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Citation: *The Journal of Chemical Physics* **145**, 224101 (2016); doi: 10.1063/1.4971211

View online: <http://dx.doi.org/10.1063/1.4971211>

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Quantum electron-vibrational dynamics at finite temperature: Thermo field dynamics approach

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(Received 20 September 2016; accepted 17 November 2016; published online 8 December 2016)

Quantum electron-vibrational dynamics in molecular systems at finite temperature is described using an approach based on the thermo field dynamics theory. This formulation treats temperature effects in the Hilbert space without introducing the Liouville space. A comparison with the theoretically equivalent density matrix formulation shows the key numerical advantages of the present approach. The solution of thermo field dynamics equations with a novel technique for the propagation of tensor trains (matrix product states) is discussed. Numerical applications to model spin-boson systems show that the present approach is a promising tool for the description of quantum dynamics of complex molecular systems at finite temperature. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4971211>]

I. INTRODUCTION

Accurate simulations of time-dependent photophysical and photochemical processes using realistic molecular potential energy surfaces are a fundamental problem of modern theoretical chemistry.^{1,2} To properly tackle finite temperature effects in such simulations, several methods have been developed which can be divided into two main classes: (i) direct propagation of the density matrix of the system and (ii) propagation of the wave function sampled over several initial conditions followed by an appropriate statistical average.

The hierarchical equations of motion (HEOM)³ and the quasi-adiabatic path integral (QUAPI)⁴ are among the most successful numerically exact methods for density matrix propagation. However, the HEOM and QUAPI methods become numerically prohibitive at low temperature.⁵ Furthermore, the HEOM application is limited to systems in which the bath spectral density may be represented in the Drude-Lorentz form, though several extensions have been proposed to overcome this problem.^{5–11} A large number of approximate methods based on density matrix formalism are also available, but their range of validity can be very limited and system dependent.^{12–21} Wave function propagation methods based on a basis set representation, such as the multiconfiguration time-dependent Hartree (MCTDH) method and its multilayer extension, (ML-MCTDH), Gaussian based MCTDH, and other basis set methods,^{22–28} are powerful tools at very low temperature,^{29,30} but become unhandy in high temperature cases, as they require a statistical sampling of the initial conditions, which introduces both theoretical and computational problems.^{31–35} On the other hand, basis set methods are very versatile, and capable of handling a large variety of Hamiltonian operators.^{36–40} A methodology that combines an accurate description of chemical processes at ambient temperature with the flexibility of a basis set representation

would be an important tool in the arsenal of quantum molecular dynamics.

The aim of this paper is twofold. First, we present a theoretical method for the simulation of time-dependent properties of electron-vibrational systems with many degrees of freedom at finite temperature based on Thermo Field Dynamics (TFD). Second, we show how to take advantage of recently developed techniques based on tensor networks to solve the resulting dynamical problem.⁴¹

TFD was introduced in the 1970's to provide a finite temperature representation of quantum mechanics.⁴² While it had a deep impact on many problems of theoretical physics,^{43–48} it did not receive much attention in molecular quantum dynamics: the first applications were reported very recently.^{49,50} In the present work, we generalize the TFD approach to treat quantum dynamics with multiple coupled electronic and vibrational degrees of freedom. We derive a new type of TFD electron-vibrational Schrödinger equation which includes the effects of temperature. Since in TFD the total number of degrees of freedom is double of that of the original system, special attention has to be paid to the numerical solution of the resulting dynamical problem. The methodology must have favorable scaling properties with respect to the number of nuclear degrees of freedom. We show how recently developed techniques based on the Tensor Train (TT) decomposition, also known as Matrix Product State (MPS) representation, can provide a robust and efficient numerical framework for the solution of the TFD Schrödinger equation.^{41,51}

The paper is organized as follows. The TFD methodology for the simulation of dynamics of quantum electron-vibrational systems is developed in Section II. Section III elaborates on the use of TTs for the solution of time-dependent TFD Schrödinger equations. Section IV shows illustrative simulations and comparisons with the exact HEOM and Stochastic Hamiltonian (SH) calculations of Ref. 5 for two representative spin-boson models. Section V is the conclusion. Appendix A contains the mathematical proof of the main working equations. Appendix B gives the derivation of the main results of

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Section II, employing the standard Liouville-von Neumann equation for the density matrix.

II. THERMO FIELD DYNAMICS FORMULATION OF ELECTRON-VIBRATIONAL DYNAMICS

A. Brief introduction to TFD and underlying equations

TFD has been reviewed and analyzed several times.^{42,44,52–54} Here we will briefly recall its physical and mathematical basis. As was first discussed by Umezawa,⁴² and later formally demonstrated by Suzuki,^{55,56} the time evolution of a system with a given Hamiltonian operator H at finite temperature can be described by a Schrödinger equation with a modified Hamiltonian \hat{H} given by

$$\hat{H} = H - \tilde{H}. \quad (1)$$

\tilde{H} is called the tildian and represents a fictitious Hamiltonian operator that can be derived from the original operator H using a well defined mathematical procedure (see below).^{42,56,57} In the following, operators with a tilde are considered as acting on the tilde states belonging to the fictitious tilde Hilbert space. The number of degrees of freedom in the new *augmented* system (real and fictitious) is double that of the original physical system. \hat{H} acts on states given by the direct product of the physical and fictitious states denoted by $|k\tilde{k}\rangle = |k\rangle|\tilde{k}\rangle$, where $|k\rangle$ ($|\tilde{k}\rangle$) are arbitrary basis vectors of the physical (fictitious) space.

Following Suzuki,⁵⁵ we define the vector

$$|\mathbf{I}\rangle = \sum_k |k\tilde{k}\rangle \quad (2)$$

(boldface symbols emphasize that we deal with both physical and tilde states) and the state

$$|\psi(t)\rangle = \rho(t)^{1/2}|\mathbf{I}\rangle, \quad (3)$$

where $\rho(t)$ is the density matrix of the original system. The time evolution of the state $|\psi(t)\rangle$ is determined by the TFD Schrödinger equation

$$i\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle \quad (4)$$

($\hbar = 1$), and the expectation value of any operator A acting in the physical Hilbert space $\{|k\rangle\}$ can be obtained as

$$\langle A(t) \rangle = \langle \psi(t) | A | \psi(t) \rangle \equiv \text{Tr}\{\rho(t)A\}. \quad (5)$$

The key difference with the standard Hilbert space formulation of quantum mechanics is that the TFD wave function $|\psi(t)\rangle$ is temperature dependent. The evaluation of $\langle A(t) \rangle$ via the TFD wave function $|\psi(t)\rangle$ and through the corresponding density matrix $\rho(t)$ is equivalent. As we show below, the solution of Equations (4) and (5) is more efficient than the solution of the Liouville equation, both from a computational and theoretical point of view.

B. Introducing vibrational temperature

Assuming that the system under investigation is at thermal equilibrium at a given temperature T , its initial state in TFD theory is obtained from Eq. (3),

$$|\psi(0)\rangle = \rho(0)^{1/2}|\mathbf{I}\rangle = Z^{-1/2}e^{-\beta H/2}|\mathbf{I}\rangle, \quad (6)$$

where Z is the overall partition function, and $\beta = (k_B T)^{-1}$ (k_B is the Boltzmann constant). The exact evaluation of the operator $e^{-\beta H/2}$ is beyond the scope of the paper, though techniques based on imaginary time propagation (which are valid for generic Hamiltonians) exist and have been successfully applied to complex systems.^{36,58–60}

In this work we consider the dynamical properties of molecular systems where usually the energies of the electronic degrees of freedom are much higher than the vibrational energies. In this case the effect of a finite temperature is to create a thermal population of excited vibrational states, while only the ground electronic state of the entire system, $|g\rangle$, is tangibly populated at thermal equilibrium. Within the validity of this condition we can safely employ the approximation

$$\rho(0) = Z^{-1}e^{-\beta H} \approx |g\rangle\langle g|\rho_{\text{vib}}. \quad (7)$$

Here ρ_{vib} is the equilibrium Boltzmann distribution of the vibrational degrees of freedom, which, in the present work, are described using harmonic approximation. Although approximation (7) may need refinements for certain systems (cf. Ref. 59) it is at the core of molecular photophysics, photochemistry, spectroscopy, as well as most of the electron and energy transfer theories, and is adopted in the present work.^{31–35} It works perfectly for molecular species at ambient temperature, since typically the electronic energy differences are of the order of a few eV, while $\beta^{-1} = 0.026$ eV at $T = 300$ K.

In time-dependent molecular processes the system is prepared in a non-stationary state $|e\rangle$, typically after interaction with an external (time-dependent) field. This process is governed by a transition operator X^\dagger , which, in the most general case, is an electron-vibrational operator that couples the electronic ground state $|g\rangle$, with high-lying electronic states,

$$|e\rangle = X^\dagger|g\rangle. \quad (8)$$

The realization of this state is almost always implicit, and henceforth we will assume the system to be initially in a generic non-stationary electronic state $|e\rangle$.

For a thermal ensemble of harmonic oscillator states

$$\rho_{\text{vib}} = Z_o^{-1}e^{-\beta H^\circ}, \quad (9)$$

where

$$H^\circ = \sum_k \omega_k a_k^\dagger a_k, \quad (10)$$

a_k^\dagger (a_k) are the creation (annihilation) Bose operators ($[a_k, a_{k'}^\dagger] = \delta_{kk'}$), and Z_o is the partition function. Hence the initial TFD wavefunction is defined as

$$|\psi(0)\rangle = |e\rangle|\tilde{e}\rangle\rho_{\text{vib}}^{1/2}|\mathbf{I}\rangle = |e\rangle Z_o^{-1/2}e^{-\beta H^\circ/2}|\mathbf{I}\rangle, \quad (11)$$

where $|e\rangle = |e\rangle|\tilde{e}\rangle$, and $|\mathbf{I}\rangle$ refers only to the vibrational subsystem. The state $Z_o^{-1/2}e^{-\beta H^\circ/2}|\mathbf{I}\rangle$ is often referred to as thermal vacuum and is denoted with the symbol $|\mathbf{0}(\beta)\rangle$. It can equivalently be rewritten as⁶¹

$$Z_o^{-1/2}e^{-\beta H^\circ/2}|\mathbf{I}\rangle = |\mathbf{0}(\beta)\rangle = e^{-iG}|\mathbf{0}\rangle, \quad (12)$$

where $|\mathbf{0}\rangle \equiv |\mathbf{0}\tilde{0}\rangle$ is the vibrational ground state of the augmented system (physical and tilde states), and the operator G is given by

$$G = -i \sum_k \theta_k (a_k \tilde{a}_k - a_k^\dagger \tilde{a}_k^\dagger) \quad (13)$$

with

$$\theta_k = \operatorname{arctanh}(e^{-\beta\omega_k/2}). \quad (14)$$

The unitary transformation defined by Equations (12) and (13) is called the Bogoliubov thermal transformation. It introduces thermal noise into the physical system by coupling it to the fictitious tilde system through the temperature-dependent mixing parameters θ_k .⁴²

Instead of solving the Schrödinger equation (4) with the initial condition (11) we prefer to apply the inverse thermal transformation to the Hamiltonian \hat{H} and solve the transformed Schrödinger equation.⁶² This is accomplished by defining a new state

$$|\varphi(t)\rangle = e^{iG}|\psi(t)\rangle, \quad (15)$$

whose time evolution is determined by the equation

$$i\frac{\partial}{\partial t}|\varphi(t)\rangle = \hat{H}_\theta|\varphi(t)\rangle \quad |\varphi(0)\rangle = |e\rangle|\mathbf{0}\rangle, \quad (16)$$

where

$$\hat{H}_\theta = e^{iG}\hat{H}e^{-iG}. \quad (17)$$

The expectation value of an observable A can now be rewritten as

$$\langle A(t) \rangle = \langle \varphi(t) | A_\theta | \varphi(t) \rangle \quad \text{with} \quad A_\theta = e^{iG} A e^{-iG}. \quad (18)$$

Equations (16) and (18), which are completely equivalent to Equations (4) and (5), are the starting point of our methodology. In order to obtain a numerical solution of the Schrödinger Equation (16) the Hamiltonian \hat{H}_θ must have an analytical representation or a form which is suitable for numerical treatment. This can be accomplished by expanding H and \tilde{H} in series in creation-annihilation operators (or position and momentum operators) and using the fundamental relations^{42,62,63}

$$e^{iG} a_k e^{-iG} = a_k \cosh(\theta_k) + \tilde{a}_k^\dagger \sinh(\theta_k), \quad (19)$$

$$e^{iG} \tilde{a}_k e^{-iG} = \tilde{a}_k \cosh(\theta_k) + a_k^\dagger \sinh(\theta_k). \quad (20)$$

The transformed Hamiltonian \hat{H}_θ depends on temperature through the parameters θ_k .

C. Electron-vibrational Hamiltonian

The above methodology is absolutely general and independent of the form of the Hamiltonian. In the remainder of the paper, we focus on a special type of the Hamiltonian operator describing a set of coupled electronic states interacting with a phonon bath,

$$H = \sum_n \varepsilon_n c_n^\dagger c_n - \sum_{n \neq m} J_{nm} c_n^\dagger c_m + \sum_k \omega_k a_k^\dagger a_k - \sum_{kn} \frac{g_{kn}}{\sqrt{2}} c_n^\dagger c_n (a_k^\dagger + a_k). \quad (21)$$

Here c_n^\dagger (c_n) creates (annihilates) electronic excitation at the electronic state n with the energy ε_n , J_{nm} are electronic couplings, ω_k are the frequencies of the bath harmonic oscillators, and the parameters g_{nk} determine the strength of the electron-phonon coupling. The Hamiltonian (21) has a large number of applications, ranging from the generic description of molecular aggregates^{64–66} to the analysis of molecular processes in the linear vibronic-coupling theory.⁶⁷

The tilde Hamiltonian is written as⁴²

$$\tilde{H} = \sum_n \varepsilon_n \tilde{c}_n^\dagger \tilde{c}_n - \sum_{n \neq m} J_{nm} \tilde{c}_n^\dagger \tilde{c}_m + \sum_k \omega_k \tilde{a}_k^\dagger \tilde{a}_k - \sum_{kn} \frac{g_{kn}}{\sqrt{2}} \tilde{c}_n^\dagger \tilde{c}_n (\tilde{a}_k^\dagger + \tilde{a}_k). \quad (22)$$

\tilde{H} is produced from H by the substitution of all the physical operators with the tilde operators. The values of the parameters ω_k , ε_n , J_{nm} , g_{nk} are the same in the two Hamiltonians.

Following the TFD prescriptions, we introduce the Hamiltonian \tilde{H} according to Eq. (1) and solve the TFD Schrödinger equation (4) with the initial condition

$$|\psi(0)\rangle = |e\rangle|\tilde{e}\rangle\rho_{\text{vib}}^{1/2}|\mathbf{I}\rangle \equiv |e\rangle|\mathbf{0}(\beta)\rangle. \quad (23)$$

Here the equilibrium vibrational distribution is defined according to Eq. (9), $|\mathbf{I}\rangle$ is specified via Eq. (2), and $|e\rangle$ is the initial electronic wave function.

In a basis-set representation, the TFD wave function $|\psi(t)\rangle$ is an array of the dimension $(N_{el} \times N_{\text{vib}})^2$, where N_{el} (N_{vib}) is the number of electronic (vibrational) basis functions and the square is due to the doubling of the degrees of freedom. The density matrix describing the current physical system has exactly the same dimensions. Hence, a straightforward application of TFD does not bring any computational gain. However, Eq. (23) introduces vibrational, but not electronic temperature. We therefore expect that the tilde part of the electronic Hamiltonian can be dropped (cf. Ref. 62). This statement is rigorously proven in Appendix A, which shows that the Schrödinger equation

$$i\frac{\partial}{\partial t}|\psi(t)\rangle = \bar{H}|\psi(t)\rangle, \quad (24)$$

where \bar{H} is defined below, with the initial condition

$$|\psi(0)\rangle = |e\rangle\rho_{\text{vib}}^{1/2}|\mathbf{I}\rangle \equiv |e\rangle|\mathbf{0}(\beta)\rangle \quad (25)$$

yields the same expectation value $\langle A(t) \rangle$ as the Schrödinger equation (4) governed by the full TFD Hamiltonian \hat{H} . We notice that the $|\tilde{e}\rangle$ term has been dropped in Eq. (25) because \bar{H} contains no tilde electronic variables. The new Hamiltonian operator \bar{H} is defined as

$$\bar{H} = H - \tilde{H}_{\text{vib}}, \quad (26)$$

where H is the physical Hamiltonian operator given by Eq. (21), and \tilde{H}_{vib} is any operator acting in the tilde vibrational space (see Appendix A). The choice of \tilde{H}_{vib} is dictated exclusively by computational convenience and does not affect the expectation value $\langle A(t) \rangle$.

In what follows we choose

$$\tilde{H}_{\text{vib}} = \sum_k \omega_k \tilde{a}_k^\dagger \tilde{a}_k. \quad (27)$$

Applying the Bogoliubov transformation to the Schrödinger equation (24), we obtain our working equation

$$i\frac{\partial}{\partial t}|\varphi(t)\rangle = \bar{H}_\theta|\varphi(t)\rangle, \quad |\varphi(0)\rangle = |e\rangle|\mathbf{0}\rangle \quad (28)$$

with the Hamiltonian

$$\begin{aligned}
\bar{H}_\theta &= e^{iG} \bar{H} e^{-iG} \\
&= \sum_n \varepsilon_n c_n^\dagger c_n + \sum_{n \neq m} J_{nm} c_n^\dagger c_m \\
&\quad + \sum_k \omega_k (a_k^\dagger a_k - \tilde{a}_k^\dagger \tilde{a}_k) \\
&\quad - \sum_{kn} \frac{g_{kn}}{\sqrt{2}} \left\{ (a_k + a_k^\dagger) \cosh(\theta_k) \right. \\
&\quad \left. + (\tilde{a}_k + \tilde{a}_k^\dagger) \sinh(\theta_k) \right\} c_n^\dagger c_n. \quad (29)
\end{aligned}$$

For deriving the above expression we used the invariance property⁴²

$$e^{iG} (a_n^\dagger a_n - \tilde{a}_n^\dagger \tilde{a}_n) e^{-iG} = a_n^\dagger a_n - \tilde{a}_n^\dagger \tilde{a}_n. \quad (30)$$

The operator \bar{H}_θ of Eq. (29) consists of two parts: a modified physical Hamiltonian in which the linear coupling terms are multiplied by $\cosh(\theta_k)$ factors, and the vibrational tilde Hamiltonian. The excitation of the tilde vibrations is caused by the linear terms $\sim \sinh(\theta_k)$. Since \tilde{H}_{vib} enters Eq. (29) with a negative sign, vibrational excitations in the tilde space correspond to a flow of energy from the physical system to the fictitious tilde system. It is this type of coupling that accounts for thermal noise.

Summarizing, the evaluation of $\langle A(t) \rangle$ can be reduced to the solution of the simplified TFD Schrödinger equation (28) with the Hamiltonian \bar{H}_θ specified by Eq. (29). In a basis-set representation, the wave function $|\varphi(t)\rangle$ is an array of dimension $N_{el} \times N_{\text{vib}}^2$. This yields a considerable reduction of the dimension in comparison with the standard TFD wave function and/or density matrix, notably for systems with multiple electronic states. $|\varphi(t)\rangle$ offers, therefore, a more compact way of storage of information on the system dynamics than the density matrix $\rho(t)$. At $T \rightarrow 0$ the mixing parameters θ_k become zero, $\sinh(\theta_k) \rightarrow 0$, the coupling to the tilde space disappears, and the standard Schrödinger equation is recovered as expected. For high-frequency modes, $\theta_k \ll 1$, $\sinh(\theta_k) \approx 0$, and $\cosh(\theta_k) \approx 1$ even at room temperature. As a rule of thumb, high-frequency modes need not be incorporated into the tilde Hamiltonian. This leads to additional reduction of the active space and computational savings. On the other hand, this trick does not work with the standard Liouville-von Neumann equation for the density matrix.

D. Generalizations and extensions

The methodology developed in Section II C is not limited to the particular form of the Hamiltonian of Eq. (21). Below we sketch its possible generalizations and extensions.

- (i) More complex forms of electron-electron, electron-phonon or phonon-phonon interactions may be considered. In fact, electronic couplings J_{nm} and electron-phonon couplings g_{nk} are allowed to depend on the vibrational degrees of freedom. If J_{nm} and g_{nk} are polynomials of the vibrational operators a_k^\dagger and a_k , then the application of the Bogoliubov transformation of Eq. (19) is quite straightforward, and the transformed Hamiltonian \bar{H}_θ will be a polynomial of the same order in a_k^\dagger , a_k , \tilde{a}_k^\dagger , and \tilde{a}_k . A common case is the presence of a bilinear coupling between high and low frequency vibrational modes. The transformed Hamiltonian \bar{H}_θ possesses the same bilinear structure. Furthermore, the

tilde contributions to the high-frequency mode can be dropped (see Section II C).

- (ii) All the parameters of the Hamiltonian of Eq. (21) may be time-dependent due to possible driving by external fields. In this case, all the equations of Section II C remain unchanged, but the proofs of Appendices A and B will require formal refinements, resulting in the replacements of the Hamiltonian propagators by the corresponding evolution operators in terms of time-ordered exponentials.
- (iii) The physical Hamiltonian of Eq. (21) can be extended to

$$H \rightarrow H + H^F(t),$$

where

$$H^F(t) = E(t)X^\dagger + E^*(t)X. \quad (31)$$

describes interaction of the system with external fields $E(t)$ and X is a transition operator defined as

$$X = \sum_{n_1=0}^1 \sum_{n_2=0}^1 \dots \sum_{n_p=0}^1 S_{n_1, n_2, \dots, n_p} (c_1^\dagger)^{n_1} (c_2^\dagger)^{n_2} \dots (c_p^\dagger)^{n_p}, \quad (32)$$

where, in general, the quantities S_{n_1, n_2, \dots, n_p} depend on the vibrational variables. After the Bogoliubov transformation (29), $X \rightarrow X_\theta$. For this extended Hamiltonian, all derivations in Section II C remain unchanged. In the simplest case of dipole transitions, we have⁶⁵

$$X = \sum_n c_n \mu_n, \quad (33)$$

where c_n are the electronic annihilation operators and μ_n are the matrix elements of the transition dipole moments. Hence the developed methodology can be used for the simulation of any photo-initiated process as well as of optical signals, both by perturbative^{65,68} and non-perturbative^{69,70} methods.

- (iv) The TFD Schrödinger equations can be approximately solved by various time-dependent variational methods. In particular, it looks promising to solve TFD Schrödinger equations via the Davydov ansatz.^{27,71} Very recently, temperature effects have been incorporated into the Davydov ansatz description by using the Glauber-Sudarshan representation of the coherent states.⁷²
- (v) The present methodology can be generalized towards dissipative nonequilibrium systems coupled to several heat baths. In this context, the work by Dzhiyev and Kosov (see Refs. 47 and 48) may become a useful starting point.

III. TENSOR-TRAIN QUANTUM DYNAMICS

The solution of the time-dependent TFD Schrödinger equation (28) requires efficient numerical methods. Since the coupling with the tilde space doubles the number of nuclear degrees of freedom, and since a thermal environment can be realistically mimicked only using hundreds or thousands of degrees of freedom, it is essential to use a methodology suitable to treat a large number of dynamical variables. Several techniques have been developed which can, at least

in principle, overcome what has been termed the *curse of dimensionality*.^{38,73} Very recently, a new type of representation of wave functions known as Tensor Train (TT) format (or Matrix Product States, MPS, in the physics literature) has turned out to be a promising approximation in high dimensional problems.^{51,73–78} In the present work, we apply the recently developed numerical techniques to efficiently solve multidimensional quantum dynamical problems using the TT format.^{76,79} Below we sketch the basic principles of the TT decomposition, and show how it can be applied to efficiently solve the TFD Schrödinger equation (28). The reader is referred to the original papers^{51,73,77} for a detailed analysis of the TT decomposition.

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

$$|\Psi\rangle = \sum_{i_1, i_2, \dots, i_d} C(i_1, \dots, i_d) |i_1\rangle \otimes |i_2\rangle \cdots |i_d\rangle, \quad (34)$$

where $|i_k\rangle$ labels the basis states of the k th dynamical variable, and the elements $C(i_1, \dots, i_d)$ are complex numbers labeled by d indices. If we truncate the summation of each index i_k , the elements $C(i_1, \dots, i_d)$ represent a tensor of rank d . The evaluation of the summation (34) requires the computation (and storage) of the n^d term, where n is the average size of the one-dimensional basis set, which becomes prohibitive for large d . Using the TT format, the tensor C is approximated as

$$C(i_1, \dots, i_d) \approx G_1(i_1)G_2(i_2) \cdots G_d(i_d), \quad (35)$$

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

$$C(i_1, \dots, i_d) = \sum_{\alpha_0 \alpha_1 \cdots \alpha_d} G_1(\alpha_0, i_1, \alpha_1) \times G_2(\alpha_1, i_2, \alpha_2) \cdots G_d(\alpha_{d-1}, i_d, \alpha_d). \quad (36)$$

The matrices G_k are three dimensional arrays, called *cores* of the TT decomposition. The ranks r_k are called compression ranks. Using the TT decomposition (35) 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 d arrays of dimensions $r_{k-1} \times n_k \times r_k$, thus the required storage dimension is of the order dnr^2 .

In a time-dependent theory the cores $G_k(i_k)$ are time dependent complex matrices whose equations of motion can be found by applying the time-dependent variational principle (TDVP) to the parametrized form of the wave function

$$|\Psi(G(t))\rangle = \sum_{i_1 \cdots i_d} G_1(i_1, t) \times G_2(i_2, t) \cdots G_d(i_d, t) |i_1\rangle \otimes |i_2\rangle \cdots |i_d\rangle. \quad (37)$$

The resulting equations of motion can be written in the form

$$\frac{d}{dt} |\Psi(G(t))\rangle = -i\hat{P}_{\pi(G(t))} H |\Psi(G(t))\rangle, \quad (38)$$

and provide an approximate solution of the original equation on the manifold of TT tensors of fixed rank, \mathcal{M}_{TT} . In Equation (38), $\hat{P}_{\pi(G(t))}$ is the orthogonal projection into the tangent space of \mathcal{M}_{TT} at $|\Psi(G(t))\rangle$. We refer the reader to Refs. 76 and 79, where the explicit differential equations are derived and their approximation properties are analyzed, and to Ref. 80 for a discussion of time-dependent TT/MPS approximations in the theoretical physics literature.

Several techniques exist to compute the time evolution of TT/MPS.^{76,81–83} Here we adopt a methodology recently developed by Lubich, Oseledets, and Vandereycken, which combines an explicit expression for the projector $\hat{P}_{\pi(G(t))}$ and an extremely efficient second order split projector integrator specifically tailored to the TT format.⁷⁶ The computations presented in this paper have been performed using a code based on the software library developed by Oseledets and coworkers.

IV. NUMERICAL EXAMPLES

In order to show the validity of the theoretical framework and the accuracy of the numerical methodology, we will consider its application to two different model systems in which two electronic states are coupled to low frequency vibrations. In the following we will refer to the current methodology with the acronym TFD-TT.

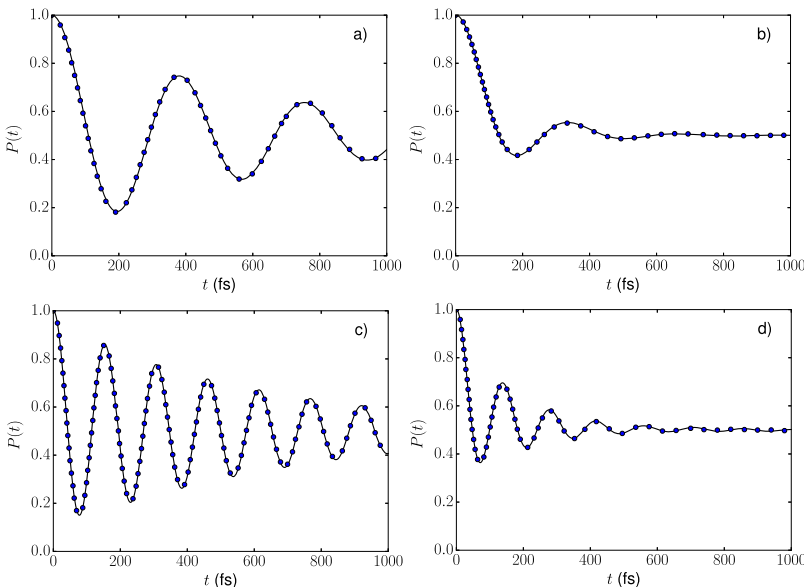


FIG. 1. Population $P(t)$ of the initial electronic state at $T = 300$ K as a function of time, for different values of $\alpha = \lambda/(2\omega_c)$; (a) $\lambda = 5$ cm^{-1} ; (b) $\lambda = 20$ cm^{-1} (both with the tunneling amplitude $J = 40$ cm^{-1}); (c) $\lambda = 20$; (d) $\lambda = 80$ (both with $J = 100$ cm^{-1}). Full lines: TFD-TT calculations. Blue dots: numerically exact HEOM calculations of Ref. 5.

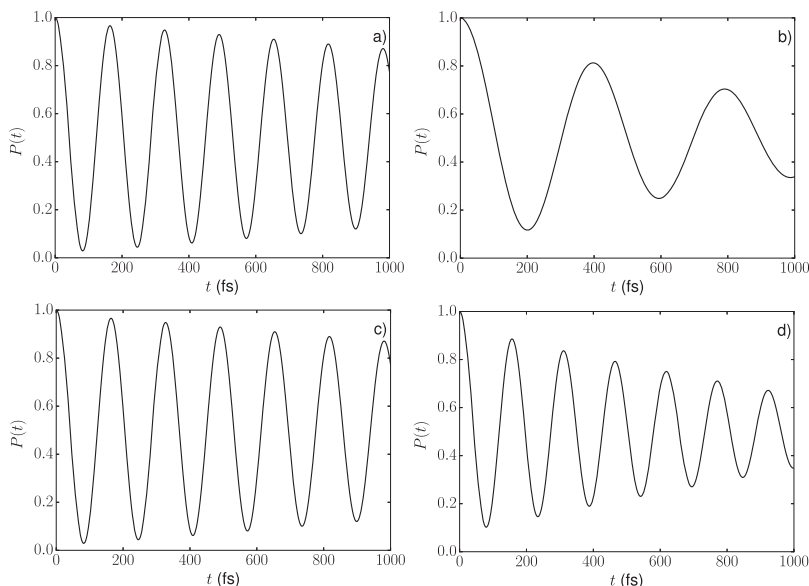


FIG. 2. Population $P(t)$ of the initial electronic state at $T = 30$ K as a function of time, for different values of $\alpha = \lambda/(2\omega_c)$; (a) $\lambda = 5\text{ cm}^{-1}$; (b) $\lambda = 20\text{ cm}^{-1}$ (both with the tunneling amplitude $J = 40\text{ cm}^{-1}$); (c) $\lambda = 20\text{ cm}^{-1}$; (d) $\lambda = 80\text{ cm}^{-1}$ (both with $J = 100\text{ cm}^{-1}$).

A. Spin-boson model

We first consider a prototypical spin-boson model in which two electronic states are coupled to low frequency vibrational modes. The thermal bath is described by the Ohmic spectral density

$$J(\omega) = \frac{\pi}{2} \alpha \omega e^{-\omega/\omega_c}. \quad (39)$$

The cut-off frequency is fixed at $\omega_c = 53\text{ cm}^{-1}$ throughout the paper. The solution of Equation (28) using a basis set representation requires the discretization of the spectral density over a finite set of frequencies. We have adopted a non uniform discretization procedure⁸⁴ that ensures a fast convergence with respect to the number of sampling points. In our calculations the spectral density is discretized with 200 degrees of freedom in the range $(0, 5\omega_c]$.

Figure 1 shows the population $P(t)$ of the initial electronic state at 300 K for the set of parameters reported in the caption. The TFD-TT results correspond to the full lines, while the blue dots correspond to the numerically exact populations computed in Ref. 5 via SH and HEOM methodologies (HEOM is a standard reference for benchmarking high-temperature simulations). Clearly, the TFD-TT and SH populations are in excellent agreement and virtually indistinguishable. The comparison unequivocally demonstrates the validity of the TFD-TT approach for this type of quantum dynamical problems.

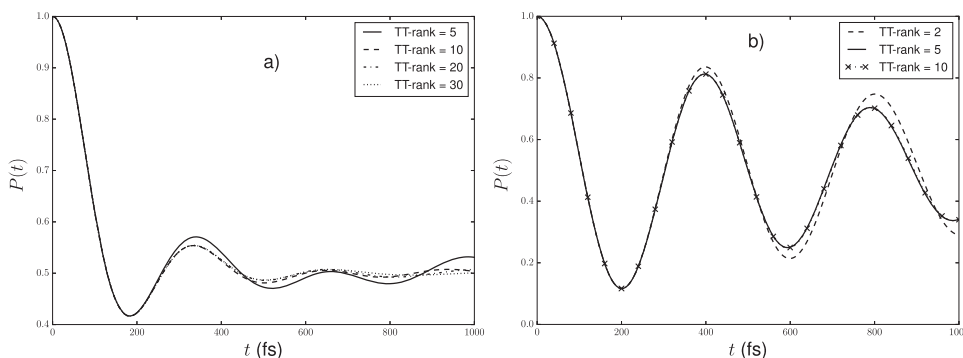


FIG. 3. Population $P(t)$ of the initial electronic state as a function of time for different values of the TT compression ranks simulated for $\alpha = (20\text{ cm}^{-1})/(2\omega_c)$ and $J = 40\text{ cm}^{-1}$. (a) $T = 300$ K; (b) $T = 30$ K.

Figure 2 shows $P(t)$ at 30 K. The more pronounced oscillations are a typical effect of the temperature decrease, due to a reduction of the number of coupled vibronic states contributing to the system dynamics.

The convergence properties of the numerical methodology are illustrated by Figure 3 which shows the population as a function of time for different values of the TT compression ranks. At a very low temperature $T = 30$ K the convergence is achieved with very low compression ranks, while at higher temperature a much higher rank is required. Since the required TT storage scales quadratically with the TT rank, this amounts to an increased computational cost of the calculation.

B. Reaction mode spin-boson

One of the key advantages of using a basis set approach is the possibility to describe a large variety of potential energy surfaces beyond linear electron-phonon couplings. This is important for the description of chemical reactions in which the surfaces can be highly anharmonic. Here we show how the TFD-TT technique can be applied to treat bilinear couplings between electrons and phonons. We consider a system of two electronic states coupled to a single harmonic oscillator mode with the frequency Ω which is in turn coupled to a set of harmonic oscillators having Ohmic spectral density. The corresponding Hamiltonian, often referred to as reaction mode spin-boson,⁸⁵ can be written as

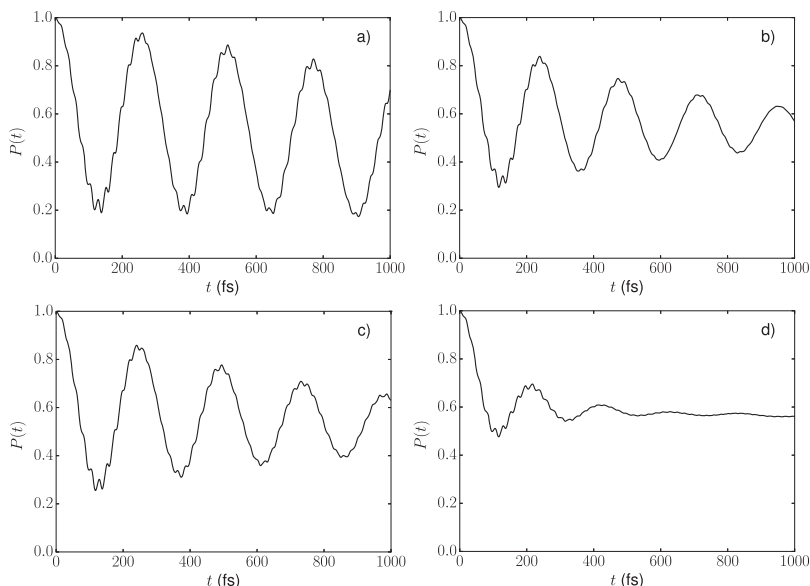


FIG. 4. The time evolution of the electronic population $P(t)$, for different values of $\alpha = \lambda/(2\omega_c)$ and for a tunneling amplitude $J = 40 \text{ cm}^{-1}$; (a) $\lambda = 20 \text{ cm}^{-1}$, $T = 30 \text{ K}$; (b) $\lambda = 20 \text{ cm}^{-1}$, $T = 300 \text{ K}$; (c) $\lambda = 80 \text{ cm}^{-1}$, $T = 30 \text{ K}$; (d) $\lambda = 80 \text{ cm}^{-1}$, $T = 300 \text{ K}$.

$$H = \epsilon\sigma_z - J\sigma_x + \Omega A^\dagger A + \sum_k \omega_k a_k^\dagger a_k + g(A^\dagger + A)\sigma_z + (A^\dagger + A) \sum_k \lambda_k (a_k^\dagger + a_k)\sigma_z, \quad (40)$$

where A , a_k (A^\dagger , a_k^\dagger) denote the annihilation (creation) operators for the reaction and bath oscillators, respectively, and the coupling coefficients λ_k satisfy the relation

$$J(\omega) = \sum_k \lambda_k^2 \delta(\omega - \omega_k) = \frac{\pi}{2} \alpha \omega e^{-\omega/\omega_c}. \quad (41)$$

The value of the parameter g determines the strength of the coupling between the high frequency mode and the electronic subsystem. In this model the phonons “drain” energy from the reaction coordinate and not directly from the spin system.

In Figure 4 the electronic population $P(t)$ at 30 K and 300 K is shown for two different values of the Kondo parameter α (see the caption of Figure 4 for the Hamiltonian parameters).

At 30 K and small α , the boson bath is not very effective in dissipating energy from the reaction coordinate. In this regime coherent oscillations of the electronic population persist at long times. When temperature increases to 300 K the damping is more evident but the oscillations remain underdamped. For larger α , the population at 30 K exhibits underdamped oscillations, while for 300 K the bath quenches the beatings at around 600 fs. The trend is natural, since the Kondo parameter controls the coupling of the reaction mode to the harmonic bath. The high-frequency modulation of the population dynamics is due to coherent vibrations of the reaction mode with a period $2\pi/\Omega \approx 22 \text{ fs}$.

Note that the population evolutions depicted in Figure 4 are fully converged and therefore numerically exact within the TT approximation.

V. CONCLUSIONS

We have developed a new approach, TFD-TT, to accurately finite-temperature quantum dynamical simulations of systems with multiple electronic and nuclear degrees of freedom. The approach is based on thermo field dynamics (TFD)

theory and tensor train (TT) decomposition. TFD describes temperature effects by the coupling of the system to a fictitious bosonic bath, so that the number of nuclear degrees of freedom is doubled. We have derived the corresponding time-dependent TFD Schrödinger equation and solved it by using a TT/MPS representation of the vibronic wave function. The use of TT decomposition enables us to handle the large number of variables: the storage of rank d tensors in TT/MPS format scales linearly with d . The results of our numerical simulations of model spin-boson systems clearly show that the methodology is very accurate and robust. It can be applied to problems with many degrees of freedom at any temperature. The present approach is based on a basis set representation of the wave function and can be applied to realistic chemical dynamics problems using computed potential energy surfaces.

In a basis-set representation, the time-dependent TFD wave function is an array of the dimension $N_{el} \times N_{vib}^2$, where N_{el} (N_{vib}) is the number of electronic (vibrational) basis functions. The density matrix describing the same problem has the dimension of $N_{el}^2 \times N_{vib}^2$. The TFD wave function offers, therefore, a more compact way of information storage in comparison with the density matrix, notably for systems with multiple electronic states. Furthermore, high-frequency modes need not be coupled to the fictitious bosonic bath. This leads to additional reduction of the active space and computational savings.

In wave function methodologies, finite temperature effects are taken into account by averaging the quantity of interest over different initial conditions. Therefore, the distribution of initial conditions must be sampled via Monte Carlo methods, and for each initial state a separate dynamical problem must be solved. Both these aspects limit the applications of such methods to large systems at room temperature. Here we have shown that using TFD theory it is possible to describe finite temperature effects without the need to solve a large number of independent dynamical problems with different initial conditions. The increased computational cost, due to the doubled number of nuclear degrees of freedom, can be kept under control by using

a TT/MPS representation of the wave function, which is very accurate for the cases discussed in this paper.

The application of the TFD-TT representation to other types of potential energy surfaces requires a straightforward extension of the methodology, however, its reliability will depend on the degree of accuracy of the TT decomposition. This aspect is under investigation and will be the subject of future work.

ACKNOWLEDGMENTS

R.B. acknowledges the CINECA award CSDYN-HP10CTEX1Q under the ISCRA initiative, for the availability of high performance computing resources and support, and the University of Torino for the Award No. BORR-RILO-16-01. M.F.G. acknowledges the support from the Deutsche Forschungsgemeinschaft (DFG) through the DFG-Cluster of Excellence “Munich-Centre for Advanced Photonics” (www.munich-photonics.de). R.B. thanks Professor Ivan Oseledets for having provided the TT software, and explained several related issues. M.F.G. thanks Danny Kosov for very useful discussions. Both of us are grateful to Professor Wolfgang Domcke for numerous stimulating conversations and support of our work.

APPENDIX A: CONSTRUCTION OF SIMPLIFIED TFD HAMILTONIAN

Consider the TFD Schrödinger equation with the physical Hamiltonian (21) and the tilde Hamiltonian (22). The expectation value of any operator A acting in the physical space can be explicitly evaluated as

$$\begin{aligned} \langle A(t) \rangle &= \langle \psi(t) | A | \psi(t) \rangle \\ &= \langle \tilde{e} | \langle e | \langle \mathbf{0}(\beta) | e^{i(H-\tilde{H})t} A e^{-i(H-\tilde{H})t} | \mathbf{0}(\beta) \rangle | e \rangle | \tilde{e} \rangle. \end{aligned} \quad (\text{A1})$$

Here $|\mathbf{0}(\beta)\rangle$ is defined via Eq. (12) and $|e\rangle$ is a certain initial electronic wave function specified per Eq. (8).

Evidently,

$$[H, \tilde{H}] = 0, \quad [\tilde{H}, A] = 0, \quad (\text{A2})$$

since the operators act on different variables, and in different spaces. Hence

$$\begin{aligned} \langle A(t) \rangle &= \langle e | \langle \mathbf{0}(\beta) | e^{iHt} A e^{-iHt} | \mathbf{0}(\beta) \rangle | e \rangle \\ &= \langle e | \langle \mathbf{0}(\beta) | e^{i(H-\tilde{H}_{\text{vib}})t} A e^{-i(H-\tilde{H}_{\text{vib}})t} | \mathbf{0}(\beta) \rangle | e \rangle, \end{aligned}$$

where \tilde{H}_{vib} is any operator depending on the tilde variables $\tilde{a}_k^\dagger, \tilde{a}_k$. Choosing \tilde{H}_{vib} as in Eq. (27) yields the TFD Hamiltonian of the present work. The commutation relations (A2) remain valid after any unitary transformation performed on the operators. Hence, they remain valid after the Bogoliubov transformation, giving

$$\begin{aligned} \langle A(t) \rangle &= \langle e | \langle \mathbf{0} | e^{iG} e^{i(H-\tilde{H}_{\text{vib}})t} A e^{-i(H-\tilde{H}_{\text{vib}})t} e^{-iG} | \mathbf{0} \rangle | e \rangle \\ &= \langle e | \langle \mathbf{0} | e^{i\tilde{H}_\theta} A_\theta e^{-i\tilde{H}_\theta t} | \mathbf{0} \rangle | e \rangle. \end{aligned} \quad (\text{A3})$$

From Equation (A3) it is clear that the evolution of the state $|e\rangle|\mathbf{0}\rangle$ generated by the operator \tilde{H}_θ determines the expectation value of any physical observable A .

APPENDIX B: DERIVATION OF EQ. (24) WITHIN THE DENSITY MATRIX FORMALISM

Consider the Liouville-von Neumann equation

$$\partial_t \rho(t) = -i[H, \rho(t)] \quad (\text{B1})$$

with the Hamiltonian H of Eq. (21). The initial condition for this equation reads

$$\rho(0) = |e\rangle\langle e| \rho_{\text{vib}}. \quad (\text{B2})$$

Here $|e\rangle$ is a certain initial electronic wave function defined by Eq. (8), and ρ_{vib} is the equilibrium vibrational distribution of Eq. (9). We wish to calculate the observable

$$\langle A(t) \rangle = \text{Tr}_{ac} \{ A \rho(t) \}, \quad (\text{B3})$$

where A is a certain operator depending on electronic and nuclear degrees of freedom and the trace is taken with respect to electronic (c refers to operators c_n^\dagger, c_n) and nuclear (a refers to operators a_k^\dagger, a_k) degrees of freedom.

Now we introduce the fictitious (tilde) Bose operators $\tilde{a}_k^\dagger, \tilde{a}_k$ and write

$$\rho_{\text{vib}} = \text{Tr}_{\tilde{a}} \{ |\mathbf{0}(\beta)\rangle\langle \mathbf{0}(\beta)| \}, \quad (\text{B4})$$

where $|\mathbf{0}(\beta)\rangle$ is defined via Eq. (12). The equivalence of Eqs. (9) and (B4) can be proven by a simple straightforward calculation.

Now consider Eq. (B1) with the initial condition

$$\rho(0) = |e\rangle\langle e| |\mathbf{0}(\beta)\rangle\langle \mathbf{0}(\beta)|. \quad (\text{B5})$$

The expectation value $\langle A(t) \rangle$ is then given via

$$\langle A(t) \rangle = \text{Tr}_{\tilde{a}} \{ A \rho(t) \}. \quad (\text{B6})$$

Eqs. (B6) and (B3) yield the same $\langle A(t) \rangle$. It does not matter whether the trace $\text{Tr}_{\tilde{a}} \{ \dots \}$ is taken with respect to the initial condition (B4) or with respect to the entire density matrix $\rho(t)$ (Eq. (B6)), because H and A are independent of the tilde operators $\tilde{a}_k^\dagger, \tilde{a}_k$.

Furthermore, we can consider the Liouville-von Neumann equation

$$\partial_t \rho(t) = -i[H - \tilde{H}_{\text{vib}}, \rho(t)], \quad (\text{B7})$$

where \tilde{H}_{vib} is any operator depending on the tilde operators $\tilde{a}_k^\dagger, \tilde{a}_k$. Eqs. (B1) and (B7) with the initial condition (B5) yield identical $\langle A(t) \rangle$, since $[\tilde{H}_{\text{vib}}, H] = 0$, $[\tilde{H}_{\text{vib}}, A] = 0$, and the evolution due to \tilde{H}_{vib} disappears upon taking the trace.

The initial condition (B5) corresponds to a pure state. Hence we can solve Eq. (B7) by writing

$$\rho(t) = |\psi(t)\rangle\langle \psi(t)|, \quad (\text{B8})$$

where

$$\partial_t |\psi(t)\rangle = -i(H - \tilde{H}_{\text{vib}}) |\psi(t)\rangle, \quad |\psi(0)\rangle = |e\rangle |\mathbf{0}(\beta)\rangle. \quad (\text{B9})$$

Eq. (B9) is identical to Eq. (24).

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