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Semiclassical Theory of Inelastic Collisions. I. Classical Picture and Semiclassical Formulation*

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This series of papers is concerned with the derivation of the equations of the classical picture of atomic collisions,

$$i\hbar \frac{d}{dt} d_i(t) = \sum_j h_{ij}(t) d_j(t),$$

which describe the "time" dependence of electronic-quantum-state amplitudes as the nuclei move along a classical trajectory. These equations are derived in two ways. In the first formulation, which coincides with the intuitive classical picture of the collision, the nuclear part of the wave function is treated as a superposition of narrow wave packets, each traveling along a classical trajectory. In the second formulation, a semiclassical approach is used. The validity and meaning of the two formulations are discussed and compared.

I. INTRODUCTION

A. Objective

It is possible to achieve a simple and accurate theoretical description of many atomic and molecular collisions by treating part of the system classically or semiclassically, and the remaining part quantally. We consider primarily the case of discrete electronic excitations in slow atomic collisions, but this approach often can be applied to other processes as well: For example, under appropriate conditions, vibrational or rotational excitation of molecules may be treated in the same way. This is the first in a pair of papers on the validity and meaning of such descriptions. In a separate series of papers, we are considering their application to the potential-curve-crossing problem.[1]

In a full quantum-mechanical description, atomic collisions are described by the Schrödinger equation

$$H(\vec{\mathbf{R}}, \vec{\mathbf{r}})\Psi(\vec{\mathbf{R}}, \vec{\mathbf{r}}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\vec{\mathbf{R}}, \vec{\mathbf{r}}, t) \tag{1}$$

together with the usual outgoing wave boundary condition. Here the electronic coordinates $\vec{\mathbf{r}}_i$ are collectively denoted by $\vec{\mathbf{r}}$, and the nuclear coordinates $\vec{\mathbf{R}}_i$ by $\vec{\mathbf{R}}$. In this condensed notation, the Hamiltonian is

$$\begin{aligned} H(\vec{\mathbf{R}}, \vec{\mathbf{r}}) &= -(\hbar^2/2M)\nabla_R^2 + V_{\text{nuc}}(\vec{\mathbf{R}}) + h(\vec{\mathbf{r}}, \vec{\mathbf{R}}) , \\ h(\vec{\mathbf{r}}, \vec{\mathbf{R}}) &= -(\hbar^2/2\mu)\nabla_r^2 + V_{\text{el}}(\vec{\mathbf{r}}) + V_{\text{el-nuc}}(\vec{\mathbf{r}}, \vec{\mathbf{R}}) . \end{aligned} \tag{2}$$

If the wave function is expanded in terms of a discrete basis $\{\phi_n(\vec{\mathbf{r}}, \vec{\mathbf{R}})\}$, which spans the space of electronic coordinates and nuclear angle variables, the result is a set of coupled equations for the nuclear wave functions[2-4]:

$$\left[\frac{1}{2M}\left(\underline{1}\frac{\hbar}{i}\frac{d}{dR} + \underline{\pi}(R)\right)^2 + \underline{1}V_{\text{nuc}}(R) + \underline{h}(R) - i\hbar\underline{1}\frac{\partial}{\partial t}\right]\underline{u}(R) = 0 , \tag{3}$$

with

$$\pi_{mn}(R) = \int \phi_m^*(\vec{\mathbf{r}}, \vec{\mathbf{R}})\left(-i\hbar\frac{\partial}{\partial R}\right)\phi_n(\vec{\mathbf{r}}, \vec{\mathbf{R}})\, d\vec{\mathbf{r}}\, d\Omega ,$$

$$h_{mn}(R) = \int \phi_m^*(\vec{r}, \vec{R}) h(\vec{r}, \vec{R}) \phi_n(\vec{r}, \vec{R})\, d\vec{r}\, d\Omega \,. \quad (4)$$

The integration here extends over the full space of electronic coordinates and nuclear angles, leaving only the scalar internuclear separation as the independent variable.

Among the simplest possible basis sets is one formed by products of atomic orbitals for the electrons and spherical harmonics for the nuclear angles. These have the property that the matrix $\underline{\pi}(R)$ vanishes identically for all R. An alternative set is based upon Born-Oppenheimer molecular wave functions, for which $\underline{h}(R)$ is diagonal, and inelastic coupling is contained in $\underline{\pi}(R)$. It should be emphasized that considerable sophistication is required in choosing a basis set, even for seemingly simple situations.[2,3] In this paper, we use a generalized representation in which coupling can be due either to $\underline{\pi}(R)$ or $\underline{h}(R)$ or both. This transcends the question of whether a diabatic, adiabatic, or some other representation is more appropriate to any given situation.

Let us now consider the following *classical picture* of a collision. Assume that the nuclei move along some classical trajectory $\vec{R}(t)$, with their positions and momenta well defined at every instant. The internuclear and nuclear-electronic potentials are then time dependent because of the motion of the nuclei. Therefore, the electronic wave function must satisfy the time-dependent Schrödinger equation

$$h(\vec{r}, \vec{R}(t))\Upsilon(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \Upsilon(\vec{r}, t) \,. \quad (5)$$

After expansion in a discrete set of electronic wave functions, this equation takes the form

$$i\hbar \frac{d}{dt} \underline{d}(t) = [\underline{h}(t) - \underline{\epsilon}(t)]\, \underline{d}(t) \,, \quad (6)$$

where $h_{mn}(t) = h_{mn}(\vec{R}(t))$, as in Eq. (4), and

$$\epsilon_{mn}(t) = \int \phi_m^*(\vec{r}, \vec{R}(t))\, i\hbar \frac{\partial}{\partial t} \phi_n(\vec{r}, \vec{R}(t))\, d\vec{r} \,. \quad (7)$$

We refer to Eqs. (5) and (6) as the "equations of the classical picture," or as the "classical-trajectory equations." The objective of these papers is to derive these equations from the quantal equations (3), displaying explicitly all assumptions and approximations. In this paper and the following one, the classical-trajectory equations are derived by several different arguments. These arguments are based upon different assumptions and approximations, and, correspondingly, they lead to different levels of interpretation of the equations. Our main concern is with the validity and meaning of the different derivations, and their relationship with one another.

The first derivation in this paper is based upon a classical-wave-packet description of the collision. In this description, the initial state is taken to be a superposition of microscopic wave packets, each of which is very small compared to the size of the interaction region. Analysis of the motion of these packets shows that they obey a classical equation of motion and that the classical-trajectory equations are valid provided that certain conditions are satisfied. These conditions are precisely strong enough to imply that the packets could (in principle) actually be observed moving along the classical trajectory. Thus, we derive the classical picture itself.

In the second derivation, we use a semiclassical approach to obtain the classical-trajectory equations under weaker, more general assumptions, which do not imply that the system actually follows the trajectory. A remarkable result follows from this derivation: The classical-trajectory equations are valid more generally than the classical picture of the collision.

B. Perspective

The classical-trajectory equations were apparently first suggested by Mott,[5] and they have become the most commonly used formulation of inelastic heavy-particle collisions. Recently, there have been several attempts at rigorous derivations of these equations, and we will try to display the relationships between them.

The narrow-wave-packet approach to single-channel processes goes back to Ehrenfest,[6] and it is discussed in all textbooks on quantum mechanics. However, it is not generally appreciated that the conditions required for the validity of the approach are very severe—an order of magnitude more severe than the conditions for the validity of the semiclassical approximation—and many misconceptions on this point still persist. The most detailed and complete study yet undertaken of the motion of wave packets is being carried out by Lebedeff.[7] On the other hand, we feel that these papers do not make clear the severe restrictions on the validity of the approach. The first attempt to develop a wave-packet theory for multichannel collisions was made by Mittleman,[8] by the use of a variational principle. While many of his results are correct, the omission of some critical steps led to an incorrect statement of the validity of the theory. More recently, Corrigall, Kuppers, and Wallace[9] have independently postulated (but not derived) the trajectory equations that result from the wave-packet theory, and they are using them to numerically study certain low-energy collision processes. For those cases, the trajectory equations being used cannot be proved to be valid.

The narrow-wave-packet formulation can be very misleading because if it is applied under inappro-

priate conditions it introduces complications which are irrelevant and unnecessary. The wave-packet theory *suggests* that the appropriate trajectory for inelastic collisions is that of the center of mass of the wave packet; it also *suggests* that certain corrections should be applied because of the energy of localization and the spreading of the packet. Before we understood the severe limitations of such a theory, we tried to apply it to a calculation of the $2p$ excitation of hydrogen atoms by protons at 30 eV, for which we had done an exact quantum calculation.[10] We found that the center-of-mass trajectory was not the best one, and that attempting to introduce the refinements suggested by the narrow-packet theory only made results worse. This illustrates the fact that narrow-wave-packet concepts have very limited applicability (to high energies only) and extrapolations to low energies based on these concepts must not be made. We here present a brief account of the narrow-packet formulation of the classical picture in order to contrast it with alternative and quite distinct derivations of the classical-trajectory equations, and thereby remove previous misconceptions; we do not believe that the packet approach leads to useful results.

The limitations of the classical picture (i.e., wave-packet approach) were previously discussed briefly by Coulson and Zalewski.[11] Recognizing that the classical picture itself is not valid at low energies, they incorrectly concluded that the equations of the classical picture are likewise not valid, and they proposed a different formulation that is less satisfactory than the trajectory description. But, by use of a semiclassical formulation, we will show that the classical equations are valid much more generally than the classical picture.

The first attempts at semiclassical derivations of the classical-trajectory equations were made by Breit and Gluckstern[12] and by Lawley and Ross,[13] but their arguments are little more than *ex post facto* rationalizations. Derivations involving the assumption of rectilinear trajectories have been given by Wilets and Wallace and by McCarroll and Salin[14]; however, the classical-trajectory formulation is valid much more generally than the rectilinear approximation.[10,15] More satisfactory derivations have been obtained independently by Cross,[16] Bates and Crothers,[17] Knudson and Thorson,[10] and Child.[18] However, we feel that these presentations have not made clear either the conditions required for their validity, or the implications of the semiclassical conditions for the interpretation of the equations. As a result, misconceptions have persisted about the accuracy of the equations as well as about their meaning.

In particular, a major objective of much prior work has been the determination of the best possible nuclear trajectory—ideally, one which conserves the total energy and angular momentum of the system.[19] But we will show that such considerations can be rigorously justified only when the corrections they introduce are unimportant; i.e., they cannot be proved to be valid unless they are unnecessary. All the derivations of the classical-trajectory equations [Eqs. (5)] implicitly assume that the various possible trajectories differ only slightly from each other, at least where inelastic coupling is important. We believe that the goal of determining in general the "best" mean trajectory cannot be achieved. For the existing derivations of Eqs. (5) a significant variation of the results with the choice of trajectory would make the derivations themselves not valid.

II. WAVE-PACKET DERIVATION OF CLASSICAL-TRAJECTORY EQUATIONS

A. Philosophy of Derivation

For an idealized scattering process, the initial state can be regarded as an incoherent superposition of wave packets, each of which is the wave function for a single particle. On the macroscopic scale of the experimental apparatus, these packets are well-enough localized that they initially have negligible interaction with the target. However, it is easy to show[20] that these individual packets are very large on an atomic scale: typically 10^4 or more atomic diameters. Thus, on an atomic scale, the actual time dependence of an incident wave packet is negligible, and the spatial dependence is that of a uniform plane wave. The fundamental result of the so-called "formal theory of scattering" is that the results of collisions can be precisely described by treating the macroscopic wave packet as if it were a stationary fully delocalized eigenstate of the Hamiltonian.

The classical approximation is directly related to the intuitive classical picture of the collision. We may regard the macroscopic wave packet (or delocalized eigenstate) as a coherent superposition of microscopic wave packets, each of which is very small compared to the potential field. As these microscopic packets evolve, the expectation values of the position and momentum operators obey the equations[21]

$$\frac{d}{dt}\,\overline{R}(t)=\frac{\overline{P}(t)}{M}\quad,\quad \frac{d}{dt}\,\overline{P}(t)=\overline{F}(R)\simeq F(\overline{R})\,,$$

so the expectation values of operators over a wave packet obey the classical equations of motion provided that the packet width is small compared to the distance over which the force changes appreciably.

Our derivation of the classical-trajectory equations follows a completely analogous approach, in

which the central assumption is that the wave function can be divided into microscopic packets which do not spread appreciably. Afterward, we will examine this assumption more closely.

B. Notation and Preliminaries

We need not be concerned with details of the motion of packets, but only with the expectation values involved. Accordingly, it is easier to carry out the derivation using a density-operator formulation.

From Eq. (6), let us define a "classical" electronic density operator (for quantal electrons and classical nuclei)

$$\underline{\rho}_c(t) = \underline{d}(t)\underline{d}^\dagger(t) , \tag{8}$$

which obeys the equation

$$i\hbar \frac{\partial}{\partial t} \underline{\rho}_c(t) = [\{\underline{h}(t) - \underline{\epsilon}(t)\}, \underline{\rho}_c(t)] . \tag{9}$$

For our purposes, Eq. (9) can be regarded as equivalent to Eq. (6); (9) is the form we will derive.

The complete density operator for the quantum system of nuclei and electrons is

$$\rho = |\Psi\rangle\langle\Psi| , \tag{10}$$

and, in the general representation discussed above, the density matrix is

$$\underline{\rho}(R, R', t) = \underline{u}(R, t)\underline{u}^\dagger(R', t) . \tag{11}$$

The equation of motion for the abstract density operator is, of course,

$$i\hbar \frac{\partial}{\partial t} \rho = H\rho - \rho H , \tag{12}$$

and in the matrix form,

$$i\hbar \frac{\partial}{\partial t} \underline{\rho}(R, R', t) = \left[\frac{1}{2M}\left(-i\hbar \underline{1} \frac{d}{dR} + \underline{\pi}(R)\right)^2 + \underline{1}V_{\text{nuc}}(R) + \underline{h}(R)\right]\underline{\rho}(R, R', t)$$

$$- \underline{\rho}(R, R', t)\left[\frac{1}{2M}\left(i\hbar \underline{1} \frac{d}{dR'} + \underline{\pi}(R')\right)^2 + \underline{1}V_{\text{nuc}}(R') + \underline{h}(R')\right] , \tag{13}$$

where, in this expression, d/dR' is considered to act *toward the left*.

A few words about the momentum and kinetic energy operators may be appropriate. In a situation involving no coupling between electronic levels, the three-dimensional momentum operator is $-i\hbar\vec{\nabla}_R$; when a single partial wave is considered, it is customary (though sloppy) to refer to $-i\hbar\partial/\partial R$ also as a momentum operator. When many electronic levels participate, this same operator becomes $\underline{1}(-i\hbar\partial/\partial R)$ if the electronic basis is R independent, or $\underline{P} = [\underline{1}(-i\hbar\partial/\partial R) + \underline{\pi}(R)]$ if the electronic basis is R dependent. It follows that the expectation value of the operator of interest is

$$\overline{P}(t) = \sum_{i,j} \int dR\, dR' \left\{\left[\delta_{ij}\left(-i\hbar \frac{d}{dR}\right) + \pi_{ij}(R)\right] \times \rho_{ji}(R, R', t)\ \delta(R - R')\right\}$$

$$= \overline{p}(t) + \overline{\pi}(t) , \tag{14}$$

where $\overline{p}$ is the expectation value of $-i\hbar\, d/dR$, and $\overline{\pi}$ is the expectation value of the $\underline{\pi}$ matrix. We refer to $\overline{P}(t)$ as the average momentum of the wave packet, and we will show that it is related to the packet speed.

Finally, let us consider the quantal electronic density matrix, averaged over nuclear coordinates

$$\underline{\rho}_{\text{el}}(t) = \text{Tr}_{\text{nuc}}\, \rho(t) ,$$

$$\underline{\rho}_{\text{el}}(t) = \int dR\, \underline{\rho}(R, R, t') . \tag{15}$$

We will show that if the wave packets are narrow throughout the collision, then $\underline{\rho}_{\text{el}}(t) = \underline{\rho}_c(t)$. Thereby we will establish the validity of the classical-trajectory equations.

C. Derivation

Once we have made clear the basic motivation and strategy, the actual derivation is trivial. The equations of motion for the average position and average momentum of the wave packet are

$$\frac{d\overline{R}}{dt} = \text{Tr}\, \frac{R[H, \rho]}{i\hbar} = \text{Tr}\, \frac{[R, H]\rho}{i\hbar}$$

$$= \text{Tr}\left(-i\hbar \underline{1} \frac{d}{dR} + \underline{\pi}(R)\right)\frac{\underline{\rho}}{i\hbar} = \overline{P}/M , \tag{16}$$

$$\frac{d\overline{P}}{dt} = \text{Tr}\, \frac{[P, H]\rho}{i\hbar} = -\text{Tr}_{\text{el}}\left(\underline{1} \frac{dV_{\text{nuc}}}{dR} + \frac{d\underline{h}(R)}{dR}\right)\underline{\rho}_{\text{el}}(t)$$

$$+ \text{Tr}\, \frac{[\underline{\pi}(R), \underline{h}(R)]\, \underline{\rho}_{\text{el}}(t)}{i\hbar} . \tag{17}$$

The above relationships are exact. If the wave packet is narrow, $V_{\text{nuc}}(R)$, $\underline{h}(R)$, and $\underline{\pi}(R)$ can be expanded in a Taylor series about $\overline{R}(t)$, with the result that

$$\frac{d\overline{P}}{dt} \simeq -\text{Tr}_{\text{el}} \frac{d}{d\overline{R}} [V_{\text{nuc}}(\overline{R})\underline{1} + \underline{h}(\overline{R})]\, \underline{\rho}_{\text{el}}(t)$$

$$+\mathrm{Tr}_{\mathrm{el}}\frac{\underline{\rho}_{\mathrm{el}}(t)[\underline{\pi}(\bar{R}),\underline{h}(\bar{R})]}{i\hbar}\,.$$

Making use of the identity

$$[\underline{P},\underline{h}(R)]=-i\hbar\frac{d\underline{h}}{dR}+[\underline{\pi}(R),\underline{h}(R)]=i\hbar\underline{F}(R)\,,$$

where

$$F_{mn}(R)=\int\phi_m^*\left(\frac{\partial}{\partial R}\,V_{\mathrm{el\text{-}nuc}}\right)\phi_n\,d\vec{r}\,,$$

this becomes

$$\frac{d\bar{P}}{dt}=\mathrm{Tr}_{\mathrm{el}}\left(\underline{F}(\bar{R})-\frac{d}{d\bar{R}}\,V_{\mathrm{nuc}}(\bar{R})\underline{1}\right)\underline{\rho}_{\mathrm{el}}(t)\,. \tag{18}$$

The effective force on the nuclei is therefore equal to the internuclear force at the center of the packet plus the electron-nuclear force averaged over the positions of the electrons. This is to be expected.

It is easy to show that the force and the resulting trajectory are independent of the electronic representation, and that the trajectory conserves energy and (in three dimensions) angular momentum.

We now show that within these same approximations, the electronic density matrix obeys the classical-trajectory equations (9). Starting from Eq. (13) we integrate over the nuclear coordinate. The part involving the electronic Hamiltonian matrix gives

$$\int[\underline{h}(R)\underline{\rho}(R,R,t)-\underline{\rho}(R,R,t)\underline{h}(R)]\,dR$$

$$\simeq\underline{h}(\bar{R})\underline{\rho}_{\mathrm{el}}(t)-\underline{\rho}_{\mathrm{el}}(t)\underline{h}(\bar{R})\,, \tag{19}$$

provided the width of the wave packet is small compared to the size of the region over which $\underline{h}(R)$ changes significantly. The terms involving $V_{\mathrm{nuc}}(R)$ cancel. The parts involving the kinetic energy operator are more complicated:

$$\int\left[-\frac{\hbar^2}{2M}\left(\frac{d^2}{dR^2}-\frac{d^2}{dR'^2}\right)\underline{\rho}(R,R',t)\right]\delta(R-R')\,dR\,dR'+\int-\frac{i\hbar}{M}\left[\underline{\pi}(R)\left(\frac{d}{dR}\,\underline{\rho}(R,R',t)\right)+\left(\frac{d}{dR'}\,\underline{\rho}(R,R',t)\right)\underline{\pi}(R')\right]$$

$$\times\delta(R-R')\,dR\,dR'+\int-\frac{i\hbar}{2M}\left(\frac{d\underline{\pi}(R)}{dR}\,\underline{\rho}(R,R,t)+\underline{\rho}(R,R,t)\frac{d\underline{\pi}(R)}{dR}\right)dR+\frac{1}{2M}\int[\underline{\pi}^2(R)\underline{\rho}(R,R,t)-\underline{\rho}(R,R,t)\underline{\pi}^2(R)]\,dR\,. \tag{20}$$

The term containing second derivatives vanishes. In the second term, $\underline{\pi}(R)$ can be approximated by $\underline{\pi}(\bar{R})$, and $-i\hbar\,d\underline{\rho}(R,R',t)/dR$ can be approximated by $\bar{p}(t)\underline{\rho}(R,R',t)$; this term then becomes approximately

$$(\bar{p}(t)/M)[\underline{\pi}(\bar{R})\underline{\rho}_{\mathrm{el}}(t)-\underline{\rho}_{\mathrm{el}}(t)\underline{\pi}(\bar{R})]\,. \tag{21}$$

Again we have neglected terms of the order of the width of the wave packet.

Now let us examine the order of magnitude of the terms. The matrix elements of $\underline{\pi}$ are of order $\hbar/a_0$, those of $\hbar(d\underline{\pi}/dR)$ and $\underline{\pi}^2$ are of order $(\hbar/a_0)^2$, while those of $\bar{p}\underline{\pi}$ are of order $(\hbar^2/\lambda\!\!\!^{-}a_0)$. Since, as we will show, a wave-packet theory necessarily involves very short wavelengths, we may neglect the last two terms in (20) and the second term in (16) to obtain

$$i\hbar\,\frac{\partial}{\partial t}\,\underline{\rho}_{\mathrm{el}}(t)\simeq[\underline{h}(\bar{R}),\underline{\rho}_{\mathrm{el}}(t)]+\frac{d\bar{R}}{dt}\,[\underline{\pi}(\bar{R}),\underline{\rho}_{\mathrm{el}}(t)]\,. \tag{22}$$

Finally, noting that

$$\underline{\epsilon}(t)=-\frac{d\bar{R}}{dt}\,\underline{\pi}(\bar{R})\,, \tag{23}$$

we see that (22) is equivalent to (9), and we have derived the classical-trajectory equations.

D. Validity

Two assumptions were made in this derivation, one explicitly and one implicitly. We explicitly assumed that the nuclear wave function could be subdivided into microscopic wave packets which remain small throughout the collision. We also implicitly assumed that when these wave packets are summed at the end of the collision, the interference between them produces no effect; hence the flux density is equal to the density of the individual packets times their velocity. However, it turns out that these assumptions are so restrictive that the wave-packet theory is of little interest in atomic-collision theory.

Let us first return to the case of single-channel scattering. By deriving a differential equation for the width of a wave packet moving in a potential, it can be shown that the width is well approximated by that of a free wave packet,

$$\Delta R(t)\simeq\Delta R(t_0)(1+\{L\lambda\!\!\!^{-}/2[\Delta R(t_0)]^2\})^{1/2},$$

where L is the distance traveled by the packet. $\Delta R(t_0)$ may be chosen in such a way as to minimize $\Delta R(t)$; the result is

$$\Delta R(t_0)=(\tfrac{1}{2}L\lambda\!\!\!^{-})^{1/2}\,,\quad \Delta R(t)=(L\lambda\!\!\!^{-})^{1/2}\,.$$

Taking $L\simeq a_0$, and since Ehrenfest's theorem requires $\Delta R(t)\ll a_0$, we obtain the condition

$$(\lambda\!\!\!^{-}/a_0)^{1/2}\ll 1\,. \tag{24}$$

The same requirement can be stated in another way: Clearly we require $\Delta R(t_0)\ll a_0$ if the packet is to behave classically near t_0; but, if it is to

remain narrow, the width in momentum space must also be small, $\Delta P \ll \bar{P}$. Since $\bar{P} = \hbar/\lambda\!\!\!^{-}$ and $\Delta P \gtrsim \hbar/\Delta R$, we must require

$$\lambda\!\!\!^{-} \ll \Delta R \ll a_0 , \tag{25}$$

a condition which is essentially equivalent to (24).

If (25) holds, then it is possible in principle to prepare a microscopic packet and actually observe its motion along the trajectory. Simultaneous measurements of position and momentum involve an error of order $\Delta P \Delta R \simeq \hbar$, and the requirement that this be relatively small leads directly to (25). Thus, in this derivation of the equations of the classical picture, we have established the validity of the classical picture itself.

In the multichannel case, it is necessary to add to the spreading of a free-particle packet the spreading that results from the fact that systems in different electronic states travel at different speeds. This spreading is small if and only if the difference between the diagonal elements of the potential matrix $\underline{h}(R)$ is small compared to the average nuclear kinetic energy. Therefore, all trajectories must approximately coincide in the region of inelastic coupling.

A numerical estimate may help to illustrate the above restrictions. For the wave-packet theory to be valid $\Delta R/a_0 \lesssim 0.1$ and $\lambda\!\!\!^{-}/a_0 \lesssim 0.01$. For particles of reduced mass 1000 (e.g., hydrogen atoms), this means $E = \hbar^2/2M\lambda\!\!\!^{-2} \gtrsim 5$ hartree $\simeq 140$ eV. Then the potential-difference spreading is small for all electronic states within 1 or 2 hartree of the ground state. This includes all discrete states and an important part of the continuum.

III. SEMICLASSICAL DERIVATION OF CLASSICAL-TRAJECTORY EQUATIONS

A. Philosophy

We have seen that the wave-packet derivation is valid only under very severe restrictions, involving energies of the order of hundreds of electron volts. But it is well known that the semiclassical approximation for elastic scattering is valid for energies down to a few eV. Therefore, it is appropriate to ask whether the classical-trajectory equations may also be valid in this energy range. To establish their validity more generally, we must abandon the classical picture and consider a totally different approach.

Just as in Sec. II, we begin with the coupled Schrödinger equations for a discrete set of internal states (3). However, we consider now only the delocalized stationary solutions to these equations,

$$\underline{u}(R, t) = \underline{u}(R) e^{-iEt/\hbar} .$$

According to the formal theory of scattering, such stationary solutions suffice to describe the results of a scattering experiment. Defining, for convenience,

$$\underline{V}(R) = \underline{1} V_{\text{nuc}}(R) + \underline{h}(R) , \tag{26}$$

the stationary Schrödinger equation is

$$\left[\frac{1}{2M}\left(-i\hbar \underline{1}\frac{d}{dR} + \underline{\pi}(R)\right)^2 + \underline{V}(R) - \underline{1}E\right]\underline{u}(R) = 0 , \tag{27}$$

and it is the starting point for the derivation. Note that it contains no reference to time.

The objective is, as before, the classical-trajectory equations (6), but this time we will derive them in the equivalent form

$$i\hbar \frac{d}{dt} c_m = \sum_n [h_{mn}(t) - \epsilon_{mn}(t)] \exp\left(\frac{i}{\hbar}\int^t (h_{mm} - h_{nn})\, dt'\right), \tag{28}$$

where

$$c_m(t) = d_m(t) \exp[-(i/\hbar)\textstyle\int^t h_{mm}(t')\, dt'] .$$

We present a derivation that does not involve the classical picture, but is based upon simple extensions of the usual semiclassical (WKB) approximation. This derivation starts from Eq. (27), and makes no reference to the classical picture of moving packets; therefore it carries no implication that any system could be observed moving along a classical trajectory, with internal-quantum-state amplitudes changing according to (28). The derivation only shows that the classical-trajectory equations correctly predict the asymptotic fluxes and the cross sections.

Two mathematical approximations are made in the derivation, the "WKB approximation" and the "± separation." These approximations are valid if three physical conditions are met: (a) the de Broglie wavelength must be small compared to the interaction region; this is the usual semiclassical condition $\lambda\!\!\!^{-}/a_0 \ll 1$ [not to be confused with the much stronger requirement $(\lambda\!\!\!^{-}/a_0)^{1/2} \ll 1$, needed for the validity of the classical picture]. (b) The differences $V_{mm}(R) - V_{nn}(R)$ must be small compared to the kinetic energy of the system, at least where inelastic coupling due to $V_{mn}(R)$ is important. (c) The inelastic coupling must be negligible near the classical turning points. These three conditions are sufficient to ensure validity of the classical-trajectory equations; it will later be shown that the third assumption is not necessary.

For simplicity, the derivations are carried out only for the two-state case, as the many-state generalization is not difficult. Also, we make the simplifying assumption that the electronic basis functions are real, so that $V_{21} = V_{12}$, $\pi_{11} = \pi_{22} = 0$, and $\pi_{12} = -\pi_{21} = -i\hbar\tau$.

B. Derivation

We write the two-state Schrödinger equation in the form

$$\left[-\frac{\hbar^2}{2M}\left(\frac{d^2}{dR^2}-\pi^2\right)+V_{11}-E\right]u_1 + \left[V_{12}-\hbar^2\left(\frac{d\pi}{dR}+2\pi\frac{d}{dR}\right)\right]u_2=0\,,$$

$$\left[-\frac{\hbar^2}{2M}\left(\frac{d^2}{dR^2}-\pi^2\right)+V_{22}-E\right]u_2 + \left[V_{21}+\hbar^2\left(\frac{d\pi}{dR}+2\pi\frac{d}{dR}\right)\right]u_1=0\,. \tag{29}$$

Let us write

$$u_j(R)=a_{j+}e^{iS_j(R)/\hbar}+a_{j-}e^{-iS_j(R)/\hbar}\,, \tag{30}$$

where

$$S_j(R)=\int_{R_{0j}}^{R}\mathcal{P}_j(R')\,dR'\,. \tag{31}$$

$\mathcal{P}_j(R)$ is the momentum classically associated with the position R:

$$[\mathcal{P}_j(R)]^2/2M+V_{jj}(R)=E\,, \tag{32}$$

and we take R_{0j} to be the classical turning point for the jth state, i.e., the point such that $\mathcal{P}_j(R_{0j})=0$. Since the two possible signs of $\mathcal{P}$ are explicitly included in (30), we consider that all $\mathcal{P}$'s are positive. The Schrödinger equations (29) can determine only two functions, but in Eq. (30) we have four quantities to be determined, so we are free to impose any two restrictions on $a_{j\pm}(R)$. The appropriate equations are

$$a'_{1+}e^{iS_1/\hbar}+a'_{1-}e^{-iS_1/\hbar}+\pi(a_{2+}e^{iS_2/\hbar}+a_{2-}e^{-iS_2/\hbar})=0\,,$$
$$a'_{2+}e^{iS_2/\hbar}+a'_{2-}e^{-iS_2/\hbar}+\pi(a_{1+}e^{iS_1/\hbar}+a_{1-}e^{-iS_1/\hbar})=0\,. \tag{33}$$

Defining

$$b_{j\pm}(R)=[\mathcal{P}_j(R)]^{1/2}a_{j\pm}(R)\,, \tag{34}$$

we obtain the equations

$$\begin{bmatrix} b'_{1+}\\ b'_{1-}\\ b'_{2+}\\ b'_{2-}\end{bmatrix}=\begin{bmatrix} 0 & (\mathcal{P}'_1/2\mathcal{P}_1)e^{-2iS_1/\hbar} & B_{12}e^{i(S_2-S_1)/\hbar} & D_{12}e^{-i(S_2+S_1)/\hbar}\\ (\mathcal{P}'_1/2\mathcal{P}_1)e^{2iS_1/\hbar} & 0 & D^*_{12}e^{i(S_2+S_1)/\hbar} & B^*_{12}e^{i(S_1-S_2)/\hbar}\\ -B^*_{12}e^{i(S_1-S_2)/\hbar} & D_{12}e^{-i(S_2+S_1)/\hbar} & 0 & (\mathcal{P}'_2/2\mathcal{P}_2)e^{-2iS_2/\hbar}\\ D^*_{12}e^{i(S_2+S_1)/\hbar} & -B_{12}e^{i(S_2-S_1)/\hbar} & (\mathcal{P}'_2/2\mathcal{P}_2)e^{2iS_2/\hbar} & 0\end{bmatrix}\begin{bmatrix} b_{1+}\\ b_{1-}\\ b_{2+}\\ b_{2-}\end{bmatrix}\,, \tag{35}$$

where

$$B_{12}=[-\tfrac{1}{2}\pi(\mathcal{P}_2+\mathcal{P}_1)-iMV_{12}/\hbar](P_1P_1)^{-1/2}$$

and

$$D_{12}=[+\tfrac{1}{2}\pi(\mathcal{P}_2-\mathcal{P}_1)-iMV_{12}/\hbar]\,(P_1P_2)^{-1/2}\,.$$

These equations are rigorously equivalent to the Schrödinger equation (27); in particular, they are valid even in the classically forbidden region, where the S_i's are purely imaginary.

We now make two approximations.

1. *WKB Approximation*

In the classically allowed region, well away from the turning points, we drop the coupling between b_{1+} and d_{1-}, and between b_{2+} and b_{2-}. The ignored terms are

$$(\mathcal{P}'_j/2\mathcal{P}_j)\,e^{\pm 2iS_j/\hbar}\,.$$

For the case of elastic scattering, in which $V_{12}=0$ and $\pi=0$, this is clearly just the WKB approximation.

2. *± Separation*

We drop the coupling between b_{1+} and b_{1-}. The ignored terms are

$$\{[\tfrac{1}{2}\pi(\mathcal{P}_2-\mathcal{P}_1)\pm MV_{12}/i\hbar]\,(\mathcal{P}_1\mathcal{P}_2)^{-1/2}\}\,e^{\pm i(S_2+S_1)/\hbar}\,,$$

and it is assumed that these are negligible compared to the remaining terms

$$\{[\tfrac{1}{2}\pi(\mathcal{P}_2+\mathcal{P}_1)\pm MV_{12}/i\hbar]\,(\mathcal{P}_1\mathcal{P}_2)^{-1/2}\}\,e^{\pm i(S_2-S_1)/\hbar}\,.$$

Physically, this corresponds to the assumption that electronic transitions cannot change the direction of the nuclear motion. Speaking loosely, one might say that if, just before the electronic transition, the nuclei were moving toward each other with speed $\mathcal{P}_1/M$, then just after the transition they will be still moving toward each other, but with speed $\mathcal{P}_2/M$. For this to be true, we require

$$|\mathcal{P}_2-\mathcal{P}_1|\ll\mathcal{P}_2+\mathcal{P}_1\,.$$

The validity of this approximation also depends upon the properties of V_{12}. First, V_{12} must be sufficiently slowly varying that $[V_{12}/(\mathcal{P}_1\mathcal{P}_2)^{1/2}]\times e^{i(S_2+S_1)/\hbar}$ approximately averages to zero. Second, we must have

$$|V_{12}|\ll(\mathcal{P}_1^2+\mathcal{P}_2^2)/2M$$

for otherwise the difference between the momenta in the adiabatic representation becomes comparable to their magnitude.

The WKB approximation and the ± separation result in the equations

$$\frac{ih(\mathcal{P}_1\mathcal{P}_2)^{1/2}}{M}\frac{d}{dR}\begin{bmatrix}b_{1\pm}\\ b_{2\pm}\end{bmatrix}=\begin{bmatrix}0 & [-i\hbar\pi(\mathcal{P}_1+\mathcal{P}_2)/M\pm V_{12}]\,e^{i(S_2-S_1)/\hbar}\\ [i\hbar\pi(\mathcal{P}_1+\mathcal{P}_2)/2M\pm V_{12}]\,e^{-i(S_2-S_1)/\hbar} & 0\end{bmatrix}\begin{bmatrix}b_{1\pm}\\ b_{2\pm}\end{bmatrix}. \quad (36)$$

To obtain the classical-trajectory equations, we define a new variable τ, having units of time, such that (TP is the turning point)

$$\tau(R_{\mathrm{TP}})=0\,,\quad \frac{d\tau}{dR}=\left(\frac{M^2}{\mathcal{P}_1(R)\mathcal{P}_2(R)}\right)^{1/2} \quad (37)$$

in the equations for b_{j+}, and

$$\frac{d\tau}{dR}=-\left(\frac{M^2}{\mathcal{P}_1(R)\mathcal{P}_2(R)}\right)^{1/2} \quad (38)$$

in the equations for b_{j-}. Then, defining $c_j(\tau)$ such that

$$\begin{aligned} c_j(\tau)&=b_{j+}(\tau)\,e^{i\pi/2}\,, \quad \tau>0\\ c_j(\tau)&=b_{j-}(\tau)\,, \quad \tau<0\end{aligned} \quad (39)$$

and approximating $(\mathcal{P}_1+\mathcal{P}_2)/2$ by $(\mathcal{P}_1\mathcal{P}_2)^{1/2}$, we obtain

$$i\hbar\frac{d}{d\tau}\begin{bmatrix}c_1(\tau)\\ c_2(\tau)\end{bmatrix}=\begin{bmatrix}0 & \left(V_{12}-i\hbar\pi\frac{dR}{d\tau}\right)\exp\left(+i\int^{\tau}\frac{(V_{11}-V_{22})d\tau'}{\hbar}\right)\\ \left(V_{21}+i\hbar\pi\frac{dR}{dt}\right)\exp\left(-i\int^{\tau}\frac{(V_{11}-V_{22})d\tau'}{\hbar}\right) & 0\end{bmatrix}\begin{bmatrix}c_1\\ c_2\end{bmatrix}. \quad (40)$$

Since $\epsilon_{12}=-\epsilon_{21}=i\hbar\pi(dR/d\tau)$, we have again arrived at the classical-trajectory equations.

C. Treatment of Nonclassical Region

Obviously the approximations used above are not valid in the classically forbidden region or near a classical turning point. For the time being, then, we neglect inelastic coupling in such a region. As shown by Fröman[22] and by Kemble,[23] Eqs. (35), with $V_{12}=0$, lead directly to the usual WKB connection formulas,

$$b_{j+}(R_{\mathrm{TP}})=e^{-i\pi/2}\,b_{j-}(R_{\mathrm{TP}})\,, \quad (41)$$

and from Eq. (39) it then follows that $c_j(\tau)$ is continuous at the turning point. A better treatment of the nonclassical region is given in Paper II of this series.

D. Many-State Case

The derivation is essentially unchanged if several quantum states are involved. Equation (35) then becomes

$$\begin{aligned} b'_{j+}=(\mathcal{P}'_j/2\mathcal{P}_j)\,e^{-2iS_j/\hbar}\,b_{j-}&+\sum_{k\neq j}\{[2MV_{jk}+\pi_{jk}(\mathcal{P}_j+\mathcal{P}_k)]/\\ &2i\hbar(\mathcal{P}_1\mathcal{P}_2)^{1/2}\}\,e^{i(S_k-S_j)/\hbar}\,b_{k+}\\ &+\sum_{k\neq j}\{[2MV_{jk}+\pi_{jk}(\mathcal{P}_j-\mathcal{P}_k)]/2i\hbar(\mathcal{P}_1\mathcal{P}_2)^{1/2}\}\\ &\times e^{i(S_k+S_j)/\hbar}\,b_{k-}\,, \end{aligned} \quad (42)$$

and after the WKB approximation and the ± separation is made, we have

$$\begin{aligned} i\hbar b'_{j+}=\sum_{k\neq j}&\{[2MV_{jk}+\pi_{jk}(\mathcal{P}_j+\mathcal{P}_k)]/2(\mathcal{P}_j\mathcal{P}_k)^{1/2}\}\\ &\times e^{i(S_k-S_j)/\hbar}\,b_{k+}\,. \end{aligned} \quad (43)$$

In order to obtain the equations of the classical picture, (28), it is necessary to choose an average velocity $\bar{v}(R)$ such that

$$\frac{(\mathcal{P}_j\mathcal{P}_k)^{1/2}}{M}\simeq\bar{v}(R)=\frac{dR}{d\tau}\,. \quad (44)$$

This approximation is valid if all elastic momenta are nearly equal, and therefore, it is consistent with the ± separation, which requires that

$$|\mathcal{P}_j-\mathcal{P}_k|\ll\mathcal{P}_j+\mathcal{P}_k \quad (45)$$

for all j, k. One may use any reasonable average trajectory in Eq. (44), and, if it makes much difference what trajectory is used, then this derivation of the classical-trajectory equations is not valid.

In other discussions and derivations of Eqs. (27) it apparently has not been recognized that the ± separation requires that the difference between the trajectories be small, and this has led to some misconceptions. Thus Cross[16] suggested that (43) is more accurate than (28) and some conclusions of Lawley and Ross[13] are based on this assumption. There may exist cases for which (43) is more accurate than (28); on the other hand, we know of cases for which (28) is more accurate than (43) (potential curve crossings near the turning point). But in general, if there is a substantial difference between the trajectories $\mathcal{P}_j(R)$, neither form is reliable, and no average trajectory can be defined.

E. Example

The ± separation can be illustrated with an exactly solvable model. In the diabatic representation, a closed-form solution exists for the case

$$\mathcal{P}_j^2=\mathrm{const}\,,\quad V_{12}=\mathrm{const}\,.$$

The exact solution to the Schrödinger equation (29) is

$$\begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \tilde{\mathcal{P}}_a^{-1/2} \left(A_+ \begin{bmatrix} d_+ \\ -d_- \end{bmatrix} e^{i\tilde{\mathcal{P}}_a R/\hbar} + A_- \begin{bmatrix} d_+ \\ -d_- \end{bmatrix} e^{-i\tilde{\mathcal{P}}_a R/\hbar} \right)$$

$$+ \tilde{\mathcal{P}}_b^{-1/2} \left(B_+ \begin{bmatrix} d_- \\ d_+ \end{bmatrix} e^{i\tilde{\mathcal{P}}_b R/\hbar} + B_- \begin{bmatrix} d_- \\ d_+ \end{bmatrix} e^{-i\tilde{\mathcal{P}}_b R/\hbar} \right) ,$$

where

$$\tilde{\mathcal{P}}_\nu^2/2M = E - \tfrac{1}{2}(V_{11} + V_{22}) \pm [\tfrac{1}{4}(V_{11} - V_{22})^2 + V_{12}^2]^{1/2} ,$$

$\nu = a, b$ for + or −, respectively,

$$d_\pm = 2^{-1/2}[1 \pm t/(1+t^2)^{1/2}]^{1/2} ,$$

$$t = (V_{22} - V_{11})/2V_{12} ,$$

and $A_\pm$, $B_\pm$ are arbitrary constants. Comparing u_j and their derivatives with Eqs. (6) and (9), we find the exact result

$$b_{1+} = (\mathcal{P}_1/\tilde{\mathcal{P}}_a)^{1/2} d_+ \{ [1 + (\tilde{\mathcal{P}}_a/\mathcal{P}_1)] A_+ e^{i(\tilde{\mathcal{P}}_a - \mathcal{P}_1)R/\hbar}$$

$$+ [1 - (\tilde{\mathcal{P}}_a/\mathcal{P}_1)] A_- e^{-i(\tilde{\mathcal{P}}_a + \mathcal{P}_1)R/\hbar} \}$$

$$+ (\mathcal{P}_1/\tilde{\mathcal{P}}_b)^{1/2} d_- \{ [1 + (\tilde{\mathcal{P}}_b/\mathcal{P}_1)] B_+ e^{i(\tilde{\mathcal{P}}_b - \mathcal{P}_1)R/\hbar}$$

$$+ [1 - (\tilde{\mathcal{P}}_b/\mathcal{P}_1)] B_- e^{-i(\tilde{\mathcal{P}}_b + \mathcal{P}_1)R/\hbar} \} \quad (46)$$

and corresponding equations for the other coefficients. The $b_{j\pm}$ contain both rapidly varying and slowly varying oscillatory terms. The rapidly oscillating terms have a wavelength about half the de Broglie wavelength; their amplitudes are small provided $|\mathcal{P}_2 - \mathcal{P}_1| \ll \mathcal{P}_2 + \mathcal{P}_1$ and $V_{12} \ll (\mathcal{P}_1^2 + \mathcal{P}_2^2)/2M$. The slowly varying terms have amplitudes of order unity and wavelength of order $\lambda_D = (\lambda_1^{-1} - \lambda_2^{-1})^{-1}$ with $\lambda_j = 2\pi\hbar/\mathcal{P}_j$.

Now we examine the results of the approximations used in the derivation. The WKB "approximation" has no effect here since $\mathcal{P}_j' = 0$. There is also no turning point, and no nonclassical region, so it causes no difficulty. Then the equations

$$\frac{i\hbar(\mathcal{P}_1\mathcal{P}_2)^{1/2}}{M} \begin{bmatrix} b_{1+}' \\ b_{1-}' \\ b_{2+}' \\ b_{2-}' \end{bmatrix} = \begin{bmatrix} 0 & 0 & V_{12}e^{i\Delta} & V_{12}e^{-i\Sigma} \\ 0 & 0 & -V_{12}e^{i\Sigma} & -V_{12}e^{-i\Delta} \\ V_{12}e^{-i\Delta} & V_{12}e^{i\Sigma} & 0 & 0 \\ -V_{12}e^{i\Sigma} & -V_{12}e^{i\Delta} & 0 & 0 \end{bmatrix} \begin{bmatrix} b_{1+} \\ b_{1-} \\ b_{2+} \\ b_{2-} \end{bmatrix} ,$$

where

$$\Delta = (\mathcal{P}_2 - \mathcal{P}_1)R/\hbar \quad \text{and} \quad \Sigma = (\mathcal{P}_1 + \mathcal{P}_2)R/\hbar$$

are rigorously equivalent to the Schrödinger equation, with the solutions (46). The ± separation gives the form (36), with $\pi = 0$. The solution to the approximate equations can be written in the form (+ case)

$$b_{1+} = \beta_1 e^{i\zeta_1 R/\hbar} , \quad b_{2+} = \beta_2 e^{i\zeta_2 R/\hbar} , \quad (47)$$

with constant β_j, ζ_j. The solutions ζ are given by

$$\zeta_j = \tfrac{1}{2}(\mathcal{P}_2 - \mathcal{P}_1) \pm [\tfrac{1}{4}(\mathcal{P}_2 - \mathcal{P}_1)^2 + (M^2V_{12}^2/\mathcal{P}_2\mathcal{P}_1)]^{1/2}$$

$$= [2MV_{12}/(\mathcal{P}_1 + \mathcal{P}_2)]$$

$$\times \{ -t \pm [t^2 + (\mathcal{P}_1 + \mathcal{P}_2)^2/4\mathcal{P}_1\mathcal{P}_2]^{1/2} \} , \quad (48)$$

where $t = (\mathcal{P}_1^2 - \mathcal{P}_2^2)/4MV_{12}$. In the exponentials of Eq. (46),

$$\tilde{\mathcal{P}}_a - \mathcal{P}_1 = [2MV_{12}/(\tilde{\mathcal{P}}_a + \mathcal{P}_1)][-t + (1+t^2)^{1/2}] ,$$

$$\tilde{\mathcal{P}}_b - \mathcal{P}_1 = [2MV_{12}/(\tilde{\mathcal{P}}_b + \mathcal{P}_1)][-t - (1+t^2)^{1/2}] . \quad (49)$$

Comparing (48) and (49), we see that the ± separation gives a good approximation to the slowly varying term in the exact solution, provided that (a) the "diabatic" momenta are not too different, and (b) the adiabatic momenta $\tilde{\mathcal{P}}_\nu$ are not too different from the diabatic momenta. The ± separation entirely ignores the smaller, rapidly oscillating terms. Clearly, if there is a substantial difference between $\tilde{\mathcal{P}}_a$ and $\tilde{\mathcal{P}}_b$, then there is no nuclear trajectory that will give an accurate answer in general.

F. Applications to H^+-H Scattering

At low energies ($\lesssim 0.5$ keV) the H^+-H system is best described in terms of Born-Oppenheimer states; the three important ones are

	separated atom	united atom	denoted here
$^2\Sigma_g^+$	$1s\sigma_g$	$1s\sigma_g$	ϕ_g
$^2\Sigma_u^+$	$1s\sigma_u$	$2p\sigma_u$	ϕ_1
$^2\Pi_u$	$2p\pi_u$	$2p\pi_u$	ϕ_2

The collision begins with amplitude distributed equally between ϕ_g and ϕ_1. As the nuclei approach each other, ϕ_1 and ϕ_2 become nearly degenerate, and they are coupled by coriolis terms in the Hamiltonian. The coupling is proportional to $1/R^2$ for small R.

This system is a particularly useful test of the derivation of the classical-trajectory equations. That derivation used three assumptions: (i) that the WKB approximation is valid in the absence of coupling, (ii) that $|\mathcal{P}_2 - \mathcal{P}_1| \ll \mathcal{P}_2 + \mathcal{P}_1$, and (iii) that the coupling is negligible near the turning points. For

TABLE I. $1s\sigma_u \rightarrow 2p\pi_u$ excitation probability for slow H^+-H collisions. Probability vs total angular momentum L (impact parameter b) for relative collision energy E: P_1, probability calculated using classical trajectory for $1s\sigma_u$ potential; P_2, using root-mean ($1s\sigma_u - 2p\pi_u$) trajectory; P_3, exact quantal results. [For the small L values involved the comparison is a good test of the WKB approximation to the radial motion; also, previous calculations (Ref. 5) have shown that the strong coupling at the turning point does not affect the validity of the classical-trajectory equations.] The tabulated data show that when the possible choices for the classical trajectory differ substantially, no significant improvement is made by the root-mean trajectory.

L	b (a.u.)	P_1	P_2	P_3
		$E=30$ eV		
1	0.031	0.0111	0.0073	0.0074
6	0.144	0.1649	0.1062	0.1204
11	0.255	0.3158	0.1968	0.2267
16	0.367	0.3304	0.2026	0.2308
21	0.478	0.2496	0.1622	0.1669
26	0.589	0.1520	0.1141	0.0907
31	0.700	0.0785	0.0773	0.0365
36	0.811	0.0352	0.0529	0.0087
41	0.922	0.0138	0.0375	0.0007
46	1.033	0.0048	0.0276	0.0000
		$E=50$ eV		
1	0.024	0.0138	0.0124	0.0124
6	0.112	0.1989	0.1749	0.1977
11	0.198	0.3831	0.3287	0.3781
16	0.284	0.4447	0.3718	0.4328
21	0.370	0.4172	0.3389	0.3985
26	0.456	0.3491	0.2746	0.3250
31	0.542	0.2699	0.2058	0.2433
36	0.628	0.1954	0.1454	0.1689
41	0.714	0.1330	0.0986	0.1101
46	0.800	0.0855	0.0650	0.0681
51	0.887	0.0520	0.0424	0.0409
56	0.973	0.0299	0.0276	0.0240
61	1.058	0.0164	0.0184	0.0139
66	1.145	0.0086	0.0126	0.0078

the H^+-H system, the first assumption is satisfied for $E \gtrsim 0.1$ hartree, the second is satisfied for $E \gtrsim 3$ hartree, and the third assumption is never satisfied.

Exact quantal calculations and semiclassical calculations using the classical-trajectory equations were performed on this system and are described in a previous paper.[10] For $E \gtrsim 3$ hartree, the two methods give almost identical results. This clearly proves that the third assumption is not necessary: The classical-trajectory equations may be valid even if there is strong coupling near the turning points.

For $E \lesssim 3$ hartree, there were substantial differences between the quantal and semiclassical calculations. In the previous calculations of Knudson and Thorson,[10] a classical trajectory determined by the $1s\sigma_u$ (initial state) elastic scattering potential was used. Here we have repeated the calculation using the geometrical-mean trajectory as suggested by Eqs. (37). As shown in Table I, the agreement is improved somewhat, but not very substantially. This shows that a geometrical-mean trajectory is not superior when turning points are involved. This is not surprising, since the whole derivation breaks down in that case. Bates and Sprevak[24] have shown that a different choice of trajectory gives an improved answer for this case. A rigorous treatment of turning-point phenomena, presented in the following paper, shows more clearly why their procedure leads to improved results.

IV. DISCUSSION

We now consider the physical meaning of the derivation given in Sec. III. The quantities $c_j(\tau)$ in Eqs. (40) appear to play the expected role of probability amplitudes. The Hermitian property of the matrix in Eqs. (40) implies the conservation law

$$|c_1(\tau)|^2 + |c_2(\tau)|^2 = 1$$

or, from Eq. (34),

$$\mathcal{P}_1(R)|a_{1+}(R)|^2 + \mathcal{P}_2(R)|a_{2+}(R)|^2 = 1 \ .$$

Also, $\mathcal{P}_j(\infty)|a_{j+}(\infty)|^2$ represents the asymptotic flux moving outward from the scattering center in the jth electronic state; hence $|c_j(\infty)|^2$ is the transition probability to the jth state. Thus it is quite natural to regard $|c_j(\tau)|^2$ as a time-dependent probability for finding the electronic system in state j during the course of collision. However, such an interpretation is not correct. The essential point is that this derivation in no way implies that the nuclei could actually be observed moving along a classical trajectory according to Eq. (38), or that the electrons change quantum-state amplitudes with time according to (40).

This is in sharp contrast with the interpretation associated with the derivation in Sec. II. There we decomposed the stationary eigenstate of formal scattering theory into microscopic packets, and showed that under sufficiently stringent conditions, these packets move along approximately classical trajectories and the electronic state amplitudes change with time according to the equations of the classical picture. The major criterion for the validity of that description is that the de Broglie wavelength be very small,

$$[\lambda\!\!\!^{-}/a_0]^{1/2} \ll 1 \ . \qquad (50)$$

This condition is much more restrictive than the usual semiclassical condition

$$(\lambda\!\!\!^{-}/a_0) \ll 1 \ . \qquad (51)$$

Under the more stringent classical conditions (50), the full classical interpretation of a system moving along a trajectory, with amplitudes $c_j(\tau)$ changing in real physical time, is valid. This state of affairs, and only this one, is the situation implied by the correspondence principle.

The derivation of Sec. III employs fully delocalized stationary states; for such wave functions no probability amplitudes actually depend on time. In principle, it is possible to measure simultaneously the electronic quantum state and the nuclear position, because the operators representing these observables commute. If one were to make such a measurement, one would find that the probability of finding the electrons in, say, the mth excited level varies with the nuclear position: It is greater in "post collision" regions of space than in "pre-collision" regions.

In Sec. II, we showed that if the wave-packet formulation is applicable, a simultaneous measurement of the nuclear position and momentum and the electronic quantum state could (in principle) be made without appreciably disturbing the system. However, under the more general semiclassical conditions, such a measurement would clearly reveal the quantum-mechanical nature of the system: The final scattering amplitudes would be completely changed. Thus, in the semiclassical case, there is no observable object moving in real time along a classical path.

Strictly speaking, the correspondence principle tells us only that there exist wave-packet states which behave like classical particles; hence, it is relevant only under the strict condition (50).

The weaker semiclassical condition (51) is not strong enough to invoke the correspondence principle. However, we have demonstrated that the classical-trajectory equations offer a valid means of computing inelastic scattering cross sections under essentially semiclassical conditions; therefore the equations of the classical picture are valid more generally than is required by the correspondence principle. There is thus a sense in which we may say that some elements of classical mechanics emerge at a much deeper level from quantum mechanics than does the correspondence principle.

V. SUMMARY

We have presented two quite different derivations of the classical-trajectory equations [in the forms (9) and (28)]. The equations are equivalent, but their interpretations are very different.

The wave-packet formulation of Sec. II describes a genuine and, in principle, observable time dependence in a suitably prepared wave packet. It is the proper mathematical expression of the intuitive classical picture of collisions, and is the only rigorous means by which we may demonstrate the truth of the correspondence principle; of course, it must therefore yield the classical formula for the elastic scattering cross section. This wave-packet formulation was extended to systems with several discrete internal quantum states, and the classical-trajectory equations [Eqs. (9)] are the result. In this case, the classical-trajectory equations express for a multichannel system the idea of the correspondence principle; the meaning of the equations is precisely that given to them intuitively by the classical picture. However, there is a price for this, i.e., the very stringent restrictions (25).

The striking empirical success of the classical-trajectory equations, even at energies far too low for these severe conditions to hold, makes it clear that the equations must have alternative and less restrictive derivations.

The formulation of Sec. III is one such derivation. It describes a mathematically approximate solution to the time-independent Schrödinger equation in configuration space. Two approximations are involved—the WKB approximation and the ± separation. These are valid if (a) the wavelength is short, (b) there is a negligible difference between the several elastic scattering trajectories associated with various internal states, and (c) the inelastic coupling is negligible near the classical turning point. These "semiclassical" conditions are sufficient to ensure the validity of the classical-trajectory equations (28).

However, it is not evident that all these conditions are necessary. In particular, calculations on the H^+-H system show that condition (c) is not necessary.

In Paper II, we present a third derivation of the classical-trajectory equations with a different condition substituted for the above condition (c). It is again a semiclassical formulation, rather than a packet theory, and involves an approximate solution to the time-independent Schrödinger equation in the *momentum* representation. Together with the formulation of Sec. III, it will permit us to offer a general semiclassical picture that is not subject to the special limitations of the WKB approximation.

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Semiclassical Theory of Inelastic Collisions. II. Momentum-Space Formulation*

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The time-dependent equations of the classical picture of inelastic collisions (classical-trajectory equations) are derived using the momentum-space semiclassical approximation. Thereby it is shown that the classical-trajectory equations remain valid in the vicinity of classical turning points provided that (a) the momentum-space semiclassical approximation is valid, (b) the trajectories for elastic scattering in the various internal states differ only slightly, and (c) the slopes of the elastic scattering potentials have the same sign. A brief review of the existing derivations of the classical-trajectory equations is given, and the general conditions for their validity are discussed.

I. INTRODUCTION

This is the second in a series of papers[1] dealing with the derivation and application of semiclassical methods to collisions involving a quantal change in the internal states of the colliding systems. We are primarily interested in discrete electronic excitations in slow atomic collisions.

The starting point is the set of coupled radial Schrödinger equations

$$\frac{-\hbar^2}{2M}\frac{d^2u_m(R)}{dR^2}+\sum_n V_{mn}(R)u_n(R)=Eu_m(R)\ . \qquad (1)$$

In this paper, we restrict ourselves to the diabatic representation; analogous results can be obtained in the adiabatic representation, but the analysis is much more complicated.

In the classical picture, we imagine the nuclei to be moving classically on some trajectory $R(t)$; in the basis $\{n\}$ the electronic system obeys the time-dependent Schrödinger equation

$$i\hbar\frac{dc_m(t)}{dt}=\sum_{n\neq m}c_n(t)V_{mn}(R(t))\times\exp\left((i/\hbar)\int^t[V_{mm}(R(t'))-V_{nn}(R(t'))]\,dt'\right) \qquad (2)$$

The objective of this series is the derivation of these classical-trajectory equations (2) from the full coupled Schrödinger equations (1) under the most general assumptions possible.

In the second derivation in Paper I, the classical-trajectory equations (2) were derived by an extension of the usual semiclassical approximation. One of the assumptions used, (c), was that inelastic coupling is negligible near the classical turning