Electron Transfer

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Non-Exponential Distance Dependence of Bridge-Mediated Electronic Coupling**

*Mattias P. Eng and Bo Albinsson**

Long-range electron transfer (ET) and triplet-energy transfer (TET) are governed by the through-bond electronic coupling (V_{DA}). As this coupling is of the exchange type and is related to orbital overlap, it is generally believed to decay exponentially with distance [Eq. (1)].

$$V_{\mathrm{DA}} = V_0 \exp\left(-\frac{\beta}{2} R_{\mathrm{DA}}\right) \tag{1}$$

In Equation (1), R_{DA} is the donor–acceptor (D–A) separation, V_0 is the electronic coupling at contact distance, and β is an attenuation factor characteristic of the intervening medium. This simple expression has been used to analyze the distance dependence for electron and energy transfer in a vast number of donor–bridge–acceptor (DBA) systems for which characteristic β values have been suggested.[1–5] In addition, it is expected that the electronic coupling is proportional to the inverse of the energy gap between the relevant bridge and donor states [Eq. (2)].

$$V_{\mathrm{DA}} = \frac{V_{\mathrm{DB}} V_{\mathrm{BA}}}{\Delta} \left(\frac{v}{\Delta}\right)^{m-1} \tag{2}$$

This relation, first derived by McConnell,[6] gives the through-bond donor–acceptor interaction for a chain of m identical units with nearest neighbor interactions v and energy gaps Δ between the relevant donor and bridge localized states. For $v/\Delta \ll 1$, it can easily be shown that Equation (2) leads to exponential distance dependence. In DBA systems with π-conjugated bridges ("wires"), it is more difficult to dissect the bridge into well-defined chain elements and the validity of Equations (1) and (2) might be questioned. In general, experimental studies of the distance dependence of ET and TET are analyzed with Equation (1) and the estimated β values regarded as bridge-specific parameters. We will show in this communication that: 1) β is not a bridge-specific parameter for π-conjugated bridges; 2) Equation (1) is not valid in cases for which the energy of the bridge states vary strongly with bridge length, that is, the distance dependence of the exchange interaction might be non-exponential.

We have been interested for quite some time in understanding bridge-mediated electronic coupling. Carefully designed DBA systems with porphyrin donors and acceptors and with different bridging structures have been investigated experimentally. The metallation states of the porphyrins were varied to allow selective studies of ET, TET, and singlet-energy transfer, SET. In one set of systems with constant D–A separation, the donor–bridge energy-gap dependence was mapped out,[7] and in another set the distance dependence was investigated.[8–10] In parallel to the experimental studies, we have developed a DFT-based quantum-mechanical method to calculate the electronic coupling for ET, TET, and SET. In particular, the calculations for TET were shown to give excellent quantitative agreement with the experiments if an appropriate conformational-averaging procedure was employed.[8] Inspired by the success of the calculations, we have expanded our study to include other important π-conjugated bridges and to specifically investigate how the distance dependence for the TET electronic coupling varies with the donor–bridge energy gap for a set of oligo(phenyleneethenylene) (OPE) bridges.

The electronic coupling V_{DA} was deduced from the TD-B3LYP/6-31G(d)-calculated (Gaussian 03[11]) energy splitting of the two lowest triplet states of the symmetric donor–bridge–donor (DBD) molecules as described in the Supporting Information. Calculating the values of V_{DA} for OPE bridges with edge–edge separations of between 12 and 37 Å ($x = 2$–5) and linear fits of $\ln V_{\mathrm{DA}}$ versus R_{DA} yielded the β values. This was done for the seven different donors (Table 1), which have calculated lowest triplet energies of between 15450 cm^{-1} and 4660 cm^{-1}. The fits are excellent (Figure 1a) and the slopes vary systematically with the variation of the donor–bridge energy gap. This shows that β is sensitive to the appended donor and acceptor and, thus, is not a bridge-specific parameter. In fact, from the McConnell model the β values are expected to vary with the donor–bridge energy gap as described in Equation (3).

$$\beta = \frac{2}{R_0} \ln\left|\frac{\Delta}{v}\right| \tag{3}$$

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[*] M. P. Eng, Prof. B. Albinsson
Chalmers University of Technology
Department of Chemical and Biological Engineering
412 96 Göteborg (Sweden)
Fax: (+46) 317-723-858
E-mail: balb@chalmers.se

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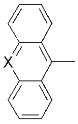
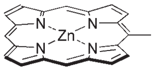
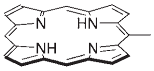
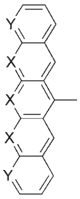
Table 1: Model systems for mapping out the donor–bridge energy gap dependence of β for the OPE bridge structure (see Table 2).

Donor		$E_D(T_1)$ [cm^{-1}]	β [Å^{-1}]
	Acr (X=N) A (X=CH)	15450 14520	0.10 0.18
	ZnPor	14340	0.19
	H_2Por	11720	0.32
	P5N (X=Y=N) P3N (X=N, Y=CH) P (X=Y=CH)	8770 6100 4660	0.39 0.43 0.47

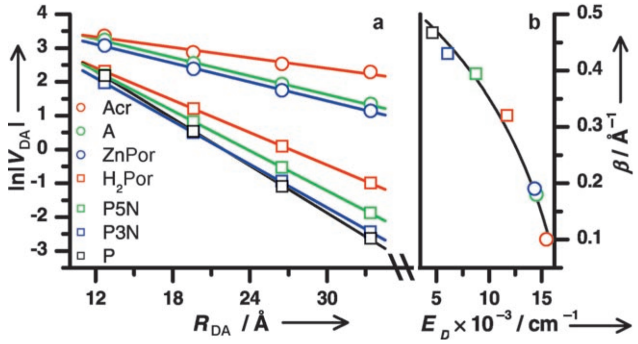


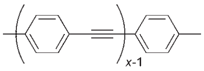
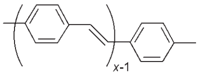
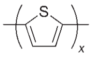
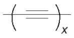
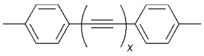
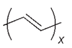
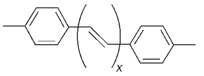
Figure 1. a) ln V_{DA} versus R_{DA} for the OPE bridges with acridine (Acr), anthracene (A), zinc(II) porphine (ZnPor), free-base porphine (H_2Por), 4,5,6,7,8-pentaazapentacene (P5N), 5,6,7-triazapentacene (P3N), and pentacene (P) as donor chromophores. b) The obtained β values plotted versus the calculated donor excitation energy (symbols) and the fit of Equation (3) to the data (solid line).

In Equation (3), $\Delta = E_{B'} - E_D$, $E_{B'}$ and R_0 are the (hypothetical) triplet energy and length of the repeating unit, respectively, and E_D is the triplet energy of the donor. Figure 1b shows this variation along with a best fit to Equation (3) to yield values for the bridge unit coupling, $v = 2944$ cm^{-1} and $E_{B'} = 19884$ cm^{-1}.[12] The coupling between the subunits of the OPE bridge is quite substantial as expected for a π-conjugated system, but the ratio $v/\Delta = 0.15$ is still small enough to give an exponential dependence on distance. It should be noted that the triplet energy of the bridge subunit extracted from the fit is significantly smaller than the triplet energy of phenyleneethynylene (26123 cm^{-1}), which demonstrates that estimating the effective energy gap in the superexchange model is quite difficult and, thus, use of Equation (3) for quantitative predictions might yield misleading results.

In another study, we calculated V_{DA} for the pentacene donor (P) with different bridging structures (see Supporting Information) Pentacene was chosen because it has the lowest triplet energy among the donors shown in Table 1 to allow for bridges that have low triplet energies.

In Table 2 the investigated bridges along with the resulting β values are listed, and the calculated electronic coupling is displayed in Figure 2. The approximate exponential dependence on distance found for the OPE bridge was also observed for the OTP and OPV bridges. However, for the bridges with non-aromatic repeating structures, OE, Ph-OE, OV, and Ph-OV, different behavior was observed. All these bridges show distinct non-exponential distance dependence; the electronic coupling increases with increasing distance in certain regions. Clearly, the data from these bridges cannot be analyzed with the McConnell superexchange model.

Table 2: Model systems for mapping out the variation of $|V_{DA}|$ with the bridge structure.[a,b]

Bridge		$E(T_1)$ range [cm^{-1}]	β [Å^{-1}]
	OPE	21600–16100	0.47
	OPV	18500–13000	0.42
	OTP	18700–11200	0.37
	OE	27200–7800	–[c]
	Ph-OE	21600–8700	–[c]
	OV	22400–5700	–[c]
	Ph-OV	18500–4900	–[c]

[a] Donor/Acceptor: Pentacene, $E(T_1) = 4660$ cm^{-1}. [b] OPE is oligo(phenyleneethenylene) (x=2–5), OPV is oligo(phenylenevinylene) (x=2–5), OTP is oligo(thiophene) (x=2–5), OE is oligo(ethylene) (x=2–11), Ph-OE is phenyl end capped oligo(ethylene) (x=1–8), OV is oligo(vinylene) (x=2–10), and Ph-OV is phenyl end capped oligo(vinylene) (x=1–10). [c] Non-exponential, see text.

As an alternative to the superexchange model, which dissects the bridge into subunits, the molecular bridges could be regarded as a single tunneling barrier of width R_{DA} and height ΔE. In contrast to the superexchange model, the variation of ΔE with R_{DA} has to be considered explicitly. For this simple model the electronic coupling is given by Equation (4).[13]

$$V_{DA} = \frac{\alpha}{\Delta E} \exp(-\rho\sqrt{\Delta E} R_{DA}) \qquad (4)$$

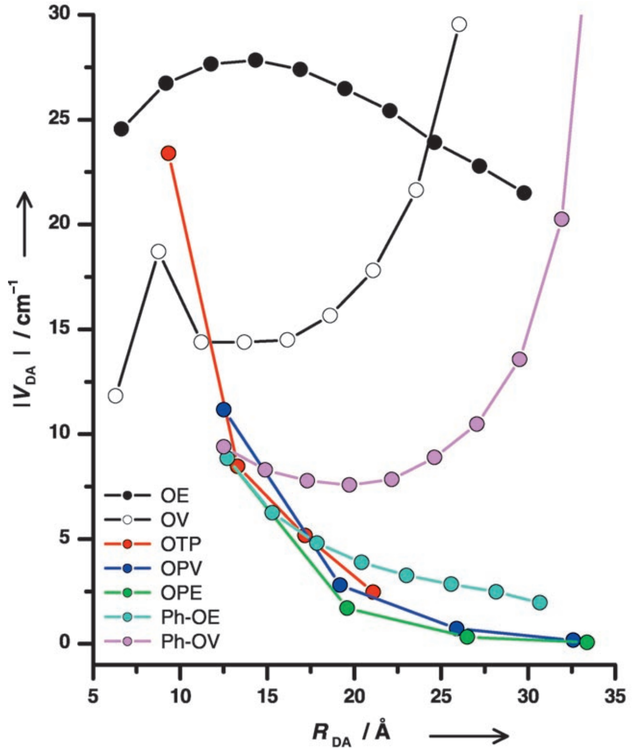


Figure 2. The calculated electronic coupling $|V_{DA}|$ versus R_{DA} for pentacene as donor chromophore with the various bridges. The electronic coupling for the OE-bridge has been multiplied by a factor of 0.15.

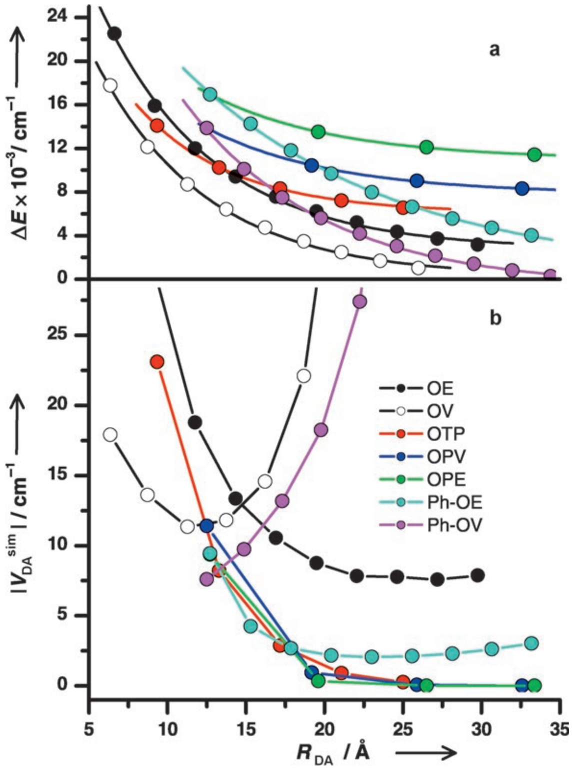


Figure 3. a) The calculated energy barrier for tunneling ΔE versus R_{DA} for various bridges with pentacene as donor chromophore and exponential fits to Equation S1 in the Supporting Information. b) The simulated electronic coupling $|V|_{DA}^{sim}$ derived by using Equation (4) and the calculated ΔE values; $\rho = 0.0057$ Å^{-1} cm$^{1/2}$ (two tunneling electrons).

In Equation (4), α is a system-specific parameter related to the donor–bridge coupling but not dependent on R_{DA}; ρ, at least in principle, is related to the effective mass of the virtual tunneling electron(s). Simulations show that Equation (4) can qualitatively describe the anomalous behavior of the OE, Ph-OE, OV, and Ph-OV bridges as well as the normal exponential behavior of the OPE, OPV, and OTP bridges (Figure 3). The distance dependence of the electronic coupling is easily accessible through Equation (4) once the distance dependence of the triplet excitation energy is known. In Figure 3a the calculated tunneling barriers, ΔE (estimated from the difference between the energies of the lowest triplet states of the bridges and pentacene), are shown together with exponential fits. The calculated energies agree almost quantitatively with the experimental energies in those cases for which the information is available (see Supporting Information). Figure 3b shows the distance dependence of the electronic coupling estimated from Equation (4) by using the calculated triplet energies and by assuming a common decay parameter, $\rho = 0.0057$ Å^{-1}cm$^{1/2}$, which corresponds to the mass of two (virtual) tunneling electrons. The simulated electronic coupling has an approximately exponential distance dependence for the OPE, OPV, and OTP bridges but shows more complex behavior for the other four bridges. This is qualitatively the same distance dependence as that observed in the quantum-mechanical calculations and below we present our reasoning for this unexpected agreement.

From Equation (4) a local β value can be analytically calculated for the tunneling model [Eq. (5)].

$$\beta^{\mathrm{loc}} = -2\frac{\mathrm{d}\ln V_{\mathrm{DA}}}{\mathrm{d}R} = 2\frac{\mathrm{d}\Delta E}{\mathrm{d}R}\left(\frac{1}{\Delta E}+\frac{\rho R}{2\sqrt{\Delta E}}\right)+2\rho\sqrt{\Delta E} \qquad (5)$$

The first term of this equation gives a negative contribution that tends to zero as R increases and the second term gives a positive contribution that tends to $2\rho\Delta E_{\infty}^{1/2}$, which is the limiting β value for a bridge long enough to show negligible variations in the energy gap. If the variation of the bridge energy is large (i.e., large $\mathrm{d}\Delta E/\mathrm{d}R$) the attenuation factor (β^{loc}) is negative. In regions where ΔE varies quickly with distance, the pre-exponential factor of Equation (4) causes the electronic coupling to increase over a limited R_{DA} range. This variation is qualitatively what has been observed for the OE, Ph-OV, and OV bridges and we conclude that in certain cases it is necessary to use a model, such as Equation (4), that allows for the interplay between the donor–bridge energy gap and donor–acceptor distance.

The simple tunneling model is not expected to give quantitative results but it is not possible to obtain correct results from the superexchange model either. In particular, for small values of ΔE the electronic coupling increases rapidly both in the tunneling model and in the quantum-mechanical calculations. This behavior is expected because at near degeneracy, the wavefunctions of the bridge and donor mix strongly and the identities of the different chromophores are lost. Experimentally, in such a situation ($\Delta E < 3000\ \text{cm}^{-1}$), a non-coherent hopping mechanism is difficult to avoid and the rate for ET or TET is no longer dictated by the direct transfer between the donor and acceptor but through a relay mechanism involving states populated at the bridge.[14] However, as can be seen in both Figure 2 and Figure 3, the anomalous distance dependence is also observed in situations for which the barrier exceeds 10000 cm^{-1} and we believe that the strong distance dependence of the excitation energies of the bridges is responsible for this effect.

In this study, we have calculated the bridge-mediated electronic coupling for TET, but the results are expected to be general for any exchange-type coupling. There are several reasons for calculating the TET couplings: 1) there are no or small solvent-reorganization energies, which for ET processes add additional distance dependence; 2) bridge and donor state energies are easily accessible; 3) there is very good correlation between the experimentally determined and calculated couplings for OPE-bridged porphyrin systems.[8]

Wasielewski and co-workers recently reported two cases for which anomalous distance dependence were experimentally observed.[14,15] Electron transfer mediated by OPV and fluorene oligomers showed a strongly non-exponential dependence on distance. However, both of these cases involve switching between a superexchange mechanism and a non-coherent hopping mechanism that uses bridge-localized states.[15] In contrast, for the systems studied in this paper (Table 2), the donor–bridge energy gap is too large to have significant contributions from a hopping mechanism, at least for the shorter members of the OE, OV, Ph-OE, and Ph-OV series. Thus, the reason for non-exponential distance dependence is different in this case.

Many experimental studies report very shallow distance dependencies for π-conjugated bridges[2,16] and also for ET in DNA.[17] In addition, the bridge-energy dependence of the β values has been suggested in a few experimental studies (most notably in DNA systems),[18] but, to the best of our knowledge, a quantitative demonstration of Equation (3) has not been previously reported. For TET between zinc and free base porphyrins through the OPE bridge, we determined experimentally a β value of 0.45 Å^{-1}.[8,19] This is quite different from the β value (0.11 Å^{-1}) previously obtained for this bridge with [Ru(terpy)$_2$]/[Os(terpy)$_2$] (terpy is 2,2′,6′,2″-terpyridine) donor–acceptor couple by Harriman et al.[2] This difference can entirely be ascribed to the difference in donor–bridge energy gaps [Equation (3)] and, thus, it shows experimentally the importance of not treating β as a bridge parameter but a system-specific parameter. We believe that the results presented in this communication are important for the future interpretation of ET and TET reactions.

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[19] It should be noted that the experimentally determined β values are averages of the conformational distribution of the OPE bridge whereas the values in this article are calculated for planar bridges. Please see reference [8] for a discussion.