

**Non-Hamiltonian commutators in quantum mechanics**

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The symplectic structure of quantum commutators is first unveiled and then exploited to describe generalized non-Hamiltonian brackets in quantum mechanics. It is easily recognized that quantum-classical systems are described by a particular realization of such a bracket. In light of previous work, this paper explains a unified approach to classical and quantum-classical non-Hamiltonian dynamics. In order to illustrate the use of non-Hamiltonian commutators, it is shown how to define thermodynamic constraints in quantum-classical systems. In particular, quantum-classical Nosé-Hoover equations of motion and the associated stationary density matrix are derived. The non-Hamiltonian commutators for both Nosé-Hoover chains and Nosé-Andersen (constant-pressure, constant-temperature) dynamics are also given. Perspectives of the formalism are discussed.

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**I. INTRODUCTION**

In order to describe phenomena in the real world, classical and quantum systems are represented by means of Hamiltonian mathematical theories [1–4]. However, when studying systems with many degrees of freedom, the need to perform numerical calculations on computers has led to the development of non-Hamiltonian mathematical structures [5–7].

In the classical case, non-Hamiltonian formalisms are typically employed to implement thermodynamic constraints [8] using just few additional degrees of freedom (whereas by using Hamiltonian theories one should resort to an infinite number of degrees of freedom). Just recently, it has been shown that the non-Hamiltonian dynamics of classical systems can be formulated in a unified way by means of generalized brackets which ensure energy conservation [9,10] and subsumes Dirac's formalism [3] for systems with holonomic constraints [11]. Other approaches to classical non-Hamiltonian brackets can be found in Refs. [12,13].

In the quantum case, the impossibility to solve on computers full quantum dynamics for interacting many-body systems has led to the development of quantum-classical theories. Indeed, a generalized bracket to treat quantum-classical systems has been proposed by various authors [14].

Since in the classical case non-Hamiltonian brackets are obtained by modifying the symplectic structure of the Poisson bracket [9,10], in order to deal with the quantum case one could first make apparent the symplectic structure of the commutator (which is the Hamiltonian bracket of quantum mechanics) and then generalize it in order to obtain a non-Hamiltonian quantum bracket (commutator). In this paper it is shown that this is indeed possible. The non-Hamiltonian commutator, which is obtained by this procedure, is then used to reformulate quantum-classical brackets [14]. Thus, it is stressed that quantum-classical dynamics can be regarded as a form of non-Hamiltonian quantum mechanics because

the quantum-classical bracket does not satisfy the Jacobi relation and, as a consequence, the time-translation invariance of the algebra is violated. In order to illustrate the use of non-Hamiltonian commutators, it is shown how to define thermodynamic constraints in quantum-classical systems. The particular case of the Nosé-Hoover thermostat [6,7] is treated in full details and the associated stationary density matrix is derived. The more general cases of Nosé-Hoover chains [15] and constant pressure and temperature [5,6,8] bring no major difference either conceptually or technically and are treated in less detail. It is worth noting that some past attempts of introducing Nosé-Hoover dynamics in quantum calculations [16,17] used a simpler form of quantum-classical dynamics which did not treat correctly the quantum back-reaction on the classical variables. The possibility of applying thermodynamic constraints to quantum-classical dynamics is a technical advance that could lead to further theoretical and computational achievements with regards to the study of open quantum systems [18,19]. With respect to this, a nontrivial major obstacle is the development of efficient algorithms to simulate longtime quantum dynamics.

Besides the technical applications of non-Hamiltonian commutators to the particular case of quantum-classical dynamics, one could appreciate on a more conceptual level that, in light of previous work, non-Hamiltonian brackets provide a unified approach to non-Hamiltonian dynamics both in the classical and quantum case. In addition, if one is willing to indulge in speculations, it is worth noting that the mathematical structure presented in this paper may be shown to generalize the formalisms that a number of authors have already presented in the literature [20–24]. In particular it is worth mentioning that non-Hamiltonian commutators could be used, in principle, in order to introduce nonlinear effects in quantum mechanics along the lines already proposed by Weinberg [22]. Therefore, one could foresee interesting applications of non-Hamiltonian commutators in various fields.

The paper is organized as follows: In Sec. II the symplectic structure of Hamiltonian quantum mechanics is unveiled and its generalization by means of the non-Hamiltonian commutator is proposed. In Sec. III it is shown that the quantum-

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classical bracket can be written in matrix form as a non-Hamiltonian commutator. Such a form easily illustrates the failure of the Jacobi relation [25]. In Sec. IV non-Hamiltonian commutators for quantum-classical systems are used in order to introduce, following Refs. [9,10], Nosé thermostatted dynamics on the classical degrees of freedom. Nosé-Hoover chains and constant-pressure, constant-temperature (NPT) equations of motion bring no major difference and are treated in less detail in the Appendix. In Sec. V it is proven that the stationary density matrix under the quantum-classical Nosé-Hoover equation of motion exists and its explicit form is given up to order  $\hbar$ . Conclusions and perspectives are given in the final section.

## II. NON-HAMILTONIAN QUANTUM MECHANICS

It is well known that classical and quantum dynamics share an analogous algebraic structure [3,4] realized by means of specific brackets: Poisson brackets in the classical case and commutators in the quantum one. It is also known that Poisson brackets have a symplectic structure that is easily represented in matrix form [1,2]. If one denotes the point in phase space as  $X=(R,P)$ , where  $R$  and  $P$  are the usual coordinates and momenta respectively, by defining the antisymmetric matrix

$$\mathcal{B} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \quad (1)$$

and the Poisson bracket of any two phase space function  $a(X)$  and  $b(X)$  can be written in matrix form as

$$\{a,b\} = \sum_{i,j=1}^{2N} \frac{\partial a}{\partial X_i} \mathcal{B}_{ij} \frac{\partial b}{\partial X_j}, \quad (2)$$

where  $2N$  is phase space dimension. In Refs. [9–11], Eq. (2) has been generalized introducing an antisymmetric tensor field  $\mathcal{B}_{ij}(X) = -\mathcal{B}_{ji}(X)$  so that a general bracket  $\{\dots, \dots\}_X$ , having the same matrix structure of that in Eq. (2), could be introduced and non-Hamiltonian equations of motion could be written as

$$\dot{X}_i = \{X_i, \mathcal{H}\}_X = \sum_{j=1}^{2N} \mathcal{B}_{ij}(X) \frac{\partial \mathcal{H}}{\partial X_j}, \quad (3)$$

where  $\mathcal{H}$  is the ‘‘Hamiltonian’’ or generalized energy.

As one could expect, the commutator can also be written in matrix form using the symplectic structure of Eq. (1). If one considers a set of quantum variables  $\hat{\chi}_\alpha$ ,  $\alpha=1, \dots, n$ , which can be canonical, noncanonical, or anticommuting variables, the commutator  $[\hat{\chi}_\alpha, \hat{\chi}_\nu] = \hat{\chi}_\alpha \hat{\chi}_\nu - \hat{\chi}_\nu \hat{\chi}_\alpha$  ( $\alpha, \nu = 1, \dots, n$ ) can be expressed as

$$[\hat{\chi}_\alpha, \hat{\chi}_\nu] = [\hat{\chi}_\alpha \ \hat{\chi}_\nu] \cdot \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \cdot \begin{bmatrix} \hat{\chi}_\alpha \\ \hat{\chi}_\nu \end{bmatrix}. \quad (4)$$

The above matrix form of the commutator permits one to appreciate the common symplectic structure of both classical and quantum mechanics.

Given the Hamiltonian operator  $\hat{H}$  of the system, the law of motion in the Heisenberg picture can also be written in matrix form as

$$\frac{d\hat{\chi}_\alpha}{dt} = \frac{i}{\hbar} [\hat{H} \ \hat{\chi}_\alpha] \cdot \mathcal{B} \cdot \begin{bmatrix} \hat{H} \\ \hat{\chi}_\alpha \end{bmatrix} = i\hat{\mathcal{L}}\hat{\chi}_\alpha, \quad (5)$$

where the Liouville operator has been introduced,

$$i\hat{\mathcal{L}} = \frac{i}{\hbar} [\hat{H} \ \dots] \cdot \mathcal{B} \cdot \begin{bmatrix} \hat{H} \\ \dots \end{bmatrix}. \quad (6)$$

The algebra of commutators is a Lie algebra. This means in particular that the commutator satisfies the following properties:

$$[\hat{\chi}_\alpha, \hat{\chi}_\nu] = -[\hat{\chi}_\nu, \hat{\chi}_\alpha], \quad (7)$$

$$[\hat{\chi}_\alpha \hat{\chi}_\nu, \hat{\chi}_\sigma] = \hat{\chi}_\alpha [\hat{\chi}_\nu, \hat{\chi}_\sigma] + [\hat{\chi}_\alpha, \hat{\chi}_\sigma] \hat{\chi}_\nu, \quad (8)$$

$$[c, \hat{\chi}_\nu] = 0, \quad (9)$$

where  $c$  is a so called  $c$  number and  $\alpha, \nu, \sigma = 1, \dots, n$ . Besides properties in Eqs. (7)–(9), in order to have a Lie algebra, it is necessary that the so-called Jacobi identity holds

$$\mathcal{J} = [\hat{\chi}_\alpha, [\hat{\chi}_\nu, \hat{\chi}_\sigma]] + [\hat{\chi}_\sigma, [\hat{\chi}_\alpha, \hat{\chi}_\nu]] + [\hat{\chi}_\nu, [\hat{\chi}_\sigma, \hat{\chi}_\alpha]] = 0. \quad (10)$$

The Jacobi identity ensures that the algebra is invariant under the law of motion and as such it states an integrability condition. In the above formalism it can be appreciated that the antisymmetry of the commutator (7) arises from the antisymmetry of the symplectic matrix  $\mathcal{B}$  and ensures that if  $\hat{H}$  is not explicitly time dependent then it is a constant of motion

$$\frac{d}{dt} \hat{H} = i\hat{\mathcal{L}}\hat{H} = 0. \quad (11)$$

The conservation of energy under time translation defined by means of antisymmetric brackets is another nice property shared both by the algebra of Poisson brackets on classical phase space and by the algebra of commutators of quantum variables.

Using the operator language of Eq. (4), one can define a generalized commutator as

$$[\hat{\chi}_\alpha, \hat{\chi}_\nu] = [\hat{\chi}_\alpha \ \hat{\chi}_\nu] \cdot \mathcal{D} \cdot \begin{bmatrix} \hat{\chi}_\alpha \\ \hat{\chi}_\nu \end{bmatrix}, \quad (12)$$

where  $\mathcal{D}$  is an antisymmetric matrix operator of the form

$$\mathcal{D} = \begin{bmatrix} 0 & \hat{\zeta} \\ -\hat{\zeta} & 0 \end{bmatrix}, \quad (13)$$

with  $\hat{\zeta}$  arbitrary operator or  $c$  number. Generalized equations of motion could then be defined as

$$\frac{d\hat{\chi}_\alpha}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{\chi}_\alpha] \cdot \mathcal{D} \cdot \begin{bmatrix} \hat{H} \\ \hat{\chi}_\alpha \end{bmatrix} = i\hat{L}\hat{\chi}_\alpha. \quad (14)$$

It must be stressed that the non-Hamiltonian commutator defined in Eq. (12) could violate the Jacobi relation (10) so that in general it does not define a Lie algebra. The non-Hamiltonian commutator of Eq. (12) defines, of course, a generalized form of quantum mechanics. However, in this generalized theory the Hamiltonian operator  $\hat{H}$  is still a constant of motion because of the antisymmetry of  $\mathcal{D}$ . It is interesting to note that  $\mathcal{D}$  could in principle depend from the quantum variables  $\hat{\chi}_\alpha$ . Then Eq. (14) can be thought of as a generalization to the Heisenberg picture of the mathematical formalism proposed by Weinberg [22] in order to introduce nonlinear effects in quantum mechanics.

In the next section it will be shown that the non-Hamiltonian commutator defined in Eq. (12) and the non-Hamiltonian equations of motion (14) provide the mathematical structure for quantum-classical evolution [14].

### III. NON-HAMILTONIAN COMMUTATORS IN QUANTUM-CLASSICAL MECHANICS

Quantum-classical systems can be treated by means of an algebraic approach. This has been already proposed by a number of authors [14] by means of a quantum-classical bracket which does not satisfy the Jacobi relation. A quantum-classical system is composed of both quantum  $\hat{\chi}$  and classical  $X$  degrees of freedom. The quantum variables depends from the classical point  $X$  so that an abstract space is defined in such a way that a Hilbert space (where quantum dynamics takes place) is attached to each phase space point. In turn, a displacement of the phase space point determines a consistent effect on quantum evolution in the Hilbert space. The energy of the system is defined in terms of a quantum-classical Hamiltonian operator  $\hat{H} = \hat{H}(X)$  coupling quantum and classical variables  $E = \text{Tr}' \int dX \hat{H}(X)$ . It has been shown [14] that the dynamical evolution of a quantum-classical operator  $\hat{\chi}(X)$  is given by

$$\partial_t \hat{\chi}(X) = \frac{i}{\hbar} [\hat{H}, \hat{\chi}(X)] - \frac{1}{2} \{\hat{H}, \hat{\chi}(X)\} + \frac{1}{2} \{\hat{\chi}(X), \hat{H}\} = (\hat{H}, \hat{\chi}(X)). \quad (15)$$

The last equality defines the quantum-classical bracket in terms of the commutator and the symmetrized sum of Poisson brackets.

Exploiting what has been done in Refs. [9,10] for the Poisson bracket and in the previous section for the commutator, the quantum-classical bracket can be easily recasted in matrix form as a non-Hamiltonian commutator. To this end, one can introduce the operator  $\Lambda$  defined in such a way that applying its negative on any pair of quantum-classical operator functions  $\hat{\chi}_\alpha(X)$  and  $\hat{\chi}_\nu(X)$ , their Poisson bracket is obtained

$$\{\hat{\chi}_\alpha, \hat{\chi}_\nu\} = -\hat{\chi}_\alpha(X) \Lambda \hat{\chi}_\nu(X) = \sum_{i,j=1}^{2N} \frac{\partial \hat{\chi}_\alpha}{\partial X_i} \mathcal{B}_{ij} \frac{\partial \hat{\chi}_\nu}{\partial X_j}. \quad (16)$$

The quantum-classical law of motion can be rewritten as

$$\partial_t \hat{\chi}_\alpha = \frac{i}{\hbar} [\hat{H}, \hat{\chi}_\alpha] \cdot \mathcal{B} \cdot \begin{bmatrix} \hat{H} \\ \hat{\chi}_\alpha \end{bmatrix} + [\hat{H}, \hat{\chi}_\alpha] \cdot \begin{bmatrix} 0 & \frac{\Lambda}{2} \\ -\frac{\Lambda}{2} & 0 \end{bmatrix} \cdot \begin{bmatrix} \hat{H} \\ \hat{\chi}_\alpha \end{bmatrix}. \quad (17)$$

A more compact form is readily found by defining the antisymmetric matrix superoperator

$$\mathcal{D} = \begin{bmatrix} 0 & 1 + \frac{\hbar\Lambda}{2i} \\ -\left(1 + \frac{\hbar\Lambda}{2i}\right) & 0 \end{bmatrix}. \quad (18)$$

Using the matrix superoperator in Eq. (18) the quantum-classical law of motion becomes

$$\partial_t \hat{\chi}_\alpha = \frac{i}{\hbar} [\hat{H}, \hat{\chi}_\alpha] \cdot \mathcal{D} \cdot \begin{bmatrix} \hat{H} \\ \hat{\chi}_\alpha \end{bmatrix} = (\hat{H}, \hat{\chi}_\alpha) = i\mathcal{L}\hat{\chi}_\alpha, \quad (19)$$

where the last equality introduces the quantum-classical Liouville operator in terms of the quantum-classical bracket. The structure of Eq. (19) is that of the non-Hamiltonian commutator given in Eq. (14) and as such generalizes the standard quantum laws of motion of Eq. (5). It is clear from its definition in Eq. (18) that the antisymmetric matrix superoperator  $\mathcal{D}$  does not have as simple a symplectic structure as  $\mathcal{B}$ . It contains the operator  $\Lambda$  defined in Eq. (16) which, in this case, has a symplectic structure. As such,  $\mathcal{D}$  introduces a mathematical structure that characterizes the time evolution of quantum-classical systems.

The Jacobi relation in quantum-classical dynamics is

$$\mathcal{J} = (\hat{\chi}_\alpha, (\hat{\chi}_\nu, \hat{\chi}_\sigma)) + (\hat{\chi}_\sigma, (\hat{\chi}_\alpha, \hat{\chi}_\nu)) + (\hat{\chi}_\nu, (\hat{\chi}_\sigma, \hat{\chi}_\alpha)). \quad (20)$$

Using the matrix formalism introduced, it is simple to calculate  $\mathcal{J}$  explicitly and to this aim one can consider the first term on the right-hand side of Eq. (20). The other two terms on the right-hand side of Eq. (20) can then be easily calculated by considering the even permutations of  $\hat{\chi}_\alpha, \hat{\chi}_\nu, \hat{\chi}_\sigma$  in the formula obtained for  $(\hat{\chi}_\alpha, (\hat{\chi}_\nu, \hat{\chi}_\sigma))$ . Finally, collecting the terms together, one gets

$$\begin{aligned} \mathcal{J} = & \frac{1}{4} \{ \hat{\chi}_\alpha \Lambda (\hat{\chi}_\nu \Lambda \hat{\chi}_\sigma) - \hat{\chi}_\alpha \Lambda (\hat{\chi}_\sigma \Lambda \hat{\chi}_\nu) - (\hat{\chi}_\nu \Lambda \hat{\chi}_\sigma) \Lambda \hat{\chi}_\alpha \\ & + (\hat{\chi}_\sigma \Lambda \hat{\chi}_\nu) \Lambda \hat{\chi}_\alpha + \hat{\chi}_\sigma \Lambda (\hat{\chi}_\alpha \Lambda \hat{\chi}_\nu) - \hat{\chi}_\nu \Lambda (\hat{\chi}_\alpha \Lambda \hat{\chi}_\sigma) \\ & - (\hat{\chi}_\alpha \Lambda \hat{\chi}_\nu) \Lambda \hat{\chi}_\sigma + (\hat{\chi}_\alpha \Lambda \hat{\chi}_\sigma) \Lambda \hat{\chi}_\nu + \hat{\chi}_\nu \Lambda (\hat{\chi}_\sigma \Lambda \hat{\chi}_\alpha) \\ & - \hat{\chi}_\sigma \Lambda (\hat{\chi}_\nu \Lambda \hat{\chi}_\alpha) - (\hat{\chi}_\sigma \Lambda \hat{\chi}_\alpha) \Lambda \hat{\chi}_\nu + (\hat{\chi}_\nu \Lambda \hat{\chi}_\alpha) \Lambda \hat{\chi}_\sigma \}. \end{aligned} \quad (21)$$

In order to easily get such expression, the relation

$$\sum_{i,j=1}^{2N} \frac{\partial \hat{\chi}_\alpha}{\partial X_i} \mathcal{B}_{ij} \partial_j (\hat{\chi}_\nu \hat{\chi}_\sigma) = \sum_{i,j=1}^{2N} \frac{\partial \hat{\chi}_\alpha}{\partial X_i} \mathcal{B}_{ij} (\partial_j \hat{\chi}_\nu) \hat{\chi}_\sigma + \frac{\partial \hat{\chi}_\alpha}{\partial X_i} \mathcal{B}_{ij} \hat{\chi}_\nu (\partial_j \hat{\chi}_\sigma) \quad (22)$$

was exploited. Thus it is found that the Jacobi relation does not hold globally for all points  $X$  of phase space ( $\mathcal{J} \neq 0$ ).

#### IV. NOSÉ DYNAMICS IN QUANTUM-CLASSICAL SYSTEMS

The antisymmetric matrix  $\mathcal{B}$  enters through  $\Lambda$  in the definition of  $\mathcal{D}$ . Following the work of Refs. [9,10] thermodynamic constraints can be imposed on the classical bath degrees of freedom in quantum-classical dynamics just by modifying the matrix  $\mathcal{B}$ . For clarity it will be explicitly shown how to generalize the derivation of quantum-classical equations of motion in the case of Nosé constant-temperature dynamics [6]. In the Nosé case the bath degrees of freedom will be

$$X \equiv (R, \eta, P, p_\eta), \quad (23)$$

where  $\eta$  and  $p_\eta$  are the Nosé coordinate and momentum. The following quantum-classical Hamiltonian is assumed:

$$\hat{H}_N = \hat{K} + \frac{P^2}{2M} + \frac{p_\eta^2}{2m_\eta} + \hat{\Phi}(\hat{\chi}, R) + gk_B T \eta, \quad (24)$$

where  $\hat{K}$  is the quantum kinetic operator,  $\hat{\Phi}$  is the potential operator coupling classical and quantum variables,  $M$  is the mass of the classical degrees of freedom,  $m_\eta$  is the Nosé inertial parameter, and  $g$  is a numerical constant whose value (as it will be shown) must be set equal to the number  $N$  of classical momenta  $P$  if one wants to obtain a sampling of the  $R, P$  coordinates in the canonical ensemble. Then the matrix  $\mathcal{B}^N$  is

$$\mathcal{B}^N = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & -P \\ 0 & -1 & P & 0 \end{bmatrix}. \quad (25)$$

Using  $\mathcal{B}^N$ , the operator  $\Lambda_N$  and the classical phase space non-Hamiltonian bracket on two generic variables  $A_1$  and  $A_2$  can be defined,

$$A_1 \Lambda_N A_2 = - \sum_{i,j=1}^{2N} \frac{\partial A_1}{\partial X_i} \mathcal{B}_{ij}^N \frac{\partial A_2}{\partial X_j}. \quad (26)$$

The explicit form of the matrix operator that defines through Eq. (19) the quantum-classical bracket and the law of motion is then given by

$$\mathcal{D}^N = \begin{bmatrix} 0 & 1 + \frac{\hbar}{2i} \Lambda_N \\ - \left( 1 + \frac{\hbar}{2i} \Lambda_N \right) & 0 \end{bmatrix}. \quad (27)$$

The quantum-classical Nosé-Liouville operator is given by

$$\frac{d}{dt} \hat{\chi} = i \mathcal{L}^N \hat{\chi} = \frac{i}{\hbar} [\hat{H}_N, \hat{\chi}] \cdot \mathcal{D}^N \cdot \begin{bmatrix} \hat{H}_N \\ \hat{\chi} \end{bmatrix}. \quad (28)$$

One is then led to consider, in the right-hand side of (28), the term given by

$$\begin{aligned} -\hat{H}_N \Lambda_N \hat{\chi} + \hat{\chi} \Lambda_N \hat{H}_N &= \frac{\partial \hat{\Phi}}{\partial R} \frac{\partial \hat{\chi}}{\partial P} + \frac{\partial \hat{\chi}}{\partial P} \frac{\partial \hat{\Phi}}{\partial R} - 2F_\eta \frac{\partial \hat{\chi}}{\partial p_\eta} - 2 \frac{P}{M} \frac{\partial \hat{\chi}}{\partial R} \\ &\quad - 2 \frac{p_\eta}{m_\eta} \frac{\partial \hat{\chi}}{\partial \eta} + 2 \frac{p_\eta}{m_\eta} P \frac{\partial \hat{\chi}}{\partial P}, \end{aligned} \quad (29)$$

where  $F_\eta = (P^2/M) - gk_B T$ . Finally, using the above result, the equation of motions for the dynamical variables are given by

$$\begin{aligned} \frac{d}{dt} \chi &= \frac{i}{\hbar} (H \hat{\chi} - \hat{\chi} H) - \frac{1}{2} \left( \frac{\partial \hat{\chi}}{\partial P} \frac{\partial \Phi}{\partial R} + \frac{\partial \Phi}{\partial R} \frac{\partial \hat{\chi}}{\partial P} \right) + \frac{P}{M} \frac{\partial \hat{\chi}}{\partial R} + \frac{p_\eta}{m_\eta} \frac{\partial \hat{\chi}}{\partial \eta} \\ &\quad - \frac{p_\eta}{m_\eta} P \frac{\partial \hat{\chi}}{\partial P} + F_\eta \frac{\partial \hat{\chi}}{\partial p_\eta}. \end{aligned} \quad (30)$$

#### Representation in the adiabatic basis

One can express the quantum-classical equations of motion in the adiabatic states. Nosé quantum-classical Hamiltonian can be rewritten as

$$\hat{H}_N = \hat{h}(R) + \frac{P^2}{2M} + \frac{p_\eta^2}{2m_\eta} + gk_B T \eta, \quad (31)$$

where it has been introduced the operator  $\hat{h}(R) = \hat{K} + \hat{\Phi}(\hat{\chi}, R)$ . Then the adiabatic states are defined by

$$\hat{h}(R) |\alpha; R\rangle = E_\alpha(R) |\alpha; R\rangle. \quad (32)$$

In the adiabatic states, Eq. (30) is easily found to be

$$\begin{aligned} \frac{d}{dt} \chi^{\alpha\alpha'} &= i \omega_{\alpha\alpha'} \chi^{\alpha\alpha'} + \frac{P}{M} \frac{\partial \chi^{\alpha\alpha'}}{\partial R} + \left( -P \frac{p_\eta}{m_\eta} \frac{\partial}{\partial P} + \frac{p_\eta}{m_\eta} \frac{\partial}{\partial \eta} \right. \\ &\quad \left. + F_\eta \frac{\partial}{\partial p_\eta} \right) \chi^{\alpha\alpha'} + \frac{P}{M} d_{\alpha\beta} \chi^{\beta\alpha'} - \frac{P}{M} \chi^{\alpha\beta'} d_{\beta'\alpha'} \\ &\quad + \frac{1}{2} \frac{\partial \chi^{\alpha\beta'}}{\partial P} F^{\beta'\alpha'} + \frac{1}{2} F^{\alpha\beta} \frac{\partial \chi^{\beta\alpha'}}{\partial P}, \end{aligned} \quad (33)$$

where  $F^{\alpha\beta} = -\langle \alpha | [(\partial \Phi) / (\partial R)] | \beta \rangle$  and  $d_{\alpha\beta} = \langle \alpha | [\partial / (\partial R)] | \beta \rangle$  is the nonadiabatic coupling vector. Equation (33) can be rewritten introducing the Liouville operator  $i \mathcal{L}^N$  such that

$$\frac{d}{dt} \chi^{\alpha\alpha'} = \sum_{\beta\beta'} i \mathcal{L}_{\alpha\alpha', \beta\beta'}^N \chi^{\beta\beta'}. \quad (34)$$

The operator is

$$\begin{aligned}
i\mathcal{L}_{\alpha\alpha',\beta\beta'}^N &= i\omega_{\alpha\alpha'}\delta_{\alpha\beta}\delta_{\alpha'\beta'} + \delta_{\alpha\beta}\delta_{\alpha'\beta'}\frac{P}{M}\frac{\partial}{\partial R} \\
&+ \delta_{\alpha\beta}\delta_{\alpha'\beta'}\left(-P\frac{p_\eta}{m_\eta}\frac{\partial}{\partial P} + \frac{p_\eta}{m_\eta}\frac{\partial}{\partial \eta} + F_\eta\frac{\partial}{\partial p_\eta}\right) \\
&+ \frac{1}{2}\delta_{\alpha\beta}F^{\beta'\alpha'}\frac{\partial}{\partial P} + \frac{1}{2}\delta_{\alpha'\beta'}F^{\alpha\beta}\frac{\partial}{\partial P} \\
&+ \frac{P}{M}d_{\alpha\beta}\delta_{\alpha'\beta'} - \frac{P}{M}d_{\beta'\alpha'}\delta_{\alpha\beta}. \quad (35)
\end{aligned}$$

The quantum-classical Liouville operator can be put into a form that makes its structure more apparent by adding and subtracting the term

$$\delta_{\alpha\beta}\delta_{\alpha'\beta'}\frac{1}{2}(F^\alpha + F^{\beta'})\frac{\partial}{\partial P}. \quad (36)$$

Then using

$$F^{\alpha\beta} = F^\alpha + (E_\alpha - E_\beta)d_{\alpha\beta} \quad (37)$$

and rearranging the terms, one obtains a classical-like Nosé-Liouville operator

$$i\hat{\mathcal{L}}_{\alpha\alpha'}^N = \frac{P}{M}\frac{\partial}{\partial R} - P\frac{p_\eta}{m_\eta}\frac{\partial}{\partial P} + \frac{p_\eta}{m_\eta}\frac{\partial}{\partial \eta} + F_\eta\frac{\partial}{\partial p_\eta} + \frac{1}{2}(F^\alpha + F^{\alpha'})\frac{\partial}{\partial P} \quad (38)$$

and a jump operator

$$\begin{aligned}
-J_{\alpha\alpha',\beta\beta'} &= \delta_{\alpha'\beta'}d_{\alpha\beta}\left[\frac{P}{M} + (E_\alpha - E_\beta)\frac{\partial}{\partial P}\right] \\
&+ \delta_{\alpha\beta}d_{\alpha'\beta'}^*\left[\frac{P}{M} + (E_{\alpha'} - E_{\beta'})\frac{\partial}{\partial P}\right] \quad (39)
\end{aligned}$$

in terms of which the quantum-classical Liouville operator is finally written as

$$i\mathcal{L}_{\alpha\alpha',\beta\beta'}^N = i\omega_{\alpha\alpha'}\delta_{\alpha\beta}\delta_{\alpha'\beta'} + \delta_{\alpha\beta}\delta_{\alpha'\beta'}i\hat{\mathcal{L}}_{\alpha\alpha'}^N - J_{\alpha\alpha',\beta\beta'}. \quad (40)$$

The jump operator  $J_{\alpha\alpha',\beta\beta'}$  is responsible for transitions between adiabatic states while the classical-like Nosé-Liouville operator  $i\hat{\mathcal{L}}_{\alpha\alpha',\beta\beta'}^N$  expresses Nosé dynamics on a constant generalized energy surface with Hellman-Feynman forces given by  $1/2(F^\alpha + F^{\alpha'})$ .

This shows that the matrix form of the non-Hamiltonian commutator is suitable for the development of generalized non-Hamiltonian dynamics for classical degrees of freedom in quantum-classical systems.

## V. STATIONARY NOSÉ DENSITY MATRIX

The average of any operator  $\hat{\chi}$  can be calculated from

$$\langle \hat{\chi} \rangle = \text{Tr}' \int dX \hat{\rho}_N \hat{\chi}(t) = \text{Tr}' \int dX \hat{\rho}_N \exp(i\mathcal{L}^N t) \hat{\chi}. \quad (41)$$

The action of  $\exp(i\mathcal{L}^N t)$  can be transferred from  $\hat{\chi}$  to  $\hat{\rho}_N$  by using the cyclic invariance of the trace and integrating by

parts the terms coming from the classical brackets. One can write

$$i\mathcal{L}^N = \frac{i}{\hbar}[\hat{H}_N, \dots] - \frac{1}{2}(\{\hat{H}_N, \dots\} - \{\dots, \hat{H}_N\}). \quad (42)$$

In this equation the classical bracket terms are written

$$\{\hat{H}_N, \dots\} - \{\dots, \hat{H}_N\} = \sum_{i,j=1}^{2N} \left( \frac{\partial \hat{H}_N}{\partial X_i} \mathcal{B}_{ij}^N \frac{\partial \dots}{\partial X_j} - \frac{\partial \dots}{\partial X_i} \mathcal{B}_{ij}^N \frac{\partial \hat{H}_N}{\partial X_j} \right). \quad (43)$$

When integrating the right-hand side by parts, one obtains a term proportional to the compressibility  $\kappa_N = \sum_{i,j=1}^{2N} [(\partial \mathcal{B}_{ij}^N) / (\partial X_i) (\partial \hat{H}_N) / (\partial X_j)]$ . As a result, the mixed quantum-classical Liouville operator, in this case, is not Hermitian,

$$(i\mathcal{L}^N)^\dagger = -i\mathcal{L}^N - \kappa_N. \quad (44)$$

The average value can then be written as

$$\langle \hat{\chi} \rangle = \text{Tr}' \int dX \hat{\chi} \exp[-(i\mathcal{L}^N + \kappa_N)t] \hat{\rho}_N. \quad (45)$$

The mixed quantum-classical Nosé density matrix evolves under the equation

$$\frac{\partial}{\partial t} \hat{\rho}_N = -\frac{i}{\hbar}[\hat{H}^N, \hat{\rho}_N] + \frac{1}{2}(\{\hat{H}^N, \hat{\rho}_N\} - \{\hat{\rho}_N, \hat{H}^N\}) - \kappa_N \hat{\rho}_N. \quad (46)$$

The stationary density matrix  $\hat{\rho}_{Ne}$  is defined by

$$(i\mathcal{L}^N + \kappa_N)\hat{\rho}_{Ne} = 0. \quad (47)$$

To find the explicit expression, one can follow Ref. [25], expand the density matrix in powers of  $\hbar$

$$\hat{\rho}_{Ne} = \sum_{n=0}^{\infty} \hbar^n \hat{\rho}_{Ne}^{(n)}, \quad (48)$$

and look for an explicit solution in the adiabatic basis. In such a basis the Nosé-Liouville operator is expressed by Eq. (40) and the Nosé Hamiltonian is given by

$$\begin{aligned}
H_N^\alpha &= \frac{P^2}{2M} + \frac{p_\eta^2}{2m_\eta} + gk_B T \eta + E_\alpha(R) \\
&= H_\alpha^P(R, P) + \frac{p_\eta^2}{2m_\eta} + gk_B T \eta. \quad (49)
\end{aligned}$$

Thus one obtains an infinite set of equations corresponding to the various power of  $\hbar$

$$iE_{\alpha\alpha'}\rho_{Ne}^{(0)\alpha\alpha'} = 0, \quad (50)$$

$$\begin{aligned}
iE_{\alpha\alpha'}\rho_{Ne}^{(n+1)\alpha\alpha'} &= -(i\mathcal{L}_{\alpha\alpha'}^N + \kappa_N)\rho_{Ne}^{(n)\alpha\alpha'} \\
&+ \sum_{\beta\beta'} J_{\alpha\alpha',\beta\beta'}\rho_{Ne}^{(n)\beta\beta'} \quad (n \geq 1). \quad (51)
\end{aligned}$$

As shown in Ref. [25], in order to ensure that a solution can

be found by recursion, one must discuss the solution of Eq. (51) when calculating the diagonal elements  $\rho_{N_e}^{(n)\alpha\alpha'}$  in terms of the off-diagonal ones  $\rho_{N_e}^{(n)\alpha\alpha'}$ . To this end, using  $\rho_{N_e}^{(n)\alpha\alpha'} = (\rho_{N_e}^{(n)\alpha'\alpha})^*$ ,  $J_{\alpha\alpha,\beta\beta'} = J_{\alpha\alpha',\beta\beta'}^*$  and the fact that  $J_{\alpha\alpha,\beta\beta} = 0$  when a real basis is chosen, it is useful to rewrite Eq. (51) in the form

$$(iL_{\alpha\alpha}^N + \kappa_N)\rho_{N_e}^{(n)\alpha\alpha} = \sum_{\beta > \beta'} 2\mathcal{R}(J_{\alpha\alpha,\beta\beta'}\rho_{N_e}^{(n)\beta\beta'}). \quad (52)$$

One has [9]  $(-iL_{\alpha\alpha}^N - \kappa_N)^\dagger = iL_{\alpha\alpha}^N$ . The right-hand side of this equation is expressed by means of the generalized bracket in Eq. (26):  $H_N^\alpha$  and any general function  $f(H_N^\alpha)$  are constants of motion under the action of  $iL_{\alpha\alpha}^N$ . The phase space compressibility  $\kappa_N$  associated with the generalized bracket in the case of Nosé dynamics is

$$\kappa_N^\alpha = -\beta \frac{d}{dt} \left( \frac{P^2}{2M} + \frac{p_\eta^2}{2m_\eta} + E_\alpha(R) \right) = -\beta N \frac{p_\eta}{m_\eta} = -\beta N \frac{d}{dt} H_T^\alpha, \quad (53)$$

where  $N$  is the number of classical momenta  $P$  in the Hamiltonian. Because of the presence of a nonzero phase space compressibility, integrals over phase space must be taken using the invariant measure [26]

$$d\mathcal{M} = \exp(-w_N^\alpha) dR dP d\eta dp_\eta, \quad (54)$$

where  $w_N^\alpha = \int dt \kappa_N^\alpha$  is the indefinite integral of the compressibility. To ensure that a solution to Eq. (52) exists, one must invoke the theorem of Fredholm alternative, requiring that the right-hand side of Eq. (52) be orthogonal to the null space of  $(iL_{\alpha\alpha}^N)^\dagger$  [27]. The null space of this operator consists of functions of the form [10]  $f(H_N^\alpha)$ , where  $f(H_N^\alpha)$  can be any function of the adiabatic Hamiltonian  $H_N^\alpha$ . Thus the condition to be satisfied is

$$\int d\mathcal{M} \sum_{\beta > \beta'} 2\mathcal{R}(J_{\alpha\alpha,\beta\beta'}\rho_{N_e}^{(n)\beta\beta'}) f(H_N^\alpha) = 0. \quad (55)$$

Apart from the integration on the additional Nosé phase space variable, there is no major difference with the proof given in Ref. [25]:  $2\mathcal{R}(J_{\alpha\alpha,\beta\beta'}\rho_{N_e}^{(n)\beta\beta'})$  and  $f(H_N^\alpha)$  are respectively an odd and an even function of  $P$ ; this guarantees the validity of Eq. (55).

Thus one can write the formal solution of Eq. (52) as

$$\rho_{N_e}^{(n)\alpha\alpha} = (iL_{\alpha\alpha}^N + \kappa_N)^{-1} \sum_{\beta > \beta'} 2\mathcal{R}(J_{\alpha\alpha,\beta\beta'}\rho_{N_e}^{(n)\beta\beta'}), \quad (56)$$

and the formal solution of Eq. (51) for  $\alpha \neq \alpha'$  as

$$\rho_{N_e}^{(n+1)\alpha\alpha'} = \frac{i}{E_{\alpha\alpha'}} (iL_{\alpha\alpha'}^N + \kappa_N)\rho_{N_e}^{(n)\alpha\alpha'} - \frac{i}{E_{\alpha\alpha'}\beta\beta'} \sum_{\beta\beta'} J_{\alpha\alpha',\beta\beta'}\rho_{N_e}^{(n)\beta\beta'}. \quad (57)$$

Equations (56) and (57) allow one to calculate  $\rho_{N_e}^{\alpha\alpha'}$  to all orders in  $\hbar$  once  $\rho_{N_e}^{(0)\alpha\alpha'}$  is given. This order zero term is obtained by the solution of  $(iL_{\alpha\alpha}^N + \kappa_N)\rho_{N_e}^{(0)\alpha\alpha} = 0$ . All higher order terms are obtained by the action of  $E_{\alpha\alpha'}$ , the imaginary

unit  $i$  and  $J_{\alpha\alpha',\beta\beta'}$  (involving factors of  $d_{\alpha\alpha'}$ ,  $P$  and derivatives with respect to  $P$ ). Hence, one can conclude that functional dependence of  $\rho_{N_e}^{(0)\alpha\alpha}$  on the Nosé variables  $\eta$  and  $p_\eta$  is preserved in higher order terms  $\rho_{N_e}^{(n)\alpha\alpha'}$ .

One can find a stationary solution to order  $\hbar$  by considering the first two equations of the set given by Eqs. (50) and (51),

$$[\hat{H}_N, \hat{\rho}_{N_e}^{(0)}] = 0 \quad (n=0), \quad (58)$$

$$i[\hat{H}_N, \hat{\rho}_{N_e}^{(1)}] = -\frac{1}{2}(\hat{H}_N \Lambda_N \hat{\rho}_{N_e}^{(0)} - \hat{\rho}_{N_e}^{(0)} \Lambda_N \hat{H}_N) \quad (n=1). \quad (59)$$

For the  $\mathcal{O}(\hbar^0)$  term one can make the ansatz

$$\hat{\rho}_{N_e}^{(0)\alpha\beta} = \frac{1}{Z} e^{w_N^\alpha} \delta(\mathcal{C} - H_N^\alpha) \delta_{\alpha\beta}, \quad (60)$$

where  $Z$  is

$$Z = \sum_\alpha \int d\mathcal{M} \delta(\mathcal{C} - H_N^\alpha), \quad (61)$$

and obtain

$$\hat{\rho}_{N_e}^{(1)\alpha\beta} = -i \frac{P}{M} d_{\alpha\beta} \hat{\rho}_{N_e}^{(0)\beta} \left[ \frac{1 - e^{-\beta(E_\alpha - E_\beta)}}{E_\beta - E_\alpha} + \frac{\beta}{2} (1 + e^{-\beta(E_\alpha - E_\beta)}) \right] \quad (62)$$

for the  $\mathcal{O}(\hbar)$  term.

Equations (60) and (62) give the explicit form of the stationary solution of the Nosé-Liouville equation up to order  $\mathcal{O}(\hbar)$ . One can now prove that, when calculating averages of quantum-classical operators depending only on physical phase space variables,  $\mathcal{G}_\alpha(R, P)$ , the canonical form of the stationary density is obtained. It can be noted that it will suffice to prove this result for the  $\mathcal{O}(\hbar^0)$  term since, as discussed before, the differences with the standard case are contained therein.

Indeed, when calculating

$$\langle \mathcal{G}_\alpha(R, P) \rangle \propto \sum_\alpha \int d\mathcal{M} \mathcal{G}_\alpha(R, P) \delta(\mathcal{C} - H_T^\alpha - g k_B T \eta). \quad (63)$$

Considering the delta function integral over Nosé variables, one has

$$\int dp_\eta d\eta e^{-N\eta} \delta(\mathcal{C} - H_T^\alpha - g k_B T \eta) = \text{const} \times \exp[-\beta(N/g)H_\alpha^T(R, P)], \quad (64)$$

and where it has been used, the property  $\delta[f(s)] = [df/ds]_{s=s_0}^{-1} \delta(s-s_0)$  [ $s_0$  is the zero of  $f(s)$ ]. Thus, at variance with what found in Ref. [16], in order to recover the canonical distribution in the quantum-classical case, one must set  $g=N$  as it is done in the classical case [6,7]. If the dynamics is ergodic and if one could integrate quantum-classical equations of motion for sufficiently long time, the phase space integral could be substituted by a time integral along the

trajectory [28]. Ergodicity could be enforced by modern advanced sampling techniques [29] but longtime stable integration of quantum-classical dynamics is still a challenge.

## VI. CONCLUSIONS AND PERSPECTIVES

In this paper a generalized non-Hamiltonian form of quantum mechanics has been presented. This has been achieved through the introduction of a suitable non-Hamiltonian commutator which has been obtained by generalizing the symplectic structure of the standard quantum mechanical commutator. Therefore, it has been demonstrated that a single idea (i.e., generalizing the symplectic structure of the bracket while retaining its antisymmetric form) is able to describe in a unified way non-Hamiltonian theories both in classical and quantum mechanics. The non-Hamiltonian form of quantum mechanics here presented provides a general mathematical structure which encompasses the ideas proposed by Weinberg to introduce nonlinear effects in quantum mechanics and whose physical content remains yet to be unveiled.

For the sake of illustrating the possible use of non-Hamiltonian commutators, it has been shown that they subsume the quantum-classical bracket proposed by other authors. Moreover, their matrix structure has been used to define Nosé dynamics on the classical degrees of freedom in quantum-classical systems. It has been also shown that the non-Hamiltonian quantum-classical bracket can be easily generalized to treat other thermodynamic constraints such as those provided by barostats or Nosé-Hoover chains (NHC). The respective stationary density matrices are easily derived. The implementation of thermodynamic constraints for the classical degrees of freedom in quantum-classical systems could be considered both as a practical and a conceptual improvement. For example, thermostatted dynamics can be useful for preparing systems into desired initial conditions or for ensuring a good thermalization of the classical bath degrees of freedom providing a way to control the nonadiabatic character of the dynamics. On the conceptual side one could note that, historically, deterministic dynamics with thermodynamic constraints for purely classical systems has provided well-defined algorithms to treat open systems both in and out of equilibrium. Thus, the possibility to use the same tool in the case of quantum-classical systems could disclose alternative routes to the numerical study of open quantum systems.

In conclusion, the non-Hamiltonian quantum formalism introduced in this paper sets a unified framework with the non-Hamiltonian classical algebra and, at the same time, discloses various routes for investigating generalized quantum and quantum-classical systems. Such studies will be performed in the future.

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## APPENDIX: NHC AND NPT

The calculations of the previous sections show that the introduction of extended system dynamics on the classical

part of the system amounts to modify the operator of Eq. (18) by simply substituting the classical bracket operator given in Eq. (16) with the one suited to express the desired extended system dynamics [9,10].

Thus, in order to couple a Nosé-Hoover chain [15] to the classical coordinates, the classical phase space point is defined as

$$X = (R, \eta_1, \eta_2, P, p_{\eta_1}, p_{\eta_2}), \quad (\text{A1})$$

where for simplicity one is considering a chain of just two thermostat coordinates  $\eta_1, \eta_2$  and momenta  $p_{\eta_1}, p_{\eta_2}$ . Also,

$$\hat{H}^{\text{NHC}} = \frac{\hat{p}^2}{2m} + \frac{P^2}{2M} + \frac{p_{\eta_1}^2}{2m_{\eta_1}} + \frac{p_{\eta_2}^2}{2m_{\eta_2}} + \hat{\Phi}(\hat{q}, R) + gk_B T \eta_1 + gk_B T \eta_2, \quad (\text{A2})$$

where  $m_{\eta_1}$  and  $m_{\eta_2}$  are the inertial parameters of the thermostat variables. As shown in Refs. [9,10], one can define an antisymmetric matrix

$$\mathcal{B}^{\text{NHC}} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & -P & 0 \\ 0 & -1 & 0 & P & 0 & -p_{\eta_1} \\ 0 & 0 & -1 & 0 & p_{\eta_1} & 0 \end{bmatrix}. \quad (\text{A3})$$

The matrix  $\mathcal{B}^{\text{NHC}}$  determines the operator  $\Lambda^{\text{NHC}}$  which in turn provides the non-Hamiltonian bracket according to Eq. (16). The Nosé-Hoover chain classical equations of motion in phase space [9] are then given by

$$\dot{X} = -X \Lambda^{\text{NHC}} \hat{H}^{\text{NHC}}. \quad (\text{A4})$$

Quantum-classical dynamics is then introduced using the matrix superoperator

$$\mathcal{D}^{\text{NHC}} = \begin{bmatrix} 0 & 1 + \frac{\hbar}{2i} \Lambda^{\text{NHC}} \\ -\left(1 + \frac{\hbar}{2i} \Lambda^{\text{NHC}}\right) & 0 \end{bmatrix}. \quad (\text{A5})$$

As previously shown by means of the latter, the quantum-classical equations of motion are then given by

$$\frac{d\hat{\chi}}{dt} = \frac{i}{\hbar} [\hat{H}^{\text{NHC}} \hat{\chi}] \cdot \mathcal{D}^{\text{NHC}} \cdot \begin{bmatrix} \hat{H}^{\text{NHC}} \\ \hat{\chi} \end{bmatrix}. \quad (\text{A6})$$

The equations of motion can be represented using the adiabatic basis obtaining the Liouville superoperator

$$i\mathcal{L}_{\alpha\alpha',\beta\beta'}^{\text{NHC}} = (i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'}^{\text{NHC}}) \delta_{\alpha\beta} \delta_{\alpha'\beta'} - J_{\alpha\alpha',\beta\beta'}, \quad (\text{A7})$$

where

$$iL_{\alpha\alpha'}^{\text{NHC}} = \frac{P}{M} \frac{\partial}{\partial R} + \frac{1}{2} (F^\alpha + F^{\alpha'}) \frac{\partial}{\partial P} + \sum_{k=1}^2 \left( \frac{p_{\eta_k}}{m_{\eta_k}} \frac{\partial}{\partial \eta_k} + F_{\eta_k} \frac{\partial}{\partial p_{\eta_k}} \right) - \frac{p_{\eta_2}}{m_{\eta_2}} p_{\eta_1} \frac{\partial}{\partial p_{\eta_1}}, \quad (\text{A8})$$

with  $F_{\eta_2} = p_{\eta_1}^2 / m_{\eta_1} - g k_B T$ . The proof of the existence of a stationary density matrix in the case of Nosé-Hoover chains follows the same logic of the simple Nosé-Hoover case. In the adiabatic basis the density matrix stationary up to order bar has the same form as given in Eqs. (60) and (62). One has just to replace Eq. (60) for the order zero term with

$$\rho_{\text{NHC}e}^{(0)\alpha\beta} = \frac{1}{Z} \exp \left\{ -\beta \left[ \frac{P^2}{2M} + E_\alpha(R) + \sum_{k=1}^2 \left( \frac{p_{\eta_k}^2}{2m_{\eta_k}} + g k_B T \eta_k \right) \right] \right\} \quad (\text{A9})$$

with obvious definition of  $Z$ .

For the case of constant pressure and temperature dynamics, the equations of motion treated in Ref. [30] are here considered. This time, the extended phase space point is

$$X = (R, \eta, V, P, p_\eta, p_V), \quad (\text{A10})$$

and the Hamiltonian quantum-classical operator is

$$\hat{H}^{\text{NPT}} = \frac{\hat{p}^2}{2m} + \frac{P^2}{2M} + \frac{p_\eta^2}{2m_{\eta_1}} + \frac{p_V^2}{2m_V} + \hat{\Phi}(\hat{q}, R) + g k_B T \eta + P_{\text{ext}} V. \quad (\text{A11})$$

The equations of motion for the classical coordinates are [9]

$$\dot{R} = \frac{P}{m_i} + R \frac{p_V}{3V m_V}, \quad (\text{A12})$$

$$\dot{p}_\eta = \frac{p_\eta}{m_\eta}, \quad (\text{A13})$$

$$\dot{V} = \frac{p_V}{m_V}, \quad (\text{A14})$$

$$\dot{P} = -\frac{\partial \Phi}{\partial R} - P \frac{p_V}{3V m_V} - P \frac{p_\eta}{m_\eta}, \quad (\text{A15})$$

$$\dot{p}_\eta = \sum_{i=1}^N \frac{P^2}{m_i} + \frac{p_V^2}{m_V} - g k_B T, \quad (\text{A16})$$

$$\dot{p}_V = F_V - p_V \frac{p_\eta}{m_\eta}, \quad (\text{A17})$$

with

$$F_V = \frac{1}{3V} \left[ \sum_{i=1}^N \frac{P^2}{M} - \frac{\partial \Phi}{\partial R} \cdot R \right] - P_{\text{ext}}. \quad (\text{A18})$$

The antisymmetric matrix to define the operator  $\Lambda^{\text{NPT}}$  in Eq. (16) is then

$$\mathcal{B}^{\text{NPT}} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & \frac{R}{3V} \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & -P & -\frac{P}{3V} \\ 0 & -1 & 0 & P & 0 & p_V \\ -\frac{R}{3V} & 0 & -1 & \frac{P}{3V} & -p_V & 0 \end{bmatrix}. \quad (\text{A19})$$

The matrix  $\mathcal{B}^{\text{NPT}}$  is the same as that given in Ref. [9] but this time the order of coordinates and momenta in the classical extended phase space point definition of Eq. (A10) ensures that  $\Lambda^{\text{NPT}}$  in Eq. (16) makes the equations of motion

$$\dot{X} = -X \Lambda^{\text{NPT}} \hat{H}^{\text{NPT}} \quad (\text{A20})$$

exactly equivalent to Eqs. (A12)–(A17). Then one can define the matrix operator  $\mathcal{D}^{\text{NPT}}$  and write down the quantum-classical equations of motion. In the adiabatic basis, the equations are written by means of the Liouville operator

$$i\mathcal{L}_{\alpha\alpha', \beta\beta'}^{\text{NPT}} = (i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'}^{\text{NPT}}) \delta_{\alpha\beta} \delta_{\alpha'\beta'} - J_{\alpha\alpha', \beta\beta'}, \quad (\text{A21})$$

with

$$iL_{\alpha\alpha'}^{\text{NPT}} = iL_{\alpha\alpha'}^{\text{NH}} + \frac{P_V}{3V m_V} R \frac{\partial}{\partial R} - \frac{P_V}{3V m_V} P \frac{\partial}{\partial P} + \frac{P_V}{m_V} \frac{\partial}{\partial V} + \left( F_V - \frac{p_\eta}{m_\eta} \right) \frac{\partial}{\partial P_V}. \quad (\text{A22})$$

The stationary density matrix is derived as usual and, in the adiabatic basis, is expressed again in the form given by Eqs. (60) and (62) with the  $\mathcal{O}(\hbar^0)$  term given by

$$\rho_{\text{NPT}e}^{(0)\alpha\beta} = \frac{1}{Z} \exp \left( -\beta \left[ \frac{P^2}{2M} + E_\alpha(R) + \frac{p_\eta^2}{2m_\eta} + g k_B T \eta + \frac{P_V^2}{2m_V} + P_{\text{ext}} V \right] \right). \quad (\text{A23})$$



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