

Liouville – von Neumann equation

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

Divide the d.o.f. into QS, CS, and CB

CB is a perturbation of the dynamics of QS and CS

Partial Wigner transform

$$\frac{\partial \hat{\rho}_W}{\partial t} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}_W] + \frac{1}{2} (\{\hat{H}, \hat{\rho}_W\} - \{\hat{\rho}_W, \hat{H}\})$$

Expansion in the adiabatic basis

$$\frac{\partial \rho_{\alpha\alpha'}}{\partial t} = -i[\omega_{\alpha\alpha'}(\mathbf{Q}_{CS}) + \hat{L}_{\alpha\alpha'}] \rho_{\alpha\alpha'} + \sum_{\beta\beta'} \hat{J}_{\alpha\alpha',\beta\beta'} \rho_{\beta\beta'}$$

Zwanzig projection on the out of diagonal elements of the density matrix

$$\frac{\partial \rho_{\alpha}}{\partial t} = -i\hat{L}_{\alpha} \rho_{\alpha} + \int_0^t dt' \sum_{\beta} \mathcal{M}_{\alpha\beta} \rho_{\beta}$$

Momentum-jump approximation

$$\hat{J}_{\alpha\rightarrow\beta} f(\mathbf{Q}_{CS}, \mathbf{\Pi}_{CS}) = f(\mathbf{Q}_{CS}, \mathbf{\Pi}_{CS} + \Delta\mathbf{\Pi}_{\alpha\beta})$$

Zwanzig projection on CB coordinates

$$\frac{\partial \rho_{CS}^{\alpha}}{\partial t} = -\hat{\Gamma}_{\alpha} \rho_{CS}^{\alpha} + \int_0^t dt' \sum_{\beta} \langle \mathcal{M}_{\alpha\beta} \rho_c(\mathcal{X}_{CB} | \mathcal{X}_{CS}) \rangle_{CB} \rho_{CS}^{\beta}$$

Markovian approximation

$$\frac{\partial \rho_{\alpha}}{\partial t} = -\hat{\Gamma}_{\alpha} \rho_{\alpha} + \sum_{\beta} m_{\alpha\beta} \hat{J}_{\alpha\rightarrow\beta} \rho_{\beta} - m_{\alpha\alpha} \rho_{\alpha}$$

# A multiscale approach to coupled nuclear and electronic dynamics. I. Quantum-stochastic Liouville equation in natural internal coordinates

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(Dated: 2 June 2023)

Multiscale methods are powerful tools to describe large and complex systems. They are based on a hierarchical partitioning of the degrees of freedom (d.o.f.) of the system, allowing one to treat each set of d.o.f. in the most computational efficient way. In the context of coupled nuclear and electronic dynamics, a multiscale approach would offer the opportunity to overcome the computational limits that, at present, do not allow one to treat a complex system (such as a biological macromolecule in explicit solvent) fully at quantum mechanical level. Based on the pioneering work of R. Kapral and G. Ciccotti [R. Kapral, G. Ciccotti, *J. Chem. Phys.* **110**, 8919 (1999)], this work is intended to present a nonadiabatic theory that describes the evolution of electronic populations coupled with the dynamics of the nuclei of a molecule in a dissipative environment (condensed phases). The two elements of novelty that are here introduced are: *i*) the casting of the theory in the natural, internal coordinates, that are bond lengths, bond angles, and dihedral angles; *ii*) the projection of those nuclear d.o.f. which can be considered at the level of a thermal bath, and therefore leading to a quantum-stochastic Liouville equation. Using natural coordinates allows the description of structure and dynamics in the way chemists are used to describe molecular geometry and its changes. The projection of the bath coordinates provides an important reduction of complexity and allows to formulate the approach that can be used directly in the statistical thermodynamics description of chemical systems.

## I. INTRODUCTION

In this work a multiscale approach for the simulation of the coupled quantum-classical dynamics of a flexible molecule in a solvent is presented. The objective is to provide a framework to interpret nonadiabatic phenomena, such as photophysical and photochemical processes (including those at the biological level),<sup>1–14</sup> as well as charge transfer processes,<sup>15–18</sup> occurring in a condensed phase. The full quantum mechanical description of the dynamics for such complex systems, based on the solution of the Liouville-von Neumann equation, is unfeasible. Therefore, approximated methods to describe the coupled electron and nuclear dynamics are required to interpret those experiments where the nuclear dynamics is in the same time scale of the evolution of the exquisitely quantum mechanical d.o.f. and/or a change of the electronic quantum state impacts the nuclear dynamics. An important example of the first scenario is the interpretation of the electronic or nuclear magnetic relaxation experiments. Here, the spin dynamics is coupled with the nuclear dynamics since in the semi-classical interpretation nuclear fluctuations are responsible for the time perturbation of the magnetic Hamiltonian of the system. To approach this problem, in 1989 Schneider and Freed<sup>19</sup> introduced the well known stochastic Liouville equation (SLE). It couples the stochastic, diffusive slow dynamics of the system with the spin relaxation dynamics without the back-effect of spin d.o.f. on the nuclei. An example of the second scenario is the photo-acoustic effect, where a system absorbs photons promoting the electrons to an excited energy level and then dissipates the electronic energy in a nonradiative way, thus transferring energy to the nuclei in the form of kinetic energy. In this case, differently from the SLE, a nonadiabatic descrip-

tion is required to describe the energy transfer between electrons and nuclei. Also, because of the fast time scales of electron dynamics, an inertial description of the time evolution of the nuclei is required.

In the vast panorama of nonadiabatic quantum-classical methods, the most popular approach is the trajectory surface hopping (TSH) for its conceptual simplicity and straightforward implementation.<sup>3,9</sup> The idea behind TSH is to compute a swarm of classical and independent trajectories to approximate the nuclear motion on the adiabatic electronic PES. The nonadiabatic transitions are ruled by a stochastic algorithm that decides if the system remains in the current electronic state or it hops to another one. The popularity of TSH has risen after the implementation known as Fewest-switches surface-hopping (FSSH), which can be derived from a quantum-classical description of the dynamics of the system.<sup>20,21</sup>

A second popular formalism is the so-called mean-field Ehrenfest dynamics.<sup>22</sup> Here, a simultaneous solution of both the quantum evolution for the electronic state to recover the density matrix elements, and the classical evolution to obtain the nuclear coordinates is carried out. This framework has two main limits. Firstly, the mean-field treatment does not allow to simulate the situation when a system leaves regions of high nonadiabatic coupling. Secondly, the principle of detailed balance is not satisfied.

Another approach is the multiple spawning method.<sup>23,24</sup> In this theory, the nuclear wavefunction is expanded in Gaussian functions that are classically propagated. The number of nuclear functions is allowed to change after spawning events to reproduce the bifurcation of the wave packet inside regions with a high nonadiabatic coupling. The bottleneck of this kind of simulations is the evaluation of the Hamiltonian matrix whose integrals are often calculated by a zero-order saddle point approximation.

Finally, the description of the dynamics based on the defini-

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tion of a quantum-classical Liouville equation<sup>25</sup> (QCLE) is introduced, as it is the approach that has inspired this work. The method is based on a partial Wigner transform (see next Section), which leads in a natural way to a hybrid quantum-classical density matrix. Its time evolution depends on a quantum mechanical Hamiltonian operator acting on the electrons and a classical Hamiltonian giving the internuclear energy. The nuclear-electronic coupling depends on both the PESs and the nonadiabatic coupling matrix obtained from the Born-Oppenheimer electronic eigenstates.

In this work, the QCLE equation is derived in the rigid body plus natural internal coordinates. The latter are bond lengths, bond angles, and dihedral angles. Despite the fact describing the dynamics in curvilinear coordinates is more complicated from a formal point of view, the advantage is the simpler description of the changes in geometry of the molecule. Moreover, adopting a philosophy similar to that followed by Kapral in his work on quantum dynamics in classical baths,<sup>26</sup> the classical (nuclear) degrees of freedom will be divided into relevant and irrelevant. Such a distinction is relative to the effect of the d.o.f. on the physical observable that is being interpreted. Here, the irrelevant d.o.f. will be intended as those nuclear degrees of freedom that are *i*) fast with respect to the relevant nuclear coordinates, and *ii*) energetically uncoupled from the quantum d.o.f.. The second requirement implies that for the irrelevant nuclear coordinates, the adiabatic Born-Oppenheimer approximation should hold. A Zwanzig projection<sup>27</sup> will be carried out, leading to a quantum-stochastic Liouville equation (QSLE), which constitutes a multiscale description of the time evolution of the system dividing the d.o.f. into three categories: quantum, classical relevant, and classical irrelevant. In what follows, we shall split the degrees of freedom in subsystem + bath. The subsystem is composed by the quantum (QS) and classical relevant (CS) d.o.f., while the classical irrelevant ones are included in the bath (CB).

This paper is organized as follows. In Section II the QCLE is briefly derived in natural internal coordinates. In Section III the QSLE is obtained by means of the Zwanzig projection. In Section IV a discussion over the obtained equation is provided, oriented especially on the numerical solution. The computation of the nonradiative jumps among the PESs will be at the center of such a discussion to introduce the work reported on the companion paper, where a model for the fast calculation of the jump rates will be presented.

## II. DERIVATION OF THE QCLE IN INTERNAL NATURAL COORDINATES

As outlined in the Introduction, a hierarchical separation of the d.o.f. is carried out according to this scheme: the system is divided into the "relevant" subsystem (S) and the "irrelevant" bath (B). The bath includes only nuclear degrees of freedom, which are treated as classical d.o.f.. As anticipated above, CB is the set of d.o.f. that are fast with respect to the relevant nuclear coordinates, and uncoupled from the relevant quantum degrees of freedom. The subsystem is divided into quantum

(QS) and classical (CS) coordinates. In a first approximation, CS will be the set of relevant nuclear coordinates, while QS will be the set of electronic coordinates. The QS set may also include nuclear coordinates that need to be treated at quantum mechanical level. However, this is beyond the scope of this paper and is postponed to further advancements of the methodology.

Figure 1 provides an example of the separation of the degrees of freedom. In what follows we shall go through the steps to define the QCLE in the set of nuclear coordinates divided into rigid body + internal. The rigid body coordinates are the center of mass translation and the global tumbling of the molecule. The natural, Z-Matrix like, internal coordinates are here chosen, which make the description of the dynamics of the molecule in line with the way chemists describe molecular geometry. The derivation of the QCLE will follow that of Grunwald and Kapral<sup>25,28</sup>, based on the partial Wigner transform of the quantum Liouville equation, followed by a Zwanzig projection of the irrelevant quantum degrees of freedom. For the classical Hamiltonian in internal coordinates, results from a recent work of Polimeno et al.<sup>29</sup> will be used.

### A. Partial Wigner transform in natural coordinates

As a starting point, it is useful to work in Cartesian coordinates. If  $\mathbf{r}$  are the positions of the electrons, and  $\mathbf{R}$  those of the nuclei, the Liouville-von Neumann equation in the position representation reads

$$\frac{\partial}{\partial t} \hat{\rho}(\mathbf{r}, \mathbf{R}, t) = -\frac{i}{\hbar} [\hat{H}(\mathbf{r}, \mathbf{R}), \hat{\rho}(\mathbf{r}, \mathbf{R}, t)] \quad (1)$$

where  $\hat{H}$  is the system Hamiltonian, and  $\hat{\rho}$  is the matrix density. From here, a partial Wigner transform with respect to the nuclei coordinates is performed, followed by the heavy mass limit.<sup>25,30</sup> This first step is fundamental to separate the quantum d.o.f. of the electrons from the classical d.o.f. of the nuclei. In this way, the Liouville equation for the mixed quantum-classical system is obtained

$$\begin{aligned} \frac{\partial \hat{\rho}_W(\mathbf{r}, \mathbf{X}, t)}{\partial t} = & -\frac{i}{\hbar} [\hat{H}_W(\mathbf{r}, \mathbf{X}), \hat{\rho}_W(\mathbf{r}, \mathbf{X}, t)] \\ & + \frac{1}{2} \{ \hat{H}_W(\mathbf{r}, \mathbf{X}), \hat{\rho}_W(\mathbf{r}, \mathbf{X}, t) \} \\ & - \frac{1}{2} \{ \hat{\rho}_W(\mathbf{r}, \mathbf{X}, t), \hat{H}_W(\mathbf{r}, \mathbf{X}) \} \end{aligned} \quad (2)$$

where  $\mathbf{X} = (\mathbf{R}, \mathbf{P})$  are the positions and momenta of the nuclei,  $\hat{\rho}_W(\mathbf{r}, \mathbf{X}, t)$  is the quantum-classical density matrix,  $\hat{H}_W(\mathbf{r}, \mathbf{X})$  is the transformed Hamiltonian (see below), the subscript W states the action of partial Wigner transform, and the Poisson brackets stand for

$$\{ \hat{H}_W, \hat{\rho}_W \} = \frac{\partial \hat{H}_W}{\partial \mathbf{R}} \cdot \frac{\partial \hat{\rho}_W}{\partial \mathbf{P}} - \frac{\partial \hat{H}_W}{\partial \mathbf{P}} \cdot \frac{\partial \hat{\rho}_W}{\partial \mathbf{R}} \quad (3)$$

where the dependence of the Hamiltonian and of the density matrix on the spatial and temporal coordinates has been



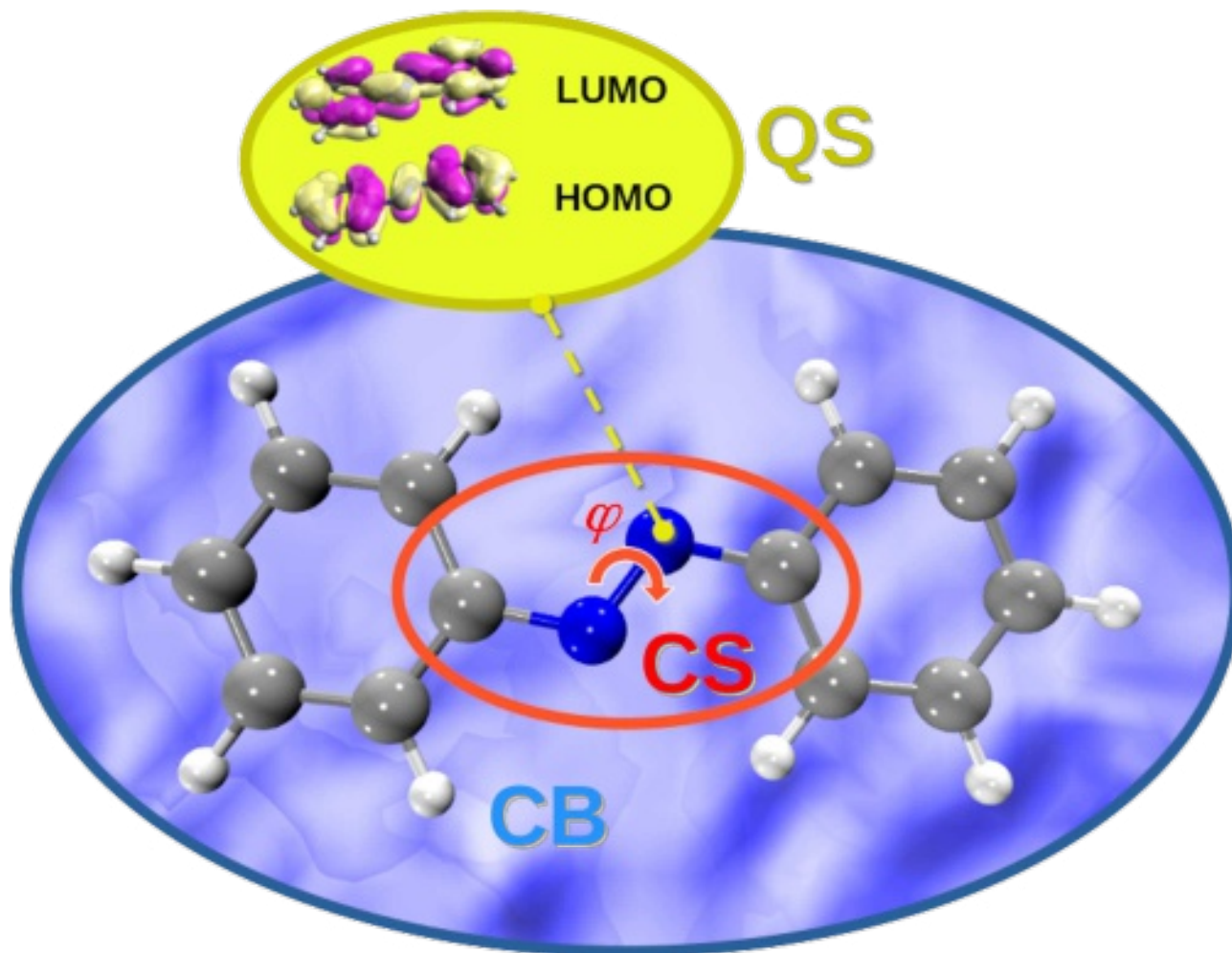


FIG. 1: A possible scheme for partitioning the coordinates of the molecular system if the QSLE approach was applied, for example, to study the photoswitching properties of azobenzene. Here, the quantum degrees of freedom of the system (QS) are the electrons, especially those responsible for the HOMO and LUMO orbitals (for this picture, obtained at B3LYP/6-31G\* level in the optimum geometry). The relevant classical internal coordinates (CS) are the rigid body roto-translations and the  $\varphi$  dihedral angle highlighted with a red arrow in the picture. Finally, all the other molecular internal degrees of freedom and the solvent coordinates (represented as a blue surface in the background) constitute the set of irrelevant bath coordinates (CB).

dropped to keep the expression more compact. The Hamiltonian has the form

$$\hat{H}_W(\mathbf{r}, \mathbf{X}) = \hat{K}(\mathbf{r}) + K(\mathbf{X}) + \hat{V}(\mathbf{r}, \mathbf{R}) = \hat{h}(\mathbf{r}, \mathbf{X}) + K(\mathbf{X}) \quad (4)$$

where the first addend is the kinetic energy operator of the electrons, the second term is the kinetic energy of the nuclei, and the third addend is the total potential energy, coupling the electrons with the nuclei. In the rightmost part of the equation, the kinetic energy of the electrons and the potential energy term have been grouped into the "electronic" Hamiltonian  $\hat{h}(\mathbf{r}, \mathbf{X})$ . As in the BO approximation, the eigenvalues of such an operator will be used to compute the PESs where the (classical) nuclear motion occurs.

From now on, we shall address only the partially Wigner transformed variables. For this reason, the subscript W is dropped from now on. An operator will be recognized as a partial Wigner transform since it will depend on the classical

nuclear momenta.

Next, the change of nuclear coordinates from Cartesian to internal is carried out. Following the work of Polimeno et al.<sup>29</sup>, the configuration of  $j$ -th molecule in the system is expressed by three sets of coordinates  $\mathbf{Q}_j = (\mathbf{R}_{CM,j}, \boldsymbol{\Omega}_j, \mathbf{p}_j)$  where  $\mathbf{R}_{CM,j}$  providing the instantaneous position of the center of mass,  $\boldsymbol{\Omega}_j$  is the instantaneous orientation, and  $\mathbf{p}_j$  are the internal coordinates providing the instantaneous conformation of the molecule.  $\boldsymbol{\Pi}_j = (\mathbf{P}_{CM,j}, \mathbf{L}_j, \mathbf{p}_j)$  is the set of the momenta conjugated to  $\mathbf{Q}_j$ , and the set of phase-space coordinates of the  $j$ -th molecule is labeled as  $\chi_j = (\mathbf{Q}_j, \boldsymbol{\Pi}_j)$ . If the system is composed by the solute (with index  $j = 0$ ) and  $N$  solvent molecules ( $j = 1, 2, \dots, N$ ), then the whole set of phase-space coordinates is  $\chi = (\chi_0, \chi_1, \dots, \chi_N)$ . According to Polimeno et al.<sup>29</sup>, equation 3 can be written as the sum of

three terms

$$\{\hat{H}, \hat{\rho}\} = \{\hat{H}, \hat{\rho}\}_{\text{TRA}} + \{\hat{H}, \hat{\rho}\}_{\text{ROT}} + \{\hat{H}, \hat{\rho}\}_{\text{INT}} \quad (5)$$

where the subscripts stand for translational (TRA), rotational (ROT), and internal (INT), and

$$\begin{aligned} \{\hat{H}, \hat{\rho}\}_{\text{TRA}} &= \sum_{j=0}^N \left[ (\hat{\nabla}_{\mathbf{R}_{\text{CM},j}} \hat{H}) \cdot \hat{\nabla}_{\mathbf{P}_{\text{CM},j}} \hat{\rho} - (\hat{\nabla}_{\mathbf{P}_{\text{CM},j}} \hat{H}) \cdot \hat{\nabla}_{\mathbf{R}_{\text{CM},j}} \hat{\rho} \right] \\ \{\hat{H}, \hat{\rho}\}_{\text{ROT}} &= \sum_{j=0}^N \left[ (\hat{\mathbf{M}}_j \hat{H}) \cdot \hat{\nabla}_{\mathbf{L}_j} \hat{\rho} - (\hat{\nabla}_{\mathbf{L}_j} \hat{H}) \cdot \hat{\mathbf{M}}_j \hat{\rho} \right. \\ &\quad \left. - \mathbf{L}_j \cdot (\hat{\nabla}_{\mathbf{L}_j} \hat{H} \times \hat{\nabla}_{\mathbf{L}_j} \hat{\rho}) \right] \\ \{\hat{H}, \hat{\rho}\}_{\text{INT}} &= \sum_{j=0}^N \left[ (\hat{\nabla}_{\mathbf{q}_j} \hat{H}) \cdot \hat{\nabla}_{\mathbf{p}_j} \hat{\rho} + (\hat{\nabla}_{\mathbf{p}_j} \hat{H}) \cdot \hat{\nabla}_{\mathbf{q}_j} \hat{\rho} \right] \end{aligned} \quad (6)$$

where  $\hat{\mathbf{M}}_j$  is the generator of infinitesimal rotations of the  $j$ -th molecule, and the gradients entering in the Poisson brackets are the elements of the gradient operator over nuclear phase-

space coordinates

$$\hat{\nabla}_{\boldsymbol{\chi}_j} = \begin{pmatrix} \hat{\nabla}_{\mathbf{Q}_j} \\ \hat{\nabla}_{\boldsymbol{\Pi}_j} \end{pmatrix} = \begin{pmatrix} \hat{\nabla}_{\mathbf{R}_{\text{CM},j}} \\ \hat{\mathbf{M}}_j \\ \hat{\nabla}_{\mathbf{q}_j} \\ \hat{\nabla}_{\mathbf{P}_{\text{CM},j}} \\ \hat{\nabla}_{\mathbf{L}_j} \\ \hat{\nabla}_{\mathbf{p}_j} \end{pmatrix} \quad (7)$$

The expression for the  $\hat{\mathbf{M}}_j$  operators depend on the way the molecular orientation is expressed. For example, if Euler angles are employed, then  $\hat{\mathbf{M}} = -i\hat{\mathbf{J}}$ , with  $\hat{\mathbf{J}}$  an angular momentum operator whose eigenfunctions are the Wigner matrices, which can be conveniently employed to span the functions of the orientation of the molecule.<sup>29</sup>

The Hamiltonian in the new set of variables is

$$\hat{H}(\mathbf{r}, \boldsymbol{\chi}) = \hat{K}(\mathbf{r}) + K(\boldsymbol{\chi}) + \hat{V}(\mathbf{r}, \mathbf{Q}) = \hat{h}(\mathbf{r}, \mathbf{Q}) + K(\boldsymbol{\chi}) \quad (8)$$

For molecules showing low anisotropy, the precessional term  $\hat{\nabla}_{\mathbf{L}_j} \hat{H} \times \hat{\nabla}_{\mathbf{L}_j} \hat{\rho}$  is responsible for second order, negligible corrections to the time evolution of the system, and for this reason it will be dropped.

The kinetic energy of the nuclei is  $K(\boldsymbol{\chi}) = \sum_{j=0}^N K_j(\boldsymbol{\chi}_j)$ , where<sup>29</sup>

$$\begin{aligned} K_j(\boldsymbol{\chi}_j) &= \boldsymbol{\Pi}_j \cdot \boldsymbol{\mu}_j^{-1}(\boldsymbol{\chi}_j) \boldsymbol{\Pi}_j = \begin{pmatrix} \mathbf{P}_{\text{CM},j} \\ \mathbf{L}_j \\ \mathbf{p}_j \end{pmatrix}^{\text{tr}} \begin{pmatrix} M_j^{-1} \mathbf{1}_3 & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{I}_j^{-1} - \mathbf{A}_j^{\text{tr}} \mathbf{g}_j \mathbf{A}_j & -\mathbf{A}_j^{\text{tr}} \mathbf{g}_j \\ \mathbf{0} & -\mathbf{g}_j \mathbf{A}_j & \mathbf{g}_j \end{pmatrix} \begin{pmatrix} \mathbf{P}_{\text{CM},j} \\ \mathbf{L}_j \\ \mathbf{p}_j \end{pmatrix} = \\ &= \frac{\mathbf{P}_{\text{CM},j} \cdot \mathbf{P}_{\text{CM},j}}{2M_j} + \frac{1}{2} \mathbf{L}_j \cdot (\mathbf{I}_j^{-1} \mathbf{L}_j) + \frac{1}{2} (\mathbf{p}_j - \mathbf{A}_j \mathbf{L}_j) \cdot \mathbf{g}_j (\mathbf{p}_j - \mathbf{A}_j \mathbf{L}_j) \end{aligned} \quad (9)$$

where  $\boldsymbol{\mu}_j(\boldsymbol{\chi}_j)$  is the generalized inertia matrix,  $M_j$  is the total mass of the  $j$ -th molecule,  $\mathbf{1}_3$  is the  $3 \times 3$  identity matrix,  $\mathbf{I}_j$  is the inertia tensor,  $\mathbf{A}_j$  is the Gauge potential matrix,  $\mathbf{g}_j$  is the contravariant metric tensor, and the superscript "tr" stands for transposition. The reader interested in the details is referred to the work of Polimeno et al.<sup>29</sup>

Different partitioning schemes of the nuclear coordinates into the relevant (CS) and the irrelevant (bath, CB) sets can be applied. In case of weak interaction between the solute and solvent molecules, the latter can be included in the thermal bath. However, in case of solutes with many degrees of freedom, part of the solute internal coordinates may be considered irrelevant (and thus, fast and weakly coupled to QS), and therefore be included in the CB set. By splitting the solute coordinates into  $\boldsymbol{\chi}_0 = (\mathbf{R}_{\text{CM},0}, \mathbf{L}_0, \mathbf{q}_0^{(\text{slow})}, \mathbf{q}_0^{(\text{fast})}) = (\boldsymbol{\chi}_{\text{CS}}, \mathbf{q}_0^{(\text{fast})})$ , since the interaction between  $\boldsymbol{\chi}_{\text{CS}}$  and  $\mathbf{q}_0^{(\text{fast})}$  is expected to build a short-time correlation, the following approximation is introduced

$$\boldsymbol{\mu}_0^{-1}(\boldsymbol{\chi}_0) \approx \begin{pmatrix} \boldsymbol{\mu}_{\text{CS}}^{-1}(\boldsymbol{\chi}_{\text{CS}}) & \mathbf{0} \\ \mathbf{0} & \mathbf{g}_0^{(\text{fast})}(\mathbf{q}_0^{(\text{fast})}) \end{pmatrix} \quad (10)$$

where  $\mathbf{g}_0^{(\text{fast})}$  is the square diagonal block of the metric contravariant tensor of the solute with the number of rows equal to the number of the fast internal coordinates. The CS submatrix reads

$$\boldsymbol{\mu}_{\text{CS}} = \begin{pmatrix} M_0^{-1} \mathbf{1}_3 & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{I}_0^{-1} - \mathbf{A}_0^{(\text{slow})} \cdot \mathbf{g}_0^{(\text{slow})} \mathbf{A}_0^{(\text{slow})} & -\mathbf{A}_j^{(\text{slow})} \cdot \mathbf{g}_0^{(\text{slow})} \\ \mathbf{0} & -\mathbf{g}_0^{(\text{slow})} \mathbf{A}_0^{(\text{slow})} & \mathbf{g}_0^{(\text{slow})} \end{pmatrix} \quad (11)$$

where  $\mathbf{A}_0^{(\text{slow})}$  and  $\mathbf{g}_0^{(\text{slow})}$  are, respectively, the Gauge and the contravariant metric tensors that have the dimensions compatible with the number of the slow internal coordinates. All the tensors in Equation 11 are computed considering the fast coordinates fixed in their minimum energy configuration.

Under such an approximation, the two sets of relevant and irrelevant coordinates read, respectively,  $\mathbf{Q}_{\text{CS}} = (\mathbf{R}_{\text{CS},0}, \mathbf{L}_0, \mathbf{q}_0^{(\text{slow})})$ , and  $\mathbf{Q}_{\text{CB}} = (\mathbf{q}_0^{(\text{fast})}, \mathbf{Q}_1, \dots, \mathbf{Q}_N)$ , and the conjugated momenta are partitioned accordingly to this scheme.

The Hamiltonian can be approximated as

$$\hat{H}(\mathbf{r}, \boldsymbol{\chi}) \approx \hat{K}(\mathbf{r}) + K(\boldsymbol{\chi}_{\text{CS}}) + K(\boldsymbol{\chi}_{\text{CB}}) + \hat{V}(\mathbf{r}, \mathbf{Q}_{\text{CS}}, \mathbf{Q}_{\text{CB}}) \quad (12)$$

where  $K(\boldsymbol{\chi}_{\text{CS}})$  and  $K(\boldsymbol{\chi}_{\text{CB}})$  are the kinetic energies of the CS and CB sets, respectively. In Equation 12, it has been made explicit the dependence of the potential energy on the three sets of coordinates (QS, CS, and CB), with the QS coordinates being the position of the electrons,  $\mathbf{r}$ .

### B. Expansion in the adiabatic basis

The next step is to represent the equation 2 in the adiabatic basis given by the eigenstates of  $\hat{h}(\mathbf{r}, \mathbf{Q})$ . Here it is introduced the approximation of small coupling between QS and CB

$$\hat{V}(\hat{\mathbf{r}}, \mathbf{Q}_{\text{CS}}, \mathbf{Q}_{\text{CB}}) \approx \hat{V}_{\text{QS-CS}}(\hat{\mathbf{r}}, \mathbf{Q}_{\text{CS}}) + V_{\text{CS-CB}}(\mathbf{Q}_{\text{CS}}, \mathbf{Q}_{\text{CB}}) \quad (13)$$

Under this approximation, the eigenstates of the electronic Hamiltonian do not depend on  $\mathbf{Q}_{\text{CB}}$ . Therefore, the adiabatic basis reads

$$\hat{h}(\mathbf{r}, \mathbf{Q}) |\alpha; \mathbf{Q}_{\text{CS}}\rangle = E_{\alpha}(\mathbf{Q}) |\alpha; \mathbf{Q}_{\text{CS}}\rangle \quad (14)$$

where  $|\alpha; \mathbf{Q}_{\text{CS}}\rangle$  is the eigenstate that in the BO notation keeps the parametric dependence on the nuclear (here only CS) coordinates, and  $\alpha$  is an index that catalogs the electronic stationary states.

Following Grunwald and Kapral<sup>28</sup>, Equation 2 is spanned over the set of adiabatic states obtained in Equation 14, leading to

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{\alpha\alpha'}(\boldsymbol{\chi}, t) = & -i [\omega_{\alpha\alpha'}(\mathbf{Q}_{\text{CS}}) + \hat{L}_{\alpha\alpha'}(\boldsymbol{\chi})] \rho_{\alpha\alpha'}(\boldsymbol{\chi}, t) \\ & + \sum_{\beta\beta'} \hat{J}_{\alpha\alpha',\beta\beta'}(\boldsymbol{\chi}) \rho_{\beta\beta'}(\boldsymbol{\chi}, t) \end{aligned} \quad (15)$$

where

$$\omega_{\alpha\alpha'}(\mathbf{Q}_{\text{CS}}) = \frac{\Delta E_{\alpha\alpha'}(\mathbf{Q}_{\text{CS}})}{\hbar} = \frac{E_{\alpha}(\mathbf{Q}) - E_{\alpha'}(\mathbf{Q})}{\hbar} \quad (16)$$

$$i\hat{L}_{\alpha\alpha'}(\boldsymbol{\chi}) = (\hat{\nabla}_{\Pi} K(\boldsymbol{\chi})) \cdot \hat{\nabla}_{\mathbf{Q}} + \frac{1}{2} (\mathbf{F}_{\alpha\alpha}(\mathbf{Q}) + \mathbf{F}_{\alpha'\alpha'}(\mathbf{Q})) \cdot \hat{\nabla}_{\Pi} \quad (17)$$

$$\begin{aligned} \hat{J}_{\alpha\alpha',\beta\beta'}(\boldsymbol{\chi}) = & -D_{\alpha\beta}^*(\boldsymbol{\chi}_{\text{CS}}) \left( 1 + \frac{\mathbf{F}_{\alpha\beta}^*(\mathbf{Q})}{2D_{\alpha\beta}^*(\boldsymbol{\chi}_{\text{CS}})} \cdot \hat{\nabla}_{\Pi_{\text{CS}}} \right) \delta_{\alpha'\beta'} \\ & - D_{\alpha'\beta'}(\boldsymbol{\chi}_{\text{CS}}) \left( 1 + \frac{\mathbf{F}_{\alpha'\beta'}(\mathbf{Q})}{2D_{\alpha'\beta'}(\boldsymbol{\chi}_{\text{CS}})} \cdot \hat{\nabla}_{\Pi_{\text{CS}}} \right) \delta_{\alpha\beta} \end{aligned} \quad (18)$$

with the force

$$\begin{aligned} \mathbf{F}_{\alpha\beta}(\mathbf{Q}) = & -\langle \alpha; \mathbf{Q}_{\text{CS}} | (\hat{\nabla}_{\mathbf{Q}} \hat{H}(\boldsymbol{\chi})) | \beta; \mathbf{Q}_{\text{CS}} \rangle \\ = & -\hat{\nabla}_{\mathbf{Q}} E_{\alpha}(\mathbf{Q}) \delta_{\alpha\beta} + \hbar \omega_{\alpha\beta}(\mathbf{Q}_{\text{CS}}) \mathbf{d}_{\alpha\beta}(\mathbf{Q}_{\text{CS}}) \end{aligned} \quad (19)$$

the nonadiabatic coupling term

$$\mathbf{d}_{\alpha\beta}(\mathbf{Q}_{\text{CS}}) = \langle \alpha; \mathbf{Q}_{\text{CS}} | \hat{\nabla}_{\mathbf{Q}_{\text{CS}}} | \beta; \mathbf{Q}_{\text{CS}} \rangle \quad (20)$$

and

$$D_{\alpha\beta}(\boldsymbol{\chi}_{\text{CS}}) = (\hat{\nabla}_{\Pi_{\text{CS}}} K(\boldsymbol{\chi}_{\text{CS}})) \cdot \mathbf{d}_{\alpha\beta}(\mathbf{Q}_{\text{CS}}) \quad (21)$$

where  $\mathbf{d}_{\alpha\beta}$  is in general a function of all the CS coordinates, including center of mass translation and molecular rotations since non-adiabatic coupling can occur even just because electrons are traveling along with the nuclei.<sup>31</sup>

The classical Liouville operator  $i\hat{L}_{\alpha\alpha'}(\boldsymbol{\chi})$  accounts for the adiabatic evolution on the mean potential energy surface given by  $E_{\alpha\alpha'}(\mathbf{Q}) = (E_{\alpha}(\mathbf{Q}) + E_{\alpha'}(\mathbf{Q}))/2$ , while the operator  $\hat{J}_{\alpha\alpha',\beta\beta'}(\boldsymbol{\chi})$  accounts for quantum transitions. The adiabatic basis is supposed to be real so that the complex conjugate superscript "\*" of the nonadiabatic coupling matrix element  $\mathbf{d}_{\alpha\beta}(\mathbf{Q}_{\text{CS}})$  is dropped.

The coherences (out of diagonal elements) of the quantum-classical density matrix can be considered fast (irrelevant) quantum d.o.f., compared to the populations (the diagonal elements). For this reason, the following Zwanzig projection operator is introduced

$$\hat{\mathcal{P}}_{\alpha\alpha',\beta\beta'} = \delta_{\alpha\alpha'} \delta_{\alpha\beta} \delta_{\alpha'\beta'} \quad (22)$$

as well as its complement

$$\hat{\mathcal{Z}}_{\alpha\alpha',\beta\beta'} = (1 - \delta_{\alpha\alpha'}) \delta_{\alpha\beta} \delta_{\alpha'\beta'} \quad (23)$$

The reader interested in the details of the Zwanzig projection is addressed to the work of Kapral and Ciccotti<sup>25</sup>. The projected evolution of the populations is given by<sup>28</sup>

$$\begin{aligned} \frac{\partial \rho_{\alpha}(\boldsymbol{\chi}, t)}{\partial t} = & -i\hat{L}_{\alpha}(\boldsymbol{\chi}) \rho_{\alpha}(\boldsymbol{\chi}, t) \\ & + \int_0^t dt' \sum_{\beta} \hat{\mathcal{M}}_{\alpha\beta}(t') \rho_{\beta}(\boldsymbol{\chi}, t-t') \end{aligned} \quad (24)$$

where  $\rho_{\alpha}(\boldsymbol{\chi}, t) \equiv \rho_{\alpha\alpha}(\boldsymbol{\chi}, t)$ ,  $i\hat{L}_{\alpha}(\boldsymbol{\chi}) \equiv i\hat{L}_{\alpha\alpha}(\boldsymbol{\chi})$ , and the memory kernel operator  $\hat{\mathcal{M}}_{\alpha\beta}(\boldsymbol{\chi}, t)$  is

$$\hat{\mathcal{M}}_{\alpha\beta}(\boldsymbol{\chi}, t) = \sum_{\nu\nu'} \sum_{\mu\mu'} \hat{J}_{\alpha\nu,\nu\mu'}(e^{-i\hat{\mathcal{Z}}_{\alpha\alpha'} t})_{\nu\nu',\mu\mu'} \hat{J}_{\mu\mu',\beta\beta} \quad (25)$$

The double hat indicates a superoperator acting in the Liouville space. In this way, a generalized master equation is obtained introducing memory effects.

### C. Momentum-jump approximation

Equation 24 is the exact result of the application of the Zwanzig projection. However, usually it is not used as it is. In particular, two approximations are introduced. One is called the momentum-jump approximation,<sup>30,32,33</sup> while the second one is the Markovian approximation. The former is introduced to simplify the action of the operator  $\hat{J}$  that enters in the memory kernel operator (Equation 25). Such an approximation is useful if one is interested in calculating trajectories, since allows for a faster and more stable algorithm.<sup>30</sup> The scope of the derivation presented in this work is slightly



different. We are interested in the direct solution of the Liouville equation. Therefore, no surface-hopping trajectories are planned and the momentum-jump approximation is not really needed. However, this approximation provides a clear interpretation of the diabatic evolution of the quantum and classical coordinates. In particular, the interpretation is that a jump between two adiabatic PESs is accompanied by a change in the kinetic energy (and thus momentum) of the nuclei. An upward electronic transition can occur only if nuclei possess sufficient momentum; a downward electronic transition is always possible, with the energy transferred to the nuclei. Therefore, we decided to adopt this approximation, which is described in this subsection. A discussion on the Markovian approximation is postponed to the next Section.

The momentum-jump approximation is here translated to the care of curvilinear internal coordinates  $\chi$ . To this purpose, Equation 21 is rewritten as

$$\begin{aligned} D_{\alpha\beta}(\chi_{CS}) &= (\boldsymbol{\mu}_{CS}^{-1}\boldsymbol{\Pi}_{CS}) \cdot \mathbf{d}_{\alpha\beta}(\mathbf{Q}_{CS}) \\ &= (\mathbf{V}\mathbf{G}_{CS}\mathbf{V}^{\text{tr}}\boldsymbol{\Pi}_{CS}) \cdot \mathbf{d}_{\alpha\beta}(\mathbf{Q}_{CS}) \\ &= (\mathbf{V}\mathbf{G}_{CS}^{1/2}\mathbf{G}_{CS}^{1/2}\mathbf{V}^{\text{tr}}\boldsymbol{\Pi}_{CS}) \cdot \mathbf{d}_{\alpha\beta}(\mathbf{Q}_{CS}) \\ &= (\mathbf{G}_{CS}^{1/2}\mathbf{V}^{\text{tr}}\boldsymbol{\Pi}_{CS}) \cdot (\mathbf{G}_{CS}^{1/2}\mathbf{V}^{\text{tr}}\mathbf{d}_{\alpha\beta}(\mathbf{Q}_{CS})) \\ &= \tilde{\boldsymbol{\Pi}}_{CS} \cdot \tilde{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{CS}) \\ &= \|\tilde{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{CS})\| \tilde{\boldsymbol{\Pi}}_{CS} \cdot \hat{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{CS}) \end{aligned} \quad (26)$$

where  $\mathbf{G}_{CS}$  and  $\mathbf{V}$  are respectively the matrix of the eigenvalues and the eigenvectors associated to  $\boldsymbol{\mu}_{CS}^{-1}$ , the tilde means pre-multiplication by  $\mathbf{G}_{CS}^{1/2}\mathbf{V}^{\text{tr}}$ ,  $\|\tilde{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{CS})\|$  and  $\hat{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{CS})$  are respectively the norm and the versor of  $\mathbf{d}_{\alpha\beta}(\mathbf{Q}_{CS})$ .

The term that depends on the gradient over the momenta in the  $\hat{J}$  operator can be reformulated as

$$\begin{aligned} \frac{\mathbf{F}_{\alpha\beta}(\mathbf{Q})}{2D_{\alpha\beta}(\chi_{CS})} \cdot \hat{\mathbf{V}}_{\boldsymbol{\Pi}_{CS}} &= \frac{\Delta E_{\alpha\beta}(\mathbf{Q}_{CS})}{2D_{\alpha\beta}(\chi_{CS})} \mathbf{d}_{\alpha\beta}(\mathbf{Q}_{CS}) \cdot \hat{\mathbf{V}}_{\boldsymbol{\Pi}_{CS}} \\ &= \frac{\Delta E_{\alpha\beta}(\mathbf{Q}_{CS})}{2\tilde{\boldsymbol{\Pi}}_{CS} \cdot \hat{\mathbf{d}}_{\alpha\beta}^{\text{INT}}(\mathbf{Q}_{CS})} \hat{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{CS}) \cdot \hat{\mathbf{V}}_{\tilde{\boldsymbol{\Pi}}_{CS}} \\ &= \Delta E_{\alpha\beta}(\mathbf{Q}_{CS}) \frac{\partial}{\partial (\tilde{\boldsymbol{\Pi}}_{CS} \cdot \hat{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{CS}))^2} \end{aligned} \quad (27)$$

Finally, the momentum-jump approximation is applied to equation 18

$$\begin{aligned} \hat{J}_{\alpha\alpha',\beta\beta'}(\chi) &= -D_{\alpha\beta}(\chi_{CS}) \hat{J}_{\alpha\beta}(\chi_{CS}) \delta_{\alpha'\beta'} \\ &\quad - D_{\alpha'\beta'}(\chi_{CS}) \hat{J}_{\alpha'\beta'}(\chi_{CS}) \delta_{\alpha\beta} \end{aligned} \quad (28)$$

and the effect of  $\hat{J}_{\alpha\beta}(\chi_{CS})$  on a generic function  $f(\chi_{CS})$  is

$$\begin{aligned} \hat{J}_{\alpha\beta}(\chi_{CS}) f(\chi_{CS}) &= e^{\Delta E_{\alpha\beta}(\mathbf{Q}_{CS}) \partial / \partial (\tilde{\boldsymbol{\Pi}}_{CS} \cdot \hat{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{CS}))^2} f(\chi_{CS}) \\ &= f(\bar{\chi}_{CS,\alpha\beta}) \end{aligned} \quad (29)$$

where  $f(\bar{\chi}_{CS,\alpha\beta})$  is the function evaluated over the same coordinates, but shifted momenta. In particular, the new phase-

space point is  $\bar{\chi}_{CS,\alpha\beta} = (\mathbf{Q}_{CS}, \boldsymbol{\Pi}_{CS} + \Delta\boldsymbol{\Pi}_{CS,\alpha\beta}(\chi_{CS}))$ , with

$$\begin{aligned} \Delta\boldsymbol{\Pi}_{CS,\alpha\beta}(\chi_{CS}) &= \mathbf{V}\mathbf{G}_{CS}^{-1/2} \hat{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{CS}) \left[ \text{sgn} \left( \tilde{\boldsymbol{\Pi}}_{CS} \cdot \hat{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{CS}) \right) \right. \\ &\quad \times \sqrt{(\tilde{\boldsymbol{\Pi}}_{CS} \cdot \hat{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{CS}))^2 + \Delta E_{\alpha\beta}(\mathbf{Q}_{CS})} \\ &\quad \left. - \tilde{\boldsymbol{\Pi}}_{CS} \cdot \hat{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{CS}) \right] \end{aligned} \quad (30)$$

In order to an upward electronic transition ( $\Delta E_{\alpha\beta} < 0$ ) to occur, the nuclei must possess sufficient kinetic energy. If not, the argument in the square root is negative and since this would lead to a complex momentum, in such a case the jump among the PESs is considered forbidden.

### III. DERIVATION OF THE QSLE

Within the momentum-jump approximation equation 24 can be recast as

$$\begin{aligned} \frac{\partial \rho_{\alpha}(\chi, t)}{\partial t} &= -i\hat{L}_{\alpha}(\chi) \rho_{\alpha}(\chi, t) \\ &\quad + \int_0^t dt' \sum_{\beta} M_{\alpha\beta}^{\alpha\beta}(\chi, t') \rho_{\beta}(\bar{\chi}_{CS,\alpha\beta,t'}, \chi_{CB,t'}, t-t') \\ &\quad + \int_0^t dt' \sum_{\beta} M_{\alpha\beta}^{\beta\alpha}(\chi, t') \rho_{\alpha}(\bar{\chi}_{CS,\alpha\beta,t'}, \chi_{CB,t'}, t-t') \end{aligned} \quad (31)$$

where the formalism of the time-reversed trajectory<sup>25,28</sup> is used

$$\bar{\chi}_{CS,\alpha\beta,t} = e^{-i\hat{L}_{\alpha\beta}(\bar{\chi}_{CS,\alpha\beta}, \chi_{CB})t} \bar{\chi}_{CS,\alpha\beta} \quad (32)$$

$$\chi_{CB,\alpha\beta,t} = e^{-i\hat{L}_{\alpha\beta}(\bar{\chi}_{CS,\alpha\beta}, \chi_{CB})t} \chi_{CB} \quad (33)$$

and

$$\bar{\chi}_{CS,\alpha\beta,t}^{\beta\alpha} = \hat{J}_{\beta\alpha}(\chi_{CS}) \bar{\chi}_{CS,\alpha\beta,t} \quad (34)$$

The memory functions  $M_{\alpha\beta}^{\alpha\beta}(\chi, t)$  and  $M_{\alpha\beta}^{\beta\alpha}(\chi, t)$  are defined as follows

$$M_{\alpha\beta}^{\alpha\beta}(\chi, t) = 2\text{Re}[W_{\alpha\beta}(\chi, t)] D_{\alpha\beta}(\chi_{CS}) D_{\alpha\beta}(\bar{\chi}_{CS,\alpha\beta,t}) \quad (35)$$

$$M_{\alpha\beta}^{\beta\alpha}(\chi, t) = 2\text{Re}[W_{\alpha\beta}(\chi, t)] D_{\alpha\beta}(\chi_{CS}) D_{\beta\alpha}(\bar{\chi}_{CS,\alpha\beta,t}) \quad (36)$$

where the phase factor is

$$W_{\alpha\beta}(\chi, t) = e^{-i \int_0^t d\tau \omega_{\alpha\beta}(\bar{\mathbf{Q}}_{CS,\alpha\beta,\tau})} \quad (37)$$

with  $\bar{\mathbf{Q}}_{CS,\alpha\beta,t} = e^{-i\hat{L}_{\alpha\beta}(\bar{\chi}_{CS,\alpha\beta}, \chi_{CB})t} \mathbf{Q}_{CS}$ . It has to be mentioned that this result is exact only for two-level systems. However, it is applicable to multilevel systems if the terms higher than quadratic order in  $\mathbf{d}_{\alpha\beta}(\mathbf{Q}_{CS})$  in the evolution operators are negligible.<sup>28</sup> Considering the fast d.o.f. of the CB, a further projection operator<sup>28,29,34</sup> is introduced

$$\hat{\mathfrak{P}} = \rho_c(\chi_{CB}|\chi_{CS}) \langle \dots \rangle_{CB} \quad (38)$$



and its complement  $\hat{\Omega}$ . The conditional equilibrium probability density,  $\rho_c(\chi_{\text{CB}}|\chi_{\text{CS}})$ , is defined as follows<sup>28,29</sup>

$$\rho_c(\chi_{\text{CB}}|\chi_{\text{CS}}) = \frac{\rho_{\text{eq}}(\chi)}{\rho_{\text{eq}}^{\text{CS}}(\chi_{\text{CS}})} \quad (39)$$

where  $\rho_{\text{eq}}(\chi)$  is the equilibrium population density independent from the state, and  $\rho_{\text{eq}}^{\text{CS}}(\chi_{\text{CS}}) = \langle \rho_{\text{eq}}(\chi) \rangle_{\text{CB}}$ . Applying the projection operator to Equation 31 and neglecting the oscillations of the memory function around its bath average lead to the following result<sup>28</sup>

$$\begin{aligned} \frac{\partial \hat{\mathcal{P}}\rho_\alpha(\chi, t)}{\partial t} = & -\hat{\mathcal{P}}i\hat{L}_\alpha(\chi)\hat{\mathcal{P}}\rho_\alpha(\chi, t) \\ & + \int_0^t dt' \hat{\mathcal{P}}i\hat{L}_\alpha(\chi) e^{-i\hat{\Omega}\hat{L}_\alpha(\chi)t'} \hat{\Omega}\hat{L}_\alpha(\chi)\hat{\mathcal{P}}\rho_\alpha(\chi, t) \\ & - \hat{\mathcal{P}}i\hat{L}_\alpha(\chi) e^{-i\hat{\Omega}\hat{L}_\alpha(\chi)t'} \hat{\Omega}\rho_\alpha(\chi, 0) \\ & + \int_0^t dt' \sum_\beta \hat{\mathcal{P}}M_{\alpha\beta}^{\alpha\beta}(\chi, t') \hat{\mathcal{P}}\rho_\beta(\bar{\chi}_{\text{CS},\alpha\beta,t'}, \chi_{\text{CB},t'}, t-t') \\ & + \int_0^t dt' \sum_\beta \hat{\mathcal{P}}M_{\alpha\beta}^{\beta\alpha}(\chi, t') \hat{\mathcal{P}}\rho_\alpha(\bar{\chi}_{\text{CS},\alpha\beta,t'}, \chi_{\text{CB},t'}, t-t') \end{aligned} \quad (40)$$

Given the subsystem density matrix population  $\rho_{\text{CS}}^\alpha(\chi_{\text{CS}}, t) = \langle \rho_\alpha(\chi, t) \rangle_{\text{CB}}$ , the initial condition

$$\rho_\alpha(\chi, 0) = \rho_{\text{CS}}^\alpha(\chi_{\text{CS}}, 0) \rho_c(\chi_{\text{CB}}|\chi_{\text{CS}}) \quad (41)$$

is assumed.<sup>29</sup> In this way, the third term of equation 40 is equal to zero. In the standard limit of fast relaxing bath coordinates, the first two terms corresponds to the Fokker-Planck evolution  $-\hat{\Gamma}_{\text{FP}}^\alpha(\chi_{\text{CS}})\rho_{\text{CS}}^\alpha(\chi_{\text{CS}}, t)$ .

The detailed derivation of the Fokker-Planck operator  $\hat{\Gamma}_{\text{FP}}^\alpha$  is found in reference 29. To make this paper self-consistent the final form of the operator is given here

$$\hat{\Gamma}_{\text{FP}}^\alpha = -k_{\text{B}}T \begin{bmatrix} \hat{\nabla}_{\text{QCS}} \\ \hat{\nabla}_{\text{ICS}} \end{bmatrix}^{\text{tr}} \begin{bmatrix} \mathbf{0} & -\mathbf{1} \\ \mathbf{1} & \boldsymbol{\xi} \end{bmatrix} \rho_{\alpha,\text{eq}} \begin{bmatrix} \hat{\nabla}_{\text{QCS}} \\ \hat{\nabla}_{\text{ICS}} \end{bmatrix} \rho_{\alpha,\text{eq}}^{-1} \quad (42)$$

where

$$\rho_{\alpha,\text{eq}}(\chi_{\text{CS}}) = \frac{\exp\{-[E_\alpha(\mathbf{Q}_{\text{CS}}) + K(\chi_{\text{CS}})]/k_{\text{B}}T\}}{\langle \exp\{-[E_\alpha(\mathbf{Q}_{\text{CS}}) + K(\chi_{\text{CS}})]/k_{\text{B}}T\} \rangle} \quad (43)$$

with  $\langle \dots \rangle$  meaning integration over  $\chi_{\text{CS}}$ . Also, in Equation 42,  $\boldsymbol{\xi}$  is the generalized friction tensor that is obtained by assuming the Markovian approximation after the Zwanzig-Mori projection of the CB degrees of freedom, and can be computed via hydrodynamic modeling.<sup>35</sup>

While usually in the QCLE the dynamics of the nuclei is treated at a deterministic level, in the QSLE the nuclear degrees of freedom that were included in the irrelevant set (acting as a thermal bath) are projected out. In this way, the dynamics of the relevant CS degrees of freedom is stochastic. The irrelevant d.o.f. affect the dynamics of CS coordinates by providing a mean field correction to the CS potential energy,

and providing fluctuation-dissipation to the momenta conjugated to the CS coordinates, where the important ingredient is the friction, which is usually obtained from hydrodynamic arguments.<sup>35</sup> It should be noticed that the projection of the CB coordinates to describe the (stochastic) dynamics of the CS coordinates only has also been presented by Kapral in Cartesian coordinates.<sup>26</sup> In fact, the work presented in this paper is based on the same philosophy of formulating a quantum-classical description of the dynamics of a molecule in liquid phases (dissipative environment), but in internal curvilinear coordinates.

The last two terms in Equation 40 involve the bath average of the memory function, that results in a decaying function on a time scale characterized by the decoherence time  $\tau_{\text{decoh}}$ .<sup>28</sup> If the characteristic time scales of the time evolution of the populations is larger than  $\tau_{\text{decoh}}$ , then the Markovian approximation can be invoked

$$\begin{aligned} \langle M_{\alpha\beta}^{\alpha\beta}(\chi, t) \rho_{\alpha,\text{CB}}^c(\chi_{\text{CB}}|\chi_{\text{CS}}) \rangle_{\text{CB}} & \approx \\ & \approx 2\delta(t) \int_0^\infty dt' \langle M_{\alpha\beta}^{\alpha\beta}(\chi, t') \rho_c(\chi_{\text{CB}}|\chi_{\text{CS}}) \rangle_{\text{CB}} \equiv \\ & \equiv 2\delta(t) m_{\alpha\beta}(\chi_{\text{CS}}) \end{aligned} \quad (44)$$

Introducing all the previous approximation into Equation 40, the QSLE is obtained

$$\begin{aligned} \frac{\partial \rho_{\text{CS}}^\alpha(\chi_{\text{CS}}, t)}{\partial t} = & -\hat{\Gamma}_{\text{FP}}^\alpha(\chi_{\text{CS}})\rho_{\text{CS}}^\alpha(\chi_{\text{CS}}, t) \\ & + \sum_\beta m_{\alpha\beta}(\chi_{\text{CS}}) \hat{j}_{\alpha\rightarrow\beta}(\chi_{\text{CS}}) \rho_{\text{CS}}^\beta(\chi_{\text{CS}}, t) \\ & - m_{\alpha\alpha}(\chi_{\text{CS}}) \rho_{\text{CS}}^\alpha(\chi_{\text{CS}}, t) \end{aligned} \quad (45)$$

where

$$m_{\alpha\alpha}(\chi_{\text{CS}}) = - \sum_\beta \int_0^\infty dt' \langle M_{\alpha\beta}^{\beta\alpha}(\chi, t') \rho_c(\chi_{\text{CB}}|\chi_{\text{CS}}) \rangle_{\text{CB}} \quad (46)$$

and the effect of  $\hat{j}_{\alpha\rightarrow\beta}(\chi_{\text{CS}})$  is equivalent to the one described in section II C except for

$$\begin{aligned} \Delta\Pi_{\text{CS},\alpha\rightarrow\beta}(\chi_{\text{CS}}) = & \mathbf{V}\mathbf{G}_{\text{CS}}^{-1/2} \hat{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{\text{CS}}) \left[ \text{sgn}(\tilde{\Pi}_{\text{CS}} \cdot \hat{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{\text{CS}})) \right. \\ & \times \left. \sqrt{(\tilde{\Pi}_{\text{CS}} \cdot \hat{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{\text{CS}}))^2 + 2\Delta E_{\alpha\beta}(\mathbf{Q}_{\text{CS}}) - \tilde{\Pi}_{\text{CS}} \cdot \hat{\mathbf{d}}_{\alpha\beta}(\mathbf{Q}_{\text{CS}})} \right] \end{aligned} \quad (47)$$

#### IV. DISCUSSION

Figure 2 summarizes in a flowchart the sequence of approximations that have been introduced in the derivation of the QSLE starting from first principles, *i.e.* the Liouville-von Neumann equation.

The partitioning of the degrees of freedom into the three sets QS, CS, and CB is the most important choice to model the dynamics of the system in such a way that it can simulate realistically the physical observable to be reproduced. The coordinates that have to be considered at quantum mechanical level of theory enter in the QS set. Of course electrons

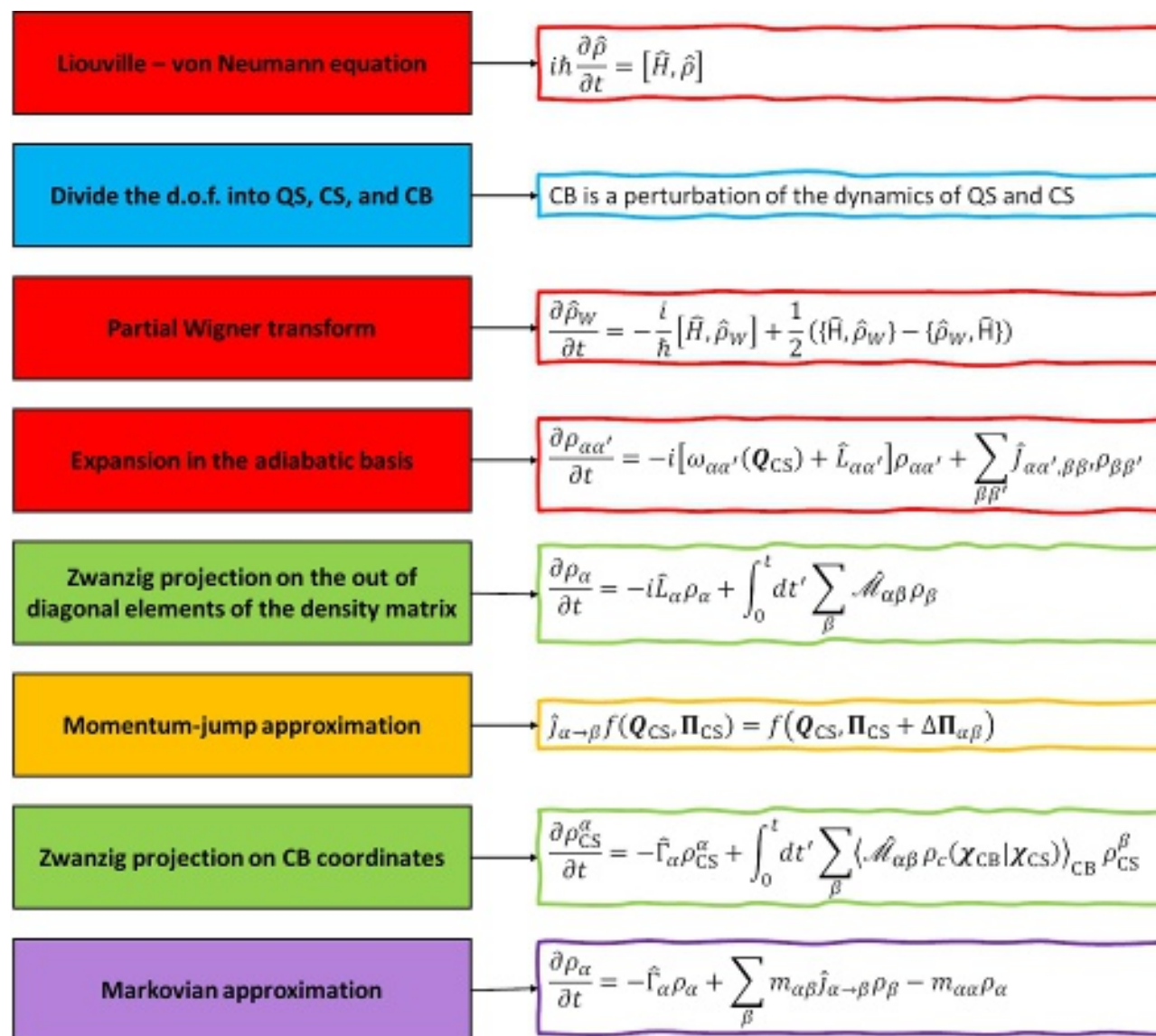


FIG. 2: Flowchart summarizing the approximations that lead from the quantum mechanical Liouville-von Neumann equation to the QSLE. On the right of each block the main resulting equation is reported. In the red boxes the dynamics is described at deterministic level. In the cyan box a decision is taken regarding the hierarchy division of the degrees of freedom of the system. In the green boxes the dynamics takes on a stochastic connotation. In the yellow box the momentum-jump approximation is carried out. The purple box summarizes the final QSLE set of equations under the Markovian approximation for the jumps among the PESs and for the dynamics of the CS degrees of freedom.

positions are automatically included here. Nuclear degrees of freedom may also be added to QS, with the necessity of calculating the adiabatic electronic and nuclear eigenstates. A way to simplify the problem, in this case, would be to assume an ansatz an harmonic dynamics of the QM nuclei. The CS set includes all the nuclear degrees of freedom treated at classical level that are considered relevant for the physical observable to be computed. As an example, if one is interested in the photoswitching properties of a molecule, such as azobenzene, then CS should contain at least the torsion angle that is responsible for the *cis-trans* change in conformation. Finally, the CB set collects all of the remaining nuclear classical d.o.f., which

are considered a perturbation to the dynamics of QS and CS, with the important approximation that the eigenstates of the QS Hamiltonian do not depend on CB. It is important to stress that in cases where the solvent can have specific interactions with the molecule (such as the formation of hydrogen bonds), it may be important to include in CS (or even in QS) the relevant solvent coordinates, which will be a small subset of all the coordinates of the solvent molecules.

The approximations that are then carried out are the following: *i*) a partial Wigner transform is used to obtain the time evolution of a quantum-classical density matrix; *ii*) such a density matrix is spanned over the adiabatic quantum states,

so that the time evolution of each element is obtained; *iii*) a Zwanzig projection is carried out over the out of diagonal elements of the density matrix that are involved in fast relaxing processes with respect to the time evolution of the populations (diagonal elements), leading to a classical evolution of CS and CB coupled to a master equation-like behavior with jumps among states; *iv*) the momentum-jump approximation is here introduced to simplify the shape of the jump operators; *v*) a Zwanzig projection is carried out over the CB d.o.f., leading to the stochastic dynamics of the CS coordinates; *vi*) finally, the Markovian approximation is carried out under the idea that in a condensed phase the memory on the populations jumps is readily lost before a changing in the conformation of the system occurs. At the end of such a process of approximations, Equation 45 is obtained, which resembles a diffusion-reaction equation. A first important difference is that the stochastic dynamics of the nuclei is not diffusive, rather it is inertial. This is important since the nuclear momenta conjugated to CS d.o.f. are affected by changes in the quantum state and, on the contrary, a change in momentum of the classical coordinates can induce a jump between quantum states. Therefore, the stochastic part is described by a Fokker-Planck operator. It should be said here that a further approximation may be introduced if part of the CS d.o.f. are not responsible for the jumps among quantum states. In this case, if such coordinates are slow with respect to the dynamics of the rest of the relevant degrees of freedom, then a further Zwanzig projection on the momenta conjugated to such slow CS coordinates may be carried out, leading to a mixed Fokker-Planck/Smoluchowski description of the nuclear dynamics. Despite the complexity to treat numerically such an equation (multiple time step strategies should be required) the advantage is the reduction on the number of coordinates that can be decisive in a computational approach.

The second difference with a diffusion-reaction equation is that usually the transitions are "vertical", *i.e.* the jump occurs between two populations evaluated in the same point in phase-space. The energy required for the jump is expected to be exchanged with the thermal bath. Here, energy exchange is expected especially between the QS and CS degrees of freedom. Therefore, a jump between two quantum states connects the probability densities of the states evaluated in two phase-space points separated by a value of the momenta of the CS subsystem such that the variation of their kinetic energy corresponds to the difference in energy of the two quantum states. As a final point of discussion, it should be mentioned that a further complexity reduction would be possible in the case part of the electronic states constitute a fast-relaxing manifold with respect to the dynamics of the remaining QS, and of the CS degrees of freedom. In this case, the projection of the dynamics over such a fast manifold leads to the motion of the nuclei over a potential of mean force surface obtained by the Boltzmann weighting of the electronic states involved in the manifold. Also, a fluctuation-dissipation effect is obtained because of the dynamics of the projected dynamics of the electrons, where the important parameter is the electronic friction.<sup>36</sup> If such an approximation can be applied, part (or all) of the random-walk over electronic PESs can be converted

in "electronic" contributions (together with the hydrodynamic ones) to the potential of mean force and to the friction.

## V. CONCLUSIONS

In this work, a quantum-stochastic Liouville equation has been formulated to describe the coupled quantum-classical dynamics of molecules in condensed phases. In the derivation of the QSLE (Equation 45), two Markovian approximations have been done because the dynamics of the molecule is occurring in a dissipative bath: *i*) on the classical dynamics of the CS d.o.f., and *ii*) on the master equation part that describes jumps among PESs. Therefore, Equation 45 is expected to be not applicable in the gas phase, or in general in inertial conditions, where the friction due to the thermal bath is low and the memory kernel given in Equation 25 is not expected to relax in a fast timescale with respect to the to the decay time of the phenomenon under consideration.<sup>37</sup> It can happen that while the Markovian approximation is possible for the dynamics of the CS subsystem, it is not applicable to the QS d.o.f. (jumps among PESs). In this case, the QSLE should be solved including memory effects.

The two main differences with respect to state-of-the-art methods based on a partial Wigner transform are that here the nuclear degrees of freedom are partitioned in the relevant and irrelevant sets, the former treated explicitly, the latter described at the level of a thermal bath inducing fluctuation and dissipation to the relevant coordinates. The second element of novelty is the derivation of the QSLE (and in an intermediate step, the derivation of the QCLE) expressed in internal natural coordinates. To pursue such a derivation the main approximation introduced was that CB and CS sets of degrees of freedom interact weakly. The introduction of curvilinear coordinates implies a mathematical treatment which is more tedious than working in Cartesian coordinates. The advantage is in the fact that using internal coordinates as bond lengths, bond angles and dihedral angles makes the interpretation of which coordinates are relevant or irrelevant very easy.

The next steps to make the approach operative are the parameterization and the numerical solution of the QSLE. To fully parameterize the equation one needs *i*) to calculate the potential energy surfaces, *i.e.* the energies of the quantum states as functions of the CS coordinates; *ii*) to estimate the friction tensor along the CS coordinates; *iii*) to evaluate the nonradiative rates  $m_{\alpha\beta}$  given in Equation 46. Energies can be obtained by finding the eigenstates of the full electronic Hamiltonian, or they can be built from a model Hamiltonian description of the relevant part of the electronic structure. For example, if  $\pi \rightarrow \pi^*$  interactions are those relevant for the system, it may be sufficient to use a Hückel-like model Hamiltonian. The friction tensor can also be easily evaluated if an hydrodynamic approach is employed. The authors developed in the past a computational tool, named DiTe2, which computes the hydrodynamic friction tensor of a flexible molecule in terms of the friction that the molecule experiences while translating, rotating, and changing conformation in a fluid medium.<sup>35</sup> Conformational changes are expressed in terms of natural in-



ternal coordinates.

The computation of transition rates needs a separate discussion. The average that must be computed inside the integral over time in Equation 46 is an integral to be carried out in the CB phase-space. Is it an integral over  $O(10^3)$ - $O(10^5)$  or even more coordinates. While in some cases unbiased or biased molecular dynamics simulations can be employed to compute such integrals, it must be noted that the average is carried out over the conditional probability density  $\rho_c(\chi_{CB}|\chi_{CS})$ . This means that the calculation of such an heavy integral may be repeated in any point of the CS phase-space. The computation is expected to become unaffordable as soon as the CS set contains just a few coordinates. A solution to this problem is to find a proper approximation that allows one to substitute the average in Equation 46 with a reasonable function. This is the work presented in paper following the present one. In paper II, an approximated expression for the calculation of  $m_{\alpha\beta}$  is presented and tested against the exact solution evaluated by molecular dynamics simulations. To keep a low computational effort, the testing is carried out over a very simple sand-box system with two quantum states and a single CS coordinate (and its conjugated momentum). A simple function with a single adjustable parameter has been obtained. In paper II, the estimation of such a parameter and the application to higher dimensional cases are discussed.

#### ACKNOWLEDGMENTS

This research has received no external funding.

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PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0148180