

Quantum Dynamics of Electronic Transitions with Gauss-Hermite Wave Packets

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A new methodology based on a superposition of time-dependent Gauss-Hermite wave packets is developed to describe the wave function of a system in which several interacting electronic states are coupled to a bath of harmonic oscillators. The equations of motion for the wave function parameters are obtained by employing the Dirac-Frenkel time-dependent variational principle. **The methodology is applied to study the quantum dynamical behaviour of model systems with two interacting electronic states characterized by a relatively large reorganization energy and a range of energy biases.** The favourable scaling properties make it a promising tool for the study of the dynamics of chemico-physical processes in molecular systems.

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I. INTRODUCTION

The study of quantum dynamics of electronic transitions is a fundamental task of the theoretical analysis of chemico-physical processes in molecular systems.¹

A number of methodologies are currently available to deal with this type of problem. Some are quite general, in the sense that they are almost “independent” on the type of Hamiltonian operator of the system, while many others are suited for dealing with a certain class of problems, identified by specific model Hamiltonians, such as spin-boson systems or similars.²⁻⁶

One of the simplest ways to describe the motion of nuclei in molecules is based on the use of Gaussian wave packets. Heller was among the first to recognize the primary role of such a simple approximation of the nuclear wave function in the study of chemico-physical problems, mainly focusing his work on semiclassical theories.⁷⁻¹¹ Since then a number of extensions have been dealing with such a method for multidimensional systems and non-adiabatic processes, *i.e.* for the treatment of electronic transitions.

Among others G-MCTDH, DD-vMCG, AIMS, are extremely general and powerful methodologies that utilizes, in different ways, linear combinations of Gaussian wave packets to define a time-dependent set of orthonormal basis functions which are then used to describe the wave function of the entire nuclear system.¹²⁻¹⁵ Pure Gaussian wave packets, *i.e.* coherent states, combined with a time-dependent DVR representation are also employed in the LCSA methodology¹⁶, and are also at the basis of the MCE methodology of Shalashilin.^{17,18} Coherent states are also the basis of the so called Davydov *ansatz* which is specifically tailored to handle polaron dynamics.¹⁹⁻²¹

Heller was also the first to suggest that a significant improvement of the semiclassical description based on Gaussian wave packets could have been obtained by introducing a polynomial prefactor to the wave function.^{7,8} Hagedorn later recognized that the natural extension of the description of quantum dynamics by Gaussian wave packet was the use of generalized Gauss-Hermite functions,²²⁻²⁵ known in the quantum optics literature as generalized coherent states,²⁶⁻²⁸ and in molecular dynamics as Hagedorn’s wave packets.^{29,30} A similar technique was developed later by Billing³¹⁻³⁴ in the framework of semiclassical mechanics as well as non-adiabatic transitions.³⁵

While semiclassical treatments are amenable for high dimensionality systems, they suffer

a number of criticality when applied to non-classical problems, i.e. to processes involving more than one potential energy surface. In these methodologies the position and momentum variables follow classical-like equations which involve only one surface at the time leading to several problems related to norm and energy conservation.

In this work we develop a methodology that uses generalized Gauss-Hermite (GH) wave packets to build a simple *ansatz* of a molecular vibronic wave function. Our approach is based on the time-dependent Dirac-Frenkel variational principle and provides a new set of equations in which position and momentum of the wave packet are dynamically coupled to the evolution of the expansion coefficients of the basis functions. The type of *ansatz* developed in the following sections is a powerful extension of the simple Gaussian wave packet approximation, and is suited to handle problems with a large number of degrees of freedom. With the purpose of showing how to apply the formalism to large size systems, the methodology is applied to the study of the dynamics of spin-boson Hamiltonians characterized by relatively large energy biases.

II. GAUSS-HERMITE WAVE PACKET ANSATZ

Let us consider a physical system which can be described as a set of N interacting electronic states and d harmonic vibrational degrees of freedom, and whose Hamiltonian operator can be written in the form

$$H = \sum_{l=1}^N \left[\sum_i^d \frac{1}{2} (-\partial_{x_{li}}^2 + \omega_{li}^2 x_{li}^2) + g_{li} x_{li} + E_l \right] |l\rangle \langle l| + \sum_{l>m} V_{lm} |l\rangle \langle m| + \text{h.c.} \quad (1)$$

where $|l\rangle$ label a set of N “electronic” degrees of freedom and $x_l = (x_{l1}, x_{l2}, \dots, x_{ld}) \in \mathbb{R}^d$ represents a set of d nuclear ~~degrees of freedom (d.o.f.)~~ of the l -th electronic state; ω_{li} are the frequencies of the i -th oscillator in the l -th electronic state; g_{li} are linear coupling between the electronic and vibrational d.o.f.’s and E_l are the electronic energies. This type of operator is representative of a wide family of chemico-physical processes whose most important ~~representatives~~ are charge and energy transfer processes.³⁶ Though not strictly necessary, we will further assume that the coupling operators V_{lm} are independent ~~on~~ nuclear coordinates and ~~on~~ time. The system dynamics is described by the Schrödinger equation

$$i\partial_t \Psi(x, t) = H\Psi(x, t), \quad \text{with } \Psi(t_0) = \Psi_0.$$

Without loosing any generality we write the wavefunction in the form

$$\Psi(x, t) = \sum_{l, K} C_{lK}(t) \Phi_{lK}(x_l, t) |l\rangle \quad (2)$$

where K is a multi-index $K = (k_1, k_2, \dots, k_d) \in \mathbb{N}_0^d$, and the Φ_{lK} 's are a complete orthonormal set of *time-dependent* basis functions defined as the product of d single-oscillator wave functions φ_{k_i}

$$\Phi_{lK}(x_{l1}, x_{l2}, \dots, t) = \prod_{i=1}^d \varphi_{l k_i}(x_{li}, t). \quad (3)$$

We choose $\varphi_{l k_i}(x_{li}, t)$ as time-dependent Gauss-Hermite wave packets^{22,31}

$$\varphi_{lk}(x, t) = 2^{-k/2} (k!)^{-1/2} a_l^{-1/2} \pi^{-1/4} H_k[a_l(x - q_l(t))] \exp \left\{ -a_l^2 (x - q_l(t))^2 / 2 + i p_l(t) (x - q_l(t)) \right\} \quad (4)$$

where $k \in \mathbb{N}_0$, $a_l, q_l, p_l \in \mathbb{R}$, q_l, p_l are functions of the time t and H_k is the Hermite polynomial of degree k . The states φ_{lk} are concentrated near the position q_l and near the momentum p_l , and for any fixed set of parameters q_l, p_l, a_l form a complete orthonormal basis in $L^2(\mathbb{R})$. Since in our approach a_l is a constant parameter, we can define a new set of scaled dimensionless coordinates $x_l \leftarrow a_l x$, and scaled parameters $q_l \leftarrow a_l q_l$, $p_l \leftarrow p_l / a_l$ and rewrite the wave packet as³⁷

$$\varphi_{lk}(x_l, t) = 2^{-k/2} (k!)^{-1/2} \pi^{-1/4} H_k[(x_l - q_l(t))] \exp \left\{ -(x_l - q_l(t))^2 / 2 + i p_l(t) (x_l - q_l(t)) \right\}. \quad (5)$$

If the scaling parameter a_l is considered as a function of time the more general form 4 should be preferred over 5. It is well known that the size of the expansion 2 is subject to an exponential growth and cannot be used for practical purposes as such. On the other hand, by introducing an explicit time dependence of the basis functions and using the time-dependent variational approach the quantum dynamical problem is formulated on a Hilbert bundle, and the Gauss-Hermite wave packets evolve in time providing a ‘‘locally optimal’’ basis for solving the Schrödinger equation. It is therefore physically sound that a truncation of the above expansion to a relatively small subset of states already provides a good description of the state of the system. Many reduction schemes can be provided, such as matrix-product states, tensor networks as well as ML-MCTDH techniques.^{2,4,38–40}

The approach developed in this work is based on the idea of partitioning the entire Hilbert space in a set of subspaces which differ in the number of vibrations allowed to

be simultaneously excited. As a consequence the entire Hilbert space \mathcal{H} spanned by the Hamiltonian of Eq. 1 can be partitioned as

$$\mathcal{H} = \bigcup_c S_c$$

where S_c is the space spanned by the states in which only c basis functions are simultaneously excited, *i.e.* have a non-zero value of k_j . Obviously for any practical purposes the basis is truncated to a maximum quantum number. Since in a system with d vibrational degrees of freedom there will be $\binom{d}{c}$ distinct combinations with c excited modes, using such a partition the wavefunction of Eq. 2 can be written in the form

$$\begin{aligned} \Psi(x, t) &= \sum_l^N \left[\sum_{c=1}^d \sum_{i_1 \dots i_c} \sum_{k_{i_1} \dots k_{i_c}} C_{lk_{i_1} \dots k_{i_c}}(t) \Phi_{lk_{i_1} \dots k_{i_c}} \right] |l\rangle \\ &= \sum_l \left[C_{l0}(t) \Phi_{l0}(x_l, t) + \sum_i \sum_{k_i=1}^d C_{lk_i}(t) \Phi_{lk_i}(x_l, t) \right. \\ &\quad \left. + \sum_{ij} \sum_{(k_i k_j)=1}^{\binom{d}{2}} C_{lk_i k_j}(t) \Phi_{lk_i k_j}(x_l, t) + \dots \right] |l\rangle. \quad (6) \end{aligned}$$

This type of partitioning has been first discussed in the field of molecular spectroscopy as a technique to simulate molecular electronic lineshapes,^{41,42} and later applied by the authors, though in a different theoretical framework, to the study of electron superexchange in molecular chains.⁶ This approach provides a remarkable restriction of the active space of the problem and of the associated numerical complexity. ~~While it might seem just an operative definition, we will later show that,~~ if properly applied, it allows to retain the most important features of the dynamical behaviour of the system.⁴

The partition 6 allows us to strongly reduce the dimension of the basis set by limiting its combinatorial explosion. Indeed, if each mode is allowed to have p basis functions, a combination with c simultaneously excited modes will introduce p^c new basis states, and since there are $\binom{d}{c}$ such combinations the dimension of the S_c subspace will be $\binom{d}{c} p^c$. ~~Thus, for $c = 1$ we will have d possible combinations and dp basis states, for $c = 2$ we will have $\binom{d}{2} p^2$ states and so on.~~ As an example, in a system with $d = 50$ and $p = 10$ (*see infra* for applications) the full tensor product basis set will have dimension 10^{50} , which is far beyond the limit of any modern numerical methodology. By assuming that only the combinations

up to $c = 3$ are relevant, the size of the basis set will be about $20 \cdot 10^6$, which is numerically treatable. This approach can be particularly fruitful in reaction path type Hamiltonian⁴³ and effective mode dynamics,^{44–47} in which the size of the basis set has to be large only for a restricted subset of nuclear degrees of freedom. Finally, ~~we notice that since~~ the parameters $(q_l(t), p_l(t))$ of the basis set are different for each electronic state, the excitation level, c , might differ as well. High energy electronic states could have a very small c values reducing the computational cost of the integration.

Of course the above partitioning of the the Hilbert space ~~has an heuristic basis and~~ does not guarantee that converged results can be obtained ~~avoiding the exponential growth of the basis set~~. In principle, the convergence can be tested by letting c vary until no significant variations of the properties of interest (*i.e.* electronic population or coherences) are observed. ~~However,~~ this can be applied only to systems with a quite small number of degrees of freedom. ~~Furthermore, in very large systems with thousands of degrees of freedom it is impossible to have an excitation level larger than $c = 2$ since the basis set would become too large for a numerical approach. For these reasons,~~ in the following we will restrict ~~our discussion~~ to the *ansatz* 6 truncated to the excitation level $c = 2$, which are the most appealing for treating systems with a large number of degrees of freedom. ~~Will will not discuss the methodology for excitation levels larger than two since, while they can certainly provide converged results, we are mainly interested to applications to large systems.~~

In the following we adopt a mathematical formulation in which all the parameters of the wave function are real hence we split each coefficient in its real and imaginary part $C_{lK}(t) = r_{lK}(t) + is_{lK}(t)$. The equations of motion for the parameters $(r_{lK}, s_{lK}, q_l, p_l)$ can be derived by using the Dirac-Frenkel time-dependent variational approach with the Lagrangian

$$L = \frac{i}{2}[\langle \Psi | \dot{\Psi} \rangle - \langle \dot{\Psi} | \Psi \rangle] - \langle \Psi | H | \Psi \rangle$$

which for a real parametrization results in the set of differential equations^{48–50}

$$\sum_j \eta_{ij} \dot{y}_j = \partial_{y_i} \mathcal{H} \quad (7)$$

where y denotes the set of parameters $(r_{lK}, s_{lK}, q_l, p_l)$, η_{ij} is a real antisymmetric tensor, and

\mathcal{H} is the Hamilton function:

$$\eta_{ij} = i[\langle \partial_{y_i} \Psi | \partial_{y_j} \Psi \rangle - \langle \partial_{y_j} \Psi | \partial_{y_i} \Psi \rangle] = -2\Im \langle \partial_{y_i} \Psi | \partial_{y_j} \Psi \rangle \quad (8)$$

$$\mathcal{H} = \langle \Psi | H | \Psi \rangle = \mathcal{H}(r_{lK}, s_{lK}, q_l, p_l). \quad (9)$$

After carrying out the calculations (see appendix) the tensor η can be written in the form

$$\eta_{r_{lK} s_{mJ}} = -2\delta_{lm} \delta_{KJ} \quad (10a)$$

$$\eta_{r_{lK} q_{mh}} = \delta_{lm} [2p_{lh} r_{lK} - \sqrt{2} (s_{l(K-1_h)} \sqrt{k_h} - s_{l(K+1_h)} \sqrt{k_h + 1})] \quad (10b)$$

$$\eta_{s_{lK} q_{mh}} = \delta_{lm} [2p_{lh} s_{lK} + \sqrt{2} (r_{l(K-1_h)} \sqrt{k_h} - r_{l(K+1_h)} \sqrt{k_h + 1})] \quad (10c)$$

$$\eta_{r_{lK} p_{mh}} = -\delta_{lm} [\sqrt{2} (r_{l(K-1_h)} \sqrt{k_h} + r_{l(K+1_h)} \sqrt{k_h + 1})] \quad (10d)$$

$$\eta_{s_{lK} p_{mh}} = -\delta_{lm} [\sqrt{2} (s_{l(K-1_h)} \sqrt{k_h} + s_{l(K+1_h)} \sqrt{k_h + 1})] \quad (10e)$$

$$\eta_{q_{lj} p_{mh}} = -\delta_{lm} \delta_{hj} \sum_K (r_{lK}^2 + s_{lK}^2). \quad (10f)$$

From the above metric tensor the final equations of motion take the form of the implicit system

$$2\dot{r}_{lK} + \sum_i^d \eta_{s_{lK} q_{li}} \dot{q}_{li} + \sum_i^d \eta_{s_{lK} p_{li}} \dot{p}_{li} = \partial_{s_{lK}} \mathcal{H} \quad (11a)$$

$$2\dot{s}_{lK} - \sum_i^d \eta_{r_{lK} q_{li}} \dot{q}_{li} - \sum_i^d \eta_{r_{lK} p_{li}} \dot{p}_{li} = -\partial_{r_{lK}} \mathcal{H} \quad (11b)$$

$$\dot{q}_{li} \sum_K (r_{lK}^2 + s_{lK}^2) - \sum_K \eta_{r_{lK} p_{li}} \dot{r}_{lK} - \sum_K \eta_{s_{lK} p_{li}} \dot{s}_{lK} = \partial_{p_{li}} \mathcal{H} \quad (11c)$$

$$\dot{p}_{li} \sum_K (r_{lK}^2 + s_{lK}^2) + \sum_K \eta_{r_{lK} q_{li}} \dot{r}_{lK} + \sum_K \eta_{s_{lK} q_{li}} \dot{s}_{lK} = -\partial_{q_{li}} \mathcal{H} \quad (11d)$$

$$\text{with } K = 1, \dots, K_{\max} \quad i = 1, \dots, d \quad l = 1, \dots, N$$

We notice that the metric tensor, η , does not directly couple the variables of two different electronic states because the electronic wavefunction is not parametrized, however, the equations are coupled by the ‘‘quantum forces’’ $\partial_{y_i} \mathcal{H}$. Equations 11a-11d constitute a set of $2 \sum_l^L (N_l + d)$ differential equations where L is the number of electronic states, N_l is the size of the basis set in the electronic state l , and d is the number of nuclear degrees of freedom.

From the definition of the Hamiltonian operator 1 the function \mathcal{H} can be partitioned as

$$\mathcal{H}(p, q, r, s) = \mathcal{H}^\circ + \mathcal{V}$$

where

$$\begin{aligned}
\mathcal{H}^\circ &= \sum_{l,i,K} \left\{ \left[E_l^\circ + \frac{\omega_{li}}{2} (p_{li}^2 + q_{li}^2) + g_{li} q_{li} + \omega_{li} k_i \right] (r_{lK}^2 + s_{lK}^2) \right\} \\
&\quad + \sum_{l,i,K} (\omega_{li} q_{li} + g_{li}) \sqrt{2(k_i + 1)} (r_{lK+1_i} r_{lK} + s_{lK+1_i} s_{lK}) \\
&\quad + \sum_{l,i,K} \omega_{li} p_{li} \sqrt{2(k_i + 1)} (r_{lK} s_{lK+1_i} - r_{lK+1_i} s_{lK}) \\
\mathcal{V} &= 2\Re \left\{ \sum_{l>m,K,J} V_{lm} \bar{C}_{lK} C_{mJ} \langle \Phi_{lK} | \Phi_{mJ} \rangle \right\}.
\end{aligned}$$

The derivatives $\partial_{y_i} \mathcal{H}$ can be easily obtained analytically

$$\partial_{s_{lK}} \mathcal{H} = 2 \left\{ E_l^\circ + \sum_i \left[\frac{\omega_{li}}{2} (p_{li}^2 + q_{li}^2) + g_{li} q_{li} + \omega_{li} k_i \right] \right\} s_{lK} \quad (12a)$$

$$\begin{aligned}
&+ \sum_i \sqrt{2(k_i + 1)} [(\omega_{li} q_{li} + g_{li}) s_{lK+1_i} - \omega_{li} p_{li} r_{lK+1_i}] \\
&+ \sum_i \sqrt{2k_i} [(\omega_{li} q_{li} + g_{li}) s_{lK-1_i} + \omega_{li} p_{li} r_{lK-1_i}] + \partial_{s_{lK}} \mathcal{V}
\end{aligned} \quad (12b)$$

$$\partial_{r_{lK}} \mathcal{H} = 2 \left\{ E_l^\circ + \sum_i \left[\frac{\omega_{li}}{2} (p_{li}^2 + q_{li}^2) + g_{li} q_{li} + \omega_{li} k_i \right] \right\} r_{lK} \quad (12c)$$

$$\begin{aligned}
&+ \sum_i \sqrt{2(k_i + 1)} [(\omega_{li} q_{li} + g_{li}) r_{lK+1_i} + \omega_{li} p_{li} s_{lK+1_i}] \\
&+ \sum_i \sqrt{2k_i} [(\omega_{li} q_{li} + g_{li}) r_{lK-1_i} - \omega_{li} p_{li} s_{lK-1_i}] + \partial_{r_{lK}} \mathcal{V}
\end{aligned} \quad (12d)$$

$$\partial_{p_{li}} \mathcal{H} = \omega_{li} p_{li} \sum_K (r_{lK}^2 + s_{lK}^2) + \sum_K \omega_{li} \sqrt{2(k_i + 1)} (r_{lK} s_{lK+1_i} - r_{lK+1_i} s_{lK}) + \partial_{p_{li}} \mathcal{V} \quad (12e)$$

$$\partial_{q_{li}} \mathcal{H} = (\omega_{li} q_{li} + g_{li}) \sum_K (r_{lK}^2 + s_{lK}^2) + \sum_K \omega_{li} \sqrt{2(k_i + 1)} (r_{lK+1_i} r_{lK} + s_{lK+1_i} s_{lK}) + \partial_{q_{li}} \mathcal{V}. \quad (12f)$$

The explicit formulae for the derivatives of \mathcal{V} are given in the appendix. ~~Equations 10, 11 and 12 and their numerical implementation and application are the main result of this work.~~

The zero-th order Hamiltonian \mathcal{H}° includes a classical-like energy part that depends explicitly on the wave packet positions and momenta $(q_l(t), p_l(t))$, and a purely quantum contribution that depends on the quantum numbers (k_1, \dots, k_d) . The terms $\langle \Phi_{lK} | \Phi_{mJ} \rangle$ appearing in the potential energy \mathcal{V} are Franck-Condon type integrals and depend on time through the variables $(q_l(t), p_l(t))$. Their evaluation is a critical step of the time propa-

gation and can be performed analytically using the recurrence relations described in the appendix.

The numerical solution of the set of differential equations 11 is not an easy task. On one hand, when the number of variables is small a pseudo-inverse of the tensor η can be computed, *e.g.* by singular value decomposition, and the system can be solved using standard methods for ordinary differential equations. On the other hand, for problems with a large number of degrees of freedom computing a pseudo-inverse of η is not feasible and methods for implicit differential equations⁵¹ must be used. Here we have used a Krylov subspace method as implemented in the DASPK package.⁵²

III. NUMERICAL TESTS

We will now consider the application of the above methodology to the case of a system in which two electronic states are coupled to an ensemble of harmonic oscillators. **We write the Hamiltonian in the standard form**

$$H = \epsilon\sigma_z + \Delta\sigma_x + \sigma_z \sum_i g_i q_i + \sum_i \frac{\omega_i}{2} (p_i^2 + q_i^2)$$

with the usual definition of the σ_x, σ_z Pauli matrices. The ensemble of harmonic oscillators is defined using a Ohmic spectral density

$$J(\omega) = \frac{\pi}{2} \alpha \omega \exp(-\omega/\omega_c)$$

where ω_c is a cutoff frequency, α is the so called Kondo parameter and determine the strength of the system-bath coupling; the quantity $\lambda = 2\alpha\omega_c$ is the reorganization energy associated to the electronic transition. In order to use a basis set approach the spectral density is discretized into N_b vibrations in the interval $(0, \omega_m]$ where ω_m is a maximum sampling frequency, ensuring that the total reorganization energy is recovered. Following established procedures,⁵³⁻⁵⁵ the frequency of the i -th mode will be given by

$$\omega_i = -\omega_c \ln\left(1 - i \frac{\omega_o}{\omega_c}\right)$$

and its linear coupling term will be

$$g_i = \sqrt{\lambda \omega_i \omega_o}$$

with $\omega_o = \omega_c(1 - e^{-\omega_m/\omega_c})/N_b$. In the following we will present two sets of calculations in which the spectral density has been discretized by using 15 and 60 degrees of freedom respectively. We point out that our aim is not to discuss exact results of spin-boson dynamics which can be found, for example, in references 56 and 57, and the discretization of a continuous spectral density is only a technique to generate an ensemble of phonons with known properties.

For all set of data we provide the result of our methodology with an excitation level up to $c = 2$ and the numerically exact results obtained using MCTDH and ML-MCTDH methodologies that are *de facto* the standard reference methods for studying quantum dynamics in molecular systems.^{2,57-59} All calculation have been performed using the MCTDH Heidelberg package version 8.5.⁵⁹

Figures 1 and 2 show the population dynamics in the system with 15 degrees of freedom for two different values of the Kondo parameter, 0.3 and 0.5, and for three values of the energy bias, $\epsilon = 0, \Delta, 2\Delta$. It is well known that systems with large energy detuning represent a difficult case for most numerical methods and, furthermore, they are the most representative of electronic transitions in molecular systems in which exact energy degeneracy between electronic states is seldom achieved. In all cases the system is initially localized in the higher energy electronic state.

In the unbiased case ($\epsilon = 0$) the agreement is almost quantitative already at excitation level $c = 1$ independently of the value of the α parameter (see fig.s1a and 2a). For $c = 2$ the Gauss-Hermite *ansatz* reproduces the exact results. For $\epsilon = \Delta$ the agreement between the MCTDH result and our *ansatz* with an excitation level $c = 2$ is again quantitative with slight deviations appearing after 500 fs.

Upon increasing the energy bias to $\epsilon = 2\Delta$ the agreement with the exact MCTDH result worsen. The maximum transition probability is about 5% lower than the exact value, and the mean lifetime is slightly longer. Interestingly, the shape of the beatings appearing after the first 100 fs are correctly reproduced. Therefore, when the electronic energy gaps are large, the results of the methodology are not quantitative, still they provide a good qualitative description of the overall electronic population dynamics.

It is also worth noticing that the increase in the Kondo parameter affects only marginally the overall behaviour of the *ansatz*. By increasing α from 0.3 to 0.5 we can observe a deterioration in the performance only in the more difficult case of $\epsilon = 2\Delta$.

We point out that in all the above calculations converged results with respect to the size of the basis set can be obtained with at most 4 functions per degree of freedom.

The behaviour observed above is also reproduced when the number of degrees of freedom is increased from 15 to 60. The results are shown in figures 3 and 4 for two different values of the Kondo parameter and in the biased case $\epsilon = \Delta$. As in the previous case the system is initially localized in the higher energy electronic state.

For $\alpha = 0.3$ (fig. 3), at the lowest degree of approximation ($c = 0$), that is by using a single Gaussian wave packet for each electronic state, the electronic population decays to a constant value of approximately 0.5, meaning that the system is not localized at infinite time. When single excitations are added to the wavefunction ($c = 1$) the transition probability becomes significantly larger, reaching a maximum of about 0.82, though a complete population exchange between the two electronic states cannot be observed. The maximum transition probability being slightly larger than 0.8. When states with two excited vibrations are included in the dynamics ($c = 2$) the localization in the lowest energy electronic states is complete after 500 fs. **From a comparison with converged numerically exact ML-MCTDH results we can observe that both methods provide the same mean lifetime and converge to completely localized state. However, after the first 200 fs the population dynamics become manifestly different, and the agreement is not quantitative.**

Thus when moving from 15 to 60 degrees of freedom we can observe a deterioration of the performances of the method. This can be understood considering that the fraction of Hilbert space explored by the *ansatz* is clearly smaller in the latter case. Notwithstanding, the qualitative behaviour of the dynamics is correctly reproduced.

For $\alpha = 0.5$ (fig. 4) the results are qualitatively similar to the preceding case however the performance of the methodology slightly worsen. Again, at the lowest degree of approx-

imation ($c = 0$) the electronic population decays to a constant value of approximately 0.4. The addition of single excitations improves the overall result, increasing the maximum transition probability to 0.75, that becomes about 0.85 when states with two excited vibrations are included in the dynamics. **As in the preceding case comparing our best result with a ML-MCTDH calculation we observe the same half-life, though the latter method converges toward larger transition probabilities.**

The difference in the performance can be ascribed to the increase in the reorganization energy with α . In this case states with higher excitation levels, not included in the dynamics, might become more relevant in the dynamics, **but as discussed in the preceding section, this is feasible only for systems with a small number of degrees of freedom.**

Thus, while all the curves exhibit the same short time behaviour, a complete localization of the system in one of the two electronic states can be observed only at excitation level $c = 2$. This result is of fundamental importance for the assessment of the methodology since it shows that it is able to correctly reproduce the qualitative behaviour of such systems at infinite time.⁶⁰

It is also clear that a superposition of single complex Gaussian wave packet cannot properly describe the quantum dynamics in strongly biased systems. The motion of a single Gaussian wave packet does not provide an efficient energy exchange between the electronic degrees of freedom and the bath, hence limiting the population transfer. On the other hand using Gauss-Hermite wave packets it is possible to improve the overall description of the wavefunction by introducing vibronic states with different quantum numbers. In this way energy can be exchanged between the electronic and vibrational subsystems in a more efficient way, leading to the expected irreversible population decay.

IV. DISCUSSIONS AND CONCLUSIONS

The Gauss-Hermite wave packet method provides a family of *ansätze* for the vibronic wave function of a molecular system with interacting electronic states. The partitioning of the Hilbert into subspaces with different levels of excitations, albeit heuristic, appears quite effective in selecting the active space. Increasing the number of simultaneously excited vibrations allows to achieve, at least in principle, converged results, however this procedure can be applied

only to small systems and more advanced truncation schemes must be developed. The method has been applied to the study of model systems comprised of two electronic states interacting with a discrete set of bosons. It has been shown that qualitatively correct results can be obtained even in the case of a system with a large energy detuning, and using at most two simultaneously excited vibrational modes. This case is of notable interest in the study of electron-transfer processes in supramolecular assemblies which is mostly controlled by the differences in the oxidation-reduction potentials of the donor-acceptor pair.⁶¹⁻⁶⁵

The theory described in the present paper provides a first fundamental step in the development of a fully variational methodology for the study of quantum dynamics using Gauss-Hermite wavepackets.

The explicit time-dependent basis and the multi-set formulation allow to strongly reduce the number of primitive functions in the calculations, which, from a numerical perspective, implies very low computer memory requirements. A foreseeable advantage of a quantum dynamical method based on Gauss-Hermite wave packet is the possibility to develop techniques for on-the-fly quantum mechanics. GH wave packets are indeed localized in the configuration space allowing, at least in principle, to compute potential energy surfaces using a small number of points. Further work is required to better address these developments.

In its current implementation, the method suffers a number of drawbacks mostly due to the accuracy of the integrator, and to the improvement of the active space. Possible solutions to these problems will be addressed in future work.

As in any basis set methodology the number of independent coefficients in the wave function expansion is of main concern. While we have not yet investigated the possibility of contraction or projection schemes^{64,66,67} the methodology could be easily extended to handle such techniques. Finally, Gauss-Hermite wave packets could also be implemented in the framework of the MCTDH theory, and work is being currently done along this line.

From a numerical point of view, the evaluation of the derivatives of the potential energy is the most crucial step of the numerical integration scheme. Indeed, it requires the calculation

of Franck-Condon type integrals between pairs of time-dependent basis functions. Here we have developed new recurrence formulae to efficiently compute this type of integrals, that are akin to the well-known recurrence relations for FC integrals between harmonic oscillators wavefunctions.^{68–72}

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Appendix A: The metric tensor η

The determination of the metric tensor η requires the evaluation of the derivatives of the wave function $\Psi(x, t)$ and of its complex conjugate $\Psi^*(x, t)$ with respect to the set of real parameters $\{r_{lK}, s_{lK}, q_{li}, p_{li}, K \in \mathbb{N}^d, i \in \mathbb{N}\}$. To ease the notation in the following we will write Φ_{lK} as a short notation for the basis function $\Phi_{lK}(x_{l1}, x_{l2}, \dots, t) = \prod_{i=1}^d \varphi_{lk_i}(x_{li}, t)$. By standard mathematical procedures we have

$$\partial_{r_{lK}} \Psi = \Phi_{lK} \quad (\text{A1a})$$

$$\partial_{s_{lK}} \Psi = i\Phi_{lK} \quad (\text{A1b})$$

$$\partial_{q_{lh}} \Psi = -ip_{lh} \sum_K (r_{lK} + is_{lK}) \Phi_{lK} + a_{lh}^{-1} \sum_K (r_{lK} + is_{lK}) \left[\sqrt{\frac{k_h + 1}{2}} \Phi_{lK+1_h} - \sqrt{\frac{k_h}{2}} \Phi_{lK-1_h} \right] \quad (\text{A1c})$$

$$\partial_{p_{lh}} \Psi = ia_{lh} \sum_K (r_{lK} + is_{lK}) \left[\sqrt{\frac{k_h + 1}{2}} \Phi_{lK+1_h} + \sqrt{\frac{k_h}{2}} \Phi_{lK-1_h} \right]. \quad (\text{A1d})$$

The notation $K - 1_h$ and alike must be read as subtracting 1 from the h -th elements of $K = (k_1, \dots, k_d)$. Of course for any real parameter y we have the relation $\partial_y \Psi^* = (\partial_y \Psi)^*$. Here we only report the explicit calculation of the $\eta_{q_{lj}p_{nh}}$ tensor elements, the others being quite straightforward. First we notice that $\eta_{q_{lj}p_{nh}} = 0$ for $l \neq n$, *i.e.* for two different electronic states. Thus we only need to compute the term $\eta_{q_{lj}p_{lh}}$. By a simple application

of the rules A1 we have

$$\begin{aligned}
-2\Im\{\partial_{q_j}\Psi^*\partial_{p_h}\Psi\} &= -2\Im\left\{ip_{lh}\sum_K(r_{lK}-is_{lK})\Phi_{lK}^*+a_{lh}^{-1}\sum_K(r_{lK}-is_{lK})\left[\sqrt{\frac{k_h+1}{2}}\Phi_{lK+1h}^*-\sqrt{\frac{k_h}{2}}\Phi_{lK-1h}^*\right]\right. \\
&\quad \left.\times ia_{lj}\sum_U(r_{lU}+is_{lU})\left[\sqrt{\frac{u_j+1}{2}}\Phi_{lU+1j}+\sqrt{\frac{u_j}{2}}\Phi_{lU-1j}\right]\right\}. \quad (\text{A2})
\end{aligned}$$

Taking the products, integrating over x and taking into account the orthonormality of the wave functions Φ_{lK} we have

$$\begin{aligned}
\eta_{q_j p_{lh}} &= 2p_{lh}a_{lj}\sum_{K,U}(r_{lK}s_{lU}-s_{lK}r_{lU})\left[\sqrt{\frac{u_j+1}{2}}\delta_{K,U+1j}+\sqrt{\frac{u_j}{2}}\delta_{K,U-1j}\right] \\
&\quad - a_{lh}^{-1}a_{lj}\sum_{K,U}(r_{lK}r_{lU}+s_{lK}s_{lU})\left[\sqrt{(k_h+1)(u_j+1)}\delta_{K+1h,U+1j}\right] \\
&\quad + a_{lh}^{-1}a_{lj}\sum_{K,U}(r_{lK}r_{lU}+s_{lK}s_{lU})\left[\sqrt{k_h u_j}\delta_{K-1h,U-1j}\right] \\
&\quad - a_{lh}^{-1}a_{lj}\sum_{K,U}(r_{lK}r_{lU}+s_{lK}s_{lU})\left[\sqrt{(k_h+1)u_j}\delta_{K+1h,U-1j}\right] \\
&\quad + a_{lh}^{-1}a_{lj}\sum_{K,U}(r_{lK}r_{lU}+s_{lK}s_{lU})\left[\sqrt{k_h(u_j+1)}\delta_{K-1h,U+1j}\right]. \quad (\text{A3})
\end{aligned}$$

In the above equations the Kronecker over the multi-indices K and U must be read as products of one-index Kronecker symbols. The two summations with the factor $2p_{lh}a_{lj}$ cancel so we are left with

$$\begin{aligned}
\eta_{q_j p_{lh}} &= -a_{lh}^{-1}a_{lj}\sum_{K,U}(r_{lK}r_{lU}+s_{lK}s_{lU})\left[\sqrt{(k_h+1)(u_j+1)}\delta_{K+1h,U+1j}\right] \\
&\quad + a_{lh}^{-1}a_{lj}\sum_{K,U}(r_{lK}r_{lU}+s_{lK}s_{lU})\left[\sqrt{k_h u_j}\delta_{K-1h,U-1j}\right] \\
&\quad - a_{lh}^{-1}a_{lj}\sum_{K,U}(r_{lK}r_{lU}+s_{lK}s_{lU})\left[\sqrt{(k_h+1)u_j}\delta_{K+1h,U-1j}\right] \\
&\quad + a_{lh}^{-1}a_{lj}\sum_{K,U}(r_{lK}r_{lU}+s_{lK}s_{lU})\left[\sqrt{k_h(u_j+1)}\delta_{K-1h,U+1j}\right]. \quad (\text{A4})
\end{aligned}$$

which can be further reduced to

$$\begin{aligned}
\eta_{q_j p_{lh}} = & -a_{lh}^{-1} a_{lj} \sum_K (r_{lK} r_{K+1h-1j} + s_{lK} s_{K+1h-1j}) \sqrt{(k_h + 1)(k_j + \delta_{hj})} \\
& + a_{lh}^{-1} a_{lj} \sum_K (r_{lK} r_{lK-1h+1j} + s_{lK} s_{lK-1h+1j}) \sqrt{k_h(k_j + 1 - \delta_{hj})} \\
& - a_{lh}^{-1} a_{lj} \sum_K (r_{lK} r_{lK+1h+1j} + s_{lK} s_{lK+1h+1j}) \sqrt{(k_h + 1)(k_j + 1 + \delta_{hj})} \\
& + a_{lh}^{-1} a_{lj} \sum_K (r_{lK} r_{lK-1h-1j} + s_{lK} s_{lK-1h-1j}) \sqrt{k_h(k_j - \delta_{hj})}. \quad (A5)
\end{aligned}$$

It is easy to verify that the third and fourth sums cancel each other leaving us with the final results

$$\begin{aligned}
\eta_{q_j p_{lh}} = & -a_{lh}^{-1} a_{lj} \sum_K (r_{lK} r_{lK+1h-1j} + s_{lK} s_{lK+1h-1j}) \sqrt{(k_h + 1)(k_j + \delta_{hj})} \\
& + a_{lh}^{-1} a_{lj} \sum_K (r_{lK} r_{lK-1h+1j} + s_{lK} s_{lK-1h+1j}) \sqrt{k_h(k_j + 1 - \delta_{hj})}. \quad (A6)
\end{aligned}$$

If $h = j$ we have

$$\eta_{q_j p_{lj}} = - \sum_{K=0} (r_{lK} r_{lK} + s_{lK} s_{lK})(k_h + 1) + \sum_{K=0} (r_{lK} r_{lK} + s_{lK} s_{lK})k_h = - \sum_{K=0} (r_{lK} r_{lK} + s_{lK} s_{lK}) \quad (A7)$$

and if $h \neq j$

$$\begin{aligned}
\eta_{q_j p_{lh}} = & -a_{lh}^{-1} a_{lj} \sum_K (r_{lK} r_{lK+1h-1j} + s_{lK} s_{lK+1h-1j}) \sqrt{(k_h + 1)k_j} \\
& + a_{lh}^{-1} a_{lj} \sum_K (r_{lK} r_{lK-1h+1j} + s_{lK} s_{lK-1h+1j}) \sqrt{k_h(k_j + 1)} = 0 \quad (A8)
\end{aligned}$$

This latter result shows that the metric η directly couple the time-dependent parameters (q_l, p_l) and the coefficients C_{lK} .

Appendix B: The Hamilton function

The Hamilton function \mathcal{H} can be easily obtained by using the formulae

$$-\partial_{x_i}^2 \varphi_k = \left[p^2 + a^2 \left(k + \frac{1}{2} \right) \right] \varphi_k - \frac{a^2}{2} \left[\sqrt{(k+1)(k+2)} \varphi_{k+2} + \sqrt{k(k-1)} \varphi_{k-2} \right] \\ + 2iap \left(\sqrt{\frac{k+1}{2}} \varphi_{k+1} - \sqrt{\frac{k}{2}} \varphi_{k-1} \right) \quad (\text{B1})$$

$$x^2 \varphi_k = \left[q^2 + a^{-2} \left(k + \frac{1}{2} \right) \right] \varphi_k + \frac{1}{2a^2} \left(\sqrt{(k+1)(k+2)} \varphi_{k+2} + \sqrt{k(k-1)} \varphi_{k-2} \right) \\ + \frac{2q}{a} \left(\sqrt{\frac{k+1}{2}} \varphi_{k+1} + \sqrt{\frac{k}{2}} \varphi_{k-1} \right) \quad (\text{B2})$$

$$x \varphi_k = q \varphi_k + \frac{1}{a} \left(\sqrt{\frac{k+1}{2}} \varphi_{k+1} + \sqrt{\frac{k}{2}} \varphi_{k-1} \right). \quad (\text{B3})$$

Furthermore, if we let $a^4 = \omega^2$ we obtain

$$\frac{1}{2} (-\partial_x^2 + \omega^2 x^2) \varphi_k = \frac{1}{2} (-\partial_x^2 + a^4 x^2) \varphi_k = \\ \frac{1}{2} \left[p^2 + a^4 q^2 + 2a^2 \left(k + \frac{1}{2} \right) \right] \varphi_k + a(a^2 q + ip) \sqrt{\frac{k+1}{2}} \varphi_{k+1} + a(a^2 q - ip) \sqrt{\frac{k}{2}} \varphi_{k-1} \quad (\text{B4})$$

thus

$$H |\Phi_{mK}\rangle |m\rangle = \left\{ \sum_l \left[\sum_i \frac{1}{2} (-\partial_{x_i}^2 + \omega_{li}^2 x_i^2) + g_{li} x_i + E_l \right] |l\rangle \langle l| + \sum_{l>m} V_{lm} |l\rangle \langle m| + \text{h.c.} \right\} |m\rangle |\Phi_{mK}\rangle \\ = |m\rangle \sum_i \left\{ \left[E_m + (p_{mi}^2 + a_{mi}^4 q_{mi}^2) / 2 + a_{mi}^2 \left(k_i + \frac{1}{2} \right) \right] |\Phi_{mK}\rangle + (a_{mi}^3 q_{mi} + i a_{mi} p_{mi}) \sqrt{\frac{k_i+1}{2}} |\Phi_{mK+1_i}\rangle \right. \\ \left. + (a_{mi}^3 q_{mi} - i a_{mi} p_{mi}) \sqrt{\frac{k_i}{2}} |\Phi_{mK-1_i}\rangle \right\} \\ + \sum_i g_{mi} q_{mi} \Phi_{mK} + \frac{1}{a_{mi}} \left(\sqrt{\frac{k_i+1}{2}} \Phi_{mK+1_i} + \sqrt{\frac{k_i}{2}} \Phi_{mK-1_i} \right) + \sum_l V_{lm} |l\rangle \quad (\text{B5})$$

Introducing a set of scaled coordinates $x_{li} \leftarrow a_{li} x$ and the set of scaled parameters $q_{li} \leftarrow a q$ and $p_{li} \leftarrow p/a_{il}$ $g_{li} \leftarrow g_{li}/a_{li}$ we obtain

$$H |\Phi_{mK}\rangle |m\rangle = |m\rangle \sum_i \left\{ \left[E_m + \omega_{mi} (p_{mi}^2 + q_{mi}^2) / 2 + \omega_{mi} \left(k_i + \frac{1}{2} \right) + g_{mi} q_{mi} \right] |\Phi_{mK}\rangle \right. \\ \left. + [\omega_{mi} (q_{mi} + ip_{mi}) + g_{mi}] \sqrt{\frac{k_i+1}{2}} |\Phi_{mK+1_i}\rangle \right. \\ \left. + [\omega_{mi} (q_{mi} - ip_{mi}) + g_{mi}] \sqrt{\frac{k_i}{2}} |\Phi_{mK-1_i}\rangle \right\} + \sum_l V_{lm} |l\rangle. \quad (\text{B6})$$

The Hamiltonian matrix elements over the basis $|\Phi_{mK}\rangle|m\rangle$ are

$$\langle\Phi_{mK}|H|\Phi_{lW}\rangle = V_{ml}\langle\Phi_{mK}|\Phi_{lW}\rangle \quad \text{for } l \neq m \quad (\text{B7})$$

$$\langle\Phi_{mK}|H|\Phi_{mK}\rangle = E_m + \sum_i \left[\omega_{mi}(p_{mi}^2 + q_{mi}^2)/2 + \omega_{mi}(k_i + \frac{1}{2}) + g_{mi}q_{mi} \right] \quad (\text{B8})$$

$$\langle\Phi_{mK}|H|\Phi_{mK+1_i}\rangle = \sum_i [\omega_{mi}(q_{mi} + ip_{mi}) + g_{mi}] \sqrt{\frac{k_i + 1}{2}} \quad \text{for } l = m. \quad (\text{B9})$$

Thus, using the orthonormality of the basis functions Φ_{lK} , we have

$$\begin{aligned} \mathcal{H} = & \sum_{miK} \left\{ \left[E_m + \omega_{mi}(p_{mi}^2 + q_{mi}^2)/2 + \omega_{mi}(k_i + \frac{1}{2}) + g_{mi}q_{mi} \right] |C_{mK}|^2 \right\} \quad (\text{B10}) \\ & + \sum_{miK} [\omega_{mi}(q_{mi} + ip_{mi}) + g_{mi}] \sqrt{\frac{k_i + 1}{2}} \bar{C}_{mK+1_i} C_{mK} \\ & + \sum_{miK} [\omega_{mi}(q_{mi} - ip_{mi}) + g_{mi}] \sqrt{\frac{k_i}{2}} \bar{C}_{mK-1_i} C_{mK} \\ & + \sum_{lmKJ} V_{lm} \bar{C}_{lK} C_{mJ} \langle\Phi_{lK}|\Phi_{mJ}\rangle + \text{h.c.} \end{aligned}$$

By letting $E_m^\circ = E_m + \sum_i \omega_{mi}/2$, we can partition the Hamiltonian as

$$\mathcal{H} = \mathcal{H}^\circ + \mathcal{V} \quad (\text{B11})$$

where

$$\begin{aligned} \mathcal{H}^\circ = & \sum_{miK} \left\{ \left[E_m^\circ + \omega_{mi}(p_{mi}^2 + q_{mi}^2)/2 + \omega_{mi}k_i + g_{mi}q_{mi} \right] (r_{mK}^2 + s_{mK}^2) \right\} \quad (\text{B12}) \\ & + \sum_{miK} (\omega_{mi}q_{mi} + g_{mi}) \sqrt{2(k_i + 1)} (r_{mK+1_i} r_{mK} + s_{mK+1_i} s_{mK}) \\ & + \sum_{miK} \omega_{mi} p_{mi} \sqrt{2(k_i + 1)} (r_{mK+1_i} s_{mK} - s_{mK+1_i} r_{mK}) \\ \mathcal{V} = & \sum_{lmKJ} V_{lm} \bar{C}_{lK} C_{mJ} \langle\Phi_{lK}|\Phi_{mJ}\rangle = \sum_{JK} \sum_{m>l} 2V_{lm} \left[(r_{lK} r_{mJ} + s_{lK} s_{mJ}) \Re \langle\Phi_{lK}|\Phi_{mJ}\rangle \right. \\ & \left. + (r_{lK} s_{mJ} - s_{lK} r_{mJ}) \Im \langle\Phi_{lK}|\Phi_{mJ}\rangle \right] \quad (\text{B13}) \end{aligned}$$

The overlap integrals $\langle\Phi_{lK}|\Phi_{mJ}\rangle$ are complex numbers, that can be evaluated by using the recurrence relations described in the next section.

The calculation of the derivatives of the Hamilton function with respect to the coefficients (r_{lK}, s_{lK}) are immediate, and those with respect to (q_{li}, p_{li}) follows easily from the application

of formulae B1,B2 and B3. After some lengthy but straightforward calculations one obtains

$$\begin{aligned} \partial_{q_{ni}} \mathcal{V} = & -2 \sum_{lKJ} V_{ln}(r_{lK}r_{nJ} + s_{lK}s_{nJ}) \left[\sqrt{\frac{j_i+1}{2}} \Re \langle \Phi_K^l | \Phi_{J+1_i}^n \rangle - \sqrt{\frac{j_i}{2}} \Re \langle \Phi_K^l | \Phi_{J-1_i}^n \rangle - p_{ni} \Im \langle \Phi_K^l | \Phi_J^n \rangle \right] \\ & + 2 \sum_{lKJ} V_{ln}(r_{lK}s_{nJ} - s_{lK}r_{nJ}) \left[\sqrt{\frac{j_i+1}{2}} \Im \langle \Phi_K^l | \Phi_{J+1_i}^n \rangle - \sqrt{\frac{j_i}{2}} \Im \langle \Phi_K^l | \Phi_{J-1_i}^n \rangle + p_{ni} \Re \langle \Phi_K^l | \Phi_J^n \rangle \right] \end{aligned} \quad (\text{B14})$$

and

$$\begin{aligned} \partial_{p_{ni}} \mathcal{V} = & -2 \sum_{lKJ} V_{ln}(r_{lK}s_{nJ} - s_{lK}r_{nJ}) \left[\sqrt{\frac{j_i+1}{2}} \Re \langle \Phi_K^l | \Phi_{J+1_i}^n \rangle + \sqrt{\frac{j_i}{2}} \Re \langle \Phi_K^l | \Phi_{J-1_i}^n \rangle \right] \\ & - 2 \sum_{lKJ} V_{ln}(r_{lK}r_{nJ} + s_{lK}s_{nJ}) \left[\sqrt{\frac{j_i+1}{2}} \Im \langle \Phi_K^l | \Phi_{J+1_i}^n \rangle + \sqrt{\frac{j_i}{2}} \Im \langle \Phi_K^l | \Phi_{J-1_i}^n \rangle \right]. \end{aligned} \quad (\text{B15})$$

Appendix C: Franck-Condon integrals

The Franck-Condon integrals $\langle \Phi_{mj} | \Phi_{lk} \rangle$, are the product of d one-dimensional overlap $\langle \varphi_{mj} | \varphi_{lk} \rangle$. By using the generating function technique it is possible to derive simple recurrence formulae which allow to compute FC integrals for any pair of quantum numbers.⁷⁰⁻⁷² After some lengthy calculation one obtain the identity

$$F_0 \exp \left\{ (\tau \ \sigma) y - \frac{1}{2} (\tau \ \sigma) A \begin{pmatrix} \tau \\ \sigma \end{pmatrix} \right\} = \sum_{j,k} \frac{\tau^j \sigma^k}{(j!k!)^{1/2}} \langle \varphi_{mj} | \varphi_{lk} \rangle \quad (\text{C1})$$

where τ, σ are dummy variables; the scalar F_0 , the matrix A , and the vector y are given by:

$$F_0 = \left(\frac{2}{1 + \alpha^2} \right)^{1/2} \exp \left[-\frac{d^2 + h^2 - i2d(p_l + \alpha p_m)}{2(1 + \alpha^2)} \right], \quad (\text{C2})$$

and

$$y = \frac{\sqrt{2}}{1 + \alpha^2} \begin{pmatrix} -(d\alpha + ih) \\ d + i\alpha h \end{pmatrix}, \quad A = \frac{1}{1 + \alpha^2} \begin{pmatrix} \alpha^2 - 1 & -2\alpha \\ -2\alpha & 1 - \alpha^2 \end{pmatrix} \quad (\text{C3})$$

with

$$d = q_m - \alpha p_l, \quad h = p_m - \alpha p_l, \quad \alpha = \sqrt{\omega_m/\omega_l}. \quad (\text{C4})$$

where ω_m, ω_l are the oscillator frequencies in the two electronic states. From the above equations it is straightforward to derive the recurrence relations^{68,70,73}

$$\sqrt{j} \langle j|k \rangle = y_1 \langle j-1|k \rangle - A_{11} \sqrt{j-1} \langle j-2|k \rangle - A_{12} \sqrt{k} \langle j-1|k-1 \rangle \quad (\text{C5})$$

$$\sqrt{k} \langle j|k \rangle = y_2 \langle j|k-1 \rangle - A_{21} \sqrt{j} \langle j-1|k-1 \rangle - A_{22} \sqrt{k} \langle j|k-2 \rangle \quad (\text{C6})$$

from which one can obtain the required integrals.

We notice that in the standard formulation of FC integrals between harmonic oscillator eigenstates y is real number and depends solely on the difference in the parameters (q_l, q_m) . In the present case y is a complex vector and depends also on the “momenta” (p_l, p_m) . If h is zero the standard recurrence relations of FC integrals between harmonic oscillators eigenstates are recovered. In the special case $\alpha = 1$, *i.e.* when the the frequency of the two basis functions is the same in both electronic states, $A_{11} = A_{22} = 0$ and the recurrence relations simplify to

$$\sqrt{j}\langle j|k\rangle = y_1\langle j-1|k\rangle + \sqrt{k}\langle j-1|k-1\rangle \quad (\text{C7})$$

$$\sqrt{k}\langle j|k\rangle = y_2\langle j|k-1\rangle + \sqrt{j}\langle j-1|k-1\rangle. \quad (\text{C8})$$

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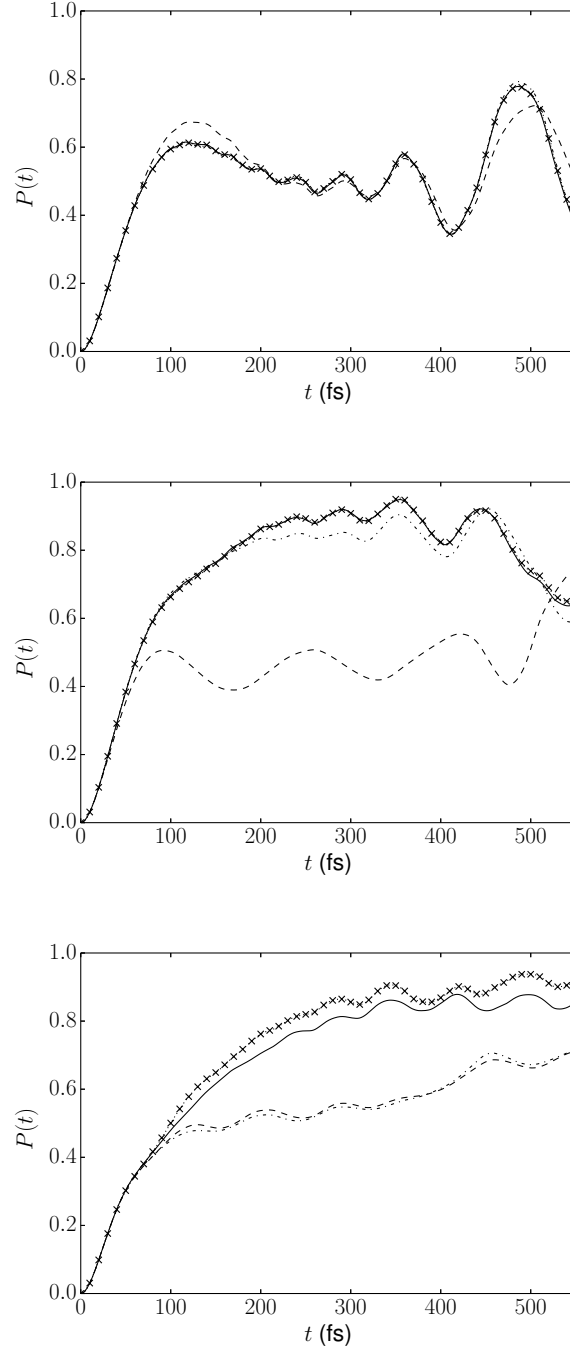


FIG. 1. Population of the lowest energy electronic state as a function of time in a two electronic state system. The parameters of the model are $\Delta = 100 \text{ cm}^{-1}$, $\omega_c = 10\Delta$, $\alpha = 0.3$; a) $\epsilon = 0$, b) $\epsilon = \Delta$ c) $\epsilon = 2\Delta$. The number of bath modes is $N_b = 15$. Dashed line (- -) excitation levels of the two electronic states $c = 0$; dash-dot line(-·-) $c = 1$; full line (-) $c_2 = 2$; (\times) MCTDH result.

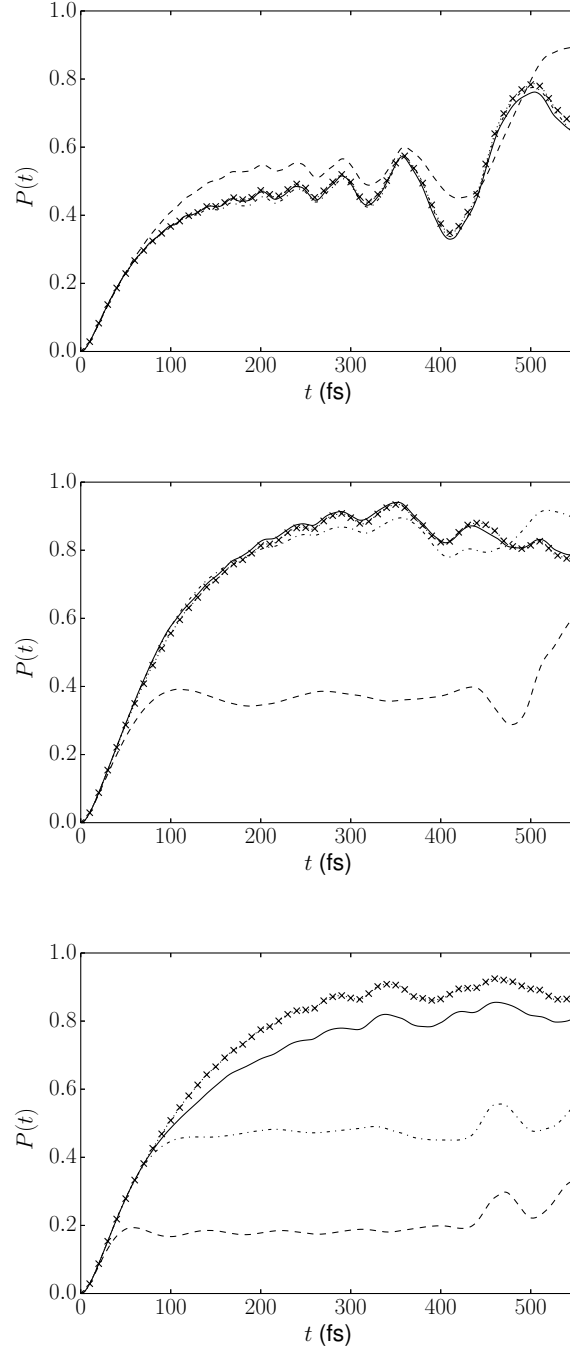


FIG. 2. Population of the lowest energy electronic state as a function of time in a two electronic state system. The parameters of the model are $\Delta = 100 \text{ cm}^{-1}$, $\omega_c = 10\Delta$, $\alpha = 0.3$ and $\epsilon = \Delta$; a) $\epsilon = 0$, b) $\epsilon = \Delta$ c) $\epsilon = 2\Delta$. The number of bath modes is $N_b = 15$. Dashed line (- -) excitation levels of the two electronic states $c = 0$; dash-dot line(-·-) $c = 1$; full line (-) $c_2 = 2$; (×) MCTDH result.

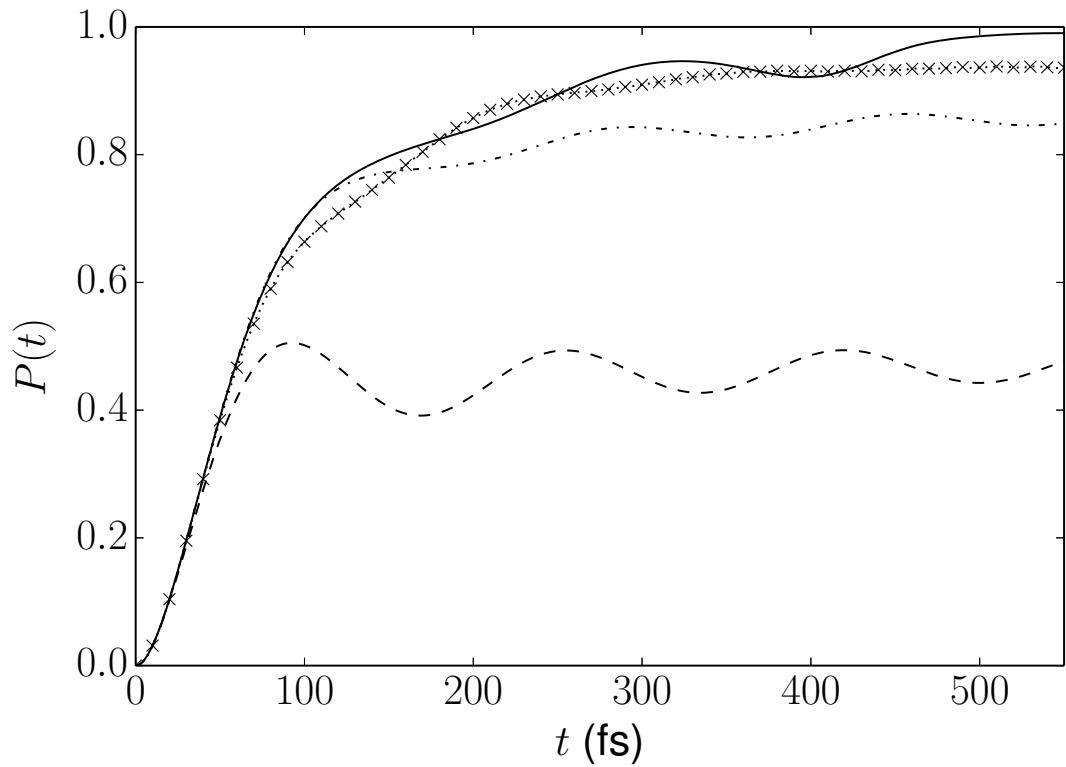


FIG. 3. Population of the lowest energy electronic state as a function of time in a model spin-boson system. The parameters of the model are $\Delta = 100 \text{ cm}^{-1}$, $\omega_c = 10\Delta$, $\alpha = 0.3$ and $\epsilon = \Delta$. The number of bath modes is $N_b = 60$. Dashed line (- -) excitation levels of the two electronic states $c_1 = 1$ and $c_2 = 2$; dash-dot line(-·) $c_1 = c_2 = 1$; full line (-) $c_1 = 1$ and $c_2 = 2$; (×) ML-MCTDH result.

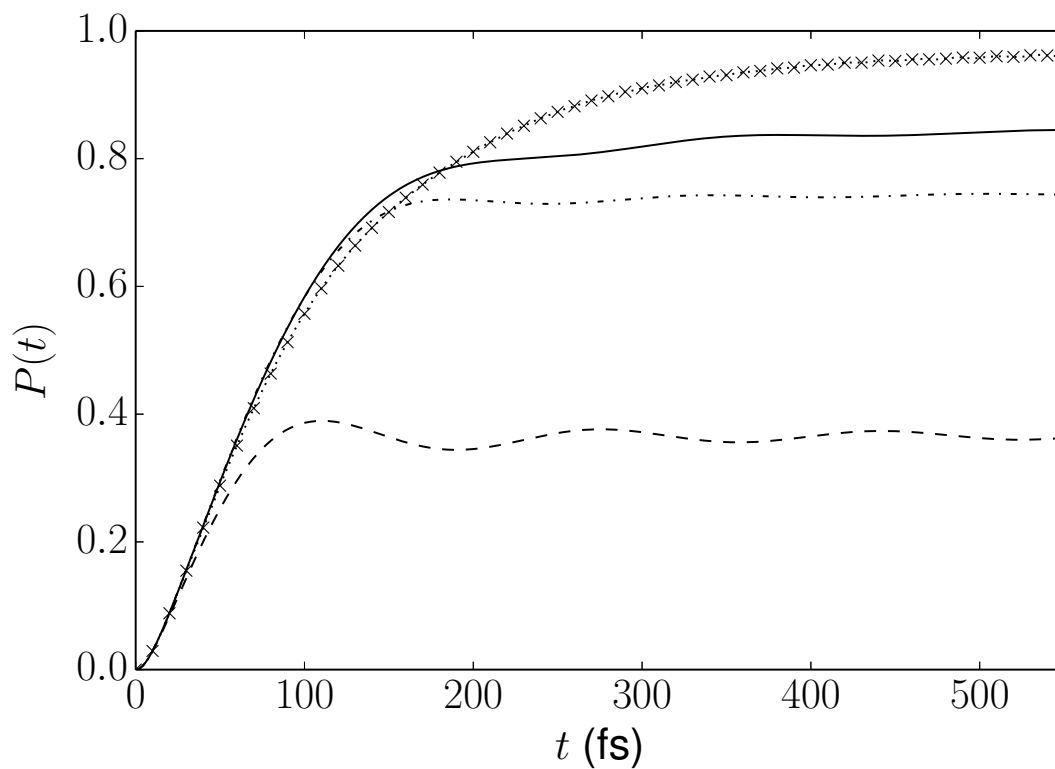


FIG. 4. Population of the lowest energy electronic state as a function of time in a model spin-boson system. The parameters of the model are $\Delta = 100 \text{ cm}^{-1}$, $\omega_c = 10\Delta$, $\alpha = 0.5$ and $\epsilon = \Delta$. The number of bath modes is $N_b = 60$. Dashed line (- -) excitation levels of the two electronic states $c_1 = 1$ and $c_2 = 2$; dash-dot line(-·) $c_1 = c_2 = 1$; full line (-) $c_1 = 1$ and $c_2 = 2$; (\times) ML-MCTDH result.