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Thermal Schrödinger Equation: Efficient Tool for Simulation of Many-Body Quantum Dynamics at Finite Temperature

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Abstract

We develop a wave-function-based method for the simulation of quantum dynamics of systems with many degrees of freedom at finite temperature. The method is inspired by the ideas of Thermo Field Dynamics (TFD). As TFD, our method is based on the doubling of the system's degrees of freedom and thermal Bogoliubov transformation. As distinct from TFD, our method implements the doubling of thermalized degrees of freedom only, and relies upon the explicitly constructed generalized thermal Bogoliubov transformation, which is not restricted to fermionic and bosonic degrees of freedom. This renders the present approach computationally efficient and applicable to a large variety of systems.

Keywords: Thermo Field Dynamics; quantum dynamics.

I. INTRODUCTION

The "open system" paradigm is the heart of dissipative quantum dynamics [1, 2]. However, operational meaning of "open system" has been changing over the years. Traditionally, "open system" was assumed to comprise a few relevant degrees of freedom which are important for the process under study, while the rest of the world was treated as a dissipative environment, responsible for relaxation and dephasing processes in the system. This approach results in the description in terms of various master equations, which can only be derived under certain approximations, such as weak coupling of the system to the environment and/or fast environment [1–3].

Enormous progress in computer facilities and rapid development of numerical methods caused two paradigm shifts.

(i) It became possible to include into "system" dozens of relevant quantum degrees of freedom and to evaluate the dynamics of such an extended system numerically exactly, assuming that the influence of the remaining quantum modes (the environment) can be neglected on the timescale of interest. This approach is represented by the multiconfiguration time-dependent Hartree (MCTDH) method and its multilayer extension (ML-MCTDH) [4–7] as well as other variational basis set methods [8–17] which solve multidimensional Schrödinger equation.

(ii) One can continue working with "system" comprising a few relevant degrees of freedom, but consider a realistic structured environment which not only possesses a finite memory but resonantly interacts with the system at certain characteristic frequencies. The dynamics of the system coupled to this environment is then evaluated numerically exactly. The hierarchical equations of motion (HEOM) [18–20] and the quasi-adiabatic path integral (QUAPI) [21] combined with realistic bath spectral density functions [22, 23] are nowadays the most powerful practical tools for the simulation of quantum dynamics within this approach, which is formulated in terms of the reduced (system) density matrix and the corresponding master equations.

Microscopic understanding of quantum effects in the functioning of various biological and artificial "open systems" under realistic conditions at ambient temperature [24] is indispensable without accurate simulations. The methods of the group (i) perform excellently at zero temperature. At ambient temperature, they require a statistical sampling of the initial

conditions [11–14, 25–27] followed, in some procedures, by a double propagation in real and imaginary time [7, 28–31]. Recently, we have suggested an alternative and computationally efficient wave-function-based method for the simulation of time-dependent properties of quantum systems with many degrees of freedom at finite temperature [32]. The method is based on the ideas of Thermo Field Dynamics (TFD) [33–37], which was introduced in the 1970’s to provide a finite temperature representation of quantum mechanics. The consideration of Ref. [32] was restricted to a system consisting of several discrete (electronic) states linearly coupled to multiple bosonic (vibrational) degrees of freedom, and the Hamiltonian of the system was considered to be time-independent. The present work lays theoretical foundation for the extension of the method towards arbitrary quantum systems described by time-dependent (driven) Hamiltonians.

II. FORMULATION OF THE PROBLEM

Let us consider a system consisting of two interacting subsystems 1 and 2. The total Hamiltonian of such a composite system (which may be time-dependent due to an external driving) is partitioned as

$$H(t) = H_1(t) + H_2(t) + V(t), \quad (1)$$

where $H_1(t)$ and $H_2(t)$ describe the subsystems 1 and 2 alone, and $V(t)$ is responsible for the coupling between the two. The dynamics of the whole system is specified by its density matrix $\rho(t)$ and is governed by the Liouville - von Neumann equation

$$\partial_t \rho(t) = -i[H(t), \rho(t)] \quad (2)$$

($\hbar = 1$). We assume that the entire system is prepared at thermal equilibrium at $t = 0$:

$$\rho(0) = \rho_B = Z^{-1} e^{-\beta H(0)}, \quad (3)$$

where Z is the partition function, $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, T is the temperature.

If characteristic energies E_1 of system 1 are (much) higher than characteristic energies E_2 of system 2, we can assume that the composite system at ambient temperature ($\beta E_1 \gg 1$, $\beta E_2 \sim 1$, $\beta^{-1} = 0.026$ eV at $T = 300$ K) resides in the ground state of subsystem 1 and

possesses thermal distribution over the degrees of freedom of subsystem 2,

$$\rho(0) = |0_1\rangle\langle 0_1|\rho_B^{(2)}, \quad (4)$$

$$\rho_B^{(2)} = Z_2^{-1}e^{-\beta H_2(0)}, \quad (5)$$

Z_2 being the corresponding partition function. The assumption (4) is rooted into Born-Oppenheimer approximation. It has a huge number of applications in molecular physics and spectroscopy [38] and is the key to the description of molecular aggregates [39–41], electron-vibrational [42] and vibration-rotational [43] systems.

The problem is to evaluate $\rho(t)$ and hence the observable

$$\langle A(t) \rangle = \text{Tr}\{A\rho(t)\}, \quad (6)$$

for any operator A acting in the vector space of the composite 1 + 2 system with many degrees of freedom. As has been mentioned in the introduction, the usual methods rely upon the computation of

$$\rho(t) = \sum_{\alpha} |\psi_{\alpha}(t)\rangle\langle\psi_{\alpha}(t)|,$$

where the wave-functions obey the Schrödinger equation

$$\partial_t|\psi_{\alpha}(t)\rangle = -iH(t)|\psi_{\alpha}(t)\rangle$$

and $|\psi_{\alpha}(0)\rangle$ are sampled from the initial distribution (3) or (4). Hence, the evaluation of the thermal averaging necessitates the solution of multiple Schrödinger equations with different initial conditions.

In the next section, we develop an alternative approach to this problem, in which the evaluation of $\langle A(t) \rangle$ requires a propagation of a single Schrödinger equation for a fictitious system in which the number of thermalized degrees of freedom is doubled. Sections III and IV deal with the initial preparation (4). This preparation is also considered in the Appendix A within the traditional TFD framework. The more general case of the correlated initial preparation (3) is considered in Section V.

III. FORMAL DERIVATION

Let us formally introduce the basis set of vectors $\{|\mathbf{k}\rangle\}$ in the Hilbert space of system 2. Following the basic idea of TFD, we also define a set of fictitious vectors $\{|\tilde{\mathbf{k}}\rangle\}$ which is a

copy of the original set $\{|\mathbf{k}\rangle\}$, but is defined on a different Hilbert space, the so-called *tilde* space. The properties of this space and its operators can be easily derived from the tilde conjugation rules of TFD theory [34]. Hereafter, we adopt the notation

$$|\mathbf{k}\tilde{\mathbf{k}}\rangle = |\mathbf{k}\rangle|\tilde{\mathbf{k}}\rangle.$$

We further introduce the unity

$$|\mathbf{I}_2\rangle = \sum_{\mathbf{k}} |\mathbf{k}\tilde{\mathbf{k}}\rangle \quad (7)$$

and the so-called thermal vacuum state [44]

$$|\mathbf{O}_2(\beta)\rangle = \sqrt{\rho_B^{(2)}} |\mathbf{I}_2\rangle = Z_2^{-1/2} \sum_{\mathbf{k}} e^{-\beta H_2(0)/2} |\mathbf{k}\tilde{\mathbf{k}}\rangle. \quad (8)$$

Clearly,

$$\rho_B^{(2)} = \text{Tr}_{\tilde{\mathbf{k}}}\{|\mathbf{O}_2(\beta)\rangle\langle\mathbf{O}_2(\beta)|\}. \quad (9)$$

The equivalence of Eqs. (5) and (9) can be proven by a straightforward calculation.

Now consider Eq. (2) with the initial condition

$$\rho(0) = |0_1\rangle\langle 0_1| |\mathbf{O}_2(\beta)\rangle\langle\mathbf{O}_2(\beta)|. \quad (10)$$

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

$$\langle A(t)\rangle = \text{Tr}_{\mathbf{3}}\{A\rho(t)\} \quad (11)$$

where the trace $\text{Tr}_{\mathbf{3}}$ is now taken over the extended vector space $\{|\mathbf{n}\rangle \otimes |\mathbf{k}\rangle \otimes |\tilde{\mathbf{k}}\rangle\}$ where $\{|\mathbf{n}\rangle\}$ specifies the states of subsystem 1.

Eqs. (11) and (6) yield the same $\langle A(t)\rangle$. It does not matter whether $\text{Tr}_{\tilde{\mathbf{k}}}\{\dots\}$ is taken with respect to the initial condition (9) or with respect to the entire density matrix $\rho(t)$, because $H(t)$ and A do not act in the tilde space. Furthermore, we can consider the Liouville - von Neumann equation

$$\partial_t \rho(t) = -i[H(t) - \tilde{h}_2(t), \rho(t)] \quad (12)$$

where $\tilde{h}_2(t)$ is any operator acting in the tilde space $\{|\tilde{\mathbf{k}}\rangle\}$. Eqs. (2) and (12) with the initial condition (10) yield identical $\langle A(t)\rangle$, since $[\tilde{h}_2(t), H(t')] = 0$, $[\tilde{h}_2(t), A] = 0$ and the time-evolution due to $\tilde{h}_2(t)$ disappears upon taking the trace. A convenient choice of $\tilde{h}_2(t)$ will be proposed in Section IV.

The initial condition (10) corresponds to a pure state in the extended vector space $\{|\mathbf{n}\rangle \otimes |\mathbf{k}\rangle \otimes |\tilde{\mathbf{k}}\rangle\}$. Hence we can solve Eq. (12) by letting

$$\rho(t) = |\psi(t)\rangle\langle\psi(t)| \quad (13)$$

where the wave function $|\psi(t)\rangle$ obeys the Schrödinger equation

$$\partial_t |\psi(t)\rangle = -i\bar{H}(t)|\psi(t)\rangle \quad (14)$$

governed by the Hamiltonian

$$\bar{H}(t) = H(t) - \tilde{h}_2(t). \quad (15)$$

Eq. (14) should be solved with the initial condition

$$|\psi(0)\rangle = |0_1\rangle|\mathbf{0}_2(\beta)\rangle \quad (16)$$

and the expectation value $\langle A(t)\rangle$ can be evaluated as

$$\langle A(t)\rangle = \langle\psi(t)|A|\psi(t)\rangle. \quad (17)$$

Note that we do not specify the time dependence of the Hamiltonian $H(t)$. If the coupling $V(t)$ between subsystems 1 and 2 is switched on infinitesimally slowly, one can prove the adiabatic theorem for the Schrödinger equation (14) (cf. Ref. [37]).

IV. BOGOLIUBOV THERMAL TRANSFORMATION

In words, the result of the derivation of the previous section can be summarized as follows: The solution of the original Liouville - von Neumann equation (2) with the initial condition (4) in the vector space $\{|\mathbf{n}\rangle \otimes |\mathbf{k}\rangle\}$ is reduced to the solution of the Schrödinger equation (13) - (14) in the extended vector space $\{|\mathbf{n}\rangle \otimes |\mathbf{k}\rangle \otimes |\tilde{\mathbf{k}}\rangle\}$. This procedure is certainly not new [45–48], but here we have explicitly taken advantage of the separation of the energy ranges of the two subsystems (Eq. (4)), avoiding the use of tilde variables for the entire system and employing them only for the thermalized degrees of freedom of subsystem 2 (cf. Refs. [46, 49]).

The thermal vacuum vector $|\mathbf{0}_2(\beta)\rangle$ possesses multiple nonzero components in the $\{|\mathbf{k}\rangle \otimes |\tilde{\mathbf{k}}\rangle\}$ subspace, and its use in practical simulations can be rather difficult, since Eq. (8) would require the explicit evaluation of the operator $e^{-\beta H_2(0)/2}$. This can be certainly done,

because efficient techniques based on imaginary time propagation have been developed and successfully applied to complex systems [7, 28–30]. However, the key advantage of the present method lies in the possibility to have a compact analytical representation of the thermal vacuum $|\mathbf{0}_2(\beta)\rangle$. Indeed, instead of the solution of the Schrödinger equation (14) with the initial condition (16) it is much more practical to introduce a unitary transformation e^{-iG} in the $\{|\mathbf{k}\rangle \otimes |\tilde{\mathbf{k}}\rangle\}$ subspace obeying the identity

$$e^{-iG}|\mathbf{0}_2\tilde{\mathbf{0}}_2\rangle = |\mathbf{0}_2(\beta)\rangle \quad (18)$$

where $|\mathbf{0}_2\tilde{\mathbf{0}}_2\rangle$ is the ground state in the $\{|\mathbf{k}\rangle \otimes |\tilde{\mathbf{k}}\rangle\}$ subspace.

Eq. (18) defines what can be called generalized thermal Bogoliubov transformation. Its application to Eq. (14) yields the transformed Schrödinger equation

$$i\partial_t|\psi_\theta(t)\rangle = \bar{H}_\theta(t)|\psi_\theta(t)\rangle \quad (19)$$

where

$$\bar{H}_\theta(t) = e^{iG}\bar{H}(t)e^{-iG}, \quad (20)$$

$$|\psi_\theta(t)\rangle = e^{iG}|\psi(t)\rangle \quad (21)$$

and

$$|\psi_\theta(0)\rangle = |0_1\rangle|\mathbf{0}_2\tilde{\mathbf{0}}_2\rangle \quad (22)$$

is the global vacuum state. The expectation value of the operator A (acting in the physical, $\{|\mathbf{n}\rangle \otimes |\mathbf{k}\rangle\}$, vector space) can now be rewritten as

$$\langle A(t)\rangle = \langle\psi_\theta(t)|A_\theta|\psi_\theta(t)\rangle \quad \text{with} \quad A_\theta = e^{iG}Ae^{-iG}. \quad (23)$$

The explicit form of thermal Bogoliubov transformation [33–37] and extensions thereof [50–52] are well known for bosons and fermions. Below we show how the generalized thermal Bogoliubov transformation of Eq. (18) can be explicitly constructed for a fairly general $H_2(0)$.

A. Harmonic oscillators

In many cases the physical observable of interest is averaged over a thermal ensemble of harmonic oscillator states with the equilibrium density matrix (5) where

$$H_2(0) = \sum_j \omega_j a_j^\dagger a_j, \quad (24)$$

a_j^\dagger (a_j) are the creation (annihilation) Bose operators ($[a_j, a_{j'}^\dagger] = \delta_{jj'}$) and ω_j are vibrational frequencies. It is worth recalling that, as pointed out by Caldeira and Leggett in their seminal work on quantum dissipative systems [53], this description of the "environment" is valid with the only restriction that "any one environmental degree of freedom is only weakly perturbed by its interaction with the system". However, this does not imply that, from the point of view of the system, the interaction is weak. The importance of this model of the environment in various applications is hardly overestimated.

The operator of thermal Bogoliubov transformation corresponding to the Hamiltonian of Eq. (24) reads [35]

$$G = -i \sum_j \theta_j (a_j \tilde{a}_j - a_j^\dagger \tilde{a}_j^\dagger) \quad (25)$$

where

$$\theta_j = \operatorname{arctanh}(e^{-\beta\omega_j/2}). \quad (26)$$

Hence thermal Bogoliubov transformation introduces thermal noise into the physical system by coupling it to the fictitious tilde system through the temperature-dependent mixing parameters θ_j . If the Hamiltonian $V(t)$ and an operator $\tilde{h}_2(t)$ are polynomials in creation-annihilation operators (this is so in many applications) then the explicit form of $\hat{H}_\theta(t)$ can be constructed by using the fundamental relations [35, 49, 54]

$$e^{iG} a_j e^{-iG} = a_j \cosh(\theta_j) + \tilde{a}_j^\dagger \sinh(\theta_j) \quad (27)$$

$$e^{iG} \tilde{a}_j e^{-iG} = \tilde{a}_j \cosh(\theta_j) + a_j^\dagger \sinh(\theta_j) \quad (28)$$

The transformed Hamiltonian $\hat{H}_\theta(t)$ depends on temperature through the parameters θ_j . An explicit expression for $\hat{H}_\theta(t)$ in the linear vibronic-coupling representation of the original Hamiltonian $H(t)$ can be found in Ref. [32]

B. General case

Usually, the system 2 at $t = 0$ can be represented as a collection of non-interacting or weakly interacting subsystems,

$$H_2(0) = \sum_j \mathcal{H}_j. \quad (29)$$

These subsystems labeled with the index j are not necessary one-dimensional, but comprise a few strongly coupled modes (see, e.g., Ref. [55] for possible strategies of making the

decomposition (29)). Hence the operator of thermal transformation can also be written as

$$G = \sum_j \mathcal{G}_j. \quad (30)$$

We assume that each of \mathcal{H}_j can be represented in a finite basis set and can therefore be directly diagonalized,

$$\mathcal{H}_j |k_j\rangle = E_k^{(j)} |k_j\rangle, \quad (31)$$

so that each subsystem j can be treated as a N_j -level system ($k_j = 0, 1, \dots, N_j$), $|k_j\rangle$ and $E_k^{(j)}$ being the corresponding eigenvectors and eigenvalues. In this notation, the basis vector $|\mathbf{k}\rangle$ in the Hilbert space of system 2 has components $|k_1, k_2, k_3, \dots\rangle$. In typical applications, \mathcal{H}_j can describe, e.g., the Morse oscillator [56] or a particle in a few-dimensional anharmonic potential treated in the discrete variable representation [57].

To construct the explicit form of the operator \mathcal{G}_j , we can rely upon the following considerations. First of all, the thermal vacuum $|0_2(\beta)\rangle = \prod_j |0_2(\beta)\rangle_j$ of Eq. (8) is uniquely determined by the vectors $|\mathbf{k}\tilde{\mathbf{k}}\rangle = \prod_j |k_j \tilde{k}_j\rangle$. Explicitly,

$$|0_2(\beta)\rangle = \sum_k \sigma_k |k, \tilde{k}\rangle, \quad \sigma_k = Z_2^{-1/2} e^{-\beta E_k/2}, \quad \sum_k \sigma_k^2 = 1 \quad (32)$$

(hereafter, the indexes j will be dropped for brevity). Therefore, the operator of the thermal transformation can be represented as

$$\mathcal{G} = \sum_{kk'} \mathcal{G}_{kk'} |k, \tilde{k}\rangle \langle k', \tilde{k}'| \quad (33)$$

The operator of thermal Bogoliubov transformation for bosons (Eq. (25)) and for fermions (see below) in the eigenfunction representation can immediately be rewritten in the form of Eq. (33) where

$$\mathcal{G}_{kk'} = -i\theta \{k' \delta_{k+1, k'} - k \delta_{k, k'+1}\}. \quad (34)$$

It is thus reasonable to assume that the operator of the thermal transformation \mathcal{G} in the eigenvalue representation can be explicitly written as

$$\mathcal{G} = -i \sum_k \theta_k \left\{ |k, \tilde{k}\rangle \langle k+1, \tilde{k}+1| - |k+1, \tilde{k}+1\rangle \langle k, \tilde{k}| \right\}, \quad (35)$$

where θ_k are unknown coefficients. The insertion of \mathcal{G} into Eq. (18) yields then a system of nonlinear equations for θ_k . Below we explicitly work out several examples and demonstrate that the system has a solution for any σ_k .

1. *2-level system*

A direct application of Eq. (35) for a system with two energy levels gives

$$-i\mathcal{G} = \theta \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \quad (-i\mathcal{G})^2 = -\theta^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

Hence

$$e^{-i\mathcal{G}} = \cos(\theta) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \sin(\theta) \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \quad (36)$$

$$|\mathbf{0}_2(\beta)\rangle = \begin{pmatrix} \sigma_2 \\ \sigma_1 \end{pmatrix}. \quad (37)$$

Plugging Eqs. (36) and (37) into Eq. (18) yields

$$\theta = \arctan(\sigma_2/\sigma_1) = \arctan(e^{-\beta(E_2-E_1)/2}).$$

This is nothing else but thermal Bogoliubov transformation for fermions [33–37].

2. *3-level system*

Eq. (35) yields

$$-i\mathcal{G} = \begin{pmatrix} 0 & \theta_1 & 0 \\ -\theta_1 & 0 & \theta_2 \\ 0 & -\theta_2 & 0 \end{pmatrix}, \quad (-i\mathcal{G})^2 = \begin{pmatrix} -\theta_1^2 & 0 & \theta_1\theta_2 \\ 0 & -\theta_{12} & 0 \\ \theta_1\theta_2 & 0 & -\theta_2^2 \end{pmatrix}, \quad (-i\mathcal{G})^3 = -\theta_{12}(-i\mathcal{G}),$$

$$\theta_{12} = \theta_1^2 + \theta_2^2.$$

Hence

$$e^{-i\mathcal{G}} = 1 + (-i\mathcal{G})X(\theta_{12}) + (-i\mathcal{G})^2Y(\theta_{12}). \quad (38)$$

Here we have introduced the functions

$$X(z) = \sum_{a=0}^{\infty} \frac{(-z)^a}{(2a+1)!}, \quad Y(z) = \sum_{a=0}^{\infty} \frac{(-z)^a}{(2a+2)!}$$

which obey the identity

$$X^2(z) + zY^2(z) = 2Y(z) \quad (39)$$

Figure 1: $X(\theta_{12})$, $Y(\theta_{12})$, and $Y(\theta_{12})/X^2(\theta_{12})$ vs θ_{12} .

that can be proven by a direct calculation. Eq. (39) is responsible for the unitarity of the operator (38) and ensures normalization of the σ_k (Eq. (32)).

Formula (22) yields a system of nonlinear algebraic equations for the thermal coefficients θ_1 and θ_2 . The introducing of polar coordinates

$$\theta_1 = \theta_{12} \cos(\phi_{12}), \quad \theta_2 = \theta_{12} \sin(\phi_{12}),$$

produces two independent equations for the unknown parameters θ_{12} and ϕ_{12} :

$$\tan(\phi_{12}) = \frac{1 - \sigma_1}{\sigma_3}, \quad (40)$$

$$\frac{Y(\theta_{12})}{X^2(\theta_{12})} = \frac{1 - \sigma_1}{\sigma_2^2}. \quad (41)$$

The functions $X(\theta_{12})$, $Y(\theta_{12})$, and $Y(\theta_{12})/X^2(\theta_{12})$ are plotted in Fig. 1. The ratio $Y(\theta_{12})/X^2(\theta_{12})$ increases with θ_{12} , starting from the value 0.5 at $\theta_{12} = 0$ and reaching ∞ at $\theta_{12} \approx 10$ ($X(10) \approx 0$). As is easy to show, the r.h.s. of Eq. (41) can also take the values from 0.5 to ∞ . Hence solution of Eqs. (40) and (41) exists for any σ_k .

3. N -level system

A few-level systems can be considered very similarly. According to the Cayley-Hamilton theorem [58], an arbitrary matrix obeys its own characteristic equation, meaning that for a N -level system

$$e^{-i\mathcal{G}} = \sum_{m=0}^{N-1} \nu_m (-i\mathcal{G})^m \quad (42)$$

where ν_m are real numbers which can be expressed in terms of θ_k . The insertion of the expansion (42) into Eq. (18) yields the system of $N - 1$ nonlinear equations for $N - 1$ unknown coefficients θ_k specifying the generalized Bogoliubov transformation (18). The transformed Hamiltonian (20) can be evaluated numerically. If N is relatively large, the θ_k can be obtained by a numerical minimization of the expression

$$\|e^{-i\mathcal{G}}|\mathbf{0}_2\tilde{\mathbf{0}}_2\rangle - |\mathbf{0}_2(\beta)\rangle\|.$$

Summarizing, we reduced the evaluation of $\langle A(t) \rangle$ to the solution of a single Schrödinger equation (19) with the thermal Hamiltonian \bar{H}_θ specified by Eq. (20). At $T \rightarrow 0$ the mixing parameters θ_k in the thermal transformation defined by Eqs. (18) and (35) become zero, $G \rightarrow 0$, the coupling to the tilde space disappears, and the standard Schrödinger equation is recovered as expected. If $\beta E_k \gg 1$, the contribution of the ground state in the equilibrium distribution (32) dominates ($\sigma_1 \rightarrow 1$, $\sigma_k \rightarrow 0$ for $k > 1$). Such modes need not be represented in the tilde space. 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. Note that the Schrödinger equation (19) permits the description of non-equilibrium dynamics, where each subsystem j is "prepared" at its own temperature T_j . The present theory can therefore be applied to the simulation of heat and/or charge transfer (cf. Refs. [59, 60]).

It is essential that the consideration of the present section does not rely upon simplifying approximations. If the Hamiltonian of the system 2 can be partitioned according to Eq. (29), the subsequent thermal Bogoliubov transformations can be numerically evaluated with any desired accuracy. Hence, the Schrödinger equation (19) and the entire methodology can be made numerically exact. For practical applications, it is important that the Hamiltonian $\bar{H}(t)$ of Eq. (15) and hence the thermally transformed Hamiltonian $\bar{H}_\theta(t)$ of Eq. (20) is not unique. The choice of $\tilde{h}_2(t)$ is dictated by convenience and simplicity of the representation of the thermal operator $\bar{H}_\theta(t)$ but does not affect $\langle A(t) \rangle$. In particular, it is convenient to set

$$\tilde{h}_2(t) = \tilde{H}_2(t). \quad (43)$$

Such a choice insures that $\bar{H}_{2\theta}(t) = \bar{H}_2(t)$, because $[G, H_2(t) - \tilde{H}_2(t)] = 0$. In the particular case of bosons and fermions, this is the result of the so-called invariance property [35]

$$e^{iG}(a_j^\dagger a_j - \tilde{a}_j^\dagger \tilde{a}_j)e^{-iG} = a_j^\dagger a_j - \tilde{a}_j^\dagger \tilde{a}_j. \quad (44)$$

The derivation of the Schrödinger equation (14) within the TFD formalism and comparison of the present approach with TFD is given in the Appendix. Importantly, in the present approach we double the degrees of freedom of the low-energy thermalized subsystem 2, while the number of the degrees of freedom of the high-energy subsystem 1 remains unchanged. In a basis-set representation, the density matrix $\rho(t)$ (Eq. (2)) and the TFD wave function $|\varphi(t)\rangle$ (Eq. (A2)) is an array of the dimension $(N_1 \times N_2)^2$, where N_1 (N_2) is the number

of the basis functions specifying the subsystem 1 (2) and the square is due to the doubling of the degrees of freedom. The wave function of the Schrödinger equation of the present work, $|\psi_\theta(t)\rangle$, is an array of the dimension $N_1 \times N_2^2$. 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. $|\psi_\theta(t)\rangle$ offers therefore a more compact way of storage of information on the system dynamics than the density matrix $\rho(t)$ or the TFD wavefunction $|\varphi(t)\rangle$.

V. THERMAL TRANSFORMATIONS FOR CORRELATED STATES

If characteristic energies of systems 1 and 2 are comparable, the simplified initial condition (4) does not hold and one has to evaluate $\langle A(t) \rangle$ with the correlated initial condition (3). Following the general scheme of TFD [33–37], one has to introduce the basis vectors $\{|\mathbf{x}\rangle\}$ and $\{|\tilde{\mathbf{x}}\rangle\}$ in the Hilbert space of the total Hamiltonian $H(0)$. One can define then the unity

$$|\mathbf{I}\rangle = \sum_{\mathbf{x}} |\mathbf{x}\tilde{\mathbf{x}}\rangle \quad (45)$$

($|\mathbf{x}\tilde{\mathbf{x}}\rangle = |\mathbf{x}\rangle|\tilde{\mathbf{x}}\rangle$), the thermal vacuum state

$$|\mathbf{0}(\beta)\rangle = \sqrt{\rho_B} |\mathbf{I}\rangle \quad (46)$$

and demonstrate that

$$\rho_B = \text{Tr}_{\tilde{\mathbf{x}}}\{|\mathbf{0}(\beta)\rangle\langle\mathbf{0}(\beta)|\}. \quad (47)$$

Closely following the derivations of Section III, one can show that the solution of the Schrödinger equation

$$\partial_t |\Psi(t)\rangle = -i\bar{\mathbf{H}}(t) |\Psi(t)\rangle \quad (48)$$

governed by the Hamiltonian

$$\bar{\mathbf{H}}(t) = H(t) - \tilde{h}(t) \quad (49)$$

($\tilde{h}(t)$ being an arbitrary operator in the tilde space) and obeying the initial condition

$$|\Psi(0)\rangle = |\mathbf{0}(\beta)\rangle \quad (50)$$

yields the expectation value

$$\langle A(t) \rangle = \langle \Psi(t) | A | \Psi(t) \rangle. \quad (51)$$

Up to now, we made standard TFD manipulations. However, the construction of thermal Bogoliubov transformation in the total $\{|\mathbf{x}\rangle \otimes |\tilde{\mathbf{x}}\rangle\}$ space has the same difficulties as the direct evaluation of Eq. (8). Indeed, it would require an explicit imaginary time evolution of the identity vector $|\mathbf{I}\rangle$, which involves summation over all the basis states and requires the introduction of sampling and convergence criteria. To alleviate this problem we suggest the following procedure. Let us introduce the Hamiltonian

$$H^\circ = H_1(0) + H_2(0) \quad (52)$$

and rewrite Eq. (46) as

$$|\mathbf{0}(\beta)\rangle = Z^{-1/2} e^{-\beta(H(0) - \tilde{H}^\circ)/2} e^{-\beta\tilde{H}^\circ/2} |\mathbf{I}\rangle = (Z/Z_\circ)^{-1/2} e^{-\beta(H(0) - \tilde{H}^\circ)/2} |\mathbf{0}^\circ(\beta)\rangle. \quad (53)$$

Here

$$|\mathbf{0}^\circ(\beta)\rangle = \sqrt{\rho_B^\circ} |\mathbf{I}\rangle = \sqrt{\tilde{\rho}_B^\circ} |\mathbf{I}\rangle \quad (54)$$

is the thermal vacuum state corresponding to the distribution

$$\rho_B^\circ = Z_\circ^{-1} e^{-\beta H^\circ}, \quad (55)$$

Z_\circ being the partition function.

Now we can introduce the thermal transformation

$$e^{-iG^\circ} |\mathbf{0}\tilde{\mathbf{0}}\rangle = |\mathbf{0}^\circ(\beta)\rangle \quad (56)$$

where $|\mathbf{0}\tilde{\mathbf{0}}\rangle$ is the ground state in the $\{|\mathbf{x}\rangle \otimes |\tilde{\mathbf{x}}\rangle\}$ space. Applying the transformation (56) to the Schrödinger equation, one obtains:

$$\langle A(t) \rangle = \frac{\langle \Psi_\theta(t) | A_\theta | \Psi_\theta(t) \rangle}{\langle \Psi_\theta(0) | \Psi_\theta(0) \rangle} \quad (57)$$

where

$$\partial_t |\Psi_\theta(t)\rangle = -i\tilde{H}_\theta(t) |\Psi_\theta(t)\rangle \quad (58)$$

and

$$|\Psi_\theta(0)\rangle = e^{-\beta\tilde{H}_\theta(0)/2} |\mathbf{0}\tilde{\mathbf{0}}\rangle. \quad (59)$$

In deriving Eq. (58), we have chosen $\tilde{h}(t) = \tilde{H}^\circ$ and made use of the identity

$$Z/Z_\circ = \langle \Psi_\theta(0) | \Psi_\theta(0) \rangle. \quad (60)$$

In the limit of high temperature ($\beta \rightarrow 0$), Eq. (59) reduces to $|\Psi_\theta(0)\rangle = |\mathbf{0}\tilde{\mathbf{0}}\rangle$.

It is important that Eqs. (57)-(60) are exact. The explicit evaluation of thermal Bogoliubov transformation (56) corresponding to uncoupled systems 1 and 2 should not be a problem. It can be done either by standard TFD methods [33–37] (if applied, e.g., to fermions, bosons, or excitons) or as described in Section IV of the present work (if applied to general Hamiltonians $H_1(0)$ and $H_2(0)$).

A practical implementation of Eqs. (57)-(60) can be done in at least three different ways as described below.

(i) Numerically exact procedure. Since $|\Psi_\theta(0)\rangle$ of Eq. (59) has to be evaluated only once, this can be done, e.g., through the propagation in the imaginary time $\beta/2$ in the $\{|\mathbf{x}\rangle \otimes |\tilde{\mathbf{x}}\rangle\}$ vector space. The subsequent propagation in t via the Schrödinger equation (58) yields $|\Psi_\theta(t)\rangle$ and $\langle A(t)\rangle$. This should be contrasted with the methodology of Refs. [7, 28–31] which, along with the propagation of wave functions in β and t in the $\{|\mathbf{x}\rangle\}$ space require sampling of the initial states, so that $\langle A(t)\rangle$ is calculated upon averaging over all $\beta - t$ "trajectories".

(ii) **Approximate procedure based on Trotter-Suzuki splitting.** One can adopt the partitioning

$$\bar{\mathbf{H}}_\theta(0) = \bar{\mathbf{H}}_\theta^\circ(0) + \bar{\mathbf{V}}_\theta(0) \quad (61)$$

($\bar{\mathbf{V}}_\theta(0)$ being the thermal transformation of the coupling operator $V(0)$) and employ the Trotter-Suzuki decomposition of the exponential operator in Eq. (59). In the leading order,

$$|\Psi_\theta(0)\rangle \approx e^{-\beta\bar{\mathbf{V}}_\theta(0)/2}|\mathbf{0}\tilde{\mathbf{0}}\rangle + O(\beta^2) \quad (62)$$

due to the identity $\exp\{-\beta\bar{\mathbf{H}}_\theta^\circ(0)/2\}|\mathbf{0}\tilde{\mathbf{0}}\rangle = |\mathbf{0}\tilde{\mathbf{0}}\rangle$. **With this approach an approximate initial state is derived that can be computed either numerically or analytically depending on the special structure of the operator V . This can be the preferred way if the direct evaluation of eq 59 is computationally demanding.** If necessary, higher-order Trotter-Suzuki decompositions can be used.

(iii) **Approximate procedure based on Hamiltonian transformation.** One can rewrite Eqs. (57)-(59) as follows:

$$\langle A(t)\rangle = Z_o/Z\langle\Psi_{\theta\beta}(t)|A_{\theta\beta}|\Psi_{\theta\beta}(t)\rangle, \quad (63)$$

$$\partial_t|\Psi_{\theta\beta}(t)\rangle = -i\bar{\mathbf{H}}_{\theta\beta}(t)|\Psi_{\theta\beta}(t)\rangle, \quad (64)$$

$$|\Psi_{\theta\beta}(0)\rangle = |\mathbf{0}\tilde{\mathbf{0}}\rangle. \quad (65)$$

Here

$$\bar{\mathbf{H}}_{\theta\beta}(t) = e^{\beta\bar{\mathbf{H}}_{\theta}(0)/2}\bar{\mathbf{H}}_{\theta}(t)e^{-\beta\bar{\mathbf{H}}_{\theta}(0)/2}, \quad A_{\theta\beta} = e^{\beta\bar{\mathbf{H}}_{\theta}(0)/2}A_{\theta}e^{-\beta\bar{\mathbf{H}}_{\theta}(0)/2}. \quad (66)$$

Note that $\bar{\mathbf{H}}_{\theta\beta}(0) = \bar{\mathbf{H}}_{\theta}(0)$. If the system Hamiltonian is time-independent, it should not therefore be transformed. While eqs. (63)-(65) are formally exact, the analytical expression of the transformed operators cannot be in general determined. However, it is always possible to approximate $\bar{\mathbf{H}}_{\theta\beta}(t)$ and $A_{\theta\beta}$ by applying the Trotter-Suzuki decomposition obtaining, to the leading order,

$$\bar{\mathbf{H}}_{\theta\beta}(t) \approx e^{\beta\bar{\mathbf{V}}_{\theta}(0)/2}\bar{\mathbf{H}}_{\theta}(t)e^{-\beta\bar{\mathbf{V}}_{\theta}(0)/2}, \quad A_{\theta\beta} \approx e^{\beta\bar{\mathbf{V}}_{\theta}(0)/2}A_{\theta}e^{-\beta\bar{\mathbf{V}}_{\theta}(0)/2}. \quad (67)$$

The main advantage of the above formulation is that in many cases of interest it is possible to find an analytical representation of the approximate transformed operators 67. Work along this direction is in progress and will be described in a forthcoming paper. Finally, we notice that the approaches iii) and ii) are equivalent but may differ significantly in their numerical implementation.

VI. CONCLUSION

We develop a wave-function-based method for the simulation of the dynamics of a driven quantum system with many degrees of freedom at finite temperature. The system is assumed to consist of two coupled subsystems 1 and 2 and is governed by a general time-dependent Hamiltonian of Eq. (1). No assumptions are made about the explicit form of the subsystem Hamiltonians and the coupling Hamiltonian. The composite initial system is assumed to be prepared at equilibrium at a certain initial time. The methodology is inspired by the ideas of the Thermo Field Dynamics [33–37], but is not equivalent to the TFD methodology. As TFD, our approach hinges upon two main ingredients, the doubling of the system’s degrees of freedom, and thermal Bogoliubov transformation. As distinct from the traditional TFD approach, we implement the doubling of only significantly thermalized degrees of freedom, and propose to solve a Schrödinger equation using a thermally transformed Hamiltonian. This renders the present approach computationally efficient.

The methodology has been developed in our previous work [32] for a particular case of a system comprising several discrete (electronic) states linearly coupled to multiple bosonic

(vibrational) degrees of freedom. The present work significantly generalizes Ref. [32] in the following three directions. (i) The system Hamiltonian is allowed to be time-dependent. (ii) The description is extended beyond fermionic and bosonic degrees of freedom. (iii) Correlated initial states are considered. The developed methodology can therefore be applied to a large variety of different quantum systems described by time-dependent (driven) Hamiltonians.

The thermal Schrödinger equations derived in the present work should be efficiently solved numerically. In Ref. [32], we considered spin-boson-type systems consisted of several electronic states coupled to multiple harmonic vibrational modes. We showed that the corresponding Schrödinger equation can efficiently be simulated numerically via the techniques based on the Tensor Train decomposition, also known as Matrix Product State representation [61, 62]. The work on the implementation of these techniques for the solution of the driven thermal Schrödinger equations of the present work beyond spin-boson-type Hamiltonians is currently in progress.

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Appendix A: TFD and its relation to the present theory

The time evolution of a system with a given Hamiltonian operator $H(t)$ at finite temperature can be described by the TFD Hamiltonian $\hat{H}(t)$ given by

$$\hat{H}(t) = H(t) - \tilde{H}(t). \quad (\text{A1})$$

$\tilde{H}(t)$ is a fictitious Hamiltonian which is identical to the original Hamiltonian $H(t)$ but acts in the tilde space [33–37]. The number of degrees of freedom in the *augmented* system (real

and fictitious) is double that of the original physical system. The time evolution of the TFD wavefunction $|\varphi(t)\rangle$ is determined by the TFD Schrödinger equation

$$\partial_t|\varphi(t)\rangle = -i\hat{H}(t)|\varphi(t)\rangle. \quad (\text{A2})$$

In the present case, the TFD Schrödinger equation must be solved with the initial condition

$$|\varphi(0)\rangle = |0_1\tilde{0}_1\rangle|\mathbf{0}_2(\beta)\rangle, \quad (\text{A3})$$

where the thermal state $|\mathbf{0}_2(\beta)\rangle$ of the low-frequency subsystem 2 is defined per Eq. (8) and the ground state of the high-frequency subsystem 1 is written as $|0_1\tilde{0}_1\rangle = |0_1\rangle|\tilde{0}_1\rangle$. The expectation value of any operator A acting in the physical Hilbert space $\{\mathbf{k}\}$ can be obtained as

$$\langle A(t)\rangle = \langle\varphi(t)|A|\varphi(t)\rangle. \quad (\text{A4})$$

Eq. (A4) is explicitly written as

$$\langle A(t)\rangle = \langle\tilde{0}_1|\langle 0_1|\langle\mathbf{0}_2(\beta)|\hat{U}(t)A\hat{U}^\dagger(t)|\mathbf{0}_2(\beta)\rangle|0_1\rangle|\tilde{0}_1\rangle \quad (\text{A5})$$

where

$$\hat{U}(t) = \hat{T}e^{-i\int_0^t \hat{H}(t')dt'} \quad (\text{A6})$$

and \hat{T} is the time-ordering operator.

Evidently,

$$[H(t), \tilde{H}(t')] = 0, \quad [\tilde{H}(t), A] = 0, \quad (\text{A7})$$

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

$$\hat{U}(t) = \tilde{U}(t)U(t)$$

where $\tilde{U}(t)$ and $U(t)$ are defined through Eq. (A6), in which \hat{H} is replaced by \tilde{H} and H , respectively. Therefore,

$$\begin{aligned} \langle A(t)\rangle &= \langle 0_1|\langle\mathbf{0}_2(\beta)|U(t)AU^\dagger(t)|\mathbf{0}_2(\beta)\rangle|0_1\rangle \\ &= \langle 0_1|\langle\mathbf{0}_2(\beta)|U(t)\tilde{U}_2(t)AU^\dagger(t)\tilde{U}_2^\dagger(t)|\mathbf{0}_2(\beta)\rangle|0_1\rangle. \end{aligned}$$

Here

$$\tilde{U}_2(t) = \hat{T}e^{-i\int_0^t \tilde{h}_2(t')dt'}$$

and $\tilde{h}_2(t)$ is any operator acting in the tilde space of the subsystem 2 (cf. Eq. (43)). The commutation relations (A7) remain valid after any unitary transformation performed on the operators. Hence, they remain valid after the thermal Bogoliubov transformation (18) yielding

$$\langle A(t) \rangle = \langle 0_1 | \langle \mathbf{0}_2 \tilde{\mathbf{0}}_2 | e^{iG} U(t) \tilde{U}_2(t) A U^\dagger(t) \tilde{U}_2^\dagger(t) e^{-iG} | \mathbf{0}_2 \tilde{\mathbf{0}}_2 \rangle | 0_1 \rangle = \langle 0_1 | \langle \mathbf{0}_2 \tilde{\mathbf{0}}_2 | \bar{U}_\theta(t) A_\theta \bar{U}_\theta^\dagger(t) | \mathbf{0}_2 \tilde{\mathbf{0}}_2 \rangle | 0_1 \rangle, \quad (\text{A8})$$

$$\bar{U}_\theta(t) = \hat{T} e^{-i \int_0^t \bar{H}_\theta(t') dt'}.$$

Eq. (A8) is equivalent to Eq. (23).

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