Zero-Point Energy Constraint in Quasi-classical Trajectory Calculations†

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A method to constrain the zero-point energy in quasi-classical trajectory calculations is proposed and applied to the Henon−Heiles system. The main idea of this method is to smoothly eliminate the coupling terms in the Hamiltonian as the energy of any mode falls below a specified value.

1. Introduction

A well-known shortcoming of the quasi-classical trajectory method is the failure to enforce zero-point energy (ZPE).[1−14] This is of course an error inherent in classical mechanics, because ZPE is a manifestation of the quantum uncertainty principle. Consequently, no matter how accurately one can assign the ZPE to each normal mode of a molecule initially, after a number of steps, the energies in these modes may fluctuate. One consequence of this energy fluctuation may be the formation of reaction products with energy less than the ZPE. This can also become a critical issue if the ZPE is comparable to the barrier height of a reaction.

The energy fluctuation between modes for a multimode Hamiltonian is caused by the mode−mode coupling. If there was only one mode in the Hamiltonian, then the mode energy would be conserved. In the case of separable modes, the energies for these modes would be conserved as well. Any coupling terms between the modes in the Hamiltonian cause energy transfer between them. Without any control of the coupling term, it is possible for one mode to transfer its energy to other modes and to lose energy less than the ZPE.

Independently, Bowman and co-workers[15] and Miller and co-workers[9] proposed a method to constrain the ZPE by changing the sign of the momentum when the energy of any mode reaches the ZPE. This method did prevent energy from going below the ZPE, however, since the momentum change occurs instantaneously, it is equivalent to an infinite impulse that is perhaps too abrupt and can cause noise in say a classical correlation function. Here, we propose another method to constrain the ZPE by smoothly switching off mode coupling when the energy in a mode drops below the ZPE. An application is made to the degenerate Henon−Heiles system.

2. Method and Application

2.1. Method. Consider a general *n*-mode Hamiltonian written as

$$H = H_0 + V_c(1,...,N) \tag{1}$$

where H_0 is a separable, zero-order Hamiltonian given by $\sum_i h_i$ and V_c is an intrinsic coupling term. The objective is to eliminate coupling when the energy in a mode or modes (defined according to H_0) drops below a specified value. How this is done for the mode(s) in question depends to some extent on how the coupling potential is represented. One possibility is to write V_c in an *n*-mode representation as follows[16]

$$V_c(1,...,N) = \sum_{i>j} V^{(2)}(i,j) + \sum_{i>j>k} V^{(3)}(i,j,k) + \cdots \tag{2}$$

Then the proposal is to modify this representation of V_c by the following expression

$$V_c(1,...,N) = \sum_{i>j} V^{(2)}(i,j)S(i)S(j) + \sum_{i>j>k} V^{(3)}(i,j,k)S(i)S(j)S(k) + \cdots \tag{3}$$

where $S(i)$ is a switching function that depends on the energy in mode *i*. One possible expression for $S(i)$ that contains the flavor of the approach is the unit step function $\theta[\epsilon_i(t) - \epsilon_{i,zpe}]$, where $\epsilon_i(t)$ is the energy of mode *i* at time *t*. Clearly, this "instantly" turns off the coupling between mode *i* and all other modes if the mode *i* energy drops below the ZPE of that mode. This is too abrupt in two important ways. First, as written, this is an explicitly time-dependent term which can "spoil" energy conservation, and second, once the mode coupling is totally eliminated, it cannot "return". This means that mode *i* is basically eliminated from further coupling in the dynamics. To deal with both of these defects, we propose a smoother switching and one that is not explicitly a function of time. Thus, we propose $S(i)$ to be given by $S[h_i - \epsilon_{i,zpe}]$, where $S(x)$ is a simple polynomial function[17]

$$S(x) = \begin{bmatrix} 0, & x < 0 \\ 10x^3 - 15x^4 + 6x^5, & 0 \le x \le 1 \\ 1, & x > 1 \end{bmatrix} \tag{4}$$

Note that in most instances h_i is given by the sum of a kinetic energy and potential. For energies near the ZPE, h_i would be well represented by a harmonic oscillator Hamiltonian although this is not essential. In any case, $S[h_i - \epsilon_{i,zpe}]$ is a polynomial in the momentum and coordinate of mode *i* and thus modifies the equations of motion in a straightforward fashion. This is illustrated in an application to the Henon−Heiles system in the next section. Before considering that application, we make some remarks on other possible forms for the coupling potential and how the switching off of mode coupling could be implemented. One form that is very widely used is a simple multinomial

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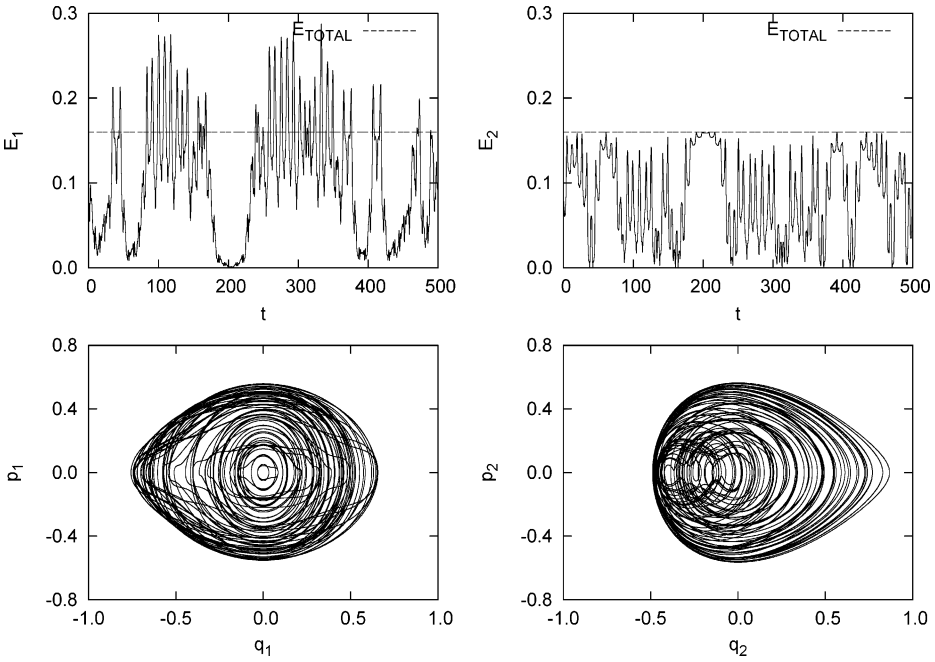

Figure 1. Mode energies E_1 and E_2 and corresponding phase−plane plots. The horizontal dashed line is the conserved total energy along the trajectory, E_{TOTAL}, which equals 0.16.

representation of V_c, that is, an expansion about a minimum

$$V_c(q_1, \cdots, q_N) = \sum C_{n_1 \cdots n_N} q_1^{n_1} \cdots q_N^{n_N} \quad (5)$$

In this case, one could simply multiply each term by the appropriate product of switching functions.

Another more general strategy is to replace each mode coordinate q_i by $S(i)q_i$. The advantage of this strategy is that it can be implemented even in the absence of an analytical expression for V_c, for example, in direct-dynamics calculations. In this case, V_c is given by the full potential (calculated "on-the-fly") minus the separable (harmonic or possible anharmonic potential). Then each coordinate is replaced by $S(i)q_i$, and $V_c(q_1, \cdots, q_N)$ is replaced by $V_c(S(1)q_1, \cdots, S(N)q_N)$. Thus, if $S(i)$ approaches zero, then the variable $S(i)q_i$ approaches zero, its reference value, and is decoupled from the coupling potential. This would probably render analytical differentiation quite complex, and one would have to resort to numerical differentiation in order to propagate the classical equations of motion.

2.2. Application. We consider the degenerate Henon−Heiles Hamiltonian of ref 15

$$H = \frac{1}{2}(p_1^2 + p_2^2 + q_1^2 + q_2^2) + q_1^2 q_2 - \frac{1}{3} q_2^3 \quad (6)$$

$h_1 = {}^1/_2(p_1^2 + q_1^2)$ is clearly the Hamiltonian for the first mode and $h_2 = {}^1/_2(p_2^2 + q_2^2) - {}^1/_3 q_2^3$ is the Hamiltonian for the second mode, and the coupling term is $V_{12} = q_1^2 q_2$.

According to eq 3, the modified Hamiltonian is

$$H = h_1(p_1,q_1) + h_2(p_2,q_2) + S(x_1)S(x_2)V_{12}(q_1,q_2) \quad (7)$$

where $x_1 = (h_1(p_1,q_1) - a_1)/(b_1 - a_1)$ and $x_2 = (h_2(p_2,q_2) - a_2)/(b_2 - a_2)$. Here a_1, a_2, b_1, and b_2 are constants that determine the range over which the switching occurs.

We used the Velocity−Verlet algorithm to integrate the equations of motion. In this algorithm, p and q are updated according to the following equations

$$q(t + \Delta t) = q(t) + \dot{q}(t)\Delta t + \frac{1}{2}\ddot{q}(t)\Delta t^2 \quad (8)$$

$$p(t + \Delta t) = p(t) + \frac{1}{2}(\dot{p}(t) + \dot{p}(t + \Delta t))\Delta t \quad (9)$$

According to Hamilton's equations

$$\dot{p}_1 = -\frac{\partial H}{\partial q_1} \equiv H_{q_1}$$

and

$$\dot{p}_2 = -\frac{\partial H}{\partial q_2} \equiv H_{q_2} \quad (10)$$

$$\dot{q}_1 = \frac{\partial H}{\partial p_1} \equiv H_{p_1}$$

and

$$\dot{q}_2 = \frac{\partial H}{\partial p_2} \equiv H_{p_2} \quad (11)$$

Thus

$$\ddot{q}_1 = \frac{\partial H_{p_1}}{\partial p_1}\dot{p}_1 + \frac{\partial H_{p_1}}{\partial p_2}\dot{p}_2 + \frac{\partial H_{p_1}}{\partial q_1}\dot{q}_1 + \frac{\partial H_{p_1}}{\partial q_2}\dot{q}_2 \quad (12)$$

$$\ddot{q}_2 = \frac{\partial H_{p_2}}{\partial p_1}\dot{p}_1 + \frac{\partial H_{p_2}}{\partial p_2}\dot{p}_2 + \frac{\partial H_{p_2}}{\partial q_1}\dot{q}_1 + \frac{\partial H_{p_2}}{\partial q_2}\dot{q}_2 \quad (13)$$

Since the Hamiltonian of the Henon−Heiles system (eq 6) and the form of the switch function (eq 4) are known analytical functions, all the derivatives can be calculated analytically. However, for this exercise, all of the time derivatives $\dot{q}_1$, $\dot{q}_2$, $\dot{p}_1$, $\dot{p}_2$, $\ddot{q}_1$, and $\ddot{q}_2$ were calculated using Mathematica 5.1.[18]

Results and Discussion

We considered the same total energy of 0.16 as in ref 15, and this energy was equally divided between the two modes at

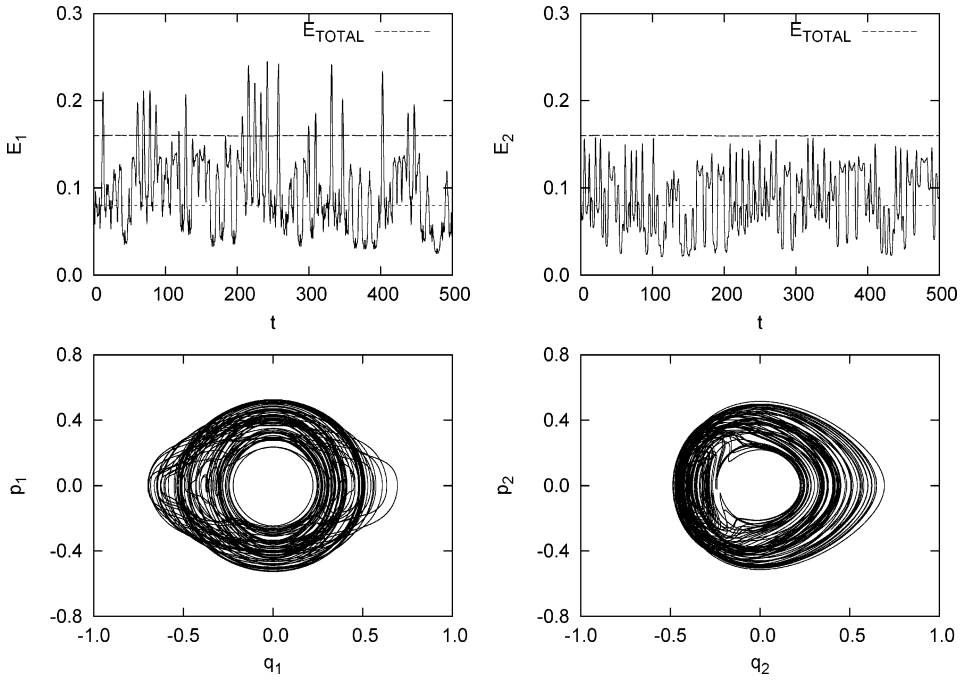

Figure 2. Same as Figure 1 except with mode switching in the range [0.00, 0.08].

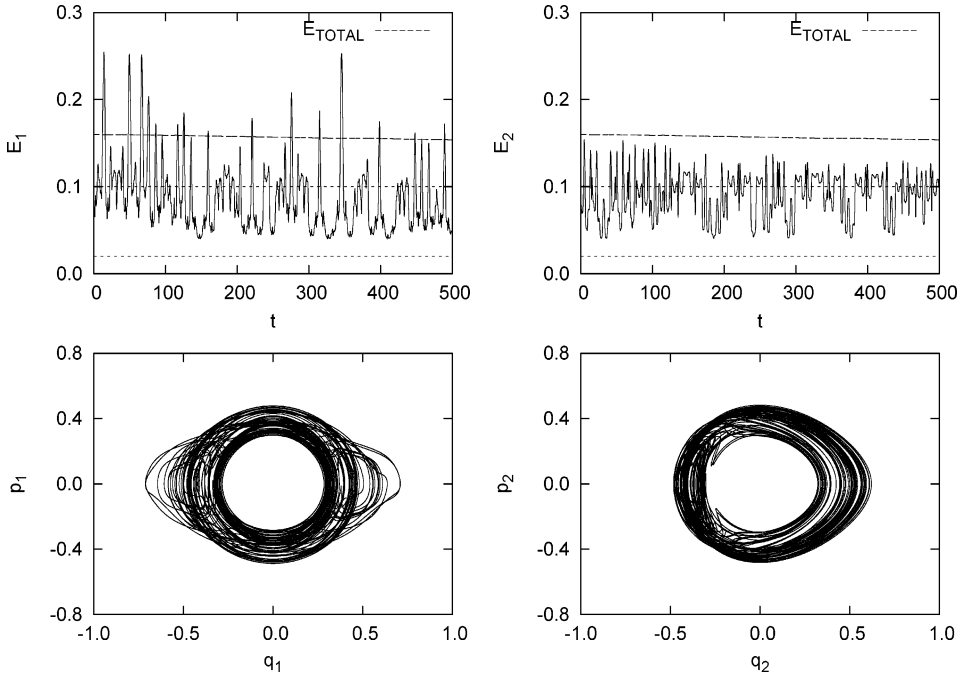

Figure 3. Same as Figure 2 except with mode switching in the range [0.02, 0.10].

$t = 0$. The phase space trajectories of these two modes for the unconstrained dynamics and the mode energies are shown in Figure 1. As seen, each mode loses all of its energy at some time during the trajectory, and there is complete energy transfer back and forth between the two modes. Also note that the energy in a given mode can exceed the total energy, as seen in this figure. This occurs when the energy in the other mode drops to near zero.

We now apply mode switching with switch ranges 0.00−0.08 and 0.02−0.10. The results for the first range are shown in Figure 2 and for the second range in Figure 3. As seen, both switch ranges work effectively and in neither case does the switching actually reach the limit of zero, and so energy exchange between the modes continues throughout this time course of this trajectory. (Note that the energy range is not meant to literally enforce the ZPE in this system, because that energy is actually above the dissociation energy of this model.)

In summary, a new method to smoothly switch off mode coupling has been proposed with the aim of mitigating the ZPE leak has been presented and demonstrated for a two-mode Henon−Heiles model.

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