Low temperature electron transfer in strongly condensed phase

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Electron transfer coupled to a collective vibronic degree of freedom is studied in strongly condensed phase and at lower temperatures where quantum fluctuations are essential. Based on an exact representation of the reduced density matrix of the electronic+reaction coordinate compound in terms of path integrals, recent findings on the overdamped limit in quantum dissipative systems are employed. This allows to give for the first time a consistent generalization of the well-known Zusman equations to the quantum domain. Detailed conditions for the range of validity are specified. Using the Wigner transform these results are also extended to the quantum dynamics in full phase space. As an important application electronic transfer rates are derived that comprise adiabatic and nonadiabatic processes in the low temperature regime including nuclear tunneling. Accurate agreement with precise quantum Monte Carlo data is observed.

I. INTRODUCTION

Electron transfer (ET) in complex environments is ubiquitous in physics, chemistry, and biology, the most prominent example being photosynthesis \[1, 2\]. In the last decade with the advent of pump-probe techniques the detection of fast electron transfer dynamics in molecular systems became accessible and meanwhile even coherent vibronic motion interacting with transfer processes has been observed in a variety of condensed phase structures \[3\]–\[14\]. Experimentally, the transfer dynamics depends very sensitively on a bunch of parameters such as temperature, electronic couplings, structure of the environmental degrees of freedom, to name but a few.

Despite this complexity theoretical foundations to describe these systems have already been laid in the 80ties with the pioneering work by Marcus et al. \[1\]. It turned out that qualitatively two dynamical domains must be distinguished: For vibronic dynamics fast compared to the bare ET, characteristic for long-distance ET, one speaks of nonadiabatic reactions, in the opposite case of very slow vibronic motion, realized e.g. in mixed-valence compounds, the reaction is said to be adiabatic. Tremendous progress towards a deeper understanding of this picture has been made for the archetypical case of donor-acceptor systems, especially based on descriptions that include the coupling to the residual molecular degrees of freedom also at lower temperatures. The common strategy starts from system+reservoir models and considers the reduced dynamics of the system (relevant degrees of freedom) only \[15\]. In this context a standard treatment has been Redfield theory \[16\]–\[19\], but also path integral approaches have been exploited \[15\], the latter one particularly suitable for strongly condensed phase systems. Within these formulations transfer rates have been successfully calculated in the nonadiabatic regime over the whole temperature range by invoking golden rule techniques. Likewise, rate calculations for adiabatic reactions at sufficiently high temperatures exploited well-established tools for activated rare events as e.g. Kramers’ flux over population method. These quite different approaches reflect the different physical processes that control the transfer, namely, in the former case the electronic coupling between diabatic donor/acceptor states, in the latter one the sluggish activated bath motion on the lower adiabatic surface. To find a formulation that interpolates, at least partially, between these distinct dynamical ranges has been one of the fundamental problems in ET theory.

A crucial step forward into this direction has been first achieved by Zusman \[20\] and then later within the path integral approach by Garg et al. \[21\]. For sufficiently high temperatures and moderately fast to slow bath modes they derived equations of motion for the electronic dynamics interacting with a damped collective degree of freedom, coined the reaction coordinate (RC). In essence, a classical overdamped RC motion (Smoluchowski limit) is coupled to the Heisenberg equations of the electronic degree of freedom. These so-called Zusman equations (ZE) not only opened the door to study the relaxation dynamics of the compound in detail \[22\], but also to derive an explicit expression for the relaxation rate \[21\]. The Marcus/Zusman rate comprises to some extent nonadiabatic and adiabatic dynamics as well, and reduces to the high temperature golden rule result for small electronic coupling and to the corresponding activated Kramers rate for large coupling. A thorough discussion of the various rate expressions and their performance in comparison with precise quantum Monte Carlo results has been given in \[26\].
The only range where so far no analytical description has been available includes moderately fast to slow bath modes as in the ZE, but at low temperatures. For a RC this domain corresponds to overdamped quantum dynamics which has been analyzed only recently in [27, 28]. There it has been shown that the position probability distribution of a RC obeys a Smoluchowski type of equation also at lower temperatures with a substantial impact of quantum fluctuations; for high temperatures the quantum Smoluchowski equation reduces to the known classical one. The basic idea of the present work is now to investigate to what extent these findings can be adapted to the ET problem and to arrive at a generalization of the ZE to the quantum domain. For that purpose the path integral representation must be utilized meaning here to start with the exact density matrix of the reduced dynamics for the electron+RC. Fortunately, the corresponding rather involved calculation has already been carried out in [29]. In the sequel, we directly built on these achievements and derive in a kind of semiclassical analysis from the exact expression approximate generalized Zusman equations (GZE). One particular advantage of the approach is that the approximations are well controlled and detailed conditions for the range of validity of the GZE can be given.

The article is organized as follows. We introduce the model and collect the main results for the reduced dynamics in Sec. II. In Sec. III we start with a discussion of the quantum Smoluchowski limit to proceed with the derivation of the generalized Zusman equations from the exact path integral expression. An extension to the full RC phase space in terms of Wigner functions is achieved in Sec. IV. As an application we derive in Sec. V an analytic expression for the ET rate which generalizes the classical Zusman result to lower temperatures and compares well with numerically exact quantum Monte Carlo data. Conclusions are given in Sec. VI.

II. MODEL HAMILTONIAN AND REDUCED DENSITY MATRIX

We consider intermolecular ET between localized electronic states, called donor and acceptor henceforth, in presence of a vibronic environment. Basically two models have been developed to describe the dynamics of this compound, namely, the spin-boson model [30] and the reaction coordinate (RC) model [21]. Within the reduced subspace of the electronic dynamics both models are completely equivalent, but they differ in the representation of the environmental degrees of freedom and thus allow to focus on different aspects of the transfer process. In the spin-boson model the electronic two-state system is linearly coupled to a bath of harmonic oscillators, while in the reaction coordinate picture the electronic system interacts with a collective bath degree of freedom (reaction coordinate) which is embedded in a harmonic environment. The latter modeling allows to study explicitly the combined dynamics of electronic and collective vibronic motion and particularly the influence of vibronic wave packet motion onto the transfer process.

A. Electron Transfer Model

The corresponding reaction coordinate Hamiltonian consists of four parts, namely,

\[ H = H_{EL} + H_{RC} + H_I + H_B \]

where

\[ H_{EL} = -\frac{\hbar \epsilon}{2} \sigma_z - \frac{\hbar \Delta}{2} \sigma_x \]

represents the bare electronic two-state system as an artificial spin-$\frac{1}{2}$ system with donor $|\text{−}\rangle$ and acceptor $|\text{+}\rangle$, a bias $\hbar \epsilon$, and an ET coupling $\hbar \Delta$ which is assumed to be independent of the nuclear degrees of freedom. The second part

\[ H_{RC} = \frac{p^2}{2m} + \frac{m \omega_0^2}{2} q^2 - c_0 q \sigma_z \]

describes a harmonic collective vibronic degree of freedom (reaction coordinate, RC) linearly coupled to the electronic system and interacting with a heat bath of residual molecular degrees of freedom

\[ H_I = -q \sum c_j y_j + q^2 \sum \frac{c_j^2}{2m_j \omega_j^2} \]

\[ H_B = \sum \left\{ \frac{p_j^2}{2m_j} + \frac{m_j \omega_j}{2} y_j^2 \right\} . \]

This way the environmental oscillators couple to the transfer system only indirectly via the reaction coordinate $q$ (secondary bath). Of course, one could transform both $q$ and $\{y_j\}$ to normal modes which leads to the spin-boson
model \[21, 31\]. Here, however, we are interested in the combined dynamics of spin+reaction coordinate and thus need to calculate the time-dependent reduced density matrix \(\rho_{\sigma, \sigma'}(q, q', t)\) obtained by integrating out the secondary bath. This can be done exactly as we have shown in \[29\], and we will summarize the main findings in the next section.

Before we do so, let us address the initial condition for the time evolution which turns out to be a crucial point, especially in the strongly condensed phase limit. We imagine a donor state as being excited from some ground state (dark state) at time \(t = 0\) (see fig. 1). The excitation pulse is assumed to be sufficiently short so that there are no correlations between the electron and its surrounding at \(t = 0\) meaning that the total initial density matrix \(W_0\) factorizes into a direct product of a projector onto a pure donor state and a density operator \(\rho_0\) of RC and secondary bath, i.e.,

\[
W_0 = |-\rangle \langle -| \otimes \rho_0 .
\]

The generalization to other electronic initial states is straightforward (see below). For \(\rho_0\) two qualitatively different cases have to be distinguished. In the first one RC and secondary bath factorize corresponding to an uncorrelated initial state. This “preparation” is well-known from Feynman-Vernon theory \[32\] and is clearly reasonable if RC and bath are only weakly coupled. In case of strong coupling, however, it is more realistic to assume a correlated initial state \[32\]

\[
\rho^\text{cor}_{0}(q, q', \{y_n\}, \{y'_n\}) = \lambda(q, q') \hat{\rho}_\beta(q, \{y_n\}, q', \{y'_n\})
\]

with the equilibrium density matrix of RC and secondary bath in the don or state \[33\]

\[
\hat{\rho}_\beta(q, \{y_n\}, q', \{y'_n\}) = \frac{1}{Z_{\text{B,RC}}(q, \{y_n\})} \exp \left[ -\beta \left( H_B + H_I + \frac{p^2}{2m} + \frac{m\omega^2}{2} q^2 + cnq \right) \right] |q', \{y'_n \}\rangle
\]

at inverse temperature \(\beta = 1/k_B T\) and with \(Z_{\text{B,RC}}\) the partition function of the bath+RC compound. Deviations from equilibrium in the RC are created by a preparation function \(\lambda(q, q')\). In fact, only starting with correlated initial states guarantees to regain from the exact quantum dynamics of the RC in the high temperature/strong damping limit the so-called Smoluchowski equation for its position probability distribution \[34, 35\].

**B. Reduced Dynamics**

Exploiting Feynman’s path integral formalism for the time propagation of the reduced density

\[
\rho(t) = \text{Tr}_B \{ \exp(-iHt/\hbar)W_0 \exp(iHt/\hbar) \}
\]

the harmonic degrees of freedom of the secondary bath can be eliminated exactly \[37, 37\]. This leads to the exact expression

\[
\rho_{\sigma_f \sigma'_f}(q_f, q'_f, t) = \int_{\sigma(0) = -1}^{\sigma(t) = \sigma_f} D\sigma \int_{\sigma(0) = -1}^{\sigma(t) = \sigma'_f} D\sigma' \exp^{i(S_{\text{EL}}[\sigma] - S_{\text{EL}}[\sigma'])} \hat{\rho}(q_f, q'_f, t; [\sigma], [\sigma']) .
\]

Here, forward and backward electronic path \(\sigma(s), \sigma'(s)\) connect in time \(t\) the initial points \(\sigma(0) = -1, \sigma'(0) = -1\) with \(\sigma_f, \sigma'_f\) where each path is weighted with the bare electronic action \(S_{\text{EL}}\) and the density matrix of the damped RC. The latter takes the form

\[
\hat{\rho}(q_f, q'_f, t; [\sigma], [\sigma']) = \frac{1}{Z} \int_{-\infty}^{\infty} dq_i dq'_i \lambda(q_i, q'_i) J(q_f, q'_f, t, q_i, q'_i; [\sigma], [\sigma'])
\]

where the propagating function \(J(\cdot)\) is a threefold path integral (two in real time, one in imaginary time) over the RC degree of freedom. The forward and backward real time paths \(q(s), q'(s)\) run in time \(t\) for given electronic paths \(\sigma(s), \sigma'(s)\) from \(q_i, q'_i\) to fixed end points \(q_f, q'_f\), while the imaginary time paths \(\tilde{q}(\tau)\) connect \(q_i\) with \(q'_i\) in the interval \(h/\beta\). The contribution of each path is weighted according to its effective action \(\Sigma_{\text{RC}}\), i.e.,

\[
\Sigma_{\text{RC}}[\tilde{q}, q, q'; \sigma, \sigma'] = iS_{\text{RC}}[\tilde{q}] + S_{\text{RC}}[q; \sigma, \sigma'] - S_{\text{RC}}[q'; \sigma, \sigma'] + \phi[\tilde{q}, q, q'] .
\]

It consists of the bare actions of the RC system according to \(H_{\text{RC}}\) \[49\] in real and imaginary time and the so-called influence functional describing the effective influence of the secondary bath onto the RC. The real time paths encode the dynamics of the RC system and the imaginary time paths specify its initial preparation, namely

\[
\hat{\rho}(q_f, q'_f, 0; \sigma_f, \sigma'_f) = \frac{1}{Z} \lambda(q_f, q'_f) \hat{\rho}_\beta(q_f, q'_f)
\]
bath oscillators which, as a classical quantity, can be obtained from molecular dynamics simulations. For real times the corresponding somewhat involved calculation to obtain the reduced density of the RC has been presented in \[29\].

The exponent $\Sigma$ is the effective action evaluated at the minimal action paths and is directly related to the macroscopic damping kernel $\gamma(s) = \frac{2}{\hbar} \int_0^\infty \frac{d\omega}{\pi} \frac{I(\omega) \cos(\omega s)}{\sinh(\omega \beta/2)}$ (15)

via $K'(s) = (m/2)\gamma(s)/ds$ and $K''(s) \to m\gamma(s)/\hbar\beta$ in the classical limit $\omega_c \hbar \beta \ll 1$ with a typical bath frequency $\omega_c$ usually taken as the bath cut-off frequency. The damping kernel produces interactions along the RC paths that are non-local in time even in cases where $\omega_c$ is very large and thus, classically, the corresponding bath memory time very short. This is due to quantum fluctuations that appear on a time scale $\hbar\beta$ and are responsible for non-Markovian behavior at lower temperatures.

C. Exact Reduced Density Matrix for the Reaction Coordinate

For given electronic paths the dissipative dynamics of the RC looks like the dynamics of a damped harmonic oscillator in presence of force fields \[33\]. The crucial difference to the case of an external force, however, is the fact that electronic forward and backward paths are not identical, but rather are dynamical degrees of freedom as well. The corresponding somewhat involved calculation to obtain the reduced density of the RC has been presented in \[29\]. Eventually, one ends up with an exact expression for the reduced dynamics of the RC

$$\tilde{\rho}(x_f,r_f,t;[\chi],[\eta]) = \frac{1}{N(t)} \int dx_i dr_i \lambda(x_i,r_i) \exp \left[ i \frac{1}{\hbar} \Sigma_{\text{ma}}(x_f,r_f,t,x_i,r_i;[\chi],[\eta]) \right]$$

where for convenience we introduced sum and difference paths for the spin

$$\chi = (\sigma - \sigma')/2, \quad \eta = (\sigma + \sigma')/2$$

and sum and difference coordinates for the RC

$$x_\alpha = q_\alpha - q'_\alpha, \quad r_\alpha = (q_\alpha + q'_\alpha)/2, \quad \alpha = i, f.$$  

The exponent $\Sigma_{\text{ma}}$ is the effective action evaluated at the minimal action paths and $N(t)$ is the normalization. The explicit form of both is not very illuminating (for details see \[29\]). $\Sigma_{\text{ma}}$ is a quadratic function of the RC-coordinates with time dependent coefficients that are functionals of $\chi(s)$ and $\eta(s)$, while $N(t)$ depends only on time. For given spin paths their time dependence can be completely expressed in terms of the real and imaginary parts of the autocorrelation function of a damped harmonic oscillator $\langle \Theta(t) \rangle$.

The exact dynamics of the electronic+RC system in presence of the residual vibronic degrees of freedom is now given by \[10\] together with \[10\]. If one would integrate over the diagonal part $\tilde{\rho}(0,r_f,t;[\chi],[\eta])$ too by putting $\lambda = 1$, one would recover the exact reduced path integral expression for the reduced spin-boson dynamics. Here, however, we are able to study the relaxation dynamics of the RC starting with nonequilibrium initial states explicitly. For that purpose what remains to be done, is an evaluation of the spin path integrals which is not possible analytically. The fundamental complication lies in the self-interactions, non-local in time, and mediated by the secondary bath. As a consequence, the dynamics of the density matrix $\rho_{\sigma\sigma'}(x_f,r_f,t)$ can in general not be determined from simple equations of motions so that one has to work within the path integral representation. Progress can be made by
applying either numerical methods like Quantum Monte Carlo techniques\[20\] or perturbative approaches like e.g. NIBA or golden rule\[15\]. As was shown by Zusman\[20\] and then in detail by Garg et al.\[21\] particularly the high temperature/strong damping limit allows for an effectively Markovian description. There, only the diagonal part

\[ P_{\sigma f,\sigma f'}(q_f,t) = \rho_{\sigma f,\sigma f'}(x_f = 0, r_f = q_f, t) \]  

(19)

is relevant and its time evolution is determined by a set of equations of motion where the bare electronic dynamics is coupled to a classical overdamped RC motion (Smoluchowski limit). Our first goal is to derive generalized Zusman equations which are also valid in the low temperature range.

### III. GENERALIZED ZUSMAN EQUATIONS

While the strong friction limit is well-known in classical mechanics\[38\], corresponding quantum systems have been analyzed only recently\[27\]. Hence, in this section we first summarize some main findings which then serve as a basis for the treatment of the ET system with overdamped RC.

#### A. Classical and Quantum Smoluchowski Limit

The strong friction limit in classical physics, known as the Smoluchowski limit, is characterized by a separation of time scales between equilibration of momentum and equilibration of position. This allows to adiabatically eliminate the momentum from the phase space Fokker-Planck equation and to gain a simple time evolution equation for the position distribution, the Smoluchowski equation\[39\]. In case of a harmonic oscillator with frequency \(\omega_0\) the basic condition then is \(\gamma \gg \omega_0\) where \(\gamma\) denotes a typical damping strength. This is defined as

\[ \gamma \equiv \hat{\gamma}(0) = \lim_{\omega \to 0} \frac{I(\omega)}{m \omega} \]  

(20)

with \(\hat{\gamma}(\omega)\) the Laplace transform of \(\gamma(t)\)\[15\]. For instance, in case of ohmic friction \(I(\omega) = \gamma m \omega\) and also for the more realistic Drude damping (also called Debye spectral density) \(I(\omega) = m \gamma \omega \omega_c/(\omega^2 + \omega_c^2)\) one has \(\gamma = \hat{\gamma}\). Since one is interested in the dynamics on long time scales where the position distribution equilibrates, only the low frequency modes of the residual degrees of freedom are relevant. Now, for overdamped quantum systems given a typical frequency \(\omega_0\) of the bare system, e.g. its ground state frequency, by strong damping we mean

\[ \frac{\gamma}{\omega_0^2} \gg \hbar \beta, \frac{1}{\omega_c}, \frac{1}{\gamma}. \]  

(21)

In other words, the time scale separation known from the classical Smoluchowski limit is extended in the quantum domain to incorporate also the time scale for quantum fluctuations \(\hbar \beta\). Correspondingly, one considers the dynamics on a coarse grained time scale \(s \gg \hbar \beta, 1/\omega_c, 1/\gamma\) in real time and \(\tau \gg 1/\omega_c, 1/\gamma\) in imaginary time. The consequences are substantial: (i) The strong friction limit suppresses non-diagonal elements of the reduced density matrix during the time evolution. This simply reflects the fact that a quantum system tends to behave more classically, the stronger coherences are destroyed in presence of a heat bath. (ii) The real-time part of the damping kernel \(K(s)\) becomes local in time so that a time evolution equation of the form \(\ddot{\rho}(t) = \mathcal{L} \rho(t)\) with a time independent operator \(\mathcal{L}\) may exist. For the quasi-ohmic case \(\omega_c \gg \gamma\) considered in the sequel the corresponding range in parameter space covered by (21) is shown in fig. 2. It is well separated from the weak friction limit region and comprises temperatures from the classical \(\gamma \hbar \beta \ll 1\) to the deep quantum domain \(\gamma \hbar \beta \gg 1\).

This way it has been shown in\[27\] that for continuous systems moving in sufficiently smooth potentials \(V(q)\) the diagonal part of the reduced density matrix \(P(q,t) = \rho(q,q,t)\) obeys the equation of motion \(\dot{P}(q,t) = \mathcal{L}_{QS} P(q,t)\) with

\[
\mathcal{L}_{QS} = \frac{1}{\gamma m} \frac{\partial}{\partial q} \left\{ V'(q) + \frac{\partial}{\partial q} \left[ \frac{1}{\beta} + AV''(q) \right] \right\}
\]  

(22)

where \(\cdot\) abbreviates \(d/dt\), \(\cdot\) stands for \(d/dq\), and \(V_{\text{eff}} = V + AV''/2\). Here

\[
\Lambda = \frac{2}{\hbar \beta} \sum_{n=1}^{\infty} \frac{1}{\nu_n^2 + \nu_n \hat{\gamma}(\nu_n)}
\]  

(23)
with Matsubara frequencies $\nu_n = 2\pi n / \hbar \beta$ measures typical quantum fluctuations in position space. In the high temperature range $\gamma \hbar \beta \ll 1$ these are negligible and one recovers the classical Smoluchowski operator $L_{\text{CLS}} = L_{\text{QS}}(\Lambda = 0)$. For low temperatures, however, quantum effects appear and for $\gamma \hbar \beta \gg 1$ we find $\Lambda \approx (\hbar / m \gamma) \ln(\gamma \hbar \beta / 2\pi)$. In the specific case of a harmonic oscillator the diffusion coefficient in $L_{\text{QS}}$ becomes independent of position and differs from the classical one just by a renormalized temperature $1 / \beta \to 1 / \beta + \Lambda m \omega_0^2$. Moreover, one has $\langle q^2 \rangle \approx \langle q_e^2 \rangle + \Lambda$.

Indeed, the strong coupling treatment even extends to classical phase space so that the Wigner transform $W(p,q,t)$ of the density matrix $\rho(q,q',t)$ satisfies a quantum Fokker-Planck equation \[25\]. As the quantum fluctuations in position are squeezed by friction, the quantum fluctuations in momentum are enhanced. Namely, for $\gamma \hbar \beta \gg 1$ they grow like $\langle p^2 \rangle \approx (m \hbar \gamma / \pi) \ln(\omega_e / \gamma)$.

Based on these results we now want to derive from the exact density matrix $\tilde{\rho_{q,q',t}}(x_f,r_f,t)$ in \[11\] approximate equations of motion for its diagonal elements in case of an overdamped RC. We know that in the classical realm $\gamma \hbar \beta \ll 1$ this leads to the so-called Zusman equations \[ZE\]. A naive expectation would be just to replace the classical operator for the RC motion $L_{\text{cl}}$ by its quantum version $L_{\text{QS}}$ meaning simply to renormalize temperature. The detailed calculation, however, shows that this covers only part of the quantum effects and that they also affect the coupling between electronic and RC system. In particular, due to the coarse graining \[21\] the short time expansion ($\gamma t \ll 1$) used in the high temperature limit by Garg et al. is not applicable at lower temperatures where $\gamma \hbar \beta \gtrsim 1$. This complicates the analysis considerably.

**B. Equations of Motions**

According to the above discussion we restrict ourselves in the sequel to the case $x_f = 0$ and consider the time evolution of $P_{\sigma_f,\sigma'_f}(q,t)$ on the coarse grained time scale \[20\] starting with preparations $\tilde{\lambda}(r_i) = \lambda(x_i = 0, r_i)$.

Then, the $x_f$-integration in \[10\] can be performed exactly and one has for the diagonal part of the RC-reduced density $\tilde{P}(q,t;[\chi],[\eta]) = \tilde{\rho}(x_f = 0, q,t;[\chi],[\eta])$ on the coarse grained time scale

$$
\tilde{P}(q,t;[\chi],[\eta]) = \frac{1}{N(t)} \int dr_i \tilde{\lambda}(r_i) \exp \left[ \frac{i}{\hbar} \tilde{\Sigma}_{\text{ma}}(q,t,r_i;[\chi],[\eta]) \right]
$$

with the normalization

$$
N(t) = \left\{ \frac{2\pi \langle q^2 \rangle}{\langle q^2 \rangle^2 + S(t)^2} \right\}^{1/2}
$$

and the effective action

$$
\frac{i}{\hbar} \tilde{\Sigma}_{\text{ma}}(q,t,r_i;[\chi],[\eta]) = -\frac{r_i^2}{2\langle q^2 \rangle} - \frac{1}{2\langle q^2 \rangle (1 - \frac{S(t)}{\langle q^2 \rangle})} \left( q - \frac{S(t)}{\langle q^2 \rangle} r_i \right)^2
$$

$$
-\Phi_q([\chi],[\eta],t) r_i - \Phi_q([\chi],[\eta],t) q - \Phi_0([\chi],[\eta],t).
$$

Here, the first term describes the equilibrium distribution of the RC with $\langle q^2 \rangle \approx 1 / m \beta \omega_0^2 + \Lambda$ the variance of the overdamped RC and $S(t)$ is the symmetrized (real) part of the position autocorrelation function

$$
\langle q(t)q \rangle = \frac{1}{2} \langle q(t)q + q(t)q \rangle - i \frac{1}{2} \langle q(t)q - q(t) \rangle = S(t) + i A(t).
$$

On the coarse grained time scale these correlation functions simplify to read

$$
S(t) \approx \langle q_e^2 \rangle e^{-\omega_0^2 t / \gamma}, \quad A(t) \approx -\frac{\hbar}{2m\gamma} e^{-\omega_0^2 t / \gamma}.
$$

Eventually, the time dependent coefficients $\Phi_j, j = r,q,0$ are functionals of the electronic paths and are specified in Appendix A.

The crucial point is now to take into account the impact of the sluggish RC motion onto the electronic dynamics. For the spin held fixed, the RC relaxes on one of the diabatic surfaces (see also fig. 1)

$$
V_0(q) = \frac{m \omega_0^2}{2} \left( q - \frac{c_0}{m \omega_0^2} \eta \right)^2
$$

(29)
where \( f \) is the function which with \( \eta(0) = -[+] \) for donor [acceptor], the relative position of which is characterized by the reorganization energy

\[
E_r = 2m\omega_0^2 q_0^2 \quad \text{with} \quad q_0 = \frac{c_0}{m\omega_0^2}. \tag{30}
\]

A dynamical spin causes transitions between these surfaces that are most likely to occur in the Landau-Zener (LZ) region around \( q = 0 \) where the diabatic potential surfaces intersect. For the motion within this region the time scale of the RC dynamics is \( t_{LZ} \) which is the typical time a RC trajectory lives in the LZ range before relaxing towards the donor/acceptor minima. The electronic dynamics starts from a diagonal state, the donor, and finally reaches the other diagonal state, the acceptor, via jumps through the non-diagonal states ("blips"). The bare spin dynamics can thus be visualized as jumps along the edges of a square where the corners represent the spin-Hilbert space. Now, this square follows the slow RC motion in such a way that blips appear substantially only if the RC lies in the LZ range, while the spin essentially rests in one of its diagonal states away from it. For sufficiently large reorganization energies \( \beta E_r \gg 1 \) the probability for the RC to be activated into the LZ region is small [of the order of the activation rate \( k_{act} \approx \omega_0 \exp(-\beta E_r) \)] and one has a separation of time scales between the dwell times of the spin in its diagonal and nondiagonal states, respectively, namely \( t_{act} = 1/k_{act} \gg t_{blip} \). This scenario allows for a perturbative treatment where it suffices to assume \( h\beta \ll t_{blip} \ll t_{LZ} \ll \gamma/\omega_0^2 \).

To summarize the situation: We assume an overdamped RC coupled to a spin, activated by a rare event into the LZ range where it diffuses for times of order \( t_{LZ} \) while the spin jumps between diagonal \((\eta = \pm 1, \chi = 0)\) and nondiagonal \((\eta = 0, \chi = \pm 1)\) states on a time scale of the order of \( t_{blip} \), i.e.,

\[
\frac{1}{\gamma} \ll h\beta \ll t_{blip} \ll t_{LZ} \ll \frac{\gamma}{\omega_0^2} \ll t_{act}. \tag{31}
\]

These conditions serve as the starting point for a perturbative approach and will be confirmed self-consistently afterwards.

The immediate consequence of (31) is that for times \( t \gg t_{blip} \) integrals in the functionals \( \Phi_j(\eta, \chi, t) \) containing \( \chi \)-spin paths are approximated by

\[
\int_0^t ds \chi(s) f(s) \approx \int_{t-t_{blip}}^t ds \chi(s) f(s) = \int_0^{t_{blip}} ds \chi(t-s) f(t-s), \tag{32}
\]

where \( f(s) \) denotes smooth time dependent functions decaying to zero on the time scale \( t_{LZ} \). The typical magnitude of these integrals is thus of order \( t_{blip} |f(t)| \) and therefore much smaller than integrals of the form

\[
\int_0^t ds \eta(s) f(s) \approx \eta(t) \int_0^t ds f(s) \tag{33}
\]

which are of order \( t_{LZ} \max_{0 \leq s \leq t} |f(s)| \). Of course, the above simplifications do not apply to all possible spin paths, but rather only to those that are assumed to give the dominant contributions to the path integral (10). Accordingly, spin dependent terms in the action (26) of the order of \( t_{blip} \Lambda \) or smaller are neglected against terms of order 1 or larger (for details see Appendix A).

Along these lines the action (26) reduces to

\[
i\frac{\hbar}{\bar{\hbar}} \sum_{\text{ma}}(q, r_i; [\chi], \eta_f) \approx -\frac{r_i^2}{2(q^2)} - \frac{1}{2(q^2)(1 - \frac{S(t)}{q^2})} \left[ q - \frac{S(t)}{(q^2)} r_i + \frac{c_0}{m\omega_0^2} \eta_f \right]^2 \tag{34}
\]

\[+ i \frac{c_0}{\hbar} \frac{\langle q^2 \rangle_{\chi\eta}}{q^2} \int_0^t ds \chi(s) \]

where we used \( \eta_f = \eta(t) \). If we take the limit \( t \to 0 \) with the exact \( S(t) \) [and not its coarse grained form (28)] only the first two terms survive: Together with \( \bar{N}(t) \) the second one gives rise to a \( \delta \) function which with \( \eta(0) = \eta_f = -1 \) restricts \( r_i \) to \( r_i = q + (c_0/m\omega_0^2) \) so that one regains from the first term the equilibrium distribution of the RC in the donor state. Deviations from this equilibrium are described by the preparation function \( \lambda(r_i) \). For finite times the first two terms describe the dynamics of an overdamped harmonic oscillator in presence of a constant external force \( \eta_f c_0/m\omega_0^2 \). The last term with the \( \chi \)-electronic path can be interpreted as an effective RC-dependent energy bias of the bare electronic system and can thus be incorporated into an effective electronic Hamiltonian

\[
H_{E,\text{eff}}(q) = -\frac{\hbar \Delta}{2} \sigma_x - \hbar \left( \frac{\epsilon + 2c_0}{\hbar \kappa} q \right) \sigma_z \tag{35}
\]
with $\kappa = \langle q^2 \rangle / \langle q^2 \rangle_{cl}$. Accordingly, in the reduced density matrix \(^{10}\) we are now able to re-express the path integrals over the electronic paths in terms of matrix elements and obtain for its diagonal part with respect to the RC

$$P_{\sigma_i,\sigma'_i}(q,t) = \frac{1}{N(t)} \int dr_i \hat{\lambda}(r_i) e^{\Sigma_{RC}(q,t;r_i;\eta_f)} \langle \sigma_f | e^{-\hat{H}_{EL} \int dt} | - \rangle \langle - | e^{\hat{H}_{EL} \int dt} | \sigma'_f \rangle$$ (36)

where $\Sigma_{RC}(q,t;r_i;\eta_f)$ comprises the first two ($\chi$ independent) terms in \(^{34}\). By replacing $\tilde{\lambda}(r_i)|-\rangle\langle -| \to \sum_{\sigma_i,\sigma'_i} \lambda_{\sigma_i,\sigma'_i}(r_i) |\sigma_i\rangle\langle \sigma'_i|$ this result applies also to more general electronic states where then $\lambda_{\sigma_i,\sigma'_i}(r_i)$ includes also the electronic preparation.

The final step is now straightforward. We take the time derivative of the matrix elements $P_{\sigma_i,\sigma'_i}(q,t)$ on the left and the right hand side of (36), express them on the right hand side as derivatives with respect to $t$ and act on time scales of order $t_{\text{blip}} \cdot (t_{\text{blip}}/t_{\text{LZ}})$ and shorter. This brings us to the central result of this paper, namely, the generalization of the ZE to include also the low temperature quantum regime, coined the generalized Zusman equations (GZE) henceforth,

$$\dot{P}_{-+}(q,t) = L^{-} P_{-+}(q,t) + \frac{i\Delta}{2} [P_{+0}(q,t) - P_{0+}(q,t)]$$

$$\dot{P}_{++}(q,t) = L^{+} P_{++}(q,t) - \frac{i\Delta}{2} [P_{-+}(q,t) - P_{+-}(q,t)]$$

$$\dot{P}_{-0}(q,t) = L^{0} P_{-0}(q,t) + \frac{i\Delta}{2} [P_{0-}(q,t) - P_{-0}(q,t)] - i \left( \epsilon + \frac{2c_0}{\hbar \kappa} \right) q P_{-0}(q,t)$$

$$\dot{P}_{0-}(q,t) = L^{0} P_{0-}(q,t) - \frac{i\Delta}{2} [P_{00}(q,t) - P_{-0}(q,t)] + i \left( \epsilon + \frac{2c_0}{\hbar \kappa} \right) q P_{0-}(q,t).$$ (37)

Here, the quantum Smoluchowski operators [see \(^{22}\)] read

$$L^n = \frac{1}{m \gamma} \frac{\partial}{\partial q} \left[ m \omega_0^2 (q - \eta q_0) + \frac{\kappa}{\beta} \frac{\partial}{\partial q} \right]$$ (38)

and describe the overdamped quantum dynamics of the RC on the donor, the acceptor, and the averaged potential surfaces, respectively. The diffusion constant is given by $\kappa/\beta = m \omega_0^2 \langle q^2 \rangle$. Apart from the replacement of the classical $L_{cl}$ by its corresponding quantum operators, the effect of quantum fluctuations also shows up in the $c_0/\kappa$ dependent coupling terms of the non-diagonal matrix elements. The coefficient $\kappa$ contains the equilibrium variance of a damped harmonic oscillator

$$\kappa \equiv \frac{\langle q^2 \rangle}{\langle q^2 \rangle_{cl}} = \hbar \beta \omega_0^2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{\omega \hat{\gamma}(-i\omega)}{(\omega_0^2 - \omega^2)^2 + \omega^2 \hat{\gamma}^2(-i\omega)} \coth(\omega \beta/2)$$ (39)

where $\hat{\gamma}$ denotes the Laplace transform of the classical damping $\gamma(t)$ [see \(^{15}\)] and the integral is determined by the real part of the dynamical susceptibility. As discussed in the previous section, for strong damping \(^{26}\) this can be written as

$$\kappa \approx 1 + m \omega_0^2 \beta \Lambda$$ (40)

with $\Lambda$ as in \(^{26}\). Exploiting the equivalence of reaction coordinate model and spin boson model an alternative representation is found to be

$$\kappa = \frac{\hbar \beta}{2} \int_0^\infty d\omega J_{SB}(\omega) \frac{\coth(\omega \beta/2)}{\coth(\omega \beta/2)},$$ (41)

where $J_{SB}$ is the spectral density within the spin boson formulation. This can be directly calculated from the spectral density $I(\omega)$ of the RC representation \(^{21,23}\). For an ohmic spectral density of the form $I(\omega) = m \gamma \omega \exp(-\omega/\omega_c)$ with a large cut-off frequency $\omega_c \gg \gamma$ one has in the overdamped limit $\gamma/\omega_0 \gg 1$ a Drude damping for the spin boson system $J_{SB} = (c_0^2/\gamma)/(\omega_0^2/\gamma^2 + \omega^2)$. Since $\kappa > 1$ for lower temperatures the effective coupling $c_0/\kappa$ between electronic and RC system is decreased by quantum fluctuations. Accordingly, the distance between the minima of the diabatic surfaces effectively shrinks, thus reflecting the fact that the activation barrier between donor and acceptor surface tends to become transparent. Indeed, below in Sec. \(^{11}\) we will see that $\kappa$ crucially influences the transfer
rate at lower temperatures and gives rise to a renormalized reorganization energy \( E_r / \kappa \). We note that this is a very important point and in contrast to the popular approach where quantum effects are taken into account \textit{ad hoc} by a simple renormalization of temperature \cite{21, 40}. This latter procedure violates the detailed balance condition and is apparently not consistent with the derivation of the GZE from the exact dynamics. Of course, in the high temperature limit \( \gamma \hbar \beta \ll 1 \) the GZE \cite{35} reduce to the ZE.

\[ t_{\text{osz}} \approx \left( \frac{\gamma}{\omega_0^2} \beta E_r \right)^{1/3} . \]

The typical dwell time in a nondiagonal state may consequently be considered as \( t_{\text{blip}} \approx t_{\text{osz}} \). Obviously, for very large \( \gamma / \omega_0 \) when the RC dynamics almost comes to rest (basically no diffusion), \( t_{\text{osz}} \) may even exceed \( 1 / \Delta \) and the situation discussed above is regained; the coherent spin dynamics lasts over large periods of times and the typical dwell time is given by \( t_{\text{blip}} \approx 1 / \Delta \). In this case quantum fluctuations in the RC are negligible and the ZE dynamics is valid anyway. Hence, in the sequel we estimate \( t_{\text{blip}} = t_{\text{osz}} \) with \( t_{\text{blip}} \ll t_{\text{LZ}} \).

Let us now come back to our assumptions for the perturbative analysis. The time coarse graining \cite{22, 24} together with the conditions \cite{31} lead first to the prerequisite for overdamped motion \( \gamma / \omega_0 \gg 1 \) and second to

\[ \frac{\hbar^2 \beta^2}{\gamma / \omega_0^2} \ll \beta E_r \ll \frac{\gamma}{\omega_0^2 / \gamma} \frac{\Delta}{\hbar \beta} . \]

By rearranging the terms and taking also into account \( \beta E_r > 1 \) we arrive at the more convenient forms

\[ \frac{E_r}{\hbar \Delta} \frac{1}{\Delta \hbar \beta}, \left( \frac{\hbar^4 E_r}{\Delta \hbar \beta} \right)^{1/2} \ll \frac{\Delta}{\omega_0^2 / \gamma}, \quad 1 < \beta E_r \ll \frac{\gamma / \omega_0^2}{\hbar \beta} . \]

Within the overdamped domain \( \gamma / \omega_0 \gg 1 \) these relations define the range of validity for the GZE. As we show in Appendix A it is exactly this range where the simplifications of the effective action described above can be applied in the sense of a semiclassical perturbation theory. In particular, the first of the above conditions determines a lower bound on temperature depending on the ratio \( E_r / \hbar \Delta \). Physically, with decreasing \( T \) tunneling of the RC becomes important that is incorporated in the GZE only in a kind of static approximation (see Sec. \ref{sec:5}) and the range of validity shrinks accordingly, see fig. 3. In comparison the ZE have additionally to obey \( \gamma \hbar \beta \ll 1 \) and consequently fail for much higher temperatures. The first condition is also readily translated into the spin boson model: for a Debye spectral density (Drude model) the full bath cut-off frequency \( \Omega_c \) is identified as \( \Omega_c \approx \omega_0^2 / \gamma \) and the spin/full-bath coupling \( \alpha \) as \( \alpha = E_r / 2 \). Then, we observe that the electronic dynamics of the GZE extends from the adiabatic \( \Delta / \Omega_c \gg 1 \) to the nonadiabatic limit \( \Delta / \Omega_c \ll 1 \) also at lower temperatures (see fig. 3). The second relation is independent of \( \Delta \) and
effectively a static field, distributed according to its equilibrium distribution, is coupled to the spin. As known from the classical limit (ZE) this evokes damped coherent oscillations in the electronic occupation probabilities [43]. For space by keeping also nondiagonal elements of the reduced density matrix with respect to the RC (conflict with the electronic dynamics. The path integral formulation allows to extract a set of equations in full phase − follows from the second one by interchanging + and −. account the equilibration process of the momentum. As already mentioned above, for continuous systems this generalization of the quantum Smoluchowski equation to a quantum Fokker-Planck equation has already been done in [28]. In particular, one can thus explicitly take into account the equilibration process of the momentum. Here, starting again with [16] and working along the lines described above, we find for the χ-independent part of the action

\[ \frac{i}{\hbar} \Sigma_{\text{RC}}(x_f, r_f, r_i; \eta_f, t) = \left. \frac{1}{2\langle q^2 \rangle} \left( - \frac{r^2}{2\langle q^2 \rangle} - i \frac{m\omega_0^2}{\hbar \gamma} x_f r_f - \frac{\langle p^2 \rangle}{2\hbar^2} x_f^2 \right) \right|_{\eta = 0} - \frac{1}{2\langle q^2 \rangle} \left( 1 - \frac{1}{\langle q^2 \rangle} \right) \left[ r_f - \frac{S(t)}{\langle q^2 \rangle} r_i - i \frac{2\omega_0^2}{\hbar \gamma} x_f + \frac{c_0}{m\omega_0^2} \eta_f \right]^2. \] (45)

In the low temperature range \( \langle p^2 \rangle \approx (m\hbar/\pi)\ln(\omega_c/\gamma) \) so that, as expected, nondiagonal elements in the RC are strongly suppressed and only takes small values, roughly of order \( 1/\sqrt{\gamma} \). The χ-dependent parts of the action are approximated as above with the result that to this order of perturbation theory (neglecting terms of order \( t_{\text{blip}}/\gamma \) or smaller) no additional \( x_f \chi \) dependent terms have to be retained.

In a next step we go over to a phase space formulation by taking the Wigner transform of \( \rho_{\sigma_f,\sigma'_f}(x_f, r_f, t) \), i.e.,

\[ W_{\sigma_f,\sigma'_f}(p, q, t) = \frac{1}{2\pi \hbar} \int dx_f \rho_{\sigma_f,\sigma'_f}(x_f, r_f, t) e^{-\frac{i}{\hbar} px_f}. \] (46)

The corresponding equations of motion for the matrix elements of the Wigner density matrix are then found as

\[ W_-\!(p, q, t) = L^0_{\text{QFP}} W_-\!(p, q, t) + \frac{i\Delta}{2} [W_+\!(p, q, t) - W_-\!(p, q, t)] \]

\[ W_+\!(p, q, t) = L^0_{\text{QFP}} W_+\!(p, q, t) + \frac{i\Delta}{2} [W_-\!(p, q, t) - W_+\!(p, q, t)] \]

\[ -i \left( \epsilon + \frac{2c_0}{\hbar \kappa} q \right) W_-\!(p, q, t) \] (47)

where the equation for \( W_+\! \) follows from the first one by replacing + with − and vice versa, while that for \( W_-\! \) follows from the second one by interchanging + and − and complex conjugation of its last term.

Compared to the GZE, in the above equations the quantum Smoluchowski operators are replaced by quantum Fokker-Planck operators

\[ L^0_{\text{QFP}} = \frac{\partial}{\partial p} \left[ m\omega_0^2 (q - \eta q_0) + \gamma p \right] - \frac{p}{m} \frac{\partial}{\partial p} + \gamma \langle p^2 \rangle \frac{\partial^2}{\partial p^2} + \left[ \langle q^2 \rangle - \frac{\langle p^2 \rangle}{m} \right] \frac{\partial^2}{\partial p \partial q}. \] (48)

They differ from classical Fokker-Planck operators [38] mainly by the last term that describes coupled \( pq \) diffusion and has also been found for weak damping [14, 15]. In the high temperature range \( \gamma \hbar \beta \ll 1 \) its diffusion constant
tends to zero due to the equipartition theorem and one recovers from (17), (18) the phase space equations derived by Garg et al. [21]. For low temperatures $\gamma \beta \gg 1$ its impact becomes substantial and is dominated by the growing $\langle p^2 \rangle$ variance. Numerical results with the quantum Fokker-Planck equation for a simple harmonic oscillator [28] show that for strong damping mean values like $\langle p(t) \rangle$ and correlation functions like $\langle p(t)p \rangle$ are in excellent agreement with exact results and that small deviations only occur in the short time range. Of course, if the momentum is eliminated adiabatically from (18) we regain the GZE.

With the exact equilibrium variances inserted into (18) the corresponding Fokker-Planck operator is even more general [13]: It gives for the set of initial conditions [17] and ohmic friction (supplemented by a high frequency cut-off) the exact quantum dynamics of a damped harmonic oscillator in the long time limit independent of temperature and damping strength. While in principle the range of validity of (17) is defined by the conditions [14], one might thus be tempted to think that with the “exact” $L_{\text{QFP}}$ one could also extend this range. However, a deeper analysis reveals that by weakening for lower temperatures one of the conditions in (14) additional $\chi$ and $\eta$ dependent terms in the effective action [see (26)] must be taken into account. Equations of motion with time independent coefficients are then out of reach. This suggests that the relations (14) define necessary and sufficient criteria for the existence of (simple) dynamical equations for the coupled electronic/RC motion in the strong damping domain at lower temperatures. Work to study the quantum phase space dynamics in detail is in progress and will be presented elsewhere.

V. QUANTUM TRANSFER RATES

Electron transfer rates have been calculated analytically and numerically within the RC and the spin boson representation as well. In essence, two limiting cases are distinguishable, in particular since they allow for perturbative analytical treatments (cf. fig. 3). Roughly speaking, in the nonadiabatic regime the RC crosses the LZ region fast compared to the dynamics of the spin ($\Delta/\Omega_c \ll 1$, $\Omega_c$ cut-off frequency of the full bath) so that golden rule techniques in the electronic coupling $\Delta$ can be invoked. This way, transfer rates for classical and quantum mechanical baths have been obtained [11, 40, 44]. In the opposite case of a very slow RC compared to the bare electronic motion ($\Delta/\Omega_c \gg 1$) the sluggish RC dynamics controls the transfer and established methods like e.g. Kramers flux over population approach or transitions state theory on the lower adiabatic surface are applicable [1, 24]. A crucial point is the changeover between purely adiabatic to nonadiabatic dominated transfer. As first shown by Zusman [20] and then later by Garg et al. [21] the ZE allow to derive an explicit expression for an interpolation formula that reduces to the adiabatic (nonadiabatic) rate constant in the respective limits. A detailed survey over the available analytical results and their performance compared to real-time Quantum Monte Carlo data was given recently in [26]: For $\Delta/\Omega_c \ll 1$ the nonadiabatic rate expression works quite well over the whole temperature range. The same is true for $\Delta/\Omega_c \gtrsim 1$ and higher temperatures $\Delta\beta \lesssim 1$ where the Zusman rate is valid. The only domain where no explicit rate formula is known so far is $\Delta/\Omega_c \gtrsim 1$ at lower temperatures $\Delta\beta \gtrsim 1$. It is exactly this region where the GZE apply.

The procedure to extract the rate from the ZE has been outlined in [22, 24]. It also works for the GZE so that details are omitted here. By solving formally the two equations for the nondiagonal elements (using the proper Greens function, see Appendix B) and plugging this result into the two equations for the diagonal ones, we arrive at two coupled integro-differential equations. These can be reduced to two coupled partial differential equations by exploiting the time scale separation $t_{\text{blip}} \ll t_{\text{LZ}}$ to end up with

$$
\dot{P}_{-}(q,t) = -K(q) [P_{-}(q,t) - P_{+}(q,t)] + \mathcal{L}^{-} P_{-}(q,t)
$$

$$
\dot{P}_{+}(q,t) = K(q) [P_{+}(q,t) - P_{-}(q,t)] + \mathcal{L}^{+} P_{+}(q,t).
$$

(49)

Here, the effective position dependent electronic coupling turns out to be

$$
K(q) = \frac{\Delta^2}{2} \text{Re} \int_{-\infty}^{\infty} dq' \int_{0}^{\infty} dt G_0(q',t|q)
$$

(50)

where $G_0(q',t|q)$ is the Greens function for the diffusion in the average potential that determines the nondiagonal elements. Next, the equations (49) are Laplace transformed (with respect to time) and projection operator techniques provide a mapping onto electronic populations. Finally, the transfer rate follows in the long time limit, i.e. for Laplace parameter tendency to zero, in the form

$$
k_+ = \frac{k_+^{\text{na}}}{1 + k_+^{\text{na}}/k_+^{\text{d}} + k_-^{\text{na}}/k_-^{\text{d}}}
$$

(51)

for the forward rate where $k_+^{\text{na}}$ and $k_+^{\text{d}}$ are so-called nonadiabatic and diffusive rate constants for forward and backward transfer, respectively. These are related by the detailed balance condition

$$
k_+^{\alpha}/k_-^{\alpha} = e^{\beta \epsilon_x}
$$

(52)
with $\alpha = n_a$, d. The backward rate $k_-$ follows from $k_+$ by interchanging $+ \leftrightarrow -$. Specifically, one obtains

$$k_{\pm}^{na} = \frac{1}{2\pi(q^2)} \int_{-\infty}^{\infty} dq \, K(q) \exp \left[ -\frac{(q \pm q_0)^2}{2(q^2)} \right]$$

(53)

which represents the nonadiabatic rate as an average of the effective electronic coupling over the equilibrium distribution of the donor and acceptor surfaces, respectively. The diffusion in these harmonic wells is described by the rate constants

$$\frac{1}{k_{\pm}^d} = \int_{0}^{\infty} dt \, \left\{ G_{\pm}(q_0, t|q_0) \sqrt{2\pi(q^2)} \exp \left[ \frac{(q \pm q_0)^2}{2(q^2)} \right] - 1 \right\}$$

(54)

where $G_{\pm}(q_0, t|q_0)$ denote the Greens functions for the RC motion in the donor and acceptor (see Appendix B). Both expressions can be simplified further for a sufficiently large reorganization energy $\beta E_r > 1$. It then turns out that the nonadiabatic rates coincide with golden rule rates, i.e.,

$$k_{\pm}^{na} = \frac{\hbar \Delta^2}{4} \sqrt{\frac{\pi \beta}{E_r / \kappa}} \exp \left( -\beta E_r^# \right)$$

(55)

where

$$E_r^# = \frac{(E_r / \kappa + \hbar\epsilon)^2}{4E_r / \kappa}$$

(56)

are the effective activation energies for the forward/backward rates. The diffusive rates are identical to the overdamped Kramers rates for escape on the lower adiabatic surface

$$k_{\pm}^d = \frac{\omega_0^2}{\gamma} \sqrt{\frac{\beta E_r^#}{4\pi \kappa}} \exp \left( -\beta E_r^# \right)$$

(57)

Accordingly, for the important case of a symmetric transfer ($\epsilon = 0$) the ultimate rate for equilibration, i.e. the total rate $k = k_+ + k_-$, takes the handsome form

$$k = \frac{\Delta^2}{1 + g} \sqrt{\frac{\hbar^2 \pi \beta}{4E_r / \kappa}} \exp \left( -\beta E_r / 4\kappa \right)$$

(58)

with an adiabaticity parameter

$$g = \frac{\pi \kappa}{\omega_0^2 / \gamma} \frac{h \Delta}{E_r}$$

(59)

For $g \gg 1$ one recovers the adiabatic, for $g \ll 1$ the nonadiabatic rate constant [cf. (41) and fig. 3]. The above rate expression looks like the classical Marcus/Zusman result with a renormalized reorganization energy $E_r \to E_r / \kappa$. Note that this simple renormalization only appears if quantum fluctuations in the $c_0$-coupling terms of the equations for $P_{\pm \mp}$ [see (37)] are properly taken into account. Since $\kappa \geq 1$ quantum fluctuations always reduce the effective energy barrier which is to be surmounted. Of course, in the high temperature limit ($\kappa \to 1$) we regain the known result, for lower temperature, however, significant deviations are observed. (i) The ratio $\kappa$ grows with decreasing temperature, at very low temperatures roughly linearly with $\beta$. As a consequence, keeping all other parameters fixed, $g$ becomes larger with lower $T$ meaning that one approaches the range where the transfer is dominated by adiabatic processes already for smaller values of $\Delta$. This behavior of $g$ is also consistent with the larger range of validity of the GZE at lower $T$ compared to the classical case. Moreover, it agrees with recent numerical indications (48). (ii) At lower $T$ the exponent in the rate expression $\beta E_r / \kappa$ tends to become temperature independent in contrast to the classical result. In particular, for an ohmic secondary bath $I(\omega) = m \gamma \omega \exp(-\omega / \omega_c)$ with large cut-off frequency we gain from (39) for large friction $\gamma / \omega_0 \gg 1$

$$\kappa \approx 1 + \frac{\hbar \beta \omega_0^2}{\pi \gamma} \left[ \psi \left( 1 + \hbar \beta \gamma / 2\pi \right) - \psi \left( 1 + \hbar \beta \omega_0^2 / 2\pi \gamma \right) \right]$$

(60)

where $\psi$ denotes the logarithmic derivative of the $\Gamma$-function. The corresponding quantum enhancement $\kappa / \beta$ is depicted in fig. 4 for various values of the damping strength. Since $\kappa$ enters the exponent in (58), even relatively small
deviations from the classical behavior $\kappa/\beta = 1/\beta$ substantially influence the rate. In fact, if formally the limit of very low temperatures $\gamma h \beta \gg 1, \omega_0 h \beta \gg \gamma/\omega_0$ is taken [which in a strict sense is out of the range of validity \[14\]], $\kappa/\beta$ saturates and the exponent in \[58\] becomes

$$\frac{\beta E_r}{4\kappa} \to \frac{\pi \gamma}{8\omega_0 \ln(\gamma/\omega_0)} \frac{E_r}{\hbar \omega_0}$$

which is identical to the overlap of two harmonic ground state wave packets with overdamped variance $(2\hbar/m\gamma) \ln(\gamma/\omega_0)/\pi$ localized around $\mp \omega_0$ in the donor and acceptor wells, respectively. Hence, nuclear tunneling is included in the above rate formula, at least in a nondynamical way. In comparison with precise Monte Carlo results (from \[20\]) a remarkable agreement is seen over a broad temperature range from low up to high temperatures (fig 5). The effect of nuclear tunneling is clearly observable at low $T$ where the classical rates expression is far off. Only at very low $T$ and for $\Delta/(\omega_0^2/\gamma) \lesssim 1$, i.e. close to the boundary of the range of validity (cf. fig. 3), does the quantum Zusman rate overestimate the true rate (fig. 6) but is still much better than the classical rate. In this parameter range the dynamics of the nuclear tunneling process is strongly affected by dissipation which is known to reduce the quantum rate substantially. To complete this discussion, we note that according to the numerical results in \[20\] for very low temperatures $\Delta h \beta \gg 1$ and large $\Delta/(\omega_0^2/\gamma) \gg 1$ (cf. fig. 3) transient relaxation dynamics persists up to very long times and the equilibration cannot be described by single-exponential decay. Hence, combining the golden rule expression \[15, 47\] with the above quantum Zusman rate covers almost the entire parameter range where a relaxation rate can be found at all.

\section{VI. CONCLUSIONS}

In this work we have studied electron transfer between a donor and acceptor site in strongly condensed phase and at lower temperatures where quantum effects are essential. Based on an exact path integral representation of the reduced density matrix of the electron/reaction coordinate compound we have employed recent results on the overdamped limit in the quantum regime to derive equations of motions for its diagonal part in the RC, named GZE. Utilizing the Wigner transform this was extended to include also its nondiagonal part and to obtain a description in phase space. Accordingly, we have given a rigorous derivation of time evolution equations for an overdamped collective vibronic degree of freedom in presence of electronic transitions over a wide parameter range. As another important result transfer rates have been gained from the GZE that interpolate between adiabatic and nonadiabatic dominated relaxation also in the low temperature domain.

The fundamental feature that makes the exact non-Markovian quantum dynamics effectively to behave Markovian, is a time scale separation in the overdamped RC dynamics influencing the electronic motion as well. The main findings are the following: (i) The GZE reduce to the ZE for high temperatures. (ii) At lower temperatures quantum fluctuations lead to a renormalized temperature and a renormalized RC-spin coupling that combines to a renormalized reorganization energy and thus conserves the detailed balance condition. (iii) The range of validity of the GZE can be specified in detail and comprises adiabatic and nonadiabatic domains also for $\Delta h \beta > 1$. In particular, the Smoluchowski reduction requires reorganization energies bounded from above by the damping strength. (iv) The phase space Fokker Planck equations include explicitly the momentum equilibration of the RC, but it seems to us that they do not allow for a substantial extension of the range of validity beyond that of the GZE. (v) A generalization of the Marcus/Zusman expression for the electron transfer rate contains a renormalized reorganization energy such that in the low temperature range the rate tends to become temperature independent. It thus describes (at least partially) nuclear tunneling in agreement with precise numerical date. The golden rule formula (see e.g. \[13, 47\]) and the quantum Zusman result give now a sufficiently precise description of the incoherent transfer throughout most of the relevant range of parameters.

What we have not discussed here in detail is the dynamics of the GZE and the quantum phase space equations based on numerical solutions. This is certainly an interesting subject, particularly for the latter one, and is presently under study. As discussed above, the quantum Smoluchowski limit has also been analyzed for anharmonic potential fields so that GZE for these cases may also be found \[48\]. In any case, the appealing feature of equations of motions is the straightforward procedure to solve them. Typically they are not plagued seriously by numerical instabilities and can therefore be used to describe the ET dynamics also for very long times. In contrast, while e.g. real time quantum Monte Carlo methods provide a numerically exact scheme, quantum noise in form of the so-called dynamical sign problem sets a severe limit on the simulation time. Further, the GZE give in some aspects a deeper understanding of the underlying physics since they allow for approximate analytical results.
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Appendix A: Effective Action

The exact action coefficients $\Phi_\gamma$ in (20) are read off from the results of [29]. On the coarse grained time scale $\hbar\beta, 1/\gamma \ll \gamma/\omega_0^2$ (Smoluchowski limit) they are given by the following approximate expressions

\[
\Phi_r \approx \frac{2q_0}{(q^2)_c} \frac{s(t)}{\hbar\beta} \left\{ \int_0^t ds \phi(u) A(2t - u) + i \frac{2q_0}{(q^2)_c} \frac{\hbar\beta}{\gamma/\omega_0^2} \right\}
\]

\[
\Phi_q \approx i \frac{4q_0}{(q^2)_c} \frac{\gamma/\omega_0^2}{\hbar\beta} \left\{ \int_0^t ds \phi(u) \left\{ s(t) A(t - u) + \frac{1}{\gamma/\omega_0^2} A(u) \right\} \right\}
\]

\[
\Phi_0 \approx i \frac{4q_0^2}{(q^2)_c} \frac{1}{\hbar\beta} \left\{ \frac{s(t)}{\gamma/\omega_0^2} \right\}
\]

with the abbreviation $s(t) = \left(1 - \frac{S^2(t)}{2}\right)^{-1}$ and $A(t)$ and $S(t)$ as in (28). If also the time scale separation $\hbar\beta \ll \hbar\beta < t_{blip} < t_{LZ} < t_{act}$ is applied, these coefficients reduce further. In a first step all leading order terms in $t_{blip}$ are kept

\[
\Phi_r \approx \frac{2q_0}{(q^2)_c} \frac{\gamma/\omega_0^2}{\hbar\beta} \left\{ \frac{s(t)}{\gamma/\omega_0^2} - i \frac{2q_0}{(q^2)_c} \frac{\hbar\beta}{\gamma/\omega_0^2} \right\}
\]

\[
\Phi_q \approx i \frac{4q_0^2}{(q^2)_c} \frac{\gamma/\omega_0^2}{\hbar\beta} \left\{ \frac{s(t)}{(q^2)_c} \right\}
\]

\[
\Phi_0 \approx i \frac{4q_0^4}{(q^2)_c} \frac{\gamma/\omega_0^2}{\hbar\beta} \left\{ \frac{s(t)}{(q^2)_c} \right\}
\]

with $A(0) = -\hbar/2m\gamma$ from (28). To extract in a second step the relevant terms, we estimate the order of magnitudes of the various contributions. There, $\Phi_r$ and $\Phi_q$ carry an overall factor $\beta E_r/q_0$, $\Phi_0$ a factor $\beta E_r$. Specifically, one obtains for $\Phi_r$: The $\eta_f$ term is of order $\beta E_r/q_0$, the $\chi$ term of order $\beta E_r/q_0$ with

\[
\xi = \frac{\omega_0^2 t_{blip}}{\hbar/\gamma}
\]

Next $\Phi_q$: The $\eta_f$ term is of order $\beta E_r/q_0$: the first $\chi$ term is of order $t_{blip}/(\hbar\beta\gamma) \beta E_r/q_0$, the second one of order $\beta E_r/q_0$. Finally, the $\Phi_0$ contribution: In the first line terms are of order $\beta E_r\xi$ or smaller, the second line is of order $\beta E_r$, and the third one of order $\beta E_r S t_{blip}/\hbar\beta$. It is now assumed that $\beta E_r\xi t_{blip}/\hbar\beta \ll 1$ so that all terms of this and smaller order (e.g. $\beta E_r\xi$) are negligible in the sense of a semiclassical approximation. Accordingly, the expression (33) for the effective action follows. In fact, within the range of validity of the GZE specified in (34) this assumption is indeed justified, thus proving the self-consistency of the approach.
Appendix B: Greens functions

The Greens function for the averaged potential is obtained from solving

\[
\left[ \frac{\partial}{\partial t} - \mathcal{L}^{0} + i \left( \epsilon + \frac{2c_0}{\hbar \kappa} q \right) \right] G_0(q, t - t'|q') = 0
\]

(66)

with the initial condition \( \lim_{t' \to 0} G_0(q, 0|q') = \delta(q - q') \) and the boundary conditions \( G(\pm \infty, t - t'|q') = 0 \). Details of the calculation have been reported in [22, 24]. Here, we specify the final result

\[
G_0(q, t|q') = \frac{1}{2\sqrt{\pi a(t)}} \exp \left\{ -\frac{(q - ib(q', t))^2}{4a(t)} + c(q', t) \right\},
\]

(67)

where

\[
a(t) = \frac{\langle q^2 \rangle}{2} \left( 1 - e^{-2\frac{\omega_0^2 t}{\gamma}} \right),
\]

\[
b(q', t) = -\frac{\omega_0^2}{\gamma} \langle q^2 \rangle \frac{2c_0}{\hbar \kappa} \left( 1 - e^{-2\frac{\omega_0^2 t}{\gamma}} \right)^2 + iq'e^{-2\frac{\omega_0^2 t}{\gamma}}
\]

\[
c(q', t) = \frac{\gamma}{\omega_0^2} \langle q^2 \rangle \frac{2c_0}{\hbar \kappa} \left( e^{-2\frac{\omega_0^2 t}{\gamma}} - 4e^{-2\frac{\omega_0^2 t}{\gamma}} + 3 - 2\frac{\omega_0^2 t}{\gamma} \right) + \frac{i\gamma}{\omega_0^2} \left( 1 - e^{-2\frac{\omega_0^2 t}{\gamma}} \right) \frac{2c_0}{\hbar \kappa} q'.
\]

(68)

To estimate \( t_{\text{blip}} \) (see Sec. III C) we consider times \( t \ll t_{\text{LZ}} = \gamma/\omega_0^2 \) and retain the imaginary part of the exponent in leading order given by the imaginary part to \( c(q', t) \).

The Greens functions for the donor/acceptor surfaces are gained from \( [\partial_t - \mathcal{L}^{\pm}] G^{\pm} = 0 \) and read

\[
G^{\mp}(q, t - t'|q') = \frac{1}{2\sqrt{\pi a(t)}} \exp \left\{ \frac{\left| q \pm q_0 - (q \pm q_0)e^{-\frac{\omega_0^2}{\gamma}(t-t')} \right|^2}{4a(t)} \right\}
\]

(69)

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FIGURE CAPTIONS

FIG. 1: Diabatic potential surfaces for the reaction coordinate. An equilibrium wave packet is excited by a short laser pulse from a dark state (thin line) to the donor state (thick line, minimum at \(-q_0\)). From this nonequilibrium preparation a wave packet evolves on the coupled donor and acceptor (thick line, minimum at \(+q_0\)) surfaces where the transfer occurs in the Landau-Zener region near \(q = 0\).

FIG. 2: Smoluchowski range for a harmonic RC according to (21). The dashed line separates the classical domain \(\gamma \hbar \beta \ll 1\) from the quantum domain \(\gamma \hbar \beta \gg 1\).

FIG. 3: Range of validity of the Quantum Zusman equations according to the first conditions in (44) (shaded) for fixed \(E_r/\hbar \Delta = 2\). The dashed line separates the classical (small \(\Delta \hbar \beta\)) from the quantum range (larger \(\Delta \hbar \beta\)).

FIG. 4: Quantum enhancement vs. inverse temperature for various damping strength together with the classical result \(\kappa = 1\).

FIG. 5: Electron transfer rates vs. temperature for a symmetric system (\(\epsilon = 0\)) according to the expression (58) (solid line), the classical result (\(\kappa = 1\), dashed line), and precise Quantum Monte Carlo data (diamonds, from [26]). \(E_r/\hbar \Delta = 10\) and \(\Delta/\Omega_c = 2\).

FIG. 6: Electron transfer rates vs. temperature for a symmetric system (\(\epsilon = 0\)) according to the expression (58) (solid line), the classical result (\(\kappa = 1\), dashed line), and exact Quantum Monte Carlo data (diamonds, from [26]). \(E_r/\hbar \Delta = 10\) and \(\Delta/\Omega_c = 1\).
