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Theoretical Study of Charge-Transfer Processes at Finite Temperature using a novel Thermal Schrödinger Equation

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Abstract

Quantum dynamics of electron transfer (ET) between redox pairs at finite temperature is described using an approach based on Thermo-Field Dynamics theory. This formulation treats temperature effects in the Hilbert space without introducing the Liouville space. The solution of Thermo-Field Dynamics equations with a novel technique for the propagation of Tensor Trains is implemented and discussed. The methodology is applied to the study of the electron-transfer process between the cofactors in the bacterial reaction center, and the results are compared with the second order cumulant approach, showing that the latter can reproduce both short- and long-time dynamics of the electron-transfer process.

1. Introduction

Unravelling the complex dynamics that results from the interplay of electronic and nuclear motion in charge-transfer processes is a fundamental task of modern chemical physics,[1] not only for improving the basic knowledge of these reactions, but also for guiding technological advances. Amongst others, the dynamics of charge-transfer reactions controls the efficiency of solar energy conversion, which is a cornerstone of modern scientific research.[2] However, the impossibility to properly simulate the evolution of quantum systems with many degrees of freedom at finite temperature often hampers a proper understanding of these processes.

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In the actual scenario two different classes of methodologies for the study of quantum dynamics of complex systems are prominent, namely direct density matrix propagation in the Liouville space, and wave-function propagation in the Hilbert space of the system. While both have their own advantages and disadvantages, their main difference lies in the capability to deal with finite temperature effects, which is fundamental for realistic simulations of chemico-physical processes.

Hierarchical equations of motion (HEOM)[3, 4, 5], together with the quasi-adiabatic path integral (QUAPI) [6], are powerful numerical methodologies for studying quantum dynamics of large molecular assemblies, both implementing a direct propagation of the reduced density matrix. However, they become numerically demanding for low temperature simulations[7], and when the Hilbert space of the system is very large.[8, 9, 7, 10, 11, 12, 4] Several approximate methods based on density matrix formalism are also available, but often with a limited range of validity.[13, 14, 15, 16, 17, 18, 19] Numerically accurate evolution of the large systems has also been described by the density matrix renormalization group (DMRG) methodology, and the associated time-evolution algorithms.[20, 21] Wave function propagation methods employing a basis set representation, such as the multiconfiguration time-dependent Hartree (MCTDH) method and its multilayer extension (ML-MCTDH),[22, 23, 24] Gaussian based MCTDH and other basis set methods,[25, 26, 27, 28, 29] are powerful tools at very low temperature, but become unhandy in high temperature cases, as their application requires a statistical sampling of the initial conditions.[30, 31] On the other hand, basis set methods are very versatile, and capable of handling a large variety of Hamiltonian operators.[32, 33]

Very recently Borrelli and Gelin [34, 35, 36] have developed a theoretical methodology based on Thermo Field Dynamics (TFD) theory[37, 38] that combines an accurate description of quantum dynamics at finite temperature with the flexibility of a basis set representation.[34] The theoretical framework of TFD is combined with a special representation of the wave function based on Tensor Trains (TT), henceforth the methodology will be referred to as TFD-TT. This technique has already been successfully applied to describe population dynamics in several spin-boson model systems, and energy transfer in the Fenna-Mathews-Olsen complex.[35] **The same approach has been implemented within the Davydov *ansatz* theory and successful applications to polaron problems have been reported.**[39] Here we apply the technique to the study of electron-transfer

(ET) processes. We will first present a brief review of the TFD formalism and of the computational approach used to solve the time-dependent Schrödinger equation, and then show how it is possible to describe ET dynamics in a two-state model system that includes all the intra-molecular vibrational degrees of freedom including temperature effects. Finally we will use exact TFD-TT results to assess the validity of a recently developed approach to describe ET dynamics based on the second-order cumulant expansions.[40, 15]

2. Theoretical Methodology

2.1. Thermo-Field Dynamics approach

The methodology has already been presented in detail elsewhere,[34, 36] and here we will only outline its formal structure and properties. Quantum dynamical studies of chemico-physical processes consist in the evaluation of the average of a properly chosen observable, A

$$\langle A(t) \rangle = \text{Tr}\{A(t)\rho(0)\}$$

where $\rho(0)$ is the initial density matrix of the system, and $A(t) = e^{iHt} A e^{-iHt}$ is the Heisenberg representation of the operator A , H being the system Hamiltonian. Here, the trace operation implies a weighted sum over all the thermally accessible states. In molecular systems the effect of a finite temperature is almost always to create a thermal population of excited vibrational states, while only one electronic state of the entire system, $|e\rangle$, is tangibly populated. Within the validity of this condition we can safely employ the approximation

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

Here Z is the proper partition function and ρ_{vib} is the equilibrium Boltzmann distribution of the vibrational degrees of freedom, which, in the present work, is described using harmonic approximation, and $\beta = 1/k_B T$, where T is the temperature of system and k_B the Boltzmann constant. Consequently, the trace operation involves only a summation over a thermal distribution of vibrational states, $|n_1 n_2 \dots\rangle$

$$\langle A(t) \rangle = Z^{-1} \langle e | \sum_{n_1 n_2 \dots} \langle n_1 n_2 \dots | A(t) e^{-\beta \sum_k \omega_k a_k a_k^\dagger} | n_1 n_2 \dots \rangle | e \rangle \quad (2)$$

where $a_k^\dagger, (a_k)$ are the creation (destruction) operators of the k -th bosonic degree of freedom with frequency ω_k , and the cyclic invariance of the trace operation has been used for the symmetrization. Following the Thermo Field Dynamics approach[37] the above trace can be evaluated by introducing a set of auxiliary boson operators $\tilde{a}_k^\dagger, \tilde{a}_k$ and their corresponding occupation number states $|\tilde{n}_1\tilde{n}_2\dots\rangle$, and rewriting the summation as

$$\langle A(t) \rangle = Z^{-1} \langle e | \sum_n \langle \tilde{n}_1\tilde{n}_2\dots | \langle n_1n_2\dots | A(t) e^{-\beta \sum_k \omega_k a_k a_k^\dagger} | n_1n_2\dots \rangle | \tilde{n}_1\tilde{n}_2\dots \rangle | e \rangle. \quad (3)$$

The introduction of the dummy *tilde* variables does not modify the expectation value since $A(t)$ is independent of them, and the states $|\tilde{n}\rangle$ form a complete orthonormal set. We notice that in the above summation the numerical values of $\{n_k\}$ and $\{\tilde{n}_k\}$ are identical. After a series of mathematical manipulations it is possible to rewrite the expectation value 3 as[41]

$$\langle A(t) \rangle = \langle e | \langle 0(\beta) | A(t) | 0(\beta) \rangle | e \rangle = \langle e | \langle \mathbf{0} | e^{iG} A(t) e^{-iG} | \mathbf{0} \rangle | e \rangle. \quad (4)$$

where we have defined the so-called thermal vacuum state as

$$|0(\beta)\rangle = Z^{-1/2} \exp(\sum_k e^{-\beta\omega_k/2} a_k^\dagger \tilde{a}_k^\dagger) | \mathbf{0} \rangle = e^{-iG} | \mathbf{0} \rangle \quad (5)$$

and

$$G = -i \sum_k \theta_k (a_k \tilde{a}_k - a_k^\dagger \tilde{a}_k^\dagger), \quad \theta_k = \text{arctanh}(e^{-\beta\omega_k/2}). \quad (6)$$

The above equations represent an extension of the fundamental results of Thermo Field dynamics[37, 42, 43] and the transformation e^{-iG} is often referred to as Bogoliubov thermal transformation.[44] It is immediate to verify that equation 4 can be equivalently written in the Schrödinegr picture as (see ref. 34)

$$\langle A(t) \rangle = \langle \varphi(t) | A_\theta | \varphi(t) \rangle \quad (7)$$

where the wavefunction $|\varphi(t)\rangle$ satisfies the Schrödinger equation

$$i \frac{\partial}{\partial t} |\varphi(t)\rangle = \bar{H}_\theta |\varphi(t)\rangle, \quad |\varphi(0)\rangle = |e\rangle | \mathbf{0} \rangle \quad (8)$$

with the thermal operators

$$\bar{H}_\theta = e^{iG} \bar{H} e^{-iG} \quad A_\theta = e^{iG} A e^{-iG}. \quad (9)$$

The modified Hamiltonian operator \bar{H} is defined as

$$\bar{H} = H - \tilde{H}_{\text{vib}} \quad (10)$$

where \tilde{H}_{vib} is any operator acting in the vibrational tilde space. Equations 7, 8, 9 and 10 represent the theoretical framework to evaluate finite temperature effects in quantum molecular dynamics. The evaluation of the thermal average $\langle A(t) \rangle$ can thus be reduced to the solution of the thermal Schrödinger equation 8 with the Hamiltonian \bar{H}_θ specified by eq. 9, followed by the computation of the desired expectation value.

A thermal environment can be realistically mimicked only using hundreds or thousands degrees of freedom, and the introduction of the tilde space doubles the number of nuclear degrees of freedom. For this reason the solution of the time-dependent Schrödinger equation 8 requires efficient numerical methods, suitable to treat a large number of dynamical variables.[32] Here we follow our recently proposed methodology[34] and represent the full vibronic wavefunction using the so-called Tensor-Train (TT) format (Matrix Product States, MPS, in the physics literature).[45, 46, 47] Eq. 8 is then solved using a numerical scheme based on the time-dependent variational principle (TDVP) recently developed by Lubich, Oseledets and Vandereycken.[47] The reader is referred to the original papers[48, 46] for a detailed analysis of the TT decomposition (see also ref. 34). Here we will only briefly review the TT approach for sake of clarity.

2.2. Tensor-Train Representation of Wave Function and its use

The state of a d dimensional quantum system is usually represented as a linear superposition of a basis set, in the form

$$|\Psi\rangle = \sum_{i_1, i_2, \dots, i_d} C(i_1, \dots, i_d) |i_1\rangle \otimes |i_2\rangle \cdots |i_d\rangle. \quad (11)$$

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. Upon truncation of the summation of each index i_k to a maximum value n_k the elements $C(i_1, \dots, i_d)$ represent a tensor of rank d . The evaluation of the summation 11 requires the computation (and storage) of n^d terms, where n is the average size of the one-dimensional basis set, which becomes prohibitive for large d . Tensor methods are a compact (compressed) way to store the information contained in the set of coefficients C up to a certain

a priori defined approximation threshold.[46] In the so-called tensor train approximation the coefficients C are written as

$$C(i_1, \dots, i_d) \approx G_1(i_1)G_2(i_2) \cdots G_d(i_d) \quad (12)$$

where the $\{G_k(i_k), k = 1, d\}$ are two-dimensional complex matrices. The above expression can be rewritten in the explicit index notation as

$$C(i_1, \dots, i_d) = \sum_{\alpha_0 \alpha_1 \cdots \alpha_d} G_1(\alpha_0, i_1, \alpha_1)G_2(\alpha_1, i_2, \alpha_2) \cdots G_d(\alpha_{d-1}, i_d, \alpha_d). \quad (13)$$

The matrices G_k are three dimensional arrays, called *cores* of the TT decomposition. The ranks r_k of the cores are called compression ranks. The TT format [12] allows to approximate the wave function by using d arrays of dimensions $r_{k-1} \times n_k \times r_k$ thus the required storage dimension is of the order dnr^2 . The quality of the approximation depends on the ranks r_k , larger values providing better results. **It is worth noting that the TT representation can be considered a very special and simple form of the tensor tree network used in the ML-MCTDH description of the wave-function.**[24]

For a time-dependent wave function 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

$$|\Psi(G(t))\rangle = \sum_{i_1 \cdots i_d} G_1(i_1, t)G_2(i_2, t) \cdots G_d(i_d, t)|i_1\rangle \otimes |i_2\rangle \cdots |i_d\rangle. \quad (14)$$

We refer the reader to references [49, 47], where the explicit differential equation for the wavefunction is derived and analyzed, and to reference [50] 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.[51, 52, 47] Here we adopt a methodology recently developed by Lubich, Oseledets and Vandereycken, which combines an explicit expression for the projector $\hat{P}_{\mathcal{T}(G(t))}$ and an extremely efficient second order split projector integrator specifically tailored to the TT format.[47] The computations presented in this paper have been performed using a code based on the software library developed by Oseledets and coworkers.

3. Electron-Transfer Hamiltonian at finite temperature

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 Hamiltonian operator describing two coupled electronic states $|A\rangle$ and $|F\rangle$, interacting with a phonon bath

$$H = |A\rangle H_A \langle A| + |F\rangle H_F \langle F| + V_{AF} |A\rangle \langle F| + \text{H.c.} \quad (15)$$

where $H_{A,F}$ are the vibrational Hamiltonian of the electronic states $|A\rangle$ and $|F\rangle$, respectively.

For H_A and H_F we assume that harmonic approximation holds, retaining two different sets of normal coordinates for each electronic state

$$H_A = \sum_i^N \omega_{Ai} / 2 (p_{Ai}^2 + q_{Ai}^2) + E_A^\circ \quad (16)$$

$$H_F = \sum_i^N \omega_{Fi} / 2 (p_{Fi}^2 + q_{Fi}^2) + E_F^\circ \quad (17)$$

The two sets of dimensionless normal coordinates are related by the affine transformation

$$q_F = d + Jq_A \quad (18)$$

where J is the normal mode transformation matrix and d the displacement vector.[53, 54, 55] Dimensionless coordinates are defined, as usual, in terms of mass-weighted normal coordinates, Q as

$$q_X = \gamma_X^{1/2} Q_X \quad \gamma_X = 2\pi c \omega_X / \hbar \quad X = A, F.$$

In order to simplify the analysis of the ET process we will neglect the variation of the vibrational frequencies and Duschinsky rotations. The general case that includes second order effects will be presented elsewhere. Nowadays, the parameters necessary to model H_A and H_F can be reliably obtained from electronic structure calculations, at least for medium sized and non floppy molecules[56, 57, 58].

The coupling operator V_{AF} is in general a function of the vibrational coordinates of the system, although it is quite common to assume its value constant, since electronic transitions take place in a restricted region of the nuclear coordinates.[59]

Using the transformation 18 and its conjugate for the momenta the Hamiltonian 10 can be rewritten in the form

$$H = H_S + |F\rangle\langle F| \sum_k g_k q_k + \sum_k \omega_k/2(p_k^2 + q_k^2) \quad (19)$$

where

$$H_S = |A\rangle E_A^\circ \langle A| + |F\rangle (E_F^\circ + E_r) \langle F| + V_{AF}(|A\rangle\langle F| + |F\rangle\langle A|),$$

the g_k 's and the reorganization energy E_r are defined as

$$g_k = \omega_k d_k \quad E_r = \sum_k \omega_k d_k^2/2 \quad (20)$$

and we have dropped the subscripts A, F from vibrational coordinates and frequencies.

The modified Hamiltonian operator \bar{H} used in eq. 10 is defined as

$$\bar{H} = H - \tilde{H}_{\text{vib}}, \quad (21)$$

where H is the physical Hamiltonian operator given by Eq. 19, and \tilde{H}_{vib} is any operator acting in the tilde vibrational space. 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

$$\tilde{H}_{\text{vib}} = \sum_k \omega_k/2(\tilde{p}_k^2 + \tilde{q}_k^2). \quad (22)$$

Applying the Bogoliubov transformation to the Schrödinger eq. 19, we obtain the Hamiltonian

$$\begin{aligned} \bar{H}_\theta = e^{iG} \bar{H} e^{-iG} = H_S + \sum_k \omega_k/2 (p_k^2 + q_k^2 - \tilde{p}_k^2 - \tilde{q}_k^2) \\ + |F\rangle\langle F| \sum_k g_k [q_k \cosh(\theta_k) + \tilde{q}_k \sinh(\theta_k)] \end{aligned} \quad (23)$$

In deriving the above expression we used the invariance property[37]

$$e^{iG}(p_k^2 + q_k^2 - \tilde{p}_k^2 - \tilde{q}_k^2)e^{-iG} = p_k^2 + q_k^2 - \tilde{p}_k^2 - \tilde{q}_k^2. \quad (24)$$

The operator \bar{H}_θ of eq. 23 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. Excitation of the tilde vibrations are caused by linear terms $\sim g_k \sinh(\theta_k)$. It is worth noting that for high frequency vibrations this terms can be neglected allowing to reduce the computational cost (see infra).

Since \tilde{H}_{vib} enters eq. 23 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 effects.

4. Electron-transfer in photosynthetic reactions centers

We will now consider the application of the methodology described above to the analysis of the dynamics of the electron-transfer (ET) between the accessory bacteriochlorophyll (B_A) and the bacteriopheophytin (H_A) in bacterial reactions centers.

Previous numerical studies have shown that this process can be modeled as a radiationless transition which involves mainly intramolecular vibrations which carry most of the reorganization energy.[60, 40] However, quantum dynamical results were obtained only for models including a reduced space of nuclear vibrational coordinates, and the effect of finite temperature was not take into account.[60] Here we will describe the ET process by including the entire set of the vibrational degrees of freedom of the two separate moieties and taking into account finite temperature effects.

Following a common approach,[61, 62, 63] the basis electronic states are represented as the direct product of the neutral and anionic states of the two single molecules, *i.e.* $|A\rangle = |B_A^- \rangle |H_A\rangle$ and $|F\rangle = |B_A\rangle |H_A^- \rangle$. Equilibrium geometries, normal modes, and vibrational frequencies of bacteriochlorophyll and bacteriopheophytin in their neutral and anionic forms were taken from our previous work.[40] Our model comprises 267 vibrational modes. Here we neglect Duschinsky rotations and variation of frequencies upon ET which have been shown to introduce only minor changes in the overall dynamics of the system.[40] The displacements d of the transformation 18 have been computed using the internal coordinate representation of normal modes.[64, 65, 57] This is fundamental to avoid the appearance of fictious vibrational progressions in the computed density of states.[64, 66, 67] The overall computed reorganization energy for the ET process is 1882 cm^{-1} .

The other parameters necessary for defining the Hamiltonian of Eq. 23, $V_{AF} = 90 \text{ cm}^{-1}$, $\Delta E_{AF} = 1200 \text{ cm}^{-1}$, have been taken from Ref. 40 .

Figure 1 shows the temperature-dependent spectral densities defined as[35]

$$J_p(\omega) = \sum_k g_k^2 \cosh^2(\theta_k) \delta(\omega - \omega_k) \quad J_t(\omega) = \sum_k g_k^2 \sinh^2(\theta_k) \delta(\omega - \omega_k).$$

These two functions represent the strength of the interaction between the electronic subsystem and the physical and tilde space respectively. The coupling with the tilde space is negligible for high frequency modes and not reported. It is immediate to see that as temperature increases the coupling with the low frequency part of the spectrum increases, while the high frequency region is left almost unaffected, as expected. This observation enables to analyse the relevance of temperature effects for each single degree of freedom and to reduce the computational costs by *a priori* removing some of the tilde degrees of freedom from the Hamiltonian.

In the present case the physical number of degrees of freedom is 267, which should be doubled to 534 upon inclusion of the tilde space. However, a large fraction of high frequency modes has a negligible vibronic coupling, $g_k \sinh(\theta_k)$, thus it is possible to reduce the overall number of nuclear dofs to 400 without any loss in the accuracy of the model.

Figure 2 shows the convergence behaviour of the TT methodology for different ranks of the cores. For sake of simplicity all cores have the same ranks, although different values are, in principles, allowed. As can be seen from figure 2a, the small rank approximation provides a good description of the dynamics only for short times. More specifically for $r = 10$ the dynamics is accurate up to 60 fs, while for $r = 20$ the dynamics is in almost quantitative agreement with the exact result up to 250 fs. Figure 2b shows that semiquantitative results are obtained with $r = 40$, while $r = 50$ is needed to achieve numerical convergence. Increasing r to 60 provides only slight modifications in the long-time tail of the decay. Indeed, after 800 fs the discrepancies between the population decay curves with $r = 60$ and $r = 50$ have an average relative deviation of about 5%. In all the calculations a basis set of harmonic oscillator eigenfunctions has been used with maximum quantum number 20 for all the degrees of freedom. As shown in figure 3 using 10 states per mode already provides excellent results, and increasing the basis set first to 20 and then to 30 states for all vibrations does not produce any significant change in the population dynamics. Here we have adopted the value $n = 20$ for all vibrations.

Figure 4 shows the electronic population of the initial state $|B_A^- H_A\rangle$ as a function of time at different temperatures. Temperature effects are not dramatic, as expected, since most of the vibronic activity is associated with high frequency vibrations. Increasing the temperature from 10 K to 77 K result in a very small decrease of the decay rate. This effect cannot be described in the framework of the classical ET theory and is very likely due to the highly quantized nature of the vibrational density of states at very low temperatures. A modest increase in the population decay rate upon increasing T from 77 K to 298 K is observed. This effect can be attributed to the increased number of accessible vibronic states. The overall behaviour is similar to what is found in other ET processes where large vibronic couplings are associated to highly quantized modes.[68, 69, 61]

Comparison with approximate theories

The exact results at finite temperature obtained from TFD-TT theory can be used for the assessment of approximate theories of electron-transfer. Very recently a second order cumulant approximation (SOC) has been developed to describe the dynamics of radiationless transition in large molecular assemblies.[40, 70, 15, 16] The SOC approach represent an improvement over standard rate theories, and is at the same time computationally feasible for large systems, it is thus of interest to better understand and define its range of validity.

In the SOC approach the time evolution of the electronic population of the electronic state $|A\rangle$ is described by the differential equation[40]

$$\frac{dP_A(t)}{dt} = \mathcal{K}_2(t)P_A(t) \quad (25)$$

where

$$\mathcal{K}_2(t) = -2|V_{AF}|^2 \hbar^{-2} Z_A^{-1} \text{Re} \int_0^t \text{Tr}(e^{iH_A(\tau+i\beta)} e^{-iH_F\tau}) d\tau \quad (26)$$

and the trace is taken over all the vibrational degrees of freedom. It is worth noticing that the kernel of the SOC approximation can be considered as a time-convolutionless representation of the Non-Interacting Blip Approximation (NIBA) introduced in the framework of spin-boson theory.[71, 72]

Figure 5 shows the exact TFD-TT electronic population dynamics and the SOC results. At $T = 10$ K, the SOC dynamics and the exact result match almost perfectly in the entire time interval reported. Moving to a higher temperature the agreement between the exact result and the SOC

dynamics worsen and is exact only for short times. A better analysis of the SOC methodology can be obtained by comparing the kernel $\mathcal{K}_2(t)$ of equation 25 with the generator, $\mathcal{K}(t)$, of the exact time-convolutionless differential equation[73, 74, 75]

$$\mathcal{K}(t) = \sum_n K_n(t) = \sum_{n=1}^{\infty} \frac{1}{n!} \left(\frac{-i}{\hbar} \right)^n \int_0^t d\tau_1 \cdots \int_0^t d\tau_{n-1} \langle \mathcal{T} V_I^\times(t) \dots V_I^\times(\tau_{n-1}) \rangle_c.$$

where, \mathcal{T} is the time ordering operator, I labels the interaction representation, and the operator $V_I^\times(\tau)$ is defined by its action on a generic operator O as $V_I^\times(\tau)O = [V_I(\tau), O]$. [76, 77] This generator can be easily computed from the population $P_A(t)$ obtained from the TFD-TT calculation, as

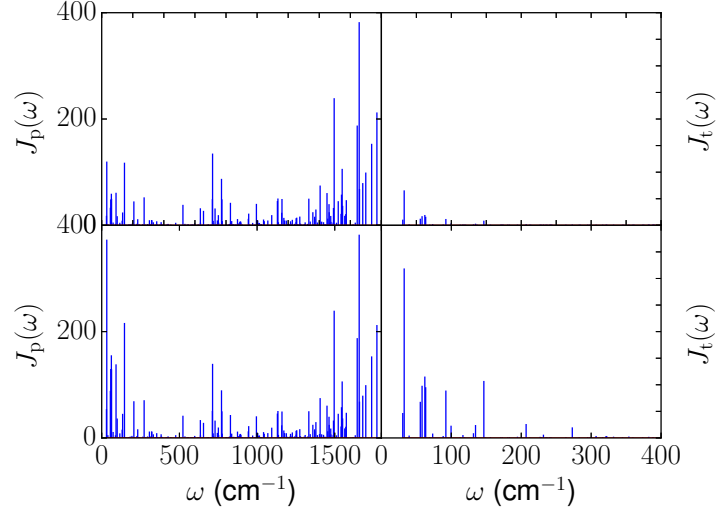
$$\mathcal{K}(t) = \dot{P}_A(t)/P_A(t). \quad (27)$$

Figure 6 shows a comparison of $\mathcal{K}(t)$ and $\mathcal{K}_2(t)$ for the electron transfer process under examination. It can be clearly seen that at low temperature $T = 10$ K, the two functions matches almost exactly. $\mathcal{K}_2(t)$ can provide a good description of the short time oscillatory behaviour of the cumulant expansion and converges to a limiting value that is very close to the exact one. At high temperature, the agreement becomes less satisfactory and the long time behaviour of the exact cumulant function is not correctly reproduced by the second order approximation. Clearly this means that higher order terms in the cumulant expansion cannot be neglected for accurate results. Yet, the SOC approximation is capable of grasping the qualitative behaviour of both the sub-picosecond and the long-time population dynamics in both hight and low temperature regimes.

5. Discussion and conclusion

We have discussed the application of the recently developed TFD-TT technique for the study of quantum dynamics of complex molecular systems at finite temperature to the electron transfer process between bacteriochlorophyll and bacteriopheophytine in bacterial PRCs. The theory allows to include temperature effects through the introduction of a set of auxiliary operators belonging to the so-called *tilde* Hilbert space. This procedure avoids the statistical sampling required in other wave-function techniques. The increased computational cost of the technique, due to the doubling of the vibrational degrees of freedom, can be partly overcome by the use of

Figure 1: Effective site spectral densities $J_p(\omega)$ and $J_t(\omega)$ describing the coupling of the physical and tilde bosonic degrees of freedom with the electronic subsystem at different temperatures. (a,b) 77 K, (c,d) 300 K.



new numerical techniques for the representation of the wave-function by tensor trains.

The results of the simulation confirm that the ET between the two cofactors in the reaction center is very fast, occurring on a sub-picosecond timescale. Temperature effects, while certainly present, are not dramatic since most of the vibronic activity during the process is associated with high frequency vibrations. Benchmark TFD-TT calculations have been used to test the range of validity of the approximate SOC expansion of the electronic population. The comparison has highlighted how the SOC theory provide a satisfactory description of the electronic dynamics in a wide range of temperatures, and is thus a valuable tool for obtaining approximate results for very large systems.

The TFD-TT methodology represent an important step toward the simulation of large molecular assemblies at finite temperature. A drawback in the use of tensor trains is represented by the necessity to increase the rank of the TT cores to obtain convergence for long time propagation. A possible approach to tackle this problem is to make use of reduced dynamical maps to obtain information for long time propagation from the short time

Figure 2: a) Electronic population of the initially populated state $|B_A^- H_A\rangle$ for different values of the TT compression ranks; b) enlargement of a) in the region between 0 and 100 fs.

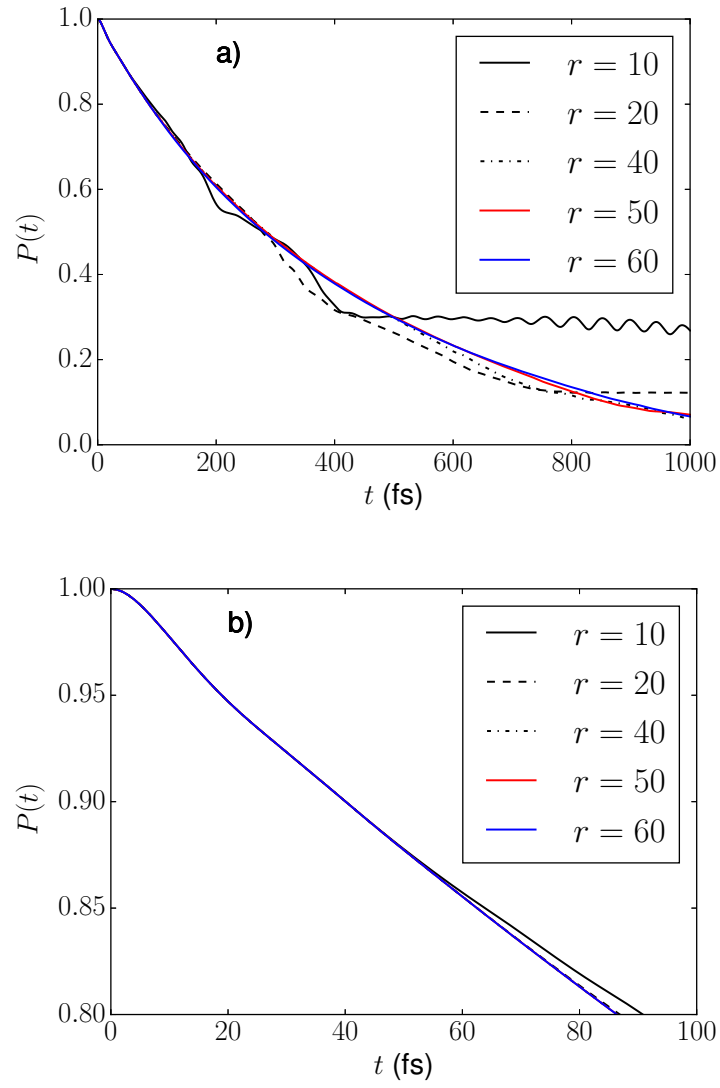


Figure 3: a) Electronic population of the initially populated state $|B_A^- H_A\rangle$ for three different values of the basis set size, $n = 10$, $n = 20$ and $n = 30$. In all cases the TT ranks are set to 50.

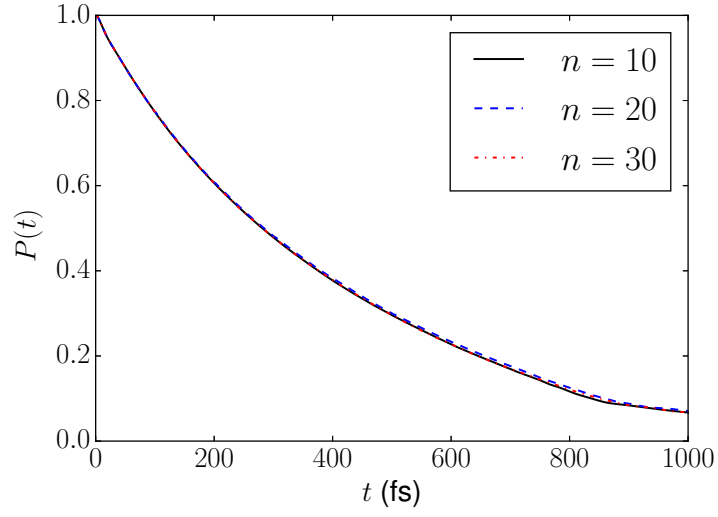


Figure 4: Electronic population of the initially populated state $|B_A^- H_A\rangle$ for different values of the temperature. In all calculations the compression rank is set to 50.

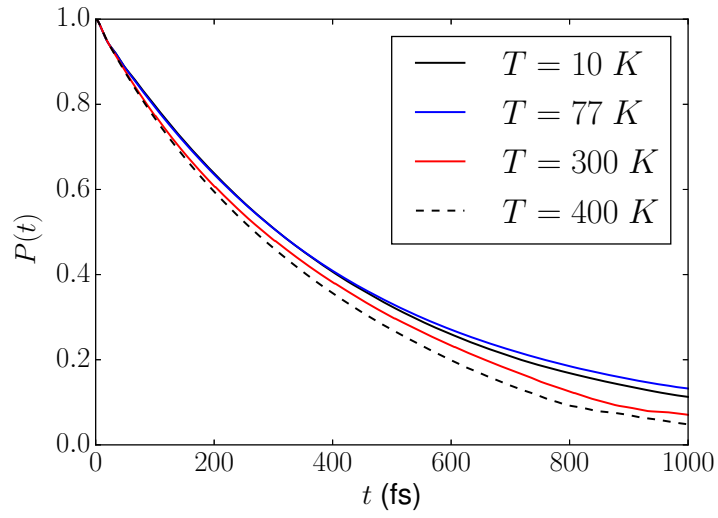


Figure 5: Electronic population of the initially populated state $|B_A^- H_A\rangle$ at $T = 10$ K, and $T = 298$ K (full lines) obtained from TFD-TT calculations; second order cumulant approximation at $T = 10$ K and $T = 298$ K (dashed line).

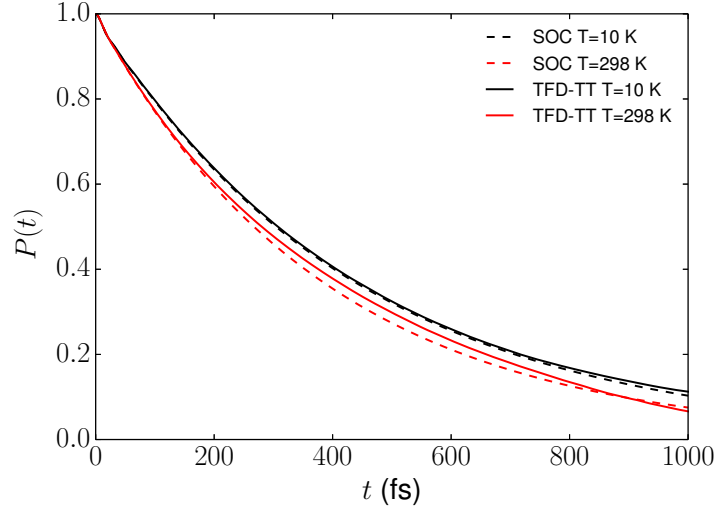
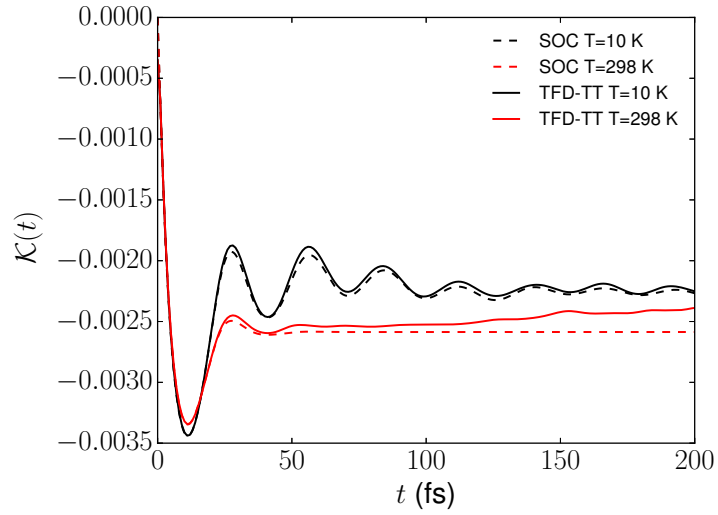


Figure 6: Second order cumulant $\mathcal{K}_2(t)$ obtained from SOC theory compared with the exact cumulant function $\mathcal{K}(t)$ obtained from TFD-TT calculations.



behaviour of the system.[78, 79, 80] Work is in progress along this direction.

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