Theory of Semiclassical Transition Probabilities (S Matrix) for Inelastic and Reactive Collisions. Uniformization with Elastic Collision Trajectories*

R. A. MARCUS
Department of Chemistry, University of Illinois, Urbana, Illinois 61801

(Received 9 September 1971)

A canonical transformation is described for uniformizing the coordinates used in Paper I of this series. For comparison with the results of Paper III, which based a uniformization on exact trajectories, the present article describes one based on elastic collision trajectories. The question of invariance of S-matrix elements with respect to semiclassical unitary transformations is also discussed.

I. INTRODUCTION

In an earlier paper,[1] hereinafter referred to as Paper III, we showed that all coordinates, including the radial motion, could be uniformized by a canonical transformation of the coordinates of Paper I.[2] It led to new coordinates, one of which was time and the others were constants of the motion. When this canonical transformation was of a symmetrical form it led to an integral expression for S_{mn} satisfying microscopic reversibility. The canonical transformation was made using exact classical trajectories.

Prior to that work and leading to it, we had investigated the possibility of generating a transformation using trajectories for elastic collisions. The results for S_{mn} are presented here for comparison purposes. In this comparison we employ a transformation which parallels that termed "TVR" in Paper III. An analogous derivation can be given paralleling the transformation labeled "FVR," but is omitted in the interests of brevity.

II. CANONICAL TRANSFORMATION AND THE WAVEFUNCTION

Again, in the interests of brevity, a familiarity with the methods employed in Paper III will be assumed. The symbols used there will be employed here. The equations of Paper III will be indicated by a prefix III.

Instead of the generating function $G_2(q,\bar{p})$ used in (III.4.6) to relate new variables $(\bar{q},\bar{p})$ to the variables (q,p) of Paper I [a $G_2(q,\bar{p})$ based on the exact trajectories], we use now a $G_2(q,p)$ based on any elastic collision. The properties of the latter are denoted by a tilde, and the turning point of the R motion in this elastic collision (for the instantaneous $\bar{E}$ and $\bar{n}$) is $\tilde{R}^T(\bar{E},\bar{n},w,R)$:

$$G_2(wR,\bar{n}\bar{E})=\sum_{i=1}^{\tau}\bar{n}_i hw_i+\int_{\tilde{R}^T}^{R}\tilde{p}_R(\tilde{R},\bar{n},\bar{E})d\tilde{R},\quad (2.1)$$

where $\bar{E}$ is obtained from the instantaneous p_R, R, and $\bar{n}_i$ by

$$\bar{E}=(p_R^2/2\mu)+V(R)+H_0^{\text{int}}(\bar{n},R).\qquad(2.2)$$

$H_0^{\text{int}}(\bar{n},R)$ is the "internal coordinate" Hamiltonian for the elastic collision, but it also includes any centrifugal potential $(n_1+\frac{1}{2})^2\hbar^2/2\mu R^2$. ($\bar{n}_1$ describes the orbital motion.) $V(R)$ is the potential energy for an elastic collision. The integral in (2.1) is evaluated along the elastic collision trajectory passing through (wR), $\tilde{p}_R(\tilde{R},\bar{n},\bar{E})$ being

$$\tilde{p}_R(\tilde{R},\bar{n},\bar{E})=\pm\{2\mu[\bar{E}-H_0^{\text{int}}(\bar{n},\tilde{R})-V(\tilde{R})]\}^{1/2},$$
$$\tilde{p}_R(\tilde{R}^T,\bar{n},\bar{E})=0.\qquad(2.3)$$

The minus sign in (2.3) refers to the ingoing portion of the trajectory.

Using the Eq. (III.4.2) for the transformation, Eqs. (2.1)–(2.3) yield the new coordinates $(\bar{w}\tau)$:

$$\bar{w}_i=\frac{\partial G_2}{\partial(\bar{n}_i h)}=w_i-\int_{\tilde{R}^T}^{R}\left(\frac{\mu\nu_i^0}{\tilde{p}_R(\tilde{R},\bar{n},\bar{E})}\right)d\tilde{R},\quad(2.4\text{a})$$

$$\tau=\frac{\partial G_2}{\partial\bar{E}}=\int_{\tilde{R}^T}^{R}\left(\frac{\mu}{p_R(\tilde{R},\bar{n},\bar{E})}\right)d\tilde{R},\qquad(2.4\text{b})$$

where ν_i^0 is $\partial H_0^{\text{int}}(\bar{n},R)/\partial(\bar{n}_i h)$, the mechanical frequency for the ith degree of freedom. Equation (2.1) also yields, from (III.4.2),

$$p_R=\partial G_2/\partial R=\tilde{p}_R(R,\bar{n},\bar{E}).\qquad(2.4\text{c})$$

Since $d\tau$ equals $(\mu/p_R)dR$, (2.4a) can be rewritten suggestively as

$$\bar{w}_i=w_i-\int_0^{\tau}\nu_i^0 d\tau,\qquad(2.4\text{d})$$

where τ is given by (2.4b) as a function of the instantaneous w, R, $\bar{n}$, and $\bar{E}$. ($\tilde{R}^T$ is a function of w, R, $\bar{n}$, and $\bar{E}$.) Equation (2.4d) shows that for an elastic collision $\bar{w}_i$ is a constant of the motion, equal to the value of w_i at the turning point.[3] For the same elastic collision trajectory, τ is the time, measured relative to the time at the turning point of that trajectory.

From (2.4c) it follows that $\tilde{p}_R$ equals the instantaneous value of p_R along the classical collision trajectory of the system. From (2.2) and (2.4c) it then follows that only at large R does $\bar{E}$ reduce to the total energy E.

In summary, the canonical transformation resulting from the generating function (2.1) utilizes the classical trajectory for an elastic collision to relate (q,p) to $(\bar{q},\bar{p})$, and the transformation equations are given by (2.4). One can verify from these equations that at large R along the trajectory of the actual system, $\bar{w}_i$ is a constant (unlike w_i or R) and that τ is, apart from an additive constant, the time variable at large R, along each arm of the actual trajectory.

Equations (III.4.3)–(III.4.5) for the wavefunction $\bar{\psi}_{nE}^{(+)}(\bar{w}\tau)$ in the new representation remain applicable here:

$$\bar{\psi}_{nE}^{(+)}(\bar{w}\tau) = \bar{A}\exp[i\bar{S}(\bar{w}\tau, nE)/\hbar], \quad (2.5)$$

where

$$\bar{S}(\bar{q}, p^0) = S(q, p^0) - G_1(q, \bar{q}), \quad (2.6)$$

$$G_1(q, \bar{q}) = G_2(q, \bar{p}) - \sum_{i=1}^{r+1} \bar{q}_i \bar{p}_i, \quad (2.7)$$

but now G_2 is given by (2.1). p^0 denotes

$$(n_1 h, \cdots, n_r h, E).$$

Using these equations and a line of argument paralleling that employed in Paper III one finds that $\bar{S}$ is

$$\frac{\bar{S}(\bar{w}\tau, nE)}{\hbar} = 2\pi \sum_{i=1}^{r} \left(\bar{n}_i \bar{w}_i - \int_{n_i}^{\bar{n}_i} w_i d\bar{n}_i \right) + \left(\frac{\bar{E}\tau}{\hbar} \right)$$

$$- \int_{-k_n}^{k} R dk + \int_0^{k} \tilde{R}(\bar{E}, \bar{n}, \tilde{k}) d\tilde{k} + \tfrac{1}{2} n_1 \pi + (\tfrac{1}{2}\pi) \quad (2.8)$$

instead of by Eq. (III.4.12). The $+(\frac{1}{2}\pi)$ term is present if (wR) is on the outgoing arm of a trajectory. The integrals over $\bar{n}_i$ and k are along the exact trajectory passing through (wR), while that over $\tilde{k}$ is along the indicated elastic collision trajectory passing through (wR) and having a constant $\bar{n}_i$ equal to the instantaneous $\bar{n}_i$ of the actual trajectory and a $\tilde{p}_R$ at (wR) equal to the instantaneous p_R.

The relation between the total energy E and the variables $\bar{n}_i$ and $\bar{E}$ is seen from (2.2) to be

$$E = \bar{E} + H_1, \qquad \partial E/\partial \bar{E} = 1 + \partial H_1/\partial \bar{E}, \quad (2.9)$$

where H_1 is the perturbation energy, i.e., the part of Hamiltonian not present in (2.2), and is expressed as a function of $(\bar{w}\tau\bar{n}\bar{E})$ using the transformation of variables given by (2.4).

Using Eq. (III.5.2) to obtain the amplitude $\bar{A}$ from $\bar{S}$, or using flux conservation, one finds that

$$\bar{A} = | \partial \bar{w}_i / \partial \bar{w}_j^0 |^{-1/2} (\partial E/\partial \bar{E})^{-1/2} h^{-1/2}, \quad (2.10)$$

where $\bar{w}_j^0$ is the initial value of $\bar{w}_j$ and where $\bar{A}$ can be complex valued and so $|\ |$ does not denote absolute value. Because of (III.5.2) the present $\bar{\psi}$ satisfies the same conditions of normalization, orthogonality, and completeness as those given there.

III. S MATRIX

The expression to be evaluated for the S-matrix S_{mn} is, as in (III.2.4),

$$S_{mn}\delta(E-E') = \int \bar{\psi}_{mE'}^{(-)*}(\bar{w}\tau) \bar{\psi}_{nE}^{(+)}(\bar{w}\tau) d\tau \prod_i d\bar{w}_i. \quad (3.1)$$

The expression for the phase $\bar{S}$ of $\bar{\psi}_{nE}^{(+)}$ is given by (2.8). Using the time-reversal arguments in Paper III the phase $\bar{S}^{(-)}(\bar{w}\tau, mE')$ is given by

$$\frac{\bar{S}^{(-)}(\bar{w}\tau, mE')}{\hbar} = 2\pi \sum_i \left(\bar{m}_i \bar{w}_i - \int_{m_i}^{\bar{m}_i} w_i d\bar{m}_i \right)$$

$$+ \left(\frac{\bar{E}'\tau}{\hbar} \right) - \int_{k_m}^{k} R dk + \int_0^{k} \tilde{R} d\tilde{k} - \tfrac{1}{2} m_1 \pi - (\tfrac{1}{2}\pi) \quad (3.2)$$

instead of (III.6.4). $\bar{A}^{(-)}$ is given by an equation similar to (2.10) but referring to the time-reversed m trajectory.

Equations (3.1), (3.2), and (2.8) yield

$$S_{mn}\delta(E-E') = \int \bar{A}\bar{A}^{(-)} \exp i\Delta' d\tau \prod_i d\bar{w}_i, \quad (3.3)$$

where

$$\Delta' = \bar{S}(\bar{w}\tau, nE) - \bar{S}^{(-)}(\bar{w}\tau, mE'). \quad (3.4)$$

Whereas in Paper III the τ integral could be evaluated exactly, yielding a δ function, this is no longer the case for (3.3), since now the $\bar{m}_i$ and k in the upper limits in (2.8) and (3.2) vary with τ. We give two approximate evaluations, which preserve the microscopic reversibility obeyed by (3.1):

(1) Apart from the $(\bar{E}-\bar{E}')\tau/\hbar$ term in Δ', the remaining portion of Δ' has only a slight dependence on τ, attaining constant values at $\tau = \pm\infty$. $\bar{A}\bar{A}^{(-)}$ also attains constant values at $\tau = \pm\infty$. If one integrates over τ the term involving $(E-\bar{E}')\tau/\hbar$, using a result[4] relating $\delta(\bar{E}-\bar{E}')$ to $\delta(E-E')$, one finds

$$S_{mn} = \int | \partial \bar{w}_i(n)/\partial \bar{w}_j^0 |^{-1/2} | \partial \bar{w}_i(m)/\partial \bar{w}_j^0 |^{-1/2} \times (\exp i\Delta) \prod_i d\bar{w}_i, \quad (3.5)$$

where

$$\Delta = 2\pi \sum_i \left[(\bar{n}_i - \bar{m}_i)\bar{w}_i - \int_{n_i}^{\bar{n}_i} w_i d\bar{n}_i - \int_{\bar{m}_i}^{m_i} w_i d\bar{m}_i \right]$$

$$- \int_{-k_n}^{k(n)} R dk - \int_{k(m)}^{k_m} R dk + \int_0^{k(n)} \tilde{R} d\tilde{k} - \int_0^{k(m)} \tilde{R} d\tilde{k} + \tfrac{1}{2}(n_1 + m_1 + 1)\pi, \quad (3.6)$$

where the (n) and (m) have been introduced, as in Paper III, to indicate the n and m trajectories. The $\bar{n}_i$, $\bar{m}_i$, $k(n)$, and $k(m)$ are the values of these variables at the given τ.

If one uses the value of the integrand at $\tau = 0$, the elastic collision integrals in (3.6) vanish, since $k(n)$ and $k(m)$ vanish at $\tau = 0$. Equations (3.5)–(3.6) are then the same as (III.7.5) and (III.7.6).

(2) An alternative approximation is to replace the integral over $\Pi_i d\bar{w}_i$ by its value at $\tau = +\infty$, when τ is positive and by its value at $\tau = -\infty$, when τ is negative. We denote these values by B_{mn} and $B_{n'm'}$,

respectively, B_{mn} being

$$B_{mn}=\int |\partial\bar{w}_i/\partial\bar{w}_j^0|^{-1/2}(\exp i\Delta)\prod_i d\bar{w}_i, \quad (3.7)$$

where now

$$\Delta=2\pi\sum_i\left[(\bar{n}_i-m_i)\bar{w}_i-\int_{n_i}^{\bar{n}_i}w_i d\bar{n}_i\right]-\int_{-k_n}^{k}Rdk$$

$$+\int_0^k\tilde{R}d\tilde{k}-\int_0^{k_m}\tilde{R}d\tilde{k}+\tfrac{1}{2}(m_1+n_1+1)\pi \quad (3.8)$$

since the integrals over $\bar{m}_i$ and k in (3.6) vanish as $\tau\rightarrow+\infty$. (When $\tau\rightarrow+\infty$ there is no collision for the time-reversed system, and so $\bar{m}_i$ and $k(m)$ tend to their initial values, m_i and k_m.) The values of $\bar{n}_i$ and k in (3.8) now refer to the postcollision values for the n trajectory. $B_{n'm'}$ is obtained from B_{mn} by time reversal. We now have

$$S_{mn}\delta(E-E')\cong B_{n'm'}\int_{-\infty}^{0}\left[\exp\left(\frac{i(\bar{E}-\bar{E}')\tau}{\hbar}\right)\right]\left(\frac{\partial\bar{E}}{\partial E}\right)^{-1}\frac{d\tau}{h}$$

$$+B_{mn}\int_0^{\infty}\left[\exp\left(\frac{i(\bar{E}-\bar{E}')\tau}{\hbar}\right)\right]\left(\frac{\partial\bar{E}}{\partial E}\right)^{-1}\frac{d\tau}{h}. \quad (3.9)$$

Upon integrating (3.9) over E' one obtains[5]

$$S_{mn}\cong\tfrac{1}{2}(B_{n'm'}+B_{mn}). \quad (3.10)$$

A numerical test of (3.10) is given in Ref. 6. When the elastic collision used in G_2 is based on a zero-interaction Hamiltonian, the $\tilde{k}$ integrals in (3.8) equal $\frac{1}{2}(\bar{n}_1+\frac{1}{2})\pi$ and $-\frac{1}{2}(m_1+\frac{1}{2})\pi$, respectively. Equation (3.10) then reduces to (III.7.9), apart from an added factor in the integrand of B_{mn}, $\exp\frac{1}{2}(\bar{n}_1-m_1)\pi i$, and apart from one in that of $B_{n'm'}$, $\exp\frac{1}{2}(n_1-\bar{m}_1)\pi i$. These factors become unity in the stationary phase approximation to the respective integrals, noted below.

The points of stationary phase in (3.6) or (3.8) are the solutions of

$$\partial\Delta/\partial\bar{w}_i=\bar{n}_i-\bar{m}_i=0, \qquad (\text{for } 3.6)$$

$$\partial\Delta/\partial\bar{w}_i=\bar{n}_i-m_i=0, \qquad (\text{for } 3.8). \quad (3.11)$$

In the stationary phase approximation, it can readily be shown that S_{mn} equals B_{mn} and, in turn, $B_{n'm'}$, and that it also equals the S_{mn} in Paper III, both the (TVR) there and the (FVR). Thus, just as the exact S_{mn} is invariant to unitary transformations of the wavefunction, the asymptotic expression (e.g., stationary phase approximation) to S_{mn} is invariant to semiclassical unitary transformations of the semiclassical wavefunction. (This invariance, pointed out previously,[7] was also seen in Paper III.) The integral expression for the semiclassical S_{mn} is not, however, invariant, as one sees both in Paper III and in comparing (3.9) with (III.7.6) or (III.7.9). Nevertheless, it is interesting that an integral expression is sometimes the more accurate,[8] probably when the phase of the integrand is only slowly varying.

In balance, the derivation of an integral expression for S_{mn} given in Paper III, e.g., Eqs. (III.7.6) or (III.7.9), is preferable to that in the present paper, since no approximation was needed in evaluating the τ integral there. The results are nevertheless of comparable accuracy[6] and, in the stationary phase approximation, are identical.

ACKNOWLEDGMENTS

I have benefitted from helpful discussions with my co-worker, Dr. Wing Wong, during the course of our work in Ref. 6. The present manuscript was completed while I was a member of the Aspen Center for Physics, and I am happy to acknowledge the hospitality of the personnel there.

* Acknowledgement is made to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research.

[1] R. A. Marcus, J. Chem. Phys. **56**, 311 (1972).

[2] R. A. Marcus, Chem. Phys. Letters **7**, 525 (1970); J. Chem. Phys. **54**, 3965 (1971).

[3] For an elastic collision, $dw_i/d\tau$ equals ν_i^0.

[4] We use the fact that

$$\int_{-\infty}^{\infty}\left[\exp\left(\frac{i(\bar{E}-\bar{E}')\tau}{\hbar}\right)\right]\frac{d\tau}{h}=\delta(\bar{E}-\bar{E}')$$

and that $\delta(\bar{E}-\bar{E}')=(\partial\bar{E}/\partial E)\delta(E-E')$; cf. A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1963), pp. 469–470, Eqs. (A.22) and (A.18).

[5] Equation (3.9) is first integrated over τ, letting two of the limits be $-T$ and $+T$, instead of $-\infty$ and $+\infty$, where $T\rightarrow\infty$. Each resulting complex exponential is subsequently written as a sum of a cosine and a sine, thus yielding some integrands which are odd functions of $\bar{E}-\bar{E}'$ and others which are even functions. Examples of the former contain factors such as

$$(\partial E/\partial\bar{E})^{-1}dE/(\bar{E}-\bar{E}')$$

or

$$(\partial E/\partial\bar{E})^{-1}dE[\cos(\bar{E}-\bar{E}')T/\hbar](\bar{E}-\bar{E}')^{-1},$$

and examples of the latter contain

$$(\partial E/\partial\bar{E})^{-1}dE[\sin(\bar{E}-\bar{E}')T/\hbar](\bar{E}-\bar{E}')^{-1}.$$

[We note that $(\partial E/\partial\bar{E})^{-1}dE$ equals $d\bar{E}$.] Integration over $\bar{E}$ causes the former to vanish and the latter to yield (3.10).

[6] W. H. Wong and R. A. Marcus, J. Chem. Phys. **55**, 5663 (1971). (In Col. 3 of Table II, for 2.44 read 0.244.)

[7] W. H. Miller, J. Chem. Phys. **53**, 3578 (1970).

[8] Compare the results for the 1–1 transition in Tables III and IV of Ref. 7.