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Density Matrix Dynamics in Twin-Formulation: an efficient methodology based on Tensor-Train Representation of Reduced Equations of Motion

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The twin-formulation of quantum statistical mechanics is employed to describe a new methodology for the solution of the equations of motion of the reduced density matrix in their hierarchical formulation. It is shown that the introduction of tilde operators and of their algebra in the dual space greatly simplifies the application of numerical techniques for the propagation of the density matrix. The application of tensor-train representation of a vector to solve complex quantum dynamical problems within the framework of the twin-formulation is discussed. Next, applications of the hierarchical equations of motion to a dissipative polaron model are presented showing the validity and accuracy of the new approach.

Keywords: Quantum Dynamics, Reduced Equations of Motion, Hierarchic Equation of Motion, Tensor-Trains, Double Space

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I. INTRODUCTION

The theoretical study of the time evolution of complex chemico-physical processes can provide a deep understanding of their basic mechanisms in terms of development of populations of specific quantum states, and of coherences (entanglement) between subsystems, both of which can be probed using specifically designed non-linear spectroscopy experiments.[1]

Two main classes of methodologies for the study of quantum dynamics of complex systems exists, which are based on the density matrix, and on the wave-function propagation respectively. While each has its own advantages and disadvantages, the main difference lies in their capability to deal with canonical distribution of states, i.e. with finite temperature effects, which is fundamental for the simulation of real chemico-physical processes.

Density matrix formalism has been the subject of intense research mostly for the possibility to describe the dynamics of a subsystem of interest via the so-called reduced density matrix. This approach is at the basis of several types of approximate methodologies,[2–8] and of the formally exact hierarchical equations of motion (HEOM) theory.[9–11]. Numerically accurate evolution of large systems has also been described by the density matrix renormalization group (DMRG) methodology, and the associated time-evolution algorithms.[12–14] Wave function propagation methods employing a basis set representation, such as the multi-configuration time-dependent Hartree (MCTDH) method and its multilayer extension (ML-MCTDH),[15–17] Gaussian based MCTDH and other basis set methods,[18–22] are powerful tools at very low temperature but become unhandy in high temperature cases, as their application requires a statistical sampling of the initial conditions.[23–25] On the other hand, basis set methods are very versatile, and capable of handling a large variety of Hamiltonian operators.[26,27] Density matrix propagation usig MCTDH is also possible[28,29] and implemented in the double space formalism.

Very recently Borrelli and Gelin[30–32] have developed a theoretical methodology based on Thermo Field Dynamics (TFD) theory[33,34] that combines an accurate description of quantum dynamics at finite temperature with the flexibility of a basis set representation.[30] The theoretical framework of TFD is combined with a special representation of the wave function based on Tensor Trains (TT), also known as Matrix Product States (MPS), and the methodology is referred to as TFD-TT. This technique has already been successfully applied to describe population dynamics in spin-boson systems, energy transfer in the Fenna-

Mathews-Olsen complex, and electron-transfer processes in bacterial reaction centers.[31,35,36] The same approach has been implemented within the Davydov *ansatz* theory and successful applications to polaron problems have been reported.[37]

The mathematical background of the TFD-TT technique lies in the formulation of Liouville-von Neumann equation using the algebra of superoperators. This type of formalism if also referred to as twin-formulation of statistical mechanics.[38] While the very idea of using the formalism of Hilbert space to the study of the density matrix evolution is not new[39], the mathematical structure provided by the twin-formulation has been developed only in the late 70's. More specifically, the twin-formulation can be used to rewrite the anticommutators of the von Neumann equation as operators of new "superfermions" and "superboson" particles.[38] This mathematical structure allows to use standard vector formalism, i.e. the superposition principle, in a new space which has the double of the physical degrees of freedom, leaving the underlying physics unchanged.[40,41]

Here we show how this approach can be fruitfully employed in the description of quantum dynamics of complex systems at finite temperature, allowing the direct application of quantum dynamical methods for wave-function propagation to the study of density matrix. We will futher show that the Tensor-Train representation[42,43] of a multi-dimensional vector is especially suited to describe the density matrix of a system and can be fully exploited by the introduction of the twin-formulation. Finally the application of the HEOM to a dissipative polaron model will be discussed.

II.   LIOUVILLE-VON NEUMANN EQUATION IN TWIN-FORMULATION

The standard double-space formulation of statistical mechanics is well known from textbooks[1,44], yet the introduction of the so-called *tilde operators* as a new mathematical structure in the dual space, and their use in the derivation of equations of motion, are seldom discussed. Here we will outline the main peculiarities of the twin-space formulation.

In the twin-formulation a double Hilbert space is defined, also referred to as Liouville space, $\mathcal{L} = (\mathcal{H} \otimes \tilde{\mathcal{H}})$ where $\tilde{\mathcal{H}}$ is the Hilbert space of a fictitious dynamical system identical to the original Hilbert space $\mathcal{H}$ of the real physical systems.[38,41,45] If $\{\left|m\tilde{n}\right\rangle\}$ is an orthonormal

basis of $\mathcal{L}$ then

$$\langle m\tilde{n}|m'\tilde{n}'\rangle = \delta_{mm'}\delta_{\tilde{n}\tilde{n}'} \qquad \sum_{mn}|m\tilde{n}\rangle\langle m\tilde{n}| = 1.$$

The identity vector $|I\rangle$ is further defined as

$$|I\rangle = \sum_m |m\tilde{m}\rangle. \tag{1}$$

This special vector allows to define a mapping between the dual space of $\mathcal{H}$ (*i.e.* the bra space) and the tilde space, indeed we have

$$\langle m|I\rangle = |\tilde{m}\rangle \qquad \langle \tilde{m}|I\rangle = |m\rangle. \tag{2}$$

Using this relations it is possible to associate a vector of the $\mathcal{L}$ space to each operator A acting in the $\mathcal{H}$ space

$$|A\rangle = A|I\rangle. \tag{3}$$

Similarly, we can define a state vector $|\rho(t)\rangle = \rho(t)|I\rangle$, where $\rho(t)$ is the density matrix of the system. Accordingly, the expectation value of A is defined as the scalar product

$$\langle A\rangle = \langle A|\rho(t)\rangle = \langle I|A\rho(t)|I\rangle \equiv \mathrm{tr}(A\rho(t)). \tag{4}$$

The meaning of the above notation can be easily understood using the closure relation

$$|A\rangle = A|I\rangle = \sum_{mn}|m\tilde{n}\rangle\langle m\tilde{n}|A|I\rangle = \sum_{mn}\langle m|A|n\rangle|m\tilde{n}\rangle = \sum_{mn}A_{mn}|m\tilde{n}\rangle$$

whence it is clear that the vector $|A\rangle$ is a linear combination of a basis of $\mathcal{L}$ with coefficients given by the matrix elements A_{mn}. Together with operators acting in the space $\mathcal{H}$ it is possible to define a set of operators acting on the $\tilde{\mathcal{H}}$ space. In particular, following Suzuki[41], two operators A and B are weakly equivalent if

$$A|I\rangle = B|I\rangle \tag{5}$$

and we write

$$A \simeq B. \tag{6}$$

For each Hermitian operator A acting in the $\mathcal{H}$ space it is possible to define a tilde operator $\tilde{A}$ that is weakly equivalent to A as

$$A|I\rangle = \tilde{A}^\dagger|I\rangle \longrightarrow A \simeq \tilde{A}^\dagger \tag{7}$$

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where the dag operator implies the Hermitian conjugation. Consequently, for Hermitian operators

$$A \simeq \tilde{A}. \tag{8}$$

The tilde operator can be obtained from the original operators by the so-called tilde conjugation rules

$$(AB)^\sim = \tilde{A}\tilde{B} \qquad (c_1 A + c_2 B)^\sim = c_1^* \tilde{A} + c_2^* \tilde{B}. \tag{9}$$

If A, B are two operators of the $\mathcal{H}$ space and $\hat{A} = A - \tilde{A}^\dagger$ then

$$\hat{A}B\big|I\big\rangle = (A - \tilde{A}^\dagger)B\big|I\big\rangle = (AB - B\tilde{A}^\dagger)\big|I\big\rangle = (AB - BA)\big|I\big\rangle = [A, B]\big|I\big\rangle \tag{10}$$

proving the fundamental property of the twin-space fomalism

$$[A, B] \simeq \hat{A}B. \tag{11}$$

Equation 11 allows to rewrite quantum statistical mechanics in a commutator-free way. Indeed, it is easy to demonstrate that the evolution of the vector $\big|\rho(t)\big\rangle$ is given by the equation

$$\frac{\partial}{\partial t}\big|\rho(t)\big\rangle = (H - \tilde{H})\big|\rho(t)\big\rangle = \hat{H}\big|\rho(t)\big\rangle \qquad \big|\rho(0)\big\rangle = \big|\rho_0\big\rangle \tag{12}$$

where $\tilde{H}$ is an Hamiltonian operator identical to the physical Hamiltonian H but acting in the *tilde* space $\mathcal{H}$. The superoperator $\hat{H} = H - \tilde{H}$ acts on the entire $\mathcal{L}$ space and is the Liouville operator rewritten as a superoperator of the $\mathcal{L}$ space. We leave the reader to the demonstration reported in the original papers by Schmutz [38] and by Suzuki [41]. When the initial condition of the system can be described by a Boltzmann distribution of a certain zero-order Hamiltonian operator H_0 we have

$$\big|\rho(0)\big\rangle = Z^{-1} e^{-\beta H_0}\big|I\big\rangle. \tag{13}$$

A comparison with the common double-space theory is now mandatory for clarifying similarities and differences of the two approaches. In double space the notation $\big|mn\big\rangle\big\rangle = \big|m\big\rangle\big\langle n\big|$ is often used to identify a state of a space that is the direct product of $\mathcal{H}$ and its dual.[1,46] Once we let the tilde space and the dual space coincide this approach and the twin formalism seem identical.[40] However, in standard double-space formulation what is often referred to as Liouville superoperator is a mere symbol for a commutator, $L = [H, \cdot]$, which induces a Lie algebra on the Liouville space. In the twin-formulation outlined above the

introduction of the tilde space and of its operators allows to eliminate all the commutators, overcoming the difficulties inherent in their evaluation, and replace them with the action of an operator in a Hilbert space. On the other hand, in most current implementations of the propagation of von Neumann equation the Liouville operator is transformed into a linear operator by the identity

$$H\rho - \rho H = (I \otimes H - H \otimes I)\mathrm{vec}(\rho) \qquad (14)$$

where $\mathrm{vec}(\rho)$ is a vectorization operator that transforms a matrix to a vector by ordering its columns. Using tilde operators we can write such a linear equation already at operator level. This provides an alternative approach to the construction of the Liouville super-operator which becomes particularly important when the density matrix is approximated using some form of tensor network, such as tensor trains or ML-MCTDH.

While the above formulation is based on a Hilbert space it is not a "wave-function" approach as Thermo-Field Dynamics,[20,32,33] since the expectation value of an operator is not given by the prescriptions valid for pure quantum states. Indeed, the average value of an observable A is defined as the scalar product of eq. 4. Yet, since the density matrix evolution can be mapped to the evolution of a vector in a new Hilbert space with a special "Hamiltonian" superoperator $\hat{H}$ (the Liouvillian), we can take full advantage of the techniques developed for the propagation of multi-dimensional wave-function in Hamiltonian systems. The ML-MCTDH and the TT representation of the wave-function seem to be the most promising due to their proven capability to treat systems with thousands or more degrees of freedom.[23,26,30] It must be noted that although the TT approximation represents a special case of the very general ML-MCTDH tree-expansion, its very structure has allowed the development of extremely efficient algorithms for handling operators and vectors in TT format. For this reason we prefer to choose this format for the numerical investigation of equation 12.

III. REDUCED DENSITY MATRIX DYNAMICS

The possibility to introduce "bath" degrees of freedom and project them out of the dynamical map of a system is one of the fundamental prerogative of the density matrix formalism,[44] and certainly one of the reasons for being the method of choice when dealing with mesoscopic (size) systems.[47]

The twin-formulation allows to define a reduced state vector analogous to the familiar reduced density matrix. This was first discussed by Arimitsu[40] using projection operator techniques and lead to a set of equations which share the same structure of the standard reduced density matrix approaches, but makes explicit use of tilde operators. Here we will briefly report its derivation, and then present a new formulation of an exact second-order cumulant approach based on a hierachical solver (see infra).[9]

Let us consider a system described by a Hamiltonian operator

$$H = H_A + H_B + V = H_0 + V \tag{15}$$

where A is the subsystem of interest, B the "bath" i.e. the irrelevant subsystem, V their coupling, and $H_0 = H_A + H_B$. The Liouville super-operator is thus given by

$$\hat{H} = H_A + H_B + V - \tilde{H}_A - \tilde{H}_B - \tilde{V} = \hat{H}_A + \hat{H}_B + \hat{V} = \hat{H}_0 + \hat{V} \tag{16}$$

where $\hat{H}_A = H_A - \tilde{H}_A$ and so on. Let us now introduce the projection operator

$$P = \big|\rho_B(0)\big\rangle\big\langle 1_B\big| \tag{17}$$

which projects out the degrees of freedom on subsystem B (i.e. the bath degrees of freedom) which are not relevant for the evaluation of the properties of interest. The unit vector $|1_B\rangle$ is defined as in eq. 3 but the summation includes only the states of the B subsystem. In the interaction representation the reduced state $\big|\rho_A(t)\big\rangle_I$ is defined as

$$\big|\rho_A\big\rangle_I = P\big|\rho(t)\big\rangle_I \tag{18}$$

where

$$\big|\rho(t)\big\rangle_I = e^{i\hat{H}_0 t}\big|\rho(t)\big\rangle \tag{19}$$

from which

$$\big|\rho_A\big\rangle_I = \langle 1_B|\rho(t)\rangle_I = e^{i\hat{H}_A}\langle 1_B|\rho\rangle = e^{i\hat{H}_A}\big|\rho_A\big\rangle \tag{20}$$

Using standard projection operator technique[48] it is possible to show that the reduced density matrix at a given time t is given by

$$\big|\rho_A(t)\big\rangle_I = T_+ \exp\left(\int_0^t \hat{K}_I(s)ds\right)\big|\rho(0)\big\rangle_I \tag{21}$$

where

$$\hat{K}_I(t) = \sum_n (-i)^n \hat{K}_I^{(n)}(t) \qquad \hat{K}_I^{(n)}(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 ... \int_0^{t_{n-2}} dt_{n-1} \langle \hat{V}(t)\hat{V}(t_1)...\hat{V}(t_{n-1})\rangle_c$$

(22)

$\hat{V}(t) = e^{i\hat{H}_0 t}\hat{V}e^{-i\hat{H}_0 t}$ being the coupling between subsystems A and B in the interaction picture. Again we point out that while the above equation share the same formal structure with that developed in standard density matrix theory, the introduction of the tilde operators completely removes the necessity to evaluate commutators. In the above equation the average operation is defined as

$$\langle ... \rangle = \langle 1_B | ... | \rho_B(0) \rangle$$

(23)

Equation 21 is the starting point for the derivation of a myriad of approximated theories based on the truncation of the cumulant expansion, and on specialized techniques which are often system dependent. The so-called hierarchical equation of motion (HEOM) theory by Kubo and Tanimura[9] is certainly one of the most important theoretical developments for the study of open systems. It was originally formulated as a methodology to describe a system interacting with a non-Markovian Gaussian environment, and has later been extended to treat other types of system-bath interactions.[9,10,49] Here we will show how it is possible to recast the HEOM methodology in the framework of the twin-formulation making explicit use of tilde operators.

A fundamental assumption of HEOM theory is that the system-bath interaction can be factorized as

$$V = \sum_k S_k Q_k$$

(24)

where S_k and Q_k are system and bath operators respectively. Furthermore, the bath operators are described as a linear combination of position operators q_j of harmonic oscillators

$$Q_k = \sum_j g_{kj} q_j.$$

(25)

The coupling super-operator is thus given by

$$\hat{V} = \sum_k S_k Q_k - \sum_k \tilde{S}_k \tilde{Q}_k.$$

(26)

Under this conditions it is possible to demostrate that all cumulants of eq. 22 higher than the second vanish giving[50,51]

$$|\rho_A(t)\rangle_I = T_+ \exp\left(-\int_0^t \hat{K}_I^{(2)}(s)ds\right)|\rho(0)\rangle_I.$$

(27)

where

$$\hat{K}_I^{(2)}(s) = \int_0^s d\tau \langle \hat{V}(s)\hat{V}(\tau)\rangle. \tag{28}$$

Differentiating the above expression one obtains[52]

$$\frac{\partial}{\partial t}|\rho_A(t)\rangle_I = -T_+ \int_0^t d\tau \langle \hat{V}(t)\hat{V}(\tau)\rangle \exp\left(-\int_0^t \hat{K}_I^{(2)}(s)ds\right)|\rho(0)\rangle_I. \tag{29}$$

It is fundamental to note that the variable τ in the integral above ranges over all times, so that, for $\tau < s$ the time ordering operator mixes $\hat{V}(\tau)$ with all the terms of the expansion of the exponential operator $\exp\left(-\int_0^t \hat{K}_I^{(2)}(s)ds\right)$, making it impossible to obtain an explicit equation for $|\rho_A(t)\rangle_I$. The hierarchical equation of motion represents a methodology to disentangle the above equation in the special case of a Gaussian bath. After some easy manipulations the second order cumulant can be written as (see appendix)

$$\hat{K}_I^{(2)}(t) = \sum_k [S_k(t) - \tilde{S}_k(t)]\left\{\int_0^t dt_1 \langle Q_k(t)Q_k(t_1)\rangle S_k(t_1) - \int_0^t dt_1 \langle Q_k(t_1)Q_k(t)\rangle \tilde{S}_k(t_1)\right\} \tag{30}$$

where property 7 has been used repeatedly. Taking advantage of the conjugation relation $\langle Q_k(t_1)Q_k(t)\rangle = \langle Q_k(t)Q_k(t_1)\rangle^*$ it is possible to write

$$\hat{K}_I^{(2)}(t) = \sum_k [S_k(t) - \tilde{S}_k(t)]\left\{\int_0^t dt_1 C_k'(t-t_1)[S_k(t_1) - \tilde{S}_k(t_1)] - i\int_0^t dt_1 C_k''(t-t_1)[S_k(t_1) + \tilde{S}_k(t_1)]\right\} \tag{31}$$

where

$$C_k'(t-t_1) = \Re\langle Q_k(t_1)Q_k(t)\rangle \qquad C_k''(t-t_1) = \Im\langle Q_k(t_1)Q_k(t)\rangle. \tag{32}$$

It is readily verified that upon substitution of eq. 25 one obtains

$$C_k'(t-t_1) = 1/2 \sum_j g_{kj}^2 \coth(\beta\omega_j/2)\cos(\omega_j(t-t_1)) \tag{33}$$

$$C_k''(t-t_1) = 1/2 \sum_j g_{kj}^2 \sin(\omega_j(t-t_1)) \tag{34}$$

which, in the limit of a continuous distribution of frequencies, become[1,44]

$$C_k'(t-t_1) = \frac{1}{\pi}\int_0^\infty J_k(\omega)\coth(\beta\omega/2)\cos(\omega(t_1-t)) \qquad C_k''(t-t_1) = \frac{1}{\pi}\int_0^\infty d\omega J_k(\omega)\sin(\omega(t_1-t)) \tag{35}$$

where $J_k(\omega)$ is the spectral density describing the system-bath interaction

$$J_k(\omega) = \frac{\pi}{2}\sum_j g_{kj}^2 \delta(\omega - \omega_j). \tag{36}$$

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These are well know results of time auto-correlation function theory.[1] At this point we model the system-bath interaction as a non-Markovian Gaussian process described by a Drude-Lorentz spectral density

$$J_k(\omega) = 2\lambda_k \frac{\omega\gamma_k}{\omega^2 + \gamma_k^2}. \tag{37}$$

resulting in the expressions[53]

$$C_k'(t - t_1) = \lambda_k\gamma_k \cot\left(\frac{\beta\gamma_k}{2}\right) e^{-\gamma_k|t-t_1|} + \sum_{j=1}^{\infty} \frac{4\lambda_k\gamma_k}{\beta} \frac{\omega_{kj}}{\omega_{kj}^2 - \gamma_k^2} e^{-\omega_{kj}|t-t_1|} \tag{38}$$

$$C_k''(t - t_1) = \lambda_k\gamma_k e^{-\gamma_k|t-t_1|}. \tag{39}$$

with $\omega_{kj} = 2\pi k/\beta$. Here the parameter λ_k defines the strength of the system-bath interaction while γ_k is a characteristic bath frequency. Introducing the super-operators

$$\hat{S}_k(t) = [S_k(t) - \tilde{S}_k(t)] \tag{40}$$

$$\hat{R}_{kj}(t) = c_{kj}S_k(t) - c_{kj}^*\tilde{S}_k(t) \tag{41}$$

where the coefficient c_{kj} are defined from equation 38 in such a way that

$$C_k(t - t_1) = C_k'(t - t_1) + iC_k''(t - t_1) = \sum_j c_{kj} e^{-\gamma_{kj}|t-t_1|} \tag{42}$$

the second order cumulant can be written as

$$\hat{K}_I^{(2)}(t) = \sum_{kj} \hat{S}_k(t) \int_0^t d\tau e^{-\gamma_{kj}|t-\tau|} \hat{R}_{kj}(\tau). \tag{43}$$

Following a standard approach we can now define a set of auxiliary state vectors[9,54]

$$\left|\rho_A^{\mathbf{m}}(t)\right\rangle = T_+ \prod_{kj} (m_{kj}!|c_{kj}|^{m_{kj}})^{-1/2} \left(i\int_0^t dt_1 e^{-\gamma_k|t-t_1|}\hat{R}_{kj}(\tau)\right)^{m_{kj}} \exp\left(-\int_0^t \hat{K}_I^{(2)}(s)ds\right) \left|\rho_A(0)\right\rangle_I \tag{44}$$

where $\mathbf{m} = \{m_{kj}\}$ is a set of non-negative integers. Here, the index k labels the number of spectral densities and the index j labels the number of Matsubara terms in the expansion of each spectral density. If the system is characterized by M spectral densities each having K Matsubara terms, then we have $M \cdot K$ auxiliary spectral density vectors, and the indices k, j can assume the values $k = 1, 2, ..., M$, and $j = 1, 2, ...K$. Different spectral densities can have a different number of expansion terms but this would only make notation slightly

more involved. It is readily verified that the vector $|\rho_A(t)\rangle_I$, describing the physical state of our system, corresponds to the auxiliary state vector having all indices $m_{kj} = 0$, *i.e.* $|\rho_A(t)\rangle_I = |\rho_A^{\mathbf{0}}(t)\rangle$. The above definition takes into account the scaling originally proposed by Shi and coworkers which improves the numerical stability of the final system of equations.[55,56] HEOM are readily derived upon repeated differentiation of the $|\rho^{\mathbf{m}}\rangle$ with respect to time. Moving to the Schrödinger representation the set of equations

$$\frac{\partial}{\partial t}|\rho_A^{\mathbf{m}}\rangle = -\left(i\hat{H}_A + \sum_{kj} m_{kj}\gamma_{kj}\right)|\rho_A^{\mathbf{m}}\rangle - i\sum_{kj} \sqrt{m_{kj}/|c_{kj}|}(c_{kj}S_k - c_{kj}^*\tilde{S}_k)|\rho_A^{\mathbf{m}-1_{kj}}\rangle$$
$$-i\sum_{kj} \sqrt{(m_{kj}+1)|c_{kj}|}(S_k - \tilde{S}_k)|\rho_A^{\mathbf{m}+1_{kj}}\rangle \quad (45)$$

is obtained, where $\mathbf{m} \pm 1_{kj} = (m_{10}, ..., m_{kj} \pm 1, ...)$, and the explicit time dependence of the auxiliary vectors has been dropped. The price to pay for disentangling the time ordering operation of eq. 29 is that HEOM constitutes an infinite set of first-order ordinary differential equations. This means that the infinite series of equation 22 has just been replaced by a different type of problem. Fortunately, using the hierarchy it is possible to devise very efficient truncation schemes which allow to obtain highly accurate results with a finite system. The reader is referred to the original papers for the derivation of an optimal truncation scheme.[9,57] In the above derivation we have not considered low-temperature corrections which can be included straightforwardly from a direct application of the original approach suggested by Ishizaki and Tanimura.[57]

The above equations resemble very closely the results of HEOM theory in the density matrix formalism (see for example Ref. 54), but here the commutators and anti-commutators are replaced by differences and sums of tilde and non-tilde operators. As we shall see in the next section, this results in several benefits for the numerical implementation of the propagator.

To further simplify the structure of the HEOMs we follow Tanimura[10] and introduce a set of vectors $|\mathbf{m}\rangle = |m_{10}m_{11}...m_{1K}m_{20}...m_{MK}\rangle$, and their corresponding boson-like creation-annihilation operators b_{kj}^+, b_{kj}^-

$$b_{kj}^+|\mathbf{m}\rangle = \sqrt{(m_{kj}+1)}|\mathbf{m}+1_{kj}\rangle \qquad b_{kj}^-|\mathbf{m}\rangle = \sqrt{m_{kj}}|\mathbf{m}-1_{kj}\rangle \qquad b_{kj}^+b_{kj}^-|\mathbf{m}\rangle = m_{kj}|\mathbf{m}\rangle \quad (46)$$

and the vector

$$|\Psi\rangle = \sum_{\mathbf{m}} |\rho_A^{\mathbf{m}}\rangle|\mathbf{m}\rangle \quad (47)$$

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and rewrite the hierachical equations of motion in the compact form

$$\frac{\partial}{\partial t}\big|\Psi\big\rangle = \left(-i\hat{H}_A - \sum_{kj}\gamma_{kj}b_{kj}^+b_{kj}^- - i\sum_{kj}\sqrt{|c_{kj}|}(S_k - \tilde{S}_k)b_{kj}^- - i\sum_{kj}\frac{(c_{kj}S_k - c_{kj}^*\tilde{S}_k)}{\sqrt{|c_{kj}|}}b_{kj}^+ \right)\big|\Psi\big\rangle,$$

(48)

with the initial condition given by $\big|\Psi(0)\big\rangle = \big|\rho_A(0)\big\rangle\big|\mathbf{0}\big\rangle$.

IV. TENSOR-TRAIN REPRESENTATION OF THE DENSITY VECTOR

The solution of the set of equations 45 requires efficient numerical methods, suitable to accurately treat a large number of dynamical variables. In the present work we apply recently developed numerical techniques to efficiently solve multidimensional quantum dynamical problems using the TT format.[42,43,58–61] Below we sketch the basic principles of the TT decomposition, and show how it can be applied to solve the HEOM equation in twin-formulation. The reader is referred to the original papers[42,59,60] for a detailed analysis of the TT decomposition. We also point out that this type of representation has very recently been applied to HEOM within the classical density matrix approach.[62]

Let us consider a generic expression of a state of a N dimensional quantum system in the form

$$\big|\Psi\big\rangle = \sum_{i_1,i_2,...,i_N} C(i_1,...,i_N)\big|i_1\big\rangle \otimes \big|i_2\big\rangle \cdots \big|i_N\big\rangle.$$

(49)

where $\big|i_k\big\rangle$ labels the basis states of the k-th dynamical variable, and the elements $C(i_1,...,i_N)$ are complex numbers labeled by N indices. If we truncate the summation of each index i_k the elements $C(i_1,...,i_N)$ represent a tensor of rank N. The evaluation of the summation 49 requires the computation (and storage) of p^N terms, where p is the average size of the one-dimensional basis set, which becomes prohibitive for large N. Using the TT format, the tensor C is approximated as

$$C(i_1,...,i_N) \approx G_1(i_1)G_2(i_2)\cdots G_N(i_N)$$

(50)

where $G_k(i_k)$ is a $r_{k-1} \times r_k$ complex matrix. In the explicit index notation

$$C(i_1,...,i_N) = \sum_{\alpha_0\alpha_1\cdots\alpha_N} G_1(\alpha_0,i_1,\alpha_1)G_2(\alpha_1,i_2,\alpha_2)\cdots G_d(\alpha_{N-1},i_N,\alpha_N).$$

(51)

The matrices G_k are three dimensional arrays, called *cores* of the TT decomposition. The dimensions r_k are called compression ranks. In the matrix-product state (MPS) language the ranks are referred to as *bond dimensions*. Using the TT decomposition 50 it is possible, at least in principle, to overcome most of the difficulties caused by the dimensions of the problem. Indeed, the wave function is entirely defined by N arrays of dimensions $r_{k-1} \times n_k \times r_k$ thus requiring a storage dimension of the order Npr^2.

We notice that if all the ranks of the cores are 1, the TT format is equivalent to a Kronecker product. From this point of view it constitutes the simplest extension of a direct product to entangled system. The higher the entanglement, that is the correlation between two degrees of freedom, the larger the ranks of the TT cores connecting their respective indices. Indeed, a fundamental problem of the TT representation is to define the sequence of indices $i_k, k = 1, ..., N$ with the minimum rank decomposition of the state vector, and of the operators. We do not aim to tackle this complex mathematical problem, however we can exploit the twin-space formalism to optimize the TT representation of the vector $|\Psi(t)\rangle$.

If d is the dimensionality of the original Hilbert space of our system, that is the number of degrees of freedom of the H_A Hamiltonian operator, and if the dissipating environment is described using M uncorrelated spectral densities $J_k(\omega)$ each expanded into K Matstubara terms, the vector $|\Psi(t)\rangle$ of eq. 47 can be considered as a tensor with $N = 2d + KM$ indices. Therefore, one possible way to represent $|\Psi(t)\rangle$ in TT format is to employ a product of $2d + MK$ low rank matrices. For sake of simplicity, in the following only one Matsubara term is considered for each spectral density, $K = 1$, the generalization to $K > 1$ having only a slightly more involved notation. If we label with $\mu_k(m_k)$ the TT core matrices associated with the i-th spectral density and with $\rho_{2f-1}(i_f)$, $(\rho_{2f}(\tilde{j}_f))$ the TT core matrices associated with the f-th physical (tilde) degrees of freedom, $|\Psi(t)\rangle$ can be written in TT form as

$$|\Psi(t)\rangle = \sum_{\substack{m_1, m_2, ... \\ i_1 \tilde{j}_1 ... i_d, \tilde{j}_d}} \mu_1(m_1)...\mu_M(m_M)\rho_1(i_1)\rho_2(\tilde{j}_1)...\rho_{2d-1}(i_d)\rho_{2d}(\tilde{j}_d)|m_1...m_K; i_1\tilde{j}_1...i_d\tilde{j}_d\rangle. \quad (52)$$

In the above expression only the component with $\{m_k = 0, k = 1, ..., M\}$ is required for the computation of physical observables, that is

$$|\rho_A(t)\rangle = \mu_1(0)...\mu_M(0) \sum_{i_1\tilde{j}_1...i_d,\tilde{j}_d} \rho_1(i_1)\rho_2(\tilde{j}_1)...\rho_{2d-1}(i_d)\rho_{2d}(\tilde{j}_d)|i_1\tilde{j}_1...i_d\tilde{j}_d\rangle. \quad (53)$$

The alternation of the indices $i_k, \tilde{j}_k$ provide a very convenient scheme for the computation of expectation values of observables. Indeed, the identity vector can easily be written as a

direct product

$$|I\rangle = \sum_{i_1}|i_1\rangle|\tilde{i}_1\rangle \otimes \sum_{i_2}|i_2\rangle|\tilde{i}_2\rangle \otimes ... \otimes \sum_{i_d}|i_d\rangle|\tilde{i}_d\rangle \qquad (54)$$

which can be directly translated into the TT format, since the Kronecker product can be considered a special TT representation in which all the ranks of the cores are 1. From the above expression it is immediate to derive TT representations of the vectors corresponding to observables using equation 3. We notice that a different order of the indices would make the summations not separable increasing the overall computational cost. Finally, the use of tilde operators allows to easily perform grouping of variables that are strongly correlated.[15]

In a time-dependent theory the cores, are time dependent complex matrices whose equations of motion can be found by applying the time-dependent variational principle (TDVP) to the parametrised form of the state given by eq. 52 The resulting equations of motion can be written in the form

$$\frac{d}{dt}\big|\Psi(G(t))\big\rangle = -i\hat{P}_{\mathcal{T}(G(t))}X\big|\Psi(G(t))\big\rangle, \qquad (55)$$

where G labels all the cores of the TT representation 52, X is the operator defined by the right hand side of eq. 48, and $\hat{P}_{\mathcal{T}(\Psi(G(t)))}$ is the orthogonal projection into the tangent space of $\mathcal{M}_{TT}$ at $\big|\Psi(G(t))\big\rangle$. Eq. 55 provide an approximate solution of the original equation on the manifold of TT tensors of fixed rank, $\mathcal{M}_{TT}$. We refer the reader to references 43,58,and 63, where the explicit differential equations are derived and their approximation properties are analyzed, and to reference 64 for a discussion of time-dependent TT/MPS approximations in the theoretical physics literature. We point out that in order to employ the TT representation of the density matrix, a TT form of the evolution operator X is also required. This can be obtained from a series of sums and subsequent contractions (rounding operations) of matrix operators written in direct product form. We refer the reader to references 42 and 58 for further details.

Several techiques exists to compute the time evolution of TT/MPS.[43,63,65,66] Here we adopt a methodology recently developed by Lubich, Oseledets and Vandereycken, which combines an explicit expression for the projector $\hat{P}_{\mathcal{T}(G(t))}$ and an extremely efficient second order split projector integrator specifically tailored to the TT format.[43]

V. APPLICATION TO DISSIPATIVE EXCITON-POLARON DYNAMICS

The fields of application of HEOM encompass fundamental molecular physical processes as well as solid state and material physics. The methodological approach suggested in this work is especially suited for cases in which the system comprises a relatively large number of interacting degrees of freedom. In this respect, we show how to explicitly take advantage of the double space implementation to tackle a class of problems, referred to as exciton-polaron systems, which is becoming increasingly popular among different scientific communities. These systems comprise a set of interacting electronic sites, coupled to high frequency nuclear vibrations. The physical processes that can be reduced to this type of models is extremely vast including, among others, charge transport in organic semiconductors, energy transfer in molecular aggregates, as well as electron transfer in biochemical and artificial systems. The explicit expressions of the operators H_A, H_B and V of eq. 15 for each specific case are given in the supplementary information.

We first consider the case in which each electronic site is coupled to an independent overdamped thermal reservoir. The system operators describing the interaction with the bath are diagonal, *i.e.* $S_n = |n\rangle\langle n|$. Within this model the strength of the system-bath coupling determines the reorganization energy E_r of each site thorough the relation

$$E_r = \frac{1}{\pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega} = \lambda \tag{56}$$

More specifically, we consider of a system comprised of seven sites with nearest-neighbour interactions, and periodic boundary conditions (*i.e.* first and last site coupled). Each site is linearly coupled to a high frequency vibration with $\omega = 1500 \text{ cm}^{-1}$. The vibronic interaction strength is set to 800 cm^{-1} corresponding to a reorganization energy of 214 cm^{-1}, and the nearest-neighbour inter-site coupling is $\epsilon = 100 \text{ cm}^{-1}$. In all cases the bath characteristic frequency is $\gamma = 53 \text{ cm}^{-1}$ corresponding to a relaxation time of 100 fs.

Figure 1 shows the results of the site population dynamics of the above model for two different values of the bath reorganization energy. For $\lambda < \epsilon$ (fig. 1a) a typical underdamped decay can be observed. Very fast oscillations with a period of 22 fs, which originate from the coherent motion of the vibrational modes at 1500 cm^{-1}, are superimposed on the overall population dynamics. For $\lambda \approx \epsilon$ (fig. 1b) the population dynamics is manifestly overdamped. Again, oscillations with a period of 22 fs, reveal the vibrational modes at 1500

15

cm^{-1}. It is interesting to note that the short time decay appears the same in both cases and is governed by the pure excitonic coupling.

The effect of the bath interaction is to provide a fast relaxation mechanism leading to an equilibrium population on each site. Since the system has periodic boundary conditions the equilibrium populations are the same on all sites. For very large bath reorganization energies the time to reach equilibrium populations increases as expected due to a renormalization effect of the inter-site coupling. Within the framework of rate theory this corresponds to an increase of the activation energy for the inter-site hopping with a consequent decrease of the corresponding kinetic constant. While many approximate treatments of system-bath interactions are available, leading to similar results, here we combine the exact treatment of a large number of discrete vibronic sites with a set of independent (uncorrelated) thermal baths. To our knowledge such a complex calculation has not yet been described in the literature.

We further examine the effect of the thermal environment on the inter-site coupling. Indeed, in realistic systems the fluctuation of the couplings due to the low frequency motion of the environment can be rather large, often of the same order of magnitude of the coupling itself. This is believed to be a common feature in organic semi-condutor materials and also of charge migration processes in DNA,[67,68] having important implications for a proper description of the charge-carrier mobility.[37,69,70]

In this model, the strength λ of the system-bath interaction (see eq. 37) determines the dynamical dispersion of the coupling through the relation

$$\langle \epsilon_{nm} \rangle = \epsilon_{nm} \pm \Delta_{nm} \tag{57}$$

with

$$\Delta_{nm} = \sqrt{\left\langle \sum_i (g_{nmi} q_{nmi})^2 \right\rangle} \equiv \frac{1}{\pi} \int_0^\infty \coth(\beta\omega/2) J(\omega) d\omega \approx \sqrt{\frac{2\lambda}{\beta}}. \tag{58}$$

Clearly the higher the temperature the larger the dispersion Δ_{nm} of the coupling. The assumption of a Debye spectral density is equivalent to describing the modulation of the coupling as originated by an overdamped vibrational mode.[1,71]

In figure 2 the population dynamics of a seven site system with neareast-neighbour interaction is reported for $\lambda = 10, 25$ cm^{-1} corresponding to a dispersion of the coupling of about 60 cm^{-1} and 100 cm^{-1} at room temperature. The other model parameters are identical to those of figure 1. In both cases an under-damped dynamics with a period of 220

fs, depending exclusively on the polaronic system, is clearly observable. As can be seen, the stronger the system-bath interaction (λ), *i.e.* the larger the dynamic disorder of the coupling, the stronger the damping and, consequently, the shorter the time to reach an equilibrium condition. Therefore, while dynamical disorder of the site energies induces a renormalization of the inter-site coupling leading to lower transition rate with increasing the system-bath interaction strength, fluctuations of the off-diagonal (excitonic) couplings increase the overall transition rate.

Figure 3 shows the population dynamics for the model system of figure 2 but for two different values of the bath characteristic frequency. The differences between the two population dynamics are clearly visible after the first 200 fs. Indeed, the population of site 1 is modulated by a second slow component associated with the bath relaxation time of 1 ps ($\gamma = 5.3$ cm^{-1}).

To show the potential range of application of the methodology we further analyse a model for the charge transfer (CT) process between two identical molecular sites. Both sites are linearly coupled to a set of seven nuclear vibrations. The parameters of the vibronic model are given in the supplementary information and have been used to describe the CT process in a pentacene dimer.[72,73] In figure 4 the population dynamics of the two site system is reported for two different system-bath couplings $\lambda = 300$ cm^{-1} and 90 cm^{-1}. In both cases the characteristic bath frequency is $\gamma = 53$ cm^{-1}. Due to the complexity of the model and the number of vibronically active degrees of freedom it is not easy to disentangle the different contribution to the population dynamics. The initial fast decay of the populations is very likely due to pure excitonic couplings while the small oscillations with periods of about 20 fs, clearly evident at longer times, are caused by the vibronic activity of several high frequency modes. For $\lambda = 90$ cm^{-1} the CT dynamics is underdamped while an overall overdamped behaviour can be observed for $\lambda = 300$ cm^{-1}.

Finally, the convergence properties of the numerical methodology are illustrated in fig. 5 where the population of the two states of the dimer model as a function of time for different values of the TT compression ranks are compared. Considering the relatively small number of degrees of freedom the ranks necessary to reach a converged dynamics are considerably large. Figure 5 also shows the norm of the state vector as a function of time. As can be readily seen for very small ranks the norm drastically decreases, by about 20%, after a very short time and even for very large ranks ($r = 115$) there is a 1% loss after 800 fs.

FIG. 1. Population dynamics of a 7 site polaron model linearly coupled to seven uncorrelated baths with reorganization energis of a) $\lambda = 30$ cm^{-1} and b) $\lambda = 300$ cm^{-1}. Initial conditons are $P_1(0) = 1, P_{2-7}(0) = 0$. Converged results are obtained with TT ranks 85. The hierarchy level is truncated at $m = 10$ on each bath.
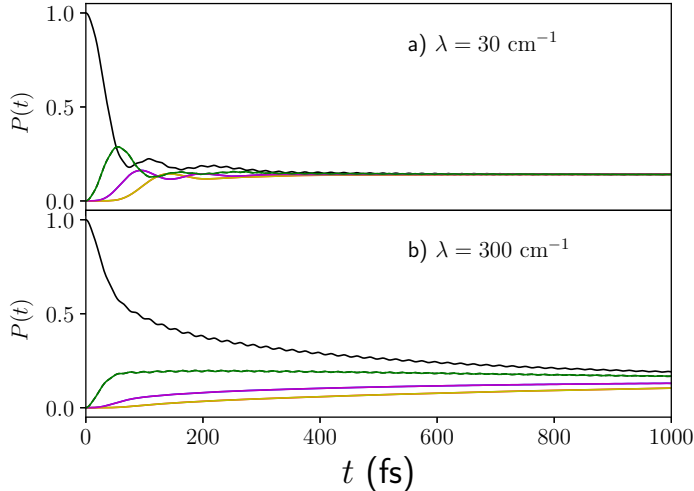
This behaviour can be traced back to the combination of the reduced Liouville equation with the TDVP solver.[74,75] Indeed, this methodology preserves the norm $\langle \Psi | \Psi \rangle$ and the "energy" $\bar{X} = \langle \Psi | X | \Psi \rangle$ during the evolution. Both quantities however have no direct physical meaning. In our formalism the true norm to be preserved during the evolution is $\langle 1 | \rho^{\mathbf{0}_A(t)} \rangle = \mathrm{tr}\rho_A^{\mathbf{0}}(t) = 1$. As can be expected this problem introduces artefacts which can be alleviated by increasing the ranks of the TT cores. However, this easily becomes a limiting factor since the required TT storage scales quadratically with the TT ranks.

Very recently it has been shown that a perturbation of the initial state can improve performances of the TVDP integration scheme for the Liouville-von Neumann equation, however the structure of the HEOM system does not allow to easily implement that type of correction.[76] Work is in progress to address this problem, and to use alternative integration schemes.

VI. DISCUSSION AND CONCLUSIONS

We have discussed the application of the twin formulation of statistical mechanics including the explicit use of tilde operators for the derivation of a set of hierarchical equations of

FIG. 2. Population dynamics of a 7 site polaron model with dynamic disorder on the inter-site couplings for two different values of the system-bath interaction strength: a) $\lambda = 25$ cm^{-1} and b) $\lambda = 10$ cm^{-1}. In both cases the characteristic bath frequency is $\gamma = 53$ cm^{-1}. Initial conditons are $P_1(0) = 1, P_{2-7}(0) = 0$. Converged results are obtained with TT ranks 95. The hierarchy level is truncated at $m = 10$ on each bath.
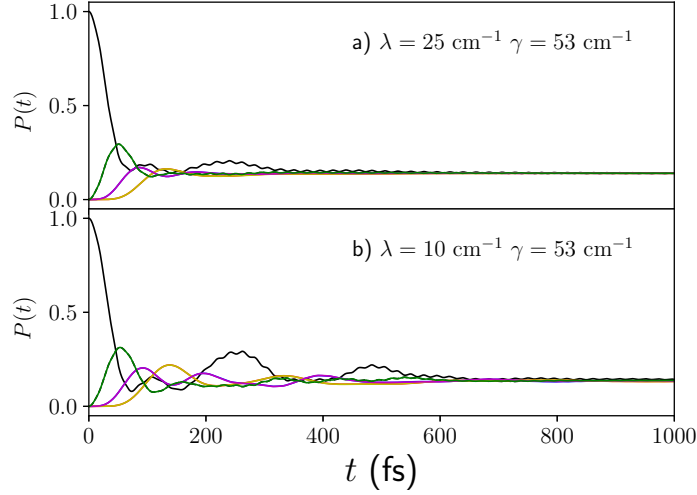

FIG. 3. Population dynamics of a 7 site polaron model with dynamic disorder on the inter-site couplings for two different values of the bath characteristic frequency (relaxation time): a) $\gamma = 53$ cm^{-1} and b) $\gamma = 5.3$ cm^{-1}. In both cases the reorganization energy is $\lambda = 25$ cm^{-1}. Initial conditons are $P_1(0) = 1, P_{2-7}(0) = 0$. The system-bath interaction strength is 25 cm^{-1}. Converged results are obtained with a TT rank 95. The hierarchy level is truncated at $m = 10$ on each bath.
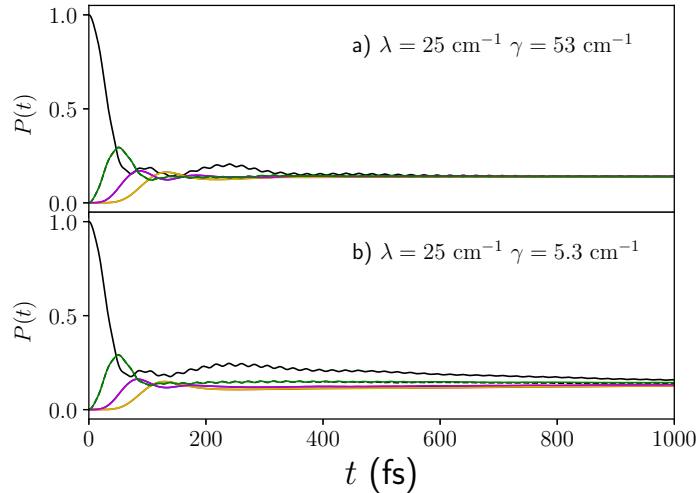
FIG. 4. Population dynamics of a homodimer with 14 nuclear vibrations. Bath reorganization energies are a) 90 cm^{-1} b) 300 cm^{-1}. Converged results are obtained with TT ranks 115. The hierarchy level is truncated at $m = 10$ on each bath
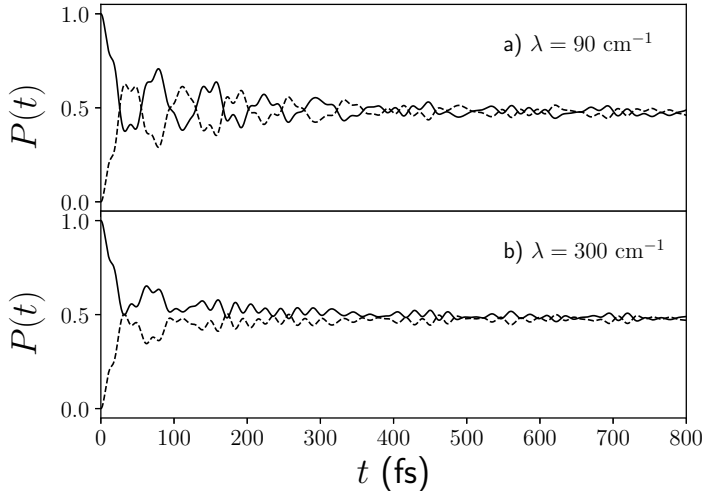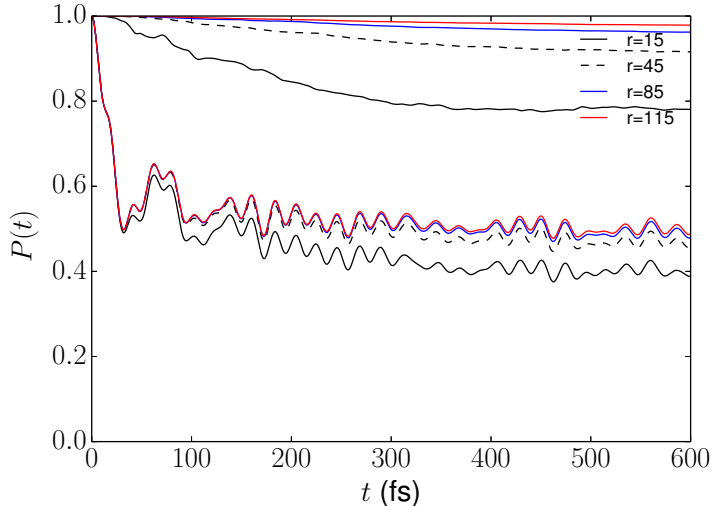

FIG. 5. Population dynamics of the initial electronic state of the homodimer model, and overall norm of the state vector for different TT truncation ranks as indicated in the legend. The hierarchy level is truncated at $m = 10$ on each bath.

motion capable to describe the exact dynamics of the reduced density matrix of a system. This new methodology allows to treat the dynamics of a complex molecular system including a large number of high frequency modes, with possibly non-linear interactions, and a dissipative non-Markovian bath.

By employing the twin formulation of quantum statistical mechanics it is possible to extend the use of numerical methods suitable for wave-packet propagation directly to the study of density matrix evolution without any modification to the original code but simply changing the definition of the Hamiltonian operator.

In the proposed approach the trace operation is replaced by a standard scalar product of two vectors, introducing a significant benefit to the actual numerical implementation in the calculations of expectation values of dynamical operators of system variables. While this approach is implicitly used in other techniques dealing with matrix products operators and matrix product states[?] here we suggest a mathematical description that allows to fully exploit the TT formalism in the Liouville space.

On the other hand, since the methodology is based on the same fundamental equations of other HEOM approaches it also benefits of several extensions already discussed in the literature. As an example, the spectral densities need not be limited to the simple Drude-Lorentz form but any linear combination of shifted Lorentzian functions is possible, which can be used to fit more complex spectral densities possibly obtained from numerical simulations of specific systems. The only fundamental requirement of the theory lies in the linear form of the bath operator in the system-bath coupling and and the second-order cumulant truncation of the evolution operator.

The numerical integration scheme based on the TDVP applied to density matrix poses some problems which do not have an immediate solution. Work is in progress to address the convergence issues. Further applications of the methodology to spin glasses coupled to a heat bath are in progress.[77]

As a concluding remark we would like to point out that HEOM methodology has been very recently implemented within the TT approximation but with a focus on the structure induced by the spectral density variable on the hierarchy.[62] The approach herein developed follows a different route for the numerical implementation of HEOM based on the use of the double space formalism followed by the tensorization of the Liuoville as well as of the relaxation super-operators. One key advantage of our approach is that no restrictions are imposed on the type of system under examination meaning that highly non-linear systems can be analysed as long as the system-bath interaction is linear in the bath degrees of freedom.

VII. SUPPLEMENTARY MATERIAL

See the supplementary material for a description of the vibronic model Hamiltonian operator and for the full set of parameters of the charge-transfer model of figure 4.

VIII. ACKNOWLEDGEMENTS

Appendix A: Derivation of $K_I^{(2)}(t)$

We start from

$$\hat{K}_I^{(2)}(t) = \int_0^t dt_1 \langle V(t)V(t_1) \rangle - \int_0^t dt_1 \langle \tilde{V}(t)V(t_1) \rangle - \int_0^t dt_1 \langle V(t)\tilde{V}(t_1) \rangle + \int_0^t dt_1 \langle \tilde{V}(t)\tilde{V}(t_1) \rangle \tag{A1}$$

which gives

$$\hat{K}_I^{(2)}(t) = S(t) \int_0^t dt_1 \langle Q(t)Q(t_1) \rangle S(t_1) - \int_0^t dt_1 \tilde{S}(t) \langle \tilde{Q}(t)Q(t_1) \rangle S(t_1)$$
$$- S(t) \int_0^t dt_1 \langle Q(t)\tilde{Q}(t_1) \rangle \tilde{S}(t_1) + \tilde{S}(t) \int_0^t dt_1 \langle \tilde{Q}(t)\tilde{Q}(t_1) \rangle \tilde{S}(t_1) \tag{A2}$$

Since

$$\langle \tilde{Q}(t)Q(t_1) \rangle = \langle 1_B | \tilde{Q}(t)Q(t_1) | \rho_B \rangle = \langle Q(t_1)Q(t) \rangle \tag{A3}$$

$$\langle Q(t)\tilde{Q}(t_1) \rangle = \langle \tilde{Q}(t_1)Q(t) \rangle = \langle Q(t_1)Q(t) \rangle = \langle Q(t)Q(t_1) \rangle^* \tag{A4}$$

$$\langle \tilde{Q}(t)\tilde{Q}(t_1) \rangle = \langle Q(t)\tilde{Q}(t) \rangle = \langle \tilde{Q}(t_1)Q(t) \rangle = \langle Q(t_1)Q(t) \rangle = \langle Q(t)Q(t_1) \rangle^* \tag{A5}$$

we have

$$\hat{K}_I^{(2)}(t) = S(t) \int_0^t dt_1 \langle Q(t)Q(t_1) \rangle S(t_1) - \tilde{S}(t) \int_0^t dt_1 \langle Q(t)Q(t_1) \rangle S(t_1)$$

$$- S(t) \int_0^t dt_1 \langle Q(t)Q(t_1) \rangle^* \tilde{S}(t_1) + \tilde{S}(t) \int_0^t dt_1 \langle Q(t)Q(t_1) \rangle^* \tilde{S}(t_1)$$

$$= [S(t) - \tilde{S}(t)] \int_0^t dt_1 \langle Q(t)Q(t_1) \rangle S(t_1) - [S(t) - \tilde{S}(t)] \int_0^t dt_1 \langle Q(t)Q(t_1) \rangle^* \tilde{S}(t_1)$$

$$= [S(t) - \tilde{S}(t)] \int_0^t dt_1 \langle Q(t)Q(t_1) \rangle S(t_1) - \int_0^t dt_1 \langle Q(t)Q(t_1) \rangle^* \tilde{S}(t_1)$$

$$= [S(t) - \tilde{S}(t)] \int_0^t dt_1 \langle Q(t_1)Q(t) \rangle^* S(t_1) - \int_0^t dt_1 \langle Q(t_1)Q(t) \rangle \tilde{S}(t_1)$$

$$= [S(t) - \tilde{S}(t)] \left\{ \int_0^t dt_1 \Re \langle Q(t_1)Q(t) \rangle [S(t_1) - \tilde{S}(t_1)] - i \int_0^t dt_1 \Im \langle Q(t_1)Q(t) \rangle [S(t_1) + \tilde{S}(t_1)] \right\}$$

(A6)

In the Schrödinger representation we have

$$\hat{K}^{(2)}(t) = e^{-i\hat{H}_A t} \hat{K}_I^{(2)}(t) e^{-i\hat{H}_A t}$$

$$= [S - \tilde{S}] \left\{ \int_0^t dt_1 \Re \langle Q(t_1)Q \rangle [S(t_1) - \tilde{S}(t_1)] - i \int_0^t dt_1 \Im \langle Q(t_1)Q \rangle [S(t_1) + \tilde{S}(t_1)] \right\}. \quad (A7)$$

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