2/40$.

E_{tot}, Σ	i	f	P_{if}^{QT}	P_{if}^{SJ}	E_{tot}, Σ	i	f	P_{if}^{QT}	P_{if}^{SJ}
3	0	0	0.984	[0.978]	6	1	4	0.417 (-3)	...
3	0	1	0.0240**	0.0221**	6	1	5	0.827 (-7)	...
3	0	2	0.701 (-5)	...	Σ_{1n}			1.006	1.000
Σ_{0n}			1.008	1.000	6	2	0	0.0806*	0.0678*
3	1	0	0.0373*	0.0221*	6	2	1	0.378	0.345
3	1	1	0.967	[0.977]	6	2	2	0.340	[0.348]
3	1	2	0.433 (-2)*	0.898 (-3)*	6	2	3	0.197	0.233
Σ_{1n}			1.008	1.000	6	2	4	0.945 (-2)**	0.606 (-2)**
3	2	0	0.405 (-11)*	...	6	2	5	0.167 (-4)	...
3	2	1	0.229 (-4)*	0.898 (-3)*	Σ_{2n}			1.004	1.000
3	2	2	0.9989	0.9991	8	0	0	0.177	[0.196]
Σ_{2n}			0.9989	1.000	8	0	1	0.421	0.434
4	0	0	0.896	[0.891]	8	0	2	0.312	0.291
4	0	1	0.110	0.108	8	0	3	0.0842	0.0713
4	0	2	0.134 (-2)	0.122 (-2)	8	0	4	0.759 (-2)	...
4	0	3	0.201 (-6)	...	8	0	5	0.170 (-3)	...
Σ_{0n}			1.008	1.000	8	0	6	0.452 (-6)	...
4	1	0	0.129	0.108	8	0	7	0.118 (-10)	...
4	1	1	0.851	[0.850]	Σ_{0n}			1.008	1.000
4	1	2	0.0332	0.0418	8	1	0	0.442	0.434
4	1	3	0.128 (-3)	...	8	1	1	0.035	0.032
Σ_{1n}			1.013	1.000	8	1	2	0.200	[0.220]
4	2	0	0.357 (-2)	0.122 (-2)	8	1	3	0.263	0.261
4	2	1	0.0602	0.0418	8	1	4	0.0557	0.0512
4	2	2	0.941	[0.956]	8	1	5	0.233 (-2)	...
4	2	3	0.304 (-2)	0.133 (-2)	8	1	6	0.619 (-5)	...
Σ_{2n}			1.008	1.000	8	1	7	0.404 (-6)	...
5	0	0	0.711	[0.733]	Σ_{1n}			0.997	1.000
5	0	1	0.274	0.252	8	2	0	0.321	0.291
5	0	2	0.0183	0.0152	8	2	1	0.231	0.220
5	0	3	0.138 (-3)	...	8	2	2	0.0288	[0.0334]
5	0	4	0.124 (-7)	...	8	2	3	0.207	0.250
Σ_{0n}			1.003	1.000	8	2	4	0.199	0.189
5	1	0	0.283	0.252	8	2	5	0.0182	0.0164
5	1	1	0.523	[0.563]	8	2	6	0.182 (-3)	...
5	1	2	0.171	0.182	8	2	7	0.127 (-4)	...
5	1	3	0.596 (-2)	0.331 (-2)	Σ_{2n}			1.006	1.000
5	1	4	0.261 (-4)	...	10	0	0	0.0388*	[0.0420]*
Σ_{1n}			1.002	1.000	10	0	1	0.195	0.218
5	2	0	0.0254	0.0152	10	0	2	0.354	0.366
5	2	1	0.217	0.182	10	0	3	0.286	0.267
5	2	2	0.690	[0.743]	10	0	4	0.106**	0.089**
5	2	3	0.0567	0.0593	10	0	5	0.017	...
5	2	4	0.778 (-4)	...	10	0	6	0.950 (-3)	...
Σ_{2n}			0.990	1.000	10	0	7	0.136 (-4)	...
6	0	0	0.509	[0.535]	10	0	8	0.228 (-7)	...
6	0	1	0.412	0.394	10	0	9	0.350 (-12)	...
6	0	2	0.781**	0.0678**	Σ_{0n}			0.998	1.000
6	0	3	0.326 (-2)	...	10	1	0	0.215	0.218
6	0	4	0.160 (-4)	...	10	1	1	0.276	[0.278]
6	0	5	0.835 (-9)	...	10	1	2	0.993 (-2)	0.854 (-2)
Σ_{0n}			1.002	1.000	10	1	3	0.155	0.170
6	1	0	0.415	0.394	10	1	4	0.243	0.240
6	1	1	0.221	0.224	10	1	5	0.0835**	0.0769**
6	1	2	0.328	0.345	10	1	6	0.931 (-2)	...
6	1	3	0.0423**	0.0370**	10	1	7	0.254 (-3)	...
					10	1	8	0.796 (-5)	...
					10	1	9	0.952 (-7)	...
					Σ_{1n}			0.992	1.000

TABLE I (Continued)

E_{tot}, Σ	i	f	P_{if}^{ST}	P_{if}^{SJ}
10	2	0	0.392	0.366
10	2	1	0.644 (-2)	0.854 (-2)
10	2	2	0.186	[0.206]
10	2	3	0.0230	0.0176
10	2	4	0.146	0.169
10	2	5	0.197	0.194
10	2	6	0.0406**	0.0371**
10	2	7	0.204 (-2)	...
10	2	8	0.667 (-4)	...
10	2	9	0.406 (-5)	...
Σ_{2n}			0.993	1.000

can result in nonsense, otherwise the results retain their character almost to eyeball accuracy in Fig. 2, for example, although very small transition probabilities may change more on a percent basis. There is, however, a definite tendency for less extended wave packets to give over-all better agreement with the exact values, as would be expected.

We have reason to suspect that use of the controlled collisional state representation will provide even better results than have been obtained so far, because of the greater flexibility in choosing well-localized packets.

Finally, we present in Table III results for a different set of parameters, namely $a = 0.114$ and $M_x = 0.5$. This system was chosen because the exact transition probabilities computed by Secrest and Johnson¹⁵ are extremely small. Nonetheless, the accuracy of the quantum trajectory results is still good, although not surprisingly the results were more sensitive to numerical errors (the t -step size was reduced to 0.015). The good agreement is partly explained by the fact that the wavepackets were very well behaved on this extremely smooth potential surface.

VI. EXTENSIONS AND FURTHER WORK

In previous sections we found that it was possible to include all quadratic terms in the Taylor expansion of the potential about the center of the wave packet and still obtain an exact solution, for each Gaussian wave packet,

TABLE II. Results for He + H₂ system with E_{osc} initially $i + \frac{1}{2}$, where i is initial oscillator state. $\alpha_0 = (p_x^0)/30$.

E_{tot}, Σ	i	f	P_{if}^{ST}	P_{if}^{SJ}
5	0	0	0.735	[0.733]
5	0	1	0.236	0.252
5	0	2	0.177	0.0152
5	0	3	0.192 (-3)	...
5	0	4	0.145 (-6)	...
Σ_{0n}			0.989	1.000
5	1	0	0.276	0.252
5	1	1	0.581	[0.563]
5	1	2	0.144	0.182
5	1	3	0.651 (-2)	0.331 (-2)
5	1	4	0.954 (-4)	...
Σ_{1n}			1.007	1.000

TABLE III. Transition probabilities for Secrest and Johnson system number II, $M_x = 0.5$, $\alpha = 0.114$.^a

E_{tot}	i	f	P_{if}^{ST}	P_{if}^{SJ}
3.8	0	0	1.0027	[0.99996]
3.8	0	1	0.534 (-4)	0.430 (-4)
3.8	0	2	0.381 (-10)	0.128 (-10)
4.4	0	0	1.0018	[0.9998]
4.4	0	1	0.213 (-3)	0.203 (-3)
4.4	0	2	0.117 (-8)	0.113 (-8)

^aSix quantum trajectories were used at each of the two energies, $E_{\text{tot}} = 3.8$ and 4.4. $\alpha_0 = (p_x^0)^2/100$. E_{osc} is initially $(i + \frac{1}{2})$.

to the effective time-dependent Hamiltonian. One may ask if it is possible to include cubic and higher derivatives of the potential in the effective Hamiltonian. The answer is yes, if we are willing to give up finding an exact solution to the approximate, time-dependent Hamiltonian.

The procedure which generalizes the Gaussian approach used up to now is to write the wavefunction in the form

$$\psi(x, t) = N(x, t) \exp[i/\hbar Q(x, t)], \quad (6.1)$$

where $N(x, t)$ is a polynomial of degree N , of the form

$$N(x, t) = 1 + n_1 x + n_2 x^2 + \dots \quad (6.2)$$

$Q(t)$ is again a quadratic. Substitution of the form (6.1) into the Schrödinger equation, followed by identification of coefficients of like powers of x , results in the problem that the term

$$V(x, t)N(x, t) \exp[i/\hbar Q(x, t)], \quad (6.3)$$

where V is the time-dependent effective potential, generates powers of x greater than $N+2$, if V is a polynomial of degree greater than 2. But $N+2$ is the limit on powers of x for which unknowns are available. The only alternative is to truncate Eq. (6.3) to terms of power $N+2$ or lower. This procedure should result in an improvement in accuracy over the purely Gaussian form, but some simplicity is lost.

If for some reason (e.g., tunneling) a Gaussian wave packet should break up into two or more packets, not even Eq. (6.1) will help. We might pick a wavefunction which is a sum of several Gaussians and see what happens. We are straying into the subject matter of a following paper,¹⁶ where we develop the notion that much more general guesses for the time-dependent form of the wavefunction may prove useful in semiclassical dynamics. We also break away from the Taylor expansion of the potential and consider a more powerful time-dependent variational approach.

However, much remains to be done with the strictly Gaussian wave packet methods developed here. For example, we don't yet know the optimum way of extracting bound states for nonharmonic potentials. And, as mentioned before, barrier tunneling seems to be a problem requiring further attention. Wave packets in non-Cartesian coordinates need to be investigated. And potential applications to a variety of physical systems lie ahead.

CONCLUSION

In spite of the intuitive appeal of an explicitly time-dependent, particle-like description of semiclassical dynamics, efforts along these lines have been rather sparse. In quantum mechanics, it is usually much easier to directly construct eigenstates than to propagate time-dependent wavefunctions. However, the explicitly time-dependent procedures successfully employed in classical dynamics suggest that similar techniques may become practical in the semiclassical limit. In this paper we have discussed such a technique, which does indeed seem to benefit from this time dependent view of the correspondence principle. The first order equations of motion derived previously are simply Hamilton's equations for the classical variables, while the quantum variables obey formally similar first order quantum equations. Given a set of initial conditions, the whole system of variables simply executes appropriate classical or quantum trajectories.

Several of the previous attempts to exploit or examine the time-dependent wave packet version of quantum mechanics are especially worthy of mention in the context of this paper. McCullough and Wyatt¹⁷ have undertaken a careful study of the explicit quantum dynamics of wave packets on a collinear $H+H_2$ surface. Their wave packets were not chosen to be optimally "small" during the collision, but their results give several insights into the dynamics, not the least of which is the appearance of vortices in the wavefunctions. Recently, Hirschfelder, Goebel, and Bruch¹⁸ have noted that such vortices must form about nodes in the wavefunction.

Perhaps closest in spirit to the work reported in the preceding sections is the work of Lebedeff.¹⁹ He also considered the propagation of Gaussian wave packets. However, his formalism prevented the inclusion of any terms in the potential higher than linear in the coordinates. Thus, the resulting wave packets are uncorrelated (missing any analogue of the λ term in Eq. (3.5), a fact which would lead to serious error in the $He+H_2$ calculations of Sec. V. A more serious error arises because even a linear harmonic oscillator is propagated incorrectly. Nonetheless, Lebedeff's work represents a significant step in the direction we have chosen in this paper.

Recently Hirschfelder, Palke, and Christoph²⁰ have studied time-independent wave packets (in the form of focused beams) in a study motivated by the hydrodynamic form of the Schrödinger equation. Their study emphasizes nicely the differences between a wave packet description and the stationary phase, $\hbar \rightarrow 0$ version of quantum mechanics. For example, the stationary phase analogue of their wave packet does not show any diffraction, nor does it describe the Goos-Hänchen shift properly. Wave packets have the ability to overcome many of the "caustic" difficulties of the stationary phase approximation.

It is worthwhile to point out some additional comparisons between a wave packet approach and a stationary phase approach. To a large extent both techniques are "classical mechanics plus quantum superposition." Our

methods require that we solve for the classical and quantum trajectories, add coherently the results of several such trajectories, and project the results onto the desired energy surface. Since each quantum trajectory contains dynamical information about a region of phase space, each wave packet has some information to contribute regarding a specific quantum transition. Thus, the classical action of the wave packets need not conform to integer values, for example, as in the classical S-matrix theory. The requisite trajectories for a particular calculation are determined at the outset, not by a search procedure. However, on the other side of the coin, it may be necessary to run several quantum trajectories corresponding to a single classical trajectory in order to find initial conditions which keep the wave packets well localized during collision.

The fact that the approach presented in this paper is exact for harmonic potentials is encouraging for applications to molecular dynamics, where the oscillator description has long been a good starting point. Thus, the method may be useful in the study of intra- and intermolecular energy exchange and unimolecular decomposition. Since wavefunctions are obtainable from the wave packet trajectories, photodissociation cross sections can be calculated. Because the wavefunctions are represented as sums of Gaussians (see the Appendix, for example), the requisite integrals are greatly simplified.

Other important processes which have a direct classical analogue will be amenable to the quantum trajectory approach. Still others, which have significant nonclassical aspects (such as curve crossing and reactive tunneling) require generalizations of the present work that are currently under investigation. A more general and powerful variational approach to time dependent semiclassical dynamics is discussed in a following paper.¹⁶

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APPENDIX: APPROXIMATE REPRESENTATION OF OSCILLATOR EIGENSTATES AS DISCRETE SUMS OF GAUSSIAN WAVE PACKETS

The time-dependent, oscillating Gaussian wave packet, Eq. (2.26a), has a representation in terms of the unit normalized, time independent oscillator eigenfunctions of the form

$$\psi(y, t) \propto \sum_n \exp[-i(n + \frac{1}{2})\omega t] \beta_0^n / \sqrt{n!} \times \psi_n. \quad (A1)$$

The ψ_n 's are the eigenstates we seek to represent as finite wave packet sums. It is clear from Eq. (A1) that

$$\psi_n \propto \int_0^{2\pi/\omega} \exp[i(n + \frac{1}{2})\omega t] \psi(y, t) dt \quad (A2)$$

$$\propto \sum_{n'} \int_0^{2\pi/\omega} \exp[i(n-n')\omega t] \beta_0^{n'} / \sqrt{n'!} \psi_{n'} . \quad (\text{A3})$$

Replacing the integral in Eq. (A3) with a discrete quadrature in t , we choose $t_p = 2\pi p/(N\omega)$ and we have

$$\tilde{\psi}_n \propto \frac{2\pi}{N\omega} \sum_{p=1}^N \sum_{n'=0}^{\infty} \exp[i(n-n')2\pi p/N] (\beta_0^{n'} / \sqrt{n'!}) \psi_{n'} , \quad (\text{A4})$$

where the tilde reminds us that we now have an approximate ψ_n . Since

$$\frac{1}{N} \sum_{p=1}^N \exp[i(n-n')2\pi p/N] = \delta_{n,n'} + \delta_{N, |n-n'|} + \delta_{2N, |n-n'|} + \dots , \quad (\text{A5})$$

we have from Eq. (A4) that

$$\langle \psi_{n'} | \tilde{\psi}_n \rangle \propto \frac{\beta_0^n}{\sqrt{n!}} \delta_{nn'} + \frac{\beta_0^{n \pm N}}{\sqrt{(n \pm N)!}} \delta_{N, |n-n'|} + \dots . \quad (\text{A6})$$

Thus, for example, $\tilde{\psi}_n$ has no components in the nearest $(N-1)$ oscillator states on either side of n . The exact formula for $\tilde{\psi}_n$ is just Eq. (2.31), with $\omega/2\pi \int_0^{2\pi/\omega} dt$ replaced by $1/N \sum_{p=1}^N$; $t_p = 2\pi p/(N\omega)$, i.e.,

$$\tilde{\psi}_n = \left(\frac{m\omega}{\pi\hbar} \right)^{1/2} \exp(|\beta_0|^2/2) \beta_0^{-n} \sqrt{n!} \frac{1}{N} \sum_{p=1}^N \exp \left[-\frac{m\omega}{2\hbar} (y - y_p)^2 + \frac{i}{\hbar} p_p (y - y_p) + \frac{1}{2\hbar} (p_p y_p - p_0 y_0) + in \times 2\pi p/N \right] , \quad (\text{A7})$$

where

$$y_p = y_0 \cos(2\pi p/N) + (p_0/m\omega) \sin(2\pi p/N), \text{ etc.}$$

Equation (A7) is simply a sum of Gaussian wavefunctions. Note that as long as $E_0 = p_0^2/2m + \frac{1}{2}m\omega^2 y_0^2 > 0$, any ψ_n can be approximated using (A7). However, the error terms for $\tilde{\psi}_n$ will be smallest [see Eq. (A6)] if $\beta_0^{n'}/\sqrt{n'!}$ is a maximum for $n'=n$. [As before, we define β_0 as $\beta_0 = (m\omega/2\hbar)^{1/2} (y_0 + ip_0/m\omega)$.] This maximum occurs if $E_0 \simeq (n + \frac{1}{2})\omega$.

Finally, we note that Eq. (A7) may be of use in other circumstances. For example, if we wish to perform the integrals

$$I_n = \int_{-\infty}^{\infty} f(y) \psi_n(y) dy \quad (\text{A8a})$$

or

$$I_{nn'} = \int_{-\infty}^{\infty} \psi_n(y) f(y) \psi_{n'}(y) dy , \quad (\text{A8b})$$

where $\psi_{n'}$'s are oscillator eigenfunctions, we can substitute Eq. (A7) into Eqs. (A8). The $\psi_{n'}$'s are then replaced by Gaussians, and the new integrals will usually be much easier to perform analytically.

We call this technique a nonlocal Gaussian quadrature. It has some features analogous to the usual theory of Gaussian quadrature.²¹ For example, suppose Eq. (A8a) is of the form

$$I_n = \int_{-\infty}^{\infty} \exp[-y^2/2] H_n(y) p(y) dy \propto \int_{-\infty}^{\infty} \psi_n(y) p(y) dy , \quad (\text{A9})$$

where $H_n(y)$ is the n th Hermite polynomial and $p(y)$ is a polynomial of degree $2n$ or less. Then I_n is given exactly if we substitute $\tilde{\psi}_n$ for ψ_n in Eq. (A9) with N in Eq. (A7) at least as large as $n+1$.

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