

- ⁸ M. Menzinger and R. Wolfgang, *Angew. Chem.* **8**, 438 (1969).
⁹ D. G. Truhlar, *J. Chem. Phys.* **53**, 2041 (1970).
¹⁰ S. H. Lin and H. Eyring, *Proc. Natl. Acad. Sci. U.S.* **68**, 402 (1971).
¹¹ J. L. Kinsey, *J. Chem. Phys.* **54**, 1206 (1971).
¹² F. T. Smith, *J. Chem. Phys.* **36**, 248 (1962).
¹³ B. Shizgal and M. Karplus, *J. Chem. Phys.* **52**, 4264 (1970); **54**, 4344, 4357 (1971).
¹⁴ J. C. Light, J. Ross, and K. E. Shuler, *Kinetic Processes in Gases and Plasmas*, edited by A. R. Hochstim (Academic, New York, 1969), p. 281.
¹⁵ W. Forst and Z. Prášil, *J. Chem. Phys.* **53**, 3065 (1970).
¹⁶ J. Ross and P. Mazur, *J. Chem. Phys.* **35**, 19 (1961).
¹⁷ N. S. Snider and J. Ross, *J. Chem. Phys.* **44**, 1087 (1966).
¹⁸ N. Davidson, *Statistical Mechanics* (McGraw-Hill, New York, 1962).
¹⁹ S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, (McGraw-Hill, New York, 1940).
²⁰ K. J. Laidler, *Theories of Chemical Reaction Rates*, (McGraw-Hill, New York, 1969).
²¹ H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (Wiley, New York, 1944).
²² K. H. Lau and S. H. Lin, *J. Phys. Chem.* **75**, 2458 (1971).
²³ M. R. Hoare and Th. W. Ruijgrok, *J. Chem. Phys.* **52**, 113 (1970).
²⁴ W. Forst, and Z. Prášil, *J. Chem. Phys.* **51**, 3006 (1969); **48**, 1431 (1968); also, Ref. 15.
²⁵ S. H. Lin and H. Eyring, *J. Chem. Phys.* **43**, 2153 (1965); J. C. Tou and S. H. Lin *ibid.* **49**, 4187 (1968); K. H. Lau and S. H. Lin, *J. Phys. Chem.* **75**, 981 (1971).
²⁶ To be more exact,

$$\bar{\sigma}(E) = \frac{h^2}{8\pi\mu} [W_E(E)]^{-1} (2\pi i)^{-1} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{d\beta}{\beta} e^{\beta E} \kappa(\beta) Q_{\dagger}^{\text{int}}(\beta).$$

Equation (3.19) holds only when $\kappa(\beta)$ is assumed to be independent of β .
²⁷ S. H. Lin (unpublished).
²⁸ M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.* **45**, 3871 (1966).
²⁹ M. R. Hoare, *J. Chem. Phys.* **52**, 5695 (1970).
³⁰ S. H. Lin, *Mol. Phys.* **20**, 953 (1971).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 55, NUMBER 12 15 DECEMBER 1971

Semiclassical Transition Probabilities (S Matrix) of Vibrational-Translational Energy Transfer*

W. H. WONG† AND R. A. MARCUS

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801

(Received 4 August 1971)

Uniformized coordinates and an integral expression for the semiclassical S matrix, derived elsewhere, are described and applied to vibrational transition probabilities. The expression obeys microscopic reversibility. The numerical results are compared with the exact quantum mechanical results of Secrest and Johnson.

INTRODUCTION

Recent advances in the semiclassical treatment of molecular collisions are beginning to yield results of useful accuracy, in addition to providing added physical insight. One recent formulation¹ is to construct the WKB wavefunction of the n -dimensional scattering system in the asymptotic regions, using exact classical mechanical trajectories to determine the phase and amplitude of the wavefunction. The elements of the S matrix, S_{mn} , are then obtained by projecting the system wavefunction onto the final channels. In the stationary phase-type approximation, this expression is equivalent² to that obtained by Miller,³ whose formulation was based on a semiclassical approximation of Feynman's propagator.⁴

These semiclassical approaches can be applied either in the form of their asymptotic approximations or in the form of integral expressions. When the plot of final "quantum number" $\bar{n}$ vs initial phase w^0 of the vibrational motions is a relatively simple sinusoidlike function, the asymptotic method can be applied fairly readily, at least in one dimension.¹⁻³ In other situations

many points of stationary phase may occur for some transitions and an integral expression is easier to apply, for the one-dimensional integral at least.

An example of a simple $\bar{n}$ -vs- w^0 plot occurs in the linear collision of an atom and a harmonic oscillator interacting via an exponential repulsion potential energy. The same system, but interacting via a Lennard-Jones potential, is an example of the more complicated $\bar{n}$ -vs- w^0 plot, according to our preliminary classical trajectory results.⁵

Miller has tested an integral expression for the linear collision of an atom and a harmonic oscillator (exponential repulsion)^{3b}: The integral gave quite good results for $|S_{mn}|^2$, except at low transition probabilities, where major deviations from the principle of microscopic reversibility and from the correct answer began to occur. Recently, canonical transformation theory has been applied⁶ to the wavefunction in Ref. 1 and has been used to derive two integral expressions, both obeying microscopic reversibility:

(a) The first expression (which was derived first) used any elastic collision to uniformize all coordinates

(i.e., to remove all singularities from the WKB wavefunction) and then introduced an approximation in the integral to evaluate it.

(b) The second expression, whose development was prompted by first, used the exact classical trajectories to uniformize all coordinates and was then able to avoid the subsequent approximation.

In the present paper we present several figures illustrating the uniformization of all coordinates and describe numerical tests of (a). Numerical tests of (b) will be given in a second paper.⁷ The tests are made by comparing with the exact quantum mechanical results of Secrest and Johnson⁸ for the linear collision of an atom with a harmonic oscillator (exponential repulsion).

CANONICAL TRANSFORMATION AND THE S MATRIX

In this section, we summarize the essential features of the canonical transformation adopted in method (a) and briefly describe the derivation of the integral expression for the S matrix. For the details of the arguments, one should refer to Refs. 1 and 6.

The coordinates q are the radial coordinate R and the angle variables w_i for all other degrees of freedom. Conjugate variables are the radial momentum p_R and "quantum numbers in units of $\hbar$," $\bar{n}\hbar$.⁶ A canonical transformation was introduced via a generating function $G_2(q, \bar{p})$ to convert these coordinates to new coordinates $\bar{w}_i$ and τ . In method (a), G_2 was based on the properties of an elastic collision (this step in itself is no approximation) and yielded $\bar{w}_i$ which were constants initially and constants finally, while τ was a timelike variable. The $\bar{p}$ conjugate to $\bar{w}$ proved to be $\bar{n}\hbar$, and so that symbol can be retained for such $\bar{p}$ without loss of generality. For the case of one internal coordinate we had⁶

$$G_2(w, R, \bar{n}\hbar, \bar{E}) = \bar{n}\hbar w + \int_{r_0}^R \bar{p}_R(\bar{R}, \bar{n}\bar{E}) d\bar{R}, \quad (1)$$

where the integral involving the tilde quantities is evaluated along the elastic collision trajectory having instantaneous values of $\bar{n}$ and (at $\bar{R}=R$) $\bar{p}_R$ of the real trajectory; r_0 and $\bar{E}$ are the distance of closest approach and instantaneous energy of an elastic collision whose interaction potential energy is $V_0(\bar{R})$:

$$\bar{E} = \bar{p}_R^2/2\mu + V_0(\bar{R}) + H_0(\bar{n}\hbar), \quad (2)$$

where H_0 is the Hamiltonian for the internal motion. The new coordinates were then obtained by the standard procedure,⁹

$$\begin{aligned} \bar{w} &= \partial G_2(w, R, \bar{n}\bar{E}) / \partial(\bar{n}\hbar) \\ &= w - \int_{r_0}^R \frac{\mu \bar{w}}{\bar{p}_R(\bar{R}, \bar{n}\bar{E})} d\bar{R} \end{aligned} \quad (3a)$$

and

$$\tau = \frac{\partial G_2}{\partial \bar{E}} = \int_{r_0}^R \frac{\mu}{\bar{p}_R(\bar{R}, \bar{n}\bar{E})} d\bar{R}, \quad (3b)$$

where $\bar{v}$ is the instantaneous frequency of the internal motion in the elastic collision, $\partial H_0 / \partial(\bar{n}\hbar)$. The momenta conjugate to w and R in the actual system are $\partial G_2 / \partial w$ and $\partial G_2 / \partial R$, namely $\bar{n}\hbar$ and $\bar{p}_R$. They are seen from (1) to equal the $\bar{p}$ conjugate to $\bar{w}$, i.e., $\bar{n}\hbar$, and the $\bar{p}_R$, respectively. Thus

$$p_R = \bar{p}_R(\bar{R}, \bar{n}, \bar{E}) \quad \text{at} \quad \bar{R} = R. \quad (4)$$

The essence of this transformation is to relate each point of the real trajectory to a point of an elastic collision trajectory having instantaneous momentum components at that point equal to those of the real one. When R is outside the range of interaction, the inelastic and elastic trajectories coincide completely. The new $\bar{w}$ reaches a constant value, as is readily seen by differentiating (3a) with respect to time in the non-interacting region where $\bar{v}$ is constant.

The application of a canonical transformation of the coordinates provided a unitary transformation of the semiclassical wavefunction^{6,10} which then became⁶

$$\bar{\Psi}_{nE}^{(+)}(\bar{w}, \tau) = \bar{A} \exp[i\bar{S}(\bar{w}\tau, \bar{n}\bar{E})/\hbar], \quad (5)$$

where the amplitude $\bar{A}$, a Jacobian relating the initial flux at the initial $\bar{w}$ ($\bar{w}=\bar{w}_0$) and $\tau=-\infty$, to the flux at $\bar{w}$ and τ , was given by (6) and the phase $\bar{S}$ by (7),

$$\begin{aligned} A &= [(\partial \bar{w} / \partial \bar{w}_0)(\partial \bar{E} / \partial E)\hbar]^{-1/2}, \\ \frac{\bar{S}(\bar{w}\tau, \bar{n}\bar{E})}{\hbar} &= 2\pi \left(\bar{n}\bar{w} - \int_n^{\bar{n}} w d\bar{n} \right) + \frac{\bar{E}\tau}{\hbar} \\ &\quad - \int_{-k_n}^k R dk + \int_0^k \bar{R} d\bar{k} + \frac{1}{2}\pi. \end{aligned} \quad (6)$$

[Both in (2) and (7) the orbital contribution present in Ref. 6 is omitted here since the formulation is applied in the present paper to collinear collisions.] The time-reversed wavefunction, $\bar{\Psi}_{mE'}^{(-)}$, also needed for the S matrix calculation in Ref. 6, is constructed with extreme care because of the subtleties involved in the time-reversal behavior of the action-angle variables. The detailed discussion on this aspect is given there. When both $\bar{\Psi}^{(+)}$ and $\bar{\Psi}^{(-)}$ were introduced into a standard expression for the on-the-energy-shell S -matrix element S_{mn} ,

$$S_{mn}\delta(E-E') = \int \bar{\Psi}_{mE'}^{(-)*} \bar{\Psi}_{nE}^{(+)} d\tau d\bar{w}, \quad (8)$$

one obtained

$$S_{mn} \cong \frac{1}{2}(B_{mn} + B_{nm}), \quad (9a)$$

where

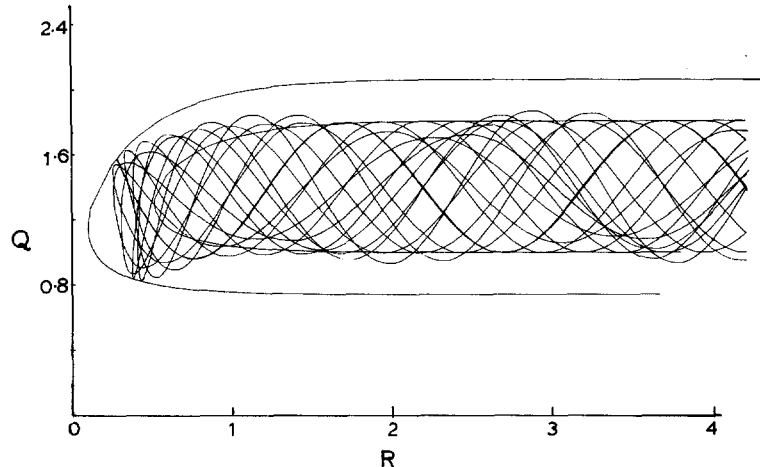
$$B_{mn} = \int (\partial \bar{w} / \partial \bar{w}_0)^{-1/2} (\exp i\Delta) d\bar{w} \quad (9b)$$

and

$$\begin{aligned} \Delta &= 2\pi \left[(\bar{n}-m)\bar{w} - \int_n^{\bar{n}} w d\bar{n} \right] - \int_{-k_n}^k R dk \\ &\quad + \int_0^k \bar{R} d\bar{k} - \int_0^{k_m} \bar{R} d\bar{k} + \frac{1}{2}\pi. \end{aligned} \quad (9c)$$

The upper limits $\bar{n}$ and k in (9c) were those for the

FIG. 1. Collisional trajectories in (Q, R) representation; $E=8$, $\mu=\frac{2}{3}$, $\alpha=0.3$, $n=1$.



actual trajectory beginning at $(\bar{w}_0, n)$. The expression for B_{nm} is similar to (9b) and (9c), but with suitable change of subscripts. The S_{mn} thus obtained satisfied microscopic reversibility.

The $\partial\bar{E}/\partial E$ appearing in (6), not needed for (9) but used to examine the amplitude $\bar{A}$ of $\bar{\psi}$, is

$$\partial\bar{E}/\partial E = 1 + \partial H_1/\partial E, \quad (10)$$

where H_1 is the perturbation, expressed in terms of the new coordinates and momenta.

Equations (9) would be independent of the elastic collision used, had there been no approximations. When the elastic collision is chosen to be, in the limit, that for a hard-sphere interaction potential [i.e., $V_0=0$, except at the actual R -turning point, where $V_0=\infty$], Eqs. (9a) and (9b) are unaffected, but (9c) simplifies to

$$\Delta = 2\pi(\bar{n} - m)w - \int_n^{\bar{n}} w d\bar{n} - \int_{-k_n}^k R dk + \frac{1}{2}\pi \quad (11)$$

and Eq. (3a) for $\bar{w}$ reduces to

$$\bar{w} = w - (R\mu\nu/p_R). \quad (12)$$

For this case, τ , given by (3b), becomes meaningless in the immediate vicinity of $\tau=0$, but is not needed for S_{mn} .

Equations (9a) and (9b) together with (9c) plus (3a) or (11) plus (12), are tested in the next section. Equations (9b), (11), and (12), with S_{mn} equal to B_{mn} , instead of to $\frac{1}{2}(B_{mn} + B_{nm})$, had previously been given by Miller.³

COLLINEAR COLLISION BETWEEN AN ATOM AND A HARMONIC OSCILLATOR

In terms of action-angle variables $(\bar{n}, w)$ and in dimensionless units of Secrest and Johnson,^{3b,8,11} the oscillator displacement coordinate Q equals $(2\bar{n}+1)^{1/2} \cos 2\pi w$, and the interaction potential is $\exp[-\alpha(R-Q)]$. The classical mechanical Hamiltonian for the system of a

collinear collision of an atom and an oscillator is then

$$H = (p_R^2/2\mu) + (\bar{n} + \frac{1}{2}) + \exp[-\alpha R + \alpha(2\bar{n}+1)^{1/2} \cos 2\pi w], \quad (13)$$

where μ and α are the two parameters of this model system. Hamilton's equations are given by $\dot{q}_i$ and $\dot{p}_i$ equal to $\partial H/\partial p_i$ and $-\partial H/\partial q_i$, respectively ($i=1, 2$). When the elastic collision potential V_0 is taken to be $\exp(-\alpha R)$, the instantaneous momentum along the elastic trajectory, $\pm\{2\mu[\bar{p}_R^2/2\mu - V_0(\bar{R})]\}^{1/2}$, is readily found to be

$$\bar{p}_R = \bar{p}_R^0 \tanh \theta, \quad (14a)$$

where

$$\theta = \pm \operatorname{sech}^{-1}[(2\mu/\bar{p}_R^0)^2 \exp(-\alpha R)]^{1/2} \quad (14b)$$

and $\bar{p}_R^0$ is the initial momentum of the elastic trajectory having an instantaneous $\bar{p}_R$ at R . The plus sign in (14b) occurs at R 's before the turning point.

Substituting these expressions into (3a) and (3b), we obtain the new variables along the trajectory. To illustrate the uniformizing properties of these variables, we trace out a set of trajectories in three sets of coordinates. The trajectories shown in Fig. 1 were made using the conventional Cartesian coordinates, R and Q , for the system. The numerous crossings of adjacent trajectories imply, by arguments of flux conservation, infinite amplitude of the simple exponential (or sum of exponentials) form of the semiclassical wavefunction at these points.

In Fig. 2, trajectories are drawn using the (w, R) coordinates. At the crossings of these trajectories at the R turning-point region and at large post-collisional separation, the Jacobian, $\partial w/\partial w_0$, vanishes and the amplitude of the wavefunction again becomes infinite at these points, but now there are many fewer such points. Wherever crossings occur in Figs. 1 and 2 it would be necessary to use for the semiclassical wavefunction an Airy function instead of a simple exponential or sum of exponentials. The crossings at large R in

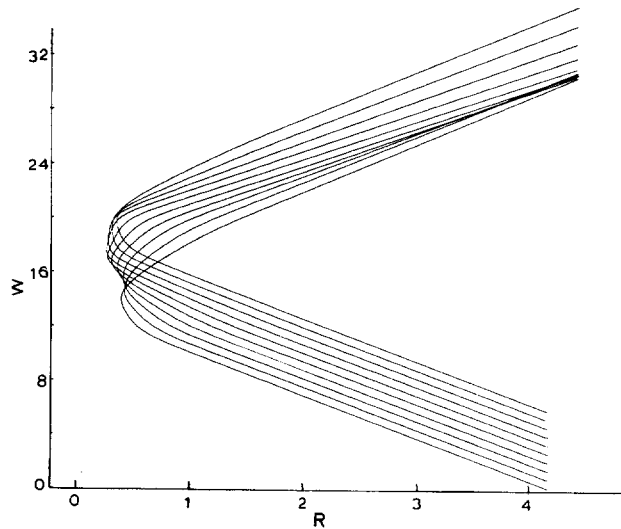


FIG. 2. Collisional trajectories in (w, R) representation; parameters same as in Fig. 1.

TABLE I. Transition probabilities calculated with $V_0 = \exp(-\alpha R)$.^a

Transitions	$ B_{mn} ^2$	$ S_{mn} ^2$	Exact
$\mu, \alpha, E = (\frac{2}{3}, 0.3, 6)$ ^b			
1-1	0.973	0.973	(0.977) ^c
1-2 ^d	$1.4 \times 10^{-3}, 3.4 \times 10^{-4}$	7.3×10^{-4}	8.98×10^{-4}
2-2	0.999	0.999	(0.999)
$\mu, \alpha, E = (\frac{2}{3}, 0.3, 8)$ ^b			
1-1	0.822	0.822	(0.856)
1-2 ^d	$5.3 \times 10^{-2}, 4.3 \times 10^{-2}$	4.9×10^{-2}	4.18×10^{-2}
1-3 ^d	$2.5 \times 10^{-4}, 1.8 \times 10^{-6}$	5.5×10^{-5}	1.46×10^{-5}
2-2	0.953	0.953	(0.956)
2-3 ^d	$1.7 \times 10^{-3}, 4.6 \times 10^{-4}$	0.90×10^{-3}	1.33×10^{-3}
$\mu, \alpha, E = (\frac{2}{3}, 0.3, 12)$ ^b			
2-2	0.315	0.315	(0.348)
2-3	0.258, 0.234	0.246	0.233
2-4 ^d	$7.0 \times 10^{-3}, 6.8 \times 10^{-3}$	6.4×10^{-3}	6.00×10^{-3}
$\mu, b, \alpha, E = (1/13, 0.1287, 16.8364)$ ^b			
2-2	1.9×10^{-4}	1.9×10^{-4}	e
2-3	0.322, 0.299	0.305	0.321
2-4	0.181, 0.168	0.174	0.167
2-5 ^d	$1.7 \times 10^{-2}, 1.8 \times 10^{-2}$	1.7×10^{-2}	1.70×10^{-2}

^a The second value in the second column is $|B_{nm}|^2$.

^b These are the dimensionless parameters in the model of Secrest and Johnson.

^c The values in parentheses were obtained by difference.

^d Classically inaccessible transitions.

^e Too small (0.002 or less) to be determined accurately by difference.

Fig. 2 had as a consequence the fact that the integral for S_{mn} in Ref. 1 needed to be evaluated by an asymptotic approximation as $R \rightarrow \infty$, as in Refs. 1 and 2.

Using the $(\bar{w}, \tau)$ coordinates, as in Fig. 3, the trajectories do not cross even in the turning-point region and hence the system's semiclassical wavefunction is well-defined throughout. A consequence is that the integral (9b) need not be evaluated by asymptotic methods as $R \rightarrow \infty$. In fact, it is independent of R . The amplitude $\bar{A}$ in Eq. (6) also contains a factor $(\partial \bar{E} / \partial E)^{1/2}$ which, for the trajectories in Fig. 3, varied between 1.3 and 0.6 and so did not cause $\bar{A}$ to become singular. In summary, when the new coordinates $(\bar{w}, \tau)$ in Fig. 3 are used no Airy functions are needed. Not shown in these figures are trajectories described in terms of coordinates $\bar{w}, \tau$ obtained using the method (b) mentioned in the Introduction and based on the exact Hamiltonian.⁶ These new trajectories are parallel to the τ axis.

For computing the transition probabilities, Hamil-

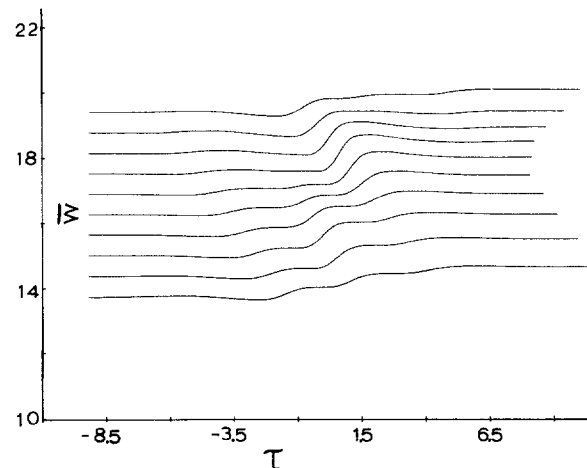


FIG. 3. Collisional trajectories in $(\bar{w}, \tau)$ representation; parameters same as in Fig. 1.

ton's equations of the collisional system were first solved in terms of the w and R ,¹² and the results were then transformed into the new coordinates by Eqs. (3). For an elastic collision potential of $\exp(-\alpha R)$ the integrals involving elastic trajectories which appear in the transformation expressions (3) and in the phase of the matrix element of (9c) were then obtained in closed form when $\tau \rightarrow \infty$. The relevant integrals were found to be

$$\int_{\tau_0}^R \frac{\nu \mu}{\bar{p}_R} d\bar{R} = \frac{\nu R \mu}{\bar{p}_R^0} - \frac{\nu \mu}{\alpha \bar{p}_R^0} \ln \frac{\mu}{2 \bar{p}_R^0} \quad (15a)$$

and

$$\int_0^{\bar{p}_R} \bar{R} d\bar{p}_R = -\frac{\bar{p}_R^0}{\alpha} \left[2 + \ln \left(\frac{\mu}{2 \bar{p}_R^0} \right) \right], \quad (15b)$$

where $-\bar{p}_R^0 = p_R$ at large separation after the turning point.

When expressions (15) and the trajectory data were substituted into (9c), the values of B_{mn} and B_{nm} were obtained by integrating (9b) with a standard 41-point Newton-Cotes formula. Test runs with 81-point integration altered the results by less than 0.3%, except for the highly improbable transitions. Two mass ratios were used for calculations. The one with parameter $\mu = \frac{2}{3}$ is in the region where the "static approximation" fails badly, and the other with $\mu = 1/13$ is the case in which this approximation holds within 5%.¹³ The calculated transition probabilities, $|S_{mn}|^2$, and the values of $|B_{mn}|^2$ are tabulated together with the exact quantum results in Table I. Reasonably good agreement is observed, except when the probability is exceedingly small.

Values of $|B_{mn}|^2$ and of $|S_{mn}|^2$ based on (9) and (11) are given in Table II. The $|B_{mn}|^2$ equals the ex-

pression given by Miller^{3b} for $|S_{mn}|^2$, but the present $|S_{mn}|^2$ is symmetrical. The agreement with the exact results of Secrest and Johnson is seen to be comparable with that in Table I. As noted earlier, if the expressions were exact, the numbers in Tables I and II would be identical. Thus, it is encouraging that the value of $|S_{mn}|^2$ given by Eq. (9) is not, in these cases at least, sensitive to the choice made for the elastic collision. The simplest choice for such a collision is, of course, the one leading to (9a), (9b) and (11), (12).

ACKNOWLEDGMENT

We are especially indebted to Mr. James Stine of this laboratory for providing us with Fig. 1.

* Acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

† Present address: Department of Chemistry, University of Toronto, Toronto, Canada.

¹ (a) R. A. Marcus, Chem. Phys. Letters **7**, 525 (1970); cf. Proc. Conf. Potential Energy Surfaces Chem., University of California, Santa Cruz, California, 1970, 58 (1971). (b) R. A. Marcus, J. Chem. Phys. **54**, 3965 (1971).

² J. N. L. Connor and R. A. Marcus, J. Chem. Phys. **55**, 5636 (1971).

³ (a) W. H. Miller, J. Chem. Phys. **53**, 1949 (1970); (b) **53**, 3578 (1970); (c) Chem. Phys. Letters **7**, 431 (1970); (d) J. Chem. Phys. **54**, 5386 (1971).

⁴ Other examples of recent semiclassical work include (a) R. D. Levine and B. R. Johnson, Chem. Phys. Letters **7**, 404 (1970); **8**, 501 (1971), which also contain an approximate integral expression for the S-matrix elements; (b) P. Pechukas, Phys. Rev. **181**, 166, 174 (1969); (c) I. L. Beigman, L. A. Varnshtein, and I. I. Sobel'man, Zh. Eksp. Teor. Fiz. **57**, 1703 (1969) [Sov. Phys. JETP **30**, 920 (1970)]; (d) I. C. Percival and D. Richards, J. Phys. B **3**, 315, 1035 (1970).

⁵ W. H. Wong and R. A. Marcus (unpublished data).

⁶ R. A. Marcus gives two alternative approximations, of which the one leading to Eq. (3.10) there is the present method (a). (Note: r_0 is denoted there by $\tilde{R}^T$ and the B_{nm} given later in Eq. (9a) is denoted there by $B_{n'm'}$). Method (b), which does not employ either of the above approximations, is given in R. A. Marcus, (unpublished). Also derived there are Eqs. (7.7)-(7.9), which are the same as the present (9a), (9b), and (11).

⁷ J. Stine, W. H. Wong, and R. A. Marcus (unpublished).

⁸ D. Secrest and B. R. Johnson, J. Chem. Phys. **45**, 4556 (1966).

⁹ H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, Mass., 1957), Chap. 8 and 9.

¹⁰ R. Schiller, Phys. Rev. **125**, 1109 (1962).

¹¹ M. Born, *The Mechanics of the Atom* (Bell and Sons, London, 1960), Chap. 1.

¹² For some conditions, though not those in Tables I and II, it would be necessary to solve Hamilton's equations in Cartesian coordinates, Q and R , and then transform the results to those in terms of w and R . Such a step is needed whenever $\tilde{n}$ becomes too near zero during a trajectory, for then w becomes inaccurate.

¹³ M. Attermeier and R. A. Marcus, J. Chem. Phys. **52**, 393 (1970).

TABLE II. Transition probabilities calculated with hard sphere V_0 .^a

Transitions	$ B_{mn} ^2$	$ S_{mn} ^2$	Exact
$\mu, \alpha, E = (\frac{2}{3}, 0.3, 6)^b$			
1-1	0.972	0.972	(0.977)
1-2 ^c	$1.6 \times 10^{-3}, 3.1 \times 10^{-4}$	7.2×10^{-4}	8.98×10^{-4}
2-2	0.998	0.998	(0.999)
$\mu, \alpha, E = (\frac{2}{3}, 0.3, 8)^b$			
1-1	0.827	0.827	(0.856)
1-2 ^c	$5.1 \times 10^{-2}, 4.4 \times 10^{-2}$	4.8×10^{-2}	4.18×10^{-2}
1-3 ^c	$2.6 \times 10^{-4}, 2.2 \times 10^{-5}$	8.4×10^{-5}	1.46×10^{-5}
2-2	0.951	0.951	(0.956)
2-3 ^c	$2.0 \times 10^{-3}, 4.5 \times 10^{-4}$	0.93×10^{-3}	1.33×10^{-3}
$\mu, \alpha, E = (\frac{2}{3}, 0.3, 12)^b$			
2-2	0.320	0.320	(0.348)
2-3	0.250, 0.233	2.44	0.233
2-4 ^c	$5.0 \times 10^{-3}, 6.9 \times 10^{-3}$	5.8×10^{-3}	6.00×10^{-3}
$\mu, \alpha, E = (1/13, 0.1287, 16.8364)^b$			
2-2	2.3×10^{-4}	2.3×10^{-4}	d
2-3	0.315, 0.303	0.309	0.321
2-4	0.183, 0.167	0.174	0.167
2-5 ^c	$2.0 \times 10^{-2}, 1.6 \times 10^{-2}$	1.7×10^{-2}	1.70×10^{-2}

^a Footnote a, Table I.

^b Footnote b, Table I.

^c Footnote d, Table I.

^d Footnote e, Table I.