Quantum-classical Liouville description of multidimensional nonadiabatic molecular dynamics

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The quantum-classical Liouville formulation gives a quantum-mechanical density-matrix description of the “quantum” particles of a problem (e.g., the electrons) and a classical phase-space-density description of the “classical” particles (e.g., the nuclei). In order to employ this formulation to describe multidimensional nonadiabatic processes in complex molecular systems, this work is concerned with an efficient Monte Carlo implementation of the quantum-classical Liouville equation. Although an exact stochastic realization of this equation is in principle available, in practice one has to cope with two major complications: (i) The representation of nonlocal phase-space operators in terms of local classical trajectories and (ii) the convergence of the Monte Carlo sampling which is cumbersome due to complex-valued trajectories with rapidly oscillating phases. Several strategies to cope with these problems are discussed, including various approximations to determine the momentum shift associated with a nonadiabatic transition, the on-the-fly generation of new trajectories at curve-crossings, and the localization of trajectories after irreversible electronic transitions. Employing several multidimensional model systems describing ultrafast photoinduced electron transfer and internal conversion, detailed numerical studies are performed which are compared to exact quantum calculations as well as to the “fewest-switches” surface-hopping method. In all cases under consideration, the Liouville calculations are in good agreement with the quantum reference. In particular, the approach is shown to provide a correct quantum-classical description of the electronic coherence.

I. INTRODUCTION

Many problems in physics allow for a partition of the system into light particles and heavy particles. This situation can be exploited to apply a mixed quantum-classical (QC) treatment, that is, to represent the light “quantum” particles by a quantum-mechanical description, while the heavy “classical” particles are represented by a trajectory description. QC theories are interesting because of (i) fundamental issues of the coupling of quantum and classical systems, e.g., in the quantum theory of measurement with a classical apparatus; (ii) the interpretation of complex quantum dynamics in terms of classical trajectories propagating in phase space; and (iii) the development of computational methods that allow us to treat multidimensional systems which are ubiquitous in chemistry and biology.

A number of mixed QC models have been proposed that aim to incorporate quantum degrees of freedom (e.g., a coupled electronic two-state system) into an essentially classical formulation, e.g., nuclear motion on an adiabatic potential-energy surface (PES). Most notably, these formulations include various mean-field1–11 and surface-hopping12–18 methods and combinations thereof.19–21 Furthermore, it has been suggested to apply quantum-mechanical bosonization techniques in order to facilitate a semiclassical description of discrete quantum degrees of freedom.12,22 In principle, a QC description may be derived by starting with a quantum-mechanically exact formulation for the complete system and performing a partial classical limit for the heavy-particle degrees of freedom. This procedure is not unique, however, since it depends on the particular dynamical formulation chosen as well as on the specific way to achieve the classical limit. Well-known examples are the Ehrenfest mean-field limit in the wave-function formulation and the stationary-phase approximation in the path-integral formulation due to Pechukas.23 In this work we consider a QC Liouville description as obtained from a partial classical limit of the density operator.24–32

Let us first consider the quantum-mechanical Liouville equation for the density operator \( \hat{\rho}(t) \),

\[
\frac{\partial}{\partial t} \hat{\rho}(t) = -i\hbar[H, \hat{\rho}(t)],
\]

where \( \hat{H} = \hat{H}(\hat{q}, \hat{p}) \) is the quantum Hamiltonian depending on position and momentum operators \( \hat{q} \) and \( \hat{p} \), respectively, and \( [\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \) denotes the usual quantum commutator. In order to obtain the classical limit of Eq. (1.1), one may introduce a quantum-mechanical phase-space representation of the operators such as the Wigner–Weyl formulation.33 Retaining only the classical (\( \hbar = 0 \)) terms, the resulting equation of motion reads
\[
\frac{\partial}{\partial t} \rho(t) = \{H, \rho(t)\},
\]
(1.2)

where \( \rho(t) = \rho(q, p, t) \) is the Wigner density function, \( H = H(q, p) \) is the classical Hamiltonian, and \( \{A, B\} = \partial_A \partial_B H - \partial_B \partial_A H \) denotes the classical Poisson bracket.

The similar appearance of the quantum and classical Liouville equations has motivated several workers to construct a mixed quantum-classical Liouville (QCL) description.\(^{25-32}\) Hereby a partial classical limit is performed for the heavy-particles dynamics, while a quantum-mechanical formulation is retained for the light particles. To be specific, throughout this paper we focus on the case that the heavy-particle degrees of freedom are nuclei with coordinates \( x = \{x_i\} \) and momenta \( p = \{p_j\} \), while the light-particle degrees of freedom are electrons described by some basis states \( |\psi_n\rangle \). The quantities \( \rho(t) \) and \( H \) in the mixed QC formulation are then operators with respect to the electronic degrees of freedom and classical functions with respect to the nuclear degrees of freedom, for example,

\[
\rho(t) = \sum_{nm} \rho_{nm}(x, p, t) |\psi_n\rangle \langle \psi_m|.
\]
(1.3)

The standard proposal for the Liouville equation for this QC density operator is

\[
\frac{\partial}{\partial t} \rho(t) = \{H, \rho(t)\}_{QC},
\]
(1.4)

\[
[A, B]_{QC} = -i\hbar [A, B] + \frac{1}{2} [A, B] - \frac{1}{2} [B, A],
\]
(1.5)

where \( \{\ldots\}_{QC} \) denotes the QC bracket that contains the pure quantum bracket \( \{\ldots\} \) in Eq. (1.1) and the pure classical bracket \( \{\ldots\} \) as limiting cases. Equation (1.4) can be derived via a number of approaches, for example, by requiring certain axioms for the QC bracket to be satisfied,\(^{26}\) by replacing nuclear commutators by Poisson brackets and nuclear anticommutators by products of Operators,\(^{28}\) and by performing the partial classical limit in the Wigner phase-space representation.\(^{29-32}\)

It should be noted, however, that the QC equation (1.4) is neither unique nor does any of the QC formulations proposed fulfill all desirable conditions on such a description. The first issue has to do with the ambiguity of the classical limit imposed. Starting with an alternative quantum-mechanical phase-space representation, one also may obtain a different QC bracket.\(^{29}\) Concerning the second issue, a QC formulation needs to satisfy a number of requirements which are also fulfilled by the pure quantum and pure classical Liouville equations. For example, the QC bracket should be linear, antisymmetric (i.e., \( [A, B]_{QC} = -[B, A]_{QC} \)), to ensure conservation of energy for time-independent Hamiltonians), and invariant under canonical transformations of the classical variables and unitary transformations of the quantum variables. Furthermore, the time evolution of \( \rho(t) \) should preserve the reality or Hermiticity conditions on the observables and also preserve the positivity of \( \rho(t) \). The trouble of QC formulations to fulfill all these requirements is due to the fact that Planck’s constant \( \hbar \) enters the classical and quantum subsystem to different order. As a consequence, the QC bracket in general does not satisfy the Jacobi identity and Leibnitz’s Rule, which may result in inconsistencies regarding the quantum back-reaction and the positivity of \( \rho(t) \).\(^{27,31}\)

As most QC formulations are plagued by some kind of consistency problem\(^{33,34}\) and since there is an increasing interest in the QC correspondence in phase space (see, for example, Ref. 2,35,36), the QCL equation nevertheless represents an interesting and promising approach.

Being a partial differential equation involving nonlocal operators, the numerical implementation of Eq. (1.4) is only straightforward on a full grid in phase space.\(^{28}\) Furthermore, one may attempt to directly propagate the classical distribution functions \( \rho_{nm}(x, p, t) \).\(^{37,38}\) Similar to a full quantum calculation, however, the numerical effort for these strategies appears to scale exponentially with the number of quantum and classical degrees of freedom. To obtain a numerical method that is directly applicable to truly multidimensional systems, it would be desirable to employ a stochastic scheme involving a Monte Carlo sampling of local classical trajectories. Based on a stochastic description of quantum-mechanical time evolution,\(^{39,40}\) several works have addressed the closely related problem of a Monte Carlo implementation of the quantum-mechanical Wigner–Moyal equation.\(^{41-43}\) Such an approach has to cope with two major complications, that is, the representation of nonlocal phase-space operators and the convergence of the sampling procedure which is cumbersome due to complex-valued trajectories with rapidly oscillating phases. The latter is related to the so-called dynamical sign problem which is well-known from real-time path-integral\(^{44}\) and time-dependent semiclassical\(^{35}\) calculations. Only very recently, a first stochastic trajectory implementation of the QCL equation has been suggested.\(^{46}\) Employing a representation of the nonlocal quantum-jump operator that is not easily generalized to multidimensional problems, however, this work was concerned with one-dimensional model systems only.

In order to describe multidimensional nonadiabatic molecular problems, in this work we are concerned with an efficient stochastic implementation of the QCL equation. Adopting the adiabatic electronic representation, various strategies to solve the sampling problem and to approximate the nonlocal quantum-jump operators are investigated. Employing several multidimensional model systems describing ultrafast photoinduced electron transfer and internal conversion, we perform detailed numerical studies which are compared to exact quantum reference calculations as well as to the “fewest-switches” surface-hopping method due to Tully.\(^{15}\) The virtues and shortcomings of various numerical strategies as well as the overall performance of the method are discussed in some detail.

II. QUANTUM-CLASSICAL LIOUVILLE EQUATION IN THE ADIABATIC REPRESENTATION

To give a self-contained description and define the notation employed, the following section briefly reviews the derivation of the QCL equation as given by Kapral and Cicotti.\(^{30}\) Performing a partial Wigner transformation with respect to the nuclear variables, the molecular Hamiltonian can be written as
\[ H = \sum_j p_j^2 / 2m_j + h(x), \]

where the nuclear coordinates \( x \) and momenta \( p \) are now classical degrees of freedom. For given values \( x \) of the classical coordinates, the operator \( h(x) \) is the Hamiltonian of the quantum system,

\[ h(x) = T_q + V(q, x). \]  

(2.2)

Here \( q \) represents the coordinates of the quantum particles and \( T_q \) denotes the corresponding kinetic energy operator. The quantum subsystem will be described in the adiabatic electronic representation with basis states \( \{|\psi_n(x)\rangle\} \). For each value of \( x \), the electronic Hamiltonian \( h(x) \) is diagonal in this representation,

\[ h(x)|\psi_n(x)\rangle = W_n(x)|\psi_n(x)\rangle, \]

(2.3)

with \( W_n(x) \) being the adiabatic PESs. The corresponding electronic matrix elements of the partial Wigner transformed density operator \( \rho(x, p, t) \) are given by

\[ \rho_{nn}(x, p, t) = \langle \psi_n(x)|\rho(x, p, t)|\psi_n(x)\rangle. \]

(2.4)

For notational convenience, in the following we will usually drop the dependency on the nuclear variables \( x, p \).

Insertion of Eqs. (2.1)–(2.4) into the QCL equation (1.4) yields the equations of motion for the QC density matrix in the adiabatic representation

\[ \frac{\partial}{\partial t} \rho_{nm}(t) = \langle \psi_n(t)| - i\hbar[H, \rho] + \frac{i}{2}\{H, \rho\} - \frac{i}{2}\{\rho, H\}|\psi_m(t)\rangle = -i\hbar(W_n - W_m)\rho_{nm}(t) + \sum_j \langle \psi_n| \frac{1}{2} \left( \frac{\partial V}{\partial x_j} \frac{\partial \rho}{\partial p_j} + \frac{\partial \rho(t)}{\partial p_j} \frac{\partial V}{\partial x_j} \right) - \frac{p_j}{m_j} \frac{\partial \rho}{\partial x_j} |\psi_m\rangle. \]

(2.5)

Introducing first-order nonadiabatic couplings,

\[ d_n^{(j)}(x) = \langle\psi_n(x)| \frac{\partial}{\partial x_j} |\psi_m(x)\rangle, \]

(2.6)

and the Hellman–Feynman force matrices,

\[ F_n^{(j)}(x) = \langle\psi_n(x)| \frac{\partial V(x)}{\partial x_j} |\psi_m(x)\rangle. \]

(2.7)

the QCL equation can be rewritten as

\[ \frac{\partial}{\partial t} \rho_{nm}(t) = -i\hbar(W_n - W_m)\rho_{nm}(t) - \sum_j \frac{p_j}{m_j} \frac{\partial \rho_{nm}(t)}{\partial x_j} + \sum_j \sum_k \left( \frac{1}{2} F_n^{(j)k} \frac{\partial p_{km}(t)}{\partial p_j} + \frac{1}{2} \frac{\partial p_{nm}(t)}{\partial p_j} F_k^{(i)j} \right) - \sum_j \left( \frac{p_j}{m_j} d_n^{(j)}(x) p_{km}(t) + p_{nk}(t) d_m^{(j)}(x) \right). \]

(2.8)

It is noted that, contrary to a full quantum-mechanical description, the QC formulation does not consider second-order nonadiabatic couplings such as \( \langle\psi_n| \frac{\partial^2}{\partial x_j^2} |\psi_m\rangle \). This is because the time evolution of the nuclear degrees of freedom is described by a Poisson bracket which introduces only first-order derivatives.

Employing a superoperator notation, the equations of motion may be cast into the suggestive form,

\[ \frac{\partial}{\partial t} \rho_{nm} = \sum_{m', m''} \mathcal{L}_{nm', m''}\rho_{m''}, \]

\[ = \sum_{m', m''} \left( \mathcal{L}^Q_{nm', m''} + \mathcal{L}^C_{nm', m''} + \mathcal{L}^{QC}_{nm', m''} \right) \rho_{m''}, \]

(2.9)

where

\[ \mathcal{L}^Q_{nm', m''} = -i\hbar(W_n - W_m)\delta_{nm}\delta_{m'm''}, \]

(2.10)

\[ \mathcal{L}^C_{nm', m''} = \sum_j \left( -\frac{p_j}{m_j} \frac{\partial}{\partial x_j} + \frac{1}{2} \left( F_n^{(j)k} + F_k^{(j)l} \right) \frac{\partial}{\partial p_j} \right) \delta_{nm}\delta_{m'm''}, \]

(2.11)

account for the pure quantum-mechanical and the pure classical time evolution of the density matrix, respectively.

Hereby, the quantum part \( \mathcal{L}^Q \) introduces the phase \( (W_n - W_m)\hbar \) to the off-diagonal matrix elements of the density matrix, while the classical part \( \mathcal{L}^C \) describes standard Newtonian dynamics with respect to the adiabatic potential energy \( (W_n + W_m)/2 \). It is noted that the evaluation of the equations of motion (2.9) requires the propagation of classical trajectories in diagonal and off-diagonal matrix elements of the electronic density matrix. That is, if \( N \) electronic states are considered, classical equations of motion have to be solved for \( N(N - 1)/2 \) potential-energy functions \( V_{nm'} \). This is in contrast to usual surface-hopping methods based on a wave-function ansatz. These formulations do not explicitly account for the coherences \( \rho_{nm}(t) \) and therefore only require the propagation of classical trajectories in diagonal potential-matrix elements \( V_{nn} \).

The quantum-classical part of the Liouville operator,

\[ \mathcal{L}^{QC}_{nm', m''} = -\sum_j \frac{p_j}{m_j} d_n^{(j)}(x) \left( 1 + \sum_i S_{nm}^{(i)} \frac{\partial}{\partial p_i} \right) \times \delta_{nm}(1 - \delta_{nm}\delta_{m'm''}) + \text{h.c.}, \]

(2.12)

\[ S_n^{(i)} = \frac{(W_n - W_m)}{2\Sigma_j d_n^{(j)}(x) p_j / m_j} d_n^{(i)}(x), \]

(2.13)

accounts for the coupling between quantum and classical subsystems thus describing nonadiabatic transitions between electronic states. Note that in a standard quantum-mechanical formulation only the first part of \( \mathcal{L}^{QC} \) appears, that is, the term \( \propto \mathbf{p} \cdot \mathbf{d}_{nm} \). In this case, \( \mathbf{p} \) and \( \mathbf{d}_{nm} \) represent nonlocal quantum operators with respect to the nuclear degrees of freedom. In the QC case considered here, however, \( \mathbf{p} \) and \( \mathbf{d}_{nm} \) are classical functions. Here the nonlocal nature of the nonadiabatic transition is accounted for by the term \( \propto \mathbf{d}_{nm} \cdot \partial / \partial \mathbf{p} \), which affects a momentum change of the clas-
sical trajectory. This shift of nuclear momenta associated with the transition between adiabatic PESs has been discussed in various semiclassical theories of nonadiabatic processes.14–18

It should be noted that the momentum derivatives of the coupling elements (2.12) represent a problem for a practical trajectory-based evaluation of the QCL equation. These terms require the knowledge of the function in question not only at a particular point in phase space but at the same time also at nearby points. A possible solution is to represent the differential operator \( \partial / \partial p_j \) in terms of an integral equation with respect to the derivative of the \( \delta \)-function.31–43 Hereby the latter is approximated by a sharply peaked Gaussian in order to sample from the resulting distribution. In practice, however, it is rather cumbersome to converge this ansatz with respect to the width of the Gaussian employed. Recently, Wan and Schofield presented an alternative approach, which seems to circumvent the problem by instantaneously diagonalizing the force matrix, thus eliminating the off-diagonal forces.46 However, this approach has been applied only to a one-dimensional system, where the force vectors have a single component. It is not obvious how to extend this method to systems with more than one classical coordinate.

A general yet approximate ansatz has been suggested by Kapral and Cicotti,30 who considered the limit of small momentum changes

\[
\delta p_j = \frac{S_{nm}^{(j)}}{p_j} < 1, \tag{2.14}
\]

where \( p_j \) refers to the nuclear momenta before the electronic transition. In this case, one may approximate the derivative term in Eq. (2.12) as

\[
1 + \sum S_{nm}^{(j)} \delta \partial p_j \approx \exp \left( \sum S_{nm}^{(j)} \delta \partial p_j \right). \tag{2.15}
\]

Since \( \exp \delta \partial f(p) = f(p + S) \), the approximation reduces action of the differential operator to a simple shift of momenta. The nonadiabatic transition operator assumes the simple form

\[
\mathcal{L}_{QC}^{n\prime,n} = - \sum \frac{p_j}{m_j} d_{nm}^{(j)} \exp \left( \sum S_{nm}^{(j)} \delta \partial p_j \right) \times \delta_{n\prime,m} \left( 1 - \delta nm \delta_{n\prime,m} \right) + \text{h.c.} \tag{2.16}
\]

Note that, apart from the magnitude of \( \delta p_j \), the accuracy of this approximation also depends on the specific shape of the density functions \( \rho_{nm}(t) \) as compared to the spatial regions of strong nonadiabatic coupling. The numerical studies presented below will employ this approximation and also check its validity.

The approximation (2.15) resembles the usual momentum-jump ansatz employed in various surface-hopping methods.12–18 In order to determine the momentum shift of a trajectory, however, the latter formulations typically require the conservation of nuclear energy

\[
W_1 + T_1 = W_2 + T_2, \tag{2.17}
\]

where \( T_1 \) and \( T_2 \) denote the kinetic energy of the trajectory on the adiabatic PES \( W_1 \) and \( W_2 \), respectively. This ansatz gives rise to the problem of classically forbidden transitions, i.e., transitions that are required by the hopping algorithm but have to be rejected because of a lack of kinetic energy.47

The QCL formulation, on the other hand, does not conserve the energy of an individual trajectory but the energy of trajectory average. Only in the limiting case of vanishing momentum changes, the approximation (2.15) satisfies condition (2.17). It therefore may be expected that the present formulation does not suffer from the problem of classically forbidden transitions, which may represent a serious consistency problem for standard surface-hopping methods.47

III. STOCHASTIC TRAJECTORY ALGORITHM

The formal solution of the QCL equation reads

\[
\rho(t) = e^{-i \hbar \mathcal{L}t} \rho(0) = e^{-i \hbar \mathcal{L}_{QC}^{0} (t)} \rho(0), \tag{3.1}
\]

where the Liouville operator \( \mathcal{L} \) has been decomposed into a zero-order part \( \mathcal{L}_0 \), which is easy to evaluate and a nonadiabatic transition part \( \mathcal{L}_{QC}^{0} \) whose evaluation is difficult. The splitting suggests to employ a short time expansion of the full exponential by use of a first-order Trotter formula,

\[
\rho(t + \delta t) = e^{-i \hbar \mathcal{L}_{QC}^{0} (t + \delta t) \delta t} \rho(t) = e^{-i \hbar \delta t \mathcal{L}^{0} } ( 1 - i \hbar \mathcal{L}_{QC}^{0} \delta t \rho(t) + O(\delta t^2) ), \tag{3.2}
\]

and to solve the equations of motion for a small time step \( \delta t \) by imposing two basic processes on \( \rho(t) \) to obtain \( \rho(t + \delta t) \):

(i) classical propagation and phase accumulation on the corresponding PES described by \( \mathcal{L}^{0} \); and

(ii) transitions between coupled potential-energy surfaces induced by \( \mathcal{L}_{QC}^{0} \).

While this scheme is straightforward to evaluate using a grid in phase space,33–35 its implementation on a grid becomes prohibitive in the case of multidimensional systems. Following previous work,39–43 we therefore introduce a stochastic algorithm which uses a Monte Carlo sampling of local classical trajectories. To this end, the density matrix is represented as an ensemble of phase-space points described by the weight functions \( W_{nm}(x,p,t) \), the phase functions \( \sigma_{nm}(x,p,t) \), and the density \( P_{nm}(x,p,t) \).

\[
\rho_{nm}(x,p,t) = W_{nm}(x,p,t) \sigma_{nm}(x,p,t) P_{nm}(x,p,t). \tag{3.3}
\]

The density is assumed to be positive and normalized

\[
\sum_{n,m} \int \text{d}x \text{d}p P_{nm}(x,p,t) = 1 \tag{3.4}
\]

and we have \( |\sigma_{nm}(x,p,t)| = 1 \).

Let us investigate the change of the various components of the density matrix under propagation from time \( t \) to \( t + \delta t \). We first consider the action of \( \mathcal{L}_0 \). Due to this operator, the density matrix element \( \rho_{nm}(t) \) attains a phase factor

\[
\exp \left( -i \hbar (W_{n} - W_{m}) \delta t \right), \tag{3.5}
\]

and is subject to propagation in phase space driven by

\[
\exp \left( \sum_j \frac{1}{2} (F_{nm}^{(j)} + F_{nm}^{(j)} \delta p_j / \delta \partial p_j / m_j \delta x_j) \delta t. \tag{3.6}
\]

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While the weights $W_{nm}(x,p,t)$ do not change under these operations, the densities $P_{nm}(x,p,t)$ are affected by the propagation (3.6). Furthermore, the sign functions $\sigma_{nm}(x,p,t)$ accumulate a phase (3.5) according to the (adiabatic) energy difference at the spatial position $x$. \cite{41} In the absence of nonadiabatic transition (i.e., for $\mathcal{L}^{QC}=0$), a stochastic realization of the propagation process is thus straightforward: Assuming that the initial phase-space distributions $\rho_{nm}(x,p,t=0)$ are given in analytical form, initial positions and momenta are sampled from this distribution, thus determining the densities $P_{nm}(x,p,0)$. Furthermore, the initial weights and phases are chosen to correctly represent the initial state of the density matrix. The time evolution of the density matrix is then described by Eqs. (3.5) and (3.6) as explained above.

Let us now consider the stochastic realization of the off-diagonal operator $\mathcal{L}^{QC}$, which represents the main difficulty of the numerical implementation. $\mathcal{L}^{QC}$ can be viewed as a branching or hopping term which causes transitions between the different components of the density matrix. Apart from acting on the densities and the sign functions, this operator therefore also modifies the weights $W_{nm}(x,p,t)$ of the density matrix. To introduce a statistical interpretation of this process, let us consider a general matrix $\mathbf{M}$. Writing

$$M_{ab} = \left( \sum_{ij} |\mathbf{M}_{ij}| \right)^{-1} \frac{|\mathbf{M}_{ab}|}{\sum_{ij} |\mathbf{M}_{ij}|},$$

(3.7)

the matrix $\mathbf{M}$ is decomposed into a scalar weight factor $w = \sum_{ij} |\mathbf{M}_{ij}|$, a phase $\phi_{ab} = M_{ab}/|\mathbf{M}_{ab}|$, and a matrix with elements

$$T_{ab} = \frac{|\mathbf{M}_{ab}|}{(\sum_{ij} |\mathbf{M}_{ij}|)}.$$  

(3.8)

Since

$$\sum_{a,b} T_{ab} = 1, \quad T_{ab} \geq 0,$$

(3.9)

$\mathbf{T}$ may be regarded as a matrix of probabilities.

We now assume that $\mathbf{M} = \mathbf{M}(t)$ is a Liouville operator acting on the Liouville vector $\rho(t)$ to give $\rho(t+\delta t)$. Employing Eq. (3.3), $\rho(t+\delta t)$ can be calculated as

$$\rho_a(t+\delta t) = \sum_b M_{ab}(t)\rho_b(t)$$

$$= \sum_b M_{ab}(t) P_b(t)\sigma_b(t)$$

$$= \sum_b T_{ab}(t) P_b(t)\sigma_b(t).$$

(3.10)

Thus, $\rho(t+\delta t)$ is a sum of contributions with the phase factors $(\phi_{ab}(t)\sigma_a(t))$, the weight factors $(w(t)W_{ab}(t))$, and phase-space distributions $P_b(t)$ which appear with a probability $T_{ab}(t)$. Associating $\mathbf{M}$ with the Liouville operator $1-i\hbar\mathcal{L}^{QC}\delta t$, the scheme becomes somewhat more involved. In addition to the hopping probabilities, $\mathcal{L}^{QC}$ also includes a momentum shift. Hence the expression $T_{ab}(t)P_b(t)$ describes a transition from component $b$ to component $a$, accompanied by an instantaneous change of momenta according to Eq. (2.15). A further subtlety should be mentioned. Since the momentum correction (2.13) itself explicitly depends on the momentum $p$, the application of the momentum shift operator (2.15) can cause contractions (or expansions) of phase space, thereby modifying the weight. For the model systems considered, however, these contractions have been found to be negligible.

Combining the steps described above, a simple stochastic algorithm for a trajectory-based propagation of the QCL equation can be constructed as follows:

(i) Sample the initial distribution function $P_{nm}(x,p,t=0)$ by a set of “random walkers.” The $i$-th random walker carries the information of its phase-space position $(x_i,p_i)$, density-matrix component $(nm)_i$, weight $W(x_i,p_i,t)$, and phase $\sigma(x_i,p_i,t)$. Divide the whole time interval into $N$ small enough pieces such that the desired accuracy of the Trotter scheme is guaranteed.

(ii) During a single time step,

(a) Propagate the random walker according to the local forces on the PES with index $nm$;

(b) Multiply the phase of the random walker by $e^{-i\hbar}\mathcal{L}^{QC}\delta t$.

(c) Make a nonadiabatic transition $|\psi_a\rangle \rightarrow |\psi_b\rangle$ if required: To this end, generate a random number $0<\zeta<1$. Stay on the current surface $a$ if $\zeta<T_{aa}$. Otherwise, jump to the surface $b$ that satisfies the condition $\sum_{a=1}^b T_{ab} \zeta < \sum_{b=1}^B T_{ab}$. Change the momenta according to $p^b_j = p^a_j + \sum_{a=1}^B T_{ab}(x^a,p^a)^{(x^a,p^a)}$;

(d) Multiply the weight with $w$ and the phase with $\phi_{ab}$;

(iii) Calculate the molecular observables of interest;

(iv) Iterate from step (i) and run as many trajectories as needed to reach statistical convergence.

Within the momentum-jump approximation (2.15), the algorithm provides as in principle, exact stochastic realization of the QCL equation. Apart from practical problems to be discussed below, the trajectory implementation therefore represents a well-defined computational scheme.

Similar to path-integral\cite{42} and semiclassical\cite{43} propagation methods, however, the Monte Carlo evaluation of the QCL equation is plagued by the so-called “sign-problem,” which is caused by exponentially increasing weights $W$ accompanied by rapidly varying phases. As a consequence, the signal to noise ratio of the sampling deteriorates in the course of propagation time, or in other words, the sampling effort increases exponentially in time. As shown in the QCL calculations below, this problem manifests itself in the fact that most of random walkers generated by the algorithm do not contribute but cancel each other in the phase average.

A well-known strategy to overcome this fundamental problem is to reorganize the sum over complex paths in a way that facilitates this canceling. In our example this effect can be achieved by generating new random walkers at each surface hop: Whenever in step (ii,c) a hop is requested, a
copy of the random walker is made. While the original walker stays on the PES, the copy starts out on the new surface, whereby its phase and momenta are updated. Finally, the copy is added to the collection of random walkers already present, where the weights are adjusted accordingly. Proceeding this way, one may expect that at any time a sufficiently large number of random walkers is present to yield a reliable description of the density matrix. Although it is clear that the gain of accuracy has to be paid through an exponential rise of newly generated random walkers, it is found that the convergence of this scheme is considerably better than simply increasing the number of initially starting random walkers (see below).

The concept of generating new random walkers at curve crossings is quite similar to the “spawning” scheme suggested by Martinez and co-workers.\textsuperscript{46,50} In the “full multiple spawning” algorithm, trajectories are generated on the fly in order to serve as an efficient adaptive basis set. While the underlying theories are quite different (QCL equation vs Gaussian wave packets approximation\textsuperscript{51} to Schrödinger’s equation), both methods employ the same idea to improve convergence. The spawning concept is also utilized in the “localized threads”-algorithm suggested to solve the QCL equation.\textsuperscript{46} It should be emphasized, however, that the latter scheme differs from the procedure outline above in that new random walkers are generated at every time step and for every matrix element, thus requiring a much larger computational effort. In both methods, however, the increasing number of walkers represents a significant problem if longer propagation times are considered.

IV. COMPUTATIONAL RESULTS

A. Model

To demonstrate the capability of the QC approach introduced above, we consider various well-studied electronic two-state problems as a test example. Adopting a diabatic electronic representation with basis states $|\psi_{nm}\rangle$, the molecular model Hamiltonian reads\textsuperscript{52,53}

$$H^0 = T + \sum_{n,m=1,2} |\psi_{nm}\rangle V_{nm} \langle \psi_{nm}|. \quad (4.1)$$

Here $T$ denotes the kinetic-energy operator, $L$ is the unit matrix, and $V_{nm}$ represents the elements of the diabatic potential matrix. Within the harmonic approximation, the diagonal matrix elements are given by

$$V_{nn}(x) = E_n + \frac{1}{2} \sum_j \omega_j(x_j + \kappa_j^{(n)})^2, \quad (4.2)$$

where $\omega_j$ is the vibrational frequency and $x_j$ is the dimensionless position of the $j$th vibrational mode. $E_n$ denotes the vertical transition energy of the diabatic state $|\psi_{nm}\rangle$ and $\kappa_j^{(n)}$ represents the gradient of the corresponding PES along the $j$th vibrational mode.

In the simplest case, the off-diagonal matrix elements are assumed to be constant ($V_{12} = V_{21} = g$), thus resulting in an avoided crossing of the diabatic PESs. This ansatz, often referred to as “spin-boson model,” has been employed to describe a large variety of phenomena in chemical and solid-state physics, including, for example, photoinduced electron transfer in the condensed phase.\textsuperscript{54,55} In general, however, the diabatic coupling $V_{12}$ is a function of nuclear coordinates, thus giving rise to a conical intersection of the diabatic PESs.\textsuperscript{52,53,56,57} Since avoided and true surface-crossings may exhibit quite different electronic and vibrational relaxation dynamics, both cases are considered in this work.

The diabatic states $|\psi_n\rangle$ employed in the QC formulation described above and the diabatic states $|\psi_{nm}\rangle$ used to define the model Hamiltonian are related through a unitary transformation $S$,

$$|\psi_{nm}\rangle = \sum_m S_{nm} |\psi_m\rangle. \quad (4.3)$$

This transformation diagonalizes the diabatic potential matrix to give the corresponding adiabatic PESs,

$$W_{12}(x) = \frac{1}{2} (V_{11} + V_{22} + g \sqrt{(V_{12} - V_{11})^2 + 4V_{12}}). \quad (4.4)$$

The corresponding first-order nonadiabatic coupling for a linearly shifted vibrational mode $x_j$ is given by\textsuperscript{52}

$$d^{(1)}_{12}(x_j) = \frac{V_{12}(\kappa_j^{(1)} - \kappa_j^{(2)})}{(V_{22} - V_{11})^2 + 4V_{12}}. \quad (4.5)$$

In the present work we are interested in the time-dependent dynamics of the model (4.1) with respect to an initial state of the form,

$$\rho(0) = |\psi_2\rangle \langle \psi_2| \langle \psi_2|. \quad (4.6)$$

This preparation of the system can be achieved, for example, by assuming that the molecule is impulsively excited from its electronic and vibrational ground state to the optically bright electronic state $|\psi_2\rangle$. The photoexcitation creates a vibrational wave packet, which evolves on the coupled PESs thereby undergoing nonadiabatic transitions.\textsuperscript{53} A useful quantity to describe this photoinduced non-Born–Oppenheimer dynamics is the time-dependent population probability of the upper adiabatic electronic state\textsuperscript{52,53}

$$P^{ad}(t) = \text{Tr}(\rho(t) |\psi_2\rangle \langle \psi_2| \langle \psi_2|) \approx \text{Tr}_e(\rho_{22}(t)), \quad (4.7)$$

where $\text{Tr}_e$ denotes the trace with respect to the vibrational degrees of freedom. Apart from the diagonal elements (the populations), the off-diagonal elements of the electronic density matrix (the coherences) are of interest

$$C^{ad}(t) = \text{Tr}(\rho(t) (|\psi_1\rangle \langle \psi_2| + |\psi_2\rangle \langle \psi_1|)) = 2 \text{Re} \text{Tr}_e(\rho_{12}(t)). \quad (4.8)$$

Alternatively, one may change to the diabatic representation and consider, for example, the population probability of the upper diabatic electronic state,

$$P^{ad}(t) = \text{Tr}(\rho(t) |\psi_2\rangle \langle \psi_2| \langle \psi_2| \langle \psi_2|). \quad (4.9)$$

As discussed elsewhere,\textsuperscript{53} transitions between diabatic electronic states are important for the interpretation of spectroscopic data. This is because in the vicinity of a surface crossing the electronic dipole transition operator is only smooth in the diabatic representation. The diabatic representation, on
the other hand, is unique and is often advantageous for the interpretation of nonadiabatic relaxation processes.

To evaluate the time-dependent observables within the QCL formulation, the quantum-mechanical trace over vibrational degrees of freedom is replaced by a phase-space integral. For the adiabatic excited-state population probability, for example, we obtain

\[ P(t) = \int dx \int dp \rho_{22}(x,p,t). \]  

(4.10)

The initial quasiclassical phase-space distributions \( \rho_{2a}(x,p,t=0) \) are provided through a Monte Carlo sampling of the Wigner transform of the quantum-mechanical initial state (4.6). Within the harmonic approximation, one thereby obtains a Gaussian phase-space distribution for the vibrational ground state.

Let us briefly mention some computational details. The QCL calculations used the first-order Trotter scheme (3.2) with a time step \( \delta t = 0.05 \) fs. Integration of the classical Hamilton equations for \( x \) and \( p \) has been performed using a standard Runge-Kutta routine. If not noted otherwise, we have employed the momentum-jump approximation (2.16) and the initial number of random-walkers employed was \( N = 50,000 \). To obtain quantum-mechanical reference data, we have performed exact time-dependent wave packet propagations, employing a direct product basis constructed from diabatic electronic states and harmonic-oscillator states for the vibrational degrees of freedom (see, e.g., Refs. 52 and 53).

### B. One-dimensional example

In order to get a first impression on the performance of the QC Liouville approach, it is instructive to start with a simple one-mode spin-boson model with constant diabatic coupling. Employing the parameters \( E_a = 0 \), \( g = 0.1 \text{ eV} \), \( \omega = g \), and \( \kappa^{(1)} = \kappa^{(2)} = 0.5g \), the adiabatic potential-energy curves of the system exhibit an avoided curve crossing at \( x = 0 \). As initial mean position of the system we have chosen \( x(0) = 3 \), thereby assuming that the wave packet starts in some distance of the curve crossing. The initial mean momentum is \( p(0) = 0 \), and the width of the Gaussian distribution corresponds to the ground state of the harmonic-oscillator potential. Employing an analysis in terms of vibronic period-orbits, recently the time-dependent electronic and vibrational dynamics of this model problem has been discussed in detail.\(^5^8\)

Figure 1 shows (a) the adiabatic population \( P^{ad}(t) \), (b) the diabatic population \( P^{di}(t) \), and (c) the adiabatic coherence \( C^{ad}(t) \) for the one-mode two-state model under consideration. As discussed above, photoexcitation at time \( t = 0 \) prepares a vibrational wave packet which starts to slide down the upper adiabatic PES. Reaching the crossing region at \( \approx 20 \) fs, the wave packet bifurcates into two components evolving on the upper and lower electronic surface, respectively. Performing quasiperiodic oscillations on coupled PESs, in the course of time the molecule undergoes nonadiabatic transitions whenever the wave packet approaches the curve crossing. The adiabatic population probability \( P^{ad}(t) \) clearly reflects this behavior: Whenever the wave packet reaches the curve crossing, the adiabatic population is seen to drop rapidly, while it is approximately constant when the wave packet is away from the crossing region. In addition to this oscillation, the diabatic population \( P^{di}(t) \) and the coherence \( C^{ad}(t) \) exhibit a beating with a shorter period.\(^5^8\) Also shown in Fig. 1 is the comparison of quantum (thick lines) and QCL (thin lines) results. For short times, the QCL calculations are in quantitative agreement with the quantum reference data, for larger times the agreement deteriorates. Similar to the quality of these results, the norm of the QC density matrix [dotted line in Fig. 1(a)] is seen to deviate from unity with increasing time. This finding indicates that the loss of accuracy may be a problem of numerical convergence rather than an intrinsic problem of the QCL formulation.

In order to study the origin of the deviations observed, we first consider the statistical convergence of the QCL data. As a representative example, Fig. 2 shows the absolute error of the adiabatic population as a function of the number of iterations \( N \), that is, the number of initially starting random walkers. The data clearly reveal the well-known \( 1/\sqrt{N} \) convergence expected for Monte Carlo sampling. We also note the occurrence of the “sign-problem” mentioned above. It manifests itself in the fact that the number of iterations increases almost exponentially with propagation time: While at time \( t = 10 \text{ fs} \) only 200 iterations are sufficient to obtain an accuracy of \( 2\% \), one needs \( N = 10,000 \) at \( t = 50 \text{ fs} \).
As explained above, the calculations employ an algorithm which generates new random walkers when a nonadiabatic transition is requested. To illustrate the performance of this scheme, Fig. 3 shows the average number of random walkers which has been generated from a single initial random walker during the propagation (i.e., for a single iteration). Here, the full and short dashed lines represent the numbers pertaining to the upper \( \rho_{22} \) and lower \( \rho_{11} \) electronic state, respectively, while the long dashed line represent the number of random walkers being in the coherences \( \rho_{12}, \rho_{21} \) of the electronic density matrix. As has been anticipated, the number of random walkers increases exponentially in time: The first step in the decay of the adiabatic population at time \( \approx 20 \text{ fs} \) [cf. Fig. 1(a)] requires in the average only the generation of about three more random walkers in total, while the second step at \( t \approx 50 \text{ fs} \) already requires about 40 more random walkers. Furthermore, it is noted that already after \( \approx 30 \text{ fs} \) the random walkers are in the average equally distributed between the four elements of the electronic density matrix. This distribution is a consequence of the fact that the probabilities to change from a coherence to the upper and to the lower state are the same.\(^{60}\) Compared to the alternative scheme of simply increasing the number of initially starting random walkers, the present algorithm provides a speedup of about a order of magnitude.\(^{60}\)

Let us turn to the other main difficulty of a Monte Carlo implementation of the QCL approach, that is, the representation of the nonlocal operator (2.13) in terms of local classical trajectories. In the calculations presented above, the action of the derivative operator has been approximated by a local momentum jump (2.15) of the trajectory. To check the quality of this approximation, it is instructive to monitor the conservation of total energy in the QCL calculation. As shown in Fig. 4(a), the total energy of the system is conserved up to \( t \approx 30 \text{ fs} \), where is suddenly starts to oscillate. For \( t \geq 60 \text{ fs} \), the conservation of energy breaks down completely. To explain this somewhat surprising flaw of the QCL calculation, Fig. 4(b) shows the expectation value of the nuclear momentum. Starting at \( \langle p(0) \rangle = 0 \), the mean momentum oscillates with a period of \( \approx 40 \text{ fs} \) corresponding to the vibrational frequency \( \omega = 0.1 \text{ eV} \) employed in the model. Comparing Figs. 4(a) and (b), it is found that the onset of the energy fluctuations at \( t \approx 30 \text{ and } 60 \text{ fs} \) coincides with the times the mean momentum approaches zero, i.e., the turning points of the motion. This finding elucidates a problem of the
momentum-jump approximation (2.15), which assumes a small relative momentum transfer \( \delta p = S_{nm}/p \). For vanishing momentum \( p \), however, \( \delta p \) may diverge. To prove this conjecture, we have changed the algorithm and excluded all trajectories with \( \delta p > 1 \). Figure 4(a) shows that the modified algorithm (dashed line) does conserve total energy. This reconfirms our assumption that the large deviations of total energy in the original QCL scheme is indeed caused by nonadiabatic transitions at turning points. Figure 4 furthermore shows quantum and QCL results obtained for the mean nuclear momentum and the diabatic population probability. While the momenta are in excellent agreement in all cases, the diabatic population obtained for the momentum-restricted QCL scheme appears to be somewhat less accurate than the results of the standard QCL calculation shown in Fig. 1(b). We have also checked the performance of the QCL method in the case that the energy conservation of each individual trajectory is requested [cf. Eq. (2.17)]. The results obtained are found to be rather similar to the momentum-restricted QCL scheme.

Let us finally make contact to the popular ‘‘fewest-switches surface-hopping’’ (SH) method due to Tully,\(^{13}\) which has been described in numerous publications.\(^{61}\) Compared to the QCL approach presented above, this method has the following features: (i) It propagates trajectories only when the system is in a diagonal element of the electronic density matrix, but not during coherences. As a consequence, the method does not account for interferences between individual trajectories and does not suffer from the sign problem. (ii) It uses the ‘‘fewest switches’’ criterion to decide upon nonadiabatic transitions. While providing an exact stochastic realization of the dynamics of a pure \( N \)-level system, this ansatz represents an approximate stochastic description for a coordinate-dependent \( N \)-state system, thus possibly leading to consistency problems.\(^{27,62}\) (iii) It requires the energy conservation of each individual trajectory and therefore needs to reject energetically forbidden transitions.

Figure 1 shows a comparison of SH (dashed lines), QCL (thin lines), and quantum (thick lines) results as obtained for the two-state one-mode model under consideration. The SH results are seen to underestimate the back transfer of the adiabatic population at \( t \sim 50 \) and 80 fs. This is because the back reaction would require energetically forbidden electronic transitions which are not possible in the SH algorithm. While the diabatic population is reproduced qualitatively for the first 40 fs, the SH results for the electronic coherence are found to deviate drastically from the quantum reference. This failure of the SH description may be attributed to the approximate description of electronic coherences as discussed in (i). As a remedy, it has been suggested to augment the SH method with a ‘‘decocherence’’ function which affects a rapid decay of the electronic coherence.\(^{60}\) The results presented here indicate that no such ansatz is necessary if the QC formulation treats quantum coherences in an appropriate way. Comparing the results of the QCL and the SH calculations, the quality of the QCL data is clearly superior, in particular in the description of the electronic coherence. It should be noted, however, that the SH method does not suffer from the sign problem and is therefore much easier to converge. In the

![FIG. 5. Comparison of quantum (thick lines), QCL (thin lines) and SH (dashed lines) results as obtained for a three-mode two-state model. Shown are (a) the adiabatic population \( P_{ad}(t) \), (b) the diabatic population \( P_{di}(t) \), and (c) the electronic coherence \( c_{ad}(t) \).

SH calculations, for example, 1000 trajectories were found to be sufficient, whereas the QCL calculations required 50 000 iterations.

C. Multidimensional examples

It is important to investigate how the virtues of the QCL approach found for the one-mode model transfer to the general case of multimode dynamics. Due to the ultrafast decay of quantum coherences one may in some sense expect that multidimensional problems are actually easier to handle for a QC description.\(^{69}\) Furthermore, a multidimensional molecular system typically undergoes only a few electronic transitions and then remains on the lower adiabatic PES. This is advantageous for the QCL description, whose problems only occur during nonadiabatic transitions. On the other hand, quantum-chemical investigations have shown that multimode systems typically exhibit conical intersections of adiabatic PESs.\(^ {53,56,57}\) True intersections rather than avoided crossings may pose a problem for calculations using the adiabatic representation, since the nonadiabatic couplings (4.5) are singular on the crossing surface. Furthermore, the sampling of phase space and the convergence of the QCL scheme may be more tedious in many dimensions.

To check these ideas step by step, it is instructive to first consider a direct extension of the study above, that is, a three-mode spin-boson system with the parameters \( E_g = 0 \), \( g = 0.1 \) eV, \( \omega_1 = g \), \( \omega_2 = 1.2 g \), \( \omega_3 = 0.9 g \), \( \kappa_{ij}^{(1)} = -\kappa_{ij}^{(2)} = 0.5 g \) \( (j = 1, 2, 3) \). Figure 5 compares results obtained by
quantum (thick lines), QCL (thin lines), and SH (dashed lines) calculations for this model, showing the (a) adiabatic and (b) diabatic populations as well as (c) the electronic coherence. The simple vibrational pattern observed in the one-mode calculations is seen to be replaced by a more complex behavior resembling irreversible relaxation. In particular, both electronic populations exhibit an initial decay to a value of 0.5, which is the expected long-time limit of the electronic population due to the symmetry of the model. The populations remain constant for almost 40 fs, followed by oscillatory structures. The QCL calculations are found to be in good agreement with the quantum reference for all observables. The convergence of the algorithm was found to be similar as in the one-dimensional case. The SH results, on the other hand, only account for the short-time dynamics of the system. The calculations match the initial decay and the constant part of the electronic populations, but completely fail to reproduce the second step of the reaction. From the discussion of the SH method given above [cf. point (i)], it may be expected that this failure is due to the neglect of interferences between trajectories.

As a representative example for a conical intersection, we adopt a two-state three-mode model of the $S_2 \rightarrow S_1$ internal conversion process in pyrazine. Compared are quantum (thick line), standard QCL (thin full line), and energy-conserving QCL (dotted line) calculations.

![Initial decay of the adiabatic population probability obtained for the three-mode model of the $S_2 \rightarrow S_1$ internal-conversion process in pyrazine.](image)

Due to the large level density of the lower-lying adiabatic electronic state, the chances of a back transfer of the adiabatic population are quite small for a multidimensional molecular system. In the present example, the adiabatic population exhibits only minor recurrences at larger times and fluctuates around a long-time limit of $\approx 0.05$ (data not shown), thus reflecting the finite level density of the three-mode system. To a good approximation, one may therefore assume that subsequent to an electronic transition a random walker will stay on the lower adiabatic PES. This observation suggest a physically appealing computational scheme to calculate the time evolution of the system for longer times. First, the initial decay of the adiabatic population is calculated within the QCL approach up to a time $t_0$, when the system is (almost) completely localized in the lower adiabatic electronic state $|\psi_1\rangle$. In a second step, we take the resulting phase-space distribution $p_{11}(x,p,t_0)$ as an initial state for a standard quasiclassical trajectory propagation on the lower adiabatic PES. While the adiabatic electronic population is constant by construction, the scheme yields diabatic electronic quantities as well as observables of the nuclear motion such as the time-dependent mean positions and momenta.

As an example, Fig. 7 shows the diabatic electronic population probability for the three-mode model of pyrazine. As discussed elsewhere, the diabatic population exhibits an oscillatory initial decay on a time scale of 50 fs, which is followed by prominent recurrences of the diabatic population. The beating reflects nuclear wave packet motion on coupled PESs and can be monitored in femtosecond time-resolved experiments. The quantum-mechanical results (thick line) are reproduced well by the QCL calculations, which have assumed a “localization time” of $t_0=20$ fs. The results obtained for the standard QCL (thin full line) and the energy-conserving QCL (dotted line) are of similar quality, thus indicating that the phase-space distribution $p_{11}(x,p)$ at $t_0=20$ fs is similar for the two schemes. Also shown in Fig. 7 are the results obtained for a standard SH calculation (dashed line), which largely fail to match the quantum reference. As discussed in Refs. 47 and 62, this failure is a consequence of the consistency problems associated with classically forbidden hops.
V. CONCLUSIONS

We have outlined an efficient Monte Carlo implementation of the QCL formulation. To this end, a trajectory-based algorithm has been suggested that represents an exact stochastic realization of the QCL equation. The ubiquitous sign problem inherent to the stochastic evaluation has been discussed in detail. Various strategies to overcome this problem have been considered, including on-the-fly generation of new trajectories at curve-crossings and the localization of trajectories after irreversible electronic transitions. Furthermore, it has been shown that the accuracy of QCL calculations depends quite sensitively on the way the nonlocal quantum-jump operator is approximated.

Employing various spin-boson models including up to three vibrational degrees of freedom, the virtues and shortcomings of the algorithm have been studied in detail. Being a bound-state problem with long-lived electronic and vibrational coherences, these presumably simple examples have been found to represent a stringent test, which in several respects is much harder than the scattering problems usually considered. In all cases studied, nevertheless, the QCL calculations have been shown to yield good agreement with exact quantum reference data. In particular, the QCL results represent a significant improvement over the standard SH calculations, however, at the price of being computationally more demanding. Since nonadiabatic photoreactions in large molecules are typically irreversible, it therefore has been suggested to divide up the theoretical description in two steps: (i) A full QCL calculation to describe the initial nonadiabatic photoreaction, followed by (ii) a standard quasiclassical trajectory propagation on the lower adiabatic PES. This physically appealing scheme may provide an appropriate but computationally still affordable theoretical description of nonadiabatic photoprocesses in complex molecular systems.

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It is noted that the operations (3.5) and (3.6) do not commute. However, the ordering affects only terms of the order $\delta t^2$.


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This general feature of the stochastic scheme may cause convergence problems. For example, consider a situation in which the molecular system is predominately in a single state, say $\rho_{11}$. Although the expectation values of the population $P_2 = \text{Tr} \rho_{22}$ and the corresponding coherences are zero, nevertheless, there are the same number of random walkers in these states which need to cancel themselves in the phase average.

Assuming that in the average each random walker is propagated for half of the end time $t$, and requesting an accuracy of 2% at $t = 50$ fs, the present scheme requires a total number of $\sim 10^5$ random walkers to be propagated. Increasing simply the number of initially starting random walkers, on the other hand, $\sim 10^6$ random walkers would be required.

See, for example, the reviews of Coker (Ref. 17) and Tully in Ref. 3.


