

Theory of Reactive Collisions: Conformal Transformation*

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Conformal mapping techniques are applied to the Schrödinger equation for a bimolecular exchange reaction, with all three atoms lying on a line. For the case of a very heavy central mass, the extension of the theory to three dimensions is indicated. An angle-shaped region of the potential-energy surface is mapped onto an infinite strip in order to simplify the theoretical treatment of the boundary conditions. The mapping function is determined with the help of the Schwarz-Christoffel formula, and its properties described. The transformed Schrödinger equation is converted into an integral equation using the method of Green's functions, and integral representations for the reflection and transmission coefficients are obtained.

I. INTRODUCTION

A well-known difficulty in the quantum-mechanical treatment of the bimolecular exchange reaction



is that, in the center-of-mass reference frame, the coordinates appropriate to asymptotic reactant configurations differ from those appropriate to asymptotic product configurations.¹

In the present paper, we overcome this difficulty by applying the theory of conformal transformations² to the reactive collision (1.1), for the case that all three atoms lie on a line. (The analysis is also valid when the line is allowed to rotate in three-dimensional space.^{3,4}) When the atom B of Reaction (1.1) possesses a very heavy mass, the theory may be extended to three dimensions in a straightforward way.

The development of the theory depends directly on the fact that the Schrödinger equation for a collinear collision depends on two (real) variables, which may be identified with the real and imaginary parts of a single complex variable. The basic feature of our approach is to map an angle-shaped region of the potential-energy surface onto an infinite strip (see Figs. 1 and 2). In this new space, the coordinates appropriate to reactants change smoothly to those appropriate to products, and numerical techniques developed for nonrearrangement collisions⁵ may be applied to the transformed Schrödinger equation. However, this simplification in the treatment of the boundary conditions is obtained at the expense of a more complicated Schrödinger equation.

Section II considers the general properties of the Schrödinger equation under a conformal transformation. Section III is devoted to the determination of the function that maps the angle-shaped region of Fig. 1 onto the infinite strip of Fig. 2; this is accomplished with the help of the Schwarz-Christoffel formula.³ Finally, in Sec. IV, the transformed Schrödinger equation is converted into an integral equation by the method of Green's functions, and integral representations for the reflection and transmission coefficients are obtained.

A useful discussion of the application of conformal mapping methods to wave equations is given in Ref. 6.

Another method for overcoming the initial and final state coordinate problem mentioned above is the introduction of natural collision coordinates.^{4,7} Both sets of coordinates are orthogonal; in the present set both coordinates are curvilinear (see Fig. 4) while in the natural collision coordinate set, the reaction coordinate is curvilinear and the vibrational coordinate curves are straight lines.

II. SCHRÖDINGER EQUATION

For the electronically adiabatic reaction (1.1) with the three atoms on a line, let ρ and r be the distance from A to the center of mass of BC and the BC distance, respectively, and let $\mu = m_A(m_B + m_C)/(m_A + m_B + m_C)$ and $m = m_B m_C/(m_B + m_C)$, where m_A , m_B , m_C are the masses of the atoms A, B, C, respectively. Then in terms of the mass-weighted coordinates $x = \mu^{1/2}\rho$ and $y = m^{1/2}r$, the Schrödinger equation in the center-of-mass reference frame is

$$\{(\partial^2/\partial x^2) + (\partial^2/\partial y^2) + (2/\hbar^2)[E - V(x, y)]\}\psi(x, y) = 0 \quad (2.1)$$

with boundary conditions representing incident, reflected, and transmitted waves. In Eq. (2.1), E is the total energy and $V(x, y)$ is the potential energy.

Typically the potential is plotted in an axis system skewed at an angle $\gamma\pi$, defined by $\tan\gamma\pi = [m_B(m_A + m_B + m_C)/m_A m_C]^{1/2}$, as shown in Fig. 1.

It is assumed that the energetically accessible regions of $V(x, y)$ may be contained within the open polygon formed from the limit of ABCD in Fig. 1. This may be accomplished by a suitable choice of the widths b and c and by scaling the potential surface if necessary. The domain D_s defined by this open polygon may be mapped onto the domain D_w , which is the strip of width d shown in Fig. 2. For the development of the theory in the next section, it actually proves more convenient to consider the inverse mapping to this one: i.e., the domain D_w is mapped onto D_s by the transformation $z = f(w)$, where

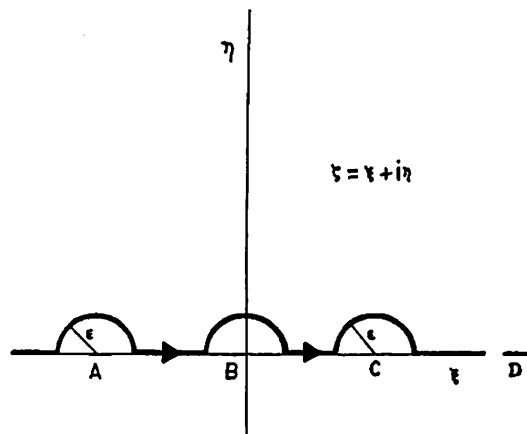


FIG. 3. The complex $z = x + iy$ plane. The domain D_1 is the upper half of this plane. The image points A, B, C, D, are $A = (-1, 0)$, $B = (0, 0)$, $C = (\alpha, 0)$, and $D = (\infty, 0)$.

in the ζ plane.² Regarding the domain D_1 as the limiting form of the polygon ABCD in Fig. 1, it is seen that the interior angles of this open polygon are $0, \gamma\pi, 0, 2\pi - \gamma\pi$. On the real axis in the ζ plane, we choose the image points to correspond with these vertices $-1, 0, \alpha, \infty$, where α is to be determined (three image points may be chosen arbitrarily²).

In terms of these angles and image points, the Schwarz-Christoffel transformation is [from Eq. (7) on p. 221 of Ref. 2]

$$z = \bar{A} \int \zeta^{\gamma-1} (\zeta+1)^{-1} (\zeta-\alpha)^{-1} d\zeta + \bar{B},$$

where $\bar{A}$ and $\bar{B}$ are to be determined. Since $\zeta=0$ for $z=0$, $\bar{B}$ is equal to zero if the lower limit of the integral is set equal to zero. Thus the transformation becomes

$$z = \bar{A} \int_0^\zeta \zeta^{\gamma-1} (\zeta+1)^{-1} (\zeta-\alpha)^{-1} d\zeta. \quad (3.1)$$

The constants $\bar{A}$ and α may be found from the change in ζ around small semicircles of radius ϵ about the points A and C (see Fig. 3) together with the corresponding changes in z . For example, as ζ travels from $-\epsilon$ to $+\epsilon$ around C, z changes by $(\infty + ib) - (\infty + i0)$, i.e., ib , so that

$$ib = \bar{A} \int_{-\epsilon}^{+\epsilon} \zeta^{\gamma-1} (\zeta+1)^{-1} (\zeta-\alpha)^{-1} d\zeta \quad (3.2)$$

and upon evaluating the integral by Cauchy's integral formula

$$\bar{A} = -\alpha^{1-\gamma} (1+\alpha) b / \pi. \quad (3.3)$$

A second equation for $\bar{A}$ and α is found by considering the change in ζ around the point A. From the geometry in Fig. 1, the corresponding change in z is $ic \exp(i\gamma\pi)$, and in a similar way as above, it is found that

$$\bar{A} = -(1+\alpha) c / \pi. \quad (3.4)$$

Solving Eqs. (3.3) and (3.4) for A and α gives

$$\alpha = (c/b)^{1/(1-\gamma)}, \quad (3.5)$$

$$A = -[1 + (c/b)^{1/(1-\gamma)}] c / \pi. \quad (3.6)$$

Note that for $b=c$, $\alpha=1$ and $A = -2c/\pi$, whilst for $b=c=\pi$, $\alpha=1$ and $\bar{A} = -2$.

Writing $t = \zeta^\gamma$ in Eq. (3.1) allows the integral to be written

$$z = \bar{A} [\gamma(1+\alpha)]^{-1} \left(\int_0^t (t^{1/\gamma} - \alpha)^{-1} dt - \int_0^t (t^{1/\gamma} + 1)^{-1} dt \right). \quad (3.7)$$

For $1/\gamma = \text{positive integer}$, the above integrals can always be evaluated.⁹ The integrals in Eq. (3.7) may also be written¹⁰

$$z = c \zeta^\gamma (\pi \alpha \gamma)^{-1} [F(1, \gamma; \gamma+1; \zeta/\alpha) + \alpha F(1, \gamma; \gamma+1; -\zeta)], \quad (3.8)$$

where $F(\alpha, \beta; \gamma; \delta)$ is the hypergeometric function.

As examples of the above transformations, consider the case of an infinite mass for B so that $\gamma = \frac{1}{2}$ and let $b=c=\pi$, so that $\alpha=1$, $\bar{A} = -2$. Then from Eq. (3.7) or (3.8)

$$z = 2(\tanh^{-1} \zeta^{1/2} + \tan^{-1} \zeta^{1/2}). \quad (3.9a)$$

As a second example, consider the $H + H_2 \rightarrow H_2 + H$ reaction in which $\gamma = \frac{1}{3}$, then with $b=c$ so that $\alpha=1$, $\bar{A} = -2c/\pi$, we have from Eq. (3.7)

$$z = (c/\pi) \{ 3 \tanh^{-1} \zeta^{1/3} - \tanh^{-1} \zeta + 3^{1/2} \tan^{-1} [3^{1/2} \zeta^{1/3} / (1 - \zeta^{2/3})] \}. \quad (3.9b)$$

B. The Mapping $h: D_1 \rightarrow D_w$

In Fig. 2, we consider the strip as the limiting form of the triangle ABC and hence possessing interior angles of $0, \pi, 0$. The images of the vertices in the ζ plane are assigned the points $-1, 0, \alpha$, where α is given by Eq. (3.5). Since Fig. 2 may be regarded as a special case of Fig. 1 with $\gamma=1$ and $c=d$, we may proceed directly from Eq. (3.8). Using the result¹¹ $F(1, 1; 2; \pm z) = \mp z^{-1} \ln(1 \mp z)$, it follows that

$$w = (d/\pi) \ln[(1+\zeta)/(1-\zeta/\alpha)], \quad (3.10)$$

or, inverting this equation to give $h^{-1}: D_w \rightarrow D_1$, yields

$$\zeta = [\exp(w\pi/d) - 1] / [\exp(w\pi/d) / \alpha + 1]. \quad (3.11)$$

For $\alpha=1$ (i.e., $b=c$), Eq. (3.11) simplifies to

$$\zeta = \tanh(w\pi/2d). \quad (3.12)$$

The point $D = (\infty, 0)$ in the ζ plane corresponds to $((d/\pi) \ln \alpha, d)$ in the w plane. An alternative derivation of Eqs. (3.10)–(3.12) follows the lines of that used for g .

It is clear from the preceding equations that, from a theoretical point of view, the simplest choice of channel widths is $b=c=d=\pi$. Figure 4 shows the domain D_z that corresponds to a rectangular grid of lines in D_w with $\gamma=\frac{1}{2}$ and $b=c=d=5$. [Equations (3.9b) and (3.12) were used.] Notice that, since the mapping is conformal, lines that are orthogonal in D_w are also orthogonal in D_z . In adiabatic or near-adiabatic theories of chemical reactions,^{4,7} motion perpendicular to a reaction coordinate plays an important role and it is seen that this property is retained in the transformed space.

It is clear from Figs. 1, 2, and 4 that for $b=c$, points symmetrical about BD in D_w correspond to points symmetrical about BD in D_z . From the geometry of Figs. 1 and 2, the symmetrical points w and $-w^*$ in D_w correspond with $z[=f(w)]$ and $(-1)^{\gamma}z^*$ in D_z , respectively, and this may also be verified analytically from Eqs. (3.7) and (3.12).

C. Jacobian

The Jacobian $J(u, v)$ may be found from Eqs. (2.3), (3.1), and (3.10):

$$\frac{dz}{dw} = \frac{dz/d\xi}{dw/d\xi} = \frac{c}{d} \xi^{\gamma-1}.$$

Thus

$$\begin{aligned} J(u, v) &= \frac{c^2}{d^2} \left| \left[\exp\left(\frac{w\pi}{d}\right) - 1 \right] / \left(\frac{\exp(w\pi/d)}{\alpha} + 1 \right) \right|^{\gamma-1} \\ &= \frac{bc}{d^2} \left(\frac{\cosh[(u\pi/d) - \ln\alpha] + \cos(v\pi/d)}{\cosh(u\pi/d) - \cos(v\pi/d)} \right)^{1-\gamma}. \end{aligned} \quad (3.13)$$

$J(u, v)$ is clearly not separable in u and v . Notice that as expected, the Jacobian reduces to unity for $b=c=d$ and $\gamma=1$ since then we have the identity mapping. Equation (3.13) also shows that $J(u, v)$ is singular at the points $(0, 0)$ and $((d/\pi) \ln\alpha, d)$; these correspond to the points B and D in D_z at which the transformation is no longer conformal. For large u , $J(u, v)$ becomes independent of v and equal to a constant:

$$J(+\infty, v) = b^2/d^2, \quad J(-\infty, v) = c^2/d^2. \quad (3.14)$$

When $\alpha=1$, Eq. (3.13) simplifies to

$$J(u, v) = \frac{c^2}{d^2} \left(\frac{\cosh(u\pi/d) + \cos(v\pi/d)}{\cosh(u\pi/d) - \cos(v\pi/d)} \right)^{1-\gamma}. \quad (3.15)$$

$J(u, v)$ is even in u , which reflects the symmetry of the domains D_z and D_w about BD in this case [$J(u, v)$ is also even in v].

The coefficients of $J(u, v)$ in Eq. (3.15) as an expansion in powers of $[\cos(v\pi/d)/\cosh(u\pi/d)]$ are the Mittag-Leffler polynomials,¹² a result that is useful in

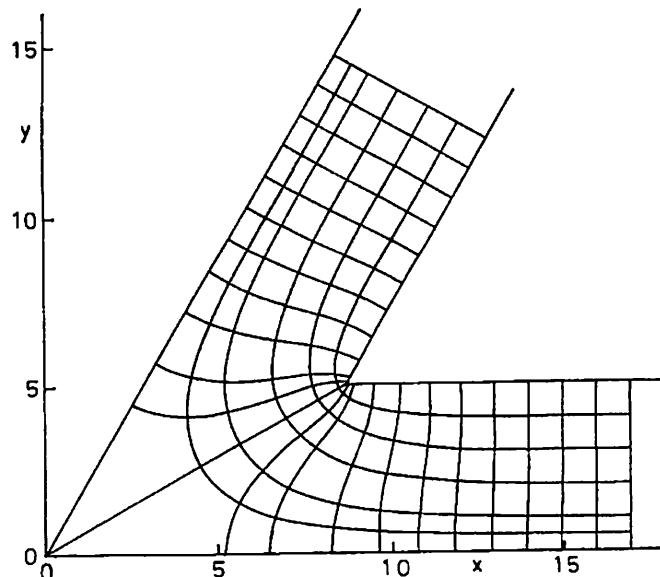


FIG. 4. The domain D_z that corresponds to a rectangular grid of lines in D_w for $\gamma=\frac{1}{2}$ and $b=c=d=5$. Equations (3.9b) and (3.12) were used.

integrals containing $J(u, v)$ (see next section):

$$J(u, v) = \frac{c^2}{d^2} \sum_{n=0}^{\infty} g_n(\beta) \left(\frac{\cos(v\pi/d)}{\cosh(u\pi/d)} \right)^n, \quad (3.16)$$

where

$$g_n(\beta) = [(\beta)_n/n!] F(-n, -\beta; 1-n-\beta; -1) \quad (3.17)$$

$$= \sum_{m=0}^n \frac{(-1)^m (\beta)_{n-m} (-\beta)_m}{(n-m)! m!}. \quad (3.18)$$

In Eqs. (3.16)–(3.18), $\beta=1-\gamma$, and $(\beta)_n$ is Pochhammer's symbol, i.e.,

$$(\beta)_0 = 1, \quad (\beta)_n = \beta(\beta+1) \cdots (\beta+n-1).$$

IV. INTEGRAL EQUATION

In this section, the differential equation (2.2) is converted into an integral equation, and integral representations obtained for the reflection and transmission coefficients. The inversion uses the method of Green's functions.¹³ Another method for obtaining the reflection and transmission coefficients that may be applied to the present problem has been described in Ref. 14 and 7(a).

It is convenient to rewrite Eq. (2.2) in the form

$$[(\partial^2/\partial u^2) + (\partial^2/\partial v^2) + k^2(u, v)]\psi(u, v) = 0, \quad (4.1)$$

where

$$k^2(u, v) = (2/\hbar^2) J(u, v) [E - V(u, v)].$$

It will also prove useful to define

$$k^{(\pm)2} = (2/\hbar^2) J(\pm\infty, v) E \quad (4.2)$$

and

$$U(\pm\infty, v) = (2/\hbar^2) J(\pm\infty, v) V(\pm\infty, v), \quad (4.3)$$

where $J(\pm\infty, v)$ is given by Eq. (3.14). We now have

$$k^2(\pm\infty, v) = k^2(\pm\infty) - U(\pm\infty, v). \quad (4.4)$$

The boundary conditions satisfied by Eq. (4.1) represent incident, reflected, and transmitted waves with the incident wave moving from right to left:

$$\begin{aligned} \psi(u, v) &\sim \phi_n^{(+)}(v) \exp(-ik_n^{(+)}u) \\ &+ \sum_{n'=0}^{\infty} R_{nn'} \phi_{n'}^{(+)}(v) \exp(ik_{n'}^{(+)}u) \\ &\sim \sum_{n'=0}^{\infty} T_{nn'} \phi_{n'}^{(-)}(v) \exp(-ik_{n'}^{(-)}u). \end{aligned} \quad (4.5)$$

In (4.5), $\{\phi_n^{(\pm)}(v)\}$ are the asymptotic vibrational wavefunctions with eigenvalues $\{\epsilon_n^{(\pm)}\}$

$$[-(d^2/dv^2) + U(\pm\infty, v)]\phi_n^{(\pm)}(v) = \epsilon_n^{(\pm)}\phi_n^{(\pm)}(v), \quad n=0, 1, 2, \dots,$$

and $k_n^{(\pm)}$ is defined by

$$k_n^{(\pm)2} = k^2(\pm\infty) - \epsilon_n^{(\pm)},$$

where the definitions of Eqs. (4.2)–(4.4) have been used. $R_{nn'}$ and $T_{nn'}$ are the reflection and transmission coefficients from an initial state n to a final state n' , respectively. The summations are understood to be in accord with the conservation of energy.

If Eq. (4.1) is written as

$$[(\partial^2/\partial u^2) + (\partial^2/\partial v^2) + k^2(\pm\infty, v)]\psi^{(\pm)}(u, v) = K^{(\pm)}(u, v)\psi^{(\pm)}(u, v), \quad (4.6)$$

where the $(\pm)$ signs on the wavefunction correspond to those in $k^2(\pm\infty, v)$ and

$$K^{(\pm)}(u, v) = k^2(\pm\infty, v) - k^2(u, v),$$

then the method of Green's functions can be used to convert (4.6) into an integral equation. The Green's function is defined by

$$[(\partial^2/\partial u^2) + (\partial^2/\partial v^2) + k^2(\pm\infty, v)]G^{(\pm)}(u, v; u', v') = \delta(u-u')\delta(v-v') \quad (4.7)$$

and by the condition that it be the outgoing solution. Since the differential operators in Eq. (4.7) commute, the Green's function is¹³ for $k_n^{(\pm)} \neq 0$,

$$G^{(\pm)}(u, v; u', v') = \sum_{n=0}^{\infty} \frac{\phi_n^{(\pm)}(v)\phi_n^{(\pm)}(v')^* \exp(ik_n^{(\pm)}|u-u'|)}{2ik_n^{(\pm)}}. \quad (4.8)$$

Two representations for the Green's function have been chosen since, as will become apparent below, one is more appropriate for the reactive scattering and the other for the nonreactive scattering.

From Eqs. (4.6)–(4.8), it follows that $\psi^{(\pm)}(u, v)$

satisfies the integral equation

$$\begin{aligned} \psi^{(\pm)}(u, v) &= \psi_n^{(\pm)}(u, v) + \sum_{n=0}^{\infty} \frac{\phi_n^{(\pm)}(v) \exp(ik_n^{(\pm)}u)}{2ik_n^{(\pm)}} \\ &\times \int_{-\infty}^u du' \int_0^d dv' \exp(-ik_n^{(\pm)}u') \phi_n^{(\pm)}(v')^* \\ &\times K^{(\pm)}(u', v') \psi^{(\pm)}(u', v') + \sum_{n=0}^{\infty} \frac{\phi_n^{(\pm)}(v) \exp(-ik_n^{(\pm)}u)}{2ik_n^{(\pm)}} \\ &\times \int_u^{\infty} du' \int_0^d dv' \exp(ik_n^{(\pm)}u') \phi_n^{(\pm)}(v')^* \\ &\times K^{(\pm)}(u', v') \psi^{(\pm)}(u', v'). \end{aligned} \quad (4.9)$$

In Eq. (4.9), $\psi_n^{(\pm)}(u, v)$ is a solution of Eq. (4.6) with the right-hand side set equal to zero. From the form of the boundary conditions (4.5), $\psi_n^{(\pm)}(u, v)$ is chosen as

$$\begin{aligned} \psi_n^{(\pm)}(u, v) &= \phi_n^{(+)}(v) \exp(-ik_n^{(+)}u) \text{ for } (+) \text{ solution} \\ &= 0 \text{ for } (-) \text{ solution.} \end{aligned}$$

Comparison of Eq. (4.9) with the boundary conditions (4.5) shows that $R_{nn'}$ is obtained by taking $u \rightarrow \infty$ and the $(+)$ solution, while $T_{nn'}$ is obtained from $u \rightarrow -\infty$ and the $(-)$ solution. Thus,

$$\begin{aligned} R_{nn'} &= [2ik_n^{(+)}]^{-1} \int_{-\infty}^{\infty} du' \int_0^d dv' \exp(-ik_n^{(+)}u') \\ &\times \phi_n^{(+)}(v')^* K^{(+)}(u', v') \psi^{(+)}(u', v'), \end{aligned} \quad (4.10)$$

$$\begin{aligned} T_{nn'} &= [2ik_n^{(-)}]^{-1} \int_{-\infty}^{\infty} du' \int_0^d dv' \exp(ik_n^{(-)}u') \\ &\times \phi_n^{(-)}(v')^* K^{(-)}(u', v') \psi^{(-)}(u', v'). \end{aligned} \quad (4.11)$$

Another method of dealing with the partial differential equation (4.1) is to convert it into a set of coupled ordinary differential equations by expanding $\psi(u, v)$ in terms of some vibrational basis set,^{4,7} but, as a similar formalism can be applied in the present case, it is not considered here. Numerical application of these coupled differential equations arising from Eq. (4.1) is currently being undertaken.¹⁵

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