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2008 J. Phys. A: Math. Theor. 41 355304

(http://iopscience.iop.org/1751-8121/41/35/355304)

IOP PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND THEORETICAL

J. Phys. A: Math. Theor. **41** (2008) 355304 (14pp) doi:10.1088/1751-8113/41/35/355304

Nosè–Hoover dynamics in quantum phase space

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Received 18 March 2008, in final form 3 July 2008
Published 28 July 2008
Online at stacks.iop.org/JPhysA/41/355304

Abstract
Thermal fluctuations in time-dependent quantum processes are treated by a constant-temperature generalization of Wigner's formulation of quantum mechanics in phase space. To this end, quantum Nosè–Hoover dynamics is defined by generalizing the Moyal bracket. Computational applications of the formalism, together with further theoretical developments, are discussed.

PACS numbers: 03.65.−w, 05.30.−d, 02.70.−c

1. Introduction

In recent years it has become clear that the field of open quantum systems [1] and quantum information [2] are intertwined: advancement in the theoretical and numerical techniques to study open systems might as well lead to novel schemes to manipulate quantum information. Typically, the growing field of cold quantum gases [3] and optical lattices [4], which is deeply related to the field of quantum information, calls for novel simulation methods [5].

In this paper, we generalize the Moyal bracket within the Wigner's formulation of quantum mechanics in phase space. We show how such a generalized bracket can be used to introduce the control of temperature in quantum dynamics in phase space. This is realized by re-formulating into quantum phase space the well-known dynamics of Nosè–Hoover, which is widely used in the field of classical molecular dynamics simulations, by means of a Nosè–Moyal bracket. We also illustrate by means of a numerical calculation on a model system how the Nosè–Moyal bracket can be used to study dissipation effects in quantum dynamics, so that one effectively addresses open systems by means of a deterministic evolution. The work presented here is related to previous formulations of thermostatted dynamics both in the Schrödinger picture [6] and in the coherent state formulation of quantum dynamics [7].

This paper is organized as follows. In section 2 we briefly sketch Wigner's formulation of quantum mechanics in a form suitable to further generalizations. In section 3 we generalized the Moyal bracket and, by means of it, introduce non-unitary evolution for the Wigner

function. In section 4 we introduce Nosè equations of motion in quantum phase space so as to define a Nosè–Wigner dynamics. For computational purposes, we take a quantum-classical approximation of the Nosè–Wigner dynamics in section 5 and show how to construct a stationary Wigner function in terms of even powers of $\hbar$. Details of the derivation are given in the appendix. In section 6 we apply the Nosè–Wigner dynamics to simulate the deterministic cooling of a system of phonons, which might represent the fluctuation of a boson gas. Our conclusion and comments are given in section 7.

2. Wigner's quantum statistical mechanics

Quantum statistical averages of generic observables $\hat{\chi}$ can be calculated my means of the density matrix operator $\hat{\rho}$ as

$$\langle\hat{\chi}\rangle(t) = \mathrm{Tr}\{\hat{\chi}\hat{\rho}(t)\}. \tag{1}$$

Time-dependent effects are addressed by solving the equation of motion for the density matrix [8]

$$\frac{\partial\hat{\rho}}{\partial t} = -\frac{\mathrm{i}}{\hbar}[\hat{H}, \hat{\rho}], \tag{2}$$

where $\hat{H} = \hat{p}^2/(2m) + \hat{V}(\hat{r})$ is the Hamiltonian operator of the system, $\hat{r}$ and $\hat{p}$ are the position and momentum operators respectively, and m is the particle mass.

Quantum mechanics can be represented in phase space by means of the Wigner function $f_W(r, p)$ [9, 10], which is defined as

$$f_W(r, p) = \frac{1}{(2\pi\hbar)^N}\int \mathrm{d}^N\xi \exp\left[\frac{\mathrm{i}}{\hbar}p\cdot\xi\right]\left\langle r - \frac{\xi}{2}|\hat{\rho}|r + \frac{\xi}{2}\right\rangle \tag{3}$$

$$= \frac{1}{(2\pi\hbar)^N}\mathcal{W}[\hat{\rho}], \tag{4}$$

where N is the number of particles in the system, and we have adopted a compact notation for the coordinates so that, for example, $\xi \equiv (\xi_1, \xi_2, \ldots, \xi_N)$. The right-hand-side of equation (4) defines the operator $\mathcal{W}$ which realizes the Wigner transform. In terms of the latter the Wigner transform of the generic observable $\hat{\chi}$ is defined as

$$\chi_W(r, p) = \mathcal{W}[\hat{\chi}]. \tag{5}$$

Therefore, quantum averages (1) are expressed in quantum (Wigner) phase space as

$$\mathrm{Tr}\{\hat{\rho}(t)\hat{\chi}\} \equiv \int d^N r d^N p f_W(r, p; t)\chi(r, p). \tag{6}$$

In order to define the time evolution of the Wigner function, one has to consider the Wigner transform of the commutator appearing in equation (2). To this end, consider two generic operators $\hat{\chi}^1$ and $\hat{\chi}^2$, together with their corresponding Wigner transforms $\mathcal{W}[\hat{\chi}^1] = \chi_W^1(r, p)$ and $\mathcal{W}[\hat{\chi}^2] = \chi_W^2(r, p)$. The Wigner transform of the product $\hat{\chi}^1\cdot\hat{\chi}^2$ is known to be [11]

$$\mathcal{W}\{\hat{\chi}^1\cdot\hat{\chi}^2\} \equiv \chi_W^1(r, p)\,\mathrm{e}^{(\hbar/2i)\Lambda}\chi_W^2(r, p), \tag{7}$$

where Λ is an operator acting as the negative of the Poisson bracket; e.g., for two arbitrary phase space functions, a and b, it is defined as

$$a(r, p)\Lambda b(r, p) = -\{a, b\} = -\frac{\partial a}{\partial r}\frac{\partial b}{\partial p} + \frac{\partial a}{\partial p}\frac{\partial b}{\partial r}, \tag{8}$$

where $\{a, b\}$ in the right-hand-side denotes the Poisson bracket.

Then, upon taking the Wigner transform of equation (2), one obtains the quantum phase space equation of motion

$$\frac{\partial}{\partial t} f_W(r, p, t) = -\frac{\mathrm{i}}{\hbar}(H_W \, \mathrm{e}^{(\hbar/2\mathrm{i})\Lambda} f_W(t) - f_W(t) \, \mathrm{e}^{(\hbar/2\mathrm{i})\Lambda} H_W)$$
$$= -\frac{\mathrm{i}}{\hbar} \{H_W, f_W(t)\}_{\mathrm{M}}, \tag{9}$$

where the right-hand-side defines the Moyal bracket [12]. The formal solution of equation (9) can be compactly written as

$$f_W(r, p, t) = \exp\left[-\frac{\mathrm{i}t}{\hbar} \{H_W, \ldots\}_{\mathrm{M}}\right] f_W(r, p, 0). \tag{10}$$

The right-hand-side of equation (10) defines the quantum propagator in phase space $\exp[(\mathrm{i}t/\hbar)\{H_W, \ldots\}_{\mathrm{M}}]$, which is defined in terms of its series expansion. Equivalently, time averages can be calculated by considering the Wigner function at the initial time and evolving Wigner transformed operators according to

$$\chi_W(r, p, t) = \exp\left[\frac{\mathrm{i}t}{\hbar} \{H_W, \ldots\}_{\mathrm{M}}\right] \chi_W(r, p, 0). \tag{11}$$

From the above equation one sees that the time evolution is unitary.

3. Generalized Moyal bracket

It has been noted some time ago [13] that the Moyal bracket defines a non-canonical dynamics in quantum phase space. Here we want to show how the mathematical structure underlying such a bracket is more general. To this end, let us introduce the canonical antisymmetric matrix in block form

$$\boldsymbol{\mathcal{B}}^c = \begin{bmatrix} \mathbf{0} & \mathbf{1} \\ -\mathbf{1} & \mathbf{0} \end{bmatrix}. \tag{12}$$

It is well known that Poisson brackets in phase space can be written in terms of $\boldsymbol{\mathcal{B}}^c$; accordingly the Λ operator can be written as

$$\Lambda = -\sum_{i,j=1}^{2N} \frac{\overleftarrow{\partial}}{\partial x_i} \mathcal{B}^c_{ij} \frac{\overrightarrow{\partial}}{\partial x_j}, \tag{13}$$

where we have used a compact notation for the phase space point: $x = (r, p)$. The antisymmetric matrix $\boldsymbol{\mathcal{B}}^c$ can be used to re-write the Moyal bracket. However, in the present context, we want to consider the modification of the equations of motion in quantum phase space arising from the introduction of a general antisymmetric matrix [14, 17], $\mathcal{B}_{ij} = -\mathcal{B}_{ji}$, which is no longer restricted to the canonical form of equation (12). In terms of $\boldsymbol{\mathcal{B}}$ a generalized Moyal bracket can be introduced as

$$\left\{\chi^1_W, \chi^2_W\right\}_{\mathrm{M}} = \chi^1_W \, \mathrm{e}^{(\mathrm{i}\hbar/2)\overleftarrow{\partial_i}\mathcal{B}_{ij}\overrightarrow{\partial_j}} \chi^2_W - \chi^2_W \, \mathrm{e}^{\frac{\mathrm{i}\hbar}{2}\overleftarrow{\partial_i}\mathcal{B}_{ij}\overrightarrow{\partial_j}} \chi^1_W, \tag{14}$$

where the summation over repeated indices is understood.

Generalized equations of motion for Wigner transformed operators can now be written as

$$\partial_t \chi_W(x, t) = \frac{\mathrm{i}}{\hbar}\left[H_W \, \mathrm{e}^{\frac{\mathrm{i}\hbar}{2}\overleftarrow{\partial_i}\mathcal{B}_{ij}\overrightarrow{\partial_j}} \chi_W - \chi_W \, \mathrm{e}^{\frac{\mathrm{i}\hbar}{2}\overleftarrow{\partial_i}\mathcal{B}_{ij}\overrightarrow{\partial_j}} H_W\right]$$
$$= \frac{\mathrm{i}}{\hbar}\left[H_W \, \mathrm{e}^{\frac{\mathrm{i}\hbar}{2}\overleftarrow{\partial_i}\mathcal{B}_{ij}\overrightarrow{\partial_j}} - H_W \, \mathrm{e}^{-\frac{\mathrm{i}\hbar}{2}\overleftarrow{\partial_i}\mathcal{B}_{ij}\overrightarrow{\partial_j}}\right]\chi_W, \tag{15}$$

where we have used the antisymmetry of $\mathcal{B}$. We can now define the generalized Moyal propagator

$$\exp\left\{\frac{\mathrm{i}t}{\hbar}\mathcal{M}\right\} = \exp\left\{\frac{\mathrm{i}t}{\hbar}\left[H_W\,\mathrm{e}^{\frac{i\hbar}{2}\overleftarrow{\partial_i}\mathcal{B}_{ij}\overrightarrow{\partial_j}} - H_W\,\mathrm{e}^{-\frac{i\hbar}{2}\overleftarrow{\partial_i}\mathcal{B}_{ij}\overrightarrow{\partial_j}}\right]\right\}, \tag{16}$$

and write quantum averages in phase space as

$$\langle\chi_W(t)\rangle = \int \mathrm{d}x\; f_W(x,0)\,\mathrm{e}^{\frac{it}{\hbar}\overrightarrow{\mathcal{M}}}\chi_W(x,0) = \int \mathrm{d}x\; f_W(x,0)\chi_W(x,t). \tag{17}$$

In order to find the generalized equations of motion for the Wigner function we must obtain a scheme of motion in which the Wigner transformed operators are evaluated at the initial time while the Wigner function evolves in time. To show how this can be achieved, let us consider the integral

$$\begin{aligned}
\int \mathrm{d}x\; f_W\frac{\mathrm{d}\chi_W}{\mathrm{d}t} &\equiv \frac{\mathrm{i}}{\hbar}\int \mathrm{d}x\; f_W\left[H_W\,\mathrm{e}^{\frac{i\hbar}{2}\overleftarrow{\partial_i}\mathcal{B}_{ij}\overrightarrow{\partial_j}} - H_W\,\mathrm{e}^{-\frac{i\hbar}{2}\overleftarrow{\partial_i}\mathcal{B}_{ij}\overrightarrow{\partial_j}}\right]\chi_W \\
&= \frac{\mathrm{i}}{\hbar}\int \mathrm{d}x\; f_W\left[H_W\,\mathrm{e}^{-\frac{i\hbar}{2}\overleftarrow{\partial_i}\mathcal{B}_{ij}\overleftarrow{\partial_j}} - H_W\,\mathrm{e}^{\frac{i\hbar}{2}\overleftarrow{\partial_i}\mathcal{B}_{ij}\overleftarrow{\partial_j}}\right]\chi_W \\
&= \frac{\mathrm{i}}{\hbar}\int \mathrm{d}x\; f_W\left[\mathrm{e}^{-\frac{i\hbar}{2}(\overleftarrow{\partial_j}\mathcal{B}_{ij}\overrightarrow{\partial_i}+(\partial_j\mathcal{B}_{ij})\overrightarrow{\partial_i})}H_W - \mathrm{e}^{\frac{i\hbar}{2}(\overleftarrow{\partial_j}\mathcal{B}_{ij}\overrightarrow{\partial_i}+(\partial_j\mathcal{B}_{ij})\overrightarrow{\partial_i})}H_W\right]\chi_W \\
&= -\frac{\mathrm{i}}{\hbar}\int \mathrm{d}x\; f_W\left[\mathrm{e}^{\frac{i\hbar}{2}(\overleftarrow{\partial_j}\mathcal{B}_{ij}\overrightarrow{\partial_i}+(\partial_j\mathcal{B}_{ij})\overrightarrow{\partial_i})}H_W - \mathrm{e}^{-\frac{i\hbar}{2}(\overleftarrow{\partial_j}\mathcal{B}_{ij}\overrightarrow{\partial_i}+(\partial_j\mathcal{B}_{ij})\overrightarrow{\partial_i})}H_W\right]\chi_W.
\end{aligned} \tag{18}$$

Note that in the above formula, ∂_i acts only on H_W (not on χ_W) and ∂_j acts on f_W. This defines an operator

$$\overrightarrow{\mathcal{M}}^\dagger = H_W\,\mathrm{e}^{\frac{i\hbar}{2}(\overleftarrow{\partial_i}\mathcal{B}_{ij}\overrightarrow{\partial_j}+\overleftarrow{\partial_i}(\partial_j\mathcal{B}_{ij}))} - H_W\,\mathrm{e}^{-\frac{i\hbar}{2}(\overleftarrow{\partial_i}\mathcal{B}_{ij}\overrightarrow{\partial_j}+\overleftarrow{\partial_i}(\partial_j\mathcal{B}_{ij}))}. \tag{19}$$

The time derivative of the Wigner function under Nosè–Wigner dynamics is defined as

$$\partial_t f_W = -\frac{\mathrm{i}}{\hbar}\overrightarrow{\mathcal{M}}^\dagger f_W \tag{20}$$

and the time-dependent function is

$$f_W(t) = \mathrm{e}^{-\frac{it}{\hbar}\overrightarrow{\mathcal{M}}^\dagger} f_W(0). \tag{21}$$

Equations (19) and (21) show that when $\partial_j\mathcal{B}_{ij} \neq 0$ the generalized Wigner bracket defines a non-unitary evolution. Note that we introduce such a generalization of the Moyal's bracket not in order to modify quantum mechanics but for devising novel computational schemes which may be of interest to address open quantum systems dynamics. In fact, in the following sections, we will show how to exploit the generalized Wigner bracket to introduce constant-temperature dynamics in quantum phase space.

4. Nosè–Wigner equations of motions

It is known that constant-temperature Nosè–Hoover dynamics in classical phase space can be introduced by means of the following extended Hamiltonian [19]:

$$H_W^{\mathrm{N}} = \frac{p^2}{2m} + \frac{p_\eta^2}{2m_\eta} + V(r) + gk_BT\eta, \tag{22}$$

where (r, p) are the coordinates and momenta, respectively, of number N of relevant degrees of freedom (m is the mass) while (η, p_η) are the additional Nosè variables with their fictitious

mass m_η. The other constants appearing in equation (22) are the Boltzmann constant k_B, the external temperature T and $g = N$ is a constant. The extended point in phase space may be written as $x = (r, \eta, p, p_\eta)$.

The well-known Nosè equations of motion

$$\dot{r} = \frac{p}{m} \tag{23}$$

$$\dot{\eta} = \frac{p_\eta}{m_\eta} \tag{24}$$

$$\dot{p} = -\frac{\partial V}{\partial r} - \frac{p_\eta}{m_\eta} p \tag{25}$$

$$\dot{p}_\eta = \frac{p^2}{m} - g k_B T \tag{26}$$

can be written in compact form [14]

$$\dot{x}_i = \mathcal{B}^{\mathrm{N}}_{ij} \frac{\partial H^{\mathrm{N}}}{\partial x_j} \tag{27}$$

upon introducing the antisymmetric matrix

$$\boldsymbol{\mathcal{B}}^{\mathrm{N}} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & -p \\ 0 & -1 & p & 0 \end{bmatrix}. \tag{28}$$

The Nosè–Liouville operator is then

$$\mathrm{i}L^{\mathrm{N}} = \mathcal{B}_{ij} \frac{\partial H^{\mathrm{N}}}{\partial x_i} \frac{\partial}{\partial x_i} \tag{29}$$

$$= \frac{p}{m} \frac{\partial}{\partial r} + \frac{p_\eta}{m_\eta} \frac{\partial}{\partial \eta} + \left(-\frac{\partial V}{\partial r} - \frac{p_\eta}{m_\eta} p \right) \frac{\partial}{\partial p} + \left(\frac{p^2}{m} - g k_B T \right) \frac{\partial}{\partial p_\eta}. \tag{30}$$

The above equations allow one to define Nosè–Hoover dynamics in classical phase space. It is worth noting that the coupling between the Nosè variables and the physical coordinates (r, p) is not present in the extended Hamiltonian in equation (22). Such a coupling is achieved only through the equations of motion (23)–(26), which, as can be seen from their compact form in equation (27), are defined by means of the generalized antisymmetric matrix in equation (28). The physical idea behind the Nosè–Hoover equations of motion is best understood by looking at equation (25): this introduces a dynamical friction acting on the momenta of the physical coordinates, which rescales them according to the unbalance between the internal kinetic energy and the temperature of the external bath, as dictated by equation (26). From the point of view of statistical mechanics, it can be rigorously proven that, when the dynamics is ergodic, the calculation of phase space averages in the microcanonical ensemble of the extended system (we recall here that the extended system is defined by the coordinates r, η, p, p_η) of functions of the (r, p) coordinates alone amounts to a canonical average in the ensemble at constant temperature. For details of such a proof, we refer the reader to [14] and to the original papers where the Nosè–Hoover dynamics was introduced for the first time [19] (in the present paper, the steps of the proof are generalized in section 5 to a quantum-classical context so that the statistical validity of Nosè–Hoover dynamics in Wigner phase space can be verified).

Although the theory of the Nosè–Hoover dynamics has been described in a generalized non-Hamiltonian form only recently [14], it has been known and used extensively for some time in the field of molecular dynamics simulations and it is also described in textbooks [15, 16]. The method of Nosè–Hoover dynamics provides a numerical non-perturbative approach to the calculation of statical and dynamical quantities of many-body systems at constant temperature. No explicit approximation about the memory effects in the many-body system is taken (as such the underlying philosophy of the approach is very different from that governing the use of master equations): within the approach of molecular dynamics simulation in general, once the interaction potential between the degrees of freedom of a many-body system is modeled, brute force computer calculations are employed to study the effects of interest. From this point of view, when applicable, the Nosè–Hoover equations of motion naturally provide a non-Markovian formulation of the dynamics of a many-body system which could be used to test other approximated approach to open system dynamics.

The matrix form of the generalized Wigner bracket can be used to generalize the Nosè–Hoover equations of motion to the quantum case. To this end, one can define a quantum extended Hamiltonian in phase space as

$$H_W^{\mathrm{N}} = H^{\mathrm{N}}. \tag{31}$$

From the logical point of view, this amounts to consider first the quantum Hamiltonian $\hat{H} = \hat{p}^2/2m + V(\hat{r})$, perform the Wigner transform in order to obtain the function $H_W = p^2/2m + V(r)$, and then augment the quantum phase space by the Nosè variables so as to obtain H_W^{N}. Therefore, we can use the matrix $\boldsymbol{\mathcal{B}}^{\mathrm{N}}$ to define the quantum equations

$$\begin{aligned}
\frac{\partial f_W}{\partial t} &= -\frac{\mathrm{i}}{\hbar}\overrightarrow{\mathcal{M}}^{\mathrm{N},\dagger} f_W \\
&= -\frac{\mathrm{i}}{\hbar} H_W^{\mathrm{N}}\left[\mathrm{e}^{\frac{\mathrm{i}\hbar}{2}\left(\overleftarrow{\partial_i}\mathcal{B}_{ij}^{\mathrm{N}}\overrightarrow{\partial_j}+\overleftarrow{\partial_i}\left(\partial_j\mathcal{B}_{ij}^{\mathrm{N}}\right)\right)} - \mathrm{e}^{-\frac{\mathrm{i}\hbar}{2}\left(\overleftarrow{\partial_i}\mathcal{B}_{ij}^{\mathrm{N}}\overrightarrow{\partial_j}+\overleftarrow{\partial_i}\left(\partial_j\mathcal{B}_{ij}^{\mathrm{N}}\right)\right)}\right] f_W \\
&= \frac{2}{\hbar} H_W^{\mathrm{N}} \sin\left[\frac{\hbar}{2}\left(\overleftarrow{\partial_i}\mathcal{B}_{ij}^{\mathrm{N}}\overrightarrow{\partial_j} + \overleftarrow{\partial_i}\left(\partial_j\mathcal{B}_{ij}^{\mathrm{N}}\right)\right)\right] f_W \\
&= H_W \overleftarrow{\partial_i}\mathcal{B}_{ij}^{\mathrm{N}}\overrightarrow{\partial_j} f_W + H_W^{\mathrm{N}}\overleftarrow{\partial_i}\left(\partial_j\mathcal{B}_{ij}^{\mathrm{N}}\right) f_W \\
&\quad + \sum_{n=3,5,7,\ldots} \frac{1}{n!}\left(\frac{\mathrm{i}\hbar}{2}\right)^{n-1} H_W^{\mathrm{N}}\left[\overleftarrow{\partial_i}\mathcal{B}_{ij}^{\mathrm{N}}\overrightarrow{\partial_j} + \overleftarrow{\partial_i}\left(\partial_j\mathcal{B}_{ij}^{\mathrm{N}}\right)\right]^n f_W.
\end{aligned} \tag{32}$$

Defining the phase space compressibility as

$$\kappa = \left(\partial_j B_{ji}^{\mathrm{N}}\right)\partial_i H_W^{\mathrm{N}}, \tag{33}$$

the Nosè–Wigner equations can be written as

$$\begin{aligned}
\partial_t f_W &= -\mathrm{i}L^{\mathrm{N}} f_W - \kappa f_W \\
&\quad + \sum_{n=3,5,7,\ldots} \frac{1}{n!}\left(\frac{\mathrm{i}\hbar}{2}\right)^{n-1} H_W^{\mathrm{N}}\left[\overleftarrow{\partial_i}\mathcal{B}_{ij}^{\mathrm{N}}\overrightarrow{\partial_j} + \overleftarrow{\partial_i}\left(\partial_j\mathcal{B}_{ij}^{\mathrm{N}}\right)\right]^n f_W,
\end{aligned} \tag{34}$$

where the Nosè–Liouville operator is defined as in equation (30) with H_W^{N} replacing H^{N}.

To zero order in $\hbar$ the Nosè–Wigner equations of motion coincide with the classical equations of motion. Higher powers of $\hbar$ provide the quantum corrections to the dynamics. Such quantum corrections can be found considering the term

$$H_W^{\mathrm{N}}\left[\overleftarrow{\partial_i}\mathcal{B}_{ij}^{\mathrm{N}}\overrightarrow{\partial_j} + \overleftarrow{\partial_i}\left(\partial_j\mathcal{B}_{ij}^{\mathrm{N}}\right)\right]^n f_W. \tag{35}$$

The general quantum correction term in equation (35) can be simplified. To this end, we note that $\partial\boldsymbol{\mathcal{B}}^{\mathrm{N}}/\partial x_1 = \partial\boldsymbol{\mathcal{B}}^{\mathrm{N}}/\partial r = 0$, $\partial\boldsymbol{\mathcal{B}}^{\mathrm{N}}/\partial x_2 = \partial\boldsymbol{\mathcal{B}}^{\mathrm{N}}/\partial\eta = 0$, $\partial\boldsymbol{\mathcal{B}}^{\mathrm{N}}/\partial x_4 = \partial\boldsymbol{\mathcal{B}}^{\mathrm{N}}/\partial p_\eta = 0$, while

the only nonzero terms are $\partial\mathcal{B}^{\mathrm{N}}_{34}/\partial x_3 = \partial\mathcal{B}^{\mathrm{N}}_{34}/\partial p = -1$ and $\partial\mathcal{B}^{\mathrm{N}}_{43}/\partial x_3 = \partial\mathcal{B}^{\mathrm{N}}_{43}/\partial p = 1$. Therefore, one obtains

$$\overleftarrow{\partial}_i\left(\partial_j\mathcal{B}^{\mathrm{N}}_{ij}\right) = \overleftarrow{\partial}_4\left(\partial_3\mathcal{B}^{\mathrm{N}}_{43}\right) = \frac{\overleftarrow{\partial}}{\partial p_\eta}. \tag{36}$$

Collecting the above results, it is not difficult to verify that

$$\overleftarrow{\partial}_i\mathcal{B}^{\mathrm{N}}_{ij}\overrightarrow{\partial}_j = \frac{\overleftarrow{\partial}}{\partial r}\frac{\overrightarrow{\partial}}{\partial p} + \frac{\overleftarrow{\partial}}{\partial \eta}\frac{\overrightarrow{\partial}}{\partial p_\eta} - \frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial r} - \frac{\overleftarrow{\partial}}{\partial p}p\frac{\overrightarrow{\partial}}{\partial p_\eta} - \frac{\overleftarrow{\partial}}{\partial p_\eta}\frac{\overrightarrow{\partial}}{\partial \eta} + \frac{\overleftarrow{\partial}}{\partial p_\eta}p\frac{\overrightarrow{\partial}}{\partial p}. \tag{37}$$

The quantum correction terms can then be written as

$$\sum_{n=3,5,7,\ldots}\frac{1}{n!}\left(\frac{\mathrm{i}\hbar}{2}\right)^{n-1}H_W\left[\frac{\overleftarrow{\partial}}{\partial r}\frac{\overrightarrow{\partial}}{\partial p} + \frac{\overleftarrow{\partial}}{\partial \eta}\frac{\overrightarrow{\partial}}{\partial p_\eta} - \frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial r} - \frac{\overleftarrow{\partial}}{\partial p}p\frac{\overrightarrow{\partial}}{\partial p_\eta} - \frac{\overleftarrow{\partial}}{\partial p_\eta}\frac{\overrightarrow{\partial}}{\partial \eta} + \frac{\overleftarrow{\partial}}{\partial p_\eta}p\frac{\overrightarrow{\partial}}{\partial p}\right]^n f_w. \tag{38}$$

The above expression can be simplified further by making the following considerations. Recalling the form of the quantum Nosè Hamiltonian, one can note that all the mixed derivatives of the form $\partial^2 H^{\mathrm{N}}_W/\partial x_i\partial x_j = 0$ when $i \neq j$. Therefore, when evaluating the nth power of the differential operator in the quantum correction terms, one can disregard the cross products of such a type. Since, in the quantum correction n is odd and $\geqslant 3$, it is not difficult to see that another null term is $\left(\partial^n H^{\mathrm{N}}_W/\partial x_i^n\right)\left(\partial^n f_W/\partial x_j^n\right) = 0$. An important nonzero term, containing spatial derivatives of the interaction potential, is given by

$$H^{\mathrm{N}}_W\frac{\overleftarrow{\partial^n}}{\partial x_i^n}\frac{\overrightarrow{\partial^n}}{\partial x_j^n}f_W = V(r)\frac{\overleftarrow{\partial^n}}{\partial r^n}\frac{\overrightarrow{\partial^n}}{\partial p^n}f_W. \tag{39}$$

Other terms which are different from zero are

$$H^{\mathrm{N}}_W\left[-\frac{\overleftarrow{\partial}}{\partial p}p\frac{\overrightarrow{\partial}}{\partial p_\eta}\right]^n f_W \neq 0, \tag{40}$$

$$H^{\mathrm{N}}_W\left(\frac{\overleftarrow{\partial}}{\partial p_\eta}p\frac{\overrightarrow{\partial}}{\partial p}\right)\left(-\frac{\overleftarrow{\partial}}{\partial p}p\frac{\overrightarrow{\partial}}{\partial p_\eta}\right)^{n-1} f_W \neq 0, \tag{41}$$

$$H^{\mathrm{N}}_W\left(\frac{\overleftarrow{\partial}}{\partial p_\eta}p\frac{\overrightarrow{\partial}}{\partial p}\right)^2\left(-\frac{\overleftarrow{\partial}}{\partial p}p\frac{\overrightarrow{\partial}}{\partial p_\eta}\right)^{n-2} f_W \neq 0, \tag{42}$$

$$H^{\mathrm{N}}_W\left(-\frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial r}\right)\left(-\frac{\overleftarrow{\partial}}{\partial p}p\frac{\overrightarrow{\partial}}{\partial p_\eta}\right)^{n-1} f_W \neq 0, \tag{43}$$

$$H^{\mathrm{N}}_W\left(-\frac{\overleftarrow{\partial}}{\partial p}p\frac{\overrightarrow{\partial}}{\partial r}\right)^2\left(-\frac{\overleftarrow{\partial}}{\partial p}p\frac{\overrightarrow{\partial}}{\partial p_\eta}\right)^{n-2} f_W \neq 0. \tag{44}$$

In summary, in order to obtain all the relevant quantum corrections to the Nosé dynamics within the Wigner phase space picture, it is sufficient to evaluate the terms arising from the expression

$$\sum_{n=3,5,7,\ldots}\frac{1}{n!}\left(\frac{\mathrm{i}\hbar}{2}\right)^{n-1}H_W\left\{\frac{\overleftarrow{\partial}^n}{\partial r^n}\frac{\overrightarrow{\partial}^n}{\partial p^n} + \left[-\frac{\overleftarrow{\partial}}{\partial p}\left(\frac{\overrightarrow{\partial}}{\partial r} - p\frac{\overrightarrow{\partial}}{\partial p_\eta}\right) + \frac{\overleftarrow{\partial}}{\partial p_\eta}\left(-\frac{\overrightarrow{\partial}}{\partial \eta} + p\frac{\overrightarrow{\partial}}{\partial p}\right)\right]^n\right\} f_W. \tag{45}$$

5. Quantum-classical Nosè–Wigner dynamics

Equation (34) contains all the quantum corrections to the dynamics of the Nosè variables. However, if one desires to perturb the dynamics of the physical variables (r, p) only slightly, the value of fictitious mass m_η of the Nosè variable (which is arbitrary and does not influence the statistical properties) can be chosen to be of the same order of magnitude of the total mass of the physical system: in such a way one effectively induces a time-scale separation between the dynamics of the thermostat (whose only role is that of enforcing the desired canonical ensemble statistics) and the dynamics of (r, p), which one is really interested in. Taking such a choice, one realizes that a small expansion parameter

$$\mu = \sqrt{\frac{m}{m_\eta}} \ll 1, \tag{46}$$

where m is the mass of the physical degrees of freedom, appears in the formalism. From a physical point of view, this can be interpreted by saying that, at a given temperature, different from zero, the De Broglie wavelength associated with the Nosè variable would be much shorter than that associated with the physical variables. In such a case, it is satisfactory to adopt a quantum-classical approximation [18] so that the quantum corrections are considered only for the physical variables (r, p): this amounts to taking an average over the short De Broglie wavelength associated with the Nosè variable. Such a quantum-classical limit can be performed along the lines adopted in [20], which require that a small expansion parameter μ, given in the present case by equation (46), must be identified. In this limit, equation (34) is replaced by

$$\partial_t f_W = -\left(\mathrm{i}L_N + \kappa\right) f_W + \sum_{n=3,5,7,\ldots} \frac{1}{n!} \left(\frac{\mathrm{i}\hbar}{2}\right)^{n-1} V(\overleftarrow{\partial}_r \overrightarrow{\partial}_p)^n f_W. \tag{47}$$

The equilibrium quantum-classical statistical mechanics arising from the above equation can be defined upon finding the stationary solution, $f_{W,e}$, of equation (47). Such a stationary solution, which is defined by $\partial_t f_{W,e} = 0$, can be written as an expansion in even powers of $\hbar$

$$f_{W,e} \approx \sum_{n=0} \hbar^{2n} f_{W,e}^{(2n)}. \tag{48}$$

From equation (47), one can see that the quantum corrections start from second order in $\hbar$. The order zero, purely classical, solution $f_{W,e}^{(0)}$ is defined by the equation

$$\left(\mathrm{i}L_\mathrm{N} + \kappa\right) f_{W,e}^{(0)} = 0. \tag{49}$$

Using the theory of classical non-Hamiltonian systems [14], one can immediately write down the form of $f_{W,e}^{(0)}$ as

$$f_{W,e}^{(0)} = \delta\left(H_W^\mathrm{N}\right) \mathrm{e}^{-w}, \tag{50}$$

where $\mathrm{d}w/\mathrm{d}t = \kappa$. The stationarity of $f_{W,e}^{(0)}$ can be easily verified considering $\mathrm{i}L_\mathrm{N} f_{W,e}^{(0)} = -\kappa f_{W,e}^{(0)}$, where one has used the fact that $\mathrm{i}L_\mathrm{N}$ conserves the Nosè Hamiltonian so that $\mathrm{i}L_\mathrm{N}\delta\left(H_W^\mathrm{N}\right) = 0$. For the case of Nosè dynamics one obtains

$$f_{W,e}^{(0)} = \delta\left(H_W^\mathrm{N}\right) \mathrm{e}^{-g\eta}. \tag{51}$$

In order to calculate averages, the function $f_{W,e}^{(0)}$ is to appear inside phase space integrals over $\mathrm{d}r\,\mathrm{d}p\,\mathrm{d}p_\eta\,\mathrm{d}\eta$. The further analysis of the phase space measure can be performed upon considering the identity

$$\delta(f(\eta)) = \sum_{\eta_0} \frac{\delta(\eta - \eta_0)}{\left.\frac{\mathrm{d}f}{\mathrm{d}\eta}\right|_{\eta=\eta_0}}, \tag{52}$$

where η_0 are the zeros of $f(\eta)$. In the present case, one has

$$\eta_0 = -\frac{\beta}{g}\left(\frac{p^2}{2m} + V(r) + \frac{p_\eta^2}{2m_\eta}\right). \tag{53}$$

$$\delta\left(H_W^{\mathrm{N}}\right) = \frac{\beta}{g}\delta\left(\eta + \frac{\beta}{N}\left(\frac{p^2}{2m} + V(r) + \frac{p_\eta^2}{2m_\eta}\right)\right). \tag{54}$$

Therefore, the stationary solution has the form

$$f_{W,e}^{(0)} \propto \delta\left(\eta + \frac{\beta}{N}\left(\frac{p^2}{2m} + V(r) + \frac{p_\eta^2}{2m_\eta}\right)\right)\mathrm{e}^{-g\eta}. \tag{55}$$

Typically, one is interested in the calculation of averages of functions of (r, p). In such a case, the integration over η gives

$$f_{W,e}^{(0)}(r, p, p_\eta) \propto \exp\left[-\beta\left(\frac{p^2}{2m} + V(r) + \frac{p_\eta^2}{2m_\eta}\right)\right]. \tag{56}$$

Since the Gaussian integration over p_η can be easily performed, one finally obtains

$$f_{W,e}^{(0)}(r, p) \propto \exp\left[-\beta\left(\frac{p^2}{2m} + V(r)\right)\right]. \tag{57}$$

Equation (57) shows that, whenever one calculates averages of functions of the physical variables (r, p) alone, the stationary solution to equation (47) up to order zero in $\hbar$ has the desired canonical form.

Quantum corrections to the stationary order zero solution can be systematically obtained by considering the higher order terms in equation (47). In the present quantum-classical case, they turn out to be identical to those originally found by Wigner [9]. For example, the second-order correction is given by

$$(\mathrm{i}L_{\mathrm{N}} + \kappa)\, f_{W,e}^{(2)}(x) = -\frac{\hbar^2}{2^2 3!} V\left(\frac{\overleftarrow{\partial}}{\partial r}\cdot\frac{\overrightarrow{\partial}}{\partial p}\right)^3 f_{W,e}^{(0)}(x). \tag{58}$$

Assuming that the analytical form of the potential $V(r)$ is known, the right-hand-side of equation (58) can be calculated exactly since the order zero solution is a Boltzmann exponential.

Physical properties of the quantum subsystem, coupled to the classical Nosè bath, will be represented by averages of functions of (r, p). In such a case, an average over (η, p_η) can be performed without loosing information over the quantum subsystem. Therefore, one does not need to consider in the stationary equation the full quantum correction term given in equation (45) but it will suffice to consider its average over (η, p_η). When averaging equation (45), the linear terms in p_η give a zero contribution, since they are averaged over a Gaussian weight $\exp\left[-\beta p_\eta^2/2m_\eta\right]$. Hence, within Nosè–Hoover quantum classical dynamics, one has to consider the following stationary equation:

$$(\mathrm{i}L_{\mathrm{N}} + \kappa)\, f_{W,e}(x) = \sum_{n=3,5,7,\ldots}\frac{1}{n!}\left(\frac{\mathrm{i}\hbar}{2}\right)^{n-1} H_W^{\mathrm{N}}(\overleftarrow{\partial}_r\overrightarrow{\partial}_p)^n f_{W,e}(x). \tag{59}$$

In the case of the second-order correction, one is left with

$$\left(\frac{p}{m}\partial_r - (\partial_r V)\partial_p\right) f_{W,e}^{(2)}(r, p) = -\frac{\hbar^2}{24} V(r)(\overleftarrow{\partial}_r\overrightarrow{\partial}_p)^3 f_{W,e}^{(0)}(r, p), \tag{60}$$

where $f^{(0)}_{W,e}(r, p)$ is the Boltzmann exponential defined in equation (57). Equation (60) was solved by Wigner in his original paper [9]. The solution is

$$f^{(2)}_{W,e}(r, p) = f^{(0)}_{W,e}(r, p)\left[-\frac{\hbar^2}{24}\frac{\partial^2 V(r)}{\partial r^2}\left[3\frac{\beta^2}{m} + \beta^3\frac{p^2}{m^2}\right] - \frac{\hbar^2}{24}\frac{\beta^3}{m}\left(\frac{\partial V(r)}{\partial r}\right)^2\right]. \tag{61}$$

We give details of the derivations in appendix A. The above discussion, together with the analysis in [9], proves that, for all practical purposes, a stationary solution to the Nosè–Wigner dynamics exists because it can be constructed term by term, for the even powers of $\hbar$.

A computational scheme to calculate quantum averages in the canonical ensemble can then be based upon sampling the initial conditions from the canonical stationary Wigner function, propagating trajectories undergoing thermal fluctuations by means of the Nosè–Wigner dynamics, and finally averaging over quantum phase space. This scheme is different from those previously suggested in the literature [6, 7]. In particular, in [7] Nosè dynamics for coherent states is introduced as a means for calculating quantum averages as time averages which requires a suitable modification of the quantum Hamiltonian. Instead, in our work the dynamics arises from a generalization of the Moyal bracket while the physical part of the Hamiltonian remains unchanged. Quantum averages must be calculated by sampling initial conditions from the proper Wigner distribution and propagating observables according to the Nosè–Wigner dynamics in order to obtain the stationary state. We also note that a practical scheme to sample initial conditions from the Wigner function, which is not based on the expansion in powers of $\hbar$, has been recently proposed in [21]. Moreover, we surmise that the computational application of the Nosè–Wigner dynamics is also interesting in the case of quantum systems out of equilibrium. In this latter case, the Nosè dynamics can be used to simulate the coupling of the relevant quantum system to a thermal bath and describe quantum relaxation processes. We provide a numerical example in the following section.

6. Numerical example: cooling of phonons

In view of the raising interest in the dynamics of cool gases in optical lattices, we will consider the related problem of the cooling of phonons. To this end, let us consider a model system comprises $N = 20$ non-interacting harmonic oscillators in one spatial dimension. Let

$$H_W = \sum_{j=1}^{N}\left(\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 r_j^2\right) \tag{62}$$

be the Wigner transform quantum Hamiltonian of the model system. The numerical values of the oscillator frequencies are chosen according to

$$\omega_j = -\log(1 - j\omega_0), \tag{63}$$

where $\omega_0 = N^{-1}(1 - \mathrm{e}^{-\omega_{\max}})$. For the system defined by the Hamiltonian in equation (62) the quantum Wigner dynamics is exactly equal to classical dynamics, i.e., the quantum corrections in the Wigner equation are identically zero because the potential is harmonic. All the quantum effects are described by the initial Wigner function, which, for the model, is known analytically and it is given by

$$f_{W,e}(0) = \prod_{i=1}^{N}\frac{\tanh\left(\frac{\beta\omega_i}{2}\right)}{\pi}\exp\left[-2\tanh\left(\frac{\beta\omega_i}{2}\right)H_W\right], \tag{64}$$

where $\beta = (k_B T)^{-1}$, i.e., the Boltzmann constant k_B times the temperature of the ensemble. At equilibrium, quantum averages can be calculated by sampling initial phase space point

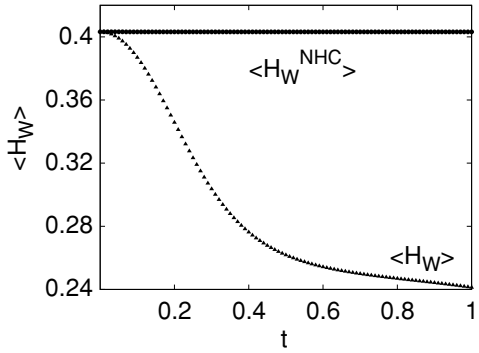

Figure 1. Average values of the quantum Nosè–Hoover chain Hamiltonian H_W^{NHC}, defined in equation (65), (black circles) and the physical Hamiltonian H_W, defined in equation (62), (black triangles) versus time. The dynamics numerically conserves the average $\langle H_W^{\mathrm{NHC}} \rangle$ while the decrease in time of $\langle H_W \rangle$ provides a clear signature of the cooling.

from $f_{W,e}$, propagating classical trajectories according to the quantum harmonic Hamiltonian (62), and averaging over phase space.

The process of cooling is a non-equilibrium phenomenon. Here, we want to simulate it by coupling the system, which is initially at equilibrium at temperature $(k_B\beta)^{-1}$, to a heat bath characterized by $\beta_1 > \beta$. This can be achieved by sampling initial conditions from the Wigner distribution in equation (64) and propagating phase space points according to a constant-temperature dynamics defined in terms of β_1. In practice we have considered $\beta = 0.01$ and $\beta_1 = 1$. In order to deal with ergodicity problems in quantum phase space, we adopt a Nosè–Hoover chain [22]. The Nosè–Hoover chain method is a more sophisticated approach in order to control the temperature of a system. It is based on the same dynamical idea of the standard Nosè–Hoover thermostat, but it exploits a series of thermostat variables which are coupled as in a chain in order to control the fluctuations of the previous member of the chain. In such a way, it has been shown numerically [22] that ergodicity can also be achieved in stiff dynamical systems, such as harmonic oscillators, where the simpler Nosè–Hoover thermostat fails. In the following, we will adopt a minimal chain composed of just two thermostats. Therefore, we introduce a quantum extended Hamiltonian in phase space

$$H_W^{\mathrm{NHC}} = H_W + \frac{p_{\eta_1}^2}{2m_{\eta_1}} + \frac{p_{\eta_2}^2}{2m_{\eta_2}} + \frac{N\eta_1}{\beta_1} + \frac{\eta_2}{\beta_2} \tag{65}$$

with the thermostat variables $(\eta_1, p_{\eta_1}, \eta_2, p_{\eta 2})$ and inertial parameters (m_{η_1}, m_{η_2}). In order to define a quantum Wigner Nosè–Hoover dynamics the generalized Moyal bracket must be defined in terms of the antisymmetric matrix

$$\mathcal{B}^{\mathrm{NHC}} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & -p & 0 \\ 0 & -1 & 0 & p & 0 & -p_{\eta_1} \\ 0 & 0 & -1 & 0 & p_{\eta_1} & 0 \end{bmatrix}. \tag{66}$$

As in the case of the Nosè–Hoover thermostat, the coupling between the extended degrees of freedom is realized by means of the antisymmetric matrix $\mathcal{B}^{\mathrm{NHC}}$, which enters into the

definition of the equations of motion [14]. Therefore, if one samples initial phase space points from $f_{W,e}(\beta)$ and propagates the dynamics defined by the Hamiltonian $H_W^{\mathrm{NHC}}(\beta_1)$, non-equilibrium quantum averages can be numerically calculated. Figure 1 shows the time dependence of the average value of the model Hamiltonian H_W under the quantum Nosè–Hoover chain dynamics. For comparison, the figure also shows the average value of the conserved quantity H_W^{NHC}. The rate of dissipation for H_W is controlled by the numerical values of m_{η_1} and m_{η_2}, which were set equal to 100 and 10, respectively.

7. Conclusions

We have generalized the Moyal bracket exploiting its underlying antisymmetric matrix structure. This naturally introduces a non-unitary evolution in quantum phase space whose implications may be of interest for open system dynamics. The generalized Moyal bracket can be used in order to introduce Nosè Wigner dynamics in phase space. Upon taking a quantum-classical approximation, according to which the system of interest retains its full quantum nature while the Nosè variables are treated classically, we have shown how to construct stationary solutions of the Wigner function under Nosè–Wigner dynamics. We surmise that Nosè–Wigner evolution is of particular interest for non-equilibrium dynamics. To this end, we have shown how such a dynamics can be used to simulate the non-equilibrium cooling of a quantum boson gas. This suggests a novel route to tackle the simulation of non-equilibrium processes in quantum gases in optical lattices. Further numerical studies are ongoing.

Acknowledgments

This work is based upon research supported by the South African Research Chair Initiative of the Department of Science and Technology and National Research Foundation.

Appendix. Second-order correction to the stationary quantum-classical Nosè–Wigner function

To show how equation (60) can be solved, we consider a one-dimensional system and write

$$f_{W,e}^{(2)}(r,p) = f_{W,e}^{(0)}(r,p) g_{W,e}^{(2)}(r,p). \tag{A.1}$$

Equation (60) becomes

$$f_{W,e}^{(0)} \left(\frac{p}{m}\partial_r - (\partial_r V)\partial_p \right) g_{W,e}^{(2)} = -\frac{\hbar^2}{24} V(r) (\overleftarrow{\partial}_r \overrightarrow{\partial}_p)^3 f_{W,e}^{(0)}, \tag{A.2}$$

where we have used

$$((p/m)\partial_r - (\partial_r V)\partial_p) f_{W,e}^{(0)} = 0. \tag{A.3}$$

We can also write

$$\begin{aligned} f_{W,e}^{(0)} \left(\frac{p}{m}\partial_r - (\partial_r V)\partial_p \right) g_{W,e}^{(2)} &= -\frac{\hbar^2}{24} \frac{\partial^3 V(r)}{\partial r^3} \frac{\partial^3 f_{W,e}^{(0)}}{\partial p^3}, \\ f_{W,e}^{(0)} \left(\frac{p}{m} \frac{\partial g_{W,e}^{(2)}}{\partial r} - \frac{\partial V}{\partial r} \frac{\partial g_{W,e}^{(2)}}{\partial p} \right) &= -\frac{\hbar^2}{24} \frac{\partial^3 V(r)}{\partial r^3} \frac{\partial^3 f_{W,e}^{(0)}}{\partial p^3}. \end{aligned} \tag{A.4}$$

Considering

$$\begin{aligned}
\frac{\partial f_{W,e}^{(0)}}{\partial p} &= -\beta \frac{p}{m} f_{W,e}^{(0)}, \\
\frac{\partial^2 f_{W,e}^{(0)}}{\partial p^2} &= -\frac{\beta}{m} f_{W,e}^{(0)} + \left(\beta \frac{p}{m}\right)^2 f_{W,e}^{(0)}, \\
\frac{\partial^3 f_{W,e}^{(0)}}{\partial p^3} &= +3\left(\frac{\beta}{m}\right)^2 p f_{W,e}^{(0)} + \left(\beta \frac{p}{m}\right)^3 f_{W,e}^{(0)},
\end{aligned} \tag{A.5}$$

Equation (A.2) becomes

$$\frac{p}{m}\frac{\partial g_{W,e}^{(2)}}{\partial r} - \frac{\partial V}{\partial r}\frac{\partial g_{W,e}^{(2)}}{\partial p} = -\frac{\hbar^2}{24}\frac{\partial^3 V(r)}{\partial r^3}\left[3\left(\frac{\beta}{m}\right)^2 p + \left(\beta \frac{p}{m}\right)^3\right] \tag{A.6}$$

$$= -\frac{\hbar^2}{24}\frac{p}{m}\frac{\partial^3 V(r)}{\partial r^3}\left[3\frac{\beta^2}{m} + \beta^3 \frac{p^2}{m^2}\right]. \tag{A.7}$$

It is easy to see that upon defining

$$g_{W,e}^{(2)\prime} = -\frac{\hbar^2}{24}\frac{\partial^2 V(r)}{\partial r^2}\left[3\frac{\beta^2}{m} + \beta^3 \frac{p^2}{m^2}\right]. \tag{A.8}$$

The second right-hand-side of equation (A.2) will be exactly cancelled by the first term in the Liouville operator in the left-hand-side. Noting that

$$-\frac{\partial V}{\partial r}\frac{\partial g_{W,e}^{(2)\prime}}{\partial p} = \frac{\hbar^2}{24}\frac{\beta^3}{m}\frac{p}{m}\frac{\partial}{\partial r}\left(\frac{\partial V(r)}{\partial r}\right)^2 \tag{A.9}$$

one gets

$$g_{W,e}^{(2)} = g_{W,e}^{(2)\prime} - \frac{\hbar^2}{24}\frac{\beta^3}{m}\left(\frac{\partial V(r)}{\partial r}\right)^2. \tag{A.10}$$

Finally, the second-order correction to the stationary equation can be written as

$$g_{W,e}^{(2)} = -\frac{\hbar^2}{24}\frac{\partial^2 V(r)}{\partial r^2}\left[3\frac{\beta^2}{m} + \beta^3 \frac{p^2}{m^2}\right] - \frac{\hbar^2}{24}\frac{\beta^3}{m}\left(\frac{\partial V(r)}{\partial r}\right)^2. \tag{A.11}$$

Higher order terms can be found in an analogous manner.

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