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Quantum dynamics in classical thermal baths

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ABSTRACT

A particular type of open quantum system dynamics is achieved by embedding a quantum system in a classical thermal bath. Such a bath can be represented in terms of the non-Hamiltonian evolution of few variables by means of the so-called Nosè–Hoover Power thermostat. The classical dynamics of the thermostat is integrated by means of time-reversible measure-preserving algorithms. In this work we show that the Nosè–Hoover Power thermostat, when applied to the dissipative evolution of a quantum spin, provides numerical results which agree with those obtained using Nosè–Hoover chains. However, since a fewer number of variables are needed to achieve the correct sampling of the canonical distribution at equilibrium, the Nosè–Hoover Power thermostat promises to be better suited for the simulation of low dimensional open quantum system on discrete grids.

1. Introduction

The open dynamics of quantum systems is usually formulated by means of influence functionals [1] or master equations [2]. Alternatively, a Hamiltonian approach [3] requires one to embed the system of interest in a bath with a great number of degrees of freedom, to calculate the evolution of the total system, and to integrate out the coordinates of the bath in order to finally obtain an open system description. The numerical implementation of this latter technique would be too demanding computationally. A classical bath of degrees of freedom can also be considered in order to generate the open dynamics of a quantum subsystem. In this case, it has been recently shown how to formulate master equations which are thermodynamically consistent [4–9]. Within the Hamiltonian approach to dissipation [3], one can obtain a phase space representation of the bath by performing a partial Wigner transform only over the coordinates coupled to the quantum subsystem [10]. Upon taking a suitable approximation, a combined quantum–classical law of motion for the quantum subsystem coupled to the bath coordinates is obtained [11]. This representation still requires one to calculate the dynamics of the total system and it is also computationally demanding. However, once the classical bath coordinates are represented in phase space through a partial Wigner transform, well established non-Hamiltonian molecular dynamics equations of motion [12–15] become available in order to represent the thermal bath by means of a minimal number of degrees of freedom. Hence, one can use a non-Hamiltonian bath with few degrees of freedom to simulate on the computer a Hamiltonian bath with many degrees of freedom. This approach has been recently suggested in [16,17]. In particular, in Ref. [17] the dynamics was represented in terms of a swarm of trajectories and the Nosè–Hoover chains (NHC) [18] were used to simulate the thermal bath. However, there are many instances in which the dynamics of open quantum systems might be represented on discrete numerical grids. In such cases, the thermostat variables of the NHC will increase the dimensionality of the grids and one would be interested in having an efficient thermostat with the smallest possible number of additional degrees of freedom. The Nosè–Hoover (NH) thermostat uses fewer variables than the NHC; however, it is not able to sample the canonical distribution for stiff systems.

Hence, in this work we adopt the so called Nosè–Hoover Power (NHP) thermostat [12]. Such a thermostat uses the same number of variables as the NH and is defined by a set of equations of motion that, using only two additional phase space variables, are able to provide a correct sampling of the canonical distribution function for stiff systems. The Nosè–Hoover Chain (NHC) thermostat [18] is also able to produce chaotic dynamics, but it requires at least four additional thermostat variables in phase space and so does the Bulgac–Kusnezov (BK) thermostat [19–21]. Since our final aim is to implement the thermostat in quantum–classical dynamics, in order to simulate a thermal environment interacting with a quantum system, the NHP thermostat has the nice feature of generating a thermal bath by means of the smallest possible number of degrees of freedom. In this work, we adopt the time-reversible measure-preserving algorithms introduced by Ezra [22] (and recently applied to various constant-temperature equations of motion [23])

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and derive an integrator for the classical NHP thermostat. The standard test for a non-Hamiltonian thermostat is a stiff harmonic oscillator, with potential $V(R) = (K/2)R^2$. We have numerically studied such a system in order to test the NHP thermostat and the measure-preserving integrator. Then the NHP thermostat is generalized to quantum–classical dynamics in order to be applied to the study of quantum systems embedded in a classical thermal bath.

This paper is organized as follows. In Section 2 we briefly sketch classical NHP dynamics and formulate time-reversible measure-preserving algorithms for its integration. In Section 3 we extend the NHP thermostat to quantum–classical dynamics and apply it to describe the relaxation of an excited spin in a thermal bath. Conclusions and perspectives are discussed in Section 4.

2. Classical Nosè–Hoover power thermostat

The NHP thermostat was introduced in [12]. Here we briefly sketch its theory and provide an algorithm of integration based on the elegant time-reversible measure-preserving approach of Ezra [22].

Consider the Hamiltonian describing a classical system of physical interest

$$H_C = \frac{P^2}{2M} + V(R), \tag{1}$$

where R and P are the coordinates and momenta, respectively, M are the masses and $V(R)$ is the interaction potential. The NHP Hamiltonian is then defined as

$$H^{\mathrm{NHP}} = H_C + \frac{P_\eta^2}{2M_\eta} + gk_BT\eta, \tag{2}$$

where η is the fictitious thermostat variable, P_η is its associated momentum, M_η is an inertial parameter controlling the dynamical properties of the thermostat, k_B is the Boltzmann constant, T is the temperature of the thermal bath, and g is a constant equal to the number of coordinates R whose temperature needs to be controlled. The extended system Hamiltonian in Eq. (2) is identical to the original Nosè–Hoover Hamiltonian. The NHP thermostat requires the introduction of the antisymmetric matrix [12]

$$\boldsymbol{\mathcal{B}} = \begin{bmatrix} 0 & 0 & 1 & sP/M \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & -P \\ -sP/M & -1 & P & 0 \end{bmatrix}, \tag{3}$$

where s is a free-parameter with the dimension of time. Hence, the corresponding non-Hamiltonian equations of motion are defined by means of a generalized bracket [12,13]

$$\dot{X} = \left\{X, H^{\mathrm{NHP}}\right\}_{\boldsymbol{\mathcal{B}}} = \sum_{jk} \frac{\partial X}{\partial X_j} \mathcal{B}_{jk} \frac{\partial H^{\mathrm{NHP}}}{\partial X_k}, \tag{4}$$

where $X = (R, \eta, P, P_\eta)$. The equations of motion (4) have a phase space compressibility

$$\kappa = \sum_{jk} \frac{\partial \mathcal{B}_{jk}}{\partial X_j} \frac{\partial H^{\mathrm{NHP}}}{\partial X_k} = -g\dot{\eta}. \tag{5}$$

From Eq. (5), using techniques which have now become standard in non-Hamiltonian dynamics with a conserved energy [12–15], one can prove that the equilibrium distribution, followed by the dynamical sampling of the physical coordinates (R, P), has a canonical form. In other words, the NHP dynamics of the coordinates (R, η, P, P_η), which admits the conserved Hamiltonian H^{NHP}, simulates the open dynamics of the physical degrees of freedom (R, P) in the canonical thermodynamic ensemble.

As shown by Ezra in [22], the generalized antisymmetric structure of the conservative non-Hamiltonian Eqs. (4) can be exploited to introduce measure-preserving time-reversible algorithms. For NHP dynamics one can split the Liouville operator as

$$L = \sum_{\alpha=1}^{4} L_\alpha, \tag{6}$$

where each L_α, defined as

$$L_\alpha = \mathcal{B}_{jk} \frac{\partial H_\alpha^{\mathrm{NHP}}}{\partial X_k} \frac{\partial}{\partial X_j}, \tag{7}$$

preserves the invariant measure of phase space [22]. The NHP Hamiltonian can be naturally split into the sum of four terms $H^{\mathrm{NHP}} = \sum_{\alpha=1}^{4} H_\alpha$, where

$$H_1 = \frac{P^2}{2M} \tag{8}$$

$$H_2 = V(R) \tag{9}$$

$$H_3 = \frac{P_\eta^2}{2M_\eta} \tag{10}$$

$$H_4 = gk_BT\eta. \tag{11}$$

This leads to the following explicit form of the Liouville operators:

$$L_1 = \frac{P}{M}\frac{\partial}{\partial R} + \frac{P^2}{M}\frac{\partial}{\partial P_\eta} \tag{12}$$

$$L_2 = -\frac{\partial V}{\partial R}\left[\frac{\partial}{\partial P} + s\frac{P}{M}\frac{\partial}{\partial P_\eta}\right] \tag{13}$$

$$L_3 = \frac{P_\eta}{M_\eta}\left[s\frac{P}{M}\frac{\partial}{\partial R} + \frac{\partial}{\partial \eta} - P\frac{\partial}{\partial P}\right] \tag{14}$$

$$L_4 = -gk_BT\frac{\partial}{\partial P_\eta}. \tag{15}$$

It is useful to combine L_1 and L_4 together by defining $L_A = L_1 + L_4$ and to make the notation homogeneous also defining $L_B = L_2$ and $L_C = L_3$. Denoting a single numerical time step as τ, one can introduce the propagators associated with the Liouville operators in Eqs. (12)–(15) as

$$U_Y(\tau) = \exp\left[\tau L_Y\right] \qquad Y = A, B, C. \tag{16}$$

A possible measure-preserving time integrator for the NHP dynamics is then determined by the approximated propagator

$$U(\tau) = U_B(\tau/2)U_C(\tau/2)U_A(\tau)U_C(\tau/2)U_B(\tau/2) + \mathcal{O}(\tau^3). \tag{17}$$

The action of the propagators $U_Y(\tau)$, $Y = A, B, C$ is defined below:

$$\left.\begin{aligned} P_\eta &\to P_\eta + \frac{\tau s}{M} F_R\left(P + \frac{\tau}{2}F_R\right) \\ P &\to P + \tau F_R \end{aligned}\right\} : U_B(\tau) \tag{18}$$

$$\left.\begin{aligned} \eta &\to \eta + \tau\frac{P_\eta}{M_\eta} \\ R &\to R + \frac{s}{M}P\left[1 - \exp\left(-\tau\frac{P_\eta}{M_\eta}\right)\right] \\ P &\to P\ \exp\left[-\tau\frac{P_\eta}{M_\eta}\right] \end{aligned}\right\} : U_C(\tau), \tag{19}$$

$$\left.\begin{aligned} R &\to R + \tau\frac{P}{M} \\ P_\eta &\to P_\eta + \tau F_p \end{aligned}\right\} : U_A(h) \tag{20}$$