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Effect of a thermal bath on electronic resonance decay: A numerical path-integral study

Heiko Plöhn and Michael Thoss
Institute of Physical and Theoretical Chemistry, Technical University of Munich, D-85747 Garching, Germany

Manfred Winterstetter
II. Institute of Theoretical Physics, University of Stuttgart, D-70550 Stuttgart, Germany

Wolfgang Domcke
Institute of Theoretical Chemistry, University of Duesseldorf, D-40225 Duesseldorf, Germany

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The effect of electron-vibrational coupling on the decay of a metastable electronic state is treated by a real-time path-integral method. The electronic resonance is described within the framework of the projection operator formalism of scattering theory. The effect of the bath is taken into account by the Feynman-Vernon influence functional technique. In this formulation, neither Born-type nor Markov-type approximations are invoked. The numerical evaluation of the time-discretized path integral is made possible by a recursive partial summation technique. This approach, which has previously been formulated for scattering amplitudes, is generalized to population probabilities that are given by a forward-backward double path integral. The performance of the method is demonstrated for model systems describing a *d*-wave shape resonance, which is linearly coupled to a bath with Ohmic spectral function. The effect of the bath is investigated as a function of coupling strength and temperature. [S1050-2947(98)05507-3]

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I. INTRODUCTION

Short-lived electronic states that decay by electron emission into a continuum are commonly encountered in atomic and molecular physics. They appear, for example, as resonances in electron-scattering or photoionization cross sections [1,2]. As is well known, these resonances can be classified into shape resonances (which decay by tunneling of the electron through a barrier of the effective interaction potential) and Feshbach resonances (which decay via electronic interchannel coupling induced by electron-electron correlations) [3]. In either case, an isolated resonance can be understood as a discrete electronic state that is coupled to an electronic continuum (or possibly several electronic continua). The formal basis of this description is provided by the projection-operator formalism of Feshbach [4] or by Fano's theory of configuration interaction in the continuum [5].

As has repeatedly been discussed in the literature (see, for example, Refs. [6–13]), the time-dependent decay law of a resonance is completely specified if the discrete-continuum coupling matrix element is given as a function of energy. The time-dependent decay is generally described by the survival amplitude, that is, the overlap of the discrete state with the time-dependent wave function of the system. As is well known, the decay of the survival probability (given by the absolute square of the survival amplitude) deviates from the exponential decay law at both short and long times [6–13]. If the resolvent of the system possesses bound-state poles, the decay is generally incomplete, i.e., the survival probability approaches a nonzero value for $t \to \infty$ [14].

In molecules the electronic resonance decay is generally significantly modified by nuclear motion, in particular vibrational motion. The theory of resonant electron-molecule scattering is well developed for diatomic molecules; see Refs. [15,16] for reviews. Following pioneering works of Chen, O'Malley, Bardsley, and Nakamura [17–20], the projection-operator formalism as well as other approaches such as the *R*-matrix method [21] have been widely employed to compute inelastic and reactive cross sections. More recently, a time-dependent formulation of resonant electron-molecule scattering has been elaborated within the projection-operator formalism [22]. The time-dependent picture yields more direct insight into the complex interplay of electronic resonance decay and vibrational motion [22,23]. It reveals, in particular, the importance of memory effects and deviations from the exponential decay law, which can be pronounced for short-lived resonances as well as in the presence of threshold effects [16,24,25].

In the present work we wish to consider basic aspects of electronic resonance decay in polyatomic systems, e.g., polyatomic molecules, molecular aggregates, or molecules adsorbed on surfaces. In such systems the electronic dynamics is coupled to a large number of vibrational modes. In the limit of very large molecules and clusters we can assume a quasicontinuous distribution of vibrational frequencies. We can assume, moreover, that the unperturbed occupation probability of vibrational levels is given by the Boltzmann distribution. It appears natural to ask how the electronic barrier tunneling process is modified by the coupling of the resonance to such a thermal heat bath.

The effect of dissipation on tunneling dynamics has extensively been investigated for the case of a two-level system that is linearly coupled to a bath of harmonic oscillators, the so-called spin-boson model [26]. Among the many applications of this model are electron-transfer processes in chemical and biological systems [27,28], defect tunneling in solids [29] and the flux-dynamics in superconducting quantum interference devices [30]. The Feynman-Vernon functional-integral approach [31] allows the oscillator degrees of freedom to be integrated out analytically, resulting in an effective two-level dynamics governed by a time-nonlocal influence functional [26]. The properties of the influence functional are determined by the spectral function of the bath: in analogy to the electronic resonance decay discussed above, the importance of non-Markovian effects in the real-time dynamics are governed by the frequency dependence of the spectral function.

Electronic resonance decay in the presence of dissipation involves two continua, the electronic scattering continuum as well as the continuum of vibrational frequencies, and represents thus a more general and more involved problem than the spin-boson model. Barrier tunneling in the presence of a dissipative environment has extensively been discussed in the chemical physics literature within the context of the famous Kramers problem, that is, noise-activated escape over a potential barrier; see Ref. [32] for a comprehensive review. In this case the de Broglie wavelength of the particle is typically very short such that semiclassical approximations can be invoked within the path-integral formulation to obtain analytical results [32–37].

In the case of the decay of an electronic shape resonance, a fully quantum mechanical description of the electronic dynamics is required owing to the small mass and thus very long wavelength of the electron. Quasiclassical approximations are probably not useful in this regime. On the other hand, electronic tunneling is a very fast process, occurring typically on a time scale of a few tens of femtoseconds. This suggests the feasibility of a direct numerical evaluation of the discrete path sum resulting from the time discretization of the real-time Feynman path integral.

The exponential growth of the number of paths with the number of elementary time slices limits the brute-force numerical evaluation of real-time path integrals to about 30 time intervals and thus extremely short time scales. The so-called sign problem is a severe obstacle for the application of Monte Carlo importance sampling techniques, which have proven to be efficient for the evaluation of imaginary-time path integrals. Considerable progress has recently been made, however, in a variety of real-time path-integral applications by employing filtering techniques, short-memory approximations, or partial summations over subsets of paths [28,38,39].

The partial-summation approach has been applied earlier to calculate T-matrix elements for resonant electron-molecular scattering with multimode vibrational coupling [40]. The basic idea is the replacement of the sum over paths, which becomes computationally intractable for more than about 30 time steps, by a manageable sum over subsets (so-called classes) of paths. The contribution of each class is given by the product of the combinatorial weight of the class and the average of the multimode vibrational propagator, taken over all paths within the class. The class averages are evaluated by recursion with respect to the length of the path [39,40]. In the present work this theory is extended to deal directly with the time-dependent population probability of the resonance, which is given by a forward-backward double path integral. The class-averaging concept has to be generalized accordingly.

In this communication we are primarily concerned with the description of the method and its computational implementation. We demonstrate the feasibility of converged numerical path-integral computations for two models of an electronic resonance that is coupled to a so-called Ohmic bath [26]. We shall investigate the effect of the bath on the electronic decay dynamics as a function of the coupling strength and the temperature.

II. DEFINITION OF THE PROBLEM

We consider an isolated electronic resonance in electron-molecule scattering. Adopting the projection-operator formalism [4,16], we use a diabatic basis [41] consisting of a discrete state $|\varphi_d\rangle$ (describing the resonance) and an orthogonal background scattering continuum $|\varphi_k\rangle$. The corresponding projectors within the electronic Hilbert space are defined by

$$\mathbf{P}=|\varphi_d\rangle\langle\varphi_d|, \tag{2.1a}$$

$$\mathbf{Q}=\int k dk d\Omega_k|\varphi_k\rangle\langle\varphi_k|. \tag{2.1b}$$

By construction the relations

$$\mathbf{P}+\mathbf{Q}=\mathbf{1}, \quad \mathbf{PQ}=\mathbf{0} \tag{2.2}$$

hold. Here **1** denotes the identity in the Hilbert space of the electronic states.

The Hamiltonian represented in this diabatic electronic basis reads (see Ref. [16] for more details)

$$H=|\varphi_d\rangle H_d\langle\varphi_d|+\int k\ dk\ d\Omega_k|\varphi_k\rangle(H_0+\varepsilon_k)\langle\varphi_k| + \int k\ dk\ d\Omega_k\{|\varphi_d\rangle V_{dk}\langle\varphi_k|+\text{H.c.}\}. \tag{2.3}$$

Here H_0 is the vibrational Hamiltonian of the target molecule, while H_d describes vibrational motion in the discrete state. $\varepsilon_k=\hbar^2k^2/2m_e$ denotes the asymptotic energy of a continuum electron and V_{dk} is the discrete-continuum coupling element.

We adopt the harmonic oscillator approximation for the multidimensional vibrational motion of the target molecule ($\hbar=1$ in the following)

$$H_0=\frac{1}{2}\sum_j \omega_j\left(-\frac{\partial^2}{\partial q_j^2}+q_j^2\right). \tag{2.4}$$

The q_j are dimensionless normal coordinates of the target molecule and the ω_j are the associated harmonic vibrational frequencies.

The multidimensional potential-energy function of the discrete electronic state differs from that of the ground state. In the approximation of linear electronic-vibrational coupling [42] we write

$$H_d=H_0+\varepsilon_d+V_d \tag{2.5}$$

with

$$V_d=\sum_j c_j q_j, \tag{2.6}$$

where ε_d is the discrete-state energy at the equilibrium geometry of the target and c_j represents the gradient of the discrete-state energy with respect to the normal coordinate q_j.

The discrete-continuum coupling elements V_{dk} are specified by the width function

$$\Gamma(E)=2\pi\int d\Omega_k|V_{dk}|^2. \tag{2.7}$$

$\Gamma(E)$ is the energy-dependent decay width of the resonance. We assume, for simplicity, that the V_{dk} and thus $\Gamma(E)$ do not depend on the nuclear coordinates.

In the discussion of the models in Sec. V we will specify the width function by its threshold onset together with a convenient high-energy cutoff function

$$\Gamma(E)=A(E/B)^{\alpha_l}\exp(-E/B). \tag{2.8}$$

The threshold exponent α_l (we denote it here by α_l to avoid confusion with the Kondo parameter α) is given by

$$\alpha_l=l+\tfrac{1}{2}, \tag{2.9}$$

where l is the lowest partial wave into which the resonance can decay according to symmetry selection rules. The time-nonlocal kernel determining the time dependence of the survival probability of the resonant state is given by the Laplace transform of the width function [22]

$$\gamma(t)=\sum_k |V_{dk}|^2\exp(-i\varepsilon_k t)=\int_0^\infty \frac{dE}{2\pi}\Gamma(E)\exp(-iEt). \tag{2.10}$$

The time-dependent memory function corresponding to the parametrization (2.8) reads

$$\gamma(t)=\frac{AB}{2\pi}\Gamma(1+\alpha_l)(1+iBt)^{-\alpha_l-1}, \tag{2.11}$$

where $\Gamma(x)$ is the gamma function [43]. For all model systems discussed in Sec. V we have $\alpha_l=2.5$, corresponding to d-wave scattering.

The coupling of the electronic resonance with the vibrational modes is determined by the coupling constants c_j in Eq. (2.5). It is convenient to introduce the spectral density function

$$J(\omega)=\frac{\pi}{2}\sum_j c_j^2\delta(\omega-\omega_j), \tag{2.12}$$

which contains the information on both the vibrational frequencies and individual coupling strengths of all vibrational modes. Considering systems with many nuclear degrees of freedom, it is appropriate to approximate the distribution $J(\omega)$ by a continuous function. We adopt here the so-called Ohmic spectral density with exponential cutoff

$$J(\omega)=2\pi\alpha\omega\,\exp(-\omega/\omega_c). \tag{2.13}$$

Here α is the dimensionless Kondo parameter measuring the overall coupling strength of the vibrational degrees of freedom and ω_c is a high-energy cutoff frequency. This spectral function is well known from the extensive literature on the spin-boson problem [26]. The Ohmic bath is the standard model for a dissipative environment as it leads, in the classical limit, to a frictional force that is proportional to the velocity [26,44]. It should be noted that the numerical path-integral method of the present work is not restricted to this special form of the spectral function.

We wish to investigate the time-dependent survival probability of the resonance and its modification by the coupling to the vibrational bath. We assume that at $t=0$ an electron hops into the discrete state (see Ref. [16] for a discussion of the connection of this initial condition with time-independent scattering theory). For a zero-temperature bath, all vibrational modes are in their ground state and the survival probability is given by

$$P_d(t)=\langle\varphi_d|\langle\mathbf{0}|e^{iHt}\mathbf{P}e^{-iHt}|\mathbf{0}\rangle|\varphi_d\rangle, \tag{2.14}$$

where

$$|\mathbf{0}\rangle=\prod_j |\mathbf{0}_j\rangle \tag{2.15}$$

denotes the product of ground states of the bath modes.

For finite temperature, the bath is initially in thermal equilibrium and the product initial state of the bath must be replaced by a Boltzmann weighted sum of product states. We have

$$P_d(t)=\frac{1}{Z_B}\langle\varphi_d|tr_B\{e^{iHt}\mathbf{P}e^{-iHt}e^{-\beta H_0}\}|\varphi_d\rangle \tag{2.16}$$

with

$$Z_B=\mathrm{tr}_B(e^{-\beta H_0}), \tag{2.17}$$

where tr_B denotes the trace over the bath and $\beta=(k_\mathrm{B}T)^{-1}$.

III. PATH-INTEGRAL FORMULATION

In this section we review the derivation of a discretized real-time path-integral expression for the survival probability defined by Eqs. (2.14) and (2.16). The time interval $[0,t]$ is divided into N time slices of equal length $\varepsilon=t/N$. At all intermediate times a complete basis of the electronic Hilbert space is inserted. Making use of the projection-operator properties (2.2) we can write $P_d(t)$ as

$$\begin{aligned}P_d(t)=\langle&\mathbf{P}U(-\varepsilon)[(\mathbf{P}+\mathbf{Q})U(-\varepsilon)]^{N-1}\mathbf{P}U(\varepsilon)\\&\times[(\mathbf{P}+\mathbf{Q})U(\varepsilon)]^{N-1}\mathbf{P}\rangle.\end{aligned} \tag{3.1}$$

Here $U(\varepsilon)=e^{-i\varepsilon H}$ is the elementary time evolution operator of the system and the brackets $\langle\cdots\rangle$ denote the expectation value with respect to the initial state of the vibrational degrees of freedom. Within each elementary time interval the exact propagator is replaced by a first-order approximation, for which the electronic and vibrational degrees of freedom are disentangled. In the limit $N\to\infty$ the discretized path sum converges to the correct result for any fixed propagation time

t according to the Trotter theorem [45]. The elements of the first-order propagator $U^{(1)}(\varepsilon)$ read (see Appendix A in [39] for details)

$$U^{(1)}_{dd}(\varepsilon)=\cos(\varepsilon\sqrt{g})\exp[-i\varepsilon(H_0+V_d+\varepsilon_d)], \tag{3.2}$$

$$U^{(1)}_{dk}(\varepsilon)=-iV_{dk}\sqrt{g}\sin(\varepsilon\sqrt{g}) \times\exp[-i\varepsilon(H_0+V_d/2+\varepsilon_k/2+\varepsilon_d/2)], \tag{3.3}$$

$$U^{(1)}_{kd}(\varepsilon)=-iV^{*}_{dk}\sqrt{g}\sin(\varepsilon\sqrt{g}) \times\exp[-i\varepsilon(H_0+V_d/2+\varepsilon_k/2+\varepsilon_d/2)], \tag{3.4}$$

$$U^{(1)}_{kk'}(\varepsilon)=\delta_{kk'}\exp[-i\varepsilon(H_0+\varepsilon_k/2+\varepsilon_{k'}/2)], \tag{3.5}$$

with

$$g=\int k\ dk\ d\Omega_k|V_{dk}|^2=\int dE\,\frac{\Gamma(E)}{2\pi}. \tag{3.6}$$

The resulting discretized path sum, consisting of $4^{(N-1)}$ paths for N time slices, can be written as a double sum describing all possible combinations of forward and backward paths labeled by the vectors $\vec{f}_f$ and $\vec{f}_b$ of dimension N, respectively. Thereby the propagator associated with the forward path is a product of the N factors in Eq. (3.1), which contain matrix elements of $U^{(1)}(\varepsilon)$, while the propagator associated with the backward path contains matrix elements $U^{(1)}(-\varepsilon)$. The components of these vectors are defined to be 0, if the system propagates in the continuum within the respective interval. If the system propagates in the discrete state, the corresponding component is defined to be 1. If the system undergoes a transition from the discrete state into the continuum or vice versa, it is 1/2. Thereby we assume that during a transition interval the vibrational dynamics is determined by an averaged potential. This third possible value of the components of $\vec{f}_f$ and $\vec{f}_b$ originates in the discretization precedure and should not be confused with a path-integral formulation of a three-state system. For each path the electronic and vibrational degrees of freedom are disentangled due to the construction of the elementary propagator $U^{(1)}(\varepsilon)$. Each vector labeling a forward or backward path defines a piecewise constant function giving rise to an explicitly time-dependent vibrational Hamiltonian for each individual path in a straightforward manner [39].

The survival probability at time t can thus be written as

$$P_d(t)=\sum_{\vec{f}_b}\sum_{\vec{f}_f}P_{\rm el}(\vec{f}_b)P_{\rm el}(\vec{f}_f)\exp[-\Phi(\vec{f}_b,\vec{f}_f)]. \tag{3.7}$$

Here $P_{\rm el}(\vec{f}_f)$ and $P_{\rm el}(\vec{f}_b)$ denote the propagators of the electronic system of the forward and backward path, respectively. $\Phi(\vec{f}_b,\vec{f}_f)$ is the influence functional of Feynman and Vernon describing the influence of the bath on the electronic system [31]. Besides including the time-nonlocal effects concerning the forward (backward) path, the influence functional also takes into account time-nonlocal correlations between the forward and the backward path, which originate from the trace over the bath at the final time $t=N\varepsilon$.

For a double path labeled by the forward vector $\vec{f}_f$ and backward vector $\vec{f}_b$ we introduce the symmetric and antisymmetric variables [28]

$$\vec{\eta}=\vec{f}_f+\vec{f}_b, \tag{3.8}$$

$$\vec{\chi}=\vec{f}_f-\vec{f}_b. \tag{3.9}$$

The corresponding piecewise constant functions are defined analogously. In terms of the new variables the discretized double path sum can formally be written as

$$P_d(t)=\sum_{\{\vec{\chi},\vec{\eta}\}}P_{\rm el}(\vec{\chi},\vec{\eta})\exp[-\Phi(\vec{\chi},\vec{\eta})]. \tag{3.10}$$

In this representation the influence functional reads

$$\Phi(\vec{\eta},\vec{\chi})=\frac{1}{4}\sum_{j=1}^{N}\sum_{k=1}^{j}(\chi_j\chi_kL'_{jk}+i\chi_j\eta_kL''_{jk}). \tag{3.11}$$

The imaginary part of the influence functional depends linearly on the symmetric variable. L'_{jk} and L''_{jk} denote the real and imaginary parts of [46]

$$L_{jk}=\frac{2}{\pi}\int_0^\infty d\omega\,\frac{J(\omega)}{\omega^2}[1-\cos(\omega\epsilon)]\{\coth(\omega\beta/2) \times\cos[\omega\epsilon(j-k)]+i\ \sin[\omega\epsilon(j-k)]\},$$

$$L_{jj}=\frac{1}{\pi}\int_0^\infty d\omega\,\frac{J(\omega)}{\omega^2}\{\coth(\omega\beta/2)[1-\cos(\omega\epsilon)] +i[\sin(\omega\epsilon)-\omega\epsilon]\}. \tag{3.12}$$

For a finite number of vibrational modes or an Ohmic form of the spectral density, the integrals (3.12) can be evaluated in analytical form [28].

Let us now specify the electronic contribution $P_{\rm el}(\vec{\chi},\vec{\eta})$ of Eq. (3.10). It is given by

$$P_{\rm el}(\vec{\chi},\vec{\eta})=\tilde{P}(\vec{\chi},\vec{\eta})P_{\rm mem}(\vec{\chi},\vec{\eta}). \tag{3.13}$$

We now derive an expression for the electronic memory function within the discretized path-integral approach. Suppose a path is hopping from the discrete state into the continuum and propagating there for a certain time interval of length $m\varepsilon$ until it finally returns to the discrete state, which represents a kink of length $m\varepsilon$. According to the matrix elements of the first-order elementary propagator $U(\varepsilon)$, the following propagator corresponds to a kink

$$\sum_{k_{m-1}}\cdots\sum_{k1}U^{(1)}_{dk_{m-1}}(\varepsilon)U^{(1)}_{k_{m-1}k_{m-2}}(\varepsilon)\cdots U^{(1)}_{k_1d}(\varepsilon) =-\frac{1}{g}[\sin(\sqrt{g}\varepsilon)]^2\gamma(m\varepsilon)\exp\{-i\varepsilon[(m+1)H_d]\}. \tag{3.14}$$

Therefore the first factor in Eq. (3.13) is given by

$$\tilde{P}(\vec{\chi},\vec{\eta})=\left(\frac{\sin(\sqrt{g}\varepsilon)}{\sqrt{g}}\right)^{2M_f+2M_b} \times[\cos(\sqrt{g}\varepsilon)]^{2N-M_f-L_f-M_b-L_b} \times\exp[-i\varepsilon(L_f-L_b)\varepsilon_d], \tag{3.15}$$

while P_{mem} reads

$$P_{\mathrm{mem}}(\vec{\chi},\vec{\eta})=\left[\prod_{j=1}^{M_f}\gamma(m_{fj}\varepsilon)\right]\left[\prod_{j=1}^{M_b}\gamma^*(m_{bj}\varepsilon)\right]. \tag{3.16}$$

M_f and M_b are the numbers of kinks in the forward and backward path, and L_f and L_b are the collective numbers of intervals in the continuum for the forward and the backward path, respectively. In Eq. (3.16), $\gamma(t)$ is the electronic memory function defined in Eq. (2.10) arising from the summation over the electronic continuum states during an intermediate propagation in the continuum. Even in the absence of vibrational degrees of freedom, this memory function renders the electronic population dynamics non-Markovian.

Thus the path sum (3.10) can be interpreted as a path sum of a four-state system representing the elements of the effective reduced density matrix. We shall refer to these states as dd if both the forward and backward path are in the discrete state, dk for the forward path in the discrete state and the backward path in the continuum, kd for the forward path in the continuum and the backward path in the discrete state, and kk for both states in the continuum.

The vibrational propagator for a single path is given by a product of propagators of driven harmonic oscillators, reflecting the different electronic-vibronic coupling in the discrete resonance state and the continuum states. As the oscillators are unshifted in the continuum, the vibrational dynamics is equivalent to that of an electronic two-state system. The coupled dynamics, however, differs essentially from the dynamics of the spin-boson model. In the absence of the bath the two-state dynamics exhibits clockwise oscillations in the spin-boson model, whereas the population of the discrete state in the model investigated in this work decays asymptotically due to the coupling to the electronic continuum.

IV. APPROXIMATION METHODS

The numerical evaluation of the path sum given by Eq. (3.10) constitutes a challenging task because of the exponential growth of the number of possible path configurations with the number of elementary intervals. In most practical applications it is impossible to systematically generate and evaluate all configurations. Besides the untractable size of the path sum, its evaluation suffers from the so-called sign problem. It originates from the cancellation of a huge number of complex valued contributions, leading to numerical inaccuracies.

In this work we follow a strategy that is based on the concept of grouping the paths into path classes [39]. This approach has been successfully applied to the calculation of cross sections in resonant electron-molecule scattering, the calculation of absorption spectra of molecules, as well as to the investigation of electron transfer [40,47–51].

The path sum is replaced by a sum over path classes. The exact subsums over the path classes are replaced by approximate, effective expressions, depending on a limited number of parameters only, which can be calculated iteratively. The definition of the path classes is not unique. In the limiting case where each path class consists of a single path only, this approach is, of course, equivalent to the evaluation of the original discretized path sum. The contribution of each path belonging to a certain path class can be considered to factorize into a product of two contributions. One of these factors is invariant within the class, whereas the other varies within the path class. Thus rapidly oscillating contributions are extracted from the subsums over the path classes. If a feasible approximation can be found for the sum over the varying contributions, whose parameters can be calculated iteratively with respect to the length of the path, the sign problem can effectively be reduced.

The paths can be classified by different criteria, rendering the concept very flexible. Choosing a coarse classification, the computational cost can be reduced significantly, but the accuracy of the approximation might become poor. Thus, according to the problem one is dealing with, a compromise between computational effort and desired accuracy of the approximations has to be found.

Let us now specify the classification used in the present work. The contribution $C_{\Upsilon[N,I]}$ of a class $\Upsilon[N,I]$ is defined as the sum over all paths of length N, which end in one of the four states $s\in\{dd,dk,kd,kk\}$ of the reduced system. They are labeled by an additional set of indices I. Here I is chosen as the average of the antisymmetric variable χ, denoted $\overline{\chi}$, and the lengths of the final kink in the forward and backward path, denoted l_f and l_b, respectively. Therefore all paths within a class exhibit the same phase originating from the resonance energy. Note that the final state of the system can always be determined from the indices l_f and l_b. The contribution of a class $\Upsilon[N,\overline{\chi},l_f,l_b]$ to the path sum of the electronic dynamics can thus be formally expressed as

$$\begin{aligned} C_{\Upsilon[N,\overline{\chi},l_f,l_b]} &= P_{\mathrm{inv,el}}(\Upsilon[N,\overline{\chi},l_f,l_b]) \\ &\quad\times\sum_{(\vec{\chi},\vec{\eta})\in\Upsilon[N,\overline{\chi},l_f,l_b]} P_{\mathrm{var,el}}(\vec{\chi},\vec{\eta})\exp[-\Phi(\vec{\chi},\vec{\eta})]. \end{aligned}\tag{4.1}$$

Equation (4.1) is just an exact reformulation of the subsum over all paths within the class $\Upsilon[N,\overline{\chi},l_f,l_b]$, taking into account the explicit definition of the path classes. The phase factor due to the electronic energy is encapsulated in the invariant contribution

$$P_{\mathrm{inv,el}}(\Upsilon[N,\overline{\chi},l_f,l_b])=\exp(-i\varepsilon\overline{\chi}\varepsilon_d). \tag{4.2}$$

The variant contributions $P_{\mathrm{var,el}}(\Upsilon[N,\overline{\chi},l_f,l_b])$ are given in terms of the matrix elements of Eq. (3.15) with ε_d set to zero. The influence functional is given by Eq. (3.11).

Next we outline the recursion for the partial sums in the absence of vibrational degrees of freedom. If we want to calculate the class contributions for N elementary intervals, given the results for $N-1$ elementary intervals, we are faced with the problem that the contribution of a kink can only be evaluated at its end. The reason for this is the fact that no simple functional relation holds for the electronic memory function, i.e., $\gamma(t_1+t_2)\neq\gamma(t_1)\gamma(t_2)$. As a consequence, there is no straightforward scheme for propagation in time. In this respect the present electronic continuum problem differs fundamentally from the electronic two-level problem. To circumvent this problem, we keep track of the lengths of the last kinks in both the forward and backward paths when the system propagates in one of the states $s\in\{dk,kd,kk\}$. Whenever it undergoes a transition into the resonance state, either in the forward and/or backward path the electronic memory function for the forward and/or backward path is multiplied to the corresponding class contribution. Therefore the propagator of the electronic effective reduced system must depend on the lengths of the kinks in the forward and backward paths. Its elements are denoted by $U_{\mathrm{el}}^{(r,s)}(l_f,l_b)$ (see Appendix). Only when at least one of the indices l_f and l_b is zero can the memory function be evaluated. Otherwise the intermediate propagator is simply set to unity. This trick enables us to write down a simple recursion relation for the variant class contributions:

$$
\begin{aligned}
P_{\mathrm{var,el}}(\Upsilon[N+1,\overline{\chi},l_f,l_b])
&= \sum_{\Upsilon[N,\overline{\chi}-\chi_N,l_f',l_b']} U_{\mathrm{el}}^{(l_b,l_f)}(l_f',l_b') \\
&\quad \times P_{\mathrm{var,el}}(\Upsilon[N,\overline{\chi}-\chi_{N+1},l_f',l_b']). \qquad (4.3)
\end{aligned}
$$

If we treat a system without vibrational degrees of freedom, these recursion relations yield the numerically exact result within the chosen discretization. The major difficulty, however, arises from the fact that the vibrational continuum leads to additional non-Markovian memory effects. Therefore we have to introduce a suitable approximation scheme for the vibrational contributions to the path classes, which allows one to construct a propagation scheme consistent with the one introduced for the electronic degrees of freedom.

Let us first inspect the structure of the influence functional given by Eq. (3.11). Consider a path of length $N+1$ labeled by the vectors $\vec{\chi}$ and $\vec{\eta}$. We can write the corresponding influence functional as

$$
\begin{aligned}
\Phi(\vec{\chi},\vec{\eta})[N+1] &= \chi_{N+1}^2 L'_{N+1,N+1} + i\chi_{N+1}\eta_{N+1}L''_{N+1,N+1} \\
&\quad + \Phi(\vec{\chi},\vec{\eta})[N] + \chi_{N+1} \\
&\quad \times \sum_{k=1}^{N} (\chi_k L'_{N+1,k} + i\eta_k L''_{N+1,k}). \qquad (4.4)
\end{aligned}
$$

The first term on the right-hand side of Eq. (4.4) is a local contribution, which only depends on the actual interval and will be denoted Φ_{loc}. The second term describes the influence functional corresponding to the path without the last interval, while the last term describes the correlation of the actual interval with the preceding intervals, which we denote $\delta\Phi$. This last term is the starting point for the definition of our approximation of the vibrational dynamics of the system [51]. From Eq. (4.4) it is clear that the influence functional remains unaltered if the actual interval corresponds to a diagonal state ($\chi_{N+1}=0$). Otherwise the local term can easily be incorporated into the propagator of the electronic system. For a single path the term $\delta\Phi$ can easily be calculated. It is, however, impossible to store all path contributions individually, and therefore approximations are unavoidable. Suppose the path with N intervals lies in the path class $\Upsilon[N,\overline{\chi}-\chi_N,l_f,l_b]$. Then we replace the individual contribution by the mean value over the class it belongs to, that is, $\langle\chi_k\rangle_{\Upsilon[N,\overline{\chi}-\chi_N,l_f,l_b]}$ and $\langle\eta_k\rangle_{\Upsilon[N,\overline{\chi}-\chi_N,l_f,l_b]}$. These mean values can easily be calculated iteratively. We have thus obtained an approximation method in which both the contributions of the electronic as well as the vibrational degrees of freedom are treated in a fully non-Markovian manner.

The chosen classification of paths is demanding, concerning the required memory and CPU time for longer times of propagation. When no cutoffs are applied, the required memory scales as N^3 and the CPU time as N^4, N being the number of elementary intervals.

V. RESULTS

In this work we have considered three model systems. Our primary aim is the demonstration of the feasibility of reliable numerical computations of the short-time decay of an electronic resonance that is coupled to a thermal bath. We are not aware of any results of this kind in the published literature. In future work we plan to explore in more detail the physical mechanisms as well as the application of these techniques to real systems.

Model I pertains to a diatomic molecule. It has been developed previously [22,52] to describe the $^2\Pi_g$ d-wave shape resonance in the electron-N_2 scattering. The $^2\Pi_g$ shape resonance in electron-N_2 scattering is the prototype of a resonance with a lifetime that is comparable to the vibrational frequency. The electron-vibrational coupling is strong and the electronic decay is strongly modified by the vibrational motion. For a more detailed discussion of this system we refer to the literature [16,53,54]. We consider this model here because it allows us to check the path-integral results against a numerically exact calculation. Such benchmarks are not possible for calculations with a multidimensional bath. The parameter values specifying model I are $\varepsilon_d=2.35$ eV, ω=0.29 eV, $c=-0.38$ eV, $A=0.874$ eV, and $B=1.316$ eV.

Figure 1 displays the decay of the resonance on a time scale of 15 fs. The solid line shows the decay of the resonance state in the absence of coupling to the vibrational mode. The decay dynamics is seen to change qualitatively when the electronic dynamics is coupled to the vibrational mode. During the first few femtoseconds the fast decay persists. Between ≈4 and ≈10 fs the population of the resonance exhibits a pronounced plateau that results from the motion of the vibrational wave packet to larger internuclear distances where the electronic decay is slower. Within a vibrational period the wave packet returns to the Franck-Condon region leading again to rapid decay. The plateau reflects the strong coupling between the electronic and the vibrational motions.

The long-dashed curve in Fig. 1 represents the PI calculation, while the short-dashed curve gives the exact reference. Despite the approximate treatment of the vibrational

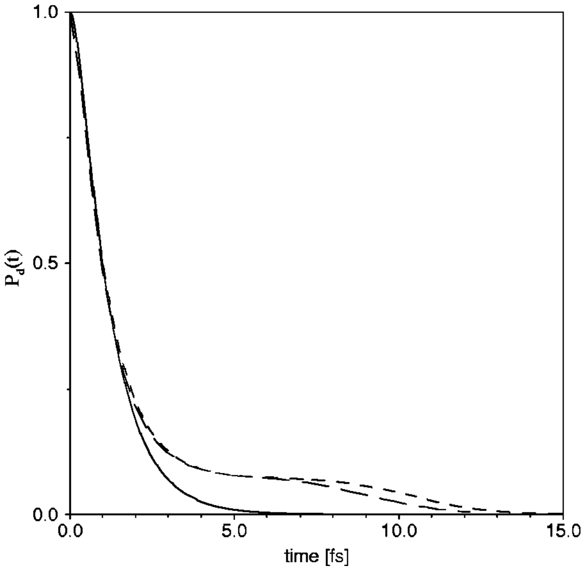

FIG. 1. Population probability $P_d(t)$ for model I. The short dashed line is the reference, the long dashed line gives the result obtained by the PI method. The full line represents the decay of the wave packet in the absence of coupling to the vibrational mode.

dynamics in the PI calculation, the exact result is reproduced very accurately up to 7 fs and qualitatively correctly for longer times.

It should be stressed that this one-dimensional model represents a demanding test of the numerical path-integral approach. The electron-vibration coupling is very strong and the kernel of the influence functional is strictly periodic in this case, i.e., vibrational memory effects persist forever. In multidimensional models, in particular those involving an Ohmic bath, the electron-vibrational coupling strength for each single mode is small and the memory kernel of the influence functional decays rapidly. We are thus confident that the present numerical path-integral calculations are of quantitative accuracy for the model systems that involve an Ohmic bath.

We mention briefly some technical details of the path-integral calculation. A time step of 0.35 fs has been employed. We have evaluated $P_d(t)$ for 87 time steps, which requires 2 Gbyte of computer core memory. The calculation takes about 1 h on a modern workstation. Because the electronic memory function $\gamma(t)$ decays rapidly, we can restrict for the models discussed in this work the numbers $\overline{\chi}, l_h, l_r$ to values below 60. Hence we can reduce the necessary amount of memory and the computation time significantly. For the single-mode case, the path-integral method is of course not competitive with the direct numerical solution of the time-dependent Schrödinger equation. However, the computational cost of the latter approach scales exponentially with the number of vibrational degrees of freedom, while the cost of the former is (for the models considered here) independent of the dimension of the vibrational system.

Model II is obtained from model I by replacing the single vibrational mode by an Ohmic bath, with $\omega_c = 0.2$ eV. The overall electron-vibrational coupling strength, described by the Kondo parameter α, is taken as a variable parameter.

In Fig. 2 we show results for four different vibrational coupling strengths and zero temperature. The solid line corresponds to the case $\alpha = 0$ (same as in Fig. 1), the dotted line gives the population for $\alpha = 0.125$, the dashed line is the result for $\alpha = 0.25$, and the dash-dotted line represents the result for $\alpha = 0.5$. Increasing the coupling strength of the bath systematically reduces the decay rate of the resonance state at intermediate and long times. The effect appears to be qualitatively the same as in the one-dimensional model. Through the coupling to the vibrational modes, the wave packet moves toward the equilibrium configuration of the bath where the electronic decay rate is smaller due to the lowering of the resonance energy.

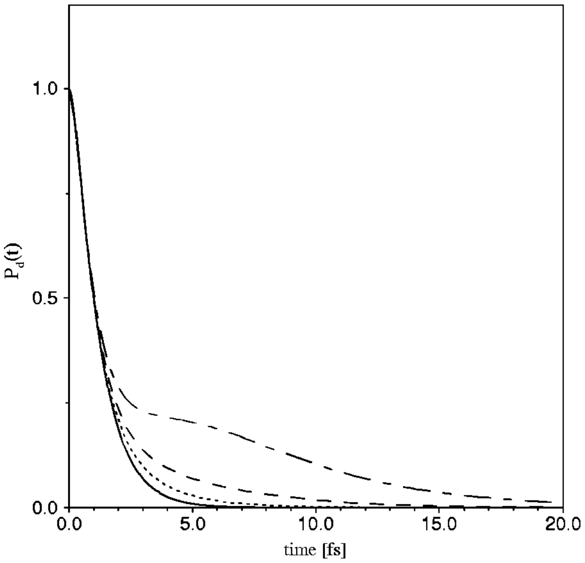

FIG. 2. Population probability for model II for $T = 0$ and different Kondo parameters, $\alpha = 0$ (solid line), $\alpha = 0.125$ (dotted line), $\alpha = 0.25$ (dashed line), and $\alpha = 0.5$ (dash-dotted line).

Figure 3 represents the population dynamics of model II for $\alpha = 0.25$ and different temperatures. The solid line is the result for $T = 0$. The dotted line corresponds to the case

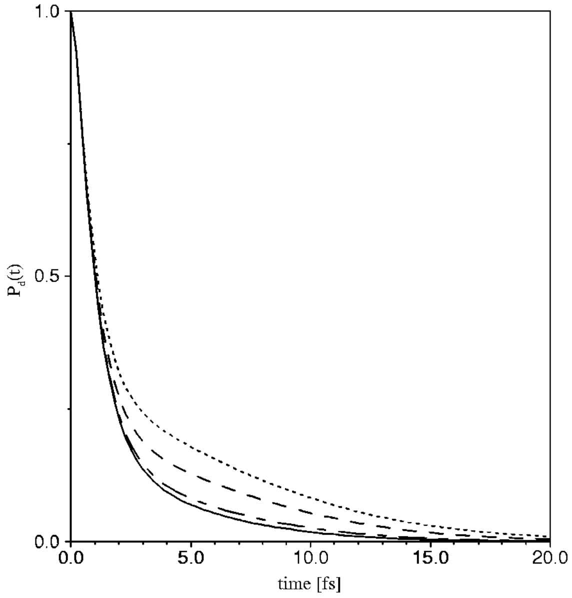

FIG. 3. Population probability for model II for $\alpha = 0.25$ and different temperatures, $T = 0$ (solid line), $\beta = 1.0$ eV^{-1} (dotted line), $\beta = 2.5$ eV^{-1} (dashed line), and $\beta = 10.0$ eV^{-1} (dash-dotted line).

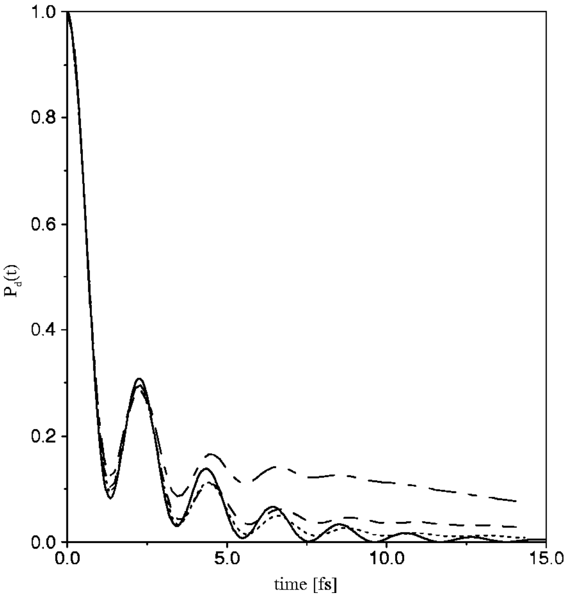

FIG. 4. Population probability for model III, with and without coupling to the bath, at $T=0$. The solid line gives the result without coupling to the bath. The dotted line gives the result for $\alpha=0.125$, the dashed line is the result for $\alpha=0.25$, while the dash-dotted line represents the result for $\alpha=0.5$.

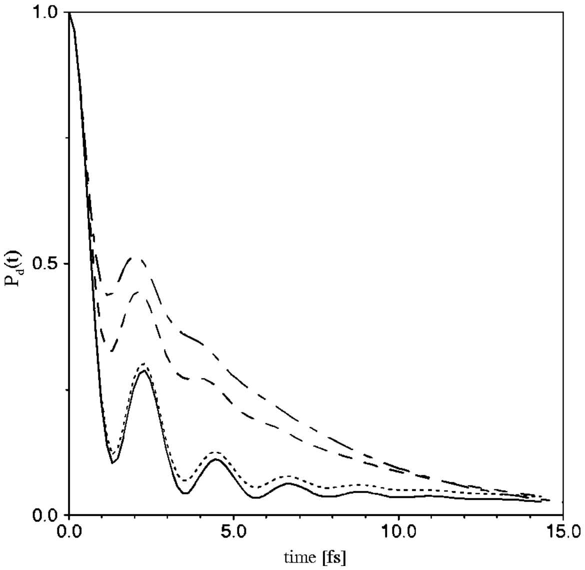

FIG. 5. Population probability for model III, $\alpha=0.25$, and different temperatures. The solid line gives the result for $T=0$. The dotted line represents the result for $\beta=10.0$ eV^{-1}, the dashed line is the result for $\beta=1.0$ eV^{-1}, and the dash-dotted line is the result for $\beta=0.5$ eV^{-1}.

$\beta=1.0$ eV^{-1}, the dashed line gives the result for $\beta=2.5$ eV^{-1}, and the dash-dotted line is the population for $\beta=10.0$ eV^{-1}. One recognizes that the decay at intermediate and long times slows down with raising temperature. This is presumably a consequence of the delocalization of the nuclear density distribution. As we increase temperature, we are initially preparing higher vibrational levels. This widens the Franck-Condon region and thus increases the lifetime of the resonance.

We obtained the results for model II by computing $P_d(t)$ for 100 time steps with a time slice of 0.23 fs. We restricted $\overline{\chi}, l_h, l_r$ to 50, which results in a memory requirement of 227 MB. These calculations take approximately 30 min on a workstation.

In model III we have changed the parameters of the electronic resonance with respect to models I and II. The discrete-state energy ε_d is chosen as 1.5 eV, 1 eV lower than before. The resonance lies thus closer to the threshold. The width function of model II is specified by the parameters $A=3.833$ eV, $B=0.3$ eV. This implies an increase and simultaneously a narrowing of the width function $\Gamma(E)$ such that the overall discrete-continuum coupling strength defined in Eq. (3.6) remains constant. $\Gamma(E)$ is now a more rapidly varying function of energy and electronic memory effects are thus more pronounced than in models I,II. An analysis of the poles of the analytically continued resolvent of model III (in the absence of coupling to the bath) reveals that there are two resonance poles with energies of $\approx$0.06 eV and $\approx$1.9 eV and lifetimes of $\approx$2.8 fs and $\approx$50 fs, respectively. The presence of two poles reflects a breakdown of the Wigner-Weisskopf single-pole approximation.

Figure 4 shows the time evolution of the survival probability for model III with and without coupling to the bath. Let us first discuss the dynamics of the electronic system without coupling to a bath, which is given by the full line. The dynamics exhibits pronounced coherent oscillations with a period of about 2.4 fs, which are a result of the quantum beating of the low-lying and the high-lying resonance, which are separated by 1.8 eV. The envelope decays on a time scale of ≈ 3fs, which corresponds to the lifetime of the high-lying broad resonance.

The remaining curves in Fig. 4 represent $P_d(t)$ obtained for four different vibronic coupling strengths, i.e., $\alpha=0.125$ (dotted line), $\alpha=0.25$ (dashed line), and $\alpha=0.5$ (dash-dotted line), all at $T=0$. It is seen that the lifetime of the electronic population increases with coupling to the bath. Although the time range of our calculations is presently limited to values below 30 fs, we can say that this model is an example where the temporary attachment of the electron is strongly enhanced through the coupling to the Ohmic bath. We also see from Fig. 4 that the amplitude of the quantum beating of the electronic system is suppressed by the coupling to the bath, demonstrating the interference of electronic and vibrational memory effects in this system.

In Fig. 5 we show for $\alpha=0.25$ the population dynamics obtained for four different temperatures, i.e., $T=0$ (solid line), $\beta=10.0$ eV^{-1} (dotted line), $\beta=1.0$ eV^{-1} (dashed line), and $\beta=0.5$ eV^{-1} (dash-dotted line). We recognize that with increasing temperature the coherent oscillations are damped out and the decay of the population slows down.

VI. CONCLUSIONS

We have described a numerical path-integral method that allows the calculation of the time-dependent population dynamics of a metastable electronic state that is coupled to a thermal vibrational bath. The approach is based on the implementation of the well-known Feynman-Vernon influence functional, which accounts for the effects of the vibrational degrees of freedom, into a path-integral description of electronic resonance decay. The numerical evaluation of the path-integral expression is made possible through a recursive partial-summation scheme. This approach allows us to deal with the interplay of quantum mechanical electronic tunneling and dissipative vibrational dynamics without introducing any Born-type or Markov-type approximation. In the present implementation of the method, we can cover a time scale of $\approx$50 fs, which is sufficient for the investigation of environmental effects on the decay of typical shape resonances.

To demonstrate the performance of the method and to check the somewhat complex computer program, we have evaluated the time-dependent electronic population probability for a one-dimensional model problem, for which exact results are available. The new method has then been applied to investigate the effect of Ohmic dissipation on electronic resonance decay, as a function of the coupling strength and the temperature of the bath. For the models considered, the coupling to the bath appears to suppress the electronic decay. The effect increases with the coupling strength and the temperature of the bath.

As far as we know, these are the first quantitative results for any problem of this type. The results obtained in the present work may serve as a benchmark for the testing of more approximate treatments.

The performance of the present path-integral method should be largely independent of the choice of the spectral density of the bath. In the future we plan to consider more general spectral functions, e.g., the case of a strongly coupled reaction mode that in turn is coupled to a thermal bath. An alternative line of future research is the development of approximations that allow the evaluation of the path integral for significantly longer time scales. With such techniques we hope to investigate the expected crossover from quantum mechanical tunneling decay to noise-activated detachment as a function of temperature.

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[1] G. J. Schulz, Rev. Mod. Phys. **45**, 378 (1973).
[2] G. J. Schulz, Rev. Mod. Phys. **45**, 423 (1973).
[3] H. S. Taylor, Adv. Chem. Phys. **18**, 91 (1970).
[4] H. Feshbach, Ann. Phys. (N.Y.) **19**, 287 (1962).
[5] U. Fano, Phys. Rev. **124**, 1866 (1961).
[6] M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964).
[7] L. A. Khalfin, Zh. Éksp. Teor. Fiz. **6**, 1053 (1958) [Sov. Phys. JETP **6(33)**, 1053 (1958)].
[8] R. G. Winter, Phys. Rev. **123**, 1503 (1961).
[9] L. Fonda, G. C. Ghirardi, and A. Rimini, Rep. Prog. Phys. **41**, 588 (1978).
[10] G. Duerinckx, J. Phys. A **17**, 385 (1984).
[11] E. C. G. Sudarshan, C. B. Chiu, and G. Bhamathi, Adv. Chem. Phys. **99**, 121 (1997).
[12] T. Mercouris and C. A. Nicolaides, J. Phys. B **30**, 811 (1997).
[13] A. K. Kazansky, J. Phys. B **30**, 1401 (1997).
[14] B. Gaveau and L. S. Schulman, J. Phys. A **28**, 7359 (1995).
[15] N. F. Lane, Rev. Mod. Phys. **52**, 29 (1980).
[16] W. Domcke, Phys. Rep. **208**, 97 (1991).
[17] J. C. Y. Chen, Phys. Rev. **148**, 66 (1966).
[18] T. F. O'Malley, Phys. Rev. **150**, 14 (1966); **156**, 230 (1967).
[19] J. N. Bardsley, J. Phys. B **1**, 349 (1968); **1**, 365 (1968).
[20] H. Nakamura, J. Phys. Soc. Jpn. **26**, 1473 (1969).
[21] C. J. Gillan, O. Nagy, P. G. Burke, L. A. Morgan, and C. J. Noble, J. Phys. B **20**, 4585 (1987).
[22] H. Estrada and W. Domcke, Phys. Rev. A **40**, 1262 (1989).
[23] C. W. McCurdy and J. L. Turner, J. Chem. Phys. **78**, 6773 (1983).
[24] P. L. Gertitschke and W. Domcke, Phys. Rev. A **47**, 1031 (1993).
[25] P. L. Gertitschke and W. Domcke, Z. Phys. D **31**, 171 (1994).
[26] A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).
[27] R. A. Marcus and N. Sutin, Biochim. Biophys. Acta **811**, 265 (1985).
[28] R. Egger and C. H. Mak, Phys. Rev. B **50**, 15 210 (1994).
[29] H. Grabert and H. Wipf, in *Advances in Solid State Physics*, Vol. 30 (Vieweg, Braunschweig, 1990), p. 1.
[30] S. Han, J. Lapointe, and J. E. Lukens, Phys. Rev. Lett. **66**, 810 (1991).
[31] R. P. Feynman and F. L. Vernon, Ann. Phys. (N.Y.) **24**, 118 (1963).
[32] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).
[33] W. Zwerger, Phys. Rev. A **31**, 1745 (1985).
[34] J. Ankerhold, H. Grabert, and G.-L. Ingold, Phys. Rev. E **51**, 4267 (1995).
[35] J. Ankerhold and H. Grabert, Chem. Phys. **204**, 27 (1996).
[36] H. Grabert and U. Weiss, Z. Phys. B **56**, 171 (1984).
[37] A. O. Caldeira and A. J. Leggett, Ann. Phys. (N.Y.) **149**, 374 (1983).
[38] N. Makri and D. E. Makarov, J. Chem. Phys. **102**, 4600 (1995).
[39] M. Winterstetter and W. Domcke, Phys. Rev. A **47**, 2838 (1993).
[40] M. Winterstetter and W. Domcke, Phys. Rev. A **48**, 4272 (1993).
[41] F. T. Smith, Phys. Rev. **179**, 111 (1969).
[42] L. S. Cederbaum and W. Domcke, J. Chem. Phys. **60**, 2878 (1974).
[43] *Handbook of Mathematical Functions*, edited by M. A. Abramowitz and I. A. Stegun (Dover, New York, 1965).
[44] A. Garg, J. N. Onuchic, and V. Ambegaokar, J. Chem. Phys. **83**, 4491 (1985).
[45] E. Nelson, J. Math. Phys. **5**, 332 (1964).

[46] U. Weiss, *Quantum Dissipative Systems* (World Scientific, Singapore, 1993).

[47] S. Krempl, M. Winterstetter, H. Plöhn, and W. Domcke, J. Chem. Phys. **100**, 926 (1994).

[48] S. Krempl, M. Winterstetter, and W. Domcke, J. Chem. Phys. **102**, 6499 (1995).

[49] H. Plöhn, S. Krempl, M. Winterstetter, and W. Domcke, Chem. Phys. **200**, 11 (1995).

[50] M. Winterstetter and W. Domcke, Chem. Phys. Lett. **236**, 445 (1995).

[51] M. Winterstetter and U. Weiss, Chem. Phys. **209**, 1 (1996).

[52] P. L. Gertitschke and W. Domcke, J. Phys. B **26**, 2927 (1993).

[53] A. U. Hazi, T. N. Rescigno, and M. Kurilla, Phys. Rev. A **23**, 1089 (1981).

[54] A. Herzenberg, J. Phys. B **1**, 548 (1968).