Temperature Controlled Open Quantum System Dynamics using Time-dependent Variational Method

Mantas Jakučionis1, Darius Abramavičius1
1 Institute of Chemical Physics, Vilnius University, Sauletekio Ave. 9-III, LT-10222 Vilnius, Lithuania

Dirac-Frenkel variational method with Davydov D2 trial wavefunction is extended by introducing a thermalization algorithm and applied to simulate dynamics of a general open quantum system. The algorithm allows to control temperature variations of a harmonic finite size bath, when in contact with the quantum system. Thermalization of the bath vibrational modes is realised via stochastic scatters, implemented as a discrete-time Bernoulli process with Poisson statistics. It controls bath temperature by steering vibrational modes’ evolution towards their canonical thermal equilibrium. Numerical analysis of the exciton relaxation dynamics in a small molecular cluster reveals that thermalization additionally provides significant calculation speed up due to reduced number of vibrational modes needed to obtain the convergence.

I. INTRODUCTION

Obtaining dynamics of open quantum systems, i.e., quantum systems that are identified as separate from its environment, yet remain in thermal contact with it, is one of the most general quantum mechanical problems. Its applicability range from excited state relaxation in optical response [1, 2], energy transport in molecular aggregates [3–8], photosynthetic complexes [9–12] and others [13–17]. Prevalent theoretical description is given in terms of system-bath model in constant temperature bath conditions [18, 19], where the system degrees of freedom are coupled to the bath-induced thermal fluctuations representing the environment, e.g., phonons or vibrational motion of surrounding molecules. Fluctuations are modeled by an infinite number of quantum harmonic oscillators constituting the quantum bath at thermal equilibrium.

These conditions can be fulfilled using the reduced density matrix approach [2, 7]. First perturbation order, with respect to the system-bath coupling, leads to the reduced equations of motion of the system-only variables, while the bath is averaged out. Then the system variables indirectly depend on the bath degrees of freedom via fluctuation correlation functions, which are well-behaved analytical functions. At the second perturbation order [7, 18], equations of motion are reminiscent of the Pauli master equation with relaxation coefficients calculated with respect to the thermal equilibrium. However, now the resulting equations can lead to unphysical results, e.g., negative probabilities [20]. The more complicated fourth order equations of motion include divergent parameters and are often avoided [21]. Non-perturbative, numerically exact approach of hierarchical equations of motion for the exponential fluctuation correlation functions is available to obtain exact dynamics [22–24], chain-mapping techniques together with the time-dependent density matrix renormalization group are alternatively possible for structured environments [23, 20]. However, computational costs limit these methods to models with just few degrees of freedom. A well known method of stochastic Schrödinger equation requires averaging over many entangled trajectories to obtain dynamics at finite temperature [27–32]. Its hierarchical realisation [32] improves convergence, meanwhile, thermofield dynamics approach tries to directly compute thermally averaged dynamics by mapping the initial thermal density matrix onto a fictitious bath vacuum state and then coupling system to it [33, 34]. Alternatively, dissipative dynamics can be obtained by straightforward addition of a linear friction coefficient to the model Hamiltonian [35], however, it only applies at zero temperature. Yet, in all these cases, thermal state of the nearest surrounding is not under control.

An important aspect of the bath, more explicitly, of the finite number of bath oscillators, is its heat capacity. For a single quantum harmonic oscillator the heat capacity in the limit of weak system-bath coupling is given by

\[ C_{\beta} = 2 \beta \omega \exp(\beta \omega), \]

here throughout the paper \( \hbar = 1 \), \( \beta = \left( k_B T \right)^{-1} \) is an inverse temperature, \( \omega \) is the oscillator frequency. When the system exchanges energy with a bath made of such oscillators, its temperature may be affected. If the system-bath energy exchange is excessively large, the thermal energy can accumulate in the bath oscillators and this will effectively change thermostat temperature [39]. In most cases, the bath heating effect is undesirable as, in the system-bath models, the bath is generally supposed to represent a constant temperature thermostat.

On the other hand, the bath heating effect could be related to the natural phenomenon of molecular local heating [40, 41], i.e., if a molecule quickly dissipates a large amount of thermal energy to its environment, e.g., due to exciton-exciton annihilation [42–44] or ultrafast molecular internal-conversion [45, 46], the local heating of the molecule nearest surrounding takes place and the further cooling process, the quantum thermalization [47, 48], becomes an important ingredient to consider when describing the corresponding experiments.

In this work, we introduce the thermalization algo-
rithm to the time dependent variational theory that al-

dows explicit control over the bath temperature. By vary-
ing the bath size and the thermalization rate, both the
degree of bath heating and the cooling time can be ad-
justed. These properties allow to mimic realistic physical
conditions, making presented approach superior to the
density operator based approaches, where the bath heat-
ing is excluded, and to the explicit bath models, where the
bath temperature is not controlled.

II. FLUCTUATING EXCITON MODEL

We consider a molecular aggregate made of \( N \) cou-
pled chromophores at specific sites. In the simplest case,
the sites represent distinct molecules that can be elec-
tronically excited by, e.g., laser or sunlight irradiation
in visible spectral region. Vibrational normal modes
of molecules and of the surrounding medium will be
in the visible spectral region. Vibrational normal modes
will be treated as the baths of harmonic oscillators. Each chro-

mophore is directly affected only by its own intramole-
cular vibrations and of its closest environment, therefore,
a separate and uncorrelated (local) manifold of vibrational
tions \( q = 1, 2, \ldots, Q \) is associated with each chro-

mophore. Such model is characterized by a Hamiltonian
\( H = H_S + H_B + H_{SB} \), with system, bath and system-bath
coupling terms being

\[
\hat{H}_S = \sum_n \varepsilon_n \hat{a}_n^\dagger \hat{a}_n + \sum_{n,m} J_{nm} \hat{a}_n^\dagger \hat{a}_m ,
\]

\[
\hat{H}_B = \sum_{n,q} \omega_{nq} \hat{b}_n^\dagger \hat{b}_n ,
\]

\[
\hat{H}_{SB} = - \sum_n \sum_{q} \omega_{nq} g_{nq} \left( \hat{b}_n^\dagger \hat{b}_n + \hat{b}_n^\dagger \hat{b}_n \right) .
\]

Here \( \varepsilon_n \) denotes \( n \)th chromophore electronic excitation
energy \( J_{nm} \) is the resonant coupling between \( n \)th and
\( m \)th chromophores, while \( \hat{a}_n^\dagger \) and \( \hat{a}_n \) are the corre-
sponding electronic excitation creation and annihilation
bosonic operators. Frequency of the \( q \)th vibrational mode
in the \( n \)th bath is \( \omega_{nq} \), the electron-vibrational coupling
is characterized by \( g_{nq} \), while \( \hat{b}_n^\dagger \) and \( \hat{b}_n \) are the creation
and annihilation bosonic operators of the \( q \)th mode in the
\( n \)th bath.

In the following we consider only single electronic ex-
citation in the time evolution of a non-equilibrium state is described by Davydov D2 wavefunc-

\[
|\Psi_{D2}\rangle = \sum_n \alpha_n(t) |\hat{a}_n^\dagger |0\rangle_{el} \times \prod_{m,q} |\lambda_{mq}(t)\rangle ,
\]

where \( \alpha_n(t) \) is the electronic excitation amplitude,
\( |0\rangle_{el} = \prod_n |0\rangle_n \) is the global ground state, when all sites
are in their electronic ground states. \( |\lambda_{mq}(t)\rangle \) is the co-
herent state of the \( q \)th mode in the \( m \)th bath.

It is fully described by the time-dependent complex dis-
placements, \( \lambda_{mq}(t) \). The time dependent Dirac-Frenkel
variational method allows to obtain equations of motion
for parameters \( \alpha_n, \lambda_{mq} \).

\[
\frac{d\alpha_n(t)}{dt} = -i\alpha_n(t) \varepsilon_n - i \sum_{m \neq n} \alpha_m(t) J_{nm} + i\alpha_n(t) \sum_q \omega_{nq} (2g_{nq} - h_q) \text{Re}(\lambda_{mq}(t)) ,
\]

\[
\frac{d\lambda_{mq}(t)}{dt} = -i\omega_{nq} (\lambda_{mq}(t) - h_q(t)) .
\]

Here \( h_q(t) = \sum_i g_{iq} |\alpha_i(t)|^2 \) is the site popula-
tion-weighted electron-vibrational coupling strength. First
line in Eq. (6) describes dynamics of an isolated sys-
tem. Accordingly, the first term on the right hand side of
Eq. (7) describes isolated oscillators. Other terms are
due to the system-bath interaction.

Description of the model at the given temperature \( T \)
requires creation of statistical ensemble. This is achieved
by Monte Carlo sampling over a statistical thermal en-
semble, i.e., initial bath oscillator displacements \( \lambda_{mq}(0) \), sampled from the Glauber-Sudarshan prob-
ability distribution

\[
P(\lambda_{mq}) = Z^{-1} \exp \left( -|\lambda_{mq}|^2 [e^{\beta \omega_{mq}} - 1] \right) .
\]

The ensemble describes canonical statistics of quantum
harmonic oscillators, which applies to our model prior to
external perturbations. The ensemble averaged quanti-
ties will be denoted by \( \langle \cdots \rangle_{th} \). The ensemble of exciton
trajectories allows to describe irreversible excitation en-
ergy relaxation. While the initial thermal state before ex-
citation can be properly defined, the bath accepts energy
during exciton relaxation and the state of the bath after
relaxation is away from equilibrium. Equations of mo-
tion guarantee energy conservation, hence the combined
system-bath cannot thermalize. In order to thermalize
the bath, we extend the original model by introducing the
secondary bath (we will refer to the local baths as the
primary baths). Effective heat capacity of the secondary
bath is infinite, hence, the bath can be characterized by
a constant temperature, \( T_\infty \). The secondary bath will
not be treated explicitly: modes of the primary baths
interact with the secondary bath via stochastic scattering
events, or quantum jumps \cite{56,57}, which affect the
kinetic energy of primary baths modes.

The scattering statistics follows Poisson distribution
\( P_{mq}(\theta,\tau) = \frac{1}{\lambda_{mq}} \exp(-\lambda_{mq} \theta \tau) \), which defines the prob-
ability of observing \( \theta \) scattering events per time interval \( \tau \)
with individual event scattering rate \( \nu_{mq} \). Poisson statis-
tics is obtained by simulating a discrete-time Bernoulli
process \cite{55,56} in a limit of \( \tau \to 0 \) and \( \nu_{mq} \tau \ll 1 \). This
is realized in simulations by dividing the total evolution
time \( t_{total} \) into equidistant length \( \tau \) intervals. At the
end of each interval, for each mode in the primary bath,
we flip a biased coin with probability \( \nu_{mq} \tau \) of landing
Along a closed trajectory around the oscillator, in the absence of thermalization, evolves \( \nu \) calculated with various scattering rates \( \nu \). Initial temperature of the primary bath is \( T_1 (0) = 300 \) K and the secondary bath is at a constant temperature \( T_\infty = 200 \) K. Scattering step size is \( \tau = 0.01 \) ps. Wiggles in dynamics are due to finite size ensemble averaging (5000 trajectories).

"heads". If the coin lands heads, we shift momentum of the mode \( p_{mq} (kt) = \sqrt{2} \text{Im} \lambda_{mq} (kt) \) to a value drawn from the Glauber-Sudarshan distribution, see Eq. [8], while the coordinate remains unchanged. Otherwise, if coin lands tails, no changes are done. To obtain converged statistics, we apply the thermalization algorithm to every trajectory of the thermal ensemble.

### III. Simulation Results

We first demonstrate control of the primary bath temperature of the simplest possible system, a single, \( N = 1 \), chromophore unit. For demonstration we set up artificial conditions: the initial primary bath temperature \( T_1 (0) = 300 \) K, the secondary bath is at \( T_\infty = 200 \) K. The primary bath consists of \( Q = 750 \) vibrational modes with frequencies, \( \omega_q = \omega_0 + (q - 1) \Delta \omega \). An offset by \( \omega_0 = 0.01 \) cm\(^{-1} \) is introduced for stability and a step size \( \Delta \omega = 1 \) cm\(^{-1} \). The coupling parameters \( g_{mq} \) follow the super-Ohmic spectral density function \( C^* (\omega) = \omega^s \exp ( -\omega/\omega_s ) \) with \( s = 2, \omega_s = 100 \) cm\(^{-1} \) [3, 60]. The number of modes and discretization parameters are sufficient to obtain convergent model dynamics. For thermalization, we consider scattering rates of all modes to be equal \( \nu_{mq} \to \nu \), and the scattering step size \( \tau = 0.01 \) ps\(^{-1} \). Thermal ensemble consists of 5000 trajectories.

In Fig. 1 the coordinate \( \langle x_{1q} \rangle_{th} \) and momentum \( \langle p_{1q} \rangle_{th} \) phase space trajectory of a single 100 cm\(^{-1} \) frequency vibrational mode, calculated with various scattering rates \( \nu \) is presented. The oscillator, in the absence of thermalization, evolves along a closed trajectory around \( x_{1q}^{\min} = \sqrt{2} g_{1q} \). Applying thermalization procedure, a dissipative type trajectory is observed. The coordinate \( \langle x_{1q} \rangle_{th} \) equilibrates to \( x_{1q}^{\min} \) (equilibrium is shifted from zero due to coupling with the system), while momentum \( \langle p_{1q} \rangle_{th} \) approaches zero. The thermalization time can be adjusted by changing the scattering rate, \( \nu \). Both weakly damped and overdamped regimes become available.

Transient temperature of the primary bath can be estimated [30] by computing the average kinetic energy \( \langle K_{mq} (t, \epsilon) \rangle_{th} \) over time interval \( \epsilon \). The parameter \( \epsilon \) then implies the resolution. For the whole primary bath the transient temperature is then given by

\[
T_m (t) = \frac{1}{k_B Q} \sum_{q=1}^{Q} \omega_{mq} \ln \left( 1 + \frac{\omega_{mq}}{2 \langle K_{mq} (t, \epsilon) \rangle_{th}} \right)^{-1}.
\]

In Fig. 2 we present the primary bath temperature calculated with \( \epsilon = 50 \) fs and various scattering rates, \( \nu \). In the absence of thermalization, the primary bath temperature remains at the initial value of \( T_1 (0) = 300 \) K. Meanwhile, thermalization introduces cooling of the primary bath down to the temperature of the secondary bath. The scattering rate, \( \nu \), allows to control the thermalization time.

The temperature control and stability considerably affects the electronic excitation dynamics. To demonstrate the sensitivity of the excitation evolution to the thermalization we consider a linear \( N = 3 \) chromophore aggregate, with chromophore transition energies \( 0, 250, 500 \) cm\(^{-1} \), and nearest neighbor coupling \( J = 100 \) cm\(^{-1} \). Excited states of such chromophore aggregate are excitons [7, 61]. They represent electronic excitations delocalized over several sites with time dependent delocalization length [62]. Hence, we switch to the eigenstate basis (exciton representation, defined by \( \hat{H}_B \psi_{(exc)} = \epsilon \psi_{(exc)} \); \( \rho_{e} \psi_{(exc)} (t) = \sum_{n,m} \left( \psi_{(exc)} \right)^{\dagger} (\alpha_n^* (t) \alpha_m (t))_{th} \psi_{(exc)} \)). The initial electronic state correspond to the optically excited highest
Figure 3. Multi site-bath model exciton state populations $\rho^{\text{exc}}_m(t)$ and local bath temperatures $T_m(t)$ calculated in (i) the dense primary bath discretization regime without thermalization, (ii) the sparse discretization regime without thermalization and (iii) the sparcely discretized bath with thermalization ($\nu = 2.5 \text{ ps}^{-1}$).

Introducing the bath thermalization in model (iii). Looking at Fig. 3E, we see that the exciton population dynamics and steady state values for model (iii) become quantitatively comparable to case of model (i).

IV. DISCUSSION

A single quantum harmonic oscillator is characterized by a specific heat $c(\beta^{-1}) < k_B$, which depends on temperature as given by Eq. (1). For a given set of bath oscillators the specific heat at a given temperature can be estimated, however, the harmonic oscillators of the bath as defined by Eq. (2) do not exchange energy. Accordingly, as the system relaxes, only a few in-resonant oscillators accept the energy and diverges away from equilibrium. Hence, the temperature at which excitation dynamics occur no longer match the initial bath temperature - local heating takes place.

A straightforward approach to avoid heating is to increase the bath density of states until dynamics of interest converges (in our model, this is achieved by increasing the number of bath oscillators). However, this is acceptable only for small systems, since computation effort scales quadratically with both number of sites and bath oscillators. Thermalization can be utilized to steer the bath to the required temperature. Additional merit of thermalization is the significant reduction of the the number of vibrational modes needed per bath. Our simulations show convergence with just 15 modes per bath while maintaining comparable exciton relaxation dynamics (Fig. 3).

In effort to reduce the computational effort, Wang et al. have used a logarithmic bath discretization. However, high frequency representation of the continuous spectral density becomes poor. Our model is in line with explicit surrogate Hamiltonian and its stochastic realization, while our approach does not require the explicit modeling of the secondary bath, it still maintaining proper quantum dynamics in the system.

The time-dependent variational approach with Davydov ansatz can be improved by considering more complex Davydov ansätze family members, e.g., multitude of $D_1$ ansatz (multi-$D_1$) and multi-$D_2$ or its Born-Oppenheimer approximated variant s$D_2$. In either way, they all suffer from finite bath heating capacity, in most cases, even stronger than the $D_2$ ansatz, because of significantly increased computational effort needed to propagate numerous bath oscillators. Work is in progress on adapting the presented thermalization algorithm to these more intricate ansätze.

In conclusion, we present a system-bath model with stochastic bath thermalization using the time-dependent variational approach with Davydov $D_2$ ansatz. Thermalization allows to steer bath vibrational modes evolution towards equilibrium thermal state of selected temperature in a controlled way, and at the same time, for the bath to still maintain an aspect of being coupled to the...
system. In addition, by analysing exciton relaxation dynamics of a chromophore aggregate with thermalization, we found the exciton dynamics to converge with much smaller number of bath modes, significantly speeding up numerical computation.

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