Reply to comment on “Checking the influence of numerically induced chaos in the computational study of intramolecular dynamics using trajectory equivalence”

Jeong Hee Moon, Sang Tae Park, Myung Soo Kim*

National Creative Research Initiative Center for Control of Reaction Dynamics, School of Chemistry, Seoul National University, 151-742 Seoul, Republic of Korea

Received 24 October 2001

Abstract

Time evolutions of mode energies averaged over equivalent trajectories are presented for an uncoupled two-dimensional harmonic oscillator. The mode energies hardly show any significant damping. Hence, our previous interpretation that the excessive damping observed for HOD was due to the onset of numerically induced chaos caused by the coupling terms in the Hamiltonian is upheld. © 2002 Elsevier Science B.V. All rights reserved.

In one of our recent articles, intramolecular dynamics of HOD was investigated with the classical trajectory method using a model potential [1]. Since an internal coordinate system was used in expressing the Hamiltonian, the kinetic coupling was incorporated, leading to interaction among vibrational modes. The main finding of the study was the persistent periodic energy exchange, that is, a vibrational recurrence between the bending and OD stretching modes. Even though the bend–stretch recurrence was observed for all the individual trajectories calculated, the mode energies averaged over 1000 trajectories displayed rapid damping. Namely, it looked as if the intramolecular vibrational redistribution had been completed during this time span and the average energy in each mode remained constant thereafter, even though the actual cause for the apparent damping was dephasing. In the subsequent Letter [2], we investigated the possibility that the dephasing observed was an artifact arising from the numerical round-off error in computation. The scaling theorem in classical dynamics reported previously [3] was utilized for this purpose. Namely, 1000 equivalent, or theoretically identical, trajectories were run and the time evolution of the average bending energy was calculated to observe the influence of the numerical round-off error on dephasing. Rapid damping of the bend–stretch recurrence was observed here also, the effective damping time having been dependent on the arithmetic precision adopted in the computation. The damping observed was much more severe than normally expected for uncoupled systems. It is well
known that tiny round-off error can accumulate rapidly and alter the course of a trajectory significantly. For the present system of coupled oscillators displaying bend–stretch recurrence, the same can lead to significant phase error which differs for different, but theoretically equivalent, trajectories and eventually to complete damping as observed.

In the comment to the above work by Probert [4], a similar investigation was made for harmonic oscillator which is intrinsically non-chaotic. Some equivalent trajectories were run using the velocity-Verlet integrator and time evolutions of the average potential energy were evaluated. Since these averages also displayed damping, it was suggested that the rapid damping was simply due to phase cancellation among different trajectories and not due to numerical chaos. There is no difference in opinion between the original Letter [2] and the comment by Probert on the point that the damping observed in the former was caused by dephasing originating from the round-off error. The point of controversy is whether the chaos has anything to do with the damping.

To clarify the issue, we present the results for an uncoupled two-dimensional oscillator, which is intrinsically non-chaotic, obtained by calculations similar to those in the original Letter [2]. The potential energy used in the calculation is

\[ V = \frac{1}{2}k_1 x^2 + \frac{1}{2}k_2 y^2. \]  

The force constants used were 235.7 and 132.6 kg s\(^{-2}\), respectively, for \( k_1 \) and \( k_2 \) and the effective masses of the oscillators were taken such that the vibrational periods for the mode 1 and 2 are 16.7 and 22.2 fs, respectively. As the trajectory initial condition, 40 and 10 kcal mol\(^{-1}\) kinetic energies were supplied to the modes 1 and 2, respectively, at \( x = y = 0 \). The fourth-order Runge–Kutta (RK4) integrator was used as before with the integration time step of 0.01 fs. Force constants, initial mode energies, and the time step were adjusted in the calculations of equivalent trajectories with the scale factors \( s = 1, 1.001, \ldots, 1.999 \) as dictated in [2]. Mode energies along the trajectories were obtained as the sum of the kinetic and potential parts. Calculations were done with single (32 bit), double (64 bit), and extended double (128 bit) precisions. Only the results from the double precision calculation will be presented here because the general trend is similar regardless of the precision adopted. Also, the results to be presented are quite general in the sense that use of parameter values different from the above leads to the same trend.

Time evolutions of the mode energies averaged over 1000 equivalent trajectories for the above two-dimensional oscillator are shown in Fig. 1a. It is to be noted that the average mode energies do not display any noticeable damping for this intrinsically non-chaotic system. This is in sharp contrast with severe damping observed for the coupled oscillator (HOD) in the previous report ([2, Fig. 2b] is reproduced as Fig. 1b). This was the reason why the latter was interpreted in the pre-
vious work as due to the chaos induced by numerical round-off error. To compare with the previous work, we have also calculated the time evolution of $\log(|\tilde{q}_1 - \tilde{q}_1|/|\tilde{q}_1|)$ along the trajectory for the two-dimensional harmonic oscillator in Fig. 1a is shown as filled squares. Similar data for the coupled HOD system are shown as open squares [2]. Double precision calculation with 0.01 fs time step using the RK4 integrator. The scaled trajectories were run using the scale factor ($s$) of 3.

Finally, we attempted to reproduce the result for the simple one-dimensional oscillator in [4]. As described in the reference, the initial energy was provided as the kinetic energy, $\pi/100$ of the vibrational period was taken as the time step, velocity-Verlet integrator was used, and single precision arithmetic was adopted. Then, the potential energy at a time when the oscillator was expected to be at the classical turning point in each cycle was calculated to obtain the mode energy. We could not reproduce the results in [4] exactly even though the general trend was similar, possibly because the parameters used in the calculation were different from those used in [4]. Fig. 3 shows the time evolutions of the potential energies at the turning point for the original ($s = 1$) and scaled ($s = 1.1$ and 1.2) trajectories during 10000000 time steps. It is curious to note that the mode energy obtained by calculating the potential energy at the nominal turning point displays oscillatory behavior. It seems as if there is an error in locating the turning point, or phase error in position, which accumulates as time goes on. There were slight differences in the scaled energies obtained from the three equivalent trajectories. However, the differences were not significant. We repeated the same calculation using the RK4 integrator. The results are also shown in Fig. 3. With this integrator, the mode energy obtained by calculating the potential energy at the nominal turning point remains essentially constant, or hardly shows any numerically induced dephasing.

To conclude, damping of the HOD bending energy averaged over the equivalent trajectories observed in the original work is more serious than observed for an uncoupled oscillator by many orders of magnitude. In light of this, previous interpretation that the excessive damping observed for HOD was due to the onset of numerically induced chaos caused by the coupling terms in the Hamiltonian should be upheld. Also, the excessive phase error observed in [4] may have something to do with the integrator used, velocity-Verlet. The phase error was not serious at all with the RK4.
integrator, at least during the limited time span of integration used.

Acknowledgements

This work was supported financially by CRI, the ministry of Science and Technology, Republic of Korea. J.H. Moon and S.T. Park thank the Ministry of Education for the Brain Korea 21 fellowship.

References