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THE DOUBLE-MORSE WELL AND TOPOLOGICAL CHAOS

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For a triatomic system with masses m , M and m moving in a symmetric collinear double-Morse well, it is shown that topological chaos exists and determines the flow of scattering trajectories. Three types of hyperbolic periodic orbits are found. Their stable and unstable asymptotic manifolds are numerically demonstrated to cross in transverse homoclinic and heteroclinic points, respectively, leading to chaos. This situation seems to prevail for a wide range of energies and mass ratios, but structural details of the manifolds, and the amount of chaos induced in the scattering, depend in an oscillatory manner on the mass ratio m/M .

1. Introduction

Irregular "chaotic" trajectories in elastic and reactive molecular scattering have been observed in computational trajectory studies since Rankin and Miller [1]. These authors found that in a system modelling the reaction $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$, the dependence of the vibrational quantum after collision, v' , on the vibrational phase before collision, φ , was "statistical" in part of the phase space. Since then, chaotic trajectories have been regularly discussed, though mostly for bound rather than scattering situations. Indeed, a scattering trajectory as such cannot be chaotic in the mathematical sense, since this would mean that the irregular properties (e.g. ergodicity, exponential divergence of the surrounding flow) should hold for infinite time, which they obviously do not (cf. also ref. [2]). Instead, the parameter space of the initial conditions contains a Cantor set of points leading to sticking collisions which are chaotic for infinite forward times and influence nearby scattering trajectories. This was first shown by Churchill et al. [3] for the Hénon-Heiles potential (which is not constant for $R \rightarrow \infty$, and therefore not a permissible intermolecular potential), and subsequently by Jung and Scholz [4] for a similar potential acceptable for potential scattering, though not allowing inelastic or reactive processes.

To the best of our knowledge there has never been

proof of chaos in a "normal" intermolecular well potential characterized by a deep trough (relative to the collision energy), and two (in 1D) or three (in 3D) asymptotic product valleys. Instead, people have used a variety of arguments to show that "chaos" prevails, among which we mention the following:

(1) "Snarled" trajectories filling the whole phase space rather than being limited to a torus.

(2) "Chattering" trajectories whose final properties depend randomly on the initial conditions as mentioned above [1]. More recently, the function $v'(\varphi)$ has numerically been demonstrated to be fractal with dimension two in one example.

(3) Exponential divergence of adjacent trajectories, or positive local Ljapunov exponents of such trajectories [6].

(4) Fourier spectra of coordinates and momenta as a function of time, which are "grassy".

(5) Self-similarity of increasingly finer structures of the dependence of some final property of the trajectories on some initial condition (the others being kept fixed) [7-9].

In each case evidence was presented to the effect that the trajectories behaved as expected from chaotic dynamics, but the numerical "depth" of such evidence is generally small. Improving this depth means in all cases better resolution and/or longer trajectories, which in turn means an exponential increase in computation time. For example, to test the fractal dimension in ref. [5] with a 300×300 grid

instead of a 30×30 would involve computing 10^6 trajectories instead of the 10^4 actually computed. Still it is clear that the true fractal behaviour, if any, can only lie in those infinitely many trajectories which were *not* computed.

In contrast, the approach of refs. [3,4], which we will also use, depends only on the demonstration that there is an unstable hyperbolic periodic orbit whose stable and unstable asymptotic manifolds cross transversely. In this case, embedded Smale horseshoe chaos, or "topological chaos" is guaranteed by general theorems [10]. To be a valid proof this demonstration needs error control, but *not* infinite resolution! (In addition, the existence of hyperbolic periodic orbits has in some cases been shown analytically [11].) This situation will be exploited in the present paper. We find three simple unstable periodic orbits, which are shown numerically to be hyperbolic, and search for their stable and unstable asymptotic manifolds. In most cases these cross in homoclinic points; moreover, some of the manifolds of different orbits also cross in heteroclinic points. So there are several mechanisms leading to topological chaos for this potential.

The plan of the paper is as follows: section 2 gives some computational details and identifies the unstable periodic orbits. Section 3 shows their asymptotic manifolds, while section 4 contains a general discussion.

2. Computational background

We follow our computations in ref. [12]. The Hamiltonian is

$$H = \frac{1}{2}(p_1^2 + p_2^2) - \delta p_1 p_2 + V_M(r_1) + V_M(r_2). \quad (1)$$

Here $V_M(r_i) = D(1 - e^{-r_i})^2$, where r_i are displacement coordinates in units of the reciprocal Morse parameter β^{-1} , and $\delta = m/(m+M)$. As before, we also use $y = (1 + 2m/M)^{1/2}$. Total energy is expressed as $\epsilon = (E + D)/D$, where D is the well depth as measured from the reactant channel. The actual calculation was done with potential parameters simulating H_3^+ ($D = 4.74615$ eV, $\beta = 1.974$ Å⁻¹, $r_e = 0.74127$ Å), but its applicability is much wider since many intermolecular wells can be approximated by

a double-Morse potential^{#1}, and energies and lengths may be scaled. The initial conditions for scattering trajectories are expressed in terms of the relative vibrational action $\eta = n/n_{\text{max}}(\epsilon)$ and the vibrational phase ϕ . In the interior of the well we start trajectories on the symmetry line $r_1 = r_2$, where we use the coordinates $Q_1 = r_1 + r_2$ and $Q_2 = r_1 - r_2$, and their conjugate momenta denoted P_1 and P_2 . Poincaré surfaces of section are taken at the symmetry line $Q_2 = 0$, or at fixed Q_1 . The integration was carried out with our usual Gear integrator specialized to four variables.

The calculations shown in this Letter were done at $E = 1.0$ eV, or $\epsilon \approx 1.20$. Three types of periodic orbits have been found of interest to us here, cf. fig. 1. The first, of course, is the symmetric stretch. Connecting two different equipotential lines $V_0 = E$ it is also a "periodic orbit dividing surface" (PODS for short [14]), and the number, N , of crossings of this line is a characteristic of each scattering trajectory. The stability of this orbit has already been approximately

^{#1} See, e.g., ref. [13], in which this type of potential for Ar_3 clusters is used.

Fig. 1. Periodic orbits in the potential well of the double-Morse potential. Equipotential lines are shown from -4.0 to $+1.0$ eV in steps of 1.0 eV. Three periodic orbits have been drawn for masses $1.0, 1.12, 1.0$: the symmetric stretch ($r_1 = r_2$), a periodic orbit on the border of the stable region surrounding the asymmetric stretch (started at $Q_1 = 4.806057$ au, $Q_2 = 0$, $P_1 = 0$), and the pair of "infinitely distant" periodic orbits of the separated diatom.

determined by Thiele and Wilson [15]. The true stability diagram using the appropriate Hill's equation is qualitatively the same as that of Mathieu's equation [16]. As expected, for $\epsilon \ll 1$ the orbit is stable, but is unstable for almost all energies above $\epsilon \approx 0.6$.

Secondly, there is the asymmetric stretch. It has the simple shape shown, e.g. in fig. 4 of ref. [17], but is not shown in fig. 1 to avoid cluttering the figure. It is stable, and surrounded by a regular part of phase space, whose size depends on δ and goes up to 20% of the total phase space for some δ . At $\epsilon > 1$ this part of phase space cannot be reached by scattering trajectories (cf. the situation in the similar DIM potential for H_2^+ [17]). Only for certain combinations of δ and ϵ is the asymmetric stretch unstable, but this is not generic. Poincaré plots for $\epsilon = 1.0$ and several values of δ are shown in ref. [18]. Being an elliptic fixed point the asymmetric stretch thus plays no role in producing chaos. However, simple unstable periodic orbits can be found on the border of the regular region, which do play such a role. An example is shown in fig. 1. This type of orbit is a prominent feature in many pictures of scattering trajectories. We call it the asymmetric boundary orbit.

Thirdly, we must discuss here the periodic motion when r_1 or r_2 are at infinity. We call this the pair of "infinitely distant" periodic orbits. Though it is not clear to us how much of the general theorems will hold in this limiting case, it is the easiest one to intuitively understand how topological chaos is produced. The situation is similar to the case of H_3 (a barrier potential), where for certain energies a pair of outer repulsive PODS exist, which contribute to chaos [8]. We will come back to this situation later.

3. Asymptotic manifolds

Having found the hyperbolic periodic orbits, it is relatively easy to find their stable and unstable asymptotic manifolds. They are defined as those points which move onto the hyperbolic fixed point (=periodic orbit) for $t \rightarrow \infty$ and $t \rightarrow -\infty$, respectively. Physically, any trajectory approaching the stable manifold is attracted to the fixed point along with it, and pushed away from the fixed point with the unstable manifold. To find an unstable manifold one starts a group of trajectories on, or slightly besides,

the unstable periodic orbit, and plots their development on the Poincaré section. (In some cases one has first to determine from the linearized problem in which directions the manifolds leave the fixed point.) Stable manifolds are generated from unstable manifolds in time-reversed dynamics, which in our case can be substituted by geometric symmetry. We show figures here for two mass ratios: 1, 2.5, 1 and 1, 1.12, 1. In the language of ref. [12] this means $\Pi \approx 2.5$ and $\Pi \approx 3$, respectively. Here Π stands for the period, and is equal to $0.52 + 1.48y^{*2}$. In ref. [12] we showed that the dynamics of our system depend periodically on this function Π (which is also slightly dependent on energy). In particular, integer and half-integer Π mean little and much chaos in the scattering, and indicate non-RRKM and RRKM behaviour for the unimolecular decay as detailed in ref. [12]. It seems that the whole dynamics is periodically changing with integer and half-integer Π .

Fig. 2 shows the asymptotic manifold of the symmetric stretch for masses 1.0, 2.5, 1.0 ($\Pi \approx 2.5$) in a section at fixed $Q_1 = 3.02 a_0$. The angle at which W_u (the unstable manifold) and W_s (the stable one) cross depends on Π , it goes through zero, i.e. the fixed

^{#2} See also ref. [20], where the period Π was called x_0 .

Fig. 2. Poincaré surface of section (at $Q_1 = 3.02 \text{ au}$, $P_1 \geq 0$) showing the symmetric stretch as a fixed point and its asymptotic manifolds (thin line: stable W_s , thick line: unstable W_u). Masses 1.0, 2.5, 1.0, energy 1.0 eV. The lines are the result of starting 250 trajectories near the fixed point.

point is not hyperbolic, for some Π near 3.0. This is further discussed below. The upper part of fig. 3 shows the same manifolds as before in the $Q_2=0$ section, where the symmetric stretch is the outer rim of the picture. Several homoclinic crossings of W_u and W_s can be seen clearly showing topological chaos.

Fig. 4 shows the same section for masses 1.0, 1.12, 1.0 ($\Pi \approx 3$). The homoclinic points are shifted, and one suspects that there is a mass ratio δ where the inner branches of W_u and W_s do not cross transversely. More resolution shows that at this energy the symmetric stretch is stable for masses between 1.095

Fig. 3. Upper panel: Poincaré surface of section (at $Q_1=0, P_2 \geq 0$) of the same manifolds of the symmetric stretch shown in fig. 2. The symmetric stretch itself is the outer boundary of phase space. Lower panel: The same surface of section showing three iterations of W_u (thick, designated $1_u, 2_u, 3_u$) plus one of W_s (thin, 1_s) of the "infinitely distant" stretches (see text). The lower tail of 3_u winds infinitely often around 1_u , cf. also fig. 5. In addition, the cross at $Q_1=4.5527, P_1=0$ denotes the asymmetric stretch, which is an elliptic fixed point. The stable region of phase space is limited by the asymptotic manifolds of the boundary orbit of fig. 1, which itself consists of the three points where the manifolds cross. The manifolds are designated here by the arrows.

Fig. 4. Same situation as in fig. 3, only the masses have been changed to 1.0, 1.12, 1.0. Upper panel: W_u and W_s have now three branches, where they leave the symmetric stretch (the rim). Lower panel: The manifolds 3_u and 1_s are now nearly coincident. Actually they cross in four points. The fixed point at $Q_1=4.5435, P_1=0$ is the stable asymmetric stretch. Another typical quasiperiodic (stable) orbit is plotted. Further out we show the saddle connection of a (seemingly) unstable trajectory of winding number 22, which is at the border of the stable fraction of phase space surrounding the asymmetric stretch. It is the simplest such trajectory we could find. The saddle connections enclose islands around a stable orbit of the same winding number (not shown).

and 1.14. The hyperbolic fixed point has bifurcated into an elliptic point and an adjacent pair of hyperbolic points. For all practical purposes this pair plays the role of the single hyperbolic point, which exists under most other conditions.

Figs. 3 and 4 also show the manifolds belonging to the infinitely distant stretches. They are produced by starting trajectories from the outside with practically all their energy in vibration ($\eta=0.99$). We show three iterations of W_u at the reactant side and one of W_s at the product side. Trajectories started from the outside with smaller η lie inside the "eggs" of W_u . All

trajectories which fall inside W_s in some iteration escape from the scattering complex and go to infinity, while trajectories adjacent to it on the outside cannot leave the complex because a minute amount of translational energy is missing. The first time for an escape to happen will be after the second or third iteration (or symmetry crossing, to remember) for $\Pi \approx 2.5$, and after the third for $\Pi \approx 3$. (Generally the first iteration to allow escape is the Π th for integer Π , and the $(\Pi - \frac{1}{2})$ th and $(\Pi + \frac{1}{2})$ th for half-integer Π .) From the figures it is clear that in both cases homoclinic points connect the second and/or third iterate of W_u with W_s , thus leading to chaos.

The figures also show why there is so little chaos near $\Pi = 3.0$, or, more generally, near integer Π [12,19]. The approximate congruence of 3_u and 1_s (in fig. 4) means that after three iterations most trajectories escape. In addition, the lack of immediate crossings of 3_u with stable manifolds of other hyperbolic periodic orbits means that this situation is not easily disturbed. So, there is no early contribution of, e.g., the symmetric stretch to the development of chaos in the trajectory. This difference was noticed earlier in refs. [19,20], where "short-range" and "long-range complexes" were distinguished. Actually, the production of long-range chaos is easily understood. It is similar to the "bouncing ball" example treated in ref. [10]: A ball bounces off a vibrating plane. If this plane vibrates fast enough, the correlation of the ball's phase with that of the vibration is lost. Ref. [10] describes how "horseshoe chaos" is directly produced by mapping from one bounce to the next. In our case the situation is similar: the system tries to escape to infinity but falls short of it. It falls back into the potential well with an effectively random phase. Fig. 5 shows how a small section of reactant phase space (a rectangle in η, φ coordinates) is mapped to several horizontal strips by the fourth iterate, i.e. the long-range return. We feel that this is a direct demonstration of a Smale horseshoe embedded in this part of the dynamics. It also explains the long lifetimes noted for near integer Π in refs. [12,19]: The fundamental time interval for this type of chaos is the return time from the outbound legs of the potential, which is much longer than a typical vibrational period within the well. We would conjecture that the unimolecular decay, which was found to be non-exponential [19,20], is actually ex-

Fig. 5. The upper panel shows a Poincaré surface of section (similar to fig. 4), where 1600 trajectories have been started on the lowest pair of V-shaped lines. Trajectories started where the legs of the "V" are within the white "egg" could have been started as scattering trajectories with $\eta = 0 \dots 1$ and two (approximately) constant values of φ , piercing the surface of section for the first time on the "V". Those trajectories which have their third iterate within 1_s of fig. 4 escape, for the others six iterates are shown. The lower panel shows in enlarged form how the fourth iterate multiply maps the "V" (in fact infinitely often) around the lower "egg" (1_u).

ponential if one waits long enough. It is also not RRKM-like due to the large fraction of the phase flux escaping after the first Π symmetry crossings.

On the lower panel of fig. 4 we show an unstable orbit at the border of the stable region surrounding the asymmetric stretch. In this case the manifolds appear to be only saddle connections without having heteroclinic crossings with the manifolds of other orbits. If this is the case this border orbit will not contribute to the global chaos, but details must still be determined.

4. Discussion

The calculations show that the dynamics of the double-Morse potential includes topological chaos near an energy $\epsilon \approx 1.2$. Our general experience leads us to conjecture that this chaos is generic in this and similar potentials for $1 \leq \epsilon < 2$ with the exception of some small (ϵ, δ) regions (in analogy to the stability map of the Mathieu equation). To have a picture, one should imagine that the inbound scattering trajectories are attracted by the stable manifolds of the unstable periodic orbits, then repelled by the unstable ones, and switched to another periodic orbit at the heteroclinic crossings of two manifolds. This explains why a great deal of the dynamics of the "chaotic" scattering trajectories can be described by writing down which periodic orbits are "visited" in order [4,8].

Our evidence is not mathematically exact, but we believe that it could be made so by careful error control on the numerical calculations. For scattering theory and practical applications the more interesting question is how the Cantor set of chaotic inbound trajectories influences all other trajectories. This is, of course, no longer a question of topology but of geometry. Work is underway to find out which part of the initial parameter space $(\epsilon, \eta, \varphi)$ is in the neighbourhood of this Cantor set, and how the structure of the manifolds is connected with the "amount of chaos" found in scattering.

Finally, one has to see what happens when one goes from the collinear to the real, 3D world. Former calculations show that the periodic mass dependence of the dynamic properties is lost [12,19]. If one notes that for a fixed bend angle $\alpha \neq \pi$ of the triatomic molecule the coupling in the Hamiltonian becomes $-\delta p_1 p_2 \cos \alpha$, it is clear that allowing the molecule to bend must have a similar effect to averaging the dynamics over a certain range of mass ratios m/M . It remains to be seen whether this is the main effect of going from 1D to 3D, or whether other dimension-dependent effects like, e.g., Arnold diffusion play an addition role.

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