Quantum-Classical Dynamics of Wave Fields

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The recent approach to the quantum-classical mechanics of phase space dependent operators is recast into a formalism for wave fields. It turns out that such wave fields obey a system of coupled non-linear equations where each equation is not Hermitian. However, backward and forward time-evolution is combined in such a way as to conserve probability. Notwithstanding their non-linear form, the equations of motion for such phase space dependent wave fields can be expressed by means of a suitable non-Hamiltonian bracket. Thus, it can be realized that the non-Hamiltonian dynamics of quantum-classical wave fields is a straightforward generalization of the formalism for non-linear quantum mechanics that Weinberg proposed recently.

I. INTRODUCTION

There are many instances where a quantum-classical description is a useful approximation to full quantum dynamics. Typically, a quantum-classical picture often allows one to implement calculable algorithms on the computer whenever charge transfer is considered within complex environments, such as those provided by proteins or nano-systems in general [1]. With respect to this, an algebraic approach has been recently proposed [2] in order to formulate the dynamics and the statistical mechanics [3] of quantum-classical systems. Such an approach represents quantum-classical dynamics by means of suitable brackets of phase space dependent operators and describes consistently the back-reaction between quantum and classical degrees of freedom. Notably, one particular implementation of this formalism has been used to calculate nonadiabatic rate constants in systems modeling the condensed phase [4]. So far, these schemes have only permitted the simulation of short-time dynamics because of the time-growing statistical error of the algorithms. It can be safely said that, so far, any approach to quantum dynamics has shown this drawback. Nevertheless, the algebraic approach [2], underlying the algorithms of Refs. [4], has some very nice features, such as the (above mentioned) proper description of the back-reaction between degrees of freedom, that one would not want to give up when addressing quantum-classical statistical mechanics. In particular, quantum-classical brackets define a non-Hamiltonian algebra [5]. The matrix structure of such brackets allows one to introduce quantum-classical Nosé-Hoover dynamics [5] and to define the statistical mechanics of quantum-classical systems with holonomic constraints [6].

It is interesting to note that when the time evolution of phase space dependent operators is implemented on computers, a particular representation of quantum-classical nonadiabatic dynamics is found. Such a representation is different from that provided by the original surface-hopping schemes [7]. In fact, these latter were formulated addressing the dynamics of wave functions and classical particle coordinates separately, instead of the unique consistent dynamics of quantum-classical operators [2]. These two approaches to quantum-classical nonadiabatic dynamics require different algorithms and numerical recipes. They also have different drawbacks. Typically, as above mentioned, the quantum-classical theory of phase space dependent operators is very satisfying, especially as for statistical mechanics is concerned [3], but is also in need of new recipes for extending the time range spanned by the calculations. Now, it is known that, within standard quantum mechanics, problems that are formidable to solve by means of the mechanics of operators become much simpler to handle when, instead, the mechanics of wave functions is used [8]. Thus, there are reasonable expectations that, also within quantum-classical mechanics, mapping time-evolving operators into quantum-classical wave functions could open new possibilities for useful approximations in order to carry long-time calculations efficiently. To this end, mapping the dynamics of quantum-classical operators into a wave picture requires to overcame a few subtle points. In fact, while in ordinary quantum mechanics, which is a Hamiltonian theory, the correspondence between the Heisenberg and Schrödinger pictures is particularly simple and rests ultimately on an operator identity [8], such simple identity cannot be found for the case of quantum-classical operators, which, obey a non-Hamiltonian algebra [5, 6]. Notably, it turns out that the phase space part of the quantum-classical bracket causes the appearance of operator-ordering problems in the needed operator identity [3]. Notwithstanding this contingency, a wave picture for quantum-classical dynamics can be found by direct algebraic manipulation of the equation of motion for the density matrix. In practice, the single equation for the quantum-classical density matrix is mapped onto two coupled non-linear equations for quantum-classical wave fields. These equations are non-Hermitian so that backward and forward evolution in time of the quantum-classical wave fields is realized according to different laws. However, such an emergent scheme is different from those of the already known non-Hermitian formulations of quantum mechanics [9]. The quantum-classical dynamics of phase space

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dependent wave fields is the mirror image of the dynamics of phase space dependent operators [2]. It has some interesting features that could lead to novel simulation algorithms and, at the same time, throws light onto the nature of quantum-classical dynamics in phase space and its non-linear character, as it will be explained in the following.

On a more general and speculative level, it is worth to note that the wave schemes of motion, introduced in this paper, generalizes the elegant formalism which Weinberg [10], following a line of research that investigates the relations between classical and quantum theories [11], proposed for describing eventual non-linear effects in quantum mechanics [12].

This paper is organized as follows. In Section II the non-Hamiltonian algebra of phase space dependent operators is briefly summarized. In Section III the quantum-classical dynamics of operators, is transformed into a theory for phase space dependent wave fields evolving in time. Such a theory for wave fields is also expressed by means of suitable non-Hamiltonian brackets: in this way a link is found with the generalization of Weinberg's non-linear formalism given in Appendix A. In Section IV the abstract non-linear equations of motion for quantum classical fields are represented in the adiabatic basis and some considerations, which are pertinent for a possible numerical implementation, are made. In Appendix A, Weinberg's formalism is briefly reviewed and its symplectic structure is unveiled. Then, this structure is generalized by means of non-Hamiltonian brackets. Therefore, one can appreciate how the generalized Weinberg's formalism establishes a more comprehensive mathematical framework for non-linear equations of motion which comprises phase space dependent wave fields as a special case. Section V is devoted to conclusions and perspectives.

II. NON-HAMILTONIAN MECHANICS OF QUANTUM-CLASSICAL OPERATORS

A quantum-classical system is composed of both quantum $\hat{\chi}$ and classical X degrees of freedom, where $X = (R, P)$ is the phase space point, with R and P coordinates and momenta, respectively. Within the operator formalism of Refs. [2, 5, 6], the quantum variables depends from the classical point X of phase space. The energy of the system is defined in terms of a Hamiltonian operator $\hat{H} = \hat{H}(X)$ which couples quantum and classical variables, by $E = \mathrm{Tr}' \int dX \hat{H}(X)$. The dynamical evolution of a quantum-classical operator $\hat{\chi}(X)$ is given by [2]

$$\frac{d}{dt}\hat{\chi}(X,t) = \frac{i}{\hbar}\left[\hat{H},\hat{\chi}(X,t)\right]_{\boldsymbol{\mathcal{B}}} - \frac{1}{2}\left\{\hat{H},\hat{\chi}(X,t)\right\}_{\boldsymbol{\mathcal{B}}} + \frac{1}{2}\left\{\hat{\chi}(X,t),\hat{H}\right\}_{\boldsymbol{\mathcal{B}}} = \left(\hat{H},\hat{\chi}(X,t)\right) , \quad (1)$$

where

$$\left[\hat{H},\hat{\chi}\right]_{\boldsymbol{\mathcal{B}}} = \left[\begin{array}{cc}\hat{H} & \hat{\chi}_\alpha\end{array}\right]\cdot\boldsymbol{\mathcal{B}}\cdot\left[\begin{array}{c}\hat{H}\\ \hat{\chi}_\alpha\end{array}\right] \quad (2)$$

is the commutator and

$$\{\hat{H},\hat{\chi}\}_{\boldsymbol{\mathcal{B}}} = \sum_{i,j=1}^{2N}\frac{\partial\hat{\chi}_\alpha}{\partial X_i}\mathcal{B}_{ij}\frac{\partial\hat{\chi}_\nu}{\partial X_j} \quad (3)$$

is the Poisson bracket [13]. Both the commutator and the Poisson bracket are defined in terms of the antisymmetric matrix

$$\boldsymbol{\mathcal{B}} = \left[\begin{array}{cc}0 & 1\\ -1 & 0\end{array}\right] . \quad (4)$$

The last equality in Eq. (1) defines the quantum-classical bracket. Following Refs. [5, 6, 14], the quantum-classical law of motion can be easily recasted in matrix form as

$$\frac{d}{dt}\hat{\chi}_\alpha = \frac{i}{\hbar}\left[\begin{array}{cc}\hat{H} & \hat{\chi}_\alpha\end{array}\right]\cdot\boldsymbol{\mathcal{D}}\cdot\left[\begin{array}{c}\hat{H}\\ \hat{\chi}_\alpha\end{array}\right] = \frac{i}{\hbar}[\hat{H},\hat{\chi}_\alpha]_{\boldsymbol{\mathcal{D}}} , \quad (5)$$

where

$$\boldsymbol{\mathcal{D}} = \left[\begin{array}{cc}0 & 1-\frac{\hbar}{2i}\{\ldots,\ldots\}_{\boldsymbol{\mathcal{B}}}\\ -1+\frac{\hbar}{2i}\{\ldots,\ldots\}_{\boldsymbol{\mathcal{B}}} & 0\end{array}\right] . \quad (6)$$

The structure of Eq. (5) is that of a non-Hamiltonian commutator, which will be defined below in Eq. (10), and as such generalizes the standard quantum law of motion [5]. The antisymmetric super-operator $\boldsymbol{\mathcal{D}}$ in Eq. (6) introduces a novel mathematical structure that characterizes the time evolution of quantum-classical systems. The Jacobi relation in quantum-classical dynamics is

$$\mathcal{J} = [\hat{\chi}_\alpha,[\hat{\chi}_\nu,\hat{\chi}_\sigma]_{\boldsymbol{\mathcal{D}}}]_{\boldsymbol{\mathcal{D}}}+[\hat{\chi}_\sigma,[\hat{\chi}_\alpha,\hat{\chi}_\nu]_{\boldsymbol{\mathcal{D}}}]_{\boldsymbol{\mathcal{D}}}+[\hat{\chi}_\nu,[\hat{\chi}_\sigma,\hat{\chi}_\alpha]_{\boldsymbol{\mathcal{D}}}]_{\boldsymbol{\mathcal{D}}} . \quad (7)$$

The explicit expression of $\mathcal{J}$ has been given in Ref. [5] where it was shown that it may not be zero for all points X of phase space: for this reason the quantum-classical theory of Refs [2, 5, 6] can be classified as a non-Hamiltonian theory.

It is worth to note that the quantum-classical law of motion in Eq. (5) is a particular example of a more general form of quantum mechanics where time evolution is defined by means of non-Hamiltonian commutators. The non-Hamiltonian commutator between two arbitrary operators χ_α and χ_ν is defined by

$$[\hat{\chi}_\alpha,\hat{\chi}_\nu]_{\boldsymbol{\Omega}} = \left[\begin{array}{cc}\hat{\chi}_\alpha & \hat{\chi}_\nu\end{array}\right]\cdot\boldsymbol{\Omega}\cdot\left[\begin{array}{c}\hat{\chi}_\alpha\\ \hat{\chi}_\nu\end{array}\right] , \quad (8)$$

where $\boldsymbol{\Omega}$ is an antisymmetric matrix operator of the form

$$\boldsymbol{\Omega} = \left[\begin{array}{cc}0 & f[\hat{\chi}]\\ -f[\hat{\chi}] & 0\end{array}\right] , \quad (9)$$

where $f[\hat{\chi}]$ can be another arbitrary operator or functional of operators. Then, generalized equations of motion can be defined as

$$\begin{aligned}\frac{d\hat{\chi}_\alpha}{dt} &= \frac{i}{\hbar}\left[\begin{array}{cc}\hat{H} & \hat{\chi}_\alpha\end{array}\right]\cdot\mathbf{\Omega}\cdot\left[\begin{array}{c}\hat{H}\\ \hat{\chi}_\alpha\end{array}\right]\\ &= \frac{i}{\hbar}[\hat{H},\hat{\chi}_\alpha]_{\mathbf{\Omega}}\,. \end{aligned} \tag{10}$$

The non-Hamiltonian commutator of Eq. (8) defines a generalized form of quantum mechanics where, nevertheless, the Hamiltonian operator $\hat{H}$ is still a constant of motion because of the antisymmetry of $\mathbf{\Omega}$.

III. QUANTUM-CLASSICAL WAVE DYNAMICS

In Refs. [2], quantum-classical evolution has been formulated in terms of phase space dependent operators. In this scheme of motion operators evolve according to

$$\begin{aligned}\hat{\chi}(X,t) &= \exp\left\{t\left[\hat{H},\ldots\right]_{\boldsymbol{\mathcal{D}}}\right\}\hat{\chi}(X)\\ &= \exp\left\{it\mathcal{L}\right\}\hat{\chi}(X)\,, \end{aligned} \tag{11}$$

where the last equality defines the quantum-classical Liouville propagator. Quantum-classical averages are calculated as

$$\begin{aligned}\langle\hat{\chi}\rangle(t) &= \mathrm{Tr}'\int dX\hat{\rho}(X)\hat{\chi}(X,t)\\ &= \mathrm{Tr}'\int dX\hat{\rho}(X,t)\hat{\chi}(X)\,, \end{aligned} \tag{12}$$

where $\hat{\rho}(X)$ is the quantum-classical density matrix and $\hat{\rho}(X,t) = \exp\{-it\mathcal{L}\}\,\hat{\rho}(X)$. Either evolving the dynamical variables or the density matrix, one is still dealing with phase space dependent operators: *viz.* a form of generalized quantum-classical matrix mechanics. This theory has interesting formal features and a certain number of numerical schemes have been proposed to integrate the dynamics and calculate correlation functions [4, 15]. However, the algorithms have been limited, so far, to short-time dynamics because statistical uncertainties grows with time beyond numerical tolerance. With this in mind, it is interesting to see which features are found when the quantum-classical theory of Refs. [2] is mapped into a scheme of motion where phase space dependent wave fields, instead of operators, are used to represent the dynamics. As it is well known [8], in standard quantum mechanics, the correspondence between dynamics in the Heisenberg and in the Schrödinger picture rests ultimately on the following operator identity:

$$e^{\hat{Y}}\hat{X}e^{-\hat{Y}} = e^{[\hat{Y},\ldots]}\hat{X}\,, \tag{13}$$

where $[\hat{Y},\ldots]\hat{X}\equiv[\hat{Y},\hat{X}]$. Thus, in quantum-classical theory, one would like to derive an operator identity analogous to that in Eq. (13). However, as already shown in Ref. [3], because of the non associativity of the quantum-classical bracket in Eq. (5), the identity that can be derived is

$$e^{\frac{it}{\hbar}\,[\hat{H},\ldots]_{\boldsymbol{\mathcal{D}}}\hat{\chi}} = \mathcal{S}\left(e^{\frac{it}{\hbar}\overrightarrow{\mathcal{H}}}\hat{\chi}e^{-\frac{it}{\hbar}\overleftarrow{\mathcal{H}}}\right)\,, \tag{14}$$

where the two operators

$$\overrightarrow{\mathcal{H}} = \hat{H} - \frac{\hbar}{2i}\left\{\hat{H},\ldots\right\}_{\boldsymbol{\mathcal{B}}} \tag{15}$$

$$\overleftarrow{\mathcal{H}} = \hat{H} - \frac{\hbar}{2i}\left\{\ldots,\hat{H}\right\}_{\boldsymbol{\mathcal{B}}} \tag{16}$$

have been introduced and $\mathcal{S}$ is an ordering operator which is chosen so that the left and the right hand side of Eq. (14), when the exponential operators are substituted with their series expansion, coincide by construction [3]. The existence of such an ordering problem, and of the ordering operator $\mathcal{S}$, in Eq. (14) is caused by the Poisson bracket parts of the operators in Eqs. (15) and (16). Thus, one can imagine that, by dealing properly with this bracket part, a solution can be found. Indeed, this can be achieved. To this end, one can start from the quantum-classical equation of motion for the density matrix written as

$$\begin{aligned}\frac{\partial\hat{\rho}}{\partial t} &= -\frac{i}{\hbar}\left[\begin{array}{cc}\hat{H} & \hat{\rho}\end{array}\right]\\ &\cdot\left[\begin{array}{cc}0 & 1-\frac{\hbar}{2i}\{\ldots,\ldots\}_{\boldsymbol{\mathcal{B}}}\\ -1+\frac{\hbar}{2i}\{\ldots,\ldots\}_{\boldsymbol{\mathcal{B}}} & 0\end{array}\right]\cdot\left[\begin{array}{c}\hat{H}\\ \hat{\rho}\end{array}\right]. \end{aligned} \tag{17}$$

As above discussed, in Eq. (17) the ordering problem arises from the terms in the right hand side containing the Poisson bracket operator $\{\ldots,\ldots\}_{\boldsymbol{\mathcal{B}}}$. Then, considering the identity $1=\hat{\rho}\cdot\hat{\rho}^{-1}=\hat{\rho}^{-1}\cdot\hat{\rho}$, Eq. (17) can be rewritten as

$$\begin{aligned}\partial_t\hat{\rho} &= -\frac{i}{\hbar}\left[\begin{array}{cc}\hat{H} & \hat{1}\end{array}\right]\\ &\cdot\left[\begin{array}{cc}0 & 1-\frac{\hbar}{2i}\{\ldots,\hat{\rho}\}_{\boldsymbol{\mathcal{B}}}\\ -1+\frac{\hbar}{2i}\{\hat{\rho},\ldots\}_{\boldsymbol{\mathcal{B}}} & 0\end{array}\right]\cdot\left[\begin{array}{c}\hat{H}\\ \hat{1}\end{array}\right]\\ &= -\frac{i}{\hbar}\left[\begin{array}{cc}\hat{H} & \hat{\rho}\hat{\rho}^{-1}\end{array}\right]\\ &\cdot\left[\begin{array}{cc}0 & 1-\frac{\hbar}{2i}\{\ldots,\hat{\rho}\}_{\boldsymbol{\mathcal{B}}}\\ -1+\frac{\hbar}{2i}\{\hat{\rho},\ldots\}_{\boldsymbol{\mathcal{B}}} & 0\end{array}\right]\cdot\left[\begin{array}{c}\hat{H}\\ \hat{\rho}^{-1}\hat{\rho}\end{array}\right]\\ &= -\frac{i}{\hbar}\left[\begin{array}{cc}\hat{H} & \hat{\rho}\end{array}\right]\cdot\boldsymbol{\mathcal{D}}_{\boldsymbol{\mathcal{B}},[\hat{\rho}]}\cdot\left[\begin{array}{c}\hat{H}\\ \hat{\rho}\end{array}\right], \end{aligned} \tag{18}$$

where

$$\boldsymbol{\mathcal{D}}_{\boldsymbol{\mathcal{B}},[\hat{\rho}]} = \left[\begin{array}{cc}0 & 1-\frac{\hbar}{2i}\{\ldots,\ln(\hat{\rho})\}_{\boldsymbol{\mathcal{B}}}\\ -1+\frac{\hbar}{2i}\{\ln(\hat{\rho}),\ldots\}_{\boldsymbol{\mathcal{B}}} & 0\end{array}\right] \tag{19}$$

The operator $\boldsymbol{\mathcal{D}}_{\boldsymbol{\mathcal{B}},[\hat{\rho}]}$ in Eq. (19) depends from the quantum-classical density matrix, $\hat{\rho}$, itself. However, if

one momentarily disregards this non-linear dependence, Eq. (18) can be manipulated algebraically in order to develop a wave picture of quantum-classical mechanics. To this end, one can introduce quantum-classical wave fields, $|\psi(X)\rangle$ and $\langle\psi(X)|$, and make the following *ansatz* for the density matrix

$$\hat{\rho}(X) \;=\; \sum_{\iota} w_{\iota} |\psi^{\iota}(X)\rangle\langle\psi^{\iota}(X)| \;, \tag{20}$$

where one has assumed that, because of thermal disorder, there can be many microscopic states $|\psi^{\iota}(X)\rangle$ ($\iota = 1,\ldots,l$) determining the same values for the macroscopic relevant observables [16]. In terms of the quantum-classical wave fields $|\psi^{\iota}(X)\rangle$ and $\langle\psi^{\iota}(X)|$, and considering the single state labeled by ι, Eq. (18) becomes

$$\begin{aligned} |\dot{\psi}^{\iota}(X)\rangle\langle\psi^{\iota}(X)| \;+\; |\psi^{\iota}(X)\rangle\langle\dot{\psi}^{\iota}(X)| \;=\; \\ -\; \frac{i}{\hbar}\Big(\hat{H}|\psi^{\iota}(X)\rangle\langle\psi^{\iota}(X)| \\ +\; |\psi^{\iota}(X)\rangle\langle\psi^{\iota}(X)|\hat{H}\Big) \\ +\; \frac{1}{2}\Big(\Big\{\hat{H},\ln(\hat{\rho})\Big\}_{\mathcal{B}}|\psi^{\iota}(X)\rangle\langle\psi^{\iota}(X)| \\ -\; |\psi^{\iota}(X)\rangle\langle\psi^{\iota}(X)|\Big\{\ln(\hat{\rho}),\hat{H}\Big\}_{\mathcal{B}}\Big) \;. \end{aligned} \tag{21}$$

Equation (21) can be written as a system of two coupled equations for the wave fields [17]:

$$\begin{cases} i\hbar\frac{d}{dt}|\psi^{\iota}_{(X,t)}\rangle \;=\; \Big(\hat{H} - \frac{\hbar}{2i}\Big\{\hat{H},\ln(\hat{\rho}_{(X,t)})\Big\}_{\mathcal{B}}\Big)|\psi^{\iota}_{(X,t)}\rangle \\ -i\hbar\langle\psi^{\iota}_{(X,t)}|\overleftarrow{\frac{d}{dt}} \;=\; \langle\psi^{\iota}_{(X,t)}|\Big(\hat{H} - \frac{\hbar}{2i}\Big\{\ln(\hat{\rho}_{(X,t)}),\hat{H}\Big\}_{\mathcal{B}}\Big) \end{cases} \tag{22}$$

The equations for the wave fields in the set (22) are non-linear since their solution depends self-consistently from the density matrix defined in Eq. (20). These equations are also non-Hermitian since the operators $\Big\{\hat{H},\ln(\hat{\rho})\Big\}_{\mathcal{B}}$ and $\Big\{\ln(\hat{\rho}),\hat{H}\Big\}_{\mathcal{B}}$ are not Hermitian. However, this does not cause problems for the conservation of probability. The wave fields $|\psi^{\iota}\rangle$ and $\langle\psi^{\iota}|$ evolve according to the different propagators

$$\overrightarrow{\mathcal{U}}_{\mathcal{B},[\hat{\rho}]}(t) \;=\; \exp\left[-\frac{it}{\hbar}\left(\hat{H} - \frac{\hbar}{2i}\Big\{\hat{H},\ln(\hat{\rho})\Big\}_{\mathcal{B}}\right)\right] \tag{23}$$

$$\overleftarrow{\mathcal{U}}_{\mathcal{B},[\hat{\rho}]}(t) \;=\; \exp\left[-\frac{it}{\hbar}\left(\hat{H} - \frac{\hbar}{2i}\Big\{\ln(\hat{\rho}),\hat{H}\Big\}_{\mathcal{B}}\right)\right] \tag{24}$$

and time-propagating wave fields are defined by

$$|\psi^{\iota}(X,t)\rangle \;=\; \overrightarrow{\mathcal{U}}_{\mathcal{B},[\hat{\rho}]}(t)|\psi^{\iota}(X)\rangle \tag{25}$$

$$\langle\psi^{\iota}(X,t)| \;=\; \langle\psi^{\iota}(X,)|\overleftarrow{\mathcal{U}}_{\mathcal{B},[\hat{\rho}]}(t) \;. \tag{26}$$

Quantum classical averages can be written as

$$\langle\hat{\chi}\rangle(t) \;=\; \int dX \sum_{\iota} w_{\iota}\langle\psi^{\iota}(X,t)|\hat{\chi}|\psi^{\iota}(X,t)\rangle \;. \tag{27}$$

One can always transform back to the operator picture to show that probability is conserved.

A. Non-linear wave dynamics by means of non-Hamiltonian brackets

The wave equations in (22) were derived starting from the non-Hamiltonian commutator expressing the dynamics of phase space dependent operators [5]. It is interesting to recast quantum-classical wave dynamics itself by means of non-Hamiltonian brackets. It turns out that this form of the wave equations generalizes the mathematical formalism first proposed by Weinberg [10] in order to study possible non-linear effects in quantum mechanics (see Appendix A).

Consider a case in which a single state is present, *i.e.* $\iota = 1$. Then, consider the wave fields $|\psi\rangle$ and $\langle\psi|$ as coordinates of an abstract space, and denote the point of such a space as

$$\zeta = \begin{bmatrix} |\psi\rangle \\ \langle\psi| \end{bmatrix} \;. \tag{28}$$

Introduce the function

$$\mathcal{H} = \langle\psi|\hat{H}|\psi\rangle \;, \tag{29}$$

and the antisimmetric matrix operator

$$\mathbf{\Omega} = \begin{bmatrix} 0 & 1 - \frac{\hbar}{2i}\frac{\left\{\hat{H},\ln(\hat{\rho})\right\}_{\mathcal{B}}|\psi\rangle}{\hat{H}|\psi\rangle} \\ -1 + \frac{\hbar}{2i}\frac{\left\{\ln(\hat{\rho}),\hat{H}\right\}_{\mathcal{B}}|\psi\rangle}{\langle\psi|\hat{H}} & 0 \end{bmatrix} \tag{30}$$

Equations (22) can be written in compact form as

$$\begin{aligned} \frac{\partial\zeta}{\partial t} \;&=\; -\frac{i}{\hbar}\begin{bmatrix} \frac{\partial\mathcal{H}}{\partial|\psi\rangle} & \frac{\partial\mathcal{H}}{\partial\langle\psi|} \end{bmatrix}\cdot\mathbf{\Omega}\cdot\begin{bmatrix} \frac{\partial\zeta}{\partial|\psi\rangle} \\ \frac{\partial\zeta}{\partial\langle\psi|} \end{bmatrix} \\ &=\; -\frac{i}{\hbar}\{\mathcal{H},\zeta\}_{\mathbf{\Omega};\zeta} \;. \end{aligned} \tag{31}$$

Equations (22), or their compact "Weinberg-like" form in Eq. (31), express the wave picture for the quantum-classical dynamics of phase space dependent quantum degrees of freedom [2]. Such a wave picture makes one recognize the intrinsic non-linearity of quantum-classical dynamics. This specific features will be discussed, among other issues, in the next section.

IV. ADIABATIC BASIS REPRESENTATION AND SURFACE-HOPPING SCHEMES

Equations (22) are written in an abstract form. In order to devise a numerical algorithm to solve them one has to obtain a representation in some basis. Of course, any basis can be used but, since one would like to find a comparison with surface-hopping schemes, the adiabatic basis is a good choice. To this end, consider the following form of the quantum-classical Hamiltonian operator:

$$\hat{H} = \frac{P^2}{2M} + \hat{h}(R) \;, \tag{32}$$

where the first term provides the kinetic energy of the classical degrees of freedom with mass M while $\hat{h}(R)$ describes the quantum sub-system and its coupling with the classical coordinates R. The adiabatic basis is then defined by the following eigenvalue equation:

$$\hat{h}|\alpha;R\rangle = E_\alpha(R)|\alpha;R\rangle \ . \tag{33}$$

Since the non-linear wave equations in (22) have been derived from the bracket equation for the quantum-classical density matrix (17), simply by dealing in a suitable manner with the Poisson bracket terms, the most simple way to find the representation of the wave equations (22) in the adiabatic basis is first to represent Eq. (17) in such a basis and then to deal with the terms arising from the Poisson brackets. The adiabatic representation of Eq. (17) is [18]

$$\partial_t \rho_{\alpha\alpha'}(X,t) \ = \ -\sum_{beta\beta'} i\mathcal{L}_{\alpha\alpha',\beta\beta'}\rho_{\beta\beta'}(X,t) \ , \tag{34}$$

where

$$\begin{aligned} i\mathcal{L}_{\alpha\alpha',\beta\beta'} \ &= \ i\mathcal{L}^{(0)}_{\alpha\alpha',\beta\beta'}\delta_{\alpha\beta}\delta_{\alpha'\beta'} - J_{\alpha\alpha',\beta\beta'} \\ &= \ \left(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'}\right)\delta_{\alpha\beta}\delta_{\alpha'\beta'} - J_{\alpha\alpha',\beta\beta'} \end{aligned} \tag{35}$$

Here, $\omega_{\alpha\alpha'} = \left(E_\alpha(R) - E_{\alpha'}(R)\right)/\hbar \equiv E_{\alpha\alpha'}/\hbar$ and

$$iL_{\alpha\alpha'} = \frac{P}{M}\cdot\frac{\partial}{\partial R} + \frac{1}{2}\left(F_\alpha + F_{\alpha'}\right)\frac{\partial}{\partial P} \ , \tag{36}$$

where

$$F_\alpha = -\langle\alpha;R|\frac{\partial\hat{h}(R)}{\partial R}|\alpha;R\rangle \tag{37}$$

is the Hellmann-Feynman force for state α. The operator J that gives rise to nonadiabatic dynamics is

$$\begin{aligned} J_{\alpha\alpha',\beta\beta'} \ &= \ -\frac{P}{M}\cdot d_{\alpha\beta}\left(1+\frac{1}{2}S_{\alpha\beta}\cdot\frac{\partial}{\partial P}\right)\delta_{\alpha'\beta'} \\ &\quad -\frac{P}{M}\cdot d^*_{\alpha'\beta'}\left(1+\frac{1}{2}S^*_{\alpha'\beta'}\cdot\frac{\partial}{\partial P}\right)\delta_{\alpha\beta} \ , \end{aligned} \tag{38}$$

where $d_{\alpha\beta} = \langle\alpha;R|(\partial/\partial R)|\beta;R\rangle$ is the nonadiabatic coupling vector and

$$S_{\alpha\beta} = E_{\alpha\beta}d_{\alpha\beta}\left(\frac{P}{M}\cdot d_{\alpha\beta}\right)^{-1} \ . \tag{39}$$

Using Eqs. (36) and (38), the equation of motion for the density matrix in the adiabatic basis can be written explicitly as

$$\begin{aligned} \partial_t\rho_{\alpha\alpha'} \ &= \ -i\omega_{\alpha\alpha'}\rho_{\alpha\alpha'} - \frac{P}{M}\cdot\frac{\partial}{\partial R}\rho_{\alpha\alpha'} \\ &\quad -\frac{1}{2}\left(F_\alpha + F_{\alpha'}\right)\cdot\frac{\partial}{\partial P}\rho_{\alpha\alpha'} \\ &\quad -\sum_\beta \frac{P}{M}\cdot d_{\alpha\beta}\left(1+\frac{1}{2}S_{\alpha\beta}\cdot\frac{\partial}{\partial P}\right)\rho_{\beta\alpha'} \\ &\quad -\sum_{\beta'} \frac{P}{M}\cdot d^*_{\alpha'\beta'}\left(1+\frac{1}{2}S^*_{\alpha'\beta'}\cdot\frac{\partial}{\partial P}\right)\rho_{\alpha\beta'} \ . \end{aligned} \tag{40}$$

The wave fields $|\psi(X)\rangle$ and $\langle\psi(X)|$ can be expanded in the adiabatic basis as

$$\begin{aligned} |\psi(X)\rangle \ &= \ \sum_\alpha |\alpha;R\rangle\langle\alpha;R|\psi(X)\rangle = \sum_\alpha C_\alpha|\alpha;R\rangle \\ \langle\psi(X)| \ &= \ \sum_\alpha \langle\psi|\alpha;R\rangle\langle\alpha;R| = \sum_\alpha \langle\alpha;R|C^*_\alpha(X) \ , \end{aligned} \tag{41}$$

and the density matrix in Eq. (20) becomes

$$\rho_{\alpha\alpha'}(X,T) \ = \ \sum_\iota w_\iota C^\iota_\alpha(X,T)C^{\iota*}_{\alpha'}(X,T) \ . \tag{42}$$

In order to find two separate equations for C^ι_α and $C^{\iota*}_{\alpha'}$, one cannot insert Eq. (42) directly into Eq. (40) because of the presence of the derivatives with respect to the phase space coordinates R ad P. One must set Eq. (40) into the form of a multiplicative operator acting on $\rho_{\alpha\alpha'}$. To this end, for example, consider

$$\begin{aligned} \frac{\partial}{\partial P}\rho_{\beta\alpha'} \ &= \ \sum_\gamma\left(\frac{\partial}{\partial P}\rho_{\beta\gamma}\right)\delta_{\gamma\alpha'} = \sum_{\gamma\mu}\left(\frac{\partial}{\partial P}\rho_{\beta\gamma}\right)\rho^{-1}_{\gamma\mu}\rho_{\mu\alpha'} \\ &= \ \sum_\mu \frac{\partial(\ln\hat{\rho})_{\beta\mu}}{\partial P}\rho_{\mu\alpha'} \ . \end{aligned} \tag{43}$$

Equation (43) shows how to transform formally a derivative operator acting on $\hat{\rho}$ into a multiplicative operator which, however, depends on $\hat{\rho}$ itself. Therefore, Eq. (40) becomes

$$\begin{aligned} \partial_t\rho_{\alpha\alpha'} \ &= \ -\frac{i}{2}\omega_{\alpha\alpha'}\rho_{\alpha\alpha'} - \frac{i}{2}\omega_{\alpha\alpha'}\rho_{\alpha\alpha'} \\ &- \ \sum_\beta \frac{P}{M}\cdot d_{\alpha\beta}\rho_{\beta\alpha'} - \sum_{\beta'}\frac{P}{M}\cdot d^*_{\alpha'\beta'}\rho_{\alpha\beta'} \\ &- \ \frac{1}{2}\sum_\mu \frac{P}{M}\cdot\frac{\partial(\ln\rho)_{\alpha\mu}}{\partial R}\rho_{\mu\alpha'} - \frac{1}{2}\sum_\mu\frac{P}{M}\cdot\frac{\partial(\ln\rho)_{\mu\alpha'}}{\partial R}\rho_{\alpha\mu} \\ &- \ \frac{1}{2}\sum_\mu F_\alpha\frac{\partial(\ln\rho)_{\alpha\mu}}{\partial P}\rho_{\mu\alpha'} - \frac{1}{2}\sum_\mu F_{\alpha'}\cdot\frac{\partial(\ln\rho)_{\mu\alpha'}}{\partial P}\rho_{\alpha\mu} \\ &- \ \frac{1}{2}\sum_{\beta,\mu}\frac{P}{M}\cdot d_{\alpha\beta}S_{\alpha\beta}\cdot\frac{\partial(\ln\hat{\rho})_{\beta\mu}}{\partial P}\rho_{\mu\alpha'} \\ &- \ \frac{1}{2}\sum_{\beta',\mu}\frac{P}{M}\cdot d^*_{\alpha'\beta'}S^*_{\alpha'\beta'}\cdot\frac{\partial(\ln\hat{\rho})_{\mu\beta'}}{\partial P}\rho_{\alpha\mu} \ . \end{aligned} \tag{44}$$

Inserting the adiabatic expression for the density matrix, given in Eq. (42), into Eq. (44), one obtains, for each

quantum state ι, the following two coupled equations

$$\begin{aligned}
\dot{C}^{\iota}_{\alpha}(X,t) &= -\frac{i}{2}\omega_{\alpha\alpha'}C^{\iota}_{\alpha}(X,t) - \sum_{\beta}\frac{P}{M}\cdot d_{\alpha\beta}C^{\iota}_{\beta}(X,t) \\
&- \frac{1}{2}\sum_{\beta,\mu}\frac{P}{M}\cdot d_{\alpha\beta}S_{\alpha\beta}\cdot\frac{\partial(\ln\hat{\rho})_{\beta\mu}}{\partial P}C^{\iota}_{\mu}(X,t) \\
&- \frac{1}{2}\sum_{\mu}\frac{P}{M}\cdot\frac{\partial(\ln\rho)_{\alpha\mu}}{\partial R}C^{\iota}_{\mu}(X,t) \\
&- \frac{1}{2}\sum_{\mu}F_{\alpha}\frac{\partial(\ln\rho)_{\alpha\mu}}{\partial P}C^{\iota}_{\mu}(X,t) \qquad (45)
\end{aligned}$$

$$\begin{aligned}
C^{\iota *}_{\alpha'}(X,t) &= -\frac{i}{2}\omega_{\alpha\alpha'}C^{\iota *}_{\alpha'} - \sum_{\beta'}\frac{P}{M}\cdot d^{*}_{\alpha'\beta'}C^{\iota *}_{\beta'}(X,t) \\
&- \frac{1}{2}\sum_{\beta',\mu}\frac{P}{M}\cdot d^{*}_{\alpha'\beta'}S^{*}_{\alpha'\beta'}\cdot\frac{\partial(\ln\hat{\rho})_{\mu\beta'}}{\partial P}C^{\iota *}_{\mu}(X,t) \\
&- \frac{1}{2}\sum_{\mu}\frac{P}{M}\cdot\frac{\partial(\ln\rho)_{\mu\alpha'}}{\partial R}C^{\iota *}_{\mu}(X,t) \\
&- \frac{1}{2}\sum_{\mu}F_{\alpha'}\cdot\frac{\partial(\ln\rho)_{\mu\alpha'}}{\partial P}C^{\iota *}_{\mu}(X,t)\ . \qquad (46)
\end{aligned}$$

Quantum-classical averages of arbitrary observables can be calculated in the adiabatic as

$$\langle\hat{\chi}\rangle(t) = \sum_{\iota}w_{\iota}\sum_{\alpha\alpha'}\int dX C^{\iota}_{\alpha}(X,t)C^{\iota *}_{\alpha'}(X,t)\chi_{\alpha'\alpha}(X)\ , \qquad (47)$$

where the coefficients $C^{\iota}_{\alpha}(X,t)$ and $C^{\iota *}_{\alpha'}(X,t)$ are evolved according to Eqs. (45) and (46), respectively. Equations (45) and (46) are non-linear equations which couple all the adiabatic states used to analyze the system.

At this stage, a general discussion about such a non-linear character is required. With a wide consensus, quantum mechanics is seen as a linear theory. This leads to visualize quantum transitions as instantaneous *quantum jumps*. The linearity of the theory leads also to the need of considering infinite perturbative series which must be re-summed in some way in order to extract meaningful predictions. Density Functional Theory is an example of a non-linear theory [19] but it is usually considered just as a computational tool. However, there are other approaches to quantum classical theory that represent interactions by an intrinsic non-linear scheme [20]. It is not difficult to see how this is possible. Matter is represented by waves, this very same waves enter into the definition of the fields defining their interaction [21]. This point of view has been pursued by Jaynes [22] and Barut [23], among others. These non-linear approaches depicts quantum transitions as abrupt but continuous events [20] in which, to go from state $|1\rangle$ to state $|2\rangle$, the system is first brought by the interaction in a superposition $\alpha|1\rangle + \beta|2\rangle$, and then, as the interaction ends, it finally goes to state $|2\rangle$. It is understood that this is made possible by the non-linearity of such theories because, instead, a linear theory would preserve the superposition indefinitely. Incidentally, the picture of the transition process just depicted also emerges from the numerical implementation [4] of the nonadiabatic quantum-classical dynamics of phase space dependent operators [2]: The action of the operator J in Eq. (35) can build and destroy coherence in the system by creating and destroying superposition of states. As explained above, this is a feature of a non-linear theory. Such a non-linear character is simply hidden in the operator version of quantum-classical dynamics and clearly manifested in the wave picture of the very same quantum-classical evolution, which has been introduced in this paper.

Since Eqs. (45) and (46) are manifestly non-linear, their numerical integration require either to adopt an iterative self-consistent procedure, according to which one makes a first guess of $\rho_{\alpha\alpha'}$, as dictated by Eq. (42), calculates the evolved $C^{\iota}_{\alpha}(X,t)$ and $C^{\iota *}_{\alpha'}(X,t)$, and then continues until numerical convergence is obtained, or to choose a definite form for $\rho^{G}_{\alpha\alpha'}$, following physical intuition, and then calculating the time evolution, according to the form of Eqs. (45) and (46) which is obtained by using $\rho^{G}_{\alpha\alpha'}$. This last idea is already known within the Wigner formulation of quantum mechanics [24] as the method of *Wigner trajectories* [25]. It is also important to find some importance sampling scheme for the phase space integral in Eq. (47). Such sampling scheme may depend on the specific form $\chi_{\alpha\alpha'}$ of the observable. It is interesting to note that Eqs. (45), (46), and (47) can be used to address both equilibrium and non-equilibrium problems on the same footing. However, the dynamical picture provided by Eqs. (45) and (46) is very different both from that of the usual surface-hopping schemes [7] and from that of the nonadiabatic evolution of quantum-classical operators [4]. In order to appreciate this, for simplicity, one can consider a situation in which there is no thermal disorder in the quantum degrees of freedom so that $\iota = 1$: *viz.*, the density matrix becomes that of a pure state $\rho_{\alpha\alpha'}(X,t) \to C_{\alpha}(X,t)C^{*}_{\alpha'}(X,t)$. Then, equations (45) and (46) remain unaltered and one has just to remove the index ι from the coefficients. Therefore, it can be realized that no classical trajectory propagation, and no state switching are involved by Eqs. (45) and (46). Instead, one has to sample one phase space point and integrate the matrix equations.

Further study is required to devise efficient numerical algorithms to integrate Eqs. (45) and (46) and calculate averages.

V. CONCLUSIONS

In this paper the approach to the quantum-classical mechanics of phase space dependent operators has been recasted into a non-linear formalism for wave fields. To a single equation for the quantum-classical density matrix there correspond two coupled non-linear equations for phase space dependent wave fields. Such equations are not Hermitian but they define backward and forward

time-evolution in such a way as to conserve probability. The equations of motion for the wave fields have been re-expressed by means of a suitable non-Hamiltonian bracket and it has been shown that the emerging formalism generalizes the non-linear quantum mechanics proposed recently by Weinberg. Finally the non-linear wave equations have been represented into the adiabatic basis and some considerations have been made in order to devise effective numerical integration schemes. Future works will be devoted specifically to the investigation of numerical algorithms for simulating the quantum-classical dynamics of wave functions and for calculating averages within this approach.

Non-Hermitian, non-linear and non-Hamiltonian quantum theories might appear too speculative to some readers. Therefore, a general comment on the philosophy behind the approach developed in this paper may be useful. As far as it is currently known, nature obeys quantum mechanics which is a Hamiltonian and linear theory (this latter is a subtle issue, indeed; consider, for example, the discussion in Sec. IV). However, it is also widely known that computational methods for solving time-dependent quantum problems have limited applicability. A general strategy of computer simulation [26] is to relax some mathematical constraints of intractable theories in order to define generalized formalisms which are, instead, numerically tractable. In other words, the step from a linear and Hamiltonian theory to a non-linear and non-Hamiltonian formalism can be taken for trying new routes toward effective computational methods. This has been the spirit animating the development of the formalism presented in this paper.

Acknowledgment

I acknowledge Professor Kapral for suggesting the possibility of mapping the quantum-classical dynamics of operators into a wave scheme of motion. I am also very grateful to Professor P. V. Giaquinta for continuous encouragement and suggestions.

APPENDIX A: WEINBERG'S FORMALISM

Consider a quantum system in a state described by the wave fields $|\Psi\rangle$ and $\langle\Psi|$, where Dirac's bra-ket notation is used to denote $\Psi(r) \equiv \langle r|\Psi\rangle$ and $\Psi^*(r) \equiv \langle\Psi|r\rangle$. Observables are defined by functions of the type

$$a = \langle\Psi|\hat{A}|\Psi\rangle \ , \tag{A1}$$

where the operators are Hermitian, $\hat{A} = \hat{A}^\dagger$. Weinberg's formalism can be introduced by defining Poisson brackets in terms of the wave fields $|\Psi\rangle$ and $\langle\Psi|$. To this end, one considers the wave fields as "phase space" coordinates $\zeta \equiv (|\Psi\rangle, \langle\Psi|)$, so that $\zeta_1 = |\Psi\rangle$ and $\zeta_2 = \langle\Psi|$, and then introduce brackets of observables as

$$\{a, b\}_{\mathcal{B}} \ = \ \sum_{\alpha=1}^{2} \frac{\partial a}{\partial \zeta_\alpha} \mathcal{B}_{\alpha\beta} \frac{\partial b}{\partial \zeta_\beta} \ . \tag{A2}$$

The bracket in Eq. (A2) defines a Lie algebra and a Hamiltonian systems. Typically, the Jacobi relation is satisfied, *i.e.* $\mathcal{J} = \{a, \{b, c\}_{\mathcal{B}}\}_{\mathcal{B}} + \{c\,\{a, b\}_{\mathcal{B}}\}_{\mathcal{B}} + \{b, \{c, a\}_{\mathcal{B}}\}_{\mathcal{B}} = 0$. In order to obtain the usual quantum formalism, one can introduce the Hamiltonian functional in the form

$$\mathcal{H}[|\psi\rangle, \langle\psi|] \equiv \mathcal{H}[\zeta] = \langle\psi|\hat{H}|\psi\rangle \ , \tag{A3}$$

where $\hat{H}$ is the Hamiltonian operator of the system. Equations of motion for the wave fields can be written in compact form as

$$\frac{\partial \zeta}{\partial t} = \frac{i}{\hbar} \{\mathcal{H}[\zeta], \zeta\}_{\mathcal{B}} \ . \tag{A4}$$

The compact form of Eq. (A4) can be set into an explicit form as

$$\frac{\partial}{\partial t}|\Psi\rangle \ = \ \frac{i}{\hbar} \frac{\partial \mathcal{H}}{\partial \langle\Psi|} \mathcal{B}_{21} \tag{A5}$$

$$\frac{\partial}{\partial t}\langle\Psi| \ = \ \frac{i}{\hbar} \frac{\partial \mathcal{H}}{\partial |\Psi\rangle} \mathcal{B}_{12} \ . \tag{A6}$$

It is easy to see that, when the Hamiltonian function is chosen as in Eq. (A3), Eqs. (A4), or their explicit form (A5-A6), gives the usual formalism of quantum mechanics. It is worth to remark that in order not to alter gauge invariance, the Hamiltonian and the other observables must obey the homogeneity condition

$$\mathcal{H} = \langle\Psi|(\partial\mathcal{H}/\partial\zeta_2)\rangle = \langle(\partial\mathcal{H}/\partial\zeta_1)|\Psi\rangle \ . \tag{A7}$$

Weinberg showed how the formalism above given can be generalized in order to describe non-linear effects in quantum mechanics [10]. To this end, one must maintain the homogeneity condition, Eq. (A7), on the Hamiltonian but relax the constraint which assumes that the Hamiltonian must be a bilinear function of the wave fields. Thus, the Hamiltonian can be a general function given by

$$\tilde{\mathcal{H}} = \sum_{i=1}^{n} \rho^{-i} \mathcal{H}_i \ , \tag{A8}$$

where n is arbitrary integer that fixes the order of the correction, $\mathcal{H}_0 = h$, and

$$\begin{aligned} \mathcal{H}_1 \ &= \ \rho^{-1} \int dr dr' dr'' dr''' \Psi^*(r) \Psi^*(r') \\ &\times \ G(r, r', r'', r''') \Psi(r'') \Psi(r''') \ , \end{aligned} \tag{A9}$$

with analogous expressions for higher order terms. Applications and thorough discussions of the above formalism can be found in Ref. [10].

Once Weinberg's formalism is expressed by means of the symplectic form in Eq. (A4), it can be generalized very easily in order to obtain a non-Hamiltonian quantum algebra. To this end, one can substitute the antisymmetric matrix $\boldsymbol{\mathcal{B}}$ with another antisymmetric matrix $\boldsymbol{\Omega} = \boldsymbol{\Omega}[\zeta]$, whose elements might be functionals of $\zeta \equiv (|\Psi\rangle, \langle\Psi|)$ obeying the homogeneity condition in Eq. (A7). By means of $\boldsymbol{\Omega}$ a non-Hamiltonian bracket $\{\ldots,\ldots\}_{\boldsymbol{\Omega}}$ can be defined as

$$\{a,b\}_{\boldsymbol{\Omega}} \;=\; \sum_{\alpha=1}^{2} \frac{\partial a}{\partial \zeta\alpha} \Omega_{\alpha\beta}[\zeta] \frac{\partial b}{\partial \zeta\beta} \;. \tag{A10}$$

In general, the bracket in Eq. (A10) does no longer satisfy the Jacobi relation

$$\mathcal{J} = \{a,\{b,c\}_{\boldsymbol{\Omega}}\}_{\boldsymbol{\Omega}} + \{c\,\{a,b\}_{\boldsymbol{\Omega}}\}_{\boldsymbol{\Omega}} + \{b,\{c,a\}_{\boldsymbol{\Omega}}\}_{\boldsymbol{\Omega}} \neq 0 \;. \tag{A11}$$

Thus, non-Hamiltonian equations of motion can be written as

$$\frac{\partial \chi}{\partial t} = \frac{i}{\hbar}\{\mathcal{H},\zeta\}_{\boldsymbol{\Omega}} \;. \tag{A12}$$

In principle, the non-Hamiltonian theory, specified by Eqs. (A10), (A11), and (A12), can be used to address the problem of non-linear correction to quantum mechanics, as it was done in Refs. [10]. In the present paper, it has been shown that such a non-Hamiltonian and non-linear version of quantum mechanics is already implied when one formulates quantum-classical dynamics of operators by means of suitable brackets. As a matter of fact, it was shown that the quantum-classical theories of Refs. [2] can be mapped onto a wave formalism which has precisely the same form specified by Eqs. (A10), (A11), and (A12).

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