Nonadiabatic donor–acceptor electron transfer mediated by a molecular bridge: A unified theoretical description of the superexchange and hopping mechanism

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Nonadiabatic bridge-assisted electron transfer (ET) is described by a set of kinetic equations which simultaneously account for the sequential (hopping) as well as the superexchange mechanism. The analysis is based on the introduction of a certain reduced density operator describing a particular set of electron-vibrational levels of the molecular units (sites) involved in the transfer act. For the limiting case of intrasite relaxations proceeding fast compared to intersite transitions a set of rate equations is obtained. This set describes the time evolution of the electronic site populations and is valid for bridges with an arbitrary number of units. If the rate constants for the transition from the bridge to the donor as well as to the acceptor exceed those for the reverse transitions the ET reduces to a single-exponential process with an effective forward and backward transfer rate. These effective rates contain a contribution from the sequential and a contribution from the superexchange mechanisms. A detailed analysis of both mechanisms is given showing their temperature dependence, their dependence on the number of bridge units, and the influence of the energy gap and the driving force. It is demonstrated that for integral bridge populations less than 10^{-3} the complicated bridge-mediated ET reduces to a donor–acceptor ET with an effective overall transfer rate. This transfer rate contains contributions from the sequential as well as the superexchange mechanisms, and thus can be used for a quantitative analysis of the efficiency of different electron pathways. For room-temperature conditions and even at a very small bridge population of 10^{-4}–10^{-10} the superexchange mechanism is superimposed by the sequential one if the number of bridge units exceeds 4 or 5. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1404389]

I. INTRODUCTION

The importance of bridging molecular structures for the observation of long-range electron transfer (ET) has been anticipated years ago (see the different overviews in Ref. 1). There are numerous contributions which describe ET reactions proceeding via a molecular bridge (B) between donor (D) and acceptor (A) redox centers (to mention some recent contributions we refer to (Refs. 2–11) or between microelectrodes (see, e.g., Refs. 12–18). In many cases the bridge induces an effective D–A (or electrode–electrode) coupling via the well-known superexchange mechanism, making long-range ET possible even at low temperatures.[4] In complex molecular structures like proteins the concept of the superexchange mechanism has been used to introduce ET pathways connecting the D and the A sites.[5–7] Apart from the formation of superexchange couplings the bridging molecular groups in donor–bridge–acceptor (D–B–A) systems can also mediate different types of thermally activated transfer including the thermal deliver of an electron into extended bridge states[9,19–22] or resulting in sequential hopping from bridge unit to bridge unit.[16–18,23–25]

In recent years, the interest in studying distant D–A–ET has been renewed according to the observation of ET reac-

tions in DNA fragments.[26,27] The energy gap of the reaction has been determined of about 0.2 eV what is quite enough for the thermal activation of the sequential ET process (see the discussion in Ref. 22). Apart from the DNA, somewhat older studies concentrated on systems with bridging units either connected by conjugated bonds like in polythiophene or oligoporphyrin chains,[14] or with bridging units containing metallic ions, for example as in the repeating structure of the compound $Mn(II)Cu(II)pba3H_2O \cdot 2H_2O$.[28] All these D–B–A systems are among candidates which could mediate sequential bridge-assisted D–A ET (due to their rather good affinity to bond an extra electron). If however the energy gap between the D and the B amounts about 1 eV the sequential mechanism only works at room temperature if the electron to be transferred has been raised into the donor LUMO level. This becomes possible via photoexcitation of the D by an appropriated light quantum or by the reduction of the D with a reducing radical R^-. Accordingly, the D–A–ET proceeds either as a charge separating photo-induced reaction $h\nu$ + DBA→D*BA→D$^+$BA$^-$ or as a pure ET reaction, D$^-$BA→DBA$^-$. The first type of reaction is usually realized via flash photolysis while the second one utilizes pulse radiolysis.

Just with these methods a number of experimental re-

sults on the distant dependency of oligopeptide-mediated long-range D–A ET have been obtained.[29,30] At room temperature, the character of the ET reaction changed when the number of proline containing bridging groups reaches 2 and up to 4. Several attempts have been undertaken to explain this effect, using a combination of different types of superexchange mechanisms with the inclusion of through-space, through-bond, and through nonbonded interactions (see the discussion in Ref. 30). However, a univocal and quantitative explanation could not be presented up to now.

In the present paper we will offer an explanation which is based on the simultaneous consideration of the superexchange and the sequential mechanism of D–A ET. A similar point of view has been used to understand ET reactions in the DNA (see Refs. 22, 31, 32). But already more than 10 years ago one of us (E.G.P) suggested in Ref. 20 the combination of the superexchange and sequential mechanism of D–A–ET. This has been done to explain earlier experiments of Isied and co-workers[29] on D–A ET along proline oligomers with Os(II) and Co(III) as the D and A site, respectively. In Ref. 20 it has been noted that the chain-mediated tunneling superexchange ET forms an electron pathway for a number N of bridging units up to 3 or 4. For $N > 4$, however, this ET mechanisms becomes so inefficient that the activation mechanism largely exceeds the superexchange one.

These early experiments on which the theoretical studies of Ref. 20 have been focused could only be carried out with proline oligomers up to four units. Meanwhile, experimental data on much larger oligomers are available, and thus it is a challenge to develop the theoretical description in much more detail. We will demonstrate that the data available for larger proline oligomers can be understood as the result of the competition between the superexchange and the sequential mechanism of bridge-assisted D–A ET. The corresponding energy gap for the thermal activation of the sequential mechanism in peptide-mediated D–A ET is found to be around 0.21 eV which is close to that reported for the DNA.[22] Note, however, that for a small energy gap of the order of 0.2–0.3 eV, the influence of the superexchange mechanism remains large as well. Consequently, it becomes necessary to specify the conditions at which the superexchange or the sequential mechanism dominates the overall transfer rate. Therefore, a unified description of all ET mechanisms will be formulated in this paper based on a common set of parameters (energy gaps, driving forces, intersite couplings, etc.). This will enable us to decide on the relative importance of both ET mechanisms. Since we have in mind situations where the sequential ET in the bridge is of the nonadiabatic type our considerations will differ basically from those in Ref. 22, where adiabatic ET in the bridge has been provided. Our attempt for a unified description of nonadiabatic D–A ET offers a description of bridges with an arbitrary number of units. Therefore, we can explain the already mentioned results on intramolecular D–A ET along polyproline oligomers.[30]

A decade ago an attempt to achieve such a unifying description has been curried out in Refs. 25 and 33 (see also the more recent description in Refs. 22, 34, 35). It is based on the derivation of a Generalized Master Equation for the total electronic population of a D–B–A system. To derive the kernel of the respective equations (the generalized rate expressions) the approach utilizes the so-called Liouville-space representation and introduces formal pathways which correspond to the superexchange or the sequential ET mechanism. The pathways give a classification of the various rate expressions, but their concrete calculation requires a tremendous effort. Existing computations are restricted to a D–A complex without and with a single bridge unit.[25,33,35] Despite the computational difficulties the derived rate expressions are of a very general type. They are determined by the spectral densities which describe the coupling of the transferred electron to the vibrational degrees of freedom and which enter the rate expressions beyond any perturbation theory. Similar results have been obtained within the spin boson model (simple D–A complex) but using path integral techniques.[36] In the recent paper[22] the Liouville-space approach has been extended to a D–B–A system with an arbitrary number of bridging units. This became possible by introducing the extended basis of B states what results in a separate coupling of the D as well as the A to a single B state allowing a treatment similar to that used in Refs. 25, 33. But the introduction of the extended B-state basis let become the approach valid for an arbitrary intersite coupling within the B.

In an alternative approach to a unifying description of superexchange and sequential ET one applies the method of the reduced density matrix (see, e.g., Refs. 24, 34, 37). This type of description uses the picture of active vibrational coordinates (reaction coordinates) which are coupled to passive coordinates forming a thermal reservoir (heat bath). The density matrix defined in the representation of the active electron vibrational states is obtained by solving respective equations of motion.[16,17,21,38–42] In this manner one may account for the intersite coupling (transfer integrals) as well as for the coupling of the active vibrational coordinates to the electronic levels without any approximation. Indeed, a simultaneous description of sequential and superexchange ET is obtained.[43] The disadvantage of this approach, however, is related to the fact that even the restriction to a single reaction coordinate desires a numerical solution of the density matrix equations. To treat systems with some 10 reaction coordinates is practically impossible.

In the present paper we propose a treatment which benefits from both mentioned approaches, the one ending up with a Liouville-space classification of intersite ET rates and the other based on a direct solution of the electron-vibrational density matrix in site representation. Our approach will enable us to derive rate equations for the total electronic level populations of each site of the D–B–A system independently on the concrete structure of its site sublevels and the number of bridge units. And, our treatment accounts for a realistic number of reaction coordinates. Since their coupling to a thermal reservoir of passive coordinates is also considered it becomes possible to introduce a coarse-grained description of the ET processes. Just as a consequence of the coarse-grained description we can essentially reduce the number of equations ending up with rate equations for the total electronic population of each unit of the

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Nonadiabatic electron transfer   7109

D–B–A system. The reduction to rate equations becomes possible since we restrict our approach to those ET systems where intrasite relaxation is achieved within a characteristic time τ_{rel} which should be short compared to the characteristic time of the ET process, τ_{ET}, i.e., we provide the inequality

$$\tau_{\text{rel}} \ll \tau_{\text{ET}}. \tag{1}$$

This relation indicates that on a time scale of the order of τ_{rel} electronic population transfer between different sites is nearly absent. On the contrary complete intrasite relaxation took place before any ET event. This well-known situation which leads to rate equations for the electronic site populations (see, e.g., Refs. 38–40) is analyzed a new in starting from basic density matrix equations. Since the characteristic time τ_{rel} is typically of the order of 0.1–10 ps (Refs. 35, 41) the theory introduced below is valid for those ET systems where the rates do not exceed values of 10^{11}–10^{13} s^{-1}. Such a situation is definitely valid for nonadiabatic bridge-mediated ET where the electronic couplings between neighboring sites are too small to form an electronic band covering the whole bridge.

Below we introduce the ET model and derive rate equations for the electronic level populations. For a particular relation among the system parameters it will be shown that the hopping mechanism dominates the superexchange one, even though the population of the bridge by the transferred electron is very small (of the order of 10^{-4}–10^{-10}, depending on the concrete value of the energy gap). We consider this as a new result since in such a case of low bridge population the standard treatment of bridge mediated nonadiabatic ET exclusively concentrates on the superexchange mechanism.

The paper is organized as follows: In Sec. II, the theoretical model is discussed and coarse-grained kinetic equations like Pauli's balance equations are derived. In Sec. III, the nonadiabatic ET through a linear molecular bridge is considered in detail. The competition between the superexchange and hopping mechanism is analyzed with respect to the number of bridge units and the dependence on other parameters of the D–B–A system. Section IV deals with an application of the theory to explain experimental data on D–A ET through a bridge formed by proline oligomers. Finally, some general remarks on the interplay of sequential and superexchange ET are given in the concluding Sec. V.

II. MODEL AND KINETIC THEORY

Let us start with the standard model for bridge mediated ET [cf. Fig. 1(a)], where the D and A center are interconnected by a linear chain of N molecular bridging units. Each bridging unit as well as the D and the A centers are characterized by a set of local states $|m\alpha\rangle$ with corresponding energies $E_{m\alpha}$ where the m label the sites of the whole ET system [$m =$ D,1,2,...,N,A, Fig. 1(b)]. Such a D–B–A model with each site characterized by several sublevels gives the basic model of distant D–A–ET (see, e.g., Refs. 1, 18, 21, 34). In the following we will quote the respective ET-Hamiltonian and derive rate equations starting from fundamental density operator relations.

A. The ET-Hamiltonian

Let $|\varphi_m\rangle$ be the electronic Born–Oppenheimer *eigenstates* related to the mth site of the D–B–A system. Since nonadiabatic ET will be considered, we can provide that the overlap between the wave functions related to different sites m and n is small. In such a case it is of some advantage to expand the total Hamiltonian of the ET system with respect to these states resulting in[1,34,44]

$$H_{\text{D–B–A}} = \sum_{m,n} (\delta_{m,n} H_m(q) + (1 - \delta_{m,n}) V_{mn}(q)) |\varphi_m\rangle\langle\varphi_n|. \tag{2}$$

Here, the vibrational Hamiltonian $H_m(q)$ and the transfer coupling $V_{mn}(q)$ depend both on the set of vibrational coordinates q which are involved in the ET reaction (active coordinates). There is no need to establish any restriction for the definition of the active vibrational coordinates. We only provide that all those coordinates which couple strongly to the transferred electron as well as one to another contribute to this set.

Despite the given representation where the electronic states $|\varphi_m\rangle$ can be understood as diabatic states located at the various fragments of the ET system, other interpretations are possible, too. For example, if the bridging molecular structure is given by a chain of hydrogen bonds, each bridging unit can be described by a single ground and a single excited electronic level corresponding the respective proton location within the two wells.

Next, we introduce the *eigenstates* $|\chi_{m\alpha}\rangle$ and *eigenenergies* $E_{m\alpha}$ of the Hamiltonian H_m, where α denotes the set of vibrational quantum numbers corresponding to the set of active coordinates. Having these vibrational states at hand it is easy to give a complete expansion of the D–B–A-Hamiltonian $H_{\text{D–B–A}}$, Eq. (2) with respect to the electron vibrational states

$$|m\alpha\rangle = |\chi_{m\alpha}\rangle |\varphi_m\rangle. \tag{3}$$

This representation using local electronic states is appropriate to carry out the coarse-graining procedure already announced in the Introduction. Since the density matrix theory will be utilized in the following we identify the D–B–A-Hamiltonian, Eq. (2) with the active system Hamiltonian H_S usually introduced in dissipative quantum dynamics.[34,36] We take the representation by means of the states $|m\alpha\rangle$ and get from Eq. (2),[17,34,39]

$$H_S \equiv H_{\text{D–B–A}} = H_0 + V_{\text{tr}}, \tag{4}$$

where the part

$$H_0 = \sum_{m\alpha} E_{m\alpha} |m\alpha\rangle\langle m\alpha|, \tag{5}$$

describes the electron-vibrational energy levels of the various fragments. The intersite coupling is contained in

$$V_{\text{tr}} = \sum_{m,n} (1 - \delta_{m,n}) \sum_{\alpha\beta} V_{m\alpha,n\beta} |m\alpha\rangle\langle n\beta|. \tag{6}$$
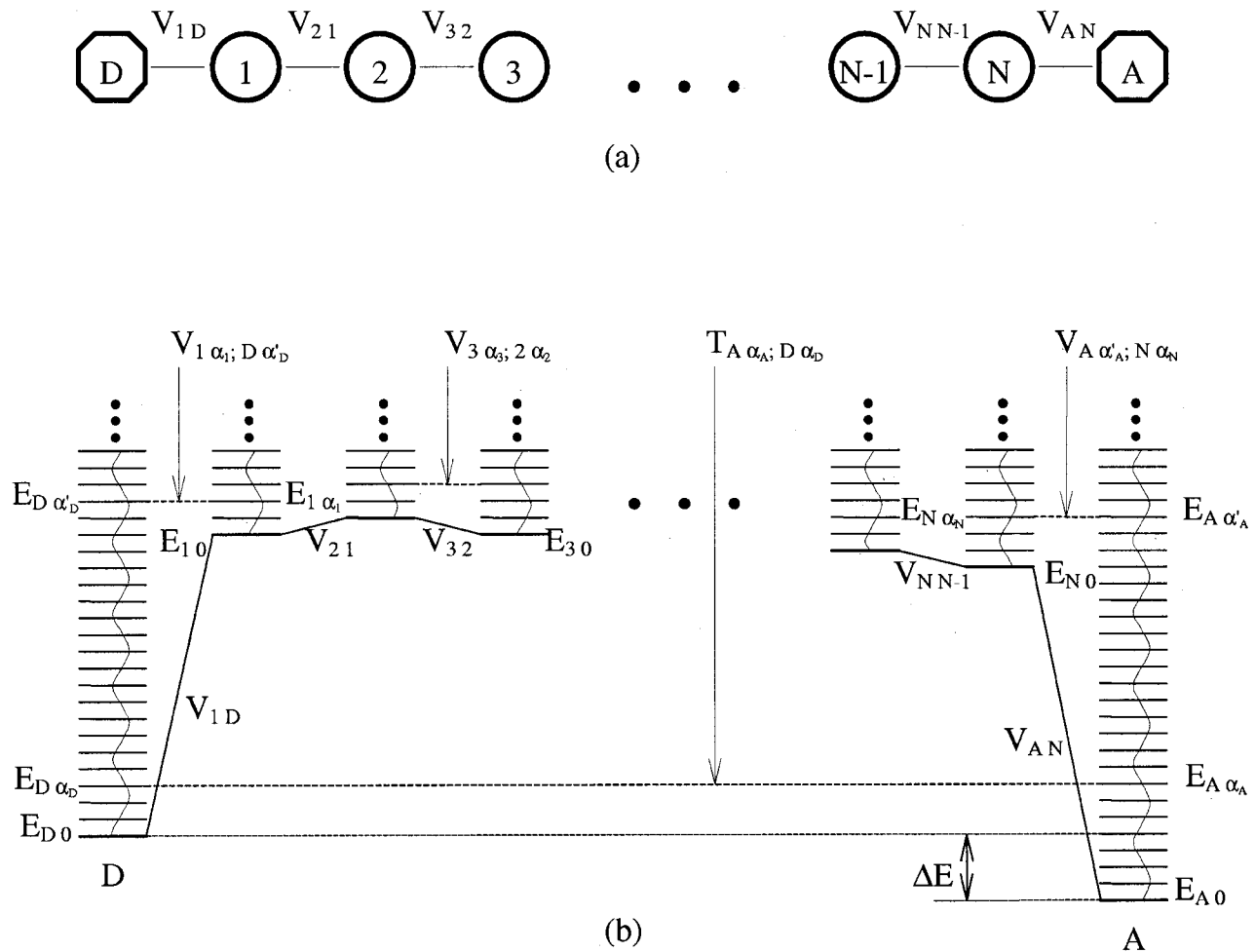
FIG. 1. Linear molecular D–B–A nanostructure built up by N bridging units. The interactions between neighboring sites are characterized by pure electronic off-diagonal couplings V_{1D}, V_{21},...,V_{NN-1}, V_{AN} (a). The ET transitions occur as a result of off-diagonal couplings $V_{m\alpha_m n\alpha_n}$ between the energy levels $E_{n\alpha_n} \approx E_{m\alpha_m}$ related to neighboring sites n and m, $(n,m=D,1,2,...,N-1,A)$, and as a result of the superexchange coupling $T_{A_{\alpha_A}D_{\alpha_D}}$ between the separated D and A (b).

Here, the matrix elements $V_{m\alpha,n\beta}=\langle \chi_{m\alpha}|V_{mn}|\chi_{n\beta}\rangle$ determine the coupling between states belonging to neighboring sites of the D–B–A system [see Fig. 1(b)] and thus specify the transitions among the sites. (Usually one takes the Condon-approximation according to which $V_{m\alpha n\beta}$ splits off into the pure electronic transfer coupling V_{mn} and into the Franck–Condon overlap integrals $\langle \chi_{m\alpha}|\chi_{n\beta}\rangle$.)

To incorporate into the description vibrational relaxation of the active coordinates we couple them to a thermal bath of passive coordinates Z with coupling Hamiltonian,

$$V_{SB}=\sum_m F_m(q,Z)|\varphi_m\rangle\langle\varphi_m|. \tag{7}$$

After changing to the representation with respect to the electron vibrational states it reads

$$V_{SB}=\sum_m \sum_{\alpha,\beta} (1-\delta_{\alpha,\beta})F^{(m)}_{\alpha\beta}(Z)|m\alpha\rangle\langle m\beta|. \tag{8}$$

The matrix elements $F^{(m)}_{\alpha\beta}(Z)$ are just a functions of the bath coordinates and characterize the coupling to the heat bath at any site of the D–B–A system. This coupling is off-diagonal in the local vibrational states $|\chi_{m\alpha}\rangle$ and responsible for re-laxation processes in the D–B–A system, in particular for reaching thermal equilibrium among the vibrational levels of any site. The concrete form of the matrix elements is determined by the structure of the nonadiabatic or the derivative coupling matrix (see, e.g., Refs. 44 and 45). Equation (8) does not contain diagonal contributions since the local states $|m\alpha\rangle$ are defined with respect to the minimum of the potential energy surface (PES) belonging to the level m. To be complete we have to mention that one has to add to the Hamiltonian H_S and V_{SB} the bath Hamiltonian H_B. But for the following considerations there is no need to specify this Hamiltonian in more detail.

B. Reduced density matrix theory of ET

According to the definition of the active system given in the preceding section we can introduce a related reduced density operator,

$$\rho(t)=\text{tr}_B\{\rho_{\text{tot}}(t)\}, \tag{9}$$

where ρ_{tot} denotes the density operator of the total system given by the active system plus the bath. A trace expression reduces ρ_{tot} to the state-space of the active system. Since all

vibrational modes which couple strongly to the transferred electron as well as one to another should contribute to the active system, it is reasonable to assume that the remaining coupling to passive coordinates is weak. This weak-coupling case enables us to use standard density matrix equations in the second Born approximation with respect to the system–bath coupling, Eq. (7), what offers a well-established approach (see, for example, Refs. 18, 21, 24, 34, 37).

According to the chosen states used to expand the total Hamiltonian we introduce the density matrix according to

$$\rho_{m\alpha n\beta}(t) = \langle m\alpha | \rho(t) | n\beta \rangle. \tag{10}$$

Conditions to be fulfilled for a description based on localized states are discussed given in Refs. 17 and 39. In particular, the correct long-time limit is reached if the ET process mainly proceeds via isoenergetic intersite transitions, $E_{m\alpha} \approx E_{n\beta}$ originated by small intersite couplings $V_{m\alpha n\beta}$ [cf. Fig. 1(b)]. Just the condition $E_{m\alpha} \approx E_{n\beta}$ guarantees the establishment of a Boltzmann distribution between all energy levels of the D–B–A system when the ET is completed. This fact is well known in the theory of bridge-assisted nonadiabatic D–A–ET. In the most popular approaches [among them a quantum version of the Marcus theory of ET (Refs. 2, 4, 12) and the spin-boson model of ET (Refs. 36, 46, 47)] the local energies $E_{m\alpha}$ are associated with vibrational levels of the respective site. Below, it will be assumed that the condition $E_{m\alpha} \approx E_{n\beta}$ is valid.

For the present purposes of distant D–A–ET it is sufficient to take the density matrix equations in the Markov approximation. This approximation is well justified since the system–bath interaction is characterized by the inequality $\tau_c \ll \tau_{ET}$, where τ_c denotes the bath correlation time (for τ_{ET} see above). Accordingly the density matrix equations (Redfield-type equations) read (see, also Refs. 17, 34, 38–40)

$$\dot{\rho}_{m\alpha n\beta}(t) = -i\omega_{m\alpha n\beta}\rho_{m\alpha n\beta}(t) - \frac{i}{\hbar}\sum_{k\xi}(V_{m\alpha k\xi}\rho_{k\xi n\beta}(t)$$
$$-V_{k\xi n\beta}\rho_{m\alpha k\xi}(t)) - (1-\delta_{m,n})$$
$$\times \frac{1}{2}(\tau_{m\alpha}^{-1} + \tau_{n\beta}^{-1})\rho_{m\alpha n\beta}(t)$$
$$-\delta_{m,n}\delta_{\alpha,\beta}\sum_{\alpha'}(w_{\alpha\to\alpha'}^{(m)}\rho_{m\alpha m\alpha}(t)$$
$$-w_{\alpha'\to\alpha}^{(m)}\rho_{m\alpha' m\alpha'}(t)). \tag{11}$$

The quantities $\tau_{m\alpha}^{-1}$ define the inverse lifetime of the state $|m\alpha\rangle$ and read

$$\tau_{m\alpha}^{-1} = \sum_{\alpha'} w_{\alpha\to\alpha'}^{(m)}. \tag{12}$$

The rates

$$w_{\alpha\to\alpha'}^{(m)} = e^{\hbar\omega_{\alpha\alpha'}^{(m)}/k_B T}w_{\alpha'\to\alpha}^{(m)}$$
$$= \frac{1}{\hbar^2}\int_{-\infty}^{\infty}d\tau e^{-i\omega_{\alpha\alpha'}^{(m)}\tau}\langle e^{-iH_B\tau/\hbar}F_{\alpha\alpha'}^{(m)}e^{iH_B\tau/\hbar}F_{\alpha'\alpha}^{(m)}\rangle \tag{13}$$

characterize the intrasite relaxation from state $|m\alpha\rangle$ to state $|m\alpha'\rangle$, separated by the transition energy $E_{m\alpha} - E_{m\alpha'} = \hbar\omega_{\alpha\alpha'}^{(m)}$. In Eq. (12) the bracket $\langle\cdots\rangle$ denotes the thermal average with respect to the equilibrium state of the heat bath.

The density matrix equations (11) are appropriate to derive coarse-grained kinetic equations (for the site populations) which are valid on a time scale $\Delta t \gg \tau_c$, τ_{rel}. In the following we will motivate this approximation (some more details can be found in Appendix A). The coarse-grained approximation is based on the fundamental inequality (1) and, consequently, is essential for describing long-range bridge mediated ET reactions. Inequality (1) states that the type of ET considered here takes place on a time scale $\Delta t \gg \tau_{rel}$. This enables us to consider the ET reaction as a transfer which proceeds on the background of quasiequilibrium distributions within each bridge unit as well as within the D and A centers. Noting the definition of the density matrix, Eq. (10) one can state that on the time scale $\Delta t \gg \tau_{rel}$ all off-diagonal matrix elements related to a given site m vanish while the diagonal matrix elements, i.e., the partial site populations $\rho_{m\alpha m\alpha}(t)$ describe a thermal equilibrium (Boltzmann) distribution vs the states $|\chi_{m\alpha}\rangle$. Accordingly we can set

$$\rho_{m\alpha m\beta}(t) = \delta_{\alpha,\beta}W(E_{m\alpha})P_m(t). \tag{14}$$

Here, we introduced the complete electronic site population (integral population)

$$P_m(t) = \sum_{\alpha}\rho_{m\alpha m\alpha}(t), \tag{15}$$

and the Boltzmann equilibrium distribution functions of site m,

$$W(E_{m\alpha}) = \exp(-E_{m\alpha}/k_B T)\left/\sum_{\alpha'}\exp(-E_{m\alpha'}/k_B T)\right. \tag{16}$$

Relation (14) displays the main point of the chosen coarse-grained description. According to the fast intrasite relaxation, the populations $P_{m\alpha}(t) \equiv \rho_{m\alpha m\alpha}(t)$ varies only via an alteration of the total site populations $P_m(t)$. If one inserts the factorized distribution (14) into Eq. (11) it results in the following equations for the integral site population (for details see Appendix A):

$$\dot{P}_m(t) = -\frac{i}{\hbar}\sum_{\alpha}\sum_{k\xi}(V_{m\alpha k\xi}\rho_{k\xi m\alpha}(t) - V_{k\xi m\alpha}\rho_{m\alpha k\xi}(t)). \tag{17}$$

But these equations have to be completed by equations for the off-diagonal density matrix elements, directly obtained from Eq. (11),

$$\dot{\rho}_{m\alpha n\beta}(t) = -[i\omega_{m\alpha n\beta} + \frac{1}{2}(\tau_{m\alpha}^{-1} + \tau_{n\beta}^{-1})]\rho_{m\alpha n\beta}(t)$$
$$-\frac{i}{\hbar}\sum_{k\xi}(V_{m\alpha,k\xi}\rho_{k\xi n\beta}(t) - V_{k\xi,n\beta}\rho_{m\alpha k\xi}(t)). \tag{18}$$

Concentrating on the time region where the ET process takes place and which is large compared to $\tau_{\rm rel} \approx \tau_{m\alpha}$ we can neglect the time derivative of $\rho_{m\alpha n\beta}(t)$ in comparison to the first term of the right-hand side. It follows

$$\rho_{m\alpha n\beta}(t) = \frac{1}{\Delta E_{m\alpha n\beta} - i\Gamma_{m\alpha n\beta}} \sum_{k\xi} (V_{k\xi n\beta}\rho_{m\alpha k\xi}(t)$$
$$- V_{m\alpha k\xi}\rho_{k\xi n\beta}(t)), \qquad (19)$$

where we changed from the transition frequencies and inverse lifetimes to transition energies $\Delta E_{m\alpha n\beta} \equiv \hbar\omega_{m\alpha n\beta}$ and the level broadening $\Gamma_{m\alpha n\beta} \equiv (\hbar/2)(\tau_{m\alpha}^{-1} + \tau_{n\beta}^{-1})$.

Equations (17) and (19) along with relation (14) offer the basis for a coarse-grained description of nonadaibatic bridge-mediated ET. Closed equations for the site populations $P_m(t)$ are obtained in two steps. First one has to iterate Eq. (19) to get density matrix elements which are diagonal with respect to the site index. And second one uses an expression like Eq. (14) (but generalized to the case being also off-diagonal with respect to the quantum number α) to replace the density matrix element by the site population $P_m(t)$ and the thermal distribution $W(E_{m\alpha})$. It results an iteration procedure characterized by small parameters like

$$\frac{|V_{m\alpha n\beta}|^2}{\Delta E_{m\alpha n\beta}^2 + \Gamma_{m\alpha n\beta}^2} \ll 1. \qquad (20)$$

Details of the perturbation expansion with respect to this small parameter are given in Appendix B. In the next section we discuss different examples of ET reactions in D–A systems with a bridge. Emphasis is put on the interplay of the sequential and superexchange mechanism.

III. RESULTS AND DISCUSSION

In studying the role of the sequential (hopping) and the superexchange mechanisms of D–A–ET mediated by a chain of N bridging units we will concentrate on interrelation between the population of the bridge and the way the D–A ET process takes place. In a first part the case will be discussed of a bridge with a single site. Afterwards a bridge with N identical sites is considered. A detailed derivation of the used rate expressions can be found in Appendix B.

A. Bridge with a single unit

To have the most simple but nontrivial case of bridge mediated ET at hand we start with the discussion of a D–B–A system with a single bridge unit as depicted in Fig. 2. Such a system has been already discussed in Refs. 25, 35, 52 to study the efficiency of the sequential and the superexchange mechanisms. The coarse-grained description proposed here enables us to obtain suitable analytic results that simplify the analysis of D–A–ET reactions. We notice the set of kinetic equations (B18) introduced in Appendix B and redefine the rate constants in correspondence to Fig. 2 as $\kappa_{D(A)\to 1} \equiv \kappa_{1(2)}$, $\kappa_{1\to D(A)} \equiv \kappa_{-1(-2)}$, $\kappa_{D(A)\to A(D)} \equiv \kappa_{3(-3)}$. Accordingly we get the following rate equations:

$$\dot{P}_D(t) = -(\kappa_{-1} + \kappa_3)P_D(t) + \kappa_1 P_B(t) + \kappa_{-3}P_A(t),$$
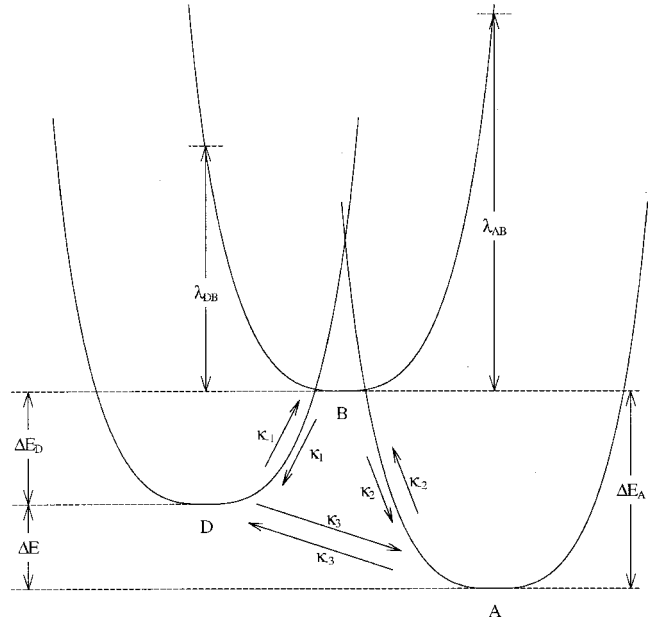$$\dot{P}_B(t) = -(\kappa_1 + \kappa_2)P_B(t) + \kappa_{-1}P_D(t) + \kappa_{-2}P_A(t), \qquad (21)$$

FIG. 2. Scheme of the ET reaction in the D–B–A system with a single bridging unit. All sites have identical vibrational spectra which are represented by identical parabola (vibrational levels are not shown).

$$\dot{P}_A(t) = -(\kappa_{-2} + \kappa_{-3})P_A(t) + \kappa_3 P_D(t) + \kappa_2 P_B(t).$$

Bearing in mind the conservation of probability, Eq. (B19) and the initial conditions

$$P_D(0) = 1, \quad P_A(0) = 0, \quad P_B(0) = 0, \qquad (22)$$

it is possible to derive an exact solution for the three populations under consideration, namely,

$$P_D(t) = \frac{a_1\kappa_1 + d_2\kappa_2}{K_1 K_2}\left[1 - \frac{1}{K_1 - K_2}(K_1 e^{-K_2 t} - K_2 e^{-K_1 t})\right]$$
$$+ \frac{1}{K_1 - K_2}[(a_1 + \kappa_1)(e^{-K_2 t} - e^{-K_1 t})$$
$$+ K_1 e^{-K_1 t} - K_2 e^{-K_2 t}],$$

$$P_A(t) = \frac{a_2\kappa_1 + d_1\kappa_2}{K_1 K_2}\left[1 - \frac{1}{K_1 - K_2}(K_1 e^{-K_2 t} - K_2 e^{-K_1 t})\right]$$
$$+ \frac{a_2 + \kappa_2}{K_1 - K_2}(e^{-K_2 t} - e^{-K_1 t}), \qquad (23)$$

$$P_B(t) = 1 - P_D(t) - P_A(t).$$

There appear two overall transfer rates which are defined as

$$K_{1,2} = \tfrac{1}{2}(a_1 + d_1 \pm \sqrt{(a_1 - d_1)^2 + 4a_2 d_2}) \qquad (24)$$

with

$$a_1 \equiv \kappa_2 + \kappa_{-2} + \kappa_{-3}, \quad a_2 \equiv \kappa_3 - \kappa_2,$$
$$d_1 \equiv \kappa_1 + \kappa_{-1} + \kappa_3, \quad d_2 \equiv \kappa_{-3} - \kappa_1. \qquad (25)$$

The general solution (23) which is characterized by double exponential kinetics can be used to discuss the various re-

gimes of bridge-assisted ET. If, however, the two rates deviate one from another considerably, i.e., if we have

$$K_1 \gg K_2, \tag{26}$$

a single-exponential type of kinetics follows. We will consider this particular case to motivate the introduction of a parameter [see Eq. (28)] which is appropriate to compare the sequential and the superexchange portion of the complete ET reaction. Within the time domain $0 \leq t \ll K_2^{-1}$ the time-dependence of all three populations is defined via the fast rate K_1 only [$\exp(-K_2 t) \simeq 1$]. Then, for $t \gg K_1^{-1}$, the fast part of the kinetic process is finished. Afterwards, when $t \gg K_1^{-1}$ but $t \ll K_2^{-1}$ the second much slower part of the kinetics starts. For this second kinetic phase one can introduce new initial conditions formed by the fast part of the kinetics,

$$P_D(+0) = 1 - \frac{\kappa_{-1} + \kappa_3}{\kappa_1 + \kappa_2},$$

$$P_A(+0) = \frac{\kappa_3}{\kappa_1 + \kappa_2}, \tag{27}$$

$$P_B(+0) = \frac{\kappa_{-1}}{\kappa_1 + \kappa_2}.$$

They are easily derived from Eq. (23) in using $\exp(-K_1 t) = 0$ and $\exp(-K_2 t) = 1$, and in taking into account inequality (26). Here, the sign $+0$ indicates the "slippage" of the initial conditions. It results the new conditions valid for the second type of kinetics where $t \gg K_1^{-1}$. In particular, these initial conditions define an intermediate population of the B and A site with the characteristic ratio,

$$\eta_0 \equiv P_B(+0)/P_A(+0) = \kappa_{-1}/\kappa_3. \tag{28}$$

This quantity can be employed as the main parameter characterizing the mutual relation of the sequential and superexchange part of the ET reaction (see below). So, at $t \gg K_1^{-1}$, the ET process is described by a single exponent only,

$$P_n(t) \simeq (P_n(+0) - P_n(\infty))e^{-Kt} + P_n(\infty),$$

$$(n = D, A, B), \tag{29}$$

with $K \equiv K_2$.

Next let us consider a D–B–A system where the transferred electron is mainly located at the D and A site, while the population of the bridge unit remains very small, i.e., we will deal with the case where κ_1 and κ_2 are large compared to the remaining rates. It follows a rather simple form of the rates

$$K_1 \simeq \tilde{\kappa}_1 + \tilde{\kappa}_2,$$

$$\tilde{\kappa}_a = \kappa_a \left(1 + \frac{\kappa_{-a}}{\kappa_1 + \kappa_2} \right) \approx \kappa_a, \quad (a = 1, 2), \tag{30}$$

and

$$K \equiv K_2 \simeq k_f + k_b,$$

$$k_f \equiv \kappa_3 + \frac{\kappa_{-1} \kappa_2}{\kappa_1 + \kappa_2}, \quad k_b \equiv \kappa_{-3} + \frac{\kappa_{-2} \kappa_1}{\kappa_1 + \kappa_2}. \tag{31}$$

These rates satisfy inequality (26). Thus, the ET corresponds to the kinetic process which can be evaluated by means of the simplified expressions (27) and (29). To have somewhat more concrete rate expressions at hand we use the Marcus form of the ET rate, Eqs. (B21) and (B27), which in our case read

$$\kappa_1 = \frac{2\pi}{\hbar} \frac{|V_{DB}|^2}{\sqrt{4\pi \lambda_{DB} k_B T}} \exp\left[-\frac{(\Delta E_D - \lambda_{DB})^2}{4\lambda_{DB} k_B T} \right],$$

$$\kappa_{-1} = \kappa_1 \exp\left[-\frac{\Delta E_D}{k_B T} \right],$$

$$\kappa_2 = \frac{2\pi}{\hbar} \frac{|V_{AB}|^2}{\sqrt{4\pi \lambda_{AB} k_B T}} \exp\left[-\frac{(\Delta E_A - \lambda_{AB})^2}{4\lambda_{AB} k_B T} \right],$$

$$\kappa_{-2} = \kappa_2 \exp\left[-\frac{\Delta E_A}{k_B T} \right], \tag{32}$$

$$\kappa_3 = \frac{2\pi}{\hbar} \frac{|T_{AD}|^2}{\sqrt{4\pi \lambda_{DA} k_B T}} \exp\left[-\frac{(\Delta E - \lambda_{DA})^2}{4\lambda_{D,-A} k_B T} \right],$$

$$\kappa_{-3} = \kappa_3 \exp\left[-\frac{\Delta E}{k_B T} \right].$$

The quantities $\lambda_{D(A)B}$ and λ_{DA} are the reorganization energies associated with the transitions $D(A) \rightarrow B$ and $D \rightarrow A$, respectively. The energy gaps between the B unit and the D and A centers are denoted by $\Delta E_D \equiv \Delta E_{BD}^0$ and $\Delta E_A \equiv \Delta E_{BA}^0$, respectively. And finally, $\Delta E \equiv E_{D-A}^0$ is the driving force of the DA–ET process (cf. Fig. 2). The effective superexchange coupling T_{AD} has been already quoted in Eq. (B16).

Let us first consider the double-exponential kinetics of the ET process which is described by Eq. (23) [the exact solution of the coarse-grained kinetic equations (21)]. Figure 3 shows that even at rather small energy gaps $\Delta E_D = 0.03$ eV and $\Delta E_A = 0.08$ eV, the characteristic overall rates K_1 and K_2 as well as the corresponding characteristic times K_1^{-1} and K_2^{-1} differ strongly. The fast part of the ET process can be clearly seen if one uses a time scale with a sufficient high resolution [Fig. 3(a)], whereas the slow part is well identified in choosing a more rough scale [Fig. 3(b)]. The fast part of the kinetics leads to a redistribution of electron populations between the D, A, and B units. The characteristic property of this fast part is the rise of the B and A population. We can see that for the cases with the mentioned very small ΔE_D and ΔE_A, the bridge population reaches the maximum $P_B(+0) \approx 0.2$. [Note that Eq. (27) defines a maximal population of the bridging unit.] In the slow part of the ET kinetics the main redistribution of population between the site appears. And, it is a characteristic property of the slow part that the bridge population decreases. This slow part is completed if the steady state populations $P_m(\infty)$ are reached.

It is necessary to note, however, that both parts of the D–A ET process can be observed for the very specific condition of rather small energy gaps ΔE_D and ΔE_A. Such a small gap ΔE_D can be realized in systems where the initial state of the ET reaction follows from photoexcitation of the D, while the small gap ΔE_A corresponds to a reduced A.
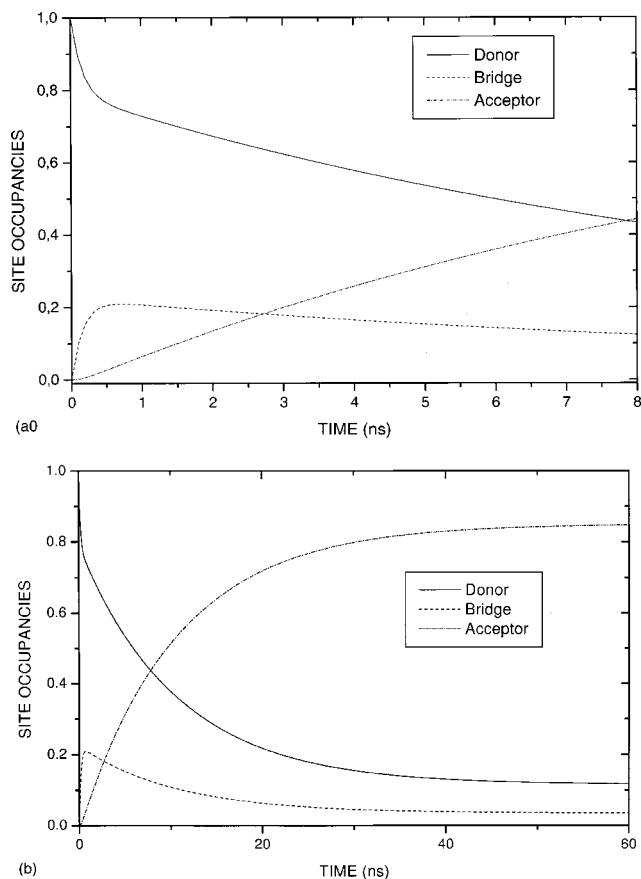
(a0)

(b)

FIG. 3. Identification of the fast (a) and the slow (b) kinetic phases of the ET process in a D–B–A system with a single bridging unit (see Fig. 2). Curves are calculated on the basis of the double-exponential rate Eqs. (23). The rate constants (32) are calculated for $\lambda_{DB}=0.8$ eV, $\lambda_{AB}=1$ eV, $\lambda_{DA}=1.4$ eV, $V_{BD}=0.02$ eV, $V_{AB}=0.01$ eV, $\Delta E_D=0.03$ eV, $\Delta E_A=0.08$ eV, and $k_BT=0.025$ eV.

(a)

(b)

FIG. 5. Relative contribution of the sequential and the superexchange mechanisms of ET for a D–B–A system with a single bridge unit in the dependency on the energy gap ΔE_D (at $k_BT=0.025$ eV) (a) and temperature T (at $\Delta E=0.1$ eV) (b). The calculations are based on Eq. (34) with $\lambda_{DB}=0.8$ eV, $\lambda_{AB}=1$ eV, $\lambda_{DA}=1.4$ eV, $V_{BD}=V_{AB}=0.05$ eV.

To be comparable with the earlier analysis of Ref. 52 we will use same parameters for the D–B–A system (the same energy gaps, reorganization energies, and the same driving force). Figure 4 demonstrates that the fast kinetic phase be-
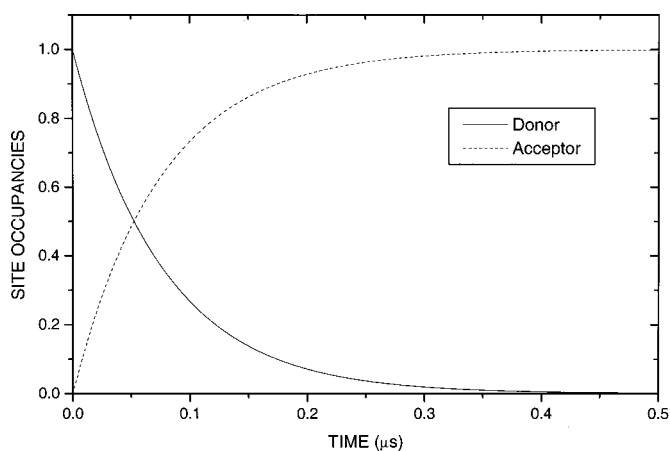

FIG. 4. Kinetics of the ET process in a D–B–A system with a single bridging unit (Fig. 2). The curves computed with rate equations based on a double-exponential decay, Eq. (23), and those based a single-exponential decay, Eq. (29) completely agree. The rate constants Eq. (32) are calculated for $\lambda_{DB}=0.8$ eV, $\lambda_{AB}=1$ eV, $\lambda_{DA}=1.4$ eV, $V_{BD}=V_{AB}=0.05$ eV, $\Delta E_D=0.4$ eV, $\Delta E=0.2$ eV, and $k_BT=0.025$ eV.
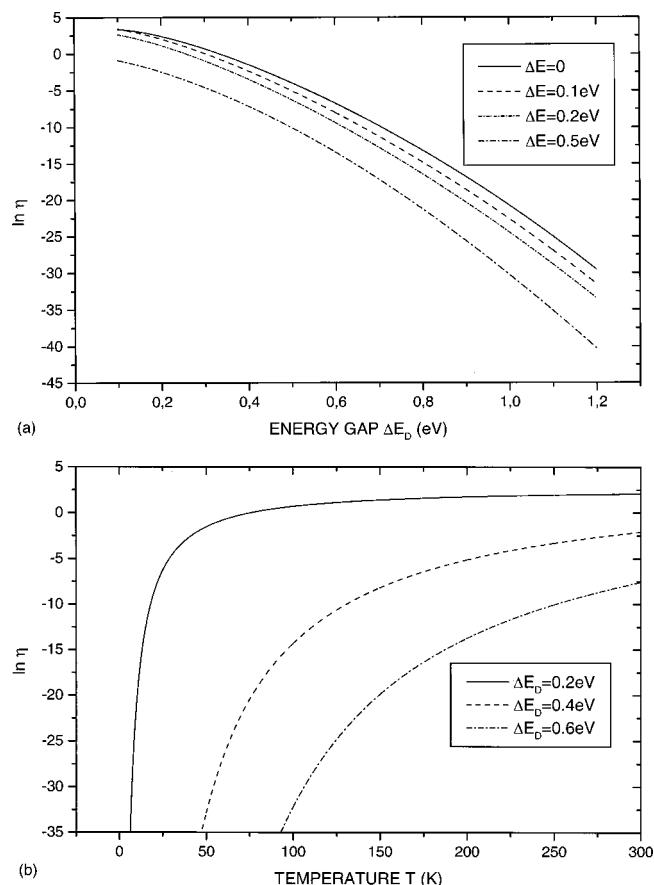
comes not visible (even so the time scale as in Fig. 3 has been chosen). This is due to the fact that for $\Delta E_D=0.8$ eV the bridge population is too small $[P_B(+0)\sim 10^{-10}]$. But, even for a smaller gap $\Delta E_D=0.25$ eV, the maximal bridge population (27) is still of such a low value, $P_B(+0)\approx 4.5 \cdot 10^{-5}$, that one can consider the ET as a process exclusively taking place between the D and A without the participation of the B unit. Such a process is described by a single effective overall transfer rate only. This becomes valid for any bridge-assisted D–A ET where the maximal bridge population does not exceed $P_B\sim 10^{-3}$. Consequently, the further analysis of the D–A–ET will be based on Eq. (29).

The single-exponential D–A–ET kinetics is characterized by the transfer time $\tau_{ET}=K^{-1}$ where the overall transfer rate $K\equiv K_2$ is given by the sum of the forward, k_f, and the backward, k_b, D–A transfer rate, Eq. (31). We note two important circumstances. The first is related to the kinetic description of the ET process. Equation (29) shows that all site populations including the bridge population $P_B(t)$, vary with the same transfer rate K. As far as this statement is also valid in a more general double-exponential description, cf. Eq. (23), we may conclude that the ET process is nothing but the redistribution of populations between the sites which participate in the ET process. The second circumstance reflects a
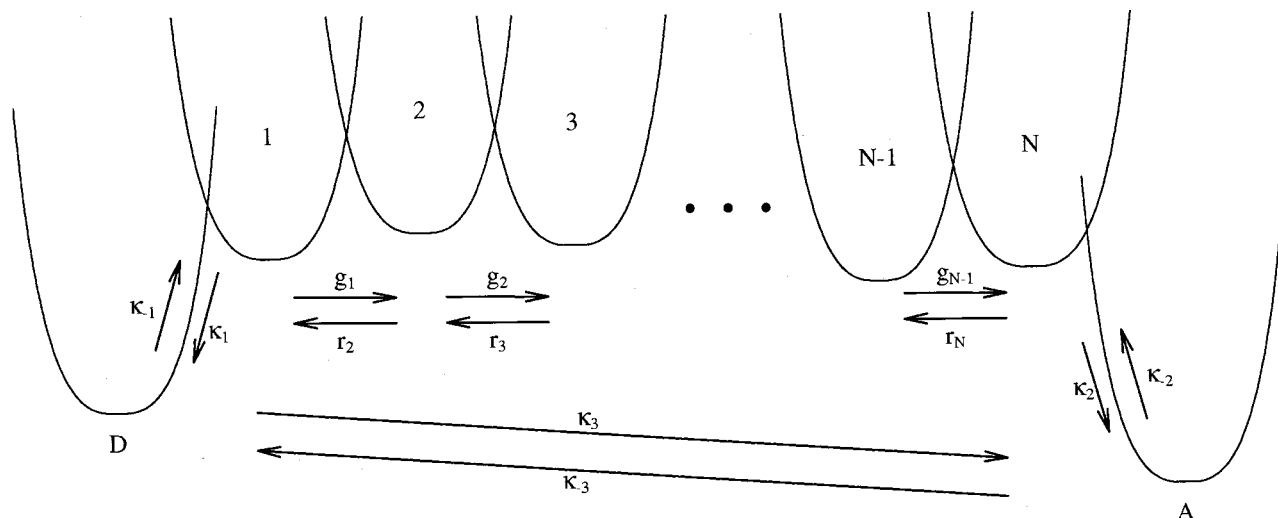
FIG. 6. The scheme of kinetic transitions in a D–B–A system (vibrational levels are not shown). Superexchange ET only occurs between the separated D and A centers.

specificity of bridge-assisted DA–ET. Namely, at small bridge population, the forward and the backward transfer rates consist of the sum of sequential (hopping) and super-exchange rate constants (the latter are denoted by κ_3 and κ_{-3}).

Despite a small maximal population of the bridge unit $[P_B(+0) \sim (10^{-10} - 10^{-4})$ for the gap ΔE_D in the region 0.8–0.22 eV] it is possible to show that the sequential mechanism can exceed the superexchange one. This important fact becomes obvious if we note that in accordance with Eqs. (31) and (32) the backward, k_b, and the overall transfer rate, $K = [1 + \exp(-\Delta E/k_B T)]k_f$, are expressed via the forward transfer rate k_f. Thus, only this transfer rate will be analyzed below. The ratio of the two contributions,

$$\eta = \eta_0 Q, \quad \left(Q \equiv \frac{\kappa_2}{\kappa_1 + \kappa_2} \right), \tag{33}$$

can be considered as the quantity which specifies the mutual relation between the two different contributions to the ET

reaction. The factor η_0 in Eq. (33) is the ratio introduced in Eq. (28). It reflects the relative population weights of the bridging and the acceptor sites which have been formed after the first fast kinetic phase of the D–A–ET process. Just this factor η_0 mainly determines the relative contribution of the sequential and superexchange mechanisms. The quantum yield of the bridge-acceptor ET reaction where the trans-ferred electron populates the bridge (even with a small prob-ability) and is captured by the A center is described in Eq. (33) by the quantity Q. In dependency on the ratio between the bridge-donor and the bridge-acceptor rate constants (κ_1 and κ_2, respectively) Q reaches its maximum $Q=1$ (at $k_1 \ll \kappa_2$) as well as its minimum $Q = \kappa_2/\kappa_1$ (at $k_1 \gg \kappa_2$). For $Q=1$, the parameter η, Eq. (33) completely coincides with the ratio η_0, Eq. (28). In this case the ratio between the intermediate populations $P_B(+0)$ and $P_A(+0)$, Eq. (27), completely specifies the relative contribution of the sequen-tial and the superexchange mechanisms. Generally, accord-ing to Eqs. (32) and (33) we have

$$\eta = \frac{\frac{\Delta E_D \Delta E_A}{|V_{AB}|^2} \sqrt{\frac{\lambda_{DA}}{\lambda_{DB}}} \exp\left\{ -\frac{1}{4k_B T} \left[\frac{(\Delta E_D + \lambda_{DB})^2}{\lambda_{DB}} - \frac{(\Delta E - \lambda_{DA})^2}{\lambda_{DA}} \right] \right\}}{1 + \left| \frac{V_{DB}}{V_{AB}} \right|^2 \sqrt{\frac{\lambda_{AB}}{\lambda_{DB}}} \exp\left\{ -\frac{1}{4k_B T} \left[\frac{(\Delta E_D - \lambda_{DB})^2}{\lambda_{DB}} - \frac{(\Delta E_A - \lambda_{AB})^2}{\lambda_{AB}} \right] \right\}}. \tag{34}$$

Figure 5(a) indicates that for a large energy gap ΔE_D the superexchange mechanism is much more effective ($\eta \ll 1$) than the sequential one (see also Ref. 52). And, the efficiency of the superexchange mechanism is further increased with the increase of the driving force ΔE. But the efficiency of the sequential mechanism can become comparable to the su-perexchange one ($\eta \approx 1$) at room temperatures and at a rather small energy gap [$\Delta E_D \approx 0.2$ eV, Fig. 5(b)]. Below we will

demonstrate that a similar efficiency increase of the sequen-tial ET mechanism can be reached by increasing the number of bridge units.

B. N bridging units

For a bridge with N units as shown in Fig. 6 set of kinetic equations reads [cf. Eq. (B18)]

$$\dot{P}_D(t) = -(\kappa_{-1} + \kappa_3)P_D(t) + \kappa_1 P_1(t) + \kappa_{-3}P_A(t),$$

$$\dot{P}_1(t) = -(\kappa_1 + g_1)P_1(t) + \kappa_{-1}P_D(t) + r_2 P_2(t),$$

$$\dot{P}_m(t) = -(g_m + r_m)P_m(t) + g_{m-1}P_{m-1}(t)$$

$$+ r_{m+1}P_{m+1}(t), \quad (m=2,3,...,N-1), \quad (35)$$

$$\dot{P}_N(t) = -(\kappa_2 + \tau_N)P_N(t) + g_{N-1}P_{N-1} + \kappa_{-2}P_A(t),$$

$$\dot{P}_A(t) = -(\kappa_{-2} + \kappa_{-3})P_A(t) + \kappa_2 P_N(t) + \kappa_3 P_D(t).$$

The rate constants κ_j and κ_{-j}, $(j=1,2,3)$ have been already defined in Eq. (32). Furthermore, we set $g_m \equiv \kappa_{m \to m+1}$ and $r_m \equiv \kappa_{m \to m-1}$.

For the most general case the analytical solution of Eqs. (35) obtains a very complicated form (for examples, see Refs. 48, 49). However, a simple expression can be derived if the hopping transitions between the bridging sites (with characteristic time $\tau_{hop} \ll \tau_{tr}$) are much faster than those between the D (A) site and the corresponding terminal site of the bridge. This will be shortly explained in the following. The mentioned ET regime is reached if all rate constants g_m and r_m largely exceed the B–D (B–A) rate constants κ_1 (κ_2). For a regular bridge where the rate constants between the B units coincide, i.e., $\kappa_B \equiv g_1 = g_2 = \cdots = g_{N-1} = r_2 = r_3 = \cdots = r_N$, the condition for fast hopping across the bridge (compared to the ET between the terminal B units and the D or A) reads

$$\kappa_B \gg \kappa_1, \kappa_2. \quad (36)$$

Let $V_B \equiv V_{mm\pm1}$ be the electronic coupling matrix element and λ_B the reorganization energy for the ET between two (neighboring) B units. Since the ET between identical B units takes place with zero driving force the Marcus form of the rate reads

$$\kappa_B = \frac{2\pi}{\hbar} \frac{|V_B|^2}{\sqrt{4\pi\lambda_B k_B T}} \exp\left[-\frac{\lambda_B}{4k_B T}\right]. \quad (37)$$

If the electronic couplings V_B and V_{DB} (V_{AB}) as well as the respective reorganization energies are comparable, condition (36) can only be satisfied if the exponential factors specifying the rates κ_1 and κ_2 in Eq. (32) strongly exceed those in Eq. (37), i.e., we have

$$\frac{(\Delta E_D - \lambda_{DB})^2}{\lambda_{DB}}, \quad \frac{(\Delta E_A - \lambda_{AB})^2}{\lambda_{AB}} > 3\lambda_B. \quad (38)$$

Now, we may introduce an additional coarse-grained description of the D–A ET bearing in mind the fact that the time scale of the ET process is the order of $\tau_{ET} \gg \tau_{hop} \sim \kappa_B^{-1}$. Therefore, the ET proceeds on the background of fast hopping processes within the bridge. (Note the presence of such hopping processes although the probability to observe the transferred electron at the bridge can be extremely small.) These fast hopping processes result in a quasiequilibrium populations of the bridging sites so that at any time $t \gg \tau_{hop}$ the ratio between populations of different bridge units follows as

$$P_m(t)/P_n(t) = Z_m/Z_n. \quad (39)$$

Here, the quantities Z_m are the partition function of the mth site [compare Eq. (16)]. According to the introduction of the complete bridge population $P_B(t)$, Eq. (B19), the site populations can be represented in the form,

$$P_m(t) = \frac{Z_m}{Z_B}P_B(t), \quad Z_B = \sum_{m=1}^{N} Z_m. \quad (40)$$

Introducing this expression into the set of Eqs. (35) one obtains a reduced set similar to that given in Eqs. (21). It is only necessary to replace the rate constants κ_1 and κ_2 by effective rate constants $\chi_1 = (Z_1/Z_B)\kappa_1$ and $\chi_2 = (Z_N/Z_B)\kappa_2$. For a regular bridge ($Z_1 = Z_2 = \cdots Z_N$) these constants read

$$\chi_1 = \frac{1}{N}\kappa_1, \quad \chi_2 = \frac{1}{N}\kappa_2. \quad (41)$$

Just these rate constants (instead of κ_1 and κ_2) specify the contribution of the sequential mechanism to the formation of the forward and backward rates, Eq. (30).

Replacing in the quantities (25) $\kappa_{1(2)}$ by $\chi_{1(2)}$ we may see that maximal population of the bridge increases proportionally to the number of bridge units,

$$P_B(N, +0) = NP_B(+0). \quad (42)$$

Here, $P_B(+0)$ is given in Eq. (27). At the same time, the sequential part of the forward and backward transfer rates (31) does not change its value [what follows from $\chi_{1(2)}/(\chi_1 + \chi_2) = \kappa_{1(2)}/(\kappa_1 + \kappa_2)$]. The contribution of the superexchange mechanism to k_f and k_b, however, decreases with an increasing number of bridge units. This conclusion follows from Eq. (B17) for the effective D–A coupling T_{AD}. In the case of a regular bridge it is given by

$$T_{AD} = T_{AD}(N) = \frac{V_{AB}V_{BD}}{\sqrt{\Delta E_D \Delta E_A}}\zeta^{N-1}, \quad \zeta \equiv \frac{V_B}{\sqrt{\Delta E_D \Delta E_A}}. \quad (43)$$

In line with Eq. (32) the superexchange rate constants, κ_3 and κ_{-3}, decrease with the increase of N as ζ^{N-1}. If the superexchange mechanism becomes ineffective compared to the sequential one the main contribution to the overall transfer rate results from the sequential mechanism. Figure 7 displays one of the possible peculiar cases. It can be clearly seen that at $N > 4$ not any pronounced distance dependency of the transfer rate on the number of bridge units exists. But it is necessary that the limiting stage of the sequential ET is the transfer process between the terminal bridge units and the adjacent D and A. The relative contribution of the sequential and the superexchange mechanisms to the overall ET rate are given in Fig. 8. This relative contribution is characterized by

$$\eta(N) = \eta\zeta^{-2(N-1)}, \quad (44)$$

where the ratio η, Eq. (34) refers to a bridge with a single bridging site. The parameters are chosen in such a way that for bridge with a single unit the superexchange mechanism dominates for all energy gaps $\Delta E_D > 0.3$ eV. Comparing the various curves shown in Fig. 8 it becomes obvious that for any given value of the gap the relative efficiency of the sequential ET increases substantially with an increasing num-
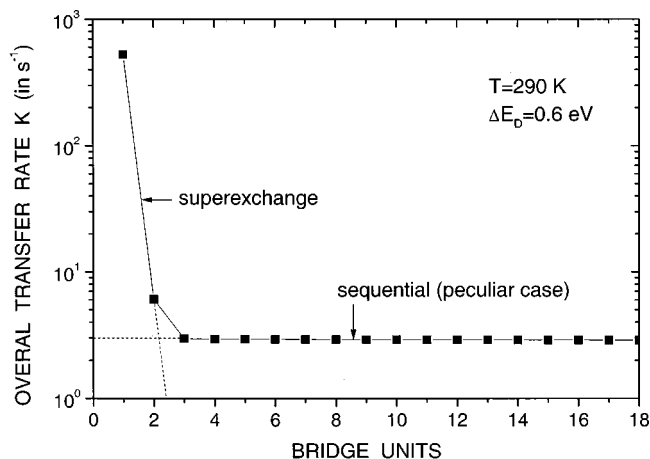
FIG. 7. Overall transfer rate of distant D–B–A ET in dependence on the number of bridge units. The particular case is considered where the limiting step of sequential ET is connected with the hopping transition between D(A) and the corresponding terminal units of the bridge. Calculations have been done on the basis of Eqs. (31)–(43) with $\lambda_{DB}=1.3$ eV, $\lambda_{AB}=1.4$ eV, $\lambda_{DA}=1.8$ eV, $\lambda_B=0.1$ eV, $V_{DB}=V_{AB}=0.02$ eV, $V_B=0.05$ eV, $\Delta E_D=0.6$ eV, $\Delta E=0.1$ eV, and $k_BT=0.025$ eV.

ber of bridging units. As a result, if $N>4$ the sequential mechanism dominates even for $\Delta E_D=0.6$ eV.

If inequality (36) is not valid the sequential contribution K^{seq} to the overall transfer rate $K=K^{sup}+K^{seq}$ depends on the number of bridge units. A similar situation occurs, for example when the hopping through the bridge is the limiting stage of the sequential D–A ET, i.e., when the inequality

$$\kappa_1, \kappa_2 \gg \kappa_B \qquad (45)$$

is fulfilled. It is seen from Fig. 8 that again the superexchange mechanism is replaced by the sequential one. But in the case under consideration, the sequential part of the overall rate depends on the number of bridge units as $K^{seq} \sim N^{-1}$. [To be more precise, at a given set of parameters the dependence reads $K^{seq}=(9.5\cdot10^6/N)\,\mathrm{s}^{-1}$.] The decrease of
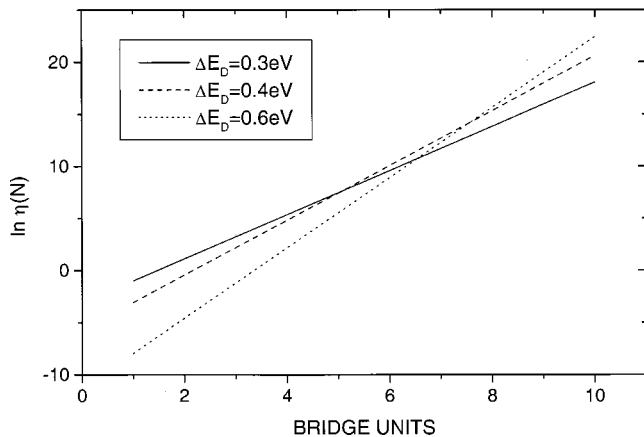

FIG. 8. Relative contribution of the sequential and the superexchange mechanisms of bridge-assisted D–A–ET in dependency on the number of bridge units at different gaps ΔE_D. The curves are calculated in using Eqs. (34) and (44) with $\lambda_{DB}=1.3$ eV, $\lambda_{AB}=1.4$ eV, $\lambda_{DA}=1.8$ eV, $V_{BD}=V_{AB}=0.08$ eV, $V_B=0.12$ eV, $\Delta E=0.1$ eV, and $k_BT=0.025$ eV.
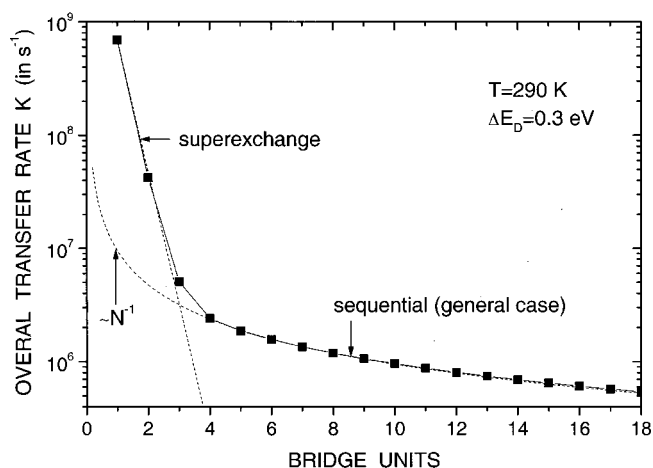

FIG. 9. Overall transfer rate of distant D–B–A ET in dependence on the number of bridge units. The particular case is considered where the limiting step of the sequential ET is the hopping transfer through bridge. Calculations have been done on the basis of a numerical solution of the set of Eqs. (35) with rates (32) and (37) and with $\lambda_{DB}=0.8$ eV, $\lambda_{AB}=0.9$ eV, $\lambda_{DA}=1.1$ eV, $\lambda_B=0.5$ eV, $V_{DB}=V_{AB}=0.04$ eV, $V_B=0.1$ eV, $\Delta E_D=0.3$ eV, $\Delta E=0.3$ eV, and $k_BT=0.025$ eV.

the overall transfer rate with increasing N follows from the law $K^{seq}\simeq AN^{-1}$ valid for hopping ET and presented earlier in Ref. 50 for long bridges.

IV. D–A ET VIA POLYPROLINE OLIGOMERS

In this section we use the results of the preceding part to explain experimental data on the distance dependence of D–A ET. The used data have been published by Isied and co-workers in Refs. 29, 30, 51 and are related to a D–B–A system with the B formed by polyproline oligomers. Ru(II) and Os(II) have been used as the D while Ru(III) or Co(III) act as the A. The reactant state of the ET has been prepared with radiolysis and flash photolysis technics. In all studied cases the fast decrease of the overall ET rate with increasing length of the polyproline oligomer is replaced by a much weaker decrease if the number of proline monomers N in the chain exceeds 3 or 4. Although different suggestions have been given in Ref. 30 to explain this behavior a univocal description is missing. Below we will demonstrate that our unified approach on superexchange and hopping ET in a D–B–A system is capable to give the correct dependence of the ET rate on the number of bridging units by using a single set of system parameters.

Figure 10 compares respective theoretical results with experimental data on the ET through an oligoproline D–A complex $(\{(bpy)_2Ru(II)L\}\cdot(Pro)_NCo(III)(NH_3)_5]^{3+}$. If one notes the rate dependence on N as shown in Fig. 10 one realizes that the superexchange mechanism gives the main contribution if $N\leqslant3$. For $N>3$, however, the hopping ET through the polyproline containing bridge governs the D–A ET process. For the corresponding activation energy we used $\Delta E_D=0.21$ eV, while the intersite coupling between the proline bridging groups is taken as $V_B=0.076$ eV. Note the rather large reorganization energy related to the acceptor, i.e., $\lambda_{AD}=3.05$ eV, and $\lambda_{AB}=1.8$. Such values correspond to the observed large inner-sphere reorganization energy for the
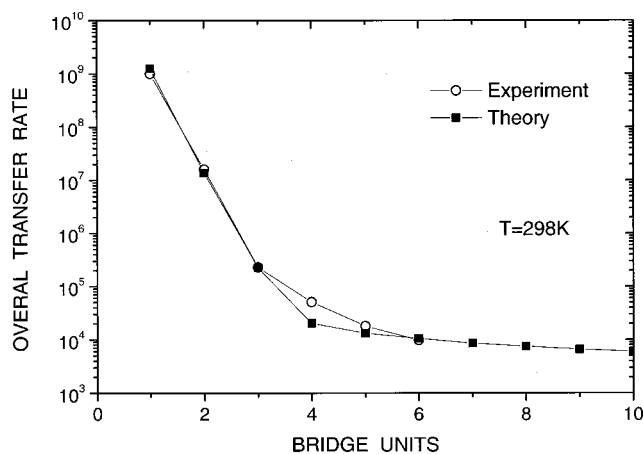
FIG. 10. Comparision with experimental data for the D-polyproline-A system $[\{(bpy)_2Ru(II)L\}\cdot(Pro)_nCo(III)(NH_3)_5]^{3+}$ (Ref. 30). Theoretical results are obtained in using Eqs. (32), (35), and (37) with $\lambda_{DB}=0.8$ eV, $\lambda_{AB}=1.8$ eV, $\lambda_{DA}=3.05$ eV, $\lambda_B=1.35$ eV, $\Delta E=1.7$ eV, $\Delta E_D=0.21$ eV, $V_{BD}=0.06$ eV, $V_{AB}=0.07$ eV, $V_B=0.08$ eV, and $T=298$ K.

Co(III)→Co(II) reaction.[30] The driving force of the reaction is also large ($\Delta E=1.7$ eV), resulting from the chosen type of ions, Ru(II) as the D and Co(III) as the A.

Of course, it would be helpful to have more experimental data on the distance dependence of the ET rate to clearly support or reject the sequential mechanism as the dominating one for $N>4$. Nevertheless, the existing results of Ref. 30 can be easily explained within our approach.

V. CONCLUSION

In the present paper we derived an approach which simultaneously accounts for the sequential as well as the superexchange mechanisms of nonadiabatic bridge-assisted D–A ET. Such a unified description of both contributions has been achieved in the framework of a coarse-graining approximation of ET dynamics. The approach is based on a reduction of the Generalized Master Equations governing the electron vibrational density matrix to a much more simple set of Pauli-type rate equations for integral site populations P_m. The coarse-grained description is well justified if the characteristic time of intersite relaxation is much smaller than the time of intersite electron hopping, Eq. (1). Such an inequality becomes valid if the intersite electron coupling is small compared to the width of energy levels belonging the sites and/or to the energetic distances between neighboring energy levels of the sites. The rate Eqs. (21) and (35) derived in the framework of the coarse-grained description form the basis for an quantitative analysis of different types of nonadiabatic D–A ET.

For the case of D–B–A ET where the rate constants of the ET process between the terminal bridge units and the corresponding D and A centers (κ_1 and κ_2) are large compared to the remaining D and A rate constants (κ_{-1}, κ_{-2}, κ_3, and κ_{-3}), we demonstrated that the complicated ET kinetics reduces to a simple single exponential behavior. It could be described by Eq. (29), with an overall transfer rate $K=k_f+k_b$, Eq. (30). The rate K incorporates contributions

from the superexchange and the sequential ET mechanisms. Note that within the coarse-grained description the form of the forward, k_f, and the backward, k_b, transfer rate follows from the general expression for the overall transfer rate $K=K_2$, Eqs. (24) and (25). Thus, it is not necessary to introduce a specific condition $\dot{P}_B(t)=0$ for the derivation of the transfer rates k_f and k_b as it has been done in Ref. 52.

If the limiting step of the common hopping process is the ET from the D(A) site to the corresponding terminal bridge unit the set of $N+2$ kinetic Eqs. (35) describing the ET process across the bridge, can be reduced to the set of three kinetic Eqs. (21). The latter possesses an exact analytical solution, Eqs. (24) and (25). But, even in the case where the $N+2$ kinetic Eqs. (35) cannot be reduced to the simpler set (21) [for example, when the D(A)-bridge rate constants are of the same order than those describing the transitions within the bridge] or when inequality (45) is fulfilled, the number of coarse-grained kinetic equations, $N+2$, is extremely small compared to the original number of density matrix Eqs. (11). This is an important result which opens a rather simple way to analyze the influence of temperature, of the bridge length, and of various energy parameters including the energy gaps, the reorganization energies, the driving force of the ET reaction, and others. To this end one has to determine the mutual relation between the superexchange and sequential mechanism of D–A ET. In the present paper the conditions have been clarified for which the nonadiabatic ET through the bridge can be really considered as a D–A ET, i.e., characterized by single-exponential kinetics, Eq. (29) with an overall transfer rate $K=k_f+k_b$. Independent on the number of bridging units we obtained the requirement that the integral bridge population (42) should not exceed 10^{-3}. Such a value is reached if the energy gap between the terminal B site and the adjacent D, ΔE_D, is larger than 0.2 eV.

A further interesting result refers to the relative contribution of the sequential and the superexchange mechanism to the D–A ET. Our detailed studies show that the contribution of these two mechanisms to the overall transfer rate $K=k_f+k_b$ substantially depends on the number of bridging units, on temperature, and on the energetic parameters of the D–B–A system. The analytic expressions (34) and (44) made it possible to specify, first, the regions where only one of the two mechanisms dominates, and, second, where both mechanisms are important. In particular, even in a D–B–A system with an energy gap $\Delta E_D>0.5$ eV, the superexchange mechanism can only exceed the sequential (hopping) one if the bridge has no more than 3 up to 5 bridging units (cf. Figs. 7–9). Of course, this conclusion depends on the driving force ΔE but is valid even at room temperatures. But if the number of bridging units exceeds the 3 or 5, the sequential mechanism dominates the ET, although the population of the bridge by the transferred electron may become extremely small (from $P_B\sim10^{-5}$ to $P_B\sim10^{-10}$ in correspondence with the gap interval from $\Delta E_D=0.3$ eV to $\Delta E_D=0.8$ eV).

This result indicates that in complicated D–B–A systems with various ET pathways like in proteins the specification of the most effective D–A pathways has to be carried out with taking into consideration the sequential mechanism, too. As a first example, we applied our theory to the descrip-

J. Chem. Phys., Vol. 115, No. 15, 15 October 2001

Nonadiabatic electron transfer   7119

tion of long-range D–B–A ET mediated by proline containing peptide chain. The sudden change of the measured ET rate if the number of proline monomers in the chains exceeds 3 up to 5 could be explained qualitatively and quantitatively by the transition from a dominating superexchange mechanism of ET to a sequential mechanism.

ACKNOWLEDGMENTS

APPENDIX A: COARSE-GRAINING APPROXIMATION

In Sec. II B we already noted that the small intersite couplings result in the inequality (1) which separates two basically different time scales one from another. Accordingly, we can represent any diagonal element of the density matrix as a product of slow and fast varying functions

$$\rho_{m\alpha m\alpha}(t) = P_m(t) f_{m\alpha}(t). \tag{A1}$$

The integral site population $P_m(t)$, Eq. (15) is assumed to change (with characteristic time τ_{ET}) under the influence of the weak intersite couplings $V_{m\alpha n\beta}$ and thus, it can be considered as a slowly varying function. In contrast the intrasite distribution function $f_{m\alpha}(t)$ changes with characteristic time τ_{rel} and describes the fast relaxation process within the site. It follows from Eq. (15) that

$$\sum_{\alpha} f_{m\alpha}(t) = 1, \tag{A2}$$

and, consequently, the quantity $f_{m\alpha}(t)$ has to be considered as the probability to find site m in a state with energy $E_{m\alpha}$. Since the integral site populations $P_m(t)$ as well as the off-diagonal elements $\rho_{m\alpha k\xi}(t)$ do not change on the time scale $\Delta t \sim \tau_{\mathrm{rel}}$ we may conclude $\dot{P}(t) = 0$ and $\rho_{n\alpha k\xi}(t) \approx \rho_{n\alpha k\xi}(0) = 0$. The latter relation follows from the initial condition which has been set up in such a manner that off-diagonal density matrix elements does not appear. The substitution of expression (A1) into Eq. (11) yields

$$\dot{f}_{m\alpha}(t) = -\sum_{\alpha'} (w^{(m)}_{\alpha \to \alpha'} f_{m\alpha}(t) - w^{(m)}_{\alpha' \to \alpha} f_{m\alpha'}(t)). \tag{A3}$$

Inserting concrete expressions for the relaxation rates this equations also allows to specify the characteristic time τ_{rel} of intrasite relaxation (see also the examples in Refs. 53–56). When $t \gg \tau_{\mathrm{rel}}$, the function $f_{m\alpha}(t)$ reduces to the equilibrium distribution $W(E_{m\alpha})$, Eq. (16). Consequently, if one describes the kinetic process on the time scale $\Delta t \gg \tau_{\mathrm{rel}}$ (coarse-grained description), we have to operate with the equilibrium function $f_{m\alpha}(t \gg \tau_{\mathrm{rel}}) = W(E_{m\alpha})$. Taking this fact into consideration [along with Eqs. (A2) and (A3)] and substituting the factorized distribution (A1) in Eq. (11), we come to an equation for the integral site population of the form,

$$\dot{P}_m(t) = -(i/\hbar) \sum_{\alpha} \sum_{k\xi} (V_{m\alpha k\xi} \rho_{k\xi m\alpha}(t)$$
$$- V_{k\xi m\alpha} \rho_{m\alpha k\xi}(t)). \tag{A4}$$

This equation will be further used in Sec. II B.

APPENDIX B: DERIVATION OF KINETIC EQUATIONS AND RATE CONSTANTS

1. BMS with a single site

The following discussion is devoted to an explanation of those derivations necessary to obtain the kinetic equations for the site populations $P_m(t)$ in starting from the coarse-grained density matrix Eqs. (19). To get the essence of the derivation let us consider a D–B–A system with a single bridging unit. For the sake of compactness we temporarily introduce the abbreviations $m \equiv m\alpha$, $n \equiv n\beta$ so that $\Delta E_{\mathrm{DB}} \equiv \Delta E_{\mathrm{D}_{\alpha_D} \mathrm{B}_{\alpha_B}}$, $\Gamma_{\mathrm{DA}} \equiv \Gamma_{\mathrm{D}_{\alpha_D} \mathrm{A}_{\alpha_A}}$, $V_{\mathrm{DB'}} \equiv V_{\mathrm{D}_{\alpha_D} \mathrm{B}_{\alpha_B'}}$, $\rho_{\mathrm{DD}} \equiv \rho_{\mathrm{D}_{\alpha_D} \mathrm{D}_{\alpha_D}}$, $\rho_{\mathrm{DA'}} \equiv \rho_{\mathrm{D}_{\alpha_D} \mathrm{A}_{\alpha_A'}}$, etc. By noting these abbreviations we obtain from the general Eq. (17) the equation valid for the complete donor population

$$\dot{P}_{\mathrm{D}}(t) = -(i/\hbar) \sum_{\alpha_D} \sum_{\alpha_B} (V_{\mathrm{DB}} \rho_{\mathrm{BD}}(t) - V_{\mathrm{BD}} \rho_{\mathrm{DB}}(t)). \tag{B1}$$

The density matrix elements on the right-hand side follow from the appropriate specified version of Eq. (19) which is of basic importance for the proposed iteration procedure. Bearing in mind the fact that on the time scale $\Delta t \gg \tau_{\mathrm{rel}}$ under consideration, the property

$$\rho_{mm'}(t) \equiv \rho_{m\alpha_m m\alpha_m'}(t)$$
$$= \rho_{m\alpha_m m\alpha_m}(t) \delta_{\alpha_m \alpha_m'} \equiv \rho_{mm}(t) \delta_{\alpha_m \alpha_m'},$$
$$(m = \mathrm{D, B, A}), \tag{B2}$$

is guaranteed independently on the concrete mechanism of intersite ET, one gets

$$\rho_{\mathrm{DB}}(t) = \rho^*_{\mathrm{BD}}(t)$$
$$= \frac{V_{\mathrm{DB}}(\rho_{\mathrm{BB}}(t) - \rho_{\mathrm{DD}}(t)) - \Sigma_{\alpha_A} V_{\mathrm{AB}} \rho_{\mathrm{DA}}(t)}{\Delta E_{\mathrm{BD}} + i \Gamma_{\mathrm{BD}}}. \tag{B3}$$

A substitution of this expression into Eq. (B1) yields

$$\dot{P}_{\mathrm{D}}(t) = -\frac{2}{\hbar} \sum_{\alpha_D} \sum_{\alpha_B} \left\{ |V_{\mathrm{DB}}|^2 \frac{\Gamma_{\mathrm{BD}}}{\Delta E^2_{\mathrm{BD}} + \Gamma^2_{\mathrm{BD}}} (\rho_{\mathrm{DD}}(t) - \rho_{\mathrm{BB}}(t)) \right\}$$
$$+ \frac{i}{\hbar} \sum_{\alpha_D} \sum_{\alpha_B} \sum_{\alpha_A} \left\{ \frac{V_{\mathrm{DB}} V_{\mathrm{BA}}}{\Delta E_{\mathrm{BD}} - i \Gamma_{\mathrm{BD}}} \rho_{\mathrm{AD}}(t) \right.$$
$$\left. - \frac{V_{\mathrm{AB}} V_{\mathrm{BD}}}{\Delta E_{\mathrm{BD}} + i \Gamma_{\mathrm{BD}}} \rho_{\mathrm{DA}}(t) \right\}. \tag{B4}$$

This expression indicates that the first step of the iteration procedure results in the formation of the sequential ET pathway. This is clearly shown by the first term of right-hand side of Eq. (B4), since it only contains diagonal elements $\rho_{\mathrm{DD}}(t)$ and $\rho_{\mathrm{BB}}(t)$. The second term, however, is expressed by off-diagonal density matrix elements $\rho_{\mathrm{AD}}(t)$ and $\rho_{\mathrm{DA}}(t)$. To ex-

press these elements by diagonal ones, it becomes necessary to take further steps in the iteration procedure. First, we note

$$\rho_{DA}(t)=\rho_{AD}^*(t)=\frac{\Sigma_{\alpha'_B}(V_{B'A}\rho_{DB'}(t)-V_{DB'}\rho_{B'A}(t))}{\Delta E_{DA}-i\Gamma_{DA}}. \quad (B5)$$

Here, the off-diagonal density matrix elements $\rho_{DA}(t)$ are related to the elements $\rho_{DB}(t)$ and $\rho_{BA}(t)$. Indeed, we need additional equations for these matrix elements which are, for example, of the form

$$\rho_{AB}(t)=\rho_{BA}^*(t)$$

$$=\frac{-\Sigma_{\alpha'_D}(V_{D'B}\rho_{AD'}(t)-V_{AB}(\rho_{AA}(t)-\rho_{BB}(t))}{\Delta E_{BA}-i\Gamma_{BA}}. \quad (B6)$$

Here, the elements $\rho_{AB}(t)$ are expressed by diagonal elements $\rho_{BB}(t)$ and $\rho_{AA}(t)$ [and off-diagonal $\rho_{AD}(t)$]. Now, by substituting the relations (B6) and (B3) into Eq. (B4) we complete the second step of the iteration procedure. This step has two effects on Eq. (B4). First, there appear corrections to the terms proportional to the difference $\rho_{DD}(t)-\rho_{BB}(t)$ which are of fourth order in the intersite couplings. According to the inequality (20) which is of basic importance for the iteration procedure we may omit these corrections. A further result of going up to the second step of the iteration consist in the appearance of principally new terms in Eq. (B4). These terms contain the difference $\rho_{DD}(t)-\rho_{AA}(t)$ and are generated as follows:

$$\frac{i}{\hbar}\sum_{\alpha_D}\sum_{\alpha_B}\sum_{\alpha_A}\left\{\frac{V_{DB}V_{BA}}{\Delta E_{BD}-i\Gamma_{BD}}\rho_{AD}(t)-\frac{V_{AB}V_{BD}}{\Delta E_{BD}+i\Gamma_{BD}}\rho_{DA}(t)\right\}$$

$$\approx\frac{i}{\hbar}\sum_{\alpha_D,\alpha_A}\sum_{\alpha_B,\alpha'_B}\left\{\frac{V_{DB}V_{BA}V_{AB'}V_{B'D}}{\Delta E_{BD}\Delta E_{B'A}}\frac{1}{\Delta E_{DA}+i\Gamma_{DA}}\right.$$

$$\left.-\frac{V_{AB}V_{BD}V_{DB'}V_{B'A}}{\Delta E_{BD}\Delta E_{B'A}}\frac{1}{\Delta E_{DA}-i\Gamma_{DA}}\right\}$$

$$\times(\rho_{AA}(t)-\rho_{DD}(t)). \quad (B7)$$

To obtain the final expression we have noted that in the discussed case of D–A ET the electronic gap between the lowest energy levels of the B and the D site, i.e., $\Delta E_{BD}^0=E_{B0}-E_{D0}$, is much larger than the energetic distance between the lowest energy levels of the D and the A sites, $\Delta E_{DA}^0\equiv E_{D0}-E_{A0}$, as well as between the neighboring energy levels within each D, A, and B [cf. Fig. 1(b)]. For such conditions the direct ET between the D and the A proceeds via transitions for which $\Delta E_{D--A}\equiv E_{D_{\alpha_D}}-E_{A_{\alpha_A}}\approx 0$ while $\Delta E_{BD}\gg\Gamma_{BD}$ and $\Delta E_{BA}\gg\Gamma_{BA}$. Noting relation (B7) the rate Eq. (B4) reduces to the form

$$\dot{P}_D(t)=-\frac{2}{\hbar}\left\{\sum_{\alpha_D}\sum_{\alpha_B}|V_{DB}|^2\frac{\Gamma_{BD}}{\Delta E_{BD}^2+\Gamma_{BD}^2}(\rho_{DD}(t)-\rho_{BB}(t))\right\}$$

$$+\sum_{\alpha_D}\sum_{\alpha_A}\left\{|T_{AD}|^2\frac{\Gamma_{D--A}}{\Delta E_{DA}^2+\Gamma_{DA}^2}(\rho_{DD}(t)-\rho_{AA}(t))\right\},$$

$$(B8)$$

where

$$|T_{AD}|^2=\frac{1}{2}\sum_{\alpha_B}\sum_{\alpha'_B}\frac{V_{AB}V_{BD}V_{DB'}V_{B'A}+V_{DB}V_{BA}V_{AB'}V_{B'D}}{\Delta E_{BD}\Delta E_{B'A}}.$$

$$(B9)$$

These results demonstrate that the second step of the iteration procedure leads to fourth-order expressions with respect to the intersite couplings. Carrying out the third iteration step one obtains sixth-order contributions with respect to the inter-site couplings. But, in the case of a single bridging unit this step only generates corrections to the terms already present in Eq. (B8).

As it has been already outlined in earlier discussions (see, e.g., Refs. 25 and 33) a rate equation like Eq. (B8) combines sequential ET given here as a hopping process between neighboring sites (D and B) and an ET reaction connecting directly the D and A unit which are separated by the B unit. This latter contribution is of fourth-order with respect to the intersite couplings whereas the hopping processes contains the off-diagonal matrix elements $V_{BD}^*=V_{DB}\equiv V_{D_{\alpha_D}B_{\alpha_B}}$ in second order.

To obtain the final form of the kinetic equation for the D-level population, we utilize Eq. (14) and obtain

$$\dot{P}_D(t)=-(\kappa_{D\to B}+\kappa_{D\to A})P_D(t)+\kappa_{B\to D}P_B(t)+\kappa_{A\to D}P_A(t).$$

$$(B10)$$

Changing back to the complete notation (including the quantum numbers α, β, etc.) we get two types of basic rate expressions, the rate

$$\kappa_{D\to B}=\frac{2\pi}{\hbar}\sum_{\alpha_D}\sum_{\alpha_B}|V_{D_{\alpha_D}B_{\alpha_B}}|^2W(E_{D_{\alpha_D}})L(E_{D_{\alpha_D}}-E_{B_{\alpha_B}}), \quad (B11)$$

and the rate

$$\kappa_{D\to A}=\frac{2\pi}{\hbar}\sum_{\alpha_D}\sum_{\alpha_A}|T_{A_{\alpha_A}D_{\alpha_D}}|^2W(E_{D_{\alpha_D}})L(E_{D_{\alpha_D}}-E_{A_{\alpha_A}}). \quad (B12)$$

All other types of transfer rates are obtained in changing the respective site indices. In Eqs. (B11) and (B12) we introduced Lorentzian functions,

$$L(E_{a\alpha}-E_{b\beta})=\frac{1}{\pi}\frac{\Gamma_{a\alpha b\beta}}{(E_{a\alpha}-E_{b\beta})^2+\Gamma_{a\alpha b\beta}^2}. \quad (B13)$$

The quantity

$$|T_{A_{\alpha_A}D_{\alpha_D}}|^2=\frac{1}{2}\sum_{\alpha_B}\sum_{\alpha'_B}\left\{\frac{V_{A_{\alpha_A}B_{\alpha_B}}V_{B_{\alpha_B}D_{\alpha_D}}V_{D_{\alpha_D}B_{\alpha'_B}}V_{B_{\alpha'_B}A_{\alpha_A}}}{\Delta E_{B_{\alpha_B}D_{\alpha_D}}\Delta E_{B_{\alpha'_B}A_{\alpha_A}}}\right.$$

$$\left.+\frac{V_{D_{\alpha_D}B_{\alpha'_B}}V_{B_{\alpha'_B}A_{\alpha_A}}V_{A_{\alpha_A}B_{\alpha_B}}V_{B_{\alpha_B}D_{\alpha_D}}}{\Delta E_{B_{\alpha'_B}D_{\alpha_D}}\Delta E_{B_{\alpha_B}A_{\alpha_A}}}\right\} \quad (B14)$$

introduced in Eq. (B12) specifies the square of the effective superexchange D–A matrix element, which directly couples the D and the A state.

If the states $|D_{\alpha_D}\rangle$, $|B_{\alpha_B}\rangle$, and $|A_{\alpha_A}\rangle$ refer to the vibrational spectrum of a single electronic state, than $V_{A_{\alpha_A}B_{\alpha_B}}=V_{AB}\langle\chi_{\alpha_A}|\chi_{\alpha_B}\rangle$, $V_{B_{\alpha_B},D_{\alpha_D}}=V_{BD}\langle\chi_{\alpha_B}|\chi_{\alpha_D}\rangle$, where V_{AB} and V_{BD} are now the pure electronic couplings while $\langle\chi_{\alpha_{D(A)}}|\chi_{\alpha_B}\rangle$

J. Chem. Phys., Vol. 115, No. 15, 15 October 2001

Nonadiabatic electron transfer   7121

are the overlap integrals between the vibrational wave functions related to localized states of the transferred electron at the D, B, and A site. If the vibrational energies are small compared to the above mentioned energy gaps ΔE_{BD}^0 and ΔE_{BA}^0, then the superexchange matrix element (B14) reduces to the somewhat simpler form,

$$T_{A_{\alpha_A} D_{\alpha_D}} = T_{AD} \langle \chi_{\alpha_A} | \chi_{\alpha_D} \rangle \tag{B15}$$

with the effective pure electronic D–A coupling,

$$T_{AD} = \frac{V_{AB} V_{BD}}{\sqrt{\Delta E_{BD}^0 \Delta E_{BA}^0}}. \tag{B16}$$

The respective expressions for $\kappa_{B \to D}$ and $\kappa_{A \to D}$ follow from Eqs. (B11) and (B12) after substituting $W(E_{B_{\alpha_B}})$ and $W(E_{A_{\alpha_A}})$ by $W(E_{D_{\alpha_D}})$. The kinetic equations for the populations $P_B(t)$ and $P_A(t)$ are derived in the same manner as those for $P_D(t)$.

2. BMS with N sites

To study the case of a bridge with N units one has to extend the iteration procedure explained in the preceeding section. As far as the inequalities like Eq. (20) hold for all bridge units we may use the lowest-order expressions for the sequential hopping terms. Therefore, we restrict ourself in the following on second-order contributions with respect to the intersite couplings. But, to obtain the superexchange coupling between the D and A centers one has to perform N times the iteration steps mentioned in in the foregoing section in relation to the treatment of a single bridge unit. In particular we are able to derive an expression for the square of the effective matrix element which is symmetric with respect to the energy gap ΔE_{BD}^0 (between the bridge unit and the D) and the energy gap ΔE_{BA}^0 [between the bridge unit and the B, cf. Eq. (B16)]. Of course, such a symmetric expression can be also derived in the case of N bridge units. Again, if the states $|m\alpha\rangle$ refer to a single electronic state and a related vibrational manifold an effective electronic D–A coupling can be introduced. It is given by Eq. (B15) but now with

$$T_{AD} = \frac{V_{AN} V_{NN-1} \cdots V_{21} V_{1D}}{\sqrt{\Delta E_{1D}^0 \Delta E_{1A}^0 \Delta E_{2D}^0 \Delta E_{2A}^0 \cdots \Delta E_{ND}^0 \Delta E_{NA}^0}}. \tag{B17}$$

Note, $V_{nn'} \equiv V_{B_n B_{n'}}$, $V_{AN} \equiv V_{AB_N}$, $V_{1D} \equiv V_{B_1 D}$.

According to inequalities like (20) the kinetic Eq. (B10) together with the rate constants given in Eqs. (B11) and (B12) remain valid. But the complete set of kinetic equations obviously contains contributions off all BMS electronic populations. Therefore, the complete set of equations reads

$$\dot{P}_D(t) = -(\kappa_{D \to 1} + \kappa_{D \to A}) P_D(t) + (\kappa_{1 \to D} P_1(t)$$
$$+ \kappa_{A \to D} P_A(t))],$$

$$\dot{P}_m(t) = -\delta_{m,1}[(\kappa_{1 \to D} + \kappa_{1 \to 2}) P_1(t) - (\kappa_{D \to 1} P_D(t)$$
$$+ \kappa_{2 \to 1} P_2(t))] - (1 - \delta_{m,1})(1 - \delta_{m,N})$$
$$\times [(\kappa_{m \to m-1} + \kappa_{m \to m+1}) P_m(t)$$

$$- (\kappa_{m-1 \to m} P_{m-1}(t) + \kappa_{m+1 \to m} P_{m+1}(t))]$$
$$- \delta_{m,N}[(\kappa_{N \to A} + \kappa_{N \to N-1}) P_N(t) - (\kappa_{A \to N} P_A(t)$$
$$+ \kappa_{N-1 \to N} P_{N-1}(t))], \tag{B18}$$

$$\dot{P}_A(t) = -(\kappa_{A \to N} + \kappa_{A \to D}) P_A(t) + (\kappa_{N \to A} P_N(t)$$
$$+ \kappa_{D \to A} P_D(t))].$$

The equations guarantee probability conservation

$$P_D(t) + P_B(t) + P_A(t) = 1, \quad \left(P_B(t) \equiv \sum_{n=1}^{N} P_n(t) \right), \tag{B19}$$

and the transfer rates between sites n and m are given by

$$\kappa_{n \to m} = \frac{2\pi}{\hbar} \sum_\alpha \sum_\beta |V_{m\beta n\alpha}|^2 W(E_{n\alpha}) L(E_{n\alpha} - E_{m\beta}) \tag{B20}$$

with Lorentzian-type functions, Eq. (B13). Note, that for $n = D$ and $m = A$ (or $n = A$ and $m = D$) the coupling matrix elements $V_{m\beta n\alpha}$ have to be replaced by the effective D–A-coupling, Eq. (B15). Generally, the iteration procedure does not only generates transfer rates which describe hopping processes between neighboring sites of the bridge but also between those with a larger spatial separation (via superexchange couplings). However, the small energetic distance between different BMS fragment levels let become such contributions of less importance. Such a conclusion can be justified by a detailed inspection of the exact solution of the three-site system, Eq. (23).

As already explained the assumption of fast intrasite relaxation used through out the whole paper results in the energy broadening $\Gamma_{n\alpha m\beta}$. These quantities are contained in the Lorentz-type function (B13) and, in particular, have to be accounted for in the case of well separated energy levels $E_{n\alpha}$ within each site n. If, however, the energy spectrum is dense, i.e., forms a quasicontinuum it is possible to ignore the level broadening and change from the Lorentzian $L(E_{n\alpha} - E_{m\beta})$ to delta-function $\delta(E_{n\alpha} - E_{m\beta})$. Furthermore, we assume that the energies $E_{n\alpha}$ correspond to a single electronic level and a set of vibrational states $|n\alpha\rangle$. Accordingly, the rate of expressions (B20) can be written as

$$\kappa_{n \to m} = \frac{2\pi}{\hbar} |V_{mn}|^2 (FC)_{nm}. \tag{B21}$$

Here, we introduced the well-known thermal averaged and Franck–Condon weighted density of states[2,4,5]

$$(FC)_{nm} = \sum_{\alpha,\beta} \langle \chi_{n\alpha} | \chi_{m\beta} \rangle^2 W(E_{n\alpha}) \delta(E_{n\alpha} - E_{m\beta}). \tag{B22}$$

If the vibrational frequencies do not change with the change of the electronic state the $(FC)_{nm}$ can be rewritten in a manner as it has been celebrated many times (see, e.g., Refs. 34, 36, 46, 47). One obtains

$$(FC)_{nm} = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} e^{-i\Delta E_{nm} t/\hbar} e^{-Q_{nm}(t)}, \tag{B23}$$

with the quantities

$$Q_{nm}(t) = 2 \int_{-\infty}^{+\infty} d\omega \, \frac{J_{nm}(\omega)}{\omega^2} \left[\coth(\hbar\omega/2k_B T) \right.$$
$$\left. \times (1 - \cos\omega t) - i\sin\omega t \right] \qquad \text{(B24)}$$

known from the spin-boson model. The functions Q_{nm} have been expressed via bath spectral functions,

$$J_{nm}(\omega) = \frac{1}{4\hbar} \sum_s m_s \omega_s^3 \Delta q_s^{(nm)2} \delta(\omega - \omega_s), \qquad \text{(B25)}$$

which define the various reorganization energies as

$$\lambda_{nm} = 2\hbar \int_0^\infty d\omega \, \frac{J_{nm}(\omega)}{\omega}. \qquad \text{(B26)}$$

In Eq. (B25), the quantities m_s, ω_s, and $\Delta q_s^{(nm)}$ are the effective mass, frequency, and displacements, respectively, related to the sth vibrational mode. In the high-temperature limit expression (B23) reduces to the Marcus-form,

$$(\text{FC})_{nm} = \frac{1}{\sqrt{4\pi\lambda_{nm}k_B T}} \exp\left(-\frac{(\Delta E_{nm}^0 - \lambda_{nm})^2}{4\lambda_{nm}k_B T} \right), \quad \text{(B27)}$$

where ΔE_{nm}^0 denotes the free energy gap between site n and m.

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