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# Fractals and resonances in collinear (He,H<sub>2</sub><sup>+</sup>) collisions

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Oscillations in the chattering region in plots of final action and collision time as a function of the initial vibrational phase of the diatom in collinear He + H<sub>2</sub><sup>+</sup> (*n<sub>i</sub>* = 0) collisions are shown to have characteristics of fractals with a capacity dimension 1.38–1.68 over a wide range of translational energies. For energies above the reaction threshold, the fractal zones are shown to occur between reactive and nonreactive bands and are related to known quantal reactive scattering resonances.

## INTRODUCTION

The first classical trajectory, computed point by point by hand, of the collinear collision between an H atom and an H<sub>2</sub> molecule was reported as early as 1936.<sup>1</sup> Results of the first classical mechanical study of collinear (H,H<sub>2</sub>) collisions using an electronic computer were published in 1958.<sup>2</sup> The number of papers published since then on the subject of classical mechanical studies of collinear atom (*A*) plus diatom (*BC*) collisions would run into several hundreds. Yet, till this date, this problem continues to be studied and one or another of its myriad fascinating facets gets uncovered.

Specification of the initial separation (*R<sub>shell</sub>*) between *A* and the center of mass of *BC*, relative translational energy (*E<sub>tr</sub>*) of the reactants, the vibrational action (*n<sub>i</sub>*) (or equivalently the vibrational energy *E<sub>v</sub><sup>i</sup>*) of *BC*, and its vibrational phase (*φ<sub>i</sub>*) would fully characterize the initial conditions for such a collision system. As early as 1958, it was realized<sup>2</sup> that the reactivity of the nonvibrating diatom was a “banded function” of *E<sub>tr</sub>*. That is, for some range of *E<sub>tr</sub>*, the collision was reactive and for some it was not. While the collision time (*τ*—defined as the time taken for the trajectory from the point of entry into the “reaction shell” till it exists in the reactant or the product channel at a distance *R<sub>shell</sub>*) was also a banded function of *E<sub>tr</sub>*, the switch from the reactive (*R*) band to the nonreactive (*NR*) or vice versa was invariably accompanied by rapid oscillations in *τ*. When the diatom was allowed to vibrate, with its zero-point energy, the reactivity depended upon *φ<sub>i</sub>* and the bandedness of *τ* with *E<sub>tr</sub>* varied with *φ<sub>i</sub>*. In a subsequent study, on a different potential-energy surface (PES), Wall and Porter<sup>3</sup> found that the final vibrational energy (*E<sub>v</sub><sup>f</sup>*) of the reactant or the product diatom also varied nonmonotonically with *E<sub>tr</sub>*; it varied particularly dramatically when there was a switch from one band to another.

There have been several papers published in the last two decades which reported on the bandedness of *E<sub>v</sub><sup>f</sup>* and *τ* as a function of *φ<sub>i</sub>* and *E<sub>tr</sub>* for a variety of different systems; sometimes on different PESs for the same chemical system. Some of them are listed in Ref. 4. We must mention in particular the work of Wright and collaborators,<sup>4(j),4(k),4(m)</sup> who investigated the bandedness in detail: its dependence on the PES and mass combination of reactants, etc. They pointed out that *E<sub>v</sub><sup>f</sup>* and *τ* reached a maximum at the band edges and

between two bands; they were oscillatory functions of *φ<sub>i</sub>*. While the trajectories in a band indicated “direct” collisions, those in the switching region involved “indirect” or “multiple” collisions and were characteristically “snarled” (complicated). Tan, Laidler, and Wright<sup>5</sup> showed that the bandedness persisted in planar (H,H<sub>2</sub>) collisions. Recently, Muga and Levine<sup>6</sup> noted the bands in three-dimensional (H,H<sub>2</sub>) collisions.

The development of semiclassical *S*-matrix theory<sup>7</sup> provided the basis on which the dependence of the final vibrational action (*n<sub>f</sub>*) (corresponding to *E<sub>v</sub><sup>f</sup>*) on *φ<sub>i</sub>* could be examined and related to the quantum-mechanical description of atom–molecule collisions: state-to-state reaction probability *P<sub>n<sub>i</sub>n<sub>f</sub></sub>*, resonances, etc. Trajectories starting from an integral *n<sub>i</sub>* and ending up with an integral *n<sub>f</sub>* are called the “root” (or stationary) trajectories and, in principle, contain the necessary information required to compute *P<sub>n<sub>i</sub>n<sub>f</sub></sub>*, which is related to the *S*-matrix element *S<sub>n<sub>i</sub>n<sub>f</sub></sub><sup>R</sup>* through

$$P_{n_i n_f}^R = |S_{n_i n_f}^R|^2. \quad (1)$$

The latter, in turn, is computed from the root trajectories connecting *n<sub>i</sub>* and *n<sub>f</sub>* which are identified from the action-angle plots. In the primitive semiclassical (PSC) approximation

$$P_{n_i n_f}^{\text{PSC}} = \sum_j S_{n_i n_f j}, \quad (2)$$

where

$$S_{n_i n_f j} = (P_{n_i n_f j})^{1/2} \exp[i\hbar^{-1}\Phi_j(n_i, n_f)]. \quad (3)$$

Each term in the sum and the subscript *j* refer to each root trajectory. The preexponential factor is evaluated from

$$P_{n_i n_f j} = [2\pi i \hbar (dn_f/d\phi_i)_j]^{-1} \quad (4)$$

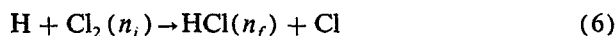
and the phase

$$\Phi_j = \lim_{\substack{t_f \rightarrow -\infty \\ t_i \rightarrow +\infty}} \left\{ \int_{t_i}^{t_f} dt [P(t)R(t) + p(t)r(t)] \right\} + P_i R_i - P_f R_f \quad (5)$$

is integrated along with the Hamilton’s equations. *r* and *R* are the coordinates for the internal motion of the diatom and the relative motion of the reactants, respectively. *p* and *P* are the corresponding momenta.

Rankin and Miller<sup>4(b)</sup> pointed out that for the collinear reaction

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there were two root trajectories in the  $R$  band. In addition, there was a “chattering” region in which  $n_f$  varied sporadically with change in  $\phi_i$  and there were many more root trajectories. But the authors concluded that the contribution by these additional root trajectories to  $P_{n,n_f}^R$  was statistical in nature. They also found that the trajectories in the chattering region were snarled. Miller<sup>7</sup> conjectured that such long-lived trajectories were related to Feshbach-type resonances.

Subsequently, Stine and Marcus<sup>4(f)</sup> pointed out that the contributions from the root trajectories in the chattering region to  $P_{n,n_f}^R$  were not additive and that they could indeed explain resonances. In their investigation of collinear  $\text{H} + \text{H}_2$  collisions, they reported,

“Between reactive branch and the nonreactive branch is a region in which atoms execute multiple collisions. Between these two reactive–nonreactive branches we have found that there is another reactive–nonreactive branch, each branch containing two stationary phase points. Between each of these is still another branch and so on.”<sup>8</sup>

When they computed  $P^R$  using root trajectories from the zero-order branch, it was a monotonically decreasing function of  $E_{tr}$ ; but on inclusion of the additional root trajectories from the first- and the second-order branches, they could reproduce semiquantitatively the oscillation in the  $P^R(E_{tr})$  curve arising from a reactive scattering resonance.

There have been several quantum-mechanical studies of reactive scattering resonances in collinear  $A + BC$  collisions (for a review up to 1984, see Ref. 9), and whenever there have been complementary classical mechanical studies, the action-angle plots revealed chattering regions suggesting a one-to-one correspondence between the existence of such chattering behavior and resonances. For example, Lagana, Hernandez, and Alvarino<sup>4(v)</sup> found scattering resonances in their quantal calculations for the reaction



and their quasiclassical trajectory (QCT) calculations showed that a plot of  $n_f$  vs  $\phi_i$  consisted of four  $R$  bands and between any two  $R$  bands there was a switchover region which on magnification revealed additional  $R$  bands and switchover regions consisting of at least one nonreactive trajectory.

The behavior of the trajectories in the chattering region is labeled “irregular” scattering in the recent literature.<sup>10</sup> It has been related to quantal resonances in a variety of other systems: nonreactive  $A + BC$  collisions, elastic scattering in a potential of certain symmetry, etc.<sup>11</sup> Interestingly, the “irregular” region contains certain regularities as illustrated above with the examples from the work of Stine and Marcus<sup>4(f)</sup> and Lagana, Hernandez, and Alvarino.<sup>4(v)</sup> While investigating collinear nonreactive  $A + BC$  collisions, using a model potential, Gottdiener<sup>12</sup> discovered that the chattering region, on magnification, revealed several “parabolas” which were placed symmetrically about the central point. The pattern repeated endlessly in a self-similar fashion with a finer resolution along the  $\phi_i$  axis. Polanyi and Wolf<sup>13</sup> discovered a similar self-repeating pattern of Gottdiener parabolas in their plots of final rotational action vs initial rota-

tional phase for inelastic molecule–surface collisions. Agmon<sup>4(t)</sup> also found a similar behavior in reactive  $\text{H} + \text{H}_2$  collisions on a model PES. But it was only in 1986, while discussing the dynamical behavior in  $(\text{He}, \text{I}_2)$  vibrational predissociation in a T-shaped geometry that Noid, Gray, and Rice<sup>14</sup> pointed out that such a behavior in the chattering region was characteristic of “fractals,”<sup>15</sup> and Davis and Gray<sup>16</sup> provided a rationale for the chattering behavior and the existence of fractals in terms of phase-space bottlenecks.<sup>16</sup> For some  $\{\phi_i\}$ ,  $n_f$  varied wildly, but on magnification the region revealed some “smooth” structures within. The authors called them “icicles” and reported the associated fractal dimension ( $D_F$ ) to be around 1.86 in contrast to the Euclidean dimension ( $D_E$ ) of two for the system. Recently, Tiyyapan and Jaffe<sup>17</sup> examined the problem in greater detail and identified the “object” that repeats itself in a self-similar fashion. They computed  $D_F$  to be 0.562 when compared to  $D_E = 1$ .<sup>18</sup> Jung and Scholz<sup>19</sup> identified fractals in elastic collisions in potentials of threefold symmetry. We have also examined fractals in rigid-rotor  $\text{HF-Li}$  collisions,<sup>20</sup> molecule–surface collisions,<sup>21</sup> and in interparticle diffusion in a model lattice.<sup>22</sup>

In our long association with the study of  $(\text{He}, \text{H}_2^+)$  collisions we have found the chattering to persist under a variety of initial conditions.<sup>4(o),4(q),4(s)</sup> Resonances in collinear  $(\text{He}, \text{H}_2^+)$  collisions have been known for some time,<sup>23</sup> and recently they have been confirmed<sup>24</sup> on the most accurate *ab initio* PES available<sup>25</sup> for the system up to now. Mayne and Wolf<sup>26</sup> had investigated the quasiperiodic motion in the system using a model PES. Therefore, on the whole, the system appeared an ideal test candidate for investigation of fractals in collinear atom–diatom collisions and relating them to resonances, if possible.

Given below is a description of our analysis of  $n_f(\phi_i)$  plots for collinear  $(\text{He}, \text{H}_2^+)$  ( $n_i = 0$ ) collisions on the *ab initio* PES in terms of fractals for a wide range of energies. For energies above the reaction threshold, we show that there are  $R$  and  $\text{NR}$  bands with the switchover region exhibiting fractal characteristics. We relate them to the known reactive scattering resonances in the  $E_{tr}$  range 0.82–1.34 eV. We also show that the fraction of collisions leading to complex formation defined in terms of the width of the chattering region decreases with increase in  $E_{tr}$ , indicating that the fraction of trajectories exhibiting chaotic behavior becomes less and less at higher energies.

## RESULTS AND DISCUSSION

Details of the PES and the dynamical approach used can be found elsewhere.<sup>27</sup> We have considered collinear  $\text{He} + \text{H}_2^+$  ( $n_i = 0$ ) collisions over a wide range of  $E_{tr}$ . For a given  $(n_i, E_{tr})$ ,  $\phi_i$  was varied systematically in the range  $0-2\pi$ . The initial separation of reactants was taken to be 10 a.u. The Hamilton’s equations were solved numerically using the fourth-order Runge–Kutta method with a stepsize of 0.215 48 fs. The results remained practically unaffected when the Gear integrator was used.

Results for  $E_{tr} = 0.5$  eV in the form of a plot of  $n_f$  as a function of  $\phi_i$  are displayed in Fig. 1(a) for a total of 8000 trajectories. It is clear that there is a smooth  $\text{NR}$  band and a

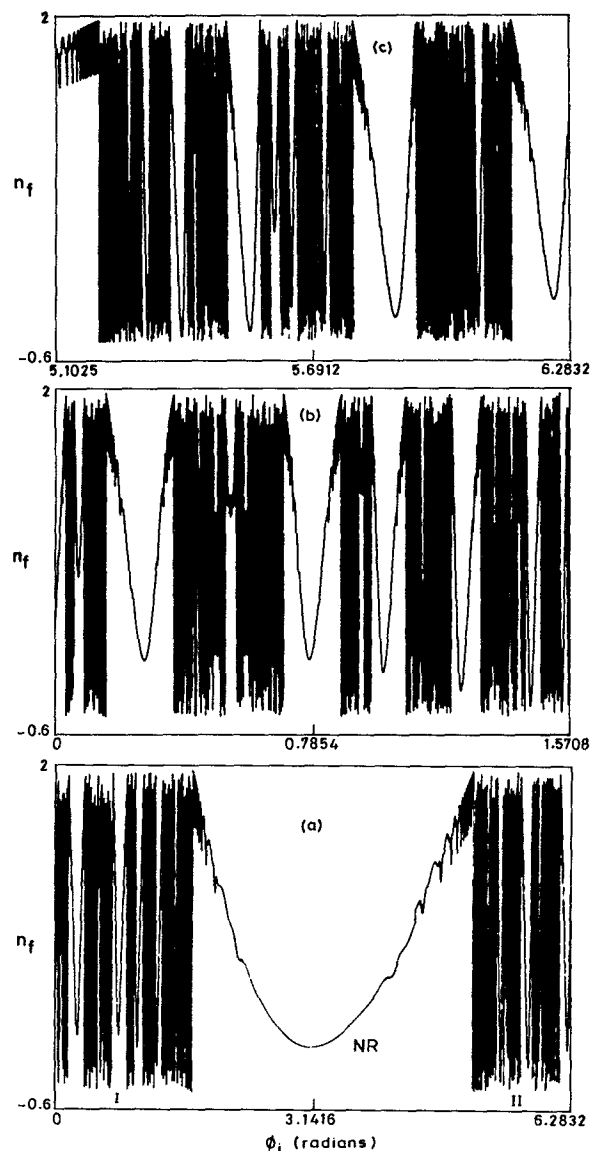


FIG. 1. (a) Final vibrational action vs initial vibrational phase plot for  $n_f = 0$  at  $E_{tr} = 0.5$  eV for 8000 trajectories. Enlargements of regions I and II using 20 000 and 15 000 trajectories in (b) and (c), respectively.

chattering region on either side of it. Since the total energy ( $E_{tr} + E_v$ ) of the system is less than the endothermicity (0.81 eV) of the reaction



there are no reactive trajectories under these conditions.

Values of  $n_f$  obtained from 20 000 and 15 000 trajectories computed in the range of  $\phi_i$  corresponding to regions I and II, respectively, are included in Figs. 1(b) and 1(c), respectively. It is clear that additional structures develop on nearly every structure in Fig. 1(a) on increasing the resolution in  $\phi_i$  by a factor of 10. In other words, in a seemingly complicated pattern there is a structure which is “self-similar”—a characteristic of fractals.<sup>15</sup> Amazingly, even the small “wiggles” on the sides of the “parabolas” are also reproduced in a self-similar fashion.

As expected, a typical trajectory in the smooth region is

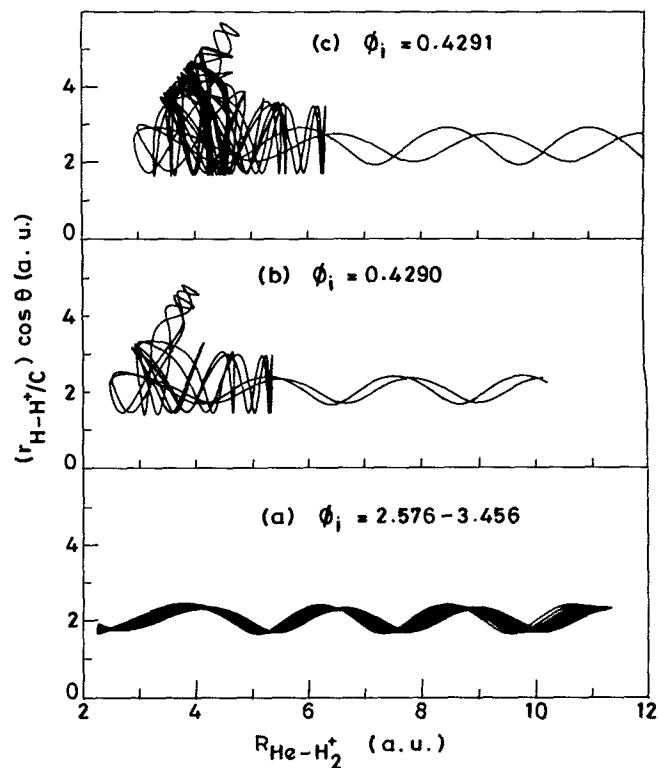


FIG. 2. Traces of individual trajectories for  $n_f = 0$  and  $E_{tr} = 0.5$  eV from (a) the NR band and (b) and (c) from the chattering region.

relatively simple as shown in Fig. 2(a). Such trajectories are “stable” and do not change significantly with a small change in the initial condition. A family of 15 trajectories in the range  $\phi_i = 2.576$ – $3.456$  radians run essentially parallel to each other. In contrast, a trajectory ( $\phi_i = 0.4290$ ) in the chattering region is much more complicated as shown in Fig. 2(b); also, it is very sensitive to the initial condition. A trajectory with a slightly different  $\phi_i$  ( $= 0.4291$ ) behaves dramatically differently as illustrated in Fig. 2(c). Investigation of such a dynamical instability has become an active area of research in the last two decades. Some of the earlier workers (see, for example, Ref. 28) tried to characterize complex formation in collisions using exponential separation as a criterion. That is, two trajectories started close to each other initially in the phase space diverge exponentially away from each other with increase in time. Equivalently, the Lyapunov characteristic exponent<sup>29</sup> (LCE) would be positive for such chaotic trajectories. For convenience, we define LCE as

$$\lambda = \lim_{N \rightarrow \infty} (1/N) \ln(\Delta n_N / \Delta \phi_i), \quad (9)$$

where  $N$  is the number of time steps along a trajectory. Plotting  $\lambda$  vs  $\phi_i$  in Fig. 3 reveals that the former is positive for the chattering trajectories and negative for the stable ones confirming that the former are indeed “chaotic” in nature.

Earlier studies on other systems had shown that  $n_f$  and  $\tau$  are strongly related to each other. For instance, Wright and co-workers<sup>4(j),4(k),4(m)</sup> pointed out that  $n_f$  reached a maximum at the band edges. That would mean that the available

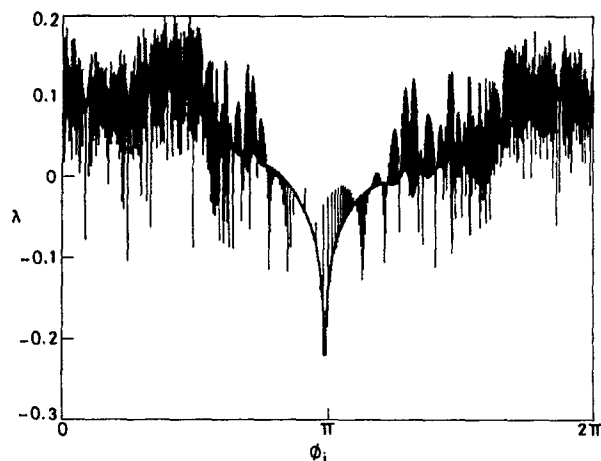


FIG. 3. Lyapunov characteristic exponent as a function of  $\phi_i$  corresponding to Fig. 1(a).

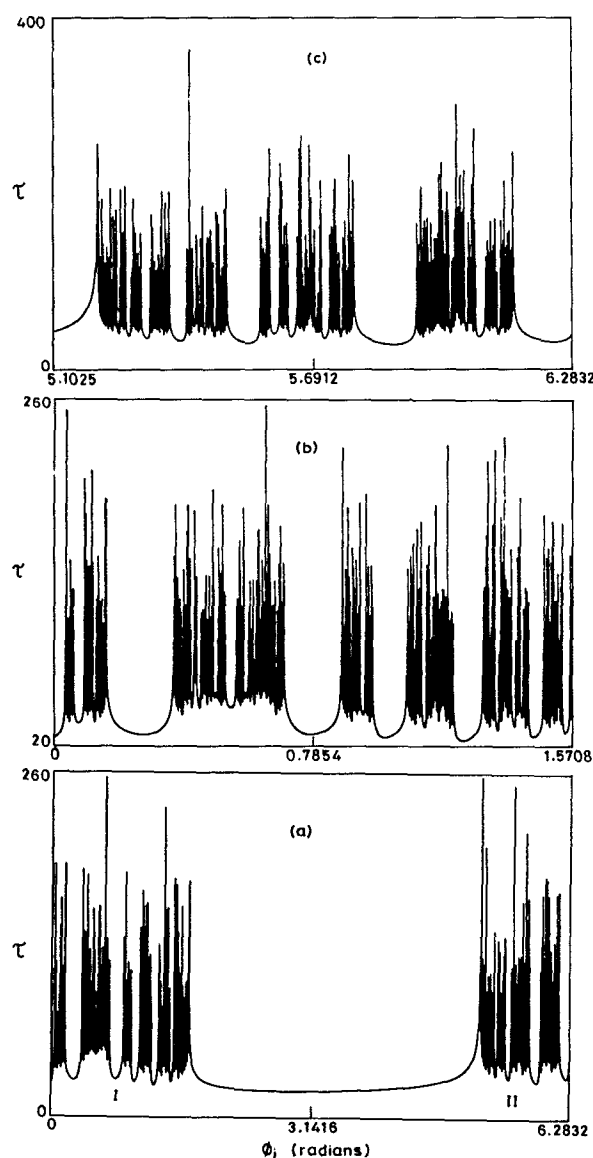


FIG. 4. Collision times of individual trajectories (in multiples of 5.387 fs) as a function of  $\phi_i$  under the conditions of Figs. 1(a)–1(c).

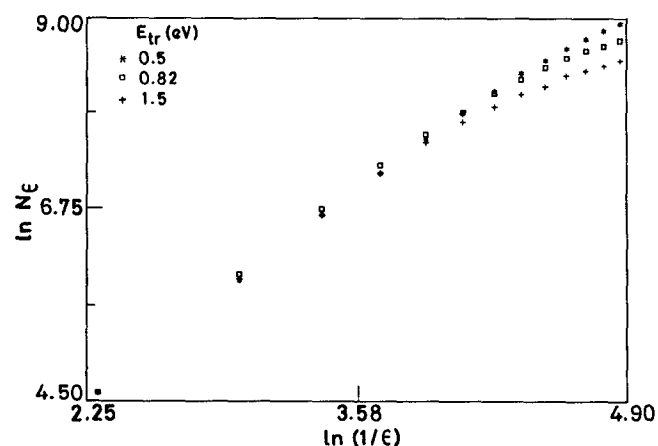


FIG. 5. Plot of  $\ln N_\epsilon$  vs  $\ln 1/\epsilon$  for calculation of the capacity dimension at three different  $E_{tr}$ .

energy in the form of relative translation is a minimum, maximizing  $\tau$ . Values of  $\tau$  for individual trajectories plotted as a function of  $\phi_i$  in Fig. 4 reflect the structure in the action-angle plots of Fig. 1. An overall structure is maintained while additional structures develop within each structure with increasing resolution in  $\phi_i$ . The “irregular” trajectories take significantly longer time and yet there is a structure in their collision time vs  $\phi_i$  plots.

A quantitative measure of characterizing a fractal set is to determine the fractal dimension  $D_F$ . Unfortunately, there does not seem to be any unique method of computing it.<sup>30</sup> Often one computes the capacity dimension  $D_{ca}$  which is identical to the Hausdorff or Fractal dimension for fractals like the Cantor set. For scattering systems,  $D_{ca}$  can be computed, as was done by Noid, Gray, and Rice,<sup>14</sup> by counting the number  $N_\epsilon$  of boxes of length  $\epsilon$  actually visited by the trajectories as follows:

$$D_{ca} = \lim_{\epsilon \rightarrow 0} [\ln N_\epsilon / \ln(1/\epsilon)]. \quad (10)$$

A plot of  $\ln N_\epsilon$  vs  $\ln(1/\epsilon)$  yields a straight line for not too large and not too small values of  $\epsilon$  as illustrated in Fig. 5 for trajectories in the chattering region I of Fig. 1(a). The slope of the straight-line portion of the curve,  $D_{ca} = 1.68 \pm 0.03$ , is substantially less than  $D_E = 2$ .

An alternative approach is to compute the correlation dimension<sup>30(a)</sup>  $D_{co}$  defined by

$$D_{co} = \lim_{r \rightarrow 0} (\ln C(r) / \ln r), \quad (11)$$

where  $C(r)$  is the correlation function giving the average fraction of points lying within a radius  $r$  from a point. If  $N$  is the total number of points and  $P(r)$  the number of points with a separation not more than  $r$ ,  $C(r) = P(r)/N^2$ . We have obtained a  $D_{co}$  of  $1.33 \pm 0.02$  by determining the slope of the  $\ln C(r)$  vs  $\ln r$  curve under the same conditions as employed in calculating  $D_{ca}$ . Clearly,  $D_{ca}$  and  $D_{co}$  differ from each other for the present problem. The reason is that the former ignores the variations in the density of points while the latter includes them. They do satisfy the relation  $D_{co} < D_{ca}$  as expected.

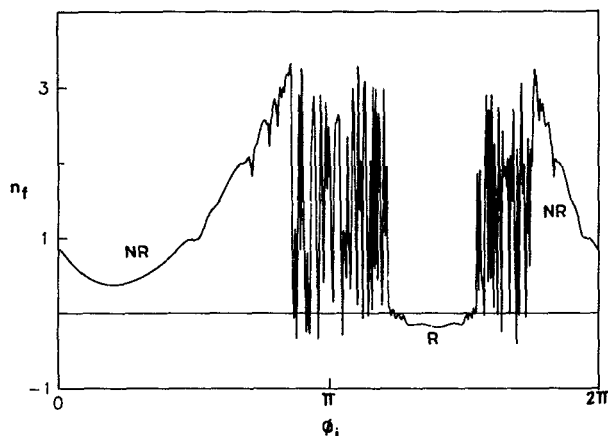


FIG. 6. Action-angle plot for  $n_i = 0$  of  $\text{H}_2^+$  obtained from 400 trajectories at  $E_{\text{tr}} = 0.82$  eV at the onset of the exchange reaction. The horizontal line at  $n_f = 0$  is shown to emphasize the adiabatic leak in the  $R$  band.

We have also tried to compute a measure of  $D_F$  using the nearest-neighbor algorithm proposed by Badii and Politi.<sup>31</sup> If  $\delta_i$  ( $i = 1, \dots, N$  with  $N$  being the total number of points in phase space) is the distance between each point and its nearest neighbor, then the  $\gamma$ th moment  $\langle \delta^\gamma \rangle$  of this distance in the large- $N$  limit is related to the dimension function  $D(\gamma)$  as

$$\left( \frac{1}{N} \sum_{i=1}^N \delta_i^\gamma \right)^{1/\gamma} \propto N^{1/D(\gamma)}. \quad (12)$$

A plot of  $D(\gamma)$  vs  $\gamma$  is made and  $D_F$  is the point at which  $D(\gamma) = \gamma$ . We used the first nearest neighbor to calculate  $D_F$  which came out to be  $1.90 \pm 0.03$  for region I in Fig. 1(a). Thus, regardless of the method used, we get a fractal dimension which is significantly less than the Euclidean dimension of two and also greater than the topological dimension of one for the  $n_f(\phi_i)$  curve.

For energies above the reaction threshold, there is an  $R$  band in addition to an NR band and there are chattering regions separating the two as illustrated in Fig. 6 for  $n_i = 0$ ,  $E_{\text{tr}} = 0.82$  eV. Out of the 400 trajectories computed, 66 are reactive giving a  $P^R = 0.165$  but only 6 of them lead to  $n_f > 0$ , implying that most of the  $P^R$  arises from the “adiabatic leak.” This is an artifact of the QCT approach and it has been found in other systems as well (for example, see Ref. 32). It could be circumvented by computing trajectories in the reverse direction and making use of the principle of microscopic reversibility to compute  $P^R$  in the forward direction as was done by Bowman, Schatz, and Kupperman<sup>33</sup> for ( $\text{F}, \text{H}_2$ ) collisions. Such an approach is being pursued but is not relevant for the present discussion.

A blowup of the  $R$  band, with a 25-fold increase in resolution along the  $\phi_i$  axis, reveals additional structures at either end of the  $R$  band as shown in Fig. 7. The fact that there are no trajectories leading to  $n_f = 0$  in the smooth region implies that there is no contribution to  $P_{00}$  from direct trajectories. Since some of the root trajectories coalesce in the chattering region, computation of the semiclassical  $S$  matrix and hence  $P_{00}^R$  using the PSC approach becomes nonpractical. It would be necessary to use the uniform semiclassical

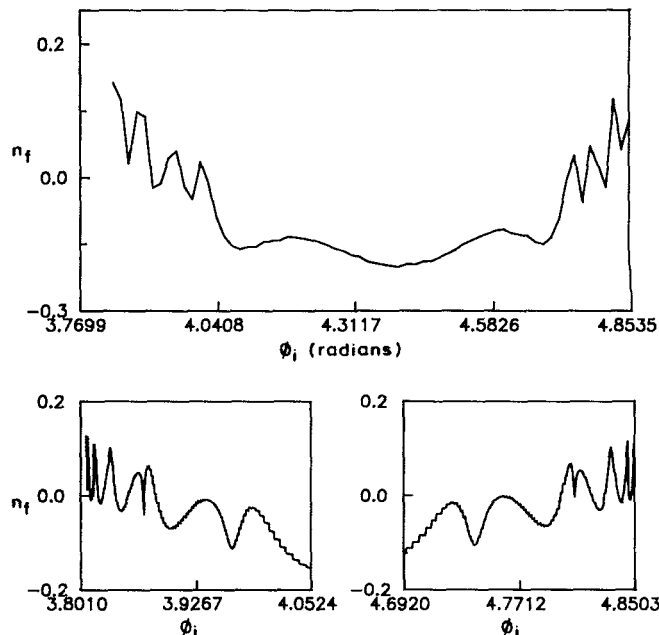


FIG. 7. A blowup of the  $R$  band shown in Fig. 6 along with further blowups of its left and right peripheries.

approximation.<sup>4(e)</sup> Since  $n_f$  is close to but not exactly equal to zero for some values of  $\phi_i$ , it may even be necessary to include some of the trajectories in the complex coordinates and momenta.<sup>34</sup> Understandably, the root trajectories in the chattering region would contribute either destructively or constructively to  $P^R$  depending upon the phase of the  $S$ -matrix element. A quantal calculation of  $P^R$  should and *does* reveal several reactive scattering resonances in the energy range  $E_{\text{tr}} = 0.82$ – $1.34$  eV.<sup>24</sup>

For the chattering region at  $E_{\text{tr}} = 0.82$  eV,  $D_{\text{ca}}$  and  $D_{\text{co}}$  have been found to be  $1.51 \pm 0.04$  and  $1.46 \pm 0.03$ , respectively. The algorithm of Badii and Politi, however, yielded a  $D_F$  of  $2.0 \pm 0.06$  which is somewhat suspect and must be arising from numerical difficulties. Results of  $n_f$  and  $\tau$  as a function of  $\phi_i$ , obtained from quasiclassical trajectories at  $E_{\text{tr}} = 1.0, 1.5, 2.0$ , and  $3.0$  eV, are displayed in Fig. 8. It is clear that the adiabatic leak persists over the entire energy range. Also, there are clearcut  $R$  and NR bands with switchover regions in between. The latter are characterized by their “raggedness” in  $\phi_i$  space.<sup>4(h)</sup> A closer examination of the switchover region around  $\phi_i = \pi$  at  $E_{\text{tr}} = 1.5$  eV reveals that there are alternating  $R$  and NR bands buried in it as illustrated in Fig. 9. The two sets of bands are so interspersed with each other that they could not be separated for the purpose of computing the  $D_F$ . For the two types of bands put together, we obtained  $D_{\text{ca}} = 1.38 \pm 0.02$  and  $D_{\text{co}} = 1.33 \pm 0.02$ . We must also add that there is a striking trend in the widths of these bands in Fig. 9. The width increases, as we go from left to right, to a maximum around  $\phi_i = 3.04$  rad and then falls off rapidly. Alternatively, we could focus attention on the “objects”  $A, B, C, \dots$ ; their widths decrease progressively by a factor 0.69–0.73.

In their study of collinear atom–diatom collisions Duff

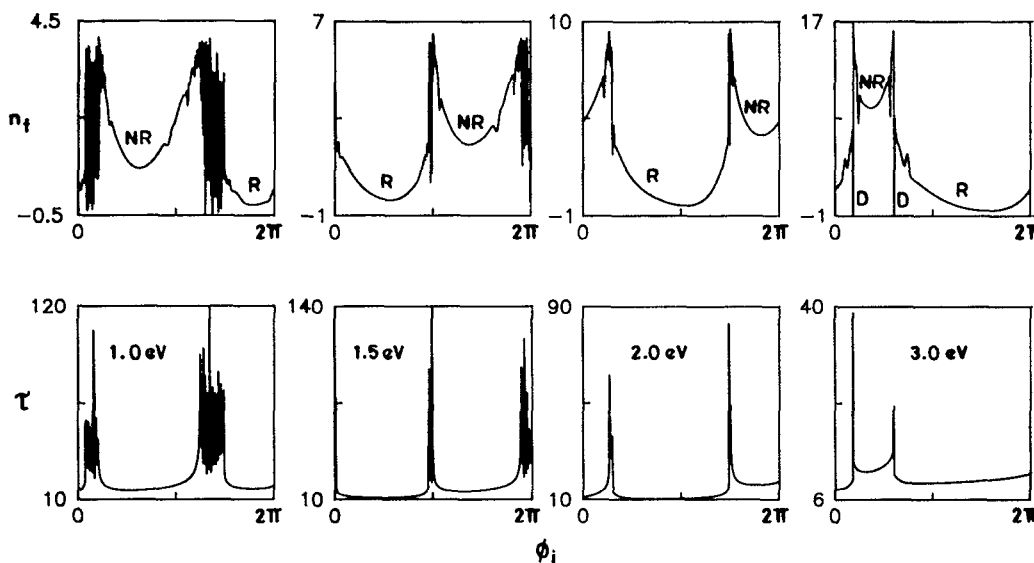


FIG. 8. Plots  $n_f$  and  $\tau$  as a function of  $\phi_i$  at different  $E_{tr}$  for  $n_i = 0$  of  $H_2^+$  to illustrate the narrowing of the chattering region with increase in energy.

and Truhlar<sup>4(c)</sup> speculated that there would be a chattering region in the  $n_f(\phi_i)$  plots, whenever the reaction probability is nonzero and less than unity. This has been found to be the case in virtually all the collinear atom-diatom systems studied to date. Now we have shown that it is also a fractal zone. We have found a similar behavior in the case of molecule-surface collisions also.<sup>21(b)</sup> Pechukas and Pollak<sup>35</sup> argued that in the switchover region there would be trapped trajectories which would live forever. This led to the identification of resonating periodic orbits and their relation to reactive scattering resonances.<sup>36</sup> Recently, Skodje<sup>37</sup> proposed a uniform adiabatic invariance analysis, which when used for the test case of  $I + HI$  reaction, could predict the structure of reactivity bands. It would be worthwhile to test his method by predicting the bands for the  $(He, H_2^+)$  collisions.

The collision time plots confirm that the trajectories in the switchover region are particularly long lived as shown in Fig. 8. We can therefore define the fraction of complex formation<sup>38</sup> in the system as the ratio of the number of trajectories in the chattering region to the total:

$$f_c = N_c/N_T. \quad (13)$$

The value of  $f_c$  decreases with increase in  $E_{tr}$  as illustrated in Fig. 10. The fact, that the capacity dimension decreases from 1.68 to 1.51 to 1.38 as  $E_{tr}$  increases from 0.5 to 0.82 to 1.5 eV, suggests that with increase in  $E_{tr}$  the tendency to chaotic scattering decreases as has been found by Bleher, Ott, and Grebogi.<sup>39</sup>

For  $H_2^+$  ( $n_i = 0$ ) at its outer turning point we found the reactivity to be a banded function of  $E_{tr}$ . Understandably, for  $E_{tr} < 0.81$  eV there is an NR band which is followed by an R band until  $E_{tr} \approx 1.5$  eV. Then there is a narrow NR band followed by an R band and an NR band for  $E_{tr} > 2.7$  eV. Values of  $n_f$  and  $\tau$  plotted as a function of  $E_{tr}$  in Fig. 11 show that along the  $E_{tr}$  axis also, switchovers between bands are characterized by chattering regions which have long-lived trajectories associated with them. A closer examination confirms their fractal characteristics. Interestingly, even below the reaction threshold,  $n_f$  and  $\tau$  are banded functions of  $E_{tr}$  implying that there would be quantal resonances for the system at these energies. An investigation<sup>24(b)</sup> of vibrational adiabatic potential in hyperspherical coordinates reveals



FIG. 9. Alternating R and NR bands in the switchover region around  $\phi_i = \pi$  for  $E_{tr} = 1.5$  eV obtained from 15 000 trajectories.

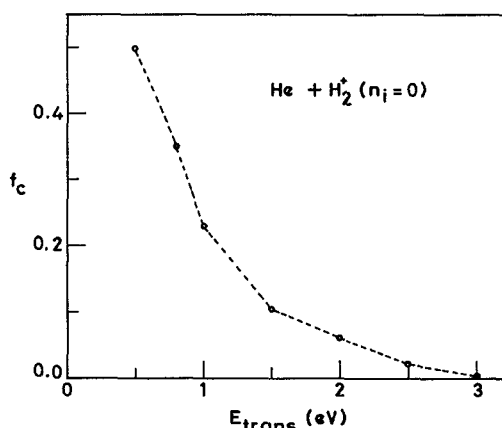


FIG. 10. Fraction of complex formation as a function of  $E_{tr}$  for collinear  $He + H_2^+$  ( $n_i = 0$ ).

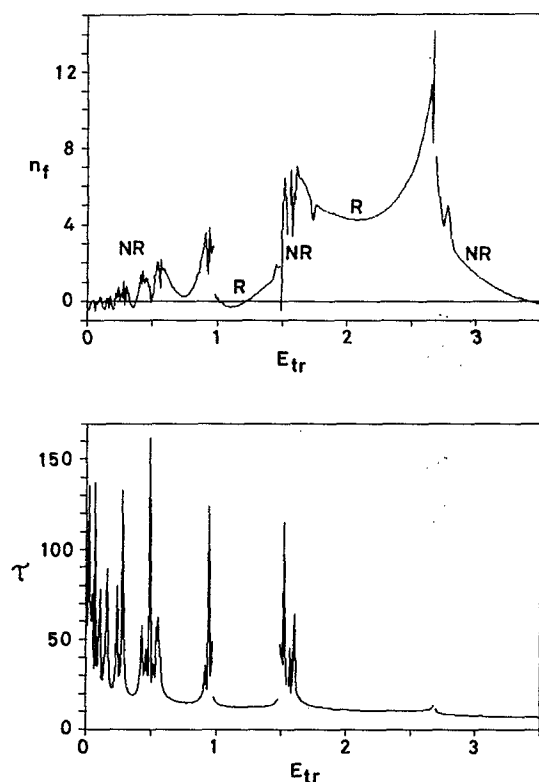


FIG. 11. Values of  $n_f$  and  $\tau$  as a function of  $E_{tr}$  for  $\text{He} + \text{H}_2^+$  ( $n_i = 0$ ) collisions with the latter at its outer turning point.

several bound states in this energy range supporting such a view.

An important question to raise at this juncture would be “Would these aspects of  $(\text{He}, \text{H}_2^+)$  dynamics survive in the 3D world?” Recently, Muga and Levine<sup>6</sup> have examined three-dimensional (3D)  $\text{H} + \text{H}_2$  collisions in terms of delay time in classical trajectories. It is clear from their plots of scattering angle, number of crossings of transition state, time delay, and final action of  $\text{H}_2$  as a function of the initial impact parameter that there is a chattering region. It would be interesting to examine if it is indeed a fractal zone. It would be worth investigating if chattering regions and fractals persist in 3D  $(\text{He}, \text{H}_2^+)$  collisions as recent quantal calculations<sup>24(c),40</sup> have revealed scattering resonances in three dimensions for zero total angular momentum.

## CONCLUSION

We have shown that the chattering regions in the action-angle plots for collinear  $\text{He} + \text{H}_2^+$  collisions exhibit fractal characteristics and that they are related to the resonances in this system. Such a finding is in conformity with the large positive delay time for the classical trajectories. We are in the process of checking whether the fractal singularities would persist in 3D collisions and if they are amenable to experimental observation.

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