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Non-resonant electron transfer efficiency of conjugated oligomers

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Abstract

We derive an exact closed expression of the Green function matrix element, which is valid for any linear conjugated molecule of the kind $M-M-\dots-M$, where M is an arbitrary monomer, and determines measurable characteristics of non-resonant electron transfer (ET) in relevant ET processes, e.g., donor–acceptor bridge assisted ET rate, ohmic conductance of molecular wires, etc. (In particular, for polymethine bridges ($M = CH$), the expression obtained restores the well-known McConnell formulè for the bridge assisted ET rate.) This result provides a tool for a quick and reliable estimate and comparison of ET efficiency of different oligomers which is aimed to facilitate the search for the most promising molecules to be used as electron transmitters in molecular electronic devices. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction and model statement

As is shown by recent development of the Green function approach to the description of the electron transfer/transmission (ET) phenomena, see Refs. [1,2] and literature cited therein, the efficiency of bridge-mediated non-resonant ET is determined by the Green function matrix element referred to the end atoms of bridging molecule which couple the bridge with the ‘outer world’, e.g., donor and acceptor, STM tip and surface of supporting conducting

layer, etc. Typically, the bridging function is performed by conjugated oligomers (O_M), i.e., by molecules which can be represented as a linear sequence of N identical groups of atoms (monomers M) connected with each other by the strong resonance interaction associated with π conjugated carbon bonds. In the case of the simplest representative of this wide class of molecules, a chain of N methine groups ($M = CH$) with non-alternating C–C bonds, the oligomer-bridge Green function reads [1,3]

$$G_{1,N}^{O_M}(E) = \frac{2}{\beta} \frac{\sqrt{E^2/4\beta^2 - 1}}{(E/2\beta + \sqrt{E^2/4\beta^2 - 1})^{N+1} - (E/2\beta - \sqrt{E^2/4\beta^2 - 1})^{N+1}}, \quad (1)$$

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where β is the energy of electron resonance transfer between adjacent carbons, and energy E is counted from the electron site energy at carbons

($E = E - \alpha_C$, α_C is the Coulomb integral of carbon atom).

The CH-bridge-mediated ET rate includes $(\beta G_{1,N}^{O_{CH}}(E))^2$ as one of principal factors [1–4] which depends only on the internal electronic properties of bridging molecule and, therefore, this quantity is referred to as the bridge electron transfer efficiency (BETE). It should be stressed that BETE has the precise physical meaning if and only if the electron energy is outside the resonance region (for the CH bridge this means that $|E| > 2|\beta|$) and the electronic coupling between the bridge and source and drain of electrons is weak. (For a detailed discussion of this point see Ref. [3].)

One of implications of Eq. (1) is that under the condition $|E/(2\beta)| \gg 1$, the ET rate is proportional to

$$(\beta G_{1,N}^{O_{CH}}(E))^2 = \left(\frac{E}{\beta}\right)^{-2N}. \quad (2)$$

This factor is often referred as the McConnell formula [5]. The ET rate that includes such a factor has been obtained by different techniques and proved to be extremely useful in a great number of applications to the description of the electron transfer processes, see Refs. [1,3,4] and references therein. However, these applications are severely restricted by the assumption of the mono-atomic structure of bridging molecule. Below, Eq. (2) and its parent expression of BETE given in Eq. (1) will be generalized to the case of conjugated bridges, whose structure can be represented as $M-M-\dots-M$, where M is an arbitrary group of atoms.

2. Physics of McConnell formula

The condition $|E/(2\beta)| > 1$ means that ET happens due to the through-bridge tunneling. To make this implication of the expression of BETE explicit, we rewrite Eq. (1) in an equivalent form

$$\beta G_{1,N}^{O_{CH}}(E) = \frac{\sin \zeta}{\sin(\zeta(N+1))}, \quad (3)$$

where ζ is related to electron energy by

$$E = 2\beta \begin{cases} \cos \zeta, & 0 \leq \zeta \leq \pi, \\ \cosh \delta, & \zeta = \pm i\delta, \\ -\cosh \delta, & \zeta = \pi \pm i\delta, \end{cases} \quad (4)$$

and has the meaning of wave vector (expressed in units of the inverse lattice constant) which can take real, $0 \leq \zeta \leq \pi$, as well as complex values: $\zeta = \pm i\delta$, if $E < -2|\beta|$, and $\zeta = \pi \pm i\delta$, if $E > 2|\beta|$ (the hopping integral β is supposed to be negative).

In these notations and under the condition $\delta(E)N \gg 1$ (for long bridges the latter condition is weaker, than $|E/(2\beta)| \gg 1$), Eq. (3) acquires the standard exponential form of tunneling probability through a potential barrier of thickness N

$$(\beta G_{1,N}^{O_{CH}}(E))^2 = 4 \sinh^2(\delta(E)) \times e^{-2\delta(E)} \times e^{-2\delta(E)N}, \quad (5)$$

where the value of $\delta(E)$ at the given energy is determined by Eq. (4).

It is obvious that under the condition $e^{\delta(E)} \gg 1$ which is equivalent to $|E/(2\beta)| \gg 1$, Eq. (5) is completely identical to the McConnell formula. However, the former reveals interesting physics hidden in Eq. (2). Namely, the first factor shows that ET rate is proportional to the electron group velocity squared, which corresponds to the given value of (complex) wave vector; the second factor, which seems to have no physical meaning, in fact represents, as we show below, the intra-monomer ET efficiency. In the case of CH bridge modeled by a mono-atomic chain, the left and right binding atoms in monomer are just one and the same carbon atom, i.e., there is no ET within monomer. (From this point of view, the mono-atomic chain represents the most efficient electron transmitter.) Finally, the third factor is a characteristic indication of the through-rectangular-barrier tunneling the form of which is independent of particular physical nature of the barrier.

In what follows it will be proved that while Eq. (2) is relevant only to the particular case of mono-atomic chain, the ET rate dependence on the bridge length and electron wave vector, electron group velocity, and intra-monomer ET efficiency, which is represented in Eq. (5), has the universal

character inherent to any conjugated bridge of the type M–M–...–M.

3. Generalization of BETE expression and McConnell formula

The matrix of one-particle tight-binding Hamiltonian in one dimension is three diagonal. Due to this fact, finding solution to the Green function equation and thus, the expression of Eq. (1), is quite straightforward [6]. The structure M–M–...–M is not one-dimensional in the true sense since at each binding site (the site of connection of monomer M with the neighboring one) as well as within monomers, electron have more than just two choices to go, i.e., not only along the chain and backward. Consequently, the Hamiltonian matrix which describes an arbitrary conjugated bridge is not three diagonal, and finding the solution of the problem becomes more complicated. (To our knowledge, it has not been solved so far.)

It is obvious, however, that though, in general, the electron dynamics within monomers can be very far from being one-dimensional, the electron motion along the chain is performed by electron transfer from one monomer to another. So, in macro-scale the system in focus is certainly one-dimensional. One may expect, therefore, that the use of one-dimensional character can be the key to the problem solution.

With this idea in mind we pass from the equation

$$(E\hat{I} - \hat{H}^{O_M})\hat{G}^{O_M} = \hat{I}, \quad (6)$$

where \hat{H}^{O_M} and \hat{G}^{O_M} are the Hamiltonian and Green function operators of oligomer, respectively, and \hat{I} is the unity operator, to the Dyson equation with the choice of the monomer Green function operator $\hat{G}^M = (E\hat{I} - \hat{H}^M)^{-1}$ as a non-perturbative solution. Precisely,

$$\hat{G}^{O_M} = \hat{G}^M + \hat{G}^M \hat{V} \hat{G}^{O_M}, \quad (7)$$

where the matrix elements of the perturbation operator \hat{V} are assumed to have non-zero value β only for the nearest-neighbor binding sites, denoted below as x_l and x_r – the coordinates of the left and right binding atoms in the monomer.

In its explicit form

$$\begin{aligned} G_{m_l, n_l}^{O_M}(E) &= \delta_{m, n} G_{x_l, x_l}^M(E) \\ &+ \beta [G_{x_l, x_l}^M(E) G_{(m-1)_l, n_l}^{O_M}(E) \\ &+ G_{x_l, x_l}^M(E) G_{(m+1)_l, n_l}^{O_M}(E)], \end{aligned} \quad (8)$$

Eq. (7) is in essence one-dimensional. Indeed, for the mono-atomic chain we have from Eq. (8)

$$E G_{m, n}^{O_{ch}}(E) = \delta_{m, n} + \beta [G_{(m-1), n}^{O_{ch}}(E) + G_{(m+1), n}^{O_{ch}}(E)]. \quad (9)$$

One can see that the structure of Eq. (8) for $G_{m_l, n_l}^{O_M}(E)$ is similar to the structure of the above equation, where the Green function matrix elements are connected by the inter-monomer interaction β only with those sites which refer to the nearest neighbors. The only distinction is that in Eq. (8) the forward and backward hopping integrals are modified but this complication does not prevent finding the closed form of solution to Eq. (8).

The use of the free-end chain boundary conditions and dispersion relation, Eq. (4), leads from Eq. (9) to Eq. (3). By analogy, the use of the same boundary conditions and the dispersion relation for the kind of oligomers under consideration [7]

$$\begin{aligned} 2\beta \cos \zeta &= \frac{1}{G_{x_l, x_l}^M(E)} [1 - \beta^2 G_{x_l, x_l}^M(E) G_{x_l, x_l}^M(E) \\ &+ (\beta G_{x_l, x_l}^M(E))^2] \end{aligned} \quad (10)$$

gives the following solution of Eq. (8) for $G_{1_l, N_l}^{O_M}(E)$

$$G_{1_l, N_l}^{O_M}(E) = \frac{G_{x_l, x_l}^M(E) \sin \zeta}{\sin \zeta N - \beta G_{x_l, x_l}^M(E) \sin \zeta (N - 1)}. \quad (11)$$

Setting in Eqs. (10) and (11) $G_{x_l, x_l}^M(E) = G_{x_r, x_r}^M(E) = G_{x_l, x_l}^M(E) = E^{-1} = (2\beta \cos \zeta)^{-1}$ immediately restores Eq. (1) and thus, the original McConnell result represented in Eq. (2).

Eqs. (10) and (11) give the exact definition of BETE. Again we emphasize that this definition makes sense only in the case of weak coupling and for energies which are outside oligomer bands and, if there are local states in the oligomer π electron spectrum, see Refs. [7–10], sufficiently distant from such states. If, in addition, for the given energy (in accordance with Eq. (10), the given E implies a certain value of complex wave vector) the condition

$\delta(E)N \gg 1$ is fulfilled, we obtain the following generalization of Eq. (5) to the case of arbitrary oligomer of the type M–M–...–M

$$(\beta G_{1_x, N_x}^O(E))^2 = 4 \sinh^2(\delta(E)) \times \frac{1}{((\beta G_{x, x}^M(E))^{-1} \pm \exp(-\delta(E)))^2} \times e^{-2\delta(E)N}, \quad (12)$$

where ‘+’ corresponds to $\zeta = \pi \pm i\delta$, and ‘-’ corresponds to $\zeta = \pm i\delta$, and δ (at the given energy) is determined by Eq. (10).

Eq. (12) represents the proof of three basic properties of bridge-mediated ET briefly mentioned above. The first one is that in the tunneling regime, the exponential decrease of ET rate with the increase of the number of monomers – repeating unites of the bridge, is universally defined in terms of the complex wave vector whose value at the given energy is determined by the dispersion relation, Eq. (10). This means that the exponent in the ET rate is identical for all bridges of the same length (in the number of monomers) provided the departure from the bridge band of tunneling electron expressed in terms of the wave vector is the same. On the contrary, for tunneling electrons which have the same separation from the bridge band in energy the exponent takes a specific value for each particular oligomer. The difference in these values is determined by distinctions in the dispersion relation of different oligomers. Secondly, the ET rate depends on how fast is the electron transfer between the binding sites of monomer. This property of bridge-assisted ET is expressed by a saturating-type dependence on $\beta G_{x, x}^M(E)$ of the pre-exponential factor in Eq. (12). One can conclude that the bridge-assisted ET rate is proportional to $(\beta G_{x, x}^M(E))^2$, if the electron transfer from one end of the monomer to another is slow (small values of $(\beta G_{x, x}^M(E))^2$), but it becomes independent of the intra-monomer ET rate, if the latter is fast (large values of $(\beta G_{x, x}^M(E))^2$). In a sense, this result shows the way of improvement of molecular wire efficiency by means of proper molecular design. And thirdly, as seen from Eq. (12), in the tunneling regime of ET the bridge-mediated ET rate is always

proportional to the square of electron group velocity determined by the oligomer band structure.

To conclude, it is shown that transmitting of electrons by tunneling through linear molecules M–M–...–M is described by an exponential dependence $\exp(-2\delta(E)N)$, where $\delta(E)$ is interrelated with the electron energy by the energy dispersion relation, Eq. (10). This kind of dependence for the bridge-assisted ET rate was first discovered by McConnell [5] for the particular case of monoatomic chain, but until now it has not been understood that expressed in the form of Eq. (12), i.e., group velocity squared times intra-monomer ET efficiency times exponential tunnel factor, it has the universal character relevant to tunneling through a sufficiently long oligomer with arbitrary electronic structure of its monomers. It is also shown that the intra-monomer ET efficiency is characterized by the saturating-type dependence on the monomer Green function matrix element which refers to the monomer binding sites.

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