

# Nonadiabatic two-electron transfer mediated by an irregular bridge

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## Abstract

Nonadiabatic two-electron transfer (TET) mediated by a linear molecular bridge is studied theoretically. Special attention is put on the case of an irregular distribution of bridge site energies as well as on the inter-site Coulomb interaction. Based on the unified description of electron transfer reactions [J. Chem. Phys. 115 (2001) 7107] a closed set of kinetic equations describing the TET process is derived. A reduction of this set to a single exponential donor–acceptor (D–A) TET is performed together with a derivation of an overall D–A TET rate. The latter contains a contribution of the stepwise as well as of the concerted route of D–A TET. The stepwise contribution is determined by two single-electron steps each of them associated with a sequential and a superexchange pathway. A two-electron unistep superexchange transition between the D and A forms the concerted contribution to the overall rate. Both contributions are analyzed in their dependency on the bridge length. The irregular distribution of the bridge site energies as well as the influence of the Coulomb interaction facilitates the D–A TET via a modification of the stepwise and the concerted part of the overall rate. At low temperatures and for short bridges with a single or two units the concerted contribution exceeds the stepwise contribution. If the bridge contains more than two units, the stepwise contribution dominates the overall rate.

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## 1. Introduction

Distant electron transfer (ET) mediated by a molecular bridge (B) is one of the basic processes responsible for oxidation–reduction reactions in chemical and biological systems (see, e.g., [1–12]). Among the various types of bridge-assisted ET reactions, the donor–acceptor (D–A) single-electron transfer (SET) process represents the most basic type. D–A SET was the subject of intensive theoretical studies during recent years promoted by experimental findings on the distant dependence of ET reactions through polypeptides [13] and DNA strands [14]. In particular, results based on a unified description of nonadiabatic SET [15–18] (see also [19–21]) allowed to derive an analytic expression for

the bridge-length dependence of the overall D–A SET rate. Conditions could be also derived at which the rate reduces to a sum of contributions related to the multi-step sequential (hopping) and the unistep superexchange (coherent) transfer [15].

The transfer process becomes more involved if it proceeds as a bridge-assisted *multi-electron* reaction. So far such types of reactions have been only studied for the case of a nonadiabatic D–A two-electron transfer (TET) mediated by a *regular* molecular bridge [22–24]. Particularly, it could be demonstrated that the D–A TET proceeds through the bridge  $B \equiv B_1 B_2 \cdots B_m \cdots B_N$  ( $B_m$  denotes the  $m$ th unit of the bridge) along stepwise and concerted routes. The stepwise route is originated by single-electron hopping transitions between neighboring sites of the DBA system. This type of transition starts from the reactant state  $D^-BA$  with the two electrons at the D. It reaches the *intermediate state* of the TET reaction  $D^-BA^- \equiv D^-B_1 B_2 \cdots B_N A^-$  via

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single-electron hoppings along the bridging states of type  $D^-B^-A$  (this notation abbreviates the manifold of states  $D^-B_1B_2\cdots B_NA$ ,  $D^-B_1B_2\cdots B_NA^-$ ,  $\dots$  and  $D^-B_1B_2\cdots B_NA^-$ ). The second part of the process starts from the intermediate state  $D^-BA^-$  and reaches the product state  $DBA^-$  via single-electron hoppings along the bridging state,  $DB^-A^-$  (which read in detail  $DB_1^-B_2\cdots B_NA^-$ ,  $DB_1B_2\cdots B_NA^-$ ,  $\dots$  and  $DB_1B_2\cdots B_NA^-$ ). Thus, the reactant state  $D^-BA$  and the product state  $DBA^-$  of the TET reaction are related one to another by the intermediate state  $D^-BA^-$ . The formation of this state is of fundamental importance for the TET (as already noted for TET reactions which proceed in the absence of a bridge [25]). In addition to the introduced states one expects some contributions from doubly reduced bridge states. It has been discussed in detail in [23] under what conditions these contributions are of minor importance.

In contrast to the stepwise route the concerted TET route follows from a direct unistep transition between the reactant and the product state (cf. [23]). This unistep transition is originated by a specific two-electron superexchange coupling between the D and the A via the above-mentioned types of bridging states  $D^-B^-A$  and  $DB^-A^-$ , as well as the intermediate state  $D^-BA^-$ . Moreover, an analytic dependence of the overall D–A TET rate on the number of bridging units could be derived in [23]. Concentrating on the special case of a regular bridge, different regimes of D–A TET have been studied.

It is the aim of the present paper to extend the approach of [22,23] to the more realistic situation of an *irregular* bridge. We will consider the influence of an intra-bridge energetic bias as well as the effect caused by the Coulombic coupling between the sites of electron localization within the DBA system. The energetic differences between the sites of the bridge may result from an externally applied electric field. Slight changes of the chemical structure of the bridge units or of the groups surrounding the bridge may also cause such differences. (In the various types of fumarate reductases the redox-chains of hemes or Fe–S clusters are characterized by a notable energetic bias [26]). The importance of the Coulomb interaction for bridge-assisted D–A SET has been already underlined in [27]. In the case of the bridge-assisted TET discussed here the Coulomb interaction leads to different contributions to the total DBA energy depending on the position of the two transferred electrons in the DBA system. The localization of the transferred electrons at the D, the A as well as the various bridge units  $B_1, B_2, \dots, B_N$  changes the site–site interaction in the DBA system. To clarify the importance of this inter-site Coulomb interaction for the efficiency of the distant TET is one task of the present paper.

The paper is organized as follows: In Section 2, the model is introduced for the description of nonadiabatic

TET through a molecular bridge and the coupled set of corresponding kinetic equations are given together with respective rate constants. The reduction of the complete set of kinetic equations to those describing the direct D–A TET process is shortly explained in Section 3. An analytic expression for the overall D–A TET transfer rate is given as well. Section 4 is devoted to the analysis of the bridge-length dependence of the stepwise and concerted contribution to the overall rate. A general discussion of the mechanisms leading to bridge-assisted D–A TET and a comparison of the results obtained for an irregular as well as a regular bridge are presented in Section 5.

## 2. Kinetic equations of nonadiabatic bridge-assisted TET

It is a basic property of bridge-assisted nonadiabatic ET reactions that they proceed against the background of fast intra-site relaxation processes. If the latter are characterized by the time-constant  $\tau_{\text{rel}}$ , then the inequality  $\Delta t \gg \tau_{\text{rel}}$  holds, where  $\Delta t$  is the characteristic time of the ET process. Accordingly, a coarse-grained description of the ET can be carried out [15,17]. It is based on the introduction of the total electronic state populations  $P_M(t) = \sum_{v_M} \langle v_M M | \rho(t) | M v_M \rangle$ , where  $\rho(t)$  is the density operator of the DBA system and the summation has been taken with respect to all vibrational substates  $v_M$  related to the electronic state  $|M\rangle$ .

In the case of bridge-assisted TET under consideration the states  $|M\rangle$  refer to all involved electronic configurations. Those cover the donor state  $|D\rangle \equiv |D^-B_1B_2\cdots B_m\cdots B_NA\rangle$ , the intermediate state  $|I\rangle \equiv |D^-B_1B_2\cdots B_m\cdots B_NA^- \rangle$ , and the acceptor state  $|A\rangle \equiv |DB_1B_2\cdots B_m\cdots B_NA^- \rangle$ , as well as two types of singly reduced bridging states  $|B_m\rangle \equiv |D^-B_1B_2\cdots B_m^- \cdots B_NA\rangle$  and  $|\tilde{B}_m\rangle \equiv |DB_1B_2\cdots B_m^- \cdots B_NA^- \rangle$  ( $m = 1, 2, \dots, N$ ). Here,  $D^{--}(A^{--})$  and  $D^-(A^-)$  denote the D(A) site with, respectively, two excess electrons and one excess electron, while  $B_m^-$  stands for the  $m$ th bridge unit with one excess electron. Of course the given electronic states have to be supplemented by those of a doubly reduced bridge. However, we will restrict our considerations to bridges which are surrounded by a nonpolar environment like lipids or nonpolar residues of a protein. Then, because of the Coulomb repulsion among the transferred electrons the doubly reduced bridge states are positioned far above the energy levels of all other states and can be neglected (for more details see [23] as well as [28,29], where this effect has been discussed for molecular wires). Accordingly, we denote the TET Hamiltonian as  $H_{\text{TET}} = H_0 + V$ , where the diagonal part

$$H_0 = \sum_M \sum_{v_M} E_{Mv_M} |Mv_M\rangle \langle Mv_M| \quad (1)$$

is defined by the electron–vibrational states  $|Mv_M\rangle$  and the respective energies  $E_{Mv_M}$  ( $M$  and  $v_M$  denote the electronic and vibrational quantum numbers, respectively). The off-diagonal part of the TET Hamiltonian,

$$V = \sum_{M,N} \sum_{v_M v'_N} \mathcal{M}_{MN} \langle v_M | v'_N \rangle |Mv_M\rangle \langle Nv'_N| \quad (2)$$

is responsible for electronic transitions between different states  $|Mv_M\rangle$  and  $|Nv'_N\rangle$ . It is written by using a Condon-like approximation (which works well in the case of bridge-assisted nonadiabatic ET). Accordingly,  $\mathcal{M}_{MN} = \langle M | \hat{V}_{tr} | N \rangle$  denotes the electronic coupling and  $\langle v_M | v'_N \rangle$  gives the vibrational overlap integral. The  $\mathcal{M}_{MN}$  are specified by employing a tight-binding model. If one restricts on a DBA system with the D and the A inter-connected by a linear bridge one obtains [23]

$$\begin{aligned} \mathcal{M}_{DB_1} &= V_{D1}, & \mathcal{M}_{IB_1} &= V'_{D1}, & \mathcal{M}_{IB_N} &= V_{AN}, \\ \mathcal{M}_{AB_N} &= V'_{AN}, & \mathcal{M}_{B_m B_{m\pm 1}} &= \mathcal{M}_{\tilde{B}_m \tilde{B}_{m\pm 1}} = V_{mm\pm 1}. \end{aligned} \quad (3)$$

The expressions show that any transition between two different electronic states  $|M\rangle$  and  $|N\rangle$  is originated by SET processes between neighboring sites of electron

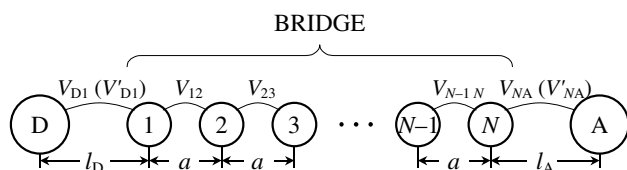


Fig. 1. Linear donor–bridge–acceptor (DBA) system. The quantities  $l_D$ ,  $a$  and  $l_A$  denote the distances between different units. (The single-electron couplings  $V_{D1}$ ,  $V_{NA}$ ,  $V'_{D1}$ ,  $V'_{NA}$ , and  $V_{mm+1}$  are discussed in the text.)

localization in the DBA system with the  $\mathcal{M}_{MN}$  expressed by inter-site single-electron coupling matrix elements  $V_{mm'}$  (cf. Fig. 1).

Based on the TET Hamiltonian one may derive kinetic equations which describe the process of bridge mediated nonadiabatic TET. Details of the derivation can be found in [15] for the case of SET, and in [23] for TET reactions. The coarse-graining procedure results in the following kinetic equations for the populations of all involved electronic states  $|M\rangle$

$$\dot{P}_M(t) = -q_M P_M(t) + \sum_{N \neq M} k_{NM} P_N(t), \quad (4)$$

where indexes  $M$  and  $N$  indicate the noted electronic DBA-states  $|D\rangle$ ,  $|B_m\rangle$ ,  $|I\rangle$ ,  $|\tilde{B}_m\rangle$  and  $|A\rangle$ . The quantities

$$\begin{aligned} q_D &\equiv g_D + k_{DI} + k_{DA}, & q_m &\equiv g_m + r_m \quad (m = 1, 2, \dots, N), \\ q_A &\equiv \tilde{r}_A + k_{AI} + k_{AD}, & \tilde{q}_n &\equiv \tilde{g}_n + \tilde{r}_n \quad (n = 1, 2, \dots, N), \\ q_I &\equiv g_I + r_I + k_{ID} + k_{IA}. \end{aligned} \quad (5)$$

are the total escape rates from the respective states. They are expressed by the rate-constants  $k_{MN}$  describing the transitions from electronic state  $|M\rangle$  to another states.

The rate constants of sequential single–electron transitions between neighboring DBA sites are indicated in the scheme (a) of Fig. 2 and read  $g_D \equiv k_{DB_1}$ ,  $g_N \equiv k_{B_N I}$ ,  $g_m \equiv k_{B_m B_{m+1}}$ ,  $\tilde{g}_I \equiv k_{I \tilde{B}_1}$ ,  $\tilde{g}_N \equiv k_{\tilde{B}_N A}$ ,  $\tilde{g}_m \equiv k_{\tilde{B}_m \tilde{B}_{m+1}}$  (and analogously for  $r_j$  and  $\tilde{r}_j$ ). The general form of this type of rate expressions is given by

$$k_{MN} = \frac{2\pi}{\hbar} |\mathcal{M}_{MN}|^2 (\text{FC})_{MN}, \quad (6)$$

where  $(\text{FC})_{MN}$  is the Franck–Condon factor for  $M \rightarrow N$  transition [1,11,15,30].

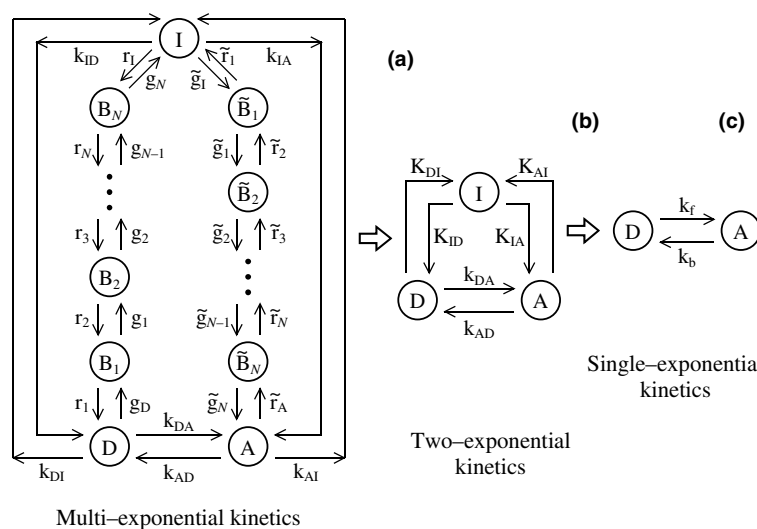


Fig. 2. Reduction of multi-exponential TET kinetics to single-exponential D–A TET kinetics. Scheme (a) involves multi-step transitions between the DBA electronic states (with rates  $g_m$ ,  $r_m$ ,  $\tilde{g}_n$ ,  $\tilde{r}_n$ ) and unistep transitions (with rates  $k_{MN}$ ). The scheme (b) shows the transitions between three basic electronic states, and scheme (c) represents the D–A TET kinetics with an overall forward and backward transfer rate.

Apart from the sequential transitions the kinetic equation (4) include processes of distant single-electron ( $D \rightleftharpoons I$  and  $I \rightleftharpoons A$ ) and two-electron ( $D \rightleftharpoons A$ ) transitions with rate expressions

$$k_{MN} = \frac{2\pi}{\hbar} |T_{MN}|^2 (\text{FC})_{MN}, \quad (7)$$

where the  $T_{MN}$  denote the respective superexchange coupling matrix elements. In the case of the SET processes  $D \rightleftharpoons I$  and  $I \rightleftharpoons A$  the squares of the related superexchange couplings read

$$|T_{DI}|^2 = \frac{|\mathcal{M}_{DB_1} \mathcal{M}_{B_1 B_2} \cdots \mathcal{M}_{B_{N-1} B_N} \mathcal{M}_{B_N I}|^2}{\prod_{m=1}^N \Delta E_{mD} \Delta E_{mI}} \quad (8)$$

and

$$|T_{IA}|^2 = \frac{|\mathcal{M}_{I \tilde{B}_1} \mathcal{M}_{\tilde{B}_1 \tilde{B}_2} \cdots \mathcal{M}_{\tilde{B}_{N-1} \tilde{B}_N} \mathcal{M}_{\tilde{B}_N A}|^2}{\prod_{m=1}^N \Delta \tilde{E}_{mI} \Delta \tilde{E}_{mA}}. \quad (9)$$

The quantity responsible for the two-electron  $D \rightleftharpoons A$  transition takes the following form:

$$|T_{DA}|^2 = \frac{|\mathcal{M}_{DB_1} \mathcal{M}_{B_1 B_2} \cdots \mathcal{M}_{B_{N-1} B_N} \mathcal{M}_{B_N I}|^2}{\prod_{m=1}^N \Delta E_{mD} \Delta E_{mA} \Delta E_{ID}} \times \frac{|\mathcal{M}_{I \tilde{B}_1} \mathcal{M}_{\tilde{B}_1 \tilde{B}_2} \cdots \mathcal{M}_{\tilde{B}_{N-1} \tilde{B}_N} \mathcal{M}_{\tilde{B}_N A}|^2}{\prod_{m=1}^N \Delta \tilde{E}_{mD} \Delta \tilde{E}_{mA} \Delta E_{IA}}. \quad (10)$$

Note that we have used the abbreviations  $\Delta E_{mD(I,A)} \equiv \Delta E_{B_m D(I,A)}$  and  $\Delta \tilde{E}_{mD(I,A)} \equiv \Delta \tilde{E}_{\tilde{B}_m D(I,A)}$ .

### 3. Overall transfer rate of the D–A TET process

The processes connected with the TET reaction are described by the  $2N + 3$  linear rate equation (4) and are depicted in scheme (a) of Fig. 2. Every state population  $P_M$  ( $M = D, I, A, B_1, \dots, B_N, \tilde{B}_1, \dots, \tilde{B}_N$ ) has a multi-exponential time-dependence  $P_M(t) = P_M(\infty) + \sum_{r=1}^{2N+2} B_M^{(r)} \exp(-K_r t)$ . The  $P_M(\infty)$  are the steady-state populations and  $K_1, K_2, \dots, K_{2N+2}$  denote the  $2N + 2$  nonzero transfer rates. Of course, analytical expressions for the rates  $K_r$  can only be derived in particular cases. One of them is the (direct) D–A TET where the populations of all bridging states  $|B_m\rangle$  and  $|\tilde{B}_n\rangle$  ( $m, n = 1, 2, \dots, N$ ) as well as of the intermediate state  $|I\rangle$  remain small during the TET. For such a situation multi-exponential kinetics are only met for the bridging states and the intermediate state which all less populated [17,23]. However, the population of the reactant state  $|D\rangle$  and the product state  $|A\rangle$  show a single-exponential time-dependence ( $M = D, A$ , the  $P_M(0)$  denote the initial populations)

$$P_M(t) = P_M(\infty) + (P_M(0) - P_M(\infty)) \exp(-K_{\text{TET}} t). \quad (11)$$

The resulting TET kinetics described by this two-state equation are shown in Fig. 2(c). The overall transfer rate  $K_{\text{TET}}$ , as demonstrated in [23] is given by the smallest rate of the set  $K_1, K_2, \dots, K_{2N+2}$ . This fact will be used to

derive an expression for  $K_{\text{TET}}$  in the general case of an irregular bridge (in [23] an analytic expression for  $K_{\text{TET}}$  has been only derived for the case of a regular bridge).

First let us change to the Laplace transform of the kinetic equation (4). According to the relation  $F_M(s) = \int_0^\infty \exp(-st) P_M(t) dt$  we obtain a linear set of algebraic equations

$$\hat{A}(s) \mathbf{F}(s) = \mathbf{C}. \quad (12)$$

The vectors  $\mathbf{F}(s)$  and  $\mathbf{C}$  are defined by its components  $F_D(s), F_I(s), \dots, F_A(s)$  and  $P_D(0), P_I(0), \dots, P_A(0)$ , respectively, and  $\hat{A}(s)$  denotes the rate matrix. The condition  $\det(s) = 0$ , where  $\det(s)$  is the determinant of  $\hat{A}$ , determines all  $2N + 3$  TET rates. They read  $K_1 = -s_1$ ,  $K_2 = -s_2, \dots, K_{2N+2} = -s_{2N+2}$  with  $s_r$  being the roots of  $\det(s)$  (one root, denoted by  $s_0$ , is equal to zero). Next we note that  $\hat{A}(s)$  depends on  $s$  only via its diagonal elements  $A_{MM}(s) = s + q_M$ . Therefore, the  $A_{MM}(s)$  are dominated by the escape rates  $q_M$  if  $|s| \ll q_M$ . Assuming that the energetic position of the bridging states as well as of the intermediate state is above the donor and the acceptor level, the escape rates  $q_1, q_N, \tilde{q}_1, \tilde{q}_N$  and  $q_I$  are much larger than  $q_D$  and  $q_A$  (see Eq. (5)). As a result, the smallest nonzero transfer rate  $K_{2N+2} \equiv K_{\text{TET}}$  strongly deviates from all other rates. Considering the diagonal elements  $A_{MM}(s)$  at  $s = -K_{\text{TET}}$  we may conclude that  $A_{MM}(s = -K_{\text{TET}}) \simeq q_M$  for all bridging states  $|B_m\rangle, |\tilde{B}_m\rangle$  as well as for the intermediate state  $|I\rangle$ . Hence, we may set  $A_{MM}(s) \simeq A_{MM}(0)$ , what exactly corresponds to the ‘‘steady-state’’ approximation for finding the populations (in our case the populations of the bridging states as well as of the intermediate state). Thus, setting  $\dot{P}_m(t) = 0, \dot{P}_n(t) = 0, \dot{P}_I(t) = 0$  and utilizing the initial condition  $P_M(0) = \delta_{MD}$  we obtain the solution, Eq. (11) with  $P_D(0) = 1, P_A = 0, P_D(\infty) = k_b/K_{\text{TET}}, P_A(\infty) = k_f/K_{\text{TET}}$ , and  $K_{\text{TET}} = k_f + k_b$ . Note that the forward ( $k_f$ ) and the backward ( $k_b$ ) component of the D–A TET rate  $K_{\text{TET}}$ ,

$$k_{f(b)} = k_{f(b)}^{(\text{step})} + k_{f(b)}^{(\text{conc})}, \quad (13)$$

contain contributions associated with the stepwise and concerted transition within the whole DBA system. The stepwise contribution is given by

$$k_f^{(\text{step})} = \frac{K_{DI} K_{IA}}{K_{ID} + K_{IA}}, \quad k_b^{(\text{step})} = \frac{K_{AI} K_{ID}}{K_{ID} + K_{IA}}. \quad (14)$$

The rates  $K_{MN}$  contain a contribution given by the superexchange mechanism of SET  $K_{MN}^{(\text{sup})}$  and by a contribution related to the sequential mechanism  $K_{MN}^{(\text{seq})}$  (cf. scheme (b) in Fig. 2). They read in detail

$$K_{DI(\text{ID})} = K_{DI(\text{ID})}^{(\text{sup})} + K_{DI(\text{ID})}^{(\text{seq})}, \quad K_{DI}^{(\text{sup})} = k_{DI}, \quad K_{DI}^{(\text{seq})} = g_D g_1 \cdots g_N / D(1, N), \quad (15)$$

$$K_{ID}^{(\text{sup})} = k_{ID}, \quad K_{ID}^{(\text{seq})} = r_I r_N \cdots r_1 / D(1, N)$$

and

$$\begin{aligned}
K_{\text{AI(IA)}} &= K_{\text{AI(IA)}}^{(\text{sup})} + K_{\text{AI(IA)}}^{(\text{seq})}, \\
K_{\text{AI}}^{(\text{sup})} &= k_{\text{AI}}, \quad K_{\text{AI}}^{(\text{seq})} = \tilde{r}_A \tilde{r}_N \cdots \tilde{r}_1 / \tilde{D}(1, N), \\
K_{\text{IA}}^{(\text{sup})} &= k_{\text{IA}}, \quad K_{\text{IA}}^{(\text{seq})} = \tilde{g}_1 \tilde{g}_1 \cdots \tilde{g}_N / \tilde{D}(1, N).
\end{aligned} \quad (16)$$

The quantity  $D(1, N)$  is the determinant of the tri-diagonal matrix

$$\hat{D} = \begin{pmatrix} q_1 & -r_2 & 0 & 0 & \cdots & 0 \\ -g_1 & q_2 & -r_3 & 0 & \cdots & 0 \\ 0 & -g_2 & q_3 & -r_4 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \cdots & \vdots \\ 0 & 0 & \cdots & -g_{N-2} & q_{N-1} & -r_N \\ 0 & 0 & \cdots & 0 & -g_{N-1} & q_N \end{pmatrix}. \quad (17)$$

Moreover,  $\tilde{D}(1, N)$  denotes the determinant of the matrix, Eq. (17) with the elements  $-g_m, -r_m$  and  $q_m$  replaced by  $-\tilde{g}_m, -\tilde{r}_m$  and  $\tilde{q}_m$ , respectively. The rate expressions given in Eqs. (15) and (16) essentially simplify for a regular bridge with identical units. If an energetic bias  $\Delta = E_{m+1} - E_m$  between neighboring bridge sites is present all forward (and backward) inter-site rate constants coincide so that

$$\begin{aligned}
g_1 = g_2 = \cdots = g_{N-1} = \tilde{g}_1 = \tilde{g}_2 = \cdots = \tilde{g}_{N-1} &\equiv \alpha, \\
r_2 = r_3 = \cdots = r_N = \tilde{r}_2 = \tilde{r}_3 = \cdots = \tilde{r}_N &\equiv \beta.
\end{aligned} \quad (18)$$

According to this specification the expressions for the sequential transfer rates  $K_{\text{DI(ID)}}^{(\text{seq})}$  and  $K_{\text{AI(IA)}}^{(\text{seq})}$  take a simpler form [23]. Furthermore, the contribution stemming from the concerted TET mechanism and entering Eq. (13) is defined via a specific unistep two-electron superexchange process between the states  $|D\rangle$  and  $|A\rangle$ . This yields

$$k_{\text{f}}^{(\text{conc})} = k_{\text{DA}}, \quad k_{\text{b}}^{(\text{conc})} = k_{\text{AD}} \quad (19)$$

with the rates  $k_{\text{DA}}$  and  $k_{\text{AD}}$  given by Eqs. (7) and (10).

The expressions given in Eqs. (11), (13)–(17), and (19) completely describe nonadiabatic D–A TET reactions mediated by a bridge of  $N$  units. Below we will concentrate on the analysis of the bridge-length dependency of the overall transfer rate  $K_{\text{TET}}$  in using a simple tight-binding description of the bridge. In accordance with this model all interstate couplings  $\mathcal{M}_{MN}$  can be expressed by the inter-site electronic couplings (cf. Eq. (3)). And, the formulas for the superexchange couplings remain valid if all energy gaps  $\Delta E_{MN}$  in Eqs. (8)–(10) are positive and satisfy the condition of deep tunneling:

$$|V_{\text{D1}}|, |V_{\text{NA}}|, |V'_{\text{D1}}|, |V'_{\text{NA}}|, |V_{\text{mm+1}}| \ll \Delta E_{\text{ID}}. \quad (20)$$

[Note that  $\Delta E_{m\text{A}} \geq \Delta E_{m\text{D}} > \Delta E_{\text{ID}}$ ,  $\Delta E_{\text{ID}} \geq \Delta E_{\text{IA}}$ , and  $\Delta \tilde{E}_{m\text{D}} \geq \Delta \tilde{E}_{m\text{A}} > \Delta \tilde{E}_{m\text{I}}$ .]

### 3.1. Bridge-length dependence in the case of regular bridge

We denote the unperturbed energies which correspond to the DBA-states  $|D\rangle, |A\rangle, |I\rangle, |B_m\rangle$  and  $|\tilde{B}_m\rangle$  by  $E_{\text{D}}^{(0)}, E_{\text{A}}^{(0)}, E_{\text{I}}^{(0)}, E_{\text{B}} \equiv E_m^{(0)}$ , and  $\tilde{E}_{\text{B}} \equiv \tilde{E}_m^{(0)}$ , respectively. In a DBA system with a regular bridge the energy gaps  $\Delta E_{MN} = \Delta E_{MN}^{(\text{reg})}$  entering the denominators of Eqs. (8)–(10), can be expressed as  $\Delta E_{m\text{D}}^{(\text{reg})} = E_{\text{B}} - E_{\text{D}}^{(0)} \equiv \Delta E_{\text{D}}$ ,  $\Delta E_{m\text{A}}^{(\text{reg})} = E_{\text{B}} - E_{\text{A}}^{(0)} \equiv \Delta E_{\text{A}}$ ,  $\Delta E_{\text{ID}}^{(\text{reg})} = E_{\text{I}}^{(0)} - E_{\text{D}}^{(0)} \equiv \Delta E_{\text{D}}$ ,  $\Delta E_{\text{I}}$ , ( $\Delta E_{\text{I}} = E_{\text{B}} - E_{\text{I}}^{(0)}$ ),  $\Delta \tilde{E}_{m\text{D}}^{(\text{reg})} = \tilde{E}_{\text{B}} - E_{\text{D}}^{(0)} \equiv \Delta \tilde{E}_{\text{D}}$ ,  $\Delta \tilde{E}_{m\text{A}}^{(\text{reg})} = \tilde{E}_{\text{B}} - E_{\text{A}}^{(0)} \equiv \Delta \tilde{E}_{\text{A}}$ ,  $\Delta E_{\text{IA}}^{(\text{reg})} = E_{\text{I}}^{(0)} - E_{\text{A}}^{(0)} = \Delta E_{\text{A}} - \Delta E_{\text{I}}$ ,  $\Delta E_{m\text{I}}^{(\text{reg})} = E_{\text{B}} - E_{\text{I}}^{(0)} \equiv \Delta E_{\text{I}}$ , and  $\Delta \tilde{E}_{m\text{I}}^{(\text{reg})} = \tilde{E}_{\text{B}} - E_{\text{I}}^{(0)} \equiv \Delta \tilde{E}_{\text{I}}$  (cf. Fig. 3). Moreover, we set  $V_{\text{mm+1}} \equiv V_{\text{B}}$ . In line with Eqs. (6), (15), (16), and (19), then, we may write (note that symbol reg stands for a regular bridge)

$$\begin{aligned}
K_{\text{DI(ID)}}^{(\text{sup-reg})} &= \frac{2\pi}{\hbar} |T_{\text{DI}}^{(\text{reg})}|^2 (\text{FC})_{\text{DI(ID)}}^{(\text{reg})}, \\
K_{\text{IA(AI)}}^{(\text{sup-reg})} &= \frac{2\pi}{\hbar} |T_{\text{IA}}^{(\text{reg})}|^2 (\text{FC})_{\text{IA(AI)}}^{(\text{reg})}
\end{aligned} \quad (21)$$

and

$$k_{\text{f(b)}}^{(\text{conc-reg})} = \frac{2\pi}{\hbar} |T_{\text{DA}}^{(\text{reg})}|^2 (\text{FC})_{\text{DA(AD)}}^{(\text{reg})}, \quad (22)$$

where the squares of superexchange couplings read

$$|T_{\text{DI(IA)}}^{(\text{reg})}(N)|^2 = |T_{\text{DI(IA)}}^{(0)}|^2 e^{-\zeta_{\text{I(2)}}(N-1)}, \quad (23)$$

$$|T_{\text{DA}}^{(\text{reg})}(N)|^2 = |T_{\text{DA}}^{(0)}|^2 e^{-\zeta(N-1)}. \quad (24)$$

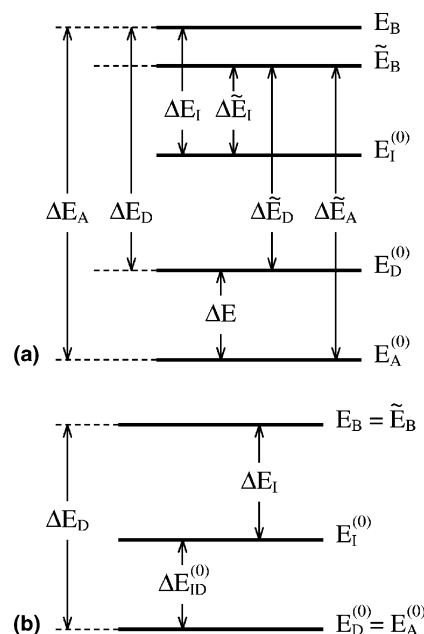


Fig. 3. Position of the electronic energy levels  $E_M \equiv E(M, \{0_M\})$  of the DBA system and respective energy gaps in the general case (panel a) and in the case of a self-exchange D–A TET reaction (panel b).

Concrete expressions for  $|T_{DI}^{(0)}|^2$ ,  $|T_{IA}^{(0)}|^2$  and  $|T_{DA}^{(0)}|^2$  as well as the decay parameters  $\zeta_1$ ,  $\zeta_2$  and  $\zeta$  can be found in [23, Eqs. (63)–(71)].

It follows from Eqs. (21) and (23) that the superexchange components of the SET rates  $K_{DI(ID)}$  and  $K_{IA(AI)}$ , Eqs. (15) and (16) which specify the stepwise contribution to the overall D–A TET rate  $K_{TET}$ , show a strong exponential decrease with an increasing number of bridge units. Analogously, an exponential decay occurs for the concerted contribution which is originated by the specific two-exponential superexchange coupling  $T_{DA}^{(reg)}(N)$ , Eq. (24).

To derive the bridge-length dependence of the sequential components of  $K_{DI(ID)}$  and  $K_{IA(AI)}$  one has to take into consideration the condition (18) as well as the fact that for a regular unbiased bridge the forward and backward intra-bridge rate constants coincide ( $\alpha = \beta$ ). Accordingly, we obtain

$$\begin{aligned} K_{DI(ID)}^{(seq-reg)} &= k_{DI(ID)}^{(0seq)} / [1 + \zeta_1(N-1)], \\ K_{IA(AI)}^{(seq-reg)} &= k_{IA(AI)}^{(0seq)} / [1 + \zeta_2(N-1)], \end{aligned} \quad (25)$$

where

$$k_{DI}^{(0seq)} = g_D g_N / (g_N + r_1), \quad k_{ID}^{(0seq)} = r_1 r_1 / (g_N + r_1), \quad (26)$$

$$k_{AI}^{(0seq)} = \tilde{r}_A \tilde{r}_1 / (\tilde{g}_N + \tilde{r}_1), \quad k_{IA}^{(0seq)} = \tilde{g}_1 \tilde{g}_N / (\tilde{g}_N + \tilde{r}_1) \quad (27)$$

are bridge-length independent quantities. The change of the sequential rates with a change of the bridge length is determined by the decay parameters

$$\zeta_1 = \frac{r_1 g_N}{\alpha(g_N + r_1)}, \quad \zeta_2 = \frac{\tilde{r}_1 \tilde{g}_N}{\alpha(\tilde{g}_N + \tilde{r}_1)}. \quad (28)$$

### 3.2. Influence of energetic perturbations on the D–A TET transfer rates

The derivation of transfer rates for the case of regular bridge as given in the previous section has been based on the supposition that the Franck–Condon factors are independent on the distance between different units of the DBA system. Such an assumption is justified by experimental data on DBA systems with a regular bridge which confirm an exponential dependence of the (single-electron) superexchange rate (see the discussion on SET through proline chains in [13,17]). However, there exist systems where an exponential dependence of the superexchange contribution to the overall D–A SET rate has not been observed (cf. the SET through DNA strands [14,16,31]). The absence of such an exponential dependence in the case of SET through a regular bridge may be related to the dependence of the reorganization energy on the D–A distance as well as to the Coulomb interaction between different sites (different redox-centers) [27].

It is the aim of the following discussion to account for the latter effect in the case of TET. Due to the presence of two transferred electrons we expect a distinct influence of the inter-site Coulomb interaction as well as of an energetic bias. Below we will consider how the exponential bridge-length dependence of superexchange rates and the hyperbolic bridge-length dependence of sequential rates changes. In order to discuss the specific influence of an energetic bias as well as of the Coulomb interaction we assume a weak dependence of the reorganization energies on the bridge length.

Let  $\epsilon_M$  be the change of the electronic energy  $E_M^{(0)} \equiv E_{M0M}^{(0)}$  caused by an inter-site Coulomb interaction as well as by the presence of an energetic bias. Then,  $E_M = E_M^{(0)} + \epsilon_M$ . A concrete expressions for  $\epsilon_M = \epsilon_M^{(bias)} + \epsilon_M^{(Coul)}$  are given in Appendix A. They cover the contributions  $\epsilon_M^{(bias)}$  originated by an externally induced energetic bias as well as the expressions  $\epsilon_M^{(Coul)}$  accounting for the inter-site Coulomb interaction. The presence of  $\epsilon_M$  changes the energy gaps  $\Delta E_{MN}^{(reg)}$  to

$$\Delta E_{MN} = \Delta E_{MN}^{(reg)} + \Delta \epsilon_{MN}. \quad (29)$$

Noting the expressions Eqs. (A.1)–(A.3), (A.13)–(A.15) for  $\epsilon_M^{(bias)}$  and  $\epsilon_M^{(Coul)}$ , respectively we may write

$$\begin{aligned} \Delta E_{mD} &= \Delta E_D - (m-1)\Delta + U_{DA}^{(2)}/r_{DA} - U_B^{(1)}/r_{Dm} \\ &\quad - U_B^{(2)}/r_{Am}, \end{aligned} \quad (30)$$

$$\begin{aligned} \Delta \tilde{E}_{mD} &= \Delta \tilde{E}_D - (m-1)\Delta - (N-1)\Delta + U_{DA}^{(2)}/r_{DA} \\ &\quad - U_B^{(2)}/r_{Dm} - U_B^{(1)}/r_{Am}, \end{aligned} \quad (31)$$

$$\begin{aligned} \Delta E_{mA} &= \Delta E_A - (m-1)\Delta + 2(N-1)\Delta + U_{DA}^{(2)}/r_{DA} \\ &\quad - U_B^{(1)}/r_{Dm} - U_B^{(2)}/r_{Am}, \end{aligned} \quad (32)$$

$$\begin{aligned} \Delta \tilde{E}_{mA} &= \Delta \tilde{E}_A + (N-m)\Delta + U_{DA}^{(2)}/r_{DA} - U_B^{(2)}/r_{Dm} \\ &\quad - U_B^{(1)}/r_{Am}, \end{aligned} \quad (33)$$

$$\begin{aligned} \Delta E_{mI} &= \Delta E_I + (N-m)\Delta + (U_{DA}^{(2)} - U_{DA}^{(1)})/r_{DA} \\ &\quad - U_B^{(1)}/r_{Dm} - U_B^{(2)}/r_{Am}, \end{aligned} \quad (34)$$

$$\begin{aligned} \Delta \tilde{E}_{mI} &= \Delta \tilde{E}_I - (m-1)\Delta + (U_{DA}^{(2)} - U_{DA}^{(1)})/r_{DA} \\ &\quad - U_B^{(2)}/r_{Dm} - U_B^{(1)}/r_{Am} \end{aligned} \quad (35)$$

and

$$\Delta E_{ID} = (\Delta E_D - \Delta E_I) - (N-1)\Delta + U_{DA}^{(1)}/r_{DA}, \quad (36)$$

$$\Delta E_{IA} = (\Delta E_A - \Delta E_I) + (N-1)\Delta + U_{DA}^{(1)}/r_{DA}, \quad (37)$$

$$\Delta E_{DA} = \Delta E + 2(N-1)\Delta \quad (\Delta E \equiv \Delta E_D - \Delta E_A). \quad (38)$$

Eqs. (30)–(38) demonstrate that the energy bias and the influence of the Coulomb interaction leads to an dependence of the energy gaps on the number of bridge

units  $N$ , thus modifying the bridge-length dependence of the superexchange couplings, Eqs. (8)–(10). Moreover, the driving forces (36)–(38) cause an additional  $N$ -dependence of the Franck–Condon factors in the superexchange rate constants, Eq. (7). Hence, a modification of the bridge-length dependence of the superexchange rate results from a change of the superexchange couplings as well as from a change of the Franck–Condon factors. Some numerical illustrations of this conclusion will be given in the next section. Here, we will derive an analytical expression which demonstrates a deviation from the exponential bridge-length dependence as found for the case of a regular bridge (cf. Eqs. (23) and (24)). We consider the case where  $\Delta\epsilon_{MN} = \epsilon_M - \epsilon_N$  is small compared to the respective energy gaps  $\Delta E_{MN}^{(\text{reg})}$ . Then, on the base of results derived in Appendix B (cf. Eqs. (B.3), (B.7) and (B.8)) we may represent the superexchange rates, Eq. (7) in the following form:

$$k_{\text{DI(IA)}} \approx \frac{2\pi}{\hbar} |T_{\text{DI(IA)}}^{(\text{reg})}(N)|^2 e^{-\theta_{1(2)}(N)} (\text{FC})_{\text{DI(IA)}}, \quad (39)$$

$$k_{\text{DA}} \approx \frac{2\pi}{\hbar} |T_{\text{DA}}^{(\text{reg})}(N)|^2 e^{-\theta(N)} (\text{FC})_{\text{DA}} \quad (40)$$

with  $|T_{\text{DI}}^{(\text{reg})}(N)|^2$ ,  $|T_{\text{IA}}^{(\text{reg})}(N)|^2$  and  $|T_{\text{DA}}^{(\text{reg})}(N)|^2$  given in Eqs. (23) and (24), respectively. The correction factors are defined by Eqs. (B.4) and (B.9).

The discussed bridge irregularities modify the sequential transfer rates in much more complicated way than the superexchange rates. If, however, only an energetic bias changes the energies of a regular bridge Eq. (25) can be transformed to

$$K_{\text{DI(IA)}}^{(\text{seq})} = \frac{k_{\text{DI(IA)}}^{(0\text{seq})}}{1 + \xi_{1(2)}(1 - \gamma^{N-1})/(1 - \gamma)}, \quad (41)$$

$$K_{\text{ID(AI)}}^{(\text{seq-reg})} = \frac{k_{\text{ID(AI)}}^{(0\text{seq})} \gamma^{N-1}}{1 + \xi_{1(2)}(1 - \gamma^{N-1})/(1 - \gamma)}.$$

Now, the sequential decay parameters read

$$\xi_1 = \frac{r_1(g_N - \alpha(1 - \gamma))}{\alpha(g_N + r_1)}, \quad \xi_2 = \frac{\tilde{r}_1(\tilde{g}_N - \alpha(1 - \gamma))}{\alpha(\tilde{g}_N + \tilde{r}_1)}, \quad (42)$$

where we introduced  $\gamma \equiv \beta/\alpha = \exp[-\Delta/k_B T]$  ( $k_B$  and  $T$  are the Boltzmann constant and temperature, respectively).

#### 4. Discussion of the results

According to Eq. (13), we may rewrite the overall transfer rate as  $K_{\text{TET}} = K^{(\text{step})} + K^{(\text{conc})}$ . Noting  $k_b = k_f \exp(-\Delta E_{\text{DA}}/k_B T)$  one obtains

$$K^{(\text{step(conc)})} = \left[ 1 + \exp\left(-\frac{\Delta E_{\text{DA}}}{k_B T}\right) \right] k_f^{(\text{step(conc)})}. \quad (43)$$

Moreover, it follows from Eq. (43) that the bridge-length dependence of  $K_{\text{TET}}$  is located once in the driving force of the D–A TET reaction,  $\Delta E_{\text{DA}}$  (cf. Eq. (38)). Furthermore, this dependence enters the forward rate  $k_f^{(\text{step})}$  (via the single-electron stepwise transfer rates  $k_{\text{DI}}$  and  $K_{\text{IA}}$ , Eqs. (15) and (16)) as well as the rate  $k_f^{(\text{conc})}$ , Eq. (19).

To let become the dependence on the bridge length more obvious we specify the Franck–Condon factors for the site-to-site transition rates eqs. (6) and (7) in using the Song–Marcus model [32,33]. The model supposes a strong coupling of the electronic transition  $M \rightarrow N$  to a single (intra-site) vibration with frequency  $\omega_{MN} > 0$  while the coupling to the surrounding bath is characterized by the reorganization energy  $\lambda_{MN}$ . In this case, one obtains Jortner’s expression [34] of the Franck–Condon factors which reads as  $(\text{FC})_{MN} = \Phi_{MN}/\hbar\omega_{MN}$ , where

$$\Phi_{MN} = \exp\left[-S_{MN} \coth\left(\frac{\hbar\omega_{MN}}{k_B T}\right)\right] \left(\frac{1 + n(\omega_{MN})}{n(\omega_{MN})}\right)^{\nu_{MN}/2} \times I_{|\nu_{MN}|}\left(2S_{MN}[n(\omega_{MN})(1 + n(\omega_{MN}))]^{1/2}\right). \quad (44)$$

This formula contains the modified Bessel function  $I_\nu(z)$ , the Bose distribution function  $n(\omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ , and we have set  $S_{MN} \equiv \lambda_{MN}/\hbar\omega_{MN}$ ,  $\nu_{MN} \equiv \Delta E_{MN}/\hbar\omega_{MN}$ . Now, we can specify all forward single-electron sequential rate constants:

$$g_D = \frac{2\pi}{\hbar^2} \frac{|V_{\text{DI}}|^2}{\omega_{\text{DI}}} \Phi_{\text{DI}}, \quad g_N = \frac{2\pi}{\hbar^2} \frac{|V_{\text{NA}}|^2}{\omega_{\text{NI}}} \Phi_{\text{NI}}, \quad (45)$$

$$\tilde{g}_I = \frac{2\pi}{\hbar^2} \frac{|V'_{\text{DI}}|^2}{\omega_{\text{I1}}} \Phi_{\text{I1}}, \quad \tilde{g}_N = \frac{2\pi}{\hbar^2} \frac{|V'_{\text{NA}}|^2}{\omega_{\text{NA}}} \Phi_{\text{I1}}, \quad (46)$$

$$g_m = \frac{2\pi}{\hbar^2} \frac{|V_{\text{B}}|^2}{\omega_{\text{B}}} \Phi_{m\bar{m}+1}, \quad \tilde{g}_m = \frac{2\pi}{\hbar^2} \frac{|V_{\text{B}}|^2}{\omega_{\text{B}}} \Phi_{\bar{m}\bar{m}+1}. \quad (47)$$

Analogously, the forward single-electron and two-electron superexchange transfer rates read

$$k_{\text{ID(IA)}} = \frac{2\pi}{\hbar^2} \frac{|T_{\text{DI(IA)}}|^2}{\omega_{\text{ID(IA)}}} \Phi_{\text{ID(IA)}}, \quad k_{\text{DA}} = \frac{2\pi}{\hbar^2} \frac{|T_{\text{DA}}|^2}{\omega_{\text{DA}}} \Phi_{\text{DA}}. \quad (48)$$

Below we will discuss the results obtained so far in analyzing the particular case of a self-exchange D–A TET reaction. In order to relate the present computations to our earlier ones of [23,24] the following calculations are carried out with parameters similar to those of [23,24]. (Note that we took into account the fact that the reorganization energies of TET reactions are, as a rule, larger than those of SET reactions; for instance, in the case of TET reactions in solvents the reorganization energies may exceed those of SET processes by 1–1.5 eV [35,36].) There will be only a single deviation from the parameters used in [23,24]. To be able to compare the

stepwise and the concerted TET mechanism also at low-temperatures the vibrational frequencies have been taken somewhat larger than in [23,24].

Fig. 4 shows that the contribution to  $K_{\text{TET}}$  caused by the stepwise mechanism exceeds the concerted one if room temperatures are considered. However, for the same energetic parameters (specifying the rates (45)–(48)) the contribution originated by the concerted mechanism increases if the temperature decreases to 150 K (compare Figs. 4 and 5). The concerted contribution becomes comparable to the stepwise contribution for a single bridge unit ( $N = 1$ ) at  $T = 150$  K as well as for two bridge units ( $N = 2$ ) at  $T = 100$  K. It exceeds the stepwise contribution at  $N = 1$  and  $T = 100$  K (compare Figs. 5(a) and (b)). Here, we have to note that in line with the Marcus-theory [37] the reorganization energies  $\lambda_{\text{DI}}$ ,  $\lambda_{\text{IA}}$  and  $\lambda_{\text{DA}}$  can depend on the D–A distance. Therefore, the transfer rates for the case  $N = 1$  does not follow automatically from the above derived rate expressions for arbitrary  $N$ . In particular, a direct TET between the D and the A would become possible which can even transform a nonadiabatic reaction to an adiabatic one. So, the case  $N = 1$  requires more involved consideration if a concrete DBA system is considered. Here, however, we would like to consider such DBA systems where the nonadiabatic character of the reaction is guaranteed by small inter-site couplings. Then, the derived kinetic equations and the corresponding rate constants can be considered to be correct, at least for  $N > 1$ .

The calculations performed with the chosen set of parameters indicate that  $K_{\text{IA}} \gg K_{\text{ID}}$ . Therefore, in line

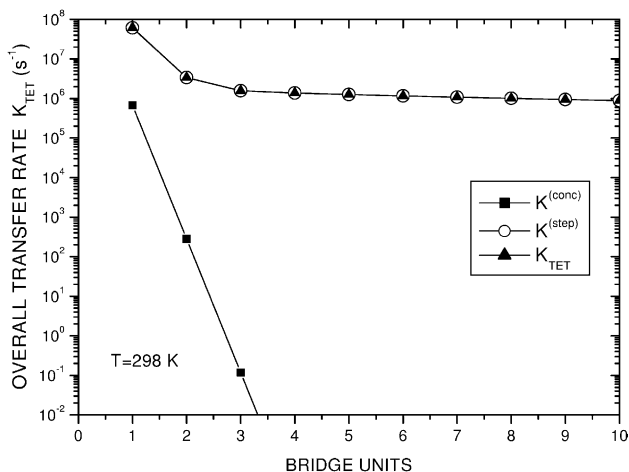
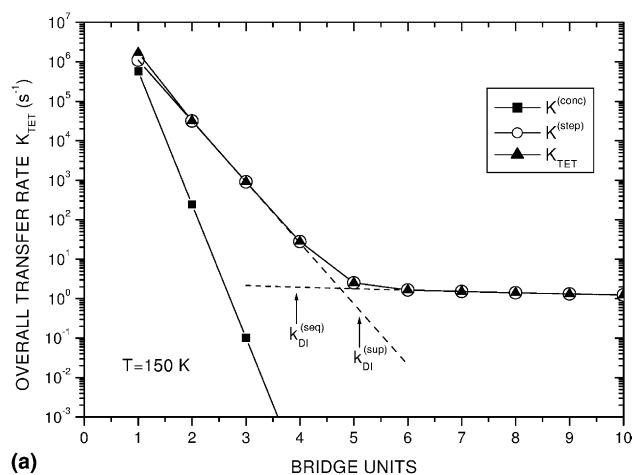
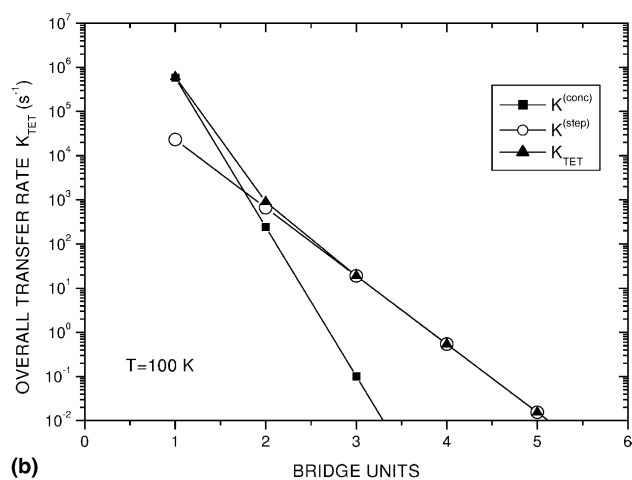


Fig. 4. Overall D–A TET rate of a DBA system with a regular bridge and for conditions where the stepwise component exceeds the concerted one at any bridge length. The calculations are based on Eqs. (6)–(10), (13)–(17), (43)–(48) for the case of self-exchange TET reaction. The following parameters have been taken:  $\Delta E_{\text{D}} = \Delta E_{\text{A}} = \Delta \bar{E}_{\text{D}} = \Delta \bar{E}_{\text{A}} = 0.35$  eV,  $\Delta E_{\text{I}} = \Delta \bar{E}_{\text{I}} = 0.25$  eV,  $\Delta E = 0$ ,  $\lambda_{\text{ID}} = \lambda_{\text{NI}} = \lambda_{\text{DI}} = \lambda_{\text{I1}} = \lambda_{\text{NA}} = \lambda_{\text{IA}} = 0.6$  eV,  $\lambda_{\text{DA}} = 0.8$  eV,  $\lambda_{\text{mm}\pm 1} \equiv \lambda_{\text{B}} = 0.3$  eV;  $\omega_{\text{MN}} = \omega_0 = 800$   $\text{cm}^{-1}$ ;  $V_{\text{D1}} = V_{\text{NA}} = V'_{\text{D1}} = V'_{\text{NA}} = 0.02$  eV,  $V_{\text{B}} = 0.04$  eV.



(a)



(b)

Fig. 5. Overall D–A TET rate of a DBA system as in Fig. 4 but for a lower temperature. The stepwise component of the overall transfer rate is caused by a single-electron sequential as well as a single-electron superexchange mechanism (panel (a)). If temperature is decreased the superexchange part in the stepwise transfer rate dominates the sequential part. Besides, in the case of a short bridge ( $N = 1, 2$ ) the concerted mechanism originated by a two-electron superexchange process between the D and the A, strongly contributes to the common rate  $K_{\text{TET}}$  (panel (b)).

with Eqs. (14) and (15) one gets  $k_{\text{f}}^{(\text{step})} \approx K_{\text{D1}}^{(\text{seq})} + K_{\text{D1}}^{(\text{sup})}$ . Fig. 5(a) shows that at  $T = 150$  K just a single-electron superexchange component,  $K_{\text{D1}}^{(\text{sup})}$ , forms the stepwise D–A TET route when the number of units of a regular bridge does not exceed  $N = 4$ . At  $T = 100$  K, the same component dominates up to  $N = 6$  (cf. Fig. 5(b)). Note again that the stepwise transfer rate,  $k_{\text{f}}^{(\text{step})}$ , Eq. (14) is defined exclusively by single-electron transitions which are responsible for the formation of the superexchange and sequential component of the common transfer rate  $k_{\text{f}}^{(\text{step})}$ .

The rise of the concerted contribution with a decrease of temperature is caused by the specific origin of the concerted mechanism. It is based on the two-electron superexchange process between the D and the A when the intermediate state  $\text{D}^- \text{BA}^-$  acts as a virtual state like



the bridging states. Therefore, the concerted mechanism works even at zero temperature while the efficiency of the stepwise mechanism is strongly limited by the need for a thermal activation of the intermediate state.

Fig. 6 demonstrates the influence of an inter-site energetic bias as well as of the Coulomb interaction on the efficiency of low-temperature D–A TET. It is seen from a comparison of Figs. 6(a) and 5(b) that the efficiency of the D–A TET increases if an energetic bias  $\Delta$  is present within the bridge. We underline two peculiarities in the dependency of  $K_{\text{TET}}$  on  $N$ . There appears a slight deviation from the exponential law for the concerted as well as the stepwise components of the D–A TET rate. Moreover, a notable alteration of the single-electron superexchange decay constant can be observed. The first peculiarity can be explained by the weak dependence of the corresponding Franck–Condon factor on the bridge length. The second one is related to the driving forces of single-electron and two-electron reactions,  $\Delta E_{\text{ID}}$  and  $\Delta E_{\text{DA}}$ . Actually, as far as at a given set of parameters the stepwise component of the overall transfer rate is mainly defined by  $k_f^{(\text{step})} \approx K_{\text{DI}}^{(\text{sup})}$  one derives  $K^{(\text{step})} \approx \exp(-\Delta E_{\text{ID}}/k_{\text{B}}T)k_{\text{ID}}$ . Bearing in mind the fact that  $k_{\text{ID}} \sim |T_{\text{DI}}|^2$  while  $\Delta E_{\text{ID}}$  contains the term  $-(N-1)\Delta$  (cf. Eq. (36)) one concludes that  $K^{(\text{step})} \sim \exp\{[(\Delta/k_{\text{B}}T - \zeta_1)(N-1)] - \zeta_{\text{DI}}N(N-1)\}$ . Here,  $\zeta_1$  specifies a rate drop for the case of regular bridge (cf. Eq. (23)) while  $\zeta_{\text{DI}} \equiv (1/2)[(\Delta/\Delta E_1) - (\Delta/\Delta E)] > 0$  gives a correction to this drop. The estimations show that  $(\Delta/k_{\text{B}}T) \gg \zeta_{\text{DA}}N$ . Therefore,

$$K^{(\text{step})} \approx K_0^{(\text{step})} e^{-\zeta_1^{(\text{eff})}(N-1)}, \quad (49)$$

where the effective decay parameter reads  $\zeta_1^{(\text{eff})} = \zeta_1 - \Delta/k_{\text{B}}T$ . As far as  $\zeta_1^{(\text{eff})} < \zeta_1$  one observes a somewhat weaker decrease of  $K^{(\text{step})}$  compared to the case of a DBA system with a regular bridge. At the same time, following from the property  $\Delta E_{\text{D}} = \Delta E_{\text{A}} = \Delta \tilde{E}_{\text{D}} = \Delta \tilde{E}_{\text{A}}$  valid for a self-exchange D–A TET reaction (compare the schemes (a) and (b) of Fig. 3), one can see from Eq. (B.9) that  $\Theta(N) = 0$ , and thus the bridge energetic bias  $\Delta$  does not alternate the two-electron superexchange coupling  $T_{\text{DA}}$ , Eq. (40). Therefore, the bridge-length dependence follows from the expression

$$K^{(\text{conc})} \approx K_0^{(\text{conc})} e^{-\zeta(N-1)}, \quad (50)$$

which has the same form as that derived for a DBA system with a regular bridge.

A slightly different situation occurs if the Coulomb interaction between the centers of electron localization in the DBA system is included into the consideration. This interaction results in different energetic shifts of the DBA system (cf. Eqs. (A.13)–(A.15)), and thus creates an energetic irregularity of the bridge. A comparison of Fig. 6(b) with Fig. 5(b) leads to the conclusion that the

Coulomb interaction modifies the energy gaps in Eqs. (8)–(10). It results an alteration of the stepwise and concerted components of the overall D–A TET rate. In

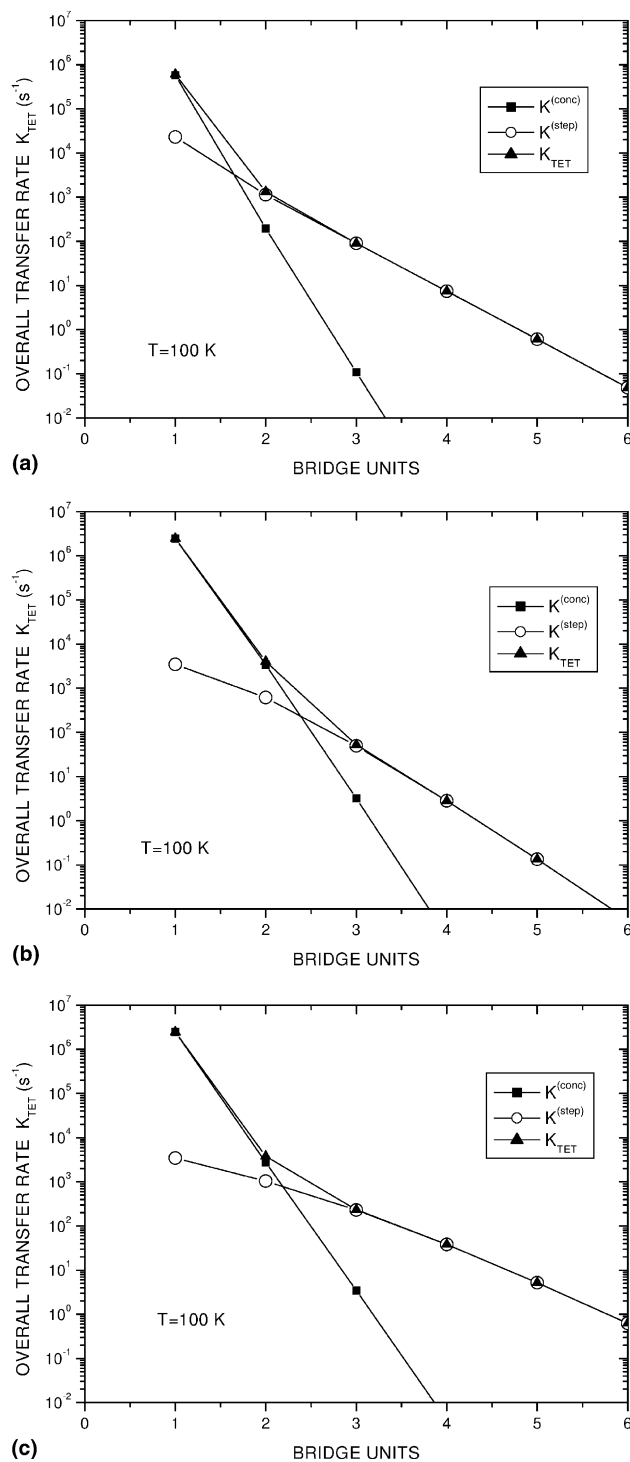


Fig. 6. Overall D–A TET rate of a DBA system with the regular arrangement of the bridge energies disturbed by an bridge-internal energetic bias (panel (a)), and by the presence of the Coulomb interaction between the centers of electron localization (panel (b)). The simultaneous presence of both mechanisms is considered in panel (c). The calculations have been done with the same parameters as in Fig. 4 except the temperature and the quantities  $\Delta = 0.01$  eV and  $Q = 0.07$  eV.

particular, the Coulomb interaction leads to a noticeable deviation of the stepwise component from the exponential law. At  $N \leq 2$  the rate  $K^{(\text{step})}$  remains smaller for an irregular bridge than for a regular. In contrast, at  $N > 2$  the rate becomes larger for an irregular bridge. This fact can directly be deduced from the expression

$$K^{(\text{step})} \approx \tilde{K}_0^{(\text{step})} e^{-\zeta_1(N-1)} e^{-\Theta_1(N)} \quad (51)$$

which is obtained from Eq. (39) with  $K^{(\text{step})} \approx \exp(-\Delta E_{\text{ID}}/k_{\text{B}}T)k_{\text{ID}}$ . Just the factor  $\Theta_1(N)$  given by Eq. (B.4) (for  $\Delta = 0$ ) mainly modifies the bridge-length behavior of  $K^{(\text{step})}$ . [The difference between  $\tilde{K}_0^{(\text{step})}$ , Eq. (51) and  $K_0^{(\text{step})}$ , Eq. (49) is caused by a different magnitude of the driving force  $\Delta E_{\text{DI}}$  at  $Q = 0$  and  $Q \neq 0$ .]

Next let us consider the concerted contribution to the total rate. It is given by Eq. (40) which can be written as

$$K^{(\text{conc})} \approx K_0^{(\text{conc})}(N) e^{-\zeta(N-1)} e^{-\Theta(N)}. \quad (52)$$

The dependence of  $K^{(\text{conc})}$  on  $N$  is mainly originated by the same factor  $\exp[-\zeta(N-1)]$  as in the case of a reg-

ular bridge. However, corrections to this  $N$ -dependence are due to the multiplier  $\exp[-\Theta(N)]$  with  $\Theta(N) = -(4Q/\Delta E_{\text{D}})[3\varphi(N) - 2N/(N+1)]$ . [Note that the Franck–Condon factor in  $K_0^{(\text{conc})}(N)$  related to superexchange transitions shows a negligible dependence on the bridge length.] Since  $\Theta(N) < 0$  for all  $N$  (remember the specificity of the bridge with  $N = 1$ ) we can conclude that the Coulomb interaction between the centers of electron localization facilitates the concerted component of overall D–A TET rate. Fig. 6(c) illustrates the combined influence of a bias as well as of the Coulomb interaction on  $K_{\text{TET}}$ . A comparison with Fig. 5(b) shows that this influence promotes the efficiency of D–A TET processes across longer bridges. Fig. 7 supports this conclusion for the case of a DBA system with a given number of bridge units ( $N = 3$ ). It shows that even a small increase of the energy bias  $\Delta$  (up to 0.01 eV) or the Coulomb interaction  $Q$  (up to 0.1 eV) can increase the overall transfer rate up to one order of magnitude compared to the case with  $\Delta = 0$  and  $Q = 0$ .

## 5. Conclusion

The general expression for an overall D–A TET rate  $K_{\text{TET}}$  (cf. Eqs. (13)–(17) and (19)) and as well as the simplified analytic forms for the superexchange couplings (Eqs. (8)–(10), (39) and (40)) and the sequential transfer rates (Eqs. (41) and (42)) have to be considered as the main results of this work. The derived formulas allowed us to understand the stepwise and the concerted mechanisms of the TET between the D and the A interconnected by a bridge  $B \equiv B_1 B_2 \dots B_N$  which may have a regular or an irregular energetic structure. It has been shown that the origin of the stepwise mechanism is the two-step single-electron transition between the donor state |D) and the intermediate state |I) (the first transfer step which is characterized by the rates  $K_{\text{DI}}$  and  $K_{\text{ID}}$ ), and between the intermediate state |I) and the acceptor state |A) (the second transfer step which is characterized by the rates  $K_{\text{IA}}$  and  $K_{\text{AI}}$ ). The first and the second step are mediated by the set of bridging states  $|B_m\rangle$  and  $|\bar{B}_m\rangle$ , respectively. During each step a single electron is not only transferred along the sequential pathway (multistep single-electron hopping between the neighboring sites). Rather the superexchange pathway (unistep single-electron hopping between the D and the A centers) is used as well.

Additionally, the common two-electron stepwise route could be identified as a thermally activated electron-transfer reaction via the intermediate state  $I \equiv D^-BA^-$  (cf. scheme (b) in Fig. 2). In contrast, the same state  $D^-BA^-$  appears as a virtual state for the concerted D–A TET. Hence, the concerted route is associated with the two-electron superexchange unistep

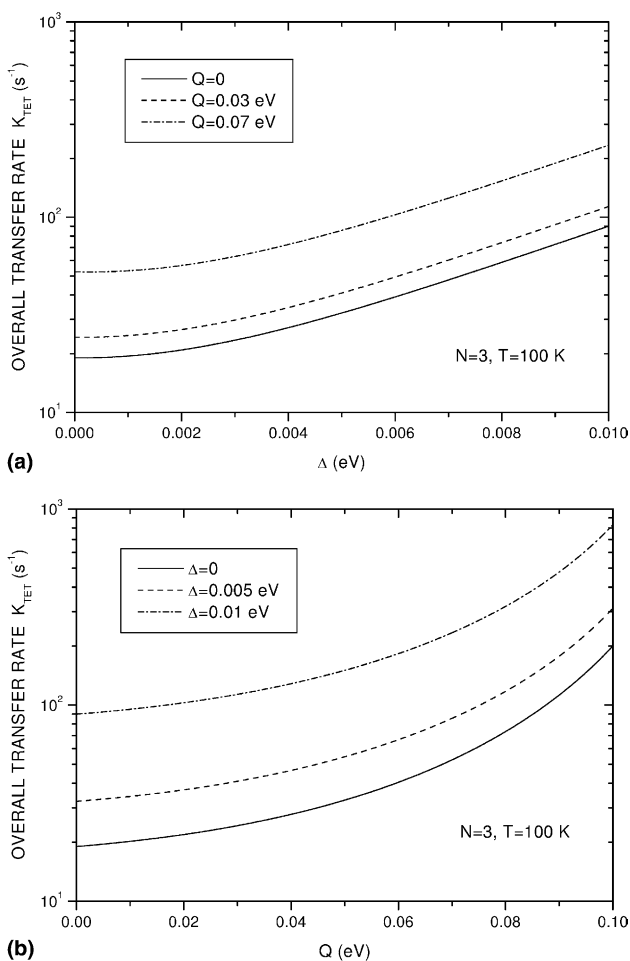


Fig. 7. Enhancement of D–A TET transfer caused by an energetic bias (panel (a)) and by the Coulomb interaction (panel (b)). The calculations have been done with the same parameters as in Fig. 4 except the temperature and the quantities  $\Delta$  and  $Q$ .

hopping between the states  $D^-BA$  and  $DBA^-$ . Such a D–A TET can take place even at  $T = 0$  K.

The derived analytical expressions for  $K_{TET}$  are quite appropriate to analyze the influence of the bridge energetic bias on the D–A TET and the effect of the Coulomb interaction between different sites which can be occupied by the transferred electrons (i.e. between the sites D, A and  $B_1, B_2, \dots, B_N$ ). Both effects may modify the identical energies of a regular bridge. The resulting irregularity can either facilitate or complicate the D–A TET depending on the strength of the perturbation and the number of bridge units.

In the present work main attention has been focused on the analysis of those D–A TET processes for which the stepwise route is determined by single-electron superexchange hopping transitions. This decision has been caused by the necessity to compare the efficiency of the stepwise and the concerted route at conditions where the routes are defined by single-electron and two-electron superexchange hopping transitions. Although the two-electron superexchange process decreases with the bridge length much stronger than the single-electron process, it could be shown that the concerted mechanism may exceed the stepwise one for a very short bridge ( $N = 1, 2$ , cf. Figs. 6(b) and (c)). This becomes possible if the energy bias and/or the Coulomb interaction perturb the regular arrangement of the site energies in the bridge. Such a result indicates the need to account for both mentioned effects when considering distant TET in molecular structures.

Finally, we point to another factor which may influence the D–A TET. In biological systems the rate of a TET process essentially depends on the pH-value of the surrounding solvent. [For instance, it has been found that just the concerted mechanism of a D–A TET can be responsible for the pH-dependence of a two-electron reduction in microthionine reductase [24.] And, it is well known from the classical studies by Marcus [37] and others [38–41] that the reorganization energy essentially determines the efficiency of the SET in solvents (see also more recent results [1,4,5,8,42]). Therefore, TET reactions in polar solvents are very specific and where the polarizability of the solvent may strongly influence the TET process [25,43]. Moreover, TET in polar solvents may proceed across more than one intermediate state so that a more complex concerted mechanism as discussed here can be formed in the course of TET [35]. We consider all this as a main challenge for further studies.

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## Appendix A. Energy level scheme for an irregular DBA system

If an energetic bias  $\Delta$  is present between neighboring units of an otherwise regular bridge the energies of the bridge states become  $E_m = E_B + \epsilon_m^{(bias)}$  and  $\tilde{E}_n = \tilde{E}_B + \tilde{\epsilon}_n^{(bias)}$  ( $m, n = 1, 2, \dots, N$ ) while  $E_D = E_D^{(0)}$ ,  $E_A = E_A^{(0)} + \epsilon_A^{(bias)}$  and  $E_I = E_I^{(0)} + \epsilon_I^{(bias)}$ . The various energetic shifts read in detail (see also [23])

$$\epsilon_D^{(bias)} = 0, \quad \epsilon_A^{(bias)} = -2(N-1)\Delta, \quad (A.1)$$

$$\epsilon_I^{(bias)} = -(N-1)\Delta, \quad \epsilon_m^{(bias)} = -(m-1)\Delta, \quad (A.2)$$

$$\tilde{\epsilon}_n^{(bias)} = -(N-1)\Delta - (n-1)\Delta. \quad (A.3)$$

In order to specify the energetic shifts caused by the Coulomb interaction between the sites  $X$  and  $Y$  of electron localization we employ the following semi-phenomenological model. We assume that already in the absence of the two excess electrons each site  $X$  is characterized by an effective charge  $q(X)$ . Hence, the inter-site Coulomb interaction reads

$$V^{(Coul)}(XY) = \frac{q(X)q(Y)}{4\pi\epsilon R_{XY}}. \quad (A.4)$$

Here,  $\epsilon$  is the medium permittivity and  $R_{XY}$  is the distance between the sites  $X$  and  $Y$ . Replacing  $X$  and  $Y$  by D, A, and  $B_m$  we get the Coulombic interaction energy of the DBA system at the absence of excess electrons. If the latter are introduced into the system the charge of the sites changes if occupied by a single excess electron or by both. In the first case, we replace  $X$  and  $Y$  in Eq. (A.4) by  $D^-$ ,  $A^-$ , and  $B_m^-$ . If a double population of the D or the A is present we have to introduce the notation  $D^{--}$ ,  $A^{--}$  into Eq. (A.4). Accordingly, we may calculate the related energetic shift  $\epsilon_M^{(Coul)}$  of the electronic state  $|M\rangle$ . As an example we consider the change of the energy  $E_D$ :

$$\begin{aligned} \epsilon_D^{(Coul)} = & \frac{q(D^{--})q(A)}{4\pi\epsilon R_{DA}} + \frac{q(D^{--})q(B)}{4\pi\epsilon} \sum_{m=1}^N \frac{1}{R_{Dm}} \\ & + \frac{q(A)q(B)}{4\pi\epsilon} \sum_{m=1}^N \frac{1}{R_{Am}} + \frac{q(B)^2}{4\pi\epsilon} \sum_{m=1}^N \sum_{n<m} \frac{1}{R_{mn}}. \end{aligned} \quad (A.5)$$

The expression implies a bridge with identical units where  $q(B) \equiv q(B_1) = q(B_2) = \dots = q(B_N)$ . In line with the scheme of Fig. 1 we obtain the distances between the redox-centers as

$$\begin{aligned} R_{DA} &= l_D + a(N-1) + l_A, & R_{Dm} &= l_D + a(m-1), \\ R_{Am} &= l_A + a(N-m), & R_{mn} &= a(|m-n|). \end{aligned} \quad (\text{A.6})$$

These relations indicate that Eq. (A.5) depends in a rather complicated manner on the number of bridge units. An essential simplification, however, appears for a DBA systems with a neutral bridge ( $q(\mathbf{B}) \approx 0$ ). Accordingly, only the first term in Eq. (A.5) remains. In what follows we assume  $q(\mathbf{B}) = 0$  and obtain

$$\epsilon_{\mathbf{D}}^{(\text{Coul})} = \frac{q(\mathbf{D}^-)q(\mathbf{A})}{4\pi\epsilon R_{DA}}, \quad (\text{A.7})$$

$$\epsilon_{\mathbf{I}}^{(\text{Coul})} = \frac{q(\mathbf{D}^-)q(\mathbf{A}^-)}{4\pi\epsilon R_{DA}}, \quad (\text{A.8})$$

$$\epsilon_{\mathbf{A}}^{(\text{Coul})} = \frac{q(\mathbf{D})q(\mathbf{A}^-)}{4\pi\epsilon R_{DA}}, \quad (\text{A.9})$$

$$\begin{aligned} \epsilon_m^{(\text{Coul})} &= \frac{q(\mathbf{D}^-)q(\mathbf{A})}{4\pi\epsilon R_{DA}} + \frac{q(\mathbf{D}^-)q(\mathbf{B}^-)}{4\pi\epsilon R_{Dm}} \\ &\quad + \frac{q(\mathbf{A})q(\mathbf{B}^-)}{4\pi\epsilon R_{Am}}, \end{aligned} \quad (\text{A.10})$$

$$\begin{aligned} \tilde{\epsilon}_n^{(\text{Coul})} &= \frac{q(\mathbf{D})q(\mathbf{A}^-)}{4\pi\epsilon R_{DA}} + \frac{q(\mathbf{D})q(\mathbf{B}^-)}{4\pi\epsilon R_{Dn}} \\ &\quad + \frac{q(\mathbf{A}^-)q(\mathbf{B}^-)}{4\pi\epsilon R_{An}}. \end{aligned} \quad (\text{A.11})$$

If the presence of two electrons at the D or at the A transform both centers into neutral states one has to put  $q(\mathbf{D}^-) \approx q(\mathbf{A}^-) = 0$ . Below we present the energetic shifts for this case by additionally assuming  $q(\mathbf{D}^-) \approx q(\mathbf{A}^-) \equiv q_1 > 0$ , and thus  $q(\mathbf{D}) \approx q(\mathbf{A}) \equiv q_2 > q_1 > 0$ . Noting that  $q(\mathbf{B}_m^-) \equiv q_B < 0$  and introducing the quantities

$$U_{DA}^{(1(2))} = \frac{q_1 q_{1(2)}}{4\pi\epsilon a}, \quad U_B^{(1(2))} = \frac{|q_B| q_{1(2)}}{4\pi\epsilon a}, \quad (\text{A.12})$$

one obtains

$$\epsilon_{\mathbf{D}}^{(\text{Coul})} = 0, \quad \epsilon_{\mathbf{A}}^{(\text{Coul})} = 0, \quad \epsilon_{\mathbf{I}}^{(\text{Coul})} = U_{DA}^{(1)}/r_{DA}, \quad (\text{A.13})$$

$$\epsilon_m^{(\text{Coul})} = U_{DA}^{(2)}/r_{DA} - U_B^{(1)}/r_{Dm} - U_B^{(2)}/r_{Am}, \quad (\text{A.14})$$

$$\tilde{\epsilon}_n^{(\text{Coul})} = U_{DA}^{(1)}/r_{DA} - U_B^{(2)}/r_{Dn} - U_B^{(1)}/r_{An}. \quad (\text{A.15})$$

Here, we have introduced the dimensionless distances  $r_{DA} \equiv R_{DA}/a$ ,  $r_{Dm} \equiv R_{Dm}/a$ , and  $r_{An} \equiv R_{An}/a$ .

## Appendix B. Corrections for the superexchange matrix elements

To derive analytic expressions for the matrix elements we start from Eqs. (8)–(10) supplemented by Eq. (3) and consider the product  $\prod_{m=1}^N \Delta E_{mD}$ . According to the identity

$$\begin{aligned} \prod_{m=1}^N \Delta E_{mD} &= (\Delta E_D)^N \prod_{m=1}^N [1 + (\Delta\epsilon_{mD}/\Delta E_D)] \\ &= (\Delta E_D)^N \exp \left\{ \sum_{m=1}^N \ln[1 + (\Delta\epsilon_{mD}/\Delta E_D)] \right\} \end{aligned} \quad (\text{B.1})$$

and by noting the condition  $|\Delta\epsilon_{mD}| \ll \Delta E_D$ , one can expand  $\ln[1 + (\Delta\epsilon_{mD}/\Delta E_D)]$  with respect to  $(\Delta\epsilon_{mD}/\Delta E_D)$ . The lowest order contribution gives

$$\prod_{m=1}^N \Delta E_{mD} = (\Delta E_D)^N \exp \left\{ \sum_{m=1}^N (\Delta\epsilon_{mD}/\Delta E_D) \right\}. \quad (\text{B.2})$$

In the same way one can specify the approximate form of the product  $\prod_{m=1}^N \Delta E_{mI}$ . Therefore, in accordance with Eq. (8) one derives

$$|T_{DI}|^2 \approx |T_{DI}^{(\text{reg})}(N)|^2 e^{-\Theta_1(N)}. \quad (\text{B.3})$$

To determine factor  $\Theta_1(N) = \sum_{m=1}^N [(\Delta\epsilon_{mD}/\Delta E_D) + (\Delta\epsilon_{mI}/\Delta E_I)]$  one has to use Eqs. (29), (30) and (34). As an example, we consider a DBA system where  $l_D = a = l_A$  (cf. Fig. 1) and  $q_2 = 2q_1 > 0$ ,  $q_B = -q_1$ . Then, one obtains (cf. Eq. (A.12))  $U_{DA}^{(2)} = 2U_{DA}^{(1)} \equiv 2Q$  and  $U_B^{(2)} = U_B^{(1)} = 2Q$  ( $Q \equiv q_1^2/4\pi\epsilon a$ ). Therefore,

$$\begin{aligned} \Theta_1(N) &= \left( \frac{2Q}{\Delta E_D} + \frac{Q}{\Delta E_I} \right) \frac{N}{N+1} - 3 \left( \frac{Q}{\Delta E_D} + \frac{Q}{\Delta E_I} \right) \\ &\quad \times \varphi_1(N) + \left( \frac{\Delta}{\Delta E_I} - \frac{\Delta}{\Delta E_D} \right) \varphi_2(N), \end{aligned} \quad (\text{B.4})$$

where the distance dependence is contained in the function ( $C \approx 0.577$  is Euler's constant)

$$\begin{aligned} \varphi_1(N) &= \sum_{m=1}^N \frac{1}{m} = \sum_{m=1}^N \frac{1}{N-m+1} \\ &\approx C + \ln N + \frac{1}{2N} - \frac{1}{12N(N-1)} + \dots, \end{aligned} \quad (\text{B.5})$$

and in the function

$$\begin{aligned} \varphi_2(N) &= \sum_{m=1}^N (m-1) = \sum_{m=1}^N (N-m) \\ &= \frac{1}{2}N(N-1). \end{aligned} \quad (\text{B.6})$$

Analogously one obtains

$$|T_{IA}|^2 \approx |T_{IA}^{(\text{reg})}(N)|^2 e^{-\Theta_2(N)}, \quad (\text{B.7})$$

with an expression for  $\Theta_2(N)$  which follows from Eq. (B.4) after replacing  $\Delta E_D$  and  $\Delta E_I$  by  $\Delta \tilde{E}_A$  and  $\Delta \tilde{E}_I$ , respectively. The same way allows to transform Eq. (10) into

$$|T_{DA}|^2 \approx |T_{DA}^{(\text{reg})}(N)|^2 e^{-\Theta(N)} \quad (\text{B.8})$$

with

$$\begin{aligned} \Theta(N) = & - \left( \frac{Q}{\Delta E_D} + \frac{Q}{\Delta E_A} + \frac{Q}{\Delta \tilde{E}_D} + \frac{Q}{\Delta \tilde{E}_A} \right) \\ & \times \left( 3\varphi_1(N) - 2\frac{N}{N+1} \right) \\ & + \left( \frac{\Delta}{\Delta E_A} - \frac{\Delta}{\Delta E_D} + \frac{\Delta}{\Delta \tilde{E}_A} - \frac{\Delta}{\Delta \tilde{E}_D} \right) \varphi_2(N) \\ & + \left( \frac{\Delta}{\Delta E_A} - \frac{\Delta}{\Delta \tilde{E}_D} \right) N(N-1). \end{aligned} \quad (\text{B.9})$$

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