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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

points. However, calculations on the H^+-H system[1-3] and other considerations[1,4] prove that assumption (c) is not necessary for the validity of the classical-trajectory equations. In this paper, the momentum-space form of the semiclassical approximation[5] is taken as the starting point. Using this approach, we show that assumption (c) can be replaced by an alternate assumption: (c′) The forces $F_i = -dV_{ii}/dR$ have the same sign near the classical turning point. The significance of this assumption is discussed in Sec. IV.

A special case of this analysis was presented by Bykhovskii, Nikitin, and Ovchinnikova.[6] They showed that for the Landau-Zener-Stueckelberg (LZS) model of linear potentials and constant coupling, the classical-trajectory equations are completely equivalent to the Schrödinger equations. The present paper shows that similar ideas can be applied to more realistic models.

In Sec. II we review the momentum-space semiclassical approximation.[5] The derivation of the classical-trajectory equations, and the relationship of this formulation to the configuration-space approach, is presented in Sec. III. Finally, in Sec. IV the assumptions used in this as well as other derivations of the classical-trajectory equations are summarized and compared.

II. MOMENTUM-SPACE SEMICLASSICAL APPROXIMATION

For the purposes of this paper, we may use the term "momentum-space wave function" to refer to the Fourier transform

$$v_m(P) = \int e^{-iPR/\hbar}\, u_m(R)\, dR \,. \tag{3}$$

The integral goes from zero to infinity, or it may be extended to minus infinity if $u_m(-R)$ is suitably defined.[5] In the absence of coupling, $v_m(P)$ obeys the differential equation

$$\left[\frac{P^2}{2M} + V_{mm}\left(i\hbar\frac{d}{dP}\right) - E\right] v_m(P) = 0 \,, \tag{4}$$

with the potential energy operator defined by its Taylor expansion. Let us write

$$v_m(P) = \hat{a}_m(P)\, e^{-i\hat{S}_m(P)/\hbar} \tag{5}$$

and denote

$$\frac{d\hat{S}_m}{dP} \equiv \mathcal{R}_m(P) \,. \tag{6}$$

It follows that $\hat{a}_m$ obeys the differential equation

$$\left[\frac{P^2}{2M} + V_{mm}\left(\mathcal{R}_m(P) + i\hbar\frac{d}{dP}\right) - E\right]\hat{a}_m(P) = 0 \,. \tag{7}$$

The semiclassical approximation is obtained by assuming that $\hat{a}(P)$ and $\mathcal{R}(P)$ are slowly varying functions; and thereby treating $i\hbar\, d/dP$ as a "small" quantity. By using the Taylor expansion for functions of two noncommuting variables,[5,7] the potential energy operator can be put in the form

$$V\left(\mathcal{R} + i\hbar\frac{d}{dP}\right) = V(\mathcal{R}) + i\hbar\left(V^{[1]}(\mathcal{R})\frac{d}{dP} + \tfrac{1}{2}V^{[2]}(\mathcal{R})\frac{d\mathcal{R}}{dP}\right)$$
$$+ (i\hbar)^2\left\{\tfrac{1}{2}V^{[2]}(\mathcal{R})\frac{d^2}{dP^2} - \tfrac{1}{6}V^{[3]}(\mathcal{R})\left[\frac{d^2\mathcal{R}}{dP^2} + 3\left(\frac{d\mathcal{R}}{dP}\right)\frac{d}{dP}\right]\right.$$
$$\left. + \tfrac{1}{24}V^{[4]}(\mathcal{R})\left(\frac{d\mathcal{R}}{dP}\right)^2\right\} + \cdots \,, \tag{8}$$

where

$$V^{[k]}(\mathcal{R}) = \frac{d^k V(\mathcal{R})}{\mathcal{R}\, d\mathcal{R}^k} \,.$$

Using (8) in (7), we see that it is natural to choose $\mathcal{R}_m(P)$ such that the zero-order term vanishes:

$$P^2/2M + V_{mm}(\mathcal{R}_m(P)) - E = 0 \,. \tag{9}$$

Then $\mathcal{R}_m(P)$ is the position that is associated classically with the momentum P; also

$$\hat{S}_m(P) = \int \mathcal{R}_m(P')\, dP' \,. \tag{10}$$

The momentum-space semiclassical approximation consists in neglecting terms of second order and higher in (8). From this it follows that

$$\hat{a}_m(P) \simeq \left|F_m(\mathcal{R}_m(P))\right|^{-1/2} \,, \tag{11}$$

where

$$F_m(\mathcal{R}) = -\frac{dV_{mm}(\mathcal{R})}{d\mathcal{R}} \,.$$

The important feature of this approximation is that it remains valid at small momenta; therefore it can give an adequate description of a system in the vicinity of classical turning points. The approximation breaks down near points in momentum space, P_0, such that $F_m(\mathcal{R}_m(P_0)) = 0$; such points could be called "momentum-space classical turning points," since the momenta P_0 are extrema of the classically accessible values. In collision problems these points occur at infinity, and at any point for which the potential has a maximum or a minimum. We have shown elsewhere[5] that a general criterion for the validity of the momentum-space semiclassical approximation is the condition

$$\left|\left(\frac{\hbar P}{MF_m}\right)\left(\frac{1}{F_m}\frac{dF_m}{dR}\right)^2\right| \ll 1 \,, \tag{12}$$

where

$$F_m = F_m(\mathcal{R}_m(P)) \,.$$

In classical mechanics a strict correlation exists between P and R for a specified dynamical state (trajectory). The essence of the semiclassical approximation is that on the average some such correlation persists, in the sense that contributions to $u_m(R)$ come mainly from momentum eigenstates near the classical value $P = \mathcal{P}(R)$, while contributions to $v_m(P)$ come mainly from position eigenstates near $\mathcal{R}(P)$. For such a case it follows that

the Fourier transform (3) and its inverse can be approximated by the method of stationary phase, provided that points of stationary phase do not lie too close together.[5] Therefore it is possible to represent the state vector for a semiclassical collision by using the configuration-space semiclassical approximation at $R \to \infty$ and near potential extrema, using the momentum-space semiclassical approximation near classical turning points, and transforming from one representation to the other by the method of stationary phase in the regions where both approximations hold. In this paper this procedure is used to extend the domain of validity of the classical-trajectory equations.

III. CLASSICAL-TRAJECTORY EQUATIONS

Now, using the momentum-space semiclassical approximation as a starting point, we obtain the classical-trajectory equations (2) by a method analogous to that used in the second derivation given in I.

A. Derivation

The two-channel momentum-space Schrödinger equation is

$$\left[\frac{P^2}{2M} + V_{11}\left(i\hbar\,\frac{d}{dP}\right) - E\right] v_1(P) + V_{12}\left(i\hbar\,\frac{d}{dP}\right) v_2(P) = 0\ , \tag{13}$$

$$\left[\frac{P^2}{2M} + V_{22}\left(i\hbar\,\frac{d}{dP}\right) - E\right] v_2(P) + V_{21}\left(i\hbar\,\frac{d}{dP}\right) v_1(P) = 0\ .$$

Using (5) and (6), we obtain without approximation

$$\left[\frac{P^2}{2M} + V_{11}\left(\mathcal{R}_1 + i\hbar\,\frac{d}{dP}\right) - E\right] \hat{a}_1(P) = -e^{(i/\hbar)(\hat{S}_1 - \hat{S}_2)}\, V_{12}\left(\mathcal{R}_2 + i\hbar\,\frac{d}{dP}\right)\hat{a}_2\ , \tag{14}$$

$$\left[\frac{P^2}{2M} + V_{12}\left(\mathcal{R}_2 + i\hbar\,\frac{d}{dP}\right) - E\right]\hat{a}_2(P) = -e^{(i/\hbar)(\hat{S}_2 - \hat{S}_1)}\, V_{21}\left(\mathcal{R}_1 + i\hbar\,\frac{d}{dP}\right)\hat{a}_1\ .$$

We now use the Taylor expansion (8) for $V_{mn}(\mathcal{R}_n + i\hbar(d/dP))$; in collecting terms, we consider that all inelastic coupling terms [right-hand side of Eqs. (14)] are one order higher than corresponding elastic scattering terms. Thus, the resulting "zero-order" equations are (9), and the "first-order" equations are

$$i\hbar\left(V_{11}^{[1]}(\mathcal{R}_1)\,\frac{d\hat{a}_1}{dP} + \tfrac{1}{2}\,V_{11}^{[2]}(\mathcal{R}_1)\,\frac{d\mathcal{R}_1}{dP}\,\hat{a}_1\right) = -e^{i(\hat{S}_1 - \hat{S}_2)/\hbar}\, V_{12}(\mathcal{R}_2)\,\hat{a}_2\ , \tag{15}$$

with a corresponding equation for $\hat{a}_2$. Here we have equated the first term from the Taylor expansion of V_{12} with the second term from the expansion of V_{11}.[8] This approximation is valid if first-order and higher terms in V_{12} and second-order and higher terms in V_{11}, V_{22} can be neglected. An estimate of these higher terms consistent with the validity of (15) can be made using Eq. (8) and

$$\left|\frac{1}{\hat{a}_m}\,\frac{d\hat{a}_m}{dP}\right| \sim \left|\frac{(\mathcal{R}_2 - \mathcal{R}_1)}{\hbar}\right|\ ,$$

which follows from (15). Generally, Eq. (15) is valid if two conditions are satisfied: (a′) The momentum-space semiclassical approximation is valid in the absence of coupling, i.e., the inequality (12) holds; (b′) The difference between the elastic scattering trajectories is small,

$$|\mathcal{R}_2 - \mathcal{R}_1|/a_0 \ll 1\ . \tag{16}$$

This requirement implies another; if the trajectories are to be approximately the same, the forces cannot be too different,

$$|(F_2 - F_1)/(F_2 + F_1)| \ll 1\ . \tag{17}$$

Inequalities (12), (16), and (17) are the conditions for validity of (15).

We now define

$$\hat{b}_m(P) = \hat{a}_m(P)\,[F_m(\mathcal{R}_m(P))]^{1/2}\ ; \tag{18}$$

then

$$\pm i\hbar\,|F_1(\mathcal{R}_1)\,F_2(\mathcal{R}_2)|^{1/2}\,\frac{d\hat{b}_1}{dP} = V_{12}(\mathcal{R}_2)\,e^{i(\hat{S}_1 - \hat{S}_2')/\hbar}\,\hat{b}_2\ , \tag{19a}$$

$$\pm i\hbar\,|F_1(\mathcal{R}_1)\,F_2(\mathcal{R}_2)|^{1/2}\,\frac{d\hat{b}_2}{dP} = V_{21}(\mathcal{R}_1)\,e^{-i(\hat{S}_1 - \hat{S}_2)/\hbar}\,\hat{b}_1\ . \tag{19b}$$

In Eq. (19a), the sign to be used is the sign of F_1, while in Eq. (19b) the sign is that of F_2. If the forces have opposite signs, the equations are very similar to the classical-trajectory equations, but the matrix involved is anti-Hermitian and does not conserve probability. We must therefore make a third assumption: (c′) The forces all have the same sign. Equation (19) then simplify using (16) and (17) to

$$i\hbar\,\bar{F}(\bar{\mathcal{R}}(P))\,\frac{d}{dP}\begin{bmatrix}\hat{b}_1\\ \hat{b}_2\end{bmatrix} = \begin{bmatrix}0 & V_{12}(\bar{\mathcal{R}})\,e^{i(\hat{S}_1 - \hat{S}_2)/\hbar}\\ V_{21}(\bar{\mathcal{R}})\,e^{-i(\hat{S}_1 - \hat{S}_2)/\hbar} & 0\end{bmatrix}\begin{bmatrix}\hat{b}_1\\ \hat{b}_2\end{bmatrix}\ .$$

Defining the variable τ such that

$$\frac{d\tau}{dP} = [\bar{F}(\bar{\mathcal{R}}(P))]^{-1}\ , \tag{20}$$

we obtain

$$i\hbar\,\frac{d}{d\tau}\begin{bmatrix}\hat{b}_1\\ \hat{b}_2\end{bmatrix} = \begin{bmatrix}0 & V_{12}\,e^{i\hat{\Delta}(\tau)}\\ V_{21}\,e^{-i\hat{\Delta}(\tau)} & 0\end{bmatrix}\begin{bmatrix}\hat{b}_1\\ \hat{b}_2\end{bmatrix}\ , \tag{21}$$

with

$$\hat{\Delta}(\tau) = \int_0^\tau (\mathcal{R}_1 - \mathcal{R}_2)\,\bar{F}(\tau')\,d\tau' \tag{22a}$$

$$\simeq \int_0^\tau [V_{11}(\bar{\mathcal{R}}(\tau')) - V_{22}(\bar{\mathcal{R}}(\tau'))]\,d\tau' \tag{22b}$$

(see Appendix). Equations (21) and (22b) are the classical-trajectory equations (2).

It should be noted that this derivation, like the second one given in I, does *not* imply that the system could be observed moving along the classical trajectory with amplitudes changing according to (21). Semiclassical derivations prove the validity of the *form* of the equations of the classical picture but do not imply the *substance* of the classical picture itself.

Finally we remark that it is possible by this method to derive corrections to the classical-trajectory equations which apply if the approximations made here begin to break down. These corrections are the many-channel generalization of the well-known expansion of the elastic scattering phase shift in powers of $\hbar$.

B. Relation to Configuration-Space Formulation

The configuration-space wave function is given by the inverse Fourier transform,

$$u_m(R) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{\infty} v_m(P)\, e^{iPR/\hbar}\, dP$$

$$\simeq (2\pi\hbar)^{-1/2} \int_{-\infty}^{\infty} dP\, \hat{b}_m(P)\, |F_m(\mathcal{R}(P))|^{-1/2}$$

$$\times \exp\{-(i/\hbar)\int_0^P [\mathcal{R}_m(P') - R]\,dP'\}\,.$$

Far from the turning points, the integral can be performed by the method of stationary phase; the result for the classically allowed region is

$$u_m(R) \simeq [M/\mathcal{P}_m(R)]^{1/2}$$

$$\times\{\hat{b}_m(\mathcal{P}_m(R)) \exp[(i/\hbar)\int_{R_{om}}^R \mathcal{P}_m(R')\,dR' - \tfrac{1}{4}i\pi]$$

$$+ \hat{b}_m(-\mathcal{P}_m(R)) \exp[-(i/\hbar)\int_{R_{om}}^R \mathcal{P}_m(R')\,dR' + \tfrac{1}{4}i\pi]\}\,; \tag{23}$$

$\mathcal{P}_m(R)$ is defined in Eq. (32) of I. Comparing Eqs. (30) and (34) of I with (23), we obtain the correspondence

$$b_{m\pm}(R) \rightarrow \hat{b}_m(\pm\mathcal{P}(R))\, e^{\mp i\pi/4}$$

or, equivalently,

$$b_{m\pm}(\bar{\mathcal{R}}(P)) \rightarrow \hat{b}_m(\pm P)\, e^{\mp i\pi/4}\,.$$

The equivalence of the classical-trajectory equations in the two forms is thus definitely established. The phase factor $e^{\mp i\pi/4}$ is the same as that obtained in I via the WKB connection formulas for elastic reflection at a classical turning point; traditionally it is incorporated into the WKB phase shift.

Similarly, in the classically forbidden region, well inside all the turning points, all $u_m(R)$ are exponentially small. If R is between two turning points, one wave function is oscillatory, and the other is exponentially small. If R is close to the turning point of the mth potential R_m [i.e., the point such that $V_{mm}(R_m) = E$], then the corresponding configuration-space wave function can be shown to be

$$u_m(R) \simeq \hat{b}_m(P=0)\,\pi^{1/2}[M^2/2\hbar F_m(R_m)]^{1/6}$$

$$\times \mathrm{Ai}((2MF/\hbar^2)^{1/3}(R_m - R))\,. \tag{24}$$

Therefore, in spite of the fact that different electronic states have different turning points R_m, the momentum-space formulation shows that a classical description involving a single trajectory is uniformly valid throughout the entire turning-point region.

IV. DISCUSSION

A. Validity of Classical-Trajectory Equations

For a single-channel system, there are five well-known ways of obtaining "classical behavior" in quantum mechanics. The most intuitive but least general approach involves the use of localized wave packets. More general are the semiclassical approximations in configuration space and in momentum space. Feynman's approach most clearly displays the connection with the principle of least action.[9] The fifth approach involves the use of the Wigner distribution function, which corresponds to the classical phase-space density.[10]

Each of these approaches has been used to derive the classical-trajectory equations, which describe "classical behavior" for a multichannel system. The Feynman approach was developed by Pechukas,[4] the wave-packet formulation by Mittleman[11] and by Delos, Thorson, and Knudson,[1] and the configuration-space semiclassical approximation method by Cross,[12] Bates and Crothers,[13] Child,[14] and Delos, Thorson, and Knudson.[1] Derivation via the momentum-space semiclassical approximation is the subject of this paper, and the Wigner function development is given elsewhere.[15]

It is plausible to suppose that there can exist no derivations that are substantially more general than these already known; therefore it is appropriate now to compare the derivations to find the most general conditions under which the classical-trajectory equations are valid. Since most of the derivations give sufficient conditions for their validity, the equations are valid provided any single derivation holds. By comparing them we can obtain the weakest possible restrictions still sufficient for their validity.

The wave-packet derivation was shown to be valid provided that the microscopic wave packets remain small as they traverse the interaction region. As was extensively discussed in I, this happens if (i) the de Broglie wavelength is extremely small com-

pared to atomic dimensions $[(\lambda\!\!\!^{-}/a_0)^{1/2} \ll 1]$ and (ii) there is a negligible difference between the elastic scattering trajectories for the several internal states. The first restriction is very severe and makes this derivation much less general than the others.

Pechukas's derivation,[4] using the Feynman approach, may well be the most general, but the conditions for its validity are not at all clear.

The Wigner-function approach can easily be reduced to the semiclassical formulation or to the wave-packet formulation, so it provides no additional insight.

We therefore turn to the semiclassical derivations. In both of them, we assumed that the single-channel semiclassical approximation would be valid, either in configuration space or in momentum space, for zero inelastic coupling. This condition is expressed loosely by the requirement that the de Broglie wavelength be small compared to atomic dimensions, or more precisely, by the inequalities

$$|\hbar MF(R)/\mathcal{P}^3(R)| \ll 1 \quad \text{(configuration space)} \tag{25a}$$

or

$$|\hbar PF'^2/MF^3| \ll 1 \quad \text{(momentum space)}. \tag{25b}$$

Some such assumption is used in every derivation of the classical-trajectory equations. In spite of this, it is an odd fact that in certain systems, the inequalities (25) are not strictly necessary; for the lower states of the harmonic oscillator and the hydrogen atom, (25) are not satisfied but the semiclassical approximation to the eigenvalue spectrum is exact. Strictly speaking, conditions (25) are also not sufficient for the validity of the semiclassical approximation.[16] Nevertheless, they provide a useful guide to its validity.

The second assumption, also made in both semiclassical derivations, is that the trajectories for elastic scattering in the several internal states are similar:

$$|(\mathcal{P}_2 - \mathcal{P}_1)/(\mathcal{P}_2 + \mathcal{P}_1)| \ll 1 \quad \text{(configuration space)} \tag{26a}$$

or

$$|(\mathcal{R}_2 - \mathcal{R}_1)/a_0| \ll 1 \quad \text{(momentum space)}. \tag{26b}$$

It has not been proven that this assumption is necessary for the validity of the classical-trajectory equations. There does exist a special case for which it is violated but for which the classical-trajectory equations are exact—the case with two linear potentials and constant coupling[6]: $V_{jj} = -F_j R$; V_{12}, F_j constants, $F_1 F_2 > 0$. However, this case is unrealistic. Unless V_{12} and F_j are constant *everywhere*, the classical-trajectory equations are not exact.

It might be claimed that Pechukas's derivation[4] does not require the assumption (26), but this has yet to be proven, as the explicit conditions for the validity of his formulation are not yet known.

The data of Bates and Crothers[13] tend to support the conclusion that (26) is not necessary. However, this support is rather tenuous, since their calculation involved a crossing problem, in which (26) were satisfied throughout the region of strongest coupling.

There are strong reasons for believing that the classical-trajectory formulation requires conditions (26). Consider the following intuitive argument based on the configuration-space formulation. If (26a) is not satisfied, then the momentum of the nuclei changes drastically in an inelastic transition. In that case, only a small additional impulse would be required to also change the direction of the momentum so that the nuclei would be reflected by the coupling potential. Such a process would occur almost as frequently as excitation without change in direction. Since this process cannot be described by the classical-trajectory equations, they could not be valid under such conditions.

In any case, if the elastic trajectories differ substantially, the classical-trajectory equations offer little computational advantage over the exact coupled Schrödinger equations (1). The oscillatory factors in the classical-trajectory equations have wavelengths $\lambda\!\!\!^{-}_{ij} = \hbar/|\mathcal{P}_i - \mathcal{P}_j|$; if (26a) is not satisfied, then $\lambda\!\!\!^{-}_{ij} \simeq \min(\lambda\!\!\!^{-}_i, \lambda\!\!\!^{-}_j)$, so no great advantage is gained by using Eq. (2).

A third assumption was made in each semiclassical derivation. In the configuration-space derivation, we assumed (consistently with the other two assumptions) that the coupling is negligible near the classical turning points. In the momentum-space derivation, we assumed that the diagonal forces $F_j = -dV_{jj}/dR$ have the same sign. The classical-trajectory equations are valid unless both of these assumptions are false.

The most important case involving the simultaneous failure of these assumptions is the two-state crossing problem illustrated in Fig. 1(a). The "diabatic" curves (labeled 1 and 2) cross with slopes of opposite sign, and the "adiabatic" curves (labeled a and b), which are obtained by diagonalizing the potential energy matrix, each have an extremum near the crossing. If the turning points are close to the crossing point, then the system has an energy between E_1 and E_2. An incident particle in internal state 1 in this energy range would approach the crossing point very slowly, and pause for a long time, unable to "make up its mind" whether it should continue approaching in state 2, or recede in state 1. For energies slightly above E_1, the phenomenon could be described as tunneling through the barrier in state *a*, while for energies slightly below E_2, it could be considered as temporary trapping in a bound vibrational level of state *b*. In

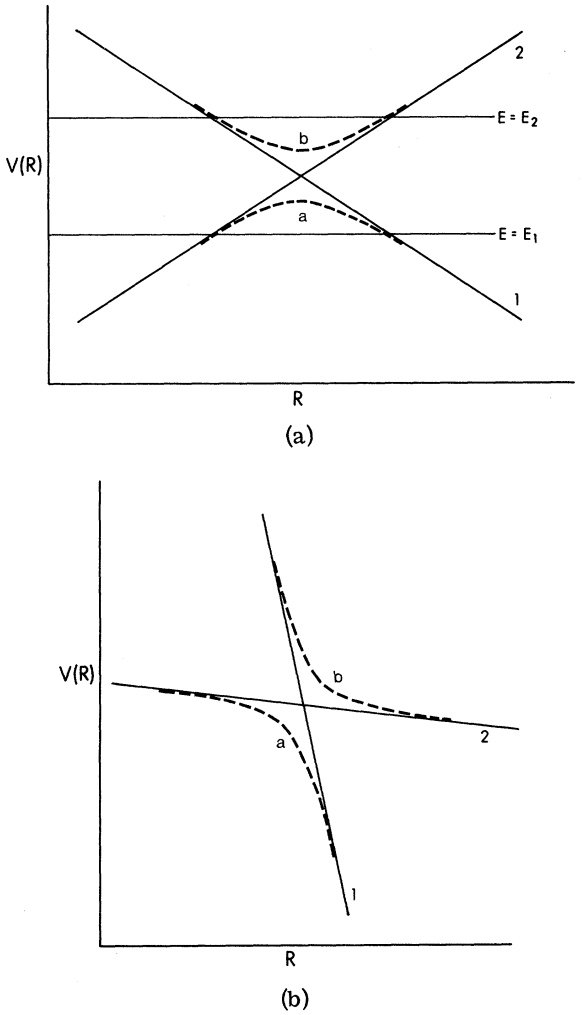

FIG. 1. Potential curves near the crossing point. "Diabatic" potentials are labeled 1, and 2, and "adiabatic" potentials are labeled a and b. The potential curves differ only in their orientation with respect to the $E=0$ axis. Nevertheless, they lead to totally different effects. (a) Forces have opposite signs. For $E_1 \leq E \leq E_2$, tunneling, orbiting, and temporary capture are possible, and classical-trajectory equations are not valid. (b) Forces have the same sign. Nonclassical effects do not occur, and classical-trajectory equations are valid at all energies.

any case, the situation cannot be described classically, so the classical-trajectory equations are not valid.

If, on the other hand, the classical turning point is far from the crossing point, then either $E \ll E_1$ or $E \gg E_2$. In the former case, tunneling is negligible, while in the latter case, the semiclassical approximation is valid for the vibrational levels of state b. Therefore, the classical-trajectory equations are again valid. Likewise, if the forces have the same sign near the crossing point [Fig. 1(b)], then the adiabatic potentials do not have an extremum, the tunneling and trapping phenomena do not exist, and the classical-trajectory equations are valid.

B. Choice of Classical Trajectory

The various derivations of the time-dependent equations suggest different choices for the classical nuclear trajectory. It is appropriate to review these here to consider their applicability to different situations.

The wave-packet derivation suggests that the appropriate trajectory is that of the center of mass of a microscopic wave packet.[1] This trajectory has great intuitive appeal,[17] since it weights the potential of each internal state in proportion to the probability of finding the system in that state. This trajectory is independent of the internal-state representation, and it satisfies the conservation laws of energy and angular momentum. However, we believe that this trajectory is unnecessarily complicated, and that it does not in general lead to results that are more accurate than those obtained from simpler trajectories. Contained in the wave-packet derivation is the assumption that the ground-state and excited-state trajectories differ negligibly from each other. Also, a calculation on the proton-hydrogen atom system showed that the wave-packet trajectory led to results that were less accurate than those obtained from the ground-state trajectory. Therefore, this approach will only lead to results that are either trivial or suspect.

The Feynman approach also leads to trajectories with considerable intuitive appeal,[4,9] as they also are independent of the internal representation, and they obey the classical conservation laws. However, they do not obey the "law" of causality, and therefore they cannot be calculated exactly by any known method. Moreover, hidden in the complicated path analysis may be the assumption that all trajectories are very similar. If so, this theory, like the wave-packet theory, would be valid only if it is unnecessary.

The semiclassical derivations explicitly contain the assumption that the trajectories are approximately the same in the region of inelastic coupling. (Elsewhere, they can be quite different—in this formulation, the scattering angle is not calculated from the nuclear trajectory, but from the phase shifts; the nuclear trajectory is only a device for calculating the amplitude for leaving the coupling region in a particular electronic state.) It follows from the above assumption that the "average trajectory" is not precisely defined by the theory. If the ground- and excited-state trajectories differ substantially, then the only reliable way to obtain accurate results is to incorporate higher-order corrections to the time-dependent equations. It is not difficult to obtain a series expansion of the

multichannel wave function that is analogous to the "expansion in powers of $\hbar$" for elastic scattering; the first term in series leads to the classical-trajectory equations and the higher terms are corrections to them.

However, it is often possible to avoid this extra effort by a very careful choice of the nuclear trajectory. We have repeatedly said in earlier sections that there is no trajectory that is best in general. On the other hand, for any given situation, there certainly exist trajectories that are rather poor. No *a priori* rule can be derived, but experience and intuition can often lead to a good choice. Several possibilities are suggested by the derivations. The configuration-space derivation uses a geometric-mean momentum at one point and an arithmetic mean at another:

$$\frac{dR}{d\tau} = \frac{[\mathcal{P}_1(R)\mathcal{P}_2(R)]^{1/2}}{M}$$

or

$$\frac{dR}{d\tau} = \frac{\frac{1}{2}[\mathcal{P}_1(R)+\mathcal{P}_2(R)]}{M} .$$

The momentum-space derivation uses a geometric-mean force at one point and an arithmetic mean at another:

$$\frac{dP}{d\tau} = [F_1(\mathcal{R}_1(P))\,F_2(\mathcal{R}_2(P))]^{1/2}$$

or

$$\frac{dP}{d\tau} = \tfrac{1}{2}[F_1(\mathcal{R}_1(P))+F_2(\mathcal{R}_2(P))] .$$

From the nature of the derivations, it follows that the geometric- or arithmetic-mean forces give better trajectories if the coupling occurs at small R, close to the turning points, where the velocities are small and the forces are strong. Clearly, the arithmetic-mean momentum becomes meaningless between the turning points, where one momentum is imaginary. The geometric-mean momentum keeps the nuclei entirely outside the outer turning point, so it does not properly sample the region between the turning points. Calculations on the H^+-H system confirm that this is not the best trajectory when coupling near the turning points is important. The geometric-mean force gives the exact solution to the (LZS) linear crossing model, so it is certainly the best choice for systems which approximate that model. The arithmetic-mean force is almost as good, and usually better if one force is very small. Since the momentum-space formulation does not involve a common turning point in configuration space, the region between the two turning points and the classically forbidden region are properly treated.

On the other hand, similar arguments can be used to show that the geometric- or arithmetic-mean momenta are better trajectories if the coupling occurs far from the turning points, at large R, where the velocities are large and the forces are weak.

Bates and Crothers[3,13] have proposed a very useful trajectory under the name of the "forced-common-turning-point procedure." The nomenclature is perhaps a bit misleading; their analysis is a configuration-space derivation of the time-dependent equations in which certain approximations lead to a particular choice of the classical trajectory. We would like to emphasize that the use of a common classical trajectory does not have to involve the use of a common turning point [see Eq. (24)]. As a consequence, the results of Bates and Crothers are valid more generally than their analysis or their nomenclature would suggest.

The essential feature of their approach is the choice of an intuitively appealing average trajectory (this choice is not derived),

$$\frac{dR}{d\tau} = \frac{(\tilde{\mathcal{P}}_1\tilde{\mathcal{P}}_2)^{1/2}}{M}\left(\frac{1-\hbar^2(l+\frac{1}{2})^2}{(\tilde{\mathcal{P}}_1\tilde{\mathcal{P}}_2)R^2}\right)^{1/2} ,$$

where $\tilde{\mathcal{P}}_j(R)$ differs from $\mathcal{P}_j(R)$ in that the latter includes the angular momentum repulsion, while the former does not. At large R, this trajectory is essentially the same as the geometric mean of $\mathcal{P}_j$, while at small R, it is very close to the trajectories that are based upon an average force. Therefore, this trajectory will give good results in a wide variety of situations.[3,13]

We conclude however by reiterating that if the difference between the initial- and final-state trajectories is very large in the region of inelastic coupling, then the classical-trajectory equations cannot be expected to provide accurate results.

V. SUMMARY

By the use of the momentum-space semiclassical approximation, we have extended the domain of validity of the classical-trajectory equations. They are valid if (a) a semiclassical approximation would be valid in the absence of coupling, (b) the potential energy difference is small compared to the kinetic energy, and (c) the coupling is negligible near the classical turning points *or* (c′) the forces have the same sign near the classical turning points. Each of these assumptions appears to be necessary for the validity of the classical-trajectory equations.

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APPENDIX

We demonstrate here the equivalence of the configuration- and momentum-space formulations. More precisely, we show that if

$$\left|(\mathcal{P}_2-\mathcal{P}_1)/(\mathcal{P}_2+\mathcal{P}_1)\right| \sim \eta ,$$

$$\left|(\mathcal{R}_2-\mathcal{R}_1)/a_0\right| \sim \eta ,$$

$$\left|(F_2-F_1)/(F_2+F_1)\right| \sim \eta ,$$

then Eqs. (20), (21), and (22a) differ from Eqs. (37) and (40) of I by terms of order η^2.

There are two possible sources of discrepancy between the two formulations. In the configuration-space formulation, V_{12} is evaluated at $R(\tau)$, which is the solution to

$$\frac{dR}{d\tau} = \frac{[\mathcal{P}_1(R(\tau))\,\mathcal{P}_2(R(\tau))]^{1/2}}{M} ,$$

while in the momentum-space formulation, V_{12} is evaluated at

$$\bar{\mathcal{R}}(\tau) = \tfrac{1}{2}(\mathcal{R}_1+\mathcal{R}_2) ,$$

where $\mathcal{R}_j(P)$ satisfies

$$P^2/2M + V_{jj}(\mathcal{R}_j(P)) - E = 0$$

and $P(\tau)$ satisfies

$$\frac{dP}{d\tau} = \bar{F} = \left|F_1(\mathcal{R}_1(P))\,F_2(\mathcal{R}_2(P))\right|^{1/2} .$$

The other possible discrepancy is between the forms of $\hat{\Delta}(\tau)$ in (22a) and (22b).

We begin by proving the intuitively obvious fact that $R(\tau)$ has the same τ dependence as $\bar{\mathcal{R}}(\tau)$. We have

$$\frac{d^2R}{d\tau^2} = (2M\mathcal{P}_1\mathcal{P}_2)^{-1}\left(\mathcal{P}_1\frac{d\mathcal{P}_2}{dR}+\mathcal{P}_2\frac{d\mathcal{P}_1}{dR}\right)\frac{dR}{d\tau} = \frac{\mathcal{P}_1^2F_2+\mathcal{P}_2^2F_1}{2M\mathcal{P}_1\mathcal{P}_2} = \frac{F_1+F_2}{2M}\left\{1+O\left[\left(\frac{\mathcal{P}_2-\mathcal{P}_1}{\mathcal{P}_2+\mathcal{P}_1}\right)\left(\frac{F_2-F_1}{F_2+F_1}\right)\right]\right\} .$$

Also

$$\frac{d}{d\tau}\left[\tfrac{1}{2}\mathcal{R}_1+\mathcal{R}_2)\right] = \tfrac{1}{2}[F_1(\mathcal{R}_1)\,F_2(\mathcal{R}_2)]^{1/2}\left(\frac{P}{MF_2(\mathcal{R}_2)}-\frac{P}{MF_1(\mathcal{R}_1)}\right) = \frac{P}{M}\left\{1+O\left[\left(\frac{F_2-F_1}{F_2+F_1}\right)^2\right]\right\}$$

and

$$\frac{d^2}{d\tau^2}\left[\tfrac{1}{2}(\mathcal{R}_1+\mathcal{R}_2)\right] = \frac{(F_1F_2)^{1/2}}{M} = \frac{F_1+F_2}{2M}\left\{1+O\left[\left(\frac{F_2-F_1}{F_2+F_1}\right)^2\right]\right\} .$$

Therefore R and $\bar{\mathcal{R}}$ obey the same second-order differential equation and the same boundary conditions, so they have the same "time" dependence. It also follows that $P(\tau)$ and $\frac{1}{2}(\mathcal{P}_1+\mathcal{P}_2)$ have the same "time" dependence.

Finally, we show that (22a) and (22b) have the same τ dependence. From Eq. (22b)

$$\frac{d^2\Delta}{d\tau^2} = [F_2(R(\tau)) - F_1(R(\tau))]\,\frac{dR}{d\tau} ,$$

whereas from Eq. (22a)

$$\frac{d^2\hat{\Delta}}{d\tau^2} = \frac{P}{M}\left[\frac{1}{F_1(\mathcal{R}_1)}-\frac{1}{F_2(\mathcal{R}_2)}\right]\bar{F}\,\frac{dP}{d\tau} + (\mathcal{R}_1-\mathcal{R}_2)\,\frac{d\bar{F}}{d\bar{\mathcal{R}}}\,\frac{d\bar{\mathcal{R}}}{dP}\,\frac{dP}{d\tau} .$$

In the first term, we use a Taylor expansion of $F_j(\mathcal{R}_j)$ about $\bar{\mathcal{R}}$. It then follows that

$$\frac{d^2\hat{\Delta}}{d\tau^2} = \frac{P}{M}\left[F_2(\bar{\mathcal{R}})-F_1(\bar{\mathcal{R}})\right] + \frac{1}{2}\frac{P}{M}(\mathcal{R}_2-\mathcal{R}_1) \times (F_2-F_1)\left(\frac{1}{F_2}\frac{dF_2}{d\mathcal{R}_2}-\frac{1}{F_1}\frac{dF_1}{d\mathcal{R}_1}\right)+\cdots .$$

The second term is of order

$$\frac{\mathcal{R}_2-\mathcal{R}_1}{a_0}\left(\frac{F_2-F_1}{F_2+F_1}\right) = O(\eta^2)$$

compared to the first. Hence, to within errors of order η^2, the second derivatives of Δ and $\hat{\Delta}$ are everywhere equal. Since the values and the first derivatives are equal at the turning point,

$$\hat{\Delta} = \int_0^\tau (V_{11}-V_{22})\,d\tau'$$

and the configuration- and momentum-space formulations are valid to within terms of order η^2.

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