Oscillating reactivity of collinear symmetric heavy + light–heavy atom reactions

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The oscillatory reaction probability (as a function of energy) of collinear heavy + light–heavy systems (e.g., \( I + HI \rightarrow IH + I \)) that has been seen in earlier quantum mechanical reactive scattering calculations is shown to be described quantitatively by a semiclassical WKB model. Because these reactions are highly vibrationally adiabatic they reduce to a two-state symmetric resonance system (analogous to symmetric charge transfer, e.g., \( H^+ + H \rightarrow H + H^+ \)) that involves only the phase shifts of the one-dimensional \( g \) (symmetric) and \( u \) (antisymmetric) combinations of the two states. Comparisons of the semiclassical and quantum mechanical reaction probabilities over a wide range of energy for the cases \( I + Mu \rightarrow IMu + I \) and \( I + HI \rightarrow IH + I \) show almost perfect agreement. The vibrationally adiabatic symmetric exchange problem is also solved classically (analytically) and is seen to have an interesting relation to the quantum/semiclassical result. The classical reaction probability is also an oscillatory function of energy, although the structure of the oscillations is different from the quantum/semiclassical ones ("saw-tooth" rather than sinusoidal) and the phase of the classical oscillations is only approximately the same as that of the quantum/semiclassical case. (In the high energy limit, the phase of the oscillations increases roughly as the square root of collision energy.) Thus, though the classical (light atom hopping between two heavy atoms) and quantum mechanical (resonance interference of \( g \) and \( u \) collision channels) interpretations of the oscillatory reactivity seem at first to be quite different, they are seen in fact to be essentially the same.

I. INTRODUCTION

Experimental studies\(^{1–3}\) of heavy + light–heavy atom reactions

\[
H + LH' \rightarrow HL + H' \tag{1.1}
\]

indicate several kinematic effects. As a rule, the translational motion of heavy atoms is not much influenced by the light atom transferred, i.e., the translational energy is roughly conserved,

\[
\langle E_{\text{trans reactant}} \rangle \approx \langle E_{\text{trans product}} \rangle. \tag{1.2}
\]

Moreover, the initial relative motion of heavy atoms is the dominant source of total angular momentum. This orbital momentum remains stored in the heavy atoms and is only marginally influenced by the light atom transfer during reaction. Angular momentum transfer then implies that the product molecule HL absorbs little rotational energy (see Refs. 8 and 9). As a consequence, the vibrational energy of thermoneutral or nearly thermoneutral reactions (1.1) is mostly conserved, e.g., for reactions

\[
\text{Cl} + \text{HO}(v) \rightarrow \text{CIH}(v') + \text{O}(^3P) \quad (\text{Ref.} \ 2–5), \tag{1.3}
\]

and

\[
\text{Cl} + \text{HCl}(v) \rightarrow \text{CIH}(v') + \text{Cl} \quad (\text{Ref.} \ 6). \tag{1.4}
\]

These kinematic propensities have been confirmed by classical trajectory studies of reaction (1.1).\(^{10–12}\) Correspondingly, information theoretic analysis indicate that vibrationally nonadiabatic \( v \rightarrow v' \neq v \) transitions, e.g., for the thermoneutral reactions

\[
F + \text{HF}(v) \rightarrow \text{FH}(v') + F \tag{1.5}
\]

and

\[
\text{Br} + \text{HBr}(v) \rightarrow \text{BrH}(v') + \text{Br} \tag{1.6}
\]

are surprising, and the surprise increases with vibrational energy mismatch.\(^{13}\)

In the ideal case of collinearly constrained heavy + light–heavy atom reactions, the absence of rotational excitation,\(^{10–12}\) multiple encounters\(^{10,14,15}\) and possible migratory pathways (for discussions, see Refs. 16–19) make the rule (1.2) even more rigorous.\(^{20}\) Nearly perfect vibrational adiabaticity holds for the symmetric collinear reactions\(^{21}\)

\[
I + HI(v) \rightarrow I + HI(v'), \tag{1.7a}
\]

\[
-\text{IH}(v') + I, \tag{1.7b}
\]

and its isotopic variant

\[
I + \text{Mu}(v) \rightarrow I + \text{Mu}(v'), \tag{1.8a}
\]

\[
-\text{IMu}(v') + I, \tag{1.8b}
\]

i.e., all \( v \rightarrow v' \neq v \) transitions are negligible for reactions (1.7) and (1.8).

The vibrational adiabaticity renders the collinear re-
actions of type (1.7) or (1.8) resonant two-state scattering processes, similar to the symmetric charge or excitation transfer reactions $H + H^+ \rightarrow H^+ + H$, $He + He^+ \rightarrow He^+ + He$, $N_2(v = 0) + N_2(v = 1) \rightarrow N_2(v = 1) + N_2(v = 0)$, etc. The transition probability for these processes is given by 

$$P = \sin^2(\eta_g - \eta_u), \quad (1.9)$$

where $\eta_g$ and $\eta_u$ are the phase shifts computed for the two one-channel problems that are the symmetric ($g$) and antisymmetric ($u$) combinations of the two states. That the collinear symmetric heavy + light-heavy atom reaction also fits into this picture has been noted by Babamov and Marcus.  

In Sec. II, we use the semiclassical WKB approximation for the two phase shifts in Eq. (1.9) and evaluate, e.g., the reaction probabilities $P = P_{g\rightarrow u}$ for the $v = 0 \rightarrow v = 0$ reactions (1.7) and (1.8). The resulting $P(E)$ oscillates as a function of collision energy $E$, in quantitative agreement with the exact quantum results.  

**Viewed as above, oscillations in the reaction probability with energy arise as an interference effect between the $g$ and $u$ states, but it is interesting that an oscillatory reaction probability has also been observed in a strictly classical theory (i.e., classical trajectory calculations). In Sec. III we go further and give the analytic solution to the classical vibrationally adiabatic symmetric exchange problem, and one indeed obtains an oscillatory reaction probability. The oscillatory structure of the classical reaction probability is of a “saw-tooth” nature, however, rather than sinusoidal, and the phase of the oscillations is an approximation to the phase shift difference in Eq. (1.9). Other aspects of the results are also discussed in Sec. III.**

**II. OSCILLATORY REACTION PROBABILITIES**

The vibrational adiabaticity of collinear symmetric heavy + light-heavy reactions

$$H + LH(v) \rightarrow HL(v) + H \quad (2.1)$$

implies the simple resonant two-state reaction probability

$$P_{g\rightarrow u} = \sin^2(\eta_g - \eta_u) \quad (2.2)$$

[cf. Eq. (1.9) and Refs. 22 and 23]. If the semiclassical WKB approximation is used for the two elastic phase shifts one obtains

$$\eta_g - \eta_u = \lim_{R \rightarrow \infty} \left[ \int_{r_{el}}^{R} dr k_{el}(r) - \int_{r_{el}}^{R} dr k_{el}(r) \right], \quad (2.3)$$

where

$$k_{el}(r) = \frac{1}{R} \sqrt{2m[E - \delta_{el}(r)] + \hbar^2/8mr^2} \quad (\lambda = g, u), \quad (2.4)$$

$E$ is the total energy, $m$ the system’s reduced mass, $r$ Delves’ radical coordinate, $\delta_{el}(r)$ the $\ell^\text{th}$ internal energy for symmetric ($\lambda = g$) and antisymmetric ($\lambda = u$) levels, modified by the centrifugal term $\hbar^2/8mr^2$, which turns out to be negligible (see Refs. 23, 26, and 27 for precise and equivalent definitions). In practice, one sets $R = r_{el}$ as upper integration limit in Eq. (2.3), where $r_{el}$ is the value of $r$ where $\delta_{el}$ and $\delta_{uu}$ are sufficiently ($5 \times 10^{-3}$) degenerate. The lower integration limits $r_{el}$ and $r_{el}$ are the classical turning points for motion along $\delta_{el}$ and $\delta_{uu}$ at collision energy $E$, respectively.  

From Eqs. (2.2)–(2.4) it is clear that the internal energies versus Delves’ (hyperspherical) coordinate $r$ determine the semiclassical reaction probability. As an example, $\delta_{el}(r)$ and $\delta_{uu}(r)$ for the $I + Mul(0) \rightarrow Mul(0) + I$ reaction (1.8) are shown in Fig. 1. At small values of $r$, $\delta_{el}$ and $\delta_{uu}$ are strongly repulsive and approximately parallel, i.e., the difference of classical turning points is approximately constant,

$$r_{el}(E) - \delta_{el}(E) \approx r_{uu} - \delta_{uu} \quad (2.5)$$

for $\gamma \leq r_{el}$ or $\gamma \leq r_{uu}$, respectively, see Fig. 1. This nearly parallel behavior in the repulsive region is due to the single-well shape of the internal interaction potential in the corner region close to the three-atom coincidence. Slight deviations from perfect parallel behavior are due to internal frequency changes along $r$. As will be shown below, this parallel behavior (as well as the deviations) yields a rather simple high energy dependence (with modifications) of the reaction probability, cf. Eq. (2.8) below.  

The low-energy dependence of reaction probabilities is influenced by the behavior of $\delta_{el}$ and $\delta_{uu}$ at larger values of $r$. There are potential wells at $r_{uu}$ and $r_{uu}$ as well barriers at $r_{el}$. Asymptotically, the quasidegenerate internal energies $\delta_{el} = \delta_{uu}$ approach the diatomic reactant (or product) vibrational level $\delta_0$. This pattern originates from the single-well-to-double-well transition of the internal potential in the interaction region.  

At very low energies, i.e., below the barrier, tunneling and resonance effects dominate. These effects have been described in detail in Refs. 23–25, and it is clear that they are also contained in Eq. (1.9); the resonant structure would appear in the $g$ phase.

![FIG. 1. Internal energies $\delta_{el}$ and $\delta_{uu}$ vs Delves radial coordinate $r$ for the symmetric and antisymmetric $v = 0$ levels of the $I + Mul(0) \rightarrow Mul(0) + I$ reaction, respectively. The inset shows the positions of potential wells $r_{uu}$, $r_{el}$, and barriers $r_{el}$. At $r_{el}$, $\delta_{el}$ and $\delta_{uu}$ are degenerate within $10^{-3}$. The behavior of $\delta_{el}$, $\delta_{uu}$ is approximately parallel for $\gamma \leq r_{el}$ and $\gamma \leq r_{uu}$, respectively.](http://jcp.aip.org/jcp/copyright.jsp)
shift (a sudden jump by \( \pi \)) and this would cause the reaction probability to go rapidly (as a function of energy) through one oscillation. Also, the WKB approximation for the phase shifts, suitably generalized (i.e., uniformized\(^{20}\)) to account for tunneling, would be expected to describe the resonance phenomena quantitatively. Our focus in this paper, however, is on the oscillatory nature of the reaction probability at higher energies, and here the "primitive" WKB phase shifts, i.e., Eq. (2.3), are completely adequate. If tunneling is neglected, in fact, then for energies below the barrier the \( g \) and \( u \) WKB phase shifts are essentially equal, leading to a zero reaction probability, and this is indeed in accord with the exact quantum results\(^{8,12}\) (with the exception of the resonance behavior).

The resulting semiclassical phase shifts \( \eta_g = \eta_g(E) \) and \( \eta_u = \eta_u(E) \) (using \( r_g = 121.75 \, \text{Å} \) in Eq. (2.3)) are plotted versus energy \( E \) in Fig. 2. Both \( \eta_g \) and \( \eta_u \) show an approximate \( E^{1/2} \) behavior at high energies, in accord with the infinitely steep wall collision model. At the lowest energies, close inspection shows that \( \eta_u \) increases more rapidly with \( E \) than \( \eta_g \), due to the very shallow well of \( \delta_u \) in comparison with \( \delta_g \). As a consequence, the difference of elastic phase shifts [Eq. (2.3)] decreases slightly at very low energies and then it increases approximately linear with \( E^{1/2} \), as shown in the top panel of Fig. 3.

In order to explain the approximately linear \( \eta_u - \eta_{us} \) vs \( E^{1/2} \) dependence more explicitly, the integrals (2.3) are split into four parts,

\[
\eta_u - \eta_{us} = \int_{r_{us}}^{r_{e}} dr \, k_g(r) + \int_{r_{e}}^{r_{g}} dr \, k_u(r) - \int_{r_{us}}^{r_{u}} dr \, k_u(r) - \int_{r_{us}}^{r_{u}} dr \, k_u(r).
\]  

(2.6)

Here the first and third terms approximately cancel each other, due to the nearly parallel behavior of \( \delta_g \) and \( \delta_u \) at high energies. In the same energy range,

\[
k_g'(r) \approx k_u'(r) \approx k_0 = (2m E_{trans}/\hbar^2)^{1/2}
\]  

(2.7)

for the second and fourth integrals of Eq. (2.6). Inserting Eqs. (2.6) and (2.7) into Eq. (2.2), it follows that:

\[
P_{\text{us}} \approx \sin^2(a + b E^{1/2})
\]  

(2.8)

for high energies. The constant \( a \) accounts for the low energy shift, whereas \( b \) depends on the mass and difference of turning points, cf. Eqs. (2.5) and (2.6). The simple relation (2.8) is verified in the bottom panel of Fig. (3) where it is seen that \( P_{\text{us}} \) in fact shows a near square sinusoidal dependence on \( E^{1/2} \) at higher energies. Deviations from this pattern at very low energies arise from the nonmonotonous behavior of \( \eta_u - \eta_{us} \), as discussed above. Deviations from Eq. (2.8) at higher energies are due to the vibrational frequency shifts at low values of \( r_e \), as discussed above.

The semiclassical result is seen to agree perfectly with the exact quantum results adapted from Ref. 21, with the expected exception of the resonance pattern close to \( E_1 \). For very high energies \( E > 100 \, \text{kJ m}^{-1} \) the present semiclassical results predict the exact quantum ones, provided that the vibrational adiabaticity continues to hold at such high energies.

Figure 4 shows the results for the \( \text{I} + \text{HI}(0) \rightarrow \text{I} \text{H}(0) \rightarrow \text{I} \) reaction in complete analogy to the results of reaction \( \text{I} + \text{M}(0) \) presented in Fig. 3. The number of high energy oscillations is smaller and the square sinusoidal behavior is less pronounced for reaction (1.7b) in com-

**FIG. 2.** Semiclassical WKB phase shifts \( \eta_g \) and \( \eta_u \) vs energy \( E \) for the symmetric and antisymmetric elastic collisions of the \( \text{I} + \text{M} \) reaction, respectively.

**FIG. 3.** Semiclassical WKB elastic phase shift difference \( \eta_u - \eta_{us} \) classical phase \( \Delta \phi = N \phi \) (\( N \) - average number of light atom jumps between the heavy atoms) and reaction probability \( P_{\text{us}} \) vs (square root of translational energy \( E_{\text{trans}}^{1/2} \)) for the \( \text{I} + \text{M} \) reaction. Continuous line --- classical approximation. Dash-dotted line --- exact quantum results for energies \( E < -100 \, \text{kJ m}^{-1} \), adapted from Ref. 21. The arrow marks the energy barrier shown in Fig. 1.
actions simple two-state resonance processes. The corresponding simple semiclassical WKB approximation yields oscillating reaction probabilities in very good agreement with exact quantum ones, and allows for a lucid interpretation of the reaction (see below). From a computational point of view then, the title actions—which have been considered as most exacting before the introduction of Delves (hyperspherical) coordinates may be considered as the world’s simplest model reaction: all one needs to evaluate numerically are the internal quantum energies (for details, see Ref. 30) as well as one-dimensional action integrals [Eq. (2.3)] in order to compute the reaction probabilities via Eq. (2.2). Interestingly, no internal wave functions, overlap integrals, etc., are required to obtain accurate results. Moreover, the semiclassical WKB approach offers the possibility of estimating error bounds for the results (see the Appendix). In contrast, all presently known exact quantum approaches, including those of Refs. 26 and 27, only allow for empirical error estimates.

It is also interesting to compare the semiclassical (which, as we have seen, is essentially the same as the quantum) picture of the vibrationally adiabatic symmetric exchange reaction with the classical picture. In the classical situation the reaction begins at large translational coordinate \( r \) in the reactant’s vibrational well. As \( r \) decreases during the incoming part of the trajectory the vibrational motion is confined to the initial well until the barrier between the reactant and product wells has decreased to the point that the vibrational energy is equal to the barrier height; let this value of \( r \) be called \( r_0 \). During the next part of the trajectory, as \( r \) decreases from \( r_0 \) to its classical turning point \( r_1 \), and then increases back to \( r_0 \), the vibrational motion passes back and forth over both potential wells, which now constitute a single “super” potential well with a bump in the middle of it (which actually vanishes for \( r < r_0 \)). Reaction occurs, or not, depending on the phase of the vibrational motion in this super potential well when the position \( r = r_0 \) is reached on the outward part of the trajectory, i.e., the point at which the particle is again trapped in one potential well or the other.

By assuming that the classical vibrational motion is adiabatic, one can obtain a simple solution for the classical reaction probability. If \( (n, q) \) are the action-angle variables for vibration in the super potential well, then the vibrationally adiabatic approximation to their time dependence is

\[
\begin{align*}
  n(t) &= n_{initial} \quad \text{(constant)}, \quad (3.1a) \\
  q(t) &= q_{initial} + \int_0^t dt' \omega(t') \quad \text{(3.1b)}
\end{align*}
\]

where \( \omega(t) \) is the time-dependent vibrational frequency. Thus, if \( q_1 \) and \( q_2 \) are the vibrational angle variables at \( r = r_0 \) on the inward and outward parts of the trajectory, respectively, then Eq. (3.1) gives

\[
q_1 = q_2 + 2\Delta\hat{\eta} \quad \text{(3.2a)}
\]

with

\[
\Delta\hat{\eta} = \int_{r_1} r_0 d\tau \frac{\omega(r)}{u(x)} \quad \text{(3.2b)}
\]

III. DISCUSSION

The vibrational adiabaticity of collinear symmetric heavy + light-heavy atom reactions renders these re-
where \( u(r) \) is the local velocity of the \( r \) motion
\[
u(r) = \sqrt{2/(\hbar m)} |E - E_c(r)| ,
\]
(3.3)
and where the time integral of Eq. (3.1b) has been changed to an integral over \( \nu \) \( d\nu = d\nu/u(r) \); the factor of 2 in Eq. (3.2a) is due to the fact that the inward and outward motion between \( r_1 \) and \( r_2 \) give an equal contribution to the vibrational phase. Note that
\[
N = 2\pi N \pi \eta
\]
(3.4)
is the (classical) number of oscillations of the light atom between its heavy partners in the interaction zone across the internal super potential. Both \( \Delta \eta \) and \( N \) are illustrated in the top panels of Figs. 3 and 4. If at \( r = r_q \) the angle interval \( (0, \pi) \) corresponds to the reactant potential well and \( (\pi, 2\pi) \) to the product potential well, then one has \( q_i \) in the interval \((0, \pi)\) and reaction if
\[
\pi < q_i < 2\pi \quad \text{(modulo } 2\pi),
\]
and nonreaction otherwise, i.e., if \( \sin q_i < 0 \). For a given value of \( q_i \), the classical reaction probability is thus
\[
P_{\text{CL}}(q_i, E) = \Omega \left[ -\sin q_i \right] = \left[ -\sin(q_i + 2\Delta \eta) \right],
\]
(3.5)
where \( \Omega \) is the usual step function
\[
\Omega(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases}
\]
The final result is obtained by averaging Eq. (3.5) over \( q_i \) in the reactant interval \((0, \pi)\),
\[
P_{\text{CL}}(E) = \frac{1}{\pi} \int_0^\pi dq_i \left[ -\sin(q_i + 2\Delta \eta) \right],
\]
and it is not hard to show that this gives
\[
P_{\text{CL}}(E) = 2 \left[ \frac{\Delta \eta}{\pi} \right] \left[ 1 - \left( \frac{\Delta \eta}{\pi} + \frac{1}{2} \right) \right],
\]
(3.6)
where here \( \left[ \right] \) denotes the greatest integer function.

It will be shown below that the quantity \( \Delta \eta \) above is an approximation to the semiclassical (or quantum) phase shift difference \( \Delta \eta = \eta_r - \eta_s \). Neglecting this difference for the moment, Eq. (3.6) is seen to have an interesting relation to the semiclassical (or quantum) reaction probability [cf. Eq. (2.2)]
\[
P_{\text{BC}}(E) = \sin^2(\Delta \eta).
\]
(3.7)
Namely, \( P_{\text{CL}} \) is zero or one at the same values of \( \Delta \eta \) for which \( P_{\text{BC}} \) is, i.e., at \( \Delta \eta = 0, \pi, 2\pi, \ldots \) and \( \Delta \eta = \pi/2, (3\pi/2), \ldots \), respectively, but as a function of \( \Delta \eta \) it consists of straight line segments connecting these points at which it is zero or one; i.e., \( P_{\text{CL}}(E) \) is a "saw tooth", rather than sinusoidal, oscillatory function of \( \Delta \eta \). This is illustrated for the \( 1 + \text{HI} \) system, e.g., in the bottom panel of Fig. 4.

To complete the classical analysis one notes that the adiabatic vibrational frequency \( \omega(r) \) is defined by
\[
\omega(r) = \frac{\delta E_c(r)}{\delta n} ,
\]
(3.8a)
where \( \delta E_c(r) \) is the classical vibrational energy as a function of the translational coordinate \( r \) and \( n \), the adiabatic vibrational action variable (the classical equivalent of the vibrational quantum number). In the classical limit vibrational levels are closely spaced, so that Eq. (3.8a) may be replaced by
\[
\omega(r) = \delta E_c(r) - \delta E_c(r),
\]
(3.8b)
and since \( n \) is the action variable for the super potential well alternate vibrational levels are \( \pi \) and \( \eta \), so that this becomes (for fixed quantum number \( \eta \))
\[
\omega(r) = \delta E_c(r) - \delta E_c(r) \quad \text{(3.9)}
\]
Equation (3.2b) for \( \Delta \eta \) thus becomes
\[
\Delta \eta = \int_{r_1}^{r_2} dr \frac{m \Delta E(r)}{\sqrt{2mE(\mu - 2\pi)}} ,
\]
(3.10)
with
\[
\Delta E(r) = \delta E_c(r) - \delta E_c(r),
\]
\[
\delta E_c(r) = \left[ \delta E_c(r) + \delta E_c(r) \right]/2 .
\]
To see that Eq. (3.10) approximates the WKB phase shift difference \( \Delta \eta \) of Eq. (2.3) one identifies \( r_q \) above as the value at which \( \Delta E(r) \) vanishes and makes the following substitution into Eq. (2.3):
\[
\delta E_c(r) = \delta E_c(r) - \frac{1}{2} \Delta E(r),
\]
\[
\delta E_c(r) = \delta E_c(r) + \frac{1}{2} \Delta E(r) ,
\]
and then expands the result to lowest order in \( \Delta \eta \); this yields \( \Delta \eta \) of Eq. (3.10). This expansion to first order in \( \Delta E \) is analogous to the usual high energy (or Jeffreys- Born) approximation for WKB phase shifts (see also Ref. 23), so that \( \Delta \eta \) of Eq. (2.3) is expected to agree with \( \Delta \eta \) of Eq. (3.10) better the higher the energy; this is indeed seen in the top panels of Figs. 3 and 4. As a consequence, the quantum (or semiclassical) and classical reaction probabilities (3.6) and (3.7) are expected to be well in phase at higher energies (provided that vibrational adiabaticity also holds for classical trajectories), but may be considerably out of phase at the lowest energies.

The above analytic classical treatment shows essentially all the features of the previously reported classical trajectory calculations, e.g., the sawtooth oscillatory dependence on energy. Since \( \Delta \eta = a + b \sqrt{E} \) [cf. Eq. (2.8)], one also understands why the curve \( P_{\text{CL}} \) vs. \( E \) is concave down when the probability is increasing from zero to one and convex up when it is decreasing from one to zero.

We have also generalized the above classical analysis to describe the asymmetric heavy-light-heavy reaction, e.g., Cl + HI = ClH + I, and will discuss this in a later publication when it can be compared to the corresponding quantum calculations that are in progress.

The foregoing discussion relates specifically to the collinear version of heavy-light-heavy reactions but of course real reactions take place in three-dimensional space. Nevertheless, it has been demonstrated repeatedly that kinematic or dynamic effects studied in the collinear world also play a role in the real world (see Refs. 31-34). Although the definitive answer as to
whether or not oscillatory reactivity appears in the
three-dimensional version of the title reactions must
await experiments (or perhaps classical trajectory
calculations), it is nevertheless interesting to speculate.
By analogy with symmetric charge transfer (e.g., H + H = H₂),
seems likely that \( P(b,E) \), the reaction probability as a function of impact parameter \( b \) and energy \( E \), will indeed be an oscillatory function of energy
for fixed \( b \) (and also an oscillatory function of \( b \) for
fixed \( E \)). Averaging this over \( b \) to obtain the total re-
active cross section
\[
\sigma_r(E) = \int_0^\infty \frac{db}{2\pi} 2n b P_r(b,E)
\]
however, will tend to quench most of the oscillatory
structure. To avoid this one needs differential cross
section measurements, i.e., the quantity \( \sigma_x(\theta,E) \), for
measuring the scattering angle has the approximate ef-
fact of undoing the impact parameter average. We
therefore expect that the energy dependence of the
reactive cross section at a fixed scattering angle will show
the type of oscillatory structure seen in our collinear
results.

There is also the interesting question of how studies
like the present one, i.e., exchange of a light atom
(e.g., H) between two heavy atoms, can be related to
hydrogen atom exchange reactions between two molecular
aggregates (e.g., CH₃ + C₂H₅ = CH₃ + C₂H₅). There is
obviously some relation, as other workers have dis-
cussed earlier. The essential question is, speaking
classically, to what extent the additional degrees of
freedom in the more complex situation damp the os-
cillation of the hydrogen atom between the two heavy
centers (e.g., by serving as an energy sink). One pos-
sibly fruitful way to approach this more complex case is
via the “system-bath” decomposition that has recently
been suggested by Schwartz and Miller.\(^{36}\) In this ap-
proach the system consists of the two collinearlike de-
grees of freedom that characterize the hydrogen atom
motion between the two heavy centers, and the remain-
ing degrees of freedom constitute the bath. The model
is thus that of a collinearlike heavy–light–heavy reac-
tion taking place in (and coupled to) a harmonic bath.
The approach of Schwartz and Miller requires the ac-
curate dynamical treatment of the system, i.e., quantum
mechanical, or perhaps semiclassical or classical,
calculations of the type discussed in the present paper,
and the effects of the bath are then incorporated ap-
proximately. At the completely classical level this
leads to a generalized Langevin equation which shows
explicitly how the friction and random force from the
bath affect the dynamics of the system. The results of
the present paper suggest that such a classical treat-
ment might be applicable for high energies, but at low
energy where tunneling and resonance effects dominate
it is clear that at least the system dynamics, and per-
haps that of the bath also, must be treated quantum
mechanically. Work of this nature should be a useful
avenue for the future.

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APPENDIX: ERROR BOUNDS FOR REACTION
PROBABILITIES

Using the semiclassical WKB approach, it is possible to evaluate error bounds for the numerical reaction
probabilities. From Eq. (2.2) it follows that:

\[
|\Delta P_{\nu-\nu'}| \leq |\Delta(\eta_{\nu} - \eta_{\nu'})|,
\]

\[
\leq |\Delta \eta_{\nu'}| + |\Delta \eta_{\nu}|.
\]

Inequalities (A1) and (A2) imply systematic and purely numerical conditions for obtaining accurate results,
respectively. The purely numerical condition is, in order to achieve reaction probabilities to an accuracy
of \( \epsilon \) (say, \( \epsilon = 0.01 \)), it is sufficient to evaluate each ac-
tion integral, cf., Eq. (2.3), to an accuracy of \( \epsilon/2 \).
From Fig. 2 one sees that the action integrals are as
large as 500 for the present systems. The relative
accuracy requirement for individual action integrals is
thus \( \epsilon/2/500 \approx 10^{-5} \). The same requirement is
imposed on the relative accuracy of the vibrational
energies \( \epsilon_{\nu}(r) \) and \( \epsilon_{\nu}(r) \) via Eqs. (2.3) and (2.4).
In practice, we used the subroutine DOIGAF of the NAG
library\(^{35}\) which is based on the Gill–Miller algorithm\(^{36}\)
and provides automatic error estimates for the integrals
of Eq. (2.3). About 400 grid points were typically
sufficient to achieve error \( \epsilon < 0.01 \). However, interest-
ing exceptions from this rule (including very rare er-
rors as large as 0.1) were observed occasionally when
the total energy \( E \) in Eq. (2.4) is accidentally close to
\( \epsilon_{\nu}(r) \) or \( \epsilon_{\nu}(r) \) at the classical turning points \( r \).
These exceptional results would have induced oscillations
superimposed on the rather smooth reaction prob-
babilities shown in Figs. 3 and 4, but the present error
analysis definitely proves the spurious origin of such
deviations, which have therefore been omitted in Figs.
3 and 4.

Systematic errors may arise from the use of (slightly)
icorrect units and conversion factors. These would
enter both action integrals [Eq. (2.3)] simultaneously,
and therefore induce partial cancellation of errors in
these integrals by evaluating their difference in Eq.
(4A1). From Figs. 3 and 4 we see that the difference
of action integrals is typically an order of magnitude
less than the action integrals themselves, implying a
minimum desired relative accuracy of \( \epsilon/50 \approx 0.5 \cdot 10^{-3}\)
for units and conversion factors. It should be noted,
too, that slight errors in conversion factors can cause
significant errors in reaction probabilities in the low
energy resonance region, in some cases even as much
as 100% error.\(^{46}\)

Although highly desirable, no equivalent direct error
estimates are presently available for exact quantum
results. However, the empirical errors derived for the quantum results, e.g., by varying grids along $r$ and $\varphi$ in Ref. 21 agree well with the present rigorous semiclassical errors. We therefore conclude that semiclassical error estimates may serve as guidelines for accuracy requirement of accurate quantum calculations.