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Citation: J. Chem. Phys. 53, 1949 (1970); doi: 10.1063/1.1674275
View online: http://dx.doi.org/10.1063/1.1674275
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v53/i5
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Semiclassical Theory of Atom–Diatom Collisions: Path Integrals and the Classical S Matrix

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(Received 23 February 1970)

The aim of this work is to show how one can use exact solutions of the classical equations of motion (numerically obtained trajectories) to construct the corresponding classical approximation to the time-independent S-matrix elements for use in quantum mechanical expressions for cross sections; it is argued that this should accurately describe many quantum effects in heavy particle collisions. The expression for the S matrix in terms of the classical trajectory is given for systems of any number of degrees of freedom, and the matter is pursued in detail for the A+BC collision system. It is shown that within this classical limit the *magnitude of* an S-matrix element is explicitly determined by its *phase*. Constancy of total angular momentum is used throughout to reduce the 12 first-order differential equations of the A+BC system in its center of mass to eight equations. A practical method is also given (in Appendix B) for further reducing the number of coupled equations to six, the minimum number possible.

I. INTRODUCTION

Perhaps the most striking features of elastic heavy particle (i.e., atom–atom) collisions at low energies are the pronounced quantum mechanical effects[1,2]: rainbows and other interference features in the differential cross section, and glory oscillations in the energy dependence of the total cross section. Aside from being interesting effects theoretically, they provide moderately simple ways of making quantitative statements about the interatomic potential (e.g., the relation of the energy dependence of the rainbow angle to the well depth of the potential).

A remarkable thing about these quantum effects, however, is that they can be accounted for, even quite quantitatively, by the following semiclassical prescription.[2] The quantum mechanical expression for the cross section is used,

$$\sigma(\theta) = |f(\theta)|^2, \tag{1}$$

$$f(\theta) = (2ik)^{-1}\sum_l (2l+1)\exp(2i\eta_l)P_l(\cos\theta), \tag{2}$$

but the phase shift η_l is computed within the WKB approximation. It is important to realize that the breakdown near rainbows, glories, and small angles, of many semiclassical results is due to the failure of approximate methods used to perform the sum (actually an integral) over l in Eq. (2) and is in no way related to inadequacy of the WKB phase shift. If the integral over l is evaluated by special techniques[2] at small angles and near the rainbow or by uniform approximations,[3,4] then these quantum effects are accurately described.

It should be recalled, however, that the WKB phase shift is a completely *classical* quantity and has been appropriately termed the classical phase.[5] It is actually the classical action integral along the classical trajectory. Correspondingly, the quantity S^l,

$$S^l = \exp[2i\eta^{\mathrm{WKB}}(l)],$$

might be called the *classical S matrix* (a 1-dimensional matrix in this case), and the scattering amplitude in Eq. (2) the classical amplitude. The point we are making is that classical dynamics is actually adequate to describe all of the above-mentioned quantum effects, provided one uses it to construct amplitudes which are then manipulated quantum mechanically; the quantum effects then arise solely as a consequence of superposition—that one adds amplitudes and squares rather than vice versa. The only feature not adequately treated in this framework is that of potential resonances, which are an intrinsically quantum dynamical effect (i.e., tunneling).

The aim of this paper is to develop the natural extension of the procedure outlined above to treat collisions of an atom and a diatomic molecule, A+BC. Therefore, analogous to Eqs. (1) and (2), one has the quantum mechanical expressions[6]

$$\sigma_{f\leftarrow i}(\theta) = |f_{f\leftarrow i}(\theta)|^2, \tag{3}$$

$$f_{f\leftarrow i}(\theta) = (2ik_i)^{-1}\sum_J (2J+1)S_{f,i}{}^J d_{M_f M_i}{}^J(\theta), \tag{4}$$

where the channel index is a collective one; i.e., $i\equiv\alpha_i$, n_i, j_i, M_i, where α labels the arrangement (whether atom A, B, or C is free), n and j are the vibrational and rotational quantum numbers of the diatom, and M is the helicity (the projection of the diatom's rotational angular momentum onto the relative velocity vector). The diagonal index J, which is summed over in Eq. (4), is the total angular momentum (rotational plus orbital), and $d_{MM'}{}^J(\theta)$ are the usual rotational matrices[7] [e.g., $d_{00}{}^J(\theta) = P_J(\cos\theta)$]. The total energy $E = \epsilon_i + \hbar^2 k_i^2/2\mu_i = \epsilon_f + \hbar^2 k_f^2/2\mu_f$ is also a diagonal index which has been suppressed (ϵ_i, ϵ_f are the internal energies of the initial and final diatom). The S matrix, $S_{f,i}{}^J(E)$, as a function of J and E is the unknown quantity which must be found to solve the scattering problem.

Our proposal is to use classical mechanics to generate the classical approximation to $S_{f,i}{}^J(E)$, and then to use this in the quantum mechanical expressions, Eqs. (3) and (4). By analogy with what one knows about

the two-body problem discussed above, it is expected that many of the quantum effects in atom–diatom collisions will be treated accurately. The principal new source of inaccuracy introduced into the three-body problem by this procedure, which is not present in the two-body problem, is that one is treating the quantized degrees of freedom (rotation and vibration) of the diatom classically, as well as the scattering (translational) degrees of freedom. One would expect this to be more serious for vibration than for rotation, but even here there are reasons for believing the error not to be serious; i.e., the Bohr–Sommerfeld quantum condition[8] is exact if the oscillator is harmonic (as are all diatomic molecules for low vibrational quantum numbers), and its accuracy increases rapidly (for any oscillator) as the quantum number increases past the few lowest values. An alternative to this procedure would be to treat the rotation–vibration degrees of freedom quantum mechanically and the translational degrees of freedom classically.[9] This is considerably more complicated and probably not warranted for the present system.

The task, then, is to show precisely how the classical S matrix can be obtained from the exact solution of the classical equations of motion (i.e., numerically obtained trajectories) for the three-body problem. The natural way to make this transcription between classical and quantum mechanics is via Feynman path integrals.[10] For our purposes it has proved simpler to employ the Hamiltonian form of classical mechanics rather than the Lagrangian form used by Feynman (there being no limitation in our case since the system has a classical Hamiltonian), the general reason being, of course, that the correspondence between classical and quantum mechanics is most direct through the Hamiltonian form. In particular, the relation between a canonical transformation in classical mechanics and a unitary transformation in quantum mechanics can be very usefully exploited. By transforming to a particular set of generalized coordinates and momenta (the coordinates being the angle-action variables[11,12]), identification of the classical S matrix is extremely simple, for the generalized momenta themselves are the quantum number labels of the S matrix.

Section II presents the general expressions for the classical propagator in canonical variables and shows its invariance upon a general canonical transformation. It is also shown how the S matrix can be easily obtained from the propagator. In Appendix A it is shown that the normalization of the propagator or any unitary matrix can be obtained from its phase alone. Section III considers the special features of the atom–diatom system in detail, and Sec. IV discusses the necessary modifications which are required in order to take rearrangement processes into account. Appendix B presents a practical procedure by which time can be eliminated from the classical equations of motion, thereby reducing them to sixth order.

II. GENERAL CONSIDERATIONS

The starting point is the classical approximation to the quantum mechanical propagator (which we call the classical propagator) as given by Feynman,[10] i.e.,

$$\langle q_2 \mid \exp[-iH(t_2-t_1)/\hbar] \mid q_1\rangle \sim \exp[i\phi(q_2, q_1)/\hbar], \quad (5)$$

where $q_2 \equiv q(t_2)$, $q_1 \equiv q(t_1)$ are the values of the coordinate at times t_2 and $t_1 (t_2 > t_1)$, H is the (time-independent) Hamiltonian governing the system, and ϕ is the classical action integral (we use ϕ for the action rather than S to avoid confusion with the S matrix) between the two space–time points:

$$\phi(q_2, q_1) = \int_{t_1}^{t_2} dt L[q(t), \dot{q}(t)]; \quad (6)$$

L is the classical Lagrangian for the system and $q(t)$ is determined by the classical equations of motion. The $\sim$ symbol used in Eq. (5) and elsewhere in the paper means that equality pertains only to the *phase* of the quantities to the left and right of it, the normalization being considered separately.

The discussion throughout this section applies equally well for multidimensional systems, the only modification being that $q(t)$ should be interpreted as an N-dimensional vector $\{q_i(t)\}$, N being the number of degrees of freedom of the system. For most of the general discussion in this section we do not use the multidimensional notation since it should be obvious how the multidimensional expressions should be written. A subscript, e.g., q_2, denotes the coordinate (possibly multidimensional) evaluated at time $t_2[q_2 = q(t_2)]$. If we need to refer to a coordinate or momentum corresponding to a particular one of the N degrees of freedom, the time variable will be indicated explicitly if necessary to avoid confusion; e.g., $q_2(t_1)$ means coordinate number two evaluated at t_1.

It is convenient to change to the Hamiltonian form of classical mechanics[13]; the momentum conjugate to q is defined as

$$p = \partial L(q, \dot{q})/\partial \dot{q}, \quad (7a)$$

and the Hamiltonian is

$$H(p, q) = p\dot{q} - L(q, \dot{q}). \quad (7b)$$

In terms of the canonical variables p and q, therefore, the phase of the classical propagator in the coordinate representation is now expressed as

$$\phi(q_2, q_1) = \int_{t_1}^{t_2} dt[p\dot{q} - H(p, q)], \quad (8)$$

where $p(t)$ and $q(t)$ are determined by Hamiltonian's equations of motion

$$\dot{q} = \partial H/\partial p, \quad (9a)$$

$$\dot{p} = -\partial H/\partial q, \quad (9b)$$

subject to the boundary condition $q(t_1) = q_1$, $q(t_2) = q_2$.

Regarding boundary conditions for Eq. (9), some simple but important points regarding classical mechanics are worth emphasizing. The classical trajectory $q(t)$ is determined by the classical equations of motion if q_1 and p_1 are specified. This trajectory is unique and determines specific values for q_2 and p_2, which may be considered as functions of q_1 and p_1. Alternatively, the values q_1 and q_2 may be the two boundary conditions used to determine the trajectory in the (t_1, t_2) time interval. This is the sense in which q_1 and q_2 are the independent variables in Eqs. (5) and (8), and p_1 and p_2 may then be considered functions of q_1 and q_2. Similarly, p_1 and p_2, q_1 and p_2 or p_1 and q_2 may be used as the pair of boundary conditions that determines the trajectory and thus may be taken as the independent variables specifying the classical path.

The questions we wish to explore next are (1) what is the classical propagator in the momentum representation, and (2) how does the classical propagator, or any quantity, transform upon changing from one set of canonical variables (p, q) to another canonical set. To answer them, we digress briefly to consider the general relation between canonical transforms in classical mechanics and unitary transformations in the classical limit of quantum mechanics.

If p and q are conjugate to one another, then the elements of the unitary transformation $\langle q \mid p \rangle$ are the familiar result[14]

$$\langle q \mid p \rangle = (2\pi i\hbar)^{-1/2} \exp(iqp/\hbar). \tag{10}$$

More generally, if (p, q) are one set of canonical variables and (P, Q) are another set, then in the classical limit $(\hbar \to 0)$ the elements of the following unitary transformations are

$$\langle q \mid P \rangle = \left(\frac{1}{2\pi i\hbar} \frac{\partial^2 F_2(q, P)}{\partial q \partial P}\right)^{1/2} \exp\left(\frac{iF_2(q, P)}{\hbar}\right), \tag{11a}$$

$$\langle q \mid Q \rangle = \left(\frac{1}{2\pi i\hbar} \frac{\partial^2 F_1(q, Q)}{\partial q \partial Q}\right)^{1/2} \exp\left(\frac{iF_1(q, Q)}{\hbar}\right), \tag{11b}$$

$$\langle p \mid P \rangle = \left(\frac{1}{2\pi i\hbar} \frac{\partial^2 F_4(p, P)}{\partial p \partial P}\right)^{1/2} \exp\left(\frac{iF_4(p, P)}{\hbar}\right), \tag{11c}$$

where F_1, F_2, and F_4 are the generators[15] of the classical canonical transformation from the set (p, q) to (P, Q). Equations (11) are one of the more general ways of stating the correspondence principle. A familiar example of these relations is Eq. (11a) for the case that q are ordinary spatial coordinates and P are the particular momenta which are the constants of the motion of H. In this case, $F_2(q, P)$ is the solution of the Hamilton–Jacobi equation,[16] and $\langle q \mid P \rangle$ is the WKB wavefunction.[17] The one point not particularly obvious is the normalization[18] of the transformation elements, and this is proved in Appendix I. It is of some practical importance that the normalization is wholly determined by, and calculable from, the phase.

To see how these transformation relations are used, suppose one has at hand the momentum representation of an operator B in one set of canonical variables (p, q),

$$\langle p_2 \mid B \mid p_1 \rangle \sim \exp[i\beta(p_2, p_1)/\hbar], \tag{12}$$

and wishes to obtain the matrix elements in the momentum representation of a new set of canonical variables (P, Q),

$$\langle P_2 \mid B \mid P_1 \rangle \sim \exp[i\bar{\beta}(P_2, P_1)/\hbar]. \tag{13}$$

That is, given β, the problem is to find $\bar{\beta}$. According to the rules of quantum mechanics, one has the transformation law of matrix algebra,

$$\langle P_2 \mid B \mid P_1 \rangle = \int dp_2' \int dp_1' \langle P_2 \mid p_2' \rangle \langle p_2' \mid B \mid p_1' \rangle \langle p_1' \mid P_1 \rangle. \tag{14}$$

In the classical limit $(\hbar \to 0)$, however, the phases of the three factors in Eq. (14) are rapidly oscillating, so that both integrals can be evaluated by stationary phase. Using Eq. (11c), the new phase $\bar{\beta}$ is given by

$$\bar{\beta}(P_2, P_1) = \beta(p_2, p_1) + F_4(p_1, P_1) - F_4(p_2, P_2), \tag{15}$$

where F_4 is the generator of the transformation from canonical variables (p, q) to (P, Q), and where p_2 and p_1 in Eq. (15) are the particular values of p_2' and p_1' which satisfy the stationary phase relations. That is, p_2 and p_1 are determined by the simultaneous equations

$$\partial\beta(p_2, p_1)/\partial p_2 - \partial F_4(p_2, P_2)/\partial p_2 = 0, \tag{16a}$$

$$\partial\beta(p_2, p_1)/\partial p_1 + \partial F_4(p_1, P_1)/\partial p_1 = 0, \tag{16b}$$

and are functions of P_1 and P_2. This procedure, of course, only determines the phase of the matrix element, but this presents no problem if the operators of interest are unitary (as are the propagator and the S operator), for the normalization of a unitary operator in any representation can be constructed from the phase (see Appendix A).

With regard to the propagator, one can show that its phase in the coordinate representation [Eq. (8)] satisfies the equations

$$\partial\phi(q_2, q_1)/\partial q_2 = p_2, \tag{17a}$$

$$\partial\phi(q_2, q_1)/\partial q_1 = -p_1, \tag{17b}$$

where p_2 and p_1 are the classical values of momentum at times t_2 and t_1, as a function of q_1 and q_2 (as discussed above). Equations (17) can be most easily proved by noting that the propagator itself is a unitary transformation, the generator of which is the Hamiltonian. Equations (17) are then seen to be the standard transformation relations for a canonical transformation whose generator is of the F_1 type.[15] To obtain the momentum representation of the propagator,

$$\langle p_2 \mid \exp[-iH(t_2 - t_1)/\hbar] \mid p_1 \rangle \equiv \int dq_2' \int dq_1' \langle p_2 \mid q_2' \rangle \times \langle q_2' \mid \exp[-iH(t_2 - t_1)/\hbar] \mid q_1' \rangle \langle q_1' \mid p_1 \rangle, \tag{18}$$

one uses Eq. (10), and in view of Eqs. (17) the stationary phase requirements [Eqs. (16)] have a very simple interpretation: the particular values of q_2' and q_1' which contribute (in a stationary phase sense) to the integral in Eq. (18) are those related to p_2 and p_1 by the classical equations of motion [i.e., $q_2(p_2, p_1)$ and $q_1(p_2, p_1)$]. If $\phi(p_2, p_1)$ is defined so that

$$\langle p_2|\exp[-iH(t_2-t_1)/\hbar]|p_1\rangle \sim \exp[i\phi(p_2, p_1)/\hbar], \quad (19)$$

then we have shown that

$$\phi(p_2, p_1) = -(p_2q_2 - p_1q_1) + \int_{t_1}^{t_2} dt[p\dot{q} - H(p, q)]$$

with q_2 and q_1 determined by p_2 and p_1. Integration by parts gives

$$\phi(p_2, p_1) = \int_{t_1}^{t_2} dt[-\dot{p}q - H(p, q)], \quad (20)$$

the desired expression for the phase of the propagator in the momentum representation.

Since the propagator is unitary, its normalization can be given explicitly (see Appendix A). The general expressions in coordinate and momentum representations are

$$\left\langle q_2 \left| \exp\left(\frac{-iH(t_2-t_1)}{\hbar}\right) \right| q_1 \right\rangle = \left(\frac{1}{2\pi i\hbar}\frac{\partial^2\phi(q_2, q_1)}{\partial q_2 \partial q_1}\right)^{1/2} \exp\left(\frac{i\phi(q_2, q_1)}{\hbar}\right), \quad (21a)$$

$$\left\langle p_2 \left| \exp\left(\frac{-iH(t_2-t_1)}{\hbar}\right) \right| p_1 \right\rangle = \left(\frac{1}{2\pi i\hbar}\frac{\partial^2\phi(p_2, p_1)}{\partial p_2 \partial p_1}\right)^{1/2} \exp\left(\frac{i\phi(p_2, p_1)}{\hbar}\right), \quad (21b)$$

where $\phi(q_2, q_1)$ and $\phi(p_2, p_1)$ are given by Eqs. (8) and (20), respectively; $q(t)$ and $p(t)$ are determined by Hamilton's equations with boundary conditions $q(t_1)=q_1$, $q(t_2)=q_2$ for Eqs. (8) and (21a), or boundary conditions $p(t_1)=p_1$, $p(t_2)=p_2$ for Eqs. (20) and (21b). It is clear that these expressions hold for *any* set of canonical variables. To see this explicitly, suppose one transforms Eq. (21b) to a new set of canonical variables (P, Q). Equation (21b) implies that the phase of the propagator in the new momentum representation is

$$\phi(P_2, P_1) = \int_{t_1}^{t_2} dt[-\dot{P}Q - H(P, Q)], \quad (22)$$

and the transformation rules established above give the phase as

$$\phi(P_2, P_1) = \phi(p_2, p_1) - F_4(p_2, P_2) + F_4(p_1, P_1), \quad (23)$$

with p_2 and p_1 determined by the stationary phase requirements

$$\partial\phi(p_2, p_1)/\partial p_2 - \partial F_4(p_2, P_2)/\partial p_2 = 0, \quad (24a)$$

$$\partial\phi(p_2, p_1)/\partial p_1 + \partial F_4(p_1, P_1)/\partial p_1 = 0. \quad (24b)$$

That Eqs. (20) and (24) imply the rhs of Eqs. (22) and (23) to be identical follows simply (by integration from t_1 to t_2) from the basic property[15] of the F_4 generator:

$$(d/dt)F_4(p, P) = Q\dot{P} - q\dot{p} + H(P, Q) - H(p, q). \quad (25)$$

Having established the form of the classical propagator in an arbitrary canonical representation, we now turn to the problem of finding the classical S matrix. This is most easily accomplished by using the fact that S matrix elements can be obtained by evaluating matrix elements of the operator S,[19]

$$S = \lim_{\substack{t_2\to+\infty \\ t_1\to-\infty}} \exp[iH_0t_2/\hbar]\exp[-iH(t_2-t_1)/\hbar] \times \exp[-iH_0t_1/\hbar] \quad (26)$$

between eigenstates of H_0, the unperturbed Hamiltonian (see Sec. IV for modifications which arise for rearrangement processes). That is, *the "indices" of the S matrix are the constants of the motion of* H_0. If (p, q) are a particular set of canonical variables which are constants of the motion of H_0, therefore, the physical S-matrix elements in this representation are

$$\begin{aligned}\langle p_2 \mid S \mid p_1\rangle &= \langle p_2 \mid \exp[iH_0t_2/\hbar]\exp[-iH(t_2-t_1)/\hbar] \times \exp[-iH_0t_1/\hbar] \mid p_1\rangle \\ &= \exp(iEt_2/\hbar)\langle p_2 \mid \exp[-iH(t_2-t_1)/\hbar] \mid p_1\rangle \times \exp(-iEt_1/\hbar), \end{aligned} \quad (27)$$

the limit $t_1\to-\infty$, $t_2\to+\infty$ being understood. Using Eq. (20), the phase of $\langle p_2 \mid S \mid p_1\rangle$ becomes

$$E(t_2-t_1) - \int_{t_1}^{t_2} dt[\dot{p}q + H(p, q)], \quad (28)$$

but $H(p, q)=E$ is time independent, so that the energy terms cancel in Eq. (28). The general expression for $\langle p_2 \mid S \mid p_1\rangle$ becomes

$$\langle p_2 \mid S \mid p_1\rangle = \left(\frac{1}{2\pi i\hbar}\frac{\partial^2\phi(p_2, p_1)}{\partial p_2 \partial p_1}\right)_{N-3}^{1/2} \exp\left(\frac{i\phi(p_2, p_1)}{\hbar}\right), \quad (29)$$

where

$$\phi(p_2, p_1) = -\int_{t_1}^{t_2} dtq(t)\dot{p}(t). \quad (30)$$

The normalization in Eq. (29) is established in the usual manner (see Appendix A) since $\langle p_2 \mid S \mid p_1\rangle$ is unitary, but the subscript $(N-3)$ indicates that three degrees of freedom of the $[q_i(t), p_i(t)]$ set are omitted in the normalizing determinant; i.e., the explicit expression for the normalization is

$$\left(\frac{1}{(2\pi i\hbar)^{N-3}}\det\left|\frac{\partial^2\phi[p(t_2), p(t_1)]}{\partial p_i(t_2)\partial p_j(t_1)}\right|_{N-3}\right)^{1/2}. \quad (31)$$

The three degrees of freedom omitted are the conserved quantities (constants of the motion): total energy, total angular momentum, and its projection along some space-fixed direction. This, in effect, factors out the delta functions[19] which conserve these quantities, so that Eqs. (29) and (30) give the S matrix "on the energy shell," as well as "on the total angular momentum shell."

The discussion in this section has been completely general and applies to systems of any number of degrees of freedom. The following section considers the details of applying these ideas to the A+BC collision.

III. ATOM-DIATOM COLLISIONS

The A+BC system in its center of mass has six degrees of freedom, but we choose canonical variables so that one degree of freedom corresponds to total angular momentum and another to its component along some space-fixed direction. Since the canonical momenta of these two degrees of freedom are conserved quantities, they appear in the classical Hamiltonian only as fixed *parameters*, and not as dynamical variables. The problem is thus reduced to four degrees of freedom.[20]

One way of choosing the four pair of canonical variables is[20]

$$\begin{aligned} p_1&=p_R, & q_1&=R,\\ p_2&=p_r, & q_2&=r,\\ p_3&=j, & q_3&=q_j,\\ p_4&=l, & q_4&=q_l; \end{aligned} \tag{32}$$

R and r are the radial coordinates of A with respect to BC and B with respect to C, respectively, and p_R and p_r are the corresponding radial momenta; j is the rotational angular momentum of BC, l is the orbital angular momentum of A with respect to BC, and q_j and q_l are angles (between 0 and 2π) conjugate to these angular momenta. In terms of these canonical variables the Hamiltonian is[20]

$$H(p,q)=(2\mu)^{-1}(p_R^2+l^2/R^2)+(2m)^{-1}(p_r^2+j^2/r^2) +v(r)+V(r,R,\gamma), \tag{33}$$

where μ and m are the translational and internal reduced masses

$$\mu=m_A(m_B+m_C)/(m_A+m_B+m_C),$$
$$m=m_Bm_C/(m_B+m_C),$$

$v(r)$ is the potential energy of the isolated BC molecule, $V(r,R,\gamma)$ is the interaction of A and BC [i.e., $v(r)+V$ is the total potential energy], and γ is the angle between the vectors $\mathbf{r}$ and $\mathbf{R}$ in which the interaction V is usually expressed. In terms of the canonical variables

$$\cos\gamma=\cos q_j\cos q_l+[(l^2+j^2-J^2)/2lj]\sin q_j\sin q_l, \tag{34}$$

where J is the total angular momentum (a fixed parameter in H).

The four momenta in Eq. (32), however, are not all appropriate for labeling the S-matrix elements. In particular, we would like a new set of canonical variables (P,Q) such that

$$\begin{aligned} P_1&=p_1=p_R,\\ P_2&=n,\\ P_3&=p_3=j,\\ P_4&=p_4=l, \end{aligned} \tag{35}$$

where n is the "vibrational quantum number" (which is continuous, of course, classically). To do this we introduce the vibration–rotation eigenvalue function $\mathcal{E}(n,j)$, defined implicitly by

$$(n+\tfrac{1}{2})\pi=\int_{r_<}^{r_>}dr\{2m[\mathcal{E}-v(r)]-j^2/r^2\}^{1/2}, \tag{36}$$

$r_<$ and $r_>$ being the zeros of the radicand. In practice one can assume that $\mathcal{E}(n,j)$ itself is known, for example, in the form of a Dunham expansion in powers of $(n+\frac{1}{2})$ and $(j+\frac{1}{2})$. Requiring the function is analogous to the situation in the quantum mechanical treatment of having to assume that the wavefunctions for the internal states are known.

The generator which effects the classical canonical transformation[15] from the (p,q) set of Eq. (32) to the (P,Q) set of Eq. (35) is

$$F_2(q,P)=q_1P_1+q_3P_3+q_4P_4 \pm\int_{r_<}^{q_2}dr\left\{2m[\mathcal{E}(P_2,P_3)-v(r)]-\frac{P_3^2}{r^2}\right\}^{1/2}. \tag{37}$$

Using the properties of this generator, one finds the Hamiltonian in terms of the new variables to be

$$H(p_Rnjl,Rq_nq_jq_l)=(2\mu)^{-1}(p_R^2+l^2/R^2) +\mathcal{E}(n,j)+V(r,R,\gamma), \tag{38}$$

with $r=r(n,j,q_n)$ determined by the equation

$$\cos^{-1}(\cos q_n) =m\frac{\partial\mathcal{E}(n,j)}{\partial n}\int_{r_<}^{r}dr'\left\{2m[\mathcal{E}(n,j)-v(r')]-\frac{j^2}{r'^2}\right\}^{-1/2}. \tag{39}$$

$\cos\gamma$ is given by Eq. (34) with the modification

$$q_j\rightarrow q_j-(-1)^{[q_n/\pi]}\int_{r_<}^{r(n,j,q_n)}dr'\left[m\frac{\partial\mathcal{E}(n,j)}{\partial j}-\frac{j}{r'^2}\right] \times\left\{2m[\mathcal{E}(n,j)-v(r')]-\frac{j^2}{r'^2}\right\}^{-1/2}, \tag{40}$$

where $[q_n/\pi]$ is the greatest integer function. The generalized coordinates q_n, q_j, q_l are angles (angle-action variables[11,12]) which have physical values[21] between 0 and 2π, and the corresponding momenta n,j,l are the quantum number labels for the S matrix. Integrating Hamilton's equations of motion [with the Hamiltonian of Eq. (38)] from t_1 (before collision) to t_2 (after collision) generates these four coordinates and

momenta as a function of time. From the general expression in Eq. (29) the S matrix in the (n,j,l) representation is

$$S_{n_2j_2l_2,n_1j_1l_1}(J) = [D/(2\pi i\hbar)^3]^{1/2} \exp[i\phi_{n_2j_2l_2,n_1j_1l_1}(J)/\hbar], \quad (41)$$

where the phase is

$$\phi_{n_2j_2l_2,n_1j_1l_1}(J) = -\int_{t_1}^{t_2} dt[R\dot{p}_R + q_n\dot{n} + q_l\dot{l} + q_j\dot{j}], \quad (42)$$

and the normalizing determinant D is given in terms of this phase by

$$D = \begin{vmatrix} \partial^2\phi/\partial n_2\partial n_1 & \partial^2\phi/\partial n_2\partial j_1 & \partial^2\phi/\partial n_2\partial l_1 \\ \partial^2\phi/\partial j_2\partial n_1 & \partial^2\phi/\partial j_2\partial j_1 & \partial^2\phi/\partial j_2\partial l_1 \\ \partial^2\phi/\partial l_2\partial n_1 & \partial^2\phi/\partial l_2\partial j_1 & \partial^2\phi/\partial l_2\partial l_1 \end{vmatrix}. \quad (43)$$

In subsequent discussion we shall concentrate attention on the phase since the normalization is derivable from it. As discussed at the end of Sec. II, the radial momentum p_R at t_2 and t_1 does not appear in the normalization since it is determined initially and finally by the other momenta and the total energy E.

In practice one must specify values for $n, j, l, R, q_n, q_j, q_l$ at time t_1, and classical mechanics determines their values at t_2 (E and J are fixed, and E determines p_R initially and finally). Keeping the initial momenta fixed at n_1, j_1, l_1, one varies the initial coordinates q_n, q_j, q_l and, in this way, generates all the possible values n_2, j_2, l_2 which can be reached from n_1, j_1, l_1. Analogous to Eq. (17), however, one can show that the phase of $\langle p_2 \mid S \mid p_1\rangle$ satisfies

$$\partial\phi(p_2,p_1)/\partial p_2 = -q_2, \quad (44a)$$

$$\partial\phi(p_2,p_1)/\partial p_1 = q_1, \quad (44b)$$

where q_1 and q_2 are the values determined classically by p_2 and p_1. From Eqs. (43) and (44b), therefore, one sees that the normalization D is equivalently given by the Jacobian of the final momenta with respect to the initial coordinates (at fixed initial momenta):

$$D^{-1} = \begin{vmatrix} \partial n(t_2)/\partial q_n(t_1) & \partial n(t_2)/\partial q_j(t_1) & \partial n(t_2)/\partial q_l(t_1) \\ \partial j(t_2)/\partial q_n(t_1) & \partial j(t_2)/\partial q_j(t_1) & \partial j(t_2)/\partial q_l(t_1) \\ \partial l(t_2)/\partial q_n(t_1) & \partial l(t_2)/\partial q_j(t_1) & \partial l(t_2)/\partial q_l(t_1) \end{vmatrix}. \quad (45)$$

This is the momentum-space analog of the normalization given by Pechukas,[22] and it has a simple physical interpretation:

$$\mid S_{n_2j_2l_2,n_1j_1l_1}(J,E) \mid^2$$

is the probability of n, j, l having the values n_2, j_2, l_2 at t_2, provided they have the values n_1, j_1, l_1 at t_1; but n_2, j_2, l_2 are uniquely related to the values of q_n, q_j, q_l at t_1. Therefore, $\mid S \mid^2$ is equal to the Jacobian in Eq. (45) times the probability that q_n, q_j, q_l have certain initial values. This probability is $1/(2\pi)^3$ since the three angles can have any value between 0 and 2π.

One further practical note: The limit $t_1 \to -\infty$, $t_2 \to +\infty$ is understood in Eq. (42). The limits have to be extended only so far, however, so that there is no further contribution to the integral which determines the phase. The fact that the four momenta are *constant* in the asymptotic region means that the form of the phase given by Eq. (42) has a natural cutoff to the time integration built in. One starts at t_1 with A and BC sufficiently far apart so that (p_R, n, j, l) are constant and integrates until after the collision they are once more constant—this determines t_2.

There is an alternative procedure for obtaining the phase given in Eq. (42). If Eqs. (39) and (40) prove too cumbersome in practice, then one can perform the numerical integration of Hamilton's equations in terms of the canonical variables of Eq. (32) and use the general transformation relations from Sec. II to transform to the canonical variables of Eq. (35). Equation (37) is the generator of this transformation, and the resulting expression for the phase of the S matrix is

$$\phi_{n_2j_2l_2,n_1j_1l_1}(J) = -\int_{t_1}^{t_2} dt[R\dot{p}_R + q_l\dot{l} + q_j\dot{j}]$$

$$+\int_{t_1}^{t_2} dt p_r\dot{r} - \mathrm{sgn}[p_r(t_2)]\int_{r_<}^{r_2} dr\{2m[\mathcal{E}_2 - v(r)] - j_2^2/r^2\}^{1/2}$$

$$+\mathrm{sgn}[p_r(t_1)]\int_{r_<}^{r_1} dr\{2m[\mathcal{E}_1 - v(r)] - j_1^2/r^2\}^{1/2}, \quad (46)$$

where $\mathcal{E}_2$ and $\mathcal{E}_1$ are the internal energies

$$(2m)^{-1}(p_r^2 + j^2/r^2) + v(r)$$

evaluated at t_2 and t_1, respectively; $p_R, p_r, j, l, R, r, q_j, q_l$ are determined as functions of t from Hamilton's equation with Hamiltonian of Eq. (33), and the values n_2 and n_1 are found by evaluating Eq. (36) with $\mathcal{E}$ and j equal to $\mathcal{E}_2$ and j_2, and $\mathcal{E}_1$ and j_1, respectively.

To use the quantum mechanical expression for the scattering amplitude given by Eq. (4) one must transform S from the above (n,j,l) representation to the (n,j,M) representation. This transformation can be carried out quantum mechanically, i.e.,

$$S_{n_2j_2M_2,n_1j_1M_1}(J) = \sum_{l_2,l_1} C(j_2Jl_2; M_2, -M_2) \times C(j_1Jl_1; M_1, -M_1)\, i^{l_2-l_1} S_{n_2j_2l_2,n_1j_1l_1}(J), \quad (47)$$

or classically [the C coefficients in Eq. (47) are Clebsch–Gordan coefficients[7]]. To effect the classical transformation, one requires the generator of the canonical transformation from the variables (p,q) to (P,Q), where $p \equiv p_R, n, j, l$ and $P = p_R, n, j, M$. This generator is

$$F_4(p,P) = q_1(P_1 - p_1) + q_2(P_2 - p_2) + q_3(P_3 - p_3) + f_4^J(M; jl), \quad (48)$$

where

$$f_4^J(M;jl) = -l\cos^{-1}\frac{M}{M_*} - M\cos^{-1}\left(\frac{l^2-J^2-j^2+2M^2}{2[(J^2-M^2)(j^2-M^2)]^{1/2}}\right) + j\cos^{-1}\left(\frac{M}{2lM_*}\frac{l^2+j^2-J^2}{(j^2-M^2)^{1/2}}\right) + J\cos^{-1}\left(\frac{M}{2lM_*}\frac{l^2+J^2-j^2}{(J^2-M^2)^{1/2}}\right), \quad (49)$$

with

$$M_* = (-l^4-J^4-j^4+2l^2j^2+2l^2J^2+2j^2J^2)^{1/2}/2l.$$

As an aside, we note that since this classical transformation must be equal to the classical limit of Eq. (47), one can identify the classical limit for the Clebsch–Gordan coefficient. The expression is

$$C(jJl;M,-M) = \left[\frac{2}{\pi}\frac{\partial^2 f_4^J(M;jl)}{\partial M\partial l}\right]^{1/2} \times\sin[\text{const}+f_4^J(M;jl)], \quad (50)$$

with f_4 defined in Eq. (49). The normalization is the usual result[23]

$$\partial^2 f_4/\partial M\partial l = (M_*^2-M^2)^{-1/2},$$

but the phase itself has defied other attempts[23] at derivation.

Using the generator above, one finds the Hamiltonian in terms of the new variables to be

$$H(p_R njM, Rq_n q_j q_M) = p_R^2/2\mu+\mathcal{E}(n,j) +[J^2+j^2-2M^2+2(J^2-M^2)^{1/2}(j^2-M^2)^{1/2}\cos q_M]/2\mu R^2 +V(r,R,\gamma), \quad (51)$$

where $r=r(n,j,q_n)$ is determined by Eq. (39), and $\cos\gamma$ is given in terms of the canonical variables by

$$\cos\gamma = (1-M^2/j^2)^{1/2}\cos q_j. \quad (52)$$

With the canonical variables determined by Hamilton's equations with the Hamiltonian in Eq. (51), the phase of S in the (n,j,M) representation is

$$\phi_{n_2j_2M_2,n_1j_1M_1}(J) = -\int_{t_1}^{t_2} dt[R\dot{p}_R+q_n\dot{n}+q_j\dot{j}+q_M\dot{M}], \quad (53)$$

and the normalization is given by a determinant similar to Eq. (43) or (45) (with l replaced by M).

The following question now arises: In which representation should the classical approximation to S be made? One can compute S classically in the (n,j,l) representation and transform to the (n,j,M) representation quantum mechanically [Eq. (47)], or one can compute S classically directly in the (n,j,M) representation. The obvious answer (or nonanswer) to this question is that one should make the classical approximation to S in that representation in which S is most nearly classical—i.e., in that representation in which the *magnitude* of S is most slowly varying. There may be some reason for believing S to be more classical-like in the (n,j,l) representation; that is, the centrifugal potential is diagonal in this representation, but not in the (n,j,M) representation. There may be situations, therefore, in which the classical approximation to S in the (n,j,l) representation is accurate, but much less accurate in the (n,j,M) representation. In such cases one should compute S in the (n,j,l) representation and transform quantum mechanically to the (n,j,M) representation.

With regard to the scattering amplitude itself, one can proceed to evaluate the integral over J in Eq. (4) using many of techniques already established in potential scattering. With the classical approximation to S in the (n,j,M) representation the amplitude is

$$f_{n_2j_2M_2\leftarrow n_1j_1M_1}(\theta) = (2ik_1)^{-1}\int_0^\infty dJ(2J+1)\,|\,S_{n_2j_2M_2,n_1j_1M_1}(J)\,| \times d_{M_2M_1}^J(\theta)\exp[i\phi_{n_2j_2M_2,n_1j_1M_1}(J)/\hbar], \quad (54)$$

and the WKB approximation for the rotation matrix[23] is

$$d_{M_2M_1}^J(\theta) = [\tfrac{1}{2}\pi\sin\theta k(\theta)]^{-1/2} \times\sin[\tfrac{1}{4}\pi+M_2\pi+W_{M_2M_1}^J(\theta)], \quad (55)$$

where

$$W_{M_2M_1}^J(\theta) = J\cos^{-1}\left(\frac{J^2\cos\theta-M_2M_1}{(J^2-M_2^2)^{1/2}(J^2-M_1^2)^{1/2}}\right) -M_2\cos^{-1}\left(\frac{M_2\cos\theta-M_1}{\sin\theta(J^2-M_2^2)^{1/2}}\right) -M_1\cos^{-1}\left(\frac{M_1\cos\theta-M_2}{\sin\theta(J^2-M_1^2)^{1/2}}\right), \quad (56)$$

$$k(\theta) = \left(J^2-\frac{M_2^2+M_1^2-2M_2M_1\cos\theta}{\sin^2\theta}\right)^{1/2}. \quad (57)$$

The sine function can be expanded as the sum of two exponentials and the integral over J done by stationary phase. The stationary phase condition is

$$\frac{d[\phi_{n_2j_2M_2,n_1j_1M_1}(J)\pm W_{M_2M_1}^J(\theta)]}{dJ} = 0,$$

and leads to the equation

$$\Theta_{n_2j_2M_2,n_1j_1M_1}(J) = \pm\theta, \quad (58)$$

where the classical deflection function is defined by

$$\Theta_{n_2j_2M_2,n_1j_1M_1}(J) = \pm\cos^{-1}\left[\frac{M_2M_1}{J^2} +\left(1-\frac{M_2^2}{J^2}\right)^{1/2}\left(1-\frac{M_1^2}{J^2}\right)^{1/2}\cos\phi_{n_2j_2M_2,n_1j_1M_1}'(J)\right]. \quad (59)$$

This is the generalization of the relation[24]

$$\Theta(J)=2\eta'(J)$$

from potential scattering. Also, as in potential scattering, there may be more than one value of J which satisfies the stationary phase relation in Eq. (58); this will lead, in the analogous manner, to interferences and rainbows. The interferences may be substantially damped, however, because the *magnitude* of S will be different at the different stationary J values. If $J_0(\theta)$ is one root of Eq. (58), then the contribution to the scattering amplitude associated with this root is

$$|S_{n_2j_2M_2,n_1j_1M_1}(J)|J^{1/2}[k_1\Theta_{n_2j_2M_2,n_1j_1M_1}'(J)\times\sin\theta(1-M_2^2/J^2)^{1/2}(1-M_1^2/J^2)^{1/2}]^{-1/2}\times\exp\{i[\text{const}+\phi_{n_2j_2M_2,n_1j_1M_1}(J)\pm W_{M_2M_1}{}^J(\theta)]\}$$

evaluated at $J=J_0(\theta)$. If two points of stationary phase are close to one another, the usual special approximations (or uniform approximations) must be used to evaluate the integral over J.

Another (and more direct) way of obtaining the deflection function of Eq. (59) is to use the fact that the phase derivative $\phi'(J)$ is related[20] to the coordinate conjugate to the total angular momentum J. This fact is not needed for integrating the equations of motion because J is constant, but once the trajectories are computed one can use the fact that

$$\phi_{n_2j_2M_2,n_1j_1M_1}'(J)=\pi-\int_{t_1}^{t_2}dt\,\frac{\partial H}{\partial J}, \tag{60}$$

and with Eq. (51) this becomes

$$\phi_{n_2j_2M_2,n_1j_1M_1}'(J)=\pi-\frac{J}{\mu}\int_{t_1}^{t_2}dtR^{-2}\times\left[1+\left(\frac{j^2-M^2}{J^2-M^2}\right)^{1/2}\cos q_M\right]; \tag{61}$$

computing $\phi'(J)$ in this manner avoids numerical differentiation. The deflection function is still given by Eq. (59).

IV. REARRANGEMENTS

The first modification necessary to include rearrangement processes (e.g., A+CB→AC+B) in the semiclassical framework is that the *operator* S itself must have labels which denote the initial and final arrangement; e.g.,

$$S_{ba}=\exp[iH_bt_2/\hbar]\exp[-iH(t_2-t_1)/\hbar]\times\exp[-iH_at_1/\hbar], \tag{62}$$

$t_2\to+\infty$, $t_1\to-\infty$, where $H_a(H_b)$ is the unperturbed Hamiltonian for the initial (final) arrangement. The generalized momenta that label S_{ba} on the b side (a side) must be constants of the motion of $H_b(H_a)$. Denoting these generalized momenta by p^b and p^a, respectively, one has

$$\langle p_2{}^b|S_{ba}|p_1{}^a\rangle=\exp[iE(t_2-t_1)/\hbar]\times\langle p_2{}^b|\exp[-iH(t_2-t_1)/\hbar]|p_1{}^a\rangle. \tag{63}$$

If we introduce the generator of the classical canonical transformation from variables (p^a, q^a) to (p^b, q^b), then the general transformation relations of Sec. II imply that the phase of S_{ba} is

$$\phi_{ba}(p_2{}^b, p_1{}^a)=F_4(p_2{}^b, p_2{}^a)-\int_{t_1}^{t_2}dtq^a\dot{p}^a, \tag{64}$$

with $p^a(t)$ and $q^a(t)$ determined by Hamilton's equations. This result is not satisfactory, however, since $\dot{p}^a$ does *not* become constant as $t_2\to+\infty$. By using the general relation in Eq. (25), however, one can show that the phase is equivalently given by

$$\phi_{ba}(p_2{}^b, p_1{}^a)=F_4[p^b(\bar{t}), p^a(\bar{t})]-\int_{t_1}^{\bar{t}}dtq^a\dot{p}^a-\int_{\bar{t}}^{t_2}dtq^b\dot{p}^b. \tag{65}$$

Equation (25) may be used to show that the phase given by Eq. (65) is independent of what intermediate time is chosen for $\bar{t}$, but for practical reasons one should choose it at some value midway in the rearrangement process. The time derivatives in the integrand of Eq. (65) *do* vanish as $t_2\to+\infty$, $t_1\to-\infty$. The physical significance of the three terms is the phase accumulated along the trajectory in arrangement a, that in arrangement b, and the phase associated with the rearrangement of canonical variables.

All of the details discussed in previous sections concerning various choices of canonical variables apply here. The total angular momentum enters just as in the nonrearrangement case, as a fixed parameter in the Hamiltonian. From the phase in Eq. (65), the S-matrix elements are constructed as in Sec. III. It is necessary, therefore, to determine explicitly the generator of the rearrangement, $F_4(p^b, p^a)$. One way of doing this is to take the classical limit of the corresponding quantum mechanical matrix element

$$\langle p^b|p^a\rangle\sim\exp[iF_4(p^b, p^a)/\hbar]. \tag{66}$$

With J fixed and $p^b\equiv p_{R_b}, n_b, j_b, M_b$, $p^a\equiv p_{R_a}, n_a, j_a, M_a$, the quantum mechanical expression is

$$\langle p^b|p^a\rangle=(2\pi\hbar)^{-1}\int_0^\infty dR_a\int_0^\infty dR_b\exp\left(\frac{i(R_ap_{R_a}-R_bp_{R_b})}{\hbar}\right)\times\Delta_{n_bj_bM_b,n_aj_aM_a}{}^J(R_b, R_a), \tag{67}$$

where Δ is the kernel which appears in the quantum mechanical atom–diatom rearrangement problem.[25]

In the (n, j, M) representation it is

$$\Delta_{n_b j_b M_b, n_a j_a M_a}{}^{J}(R_b, R_a) = R_b R_a \int_0^{\pi} d\gamma_{ba} u_{n_b j_b}(r_b) u_{n_a j_a}(r_a) \times \psi_{j_b M_b}(\gamma_b) \psi_{j_a M_a}(\gamma_a) d_{M_b M_a}{}^{J}(\gamma_{ba}), \quad (68)$$

where u_{nj} are vibrational eigenfunctions, $\psi_{jM}(\gamma) \equiv (2\pi)^{1/2} Y_{jM}(\gamma, 0)$ are rotational eigenfunctions, and the variables r_a, r_b, γ_a, γ_b are functions of R_a, R_b, and γ_{ba} given in Ref. 25. To obtain the classical limit of Eq. (67), one uses WKB wavefunctions for the vibrational and rotational wavefunctions and for the rotation matrix, and the integrals over R_a, R_b, and γ_{ba} are evaluated by stationary phase. The result is that one can identify the generator as

$$\begin{aligned} F_4(p^b, p^a) = {} & p_{R_a} R_a - p_{R_b} R_b \\ & + \int_{r_<}^{r_a} dr \left\{ 2m_a [\mathcal{E}_a(n_a, j_a) - v_a(r)] - \frac{j_a^2}{r^2} \right\}^{1/2} \\ & - \int_{r_<}^{r_b} dr \left\{ 2m_b [\mathcal{E}_b(n_b, j_b) - v_b(r)] - \frac{j_b^2}{r^2} \right\}^{1/2} \\ & + j_a \cos^{-1}\left(\frac{j_a \cos\gamma_a}{(j_a^2 - M_a^2)^{1/2}} \right) - M_a \cos^{-1}\left(\frac{M_a \cot\gamma_a}{(j_a^2 - M_a^2)^{1/2}} \right) \\ & - j_b \cos^{-1}\left(\frac{j_b \cos\gamma_b}{(j_b^2 - M_b^2)^{1/2}} \right) + M_b \cos^{-1}\left(\frac{M_b \cot\gamma_b}{(j_b^2 - M_b^2)^{1/2}} \right) \\ & + J \cos^{-1}\left(\frac{J^2 \cos\gamma_{ba} - M_b M_a}{(J^2 - M_b^2)^{1/2} (J^2 - M_a^2)^{1/2}} \right) \\ & - M_b \cos^{-1}\left(\frac{M_b \cos\gamma_{ba} - M_a}{\sin\gamma_{ba} (J^2 - M_b^2)^{1/2}} \right) \\ & - M_a \cos^{-1}\left(\frac{M_a \cos\gamma_{ba} - M_b}{\sin\gamma_{ba} (J^2 - M_a^2)^{1/2}} \right), \end{aligned} \quad (69)$$

where r_a, r_b, γ_a, γ_b are functions[25] of R_a, R_b, γ_{ba}, and where R_a, R_b, γ_{ba} have specific values determined by the stationary phase requirements

$$\frac{\partial F_4}{\partial R_a} = \frac{\partial F_4}{\partial R_b} = \frac{\partial F_4}{\partial \gamma_{ba}} = 0.$$

ACKNOWLEDGMENTS

This research has been supported in part by grants from the Research Corporation and the Petroleum Research Fund of the American Chemical Society.

APPENDIX A: NORMALIZATION OF UNITARY OPERATORS IN THE CLASSICAL LIMIT

Here we show how the normalization of the transformation elements in Eq. (11), or that of any unitary operator, is obtained. Suppose $U(x, y)$ is a "matrix" (with continuous indices x and y) of the form

$$U(x, y) = A(x, y) \exp[i\phi(x, y)/\hbar], \quad (A1)$$

where $\phi(x, y)$ is real and assumed known. The task is to determine the function A so that U is unitary; i.e., we demand

$$\int dx U(x, y) U(x, y')^* = \delta(y - y'), \quad (A2)$$

$$\int dy U(x, y) U(x', y)^* = \delta(x - x'). \quad (A3)$$

Considering Eq. (A2), for example, the requirement is that

$$\delta(y - y') = \int dx A(x, y) A(x, y')^* \times \exp\{i[\phi(x, y) - \phi(x, y')]/\hbar\}. \quad (A4)$$

In the classical limit, which we are considering, $\hbar \to 0$ so that the phase in the integrand is infinitely oscillatory except for $y \sim y'$. Expanding

$$\phi(x, y') \simeq \phi(x, y) + (y' - y)[\partial\phi(x, y)/\partial y],$$

Eq. (A4) becomes

$$\delta(y - y') = \int dx \, | A(x, y) |^2 \times \exp\left[- \frac{i(y' - y)[\partial\phi(x, y)/\partial y]}{\hbar} \right], \quad (A5)$$

where we have set $y' = y$ in A. For fixed y, the function $w(x)$ is defined by

$$w(x) = \frac{\partial\phi(x, y)/\partial y}{\hbar},$$

and *if* $w(x)$ *is monotonic*, then a change of variables in Eq. (A5) is possible,

$$\delta(y - y') = \int dw \frac{| A(x, y) |^2}{| dw/dx |} \exp[-iw(y' - y)]. \quad (A6)$$

A well-known representation of the delta function, however, is

$$\delta(y - y') = (2\pi)^{-1} \int dw \exp[-iw(y' - y)], \quad (A7)$$

so that by comparing the integrands of Eqs. (A6) and (A7), one identifies

$$| A(x, y) | = (2\pi)^{-1/2} | dw/dx |^{1/2},$$

or from the definition of w, one finally obtains

$$| A(x, y) | = \left| \frac{1}{2\pi\hbar} \frac{\partial^2\phi(x, y)}{\partial x \partial y} \right|^{1/2}. \quad (A8)$$

Equation (A8) is the most that can be deduced about the normalization in a general manner. It is clear that one can take it to be real and positive, any phase being absorbed in ϕ. It is customary, however, to assign it a constant, nonzero phase, as in Eq. (11). Clearly, no physical quantity depends on a constant over-all phase.

In the above derivation it was necessary to require that $\partial^2\phi/\partial x\partial y$ not be zero or singular for any values of the variables. The implications of this are most easily seen by considering a physical example, such as the momentum representation of the propagator. From Eq. (44b), one sees that

$$\frac{\partial^2\phi(p_2, p_1)}{\partial p_2 \partial p_1} = \left(\frac{\partial q_1}{\partial p_2}\right)_{p_1} = \left[\left(\frac{\partial p_2}{\partial q_1}\right)_{p_1}\right]^{-1}, \qquad \text{(A9)}$$

so that the requirement that the normalization be nonsingular is equivalent to the requirement that only one particular value of q_1 leads to the final momentum p_2 (for a given p_1)—i.e., that there is only one classical path connecting p_1 to p_2. There may be cases, however, for which there is more than one classical path connecting p_1 and p_2. In such cases the S matrix is the sum of the several terms (all of the usual form) corresponding to each classical path that connects p_1 and p_2.[10] The question then arises as to the *relative* phase of the several terms. Pechukas[22] has considered this problem for the case of potential scattering, and it is clear that the solution in the general case is the straightforward extension of his result. Namely, that each term adds a phase of $\frac{1}{2}\pi$ every time the quantity $(\partial p_2/\partial q_1)_{p_1}$ changes sign (i.e., passes through zero) in the time interval (t_1, t_2). This result will only be useful, however, if the two values of q_1, say, which lead to the same value of p_2 are "well separated" (isolated points of stationary phase). If this criterion is not met, then one must either transform to a different set of canonical variables for which this nonunique relationship between p_2 and q_1 (at fixed p_1) does not exist, or return to the path integral expression for the propagator[10] and go beyond the classical approximation in evaluating it.

APPENDIX B: ELIMINATION OF TIME AND REDUCTION TO SIXTH ORDER

We consider the Hamiltonian in the (n, j, l) representation as given in Eq. (38); in this Appendix, we refer to (p_R, R) explicitly and denote the internal degrees of freedom $[(n, q_n), (j, q_j)$, and $(l, q_l)]$ by (p_i, q_i). The plan is to eliminate the variable t in the equations of motion in favor of the variable R. Hamilton's equations give the R versus t relation as

$$dR/dt \equiv \dot{R} = \partial H/\partial p_R = p_R/\mu, \qquad \text{(B1)}$$

but since p_R changes sign during the collision, the over-all trajectory must be broken up into segments in each of which p_R is of one sign. This is necessary for $t(R)$, the inverse function of $R(t)$, to be single valued in each segment.

The first segment, for example, is the time interval (t_1, t_2), where $t_1 \to -\infty$, and t_2 is that time at which p_R experiences its first zero (i.e., a classical turning point). With $R(t)$ and $t(R)$ specified by Eq. (B1), we regard p_i and q_i as functions of R; e.g.,

$$q_i(t) = q_i(t(R)) \equiv q_i(R).$$

The R dependence is determined by the equations

$$\frac{dq_i}{dR} \equiv q_i'(R) = \frac{dq_i}{dt}\frac{dt}{dR} = \dot{q}_i \frac{dt}{dR},$$

or with $\dot{q}_i$ given by Hamilton's equations and dt/dR from Eq. (B1), one has

$$q_i'(R) = (\partial H/\partial p_i)(\mu/p_R). \qquad \text{(B2)}$$

Similarly, the equation determining $p_i(R)$ is

$$p_i'(R) = -(\partial H/\partial q_i)(\mu/p_R). \qquad \text{(B3)}$$

The R dependence of p_R itself can be determined by using the fact that $H(p, q)$ is time independent, i.e.,

$$H(p, q) = E. \qquad \text{(B4)}$$

H is such a simple function of p_R that one can solve Eq. (B4) for p_R as a function of (R, q_i, p_i) and the fixed parameter E:

$$p_R = -\{2\mu[E - \mathcal{E}(n, j) - V(r, R, \gamma)] - l^2/R^2\}^{1/2}, \qquad \text{(B5)}$$

with the minus sign appropriate to the present (first) segment of the trajectory. Substituting the above equation for p_R into Eqs. (B2) and (B3) provides expressions for $q_i'(R)$ and $p_i'(R)$ which are functions only of (R, q_i, p_i); E and J are fixed parameters, of course, which also appear. With values of q_i and p_i specified at $R_1(\to +\infty)$, these equations can be numerically integrated inward in R until R_2 is reached, at which $p_R = 0$. This determines the values of (q_i, p_i) at R_2 which serve as the initial values of these six variables for numerical integration outward in R in the next segment. In this second segment $p_R > 0$, so that the sign in Eq. (B5) is changed when the p_R expression is substituted into Eqs. (B2) and (B3) to obtain the equations of motion in segment two.

In most cases p_R will probably change sign only once (from minus to plus); however, it is possible for p_R to change sign several times. In any event, it is clear that there must be an *odd* number of sign changes (i.e., an *even* number of segments). The contribution to the phase of the S matrix from each segment is easily given in terms of the new independent variable R by changing integration variables in Eq. (42). One has

$$dt\dot{p}_i \equiv dt(dp_i/dt) = dRp_i'(R),$$

so it is easy to rewrite Eq. (42) in terms of R as the integration variable.

To summarize the outcome of the over-all procedure, the phase of the S matrix is given by

$$\phi_{n_2 j_2 l_2, n_1 j_1 l_1}(J, E) = \sum_{s=1}^{M} \phi_s, \qquad \text{(B6)}$$

where M is an even number ($M-1$ is the number of zeros of p_R in the complete trajectory); (n_1, j_1, l_1) are the initial values of (n, j, l); and (n_2, j_2, l_2), the final values. In each segment $s(n, j, l, q_n, q_j, q_l)$ are known at

R_s and are determined at $R_{s+1}(R_1,\ R_{M+1}\to\infty)$ by integrating the following Hamilton-like equations

$$q_i'(R)=(-1)^s(\partial H/\partial p_i)\times\mu\{2\mu[E-\mathcal{E}(n,j)-V]-l^2/R^2\}^{-1/2},\quad \text{(B7)}$$

$$p_i'(R)=-(-1)^s(\partial H/\partial q_i)\times\mu\{2\mu[E-\mathcal{E}(n,j)-V]-l^2/R^2\}^{-1/2},\quad \text{(B8)}$$

with r and $\cos\gamma$ (in V) the same functions of $(p_i,\ q_i)$ as in Sec. III. The phase ϕ_s accumulated in segments s is

$$\phi_s=(-1)^s\int_{R_s}^{R_{s+1}}dR\mu\left(2\mu[E-\mathcal{E}(n,j)-V]-\frac{l^2}{R^2}\right)^{-1/2}\times\left[R\frac{d}{dR}\left(\mathcal{E}(n,j)+V+\frac{l^2}{2\mu R^2}\right)+q_n\frac{\partial V}{\partial q_n}+q_j\frac{\partial V}{\partial q_j}+q_l\frac{\partial V}{\partial q_l}\right].\quad \text{(B9)}$$

An equivalent expression for ϕ_s is

$$\phi_s=-R\left(2\mu[E-\mathcal{E}(n,j)-V]-\frac{l^2}{R^2}\right)^{1/2}\Bigg|_{R=R_s}(\delta_{1,s}+\delta_{M,s})+\int_{R_s}^{R_{s+1}}dR\left[(-1)^s\left(2\mu[E-\mathcal{E}(n,j)-V]-\frac{l^2}{R^2}\right)^{1/2}-q_n(R)n'(R)-q_j(R)j'(R)-q_l(R)l'(R)\right].\quad \text{(B10)}$$

This completes the reduction. Equations (B7) and (B8) are the six first-order coupled differential equations which must be integrated numerically to determine $q_i(R)$ and $p_i(R)$, and then the phase is computed via Eqs. (B6)–(B10). The reader will probably recognize many similarities between the above expression for the phase and the usual expression for the WKB phase shift in potential scattering[1]. This analogy, of course, was the motivation for developing the above procedure.

An alternative method for reducing the equations of motion to sixth order is by use of the Hamilton–Jacobi equation.[16,26] This is not particularly useful for our purposes, however, for it (like the Schrödinger equation) is a *partial* differential equation and, therefore, cannot be integrated numerically. Also, the solution of the Hamilton–Jacobi has a complicated multivalued structure.[26] The above Eqs. (B7) and (B8) have the virtue of being *ordinary* differential equations and thus numerically integrable. The fact that the trajectory must be broken up into segments is related to the multivalued character of the solution of the Hamilton–Jacobi equation. This feature is handled much more easily in the above framework of ordinary differential equations which proceed stepwise along the trajectory, than via the Hamilton–Jacobi partial differential equation which essentially considers the entire path at once.

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