Recurrence plot analysis of nonlinear vibrational dynamics in \( \text{H}_3^+ \) molecule

Peter Babinec \(^{a,b,*}\), Jerzy Leszczynski \(^b\)

\(^a\) Department of Biophysics and Chemical Physics, Comenius University, MFF UK, Mlynská dolina F1, 842 48 Bratislava, Slovakia

\(^b\) Department of Chemistry, The Computational Center for Molecular Structures and Interactions, Jackson State University, Jackson, MS 39 217, USA

Abstract

An ab initio classical trajectories obtained from the simulation of vibrational mode dynamics of \( \text{H}_3^+ \) molecule were analyzed by Fourier transform and recurrence plot analysis. As has been found, at a particular value of energy supplied to vibrational modes (slightly above the zero point energy) the character of vibrational motion changes from regular to chaotic.

\( \text{C211} \) 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

In 1954 Fermi, Pasta and Ulam (FPU) performed numerical simulation of the planar motion of a one-dimensional anharmonic chain of 64 particles with fixed ends [1]. To their surprise, instead of finding a rapid redistribution of energy among the normal modes, they observed a variety of manifestly nonequilibrium and nonequipartition behaviors. Recently, Casetti et al. [2] performed extensive numerical calculations and found that there is a threshold energy, below which the dynamics appears to be regular and above stochastic. Similar behavior has been found in the numerical studies of the Henon–Heiles Hamiltonian [3],

\[
H = \frac{1}{2}(\dot{x}^2 + \dot{y}^2) + \frac{1}{2}(x^2 + y^2) + x^3y - 3y^3,
\]

where depending on the value of energy, a fully developed chaos, a coexistence of regular and chaotic regions of phase space, or only regular trajectories are observed.

The many coupling and resonances in even small molecules and the possible existence of FPU-like behavior in molecular systems, has been intriguing and persistent question for a long time [4]. The aim of this work is to study the vibrational dynamics of the simplest polyatomic molecule, \( \text{H}_3^+ \), known as a strongly anharmonic with a large amplitude motion, and to show that it exhibits similar features like that observed in FPU and Henon–Heiles systems.

2. Computational methods

For our computational purposes we have used classical trajectory method introduced by Stewart et al. to follow steepest descent paths efficiently on the semiempirical MNDO potential surface [5] and subsequently extended to an ab initio wave functions and implemented as dynamical reaction coordinate (DRC) routine into the electronic structure

\*Corresponding author. Address: Department of Biophysics and Chemical Physics, Comenius University, MFF UK, Mlynská dolina F1, 842 48 Bratislava, Slovakia. Fax: +421-2-65412305.

E-mail address: babinec@fmph.uniba.sk (P. Babinec).

0960-0779/03/S - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0960-0779(02)00646-X
program package GAMESS [6]. The DRC method may be thought of as a classical trajectory calculation “on the fly” since one does not need to determine the potential energy surface for the process of interest prior to the trajectory calculation [7]. On the other hand, because these calculations are obtained from ab initio electronic structure wave functions, they can be quite time-consuming and performing such calculations represents a substantial commitment of computer time.

Recurrence plots (RPs) are relatively new technique for the qualitative assessment of time series [8,9]. With RPs one can graphically detect hidden patterns and structural changes in data or see similarities in patterns across the time series under study. To expand a one-dimensional signal into a \( d \)-dimensional phase space, one substitutes each observation in the original signal \( X(t) \) with vector \( y(i) = \{x(i), x(i + T), x(i + 2T), \ldots, x(i + (d - 1)T)\} \), where \( i \) is the time index, \( d \) is the embedding dimension and \( T \) represents the time delay. As a result, we have series of vectors \( Y = [y(1), y(2), y(3), \ldots, y(N - (d - 1)T)] \), where \( N \) is the length of the original series. Proper choice of the time delay and the embedding dimension is critical for this type of phase space reconstruction. Once the dynamical system is reconstructed, RP can be used to show which vectors in the reconstructed or original space are close and far from each other. Distance matrix \( D_{ij} \) between vectors \( y(i) \) and \( y(j) \) in the reconstructed series is given by

\[
D_{ij} = \sqrt{(x(i) - x(j))^2 + (x(i + T) - x(j + T))^2 + \cdots + (x(i + (d - 1)T) - x(j + (d - 1)T))^2}.
\]

The next step is to choose a threshold corridor \([\delta_l, \delta_h]/\) Once the threshold corridor has been chosen, it is used to generate a thresholded recurrence matrix

\[
B(i, j) = \begin{cases} 
1 & \text{if } \delta_l \leq D(y_i, y_j) \leq \delta_h \\
0 & \text{otherwise}
\end{cases}
\]

Finally, the RP is generated by darkening all pixels \((i, j)\) that correspond to nonzero entries in matrix \( B \). The examples of the RPs are shown in Fig. 1.

---

Fig. 1. Thresholded RPs of (a) a time series derived by sampling the function \( \sin(t) \), (b) a time series of a chaotic signal (white noise), (c) a time series of a random signal (Lorenz model), and (d) a time series of the monotonically growing time sequence. The thresholds \( \delta_l = 0, \delta_h = 1/10 \) of the maximal \((i, j)\) distance, are used in all examples.
3. Results and discussion

To examine behavior of $H_3^+$ vibration dynamics depending on the amount of vibrational energy supplied, we performed DRC calculations at the HF/6-31G** computational level. As the initial conditions of DRC calculations, the same amount of vibrational energy ranging from 0.2 to 4.5 of vibrational quanta $h\nu$, was given in the positive direction.

Fig. 2. Time dependences of normal mode coordinates (left column), their Fourier transforms (middle column) and their RPs (right column) for various amounts of the energy $x \sum_{i=1}^n h\nu$ supplied to the normal modes: (a) $x = 0.5$; (b) $x = 0.75$; (c) $x = 1.5$; (d) $x = 3.5$. The thresholds $\delta_l = 0$, $\delta_u = 1/10$ of the maximal $(i,j)$ distance, are used in all RPs.
to all normal modes. In every case, the time step was set equal to 0.05 fs and simulation was carried out over 5 ps. Representative results of our extensive classical trajectory calculations are shown in the Fig. 2.

In the case of regular vibration motion (Fig. 2a) skeleton of RPs has a structure of regular lattice. This structure is similar to RP of a time series of sampled function \( \sin(t) \) (Fig. 1a), indicating periodic character of vibration motion. As the energy increases, this lattice becomes more and more dense and distorted due to presence of higher modulation frequencies. When the transition from regular to stochastic vibration motion occurs, lattice becomes at first slightly deformed (Fig. 2b and c) and when the motion becomes fully stochastic, skeleton of RPs displays a very complicated pattern (Fig. 2d), similar to chaotic (Fig. 1b) or even stochastic systems (Fig. 1c). This behavior is also evident from the Fourier transforms, which changes from sharp peaks, to a broad band spectra corresponding to chaotic motion. DRC calculations performed with 20 different values of vibrational energy supplied to all normal modes revealed transition from regular to stochastic motion at energy slightly higher than zero point vibrational energy. The threshold of this transition is lying close to \( 0.6 \sum_{i=1}^{3} h\nu_{i} \). This behavior of \( \text{H}^+_3 \) molecule resembles the dynamics of the FPU-model and Henon–Heiles Hamiltonian, indicating that an order-to-chaos transition might be characteristic feature of Hamiltonians describing also real molecules. We performed similar calculations for the molecule of water (which is in the contrast with \( \text{H}^+_3 \), known as a prototype of a harmonic molecule) up to the energy \( 6 \sum_{i=1}^{3} h\nu_{i} \) (\( \approx \) dissociation energy), but we have not observed any similar phenomena (RPs for water vibrational motions changed from the form of Fig. 1a to the form similar to that of Fig. 1d, which corresponds to dissociating molecule), which is an indication of the importance of anharmonicity for order-to-chaos transition in molecules.

Acknowledgements

This work was facilitated by NIH grant no. G1 2RR13459-21, by NSF grant no. 9805465, and by support of the Army High Performance Computing Research Center under the auspices of the Department of the Army, Army Research Laboratory cooperative agreement no. DAAH04-95-2-0003, contract no. DAAH04-95-C-0008. This work does not necessarily reflect the policy of the government, and no official endorsement should be inferred. We thank the Mississippi Center for Supercomputing Research for a generous allotment of computer time.

References