

An extension of the McConnell superexchange formula to the case of real conjugated oligomers

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Abstract

The McConnell formula of superexchange that describes the long-range, non-adiabatic bridge-mediated electron transfer (ET) is generalized to the case of conjugated bridges covered by the structural formula $M-M-\dots-M$, where M is an arbitrary monomer. An explicit definition of the exponential decay constant and pre-exponential factor (in the standard expression of the ET rate) is given in terms of the monomer Green's function. This makes it possible to address the essentials of electron transfer across large molecules at the monomer level. The obtained dependence of the ET rate on parameters of the bridge electronic structure is compared with the original McConnell result and exemplified by analytical expressions of the effective donor–acceptor through-bridge coupling for oligomers of polyene and five- and six-membered aromatic ring based oligomers. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

In 1961 McConnell published a paper [1] on donor-to-acceptor bridge-mediated electron transfer (ET). Among the other results of that work it was shown that in the tunneling regime of electron transfer, the electronic factor in the ET rate can be explicitly related to the electronic structure of the bridging molecule — in that case a polymethylene chain $(CH_2)_N$.

One of the important messages of McConnell's formula is that the well-known textbook model for electron tunneling can be deceptive if applied to the

description of long-range electron transfer in donor/bridge/acceptor (DBA) systems and that the electronic structure of the bridge has to be taken into account explicitly.

In Ref. [1], and in a number of subsequent works, where the McConnell result has been rederived in various contexts (see Ref. [2–6] to mention few) the electronic structure of the bridging molecule has been approximated by a linear sequence of one-level subunits with the electron on-site energy ε_b and coupled to each other via a constant nearest-neighbor ET interaction (hopping integral) β_b . This model is known to give a band of N discrete one-electron states with energies $\varepsilon_j = \varepsilon_b + 2\beta_b \cos[\pi j/(N+1)]$, where $j = 1, 2, \dots, N$ and N is the number of the subunits in the chain. If the zeroth-order energy of the electron at the donor (acceptor) coupled to the bridge is far from the energies ε_j , the bridge-media-

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ted donor–acceptor ET rate k_{ET} decreases exponentially with the bridge length [1],

$$k_{\text{ET}} \sim \frac{\bar{\beta}^4}{\beta_b^2} e^{-2\delta N}, \quad (1)$$

where $\bar{\beta}$ is the coupling constant between the donor (acceptor) and the end atoms of the bridging molecule and $\delta = \ln|E/\beta_b|$ is an exponential decay constant of the donor–acceptor through-bridge coupling (superexchange). In Eq. (1) E has the meaning of the electron energy in the initial (final) state of the ET event and is counted from ε_b . The latter quantity therefore, can be set equal to zero.

Apart of the restriction of the validity of Eq. (1) by the inequality $|E/2\beta_b| \gg 1$ ([1]; for a comprehensive discussion of this limitation, see Ref. [7]), it also has to be noted that Eq. (1) is useful if the donor and acceptor do not oxidize or reduce the bridge and if the interaction with the bridge $\bar{\beta}$ is not exceptionally large. The non-redox case means that if, for instance, Eq. (1) is applied to the bridge-mediated electron transfer between transition metal ions, their active ‘d’ levels must be located in the gap between the occupied and unoccupied levels of the bridge. However, the above indicated inequality is inconsistent with the donor (acceptor) unperturbed levels being placed in the π electron band gap. Not surprisingly, the simple chain model does not lead to a band gap in the molecular electron spectrum. Hence, strictly speaking, the model used to derive Eq. (1) is not adequate to describe the electron transfer associated with tunneling through the molecular band gap. The realistic Hamiltonian of a conjugated bridge must take into account the fact that the π electronic structure is of the semi-conductor type. The same concerns also the intramolecular electron transfer across saturated bridges to which the original derivation refer [1].

There exists an enormous literature aimed at improvements of the McConnell approximation. Mostly, the theoretical effort has been focused on refining the description of the bridge electronic structure by computational methods (see e.g. Refs. [8–10] and references therein) and the reviews of Newton [11] and Jordan and Paddon–Row [12]. This Letter contributes to resolving the above-mentioned problems analytically by taking advantage of the Green’s func-

tion formalism. The Green’s function technique has been extensively used for a perturbative description of bridge-mediated electron transfer [13], as well as for the development of efficient schemes to compute the electronic factor in the ET rate [14–18]. Unlike previous treatments we report and examine here a model-exact analytical expression of this factor to be derived making use of a realistic Hamiltonian for a wide class of conjugated bridges.

The central result of this work (Eq. (11)) suggests an analogue of Eq. (1) that gives a useful estimate of the ET rate due to tunneling through the band gap of the bridging molecule. The forthcoming discussion will be restricted to the case of conjugated bridges covered by the structural formula $M-M-\dots-M$, (M)-oligomers and described by a Su–Schrieffer–Heeger type of Hamiltonian [19]. With these model limitations, Eq. (1) will be proved to be applicable to the description of intramolecular non-adiabatic electron transfer with the decay constant and pre-exponential factor given in an analytical form.

2. McConnell formula in the Green’s function formalism

To make connections with relevant works reported during the last decade, we represent first the McConnell result in terms of the effective coupling T_{DA} , which describes the electronic interaction between donor and acceptor localized states due to a molecule that connects (bridges) donor and acceptor.

The ET rate in DBA systems is usually assumed to be given by an expression based on the Fermi golden rule [20]

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |T_{\text{DA}}|^2 [\text{FC}], \quad (2)$$

where [FC] is the Franck–Condon factor connected with nuclear vibrational motion in the DBA system and its surroundings; and T_{DA} (the electronic factor) given by [7]

$$T_{\text{DA}} = \bar{\beta}^2 G_{1_{\alpha_2}, N_{\alpha_r}}^{\alpha_1}, \quad (3)$$

has the meaning of half the donor (acceptor) energy splitting due to the through-bridge interaction.

In Eq. (3) the notation $G_{1_{\alpha_1}, N_{\alpha_r}}^{\alpha_1} = \langle 1_{\alpha_1} | (E\hat{I} - \hat{H}^{\alpha_1})^{-1} | N_{\alpha_r} \rangle$ is used for the bridge Green’s function

matrix element, referred to the bridge end atoms denoted as 1_{α_1} and N_{α_r} (we omit the indication of the explicit dependence of the Green's function on energy). \hat{H}^{OM} is the Hamiltonian that describes the π electron subsystem of (M)-oligomers [21]

$$\hat{H}^{OM} = \sum_{n=1}^N \left[\hat{H}_n^M + \beta_i (|n_{\alpha_1}\rangle \langle (n+1)_{\alpha_r}| + h.c.) \right], \quad (4)$$

where $|O_{\alpha_r}\rangle = |(N+1)_{\alpha_1}\rangle = 0$; ket $|n_{\alpha}\rangle$ has its usual meaning of the $2p_z$ atomic orbital of the α th atom in the n th monomer; the monomer π electron Hamiltonian is \hat{H}_n^M and the neighboring sites of adjacent left and right monomers are denoted as α_r and α_l , respectively.

The definition of the effective coupling given above implies that $|\beta_b G_{1_{\alpha_1}, N_{\alpha_r}}^{OM}| \ll 1$ and there are no discrete states in the band gap of the π electron spectrum. Commonly, the non-adiabatic electron transfer is associated with small values of effective coupling T_{DA} (see e.g. Ref. [3] and references therein). It should be stressed, however, that if the ET frequency is comparable with intramolecular vibrational frequencies of the bridge, the pure electronic problem is not useful. In other words, the concept of pure electronic effective coupling is not applicable for too long bridges.

For the McConnell model of the bridge, $\hat{H}_n^M = 0$ and the Green's function is well known [22]. It is convenient to use here its trigonometric/hyperbolic representation

$$\beta_b G_{1, N}^{OM} = \frac{\sin \xi}{\sin[\xi(N+1)]}, \quad (5)$$

where ξ is related to the electron energy by

$$E = 2\beta_b \begin{cases} \cos \xi, & 0 \leq \xi \leq \pi, \\ \cosh \delta, & \xi = \pm i\delta, \\ -\cosh \delta, & \xi = \pi \pm i\delta. \end{cases} \quad (6)$$

Eq. (3) with the Green's function matrix element defined in Eqs. (5) and (6) is applicable to the description of effective coupling, whenever $\delta N \gg 1$ [7]. Hence, $|\beta_b T_{DA}| = 2\beta^2 \sinh \delta e^{-\delta(N+1)}$, $\delta = \cosh^{-1}|E/(2\beta_b)|$. To compare this expression with Eq. (1) we have, following McConnell, to use the condition $e^\delta \gg 1$ in which case expressions $|\beta_b T_{DA}|$

$= \bar{\beta}^2 e^{-\delta N}$ and $\delta = |E/(2\beta_b)|$ restore the original result of McConnell (1).

It is seen from above that formally, the McConnell result has to be understood as an asymptotic dependence of the effective coupling as a function of the electron energy. Also, it is obvious that the Green's function matrix element $G_{1_{\alpha_1}, N_{\alpha_r}}^{OM}$ is all that we need to generalize Eq. (1) to molecules described by more realistic Hamiltonians.

3. Oligomer-bridge Green's function

Finding the solution to the equation $(E\hat{I} - \hat{H}^{OM})\hat{G}^{OM} = \hat{I}$ with the Hamiltonian (4) requires quite lengthy calculations [23]. To avoid unnecessary mathematical details, we shall use here an analogy between chains consisting of subunits with and without internal structure and also the fact that the Green's function poles give the energies of the system eigenstates.

For one-site, one-level monomers the poles of Green's function (5) are determined by

$$\sin[\xi(N+1)] = \frac{E}{\beta_b} \sin(\xi N) - \sin[\xi(N-1)] = 0. \quad (7)$$

In the general case of (M)-oligomers the above equation takes the form [21]

$$\frac{1}{\beta_b G_{\alpha_1, \alpha_r}^M} \sin(\xi N) - \sin[\xi(N-1)] = 0, \quad (8)$$

where $G_{\alpha_1, \alpha_r}^M = \langle \alpha_1 | (E\hat{I} - \hat{H}_n^M)^{-1} | \alpha_r \rangle$. From a comparison of Eqs. (7) and (8) and by noting that for one-site, one-level monomers $G_{\alpha_1, \alpha_r}^M = G_{\alpha_1, \alpha_1}^M = 1/E$, one can assume that to obtain the Green's function matrix element appearing in Eq. (3), one has to replace the denominator (7) in Eq. (5) by Eq. (8), i.e.

$$G_{1_{\alpha_1}, N_{\alpha_r}}^{OM} = \frac{\sin \xi G_{\alpha_1, \alpha_r}^M}{\sin(\xi N) - \beta_b G_{\alpha_1, \alpha_r}^M \sin[\xi(N-1)]}. \quad (9)$$

Thereby, instead of Eq. (6), the dispersion relation

$$2\beta_b G_{\alpha_1, \alpha_r}^M \cos \xi = 1 - \beta_b^2 (G_{\alpha_1, \alpha_1}^M G_{\alpha_r, \alpha_r}^M + G_{\alpha_1, \alpha_r}^{M^2}) \quad (10)$$

prescribed by Hamiltonian (4) [21] has to be used.

Eqs. (9) and (10) are valid for any energy. For in-band energies (defined in the limit $N \rightarrow \infty$) ξ takes real values $0 \leq \xi \leq \pi$; for out-of-band energies, $\xi = \pm i\delta$; and for in-gap energies $\xi = \pi \pm i\delta$, $\delta > 0$. If $\delta N \gg 1$ one has from Eqs. (3) and (9)

$$|\beta_b T_{\text{DA}}| = \bar{\beta}^2 \frac{2 \sinh \delta e^{-\delta N}}{\left| (\beta_b G_{\alpha_1, \alpha_r}^M)^{-1} \pm e^{-\delta} \right|}, \quad (11)$$

where + corresponds to $\xi = \pi \pm i\delta$, and – corresponds to $\xi = \pm i\delta$.

It should be stressed that Eq. (11) represents an explicit definition of the effective coupling in terms of the monomer Green's function elements. Since in most cases of interest the latter quantities as functions of energy are known [21,24], Eq. (11) gives an analytical dependence of the electronic factor in the ET rate on energy and relates this dependence to the particular electronic structure of the bridging molecule.

Furthermore, Eq. (11) represents the first strict proof of the exponential N -dependence of the bridge-mediated ET rate given on the basis of a realistic Hamiltonian of the bridging molecule. So far, this kind of dependence was either guessed or found numerically.

Importantly, this central result of the Letter, is applicable to the description of the tunnel current across molecular wires and can be extended to cover conjugated oligomers consisting of a linear sequence of $N - 1$ identical monomers $M = M_1 - M_2$ ended by M_1 [25].

Now we focus our attention on a comparison of Eq. (11) with Eq. (1).

4. Asymptotics of effective coupling

As shown above, in the spirit of the original derivation, Eq. (1) describes the asymptotic behavior of the effective coupling as a function of energy. Therefore, for a more detailed comparison with the McConnell result Eq. (11) has to be examined in the limit $|E/\beta_b| \gg 1$.

By using the Green's function properties the asymptotic behavior of T_{DA} can be found without specifying the molecular electronic structure. Any Green's function matrix element can be represented as a rational function of energy. In particular,

$\beta_b G_{\alpha_1, \alpha_r}^M = P'_{N'_M}(E)/P_{N_M}(E)$, where P_{N_M} and $P'_{N'_M}(E)$ are polynomials of the N_M th and N'_M th ($N'_M < N_M$) degree, respectively, and N_M is equal to or less, than the number of one-electron states in the monomer. Therefore, for energies which are sufficiently distant from the monomer π levels we can write

$$|\beta_b G_{\alpha_1, \alpha_r}^M| = \text{const} |E/\beta|^{-(N_M - N'_M)}, \quad (12)$$

where the values of const and $N_M - N'_M$ are determined by the particular electronic structure of the monomer and β is some energy scale that is convenient to use for the given monomer (see examples below).

On the other hand, it follows from Eqs. (10) and (12) that with the increase of $|E|$ such that $e^\delta \gg 1$, the pre-exponential factor in (11), rapidly saturates at unity so that

$$|\beta_b T_{\text{DA}}| = \bar{\beta}^2 e^{-\delta N}, \quad (13)$$

where

$$\delta = (N_M - N'_M) \ln |E/\beta| - \ln \text{const}. \quad (14)$$

To recall, in the McConnell formula, the positive integer in front of logarithm (energy-dependent) term, as well as const are equal to unity.

To illustrate expression (14) for particular conjugated oligomers we use in Eq. (10) explicit expressions of monomer Green's functions obtained for a five-membered heterocycle [21] and benzene [24]. This yields ($|E/\beta| \gg 1$)

$$\delta = 3 \ln |E/\beta| - \ln (\beta_b \beta_X^2 / \beta^3), \quad (15)$$

for polyheterocycle bridges and

$$\delta = 4 \ln |E/\beta| - \ln [2(\beta_b / \beta) \cosh \eta] \quad (16)$$

for poly-paraphenylene bridges with alternating C–C bonds within phenyl rings. In Eqs. (15) and (16) the parameter η distinguishes the hopping integrals associated with the double ($\beta \exp \eta$) and single ($\beta \exp(-\eta)$) C–C bonds within aromatic rings and β_X is the hopping integral between a heteroatom (X) and carbon within the heterocycle.

When using Eqs. (13)–(16) for estimates of the effective coupling, one has to keep in mind that these are referred to the π electron subsystem only. For energies that are distant from the π levels of the bridge, as is implied in the above equations, the manifold of σ electron states can and actually do suggest more efficient pathways of the donor–acceptor electron transfer.

5. In-gap values of T_{DA}

Typically, the π electron band spectrum of linear molecules described by Eqs. (8) and (10) consists of allowed (real ξ) and forbidden (complex ξ) energy zones. With the increase of the oligomer length N the number of one-electron levels within allowed zones (or bands) increases proportionally, whereas the forbidden zones (or band gaps) remain free of electron states.

The main advantage of Eq. (11) is that in contrast to the McConnell model, it is applicable for energies lying within band gaps of the bridge electron spectrum, in particular, the HOMO–LUMO (the highest occupied band–lowest unoccupied band) gap Δ_{HL} of conjugated oligomers, where the role of σ electron states is negligible.

It can be proved that zeros of the diagonal matrix elements $G_{\alpha,\alpha}^M$ are always within the oligomer band gaps [21]. Moreover, for alternant all carbon oligomers the energy that satisfies the equation

$$G_{\alpha_1,\alpha_1}^M G_{\alpha_r,\alpha_r}^M = 0 \quad (17)$$

in the HOMO–LUMO gap energy interval, corresponds to the middle of the gap, where the decay constant reaches its maximal value δ_{\max} .

At the solutions to Eq. (17) the expression of the effective coupling takes a particularly simple form

$$|\beta_b T_{DA}| = \bar{\beta}^2 |\beta_b G_{\alpha_1,\alpha_r}^M|^N \quad (18)$$

which follows directly from Eqs. (10) and (11), since we excluded the case of in-gap states, $|\beta_b G_{\alpha_1,\alpha_r}^M| < 1$ [21].

As an example, expressed in terms of parameters of Hamiltonian (4) for oligomers of polyene and poly-paraphenylene (in the polyene chain the hopping integrals associated with double and single C–C bonds are $\beta \exp \eta$ and $\beta \exp(-\eta)$, respectively and for poly-paraphenylene oligomers η is set equal to zero) one obtains from (18) $|\beta_b T_{DA}| = \bar{\beta}^2 \exp(-2\eta N)$ and $|\beta_b T_{DA}| = \bar{\beta}^2 [\beta_i / (2\beta)]^N$. With $\eta = 0.1333$, $\beta = -3.757$ eV [26] and $\beta_i = 0.92\beta$, the maximal decay constant for polyene oligomers, $\delta_{\max} = 2\eta$, is equal to 0.27 ($\Delta_{HL} = 2$ eV), and for poly-paraphenylene oligomers $\delta_{\max} = \ln(2\beta/\beta_b) = 0.78$ ($\Delta_{HL} = 3.4$ eV).

For non-alternant oligomers Eq. (18) also gives a useful estimate of the exponential decay of $|T_{DA}|$ with the oligomer length, but in that case it does not correspond to the minimal value of the effective coupling.

It is of importance to note that in accordance with Eq. (18), at the energies determined by Eq. (17) the pre-exponential factor of the effective coupling ($= 1$) is independent of the electronic structure of the (M)-oligomers.

6. Anomalies of effective coupling

As is emphasized above the concept of effective coupling is applicable to the description of electron through-bridge tunneling if $\delta N \gg 1$. The shorter the bridge, the larger δ is needed to ensure the validity of Eq. (11). Intuitively, large values of the decay constant associate with large distances in energy from the bridge levels and hence, with wide band gaps. However, such an expectation may not always be justified.

As is seen from Eq. (10), the value of δ goes to infinity, if either

$$G_{\alpha_1,\alpha_r}^M = 0, \quad (19)$$

but

$$\beta_{\text{int}}^2 G_{\alpha_1,\alpha_1}^M G_{\alpha_r,\alpha_r}^M \neq 1,$$

$$\text{or } G_{\alpha_1,\alpha_r}^M / \left[G_{\alpha_1,\alpha_1}^M G_{\alpha_r,\alpha_r}^M - (G_{\alpha_1,\alpha_r}^M)^2 \right] = 0, \quad (20)$$

but $G_{\alpha_1,\alpha_r}^M \neq 0$, is satisfied. Consequently, the effective coupling takes zero value at the energies determined by the solutions to Eqs. (19) and (20).

Such an unusual switching ability can be possessed, in particular, by five- and six-membered ring based oligomers. For poly-heterocycle oligomers the energies of zero coupling (through π electron states) are given by

$$E = -\frac{e\eta\beta}{2\beta_X^2} \times \left(\beta^2 \pm \sqrt{\beta^4 + 4\beta_X^2 e^{-\eta} (\beta^2 \varepsilon_X + \beta_X^2 e^{-3\eta})} \right), \quad (21)$$

where $\beta\varepsilon_X$ is the difference in the Coulomb integrals between the X and C atoms.

The above equation is derived for the same model Hamiltonian as Eq. (15). For typical parameters of the bridge [21] one of the two energies determined in Eq. (21) lies within the π electron spectrum, and the other one is outside of it. This latter solution to Eq. (19) significantly affects the asymptotic behavior of the effective coupling in the sense that the true asymptotic (14) is attained far from π bands of the bridge.

The energies at which the π electron states of poly-paraphenylene oligomers block the electron transfer are given by

$$E = \pm \beta \sqrt{2 \cosh(2\eta) - 1}, \quad \eta \neq 0. \quad (22)$$

These are at the distance $\approx |\beta|$ from the middle of the HOMO–LUMO gap.

7. Synopsis

Based on a realistic Hamiltonian for conjugated oligomers of the type M–M–...–M, an analytical expression for the effective through bridge coupling (superexchange) is derived. Eq. (11) extends the McConnell exponential dependence of the superexchange, a corner stone in the theory of non-adiabatic electron transfer, to a wide class of linear molecules. This greatly facilitates estimating the electronic factor of the in molecular ET rate and gives a new insight into the physics of long-range non-adiabatic electron transfer mediated by conjugated oligomers.

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