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

Theory of Semiclassical Transition Probabilities for Inelastic and Reactive Collisions. II Asymptotic Evaluation of the S Matrix*

J. N. L. CONNOR† AND R. A. MARCUS

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

(Received 29 July 1971)

The asymptotic evaluation of the integral representation for an S matrix element in a previously developed semiclassical theory of molecular collisions is considered. The integral representation is evaluated asymptotically by the method of Chester, Friedman, and Ursell to give a uniform approximation for the S matrix element which is valid for classically accessible and classically inaccessible transitions. The results unify and extend those previously derived, which were restricted to the simple semiclassical and Airy function cases. A comparison is made with the simple, Airy, and uniform semiclassical approximations that occur in Miller's semiclassical theory of molecular collisions. Although the starting point of the two theories is different, it is concluded that their asymptotic results are essentially identical. In addition, a simpler derivation of the integral representation for an S matrix element from the semiclassical wavefunction is given, one which avoids the use of Green's theorem.

I. INTRODUCTION

There has been considerable interest recently in the way classical mechanics may be incorporated into the description of atomic and molecular collisions.[1–12]

One approach[1–3] applies the WKB (semiclassical) approximation directly to the Schrödinger equation, obtaining thereby a wavefunction that consists of an incoming and outgoing term. This method avoids the resolution of the Schrödinger equation into an infinite set of coupled differential equations. The phase of the wavefunction satisfies the Hamilton–Jacobi equation of classical mechanics, whilst the amplitude satisfies an equation of continuity of flux.[1,2] The characteristics of the Hamilton–Jacobi equation are the classical equations of motion. This paper presents a further development in the theory of this semiclassical approach to collision problems.

One step in the theory developed in Refs. 1 and 2, was the derivation of an integral representation for the elements of the S matrix, from the semiclassical wavefunction mentioned above. The method previously used[1,2] involved a lengthy calculation using a multidimensional form of Green's theorem. However a shorter derivation of the S matrix is possible, and this is described in Sec. II. The method avoids the use of Green's theorem.

The integral representation for the S matrix was evaluated in Refs. 1 and 2 by means of asymptotic arguments. Results were obtained when the points of stationary phase were well separated ("simple" semiclassical analysis) or when they were close together (Airy function analysis). In this paper, we present a more extensive discussion of the asymptotic evaluation of the S matrix integral, one which unifies the previous treatment and extends it. For this purpose, Sec. III is devoted to a discussion of uniform asymptotic integration by the method of Chester, Friedman, and Ursell.[13] We give a general discussion because we feel this is clearer than if a special case had been considered, and because we have other applications of the results in mind.[3]

In Sec. IV, the general results of Sec. III are applied to the integral representation for the S matrix of Sec. II. A uniform semiclassical approximation is derived which is valid for both classically accessible and classically inaccessible transitions and which reduces, in the appropriate limit, to the simple semiclassical and Airy function results.

Miller[4–8] has presented a semiclassical theory of inelastic collisions in which he evaluates the classical approximation to the quantum mechanical propagator[14] in various representations.[15] He has demonstrated by numerical application to several model problems that his theory provides a feasible quantitative approximation scheme for the analysis of inelastic molecular collisions. In Sec. IV, we compare in some detail our results for the simple, Airy, and uniform semiclassical approximations with those of Miller. Although the starting point of the two theories is different, we conclude that their asymptotic results are essentially equivalent.

II. CALCULATION OF THE S MATRIX

In this section, we present a derivation for the elements of the S matrix which is shorter and more direct than that used previously.[1,2]

In Refs. 1 and 2, the asymptotic form of the wavefunction was found to be

$$\psi_n^{(+)} \underset{R\to\infty}{\sim} R^{-1}[(\psi_{nw}{}^0/v_n{}^{1/2})\exp(-ik_nR+i\tfrac{1}{2}n_1\pi) - v^{-1/2}\,|\,\partial w_i/\partial w_j{}^0\,|^{-1/2}\exp(i\phi^*/\hbar)], \quad (2.1)$$

where

$$\frac{\phi^*}{\hbar}=2\pi\sum_{i=1}^{r}\int_{w_i0}^{w_i}[\bar{n}_i(w_i)-n_i]dw_i+\int_{R_0}^{R}kdR+2\pi\sum_{i=1}^{r}n_iw_i-k_nR_0+(n_1+1)\tfrac{1}{2}\pi. \quad (2.2)$$

In Eq. (2.1), the first term represents an incoming partial wave in a state n. R is the radial coordinate and

$$\psi_{nw}{}^0=\exp(2\pi i\sum_{i=1}^{r}n_iw_i)$$

represents the remaining r degrees of freedom expressed in terms of action-angle variables.[16] k_n and v_n are the asymptotic wavenumber and velocity, respectively. The second term in Eq. (2.1) represents an outgoing wave. k, v, and $\bar{n}_i$ are the instantaneous wavenumber, velocity, and the action for the coordinate i, respectively.[16] The integration in Eq. (2.2) is from some initial set of values $\{w_i{}^0, R_0\}$ at the beginning of the collision, to some final set of values $\{w_i, R\}$ at the end. Finally $|\partial w_i/\partial w_j{}^0|$ denotes a Jacobian of the final angle variables with respect to the initial ones.

The elements of the S matrix are defined by[17]

$$\psi_n{}^{(+)}\underset{R\to\infty}{\sim}R^{-1}[(\psi_{nw}{}^0/v_n{}^{1/2})\exp(-ik_nR+i\tfrac{1}{2}n_1\pi)-\sum_m S_{mn}(\psi_{mw}{}^0/v_m{}^{1/2})\exp(ik_mR-i\tfrac{1}{2}m_1\pi)] \quad (2.3)$$

and the problem is to determine S_{mn} from Eqs. (2.1) and (2.3). In Refs. 1 and 2, S_{mn} was found by a lengthy calculation in which Green's theorem was used to convert an $r+1$ dimensional volume integral into an r-dimensional surface integral. Instead of doing this, however, we can realize that Eqs. (2.1) and (2.3) are two representations of the same wavefunction, $\psi_n{}^{(+)}$, and hence are equivalent. Therefore we have from Eqs. (2.1) and (2.3):

$$\sum_{m'}S_{m'n}(\psi_{m'w}{}^0/v_{m'}{}^{1/2})\exp(ik_{m'}R-i\tfrac{1}{2}m_1'\pi)=v^{-1/2}|\partial w_i/\partial w_j{}^0|^{-1/2}\exp(i\phi^*/\hbar). \quad (2.4)$$

The mnth element of the S matrix is now obtained by multiplying both sides of Eq. (2.4) by $\psi_{mw}{}^{0*}$, integrating over w, and using the orthonormality of the $\{\psi_{mw}{}^0\}$:

$$\int_0^1\cdots\int_0^1\psi_{mw}{}^{0*}\psi_{m'w}{}^0\prod_{i=1}^{r}dw_i=\delta_{mm'}.$$

This gives for S_{mn}:

$$S_{mn}=\int_0^1\cdots\int_0^1\left(\frac{v_m}{v}\right)^{1/2}\left|\frac{\partial w_i}{\partial w_j{}^0}\right|^{-1/2}\exp(i\Delta)\prod_{i=1}^{r}dw_i, \quad (2.5)$$

where

$$\Delta=2\pi\sum_{i=1}^{r}\int_{w_i0}^{w_i}[\bar{n}_i(w_i)-n_i]dw_i+\int_{R_0}^{R}kdR-k_nR_0-k_mR+2\pi\sum_{i=1}^{r}(n_i-m_i)w_i+(n_1+m_1+1)\tfrac{1}{2}\pi. \quad (2.6)$$

This completes the formal derivation of the integral representation for S_{mn}.

At first sight, Eq. (2.5) differs from the result obtained previously[1,2] by the Green's theorem method, namely

$$S_{mn}=\int_0^1\cdots\int_0^1\frac{(v+v_m)}{2(vv_m)^{1/2}}\left|\frac{\partial w_i}{\partial w_j{}^0}\right|^{-1/2}\exp(i\Delta)\prod_{i=1}^{r}dw_i. \quad (2.7)$$

However, the formal results (2.5) and (2.7) cannot be used as they stand, because S_{mn} is a function of R. This can be most easily seen by integrating by parts the integrals in Eq. (2.6) for Δ:

$$\Delta=-2\pi\sum_{i=1}^{r}\int_{n_i}^{\bar{n}_i}w_id\bar{n}_i-\int_{-k_n}^{k}Rdk+2\pi\sum_{i=1}^{r}(\bar{n}_i-m_i)w_i+(k-k_m)R+(n_1+m_1+1)\tfrac{1}{2}\pi. \quad (2.8)$$

However, if Eqs. (2.5) and (2.7) are evaluated by asymptotic methods, S_{mn} becomes independent of R and Eqs. (2.5) and (2.7) become equivalent. This follows since at a saddle point (defined by $\partial\Delta/\partial w_i=0$), we have $\bar{n}_i=m_i$ and hence $k=k_m$ and $v=v_m$. The use of an asymptotic method to evaluate the integral representation of S_{mn} is consistent with the use of an asymptotic method to derive Eq. (2.1) originally.[1,2] An exception to the use of an asymptotic evaluation of the S matrix integral is the case of elastic scattering, when both Eqs. (2.5) and (2.7) reduce to their well-known values $\exp(2i\delta_l)\delta_{mn}$, where δ_l is the semiclassical phase shift for radial motion with a single turning point.[2]

In the next paper[3] of this series, integral representations will be given which are not R dependent and one of which satisfies the principle of microscopic reversibility. The method presented in the subsequent sections will be equally applicable to them as it is to (2.5) or (2.7). In all cases, the same results are then obtained for the asymptotic result, and so the analysis of Secs. III and IV need not then be repeated in the later paper.

In the remainder of this paper, we will consider only one-dimensional integrals for simplicity of presentation, although some of the results are valid in more than one dimension. The next section deals with the theory of the asymptotic evaluation of integrals of the type (2.5) and (2.7), whilst applications will be found in Sec. IV.

III. UNIFORM ASYMPTOTIC INTEGRATION

A. Introduction

Here we apply the method of Chester, Friedman, and Ursell[13] to the asymptotic evaluation of the integral

$$I=\int_{-\infty}^{\infty} g(x)\ \exp[if(\alpha,x)]dx, \tag{3.1}$$

where α is a real parameter. It is known from studies in potential scattering that this is a very effective method for dealing with integrals of the type (3.1).[18–20] Another treatment for the uniform asymptotic integration of Eq. (3.1) has been given by Miller[5] based on a method of Carrier.[21] We have adapted the method of Chester *et al.* because of its comparative rigor. Applications and further discussion are given in the next section.

B. $f''(x_1)>0 \qquad f''(x_2)<0$

We shall suppose there exist two points of stationary phase such that

$$f'(\alpha,x_1)=0, \qquad f'(\alpha,x_2)=0. \tag{3.2}$$

For the classically accessible case (which we consider first) x_1 and x_2 are real while in the classically inaccessible case x_1 and x_2 are complex conjugates. For the classically accessible case we choose for the signs of the second derivatives

$$f''(x_1)>0 \qquad f''(x_2)<0, \tag{3.3}$$

where the primes denote differentiation with respect to x. In addition it is assumed that there exists a real α_0 and x_0 such that

$$f'(\alpha_0,x_0)=0, \qquad f''(x_0)=0, \qquad f'''(x_0)<0, \tag{3.4}$$

that is, for $\alpha=\alpha_0$ there exists a double root, but for $\alpha\neq\alpha_0$ there exists two single roots.

The absence of α in the second- and third-order derivatives in (3.3) and (3.4) indicates that $f(\alpha, x)$ depends only linearly on the parameter α. For example, in terms of Eq. (2.8), and Fig. 3 of Ref. 2, α is m, α_0 is $\hat{n}$, and x_0 is $\hat{w}$; in rainbow scattering[18,22] α is θ the scattering angle, α_0 is θ_r the rainbow angle and x_0 is l_r the value of the angular momentum quantum number at the rainbow angle. [See Eqs. (3.27) and (3.28) below.] However, it is true in general that $f''(x_0)$ and $f'''(x_0)$ can be taken as independent of α, by a suitable translation and rotation of coordinates.[13]

Throughout this section and the next it is assumed that $g(x)$ does not possess any zeros or singularities near the saddle points. If this is not the case, a modified treatment can be given.

C. Quadratic Approximation

The simplest approximation for evaluating the integral (3.1) in the classically accessible case comes by expanding $f(\alpha, x)$ around the points x_1 and x_2:

$$f(\alpha,x)=f(\alpha,x_1)+\tfrac{1}{2}f''(x_1)(x-x_1)^2$$
$$f(\alpha,x)=f(\alpha,x_2)-\tfrac{1}{2}\,|f''(x_2)|\,(x-x_2)^2 \tag{3.5}$$

which leads to the simple stationary phase result

$$I=(2\pi/|f_1''|)^{1/2}g_1\exp[i(f_1+\tfrac{1}{4}\pi)]+(2\pi/|f_2''|)^{1/2}g_2 \times\exp[i(f_2-\tfrac{1}{4}\pi)], \tag{3.6}$$

where the obvious notation $g_i=g(x_i)$, $f_i=f(\alpha, x_i)$, $f_i''=f''(x_i)$, $i=1, 2$ has been used.

D. Cubic Approximation

For α near α_0, the approximation (3.5) breaks down, and a cubic expansion of $f(\alpha, x)$ about x_0 must be used instead

$$f(\alpha,x)=f(\alpha,x_0)+f'(\alpha,x_0)(x-x_0) -\tfrac{1}{6}\,|f'''(x_0)|\,(x-x_0)^3, \tag{3.7}$$

where Eq. (3.4) has been used. For the classically accessible case, $f'(\alpha, x_0)$ is positive whereas in the classically inaccessible case $f'(\alpha, x_0)$ is negative. It will also prove useful to include the second term in the asymptotic expansion for I by writing[13,18]

$$g(x)=g(x_0)+g'(x_0)(x-x_0). \tag{3.8}$$

Inserting Eqs. (3.7) and (3.8) into the integral (3.1) and making the change of variable

$$v=-(|f'''(x_0)|/2)^{1/3}(x-x_0)$$

leads to

$$I=2\pi g_0(2/|f_0'''|)^{1/3}\exp(if_0)Ai[-f_0'(2/|f_0'''|)^{1/3}] +i2\pi g_0'(2/|f_0'''|)^{2/3}\exp(if_0)Ai'[-f_0'(2/|f_0'''|)^{1/3}], \tag{3.9}$$

where $Ai(x)$ and $Ai'(x)$ are the regular Airy function and its derivative, respectively,[23]

$$2\pi Ai(x)=\int_{-\infty}^{\infty}\exp[i(xv+\tfrac{1}{3}v^3)]dv,$$

$$2\pi Ai'(x)=i\int_{-\infty}^{\infty}v\exp[i(xv+\tfrac{1}{3}v^3)]dv.$$

For small values of the argument of the Airy function and its derivative [i.e., those for which the expansion (3.7) is valid], the first term in Eq. (3.9) will dominate the second term

In passing we note that if $f'''(x_0)=0$ but $f''''(x_0)\neq0$, the method of this subsection still holds but now the characteristic integral is

$$C(x)=\int_{-\infty}^{\infty} dv \exp[i(xv+v^4)]$$

instead of the Airy integral. In potential scattering this behavior gives rise to cubic rainbows.[24]

E. Uniform Approximation

In this subsection, a uniform approximation for the integral (3.1) is derived which reduces to Eq. (3.6) when x_1 and x_2 are far apart, and to Eq. (3.9) when they are close together, but which is also valid for intermediate values of x_1 and x_2 as well.

Chester, Friedman, and Ursell[13] have shown that a uniform approximation for the integral (3.1) may be obtained by introducing a new variable y, implicitly defined by[25] (note that this is *not* an approximation)

$$f(\alpha, x)=\tfrac{1}{3}y^3-\zeta(\alpha)y+A(\alpha), \tag{3.10}$$

where $\zeta(\alpha)$ and $A(\alpha)$ are constants. The mapping is one-to-one and uniformly analytic if the stationary points of either side of Eq. (3.10) correspond[13]:

$$x=x_1\leftrightarrow y=\zeta^{1/2},$$
$$x=x_2\leftrightarrow y=-\zeta^{1/2}. \tag{3.11}$$

Substituting Eqs. (3.11) into Eq. (3.10) yields two simultaneous equations for $\zeta(\alpha)$ and $A(\alpha)$ which may be solved to give

$$2A=f(\alpha, x_1)+f(\alpha, x_2), \tag{3.12}$$

$$\tfrac{4}{3}\zeta^{3/2}=f(\alpha, x_2)-f(\alpha, x_1). \tag{3.13}$$

In our applications, the right-hand sides of Eqs. (3.12) and (3.13) will represent the sum and difference of classical action terms, respectively.

In the classically accessible case, where x_1 and x_2 are real solutions of Eq. (3.2), A and ζ are both real and ζ may be chosen to be positive. In the classically inaccessible case, where x_1 and x_2 are complex conjugate solutions of Eq. (3.2), A and ζ are again real with ζ chosen to be negative.

The integral (3.1) now becomes

$$I=\exp(iA)\int_{-\infty}^{\infty} g\left(\frac{dx}{dy}\right)\exp[i(-\zeta y+\tfrac{1}{3}y^3)]dy. \tag{3.14}$$

In Ref. 13 it is shown that the first two terms of a suitable expansion for $g(dx/dy)$ are

$$g(dx/dy)=p_0+q_0y. \tag{3.15}$$

Inserting Eqs. (3.11) into Eq. (3.15) then gives two simultaneous equations which may be solved for p_0 and q_0:

$$p_0=\tfrac{1}{2}[g(x_1)(dx/dy)_{x_1}+g(x_2)(dx/dy)_{x_2}], \tag{3.16}$$

$$q_0=(1/2\zeta^{1/2})[g(x_1)(dx/dy)_{x_1}-g(x_2)(dx/dy)_{x_2}]. \tag{3.17}$$

The values of the derivatives may be found by differentiating the transformation equation (3.10) twice to give:

$$\frac{d^2f(\alpha,x)}{dx^2}\left(\frac{dx}{dy}\right)^2+\frac{df(\alpha,x)}{dx}\frac{d^2x}{dy^2}=2y. \tag{3.18}$$

Substituting the values (3.11) into Eq. (3.18) and using Eq. (3.2) leads to

$$(dx/dy)_{x_1}=(2\zeta^{1/2}/f_1'')^{1/2},$$
$$(dx/dy)_{x_2}=(-2\zeta^{1/2}/f_2'')^{1/2},$$

so that from Eqs. (3.16) and (3.17), p_0 and q_0 become

$$p_0=(\zeta^{1/4}/2^{1/2})\{[g_1/(f_1'')^{1/2}]+[g_2/(-f_2'')^{1/2}]\},$$

$$q_0=(1/2^{1/2}\zeta^{1/4})\{[g_1/(f_1'')^{1/2}]-[g_2/(-f_2'')^{1/2}]\}. \tag{3.19}$$

Substituting Eqs. (3.19) and (3.15) into Eq. (3.14) allows the integral I to be written in terms of the Airy function and its derivative, thus

$$\begin{aligned}I=2^{1/2}\pi\exp(iA)\{&[g_1/(f_1'')^{1/2}]\\&+[g_2/(-f_2'')^{1/2}]\}\zeta^{1/4}Ai(-\zeta)\\&-i2^{1/2}\pi\exp(iA)\{[g_1/(f_1'')^{1/2}]\\&-[g_2/(-f_2'')^{1/2}]\}\zeta^{-1/4}Ai'(-\zeta),\end{aligned} \tag{3.20}$$

where $A(\alpha)$ is given by Eq. (3.12) and $\zeta(\alpha)$ by Eq. (3.13). This is the uniform approximation we have been seeking and Eq. (3.20) is the main result of this section. Equation (3.20) is valid for both the classically accessible case and the classically inaccessible case. In the second case, x_1 and x_2 are complex conjugate solutions of Eq. (3.2) and $f(\alpha, x_1)=f(\alpha, x_2)^*$, $f''(\alpha, x_1)=f''(\alpha, x_2)^*$, $g(x_1)=g(x_2)^*$ (all these results are a consequence of the Schwarz Reflection Principle). In addition, in the classically inaccessible case, A and ζ are real with ζ negative. We can write therefore

$$g_1=ge^{i\alpha}, \qquad g_2=ge^{-i\alpha},$$
$$f_1''=f''e^{i\beta}, \qquad f_2''=f''e^{-i\beta}. \tag{3.21}$$

With Eqs. (3.21) substituted into Eq. (3.20), the equation for I does not take a particularly simple form, so we do not report it. However, the equation for $|I|^2$ (required later) does simplify and is given by

$$\begin{aligned}|I|^2=4\pi^2g^2(f'')^{-1}\{&[1-\sin(2\alpha-\beta)]|\zeta|^{1/2}Ai^2(|\zeta|)\\&+[1+\sin(2\alpha-\beta)]|\zeta|^{-1/2}Ai'^2(|\zeta|)\}.\end{aligned} \tag{3.22}$$

F. Limiting Cases

Equation (3.20) is readily shown to reduce to the simple stationary phase result (3.6) by substituting the asymptotic forms for $Ai(-\zeta)$ and $Ai'(-\zeta)$[23]

$$Ai(-\zeta) \underset{\zeta\to\infty}{\sim} \pi^{-1/2}\zeta^{-1/4}\sin(\tfrac{2}{3}\zeta^{3/2}+\tfrac{1}{4}\pi),$$
$$Ai'(-\zeta) \underset{\zeta\to\infty}{\sim} -\pi^{-1/2}\zeta^{1/4}\cos(\tfrac{2}{3}\zeta^{3/2}+\tfrac{1}{4}\pi). \quad (3.23)$$

To verify that the uniform approximation (3.20) and (3.22) reduces to the Airy result (3.9), the cubic expansion (3.7) is assumed for $f(\alpha, x)$, and the linear expansion (3.8) for $g(x)$. With the help of the stationary phase conditions (3.2) and Eq. (3.8), it is then found that

$$x_2-x_0=-(x_1-x_0)=(2f_0'/|f_0'''|)^{1/2} \quad (3.24)$$

in the classically accessible case, or

$$x_2-x_0=-(x_1-x_0)=i(2|f_0'|/|f_0'''|)^{1/2} \quad (3.25)$$

in the classically inaccessible case. Equations (3.24) and (3.25) then allow A, ζ, g_1, g_2, f_1'', f_2'', g, f'', α, and β to be determined, and it is readily shown that Eqs. (3.20) and (3.22) reduce to the Airy result (3.9).

G. $f''(x_1)<0 \quad f''(x_2)>0$

In this subsection, we consider the uniform approximation for the opposite case to that of Sec. III.B, i.e., in the classically accessible case when

$$f''(x_1)<0, \qquad f''(x_2)>0.$$

As the derivation is similar to that described in the previous subsections, we merely quote the results. Defining a new function implicitly by Eq. (3.10) and proceeding as before, we arrive at the following uniform approximation for I:

$$\begin{aligned}I=&2^{1/2}\pi\exp(iA)\{[g_2/(f_2'')^{1/2}]\\&+[g_1/(-f_1'')^{1/2})]\}\zeta^{1/4}Ai(-\zeta)\\&-i2^{1/2}\pi\exp(iA)\{[g_2/(f_2'')^{1/2}]\\&-[g_1/(-f_1'')^{1/2}]\}\zeta^{-1/4}Ai'(-\zeta),\end{aligned} \quad (3.26)$$

where

$$2A=f(\alpha,x_1)+f(\alpha,x_2)$$

and

$$\tfrac{4}{3}\zeta^{3/2}=f(\alpha,x_1)-f(\alpha,x_2).$$

If the asymptotic forms (3.23) for $Ai(-\zeta)$ and $Ai'(-\zeta)$ are substituted into Eq. (3.26), the simple stationary phase result is obtained:

$$I=g_1\left(\frac{2\pi}{|f_1''|}\right)^{1/2}\exp\left[i\left(f_1-\frac{\pi}{4}\right)\right]+g_2\left(\frac{2\pi}{|f_2''|}\right)^{1/2}\exp\left[i\left(f_2+\frac{\pi}{4}\right)\right].$$

On the other hand, if a cubic expansion for $f(\alpha, x)$ near x_0 is assumed,

$$f(\alpha,x)=f(\alpha,x_0)+f'(\alpha,x_0)(x-x_0)+\tfrac{1}{6}f'''(x_0)(x-x_0)^3$$

and the procedure described in Sec. III.F followed, then the Airy result is obtained:

$$\begin{aligned}I=&2\pi g_0(2/f_0''')^{1/3}\exp(if_0)Ai[f_0'(2/f_0''')^{1/3}]\\&-i2\pi g_0'(2/f_0''')^{2/3}\exp(if_0)Ai'[f_0'(2/f_0''')^{1/3}].\end{aligned}$$

H. Example: Potential Scattering

As an example of the use of Eq. (3.26) and as a check on our calculations, we evaluate the integral $|f_r(\theta)|^2$ where

$$f_r(\theta)=\frac{-i\exp(-i\pi/4)}{k(2\pi\sin\theta)^{1/2}}I^+ \quad (3.27)$$

and

$$I^+=\int_{-\infty}^{\infty}l^{1/2}\exp[i(2\delta_l+l\theta)]dl \quad (3.28)$$

which arises in the theory of the rainbow effect in potential scattering when the rainbow angle $\theta_r<\pi$.[18,22] In Eqs. (3.27) and (3.28) θ is the scattering angle, l the angular momentum quantum number, δ_l the semiclassical phase shift ($2d\delta_l/dl=\Theta$, the deflection function), and k is the wavenumber. Making the appropriate identifications with Eq. (3.26) we obtain[26]

$$\begin{aligned}I^+=&2^{1/2}\pi\exp(iA)\{[(l_2/\Theta_{l_2}')^{1/2}\\&+(-l_1/\Theta_{l_1}')^{1/2}]\zeta^{1/4}Ai(-\zeta)\\&-i[(l_2/\Theta_{l_2}')^{1/2}-(-l_1/\Theta_{l_1}')^{1/2}]\zeta^{-1/4}Ai'(-\zeta)\},\end{aligned} \quad (3.29)$$

where

$$2A=2(\delta_{l_1}+\delta_{l_2})+(l_1+l_2)\theta$$

and

$$\tfrac{4}{3}\zeta^{3/2}=2(\delta_{l_1}-\delta_{l_2})+(l_1-l_2)\theta.$$

Introducing the classical cross sections by

$$\sigma_i=l_i/k^2\sin\theta\,|\Theta_{l_i}'| \qquad i=1,2$$

we find from Eq. (3.29) for the case $\theta<\theta_r$

$$\begin{aligned}|f_r(\theta)|^2=&\pi(\sigma_2^{1/2}+\sigma_1^{1/2})^2\zeta^{1/2}Ai^2(-\zeta)\\&+\pi(\sigma_2^{1/2}-\sigma_1^{1/2})^2\zeta^{-1/2}Ai'^2(-\zeta)\end{aligned} \quad (3.30)$$

in agreement with Berry.[18] Equation (3.30) will provide a very illuminating analogy with a result derived in Sec. IV.

IV. DISCUSSION

The general results of Sec. III are now applied to the integral representation of the S matrix given in Sec. II, hence unifying and extending the analysis given previously.[2] It is clear that there are essentially three cases to consider: the simple stationary phase result, the Airy result, and the uniform result which encompasses the other two. For each case we will compare our results with those of Miller.[4–8]

A. Simple Semiclassical Analysis

The results of Sec. III.C are applicable here. From Eqs. (2.5)–(2.8) the points of stationary phase w_1', w_2' are given by (see also Ref. 2)

$$d\Delta/dw=2\pi[\bar{n}(w)-m]$$
$$=0 \quad \text{at} \quad w=w_1', w_2'. \tag{4.1}$$

The first line of Eq. (4.1) is the equivalent of the relation $2d\delta_l/dl=\Theta$ in potential scattering (see Sec. III.H). Then from Eqs. (2.5) or (2.7) and (3.6)

$$S_{mn}=|\,d\bar{n}/dw^0\,|_{w_1{}^{0\prime}}{}^{-1/2}\exp\{i[\Delta(w_1{}^{0\prime})+\tfrac{1}{4}\pi]\}$$
$$+\,|\,d\bar{n}/dw^0\,|_{w_2{}^{0\prime}}{}^{-1/2}\exp\{i[\Delta(w_2{}^{0\prime})-\tfrac{1}{4}\pi]\}, \tag{4.2}$$

where we have used from Eq. (4.1) the fact that

$$d^2\Delta/dw^2=2\pi d\bar{n}/dw. \tag{4.3}$$

In Eq. (4.2), $\bar{n}$ is now to be regarded as an explicit function of w^0 rather than w, and the labeling of the points of stationary phase has been changed to conform with this. Thus if

$$w=w(w^0),$$

then

$$w_i'=w(w_i{}^{0\prime}), \qquad i=1, 2.$$

Also in writing down Eq. (4.2), we have chosen the sign of the Jacobian factor

$$(dw^0/dw)_{w_i'}$$

to be positive in order that the amplitude factor A [defined by Eq. (4.23) of Ref. 2] be real. This will also be the case in the next two subsections. When the sign is negative, the analysis of this section is still valid provided appropriate modifications are made; or one may proceed directly from the integral (2.5) or (2.7) to the results of Sec. III.G. $\Delta(w_1{}^{0\prime})$ and $\Delta(w_2{}^{0\prime})$ are defined by [from Eq. (2.8)]:

$$\left.\begin{matrix}\Delta(w_1{}^{0\prime})\\ \\ \Delta(w_2{}^{0\prime})\end{matrix}\right\}=-2\pi\int_n^m w d\bar{n}-\int_{-k_n}^{k_m}Rdk+\tfrac{1}{2}\pi \tag{4.4}$$

since $n_1=m_1=0$ in the one-dimensional case we are considering. [We recall[2] that the integrals in Eq. (4.4) are *line integrals*, i.e., integrals evaluated along the actual classical trajectories. In the present case there are two trajectories which give rise to a final m.]

We can now compare Eq. (4.2) with Miller's results [Eqs. (41)–(45) of Ref. 4].[27] The expressions differ in both their amplitude and phase factors. The amplitudes differ by a factor of $\hbar$. This, however, is a consequence of the delta function normalization used in Ref. 4,[28] which apparently omitted the $\hbar$ factor. The over-all phase of the S matrix is also different in the two cases. Miller gives his S matrix an over-all phase of $-\pi/4$ in the one-dimensional case (Appendix A of Ref. 4), whereas Eq. (4.4) shows that the present S matrix has an over-all phase of $\pi/2$, or in the general case, from Eq. (2.6), an over-all phase of

$$(n_1+m_1+1)\pi/2.$$

The term $(n_1+m_1)\pi/2$ is a consequence of the boundary condition that the incoming wave in Eq. (2.1) be a partial wave, and the $\pi/2$ is a consequence of the decrease in $\pi/2$ of the wavefunction at the turning point in the R motion.[2] The transition probability is

$$P_{mn}=|\,S_{mn}\,|^2$$

and then the over-all phases are of no consequence. Thus from Eq. (4.2)

$$P_{mn}=p_1+p_2+2(p_1p_2)^{1/2}\sin[\Delta(w_2{}^{0\prime})-\Delta(w_1{}^{0\prime})], \tag{4.5}$$

where

$$p_i=(|\,d\bar{n}/dw^0\,|_{w_i{}^{0\prime}})^{-1}, \qquad i=1,2 \tag{4.6}$$

is the classical transition probability. Thus the present simple semiclassical results are equivalent to those of Miller[4,5] when the above remarks regarding the amplitude and over-all phase of the S matrix are taken into account.

B. Airy Analysis

We now wish to consider the result for S_{mn} based on the assumption of a parabolic maximum in the $\bar{n}(w)$ vs w plot[2]:

$$\bar{n}(w)=\hat{n}-(a/2\pi)(w-\hat{w})^2 \tag{4.7}$$

so that from Eq. (4.1)

$$\Delta(w)=\Delta(\hat{w})+2\pi(\hat{n}-m)(w-\hat{w})-\tfrac{1}{3}a(w-\hat{w})^3. \tag{4.8}$$

Then if we compare Eq. (4.8) with Eq. (3.7) and use Eq. (3.9), we have

$$S_{mn}=2\pi a^{-1/3}\exp[i\Delta(\hat{w})]$$
$$\times(|\,dw/dw^0\,|_{\hat{w}})^{-1/2}\,Ai[-2\pi(\hat{n}-m)/a^{1/3}] \tag{4.9}$$

and

$$P_{mn}=4\pi^2a^{-2/3}(|\,dw/dw^0\,|_{\hat{w}})^{-1}Ai^2[-2\pi(\hat{n}-m)/a^{1/3}], \tag{4.10}$$

where we have neglected the second term in Eq. (3.9) in writing down Eqs. (4.9) and (4.10) as it is dominated by the first term.[29]

The result derived previously [Eqs. (7.6) and (7.10) of Ref. 2] differs from Eq. (4.9) in that the Jacobean factor was evaluated at a saddle point w_i' rather than at the maximum of $\bar{n}(w)$, i.e., $\hat{w}$. However since w_i' is assumed to lie close to $\hat{w}$ for the quadratic expansion (4.7) to be meaningful and because the Jacobian factor is also assumed to be a slowly varying function of w, this difference will be of little importance.

This is a convenient point at which to discuss the variable of integration in Eqs. (2.5), (2.7), (4.9), and (4.10). In these equations, the integration is over w, i.e., the *final* value of the angle variable. However since there is a relation between w and w^0, the *initial* value of the angle variable, of the form

$$w=w(w^0)$$

the integration can be changed from one over w to one over w^0. The question then arises as to which variable is to be preferred: the initial angle variable or the final angle variable? Clearly the variable to use is that for which the $\bar{n}(w)$ vs w plot, or $\bar{n}(w^0)$ vs w^0 plot, is the simpler. For example, in the nonreactive linear atom–diatom collision problem, the $\bar{n}(w^0)$ vs w^0 plot has a simple sinusoidal shape (see Figs. 2 and 4 of Ref. 5), whereas the $\bar{n}(w)$ vs w plot is considerably more complicated.[30] The initial angle variable is therefore the preferred one to use in this case.

Now Eqs. (2.5), (2.7), (4.9), and (4.10) together with the analysis given previously[2] involve integrations over w, whereas Miller uses the initial angle variable.[5] Suppose however we know that $\bar{n}(w^0)$ can be represented by

$$\bar{n}(w^0)=\bar{n}(\hat{w}^0)+\tfrac{1}{2}(d^2\bar{n}/dw^{02})_{\hat{w}^0}(w^0-\hat{w}^0)^2 \quad (4.11)$$

and that

$$w^0=w^0(w)$$

with

$$\hat{w}^0=w^0(\hat{w});$$

Then it is not difficult to show that Eq. (4.11) becomes

$$\bar{n}(w)=\bar{n}(\hat{w})+\tfrac{1}{2}(d^2\bar{n}/dw^{02})_{\hat{w}^0}[(dw/dw^0)_{\hat{w}^0}]^{-2}(w-\hat{w})^2. \quad (4.12)$$

Miller uses initial angle variables in his Airy analysis [Eq. (18) of Ref. 5], so in order to make the comparison Eq. (4.7) must be identified with Eq. (4.12). When this is done, and the remarks of Sec. IV.A regarding the normalization and over-all phase of S_{mn} are taken into account, it is found that the two approximations for the transition probability agree.[27,28]

Miller actually uses a somewhat different set of variables in his treatment of the nonreactive linear atom–diatom system[5,6] from the usual action-angle variables we are using. However, the arguments leading to the various asymptotic approximations are quite general and our comparison remains valid.

Finally, by evaluating the S matrix in different representations, Miller derived another integral representation for S_{mn} which he called the initial value representation.[5] The question then arises as to the relationship between this representation and the integral representation of Eqs. (2.5) or (2.7). We have not tried to derive the initial value representation from Eqs. (2.5) or (2.7) or from the formalism of Ref. 2. However, in Part III of this series[3] a new representation of the wavefunction is achieved and yields in a natural manner an integral expression which satisfies microscopic reversibility. A comparison with Miller's initial value representation is given in Part III. The coordinates in the new representation are all "uniformized" whereas formerly only the internal coordinates were.

The method described in the present paper can be used to give an asymptotic approximation to the integral for S_{mn} given in Part III.

C. Uniform Approximation

Here we apply the uniform approximation of Sec. III to the integral (2.5) or (2.7). We consider the classically accessible case first. Making the appropriate identifications and using Eqs. (4.3) and (4.6) we have

$$S_{mn}=\pi^{1/2}\exp(iA)[(p_1^{1/2}+p_2^{1/2})\zeta^{1/4}Ai(-\zeta) - i(p_1^{1/2}-p_2^{1/2})\zeta^{-1/4}Ai'(-\zeta)], \quad (4.13)$$

where

$$A=\tfrac{1}{2}[\Delta(w_1^{0\prime})+\Delta(w_2^{0\prime})]$$

and

$$\zeta=\{\tfrac{3}{4}[\Delta(w_2^{0\prime})-\Delta(w_1^{0\prime})]\}^{2/3}$$

so that A and ζ involve the sum and difference of the classical actions, respectively. The transition probability then takes the form

$$P_{mn}=\pi(p_1^{1/2}+p_2^{1/2})^2\zeta^{1/2}Ai^2(-\zeta) +\pi(p_1^{1/2}-p_2^{1/2})^2\zeta^{-1/2}Ai'^2(-\zeta). \quad (4.14)$$

This is directly analogous to the uniform approximation for the rainbow effect in potential scattering derived in Sec. III.H [see Eq. (3.30)]. For ζ large, Eq. (4.14) goes over to the simple semiclassical result Eq. (4.5), and for ζ small, Eq. (4.14) becomes equivalent to the Airy result Eq. (4.10).

Miller has also derived a uniform approximation[5] for the transition probability which in our notation is

$$P_{mn}=\pi(p_1^{1/2}+p_2^{1/2})^2\zeta^{1/2}Ai^2(-\zeta) +\pi(p_1^{1/2}-p_2^{1/2})^2\zeta^{1/2}Bi^2(-\zeta), \quad (4.15)$$

where $Bi(-\zeta)$ is the irregular Airy function.[23] Thus, Eq. (4.15) differs from Eq. (4.14) only in that $\zeta^{1/2}Bi^2(-\zeta)$ replaces $\zeta^{-1/2}Ai'^2(-\zeta)$.

Since[23]

$$\left.\begin{array}{l}\zeta^{-1/2}Ai'^2(-\zeta)\\ \zeta^{1/2}Bi^2(-\zeta)\end{array}\right\} \underset{\zeta\to\infty}{\sim} \pi^{-1}\cos^2(\tfrac{2}{3}\zeta^{3/2}+\tfrac{1}{4}\pi)$$

it is clear that both Eqs. (4.14) and (4.15) are equivalent for large ζ [and go over to Eq. (4.5)]. When ζ is small, however,

$$\zeta^{-1/2}Ai'^2(-\zeta)\neq\zeta^{1/2}Bi^2(-\zeta)$$

but in this case, the first term in both Eqs. (4.14) and (4.15) dominates the second term, cf. Eq. (3.9). We therefore conclude that Eqs. (4.14) and (4.15) are essentially equivalent for all ζ in the classically accessible case.

We now consider the classically inaccessible case. If we write

$$(d\bar{n}/dw^0)_{w_1^0\prime}{}^{1/2}=p^{-1/2}\exp(i\beta/2),$$

then from Eqs. (3.21) and (3.22) we have

$$P_{mn}=2\pi p[(1+\sin\beta)\,|\,\zeta\,|^{1/2}Ai^2(|\,\zeta\,|)+(1-\sin\beta)\,|\,\zeta\,|^{-1/2}Ai'^2(|\,\zeta\,|)]. \quad (4.16)$$

Equations (4.14) and (4.16) are therefore the uniform approximation in the general case.

It is not difficult to show from Eqs. (4.11) and (3.25) that $\beta=\frac{1}{2}\pi$ for a quadratic expansion of $\bar{n}(w^0)$ [Eq. (4.11)], and in general we expect $\beta\approx\frac{1}{2}\pi$ to hold. With this value of β, Eq. (4.16) becomes

$$P_{mn}=4\pi p\,|\,\zeta\,|^{1/2}Ai^2(|\,\zeta\,|) \quad (4.17)$$

which is the expression used by Miller [Eq. (1a) of Ref. 6].[27,31] Therefore, we conclude that the present uniform semiclassical approximation and that of Miller are essentially equivalent for both the classically accessible and classically inaccessible cases.

ACKNOWLEDGMENT

We have benefitted from discussions with Dr. W. H. Wong.

* Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This research was also supported by a grant from the National Science Foundation at the University of Illinois.

† Present address: Department of Chemistry, University of Manchester, Manchester M13 9PL, England.

[1] R. A. Marcus, Chem. Phys. Letters **7**, 525 (1970), cf. *Proceedings of the Conference on Potential Energy Surfaces in Chemistry, 10–13 August 1970, University of California, Santa Cruz, Calif.*, edited by W. A. Lester (IBM Res. Lab., San Jose, Calif., 1971), p. 58.

[2] R. A. Marcus, J. Chem. Phys. **54**, 3965 (1971). In Eq. (6.6′) for Δ, read $\hbar\Delta$, in Eq. (7.16), for $(w-w_i')(w-w_j')$, read $(w_i-w_i')(w_j-w_j')$.

[3] R. A. Marcus, "Theory of Semiclassical Transition Probabilities (*s* Matrix) for Inelastic and Reactive Collisions. III. Uniformization Using Exact Trajectories," J. Chem. Phys. (to be published).

[4] W. H. Miller, J. Chem. Phys. **53**, 1949 (1970).

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

[6] W. H. Miller, Chem. Phys. Letters **7**, 431 (1970).

[7] W. H. Miller, J. Chem. Phys. **54**, 5386 (1971).

[8] W. H. Miller, Accounts Chem. Res. **4**, 161 (1971).

[9] R. D. Levine and B. R. Johnson, Chem. Phys. Letters **7**, 404 (1970); **8**, 501 (1971).

[10] I. C. Percival and D. Richards, J. Phys. B **3**, 315, 1035 (1970).

[11] I. L. Beĭgman, L. A. Vaĭnshtein, and I. I. Sobel'man, Zh. Eksp. Teor. Fiz. **57**, 1703 (1969) [Sov. Phys. JETP **30**, 920 (1970)].

[12] P. Pechukas, Phys. Rev. **181**, 166, 174 (1969); J. C. Y. Chen and K. M. Watson, *ibid.* **188**, 236 (1969); S. A. Lebedeff, Phys. Rev. D **1**, 1583 (1970); R. E. Olson and F. T. Smith, Phys. Rev. A **3**, 1607 (1971); R. J. Cross, J. Chem. Phys. **52**, 5703 (1970); B. C. Eu, *ibid.* **52**, 3903 (1970); M. D. Pattengill, C. F. Curtiss, and R. B. Bernstein, *ibid.* **54**, 2197 (1971); F. E. Heidrich, K. R. Wilson, and D. Rapp, *ibid.* **54**, 3885 (1971); D. R. Bates and D. S. F. Crothers, Proc. Roy. Soc. (London) **A315**, 465 (1970); G. V. Dubrovskiĭ, Zh. Eksp. Teor. Fiz. **58**, 1075 (1970) [Sov. Phys. JETP **31**, 577 (1970)].

[13] C. Chester, B. Friedman, and F. Ursell, Proc. Cambridge Phil. Soc. **53**, 599 (1957). For an introduction to this paper see B. Friedman, J. Soc. Ind. Appl. Math. **7**, 280 (1959).

[14] P. A. M. Dirac, Physik. Z. Sowjetunion **3**, 64 (1933); R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).

[15] R. Schiller, Phys. Rev. **125**, 1109 (1962); V. A. Fock, Vestnik Leningrad Univ. Ser. Fiz. Khim. **16(3)**, 67 (1959). An English translation of this paper is available from the National Translations Center, John Crerar Library, 35 West 33rd Street, Chicago, Ill. 60616. See Tech. Transl. **4**, 53 (1960), No. 60-17464.

[16] Actually, the action variable conjugate to the angle variable w_i is J_i, where $J_i=(\bar{n}_i+\delta_i)h$ and the initial value of J_i is $J_{n_i}=(n_i+\delta_i)h$, where δ_i is a constant depending on the degree of freedom i (see Ref. 2).

[17] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon, Oxford, England, 1965) 3rd ed., p. 436.

[18] M. V. Berry, Proc. Phys. Soc. (London) **89**, 479 (1966).

[19] M. V. Berry, J. Phys. B **2**, 381 (1969).

[20] U. Buck, J. Chem. Phys. **54**, 1923 (1971); R. M. Harris and J. F. Wilson, *ibid.* **54**, 2088 (1971).

[21] G. F. Carrier, J. Fluid. Mech. **24**, 641 (1966).

[22] K. W. Ford and J. A. Wheeler, Ann. Phys. **7**, 259 (1959); R. B. Bernstein, Advan. Chem. Phys. **10**, 75 (1966).

[23] M. Abramowitz and I. A. Stegun, (Eds.) Natl. Bur. Std. (U.S.), Appl. Math. Ser. **55**, 446ff (1964).

[24] J. N. L. Connor and M. S. Child, Mol. Phys. **18**, 653 (1970); see also, E. F. Greene, G. P. Reck, and J. L. J. Rosenfeld, J. Chem. Phys. **46**, 3693 (1967).

[25] Note that our procedure differs from that of Berry (Ref. 18) at this point.

[26] The position of the factor i in Eq. (3.29) differs from that of Ref. 18.

[27] In making the comparison it is necessary to remember that the domain of the initial angle variable is [0, 1] in Refs. 1–3 and the present paper, but [0, 2π] in Refs. 4–8.

[28] In Refs. 5–7 units of $\hbar=1$ are used.

[29] If one writes the velocity factor in (2.5) or (2.7) as $h(x)$, then one notes that $h(x_1)$ equals $h(x_2)$. A Taylor's expansion,

$$h(x)=h(x_0)+(x-x_0)h'(x_0)+\cdots,$$

shows that $h(x_2)-h(x_1)$ equals $(x_2-x_1)h'(x_0)$, and hence that $h'(x_0)$ is zero. Thus, the velocity factor can, to the order appropriate in (3.8), be replaced by its value at x_1 or x_2, namely by unity.

[30] W. H. Wong (private communication).

[31] Miller (Ref. 6) derived Eq. (4.17) from Eq. (4.15), a procedure which is only valid if $\beta\approx\pi/2$, as the derivation of Eq. (4.16) shows.