Few-electron transfer reactions in donor−acceptor complexes and molecular wires

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A unified description is presented for electron transfer reactions in molecular systems which proceed against the background of fast vibrational relaxation processes. By generalizing earlier treatments a common approach is developed which covers single- and two-electron transfer as well as processes with the participation of even more electrons. Different types of reactions are discussed taking place either in donor−bridge−acceptor complexes or molecular wires attached to nanolectrodes. In particular, it is underlined that measuring the dependence of the transfer rate or of the stationary current on the length of the molecular system may represent an efficient way to uncover the concrete mechanism of charge transfer.

1 Introduction

Although intensively studied during many decades, electron transfer (ET) reactions did not lose their importance for different branches of physics, chemistry, and biology. ET reactions are currently studied in complex biological systems, on a sub-picosecond time-scale, in artificial nanostructures, but also in more traditional systems given by donor−acceptor (DA) complexes of medium size dissolved in a polar or non-polar solvent. But in any case the aim of all these activities is to uncover the relation between the atomic structure and the observed details of the reaction. Of course, this requires a detailed theoretical analysis. A number of nice articles and textbooks documents the recent progress in this field (cf., for example, [1−4]).

The type of theoretical description strongly depends on the concrete nature of the ET. If it is of the ultrafast type proceeding on a 100 fs time-scale one has to simulate the whole electron-vibrational dynamics. If the ET is much slower than vibrational motion, relaxation, and IVR (intramolecular vibrational redistribution), every step of the charge transfer reaction takes place at the presence of an (instantaneously formed) vibrational equilibrium. For such a situation one may choose a description where only *thermal* distribution functions of the involved vibrational degrees of freedom (DOF) enter. In particular, these treatments cover the broad field of so-called *nonadiabatic* ET reactions.

The present paper gives a unified description of such ET reactions which proceed against the background of fast vibrational relaxation (where vibrational coherences do not influence the charge motion). It will be demonstrated that in such a case ET is well described by rate equations. We present a general way to derive such rate equations. They are valid for molecular donor−bridge−acceptor

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(DBA) systems as well as molecular wires attached to nanolectrodes and may describe single-electron transfer (SET), but also reactions with the participation of more electrons (like two-electron transfer, TET). Of course, the type of the electron distribution function as well as the expressions for the transition rates strongly depend on the concrete system to be studied.

The general ideas of the used theoretical approach are explained in the following section. In Sections 3 and 4 we shortly comment on the description of SET in molecular DA complexes and through molecular wires. Section 5 summarizes recent results on TET reactions.

2 Nonequilibrium quantum statistical description of few-electron transfer reactions

The consideration following hereafter unifies our different attempts undertaken in recent years to describe single-, two-, and few-electron transfer in DBA complexes and molecular wires [5–14]. Therefore, we will dwell upon the introduction of the model. The way to to obtain kinetic equations will also be explained in some detail.

2.1 The model

In order to achieve a unified description of electron motion through DBA complexes and molecular wires the approach has to be based on a sufficient general model. First its necessary to note that we will concentrate on the motion of *excess* electrons (holes). The exclusive motion of intrinsic electrons, for example, after an optical excitation, will be outside the scope of the following considerations. The overall Hamiltonian includes H_{mol}, which may represent either the bridge part in a DBA complex or the molecular wire attached to nanolectrodes. Furthermore, there is a coupling part to the D and A or the electrodes, denoted by H_{int}. The Hamiltonian for the D and the A part or for the metal electrodes is given by H_{sd}. The notation takes into account that those part of the whole system described by H_{sd} acts as a source or drain for electrons moving through the molecular bridge. Accordingly, we obtain the complete system Hamiltonian as

$$H = H_{mol} + H_{int} + H_{sd} \,. \tag{1}$$

The given separation of the Hamiltonian is particularly suitable if the Hamiltonian H_{int} describing the coupling to the part introduced as electron "source" and "drain" can be handled within perturbation theory.

Next we specify H_{mol} in somewhat more detail. The most direct way would be the consideration of the presence of N excess electrons ($N = 1, 2, \ldots$) in the system and the subsequent calculation of the related states $\phi_{a(N)}$ which can be considered as adiabatic (delocalized states). They comprize the ground-state of the system of N excess electrons and some excited states. Then, H_{mol} can be decomposed into the separate Hamiltonians

$$H_{mol}^{(N)} = \sum_{a(N)} H_{a(N)}(q) |\phi_{a(N)}\rangle \langle\phi_{a(N)}| \,, \tag{2}$$

valid for the concrete number N of excess electrons (cf. Fig. 1). The $H_{a(N)}(q)$ are vibrational Hamiltonians referring to the respective electronic states. This notation seems simple but it represents a formidable task to determine the states $\phi_{a(N)}$ and the related potential energy surfaces (PES) entering the $H_{a(N)}$ for a concrete molecular system.

If the part of the system given by Eq. (2) can be characterized by molecular units coupled one to another only weakly, it is more appropriate to chose a description based on states where the excess electrons are localized at the different units. This can be achieved by a so-called diabatization of the original adiabatic states $\phi_{a(N)}$, leading to different N-electron configurations. If only a single excess electron is present the possible configurations are given by the states φ_m with the electron at site (molecular unit) m (higher excited states of localized charges will be disregarded). Two excess elec-
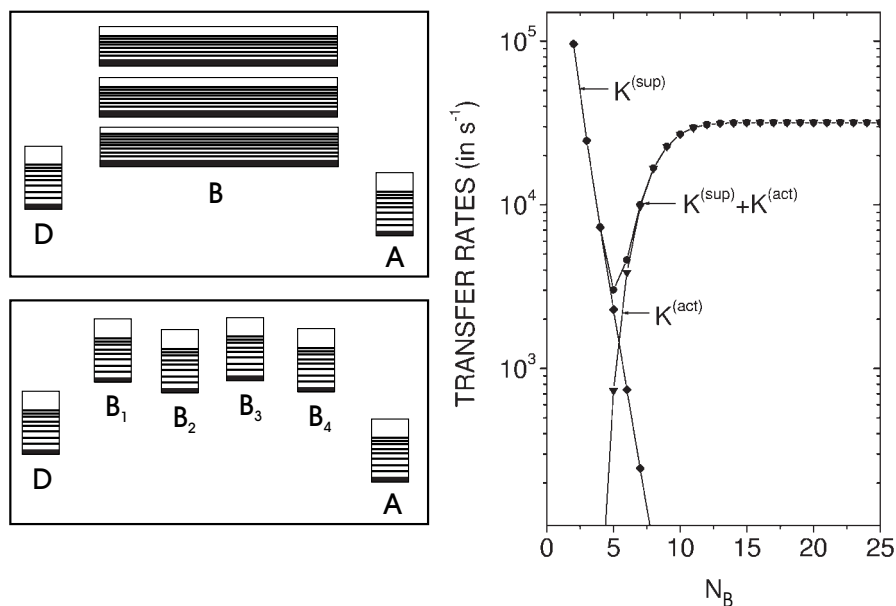
Fig. 1 Single electron transfer in a DBA complex with extended bridge states. Left panel: scheme of electron transfer in a linear DBA system with extended bridge states (upper part, shown are only three levels) and localized bridge state (lower part, every electronic level has been supplemented by the manifold of vibrational levels). Right panel: overall D–A ET rate, Eq. (18) versus the number N_B of bridge units. The rate follows as the sum of the superexchange rate $K^{(sup)}$ and the thermally activated rate $K^{(act)}$ (for details see [7]).

trons result in the states $\varphi_{m,n}$ with a single electron at site m and a single electron at site n. But states $\tilde{\varphi}_m$ with two electrons at site m are also possible. In a similar way one can classify the configurations of three excess electrons. Since the PES referring to all the localized N-electron states are the result of a diabatization they account for the Coulombic interaction energy among the excess electron states. However, as a residual effect of the Coulomb interaction we obtain the transfer coupling which connects all configurations of a given number of excess electrons. The version of the molecular Hamiltonian valid for the presence of a single excess electron reads (see also Fig. 1)

$$H_{mol}^{(1)} = \sum_{m,n} \left(\delta_{m,n} H_m(q) + (1 - \delta_{m,n}) V_{mn}(q)\right) |\varphi_m\rangle \langle\varphi_n|. \tag{3}$$

Every (diabatic) electronic state is characterized by a vibrational Hamiltonian $H_m(q)$ and is coupled to other states by the (single-electron) transfer integral $V_{mn}(q)$.

In order to specify the coupling Hamiltonian H_{int} we may proceed in a way similar to the aforementioned separation of H_{mol} into states with localized electrons. Concentrating on single electron jumps we get

$$H_{int} = \sum_{X,\mathcal{N},N} \sum_{\kappa(\mathcal{N}\pm 1)a(N\mp 1)} \sum_{\lambda(\mathcal{N})b(N)} V_X(\kappa(\mathcal{N} \mp 1)a(N \pm 1), b(N)\lambda(\mathcal{N}))$$
$$\times |\psi_{X\kappa(\mathcal{N}\mp 1)}\phi_{a(N\pm 1)}\rangle \langle\phi_{b(N)}\psi_{X\lambda(\mathcal{N})}|. \tag{4}$$

This formula needs some comments. It is obvious that it describes a transition from the molecular state $\phi_{b(N)}$ with N excess electrons to the state $\phi_{a(N\pm 1)}$ with $N \pm 1$ excess electrons. This change of the number of excess electrons results from the coupling to the additional units labeled by X. Those units might be the D or A in a DBA complex or the left (L) or right (R) electrode in a linear arrangement of two electrodes and a molecular wire.

If a DBA complex is considered the $\psi_{X\lambda(\mathcal{N})}$ and $\psi_{X\kappa(\mathcal{N}\mp 1)}$ in Eq. (4) represent states of the D or A with $\mathcal{N}$ or $\mathcal{N} \mp 1$ excess electrons. Here, it is also common to introduce a state for the whole DBA system valid for $\mathcal{N}_D$ excess electrons at the D, N excess electrons in the molecule, and $\mathcal{N}_A$ excess electrons at the A. For the case of the coupling to nanolectrodes the states ψ introduced in Eq. (4) describe the Fermi sea of metal electrons in the left as well as in the right electrode (with $\mathcal{N}_X$ or $\mathcal{N}_X \mp 1$ electrons). If a grand-canonical description is taken for the electrodes (with chemical potentials) it is also useful to denote the states as

$$|\psi_{X\lambda(\mathcal{N})}\rangle = \prod_{\mathbf{k},s} a^+_{X\mathbf{k}s} |0_X\rangle \,, \tag{5}$$

with the standard creation operators $a^+_{X\mathbf{k}s}$ of metal electrons with spin s, wavevector $\mathbf{k}$ positioned in electrode X (the whole set of s and $\mathbf{k}$ referring to the $\mathcal{N}$ electrons has been abbreviated by λ).

From all what has been discussed so far the general notation of H_{sd} is obvious. In the case of a D or an A it reads similar to that given in Eq. (2) with PES U_D and U_A included in the vibrational Hamiltonians $H_{a(N)}$ ($a =$ D, A). Specifying H_{sd} to the case of electrodes one can use the creation and annihilation operators for noninteracting electrons of a metal (the inclusion of respective phonon DOF would be of less interest).

Based on the preceding discussion we introduce the many-electron expansion basis

$$|\alpha\rangle = |\phi_{a(N)}\rangle \times \prod_X |\psi_{X\lambda(\mathcal{N})}\rangle \,. \tag{6}$$

It will find an application in the subsequent section where the kinetics of multielectron transfer are considered.

2.2 Derivation of rate equations

The following considerations focus on a derivation of rate equations governing the time evolution of the many-electron distribution

$$P_\alpha(t) = \langle\alpha| \mathrm{tr}_{\mathrm{vib}}\{\hat{W}(t)\} |\alpha\rangle \,, \tag{7}$$

defined with respect to the states introduced in Eq. (6). Moreover, the expression for P_α includes the total nonequilibrium statistical operator $\hat{W}(t)$ of the electron-vibrational system under consideration. It is transformed into a reduced form by the trace $\mathrm{tr}_{\mathrm{vib}}\{\dots\}$ taken with respect to all vibrational DOF. $P_\alpha(t)$ is ready to describe multielectron transfer reactions in a DBA system or multielectron charge transmission through a molecular wire. In the latter case it is of main interest to compute the $I\!-\!V$ characteristics with the stationary current obtained from, e.g.

$$I = -e \frac{\partial}{\partial t} \sum_{\mathbf{k},s} P_{L\mathbf{k}s}(t) \,, \tag{8}$$

where $P_{L\mathbf{k}s}(t)$ is the single-electron population of the left electrode (following from P_α, Eq. (7) after an appropriate reduction).

As already underlined in the introductory part the computations concentrate on the case of nonadiabatic ET characterized by the inequality

$$\tau_{\mathrm{rel}} \ll \tau_{\mathrm{ET}} \,. \tag{9}$$

This relation states that the overall charge motion with time constant τ_{ET} is much slower than all processes of vibrational relaxation characterized by τ_{rel}. Accordingly, the ET takes place against the background of fast vibrational relaxation. In the Refs. [5–7, 9, 12–14] we used an approach which directly notices Eq. (9). This has been achieved by modeling vibrational relaxation via a coupling of the respective DOF to secondary vibrational DOF acting as a heat bath. Here, we will chose a descrip-

tion which accounts for Eq. (9) in a somewhat different way. We assume that vibrational equilibrium is separately defined for every many-electron state $|\alpha\rangle$ (by the canonical equilibrium statistical operators $\hat{R}_\alpha$). Such an approach is known from literature (see, e.g. [4, 8, 15−17]) but has been used so far only for a description of SET (with the only exception given by us in [11]). The whole method is based on the introduction of the following projection superoperator

$$\mathcal{P} \ldots = \sum_\alpha \hat{R}_\alpha \hat{\Pi}_\alpha \, \mathrm{tr} \left\{ \hat{\Pi}_\alpha \ldots \right\} . \tag{10}$$

It contains a trace expression with respect to the complete set of electron-vibrational states and the many-electron state projection operator $\hat{\Pi}_\alpha = |\alpha\rangle\langle\alpha|$. The projector immediately gives the many-electron state population, Eq. (7) as

$$P_\alpha(t) = \langle\alpha| \, \mathrm{tr}_{\mathrm{vib}} \left\{ \mathcal{P}\hat{W}(t) \right\} |\alpha\rangle . \tag{11}$$

As in many other cases it is also possible here to apply the standard scheme of projection operator technique (see, e.g. [4]). One first derives a Nakajima−Zwanzig identity for $\mathcal{P}\hat{W}(t)$. Then the rate equation is obtained in noting Eq. (11). We neglect memory effects and obtain

$$\frac{\partial}{\partial t} P_\alpha(t) = - \sum_\beta \left(k_{\alpha\to\beta} P_\alpha(t) - k_{\beta\to\alpha} P_\beta(t) \right) . \tag{12}$$

The related many-electron transition rates are rather cumbersome expressions

$$k_{\alpha\to\beta} = \mathrm{tr} \left\{ \hat{\Pi}_\beta \mathcal{T}(\omega=0) \hat{R}_\alpha \hat{\Pi}_\alpha \right\} , \tag{13}$$

however, their meaning is simple. They describe the transition from the initial many-electron state $|\alpha\rangle$ (represented in the trace expression by the statistical operator $\hat{R}_\alpha \hat{\Pi}_\alpha$) into the final many-electron state $|\beta\rangle$. The transition is induced by the (frequency dependent) transfer superoperator $\mathcal{T}(\omega)$. If expanded with respect to the coupling part H_{int} of the total Hamiltonian, Eq. (1) one obtains

$$\mathcal{T}(\omega) = -i\mathcal{L}_{\mathrm{int}} \sum_{j=0}^\infty \left\{ \mathcal{G}_0(\omega) \, \mathcal{L}_{\mathrm{int}} \right\}^{2j+1} . \tag{14}$$

Note $\mathcal{L}_{\mathrm{int}} \ldots = [H_{\mathrm{int}}/\hbar, \ldots]_-$ and the expression for the zero-order Green's superoperator:

$$\mathcal{G}_0(\omega) = -i \int_0^\infty \mathrm{d}t \, \mathrm{e}^{i\omega t} \left[\mathcal{U}_0(t) - \mathcal{P} \right] . \tag{15}$$

It contains the zero-order time evolution superoperator $\mathcal{U}_0(t) \ldots = U_0(t) \ldots U_0^+(t)$, where $U_0(t)$ is an ordinary time−evolution operator given by the zero-order Hamiltonian $H_{\mathrm{mol}} + H_{\mathrm{sd}}$. The combination of $\mathcal{U}_0$ with $\mathcal{P}$ avoids double-counting of lower-order vibrational correlation functions (for more details see [8, 16]).

To apply the general rate Eq. (12) to concrete reactions one, first, has to specify the many-electron states $|\alpha\rangle$ and $|\beta\rangle$ to those of the particular reaction scheme and, second, one has to compute the respective transition rates. This requires to decide up to which order the perturbational expansion in Eq. (14) has to be taken.

In the following sections the whole description will be specified to SET and TET reactions in DBA complexes and molecular wires. Of most interest will be studies focusing on the dependence of the ET rate (in the case of a DBA system) or the current (in the case of a molecular wire attached to a left and a right nanoelectrode) on the length of the bridging molecular system. Here, we will concentrate on the case where the levels of the bridging molecular system are positioned energetically far above the D and A level or the nanoelectrode Fermi energies. It will be underlined that for such a level configuration the whole ET is separately determined by an addend caused by sequential charge transfer and an addend caused by the superexchange mechanism.

3 Single electron transfer reactions in a donor–bridge–acceptor complex

In studying the transfer of a single electron from the D to the A in a DBA complex two limiting cases are possible: the description of the B by localized levels for the excess electron or the description by delocalized levels common to the whole B (cf. Fig. 1). This latter case will be studied first followed by that based on the use of localized B states. In any case we will assume a linear arrangement of the D, the B units, and the A, with N_B (identical) molecular units forming the B.

3.1 Bridge with delocalized states

To study SET through a B with orbitals delocalized over the whole B the respective Hamiltonian is given by the single electron version of Eq. (2). Furthermore, we assume a weak coupling of the B to the D and A, i.e. the respective interaction introduced in its general from in Eq. (4) can be handled within perturbation theory. Such a situation is typical for oligomers with delocalized orbitals bound at its terminal sites to molecules acting as a D and a A.

To achieve a uniform description of all states of the excess electron in the DBA complex the two-state formulation in Eq. (4) via $|\psi_{D\kappa(0)}\phi_{a(1)}\rangle \langle \phi_{b(0)}\psi_{D\lambda(1)}|$ (note $X = D$) is replaced by the more compact expression $|a\rangle\langle D|$ referring to the transfer of the electron from the D into the B level a. Similar couplings are found for the reverse process as well as the transition between the B and the A. Intra B transitions originated by nonadiabatic couplings are not taken into account explicitly (see below).

The processes described so far follow from Eq. (13) in the lowest order of perturbation theory with respect to H_{int}, Eq. (4). For example, we obtain

$$k_{D\to a} = \text{tr}\left\{\hat{\Pi}_a \mathcal{L}_{int} \mathcal{G}_0(\omega = 0)\mathcal{L}_{int}\hat{R}_D\hat{\Pi}_D\right\}, \tag{16}$$

what represents a standard nonadiabatic ET-rate [3, 4], here characterizing thermal activated ET from the D into a particular B level.

If a level scheme is considered where the bottom of the PES corresponding to the excess electron states in the bridge is 1 or 2 eV above the D and the A level a direct ET from the D to the A known as the superexchange process is of some importance. It corresponds to the fourth-order term of the transfer superoperator, Eq. (14) and the rate reads

$$k_{D\to A} = \text{tr}\left\{\hat{\Pi}_A \mathcal{L}_{int} \left\{\mathcal{G}_0(\omega = 0)\, \mathcal{L}_{int}\right\}^3 \hat{R}_D\hat{\Pi}_D\right\}. \tag{17}$$

Although there are a number of different contributions following from the various commutators the rate is dominated by a single type of expression (superexchange rate) for the aforementioned level configuration [4–8, 16]. It is characterized by electronic matrix elements, appearing during the evolution of the initial density operator $\hat{R}_D\hat{\Pi}_D$, which are exclusively off-diagonal.

As a result we obtain the single-electron version of the rate Eq. (12) for the single excess electron distributions P_D, P_a, and P_A with forward rates $k_{D\to a}$, $k_{a\to A}$ and $k_{D\to A}$ and the respective backward rates. Although intra-bridge transitions have been neglected so far we can introduce them into the description by assuming the fast formation of an equilibrium distribution within the B on the time-scale of the whole ET. As a result the B can be described by a single overall population P_B. Then, the related rate equations for the three quantities P_D, P_B and P_A can be solved analytically [5–7] and different regimes of ET can be discussed.

In the initially described level configuration with the B levels far above the D and the A level one obtains the inequality $k_{B\to D}, k_{B\to A} \gg k_{D\to B}, k_{A\to B}$, i.e. ET out of the B is much more efficient than ET into the B. A detailed inspection of the solution of the rate equation shows that the DBA ET can be described by a single overall transfer rate (note $P_{m=D,B,A} \approx (P_m(t = 0) - P_m(t = \infty)) \times \exp(-K_{ET}t) + P_m(t = \infty))$

$$K_{ET} = k_{D\to A} + \frac{k_{D\to B}k_{B\to A}}{k_{B\to D} + k_{B\to A}} + k_{A\to D} + \frac{k_{A\to B}k_{B\to D}}{k_{B\to D} + k_{B\to A}}. \tag{18}$$

The first two terms correspond to the forward rate and the third and the fourth term to the backward rate. Both types of contributions indicate that the forward (or backward) rate is given by two independent addend one following from the superexchange mechanism of ET and the other from the thermally activated ET. This is not an universal result but is strongly related to the mentioned off-resonant position of the B levels [7]. It goes along with a very small bridge population in the course of the ET ($\ll 10^{-2}$). For an illustration we refer to Fig. 1 and to Ref. [7].

3.2   Bridge with localized states

If the B can be decribed by localized states for the excess electron coupled one to another by small transfer integrals V_{mn}, Eq. (3) the ET can take place via hopping transitions betwen the D and the respective terminal unit of the B, among the B units ($1 \ldots N_B$), and between the terminal unit of the B and the A (see Fig. 1). Additionally a direct transfer between the D and the A initiated by the superexchange mechanism becomes possible. Respective rate equations can be drived from Eq. (3) in a similar way as described in the preceeding section with one major exception. Since the transfer integrals V_{mn} are small, perturbation theory becomes possible when considering the superexchange transfer. In order to do this the coupling term of Eq. (3) covering all V_{mn} is removed from H_{mol} and included into the SET version of H_{int}, Eq. (4). Then, the rate $k_{D \rightarrow A}$, Eq. (17) has to be generalized to an expression with the $2N_B - 1$'th power of $\mathcal{G}_0(\omega = 0)\mathcal{L}_{int}$ and with $\mathcal{L}_{int}$ exclusively defined by the intra-bridge transfer integrals and the D−B and B−A coupling [5, 6]. In this way one may derive the standard expression for the superexchange coupling (see, e.g. [3, 4]).

In Ref. [5, 6, 9, 10] the decribed approach has been used to explain the length dependence of SET through an oligopeptide formed by the aminoacid proline and measured in [18]. As shown in Fig. 2 there is a good agreement between theory and experiment. In particular, the length dependence indi-
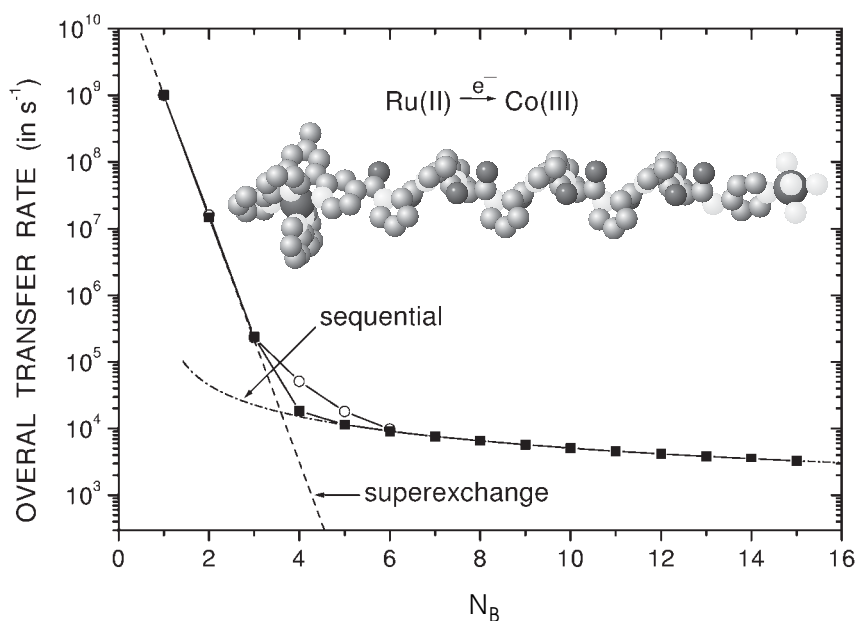
Fig. 2 Single electron transfer in a DBA complex with localized bridge states. The DBA complex is given by a ruthenium−oligoproline−cobalt complex ([(bpy)$_2$Ru(II)L $\cdot$ (Pro)$_n$Co(III)(NH$_3$)$_5$]$^{3+}$, see insert) studied in [18] (related measured data are given by open circles). Theoretical results (full squares) are obtained as described in Section 3.2 (for details of the computation see also [5, 6, 9, 10]). The curves give the rate in dependence on the number N_B of proline monomers in the polypeptide forming the bridge. The broken lines follow from a sole N_B-dependence of the superexchange and the sequential ET mechanism, respectively.

cates that the SET in the oligopeptide proceeds in a way where the bridge population remains small and the overall transfer rate is given by two independent addends, one corresponding to the sequential (hopping) ET and one to the superexchange ET. By the way, the absence of a dip like that in Fig. 1 offers strong evidence for an ET reaction which proceeds via localized and not delocalized B states. The importance of strutural and energetic disorder in the chain is underlined in the studies of Ref. [10]. An improved analytical solution of the rate equations can be found in Ref. [9]. Note that a similar picture has also been used to interpret charge motion through DNA fragments [19–22].

4 Single electron transmission through a molecular wire

When considering the case of a molecule or a molecular complex attached to nanolectrodes it has to be checked whether the electrode–molecule coupling is strong or weak. The first case is typical for a covalent bonding of the molecule to the electrode and leads to a renormalization and life-time broadening of the molecular levels (cf. [23, 24]). In the contrary case one can handle this coupling in perturbation theory [8, 11]. Such a description has been carried out in [8] for a arrangement of a left electrode, the wire and the right electrode (cf. Fig. 3) as well as for the case of strong wire-internal transfer coupling. Then, it is appropriate to introduce delocalized wire-states, and one can discuss the interplay of sequential transfer, for example from one electrode into the wire, and superexchange transfer from the left to the right electrode.

In Ref. [11] a situation has been discussed which has some similarities to that of the foregoing section. The DBA complex described there has been additionally attached with its D to a left electrode and its A to a right electrode. Instead of a rate expression, now, one has to compute the stationary current, Eq. (8) moving at a given applied voltage through the wire. This current can be drawn versus the applied voltage to give the $I-V$ characteristics, or one can draw the current at a given
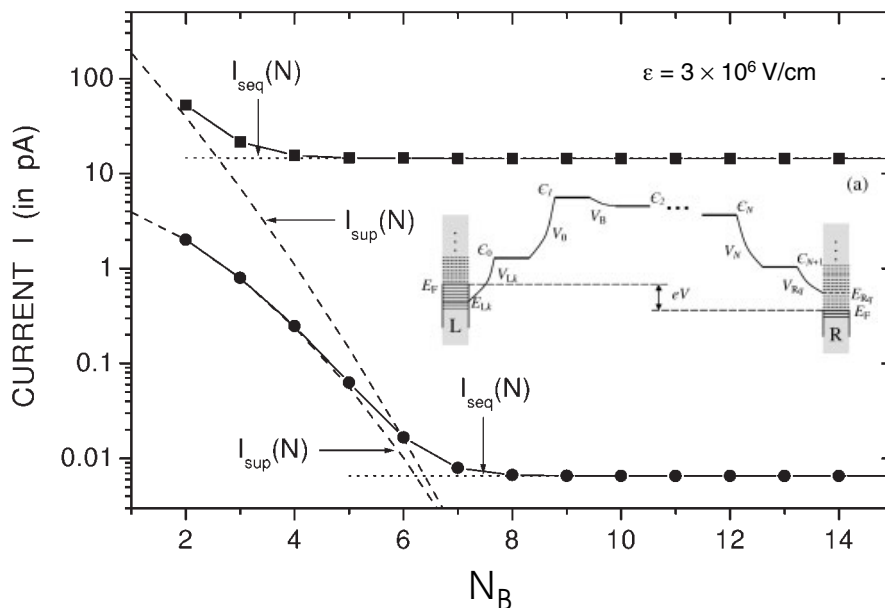
Fig. 3 Single electron transmission through a molecular wire described by weakly interacting localized states. Drawn is the stationary current through the wire in dependence on the number N_B of wire units and at fixed electric field strength ϵ (achievable by a certain increase of the applied voltage with an increase of N_B). The insert shows the left electrode–wire–right electrode arrangement together with the energetic position of all levels involved. Curve with quares: $T = 298$ K, curve with circles: $T = 180$ K. Broken lines correspond to a sole N_B–dependence of the part of the current originated by the superexchange (I_{sup}) or the sequential mechanism (I_{seq}) of charge transmission (for more details see [11]).

voltage versus the length of the wire. This has been done in Ref. [11]. It is a special feature of this approach to account for the many-electron character of the electrode states as given in Eq. (5). Then, the Fermi distribution of the left and the right electrode enter the respective transitions rates in the correct manner, for example, $k_{L \to D}$ representing the transition from the left electrode into the D. The obtained length dependence of the current is shown in Fig. 3.

5 Two-electron transfer reactions in a donor−bridge−acceptor complex

As an example for a TET reaction we will study in the following charge motion through a DBA system according to the scheme: $D^{--}BA \to D^-B^-A \to D^-BA^- \to DB^-A^- \to DBA^{--}$ (see Fig. 4). Two excess electrons initially localized at the D move via a molecular bridge to the A. The reaction scheme given in Fig. 4 excludes double population of the bridge with two excess electrons (doubly reduced B state). The neglect is reasonable for a rigid B and a rigid environment of the B which do not undergo a rearrangement if two excess charges are present (small reorganization energy). Then, the state $DB^{--}A$ is energetically unfavourable and can be removed from the reaction scheme [12–14].

Having exluded the electron configuration $DB^{--}A$ one can relate the respective electronic states to the different steps of the TET reaction which are characterized by state populations Eq. (11) and connected via transition rates, Eq. (12). After a proper computation of the related transition rates (for details see [12–14, 25, 26]) the dependence of the TET reaction on the bridge length can be calculated.

Assuming again high-lying B states the charge injection into the bridge appears to be much slower than the motion of the electron out of the B. A thermal equilibrium is established along the TET in the bridge with a small B population and the two parts $D^{--}BA \to D^-B^-A \to D^-BA^-$ and $D^-BA^- \to DB^-A^- \to DBA^{--}$ of the whole reaction can be described as the SET of Section 3.2. Here, sequential transfer of a single electron takes place as well as superexchange transitions, but
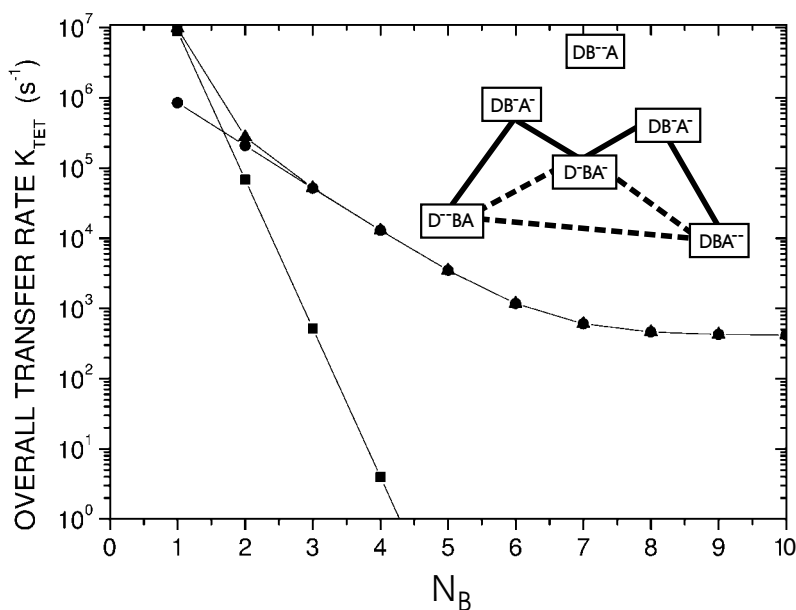
Fig. 4 Two-electron transfer in a DBA complex with localized bridge states. The insert displays the different electronic configurations together with the transfer routes (full lines indicate squential transfer and broken lines superexchange ET, the uppermost states with a doubly reduced bridge has been neglected). Drawn is the bridge-length dependence of the overall transfer rate (triangles) as well as the contributions following from the sequential transfer (circles) and the concerted two-electron superexchange transfer (squares, for more details see [14]).

described by overall rates of SET. We abbreviate the intermediate state corresponding to the electron configuration D^-BA^- by I, and get the SET rates $k_{D \to I}$ as well as $k_{I \to A}$ for the forward transitiona and $k_{I \to D}$ as well as $k_{A \to I}$ for the backward transition.

If the system parameters are of such a type that the population of the intermediate state I is also small the TET can be described by single exponential kinetics with the overall TET rate

$$K_{TET} = k_{D \to A} + \frac{k_{D \to I}k_{I \to A}}{k_{I \to D} + k_{I \to A}} + k_{A \to D} + \frac{k_{A \to I}k_{I \to D}}{k_{I \to D} + k_{I \to A}} \; . \tag{19}$$

The rate $k_{D \to A}$ describes *concerted* TET directly from the reactant states $D^{--}BA$ to the product state DBA^{--}. The second term follows from SET (which includes sequential and superexchange contributions). The third and the fourth term are the respective backward rates. A numerical illustration can be found in Fig. 4. The influence of bridge irregularities is studied in [25], and Ref. [26] generalizes the description to the case of TET through extended B states as discussed in Section 3.1 for SET reactions.

6 Conclusions

A unified theory of few-electron transfer reactions has been developed. The approach concentrates on the particular type of charge transfer proceeding against the background of fast vibrational relaxation. By considering rate equations for many-electron state populations we have been able to present a decription which covers all of our earlier theories of single and two-electron transfer in donor–bridge–acceptor complexes as well as molecular wires. The approach accounts for the many-electron states of nano-electrodes as well as for the Coulomb interaction among the states of some excess electrons in a molecular wire or in a donor–bridge–acceptor complex. But at the same time it is also capable to include the coupling to intra-molecular as well as environmental vibrations beyond any perturbation theory.

This unified theory has to be considered as the central and new result of the present paper. In order to demonstrate that the general approach comprices all earlier theories it becomes necessary to carry out a specificication to the concrete number of electrons involved in the reaction and to subsequently determine the related transition rates.

The new description of few-electron transfer reactions has the capability to adress various problems to be solved. Among them we mention two. For example, when dealing with few-electron transfer in molecular wires forthcoming investigations should study the interplay between inelastic charge transmission processes via electron-vibrational interaction and the strong coupling to the electrons of the electrode Fermi sea. Of general interest would be also the change of the charge motion by an optical excitation applied to some parts of a molecular wire or of a donor acceptor complex.

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