

parameter, but this term can be eliminated from the energy level analysis by the proper choice of coordinate axes. This involves a rotation about the c axis and results in no loss of generality in the energy level analysis. Discussion of this point can be found in J. L. Prather, Natl. Bur. Std. (U.S.) Monograph 19 (1961), or Appendix A of Ref. 39.

³¹ B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience, New York, 1965).

³² S. S. Bishton and D. J. Newman, J. Phys. C 3, 1753 (1970).

³³ K. Rajnak, J. Chem. Phys. 43, 847 (1965). A typographical error was found in the eigenvector for the $J=11/2$ level at 10 000 cm⁻¹ by checking the orthogonality of the eigenvectors. The sign of the $^2H(21)$ component should be +.

³⁴ J. C. Eisenstein, J. Chem. Phys. 39, 2128 (1963).

³⁵ K. Rajnak and B. G. Wybourne, Phys. Rev. 132, 280 (1963).

³⁶ K. Rajnak and B. G. Wybourne, Phys. Rev. 134, A596 (1964).

³⁷ B. R. Judd, Proc. Phys. Soc. 74, 330 (1959).

³⁸ C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients of the p^n , d^n , and f^n Configurations* (MIT Press, Cambridge, 1963).

³⁹ R. L. Cone, Ph.D. thesis, Yale Univ., 1971, Appendix D, University Microfilm 71-28151.

⁴⁰ For a Fortran IV listing of the program, see Ref. 39, Appendix E.

⁴¹ J. C. Morrison, P. R. Fields, and W. T. Carnall, Phys. Rev. B 2, 3526 (1970).

⁴² W. P. Wolf, Int. J. Quantum Chem. Symp. 5, 397 (1971).

⁴³ G. F. Koster, J. O. Dimmock, R. G. Wheeler, and Hermann Statz, *Properties of the Thirty-two Point Groups* (MIT Press, Cambridge, 1963).

⁴⁴ To determine the absolute sign experimentally, circularly polarized radiation must be used.

⁴⁵ Due to the crystal structure and the Ising nature of the Tb³⁺ ground state, the perpendicular components of $\mathbf{u}$ are not involved.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 57, NUMBER 11 1 DECEMBER 1972

Theory of Semiclassical Transition Probabilities for Inelastic and Reactive Collisions. V. Uniform Approximation in Multidimensional Systems*

R. A. MARCUS

Department of Chemistry, University of Illinois, Urbana, Illinois 61801

(Received 14 April 1972)

An integral semiclassical expression for the S matrix of inelastic and reactive collisions was formulated earlier in this series. In the present paper a uniform approximation for the expression is derived for the case of multidimensional systems. The method is an extension of that employed in Part II for the case of one internal coordinate. The final result, Eq. (2), is highly symmetrical, thus making some of its properties immediately clear.

I. INTRODUCTION

In semiclassical theory for inelastic or reactive collisions,¹⁻³ an inelastic transition from state n to state m is associated with a particular classical trajectory. The latter is one for which the (continuously varying) "quantum number" $\tilde{n}$ equals n before collision and m after it. Such a trajectory corresponds to a point of stationary phase of the phase term in the exponent of the integrand in a semiclassical expression for the S -matrix element S_{mn} .^{1,2} Frequently, several such trajectories contribute and give rise to interference phenomena for the transition, and for scattering. Often the stationary phase value of the integral suffices, and one then has

$$S_{mn} = \sum_j I_j, \quad (1)$$

where the sum is over all stationary phase points j of the integrand and where I_j is the contribution to S_{mn} from the j th point.

When two or more of the stationary phase points are close together, the effects of this proximity must be included (the "uniform approximation"). The case of one dimension was treated in Part II,^{1b} by adapting a method of Ursell, Chester, and Friedman.⁴ This method, which has also been used for obtaining a uniform

approximation for the rainbow and glory effects in elastic scattering,⁵ involves mapping the exponent in the integrand onto a cubic polynomial and mapping the pre-exponential factor onto a power series.⁶ One then obtains a uniform asymptotic expansion. The case of one and two dimensions has been also treated more intuitively,⁷ obtaining the latter by interpolating from various limiting cases.

Apart from the collision of a rigid rotor and an atom, inelastic or reactive molecular collisions involve at least three internal coordinates in the integral expression for S_{mn} . In the present paper we treat the multidimensional case by extending the method of Part II. We obtain

$$S_{mn} = \sum_j I_j \mathcal{B}i^{(+)}(-\zeta_{jj_1}) \cdots \mathcal{B}i^{(+)}(-\zeta_{jj_N}), \quad (2)$$

where the sum is over all stationary phase points j , the latter's neighbors being $j_1 \cdots j_N$. The points j are put into 1:1 correspondence with the corners of a hypercube and $j_1, \cdots, j_N$ are at the corners adjacent to j . The $\mathcal{B}i^{(+)}$'s are certain combinations of the Airy integral and its derivative. The magnitude of $\mathcal{B}i^{(+)}$ is usually close to unity and its phase rapidly decreases toward zero as ζ increases (as in Table I, given later). The ζ 's are related to phase integral differences between adjacent points j and j_k .

II. EVALUATION OF INTEGRAL

We begin with the case of two dimensions, the integral S_{mn} being a particular example of an integral, I ,⁸

$$I = \iint g(x, y) [\exp i f(x, y)] dx dy. \quad (3)$$

The evaluation reduces to that of one-dimensional integrals when one can separate variables, i.e., when $f(x, y) = f(x) + f(y)$ and $g(x, y) = g(x)g(y)$. However, such an approximation cannot be made in general. A typical situation is given schematically in Fig. 1, where the points of stationary phase are indicated as P_1, P_2, P_3 , and P_4 , there frequently being four points of stationary phase. Sometimes, as one sees by symmetry arguments,^{1a} there may be more, but the evaluation of the integral for S_{mn} can then be reduced by symmetry to the evaluation of one with this smaller number of points.^{1a} Sometimes, because of an unusually complicated (highly nonsinusoidal) phase integral, there may again be more points. In the separable case P_1 to P_4 are at the corners of a rectangle in this xy plane.

We introduce in Fig. 1 curvilinear coordinates u and v , and suppose the mapping $(x, y) \rightarrow (u, v)$ to be one to one and regular. The u curves are chosen such that along them one may map the phase f in Eq. (3) onto a cubic expression,

$$f(x, y) = \frac{1}{3}u^3 - \zeta u + A \quad (\text{along } u \text{ curves}). \quad (4)$$

Here, ζ and A are constant along such a curve but their values can vary from member to member of this family of u curves. Two u curves are P_1P_4 and P_2P_3 in Fig. 1. ζ and A are real, when (4) is valid over a sufficiently large region, since f is real for real x and y and hence for real u .

The points of stationary phase, P_1, P_2, P_3 , and P_4 , are those for which

$$\partial f / \partial x = \partial f / \partial y = 0 \quad (5)$$

and thereby for which, along a u curve

$$df/du = 0. \quad (6)$$

There are two solutions to (4) and (6), occurring at points which will be designated S and S' :

$$\begin{aligned} u &= -\zeta_{SS'}^{1/2} & \text{at } S \\ u &= +\zeta_{SS'}^{1/2} & \text{at } S', \end{aligned} \quad (7)$$

where $\zeta_{SS'}$ is the ζ for the u curve joining S and S' (Fig. 1). The set of points S is the curve P_1P_2 and that of S' is curve P_4P_3 there. Equations (4) and (7) yield the values $f(x, y)$ at S and S' , f_S and $f_{S'}$:

$$f_S = \frac{2}{3}\zeta_{SS'}^{3/2} + A_{SS'}, \quad f_{S'} = -\frac{2}{3}\zeta_{SS'}^{3/2} + A_{SS'} \quad (8a)$$

and so

$$f_S - f_{S'} = \frac{4}{3}\zeta_{SS'}^{3/2}, \quad f_S + f_{S'} = 2A_{SS'}. \quad (8b)$$

According as the curve SS' is taken to be P_1P_4 or P_2P_3 ,

the corresponding $\zeta_{SS'}$ is designated as ζ_{14} or ζ_{23} , respectively.

We introduce a coordinate v along curves P_1P_2 and P_4P_3 , such that

$$f(x, y) = \frac{1}{3}v^3 - \eta v + B \quad (\text{along a } v \text{ curve}). \quad (9)$$

η and B depend on the particular v curve, e.g., P_1P_2 or P_4P_3 , and are real. The stationary phase condition (5) implies that, along a v curve,

$$df/dv = 0 \quad (10)$$

at a stationary phase point, thus yielding solutions

$$\begin{aligned} v &= -\eta_{QQ'}^{1/2} & \text{at } Q \\ v &= +\eta_{QQ'}^{1/2} & \text{at } Q', \end{aligned} \quad (11)$$

where Q is P_1 or P_4 in Fig. 1 and Q' is P_2 or P_3 . Curves P_1P_2 and P_4P_3 are members of a family of v curves, as in Fig. 1.

Equations (9) and (11) applied to curves P_1P_2 and P_4P_3 lead to

$$\begin{aligned} \frac{4}{3}\eta_{12}^{3/2} &= f_1 - f_2 \\ \frac{4}{3}\eta_{43}^{3/2} &= f_4 - f_3. \end{aligned} \quad (12)$$

From the foregoing it follows that

$$\begin{aligned} P_1(-\zeta_{14}^{1/2}, -\eta_{12}^{1/2}), & \quad P_2(-\zeta_{23}^{1/2}, +\eta_{12}^{1/2}), \\ P_3(+\zeta_{23}^{1/2}, +\eta_{43}^{1/2}), & \quad P_4(+\zeta_{14}^{1/2}, -\eta_{43}^{1/2}). \end{aligned} \quad (13)$$

Of these four solutions to (5) there may be four real, or some real and some complex-valued, or four complex-valued solutions. The case of one or more real ones yields a classically accessible transition while that of four complex ones yields a classically inaccessible one.¹

The quantities ζ , A , η , and B have a useful property employed later: differentiation of (8b) with respect to v , and application of (10) when S and S' are the stationary phase points P_1 and P_4 or P_2 and P_3 , shows that along a v curve

$$d\zeta_{SS'}/dv = 0 \quad (\text{at a stationary phase point}) \quad (14a)$$

and that $dA_{SS'}/dv$ vanishes there also. Similarly using (8) but with S, S', ζ , and A replaced by Q, Q', η , and B , differentiating it with respect to u and applying (6) shows that along a u curve

$$d\eta_{QQ'}/du = 0 \quad (\text{at a stationary phase point}) \quad (14b)$$

and that $dB_{QQ'}/du$ also vanishes there.

The integral in Eq. (1) can be written as

$$I = \iint gJ [\exp i(\frac{1}{3}u^3 - \zeta u + A)] du dv, \quad (15)$$

where J denotes the actual (rather than absolute) value of the Jacobian for the transformation $(u, v) \rightarrow (x, y)$. (This is an important point, partly because one is working with complex variables x and y and their

functions.)

$$J = \begin{pmatrix} x_u & x_v \\ y_u & y_v \end{pmatrix} \equiv x_u y_v - x_v y_u; \quad (16)$$

throughout, the subscripts u, v, x, y, x^0 , and y^0 indicate a derivative, e.g., x_u denotes $\partial x / \partial u$.

We integrate (15) along any curve SS' in Fig. 1, first expanding gJ there along that curve, as in the one-dimensional analog in Part II and as in Ref. 4. The leading term is⁶

$$gJ = p_0 + q_0 u, \quad (17)$$

where p_0 and q_0 both depend on the SS' curve. [In an integration along an SS' curve, u varies and v may also. Thus, if u is used as the integration variable along SS' , any v in the integrand becomes a $v(u)$.] At the points S and S' in Fig. 1, u has the values in Eq. (7). Upon evaluation of p_0 and q_0 , Eq. (17) yields

$$gJ = \frac{1}{2}(1 - u\zeta^{-1/2})(gJ)_S + \frac{1}{2}(1 + u\zeta^{-1/2})(gJ)_{S'}, \quad (18)$$

where $(gJ)_S$ denotes the value of gJ at S .

We denote by the symbols $\mathcal{R}i^{(\pm)}$ the following integrals:

$$\mathcal{R}i^{(\pm)}(-\zeta) = (2\pi)^{-1} \int_{-\infty}^{\infty} (1 \mp u\zeta^{-1/2}) \times [\exp(i(\frac{1}{3}u^3 - \zeta u))] du. \quad (19a)$$

From the definitions⁹ of the Airy function Ai and its derivative, Ai' , we have

$$\mathcal{R}i^{(\pm)}(-\zeta) = Ai(-\zeta) \pm i\zeta^{-1/2} Ai'(-\zeta). \quad (19b)$$

Bearing in mind the asymptotic behavior of $\mathcal{R}i^{(\pm)}(-\zeta)$,⁹ it is convenient to introduce a function $\mathcal{B}i^{(\pm)}(-\zeta)$ which tends to unity at large ζ :

$$\mathcal{B}i^{(\pm)}(-\zeta) = \pi^{1/2} \zeta^{-1/4} \mathcal{R}i^{(\pm)}(-\zeta) \times \exp[\mp i(\frac{2}{3}\zeta^{3/2} - \frac{1}{4}\pi)]. \quad (19c)$$

Values of the magnitude and phase of $\mathcal{B}i^{(\pm)}(-\zeta)$ are given for various ζ 's in the range 0.01 to 3 in Table I. (The value of $\mathcal{B}i^{(\pm)}$ diverges when ζ is zero.) Its

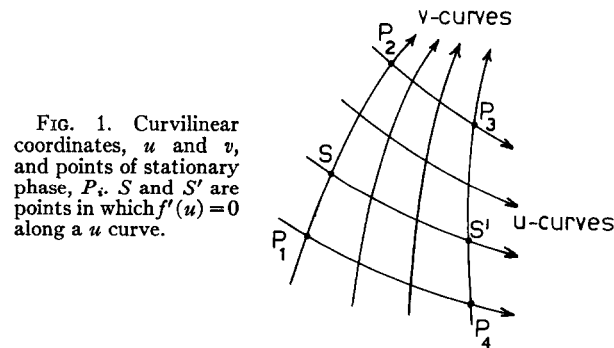


FIG. 1. Curvilinear coordinates, u and v , and points of stationary phase, P_i . S and S' are points in which $f'(u) = 0$ along a u curve.

TABLE I. Amplitude (ρ) and phase (ϕ) of $\mathcal{B}i^{(\pm)}(-\zeta)$.

ζ	ρ	ϕ	ζ	ρ	ϕ
0.01	1.464	-0.649	0.90	0.925	+0.096
0.03	1.134	-0.551	1.0	0.949	+0.100
0.05	1.016	-0.485	1.2	0.993	+0.093
0.07	0.929	-0.409	1.4	1.025	+0.072
0.10	0.894	-0.368	1.6	1.044	+0.044
0.20	0.821	-0.219	1.8	1.048	+0.015
0.30	0.807	-0.119	2.0	1.039	-0.009
0.40	0.813	-0.048	2.2	1.020	-0.024
0.50	0.829	+0.004	2.4	0.999	-0.027
0.60	0.851	+0.042	2.6	0.982	-0.017
0.70	0.874	+0.069	2.8	0.975	-0.002
0.80	0.900	+0.086	3.0	0.980	+0.016

magnitude is seen to be fairly close to unity in the region 0.1 to 3, and its phase changes from -0.37 at $\zeta = 0.1$ to values of 0.04 or less when ζ exceeds 1.6. Ultimately, the phase becomes zero and the magnitude becomes unity at large ζ . $\mathcal{B}i^{(-)}(-\zeta)$ is the complex conjugate of $\mathcal{B}i^{(+)}(-\zeta)$.

The integral in Eq. (15) can now be written as

$$I = \pi^{1/2} \int \zeta^{-1/4} \{ (gJ)_S [\exp(i(\frac{2}{3}\zeta_{SS'}^{3/2} + A - \frac{1}{4}\pi))] \times \mathcal{B}i^{(+)}(-\zeta_{SS'}) + (gJ)_{S'} [\exp(i(-\frac{2}{3}\zeta_{SS'}^{3/2} + A + \frac{1}{4}\pi))] \times \mathcal{B}i^{(-)}(-\zeta_{SS'}) \} dv. \quad (20)$$

Introducing (8a) into (20) and noting that S lies on curve P_1P_2 and that S' lies on curve P_4P_3 , Eq. (20) may be rewritten as

$$I = \pi^{1/2} \int_{P_1P_2} \zeta_{SS'}^{-1/4} gJ \mathcal{B}i^{(+)}(-\zeta_{SS'}) \exp(i(f - \frac{1}{4}\pi)) dv + \int_{P_4P_3} \zeta_{SS'}^{-1/4} gJ \mathcal{B}i^{(-)}(-\zeta_{SS'}) \exp(i(f + \frac{1}{4}\pi)) dv. \quad (21)$$

In integrating along v curves P_1P_2 and P_4P_3 one may use v as an integration variable.

When ζ is large, $\mathcal{B}i^{(\pm)}(-\zeta)$ is about unity, and so the only significant variation in phase of the integrands of (19) is due to $f(x, y)$. However, even more generally, (14a) shows that $d\zeta_{SS'}/dv$ vanishes at a stationary phase point and so $\mathcal{B}i^{(\pm)}(\zeta_{SS'})$ makes no contribution to phase variation in the integrand at such a point. One can thus treat the factors $\zeta^{-1/2} gJ \mathcal{B}i^{(\pm)}$ as in (17), whence we may set

$$\zeta_{SS'}^{-1/4} gJ \mathcal{B}i^{(\pm)}(-\zeta_{SS'}) = P_0 + Q_0 v \quad (\text{on } P_1P_2 \text{ and } P_4P_3), \quad (22)$$

and evaluate P_0 and Q_0 . The $(+)$ sign in $\mathcal{B}i$ is for P_1P_2 and the $(-)$ sign is for P_4P_3 , according to (21), and the values of P_0 and Q_0 on the first curve differ from those on the second. $\zeta_{SS'}$ is ζ_{14} at P_1 and ζ_{23} at P_2 and according to (1), v is $-\eta_{12}$ at P_1 and $+\eta_{12}$ at P_2 . Denoting by g_i and J_i the values of g and J at point P_i ,

and introducing these results into (22) to obtain P_0 and Q_0 , one finds that on curve P_1P_2

$$\begin{aligned} \zeta^{-1/4} g J \mathfrak{B} i^{(+)}(-\zeta) \\ = \frac{1}{2} \zeta_{14}^{-1/4} g_1 J_1 (1 - v \eta_{12}^{-1/2}) \mathfrak{B} i^{(+)}(-\zeta_{14}) \\ + \frac{1}{2} \zeta_{23}^{-1/4} g_2 J_2 (1 + v \eta_{12}^{-1/2}) \mathfrak{B} i^{(+)}(-\zeta_{23}). \quad (23) \end{aligned}$$

Similarly, using (14) and (22), one finds that on curve P_4P_3

$$\begin{aligned} \zeta^{-1/4} g J \mathfrak{B} i^{(-)}(-\zeta) \\ = \frac{1}{2} \zeta_{14}^{-1/4} g_4 J_4 (1 - v \eta_{43}^{-1/2}) \mathfrak{B} i^{(-)}(-\zeta_{14}) \\ + \frac{1}{2} \zeta_{23}^{-1/4} g_3 J_3 (1 + v \eta_{43}^{-1/2}) \mathfrak{B} i^{(-)}(-\zeta_{23}). \quad (24) \end{aligned}$$

We may also write the $f(x, y)$ in (21) as in (9), introduce (23) and (24) into (21), and use (19c) to write the resulting $\mathfrak{B} i^{(\pm)}$ integrals in terms of $\mathfrak{B} i^{(\pm)}$'s. When Eqs. (9) and (11) are used to simplify the resulting expression one obtains

$$\begin{aligned} I = [\pi g_1 J_1 / (\eta_{12} \zeta_{14})^{1/4}] \mathfrak{B} i^{(+)}(-\eta_{12}) \mathfrak{B} i^{(+)}(-\zeta_{14}) \\ \times \exp i(f_1 - \frac{1}{2}\pi) + [\pi g_2 J_2 / (\eta_{12} \zeta_{23})^{1/4}] \\ \times \mathfrak{B} i^{(-)}(-\eta_{12}) \mathfrak{B} i^{(+)}(-\zeta_{23}) \exp i f_2 \\ + [\pi g_3 J_3 / (\eta_{43} \zeta_{23})^{1/4}] \mathfrak{B} i^{(-)}(-\zeta_{23}) \mathfrak{B} i^{(-)}(-\eta_{43}) \\ \times \exp i(f_3 + \frac{1}{2}\pi) + [\pi g_4 J_4 / (\eta_{43} \zeta_{14})^{1/4}] \\ \times \mathfrak{B} i^{(-)}(-\zeta_{14}) \mathfrak{B} i^{(+)}(-\eta_{43}) \exp i f_4. \quad (25) \end{aligned}$$

This expression can be further simplified: The J_i 's can be expressed in terms of properties of $f(x, y)$ and so freed from those of u and v . We first note that one can readily show that the second derivatives of f with respect to x and y are related to those with respect to u and v . At a point of stationary phase one obtains the first half of (26):

$$\begin{pmatrix} x_u & y_u \\ x_v & y_v \end{pmatrix} \begin{pmatrix} f_{xx} & f_{xy} \\ f_{xy} & f_{yy} \end{pmatrix} \begin{pmatrix} x_u & x_v \\ y_u & y_v \end{pmatrix} \\ = \begin{pmatrix} f_{uu} & f_{uv} \\ f_{uv} & f_{vv} \end{pmatrix} = \begin{pmatrix} 2u & 0 \\ 0 & 2v \end{pmatrix}. \quad (26)$$

The second half of (26) is obtained by differentiating (4) and (9) with respect to u and v at a stationary phase point and using (14) (Appendix B).

The square matrices in (26) can be interpreted as signed determinants. The first factor on the left hand side then equals the third, which in turn is J , according to (16). Thus, (26) yields

$$J = 2F^{-1/2} (uv)^{1/2}, \quad (27)$$

where

$$F = \begin{pmatrix} f_{xx} & f_{xy} \\ f_{xy} & f_{yy} \end{pmatrix}, \quad (28)$$

and the quantities are to be evaluated at the cited point of stationary phase.

Further, the quantity g in Eq. (3) involves a (signed) determinant of derivatives the values of x and y with respect to initial values before the collision, x^0 and y^0 :

$$g = \begin{pmatrix} x_{x^0} & x_{y^0} \\ y_{x^0} & y_{y^0} \end{pmatrix}^{-1/2}. \quad (29)$$

Equations (27) to (29) yield

$$gJ = 2G^{-1/2} (uv)^{1/2}, \quad (30)$$

where

$$G^{-1/2} = gF^{-1/2} = \begin{pmatrix} f_{xx^0} & f_{xy^0} \\ f_{yx^0} & f_{yy^0} \end{pmatrix}^{-1/2} = \begin{pmatrix} X_{x^0} & X_{y^0} \\ Y_{x^0} & Y_{y^0} \end{pmatrix}^{-1/2}. \quad (31)$$

Here, X denotes f_x and Y denotes f_y ; X and Y are the final momenta conjugate to the final coordinates x and y , respectively.^{1,8}

When the values of $(uv)^{1/2}$ appropriate to the given stationary phase points, namely those given by (13), are introduced, Eq. (25) becomes

$$\begin{aligned} I = 2\pi \exp(i\frac{1}{2}\pi) \\ \times [G_1^{-1/2} \mathfrak{B} i^{(+)}(-\eta_{12}) \mathfrak{B} i^{(+)}(-\zeta_{14}) \exp(if_1) \\ + G_2^{-1/2} \mathfrak{B} i^{(-)}(-\eta_{12}) \mathfrak{B} i^{(+)}(-\zeta_{23}) \exp(if_2) \\ + G_3^{-1/2} \mathfrak{B} i^{(-)}(-\zeta_{23}) \mathfrak{B} i^{(-)}(-\eta_{43}) \exp(if_3) \\ + G_4^{-1/2} \mathfrak{B} i^{(-)}(-\zeta_{14}) \mathfrak{B} i^{(+)}(-\eta_{43}) \exp(if_4)]. \quad (32) \end{aligned}$$

We now introduce a completely symmetrical notation for all i and j :

$$f_i - f_j = \frac{4}{3} \zeta_{ij}^{3/2}, \quad (33)$$

where, therefore,

$$\zeta_{ij}^{3/2} = -\zeta_{ji}^{3/2}. \quad (34)$$

From these relations and from the properties of the Airy functions, it can be shown that

$$\mathfrak{B} i^{(+)}(-\zeta_{ij}) = \mathfrak{B} i^{(-)}(-\zeta_{ji}). \quad (35)$$

Equation (32) now yields

$$\begin{aligned} I = 2\pi i \sum_{j=1}^4 G_j^{-1/2} \mathfrak{B} i^{(+)}(-\zeta_{jj_1}) \\ \times \mathfrak{B} i^{(+)}(-\zeta_{jj_2}) \exp(if_j), \quad (36) \end{aligned}$$

where the sum is over all stationary phase points j and where j_1 and j_2 denote their adjacent neighbors (i.e., the points on the adjacent corners of the deformed "square" $P_1P_2P_3P_4$ in Fig. 1).

When the above type of derivation is used for the case of a one-dimensional integral, $\int g \exp(if) dx$, one obtains instead

$$I = (2\pi i)^{1/2} \sum_{j=1}^2 G_j^{-1/2} \mathfrak{B} i^{(+)}(-\zeta_{jj'}) \exp(if_j), \quad (37)$$

there being only two stationary phase points in most occasions ($j' = 2$ when $j = 1$, etc.).

The generalization of (36) and (37) to N dimensions is apparent from their highly symmetrical form, and is obtained by a straightforward extension of the above arguments. In the case of three dimensions, a three dimensional set of curvilinear coordinates (u, v, w) is introduced, together with the eight points P_i , and the curves P_{ij} ($i, j=1$ to 8), as in Fig. 2.

For the N -dimensional case one establishes [by induction, since the N -dimensional case is the "Cartesian product" of the $(N-1)$ and one dimensional cases] the following result

$$I = (2\pi i)^{N/2} \sum_j G_j^{-1/2} \mathfrak{B}^{(+)}(-\zeta_{jj1}) \cdots \mathfrak{B}^{(+)}(-\zeta_{jjN}) \times \exp(if_j). \quad (38)$$

Since the stationary phase value is given by (38) but with all $\mathfrak{B}^{(+)}$'s equal to unity, one can rewrite (38) in terms of the stationary phase contribution from the j 'th point, I_j :

$$I = \sum_{j=1}^{2^N} I_j \mathfrak{B}^{(+)}(-\zeta_{jj1}) \cdots \mathfrak{B}^{(+)}(-\zeta_{jjN}), \quad (39)$$

where

$$I_j = (2\pi i)^{N/2} G_j^{-1/2} \exp if_j. \quad (40)$$

There are in the sum (39) 2^N stationary phase points for the system examined, these being the number of corners of an N -dimensional hypercube.

III. DISCUSSION

When $\mathfrak{B}^{(+)}$ is written in terms of the Airy integral and its derivative, and when G is expressed in terms of g and F , it can be shown (Appendix A) that Eq. (37) leads to the results previously obtained in Part II for one dimension, namely Eqs. (3.20) and (3.26) there.

Again, when $\mathfrak{B}^{(+)}$ is expressed as above and Eq. (38) then specialized to the case of two dimensions it yields an equation of Miller²⁰ for the two-dimensional case, apart from one difference noted earlier^{2b}: $Bi(-\zeta)$, the irregular Airy function appears in Ref. 2 instead of the present $\zeta^{-1/2} Ai'(-\zeta)$. The difference arises from the fact that in Ref. 2 the uniform approximation was partly deduced from an interpolation of stationary phase values, and that both $\zeta^{-1/2} Ai'(-\zeta)$ and $Bi(-\zeta)$ have the same limiting values, and partly from a result of Carrier,^{7,10} which in turn omitted the second term in (15). The difference in the two functions is, as already mentioned in Part II, negligible when ζ is large, their limiting behavior being the same. When ζ is small, they do differ appreciably, but then the term which contains them is largely dominated by one which contains $Ai(-\zeta)$.

Equation (39) has, because of its symmetry, several useful properties. It shows immediately that I equals its stationary phase value $\sum_j I_j$ when the ζ 's are large, i.e., when the points of stationary phase are widely separated, since the $\mathfrak{B}^{(+)}(-\zeta)$'s approach unity at large ζ . Again, when ζ is not large but not so small that

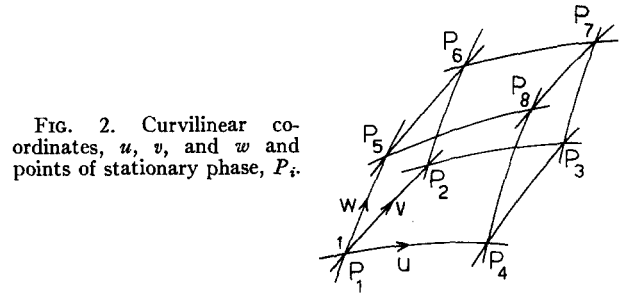


FIG. 2. Curvilinear coordinates, u , v , and w and points of stationary phase, P_i .

$\mathfrak{B}^{(+)}$ becomes singular (we note, however, that because of cancellations, I itself is not singular), one can understand from (39) the interesting empirical observation²⁰ that the quantum value for $|S_{mn}|^2$ is sometimes closer to the "classical value", $\sum_j |I_j|^2$ than it is to the stationary phase value $|\sum_j I_j|^2$. Some randomness in the ζ 's in (39) leads to some randomness in the phases of the $\mathfrak{B}^{(+)}$'s, leading to $|I|^2$ being closer, on such occasions, to $\sum_j |I_j|^2$. This value, $\sum_j |I_j|^2$, which we have called classical, was derived earlier in Part I of this series by classical arguments using slightly different notation [see Eq. (2.3) and subsequent sentence there].

To evaluate the phase of G in (34)–(38), one needs some examination of the topography of the f surface, and we consider it now.¹¹

In the case of one dimension the stationary phase point at $u = -\zeta^{1/2}$ has a negative value of f_{xx} in the classically accessible case, since f_{xx} equals $2u(du/dx)^2$ there. Since $f_{xx} < 0$ at this point (we will call it P_1) f is a maximum there, while at the other point (P_2) f is a minimum. (Indeed, $f_1 - f_2$ equals $\frac{2}{3}\zeta^{3/2}$ and is positive.) In (37) one has, denoting f_{xx} by f'' ,

$$F_1 = f_1'' = |f_1''| \exp i\pi, \quad F_2 = f_2'' = |f_2''|. \quad (41)$$

In the case of two dimensions, as in Fig. 1, there is a maximum and a minimum in f along each of the curves $P_i P_j$. Thereby, at one of the four points (P_1 , when ζ_{12} and ζ_{14} are positive) f is a maximum, while at the opposite corner, P_3 , f is a minimum. At each of the other points, P_2 and P_4 , the f surface has a col. Thereby, the phase of $F^{-1/2}$ is given by (42):

$$\begin{aligned} F_1^{-1/2} &= |F_1|^{-1/2} \exp(-i\pi), \\ F_2^{-1/2} &= |F_2|^{-1/2} \exp(-i\pi/2), \\ F_3^{-1/2} &= |F_3|^{-1/2}, \\ F_4^{-1/2} &= |F_4|^{-1/2} \exp(-i\pi/2), \end{aligned} \quad (42)$$

(e.g., when the matrix F in (28) is diagonalized in the neighborhood of a point of stationary phase of f , there are two negative values for the diagonal elements at P_1 , leading to a phase of 2π for F_1 and hence to $-\pi$ for $F_1^{-1/2}$. Related remarks apply to the other F_i 's).

In the case of three dimensions, we may consider eight points $P_1, \dots, P_8$, as in Fig. 2, with coordinates

(u, v, w) :

$$\begin{aligned}
 P_1 &(-\zeta_{14}^{1/2}, -\zeta_{12}^{1/2}, -\zeta_{15}^{1/2}), \\
 P_2 &(-\zeta_{23}^{1/2}, +\zeta_{12}^{1/2}, -\zeta_{26}^{1/2}), \\
 P_3 &(+\zeta_{23}^{1/2}, +\zeta_{43}^{1/2}, -\zeta_{37}^{1/2}), \\
 P_4 &(+\zeta_{14}^{1/2}, -\zeta_{43}^{1/2}, -\zeta_{46}^{1/2}), \\
 P_5 &(-\zeta_{58}^{1/2}, -\zeta_{56}^{1/2}, +\zeta_{15}^{1/2}), \\
 P_6 &(-\zeta_{67}^{1/2}, +\zeta_{56}^{1/2}, +\zeta_{26}^{1/2}), \\
 P_7 &(+\zeta_{67}^{1/2}, +\zeta_{87}^{1/2}, +\zeta_{37}^{1/2}), \\
 P_8 &(+\zeta_{58}^{1/2}, -\zeta_{87}^{1/2}, +\zeta_{48}^{1/2}), \quad (43)
 \end{aligned}$$

where all the ζ 's cited in (43) are positive. One can always define the (u, v, w) coordinates so that this condition is fulfilled.

From (43) one can see that P_1 is the point where the f surface has a maximum. At diagonally opposite point P_7 f has a minimum. At the other points there are various types of saddle points, those adjacent to P_1 , namely P_2, P_4 , and P_5 , having maxima in two principal directions and a minimum in a third, while those adjacent to P_7 (P_3, P_6, P_8) have minima in two principal directions and a maximum in the third. One can then deduce that

$$\begin{aligned}
 F_1^{-1/2} &= |F_1|^{-1/2} \exp(-3i\pi/2), \\
 F_2^{-1/2} &= |F_2|^{-1/2} \exp(-i\pi), \\
 F_3^{-1/2} &= |F_3|^{-1/2} \exp(-i\pi/2), \\
 F_4^{-1/2} &= |F_4|^{-1/2} \exp(-i\pi), \\
 F_5^{-1/2} &= |F_5|^{-1/2} \exp(-i\pi), \\
 F_6^{-1/2} &= |F_6|^{-1/2} \exp(-i\pi/2), \\
 F_7^{-1/2} &= |F_7|^{-1/2}, \\
 F_8^{-1/2} &= |F_8|^{-1/2} \exp(-i\pi/2), \quad (44)
 \end{aligned}$$

in the case of classically accessible cases. Once again, these results follow from (43) by noting that a minus sign before a $\zeta^{1/2}$ indicates that f is locally a maximum along that coordinate, while a plus sign indicates that it is locally a minimum. The phase of F_i equals π times the number of such minus signs.

The phase of $G_i^{-1/2}$ is the same as that of $F_i^{-1/2}$ when the phase of (29) is zero. In the actual numerical cases examined thus far in the rotation-translation and vibration-translation collisions problems, the phase of (29) has been zero at the points of stationary phase, although it has sometimes differed from zero elsewhere.¹² Thus, for these cases, the phases in (41), (42), and (43) may be used as the phases of $G^{-1/2}$. However, strictly speaking, this question regarding the possible change of phase of (29) should be checked in each instance.

In a plot of the final collisional value of the quantum number $\bar{n}_k$ for the k th degree of freedom versus (x^0, y^0) ,

the local minimum or the maximum $\bar{n}_i$ of such a plot may sometimes be near a stationary phase point of $f(x, y)$ and hence, near an m_k . In this case the stationary phase points of at least one pair approach each other and eventually coalesce when m_k equals the local maximum or minimum $\bar{n}_k$. The pair then move in opposite directions along an imaginary axis in a complex (u, v) or $(u, v, \dots)$ plane. In this case, as in the one-dimensional analog in Part II, the g 's at these two points are complex conjugates, as are the F 's. The associated ζ_{ij} value is still real but negative. With care, the change in phase from the values given in (41), (42), and (44) can be determined by analytic continuation arguments. Equation (39) remains valid for this classically inaccessible case.

Examination of Eq. (13) shows that if some P_i 's are complex-valued, the ζ_{ij} 's can also be complex. Since real ζ_{ij} 's were assumed originally, one should now modify the argument. Elsewhere, it will be shown how to modify Eq. (38) for such a case.

ACKNOWLEDGMENT

Dr. Holger Kreek of this laboratory kindly computed the data in Table I and I am pleased to acknowledge his help in this matter, and helpful discussions with Dr. Kreek and Dr. J. N. L. Connor.

APPENDIX A: COMPARISONS

One can readily show that Eq. (37) is equivalent to Eqs. (3.20) and (3.26) of Part II: according to (31) $G^{-1/2}$ equals $gF^{-1/2}$, and so (denoting f_{xx} by f'') we have

$$\begin{aligned}
 I &= (2\pi i)^{1/2} [g_1(f_1'')^{-1/2} (\exp i f_1) \mathcal{B}i^{(+)}(-\zeta_{12}) \\
 &\quad + g_2(f_2'')^{-1/2} (\exp i f_2) \mathcal{B}i^{(+)}(-\zeta_{21})]. \quad (A1)
 \end{aligned}$$

In (3.20) one had $f_1'' > 0$ and $f_2'' < 0$ for a classically accessible transition, so that f is a minimum at P_1 and a maximum at P_2 . Since $\frac{4}{3}\zeta_{21}$ equals $f_2 - f_1$, $\zeta_{21}^{3/2}$ is therefore positive and hence ζ_{21} is also; ζ_{12} is not. Setting $\mathcal{B}i^{(+)}(-\zeta_{12})$ equal to $\mathcal{B}i^{(-)}(-\zeta_{21})$, as in (35), and introducing (19) one obtains

$$\begin{aligned}
 I &= (2i)^{1/2} \pi \zeta^{1/4} \{g_1(f_1'')^{-1/2} (\exp i f_1) \\
 &\quad \times [Ai(-\zeta) - i\zeta^{-1/2} Ai'(-\zeta)] \\
 &\quad \times \exp i(\frac{2}{3}\zeta^{3/2} - \frac{1}{4}\pi) + g_2(f_2'')^{-1/2} (\exp i f_2) \\
 &\quad \times [Ai(-\zeta) + i\zeta^{-1/2} Ai'(-\zeta)] \exp -i(\frac{2}{3}\zeta^{3/2} - \frac{1}{4}\pi)\}, \quad (A2)
 \end{aligned}$$

where ζ denotes ζ_{21} .

Since f'' equals $2u(du/dx)^2$, point P_1 must be at $u = +\zeta^{1/2}$, to have $f_1'' > 0$, and point P_2 must be at $u = -\zeta^{1/2}$. Thus, f_1 equals $-\frac{2}{3}\zeta^{3/2} + A$ and f_2 equals $\frac{2}{3}\zeta^{3/2} + A$, a result which simplifies (A2). Finally, since f_1'' is $|f_1''|$ and f_2'' is $|f_2''| \exp i\pi$, f_2'' being negative, one can introduce this result and the preceding one into

(A2) and obtain (3.20) of Part II. When Eq. (3.26) of Part II is regarded as a relabeling of points 1 and 2, by changing the sign of the original coordinates, it does not constitute a separate problem.

APPENDIX B: PROOF OF SECOND HALF OF EQ. (26)

We first note that the curves labeled for convenience as u and v curves in Fig. 1 are not the usual curvilinear u -coordinate and v -coordinate curves. For example, on a u curve P_1P_4 , v is given by (11) and so is not in general constant on it. Similarly, on a v curve P_1P_2 the quantity u , given by (7), is not in general constant on it.¹³

Along a u curve, such as P_1P_4 or P_2P_3 , we have

$$df/du = \partial f/\partial u + (\partial f/\partial v)(dv/du), \quad (B1)$$

where d/du will denote differentiation along a u curve, and d/dv will denote differentiation along a v curve. (Thereby, with this notation dv/du and du/dv are not reciprocals.)

Differentiation of Eq. (B1) and of Eq. (4) along a u curve shows that

$$2u = \frac{d^2f}{du^2} = \frac{\partial^2f}{\partial u^2} + 2\frac{\partial^2f}{\partial u\partial v}\frac{dv}{du} + \frac{\partial f}{\partial v}\frac{d^2v}{du^2} + \frac{\partial^2f}{\partial v^2}\left(\frac{dv}{du}\right)^2. \quad (B2)$$

At a stationary phase point, Eqs. (11) and (14b) show that dv/du vanishes. According to (5) $\partial f/\partial v$ also vanishes there. Thus, (B2) shows that, at a stationary phase point P_i , $\partial^2f/\partial u^2$ equals $2u$, as in (26). Similarly, $\partial^2f/\partial v^2$ equals the d^2f/dv^2 computed along a v curve at a P_i and so, from (9), equals $2v$, again as in (26).

Differentiating (B1) along a v curve yields (B3). Differentiating (4) first along a u curve and then along a v curve yields (B4)

$$\begin{aligned} \frac{d(df/du)}{dv} &= \frac{\partial^2f}{\partial u\partial v} + \frac{\partial^2f}{\partial u^2}\frac{du}{dv} + \frac{\partial f}{\partial v}\frac{d[(dv/du)]}{dv} \\ &\quad + \frac{\partial^2f}{\partial v\partial u}\frac{du}{dv}\frac{dv}{du} + \frac{\partial^2f}{\partial v^2}\frac{dv}{du} \end{aligned} \quad (B3)$$

$$\frac{d(df/du)}{dv} = 2u\frac{du}{dv} - \frac{d\xi}{dv}. \quad (B4)$$

Since dv/du vanishes at a P_i , as already noted, and similarly according to (7) and (14a) du/dv and $d\xi/dv$ also vanish at a P_i , as also does $\partial f/\partial v$, (B3) and (B4) show that $\partial^2f/\partial u\partial v$ vanishes, as in (26).

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

¹ (a) R. A. Marcus, Chem. Phys. Letters **7**, 525 (1970); J. Chem. Phys. **54**, 3965 (1971) (Part I); (b) J. N. L. Connor and R. A. Marcus, *ibid.* **55**, 5636 (1971) (Part II); (c) W. H. Wong and R. A. Marcus, *ibid.* **55**, 5663 (1971); (d) R. A. Marcus, *ibid.* **56**, 311 (1972) (Part III); (e) J. Stine and R. A. Marcus, Chem. Phys. Letters **15**, 536 (1972) (Part IV).

² (a) W. H. Miller, J. Chem. Phys. **53**, 1949 (1970); (b) **53**, 3578 (1970); (c) **54**, 5386 (1971); (d) Chem. Phys. Letters **7**, 431 (1970); (e) Accts. Chem. Res. **4**, 161 (1971); (f) C. C. Rankin and W. H. Miller, J. Chem. Phys. **55**, 3150 (1971).

³ Other examples of recent semiclassical work include: (a) R. D. Levine and B. R. Johnson, Chem. Phys. Letters **7**, 404 (1970); **8**, 501 (1971); (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).

⁴ C. Chester, B. Friedman, and F. Ursell, Proc. Cambridge Phil. Soc. **53**, 599 (1957); B. Friedman, J. Soc. Ind. Appl. Math. **7**, 280 (1959).

⁵ M. V. Berry, Proc. Phys. Soc. **89**, 479 (1966); J. Phys. B **2**, 381 (1969).

⁶ In our notation, the pre-exponential factor in Ref. 4 is expanded as a sum,

$$\sum_{m=0}^{\infty} (u^2 + \xi)^m (p_m + q_m u).$$

In Part II [Ref. 2(b)] and in the present paper we use the $m=0$ term.

⁷ References 2(b)–2(c). E.g., cf discussion in Appendix A of Ref. 2(b) and in Appendix D of Ref. 2(c) [That method has also been used to treat rainbow and glory scattering. W. H. Miller, J. Chem. Phys. **48**, 464 (1968).]

⁸ In Part I, x and y angle variables are w_i 's. After a canonical transformation in Part III, they are $\tilde{w}_i$'s, which are "reduced" (constant in time) angle variables. As noted in Part III, the uniform approximations for the two integrals agree identically.

⁹ M. Abramowitz and I. A. Stegun (Eds.), National. Bur. Std. (U.S.) Appl. Math. Ser. **55**, 446 (1964).

¹⁰ G. F. Carrier, J. Fluid Mech. **24**, 641 (1966).

¹¹ The phase of the pre-exponential factor has also been discussed in terms of the eigenvalues of a Jacobian, in W. H. Miller, J. Chem. Phys. **54**, (1971).

¹² H. Kreek and J. Stine, unpublished results in this laboratory.

¹³ It is perhaps worthwhile remarking here that in Eq. (4) one should not treat ξ and A as functions of v alone: ξ and A are constant along any u curve but, as already noted, v can vary along such a curve. Thus, ξ and A are functions of both u and v , in such a way that $d\xi/du$ and dA/du vanish along u curves. Similarly, η and B in Eq. (9) can be written as $\eta(u, v)$ and $B(u, v)$, but are constant along v curves.