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Semiclassical electron transfer: Zusman equations versus Langevin approach

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Abstract

The model of a donor–acceptor electron transfer (ET) being coupled to an overdamped reaction coordinate is studied semiclassically. Starting from an archetypal ET Hamiltonian, two different routes of the semiclassical approximation are critically analyzed and mutually compared. A first path proceeds along the Caldeira–Leggett form for the master equation for the reduced density matrix of "electron + reaction coordinate" which is cast in its Wigner phase–space representation. Integrating over the momentum of the reaction coordinate then yields (in the overdamped limit) the so-termed Zusman ET-equations. The alternative route starts from the formally exact quantum Heisenberg–Langevin equations. The corresponding derivation of the equations of motion for the observables involves a sort of a mean-field semiclassical approximation. The final result are nonlinear stochastic differential equations (SDE) of the Langevin type. We compare the results of these two approaches, both in the absence and in the presence of external time-dependent driving fields. Our findings are that both methods yield good agreement for the description of symmetric ET. In contrast, however, the SDE fails to describe the ET dynamics when a strong static bias is present. The inclusion of a strong time-periodic field ET-manipulation improves the Langevin approximation scheme, providing reasonable good agreement between both routes.

1. Introduction

A wealth of basic research work to investigate open quantum systems has been put forward in recent years and applied to numerous applications in the fields of chemistry and physics [1–4]. A prominent example with ever increasing activity addresses the problem of charge transfer in a dissipative environment. There exist numerous models in the literature designed to describe electron (or proton) transfer [2]. A particularly appealing approach is based on the familiar spin-boson model [1] which provides a pragmatic, yet still realistic formulation for the physics of a dissipative donor–acceptor electron transfer (ET) [2].

Often, the dissipative influence of the environment allows for a semiclassical description, while at the same time the full quantum nature of the electron dynamics must be accounted for. Such a type of the mixed quantum-classical description is presently very much on vogue [5–11]. The literature offers several such methods, but at the same time providing no guide of how to single out a most useful and advantageous approximation scheme. In this work we compare two popular such

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approaches. The Zusman approach, introduced in Section 3, and the nonlinear Langevin model, presented in Section 4, are not solely restricted to describe ET in condensed phases; these provide a generic scheme to model a few level system coupled to a dissipative oscillator. As such these two schemes carry the potential for even broader applications in modeling the dynamics of open quantum systems.

2. Electron transfer model

Let us consider the following archetypal Hamiltonian

$$\hat{H}_{\mathrm{ET}}(t) = \frac{1}{2}[V_1(\hat{x},t) - V_2(\hat{x},t)]\hat{\sigma}_z + \frac{1}{2}\Delta\hat{\sigma}_x + \frac{1}{2}\left[\frac{\hat{p}^2}{m} + V_1(\hat{x},t) + V_2(\hat{x},t)\right]\hat{1} + \hat{H}_{\mathrm{B}} \quad (1)$$

which is widely used to describe the ET processes in condensed media [2,12]. In Eq. (1), $\hat{\sigma}_z := |1\rangle\langle 1| - |2\rangle\langle 2|$ and $\hat{\sigma}_x := |1\rangle\langle 2| + |2\rangle\langle 1|$ are the pseudo-spin operators expressed via the localized donor, $|1\rangle$, and acceptor, $|2\rangle$, states; $\hat{1}$ is the 2×2 unity matrix. Furthermore, the diabatic electronic states $V_{1,2}(\hat{x})$ constitute the Born–Oppenheimer potentials for the nuclear (reaction coordinate) motion. We consider in this work the standard harmonic oscillator potentials

$$V_1(\hat{x}) = \tfrac{1}{2}m\omega_0^2\hat{x}^2, \qquad V_2(\hat{x}) = \tfrac{1}{2}m\omega_0^2(\hat{x}-x_0)^2 - \epsilon_0, \quad (2)$$

where x_0 is the spatial displacement between the two shifted parabolic surfaces, and ϵ_0 is the energy distance between the minima. For convenience, the donor well $V_1(\hat{x})$ is centered on the coordinate origin. The curvature of the two wells is assumed to be equal and is characterized by ω_0. Moreover, the potential curves are often characterized by the so-called reorganization energy

$$E_{\mathrm{r}} = \tfrac{1}{2}m\omega_0^2 x_0^2. \quad (3)$$

The connection between the various parameters is illustrated with Fig. 1. Furthermore, the electronic states can generally be time dependent, due to the presence of a time-dependent electric field $\vec{\mathscr{E}}(t)$.

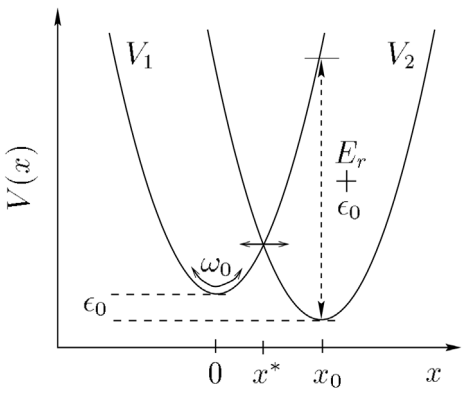

Fig. 1. The diabatic reactant V_1 and the product V_2 energy surfaces presented by harmonic functions of the reaction coordinate □ (cf. Eq. (2)). The bias ϵ_0 is the difference between the energy minima of the surfaces. E_{r} denotes the reorganization energy, and x^* is the point of intersection at which the ET takes place. The curvature of the wells is characterized by ω_0. The curved arrow indicates relaxation along the reaction coordinate and the horizontal arrows indicate the tunnelling-assisted crossing motion.

This time dependence can be accounted for in the dipole approximation as $V_{1,2}(\hat{x},t) := V_{1,2}(\hat{x}) - \vec{d}_{1,2}\vec{\mathscr{E}}(t)$. Note that the diabatic electronic dipole moments $\vec{d}_{1,2}(\hat{x})$ should generally depend on the reaction coordinate $\hat{x}$. However, we consider the corresponding dependences as a higher order effect, and put consequently $\vec{d}_1 := \vec{d}_1(0)$, $\vec{d}_2 := \vec{d}_1(x_0)$. Moreover, we assume that the reaction coordinate has no associated charge or dipole moment. These very same assumptions are commonly made also in recent works on laser driven ET [13–16]. In these models one neglects any direct influence of the external field on the reaction coordinate dynamics. The electronic coupling Δ in Eq. (1) induces the electronic transitions between the diabatic electronic states (ET). We consider this coupling in the Condon approximation, i.e., its dependence on the reaction coordinate is neglected.

The reaction coordinate with the effective mass □ and momentum □ represents some distinctive nuclear degree of freedom (e.g., a collective vibrational mode of protein) which is strongly coupled to the ET [2]. The effect of the remaining molecular nuclear degrees of freedom and of the surrounding on the reaction coordinate can be

described on the phenomenological level as a friction term. Microscopically, friction is taken into account in Eq. (1) by the bilinear coupling of the reaction coordinate to thermal bath of harmonic oscillators at frequencies ω_i and masses m_i [17,18]

$$\hat{H}_{\mathrm{B}} = \frac{1}{2}\sum_i \left\{ \frac{\hat{p}_i^2}{m_i} + m_i\omega_i^2\left[\hat{x}_i + \frac{c_i}{m_i\omega_i^2}\hat{x}\right]^2 \right\}. \tag{4}$$

This coupling can be characterized by the bath spectral density $J(\omega) = (\pi/2)\sum_i (c_i^2/m_i\omega_i)\delta(\omega - \omega_i)$ [1]. In the continuum limit we choose the smooth ohmic form $J(\omega) = \eta\omega\exp(-\omega/\omega_{\mathrm{c}})$ with the frequency cutoff $\omega_{\mathrm{c}} \to \infty$ [18] and a phenomenological friction coefficient η.

The reaction coordinate dynamics often allows for a (semi) classical treatment. This approximation is well justified when the temperature □ is sufficiently high such that the characteristic time of thermal fluctuations $\tau_{\mathrm{T}} = \hbar/(\pi k_{\mathrm{B}}T)$ is much less than the characteristic time scales for the reaction coordinate dynamics, i.e., $\tau_{\mathrm{T}} \ll \tau_{\mathrm{s}} = \min\{\omega_0^{-1}, m/\eta\}$. At $T = 300$ K, $\tau_{\mathrm{T}} \approx 8$ fs, and with the vibrations obeying $\omega_0 < 25\,\mathrm{cm}^{-1} \approx 4.7 \times 10^{12}\,\mathrm{s}^{-1}$ the reaction coordinate dynamics can be treated semiclassically. Especially, this approximation is valid at room temperatures for solvents where τ_{s} is typically of the order of several picoseconds. Our goal in this work is to compare two common, although very different ways of doing the semiclassical approximation in the ET dynamics described by the Hamiltonian (1).

3. Zusman equations

The first approach to the above stated problem utilizes the reduced density matrix method. In a first step, the master equation for the reduced density matrix $\hat{\rho}$ of the "electron + reaction coordinate" system is derived in the coordinate representation. This task can be accomplished using either the real-time path integral approach [12], or by the cumulant expansion method [19]. The resulting master equation reads within the semiclassical approximation of the bath [12,23]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}(t) = -\frac{\mathrm{i}}{\hbar}[\hat{H}_{\mathrm{ET}}(t), \hat{\rho}(t)] - \frac{\mathrm{i}\eta}{2m\hbar}[\hat{x}, [\hat{p}, \hat{\rho}(t)]_+] - \frac{\eta k_{\mathrm{B}}T}{\hbar^2}[\hat{x}, [\hat{x}, \hat{\rho}(t)]], \tag{5}$$

where $[A,B] := AB - BA$ and $[A,B]_+ := AB + BA$ denote the commutator and the anticommutator of two arbitrary operators, □ and □, respectively (note that $\hat{\rho}$ and $\hat{H}_{\mathrm{B}}$ commute). In Eq. (5) the dissipative part has the well-known Caldeira–Leggett form [18]. In the absence of external driving, this equation has been derived in Ref. [12]. Note that the external driving does not affect the dissipative part in Eq. (5). This latter approximation is fully consistent with the classical approximation for the thermal bath, where the thermal random forces are approximated by the Gaussian uncorrelated (white) noise (see below). In the next step, Eq. (5) is rewritten in terms of the Wigner function [24,25]

$$\hat{W}(x,p,t) = \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} \mathrm{d}x' \exp(-\mathrm{i}px'/\hbar) \times \langle x + x'/2|\hat{\rho}(t)|x - x'/2\rangle, \tag{6}$$

where $\hat{W}(x,p,t)$ is a 2×2 matrix. This transformation is used to mimic the approach to the classical limit, namely the Wigner function represents the probability density function (PDF) in the phase space (x,p) in the limit $\hbar \to 0$. Then, keeping only terms of leading order in $\hbar$ ($\hbar \to 0$) Eq. (5) results in a hybrid of quantum Bloch equation and the classical Fokker–Planck equation (cf. Refs. [12,23]). Finally, we assume a sluggish reaction coordinate dynamics, i.e., it is strongly overdamped, with $\gamma = \eta/m \gg \omega_0$ (while still obeying $\gamma \ll \pi k_{\mathrm{B}}T/\hbar$). In this limit the dynamics of the reaction coordinate □□□□□□□□ □ is not of relevant interest; it thus can be integrated over. In the basis of localized states, $|i\rangle$, $i = 1, 2$ we have

$$\rho_{ij}(x,t) = \int_{-\infty}^{+\infty} \mathrm{d}p\, W_{ij}(x,p,t), \tag{7}$$

where $(\ldots)_{ij} := \langle i|(\ldots)|j\rangle$. For large times $t \gg \gamma^{-1}$ the equations of motion for $\rho_{ij}(x,t)$ can be obtained by the method of an inverse friction expansion [26]. To leading order in γ^{-1} the distribution for the

reaction coordinate momentum □ at any space point □ is assumed to be Maxwellian, i.e.

$$W_{ij}(x,p,t) = \frac{1}{\sqrt{2\pi m k_B T}} \times \exp(-p^2/2mk_BT)\rho_{ij}(x,t). \quad (8)$$

The final semiclassical equations are Smoluchowski-like, reading [23]

$$\begin{aligned}
\frac{\partial}{\partial t}\rho_{11}(x,t) &= \mathscr{L}_1\rho_{11}(x,t) - \mathrm{i}\frac{\Delta}{2\hbar}[\rho_{21}(x,t) - \rho_{12}(x,t)],\\
\frac{\partial}{\partial t}\rho_{22}(x,t) &= \mathscr{L}_2\rho_{22}(x,t) - \mathrm{i}\frac{\Delta}{2\hbar}[\rho_{12}(x,t) - \rho_{21}(x,t)],\\
\frac{\partial}{\partial t}\rho_{12}(x,t) &= \mathscr{L}\rho_{12}(x,t) - \mathrm{i}\frac{\Delta}{2\hbar}[\rho_{22}(x,t) - \rho_{11}(x,t)]\\
&\quad - \frac{\mathrm{i}}{\hbar}[V_1(x) - V_2(x) + \epsilon(t)]\rho_{12}(x,t),\\
\frac{\partial}{\partial t}\rho_{21}(x,t) &= \mathscr{L}\rho_{21}(x,t) - \mathrm{i}\frac{\Delta}{2\hbar}[\rho_{11}(x,t) - \rho_{22}(x,t)]\\
&\quad + \frac{\mathrm{i}}{\hbar}[V_1(x) - V_2(x) + \epsilon(t)]\rho_{21}(x,t).
\end{aligned} \quad (9)$$

Here, the time-dependent electric field influence is contained in the function

$$\epsilon(t) = (\vec{d}_2 - \vec{d}_1)\cdot\vec{\mathscr{E}}(t). \quad (10)$$

In Eq. (9) we have introduced the two Smoluchowski operators

$$\begin{aligned}
\mathscr{L}_1 &= D\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x} + \frac{1}{k_BT}\frac{\partial}{\partial x}V_1(x)\right),\\
\mathscr{L}_2 &= D\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x} + \frac{1}{k_BT}\frac{\partial}{\partial x}V_2(x)\right),
\end{aligned} \quad (11)$$

which describe a diffusion dynamics on the energy surfaces $V_1(x)$ and $V_2(x)$, respectively. Moreover, the operator $\mathscr{L} = (\mathscr{L}_1 + \mathscr{L}_2)/2$ describes the diffusion on the averaged potential. The macroscopic diffusion constant □ is connected with the phenomenological friction coefficient η and the temperature □ by the Einstein relation

$$D = \frac{k_BT}{m\gamma} = \frac{k_BT}{\eta}. \quad (12)$$

The diagonal elements $\rho_{11}(x,t)$ and $\rho_{22}(x,t)$ can be interpreted as the PDF for the reaction coordinate position □ when the electron is situated at the donor or acceptor site, respectively. The external driving force $\epsilon(t)$ in Eq. (9) can be understood as a time-dependent modulation of the energy gap ϵ_0 between the minima of the two potential surfaces. The specific form of this modulation is defined by the time dependence of the driving field $\mathscr{E}(t)$, which is arbitrary. In this work we confine ourselves, however, to the periodic drive

$$\epsilon(t) = \hat{\epsilon}\cos(\Omega t) \quad (13)$$

with angular frequency Ω and (scaled) amplitude $\hat{\epsilon}$. Furthermore, the ET process is described by the evolution of the reduced density matrix

$$P_{ij}(t) = \int_{-\infty}^{+\infty} \mathrm{d}x\,\rho_{ij}(x,t). \quad (14)$$

We are interested in the following in the time evolution of the donor population $P_{11}(t)$ and the acceptor population $P_{22}(t)$, respectively.

In the absence of external driving, Eq. (9) have been established first by Zusman in 1980 [27]. In the field-free case, they have been analyzed in numerous works, notably in Refs. [12,27,28]. The most appealing and striking feature of the Zusman equations is that they are □□□□□□□□□□□□□□□□ in the electronic coupling strength Δ, thus these allow for the unifying treatment of both the □□□□□□□□□ and the □□□□□□□□□□□□ limits of the ET process. In the related analytical treatments the regime of sufficiently small electronic couplings $\Delta \ll E_r$ has been investigated. Especially, it has been shown that an □□□□□□□□ of the friction strength η leads to the crossover from the □□□□□□□□□□□□ (lowest order in Δ) to the □□□□□□□□□ (independent of Δ) regime of ET. It is worth noting here that, per se, the Zusman equations are not restricted to the regime $\Delta \ll E_r$. The limit of large electronic coupling, $\Delta \sim E_r$, or $\Delta \gg E_r$ can be investigated □□□□□□□□□□, but presents a challenge for the □□□□□□□□□□ treatment. A less known and seemingly problematic peculiarity is that these equations may violate the positive definiteness condition of the quantum evolution of the electronic subsystem, i.e., the matrix $P_{ij}(t)$ may cease to be (semi)positively defined at small initial times [29]. This peculiarity, however, does not matter in practice because it happens only on the small time scale of thermal fluctuations $t < \tau_T$ [30]

where the Markovian equations themselves are, strictly speaking, no longer valid. This feature does not present a real surprise since it is inherent also in the Caldeira–Leggett form of the dissipative operator in Eq. (5) [19–22]. The fact that the violation of the positivity of quantum evolution on the time scale of τ_{T} does not present a decisive criterion has been discussed previously in the literature [19,31–33].

Recently we performed a prime analysis (both numerical and analytical) of the generalized Zusman equations (9) in the presence of strong periodic driving. The results of this analysis are detailed elsewhere [23]. Here, we summarize our results for the nonadiabatic limit of ET. Within the parameter regime $\Delta \ll \{E_{\mathrm{r}}, \sqrt{2E_{\mathrm{r}}\hbar/\tau}\}$ (where $\tau = \gamma/\omega_0^2$ is the relaxation time of the overdamped reaction coordinate), fast periodic driving $\Omega \gg \Gamma_{\mathrm{NA}}$, and for an initially thermally equilibrated reaction coordinate the ET can be characterized by

$$P_{11}(t) = P_{11}(\infty) + (1 - P_{11}(\infty))\exp(-\Gamma_{\mathrm{NA}}\, t). \tag{15}$$

Eq. (15) predicts an exponential decay with a total rate constant $\Gamma_{\mathrm{NA}} = k^{+}_{\mathrm{NA}} + k^{-}_{\mathrm{NA}}$ given by the sum of forward and backward nonadiabatic rates [23],

$$\begin{aligned} k^{\pm}_{\mathrm{NA}} = \frac{\Delta^2}{2\hbar^2}\int_0^\infty \mathrm{d}t J_0\left(\frac{2\hat{\epsilon}}{\hbar\Omega}\sin\frac{\Omega t}{2}\right) \\ \times \cos\left(\frac{E_{\mathrm{r}}\tau}{\hbar}(1-\mathrm{e}^{-t/\tau}) \mp \frac{\epsilon_0}{\hbar}t\right) \\ \times \exp\left(\frac{2E_{\mathrm{r}}k_{\mathrm{B}}T\tau}{\hbar^2}\left[\left(1-\mathrm{e}^{-t/\tau}\right)\tau - t\right]\right). \end{aligned} \tag{16}$$

These rates present in fact the golden rule result in the lowest order Δ, being generalized to include the periodic field influence [23]. At long times the (averaged) asymptotic limit $P_{11}(\infty) = k^{-}/[k^{+}+k^{-}]$ is assumed. In the absence of driving, this stationary value is defined by the Boltzmann relation $P_{11}(\infty)/P_{22}(\infty) = \exp(-\epsilon_0/k_{\mathrm{B}}T)$, obeying the normalization condition $P_{11}(t) + P_{22}(t) = 1$, i.e.,

$$P_{11}(\infty) = \frac{1}{2}\left[1 - \tanh\left(\frac{\epsilon_0}{2k_{\mathrm{B}}T}\right)\right]. \tag{17}$$

4. Langevin approach

Because the Zusman equations present an analogue of the Smoluchowski-like equations we pose the question: does there exists an equivalent formulation in terms of SDEs (Langevin approach)? To answer this challenge we start from the Heisenberg equations of motion for the Hamiltonian (1) and integrate over the thermal bath variables (see, e.g., Refs. [1,3,4,17]). The final result reads

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\hat{\sigma}_x(t) &= -\frac{1}{\hbar}(\epsilon(t) + V_1(\hat{x}) - V_2(\hat{x}))\hat{\sigma}_y(t), \\ \frac{\mathrm{d}}{\mathrm{d}t}\hat{\sigma}_y(t) &= -\frac{1}{\hbar}\Delta\hat{\sigma}_z(t) + \frac{1}{\hbar}(\epsilon(t) + V_1(\hat{x}) \\ &\quad - V_2(\hat{x}))\hat{\sigma}_x(t), \\ \frac{\mathrm{d}}{\mathrm{d}t}\hat{\sigma}_z(t) &= \frac{1}{\hbar}\Delta\hat{\sigma}_y(t), m\frac{\mathrm{d}^2}{\mathrm{d}t^2}\hat{x}(t) \\ &\quad + \frac{1}{2}\frac{\partial}{\partial\hat{x}}(V_1(\hat{x}) + V_2(\hat{x})) \\ &\quad + \frac{1}{2}\frac{\partial}{\partial\hat{x}}(V_1(\hat{x}) - V_2(\hat{x}))\hat{\sigma}_z(t) \\ &= -\int_0^t \tilde{\eta}(t-t')\frac{\mathrm{d}}{\mathrm{d}t'}\hat{x}(t')\,\mathrm{d}t' + \hat{\xi}(t), \end{aligned} \tag{18}$$

where $\tilde{\eta}(t) = \frac{2}{\pi}\int_0^\infty \mathrm{d}\omega J(\omega)\cos(\omega t)/\omega$ is the frictional memory kernel, and

$$\begin{aligned} \hat{\xi}(t) = -\sum_i c_i\left[\frac{\hat{p}_i(0)}{m_i\omega_i}\sin(\omega_i t)\right. \\ \left. + \left(\hat{x}_i(0) + \frac{c_i\hat{x}(0)}{m_i\omega_i^2}\right)\cos(\omega_i t)\right] \end{aligned} \tag{19}$$

denotes the operator-valued random force. Provided that the initial distribution of $\{\hat{p}_i(0), \hat{x}_i(0)\}$ is characterized by the shifted equilibrium density matrix of the bath $\hat{\rho}_{\mathrm{B}} = \exp(-\hat{H}_{\mathrm{B}}/k_{\mathrm{B}}T)/Z$, the random force $\hat{\xi}(t)$ obeys a Gaussian statistics and is fully characterized by the autocorrelation function [1]

$$\begin{aligned} \langle\hat{\xi}(t)\hat{\xi}(0)\rangle_{\mathrm{B}} = \frac{\hbar}{\pi}\int_0^\infty J(\omega)\left[\coth\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right)\cos(\omega t)\right. \\ \left. - \mathrm{i}\sin(\omega t)\right]\mathrm{d}\omega. \end{aligned} \tag{20}$$

In the considered limit that $\omega_c \to \infty$, the ohmic friction is memoryless, i.e., $\tilde{\eta}(t) = 2\eta\delta(t)$, and the quantum correlation (20) acquires the form

$$\langle \hat{\xi}(t)\hat{\xi}(0)\rangle_B \approx \frac{1}{\pi}\frac{\hbar\eta\omega_c^2}{(1+i\omega_c t)^2} + 2k_B T\eta f(t), \qquad (21)$$

where

$$f(t) = \frac{1}{2\tau_T}\left[\frac{\tau_T^2}{t^2} - \frac{1}{\sinh^2(t/\tau_T)}\right] \qquad (22)$$

is a function that assumes a Dirac δ-function in the (high-temperature) limit $\tau_T = \hbar/(\pi k_B T) \to 0$. In Eq. (21), the first (complex-valued) term corresponds to the zero-temperature contribution and shall be neglected in our following (semi)classical approximation. Moreover, within the same approximation $f(t)$ can be replaced by $\delta(t)$. Then, the dissipative part of the quantum Langevin equations (18) precisely corresponds to the Caldeira–Leggett form of the dissipative operator within the master equation description (5). Furthermore, let us assume that the reduced density matrix $\hat{\rho}_{tot}$ of the whole system is initially factorized, i.e., $\hat{\rho}_{tot}(0) = \hat{\rho}_s(0) \otimes \hat{\rho}_B$, where $\hat{\rho}_s(0)$ is the initial reduced density matrix of the "electron + reaction coordinate" system. We are interested in the stochastic Langevin-like equations of motion for the observables $\sigma_\alpha(t) = \mathrm{Tr}_s(\hat{\rho}_s(0)\hat{\sigma}_\alpha(t))$ when additionally the semiclassical limit for the reaction coordinate and the bath degrees of freedom is invoked. In doing so, we encounter terms like $\mathrm{Tr}_s(\hat{\rho}_s(0)\hat{\sigma}_i(t)F(\hat{x}(t)))$, where □ is a function of $\hat{x}$. In the spirit of a semiclassical approximation, we use a decoupling approximation, i.e., $\mathrm{Tr}_s(\hat{\rho}_s\hat{\sigma}_i(t)F(\hat{x}(t))) \approx \sigma_i(t)F(x(t))$. This mean-field type of approximation has commonly been used in the theory of the Davydov soliton [34] and in the related field of the so-termed nonlinear dimer (see, e.g. Ref. [35] and references therein). It presently enjoys, with various modifications, an increasingly popular revival in the literature [5–7]. Performing all these approximations we obtain in the overdamped limit the result

$$\begin{aligned}
\dot{\sigma}_x(t) &= -\frac{1}{\hbar}(\epsilon(t) + V_1(x) - V_2(x))\sigma_y(t),\\
\dot{\sigma}_y(t) &= -\frac{1}{\hbar}\Delta\sigma_z(t) + \frac{1}{\hbar}(\epsilon(t) + V_1(x)\\
&\quad - V_2(x))\sigma_x(t),\\
\dot{\sigma}_z(t) &= \frac{1}{\hbar}\Delta\sigma_y(t),\\
\eta\dot{x}(t) &+ \frac{1}{2}\frac{\partial}{\partial x}(V_1(x) + V_2(x))\\
&+ \frac{1}{2}\frac{\partial}{\partial x}(V_1(x) - V_2(x))\sigma_z(t) = \xi_{cl}(t),
\end{aligned} \qquad (23)$$

where $\xi_{cl}(t)$ is a classical Gaussian white noise with the autocorrelation function $\langle \xi(t)_{cl}\xi(0)_{cl}\rangle_B = 2\eta k_B T\delta(t)$. One might expect that Eq. (23) corresponds to the Langevin counterpart of the Zusman equations (9). This, however, is not the case. An appealing feature of Eq. (23) is that the evolution of the electronic reduced density matrix

$$\hat{P}(t) = \frac{1}{2}\left(\hat{1} + \sum_{\alpha=x,y,z}\hat{\sigma}_\alpha\langle\sigma_\alpha(t)\rangle_\xi\right),$$

obtained by the averaging of Eq. (23) over stochastic realizations is positive on the □□□□□ time scale of the ET. Therefore, no □□□□□□□□ populations can emerge in principle. This can be deduced from the fact that the length of the stochastic Bloch vector $\vec{\sigma}(t) = [\sigma_x(t), \sigma_y(t), \sigma_z(t)]$ is conserved, i.e., $\sigma^2(t) = \sigma_x^2(t) + \sigma_y^2(t) + \sigma_z^2(t) = 1$. Put differently, the stochastic dynamics of pseudo-spin happens on the Bloch sphere of unit radius. Since $\langle\sigma_\alpha\rangle_\xi^2 \leqslant \langle\sigma_\alpha^2\rangle_\xi$, it follows that $\sum_{\alpha=x,y,z}\langle\sigma_\alpha(t)\rangle_\xi^2 \leqslant 1$, i.e. the length of the □□□□□□□□ Bloch vector cannot grow with time. The latter condition is equivalent to the (semi)positivity of the density matrix $P_{ij}(t)$ [36]. This prominent feature makes it clear without further analytical insights that Eq. (23) □□□□□□ represent the Langevin counterpart of the Zusman equations (9).

We next specify Eq. (23) for the case of parabolic potentials in Eq. (2). Performing the coordinate shift $y = x - x_0/2$, we end up with

$$
\begin{aligned}
\dot{\sigma}_x(t) &= -\frac{1}{\hbar}\big(\epsilon_0 + \epsilon(t) + m\omega_0^2 x_0 y(t)\big)\sigma_y(t),\\
\dot{\sigma}_y(t) &= -\frac{1}{\hbar}\Delta\sigma_z(t) + \frac{1}{\hbar}(\epsilon_0 + \epsilon(t)\\
&\quad + m\omega_0^2 x_0 y(t)\big)\sigma_x(t), \qquad (24)\\
\dot{\sigma}_z(t) &= \frac{1}{\hbar}\Delta\sigma_y(t),\\
\dot{y}(t) &= -\frac{1}{\tau}y(t) - \frac{1}{2\tau}x_0\sigma_z(t) + \sqrt{2D}\chi(t),
\end{aligned}
$$

wherein $\chi(t)$ is white Gaussian noise with correlation, $\langle\chi(t)\chi(t')\rangle_{\rm B} = \delta(t-t')$. A close inspection of Eqs. (24) reveals (after the rotation $\sigma_z \to \sigma_x$, $\sigma_x \to \sigma_z$, and a corresponding scaling of the variables) that the □□□□□□□□□ SDEs (24) present nothing but the generalization of Eq. (2.7) in Ref. [35] to the case of a nonzero and time-dependent bias: $\epsilon_0 \neq 0$, $\epsilon(t) \neq 0$. The set of equations (24) is fully equivalent to the equations derived recently in Ref. [8], cf. Appendix A. An appealing feature of Eq. (24) is the presence of the reaction force term proportional to σ_z in the equation for $\dot{y}(t)$. This latter term accounts for the back force acting from the pseudo-spin 1/2 on the thermal bath. If we were to neglect this term, we obtain a stochastic Liouville equation description, where the classical random force that accounts for the thermal bath influence, is added into the Hamiltonian, i.e., $\epsilon_0 \to \epsilon_0 + m\omega_0^2 x_0 y(t)$. In this latter case, the last equation in Eq. (24) generates the Ornstein–Uhlenbeck process with the autocorrelation time $\tau = \eta/(m\omega_0^2)$ and with a root mean square noise amplitude (rms) of $\sqrt{2E_{\rm r}k_{\rm B}T}$ (in energy units). Such Langevin-like equations which correspond to a stochastic Liouville approach (SLA) have been used for the problem of proton transfer in former work by Morillo and Cukier [9,10]. A drawback of this SLA is that it yields an asymptotic equipopulation of the energy levels, i.e. $P_{11}(\infty) = P_{22}(\infty) = 1/2$ [37]. However, it has been shown in Ref. [9,10], that this SLA Langevin description is capable to reproduce correctly (in a limiting case) the behavior of the rates. The inclusion of the reaction field in Eq. (24) thus appears to present a step forward beyond the SLA description.

Let us clarify next whether the inclusion of the reaction force in Eq. (24) indeed provides the correct asymptotic behavior of the populations. In Appendix B we derive (in the absence of driving) the following □□□□□ result

$$
P_{11}(\infty) = \frac{1}{2}\left[1 - \frac{\int_0^1 z I_0\left(\frac{\Delta}{2k_{\rm B}T}\sqrt{1-z^2}\right)\exp\left(\frac{E_{\rm r}z^2}{4k_{\rm B}T}\right)\sinh\left(\frac{z\epsilon_0}{2k_{\rm B}T}\right)\mathrm{d}z}{\int_0^1 I_0\left(\frac{\Delta}{2k_{\rm B}T}\sqrt{1-z^2}\right)\exp\left(\frac{E_{\rm r}z^2}{4k_{\rm B}T}\right)\cosh\left(\frac{z\epsilon_0}{2k_{\rm B}T}\right)\mathrm{d}z}\right], \qquad (25)
$$

where $I_0(z)$ is the modified Bessel function. In the prominent limiting case that $\Delta \ll \{E_{\rm r}, k_{\rm B}T\}$, the result in Eq. (17) is obviously correct, while Eq. (25) provides in this limit incorrect results (see the numerical examples given below). It thus appears that, by making the above semiclassical mean-field decoupling approximation we □□□□□□□□□ approximated the □□□□□□□ dynamics of the spin $S = 1/2$ with the □□□□□□□□□ spin dynamics. In conclusion, the Zusman equations (9) are more accurate in describing the quantum dynamics; to capture the back action force correctly within the Langevin-like description one needs to go beyond the mean-field decoupling approximation used in Eq. (24). The challenge to obtain a fully equivalent Langevin description thus still remains.

5. Numerical results and discussion

Let us test these preliminary conclusions numerically. The ET process within the considered model can be characterized by the following phenomenological parameters: (i) the electronic coupling Δ; (ii) the static energy bias ϵ_0; (iii) (medium's) reorganization energy $E_{\rm r}$; (iv) (medium's) autocorrelation time τ, and (v) the temperature □. We have performed our analysis with the following set of parameters being typical for a nonadiabatic ET regime: $\Delta = 10\ \mathrm{cm}^{-1}$, $E_{\rm r} = 500\ \mathrm{cm}^{-1}$, $\tau = 1$ ps, and $T = 300$ K. The static bias ϵ_0 was varied from

$\epsilon_0 = 0$ (symmetric transfer), through $\epsilon_0 = 500$ cm^{-1} (activationless ET), towards $\epsilon_0 = 800$ cm^{-1} (inverted regime of ET). Note that the parameters were deliberately chosen to justify a classical bath dynamics. In this limit, the bath dynamics is slow on the time scale characterized by the tunneling frequency λ of the two-level system, i.e., $\lambda = \sqrt{\epsilon_0^2 + \Delta^2}/\hbar$. For the symmetric situation ($\epsilon_0 = 0$), we have $\lambda\tau \sim 4$ being intermediate between the fast and the slow bath limits. For the activationless and the inverted regime we obtain the proper slow bath limit, because $\lambda\tau \gg 1$. The reasons for such a choice are twofold. First, the quasiclassical approximation leading to Eq. (24) is assumed to be well suited for the slow bath limit [5–7] and we would like to check this general assertion in our particular case of a strong coupling to the bath. Second, with the discussed choice of parameters we make it clear that the so-called slow bath limit should □□□ be confused with the adiabatic limit of ET, although both limits do overlap. In all considered cases, the resulting ET-dynamics is very close to the non-adiabatic ET-limit, being well described with the golden rule rates (cf. Figs. 2 and 3).

The numerical technique for the solution of Zusman equations (9) is detailed in Ref. [23]. We remark here, however, that we have started always from an initial preparation where the electron is fixed on the donor and the reaction coordinate is relaxed to the thermal quasi-equilibrium under this constraint. The Monte Carlo simulations for Eq. (24) have been performed with the □□□□□□□ Euler algorithm (see Appendix C). A nice feature of this algorithm is that it conserves the length of the Bloch vector for a given stochastic trajectory. In other words, the unitary character of the stochastic pseudo-spin evolution on the Bloch sphere is preserved at all times. The initial conditions have been matched to correspond to those for the Zusman equations, i.e., $\sigma_z(0) = 1$ and $x(0)$ was sampled from the Gaussian probability density, $p[x(0)] \sim \exp(-m\omega_0^2 x(0)^2/(2k_B T))$. To obtain convergent, averaged results, we did run 10^4–10^5 stochastic trajectories for each considered case.

Fig. 2 depicts the results of our comparison for the case without external driving. For symmetric ET (cf. Fig. 2a), the numerical solution of Zusman equation (full line) is in a very good agreement with the analytical result given by Eq. (15) with the golden rule rate (16). The Langevin equations (24) predict slightly different results. These results also allow for a fit with only one single-exponential relaxation term. The corresponding rate differs by 15% from the one given numerically by the Zusman equations. The agreement is nevertheless fair. For the activationless case (Fig. 2b) and for the inverted regime (Fig. 2c), however, the situation changes drastically. For the considered parameters the golden rule and the Zusman equations are again in good agreement; in contrast, the Langevin-like equations (24) fail badly. The asymptotic value $P_{11}(\infty)$ obtained from the Langevin equations (24) coincides very well with the analytical prediction in Eq. (25). This agreement provides a successful check of the consistency of our Langevin numerics. Nevertheless, this asymptotic value differs drastically from the corresponding prediction of the Zusman theory, or equivalently the golden rule result. Even worse is the finding that also the □□□□□□□□ are reproduced incorrectly. Instead of a single-exponential decay, the Langevin dynamics of Eq. (24) predict a bi-exponential dynamics with two equally weighted rates. Similar results on the breakdown of mean-field decoupling approximation have been stated in Ref. [8]. Moreover, our findings are consistent with an earlier observation [22] that the theory of Lindblad type [36] has also a problem with the asymptotic long time behavior. The similarity between the considered mean-field Langevin approach and the Lindblad theory is that both the methods conserve positivity of the quantum evolution on the whole time scale of the dissipative dynamics.

Next we demonstrate that the switch-on of a strong periodically varying driving field drastically improves the applicability of the Langevin approach in Eq. (24). We performed the calculations with the following field parameters: an angular frequency of $\Omega = 500$ cm^{-1} and with the field strength $\hat{\epsilon} = 1400$ cm^{-1}. Although the asymptotic populations are still incorrect, the ET dynamics is now much better described by Eq. (24) as compared to the undriven case (cf. Fig. 3). Thus, in the driven case the description with Eq. (24) may become fair even if these fail in the limit of an adi-

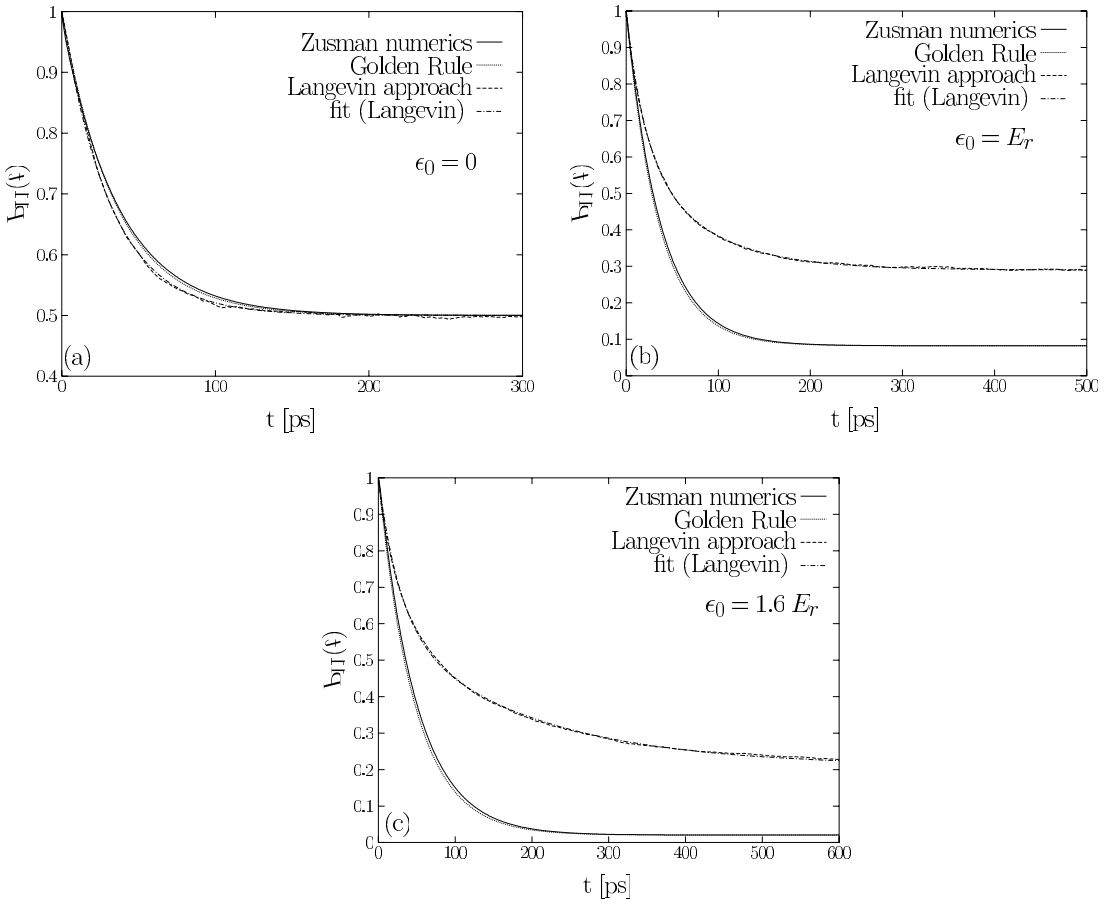

Fig. 2. Relaxation of the donor population $P_{11}(t)$ versus time for the symmetric (a), activationless (b), and the inverted (c) regimes of ET in the absence of external driving. The used set of parameters is as follows: $T = 300$ K, $E_r = 500\ \mathrm{cm}^{-1}$, $\Delta = 10\ \mathrm{cm}^{-1}$, $\tau = 1$ ps. The numerical solutions of the Zusman equations (9) are compared with both the golden rule results, cf. Eqs. (15)–(17), and the results of stochastic simulations of Eq. (24). The golden rule rates are: (a) $\Gamma_{\mathrm{NA}} = 0.0286\ (\mathrm{ps}^{-1})$; (b) $\Gamma_{\mathrm{NA}} = 0.0283\ (\mathrm{ps}^{-1})$; (c) $\Gamma_{\mathrm{NA}} = 0.0212\ (\mathrm{ps}^{-1})$. In the case of Eq. (9), the equilibrium population $P_{11}(\infty)$ is correctly reproduced by Eq. (17). In addition, the one-, or two-exponential fit to the results of stochastic simulations is depicted. These are explicitly given by: (a) $P_{11}(t) = 0.5[1 + \exp(-0.0318t)]$; (b) $P_{11}(t) = 0.29 + 0.355[\exp(-0.0510t) + \exp(-0.0136t)]$; (c) $P_{11}(t) = 0.21 + 0.395[\exp(-0.0356t) + \exp(-0.0055t)]$. The asymptotic value in this fit is taken from Eq. (25).

abatic, or even a vanishing external driving. Note also that the validity of the golden rule description, i.e. the □□□□□□□□□□□□ ET-transfer regime, is □□□ □□□□□□ in strong periodic fields [23]. In view of this fact, the □□□□□□□□□□□□ of the mean-field approximation in strong periodic fields presents indeed a surprise.

One should also emphasize that the failure of Eq. (24) for the nonadiabatic ET-transfer regime does not mean that the discussed method of doing the semiclassical approximation is generally invalid. On the contrary, this kind of approximation appears to be justified in the limit of a strong electronic coupling limit, where Δ becomes comparable to, or greater than E_r [8]. We emphasize here that in the derivation of Zusman equations neither a restriction on the relation between Δ and E_r, nor any additional approximations like the decoupling approximation has been invoked. These equations are also correct in the limit $E_r < \Delta$. To

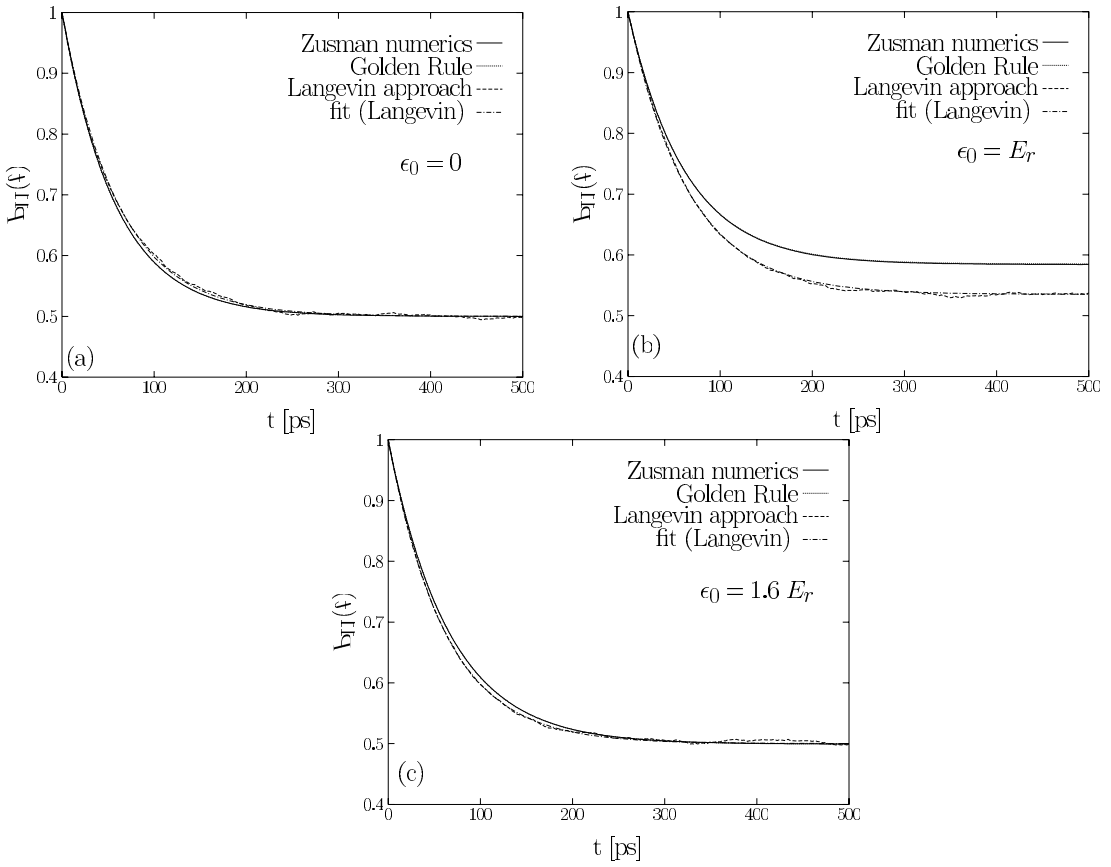

Fig. 3. The same as in Fig. 2, but in the presence of a strong periodic driving. The driving parameters are: $\Omega = 500\,\mathrm{cm}^{-1}$, $\hat{\epsilon} = 1400\,\mathrm{cm}^{-1}$. The golden rule rates are: (a) $\Gamma_{\mathrm{NA}} = 0.0173\ (\mathrm{ps}^{-1})$; (b) $\Gamma_{\mathrm{NA}} = 0.0162\ (\mathrm{ps}^{-1})$; (c) $\Gamma_{\mathrm{NA}} = 0.0152\ (\mathrm{ps}^{-1})$. The results of the stochastic simulations can be fitted by single-exponential dependences in all considered cases: (a) $P_{11}(t) = 0.5[1 + \exp(-0.0163t)]$; (b) $P_{11}(t) = 0.535 + 0.465\exp(-0.0154t)$; (c) $P_{11}(t) = 0.5[1 + \exp(-0.0163t)]$. Panel (b) depicts the inversion of populations due to the externally applied periodic field, i.e., $P_{11}(\infty) > 1/2$.

demonstrate this remarkable fact we performed our numerics for the special set of parameters used in Ref. [8] (in units of $\hbar/\tau$): $\Delta = 1$, $k_{\mathrm{B}}T = 2$, $\epsilon_0 = 0$. E_{r} was varied among three values: (a) $E_{\mathrm{r}} = 0.2$, (b) $E_{\mathrm{r}} = 0.5$ and (c) $E_{\mathrm{r}} = 1.0$. The reason for this special choice is that for these parameters good agreement has been found in Ref. [8] between the behavior of the □□□□□□□□□□□ within the stochastic description in Eq. (24) and those achieved with the tensor multiplication scheme of Makri and Makarov [40,41]. The latter results can be used as a benchmark here. The results of our stochastic simulations and the numerical integration of Zusman equations are depicted with Fig. 4. In the case (a) the agreement is remarkable indeed. The data set in (c) also demonstrates good agreement. Even for the case (b), where some discrepancy occurs, a decisive conclusion about which of two schemes (Zusman vs. Langevin approach) is closer to the tensor multiplication scheme is not really possible.

Moreover, it is worth noting that the behavior of the $\sigma_x(t)$ component of pseudo-spin is not given accurately by Eq. (24) (cf. Ref. [8]). Thus, the □□□□□ density matrix $P_{ij}(t)$ is □□□ reproduced correctly by the stochastic Langevin approach in Eq. (24)! We presume that the Zusman equations (9) do not suffer from this drawback.

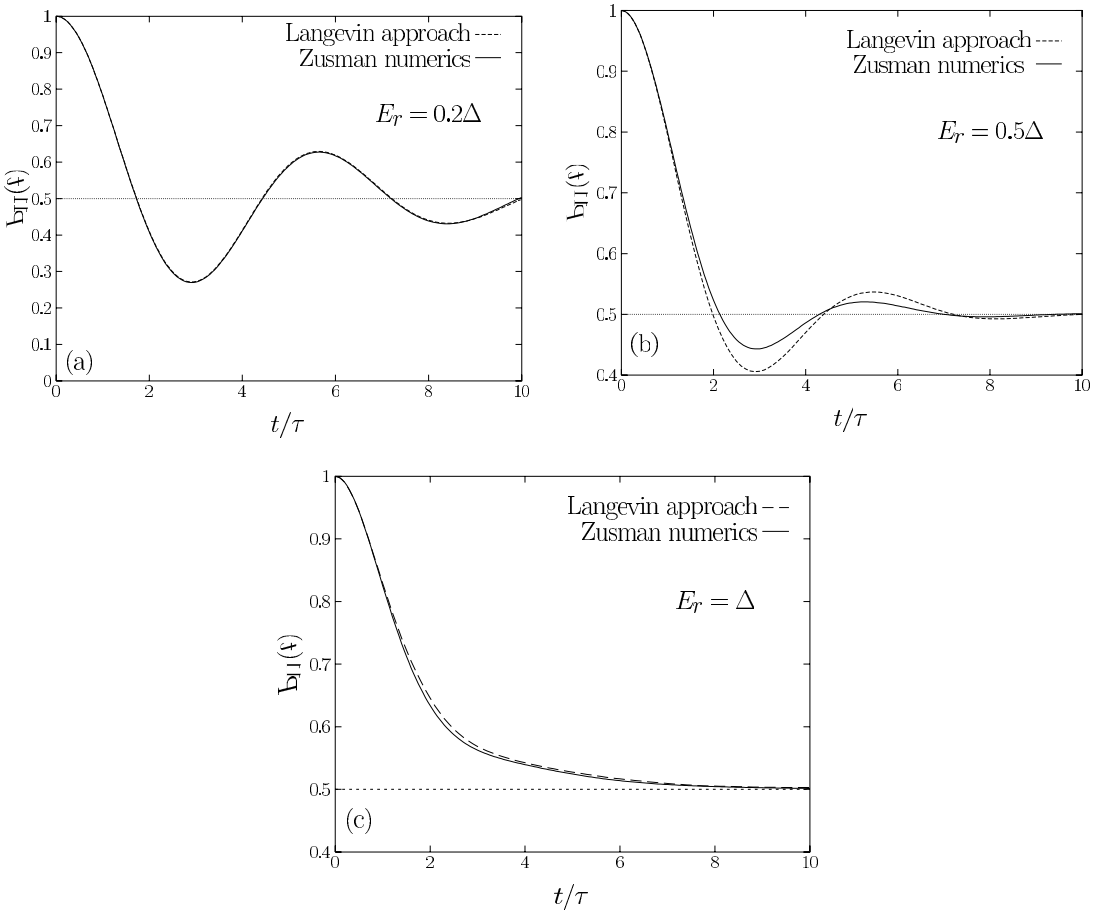

Fig. 4. Dependence of the donor population $P_{11}(t)$ on time □ for the field-free symmetric case studied in Ref. [7]. The parameters are given in units of $\hbar/\tau$: $\Delta = 1$, $k_B T = 2$, $\epsilon_0 = 0$. The reorganization energy E_r was varied among the three values: (a) $E_r = 0.2$, (b) $E_r = 0.5$ and (c) $E_r = 1.0$. The transition from coherent to incoherent behavior is well captured both by Zusman equations and Eq. (24).

6. Conclusion

With this work we primarily have performed a detailed comparison between two familiar, although very different approaches in order to implement the semiclassical approximation for the sluggish reaction coordinate dynamics of a charge transfer dynamics. These two schemes relate to a generalization of the Zusman approach and the nonlinear semiclassical Langevin dynamics. In doing so, we have considered both an undriven ET dynamics and a time-periodic ET-manipulation via external, generally strong electric fields. We demonstrate that both methods yield good agreement for the description of a symmetric ET. In contrast, however, the semiclassical nonlinear SDE method fails to describe the ET dynamics when a strong static bias is present. The inclusion of a strong time-periodic field ET-manipulation appears to cure the Langevin scheme, providing reasonable good agreement between both routes. Nevertheless, the Zusman approach is advantageous when applied to the high-temperature, semiclassical regime of an ET-dynamics. An intriguing problem however remains: What is the best scheme to correct (improve) the dynamics of the reaction field? In doing so, one must go beyond the tractable mean-field decoupling approximation. This challenge surely presents no easy task. The overall positively defined evolution of the

whole electron reduced density matrix displayed by Eqs. (23) and (24) seems appealing; this property is not necessarily guaranteed at initial short times with the Zusman equations. It should be kept in mind, however, that nonMarkovian effects then play an increasingly important role as well. Nevertheless, given the possibility to improve the simple decoupling approximation the second route with correspondingly amended nonlinear Langevin equations deserves future considerations.

Acknowledgements

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Appendix A. Equivalence of different representations of nonlinear Langevin equations

In this appendix we show the equivalence of our Eq. (24) and Eqs. (29)–(32) in Ref. [8]. To this end we simply recast the dynamics of $y(t)$ in Eq. (24) into three parts with $y(t) = y_1(t) + y_2(t) + y_0(t)$, where:

$$\dot{y}_1(t) = -y_1(t)/\tau + \sqrt{2D}\chi(t) \tag{A.1}$$

with the initial condition $y_1(0) = 0$. Moreover,

$$\dot{y}_2(t) = -y_2(t)/\tau - x_0\sigma_z(t)/(2\tau) \tag{A.2}$$

with the initial condition $y_2(0) = 0$, and

$$\dot{y}_0(t) = -y_0(t)/\tau \tag{A.3}$$

with the initial condition $y_0(0) = x(0) - x_0/2$. In Eq. (A.3), $x(0)$ denotes the initial position of the reaction coordinate. The case $x(0) = 0$ used in our calculations corresponds to the case of a non-equilibrium solvent preparation in Ref. [8] (the case $\alpha = 1$ therein). The case $x(0) = x_0/2$ corresponds to the equilibrium solvent preparation ($\alpha = 0$) in Ref. [8]. Eq. (A.3) is trivially integrated and our $y_0(t)$ represents in Eqs. (29) and (30) of Ref. [8] a transient contribution to the energy bias, i.e., $\epsilon_0 \to \epsilon_0 + y_0(t)$, which reflects the initial preparation effects. The advantage of the (y_1, y_2, y_0)-representation in Ref. [8] is that it allows to interpret the corresponding set of equations as nonlinear equations □□□□□□ by an external noise (Ornstein–Uhlenbeck process, cf. Eq. (A.1)) without any feedback onto the noise source. However, in order to perform the numerics our compact set (24) appears to be more convenient.

Appendix B. Calculation of equilibrium populations

In this appendix we give the derivation of Eq. (25). First, using standard manipulations [36] we recast the Langevin equations (24) into their Fokker–Planck counterpart, i.e.,

$$\begin{aligned}
&\frac{\partial P(\sigma_x, \sigma_y, \sigma_x, y, t)}{\partial t} \\
&= \frac{1}{\hbar}[\epsilon_0 + \epsilon(t) + m\omega_0^2 x_0 y] \\
&\quad \times \left(\sigma_y \frac{\partial}{\partial \sigma_x} - \sigma_x \frac{\partial}{\partial \sigma_y}\right) P(\sigma_x, \sigma_y, \sigma_x, y, t) \\
&\quad + \frac{1}{\hbar} \Delta \left(\sigma_z \frac{\partial}{\partial \sigma_y} - \sigma_y \frac{\partial}{\partial \sigma_z}\right) P(\sigma_x, \sigma_y, \sigma_x, y, t) \\
&\quad + \frac{1}{\tau} \frac{\partial}{\partial y}[y + \frac{1}{2} x_0 \sigma_z] P(\sigma_x, \sigma_y, \sigma_x, y, t) \\
&\quad + D \frac{\partial^2}{\partial y^2} P(\sigma_x, \sigma_y, \sigma_x, y, t).
\end{aligned} \tag{B.1}$$

Here, $P(\sigma_x, \sigma_y, \sigma_x, y, t)$ is the time-dependent PDF in the space $(\sigma_x, \sigma_y, \sigma_x, y)$. The equilibrium solution to Eq. (B.1) in the absence of driving $[\epsilon(t) = 0]$ reads

$$\begin{aligned}
&P_{\mathrm{eq}}(\sigma_x, \sigma_y, \sigma_x, y) \\
&\quad = \mathscr{C} \exp\left(- \frac{1}{2k_{\mathrm{B}}T} \left[\Delta \sigma_x + (\epsilon_0 + m\omega_0^2 x_0 y)\sigma_z \right.\right. \\
&\qquad \left.\left. + m\omega_0^2 y^2\right]\right) \delta\left(\sigma_x^2 + \sigma_y^2 + \sigma_z^2 - 1\right).
\end{aligned} \tag{B.2}$$

It can be verified by the direct substitution ($\mathscr{C}$ denotes here the normalization constant). The reduced PDF for the spin subspace

$$Q_{\mathrm{eq}}(\sigma_x,\sigma_y,\sigma_x)=\int_{-\infty}^{\infty}P_{\mathrm{eq}}(\sigma_x,\sigma_y,\sigma_x,y)\,\mathrm{d}y \qquad \text{(B.3)}$$

is obtained from Eq. (B.3). Furthermore, let us change in Eq. (B.3) to the angular variables: $\sigma_z=r\cos\theta,\quad \sigma_y=r\sin\theta\sin\phi,\quad \sigma_x=r\sin\theta\cos\phi$. Then, the value $r=1$ is fixed by the δ-function in Eq. (B.2). The reduced PDF in the probability space defined by two angular variables on the Bloch sphere then reads

$$\tilde{Q}_{\mathrm{eq}}(\theta,\phi)=\sqrt{\frac{\pi k_{\mathrm{B}}T}{E_{\mathrm{r}}}}\mathscr{C}\exp\left(-\frac{1}{2k_{\mathrm{B}}T}\left[\epsilon_0\cos\theta-\frac{1}{2}E_{\mathrm{r}}\cos^2\theta+\Delta\sin\theta\cos\phi\right]\right)\sin\theta. \qquad \text{(B.4)}$$

From Eq. (B.4) one can calculate all averaged spin projections $\langle\sigma_\alpha(\infty)\rangle_\xi$. In particular, for the z-component of the pseudo-spin $-1\leqslant z:=\sigma_z=\cos\theta\leqslant 1$ we integrate over ϕ to obtain the corresponding marginal PDF. It reads

$$\Pi(z)=\frac{I_0\left(\frac{\Delta}{2k_{\mathrm{B}}T}\sqrt{1-z^2}\right)\exp\left(\frac{E_{\mathrm{r}}z^2}{4k_{\mathrm{B}}T}-\frac{z\epsilon_0}{2k_{\mathrm{B}}T}\right)}{2\int_0^1 I_0\left(\frac{\Delta}{2k_{\mathrm{B}}T}\sqrt{1-z^2}\right)\exp\left(\frac{E_{\mathrm{r}}z^2}{4k_{\mathrm{B}}T}\right)\cosh\left(\frac{z\epsilon_0}{2k_{\mathrm{B}}T}\right)\mathrm{d}z}. \qquad \text{(B.5)}$$

By virtue of Eq. (B.5) the result in Eq. (25) follows readily.

Appendix C. Unitary Euler algorithm

In this appendix we present the unitary Euler algorithm used in our calculations. For the sake of convenience, let us change to the dimensionless representation of Eq. (24). By use of the scaling for the time $\tilde{t}=t/\tau$ and for the reaction coordinate $q=y\sqrt{m\omega_0^2/k_{\mathrm{B}}T}$, as well as the dimensionless parameters $a=\Delta\tau/\hbar,\ b=\sqrt{2E_{\mathrm{r}}k_{\mathrm{B}}T}\tau/\hbar,\ c(t)=[\epsilon_0+\epsilon(t)]\tau/\hbar,\ q_0=\sqrt{E_{\mathrm{r}}/(2k_{\mathrm{B}}T)}$ we obtain

$$\begin{aligned}\dot{\sigma}_x(\tilde{t})&=-[c(\tilde{t})+bq(\tilde{t})]\sigma_y(\tilde{t}),\\ \dot{\sigma}_y(\tilde{t})&=[c(\tilde{t})+bq(\tilde{t})]\sigma_x(\tilde{t})-a\sigma_z(\tilde{t}),\\ \dot{\sigma}_z(\tilde{t})&=a\sigma_y(\tilde{t}),\\ \dot{q}(\tilde{t})&=-q(\tilde{t})-q_0\sigma_z(\tilde{t})+\sqrt{2}\chi(\tilde{t})\end{aligned} \qquad \text{(C.1)}$$

In the following we suppress the "tilde" over □ and rewrite Eq. (C.1) in the vector form

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\vec{\sigma}(t)&=\hat{H}(q(t),t)\vec{\sigma}(t),\\ \dot{q}(t)&=-q(t)-q_0\sigma_z(\tilde{t})+\sqrt{2}\chi(\tilde{t}),\end{aligned} \qquad \text{(C.2)}$$

where

$$\hat{H}(q(t),t)=\begin{pmatrix}0 & -c(t)-bq(t) & 0\\ c(t)+bq(t) & 0 & -a\\ 0 & a & 0\end{pmatrix} \qquad \text{(C.3)}$$

The well-known stochastic Euler algorithm amounts to the solution of Eq. (C.2) with the simplest algorithm

$$\begin{aligned}\vec{\sigma}(t+\Delta t)&=\vec{\sigma}(t)+\hat{H}(q(t),t)\vec{\sigma}(t)\Delta t,\\ q(t+\Delta t)&=q(t)-[q(t)+q_0\sigma_z(\tilde{t})]\,\Delta t+\sqrt{2\,\Delta t}\,w(t),\end{aligned} \qquad \text{(C.4)}$$

where $w(t)$ is the zero-mean random Gaussian variable with unit variance [38]. Note that the first equation in Eq. (C.4) violates conservation of the length of Bloch vector. Thus, the time step Δt must be chosen sufficiently small, in order to make such numerical error negligible during the □□□□□ time of propagation.

In the spirit of □□□□□□□□□□□□ unitary algorithms [39] one can choose another discretization scheme and to replace the first equation in Eq. (C.4) with

$$\vec{\sigma}(t+\Delta t)=\exp\left(\hat{H}(q(t),t)\,\Delta t\right)\vec{\sigma}(t). \qquad \text{(C.5)}$$

Then, the length of the Bloch vector is conserved at each step of integration. The proposed algorithm thus preserves the positivity of the averaged pseudo-spin evolution, thereby being of advantageous numerical use. Clearly, our unitary stochastic Euler algorithm outperforms the standard Euler scheme. With respect to the numerical efficiency, it is comparable with the second order Heun algorithm [38], but being preferable in view of its inherent unitary physical features.

References

[1] U. Weiss, Quantum Dissipative Systems, 2nd ed., World Scientific, Singapore, 1999.
[2] J. Jortner, M. Bixon (Eds.), Electron Transfer – From Isolated Molecules to Biomolecules, Adv. Chem. Phys. 106–107 (1999).
[3] M. Grifoni, P. Hänggi, Phys. Rep. 304 (1998) 229.
[4] P. Hänggi, P. Talkner, M. Borkovec, Rev. Mod. Phys. 62 (1990) 251.
[5] G. Stock, J. Chem. Phys. 103 (1995) 1561.
[6] A.A. Golosov, S.I. Tsonchev, P. Pechukas, R. Friesner, J. Chem. Phys. 111 (1999) 9918.
[7] A.A. Golosov, R.A. Friesner, P. Pechukas, J. Chem. Phys. 112 (2000) 2095.
[8] J. Casado-Pascual, C. Denk, M. Morillo, R.I. Cukier, J. Chem. Phys. 113 (2000) 11176.
[9] M. Morillo, R.I. Cukier, J. Chem. Phys. 98 (1993) 4548.
[10] M. Morillo, R.I. Cukier, J. Chem. Phys. 110 (1999) 7966.
[11] A. Lucke, C.H. Mak, J.T. Stockburger, J. Chem. Phys. 111 (1999) 10843.
[12] A. Garg, J.N. Onuchic, V. Ambegaokar, J. Chem. Phys. 83 (1985) 4491.
[13] Yu. Dakhnovskii, R.D. Coalson, J. Chem. Phys. 103 (1995) 2908.
[14] Yu. Dakhnovskii, D.G. Evans, H.J. Kim, R.D. Coalson, J. Chem. Phys. 103 (1995) 5459.
[15] I.A. Goychuk, E.G. Petrov, V. May, Chem. Phys. Lett. 253 (1996) 428.
[16] M. Grifoni, L. Hartmann, P. Hänggi, Chem. Phys. 217 (1997) 167.
[17] V.B. Magalinskii, Sov. Phys. JETP 9 (1959) 1381.
[18] A.O. Caldeira, A.J. Leggett, Physica A 121 (1983) 587.
[19] W.J. Munro, C.W. Gardiner, Phys. Rev. A 53 (1996) 2633.
[20] V. Ambegaokar, Ber. Bunsenges. Phys. Chem. 95 (1991) 400.
[21] P. Pechukas, in: W. Gans et al. (Eds.), Large Scale Molecular Systems, Plenum Press, New York, 1991.
[22] D. Kohen, C.C. Marston, D.J. Tannor, J. Chem. Phys. 107 (1997) 5236.
[23] L. Hartmann, I. Goychuk, P. Hänggi, J. Chem. Phys. 113 (2000) 11159.
[24] E. Wigner, Phys. Rev. 40 (1932) 749.
[25] M. Hillery, R.F. O'Connell, M.O. Scully, E.P. Wigner, Phys. Rep. 106 (1984) 122.
[26] H. Risken, The Fokker–Plank Equation, Springer, Berlin, 1984.
[27] L.D. Zusman, Chem. Phys. 49 (1980) 295.
[28] D.Y. Yang, R.I. Cukier, J. Chem. Phys. 91 (1989) 281.
[29] P.A. Frantsuzov, Chem. Phys. Lett. 267 (1997) 427.
[30] M.V. Basilevsky, A.V. Soudackov, A.I. Voronin, Chem. Phys. 235 (1998) 281.
[31] A. Suarez, R. Silbey, I. Oppenheim, J. Chem. Phys. 97 (1992) 5101.
[32] P. Pechukas, Phys. Rev. Lett. 73 (1994) 1060.
[33] S. Gnutzmann, F. Haake, Z. Phys. B 101 (1996) 263.
[34] A.S. Davydov, N.I. Kislucha, Phys. Stat. Sol. B 59 (1973) 465.
[35] P. Grigolini, V.M. Kenkre, D. Vitali, Phys. Rev. A 44 (1991) 1015.
[36] N. Van Kampen, Stochastic Processes in Physics and Chemistry, second ed., North-Holland, Amsterdam, 1992.
[37] P. Reineker, in: V.M. Kenkre, P. Reineker (Eds.), Exciton Dynamics in Molecular Systems and Aggregates, Springer, Berlin,1982.
[38] T.C. Gard, Introduction to Stochastic Differential Equations, Marcel Dekker, New York, 1988.
[39] B.A. Shadwick, W.E. Buell, Phys. Rev. Lett. 79 (1997) 5189.
[40] M. Makri, D.E. Makarov, J. Chem. Phys. 102 (1995) 4600.
[41] M. Makri, D.E. Makarov, J. Chem. Phys. 102 (1995) 4611.