

## Bridge-Mediated Two-Electron Transfer via Delocalized Bridge Orbitals

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Bridge mediated two-electron transfer (TET) in a donor–acceptor (D–A) complex is studied theoretically. A type of bridge is considered where the intersite coupling in the bridge becomes so large that the TET proceeds along delocalized bridge states but against the background of fast vibrational transitions within and between these states. The assumption of fast vibrational relaxations allows us to follow our earlier approach (Petrov; et al. *J. Phys. Chem. B* 2002, 106, 3092) and to derive kinetic equations governing the populations of the states involved in the TET reaction. The conditions are explained in detail at which a reduction to distant D–A TET can be carried out. Moreover, an analytic expression for the overall D–A TET rate is given for the case of a regular bridge as well as for a bridge perturbed by an intersite energetic bias. The stepwise and the concerted route of the D–A TET is analyzed in dependence on the bridge length. It is shown that the stepwise route follows from a thermal activation of a specific intermediate state. Its contribution to the overall transfer rate is determined by two single-electron transfer steps each of them related to two single-electron pathways through the bridge. The first pathway requires a population of the extended bridge state by thermal activation and thus can be termed the thermally activated pathway. The second pathway utilizes the bridging states as virtual intermediate states and thus is termed the single-electron superexchange pathway. The concerted D–A TET mechanism uses the extended bridge states as well as the mentioned intermediate state as virtual states. Therefore, it can be understood as a two-electron unistep superexchange transition between the D and the A. This transition can take place even at zero temperature. The perturbation of a regular arrangement of bridge levels by an energetic bias favors the stepwise route because it includes thermal activation of the intermediate state. This fact also explains that the efficiency of the concerted two-electron superexchange route is larger than that of the thermally activated stepwise route if low temperatures and short bridges (one or two units) are considered.

### I. Introduction

It is of huge importance for chemistry, biochemistry, biophysics, and even molecular medicine to obtain a comprehensive understanding of the way structural and energetic factors determine the rate and efficiency of charge-transfer reactions. Besides standard single electron transfer (SET) those reactions involving the participation of two electrons found increasing interest. Current theoretical studies on two-electron transfer (TET) are based on different semiphenomenological extensions of the SET Marcus theory.<sup>1–6</sup> For the case of a TET reaction in a polar liquid such an approach allowed us to formulate the conditions necessary to let the TET take place between a donor (D) and an acceptor (A) redox center. It has been found that the TET occurs via intermediate electronic state D(e)A(e) (e denotes the presence of a single excess electron at a given center). This corresponds to the formation of a stepwise route via single-electron transitions  $D(ee)A \rightleftharpoons D(e)A(e) \rightleftharpoons DA(ee)$ . The so-called concerted route of TET is determined by the orchestrated two-electron transitions  $D(ee)A \rightleftharpoons DA(ee)$ . Here, the state D(e)A(e) only participates as an intermediate virtual electronic state.<sup>7</sup>

There are numerous cases where more than a single intermediate state mediates the TET. As an example, we mention

here the homogeneous and electrochemical TET within the  $Tl(aq)^{3+}/Tl(aq)^+$  complex.<sup>8</sup> The presence of several intermediate states is also typical for TET reactions in biosystems. Quantum-chemical calculations have already specified these intermediate states with dependency on the spatial position of the two electrons within the considered macromolecular structure.<sup>9–15</sup>

The presence of several intermediate states may result in multiexponential TET kinetics. However, it is a common observation that TET reactions displays two-exponential or single-exponential kinetics. Therefore, it is a basic theoretical challenge to find out the conditions at which the multiexponential kinetics is reduced to kinetics characterized by two overall transfer rates or even by a single rate. Usually, single-exponential kinetics is termed the D–A regime of electron-transfer reactions.

During recent years such a D–A regime related to a SET reaction has been the subject of intensive theoretical and experimental work (cf., e.g., refs 5, 6, and 16–21). In particular, the condition could be clarified at which SET kinetics can be described by a single overall transfer rate  $K_{ET}$ , even though the SET is mediated by a number of bridging states. This condition consists of the only requirement that the population of the bridging states remains small (less than  $10^{-2}$ ) during the complete course of the SET.<sup>22–24</sup> It could be shown that for such a case the rate  $K_{ET}$  is determined by the sequential and the superexchange mechanisms of distant D–A SET.<sup>5,24–26</sup>

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As demonstrated by us in refs 27–29, it is also possible to analyze D–A TET reactions in this way. The reactions can be described by a single overall transfer rate  $K_{\text{TET}}$  between the donor state  $|D\rangle \equiv |D(\text{ee})B_1B_2\dots B_NA\rangle$  and the acceptor state  $|A\rangle \equiv |DB_1B_2\dots B_NA(\text{ee})\rangle$  provided that the population of the two types of bridging states,  $|B_m\rangle \equiv |D(e)B_1B_2\dots B_m(e)\dots B_NA\rangle$  and  $|\tilde{B}_n\rangle \equiv |DB_1B_2\dots B_n(e)\dots B_NA(e)\rangle$  as well as the population of the intermediate state  $|I\rangle \equiv |D(e)B_1B_2\dots B_NA(e)\rangle$  remain small during the whole reaction. The rate expression  $K_{\text{TET}}$  contains contributions from two different TET mechanisms, the stepwise and the concerted mechanism. The first one includes two SET processes,  $|D\rangle \rightleftharpoons |B_1\rangle \rightleftharpoons |B_2\rangle \rightleftharpoons \dots \rightleftharpoons B_N \rightleftharpoons |I\rangle$  and  $|I\rangle \rightleftharpoons |\tilde{B}_1\rangle \rightleftharpoons |\tilde{B}_2\rangle \rightleftharpoons \dots \rightleftharpoons \tilde{B}_N \rightleftharpoons |A\rangle$ . Each process comprises a multistep single-electron sequential pathway and a unistep single-electron superexchange pathway. In contrast, the concerted TET results from a unistep two-electron superexchange pathway  $|D\rangle \rightleftharpoons |A\rangle$ , where the states  $|B_1\rangle, |B_2\rangle, \dots, |B_N\rangle, |\tilde{B}_1\rangle, |\tilde{B}_2\rangle, \dots, |\tilde{B}_N\rangle$ , and  $|I\rangle$  act as virtual intermediate states. All these results are valid for small intersite electronic couplings, so that the TET occurs against the background of fast intrasite vibrational relaxation.

In the present study we will concentrate on a type of bridge-mediated TET where the electronic coupling between neighboring bridge sites becomes so large that the whole bridge has to be described by extended electronic states. However, the coupling of the D and the A to the extended bridge levels should remain small enough to let the D–B and A–B transitions of the nonadiabatic type. For such a situation the TET reaction occurs against the background of fast relaxation processes within the D and A centers. At the same time, relaxation processes within the set of extended bridge states may be either faster or slower than the TET reaction itself. Recent results on distant SET<sup>23</sup> demonstrated that the sequential D–A SET is replaced by a thermally activated mechanism if the D as well as the A center couple weakly to the respective terminal bridge units. The thermally activated mechanism results in a completely different bridge-length dependence of the overall transfer rate as would be the case for a bridge with weak intersite coupling. Turning to the case of D–A TET it has to be clarified which process replaces the stepwise mechanism if the bridge-internal intersite couplings become large. And, it is also necessary to understand the mechanism forming the concerted unistep two-electron transition mediated by the bridge.

The paper is organized as follows. In the next section the model is introduced for the description of bridge-mediated TET, and the basic kinetic equations together with all rate constants are derived. Section III includes the reduction of multiexponential TET kinetics to single-exponential D–A TET kinetics as well as the derivation of an overall transfer rate  $K_{\text{TET}}$ . The main results related to the formation of stepwise and concerted routes of TET in a DBA system are presented in section IV. The paper ends with some concluding remarks in section V.

## II. Model and Theory

**A. Hamiltonian of the DBA System.** Let us consider a DBA system with a linear bridge of  $N$  units. The bridge couples to the D via terminal site  $m = 1$  and to the A via terminal site  $m = N$ . Those electronic states necessary for a complete description of the TET have already been fixed in the introductory part and are denoted as  $|M\rangle = |D\rangle, |B_m\rangle, |\tilde{B}_n\rangle, |I\rangle$ , and  $|A\rangle$  (see also refs 27 and 29). Accordingly, the electronic Hamiltonian of the whole TET system takes the following form

$$H_{\text{DBA}}^{(\text{el})} = \sum_M H_M^{(\text{el})} + H_B^{(\text{el})} + \tilde{H}_B^{(\text{el})} + H_{\text{loc-b}}^{(\text{el})} \quad (1)$$

where

$$H_M^{(\text{el})} = E_M|M\rangle\langle M| \quad (M = D, I, A) \quad (2)$$

is the Hamiltonian of the  $M$ th localized DBA state with energy  $E_M$ . Furthermore,

$$H_B^{(\text{el})} = \sum_{m=1}^N E_m|B_m\rangle\langle B_m| + \sum_{m,m'=1}^{N-1} (1 - \delta_{mm'})[\mathcal{M}_{B_m B_{m'}}|B_m\rangle\langle B_{m'}| + hc] \quad (3)$$

and

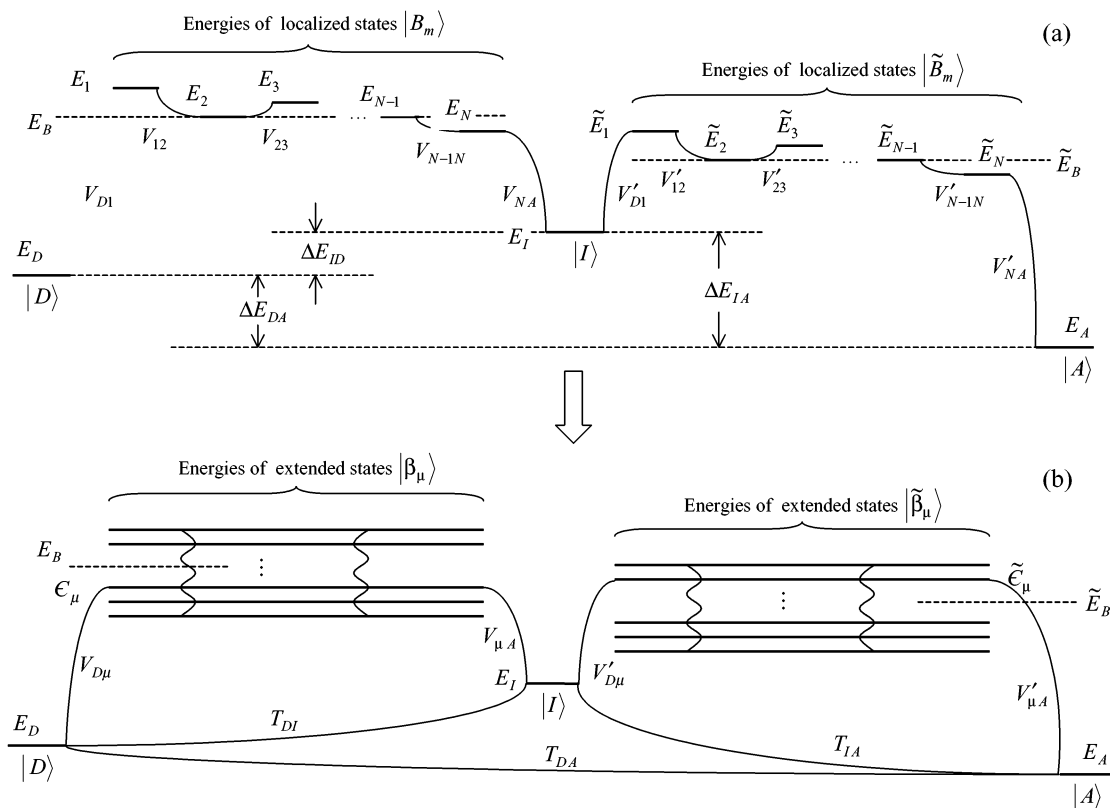
$$\tilde{H}_B^{(\text{el})} = \sum_{n=1}^N \tilde{E}_n|\tilde{B}_n\rangle\langle\tilde{B}_n| + \sum_{n,n'=1}^{N-1} (1 - \delta_{nn'})[\mathcal{M}_{\tilde{B}_n \tilde{B}_{n'}}|\tilde{B}_n\rangle\langle\tilde{B}_{n'}| + hc] \quad (4)$$

are the Hamiltonians that characterize the DBA bridging states ( $E_m$  and  $\tilde{E}_n$  are the energies of the localized bridging states  $|B_m\rangle$  and  $|\tilde{B}_n\rangle$ , respectively). Finally, the Hamiltonian

$$H_{\text{loc-b}}^{(\text{el})} = \mathcal{M}_{DB_1}|D\rangle\langle B_1| + \mathcal{M}_{IB_N}|I\rangle\langle B_N| + \mathcal{M}_{I\tilde{B}_1}|I\rangle\langle\tilde{B}_1| + \mathcal{M}_{A\tilde{B}_N}|A\rangle\langle\tilde{B}_N| + hc \quad (5)$$

describes the interaction of the localized DBA states  $|D\rangle, |I\rangle$ , and  $|A\rangle$  with the corresponding localized DBA bridging states. The matrix elements  $\mathcal{M}_{MM'} = \langle M|\hat{V}_{\text{tr}}|M'\rangle$  responsible for the transitions between the localized DBA electronic states  $|M'\rangle$  and  $|M\rangle$  are defined by the transfer operator  $\hat{V}_{\text{tr}}$ . In this paper we employ a tight binding model where  $\hat{V}_{\text{tr}}$  describes single-electron transitions between the molecular orbitals of neighboring DBA sites (D and  $B_1, B_m$  and  $B_{m\pm 1}$ , and  $B_N$  and A). One obtains  $\mathcal{M}_{DB_1} = V_{D1}$ ,  $\mathcal{M}_{B_N I} = V_{NA}$ ,  $\mathcal{M}_{I\tilde{B}_1} = V'_{D1}$ ,  $\mathcal{M}_{\tilde{B}_N A} = V'_{NA}$ ,  $\mathcal{M}_{B_m B_{m'}} = \delta_{m'm\pm 1}V_{mm\pm 1}$ , and  $\mathcal{M}_{\tilde{B}_n \tilde{B}_{n'}} = \delta_{n'n\pm 1}V'_{nn\pm 1}$ . All single-electron couplings,  $V_{ab}$  and  $V'_{ab}$ , are shown in Figure 1a together with the DBA energies of the localized states. Note that in the general case the couplings  $V'_{D1}$  and  $V'_{NA}$  do not coincide with the respective couplings  $V_{D1}$  and  $V_{NA}$ . This difference results from the fact that any charge distribution in the D and A centers strongly depends on the actual electronic states  $|D\rangle, |I\rangle$ , and  $|A\rangle$  of the whole DBA system. In contrast, the bridge-internal couplings  $V_{mm\pm 1}$  and  $V'_{nn\pm 1}$  characterizing the single-electron transitions within the bridge do not differ so much at  $n = m$ . [For the small couplings  $V_{D1}$ ,  $V'_{D1}$ ,  $V_{NA}$ , and  $V'_{NA}$  under consideration the D and A centers are not essentially effected by the overlap of bridge unit molecular orbitals.] In the case of a regular bridge we set for all sites in the bridge  $V_{mm\pm 1} = V'_{nn\pm 1} \equiv V_B$ .

If all the single-electron couplings including the  $V_{mm\pm 1}$  and  $V'_{nn\pm 1}$  are small the TET process reduces to a distant nonadiabatic transfer of two electrons through the localized bridging states  $|B_m\rangle$  and  $|\tilde{B}_n\rangle$  as well as through the intermediate state  $|I\rangle$ .<sup>27,29</sup> Such a TET occurs against the background of fast intrasite vibrational relaxation. The goal of the present studies is to consider TET reactions for the case of strong single-electron couplings between neighboring bridge units (here, strong means strong compared with the electron-vibrational interaction). In contrast to the mentioned nonadiabatic TET, here, the transfer process proceeds with the participation of the localized electronic states  $|M\rangle = |D\rangle, |I\rangle, |A\rangle$  as well as the extended bridging



**Figure 1.** Position of the localized bridging DBA levels with energies  $E_m$  and  $\tilde{E}_n$  relative to the position of the donor, the intermediate, and the acceptor electronic levels with energies  $E_D$ ,  $E_I$ , and  $E_A$ , respectively ( $E_B$  gives the position of the local DBA levels in a regular chain) (part a). When the localized bridge states  $|B_m\rangle$  and  $|\tilde{B}_n\rangle$  are transformed to extended bridge states  $|\beta_\mu\rangle$  and  $|\tilde{\beta}_\mu\rangle$ , respectively, the energies  $E_m$  and  $\tilde{E}_n$  change to  $\epsilon_\mu$  and  $\tilde{\epsilon}_\mu$ , respectively. At the same time the transformation takes place of the local couplings  $V_{D1}$  ( $V'_{D1}$ ) and  $V_{NA}$  ( $V'_{NA}$ ) into  $V_{D\mu}$  ( $V'_{D\mu}$ ) and  $V_{\mu A}$  ( $V'_{\mu A}$ ), respectively. Besides, the bridge states mediate the formation of single-electron superexchange couplings  $T_{DI}$  and  $T_{IA}$  as well as of the two-electron superexchange coupling  $T_{DA}$  (part b, wavy lines indicate the relaxation between the extended DBA levels).

electronic states  $|\beta_\mu\rangle$  and  $|\tilde{\beta}_\mu\rangle$ . The latter are obtained after diagonalizing the Hamiltonian, eqs 3 and 4

$$H_B^{(el)} = \sum_{\mu=1}^N \epsilon_\mu |\beta_\mu\rangle \langle \beta_\mu| \quad \tilde{H}_B^{(el)} = \sum_{\mu=1}^N \tilde{\epsilon}_\mu |\tilde{\beta}_\mu\rangle \langle \tilde{\beta}_\mu| \quad (6)$$

The transformations relating localized and delocalized bridge states one to another read

$$|\beta_\mu\rangle = \sum_{m=1}^N u_\mu(m) |B_m\rangle \quad |\tilde{\beta}_\mu\rangle = \sum_{n=1}^N \tilde{u}_\mu(n) |\tilde{B}_n\rangle \quad (7)$$

Obviously, the coefficients  $u_\mu(m)$  and  $\tilde{u}_\mu(n)$  as well as the energies  $\epsilon_\mu$  and  $\tilde{\epsilon}_\mu$  of the extended DBA electronic states  $|\beta_\mu\rangle$  and  $|\tilde{\beta}_\mu\rangle$  depend on the  $E_m$  and  $\tilde{E}_n$  (characterizing the energetic position of the localized levels of the DBA system) as well as on the intersite couplings  $V_{mm\pm 1}$  and  $V'_{nn\pm 1}$ . In the case of regular bridge with  $E_1 = E_2 = \dots = E_N \equiv E_B$  and  $\tilde{E}_1 = \tilde{E}_2 = \dots = \tilde{E}_N \equiv \tilde{E}_B$  the tight binding model results in the following well-known formulas

$$\begin{aligned} \epsilon_\mu^{(reg)} &\equiv \epsilon_\mu = E_B - 2V_B \cos\left[\frac{\pi\mu}{N+1}\right] \\ \tilde{\epsilon}_\mu^{(reg)} &\equiv \tilde{\epsilon}_\mu(N) = \tilde{E}_B - 2V_B \cos\left[\frac{\pi\mu}{N+1}\right] \\ u_\mu(m) = \tilde{u}_\mu(m) &= \sqrt{\frac{2}{N+1}} \sin\left[\frac{\pi m\mu}{N+1}\right]. \end{aligned} \quad (8)$$

Using the delocalized bridge state the coupling Hamiltonian eq

5 can be written as

$$H_{loc-b}^{(el)} = \sum_{\mu=1}^N [V_{D\mu} |D\rangle \langle \beta_\mu| + V_{A\mu} |I\rangle \langle \beta_\mu| + V'_{D\mu} |I\rangle \langle \tilde{\beta}_\mu| + V'_{A\mu} |A\rangle \langle \tilde{\beta}_\mu| + hc] \quad (9)$$

where the quantities

$$\begin{aligned} V_{D\mu} &= V_{D1} u_\mu(1) & V_{\mu A} &= V_{NA} u_\mu(N) \\ V'_{D\mu} &= V'_{D1} \tilde{u}_\mu(1) & V'_{\mu A} &= V'_{NA} \tilde{u}_\mu(N) \end{aligned} \quad (10)$$

are responsible for the single-electron coupling of the localized states  $|D\rangle$ ,  $|I\rangle$ ,  $|A\rangle$  to the extended bridge states  $|\beta_\mu\rangle$ ,  $|\tilde{\beta}_\mu\rangle$  (cf. also Figure 1b).

The Hamiltonian eq 1, which covers the contributions, eqs 2, 6, and 9, only accounts for the electronic part of the DBA system. Apparently, to describe the TET kinetics, we have to include the coupling to the vibrational degrees of freedom. The related vibrational Hamiltonian  $H_{vib}$  is taken as that for a set of harmonic oscillators with frequencies  $\omega_j$  and normal-mode coordinate  $Q_j$ . Let  $Q_j^{(M)}$  be the replacement of the vibrational mode in the  $M$ th electronic state (in our case,  $|M\rangle = |D\rangle$ ,  $|I\rangle$ ,  $|A\rangle$ ,  $|\beta_\mu\rangle$ ,  $|\tilde{\beta}_\mu\rangle$ ). The expansion of the electronic energies with respect to the deviations  $Q_j - Q_j^{(M)}$  results in diagonal and off-diagonal interaction terms of the electronic DBA states with the vibrational reservoir (see also refs 23 and 30). The diagonal part of the coupling to the reservoir (R) of vibrations reads

$$H_{\text{DBA-R}} = \sum_{M=D,I,A} H_{M-R} + H_{B-R} + \tilde{H}_{B-R} \quad (11)$$

The first contribution is defined by

$$H_{M-R} = -\frac{1}{2} \sum_j \hbar \omega_j Q_j^{(M)} Q_j |M\rangle \langle M| \quad (12)$$

which specifies the coupling of the localized DBA state  $|M\rangle$  to the vibrational reservoir (note that  $Q_j$  and  $Q_j^{(M)}$  are dimensionless quantities). The second contribution includes the operators  $H_{B-R}$  and  $\tilde{H}_{B-R}$ . The first,

$$H_{B-R} = \sum_{\mu=1}^N \sum_j \hbar \omega_j g_j(\mu, \mu') Q_j |\beta_\mu\rangle \langle \beta_\mu| \quad (13)$$

ouples the bridging DBA states  $|\beta_\mu\rangle$  to the vibrations with the coupling matrix

$$g_j(\mu, \mu') = -\frac{1}{2} \sum_{m=1}^N |u_\mu(m)|^2 Q_j^{(m)} \quad (14)$$

[Analogous form has an operator  $\tilde{H}_{B-R}$ .] The off-diagonal interaction between the extended bridge states and the vibrational reservoir,

$$H'_{B-R} = \sum_{\mu, \mu'=1}^N (1 - \delta_{\mu\mu'}) \sum_j \hbar \omega_j [g_j(\mu, \mu') Q_j |\beta_\mu\rangle \langle \beta_{\mu'}| + \tilde{g}_j(\mu, \mu') Q_j |\tilde{\beta}_\mu\rangle \langle \tilde{\beta}_{\mu'}|] \quad (15)$$

is responsible for transitions between the extended bridging DBA states. The first coupling reads  $g_j(\mu, \mu') = -1/2 \sum_{m=1}^N u_\mu^*(m) u_{\mu'}(m) Q_j^{(m)}$  whereas the form of the second one,  $\tilde{g}_j(\mu, \mu')$ , follows from  $g_j(\mu, \mu')$  if one substitutes the  $u_\mu(m)$  for the  $\tilde{u}_\mu(m)$ .

### B. Kinetic Equations for Description of the TET Reaction.

According to the discussion of the preceding section we denote the total Hamiltonian of the DBA system interacting with a reservoir of intramolecular as well as intermolecular vibrations as

$$H = H_{\text{DBA}}^{(\text{el})} + H_{\text{DBA-R}} + H'_{B-R} + H_{\text{vib}} \quad (16)$$

On the basis of this Hamiltonian one may derive kinetic equations that describe the TET process mediated by the extended bridge states. But, before doing this, we note that the introduction of extended bridge states instead of the localized ones becomes only possible if the following supposition is fulfilled. The broadening of the energies  $\epsilon_\mu$  and  $\tilde{\epsilon}_\mu$ , which is caused by the interaction  $H'_{B-R}$  with the reservoir has to be small compared to the differences  $|\epsilon_\mu - \epsilon_{\mu'}|$  and  $|\tilde{\epsilon}_\mu - \tilde{\epsilon}_{\mu'}|$ . Just in this case, the TET proceeds through the adiabatic (extended) bridging DBA states  $|\beta_\mu\rangle$  and  $|\tilde{\beta}_\mu\rangle$ . This is in contrast to complete nonadiabatic TET where the localized bridging DBA states  $|B_m\rangle$  and  $|\tilde{B}_m\rangle$  mediate the charge motion.<sup>27,29</sup> The condition to be fulfilled when extended bridge states are used can be formulated for a regular bridge (and for a bridge with a small energetic irregularity) by the demand that the matrix elements  $V_{mm\pm 1}$  and  $V'_{mm\pm 1}$  (that couple the localized molecular orbitals of a given bridge unit to those of the neighboring units) strongly exceed the coupling energy of the localized orbitals to the nuclear vibrations. [It is supposed that the localized molecular orbitals belonging to each of the bridge units are well separated so that the energies  $\epsilon_\mu$  and  $\tilde{\epsilon}_\mu$  correspond to the extended bridge LUMO-levels.] For the present studies we assume that the aforementioned

conditions are fulfilled and, thus, the Hamiltonians  $H_{\text{DBA}}^{(\text{el})}$ ,  $H_{\text{DBA-R}}$ , and  $H'_{B-R}$  are taken according to the eqs 1, 2, 6, and 11–13.

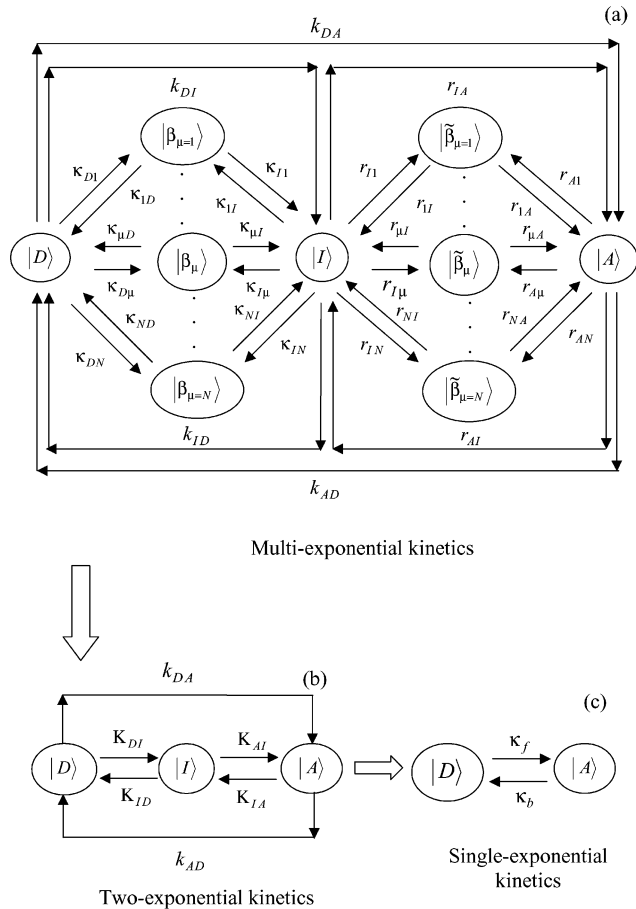
A comprehensive description of the TET can be achieved by using the generalized master equation (GME) (cf., e.g., refs 18, 31, and 32), which governs the density operator  $\rho(t)$  of the DBA system (coupled to a vibrational reservoir). How to proceed in the case of nonadiabatic TET has been explained in detail in our foregoing papers.<sup>27,29</sup> There, we demonstrated the derivation of kinetic equations for the total populations  $P_M(t) = \langle M | \text{tr}_{\text{vib}} \rho(t) | M \rangle$  of each electronic state  $|M\rangle$  participating in the TET. In particular, it has been shown that for cases where the characteristic time  $\tau_{\text{rel}}^{(m)}$  of the vibrational relaxation within the site  $m$  (of electron localization) is small compared to the transfer time, a simplified coarse-grained description of the TET process becomes possible. Then, the populations  $P_M(t)$  fulfill a set of coupled balance-like equations. A similar situation occurs if the bridge is defined via extended states. Now, the characteristic times  $\tau_{\text{rel}}^{(\mu)}$  and  $\tau_{\text{rel}}^{(M)}$  of the vibrational relaxation within the extended electronic state  $\mu$  and the localized states  $M = D, I, A$ , respectively, are supposed to be much smaller than the overall transfer time  $\tau_{\text{TET}} = K_{\text{TET}}^{-1}$ . Noting the inequality

$$\tau_{\text{TET}} \gg \tau_{\text{rel}}^{(M)}, \tau_{\text{rel}}^{(\mu)} \quad (17)$$

we may state that the kinetics of the D–A ET proceeds against the background of fast vibrational relaxations and thus can be described in the framework of the mentioned coarse-grained approach. A similar situation valid for SET reactions has been already discussed in ref 23. The basic difference from the TET kinetics studied here is only related to the presence of two types of extended states,  $|\beta_\mu\rangle$  and  $|\tilde{\beta}_\mu\rangle$ , as well as the intermediate state  $|I\rangle$ . Fortunately, according to inequality, eq 17 the procedure of deriving kinetic equations and corresponding rate constants remains identical with that explained in refs 23 and 29. Therefore, we skip any detail of the derivation and only present the resulting kinetic equations for the populations of interest. Those cover  $P_D(t)$ ,  $P_I(t)$ , and  $P_A(t)$  of the localized DBA states  $|D\rangle$ ,  $|I\rangle$ , and  $|A\rangle$ , respectively, as well as the populations  $P_\mu(t)$  and  $\tilde{P}_\mu(t)$  of the respective extended bridging DBA states  $|\beta_\mu\rangle$  and  $|\tilde{\beta}_\mu\rangle$ . Accordingly, the set of equations reads

$$\begin{aligned} \dot{P}_D(t) &= -(k_{DI} + k_{DA} + \sum_\mu k_{D\mu}) P_D(t) + k_{ID} P_I(t) + k_{AD} P_A(t) + \sum_\mu k_{\mu D} P_\mu(t) \\ \dot{P}_\mu(t) &= -(k_{\mu D} + k_{\mu I} + \sum_{\mu' \neq \mu} k_{\mu\mu'}) P_\mu(t) + k_{D\mu} P_D(t) + k_{I\mu} P_I(t) + \sum_{\mu' \neq \mu} k_{\mu'\mu} P_{\mu'}(t) \quad (\mu = 1, 2, \dots, N) \\ \dot{P}_I(t) &= -(k_{ID} + k_{IA} + \sum_\mu (k_{I\mu} + r_{I\mu})) P_I(t) + k_{DI} P_D(t) + k_{AI} P_A(t) + \sum_\mu k_{\mu I} P_\mu(t) + \sum_\mu r_{\mu I} \tilde{P}_\mu(t) \\ \dot{\tilde{P}}_\mu(t) &= -(r_{\mu I} + r_{\mu A} + \sum_{\mu' \neq \mu} r_{\mu\mu'}) \tilde{P}_\mu(t) + r_{I\mu} P_I(t) + r_{A\mu} P_A(t) + \sum_{\mu' \neq \mu} r_{\mu'\mu} \tilde{P}_{\mu'}(t) \quad (\mu = 1, 2, \dots, N) \\ \dot{P}_A(t) &= -(r_{AI} + k_{AD} + \sum_\mu r_{A\mu}) P_A(t) + r_{IA} P_I(t) + k_{DA} P_D(t) + \sum_\mu r_{\mu A} \tilde{P}_\mu(t) \quad (18) \end{aligned}$$





**Figure 2.** Kinetic scheme of the TET process with the participation of the extended bridge states  $|\beta_\mu\rangle$  and  $|\tilde{\beta}_\mu\rangle$  (part a). For a small population of the bridge states the kinetics reduces to the transitions between the three localized DBA states:  $|D\rangle$ ,  $|I\rangle$ , and  $|A\rangle$  (part b). If the population of the intermediate DBA state  $|I\rangle$  becomes also small, the two-exponential kinetics is reduced to a single-exponential D–A TET kinetics between two localized DBA states  $|D\rangle$  and  $|A\rangle$ , only (part c).

The rate constants  $k_{D\mu}$  ( $k_{\mu D}$ ) and  $k_{I\mu}$  ( $k_{\mu I}$ ) characterize single-electron hopping between the localized DBA states  $|D\rangle$  and  $|I\rangle$  and the extended bridging DBA states of the first type,  $|\beta_\mu\rangle$ . Analogously, the rate constants  $r_{I\mu}$  ( $r_{\mu I}$ ) and  $r_{A\mu}$  ( $r_{\mu A}$ ) describe single-electron hopping transitions between the localized DBA states  $|I\rangle$  or  $|A\rangle$  and the extended bridging DBA states of the second type,  $|\tilde{\beta}_\mu\rangle$ . The transitions among different extended states  $|\beta_\mu\rangle$  and  $|\tilde{\beta}_\mu\rangle$  are described by the rates  $k_{\mu\mu'}$  and  $r_{\mu\mu'}$ , respectively. Scheme a of Figure 2 displays those transitions leading to the TET process in the DBA system. It follows from this scheme as well as from the set of kinetic equations, eqs 18, that along with the above-mentioned single-electron hopping transitions between the localized states and the extended states the TET process also covers distant single-electron transitions (with rates  $k_{DI}$  ( $k_{ID}$ ) and  $r_{AI}$  ( $r_{IA}$ )) as well as distant unistep two-electron transitions (with rates  $k_{DA}$  and  $k_{AD}$ ).

All ET rate constants valid for the transitions between localized states and extended bridge states take the form (concerning  $k_{\mu\mu'}$  see the discussion in ref 23)

$$k_{\mu M} = \frac{2\pi}{\hbar} |T_{M\mu}|^2 (\text{FC})_{\mu M} \quad (M = D, I) \quad (19)$$

and

$$r_{\mu M} = \frac{2\pi}{\hbar} |\tilde{T}_{M\mu}|^2 (\text{F}\tilde{\text{C}})_{\mu M} \quad (M = I, A) \quad (20)$$

Here,  $(\text{FC})_{\mu M}$  and  $(\text{F}\tilde{\text{C}})_{\mu M}$  denote respective Franck–Condon factors. The couplings derived in the tight binding model are given by  $T_{D\mu} = V_{D\mu}$ ,  $T_{I\mu} = V_{A\mu}$ , and  $\tilde{T}_{I\mu} = V'_{D\mu}$ ,  $\tilde{T}_{A\mu} = V'_{A\mu}$ . The backward rates follow from the above given one as ( $k_B$  and  $T$  denote the Boltzmann constant and the absolute temperature, respectively)

$$k_{M\mu} = \exp[-(\epsilon_\mu - E_M)/k_B T] k_{\mu M} \quad (21)$$

and

$$r_{M\mu} = \exp[-(\tilde{\epsilon}_\mu - E_M)/k_B T] r_{\mu M} \quad (22)$$

The rate constants defining the unistep single-electron and two-electron hopping transitions are given by ( $M \neq N$ )

$$\kappa_{MN} = \frac{2\pi}{\hbar} |T_{MN}|^2 (\text{FC})_{MN} \quad (M, N = D, I, A) \quad (23)$$

with  $T_{MN}$  being the superexchange coupling between the localized states (cf. scheme b in Figure 1).

The derivation leading to the kinetic eqs 18 also results in the following expression for the squares of the single-electron superexchange couplings,

$$|T_{DI}|^2 = |V_{D1} V_{AN}|^2 \text{Re}\{G_{IN}(E_D) G_{N1}(E_I)\} \quad (24)$$

and

$$|T_{IA}|^2 = |V'_{D1} V'_{AN}|^2 \text{Re}\{\tilde{G}_{IN}(E_I) \tilde{G}_{N1}(E_A)\} \quad (25)$$

The square of two-electron superexchange couplings read (note  $\Delta E_{ID} = E_I - E_D$ ,  $\Delta E_{IA} = E_I - E_A$ ),

$$|T_{DA}|^2 = \frac{|V_{D1} V_{AN} V'_{D1} V'_{AN}|^2}{\Delta E_{ID} \Delta E_{IA}} \text{Re}\{G_{IN}(E_D) G_{N1}(E_A) \tilde{G}_{IN}(E_D) \tilde{G}_{N1}(E_A)\} \quad (26)$$

In eqs 24, 25, and 26,  $G_{IN}(E)$  and  $\tilde{G}_{N1}(E)$  are the bridge Green's functions (cf. also refs 33 and 34). In the case of small energetic irregularity they can be represented in form (cf. Appendix A)

$$G_{IN}(E) = G_{IN}^{(\text{reg})}(E) e^{-S(E)} \\ \tilde{G}_{IN}(E) = \tilde{G}_{IN}^{(\text{reg})}(E) e^{-\tilde{S}(E)} \quad (27)$$

with the Green's function of regular bridge

$$G_{IN}^{(\text{reg})}(E) = \frac{1}{|V_B|} \frac{\sinh \Lambda(E)}{\sinh[(N+1)\Lambda(E)]} \quad (28)$$

Note the introduction of a superexchange decay parameter<sup>34–36</sup>

$$\Lambda(E) = \ln[(E_B - E)/2|V_B| + \sqrt{((E_B - E)/2|V_B|)^2 - 1}] \quad (29)$$

To derive the  $\tilde{G}_{N1}(E)$ , one has only to change  $\Lambda(E)$  by  $\tilde{\Lambda}(E)$ . The latter quantity is given by the same expression as in eq 29 but with  $E_B$  replaced by  $\tilde{E}_B$ . Moreover, the correction factors  $S(E)$  and  $\tilde{S}(E)$  are defined by eqs A11 and A12.

The rate constants, eqs 19–23, contain the Franck–Condon factors

$$(\text{FC})_{MN} = \frac{1}{2\pi\hbar} \int d\tau e^{-i\Delta E_{MN}\tau/\hbar} e^{-Q_{MN}(\tau)} \quad (30)$$

Each depends on the concrete form of the vibrational spectral density  $J_{MN}(\omega)$  via<sup>18,37,38</sup>

$$Q_{MN}(\tau) = 2 \int d\omega (J_{MN}(\omega)/\omega^2) [\coth(\hbar\omega/k_B T) (1 - \cos \omega\tau) - i \sin \omega\tau]. \quad (31)$$

**C. Overall TET Rate.** The various rate constants, eqs 19–23, all contribute to the overall transfer rate  $K_{TET}$  of bridge-mediated TET. To derive a respective expression, we follow the coarse-graining approach which has been used earlier for the description of nonadiabatic TET in refs 27 and 29. There, it has been shown that single-exponential TET kinetics are related to a D–A regime of this reaction where the population of the bridging DBA states as well as the population of the intermediate state remains small in the course of the ET reaction. In the present case, a small bridge population appears if the rate constants responsible for an escape of an electron from the extended bridging state  $|\mu\rangle$  to the localized state  $|M\rangle$ , ( $M = D, I, A$ ) strongly exceed the backward rate, i.e., if the following inequality is valid

$$\begin{aligned} k_{D(I),\mu}/k_{\mu,D(I)} &= \exp[-(\epsilon_\mu - E_{D(I)})/k_B T] \ll 1 \\ r_{I(A),\mu}/r_{\mu,I(A)} &= \exp[-(\tilde{\epsilon}_\mu - E_{I(A)})/k_B T] \ll 1 \end{aligned} \quad (32)$$

A relation that guarantees a small population of the intermediate state  $|I\rangle$  will be given below. If the condition eq 32 is fulfilled, it becomes possible to derive a solution of eqs 18 by employing the steady state approximation for the populations  $P_\mu(t)$  and  $\tilde{P}_\mu(t)$ . The definite form of the solution also depends on the relation between the rate constants  $k_{\mu M}$  ( $r_{\mu M}$ ) and the intrabridge rate constants  $k_{\mu\mu'}$  ( $r_{\mu\mu'}$ ). The latter are responsible for transitions between different electronic bridging states  $|\mu\rangle$  and  $|\mu'\rangle$ . Note that the characteristic time  $\tau_B$  of these (electronic) transitions is basically different from the above introduced characteristic times  $\tau_{rel}^{(M)}$  and  $\tau_{rel}^{(\mu)}$  (related to the vibrational relaxation within electronic terms). Because the times  $\tau_{rel}^{(M)}$  and  $\tau_{rel}^{(\mu)}$  are assumed to be the fastest times of the DBA system, along with inequality (17) the relation  $\tau_B \gg \tau_{rel}^{(M)}, \tau_{rel}^{(\mu)}$  also becomes valid. Therefore, the transitions between the extended states  $|\mu\rangle$  and  $|\mu'\rangle$  can be described by the rate constants  $k_{\mu\mu'}$  and  $r_{\mu\mu'}$  and, thus, a coarse-graining procedure becomes valid for an arbitrary relation between the characteristic times  $\tau_B$  and  $\tau_{TET}$ . Provided that the rate constants  $k_{\mu\mu'}$  and  $r_{\mu\mu'}$  do not result in an overall D–A transition but only redistribute the electron population between the extended bridging states, these rate constants determine intrabridge relaxation processes.

To derive analytic results, we will consider the solution of eqs 18 for the case where the time  $\tau_B$  of the intrabridge relaxation transitions is small compared to the time  $\tau_{TET}$  as well as for the case where  $\tau_B$  is large.

**1. Fast Intrabridge Relaxation:**  $\tau_B \ll \tau_{TET}$ . In this case quasi-equilibrium distributions  $P_\mu(t)$  ( $\tilde{P}_\mu(t)$ ) across the bridge states are present on the time-scale of the TET reaction:

$$\frac{P_\mu(t)}{P_{\mu'}(t)} = e^{-(\epsilon_\mu - \epsilon_{\mu'})/k_B T} \quad \frac{\tilde{P}_\mu(t)}{\tilde{P}_{\mu'}(t)} = e^{-(\tilde{\epsilon}_\mu - \tilde{\epsilon}_{\mu'})/k_B T} \quad (33)$$

These relations, eq 33, allow us to express the populations of the bridging states by the integral populations  $P_B(t) = \sum_\mu P_\mu(t)$  and  $\tilde{P}_B(t) = \sum_\mu \tilde{P}_\mu(t)$ . Introducing the statistical weights of the extended bridging states,

$$W_B(\epsilon_\mu) = Z_B^{-1} e^{-\epsilon_\mu/k_B T} \quad (Z_B = \sum_{\mu=1}^N e^{-\epsilon_\mu/k_B T}) \quad (34)$$

and

$$W_B(\tilde{\epsilon}_\mu) = \tilde{Z}_B^{-1} e^{-\tilde{\epsilon}_\mu/k_B T} \quad (\tilde{Z}_B = \sum_{\mu=1}^N e^{-\tilde{\epsilon}_\mu/k_B T}) \quad (35)$$

one derives

$$P_\mu(t) = W_B(\epsilon_\mu) P_B(t) \quad \tilde{P}_\mu(t) = W_B(\tilde{\epsilon}_\mu) \tilde{P}_B(t) \quad (36)$$

These expressions demonstrate that the populations  $P_\mu(t)$  and  $\tilde{P}_\mu(t)$  only change in time via the integral populations  $P_B(t)$  and  $\tilde{P}_B(t)$ . Now, by introducing the  $P_\mu(t)$  and  $\tilde{P}_\mu(t)$  into eqs 18 it remains a set of kinetic equations for the populations  $P_D(t)$ ,  $P_B(t)$ ,  $P_I(t)$ ,  $\tilde{P}_B(t)$ , and  $P_A(t)$ . The following approximation is based on the small population of the bridging states and thus on the utilization of a steady state approximation. The latter reads as  $\dot{P}_B(t) = 0$  and  $\dot{\tilde{P}}_B(t) = 0$  and allows us to derive the following set of coupled kinetic equations

$$\begin{aligned} \dot{P}_D(t) &= -(K_{DI} + k_{DA})P_D(t) + K_{ID}P_I(t) + k_{AD}P_A(t) \\ \dot{P}_I(t) &= -(K_{ID} + K_{IA})P_I(t) + K_{DI}P_D(t) + K_{AI}P_I(t) \\ \dot{P}_A(t) &= -(K_{AI} + k_{AD})P_A(t) + K_{IA}P_I(t) + k_{DA}P_D(t) \end{aligned} \quad (37)$$

These equations describe the TET kinetics between the localized DBA states (cf. scheme b of Figure 2). The respective (effective) transfer rates read

$$\begin{aligned} K_{DI(ID)} &= k_{DI(ID)} + k_{DI(ID)}^{(act)} \\ K_{IA(AI)} &= k_{IA(AI)} + k_{IA(AI)}^{(act)} \end{aligned} \quad (38)$$

The rates  $k_{ID(DI)}$  and  $k_{IA(AI)}$  define single-electron superexchange transitions  $|D\rangle \rightleftharpoons |I\rangle$  and  $|I\rangle \rightleftharpoons |A\rangle$ , respectively, through extended bridge states whereas the rates

$$\begin{aligned} k_{DI(ID)}^{(act)} &= \frac{K_{D(I),B} K_{B,I(D)}}{K_{BD} + K_{BI}} \\ k_{IA(AI)}^{(act)} &= \frac{\tilde{K}_{I(A),B} \tilde{K}_{B,A(I)}}{\tilde{K}_{BA} + \tilde{K}_{BI}} \end{aligned} \quad (39)$$

are responsible for transitions comprising hopping transitions into the bridge states as well as out of the bridge states.

The rate expressions appearing in eqs 39 read in more detail

$$\begin{aligned} K_{D(I),B} &= \sum_{\mu=1}^N k_{D(I),\mu}, \quad K_{B,D(I)} = \sum_{\mu=1}^N W_B(\epsilon_\mu) k_{\mu,D(I)} \\ \tilde{K}_{I(A),B} &= \sum_{\mu=1}^N r_{I(A),\mu}, \quad \tilde{K}_{B,I(A)} = \sum_{\mu=1}^N W_B(\tilde{\epsilon}_\mu) r_{\mu,I(A)} \end{aligned} \quad (40)$$

The solution of eqs 37 take the following form:  $P_M(t) = P_M(\infty) + A_M^{(1)} e^{-K_1 t} + A_M^{(2)} e^{-K_2 t}$  ( $M = D, I, A$ ). Concrete expressions for the steady state populations  $P_M(\infty)$  as well as for the overall transfer rates  $K_1$  and  $K_2$  can be found, for instance, in ref 27. The solution describes two-exponential TET kinetics which, however, reduces to single-exponential kinetics in the time region  $t \gg K_1^{-1}$  only if  $K_1 \gg K_2$ . A detailed inspection of the related expressions shows that condition the  $K_1 \gg K_2$  is

fulfilled when

$$\begin{aligned} K_{DI}/K_{ID} &= \exp[-(E_D - E_I)/k_B T] \ll 1 \\ K_{AI}/K_{IA} &= \exp[-(E_A - E_I)/k_B T] \ll 1 \end{aligned} \quad (41)$$

Moreover, the validity of inequality eq 41 guarantees a small population of the intermediate state |I⟩, and thus it becomes possible to use the stationary condition,  $\dot{P}_I(t) = 0$ . With this condition, the solution of the eqs 37 reads

$$\begin{aligned} P_D(t) &\simeq k_b/K_{TET} + (k_f/K_{TET})e^{-K_{TET}t} \\ P_A(t) &\simeq (k_f/K_{TET})(1 - e^{-K_{TET}t}) \\ P_I(t) &\simeq 0 \end{aligned} \quad (42)$$

Indeed, this solution describes single-exponential TET kinetics, which is characterized by the overall transfer rate

$$K_{TET} = k_f + k_b \quad (43)$$

only between the states |D⟩ and |A⟩ and, thus, directly between the D and the A centers. It is important to note that  $K_{TET}$  agrees with  $K_2$  derived from the exact solution only if  $K_1 \gg K_2$ . This means that the inequality (41) represents a necessary and sufficient condition for formation of D–A TET kinetics. [Note that in the case of bridge-mediated TET under consideration the additional conditions, eq 32, also have to be fulfilled.] The overall rate  $K_{TET}$  is defined by its forward ( $k_f$ ) and backward ( $k_b$ ) components, each determined through stepwise and concerted contributions so that

$$k_{f(b)} = k_{f(b)}^{(\text{step})} + k_{f(b)}^{(\text{conc})} \quad (44)$$

where

$$\begin{aligned} k_f^{(\text{step})} &= \frac{K_{DI}K_{IA}}{K_{ID} + K_{IA}} & k_f^{(\text{conc})} &= k_{DA} \\ k_b^{(\text{step})} &= \frac{K_{AI}K_{ID}}{K_{ID} + K_{IA}} & k_b^{(\text{conc})} &= k_{AD} \end{aligned} \quad (45)$$

2. *Slow Intrabridge Relaxation:*  $\tau_B \gg \tau_{TET}$ . This case appears for small transfer rates  $k_{\mu\mu'}$  and  $r_{\mu\mu'}$ . Therefore, the TET process has been finalized before any noticeable redistribution of population within the bridging states  $|\mu\rangle$  took place. As a result, we may ignore intrabridge relaxational transitions on the time scale of the TET process and, consequently, omit the rates  $k_{\mu\mu'}$  and  $r_{\mu\mu'}$  in eqs 18. Bearing in mind the small population of the bridging states, we again arrive at eqs 37 where, however, the thermally activated components of effective transfer rates, eq 38, take the form

$$k_{ID(DI)}^{(\text{act})} = \sum_{\mu=1}^N \frac{k_{I(D),\mu} k_{\mu,D(I)}}{k_{\mu D} + k_{\mu I}}$$

and

$$k_{IA(AI)}^{(\text{act})} = \sum_{\mu=1}^N \frac{r_{I(A),\mu} r_{\mu,A(I)}}{r_{\mu A} + r_{\mu I}} \quad (46)$$

Just these expressions specify the stepwise route of the D–A TET kinetics. They have to be distinguished from those of the eqs 39 and 40. Because a small population of the intermediate

states |I⟩ has been assumed, we finally get the same expressions for the overall transfer rate as given in eqs 43–45.

### III. Discussion of the Results

The derivation and the solution of the  $2N + 3$  coupled kinetic equations, eqs 18, describing the bridge-mediated TET in a DBA system, and the construction of an analytic expression for the overall D–A TET rate  $K_{TET}$ , eqs 43–45, 38–40, and 46, have to be considered as the main result of the present paper. It could be demonstrated that for fast as well as slow relaxation among the extended DBA levels the rate  $K_{TET}$  contains two contributions related to the stepwise and the concerted TET routes. To clearly demonstrate the importance of these two different mechanisms for the overall D–A TET process, we considered the TET through a regular bridge with a weak energetic irregularities. The main attention has been put on the bridge-length dependence of the overall transfer rate.

We first emphasize that in line with eqs 80 and 82 the driving force of the D–A TET reaction,

$$\Delta E_{DA} \equiv E_D - E_A = \Delta E + (N - 1)\Delta \quad (47)$$

increases with the increase of the energetic bias  $\Delta$  ( $\Delta E = E_D^{(0)} - E_A^{(0)} \geq 0$  denotes the driving force in the absence of an energetic bias). Therefore, and following from  $k_b = \exp(-\Delta E_{DA}/k_B T)k_f$ , the backward ET processes becomes less important when the number of bridge units  $N$  increases.

Using the relation between the rates  $k_b$  and  $k_f$ , we rewrite eq 43 as

$$K_{TET} = k_f \{1 + \exp[-(\Delta E + (N - 1)\Delta)/k_B T]\} \quad (48)$$

and conclude that an analysis of the forward component  $k_f$  suffices.

Let us first consider the stepwise contribution. Because in the case of a D–A TET regime the, energy  $E_I$  exceeds  $E_D$ , the driving force

$$\Delta E_{DI} = E_D - E_I = -\Delta E_{ID}^{(0)} + (N - 1)\Delta \quad (49)$$

of the SET process  $|D\rangle \rightarrow |I\rangle$  remains negative at any finite number of bridging units (note  $\Delta E_{ID}^{(0)} \equiv E_I^{(0)} - E_D^{(0)} > 0$ ). Therefore, by denoting the stepwise contribution, eq 45, in the form

$$k_f^{(\text{step})} = e^{-\Delta E_{ID}^{(0)} - (N-1)\Delta/k_B T} \frac{K_{ID}K_{IA}}{K_{ID} + K_{IA}} \quad (50)$$

one realizes that the stepwise route of TET can be understood as a thermally activated transfer process through the intermediate state |I⟩.

Next, we note that each effective transfer rate,  $K_{ID}$  and  $K_{IA}$ , contains contributions related to the superexchange and thermally activated transfer with the superexchange contribution to  $K_{ID}$  given by the rate  $k_{ID}$ . On the basis of eqs 23, 24, and A19 it becomes obvious that at the conditions of deep tunneling the noted rate reads

$$k_{ID} = k_{ID}^{(0)} e^{-\alpha_1(N-1)} e^{\xi_1 N(N-1)} \quad (51)$$

The dependence of this rate on the number of bridge units is mainly given by the exponent including the decay parameter

$$\alpha_1 = \Lambda(E_D) + \Lambda(E_I) \quad (52)$$

This parameter characterizes the superexchange transition taking place in a regular bridge. The second exponential function in eq 51 corresponds to the perturbation caused by an energetic bias  $\Delta$  and contains the parameter (note  $\Delta E_M \equiv E_B - E_M^{(0)}$ )

$$\zeta_1 = (\Delta/\Delta E_D + \Delta/\Delta E_I)/2. \quad (53)$$

Finally, the rate expressions of eq 51

$$k_{ID}^{(0)} = \frac{2\pi}{\hbar} \frac{|V_{DI}V_{AN}|^2}{\Delta E_I \Delta E_D} (\text{FC})_{ID} \quad (54)$$

coincides with that for a bridge with a “single” unit. Note that for  $\Delta \neq 0$  the rate  $k_{ID}^{(0)}$  contains a weak  $N$  dependence via the driving force  $\Delta E_{DI}$  of the Franck–Condon factor. Moreover, in analogy to eq 51 we obtain

$$k_{IA} = k_{IA}^{(0)} e^{-\alpha_2(N-1)} e^{\zeta_2 N(N-1)} \quad (55)$$

with

$$\alpha_2 = \tilde{\Lambda}(E_A) + \tilde{\Lambda}(E_I) \quad (56)$$

$$\zeta_2 = (\Delta/\Delta \tilde{E}_A + \Delta/\Delta \tilde{E}_I)/2 \quad (57)$$

(note  $\Delta \tilde{E}_M \equiv \tilde{E}_B - E_M^{(0)}$ ), and

$$k_{IA}^{(0)} = \frac{2\pi}{\hbar} \frac{|V'_{DI}V'_{AN}|^2}{\Delta \tilde{E}_I \Delta \tilde{E}_A} (\text{FC})_{IA} \quad (58)$$

The  $N$  dependence of the thermally activated component of the rate  $K_{ID}$  is defined by the shifts  $\Delta \epsilon_\mu$  of the energies  $\epsilon_\mu$ . According to the eqs A6, A18, and 39, we may derive

$$k_{ID}^{(\text{act})} = e^{-(N-1)\Delta/2k_B T} \sum_{\mu=1}^N e^{-\epsilon_\mu - E_I^{(0)}/k_B T} \frac{k_{\mu I} k_{\mu D}}{k_{\mu I} + k_{\mu D}} \quad (59)$$

This expression is valid for slow relaxation processes between the extended bridge states. In the contrary case of fast relaxation, eqs A6, A18, and 46 result in

$$k_{ID}^{(\text{act})} = e^{-(N-1)\Delta/2k_B T} \sum_{\mu=1}^N e^{-\epsilon_\mu - E_I^{(0)}/k_B T} k_{\mu I} \frac{\sum_{\mu=1}^N W_B(\epsilon_\mu) k_{\mu D}}{\sum_{\mu=1}^N W_B(\epsilon_\mu) (k_{\mu I} + k_{\mu D})} \quad (60)$$

[Because the shifts  $\Delta \epsilon_\mu$  are independent of  $\mu$  (cf. eq A18), we may set  $W_B(\epsilon_\mu) = W_B(\epsilon_\mu)$ .] The transfer rate  $k_{IA}^{(\text{act})}$  is obtained from eqs 59 and 60 by replacing the rates  $k_{\mu D}$  and  $k_{\mu I}$  by  $r_{\mu A}$  and  $r_{\mu I}$ , respectively. Besides, one has to replace the factor  $\exp[-3(N-1)\Delta/2k_B T]$  by the factor  $\exp[-(N-1)\Delta/2k_B T]$  and the energy  $\epsilon_\mu$  by the energy  $\tilde{\epsilon}_\mu$ .

The  $N$  dependence of the stepwise transfer rate, eq 50, is completely defined by eqs 51, 55, and 59 (or eq 60). To find the  $N$  dependence of the concerted transfer rate  $k_f^{(\text{conc})}$ , eq 45, we use eqs 23, 26, and A19. It follows

$$k_f^{(\text{conc})} = k_{DA}^{(0)} e^{-\alpha(N-1)} e^{\zeta N(N-1)} \quad (61)$$

where the decay parameter

$$\alpha = \Lambda(E_D) + \Lambda(E_A) + \tilde{\Lambda}(E_D) + \tilde{\Lambda}(E_A) \quad (62)$$

characterizes the two-electron superexchange transition between the D and the A mediated by a regular bridge whereas the change of the rate caused by an energetic bias  $\Delta$  is characterized by the parameter

$$\zeta = (\Delta/\Delta E_D + \Delta/\Delta E_A)/2 + 3(\Delta/\Delta \tilde{E}_A + \Delta/\Delta \tilde{E}_A)/2 \quad (63)$$

The rate expression of eq 61

$$k_{DA}^{(0)} = \frac{2\pi}{\hbar} \frac{|V_{DI}V_{AN}V'_{DI}V'_{AN}|^2}{\Delta E_D \Delta E_A \Delta \tilde{E}_D \Delta \tilde{E}_A \Delta E_{ID} \Delta E_{IA}} (\text{FC})_{DA} \quad (64)$$

represents the two-electron superexchange rate for a bridge with a “single” unit. For  $\Delta \neq 0$  it shows a weak dependence on the bridge length via the dependence of the Franck–Condon factor on the driving force  $\Delta E_{DA}$ , eq 47.

The analytic results presented so far enable us to analyze different regimes of the D–A TET process. To do this, we utilize the simplest version of the Song–Marcus model<sup>39,40</sup> for the Franck–Condon factors. Such an approach is based on the coupling of the electronic states to a single active vibrational coordinate with frequency  $\omega_0$ . It results the well-known Jortner expression<sup>17,41</sup> for the Franck–Condon factor:

$$(\text{FC})_{MN} = \frac{1}{\hbar \omega_0} \exp(-S_{MN} \coth \hbar \omega_0 / 2k_B T) \left( \frac{1+n(\omega_0)}{n(\omega_0)} \right)^{\nu_{MN}/2} I_{|\nu_{MN}|} (2S_{MN} \sqrt{n(\omega_0)(1+n(\omega_0))}) \quad (65)$$

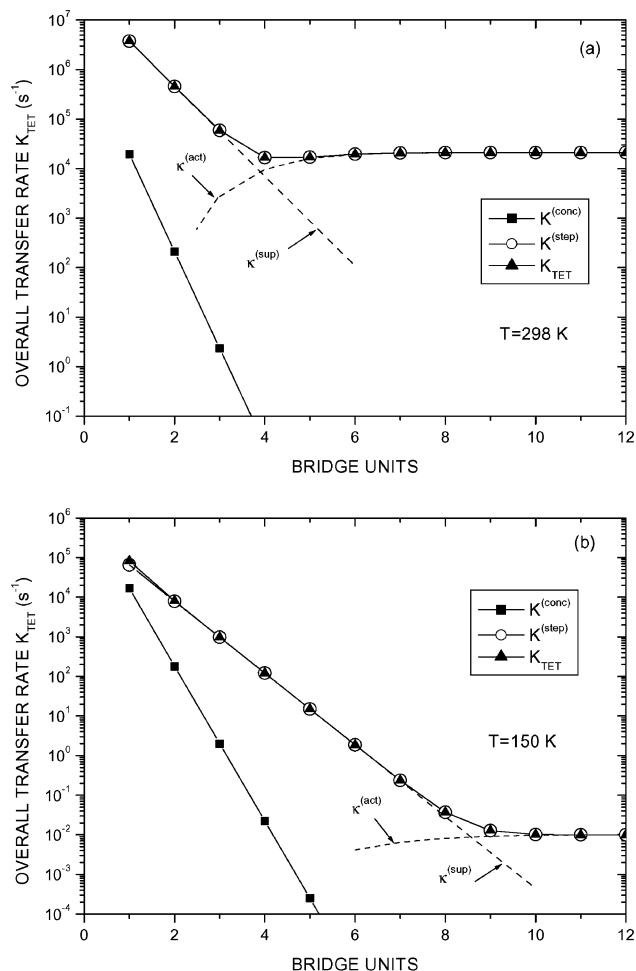
Here, we introduced  $\nu_{MN} \equiv \Delta E_{MN}/\hbar \omega_0$  (note the correspondence  $\Delta E_{MN} = E_M - E_N$  for  $M, N = D, I, A$  as well as  $\Delta E_{\mu D(I)} = \epsilon_\mu - E_{D(I)}$  and  $\Delta E_{\mu A} = \tilde{\epsilon}_\mu - E_A$ ). Moreover, we set  $S_{MN} \equiv \lambda_{MN}/\hbar \omega_0$  ( $\lambda_{MN}$  denotes the reorganization energy for the  $M \rightarrow N$  ET). Finally,  $n(\omega_0) = [\exp(\hbar \omega_0/k_B T) - 1]^{-1}$  is the Bose distribution, and  $I_\nu(z)$  stands for the modified Bessel function.

The actual value of the overall D–A TET rate is determined by all those parameters entering the elementary rate constants. In present paper we focus on the bridge-length dependence of the stepwise and concerted contributions to the  $K_{\text{TET}}$ . Therefore, all parameters are chosen in such way that allows us not only to numerically analyze the difference between the mentioned transfer rates, eq 59 and eq 60, describing the thermally activated stepwise route but also to derive a rather simple analytic form for two types of rate. In particular, we are able to show that even at room temperature both types of rates reduce to a single analytic form (cf. below, eqs 66 and 67) provided that the intrabridge transfer coupling  $|V_B|$  becomes sufficiently large.

To underline that the stepwise D–A TET route follows an activation law, let us take a look at Figure 3. It can be directly seen that at the given set of parameters a decrease of temperature leads to a remarkable decrease of the stepwise contribution  $K^{(\text{step})} = [1 + \exp(-\Delta E_{DA}/k_B T)] k_f^{(\text{step})}$  to the overall transfer rate  $K_{\text{TET}} = K^{(\text{step})} + K^{(\text{conc})}$ . In contrast, the concerted contribution  $K^{(\text{conc})} = [1 + \exp(-\Delta E_{DA}/k_B T)] k_f^{(\text{conc})}$  stays practically constant. This fact is completely explained by the two-electron superexchange nature of the rate  $k_f^{(\text{conc})} = k_{DA}$ . Thus, the concerted route of TET can even exist at zero temperature. Analyzing the stepwise contribution  $K^{(\text{step})}$  and remembering the peculiarities related to  $k_f^{(\text{conc})}$ , eq 50, we have to note that  $K^{(\text{step})}$  contains a mixture of contributions related to the thermally activated and the superexchange single-electron pathways that cannot be separated in the general case.

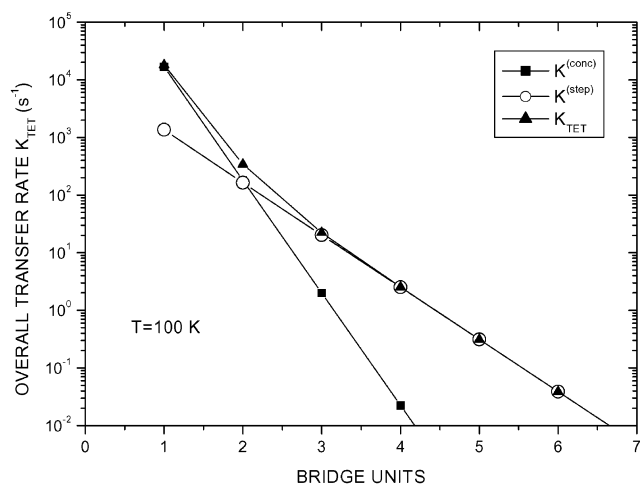
However, we may compare the efficiency of the described pathways by introducing a thermal activated component  $k^{(\text{act})}$





**Figure 3.** Bridge-length dependence of the overall D–A TET rate  $K_{\text{TET}} = K^{(\text{step})} + K^{(\text{conc})}$  as well as its stepwise,  $K^{(\text{step})}$ , and concerted,  $K^{(\text{conc})}$ , contributions at two different temperatures. The  $N$  dependence of the transfer rate exclusively accounting for the activated stepwise process,  $k^{(\text{act})}$ , and for superexchange stepwise process,  $k^{(\text{sup})}$ , is also shown (dashed lines). The curves are obtained in using the parameters:  $\Delta E_{\text{D}} = 0.75$  eV,  $\Delta E_{\text{I}} = 0.65$  eV,  $\Delta \tilde{E}_{\text{I}} = 0.75$  eV,  $\Delta E = 0$ ,  $\lambda_{\text{D1}} = \lambda_{\text{N1}} = \lambda_{\text{NA}} = 0.6$  eV,  $\lambda_{\text{D1}} = \lambda_{\text{IA}} = 0.7$  eV,  $\lambda_{\text{DA}} = 0.4$  eV,  $\omega_0 = 600$   $\text{cm}^{-1}$ ,  $\Delta = 0$ ,  $V_{\text{D1}} = V_{\text{NA}} = V'_{\text{D1}} = V'_{\text{NA}} = 0.04$  eV,  $V_{\text{B}} = 0.20$  eV.

as well as a superexchange component,  $k^{(\text{sup})}$ . Concrete expressions for both follow from eq 50 if one maintains in eqs 38 either the rates  $k_{\text{MN}}^{(\text{act})}$  or the rates  $k_{\text{MN}}$ . The single-electron superexchange component  $k^{(\text{sup})}$  is clearly represented in the stepwise contribution if one compares Figure 3a with Figure 3b. At room temperature it exceeds the activated contribution up to a number  $N = 3$  of bridge units whereas at  $T = 150$  K this is the case up to  $N = 8$ . An interesting peculiarity of the activated component represents the fact that the rate  $k^{(\text{act})}$  increases with increasing bridge length but stays nearly constant at  $N \approx 7$  (if  $T = 298$  K, Figure 3a) or at  $N \approx 12$  (if  $T = 150$  K, Figure 3b). Such a behavior can be explained in the following way. If the energy bias  $\Delta$  is zero (case of a regular bridge), the  $N$  dependence of the activated component  $k^{(\text{act})}$  is only originated by the gap  $\epsilon_{\mu} - E_1^{(0)}$  ( $\tilde{\epsilon}_{\mu} - E_1^{(0)}$ ) as well as by the rates  $k_{\mu\text{M}}$  ( $r_{\mu\text{M}}$ ), and here via the energies  $\epsilon_{\mu}$  ( $\tilde{\epsilon}_{\mu}$ ) and the transfer couplings  $T_{\mu\mu}$  ( $\tilde{T}_{\mu\mu}$ ). Let the intrasite bridge coupling  $V_{\text{B}}$  (which leads to the extended levels) to be of such a magnitude that the relation  $\exp[-(\epsilon_2 - \epsilon_1)/k_{\text{B}}T] \ll 1$  ( $\exp[-(\tilde{\epsilon}_2 - \tilde{\epsilon}_1)/k_{\text{B}}T] \ll 1$ ) is fulfilled. Then, the main contribution to the thermally activated process



**Figure 4.** Bridge-length dependence of the overall D–A TET rate  $K_{\text{TET}}$  at  $T = 100$  K. The part stemming from the concerted mechanism dominates at  $N = 1$ , it is comparable with the stepwise contribution at  $N = 2$  and becomes less important for  $N > 2$ . The use parameters are those of Figure 3.

under consideration is given by level  $\mu = 1$ . In this case both expressions, eqs 59 eq 60, reduce to the common expression

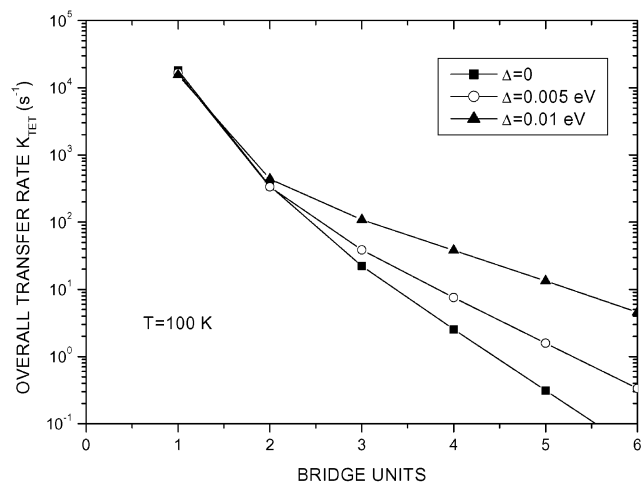
$$k_{\text{ID}}^{(\text{act})} = e^{-[\Delta E_{\text{I}} - 2|V_{\text{B}}|\cos(\pi/(N+1))]/k_{\text{B}}T} \frac{k_{\text{I1}}k_{\text{1D}}}{k_{\text{I1}} + k_{\text{1D}}} (\Delta E_{\text{I}} \equiv E_{\text{B}} - E_{\text{I}}^{(0)}) \quad (66)$$

and

$$k_{\text{IA}}^{(\text{act})} = e^{-[\Delta \tilde{E}_{\text{I}} - 2|V_{\text{B}}|\cos(\pi/(N+1))]/k_{\text{B}}T} \frac{r_{\text{I1}}r_{\text{1A}}}{r_{\text{I1}} + r_{\text{1A}}} (\Delta \tilde{E}_{\text{I}} \equiv \tilde{E}_{\text{B}} - E_{\text{I}}^{(0)}) \quad (67)$$

In the present case,  $|V_{\text{B}}| = 0.20$  eV and thus eqs 66 and 67 are satisfied for small  $N$ . Therefore, in line with eq 50 one derives  $k^{(\text{act})} \sim \exp[2|V_{\text{B}}|\cos \pi/(N+1)/k_{\text{B}}T]$ . Just such an  $N$  dependence can be seen in Figure 3a,b. It is necessary to note here that a similar behavior of the transfer rate characterizing the thermally activated ET through extended bridge states (in particular, the flat length dependence of the rate for long bridges) has been earlier found for the case of SET reactions.<sup>42</sup> (A more detailed discussion on this problem can be found in refs 23, 43, and 44.) We would only like to mention here that the difference to the TET consists of the fact that TET reactions cover two separate steps of a single electron thermally activated pathway, namely  $|\text{D}\rangle \rightleftharpoons |\text{I}\rangle$  and  $|\text{I}\rangle \rightleftharpoons |\text{A}\rangle$ .

Next let us pay attention to the fact that the single-electron superexchange decay parameters, eqs 53 and 57 are smaller than the two-electron superexchange parameter, eq 63. Therefore, at low temperatures one may observe a more pronounced decrease of the concerted contribution with increasing bridge length as compared with the stepwise contribution (cf. Figure 3b). Nevertheless, due to the activated character of the stepwise D–A TET a decreasing temperature may result in a situation where the concerted contribution to  $K_{\text{TET}}$  exceeds the stepwise one. Figure 4 displays this behavior for  $T = 100$  K. One can see that the stepwise contribution to  $K_{\text{TET}}$  dominates for  $N > 2$  whereas the D–A TET through a bridge with a single unit is determined by the concerted mechanism. At  $N = 2$  the stepwise and the concerted mechanism show the same efficiency.



**Figure 5.** Enhancement of the D–A TET efficiency caused by an energetic bias within the bridge. A comparison with Figure 4 shows that the bias mainly influences the thermal activated stepwise contribution of the  $K_{TET}$ . The use parameters are those of Figure 3.

The efficiency of the thermally activated stepwise route  $|D\rangle \rightleftharpoons |I\rangle \rightleftharpoons |A\rangle$  is very sensitive to a change of the energy gap  $\Delta E_{ID}$ . Figure 5 shows this effect for the case where the degeneracy of the local bridge levels is disturbed by the energetic bias  $\Delta$ . Now, the mentioned gap shows a linear dependence on the number of bridge units, cf. eq 49. Note that the concerted contribution which at  $N = 2$  exceeds the stepwise one (compare with Figure 4), stays practically constant at a given value of  $\Delta$ .

#### IV. Conclusion

In the present paper we considered bridge-mediated two-electron transfer (TET) for the case where the electronic couplings between neighboring bridge units strongly exceed their coupling to vibrational coordinates (of the DBA system as well as the surrounding medium). Furthermore, it has been assumed that the relaxation processes that lead to an equilibrium distribution within the vibrational states are much faster than the overall TET process (cf. inequality, eq 17). Because the characteristic time  $\tau_{rel}$  for vibrational relaxation in molecular systems is 0.1–10 ps,<sup>45,46</sup> the results presented here are valid for TET reactions taking place in a 100 ps up to 1 ns time region. The fact that the TET takes place against the background of fast vibrational relaxation processes allowed us to utilize a coarse-grained description and to derive a set of coupled balance-like eqs 18. At the same time respective rate constants have been derived, characterizing the hopping transitions between the localized DBA states ( $|D\rangle$ ,  $|I\rangle$ , and  $|A\rangle$ ) and the extended DBA states ( $|\beta_{\mu}\rangle$  and  $|\tilde{\beta}_{\mu}\rangle$ ) as well as the distant superexchange single-electron and two-electron unistep transitions between the D and the A centers (cf. scheme a in Figure 2).

The main focus has been put on the reduction of multiexponential TET kinetics to single-exponential kinetics between the donor state  $|D\rangle \equiv |D(ee)B_1B_2\dots B_NA\rangle$  and the acceptor state  $|A\rangle \equiv |DB_1B_2\dots B_NA(ee)\rangle$ , only. Such a description has been taken because the possible characterization by a single rate  $K_{TET}$  is a common observation for numerous ET processes covering biological systems, too (cf., e.g., refs 2–4, 6, 8, 9, and 16–20). In particular, it could be shown by us that such a D–A regime of the TET becomes possible if a specific relation exists between the elementary rate constants, eq 32, as well as between the effective transfer rates, eq 41. The validity of inequality 32

results in a small population of the extended bridge states, eqs 7, whereas eqs 41 guarantee a small population of the intermediate state  $|I\rangle \equiv |D(e)B_1B_2\dots B_NA(e)\rangle$ . Our estimations indicate that the limit of a direct D–A TET process is achieved if the population of the mentioned states does not exceed  $10^{-2}$ . Then, the overall D–A TET transfer rate  $K_{TET}$  only contains a contribution related to the stepwise and to the concerted mechanism. The stepwise contribution  $K^{(step)}$  is originated by two single-electron rates and the participation of a weakly populated intermediate state  $|I\rangle$ . The effective transfer rates  $K_{DI}$  and  $K_{ID}$  ( $K_{IA}$  and  $K_{AI}$ ) characterize the first (second) step; cf. scheme b of Figure 2. In line with eq 38 each effective transfer rate has a single-electron superexchange component as well as a component related to the thermal activated process.

Note that the superexchange contribution exists even at zero temperature. But due to the activation character of the stepwise route (cf. eq 50) the common contribution to the TET process drops with decreasing temperature. For a short bridge, it can become even less effective than the concerted contribution that results from a direct two-electron superexchange process (cf. Figure 4). According to the single-electron superexchange component, however, one observes a certain increase of the stepwise contribution with increasing bridge length. For instance, in Figure 3a this increase may be seen around  $N = 4$ . The presence of such a region has to be considered as the important criterion for the participation of extended bridge states in the D–A TET process. Note that such a behavior of the rate is impossible when nonadiabatic D–A TET is considered, where the thermally activated component of the stepwise route originates from the single-electron site to site hopping across the bridge.<sup>29</sup>

Our considerations concentrated on a particular part of the TET through extended DBA bridge states, the bridge-length dependence of the reaction for a regular bridge as well as for the case of rather simple energetic irregularities. It has been shown that an intersite energetic bias within the bridge may facilitate the D–A TET (cf. Figure 5). The perturbation caused by the bias mainly results in corrections of the superexchange couplings as well as in an alteration of the gaps between the specific intermediate state  $|I\rangle$  and the donor (acceptor) state  $|D\rangle$  ( $|A\rangle$ ). The change of the driving force of the corresponding reaction was of less importance.

Further work to be done in the investigation of bridge-mediated TET reactions should be related to the consideration of more complex perturbations, in particular, to the consideration of the Coulomb interaction connected with a localization of the transferred electrons within the DBA system. In the present description, we did not include this interaction but supposed that the D and the A centers are well screened by polar groups while the bridge is surrounded by a nonpolar medium (for a more detailed discussion cf. ref 29). However, this interaction may influence the transfer processes in a considerable manner. [As an example, we mention here ref 53 where the influence of the Coulomb interaction on the rate of a single-electron bridge-mediated oxidation–reduction reaction has been analyzed.]

Of course, the presented computations on TET processes have to be applied on concrete molecular systems. Two-electron reactions, for example, have been observed in a number of substrate–enzyme complexes such as xanthine oxidase<sup>47</sup> mycothione reductase,<sup>48</sup> monoxygenase,<sup>10</sup> cytochrome oxidase,<sup>11</sup> nickel–iron hydrogenase,<sup>12</sup> trimethylamine dehydrogenase,<sup>49</sup> hemocyanin,<sup>50</sup> human cytochrome P450 reductase,<sup>51</sup> mycothione reductase<sup>52</sup> and others. When considering such reactions, the main challenge is to uncover the mechanisms that orchestrate

the multielectron release along the iron-sulfur-, molybdenum-, vanadium-, manganese-, or copper-containing protein domains. Moreover, it is less understood in which way a stabilization of reactive intermediates takes place and what is the underlying mechanism for the cleavage and formation of chemical bonds. So far, the main interest has been related to the questions whether the electron transfer and the structural changes are separated or concerted and, if the dominant structural change is coupled to the first or to the second step of the transfer. The progress in understanding the mechanisms of these complex reactions could be probably achieved by not only analyzing the bridge-length dependence of the transfer rates but by the study of the dependence of the overall transfer rate on structural and external factors (including the temperature and the media acidity), too. Recently,<sup>27</sup> we used the theory of nonadiabatic bridge-mediated D–A TET to explain the dependence of the overall transfer rate on the pH value of the solvent in which two-electron reduction of microthionine reductase by NADPH takes place.

### Appendix A: Bridge Green's Function for the Case of Energetic Irregularities

The Green's function characterizing the ET through the DBA bridge states is defined as (cf. refs 33 and 34)

$$G_{1N}(E) = \langle B_1 | [E - H_B^{(el)}]^{-1} | B_N \rangle \quad (A1)$$

where  $|B_1\rangle$  and  $|B_N\rangle$  are the localized DBA states which indicate that one of the transferred electrons is located at the D center whereas the second electron is located at the first or at the  $N$ th bridge unit. The same expression is valid for Green's function  $\tilde{G}_{1N}(E)$ , which follows  $G_{1N}(E)$  when  $H_B^{(el)}$  is substituted by  $\tilde{H}_B^{(el)}$  as well as the states  $|B_1\rangle$  and  $|B_N\rangle$  by  $|\tilde{B}_1\rangle$  and  $|\tilde{B}_N\rangle$ , respectively (these states indicate that one of the transferred electrons is located at the A center whereas the second transferred electron is located at the first or the  $N$ th bridge unit). In the tight binding approximation under consideration  $G_{1N}(E)$  takes the following form

$$G_{1N}(E) = \sum_{\mu} \frac{u_{\mu}^*(1)u_{\mu}(N)}{E - \epsilon_{\mu}}. \quad (A2)$$

For a linear bridge this expression can be also rewritten as<sup>54</sup>

$$G_{1N}(E) = \frac{(-1)^{N+1} \prod_{m=1}^{N-1} V_{mm+1}}{\prod_{\mu=1}^N (\epsilon_{\mu} - E)} \quad (A3)$$

which is more suitable when approximations are carried out. If a regular bridge is considered ( $V_{12} = V_{23} = \dots V_{N-1,N} \equiv V_B$ )  $G_{1N}(E)$  changes to the form given in eq 28.

Below we derive an analytical expression for Green's function of a bridge including a small energetic perturbation. We assume for the energies of the bridge units that appear in the Hamiltonian, eq 3

$$E_m = E_B + \Delta E_m \quad (A4)$$

The deviations  $\Delta E_m$  from the mean value  $E_B$  are assumed to be small compared with the transfer couplings  $V_{mm\pm 1} = V_B$ . Therefore, in the zero-order approximation (i.e., at  $E_m \approx E_B$ ),

the energies  $\epsilon_{\mu}$  of the extended bridge states  $|\beta_{\mu}\rangle$  and the transformation coefficients  $u_{\mu}(m)$  are given by eq 8. Let  $t_{\mu\mu'} = \sum_m u_{\mu}(m)u_{\mu'}(m)\Delta E_m$  be the off-diagonal contribution caused by an energetic irregularity. If the inequality

$$|t_{\mu\mu'}| \ll |\epsilon_{\mu} - \epsilon_{\mu'}| \quad (A5)$$

is fulfilled for each  $\mu' \neq \mu$ , then in the first-order approximation with respect to the energetic perturbations one derives the following form for the energies of bridge states (note that in eq 8 and thus in the following relation the  $u_{\mu}(m)$  are real)

$$\epsilon_{\mu} \approx \epsilon_{\mu} + \Delta\epsilon_{\mu} \quad (\Delta\epsilon_{\mu} = \sum_m u_{\mu}^2(m)\Delta E_m) \quad (A6)$$

Using the identity

$$\prod_{\mu=1}^N (\epsilon_{\mu} - E) = \prod_{\mu=1}^N (\epsilon_{\mu} - E) e^{S(E)} \quad (A7)$$

where

$$S(E) = \sum_{\mu=1}^N \ln[1 + \Delta\epsilon_{\mu}/(\epsilon_{\mu} - E)] \quad (A8)$$

we arrive at eq 27, where

$$G_{1N}^{(\text{reg})}(E) = \frac{(-1)^{N+1} V_B^{N-1}}{\prod_{\mu=1}^N (\epsilon_{\mu} - E)} \quad (A9)$$

With  $\cosh \Lambda(E) \equiv (E_B - E)/2|V_B|$  this expression can be reduced to the expression given in eq 28.<sup>54</sup>

If the levels of the bridge states are energetically positioned far away the energy levels  $E = E_D, E_I, E_A$  (cf. Figure 1) so that the inequality

$$\Delta\epsilon_{\mu} \ll (\epsilon_{\mu} - E) \quad (A10)$$

is valid for all bridge states, then the correcting factor is reduced to the more simple form

$$S(E) = \sum_{\mu=1}^N [\Delta\epsilon_{\mu}/(\epsilon_{\mu} - E)] \quad (A11)$$

Analogously, one derives

$$\tilde{S}(E) = \sum_{\mu=1}^N [\Delta\tilde{\epsilon}_{\mu}/(\tilde{\epsilon}_{\mu} - E)] \quad (A12)$$

Expressions A11 and A12 are suitable for an evaluation of the corrections to superexchange couplings. Let, for instance, an energetic irregularity be defined by the intrabridge bias so that

$E_m - E_{m+1} = \tilde{E}_m - \tilde{E}_{m+1} = \Delta$ . In this case, the energies of the localized DBA states depend on the energy bias  $\Delta$  as

$$E_D = E_D^{(0)} \quad (\text{A13})$$

$$E_1 = E_1^{(0)} - (N - 1)\Delta \quad (\text{A14})$$

$$E_A = E_A^{(0)} - 2(N - 1)\Delta \quad (\text{A15})$$

$$E_m = E_B - (m - 1)\Delta \quad (m = 1, 2, \dots, N) \quad (\text{A16})$$

$$\tilde{E}_n = \tilde{E}_B - (N - 1)\Delta - (n - 1)\Delta \quad (n = 1, 2, \dots, N) \quad (\text{A17})$$

where  $E_D^{(0)}$ ,  $E_1^{(0)}$ ,  $E_A^{(0)}$ ,  $E_B \equiv E_m^{(0)}$ , and  $\tilde{E}_B \equiv \tilde{E}_n^{(0)}$  are the DBA energies in absence of the bias. On the basis of eqs A6, A16, A17, and 8 one derives

$$\Delta\epsilon_\mu = -(N - 1)\Delta/2 \quad \Delta\tilde{\epsilon}_\mu = -3(N - 1)\Delta/2 \quad (\text{A18})$$

These quantities are independent of the extended state  $|\mu\rangle$ . Therefore, to evaluate the correction factors, one has to estimate the quantity  $\sum_\mu [\epsilon_\mu - E]^{-1}$ . As an example, we consider the case of deep tunneling where  $E_B - E \gg 2|V_B|$  and thus  $\sum_\mu [\epsilon_\mu - E]^{-1} \approx N/(E_B - E)$ . Introducing the correction factor into eq 27, we get

$$G_{1N}(E) \approx \frac{1}{E_B - E} e^{-\Lambda(E)(N-1)} e^{N(N-1)\Delta/[2(E_B-E)]}$$

$$\tilde{G}_{1N}(E) \approx \frac{1}{\tilde{E}_B - E} e^{-\tilde{\Lambda}(E)(N-1)} e^{3N(N-1)\Delta/[2(\tilde{E}_B-E)]} \quad (\text{A19})$$

To derive these expressions, we have also used the fact that owing to the inequality  $\exp \Lambda(E) \gg \exp(-\Lambda(E))$  which is valid for deep tunneling, the Green's function, eq 28, of a regular bridge reduces to the form

$$G_{1N}^{(\text{reg})}(E) \approx \frac{\exp[-\Lambda(E)(N - 1)]}{E_B - E} \quad (\text{A20})$$

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