DOI: 10.1478/C1C8901002

AAPP | Atti della Accademia Peloritana dei Pericolanti
Classe di Scienze Fisiche, Matematiche e Naturali
ISSN 1825-1242

Vol. LXXXIX, No. 1, C1C8901002 (2011)

SAMPLING THE TIME EVOLUTION OF MIXED QUANTUM-CLASSICAL SYSTEMS

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ABSTRACT. Quantum mechanics is not logically closed with respect to the classical world. Its formalism unfolds as the quantization of a sub-set of classical Hamiltonians. The interpretation of quantum theory in terms of the measurement process inevitably requires to deal with systems composed by a mixture of both classical and quantum degrees of freedom. Moreover, when energy can flow between the quantum and classical degrees of freedom (*i.e.*, in the case of nonadiabatic dynamics), there are more theoretical difficulties in order to obtain a fully consistent quantum-classical formalism. In order to perform calculations, one can renounce to the usual Lie algebraic structure of well-established physical theories, adopt non-Hamiltonian brackets, and obtain a formalism for the dynamics and statistics of quantum-classical systems that has an affordable computational complexity. Recent progress in the algorithms for the sampling of nonadiabatic dynamics of quantum-classical systems at long time is reviewed here.

1. Introduction

The relation between quantum mechanics and classical theory has remained controversial since the birth of the quantum formalism [1]. It appears that the logical formulation of quantum mechanics inevitably needs a classical theory to be quantized [2]. Interestingly, recovering the classical limit from the quantized formalism is not at all trivial: the classical world seems to emerge from the quantized world through some complicated process, which is akin to a phase transition with singularities [3, 4].

Theories attempting to describe in a unified way systems comprising both classical and quantum degrees of freedom seem to be no less controversial or complicated [5]. For example, such theories are needed in cosmology to describe quantum phenomena taking place on the classical gravitational background [6, 7, 8]. Since fully quantum formalisms are in general exponentially complex and cannot be simulated by brute force, quantum-classical theories are widely used as approximate descriptions of systems where all coordinates are quantized. To this end, the quantum-classical approximation is needed to perform computer simulations of the dynamics of quantum systems in a condensed phase [5],

In this contribution, a particular approach to the formulation of quantum-classical dynamics is reviewed [9]. Such an approach is based on the partial Wigner representation of the quantum formalism. By means of a series of controllable approximations, it leads

to the formulation of the dynamics and statistical mechanics of systems comprising both quantum and classical degrees of freedom [10]. For computational purposes, such a dynamics can be represented in terms of stochastic trajectories (hopping between different energy surfaces). Such trajectories start from initial conditions that are sampled by means of Monte Carlo schemes [11]. The stochastic sampling of the dynamical trajectories is affected by numerical instabilities at long time, leading to big statistical errors. This imposes significant limitations on the application of the method. Overcoming such a problem is one of the fundamental goals of computational physics within this area. To this end, a generalized sampling algorithm has been recently shown to improve dramatically on the numerical stability of quantum-classical dynamics at long time [12, 13]. This is also reviewed.

This contribution is organized as follows. Section **2** describes the unusual relation between the classical and quantum world by looking at quantum mechanics as a theory of quantization. The importance of quantum-classical systems is discussed together with the open issues that must be faced by quantum-classical theories. Section **3** introduces a particular approach to the theory of quantum-classical systems. This is derived by means of controllable approximations from a rigorous theory where all coordinates are initially quantized. Section **4** reviews the algorithms used to sample the nonadiabatic dynamics of quantum-classical systems and shows their application to the spin-boson model. Finally, Section **5** presents conclusions and perspectives.

2. Quantization theory for classical events

Since Schrödinger's and Heisenberg's formulations (unified by Dirac's *transformation theory* [14]), quantum mechanics has never ceased to puzzle the minds of physicists. Perhaps, one of the reasons is that quantum mechanics is a logically open theory [2] that has classical mechanics as both its starting and final point. Since quantum mechanics provides results that can be experimentally tested, the final stage of a quantum process must be a classical phenomenon: the experimenter invariably observes something (*e.g.*, the instrument's readings) by means of his own senses. This means that there is nothing magical or mystical in a quantum laboratory. One does not observe waves instead of particles, or any form of smeared-out reality. There are only classical phenomena (*i.e.*, taking place in the classical world) that require a non-classical (quantum) *explanation*: we never observe a cat half-alive and half-dead; but there are some phenomena that might be interpreted in terms of a cat half-alive and half-dead. In other words, quantum mechanics provides a *hidden* mechanism for well-defined classical events whose space-time correlations are neither described nor explained by a classical theory. As usual, when using any language, some words or concepts cannot be explained in terms of other words contained in the same language and must be used with an intuitive meaning. In the same way, it is not at all easy to explain what one really means by saying that a theory is classical. Here, we just state that a theory is termed classical if it consists, at all its stages, of *events* that can be associated with well-defined probabilities. Quantum mechanics also describes events with well-defined probabilities at the end of a process. But its phenomena start from *superpositions* of events (whatever this may physically mean) that admit complex probability amplitudes. Hence, superpositions of events (and complex amplitudes) must be considered more fundamental than events (and probabilities). On the other hand, one cannot think of

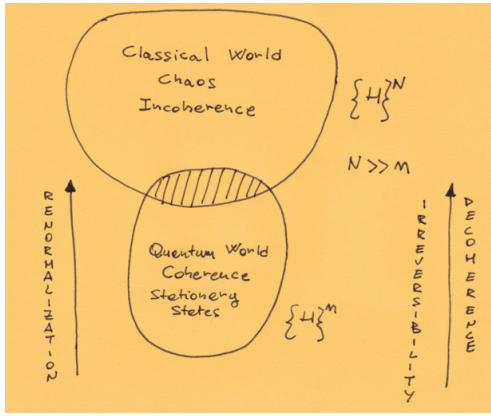

Figure 1. This picture symbolizes the peculiar relation between the quantum and the classical world. There is an overlap between the two worlds, but the classical world admits many more possible Hamiltonians, coordinates and states ($N >> n$) than the quantum world. Moreover, the processes leading from the quantum to the classical world are fundamentally irreversible. Such processes can be described by means of the integration over short wave-length degrees of freedom, as in renormalization.

superpositions of events without having first in mind well-defined events. Perhaps, it is simply this the origin of the logical openness of quantum theory.

This author has always thought of quantum mechanics as a theory of quantization. As it happens in Dirac's approach [14] (called canonical quantization), one has to start from a classical Hamiltonian, written in terms of canonical coordinates: $\{q, p\} = 1$, where $\{\ldots, \ldots\}$ is the Poisson bracket. Hence, it is possible to quantize the coordinates in such a way that $[\hat{q}, \hat{p}] = i\hbar\{\hat{q, p}\}$, where $[\ldots, \ldots]$ is the commutator. From a mathematical point of view, this constitutes the fundamental openness of quantum theory: in the author's knowledge, no method has been found so far to avoid the classical starting point of the theory. This issue was acknowledged, among many others, by Landau [2]: quantum mechanics needs a classical theory for its very formulation. Therefore, it is somewhat controversial to regard it as a fundamental theory on logical grounds. Once the quantization of the classical Hamiltonian has been performed, the Stone-von Neumann uniqueness theorem [15] (for a finite number of degrees of freedom) ensures that all the different representations can be connected through unitary transformations. This rules out (in the

majority of cases) the quantization of curvilinear and non-canonical coordinates. I believe this latter to be one of the mysteries of quantization, which still requires an understanding at a fundamental level. Figure 1 illustrates the peculiar relation between the classical and the quantum world. Classically, many more states and Hamiltonians are allowed. In fact, there are restrictions on the type of Hamiltonians that can be quantized. For example, chaotic dynamics seems to have no counterpart in the quantum realm. At the same time, there are quantum states that do not admit a classical limit. It seems that the two worlds can be connected only going through an interface region, showed in Fig. 1 as the dashed overlap of the two domains [16]. It also appears that the processes leading from the quantum to the classical world require some kind of fundamental irreversibility that can be represented in terms of the integration over short-wave length fluctuations [17], not unlike from what happens in the renormalization approach to the theory of phase transitions [18].

There are important exceptions to quantization by means of canonical commutation relations. The rigid rotor $H = L^2$, with $\{L_i, L_j\} = \epsilon_{ijk} L_k$, is an important example that is best quantized through non-canonical commutation relations: $[\hat{L}_i, \hat{L}_j] = i\hbar\{\hat{L_i, L_j}\}$ [2]. Spin degrees of freedom are also quantized in terms of non-canonical coordinates [2]. These types of non-canonical quantization procedures are studied by the approach of *Geometric Quantization* [19]. I believe that the unitary symmetry of quantum mechanics plays a fundamental role in permitting also non-canonical representations. In practice, to see which coordinates can be quantized unambiguously, one has to find whether a simple diagonal expression of the kinetic energy is possible, and then apply Dirac's correspondence rule between Poisson brackets of phase space functions and commutators of self-adjoint operators. Of course, it must be mentioned that non-local actions can be quantized through a Lagrangian approach, which was first proposed by Dirac [20] and brought to its logical completion by Feynman [21].

When dealing with systems with a continuous number of coordinates, $q_i \to q_x = \Phi(x)$, i.e., fields, some extra care is required in applying the quantization procedure. For example, the Stone-von Neumann uniqueness theorem is more subtle for such systems [15]. In practice, unitary symmetry and the form of the kinetic energy functional (together with the form of interaction, which must be polynomial) restrain the type of quantizable theories. When in doubt, one can physically discretize the field and go back to the usual quantization procedure. From such a practical point of view, there is no major conceptual difference between the quantization of particles and fields in quantum mechanics. Note that, as Feynman and Stuckelberg have shown, the creation-destruction of particles is a relativistic effect arising from the possibility of scattering backward-forward in time [22].

If one accepts the idea that classical events are generated by quantized processes and that human beings (*i.e.*, classical systems) can investigate the results of such processes, then (at least in this author's opinion) mere logic implies that classical events must also be included in the initial conditions of quantum processes. In other words, the classical experimental apparatus must be present at the beginning of a *quantum* event so that the investigation of any quantized process is possible. Hence, the following question naturally arises: should not the quantum formalism consider a mixture of classical and quantum coordinates from the very beginning? In my opinion, the affirmative answer to the previous question is the main logical motivation leading to the consideration of mixed quantum-classical theories. In order to emphasizes this point, Fig. 2 represents metaphorically the general features of

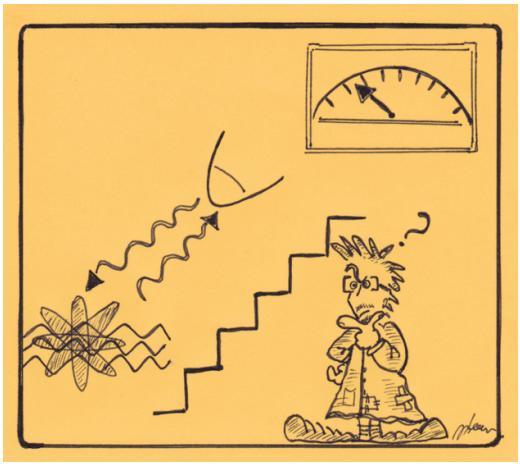

Figure 2. This picture symbolizes the general features of quantum processes. A probe interacts with a microscopic system (depicted in terms of atomic orbitals with accompanying waves) by means of the exchange of quanta (wavy lines with arrows) of some field. The stairs are a symbol for the not-so-well understood amplification (irreversible) process that must occur in order to reveal observable features by means of some instrument. The latter is depicted in the picture as a graded scale with a pointer. All this leaves the scientist puzzled.

a quantum process. Some instrument exchanges quanta (wavy lines with arrows) with a microscopic system, depicted in terms of atomic orbitals with superimposed waves. The effects of such an interaction must be amplified by a not-yet-understood process so that they are registered by a macroscopic (classical) pointer [17]. All this leaves the physicist in the picture puzzled. After a century from Planck and Einstein, the question remains: What is the quantum?

On a less fundamental level, quantum-classical theories can also be introduced as an approximation of descriptions where all coordinates are initially quantized. For example, they can approximate the yet unknown theory of quantum gravity in order to describe quantum effects on a classical gravitational background [6, 7].

Quantum-classical theories can also provide computable approximations of formalisms with exponential complexity, such as the dynamics of interacting quantum many-body systems in a condensed phase [5]. In the author's knowledge there are two main viable approaches to the calculation of quantum many-body phenomena in condensed matter systems. One is provided by time-dependent density functional theory [23] (which is so far

limited to the linear response regime), while the other approach is provided by mixed quantum-classical systems, *e.g.*, systems where one has to study few quantum degrees of freedom in a classical bath [5].

When studying quantum-classical systems there are two main situations that need to be considered. The first occurs when there is no energy flux between the quantum and the classical coordinates. Such theories are called adiabatic and they have been studied since the beginning of quantum mechanics [2]. They pose no particular problem (if one excludes the existence of so-called topological phases [24], which are, in fact, a form of nonadiabatic correction). Many equivalent formalisms are available to formulate adiabatic quantum-classical theories [25]. Perhaps, the simplest one adopts a Schrödinger's picture with a wave functional $|\Psi(X,t)\rangle$, and operators $\hat{H}(X,t)$, $\hat{\chi}(X,t)$, having a parametric dependence on the classical coordinates X.

A second situation (which is much more complicated than the adiabatic one) occurs when, instead, there is a flux of energy between the quantum and classical coordinates. Such theories are called nonadiabatic. The classical X coordinates exchange energy directly with the quantum $\hat{\chi}(X,t)$ operators. For such a reason, the Xs are dynamical degrees of freedom on the same footing as the $\hat{\chi}$s. Accordingly, the X-dependence of the quantum operator is no longer parametric. This leads to the so-called quantum back-reaction problem: when energy flows to or from the $\hat{\chi}$s, the energy of the Xs must be adjusted so that the total energy of the system is conserved. This turns out to be a difficult test for many formalisms. Typically, in the nonadiabatic case there are many different non-equivalent approaches: probably the theory does not admit a unique expression.

3. Nonadiabatic dynamics of quantum-classical systems

As it is well-known, for a system where all coordinates are quantized one can introduce an algebra in terms of the commutators of self-adjoint operators

$$[\hat{\chi}_1, \hat{\chi}_2] \quad = \quad \left[\begin{array}{cc} \hat{\chi}_1 & \hat{\chi}_2 \end{array} \right] \cdot \boldsymbol{\mathcal{B}} \cdot \left[\begin{array}{c} \hat{\chi}_1 \\ \hat{\chi}_2 \end{array} \right] \tag{1}$$

where χ_i, $i = 1, 2$, are arbitrary self-adjoint operators and the commutator is written in matrix form in terms of the co-symplectic matrix $\boldsymbol{\mathcal{B}}$:

$$\boldsymbol{\mathcal{B}} = \left[\begin{array}{cc} 0 & 1 \\ -1 & 0 \end{array} \right] . \tag{2}$$

The commutator algebra is a Lie algebra where the Jacobi relation is satisfied identically:

$$[[\hat{\chi}_1, \hat{\chi}_2], \hat{\chi}_3] + [[\hat{\chi}_3, \hat{\chi}_1], \hat{\chi}_2] + [[\hat{\chi}_2, \hat{\chi}_3], \hat{\chi}_1] = 0 . \tag{3}$$

An important consequence of the Jacobi relation is that the commutator algebra is invariant under time time translations:

$$\hat{U}(t - t_0)[\hat{\chi}_1(t_0), \hat{\chi}_2(t_0)] = [\hat{\chi}_1(t), \hat{\chi}_2(t)] , \tag{4}$$

where $\hat{U}(t-t_0)$ is the unitary operator realizing time-translations (*i.e.*, the dynamics) of the operators in the theory. In other words, relations established by means of the commutators, which appear in the expression for observable quantities of the theory (such as correlation functions), keep the same form regardless of the specific instant of time at which they are

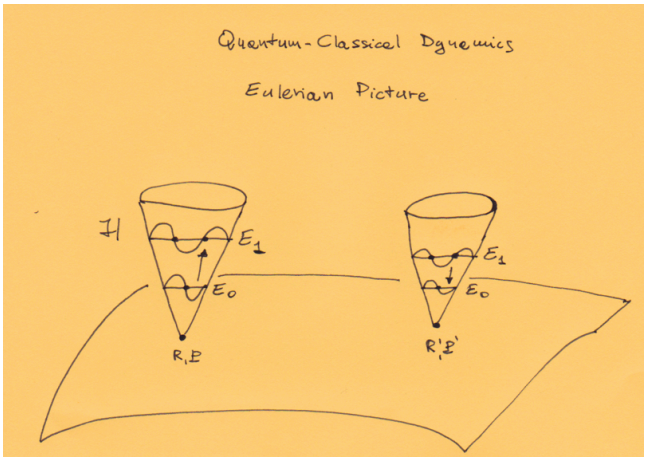

Figure 3. This drawing illustrates the so-called Eulerian picture of the quantum-classical theory. For every point in phase space, (R, P) or (R', P'), there is a Hilbert space (symbolyzed by a cone) where dynamics with transitions between energy levels takes place.

considered. This reflects the requirement that the expression of the laws (*i.e.*, the form of the equations) of physics should not depend on the instant of time considered.

It turns out that an algebra of quantum-classical operators [26] can be introduced along lines which are very close to those followed in the case of the standard Hilbert space formalism of quantum mechanics. One can start by considering hybrid mathematical objects such as $\hat{\chi}(R, P, t) = \hat{\chi}(X, t)$. These entities describes self-adjoint operators defined for every phase space coordinate $X = (R, P)$ of a classical-like manifold (see Fig. 3). For each point in the manifold, there is a Hilbert space. A generalized commutator (which was called non-Hamiltonian commutator in [26]) can be defined as

$$[\hat{\chi}_1(X), \hat{\chi}_2(X)]_{\boldsymbol{\mathcal{D}}} = \left[\begin{array}{cc} \hat{\chi}_1(X) & \hat{\chi}_2(X) \end{array} \right] \cdot \boldsymbol{\mathcal{D}} \cdot \left[\begin{array}{c} \hat{\chi}_1(X) \\ \hat{\chi}_2(X) \end{array} \right] , \tag{5}$$

where

$$\boldsymbol{\mathcal{D}} = \left[\begin{array}{cc} 0 & 1 + \frac{i\hbar}{2} \overleftarrow{\boldsymbol{\partial}} \cdot \boldsymbol{\mathcal{B}} \cdot \overrightarrow{\boldsymbol{\partial}} \\ -1 - \frac{i\hbar}{2} \overleftarrow{\boldsymbol{\partial}} \cdot \boldsymbol{\mathcal{B}} \cdot \overrightarrow{\boldsymbol{\partial}} & 0 \end{array} \right] , \tag{6}$$

with the derivative operator in phase space being defined by $\boldsymbol{\partial} = \partial/\partial X \equiv (\partial/\partial R, \partial/\partial P)$ (the arrows in Eq. (6) give the direction in which the operators act). The quantum-classical

commutator defined in Eq. (5) introduces an algebra of quantum-classical operators that has all the properties of a Lie algebra but one, *i.e.*, the Jacobi relation fails:

$$\begin{aligned}[[\hat{\chi}_1(X),\hat{\chi}_2(X)]_{\boldsymbol{\mathcal{D}}},\hat{\chi}_3(X)]_{\boldsymbol{\mathcal{D}}} &+ [[\hat{\chi}_3(X),\hat{\chi}_1(X)]_{\boldsymbol{\mathcal{D}}},\hat{\chi}_2(X)]_{\boldsymbol{\mathcal{D}}} \\ &+ [[\hat{\chi}_2(X),\hat{\chi}_3(X)]_{\boldsymbol{\mathcal{D}}},\hat{\chi}_1(X)]_{\boldsymbol{\mathcal{D}}} \neq 0 \ . \end{aligned} \tag{7}$$

Since almost all the properties of a Lie algebra are satisfied (the Jacobi relation is not), one might say that the quantum-classical commutator defines an *almost*-Lie algebra. One important consequence of the failure of the Jacobi relation is that algebraic relations between quantum-classical operators, which are defined in terms of the quantum-classical commutator in Eq. (5), are not time-translation invariant [26, 27]:

$$\hat{U}_{\boldsymbol{\mathcal{D}}}(t-t_0)[\hat{\chi}_1(t_0),\hat{\chi}_2(t_0)]_{\boldsymbol{\mathcal{D}}} \neq [\hat{\chi}_1(t),\hat{\chi}_2(t)]_{\boldsymbol{\mathcal{D}}} \ , \tag{8}$$

where $\hat{U}_{\boldsymbol{\mathcal{D}}}(t-t_0)$ is the quantum-classical propagator. In practice, this means that some relations obeyed by time dependent correlation functions within a Lie algebra are no longer valid in the almost-Lie algebra defined by the quantum-classical commutator. It is very important to note that the Heisenberg-like quantum-classical equation of motion

$$\frac{\partial}{\partial t}\hat{\chi}(X,t) = \frac{i}{\hbar}\left[\hat{H},\hat{\chi}(X,t)\right]_{\boldsymbol{\mathcal{D}}} \tag{9}$$

exactly conserves the energy. This constitutes a very nice feature of the quantum-classical (almost-Lie) algebra since it solves (at least in principle) the back-reaction problem. It must be noted that Eq. (9) is very naturally interpreted from an Eulerian point of view (see Fig. 3): fixing the phase space point X, the matrix element of $\hat{\chi}(X,t)$ can change in time. This means that Eq. (9) must be solved in principle for every X, as one would do in a field theory or, precisely, in the Eulerian picture of fluid dynamics.

The quantum-classical algebra, which has been introduced above as a postulate, can be obtained by means of controlled approximations, starting from a partial Wigner representation of Heisenberg's picture of quantum mechanics [9, 28]. One can start the derivation from the quantum Heisenberg equation of motion

$$\partial_t\hat{\chi} = \frac{i}{\hbar}[\hat{H}(\hat{r},\hat{R}),\hat{\chi}(t)] \ . \tag{10}$$

At this stage a partial Wigner transform can be defined as

$$\hat{H}_W(\hat{r},R,P) = \mathcal{W}\left\{\hat{H}(\hat{r},\hat{R})\right\} = \int dz e^{iP\cdot z/\hbar}\langle R-\frac{z}{2}|\hat{H}(\hat{r},\hat{R})|R+\frac{z}{2}\rangle \ . \tag{11}$$

Equation (11) assumes that the integral transform is taken over a subset only of the degrees of freedom of the system, *e.g.*, only over those degrees describing the bath in which the relevant quantum coordinates are embedded. The partial Wigner transform of the quantum commutator gives exactly

$$\mathcal{W}\left\{[\hat{H}(\hat{r},\hat{R}),\hat{\chi}(t)]\right\} = \hat{H}_W e^{\frac{i\hbar}{2}\overleftarrow{\boldsymbol{\partial}}\cdot\boldsymbol{\mathcal{B}}\cdot\overrightarrow{\boldsymbol{\partial}}}\hat{\chi}_W - \hat{H}_W e^{\frac{i\hbar}{2}\overleftarrow{\boldsymbol{\partial}}\cdot\boldsymbol{\mathcal{B}}\cdot\overrightarrow{\boldsymbol{\partial}}}\hat{\chi}_W \ , \tag{12}$$

and, upon taking a linear approximation of the exponential operator in Eq. (12), one obtains

$$\hat{H}_W e^{\frac{i\hbar}{2}\overleftarrow{\boldsymbol{\partial}}\cdot\boldsymbol{\mathcal{B}}\cdot\overrightarrow{\boldsymbol{\partial}}}\hat{\chi}_W \approx \hat{H}_W\hat{\chi}_W + \frac{i\hbar}{2}\hat{H}_W\overleftarrow{\boldsymbol{\partial}}\cdot\boldsymbol{\mathcal{B}}\cdot\overrightarrow{\boldsymbol{\partial}}\hat{\chi}_W \ . \tag{13}$$

This shows that the quantum-classical commutator in Eq. (5) is just a linear approximation of the partial Wigner transform of the standard quantum commutator:

$$\mathcal{W}\left\{[\hat{H},\hat{\chi}]\right\} \approx [\hat{H}_W,\hat{\chi}_W]_{\boldsymbol{\mathcal{D}}} \; . \tag{14}$$

Besides the exact energy-conservation property, another advantage of the quantum-classical algebra is that it naturally leads to a systematic definition of the statistical mechanics of quantum-classical systems [10]. To this end, one has to identify a quantum-classical Liouville operator in terms of the non-Hamiltonian commutator:

$$i\mathcal{L} = \frac{i}{\hbar}[\hat{H}_W,...]_{\boldsymbol{\mathcal{D}}} \; . \tag{15}$$

In turn, $i\mathcal{L}$ leads to the time evolution of a quantum-classical density matrix $\hat{\rho}_W(X,t)$:

$$\partial_t \hat{\rho}_W(t) = -i\mathcal{L}\hat{\rho}_W(t) \; . \tag{16}$$

On this base, statistical averages of quantum-classical properties can be rigorously calculated as

$$\langle \hat{\chi}_W(t) \rangle \;\; = \;\; \mathrm{Tr}' \int dX \hat{\rho}_W(X) e^{i\mathcal{L}t} \hat{\chi}_W(X) \; . \tag{17}$$

The statistical mechanics of equilibrium ensembles can be naturally determined by solving the equation

$$i\mathcal{L}\hat{\rho}_{W,e}(X) = 0 \; . \tag{18}$$

As it happens in the complete Wigner representation of quantum mechanics [29, 30], a solution for $\hat{\rho}_{W,e}(X)$ can be found as a series expansion in powers of $\hbar$. Linear response theory also follows from the quantum-classical Liouville equation, leading to a rigorous definition of transport coefficients [31, 32].

Despite the controlled sequence of approximations leading from the partial Wigner representation of Heisenberg quantum mechanics to the quantum-classical almost-Lie algebra, there has been a lot of controversy in the literature about the mere *possibility* of defining a consistent quantum-classical theory [33, 34, 35, 36, 37]. Here, the word "consistent" really means "Lie algebra". My opinion is that such a controversy is somewhat over-emphasized. My first objection is that we do not know very much at the moment about almost-Lie algebras, *i.e.*, not all consequences of having an almost-Lie algebra in a quantum-classical theory are known or fully understood. It might very well be that the almost-Lie algebra in a quantum-classical theory hides some deeper physics that remains to be unveiled. In the history of physics one can find plenty of concepts that were thought to be unsatisfying in the beginning and that were later regarded as cornerstones: Renormalization in quantum field theory [18] and entanglement-based non-locality [38, 39, 40] in quantum mechanics seem to me prominent examples. In any case, one can look at the almost-Lie algebra in quantum-classical theory as a theoretical *sacrifice* accepted in order to obtain a formalism with which calculations are possible in practice. This is the idea of Approximate Computational Complexity applied to theory [27]. In Approximate Computational Complexity a non-computable problem $\mathcal{P}$ characterized by a certain mathematical structure, described by constraints $\sigma_l = 0$, with $l = 1, \ldots, n_l$, is mapped onto another problem $\mathcal{P}'$ characterized by the relaxation of at least one constraint, for example $\sigma_1 \neq 0$. Typically, the mathematical structure of $\mathcal{P}'$ can be made to be dependent from some new numerical parameters

k_j, with $j = 1, \ldots, n_j$, controlling the violation of the constraint σ_1. The mapping is performed so that $\mathcal{P}'$ becomes computable. Moreover, for some specific choice of the numerical parameters k_j the solution of $\mathcal{P}'$ approximates that of $\mathcal{P}$ [27]. Almost-Lie algebras (or non-Hamiltonian theories) implement the same strategy at the level of the theory itself: by relaxing the Jacobi relation one is changing the structure of the theory. When the failure of the Jacobi relation does not affect properties of interest within a specific investigation, one has gained a computable theory (the almost-Lie algebra) in place of a non-computable one (the Lie algebra) [26, 27]. This author believes that the above discussion provides a logical (and practical) motivation for using quantum-classical approximations in the calculation of interacting quantum many-body systems.

4. Sampling algorithms

In order to devise an algorithm for the computer simulation of quantum-classical dynamics, the abstract equations of the almost-Lie algebra (*e.g*, the quantum classical Liouville equation) must be represented on some basis. The adiabatic basis is one possible convenient choice leading to a representation of nonadiabatic dynamics in quantum-classical systems in terms of surface-hopping trajectories. Without too much loss of generality, one can assume that the quantum-classical Hamiltonian is given by

$$H_W = \frac{P^2}{2M} + \hat{h}_W(\hat{r}, R) \; , \tag{19}$$

where $P^2/2M$ is the kinetic energy of the classical degrees of freedom while their potential energy, the energy of the quantum subsystem, and the coupling to the classical coordinates are given by the operator $\hat{h}_W(\hat{r}, R)$. The adiabatic basis is simply defined by the eigenstates of $\hat{h}_W(\hat{r}, R)$:

$$\hat{h}_W(\hat{r}, R)|\alpha; R\rangle = E_\alpha(R)|\alpha; R\rangle \; . \tag{20}$$

The matrix elements of the quantum-classical Liouville operators are then given by [9]

$$i\mathcal{L}_{\alpha\alpha',\beta\beta'} = \frac{i}{\hbar}\left(\omega_{\alpha\alpha'} + L_{\alpha\alpha'}\right)\delta_{\alpha\beta}\delta_{\alpha'\beta'} + J_{\alpha\alpha',\beta\beta'} \tag{21}$$

$$= i\mathcal{L}^{(0)}_{\alpha\alpha',\beta\beta'} + J_{\alpha\alpha',\beta\beta'} \; , \tag{22}$$

where a classical-like Liouville operator has been defined as

$$iL_{\alpha\alpha'} = \frac{P}{M}\cdot\nabla_R + \frac{1}{2}\left(F^{\alpha}_W + F^{\alpha'}_W\right)\cdot\nabla_P \; , \tag{23}$$

and $J_{\alpha\alpha',\beta\beta'}$ is a purely off-diagonal transition operator changing the quantum states and the momenta of the classical degrees of freedom; it is defined by

$$J_{\alpha\alpha',\beta\beta'} = \frac{P}{M}\cdot d_{\alpha\beta}(R)\left(1 + \frac{1}{2}\frac{\Delta E_{\alpha\beta} d_{\alpha\beta}(R)}{\frac{P}{M}\cdot d_{\alpha\beta}(R)}\nabla_P\right)\delta_{\alpha'\beta'} \tag{24}$$

$$+ \frac{P}{M}\cdot d^*_{\alpha'\beta'}(R)\left(1 + \frac{1}{2}\frac{\Delta E_{\alpha'\beta'} d^*_{\alpha'\beta'}(R)^*}{\frac{P}{M}\cdot d_{\alpha'\beta'}(R)}\nabla_P\right)\delta_{\alpha\beta} \tag{25}$$

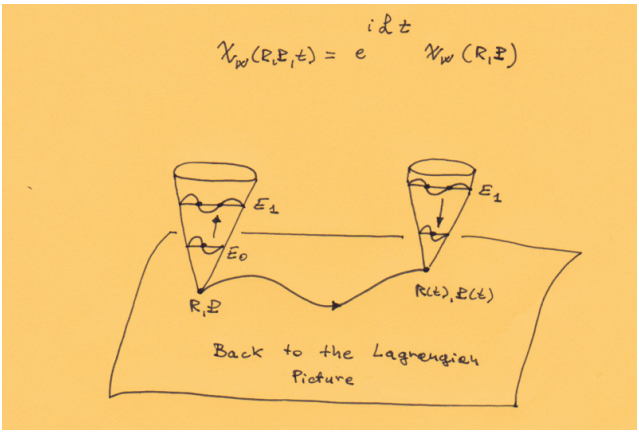

Figure 4. This drawing illustrates how the action of the quantum-classical Liouville operator, $i\mathcal{L}$, leads to a representation of the Eulerian picture of quantum-classical dynamics in terms of Lagrangian trajectories: a change of probability at (R, P) can occur because a different configuration at (R', P') is mapped onto (R, P) following a Lagrangian trajectory.

At this point, it is worth discussing one of the subtlest points of quantum-classical dynamics. In fact, in the previous section and in Fig. 3, such a dynamics has been interpreted very naturally within an Eulerian point of view, according to which X is fixed and the abstract equations of motion, Eq. (9), or their representation in the adiabatic basis, given in terms of the Liouville operators in Eq. (22), must be solved for every $X = (R, P)$, which is considered fixed. However, the total Liouville operator in the adiabatic basis is defined in terms of the classical-like Liouville operator in Eq. (23). The action of this latter operator is very naturally interpreted in terms of propagation of trajectories. As a result, the time-dependence of matrix elements of arbitrary operators $\hat{\chi}(X, t)$ in the Eulerian picture of quantum-classical dynamics can be more conveniently calculated in the adiabatic basis by using a Lagrangian point of view (see Fig. 4). According to this, for every fixed X, an ensemble of trajectories is propagated so that X will vary in time along each trajectory of the ensemble. Very different phase space points can be reached at the end of each trajectory. In any case, they all contribute to the time dependence of matrix elements at the initial X (*i.e.*, the Eulerian picture is more fundamental in quantum-classical dynamics).

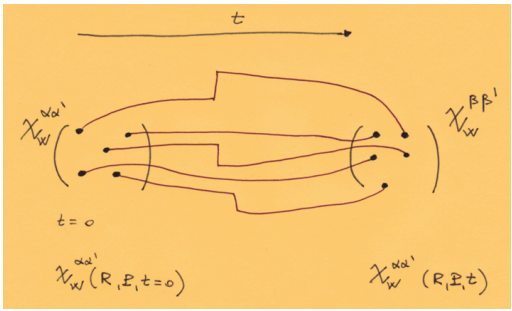

Figure 5. This picture represents the calculation of the nonadiabatic dynamics of an observable in terms of a swarm of surface-hopping trajectories. The observable $\hat{\chi}_W(X,t)$ is represented at $t = 0$ by the set of values assumed at the point X. Surface hopping trajectories are propagated so that final points $X(t)$ are obtained. The observable is evaluated at the new points and is also multiplied by the sampling weights (and phase factors) associated to its trajectory. One must remember that all this is really implementing an Eulerian picture of quantum-classical dynamics so that the final points $X(t)$ and states (β, β'), at the end of the Lagrangian trajectory, are just a means to calculate the time dependence of the matrix elements (α, α') at X. Once such a time dependence has been found, weighted averages over X can be calculated in order to obtain observable properties.

The action of the transition operator in Eq. (25) must be considered within a Lagrangian implementation of the Eulerian quantum-classical dynamics discussed above. The definition in Eq. (25) is exact but would lead to a calculation with exponential complexity because of the branching of trajectories caused by the action of the exact J operator (it is worth remembering that J represents the quantum transitions caused by the interaction with the classical coordinates). Hence, in order to obtain a computable algorithm one can perform the so-called momentum-jump approximation of the transition operator [11]:

$$J_{\alpha\alpha',\beta\beta'} \approx J^{\mathrm{MJ}}_{\alpha\alpha',\beta\beta'} \tag{26}$$

$$= \frac{P}{M}\cdot d_{\alpha\beta}(R)\exp\left[\frac{1}{2}\frac{\Delta E_{\alpha\beta} d_{\alpha\beta}(R)}{\frac{P}{M}\cdot d_{\alpha\beta}(R)}\nabla_P\right]\delta_{\alpha'\beta'} \tag{27}$$

$$+ \frac{P}{M}\cdot d^*_{\alpha'\beta'}(R)\exp\left[\frac{1}{2}\frac{\Delta E_{\alpha'\beta'} d^*_{\alpha'\beta'}(R)}{\frac{P}{M}\cdot d^*_{\alpha'\beta'}(R)}\nabla_P\right]\delta_{\alpha\beta} \tag{28}$$

$$= \mathcal{T}_{\alpha\to\beta} + \mathcal{T}_{\alpha'\to\beta'}\ . \tag{29}$$

In the momentum-jump approximation each of the two transition operators on the right hand side of Eq. (29) change the quantum state and produce a shift of the classical momenta:

$$\mathcal{T}_{\alpha\to\beta} P = P_{\alpha\to\beta} = P + \Delta^{\rm MJ}_{\alpha\beta} P \, . \tag{30}$$

Even if the momentum-jump approximation greatly simplifies the representation of nonadiabatic dynamics, the calculation of

$$\chi_W^{\alpha\alpha'}(X,t) = \sum_{\beta\beta'} \left(e^{\frac{it}{\hbar}\mathcal{L}} \right)_{\alpha\alpha',\beta\beta'} \chi_W^{\beta\beta'}(X) \tag{31}$$

cannot be performed exactly since it is still of exponential computational complexity. What one can do in order to obtain a computable algorithm is mapping the propagation onto a stochastic process with an importance sampling of the occurrence of the quantum transitions [11]. Figure 5 gives a pictorial representation of quantum-classical dynamics in terms of hopping trajectories. For small coupling strengths between the quantum and the classical subsystems, one can use a linear approximation of the quantum-classical propagator for a small time step τ:

$$\left(e^{i\mathcal{L}\tau} \right)_{\alpha\alpha',\beta\beta'} \approx e^{i\mathcal{L}^{(0)}_{\alpha\alpha'}\tau} \delta_{\alpha\beta}\delta_{\alpha'\beta'} \left(1 + \tau J^{\rm MJ}_{\alpha\alpha',\beta\beta'} \right) \, , \tag{32}$$

where at each time step one has to sample the occurrence of transitions (due to the action of $J_{\alpha\alpha',\beta\beta'}$). A trajectory of finite length is obtained by a concatenation of many short time steps. This leads to a representation of nonadiabatic dynamics in terms of piecewise deterministic trajectories, connected by quantum transitions.

A primitive sampling scheme of the nonadiabatic transitions [41] can be defined upon introducing the probability $\mathcal{P}^{(0)}_{\alpha\to\beta}$ of realizing the transition $\alpha \to \beta$, together with the probability of rejecting such a transition, $\mathcal{Q}^{(0)}_{\alpha\to\beta}$. Naturally, the normalization condition

$$\mathcal{P}^{(0)}_{\alpha\to\beta} + \mathcal{Q}^{(0)}_{\alpha\to\alpha} = 1 \tag{33}$$

must be obeyed. In the primitive scheme the transition probabilities are defined as

$$\mathcal{P}^{(0)}_{\alpha\to\beta} = \frac{\tau|\frac{P}{M}\cdot d_{\alpha\beta}|}{1+\tau|\frac{P}{M}\cdot d_{\alpha\beta}|} = \frac{\tau|\langle\alpha|\dot{\beta}\rangle|}{1+\tau|\langle\alpha|\dot{\beta}\rangle|} \, , \tag{34}$$

$$\mathcal{Q}^{(0)}_{\alpha\to\beta} = \frac{1}{1+\tau|\langle\alpha|\dot{\beta}\rangle|} \, . \tag{35}$$

The definitions (34) and (35) naturally arise by considering the weighting factor $(P/M)\cdot d_{\alpha\beta}$ appearing in the transition operator in Eq. (29). Because of the sampling scheme, each trajectory entering in a stochastic realization of the propagation in Eq. (31) acquires a multiplicative weighting factor at each time step τ equal to $[\mathcal{P}^{(0)}_{\alpha\to\beta}]^{-1}$ when the transition $\alpha \to \beta$ is accepted, and to $[\mathcal{Q}^{(0)}_{\alpha\to\beta}]^{-1}$ when it is rejected. The total weight of the trajectory grows in time and this leads to numerical instabilities, since after a certain time threshold (which varies depending on the particular model and numerical parameters of the calculation) the statistical fluctuations of the observable are amplified excessively. This numerical amplification of statistical fluctuations is an artifact of the primitive sampling scheme.

One can note that the spurious amplification of fluctuations due to the sampling weight could be tamed if a rejected transition would have a weight equal to unity (as expected in

an adiabatic scheme). In such a way the growth of the statistical weight could be limited. Since the primitive transition probabilities in Eqs. (34) and (35) are to a certain extent arbitrary, one could redefine them in terms of an additional weight $w(c_{\mathcal{E}})$ [12], depending on the numerical parameter $c_{\mathcal{E}}$. This idea leads to the expressions

$$\mathcal{P}_{\alpha\to\beta} = \frac{\tau w\left(c_{\mathcal{E}}\right)\left|\langle\alpha|\dot{\beta}\rangle\right|}{1+\tau w\left(c_{\mathcal{E}}\right)\left|\langle\alpha|\dot{\beta}\rangle\right|} , \tag{36}$$

$$\mathcal{Q}_{\alpha\to\alpha} = 1-\mathcal{P}_{\alpha\to\beta} . \tag{37}$$

Many choices for w can be devised. At the time of writing we have (successfully) tested the following recipe arising from considering the energy variation associated to a quantum transition

$$\mathcal{E}_{\alpha\alpha',\beta\beta'} = \frac{P'^2}{2M}+\frac{1}{2}\left(E_{\alpha}(R)+E_{\alpha'}(R)\right)-\frac{P^2}{2M}-\frac{1}{2}\left(E_{\beta}(R)+E_{\beta'}(R)\right) , \tag{38}$$

upon defining the generalized weight as

$$w\left(c_{\mathcal{E}}\right) = \left\{ \begin{array}{cc} 1 & \text{if } |\mathcal{E}_{\alpha\alpha',\beta\beta'}| \leq c_{\mathcal{E}} \\ 0 & \text{otherwise} \end{array} \right. . \tag{39}$$

The effect of the generalized sampling weight defined in Eqs. (36), (37), (38), and (39) is that of realizing a pruning of the allowed nonadiabatic transitions: out of the whole ensemble, only those transitions with $\mathcal{E}_{\alpha\alpha',\beta\beta'} = 0$ are performed. In those regions the variation of the momenta because of the quantum back-reaction is small. This controls the numerical validity of the momentum-jump approximation and improves the numerical stability of the sampling scheme.

This can be illustrated by performing some numerical calculations of the relaxation dynamics of the spin-boson model [12]. The spin-boson model [42] is defined by the following Hamiltonian:

$$\hat{H}_W = \hat{H}_S + H_{W,B} + \hat{H}_{W,SB} , \tag{40}$$

where the system Hamiltonian $\hat{H}_S$ describes a tunnelling spin

$$\hat{H}_S = -\Omega\hat{\sigma}_x , \tag{41}$$

the bath Hamiltonian is given in terms of a number N of harmonic oscillators

$$H_{W,B} = \sum_{J=1}^{N}\frac{P_J^2}{2}+\frac{1}{2}\omega_J^2 R_J^2 , \tag{42}$$

and the spin-oscillator coupling is linear

$$\hat{H}_{W,SB} = -\hat{\sigma}_z\sum_{J=1}^{N} c_J R_J . \tag{43}$$

In Eqs. (41) and (43), $\hat{\sigma}_x$ and $\hat{\sigma}_z$ are the Pauli spin matrices. One must note that adimensional coordinates are used [11]. The phase space coordinates of the oscillators are (R_J, P_J), while ω_J and c_J are oscillator frequencies and coupling constants of the spin, respectively. Their values are chosen in order to provide an Ohmic spectral density of the bath [42].

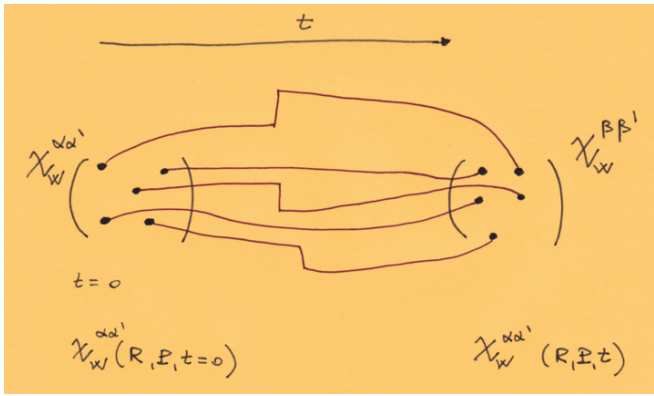

Figure 6. Comparison of the population decay calculated by means of the generalized sampling (black bullet) and by means of the primitive sampling (white triangles). The parameter values of the calculation are $\beta = 0.3$, $\Omega = 1/3$, and $\xi = 0.007$. The generalized sampling scheme remains stable, with small statistical errors, up to $t = 30$, while the primitive sampling experiences too large numerical fluctuations already at $t = 15$.

The relaxation dynamics of this model has been investigated by considering an initial density matrix (written in the subsystem basis) describing a bath in thermal equilibrium with the spin in an excited state:

$$\rho_W(t=0) = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \rho^{(\mathrm{eq})}_{W,B}(X;\beta) \; . \tag{44}$$

Time-evolution and the coupling to the bath lead to a dissipation of the population of the excited state of the spin. Figure 6 compares the decay of the population at long time calculated by means of the primitive sampling with that calculated by means of the generalized sampling scheme for the set of parameter values $\beta = 0.3$, $\Omega = 1/3$, and $\xi = 0.007$. The generalized sampling scheme remains stable, with small statistical errors, up to $t = 30$, while the primitive sampling experiences large numerical fluctuations already at $t = 15$. A more dramatic improvement is obtained for the parameter values of $\beta = 12.5$, $\Omega = 0.4$, and $\xi = 0.09$. These results are shown in Fig. 7. In this case the generalized sampling scheme remains stable up to $t = 100$ while the primitive recipe already fails at $t = 12$.

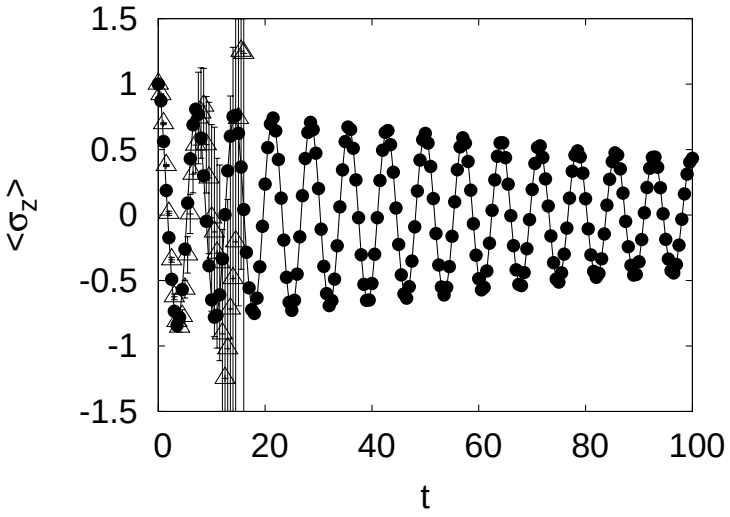

Figure 7. Comparison of the population decay calculated by means of the generalized sampling (black bullets) and by means of the primitive sampling (white triangles). The parameter values of the calculation are $\beta = 12.5$, $\Omega = 0.4$, and $\xi = 0.09$. The generalized sampling scheme remains stable, with small statistical errors, up to $t = 100$, while the primitive sampling experiences too large numerical fluctuations already at $t = 12$.

5. Conclusions and perspectives

Quantum-classical formalisms lie at the very heart of the conceptual structure of quantum mechanics. From a practical perspective, they provide an approximate computational theory of quantum dynamics. The statistical mechanics of quantum-classical systems can be rigorously defined by means of non-Hamiltonian brackets, leading to a quantum-classical Liouville equation for the density matrix. Systematic and computable approximations to the back-reaction problem can also be found. The momentum-jump approximation is one of these and it has been proven to give good numerical results. The nonadiabatic dynamics of quantum-classical systems is mapped for computational purposes onto a stochastic process comprised of adiabatic trajectory pieces and quantum jumps. A generalized mathematical structure for the long time sampling of quantum-classical dynamics has been found and shown to provide exceptionally good numerical results in the case of the relaxation dynamics of the spin-boson model.

The generalized structure for the stochastic sampling of nonadiabatic dynamics opens some interesting perspectives for future applications. One can think of applying the algorithm to processes involving quantum transport in models of both solid state devises and biological systems, where stability at long times is required. Moreover, the choice of w is by no means unique and one can imagine alternative definitions of the sampling weight specifically suited for the problem under investigation.

Acknowledgments

I am grateful to the *Accademia Peloritana dei Pericolanti* for the invitation. I am very pleased that my wife Marika drew Figure 2 in this manuscript. I plan to exploit her illustrations more and more in the future.

This work is based upon research supported by the National Research Foundation of South Africa.

References

[1] J. A. Wheeler and W. H. Zurek, *Quantum Theory and Measurement* (Princeton University Press, Princeton, 1984).
[2] L. D. Landau and L. M. Lifshitz, *Quantum Mechanics (Non Relativistic Theory)* (Butterworth-Heinemann, London, 1981).
[3] M. V. Berry, "Quantum physics on the edge of chaos", *New Scientist* **19**, 44 (1987).
[4] M. V. Berry, "Semiclassical Mechanics of regular and irregular motion" in *Les Houches Lecture Series Session XXXVI*, edited by G. Iooss, R. H. G. Helleman, and R. Stora (North Holland, Amsterdam, 1983), pp. 171-271.
[5] *Classical and Quantum Dynamics in the Condensed Phase Simulations*, edited by B. J. Berne, G. Ciccotti, and D. F. Coker (World Scientific, Singapore, 1998).
[6] N. D. Birrell and P. C. W. Davies, *Quantum Fields in Curved Space* (Cambridge University Press, Cambridge, 1994).
[7] R. M. Wald, *Quantum Field Theory in Curved Spacetime and Black Hole Thermodynamics* (The University of Chicago Press, Chicago, 1994).
[8] A. Anderson, "Quantum backreaction on classical variables", *Phys. Rev. Lett.* **74**, 621 (1995).
[9] R. Kapral and G. Ciccotti, "Mixed quantum-classical dynamics", *J. Chem. Phys.* **110**, 8919 (1999).
[10] S. Nielsen, R. Kapral, and G. Ciccotti, "Statistical mechanics of quantum-classical systems", *J. Chem. Phys.* **115**, 5805 (2001).
[11] A. Sergi, D. Mac Kernan, G. Ciccotti, and R. Kapral, "Simulating quantum dynamics in classical environments", *Theor. Chem. Acc.* **110**, 49 (2003).
[12] A. Sergi and F. Petruccione, "Sampling quantum dynamics at long time", *Phys. Rev. E* **81**, 032101 (2010).
[13] D. Uken, A. Sergi, and F. Petruccione, "Stochastic simulation of nonadiabatic dynamics at long time", *arXiv:1003.317 [quant-ph]* (2010).
[14] A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford University Press, Oxford, 1982).
[15] J. Rosenberg, "A selective history of the Stone-von Neumann theorem", *Contemp. Math.* **365**, 123 (2004).
[16] P. R. Holland, *The Quantum Theory of Motion* (Cambridge University press, Cambridge, 1993).
[17] L. E. Ballentine, *Quantum Mechanics* (World Scientific, Singapore, 2001).
[18] M. Le Bellac, *Quantum Statistical Field Theory* (Oxford University Press, Oxford, 1991).
[19] N. M. J. Woodhouse, *Geometric Quantization* (Oxford University Press, Oxford, 1997).
[20] P. A. M. Dirac, "The Lagrangian in Quantum Mechanics", *Physikalische Zeitschrift der Sowjetunion* **3**, 1 (1993).
[21] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
[22] R. P. Feynman, "The reason for antiparticles" in *Elementary particles and the Laws of Physics: The 1986 Dirac Memorial Lectures*, edited by R. P. Feynman and S. Weinberg (Cambridge University Press, Cambridge, 1999).
[23] *Time-Dependent Density Functional Theory*, edited by M. A. L. Marques, C. A. Ullrich, F. Nogueira, and A. Rubio (Springer, Berlin Heidelberg, 2006).
[24] *Geometric Phases in Physics*, edited by A. Shapere and F. Wilczek (World Scientific, Singapore, 1988).
[25] *Classical and Quantum Dynamics in Condensed Phase Simulations*, Proceedings of the International School of Physics "Computer Simulation of Rare Events and the Dynamics of Classical and Quantum Condensed-Phase Systems", edited by B. J. Berne, Giovanni Ciccotti, and D. F. Coker (World Scientific, Singapore, 1998).
[26] A. Sergi, "Non-Hamiltonian commutators in Quantum Mechanics", *Physical Review E* **72**, 066125 (2005).

[27] A. Sergi and P. V. Giaquinta, "On computational strategies in molecular dynamics simulation", *Physics Essays* **20**, 629 (2007).
[28] A. Sergi, I. Sinayskiy, and F. Petruccione, "Numerical and analytical approach to the quantum dynamics of two coupled spins in bosonic baths", *Phys. Rev. A* **80**, 012108 (2009).
[29] E. Wigner, "On the quantum correction for thermodynamic equilibrium", *Phys. Rev* **40**, 749 (1932).
[30] M. Hillery, R. F. O'Connell, M. O. Scully, and E. P. Wigner, "Distribution functions in physics: Fundamentals", *Phys. Rep.* **106**, 121 (1984).
[31] A. Sergi and R. Kapral, "Quantum-classical dynamics of nonadiabatic chemical reactions", *J. Chem. Phys.* **118**, 8566 (2003).
[32] H. Kim and R. Kapral, "Quantum reaction rates and sampling of quantum equilibrium structure", *J. Chem. Phys.* **127**, 226101 (2007).
[33] O. V. Prezhdo and V. V. Kisil, "Mixing quantum and classical mechanics", *Phys. Rev. A* **56**, 162 (1997).
[34] J. Caro and L. L. Salcedo, "Impediments to mixing classical and quantum dynamics", *Phys. Rev. A* **60**, 842 (1999).
[35] O. V. Prezhdo, "A quantum-classical bracket that satisfies the Jacobi identity", *J. Chem. Phys.* **124**, 201104 (2006).
[36] L. L. Salcedo, "Comment on 'A quantum-classical bracket that satisfies the Jacobi identity' [J. Chem. Phys. **124**, 201104 (2006)]", *J. Chem. Phys.* **126**, 057101 (2007).
[37] O. V. Prezhdo, "Reply to "Comment on 'A quantum-classical bracket that satisfies the Jacobi identity' " [J. Chem. Phys. 124, 201104 (2006)]", *J. Chem. Phys.* **126**, 057102 (2007).
[38] A. Aczel, *Entanglement* (Penguin Books, New York, 2003).
[39] M. D. Reid, P. D. Drummond, W. P. Bowen, E. G. Cavalcanti, P. K. Lam, H. A. Bachor, U. L. Andersen, and G. Leuchs, "Colloquium: The Einstein-Podolsky-Rosen paradox: From concepts to applications", *Rev. Mod. Phys.* **81**, 1727 (2009).
[40] R. Horodecki, P. Horodecki, M. Horodecki, and K. Horodecki, "Quantum entanglement", *Rev. Mod. Phys.* **81**, 865 (2009).
[41] D. Mac Kernan, R. Kapral, and G. Ciccotti, "Sequential short time propagation of quantum-classical dynamics", *J. Phys. Condens. Matter* **14**, 9069 (2002).
[42] A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fischer, A. Garg, and M. Zwerger, "Dynamics of the dissipative two-state system", *Rev. Mod. Phys.* **59**, 1 (1987).

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Presented 24 March 2010; published online 11 May 2011