

## Sampling of quantum dynamics at long time

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The principle of energy conservation leads to a generalized choice of transition probability in a piecewise adiabatic representation of quantum(-classical) dynamics. Significant improvement (almost an order of magnitude, depending on the parameters of the calculation) over previous schemes is achieved. Perspectives for theoretical calculations in coherent many-body systems are opened.

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The importance of theoretical methods for the calculation of time-dependent quantum properties cannot be emphasized enough. The lack of general algorithms, so reliable as classical molecular dynamics simulations [1], is to be contrasted with the manifold of open problems that scientists face both in condensed matter [2] and quantum information technology [3]. Lately, we are also witnessing a renaissance of quantum approaches to biological phenomena [4]: a revival of interest generated by the combination of methodologies from open quantum systems [5] and quantum information theory [3]. Undoubtedly, the possibility of performing long-time quantum dynamical simulations would be an asset for all the above fields.

When considering the calculation of time-dependent quantum properties, two main methods are available: time-dependent density functional theory [6] and quantum-classical formalisms [7]. Time-dependent density functional methods are usually limited to linear response while quantum-classical methods are restricted to perturbations around the adiabatic evolution, i.e., nonadiabatic corrections, of few relevant quantum degrees of freedom interacting with a classical bath. Nevertheless, quantum-classical methods promise to access the investigation of properties relevant to biological systems [7]. Here, we are considering the formulation of quantum-classical theory by means of algebraic brackets which was proposed originally in [8] and shown to arise from a linear approximation of the partially Wigner-transformed quantum commutator [9]. It is remarkable that, when the environmental degrees of freedom are harmonic and the coupling to the quantum subsystem is linear in the bath degrees of freedom, as in gauge theory [10], such theory becomes fully quantum. What is interesting from a computational point of view is that, within such a theory, a particular approximation (called *momentum jump* in the adiabatic basis of the total system) leads to represent nonadiabatic dynamics in terms of piecewise (adiabatic) deterministic trajectories interspersed by stochastic quantum transitions [11,12].

There is a long history of development and methods for treating nonadiabatic transitions with so called surface-hopping schemes [7]. Such schemes were originated in [13]. A more recent approach can be found in [14]. These methods are successful for the description of the dynamics but do not easily lead to an accurate formulation of the statistical mechanics of quantum-classical systems. Instead, the theory stemming from [9] allows one to address the consistent formulation of the quantum-classical statistical mechanics [15] of general hybrid systems, i.e., the theory can describe, in the non relativistic limit, *any* quantum subsystem coupled to a classical bath. It exactly conserves the energy of the total system and consistently describes the coupling between the quantum subsystem and the classical bath (or the quantum harmonic bath represented in Wigner phase space). The forms of the equations in the momentum-jump approximation also naturally provide a sampling transition probability for nonadiabatic change in state. However, when nonadiabatic effects are included, the phase space trajectories representing the quantum(-classical) dynamics do no longer conserve the energy. Despite this, in its original formulation, called sequential time-step propagation [11,12], the algorithm is successful, although limited to somewhat short-times because of numerical instabilities arising from the sampling of the nonadiabatic transitions. The instability, in practice, restricts the range of applications of the method to charge transfers and rate processes [16].

More general quantum processes require the ability of sampling at longer time. In this Brief Report, we show how to achieve this by means of a suitable generalization (implementing the principle of energy conservation) of the transition probability in the sequential time-step propagation: this is the main theoretical idea we propose and it is introduced by Eq. (5) in the following. Before providing our solution, we sketch the theory and the original version of the sequential time-step propagation, which will be referred to in the following as *primitive* algorithm. The interested reader will find more details in [12]. The theory of quantum-classical dynamics is defined by the equation [17–19].

$$\frac{d}{dt}\hat{\chi}_W(X) = \frac{i}{\hbar}[\hat{H}_W, \hat{\chi}_W] \cdot \begin{bmatrix} 0 & 1 + \frac{i\hbar}{2}\tilde{\partial} \cdot \mathcal{B}^c \cdot \tilde{\partial} \\ -1 - \frac{i\hbar}{2}\tilde{\partial} \cdot \mathcal{B}^c \cdot \tilde{\partial} & 0 \end{bmatrix} \cdot \begin{bmatrix} \hat{H}_W \\ \hat{\chi}_W \end{bmatrix}, \quad (1)$$

where  $\hat{\chi}_W(X)$  is a quantum operator in a partial Wigner representation depending on the phase space point  $X=(R,P)$ , comprised by coordinated and momenta, respectively;  $\hat{H}_W$  is the partially Wigner-transformed Hamiltonian operator of the total system,  $\mathcal{B}^c$  is the symplectic matrix, and  $\tilde{\partial}$  stands for the phase space gradient  $\partial/\partial X$ , with the arrow giving the direction of action of the operators. Without loss of generality, one can assume the form of the Hamiltonian to be  $\hat{H}_W(X) = \frac{P^2}{2M} + \hat{h}_W(R)$ . In the adiabatic basis, defined by the eigenvalue equation  $\hat{h}_W(R)|\alpha;R\rangle = E_\alpha(R)|\alpha;R\rangle$ , the quantum-classical evolution reads

$$\chi_W^{\alpha\alpha'}(X,t) = \sum_{\beta\beta'} (e^{it\mathcal{L}})_{\alpha\alpha',\beta\beta'} \chi_W^{\beta\beta'}(X), \quad (2)$$

where  $i\mathcal{L}_{\alpha\alpha',\beta\beta'} = i\mathcal{L}_{\alpha\alpha'}^0 \delta_{\alpha\beta} \delta_{\alpha'\beta'} + J_{\alpha\alpha',\beta\beta'}$ . The diagonal operator  $i\mathcal{L}_{\alpha\alpha'}^0 = (i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'}) \delta_{\alpha\beta} \delta_{\alpha'\beta'}$  is defined in terms of the quantum adiabatic frequency  $\omega_{\alpha\alpha'}(R) = [E_\alpha(R) - E_{\alpha'}(R)]/\hbar$  and of the classical-like Liouville operator  $iL_{\alpha\alpha'} = (P/M) \partial/\partial R + (1/2)(F_W^\alpha + F_W^{\alpha'}) (\partial/\partial P)$ , where  $F_W^\alpha$  are the Hellmann-Feynman forces [20]. The operator  $J_{\alpha\alpha',\beta\beta'}$  is purely off-diagonal and its action realizes the quantum nonadiabatic transitions. It is worth remarking that Eqs. (1) and (2) exactly conserve the total Hamiltonian of the system  $\hat{H}_W(X)$ .

In the momentum-jump approximation, the form of the off-diagonal operator  $J_{\alpha\alpha',\beta\beta'}$  is simplified [12]. Here, we denote such an approximation by  $J_{\alpha\alpha',\beta\beta'}^{(\text{mp})}$ . The action of  $J_{\alpha\alpha',\beta\beta'}^{(\text{mp})}$  changes the quantum state and rescales the bath momenta. The technical details can be found, among many other possible references, in [12]. Using the momentum-jump operator, one can also define a momentum-jump Liouville operator,  $i\mathcal{L}_{\alpha\alpha',\beta\beta'}^{(\text{mp})} = i\mathcal{L}_{\alpha\alpha'}^0 \delta_{\alpha\beta} \delta_{\alpha'\beta'} + J_{\alpha\alpha',\beta\beta'}^{(\text{mp})}$ , approximating the exact operator  $i\mathcal{L}_{\alpha\alpha',\beta\beta'}$  in Eq. (2).

Deterministic dynamics is too complicated to be solved, so one has to resort to stochastic schemes. A very elegant approach is provided by the sequential short time propagation [12] (the primitive algorithm). This is summarized as follows. For a small time-step  $\tau$  the quantum-classical propagator is approximated as

$$(e^{i\tau\mathcal{L}^{(\text{mp})}})_{\alpha\alpha',\beta\beta'} \approx e^{i\tau\mathcal{L}_{\alpha\alpha'}^0} (\delta_{\alpha\beta} \delta_{\alpha'\beta'} + \tau J_{\alpha\alpha',\beta\beta'}^{(\text{mp})}). \quad (3)$$

One can prove that the concatenation of short time steps, according to Eq. (3), reproduces exactly the Dyson integral expansion of the operator  $\exp(i\tau\mathcal{L}^{(\text{mp})})_{\alpha\alpha',\beta\beta'}$ . The algorithm unfolds by considering the action of  $J^{(\text{mp})}$  dictated by a stochastic process with a certain transition probability. The form

of  $J^{(\text{mp})}$  naturally suggests the following *primitive* choice of the transition probability (for example considering the  $\alpha \rightarrow \beta$  quantum transition):

$$\mathcal{P}_{\alpha\beta}^{(0)}(X,\tau) = \frac{\left| \frac{P}{M} d_{\alpha\beta}(R) \right| \tau}{1 + \left| \frac{P}{M} d_{\alpha\beta}(R) \right| \tau}, \quad (4)$$

where  $d_{\alpha\beta} = \langle \alpha;R | \partial/\partial R | \beta;R \rangle$  is the coupling vector. Normalization fixes the probability of not making any transition in the time interval  $\tau$  as  $\mathcal{Q}_{\alpha\beta}^{(0)}(X,\Delta t) = 1 - \mathcal{P}_{\alpha\beta}^{(0)}$ . The stochastic propagation amounts to deterministic trajectory segments, propagating on single or mean energy surfaces, interspersed by transitions between energy surfaces. The transitions break the conservation of energy along the single trajectory: the conservation is only satisfied in an averaged sense in the ensemble. As one can see from Eq. (4), arbitrary shifted momenta  $P'$  can arise from a sampled transition. As experience has shown, this leads in general to very big denominators in the left hand side of Eq. (4). This denominators get multiplied with each other along the trajectory to give its overall weight in the stochastic ensemble. The concatenation of big weights arising from nonadiabatic transitions produces a numerical instability, which has so far limited the application of the primitive algorithm to somewhat short times.

The principle of energy conservation, which is exactly satisfied by Eq. (1), guides us in defining a generalized transition probability as

$$\mathcal{P}_{\alpha\beta}(X,\Delta t) = \frac{\tau |\langle \alpha | \dot{\beta} \rangle| w(c_\mathcal{E}, \mathcal{E}_{\alpha\alpha',\beta\beta'})}{1 + \tau |\langle \alpha | \dot{\beta} \rangle| w(c_\mathcal{E}, \mathcal{E}_{\alpha\alpha',\beta\beta'})}, \quad (5)$$

where we have defined  $(P/M)d_{\alpha\beta}(R) = \langle \alpha | \dot{\beta} \rangle$ . Again, normalization provides  $\mathcal{Q}_{\alpha\beta}^{(0)}(X,\Delta t) = 1 - \mathcal{P}_{\alpha\beta}$ . Upon introducing the variation in energy in any quantum transition  $\mathcal{E}_{\alpha\alpha',\beta\beta'} = \frac{P'^2}{2M} + \frac{1}{2}[E_\alpha(R) + E_{\alpha'}(R)] - \frac{P^2}{2M} - \frac{1}{2}[E_\beta(R) + E_{\beta'}(R)]$ , the generalized weight introduced in Eq. (5) is defined as

$$w(c_\mathcal{E}) = \begin{cases} 1 & \text{if } |\mathcal{E}_{\alpha\alpha',\beta\beta'}| \leq c_\mathcal{E} \\ 0 & \text{otherwise,} \end{cases} \quad (6)$$

with  $c_\mathcal{E}$  tunable constants controlling the numerical error on the energy conservation.

The generalized transition probability in Eq. (5) and the energy-conserving weight in Eq. (6) are our fundamental findings, improving the primitive algorithm. Because of our choice of  $w(c_\mathcal{E})$ , the sampled transitions can only allow shifted momenta  $P'$ , which conserve (within the required numerical error specified by  $c_\mathcal{E}$ ) the energy of the system.

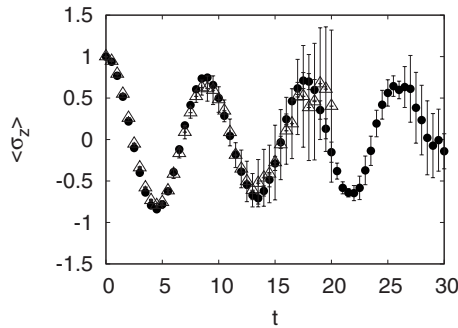


FIG. 1. Comparison of the primitive ( $\Delta$ ) and energy-conserving ( $\bullet$ ) sampling for  $\beta=0.3$ ,  $\Omega=1/3$ , and  $\xi=0.007$ . The calculation with the primitive algorithm are propagated until  $t=20$  and then stopped since already around  $t=15$  the statistical error becomes very big, as the error bars show. The calculation with the energy-conserving sampling ( $\bullet$ ), with  $c_\xi=0.01$ , can be extended further than  $t=30$ .

This in turn avoids arbitrarily big denominators in Eq. (5) and dramatically improves the stability of the algorithm.

In order to illustrate the efficiency of the energy-conserving sampling, we performed a series of calculation on the dynamics of the spin-boson model [21]. The partially Wigner-transformed Hamiltonian of this model (in scaled coordinates) is  $\hat{H}_W = -\Omega \hat{\sigma}_x + \sum_{j=1}^N (P_j^2/s + \omega_j^2 R_j^2/2 - c_j R_j \hat{\sigma}_z)$ , where  $\hat{\sigma}_x$  and  $\hat{\sigma}_z$  are the Pauli matrices, and  $R_j$  and  $P_j$  are coordinates and momenta of  $N$  harmonic degrees of freedom (in the following we have used  $N=200$ , and  $c_j$  are coupling constants defined in term of the Kondo parameter  $\xi$ ). Details of the model and definition of coordinates and parameters can be found in [12]. Figures 1 and 2 illustrate the numerical comparison between the primitive and our energy-conserving sampling for the relaxation dynamics of  $\sigma_z$  for various couplings, temperatures, and tunnel splitting  $\Omega$ . The results obtained with the primitive algorithm are displayed by white triangles while those obtained with our energy-conserving sampling by black filled circles. Figure 1 displays the results of the numerical calculation for  $\beta=0.3$ ,  $\Omega=1/3$ , and  $\xi=0.007$ . Basically, after  $t=15$  (in dimensionless units) the error bars on the primitive algorithm results grow exponentially fast and the calculation is stopped at  $t=20$ . Instead, the calculation with our generalized sampling scheme can be extended further than  $t=30$ : for this set of parameters we obtain

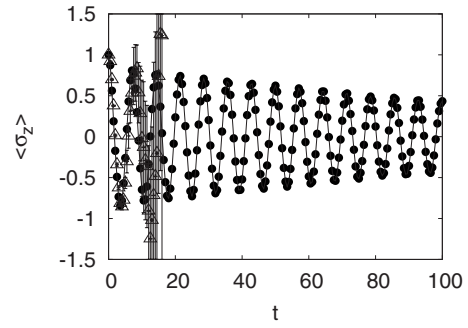


FIG. 2. Comparison of primitive ( $\Delta$ ) and energy-conserving ( $\bullet$ ) sampling for  $\beta=12.5$ ,  $\Omega=0.4$ , and  $\xi=0.09$ . The calculation with the primitive algorithm are propagated until  $t=20$  and then stopped since already around  $t=12$  the statistical error becomes very big, as the error bars show. The calculation with the energy-conserving sampling ( $\bullet$  and a continuous line to help the eye), with  $c_\xi=0.01$ , can be extended further than  $t=100$  (the error bars of the order of magnitude of the  $\bullet$  symbols).

an improvement over the time interval we can sample of at least two. Figure 2 displays the results of the numerical calculation for  $\beta=12.5$ ,  $\Omega=0.4$ , and  $\xi=0.09$ . This time, the statistical errors of the primitive algorithm start growing fast around  $t=10$ , while our scheme can reach further than  $t=100$ , providing an improvement of an order of magnitude. Summarizing, the simulation shows that the use of our energy-conserving sampling dramatically improves the stability of the elegant sequential time-step algorithm at long time.

In conclusion, it is worth mentioning that the approach, embodied by Eq. (5), to modify the transition probability in order to respect a conservation law and improving the stability is very general: it is by no means restricted to quantum(-classical) dynamics in the partial Wigner representation. On the contrary, there are reasonable expectations that the generalized scheme that we have presented here can be applied, after suitable changes, to other stochastic approaches for calculating time-dependent properties, both in the classical and quantum cases.

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