Fine structure in the dependence of final conditions on initial conditions in classical collinear H$_2$+H dynamics

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The dependence of final vibrational energy, final phase, and trajectory time on the initial phase of the H$_2$ reagent is examined on a novel potential energy surface for the collinear H$_3$ system. For the first time, the fine structure in the borders of the reactivity bands is reported in some detail. A complex, exponentially crowding structure is found in contrast to the common impression of “chaotic” behavior in these regions. The close relation of this structure to the concepts of periodic and exponentiating trajectories is discussed. A suggestion for the implications to Feshbach resonances in semiclassical theory is made.

I. INTRODUCTION

The solution of “well-behaved” ordinary differential equations is known to be a continuous function of initial conditions.$^1$ Any initial condition for which solution is defined has a neighborhood (an open set in the space of initial variables) for which solution is defined and continuous (in initial conditions). Such is the case for the solution of Hamilton’s equations of motion for the (analytic) collinear, triatomic (ABC) potential. Such a solution is known as a “classical trajectory.” Here there are four initial conditions: two coordinates $(Q_1, Q_2)$ and their two conjugate momenta $(P_1, P_2)$. Initially, one has an atom A and a diatom BC and the coordinates can be chosen as the diatomic separation $Q_1 = R_{BC}$ and the distance $Q_2$ between A and the center of mass of BC. Another choice is the angle-action coordinates of BC, i.e., its phase $\phi$ replaces $Q_1$ and its action, which is proportional to the vibrational energy $E_v$, replaces $P_1$. If $E_v$ is given (in the present work we choose $E_v$ to be that of the ground vibrational state $v = 0$), the constancy of the energy $E$ determines the relative translational energy $E_r = E - E_v$, and hence $P_2$. Because the potential $V$ is such that $\partial V/\partial Q_2 = 0$ for $Q_2 = \infty$, the value of $Q_2$ does not matter as long as it is large enough. Hence, one is left with one coordinate to vary, namely, the initial phase $\phi$.

The final configuration is either AB + C (when the trajectory is reactive) or A + BC (when the trajectory is nonreactive) and is obtained when $Q_2^f$ is large. (The final conditions shall be designated by primes.) Again, the value of $Q_2^f$ is immaterial, as long as it is large enough. In addition, the energy is constant ($E' = E$); therefore, two final conditions depend on the outcome of the trajectory, say $\phi'$ and $E'$. The dependence of $E'_r$ on $\phi$ is a fundamental function in semiclassical (“classical S-matrix”) theory.$^2$ It has therefore been calculated quite extensively for H$_3$ and other collinear triatomic systems.$^3$ It was found that this function is indeed continuous for a portion of reactive (R) phases and a portion of nonreactive (NR) phases. This is the “direct” region, corresponding to a single-collision dynamics. However, for some energies it was observed$^4$ that at the border of R/NR phases “apparent random discontinuities occur,”$^{3(e)}$ meaning that a minute variation in $\phi$ results in large changes in $E'_r$ and in the identity of the final configuration (R or NR). In view of the opening sentence of this introduction, these apparent random discontinuities must not, of course, be taken literally. Rather, they must conceal a fine structure of $E'_r = E'_r(\phi)$ in these regions.

The only case where such a fine structure had been investigated$^5$ is NR collisions on a hypothetical potential energy surface (PES) with a well (rather than a barrier, or saddle point, which is the case for H$_3$). Gottscheider observed$^6$ that these transition regions consist of an almost symmetric structure of an infinite series of “parabolas,” decreasing drastically in width from the center of the transition region outwards. Each “Gottscheider parabola” (GP) ends at the two points where $E'_r = E$. Between any two adjacent GP’s another infinite set of GP’s is found, and so on. Each additional set is composed of trajectories which execute one additional collision in the “interaction region,” before separating into the asymptotic configuration.

The present work aims to describe and partly rationalize the fine structure in final-condition functions [such an $E'_r(\phi)$] for an actual reactive system (H$_2$ on a novel PES$^6$).

This study began as a “computer experiment,” devised to introduce our third year students to classical dynamics. In Sec. II we describe briefly the PES, the trajectory program, and the exact choice of initial conditions. After a short discussion of “periodic trajectories”$^6$ (PT) in Sec. III we present results (Sec. IV) for $E'_r$, $Q'_2$, and “trajectory time”$^6$ $t$ as a function of initial phase. We observe three types of behavior, not one as Gottscheider had observed,$^6$ depending on the number of periodic trajectories$^7$ which exist for a given value of $E$. The “exponential crowding” of these functions is related to the “exponentiating” property$^{4(d)}$ of the trajectories. In Sec. V we present the conventional “quasiclassical” reaction probability for the present PES. In the conclusion (Sec. VI) we point to possible implications for Feshbach resonances$^{4(d)}$ in semiclassical theory.

II. EXPERIMENTAL

A. The potential energy surface

The present work is a first trajectory study on the novel bond order interpolation PES$^6$ for collinear H$_2$.\footnote{Present address: Department of Chemistry, California Institute of Technology, Pasadena, Cal. 91125.}
The potential used here is known to be within 1 kcal/mol of the exact H$_2$ surface,\textsuperscript{12} for energies considered in this study, except in some portions of the "repulsive region" (between the reaction coordinate and the origin). However, in that region the potential is very steep, so that any such discrepancy would result only in a small variation in the classical turning point of a trajectory.

The equipotentials for this H$_2$ PES are shown in the bottom panel of Fig. 1. The saddle point energy is equal to the \textit{ab initio} value,\textsuperscript{12} which is 9.8 kcal/mol = 15.6 hartree above the H$_2$ well.

\textbf{B. The computer program}

The computer program, written by A. Ophir and the author for use in the students' laboratory, utilizes Gear's "stiff" method\textsuperscript{13} (which is of the "predictor-corrector" type) to perform the integration of Hamilton's equations. This is done in the ($Q$, P) coordinates, as defined in the Introduction. (The appropriate reduced masses are $\mu_1 = m_H/2$ and $\mu_2 = 2m_H/3$, where $m_H$ is the mass of an H atom.)

The program was exposed to two (conventional) tests:

(i) A trajectory run backwards was seen to trace exactly the forwards trajectory path. This shows that the integrator's precision is suitable, and that the initial integration step is not too large.

(ii) Energy conservation was found to hold to five significant digits. For a reliable integrator, this is a check against errors in the analytical expressions for the derivatives of the potential. Such an error is likely to make the field (dr/d$Q$, $V_r/dr$) nonconservative. A backwards trajectory would trace itself, but $E$ would not be a constant of the motion.

\textbf{C. Input/output}

The input for the program is $E$, $E_v$, and $Q_2$, all in a.u. The integration is stopped when $Q_2^t \geq 8$ a.u.

Numerical output consists of the final values $E_f^t$, $E_v^t$, and $Q_2^f$ (the latter is corrected for the amount the last integration step exceeded 8 a.u.). The trajectory time $t$ is also calculated. $t$ is defined to be the time which it takes for the trajectory to pass from $Q_2 = 7$ a.u. (it is assumed that the initial value for $Q_2$ is $\geq 7$ a.u.) to $Q_2^t = 8$ a.u.

Graphical output consists of the three graphs shown in Fig. 1. These are $R = R_{AB}$ vs $R = R_{AB}$, $R_f$ vs time, and $P_f$ vs time (all in a.u.).

\textbf{D. Initial conditions}

As mentioned above, $E_v$ and $E_r$ determine the initial values for the $P_i$'s. In the present study we consider only trajectories with $v = 0$; hence, $E_v = 6.21$ kcal/mol = 9.89 hartree, while $E_r$ is varied. $Q_2 = Q_2^0$ large enough (the value of $Q_2^0 = 7$ a.u. is somewhat smaller than elsewhere,\textsuperscript{14} but from Fig. 1 it seems still to be large enough). Instead of varying $Q_1$ directly, we set it at a classical turning point and vary $Q_2$ in an interval.
III. PERIODIC TRAJECTORIES

There are three cases to be considered in the final conditions plots, depending on the value of the total energy $E$. There are energies where all the phases are R or all the phases are NR, and energies where some phases are R and some NR. The latter shall be classified according to the number of periodic trajectories (PT) found at that energy.

Let us consider briefly PT's of the first kind, namely, those which oscillate indefinitely between two opposite equipotentials of energy $E$. It is found$^{[10]}$ that at low energies (just above that of the saddle point) one such PT exists and passes through the saddle point. At higher energies two additional PT's appear, and move towards the exit valleys with increasing $E$. These two outer PT's mark local minima in the number of vibrational states (i.e., vibrational action) for the bound motion perpendicular to the reaction coordinate, while the central PT marks a local maximum.$^{[10,11]}$ (For a semiquantitative analysis of this behavior see Ref. 14.) It is shown$^{[10]}$ that trajectories which cross the outer PT's with a velocity component towards the central PT would also cross the central PT (which for $H_2$ is along the bisector $R_1 = R_2$). Trajectories which cross the outer PT's outwards (with a velocity component towards the asymptotic reagent/product regions) would never return. Therefore, the outer PT's are termed$^{[10,11]}$ "repulsive" while the central PT is "attractive."

IV. RESULTS

A. All phases are either R or NR

This is the simplest case. An example for an energy where all phases are R is shown in Fig. 2. It is a simple, periodic, continuous graph. Similar behavior is observed at energies where all phases are NR, below the classical threshold to reaction (e.g., $E_r = 5$ mhartree).

FIG. 2. Final vibrational energy as a function of the initial value of $Q_2$ (linearly related to initial phase $\phi$, in a harmonic approximation), for an energy where all phases are reactive. Circles denote calculated results. The line is an interpolation.

B. Some phases are reactive and some nonreactive

As implied from Sec. III, one has two typical situations: low energies, just above the threshold, where one PT exists, and higher energies, where there are three PT's.$^{[15]}

1. One PT exists

There are two transition points from R to NR phases as shown in the example of Fig. 3. When the transition regions are "blown up" (bottom panels in Fig. 3), additional oscillations of the two branches are observed. To observe an additional oscillation one has to magnify the transition region by an order of magnitude. Hence, these oscillations are exponentially crowding. More quantitatively, we determined the first transition point $Q_2$ to be at $Q_2 = 7.56345$ a.u. and plotted $E_r$ vs $\ln(Q_2 - Q_3)$ for $Q_2$ near to and smaller than $Q_2$. The results was a nearly sinusoidal graph, in agreement with an approximate quantitative analysis$^{[18]}$ of the behavior just above threshold.

Typical trajectories near the first transition point $Q_2$ are shown in Fig. 4. The figure demonstrates how the trajectories near $Q_2$ are "stuck" near the single PT that exists at this energy. The same effect is also obvious in Fig. 5 for the trajectory time.

Let us summarize the above observations as "theo- rems" on the behavior near transition points for the case of one periodic trajectory. The proof of some of these...
is sketched below, and some should be elaborated in the future.

(i) Transition points are isolated. By "isolated" is meant that there exists a small open interval around $\tilde{Q}_2$ which contains no other transition points. The proof sketch is as follows: Consider the classical turning points nearest to those of the PT, of trajectories with initial conditions near $\tilde{Q}_2$. Those turning points would be infinitesimally near that of the PT and infinitesimally near the equipotential $V = E$. Now a turning point of the PT divides the equipotential on which it lies into two disjoint open sets: Trajectories starting on its reagents' side with zero velocity go to reagents, while those which start on its products' side go to products. Hence, a turning point of the PT divides its vicinity on the equipotential into R and NR turning points. Mapping into the reagents space by back integration gives the desired result.

(ii) The number of transition points is even (for a cycle of $2\pi$ in the initial phase). This result follows immediately from the periodic nature of the graph: If, in an interval of $2\pi$, $\phi$ changes from R to NR, it must change again from NR to R in order that the periodic boundary property of the graph holds.

(iii) The graph of $E'_1(\phi)$ oscillates near the transition point. Each additional oscillation for $Q_2 - \tilde{Q}_2$ corresponds to an additional oscillation of the trajectory near the PT. Leaving the PT from its inner turning point corresponds to a low $E'_1$. Leaving it from the outer turning point (large $R_1$'s) corresponds to a large $E'_1$. This is so because the inner turning point of the symmetric $H_2$ stretch is approximately at the equilibri-

um $H_2$ distance, whereas the outer turning point corresponds to an extended $H_2$ distance.

For the results shown in Fig. 3 it was found that trajectories corresponding to the first maxima in $E'_1$ upon approaching $\tilde{Q}_2$ (upper panel) execute one full oscillation near the PT. Trajectories corresponding to the subsequent minima (two bottom panels) correspond to $\frac{1}{2}$ oscillations near the PT. Such are the pair of trajectories shown in Fig. 4. (The final $\frac{1}{2}$ oscillation already deviates from the PT.) They terminate indeed at a low $E'_1$. Trajectories corresponding to the subsequent maxima (not shown in Fig. 4) execute two full oscillations near the PT and (presumably) so on. These oscillations are also reflected in the bottom panel of Fig. 5 for $t(\tilde{Q}_2)$: When $E'_1$ is small, $E'_1$ is large; hence, $t$ decreases, and vice versa.

(iv) The oscillations are exponentially crowding, as discussed above. This follows from the fact that in each additional oscillation near the PT, the trajectory passes once more in the region of the PES which causes trajectories to separate exponentially. This is the region for which there is a direction $x$ such that the potential along $x$ is locally an inverted parabola. Therefore, the force is linear in $x$ and in the direction of motion. This causes the initial $x$ distance between two trajectories to increase exponentially (consider the solution for the equation $d^2x/dt^2 = cx$ with $c > 0$). Hence, each passage through this exponential region magnifies the differences in initial conditions.

**2. Three PT's exist**

Figure 6 shows $E'_1(\tilde{Q}_2)$ and some enlargements of the transition regions for a higher energy than that discussed above. From Fig. 7, which shows trajectories at the transition regions, it is evident that three PT's exist at this energy: A trajectory can oscillate back and forth between these points.
forth between the two extreme PT's before it finally exits into the products' or reactants' valley. Trajectory times are shown in Fig. 8.

The first thing one notes is the complexity of the present situation in comparison to those discussed above. To make our report clearer, we therefore divide this section into three parts: First, we discuss the structure of the graphs; then we try to relate it to properties of the trajectories; and finally we discuss some properties of the transition points in the present case.

(a) Rank and cycle of Gottdiener parabolas: From Figs. 6(b)–6(e) we see that the basic structural units are parabolas, similar to those observed by Gottdiener for nonreactive collisions. These we shall call Gottdiener parabolas (GP). Each GP terminates at two transition points, the nature of which we discuss in (c) below. Another significant point on a GP is its minimum, which divides it into two “branches.” The GP’s always come in pairs: one R and one NR. Hence, we can speak of an “inner” (facing its “sister GP”) and “outer” branches of a GP. The inner branch is always steeper than the outer. In each pair of GP’s the R GP is nearer the NR transition point of the direct region [the region shown in Figs. 6(a) and 8(a)], while the NR GP is facing the R transition point of the direct region.

FIG. 7. Two representative trajectories for transition regions of Fig. 6. The R trajectory is Or3 Pd6, belonging to the Rkt Cy4r GP. The NR trajectory is Or4 Pd6. Trajectories begin at upper left, as indicated by the arrows.

FIG. 6. Final vibrational energy as a function of the initial value of \( Q_2 \) for an energy where three PT's exist. The upper panel shows the "direct" region. The central panel shows fine structure revealed upon magnifications of the two transitions regions. Bottom panels show an additional magnification of two transition regions. R and NR trajectories are denoted, as above, by circles and triangles, respectively.

FIG. 8. Trajectory time in units of \( 10^3 \) a.u. (2.42×10^{-14} s) for the trajectories appearing in Fig. 6. The same notations for R and NR trajectories are used.
Next, we consider the structure of GP's revealed by a first magnification of the transition region [Figs. 6(b), (c)]. This we call "structure of the first rank," denoted by Rk1. This structure seems to consist of an infinite series of GP's. The largest pair is in the center of the transition region. We shall call it "cycle one" (Cy1). On each side of these there is a pair of narrower Cy2 GP's. The pair nearer to the R transition point of the direct region shall be denoted by Cy2r, and the other pair by Cy2w. The width of the GP's decreases exponentially with their cycle, the third cycle being already too narrow to be observed in the figures.

Between any pair of GP's of the first rank there is a finer structure of GP's, observed in the additional enlargements shown in Figs. 6(d), (e). Presumably, each of the pairs shown is only the first cycle in an infinite series of GP's. Because there is an infinite number of GP's of the first rank, we will now have an infinite number of series of Rk2 GP's.

Some of the above conclusions are yet only conjectures: The complexity of the structure makes its determination difficult. Also, the exponential enlargements bring us to the limits of the stability of the numerical integrator, e.g., the angular resolution of two adjacent trajectories in Figs. 6(d), (e) is already about $10^{-4}$.

In Fig. 8 for trajectory times we see a similar structure of GP's. This is understandable because large $E'$ implies small $E$, and hence large $t$, and conversely for small $E'$. However, there are two differences from the structure in Fig. 6. First, $t$ diverges upon approaching a transition point and second, $t$ increases with the cycle of the GP's.

(b) Order and period of trajectories: The fact that two numbers Rk and Cy were needed to specify a GP pair implies that a trajectory should have at least two characteristic numbers attached to it, in order that we can connect the GP structure to trajectory properties. These are the "order" (Or) and "period" (Pd) of the trajectory.

The existence of three PT's allows us to define an order of a trajectory quite simply as the number of times it crosses the central PT. This number is well defined because we know $R^{(k)}_d$ that there can be no more crossings of the central PT after the trajectory crosses an extreme PT outwards (or before it crosses an extreme PT inwards). The order of a trajectory is an exact measure for the intuitive concept of "multiple collisions." R collisions are always odd order and NR collisions are even order.

The fact that the PES supports vibrational motion perpendicular to the reaction coordinate enables us to define the period of a trajectory as the integer number of vibrational periods in the region of the PES bounded by the two extreme PT's (and the two $V=E$ equipotentials). Operationally, the period equals the number of classical turning points (at which the trajectory is tangent to an equipotential) in this region, minus one, divided by two.

Roughly speaking, for the region of the PES bounded by the two extreme PT's and the equipotentials $V=E$, the order and period are related to the "angle variables" for the motions parallel and perpendicular to the reaction coordinate.

How are the rank and cycle of a GP related to the order and period of the trajectories belonging to it? We summarize the main findings below:

(i) In each GP pair all trajectories (R and NR) are of the same period.

(ii) In each GP pair the R and NR GP's differ by one unit in order.

(iii) The direct region is of order 1 or 2. No Or0 trajectories exist at the present energy.

(iv) The highest period in the direct region is 2. (Upon approaching the transition points, an increasing number of oscillations in the trajectory approach an extreme PT from the outside. Hence, they do not contribute to the period.)

(v) The GP's of Rk1 Cy1 are of Pd3. Upon increasing the cycle by unity for Rk1 GP's, the period of the trajectories also increases by unity. (This is the reason for the increase in $t$ with the cycle. The narrowing of GP's with higher cycles follows from the longer time spent in the exponentiation region by trajectories of higher periods.)

As examples to the above ideas consider the trajectories shown in the figures. Figure 1 shows an Or3 Pd3 trajectory which belongs to the Rk1 Cy1 GP [center of Fig. 6(b)]. The R trajectory in Fig. 7 is Or3 Pd6 and belongs to the Rk1 Cy4 GP. The NR trajectory in Fig. 7 is Or4 Pd6. Its GP was not determined.

The relation of the order to the GP structure is not completely clear: For most Rk1 GP's we found that the NR trajectories were Or2 and the R were Or3. However, the NR Cy2r GP's are Or4. In the Rk2 GP's shown in Figs. 6(d), (e) the order increases to 4 for the NR GP's, but does not change for the R GP's. Their period is larger by unity in comparison to the adjacent Rk1 GP with the largest period.

(c) Properties of transition points: Each GP has an inner and outer transition point. Let us list the properties of transition points for the case of three PT's. These should be compared to the case of one PT, discussed in Sec. IV B 1.

(i) The transition points are not isolated: Any open interval around such a point contains additional transition points. More exactly, the transition points are only "half-isolated": Each one has an infinite series of such points converging to it either from the right or from the left.

(ii) Transition points correspond to one of the two extreme PT's which are repulsive. They could not correspond to the central, attractive PT.

(iii) On approaching a transition point from inside a GP, the increasing number of trajectory oscillations converge to the extreme PT's from the outside. (The oscillations in the exit valley become denser.) A convergence from inside (i.e., from the direction of the
central PT) would have meant nonconstancy of the period of trajectories composing a GP, in contrast to (b)(i).

On approaching a transition point from outside a GP, the trajectories' period increases indefinitely, resulting in an infinite series of transition points converging to the given transition point.

(iv) Transition points for R GP's correspond to the PT in the product's side, while those for NR GP's correspond to the PT in the reactant's side. [This is implied by (iv).] The difference between trajectories on the same GP is that the location of one of its oscillations between the extreme PT's varies.

(v) As \( E \) increases we expect the vibrational energy at which the transition points occur to tend to \( E \). This is a consequence of the observation that the two extreme PT's move outwards with increasing \( E \), thus resembling the vibrational motion in the asymptotic diatonic.

C. Other final condition functions

The other final condition, besides final vibrational energy, which depends on the initial phase is the final phase. Figure 9 shows the function \( Q''_1(Q_1) \) for the two energies discussed in Sec. IV B above. We see that already in the direct region, \( Q''_1 \) executes numerous oscillations, crowding towards the transition regions.

V. REACTION PROBABILITIES

Figure 10 collects results for the three energies discussed in Sec. IV, as well as results at other energies obtained by students in our laboratory, in the form of a plot of the reaction probability from \( v = 0 \) (\( P_{NR}^v \)) vs \( E_r \). \( P_{NR}^v \) at a certain energy is simply the ratio of the R \( Q_2 \) interval to the interval \( \Delta Q_2 \) corresponding to a variation of \( 2\pi \) in \( \phi \). The graph is in qualitative agreement with results for other available PES. (Such trajectory results, where \( E \) is chosen to correspond to an integer quantum number, are known by the somewhat misleading title quasiclassical.)

![Graph of final diatomic separation vs energy](image1)

**FIG. 9.** Final diatomic separation \( Q_2 \) at \( Q_1 = 8 \) a.u. for the two energies discussed above. Triangles and dashed line represent NR trajectories. Circles and full line represent R trajectories.

![Graph of reaction probability](image2)

**FIG. 10.** Reaction probability ("quasiclassical") from \( v = 0 \) as a function of initial translational energy (circles connected by a full/dashed line). State to state reaction probabilities from \( v = 0 \) into \( v' = 0 \) and 1 are also shown. Triangles and dashed line represent NR probabilities and relate to the scale on the right.

Also shown in Fig. 10 are R and NR probabilities from \( v = 0 \) into \( v' = 0, 1 \). These are calculated by the conventional "boxing" method, where a trajectory with final vibrational energy \( E_{nr} \) is assigned the (integer) quantum number \( n_r \), if \( E_{nr} \) is nearest to \( E_r \).

The threshold for reaction is about a quarter vibrational quantum above the barrier's energy. This reflects the fact that there is always some vibrational energy in the motion perpendicular to the reaction coordinate. The threshold for reaction into \( v' = 1 \) is lower by \( \sim 5 \) mhartree than the minimum energy needed to populate this vibrational energy in the products. This is a consequence of the boxing procedure: Quantum mechanically, the \( 0 \rightarrow 1 \) graph would begin at \( E \approx 20 \) mhartree. The increase in the population in \( v' = 1 \) is accompanied by a decrease in the population in \( v' = 0 \), so that \( P_{NR}^{v=v'} \).

VI. CONCLUSION

We have discussed two types of transition regions between R/NR bands in final condition plots on a collinear \( \text{H}_2 \) surface. These were analyzed in terms of periodic and exponentiating trajectories, introducing notions such as the order and period of a classical trajectory. More rigorous discussion and proofs of the suggested "theorems" are called for.

An important application of \( E'_v(Q_2) \) plots is in semi-classical theories, attempting to reproduce quantum effects (tunneling, resonances) by interference of classical trajectories. The plots serve for finding the "stationary trajectories," for which \( E'_v \) corresponds to an integer \( v' \). The reciprocal square roots of the slope at these points are the "classical probabilities" appearing in various versions of semiclassical theory.

The first Feshbach resonance for \( \text{H}_2 \) is expected for \( E_r \approx 25 \) mhartree=17 kcal/mol. (The resonance is manifested as a large dip in \( P_{NR}^{v=v'} \) and a smaller spike in...
The calculation shown in Fig. 6 is just below this energy. From Figs. 6(b) and 6(c) we see that at the present energy the transition region would not contribute to the semiclassical reaction probability: The minima of the GP's are just above $v' = 0$ (9.89 mhartree), while the transition points at their upper limit are below $v' = 1$. There is evidence\textsuperscript{3,5} that at the resonance energy the minima of the GP's dip below $v' = 0$, and that it is precisely the contribution from these multiple collision trajectories in the transition regions which accounts for the resonance. A similar conclusion was obtained\textsuperscript{23} from the shape of the vibrational adiabatic potential along the reaction coordinate: At the resonance energy these potentials are seen to support a quasibound state for the motion along the reaction coordinate, i.e., a multiple-collision complex. Both arguments indicate the importance of the transition regions for understanding the quantum resonances. Therefore, a closer examination of transition regions in final condition plots at the resonance energies should be performed in the future.

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\textsuperscript{15}A direct determination of PT's at different energies\textsuperscript{1} was not done for the present PES, but their location is quite obvious from characteristic trajectories shown in the figures. This situation would hopefully be remedied in subsequent undergraduate laboratories.


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