1970-02-01

Asymptotic Evaluation of WKB Matrix Elements. II. Use of Langer's Uniform Asymptotic Wavefunctions

Wesley D. Smith
smithw@byui.edu

Russell T. Pack

Follow this and additional works at: https://scholarsarchive.byu.edu/facpub

Part of the Biochemistry Commons, and the Chemistry Commons

Original Publication Citation

BYU ScholarsArchive Citation
https://scholarsarchive.byu.edu/facpub/798

This Peer-Reviewed Article is brought to you for free and open access by BYU ScholarsArchive. It has been accepted for inclusion in All Faculty Publications by an authorized administrator of BYU ScholarsArchive. For more information, please contact scholarsarchive@byu.edu, ellen_amatangelo@byu.edu.
Asymptotic Evaluation of WKB Matrix Elements. II. Use of Langer’s Uniform
Asymptotic Wavefunctions

WESLEY D. SMITH AND RUSSELL T PACK
Department of Chemistry, Brigham Young University, Provo, Utah 84601
(Received 4 August 1969)

An improvement in a previous procedure for the analytic asymptotic evaluation of integrals arising
in the quantum-mechanical theory of inelastic molecular collisions is presented. The integrals are evaluated
using Langer’s uniform asymptotic wavefunctions and the higher-order saddle-point or steepest-descents
method. It is found that the Langer functions give no better results than WKB functions, but the higher-
orde r steepest-descents corrections produce a marked improvement. The result is a simple method for
evaluating a large class of integrals with an error of 0.1%–2.1%.

I. INTRODUCTION

In order to determine the scattering cross sections in any distorted-wave treatment1 of inelastic atomic and
molecular collisions, one must evaluate certain integrals (often called β integrals2) of the form

\[ I_{mn} = \int_0^\infty G_m(r) V(r) G_n(r) dr, \]  

where \( V(r) \) is an off-diagonal matrix element of the perturbing intermolecular potential over internal-state
wavefunctions. The scattering wavefunctions \( G_i(r) \) satisfy

\[ (\partial^2 G_i/\partial r^2) + (k_i^2 - U_i) G_i = 0, \]

subject to the boundary conditions \( G_i(0) = 0 \) and

\[ G_i(r) - k_i^{-1/2} \sin(k_i r - \frac{1}{2} \pi l_i + \eta_i). \]

Here \( k_i = (2\mu E_i/\hbar^2)^{1/2} \) is the wavenumber associated with the relative motion of the two particles, \( \mu \) their
reduced mass, \( l_i \) their relative orbital angular momentum, and \( \eta_i \) the phase shift. The effective potential

\[ U_i = (2\mu/\hbar^2) W_i + l_i(l_i+1)/r^2 \]

is the sum of the intermolecular potential and a centrifugal potential.

Two problems are encountered in the evaluation of the \( I_{mn} \) term. First, exact solutions of (2) are not known for
most \( U_i \); one must either find adequate approximate solutions or integrate (2) numerically. Second, the integrand of (1) oscillates rapidly making accurate numerical evaluation difficult and tedious.

In a previous paper3 (herein called Paper I), co-authored by one of us, a means was presented by which the
\( I_{mn} \) term were evaluated by asymptotic analytic methods.

\[ G_i = (\pi/\omega_i)^{1/2} Ai(-\omega_i), \]

where \( Ai \) is the Airy function, \( \omega_i \) is given by

\[ \omega_i(r) = (\frac{1}{2} S_i)^{1/3}, \]

and the \( S_i \) are the action integrals7

\[ S_i = \int r_i p_i dr. \]

\[ \text{WKB wavefunctions were used for the } G_i \text{, and the integration was performed by the lowest-order saddle-}
\text{point method along a path on which the integrand did not oscillate. The results were surprisingly good for such}
\text{a simple method.}

In this paper, the same problem is considered, but two changes in procedure are made to improve accuracy.
Higher-order terms are included in the saddle-point or steepest-descents method, and Langer’s uniform asymptotic
wavefunctions4–6 are used instead of WKB functions. Langer’s functions are everywhere excellent approximations to the solutions of (2); far from the classical turning points they reduce to the WKB solutions, but unlike the WKB functions they remain smooth and continuous near the turning points.

The results obtained are compared with the results of Paper I and with the exact values of \( I_{mn} \), using the
respective exponential potential as an example.

II. EVALUATION OF THE MATRIX ELEMENTS

A. The Uniform Asymptotic Wavefunctions

Let the potentials \( U_i \) be repulsive in the turning-point region (see Fig. 1) so that each state has only
one turning point.3 In this case the appropriate Langer functions are4–6

\[ G_i = (\pi/\omega_i)^{1/2} Ai(-\omega_i), \]

where \( Ai \) is the Airy function, \( \omega_i \) is given by

\[ \omega_i(r) = (\frac{1}{2} S_i)^{1/3}, \]

and the \( S_i \) are the action integrals7
Thus defined, both \( q_i \) and \( S_i \) are real and positive for real \( r < r_0 \). Then (8) becomes

\[
G_i = \text{Re} \left( \pi S_i e^{ir/2q_i} \right)^{1/2} e^{ir/2q_i} H_{1/20}^{(0)}(\rho) \left( e^{ir/2q_i} S_i \right),
\]

\[
= (\pi S_i e^{ir/2q_i})^{1/2} e^{ir/2q_i} H_{1/20}^{(0)}(\rho) \left( e^{ir/2q_i} S_i \right)
\]

\[
+ (\pi S_i e^{-ir/2q_i})^{1/2} e^{-ir/2q_i} H_{1/20}^{(0)}(\rho) \left( e^{-ir/2q_i} S_i \right),
\]

\[
= (\pi S_i e^{ir/2q_i})^{1/2} e^{ir/2q_i} H_{1/20}^{(0)}(S_i) - e^{-ir/2q_i} H_{1/20}^{(0)}(S_i) \left( e^{-ir/2q_i} S_i \right).
\]

(13)

Using the analytic continuation formulas\(^9\) for \( H_{1/20}^{(0)} \) in (13), one recovers (6) as asserted.

We can also write (3) in terms of Bessel functions another convenient way. By letting \( S_i = e^{-ir/2} S_i \) in (6) and by employing the analytic continuation formulas\(^9\) one obtains

\[
G_i = (\pi S_i / 8 q_i)^{1/2} e^{ir/2q_i} H_{1/20}^{(0)}(S_i).
\]

(14)

In this expression, \( \arg S_i \) stays in the domain on which the Hankel functions are analytic for all \( r \) of interest.

**B. The Matrix Elements**

Consider a typical molecular collision problem in which \( U_m \) nearly equals \( U_n \) in which \( k_m > k_n \), so that \( r_m < r_n \) (see Fig. 1). In this case it was shown in Paper I that the WKB integrand of (1) could be put into a form which had a saddle point at \( R < r_m \). Since the Langer functions reduce to the WKB functions except near the turning points, the Langer integrand of (1) is expected to behave similarly. Hence, we split the integral into two parts:

\[
I_{mn} = I_1 + I_2,
\]

(15)

where

\[
I_1 = \int_0^R G_m(r) V(r) G_n(r) dr,
\]

(16)

and

\[
I_2 = \int_R^\infty G_m(r) V(r) G_n(r) dr.
\]

(17)

---

Footnotes:


9 Reference 8, p. 361.
By using (14) for both \( G_m \) and \( G_a \) in (16), we can write \( I_1 \) in the form

\[
I_1 = \left( \frac{3}{i} \right) e^{i \frac{t}{3}} \int_0^R V(r) \left( \frac{S_m S_a}{p_m p_a} \right)^{1/2} H_{1/3}^{(3)}(S_m) H_{1/3}^{(3)}(S_a) \, dr. \tag{18}
\]

This integrand dies exponentially on this interval making \( I_1 \) very small and readily estimated using either numerical or analytic methods.

Since \( G_a \) and the range of integration are both real, we can substitute (8) for \( G_a \) in (17) and then (14) for \( G_a \) to obtain

\[
I_2 = \text{Re} \left( \frac{3}{i} \right) e^{i \frac{t}{3}} \int_R^\infty V(r) \left( \frac{S_m S_a}{p_m p_a} \right)^{1/2} \times H_{1/2}^{(3)}(S_m) H_{1/2}^{(3)}(S_a) \, dr. \tag{19}
\]

The evaluation of this integral is greatly facilitated by the fact that the integrand has a saddle point at \( R \) on the real axis. [Substitution of either (3) or (6) into (1) yields an integrand which does not.] In addition, the integrand is an analytic function, so that we are free (by Cauchy’s theorem) to deform the contour of integration to follow \( C_0 \), the path of steepest descents, as shown in Fig. 2. On such a path the integrand no longer oscillates, and the difficulties inherent in (1) are avoided.

At this point probably the most accurate method of evaluating \( I_m \) would be by numerical contour integration of \( I_1 \) and \( I_2 \) along \( C_1 \) and \( C_2 \), respectively. However, it is usually possible to continue analytically and obtain a value for \( I_m \) which has better accuracy than is either needed or justified by the distorted-wave approximation that gave rise to the integrals.

Let us first consider \( I_1 \). Since \( I_1 \) is expected to be small (it was neglected in Paper I), and since the saddle point \( R \) usually lies far to the left of \( r_m \), \( I_1 \) can be approximated with sufficient accuracy by employing the first terms of the Hankel functions’ asymptotic expansions—the WKB functions. Changing to the real quantities \( q_m \) and \( s_m \), one then finds that

\[
I_1 \sim -\frac{1}{4} \int_0^R V(r) (q_m q_a)^{-1/2} \exp(-S_m - S_a) \, dr. \tag{20}
\]

An asymptotic representation of \( I_1 \) can be obtained by the method of integration by parts.\(^{13}\) We write

\[
I_1 \sim -\frac{1}{4} \int_0^R \left( \frac{d}{dr} \right) \exp(-S_m - S_a) \, dr.
\]

Integrating by parts and noting that \( \exp(-S_m - S_a) \to 0 \) as \( r \to 0 \) for most potentials, we find that

\[
I_1 \sim -\frac{1}{4} \int_0^R \left( \frac{d}{dr} \right) \left[ V(r) (q_m q_a)^{-1/2} (q_m + q_a)^{-1} \right] \exp(-S_m - S_a) \, dr.
\]
where
\[ h(z) = S_m - S_n + \ln V(z) - \frac{1}{2} \ln \alpha_{in} q_n, \] (26)
and
\[ g(z) = D_m C_n. \] (27)

Now in the usual higher-order steepest-descent method \( g(z) \) and its derivatives would be involved in the determination of the path of steepest descents. However, like many asymptotic series, those in \( g(z) \) are not usually differentiable. Hence, the best estimate possible for the effect of \( g(z) \) is that of the lowest-order steepest descents or saddle-point method,
\[ I_z = - \text{Re} \frac{1}{2} i g(R) \int_{C_z} \exp[h(z)] \, dz. \] (28)

However, we do want to find higher-order terms due to \( h(z) \). Following Copson,\textsuperscript{16} we let
\[ h(z) = h(R) - \ell. \] (29)
The saddle point \( R \) is the point at which \( h'(R) = 0 \). The path of steepest descent is that path \( C_z \) on which \( \ell \) is real and positive. Thus, (28) becomes
\[ I_z = - \text{Re} \frac{1}{2} i g(R) \exp[h(R)] \int_0^\infty \exp(-\ell) \, \frac{dz}{dl}. \] (30)
Expanding \( dz/dl \) in an asymptotic power series,
\[ \frac{dz}{dl} = \sum_{n=0}^N A_n e^{n \ell}, \] (31)
one obtains
\[ I_z = - \text{Re} \frac{1}{2} i g(R) \exp[h(R)] \sum_{n=0}^N A_n \int_0^\infty \exp(-\ell) \ell^n \, dl, \] (32)
\[ = - \text{Re} \frac{1}{2} i g(R) \exp[h(R)] \sum_{n=0}^N A_n \Gamma[(n+1)/2]. \] (33)
The coefficients \( A_n \) are given by the residues\textsuperscript{16}
\[ A_n = (2\pi i)^{-1} \int C_z \left[ h(R) - h(z) \right]^{-\ell(n+1)/2} \, dz, \] (34)
in which the path of integration is a small closed contour around \( R \). The \( A_n \) are readily evaluated and expressed in the form
\[ A_n = \exp[i\pi (n+1)/2] \frac{2}{h^{(2)}(R)} \Gamma^{(n+1)/2} \alpha_n, \] (35)
where \( h^{(n)}(R) \) are the derivatives of \( h(z) \) evaluated at
\[ R. \] The first few \( \alpha_n \) are
\[ \alpha_0 = 1, \]
\[ \alpha_1 = -d_1, \]
\[ \alpha_2 = -\frac{3}{2} d_2 + (15/8) d_3^2, \]
\[ \alpha_3 = -2 d_3 + 6 d_2 d_2 - 4 d_4^3, \]
\[ \alpha_4 = -\frac{6}{5} d_4 + \frac{3}{2} d_3 d_2 + \frac{3}{2} d_2^2 - \frac{3}{4} d_1 d_2^2, \]
\[ \alpha_5 = -3 d_5 + 12 (d_3 d_3 + d_2 d_4) - 30 (d_3^2 d_2 + d_5 d_2^2) \]
\[ + 60 d_4^2 d_2 - 21 d_4^3, \]
\[ \alpha_6 = -\frac{7}{8} d_6 + \frac{3}{4} d_3 (d_3 d_2 + d_2 d_4) + \frac{3}{8} d_2^2 - \frac{3}{4} d_1 d_2^2 + \frac{3}{8} d_1^3 - \frac{5}{3} d_6^2 d_2 + \frac{1}{2} d_6^3, \] (36)
where the \( d_n \) are given by the ratios
\[ d_n = 2 h^{(n+1)}(R) [n + 2] \Gamma^{(n+1)/2} \Gamma^{(n+1)/2}. \] (37)
Now the \( \alpha_n \) are real and \( h^{(2)}(R) \) is positive; thus, \( I_z \) becomes
\[ I_z = \frac{1}{2} g(R) \exp[h(R)] \sum_{n=0}^N \left( \frac{2}{h^{(2)}(R)} \right)^{(n+1)/2} \times \Gamma\left(\frac{(n+1)}{2}\right) \alpha_n \text{Re}(e^{i\pi/2}). \] Since only terms with \( n \) even will make any contribution, we let \( n = 2k \) and write
\[ I_z = \frac{1}{2} g(R) \exp[h(R)] \times \sum_{k=0}^K (-1)^k \left( \frac{2}{h^{(2)}(R)} \right)^{k+1/2} \Gamma(k+1/2) \alpha_{2k}. \] (38)
The first term in the sum is the result of Paper I. If it is factored out, we can write
\[ I_z = g g(R) T(R), \] (39)
where
\[ g = \frac{1}{2} \exp[h(R)] \pi/2 h^{(2)}(R) \] (40)
is the approximation for \( I_{mn} \) obtained in Paper I, and,
\[ T(R) = \sum_{k=0}^K (-1)^k \left( \frac{2}{h^{(2)}(R)} \right)^k \pi^{1/2} \Gamma(k+1/2) \alpha_{2k}. \] (41)
is a correction due to the higher-order steepest-descent method. The series \( T(R) \) converges for a few terms and then begins to diverge—a behavior typical of asymptotic series. The maximum accuracy possible with such series is achieved by truncating them at the smallest term, and the error is of the same order of magnitude as the smallest term.\textsuperscript{17} The other asymptotic series in (39),
\[ ^{16} \text{Reference 6, p. 11; Ref. 13, p. 6.} \]
$g(R)$, which represents the difference between the Langer functions and the WKB functions, is a correction for the divergences of the WKB functions.

We have thus obtained formulas (21) and (39) as an asymptotic estimate of $I_{mn} = I_1 + I_2$. The determination of the $S_c$ (discussed in Paper I) completes the evaluation of the matrix element.

III. EXAMPLE. THE REPULSIVE EXPONENTIAL POTENTIAL

Consider again the example used in Paper I. Let $l_p = l_q = 0$, $W_p = W_q = C \exp(-r/a)$, and $V = (2\mu/k^2) W$. If $r$ is measured in units of $a$ (about 0.2 Å) and $E$ in units of $h^2/2ma^2$ (typically about 40°K), then one has $E_i = k_i^2$ and $U = D e^{-r}$ with $D \approx 4 \times 10^{-8}$. In these units typical vibrational and rotational constants are $\theta_v = 2000°K = 50$ and $\theta_i = 2°K = 0.05$.

Jackson and Mott have solved both (2) and (1) exactly for this potential. We now compare our asymptotic results with their exact formula in the limits of large (vibrational) energy exchange and small (resonance) energy exchange. The results for rotational transitions lie between those of these two limits but are not discussed here because they do not reduce to simple formulas.

A. Vibrational Transitions

If vibrational energy is exchanged, we have $k_m^2 - k_n^2 \geq 50$, and for energies slightly above threshold, the exact result reduces to

$$I_{mn} \text{(exact)} = \pi(k_m^2 - k_n^2) \exp[-(k_m - k_n)^2].$$

As in Paper I, the saddle point $R$ is determined to a good approximation by

$$U(R) = (k_m^2 - k_n^2)^2,$$

and the WKB lowest-order saddle-point result of Paper I is

$$\sigma = \epsilon(2\pi)^{-1/2} I_{mn} \text{(exact)};$$

hence, $I_{mn} \text{(asymptotic)}$, as obtained in the previous section of this paper, becomes

$$I_{mn} \text{(asymptotic)} = I_1 + g(R) T(R) \epsilon(2\pi)^{-1/2} I_{mn} \text{(exact)}.$$  

(45)

Using (43) one finds that for $n \geq 2$,

$$\hbar^{(n)}(R) = 2^{-n},$$

(46)

approximately. Upon evaluating the $A_{2k}$, we then obtain

$$T(R) = (1 - 1/12 + 0.0034722 + 0.0026813 + \cdots),$$

(47)

where we have truncated at the smallest term ($K = 3$).

The correction term $g(R)$ depends on the values of $k_m$ and $k_n$ and does not reduce to a simpler expression. Its values can be calculated using (23), (24) and the formula

$$S_a^2 = 2[U(R) - k_n^2]^{1/2} - 2k_i \tan^{-1}[U(R) - k_n^2]^{1/2} k_i^{-1}].$$

(48)

Typical values, which are always slightly greater than one, are tabulated in Table I.

<table>
<thead>
<tr>
<th>$E_i$ ($°K$)</th>
<th>$k_i^2$</th>
<th>$k_n^2$</th>
<th>$g(R)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1</td>
<td>51</td>
<td>1.0002</td>
</tr>
<tr>
<td>160</td>
<td>4</td>
<td>54</td>
<td>1.0002</td>
</tr>
<tr>
<td>280</td>
<td>7</td>
<td>57</td>
<td>1.0001</td>
</tr>
<tr>
<td>360</td>
<td>9</td>
<td>59</td>
<td>1.0001</td>
</tr>
<tr>
<td>640</td>
<td>16</td>
<td>66</td>
<td>1.0001</td>
</tr>
<tr>
<td>1440</td>
<td>36</td>
<td>86</td>
<td>1.0001</td>
</tr>
<tr>
<td>4000</td>
<td>100</td>
<td>150</td>
<td>1.0001</td>
</tr>
</tbody>
</table>

Table I. Correction terms for vibrational transitions with $k_m^2 - k_n^2 = 50$.

B. Resonant Transfer of Internal Energy

For resonant transition, $k_m^2 = k_n^2 = k_i^2$, and the exact result reduces to

$$I_{mn} \text{(exact)} = k.$$  

(51)

In this case \( R \) is defined by \( U(R) = 2k^2 \) and the result of Paper I is

\[
\delta = \left( \frac{3}{4} \pi \right)^{1/2} I_{mn}(\text{exact});
\]

(52)

thus, the result of this paper is

\[
I_{mn}(\text{asymptotic}) = I_1 + g(R) T(R) \left( \frac{3}{4} \pi \right)^{1/2} I_{mn}(\text{exact}).
\]

(53)

Here the \( h(n) \), for \( n = 2 \) through 6, are 1, 3, 13, 75, and 541, respectively, so that from (47),

\[
T(R) = \left( 1 - \frac{1}{4} + 0.03125 + \cdots \right) = 0.78125,
\]

(54)

where we have again truncated the sum at the smallest term \( (K = 2) \). Ignoring \( g(R) \) and \( I_1 \), we find

\[
I_{mn}(\text{WKB}) = 0.9792 I_{mn}(\text{exact}).
\]

(55)

The corrections \( I_1 \) and \( g(R) \) are obtained by noting that the action integrals in this case reduce to

\[
S_m = S_n = (2 - \pi/2) k = 0.4202 k,
\]

(56)

so that (21) becomes

\[
I \sim 0.5 \exp(-0.8584k).
\]

(57)

Values of \( g(R) \) and \( I_1 \) calculated for a range of \( k \) values are listed in Table II. It is clear that in

\[
I_{mn}(\text{asymptotic}) = I_1 + g(R) (0.9792) I_{mn}(\text{exact})
\]

(58)

they make significant changes, but that those changes do not constitute any systematic improvement.

IV. DISCUSSION

From the results on the example problem we can make a number of observations and conclusions which should apply to any potential which has a shape similar to the repulsive exponential. First, the corrections \( I_1 \), due to the exponentially dying part of the integrand, and \( g(R) \), due to the use of the Langer functions, do not improve the results; they serve only as indices of the validity of the asymptotic approximations used.14 Equally good or better results are obtained much more simply using WKB functions (including higher-order steepest-descents terms). Second, the accuracy obtained with the WKB functions, 0.07%–2.08%, indicates that asymptotic methods and asymptotic wavefunctions are capable of giving very nearly exact results. It is possible that the 0.07% is somewhat fortuitous. Both (43) and (44) are approximate, and numerical calculations indicate that these approximations may change the asymptotic result by almost 1%. In either case, the error is considerably less than the error inherent in the distorted-wave approximation which is implied when the integrals (1) are used to calculate cross sections. These asymptotic methods are easily applied to different problems; hence, laborious numerical integration of (2) and (1) should usually be unnecessary.

Finally, let us comment on some earlier work using Langer and WKB functions. Using methods similar to those presented here and in Paper I, Shin15 has evaluated matrix elements equivalent to these for the repulsive exponential potential. The error in his results was a few tenths of a percent at higher energies but became much larger at lower energies. However, as Shin noted, and as (50) also shows, this error was due to approximations made in calculating the action integrals \( S_i \) and was not due to the WKB approximation.

Langer's wavefunctions have been used by Hartmann and Slawsky16 in the numerical integration of matrix elements equivalent to \( I_{mn} \) using the SSH potential,

\[
W = C \exp(-r/a) - \epsilon.
\]

Their results differ from the exact results by 0.4% at high energies but as much as 22.3% at low energies. Since the SSH potential differs from the repulsive exponential only by a constant, one has the same equation (2) to solve for the \( G_i \) except that \( E_i \) is replaced by \( E_i + \epsilon \). Hence, our analysis using this potential gives the same formulas as those for the repulsive exponential potential except with a shifted \( k \). Furthermore, (42) is valid for the entire energy range they considered. Hence, our (49) holds, and it is clear that the large error in Hartmann and Slawsky's result at low energies is an error in their numerical integration rather than in the Langer functions. Shin15 has attempted unsuccessfully to match Hartmann and Slawsky's results for the SSH potential using WKB functions. From (50) we see that the discrepancy is not a consequence of the WKB approximation but is probably due to Shin's use of a different range parameter, \( a \).

ACKNOWLEDGMENT

We thank Professor John S. Dahler for his suggestions and encouragement on this problem.