Nonadiabatic Electron Transfer: Exact Analytical Expression of through-Conjugated-Bridge Effective Coupling and Its Asymptotics and Zeros

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Received: September 26, 1997; In Final Form: March 2, 1998

For the conjugated oligomers of the type $(M)_N$ described by a tight-binding Hamiltonian with the nearest-neighbor interaction between monomers M of otherwise arbitrary electronic structure, the bridge-mediated donor−acceptor effective coupling is proved to be ruled by an exponential law $T^0_{DA}\exp(-\delta N)$. Previously, this kind of dependence has been recovered in many numerical treatments or guessed on phenomenological basis. The exact expressions of the decay constant δ and pre-exponential factor T^0_{DA} obtained in terms of the monomer Green function provide, for the first time, an analytical relationship between the oligomer π electronic structure and through-conjugated-bridge tunneling efficiency. For the fundamental band gap a simple analytical approximation of the effective coupling that relates δ to the model of through-rectangular-barrier tunneling is also given. The dependence of the effective coupling on energy of tunneling electron (hole) is examined in detail and illustrated for oligomers of polyenes, polyparaphenylenes, and polyheterocycles. The results obtained suggest a quick and reliable estimate of the effective coupling with a deep insight into the physical origins of related switching abilities of conjugated oligomers as a useful alternative to lengthy numerical calculations.

I. Introduction

Numerous processes that are met in physics, chemistry, and biology can be put onto a formal scheme $\tilde{D}BA \rightarrow DB\tilde{A}$ that implies the transfer of charge or excitation from (conditionally) donor (D) to acceptor (A) through a bridge B. Generally speaking, the interaction between donor and acceptor, which makes possible that kind of processes, involves all states of bridging subsystem. However, under certain conditions the D−A interaction can be characterized by a single energy dependent parameter—effective trough−bridge coupling, which has been proven to play the fundamental role in charge and excitation energy transfer phenomena.[1−6]

It is now well established[2−6] that the effective coupling in donor/bridge/acceptor (DBA) systems can be expressed in terms of a bridge Green function which suggests the physically clear basis for computing this quantity explicitly or implicitly in various contexts.[2−14] For a bridge modeled by a monoatomic chain, the explicit expression of Green function can also be found,[4,6,15] and thus far, this model remains dominating in relevant analytical and semi-analytical treatments.[2,4,6,8−13] The focus of this work is just on this latter aspect of the problem pioneered by McConnell,[1] who found the asymptotic energy dependence of effective coupling through a nonalternating CH_2 chain in the bridge assisted electron transfer.

Specifically, we consider an important class of bridging molecules−conjugated oligomers, which can be approached by the Green function formalism up to obtaining the exact closed expression which relates the effective coupling to the monomer (oligomer building blocks) Green function. In general terms, this makes possible to oversee the electron transmitting properties of conjugated bridges at the monomer level.

The effective through-bridge coupling squared enters the intramolecular donor-acceptor electron transfer rate as a principal factor.[16,17] The linear-response tunnel conductance of metal-molecular heterojunctions,[11,14,18] where a molecule spanned between electrodes acts as a molecular wire,[19−21] is proportional to this same quantity. Therefore, the present detailed discussion of the through-bridge effective coupling on the basis of the exact expression of the Green function for conjugated oligomers, that has been found by us recently,[22] is of immediate use not only in the field of the electron transfer but also for measurements of current-voltage characteristics in metal−molecule−metal heterostructures.[19−21] From this perspective our work aims at the development of a realistic analytical description of electrical current across a single molecule. This work concerns only the tunnel current and related switching abilities of conjugated oligomers. In a subsequent publication we shall discuss the resonance transmission spectrum of "elastic" metal−molecular heterojunctions.

The paper is organized as follows. Section II proceeds with a brief formal introduction of the effective coupling and gives its exact analytical definition in terms of the monomer Green function for a tight-binding Hamiltonian of conjugated bridges. We establish the interrelation between the monomer Green function and the asymptotic behavior and zeros of effective coupling as a function of energy in sections III and IV, respectively. Section V exemplifies the analytical relations derived in preceding Sections by oligomers of polyene, polyparaphenylene, and polyheterocycles. A brief discussion of some related results is also given in Section V. The concluding remarks of section VI outline the main findings of this presentation.

II. Bridge-Mediated Effective Coupling

In this section we introduce the concept of effective coupling which is broadly used in the theory of non-adiabatic bridge-

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S1089-5639(97)03135-6 CCC: $15.00
Published on Web 05/02/1998

assisted electron (hole) transfer, see refs 1−6, 16, and 17, and literature given therein. Briefly, the electron transfer event is thought to occur under the influence of a weak donor−acceptor interaction, whenever electron has the same energy in the initial (at donor) and final (at acceptor) states, and at a fixed geometry of the bridging molecule, whose end atoms are coupled with donor and acceptor via the electron-transfer resonance interaction.

To put this concept on formal basis, it is usually assumed that the presence of electron at donor (acceptor) described by the Hamiltonian $\hat{H}^{\mathrm{D}}$ ($\hat{H}^{\mathrm{A}}$) can be approximated by a single orbital $|\mathrm{D}\rangle$ ($|\mathrm{A}\rangle$), $\hat{H}^{\mathrm{D}}|\mathrm{D}\rangle = \epsilon|\mathrm{D}\rangle$ ($\hat{H}^{\mathrm{A}}|\mathrm{A}\rangle = \epsilon|\mathrm{A}\rangle$), whose overlap with the bridge end-atom orbitals $|1_{\alpha_l}\rangle$ and $|N_{\alpha_r}\rangle$ is represented by the identical hopping integral $\bar{\beta}$. Then, denoting the Hamiltonians of DBA system and bridging molecule (in the present context the latter is associated with an oligomer of N monomers M in conjugation) as $\hat{H}$ and $\hat{H}^{\mathrm{O_M}}$, respectively, and the operator of the Green function of the bridging molecule as $\hat{G}^{\mathrm{O_M}} = (E - \hat{H}^{\mathrm{O_M}})^{-1}$, the eigenvalue problem for the DBA system, $\det|H_{m_\alpha,n_{\alpha'}} - \delta_{m,n}\delta_{\alpha,\alpha'}E| = 0$, can be expressed in the form[23]

$$E = \epsilon + \bar{\beta}^2\,[G^{\mathrm{O_M}}_{1_{\alpha_l},1_{\alpha_l}}(E) \pm G^{\mathrm{O_M}}_{1_{\alpha_l},N_{\alpha_r}}(E)] \qquad (1)$$

The notations introduced above have the following meanings: $H_{m_\alpha,n_{\alpha'}} = \langle m_\alpha|\hat{H}|n_{\alpha'}\rangle$, $\hat{H} = \hat{H}^{\mathrm{O_M}} + \hat{H}^{\mathrm{D}} + \hat{H}^{\mathrm{A}} + \bar{\beta}(|\mathrm{D}\rangle\langle 1_{\alpha_l}| + |\mathrm{A}\rangle\langle N_{\alpha_r}| + \mathrm{h.c.})$, $G^{\mathrm{O_M}}_{m_{\alpha_l},n_{\alpha_r}}(E) = \langle m_{\alpha_l}|\,(E - \hat{H}^{\mathrm{O_M}})^{-1}|n_{\alpha_r}\rangle$, $|n_\alpha\rangle = |\mathrm{D}\rangle, |\mathrm{A}\rangle$, when $n = 0, (N + 1)$, respectively, and ket $|n_\alpha\rangle$, where n runs over all monomers of the bridge (from the first to Nth), identifies the $2p_z$ atomic orbital of the αth atom in the nth monomer, and these orbitals are supposed to form a complete orthonormalized basis of the bridge states; indexes l and r refer to the left and right binding sites (atoms) of the monomer in the oligomer chain. At this stage the Hamiltonian $\hat{H}^{\mathrm{O_M}}$ is not needed to be specified.

The solutions to the above set of equations determine (exactly) all one-electron energies in the system except those corresponding to degenerate oligomer bands.[24] If the contribution of bridge states to the donor (acceptor) state and vice versa is small (see the extensive discussion of this point in ref 6) the two energies of originally degenerate donor and acceptor levels can (approximately) be defined as

$$E_\pm = \epsilon + \bar{\beta}^2 G^{\mathrm{O_M}}_{1_{\alpha_l},1_{\alpha_l}}(\epsilon) \pm \bar{\beta}^2 G^{\mathrm{O_M}}_{1_{\alpha_l},N_{\alpha_r}}(\epsilon) \qquad (2)$$

where, unlike the exact eq 1, the argument of the bridge Green function matrix elements E is replaced by the zero-order donor (acceptor) energy ϵ.

As it is seen from eq 2, the quantity

$$T_{\mathrm{DA}} = \frac{1}{2}|E_+ - E_-| = \bar{\beta}^2|G^{\mathrm{O_M}}_{1_{\alpha_l},N_{\alpha_r}}(E = \epsilon)| \qquad (3)$$

plays the role of the bridge mediated effective coupling between donor and acceptor that removes the donor-acceptor degeneracy. In an isolated DBA system described by Hamiltonian $\hat{H}$, such a coupling leads to oscillations of the electron density at donor and acceptor with the frequency $T_{\mathrm{DA}}/\hbar$[4,6] (reversible electron transfer from donor to acceptor and backward). Under certain conditions regarding the interaction of DBA with the outer world, which can be further specified (see, e.g., refs 1−6, 8, 9, 16, and 17), but this is outside the scope of this presentation: the effective coupling gives rise to irreversible donor−acceptor electron transfer with the rate proportional to T^2_{DA}.[1−4,6,16,17]

The validity of approximation 2 has already been examined in detail.[6] Therefore, we restrict ourselves to a few remarks about its applicability. Obviously, eq 2 is valid if and only if both the renormalization correction to the donor (acceptor) zeroth order energy ϵ (the second term of the right hand side in eq 2) and the splitting (third) term are small in comparison with the difference $\Delta\epsilon$ between ϵ and the bridge band edges expressed in units of the intermonomer electron-transfer resonance interaction $\beta_{\mathrm{C-C}}$. This condition is satisfied if, firstly, $|T_{\mathrm{DA}}/\beta_{\mathrm{C-C}}| \ll \Delta\epsilon$, and, secondly, if both energies E_+ and E_- are outside the oligomer one-electron bands defined in the limit $N \to \infty$. The latter restriction of the validity of the two-state description of DBA systems and thus, of the validity of the concept of effective coupling, is particularly important. It has been implied rather than emphasized previously.[6] Moreover, it was rarely controlled in numerous computations of the effective coupling.

Since the width of band gaps of linear conjugated molecules is of the order of $|\beta_{\mathrm{C-C}}|$ or less, introducing the effective coupling makes sense if $|T_{\mathrm{DA}}/\beta_{\mathrm{C-C}}| \ll 1$. For comparable values of $|\bar{\beta}|$ and $|\beta_{\mathrm{C-C}}|$ the latter inequality is equivalent to

$$|\beta_{\mathrm{C-C}} G^{\mathrm{O_M}}_{1_{\alpha_l},N_{\alpha_r}}(\epsilon)| \ll 1 \qquad (4)$$

that, in physical terms, implies donor−acceptor electron transfer occurring due to tunneling across the bridging molecule.

The above derivation of effective coupling is essentially based on the method of Lifshits[25] and Koster and Slater[26] that in the same context has been used previously.[2,12] The expression of effective coupling in terms of the Green function of bridging molecule given in eq 3 can also be obtained by using the Löwdin partitioning technique,[27] see, e.g., refs 3 and 6.

To advance this derivation further we shall define the bridge Green function appeared in eq 3. For the conjugated oligomers of the type M−M−···−M it takes the form[22]

$$G^{\mathrm{O_M}}_{1_{\alpha_l},N_{\alpha_r}}(E) = \frac{G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E)\sin\xi}{\sin(\xi N) - \beta_{\mathrm{C-C}} G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E)\sin[\xi(N-1)]} \qquad (5)$$

where $G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E)$ is the monomer Green function matrix element referred to binding sites α_l and α_r, the sites of the intermonomer interaction, and ξ is related to the electron energy in the DBA system by the following equation[24]

$$2\cos\xi = f(E) \qquad (6)$$

where

$$\beta_{\mathrm{C-C}} G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E) f(E) = 1 - \beta^2_{\mathrm{C-C}}\,[G^{\mathrm{M}}_{\alpha_l,\alpha_l}(E)\,G^{\mathrm{M}}_{\alpha_r,\alpha_r}(E) - (G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E))^2] \qquad (7)$$

The expression 5 has been obtained under the only limitation with respect to the electronic Hamiltonian $\hat{H}^{\mathrm{O_M}}$:[22] the assumption of nearest-neighbor interaction between monomers in the oligomer chain. In the particular case of polyene oligomers, an equivalent expression was suggested in ref 6. Earlier,[28] all matrix elements of the polyene Green function for the tight-binding Hamiltonian have been found.

Equations 5−7 are valid for any energies. Equation 6 has the meaning of the dispersion relation and, as such, determines the allowed and forbidden zones, i.e., the bands and gaps in the energy spectrum of linear sequence M−M−···−M in the limit $N \to \infty$.[24] The (dimensionless) wave vector ξ is real within the band energy intervals, $0 \le \xi \le \pi$, but it acquires complex

values, $\xi = \pm\, \mathrm{i}\delta$ or $\xi = \pi \pm \mathrm{i}\delta$, within the band gaps. In this latter case, the dependence of δ on energy is given by the equation

$$\delta = \ln\left(|f(E)|/2 + \sqrt{[f(E)/2]^2 - 1}\right) \tag{8}$$

that directly follows from eq 6 for $|f(E)|/2 \geq 1$. The gap boundaries (band edges) can also be found from eq 6, often in an analytical form.[24,29]

The replacement of ξ in eq 5 by the complex wave vector gives

$$G^{\mathrm{O_M}}_{1_{\alpha_l},N_{\alpha_r}}(E) = \frac{(\mp 1)^N G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E)\sinh\delta}{\sinh(\delta N) \pm \beta_{\mathrm{C-C}} G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E)\sinh[\delta(N-1)]} \tag{9}$$

where the upper signs correspond to $\xi = \pi \pm \mathrm{i}\delta$, and lower signs correspond to $\xi = \pm\mathrm{i}\delta$, and $\delta > 0$. Inequality 4 can be satisfied, if $e^{\delta N} \gg 1$. Hence, under the latter condition we have from eqs 3 and 9

$$T_{\mathrm{DA}} = T^0_{\mathrm{DA}}\, \mathrm{e}^{-\delta N} \tag{10}$$

where the preexponential factor is given by

$$T^0_{\mathrm{DA}} = \bar{\beta}^2 \left| \frac{2\sinh(\delta) G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E)}{1 \pm \beta_{\mathrm{C-C}} G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E)\, \mathrm{e}^{-\delta}} \right| \tag{11}$$

As is shown by us previously,[24] if $|\beta_{\mathrm{C-C}} G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E)| > 1$, the π electron spectrum of the oligomer contains ingap (local) states at the energies, where $G^{\mathrm{M}}_{\alpha_l,\alpha_l}(E) = 0$. (If $|\beta_{\mathrm{C-C}} G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E)| = 1$, the neighboring bands join each other at the energies, where $G^{\mathrm{M}}_{\alpha_l,\alpha_l}(E) = 0$,[24] so that at these energies the concept of effective coupling is not applicable.) In such a special case further analysis is required that will be published elsewhere. Here, we only note that, if the denominator of the right-hand side of eq 11 turns to zero or has nearly zero value (and this can be the case only if $|\beta_{\mathrm{C-C}} G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E)| > 1$), the definition of the preexponential factor given in eq 11 is incorrect. Nevertheless, exponential dependence in eq 10 with δ given in eq 8 remains to be valid but with another definition of T^0_{DA} and at larger oligomer lengths, i.e., at the energies of ingap states and close to them the condition $e^{\delta N} \gg 1$ becomes to be insufficient.

With account to the restrictions just specified, eq 10 with the exponential decay constant and preexponential factor determined by eqs 8 and 11, respectively, represent a physically consistent definition of donor-acceptor through bridge coupling. Above all, the derivation of this equation presents a proof that tunneling across the band gap of a linear molecule is described by the same dependence on the molecule length as the probability W of tunneling across a rectangular barrier of height V on the barrier width $L = aN$: $W \sim \mathrm{e}^{-2\kappa L}$, where $\kappa = \hbar^{-1}\sqrt{2m^*(V-E)}$, E is the energy of tunneling electron, m^* is the electron effective mass, and a is the lattice constant of the linear molecule. Earlier, such a dependence was often guessed[14,30,31] but never proved.

Furthermore, provided the monomer Green functions $G^{\mathrm{M}}_{\alpha_l,\alpha_l}(E)$, $G^{\mathrm{M}}_{\alpha_r,\alpha_r}(E)$ and $G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E)$ are known (and these can quite easily be found in many cases described by the tight-binding Hamiltonian, see below), eq 10 gives an analytical relationship between the value of T_{DA} (that is probability of electron tunneling across the bridge) and the electronic structure of the bridge and its length. Importantly, this relationship is obtained in the framework of a model that has been proven to give an adequate description of linear conjugated molecules.[32]

Note also that with the replacement $\bar{\beta}^2$ by the spectral density, the square of the effective coupling, $(T_{\mathrm{DA}}/\beta_{\mathrm{C-C}})^2$, determines the tunnel conductance in the linear-response theory.[11,18] Therefore, the model-exact expression of the effective coupling derived above gives an analytical solution to a particular problem of current experimental[19−21] and theoretical[14,21,31] interest. Moreover, eqs 8−11 can be generalized to the case of oligomers of the kind M−M−···−M−$\mathrm{M_1}$, where M is a two-component monomer $\mathrm{M_1}$−$\mathrm{M_2}$[18] (such as oligomers of poly(phenylene−vinylene), polyaniline, etc.). Thus, an analytical exponential dependence, that has been originally found by McConnell for a chain of one site, one level monomers, is extended to cover essentially all conjugated oligomers.

Setting in eq 11 $G^{\mathrm{M}}_{\alpha_l,\alpha_l}(E) = G^{\mathrm{M}}_{\alpha_r,\alpha_r}(E) = G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E) = E^{-1} = -(2\beta_{\mathrm{C-C}}\cosh\delta)^{-1}$ and substituting the result in eq 10, one obtains

$$|T_{\mathrm{DA}}| = \frac{2\bar{\beta}^2 \sinh\delta}{|\beta_{\mathrm{C-C}}|}\, \mathrm{e}^{-\delta(N+1)} \tag{12}$$

where

$$\delta = \ln\left(|E/(2\beta_{\mathrm{C-C}})| + \sqrt{[E/(2\beta_{\mathrm{C-C}})]^2 - 1}\right)$$

To restore the McConnell original result, one has to set in eq 12 $|E/(2\beta_{\mathrm{C-C}})| \gg 1$. Then, one gets $T_{\mathrm{DA}} = (\bar{\beta}^2/|\beta_{\mathrm{C-C}}|)\mathrm{e}^{-\delta N}$, where $\delta = \ln|E/\beta_{\mathrm{C-C}}|$.[1]

One of the disappointing features of this result is that its validity requires the energy of tunneling electron to be remote from the bridge states. From the mathematical point of view, the McConnell formula describes the asymptotic behavior of effective coupling as a function of energy. Nevertheless, it is of interest to answer the question: does or does not survive the McConnell result, if building blocks of the bridging molecule possess some internal structure?

III. Asymptotic Behavior of Effective Coupling

Any Green function matrix element can be represented as a rational function. In particular, $\beta_{\mathrm{C-C}} G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E) = P'_{N'_{\mathrm{M}}}(E)/P_{N_{\mathrm{M}}}(E)$, where $P_{N_{\mathrm{M}}}(E)$ and $P'_{N'_{\mathrm{M}}}(E)$ are polynomials of the N_{M}th and N'_{M}th ($N'_{\mathrm{M}} < N_{\mathrm{M}}$) degree, respectively, and N_{M} is equal to, or less, than the number of π electron centers in the monomer. Therefore, for energies which are sufficiently distant from the oligomer bands, we can write

$$\lim_{|E|\to\infty}\left|\beta_{\mathrm{C-C}} G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E)\right| = \lim_{|E|\to\infty}\left|\frac{\beta_{\mathrm{C-C}}}{\beta} G^{\mathrm{M}}_{\alpha_l,\alpha_r}\left(\frac{E}{\beta}\right)\right| = C\left|\frac{E}{\beta}\right|^{-(N_{\mathrm{M}}-N'_{\mathrm{M}})} \tag{13}$$

where the values of C and $N_{\mathrm{M}} - N'_{\mathrm{M}}$ are determined by the particular electronic structure of monomer, and β is some energy scale which is convenient to use for the given monomer, see below.

On the other hand, under the assumption that polynomial $P'_{N'_{\mathrm{M}}}(E)$ does not have roots outside π electron bands (the special case $G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E) = 0$ is discussed later) it follows from eqs 8 and 13 that for large values of $|E|$ and e^{δ} we have $\mathrm{e}^{\delta} = |\beta_{\mathrm{C-C}} G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E)|^{-1}$. Then, eq 10 transforms into $T_{\mathrm{DA}} = (\bar{\beta}^2/|\beta_{\mathrm{C-C}}|)\ \mathrm{e}^{-\delta N}$ or, equivalently, $T_{\mathrm{DA}} = (\bar{\beta}^2/|\beta_{\mathrm{C-C}}|)|\beta_{\mathrm{C-C}} G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E)|^N$. Thus, with account to eq 13

$$\delta = -\ln|\beta_{C-C} G^{M}_{\alpha_l,\alpha_r}(E)| = (N_M - N'_M)\ln\left|\frac{E}{\beta}\right| - \ln C \quad (14)$$

Hence, the asymptotics of the effective donor−acceptor coupling through an oligomer is determined by the asymptotic behavior of the corresponding monomer Green function.

It may seem at first sight that the larger is the number of π centers in the monomer, i.e., the larger is the number N_M, the larger is the decay constant of effective coupling. But in applications of the above equation, one should take into account the real distance which corresponds to the chain of N monomers. For example, for nonalternating CH_2-bridge ($M = CH_2$) $N_M - N'_M = C = 1$, and for polyene bridge ($M = C_2H_2$) $N_M - N'_M = 2$, $C = 1$, i.e., according to eq 14, the decay constant for the latter bridge is two times larger. But the chain of N vinylene groups is equal (in the number of carbons) to the length of the chain of $2N$ CH groups, so that the effective coupling across these two bridges is, as expected, identical if compared far from the bridge states.

IV. Zeros of Effective Coupling

By the definition given in eq 3, the effective coupling vanishes at energies, where the bridge Green function $G^{O_M}_{1_{\alpha_l},N_{\alpha_r}}(E) = 0$ which is the case, whenever (see eqs 10 and 11)

$$G^{M}_{\alpha_l,\alpha_r}(E) = 0 \quad (15)$$

The above equation states that zeros of effective coupling coincide with zeros of the nondiagonal *monomer* Green function element which refers to the binding sites of monomer in the given oligomer bridge. It can be concluded, therefore, the bridging molecules, whose building blocks possess the property expressed in eq 15, will break the electronic contact at energies given by solutions to the above equation.

As it follows from eq 8, if $\beta^2_{C-C}\, G^{M}_{\alpha_l,\alpha_l}(E) G^{M}_{\alpha_r,\alpha_r}(E) \neq 1$, zeros of $G^{M}_{\alpha_l,\alpha_r}(E)$ are reflected in the singular behavior of decay constant as a function of energy. But if equation

$$\beta^2_{C-C}\, G^{M}_{\alpha_l,\alpha_l}(E) G^{M}_{\alpha_r,\alpha_r}(E) = 1 \quad (16)$$

is satisfied simultaneously with eq 15, the decay constant becomes indefinite, see eqs 6 and 7. This can be the case of certain relations between parameters determining the monomer electronic structure that has to be examined separately.[24]

It is also seen from eqs 6 and 7 that except for the case of the gap closing,[24] eq 15 can have solutions only outside oligomer π electron bands.[33] If such solutions do exist, the monotonic behavior of the decay constant discussed in the preceding section, will be replaced by a singular (highly nonmonotonic) dependence near energies determined by eq 15. Accordingly, the singularities of decay constant reveal themselves as zeros of effective coupling as a function of energy, see illustrative examples represented below. This result is in an obvious conflict with expectations based on the CH_2-chain model which predicts the monotonic decrease of T_{DA} with increase of $|E|$, see eq 12.

Equation 15 that determines zeros of effective coupling directly follows from the definition of the bridge Green function 9. Apart eq 15, there is another, somewhat less obvious condition, the fulfillment of which also nullifies through bridge coupling. As it is seen from eqs 8 and 10, for nonzero $G^{M}_{\alpha_l,\alpha_r}(E)$ the value of T_{DA} can still be equal to zero, if among poles of the bilinear combination

$$G^{M}_{\alpha_l,\alpha_l}(E) G^{M}_{\alpha_r,\alpha_r}(E) - (G^{M}_{\alpha_l,\alpha_r}(E))^2 \quad (17)$$

there are others than the poles of $G^{M}_{\alpha_l,\alpha_r}(E)$, or if the poles of the former function are of higher order than those of the latter. Then, at the energies which are solutions to equation

$$\frac{G^{M}_{\alpha_l,\alpha_r}(E)}{G^{M}_{\alpha_l,\alpha_l}(E) G^{M}_{\alpha_r,\alpha_r}(E) - [G^{M}_{\alpha_l,\alpha_r}(E)]^2} = 0 \quad (18)$$

the decay constant is infinite, see eq 8, and consequently, the bridge Green function, as well as the effective coupling are equal to zero.

To notice, the number of poles of bilinear combination 17 is restricted by the number of π centers in monomer and can be larger than the number of poles of diagonal and nondiagonal Green function matrix elements which enter this combination. We can prove this statement in the general case and it will be illustrated in the next section by a particular example.

Since the solutions of eq 18 correspond to monomer levels, and therefore, the interaction between donor (acceptor) and bridging molecule cannot be regarded as a small perturbation, it is the right place to emphasize that zeros of effective coupling have the clear physical consequence: the break of through-bridge electronic coupling, independent of the values of electron energy to which they refer. The particular manifestation of this property, e.g., the character of the dependence of physical quantities related to the effective coupling on electron energy, presents another problem which has to be examined separately and in its particular context.[34]

To this point, the relations obtained and conclusions made are rather general and can be applied to any linear molecules consisting of repeating units of arbitrary complexity and coupled via the nearest-neighbor interaction. Below, we center our attention on some particular oligomers which are of interest as potential molecular wires.[19−21]

V. Comparison of Effective Coupling through Different Oligomers

It is instructive to illustrate the above general discussion by comparing the effective coupling for representative oligomer-bridges such as polyenes, polyparaphenylenes (PPP), and polyheterocycles shown in Figure 1. It is also the aim of this section to specify the analytical expression of effective coupling for a number of particular cases.

To calculate $G^{M}_{\alpha,\alpha'}(E) = \langle\alpha|(E - \hat{H}^{M})^{-1}|\alpha'\rangle$, where $\alpha, \alpha' = \alpha_{l(r)}$, we have to define the Hamiltonian $\hat{H}^{M}$ of the corresponding monomers: vinylene group ($M = C_2H_2$), phenyl ring ($M = C_6H_4$), and heterocycle ($M = C_4H_2X$), where X denotes heteroatom, e.g., sulfur, nitrogen, or oxygen.

Due to the comparatively small number of atoms, the monomer Green functions (and hence, the bridge Green function) can be found with very high accuracy, and this is one but not the only strong side of the present approach. For the sake of simplicity and to proceed analytically, we use here the standard one-electron Hückel model which operates with two types of integrals only:[35] the Coulomb integral, which determines the electron site energy at the given atom, and hopping integral, which determines the resonance electron transfer energy between neighboring atoms. Using the Coulomb integral for carbon as the energy reference point which is set equal to zero, and denoting the hopping integrals associated with double (C=C) and single (C−C) carbon−carbon bonds in polyene chain, and within monomers C_6H_4 and C_4H_2X (see Figure 1)

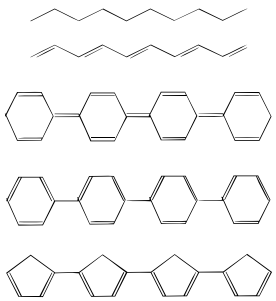

Figure 1. Oligomers of nonalternated CH-chain, polyene, polyparaphenylene in quinoid (up) and aromatic (down) conformations, and polyheterocycle.

as βe^{η} and $\beta e^{-\eta}$, respectively, for the monomers specified above we find[24,29]

$$\beta_{\mathrm{C-C}} G^{\mathrm{M}}_{\alpha_l,\alpha_r}(E) = \gamma_{\mathrm{int}} \begin{cases} \dfrac{\mathrm{e}^{\eta}}{E^2 - \mathrm{e}^{2\eta}}, \text{ vinylene group} \\ \dfrac{2\mathrm{e}^{-\eta}}{(E^2 - 2\mathrm{e}^{-2\eta})^2 - E^2\mathrm{e}^{2\eta}}, \text{ phenyl ring (quinoid form)} \\ \dfrac{2\cosh\eta}{(E^2 - 2\cosh(2\eta) + 1)(E^2 - 4\cosh^2\eta)}, \\ \qquad\qquad \text{phenyl ring (aromatic form)} \\ \dfrac{\mathrm{e}^{\eta}(E - \epsilon_{\mathrm{X}}) + \gamma_{\mathrm{X}}^2(E^2 - \mathrm{e}^{-2\eta})}{(E^2 + E\mathrm{e}^{-\eta} - \mathrm{e}^{2\eta})[(E - \epsilon_{\mathrm{X}})(E^2 - E\mathrm{e}^{-\eta} - \mathrm{e}^{2\eta}) - 2\gamma_{\mathrm{X}}^2(E - \mathrm{e}^{-\eta})]} \\ \qquad\qquad \text{heterocycle} \end{cases} \tag{19}$$

and

$$\beta_{\mathrm{C-C}} G^{\mathrm{M}}_{\alpha_l,\alpha_l}(E) = \beta_{\mathrm{C-C}} G^{\mathrm{M}}_{\alpha_r,\alpha_r}(E) = \gamma_{\mathrm{int}} \begin{cases} \dfrac{E}{E^2 - \mathrm{e}^{2\eta}}, \text{ vinylene group} \\ \dfrac{E(E^2 - \mathrm{e}^{2\eta} - 2\mathrm{e}^{-2\eta})}{(E^2 - 2\mathrm{e}^{-2\eta})^2 - E^2\mathrm{e}^{2\eta}}, \text{ phenyl ring (quinoid form)} \\ \dfrac{E[E^2 - 2\cosh(2\eta) - 1]}{(E^2 - 2\cosh(2\eta) + 1)(E^2 - 4\cosh^2\eta)}, \\ \qquad\qquad \text{phenyl ring (aromatic form)} \\ \dfrac{E(E - \epsilon_{\mathrm{X}})[E^2 - 2\cosh(2\eta)] - \gamma_{\mathrm{X}}^2(E^2 - \mathrm{e}^{-2\eta})}{(E^2 + E\mathrm{e}^{-\eta} - \mathrm{e}^{2\eta})[(E - \epsilon_{\mathrm{X}})(E^2 - E\mathrm{e}^{-\eta} - \mathrm{e}^{2\eta}) - 2\gamma_{\mathrm{X}}^2(E - \mathrm{e}^{-\eta})]}, \\ \qquad\qquad \text{heterocycle} \end{cases} \tag{20}$$

where parameter $\gamma_{\mathrm{int}} = \beta_{\mathrm{C-C}}/\beta$ represents the intermonomer resonance interaction energy; ϵ_{X} is the difference in Coulomb integrals of heteroatom X and carbon C, and γ_{X} is the X−C resonance interaction energy. In eqs 19, 20, and henceforth, the electron energy is expressed in units of β without changes in notation. Note that for polyene $\gamma_{\mathrm{int}} = e^{-\eta}$, and for PPP, and heterocyclic oligomers, parameter γ_{int} accounts for possible deviations of the carbon backbone from the ideally alternated carbon chain. For more details on the monomer Green functions see refs 24 and 29.

A. Asymptotics of Effective Coupling. Using the asymptotics of the monomer Green functions 19 in eq 13, one can easily obtain the following expressions for the decay constants of conjugated bridges represented by oligomers of polyene, PPP, and polyheterocycles (the case of CH_2-chain is also supplemented for comparison)

$$N_{\mathrm{M}} - N'_{\mathrm{M}} = \begin{cases} 1 \\ 2 \\ 4 \\ 4 \\ 3 \end{cases}$$

$$C = \begin{cases} 1 & \mathrm{CH_2}\text{ chain} \\ & \quad\text{(the McConnell result, 1)} \\ 1 & \text{polyene} \\ 2\gamma_{\mathrm{int}}\mathrm{e}^{-\eta} & \text{PPP (quinoid form)} \\ 2\gamma_{\mathrm{int}}\cosh\eta & \text{PPP (aromatic form)} \\ \gamma_{\mathrm{int}}\gamma_{\mathrm{X}}^2 & \text{polyheterocycle} \end{cases} \tag{21}$$

Equation 21 gives an interesting insight into the nature of electron tunneling across aromatic-ring-based oligomers. Firstly, it makes apparent that the noncoplanarity of monomers in the bridging molecule can substantially affect (suppress) the effective coupling, if the electron energy is not too distant from the oligomer π bands, so that the second term in the right-hand side of eq 14 can compete with the first one. The physical explanation of the effect is as follows: the twisting of aromatic rings with respect to each other reduces the degree of π conjugation. Therefore, it is expected that in noncoplanar oligomers γ_{int} is less than unity and that this parameter decreases monotonically with the increase of torsion angle between neighboring monomers.[36] This gives an increasing contribution to the decay constant which is linear in $|\ln \gamma_{\mathrm{int}}|$.

Secondly, eq 21 shows that the Peierls distortions which result in the quinoidlike geometry of carbon backbone of PPP, $\gamma_{\mathrm{int}} \sim \mathrm{e}^{\eta}$, produce no or negligible effect on the decay constant δ. By contrast, in the aromatic form of PPP, $\gamma_{\mathrm{int}} \sim \mathrm{e}^{-\eta}$, δ increases linearly with the increase of alternation parameter. This conclusion is based on the assumption that the dependence of γ_{int} on η is the same as in a polyparaphenylene chain with regularly alternating C−C bonds, where $\gamma_{\mathrm{int}} = e^{\eta}$ and $\gamma_{\mathrm{int}} = \mathrm{e}^{-\eta}$ ($\eta > 0$) in the quinoid and aromatic conformations of the carbon backbone, respectively.

And thirdly, at the energies which are far from the oligomer π bands (deep tunneling), the comparison of through-bridge effective coupling due to oligomers of PPP and heterocyclic oligomers is undoubtedly in favor of the latter, since the asymptotics of decay constant for PPP bridges is substantially larger. It should be emphasized however, that because of an unusual behavior of δ in polyheterocycles (as discussed below), the energies of truly asymptotic behavior of decay constant can be too large to be of any practical significance, while for lesser energies the decay constant for heterocyclic oligomers can turn to be much larger than that for PPP oligomers.

The asymptotic behavior of the decay constant, eq 14, with $N_{\mathrm{M}} - N'_{\mathrm{M}}$ and C defined in eq 21 and the characteristic parameters taken from literature, is visualized in Figure 2a by solid curves. The exact dependence of δ on E, eq 8, above the upper ($E^{\mathrm{edge}}_{\mathrm{upper}}$) and below the lower ($E^{\mathrm{edge}}_{\mathrm{lower}}$) π band edges is shown by bold-faced lines in the same figure. A singular-type dependence in the case of polythiophene (PTh) oligomers is in focus of the forthcoming discussion.

B. Deeps (Antiresonances) in Effective Coupling. In the examples represented by eq 19, the only monomer which possesses the "electronic contact breaking ability" expressed in eq 15 is a five-membered heterocycle. According to eqs 15 and 19, the oligomers of polyheterocycle block the transfer of electrons at two energies

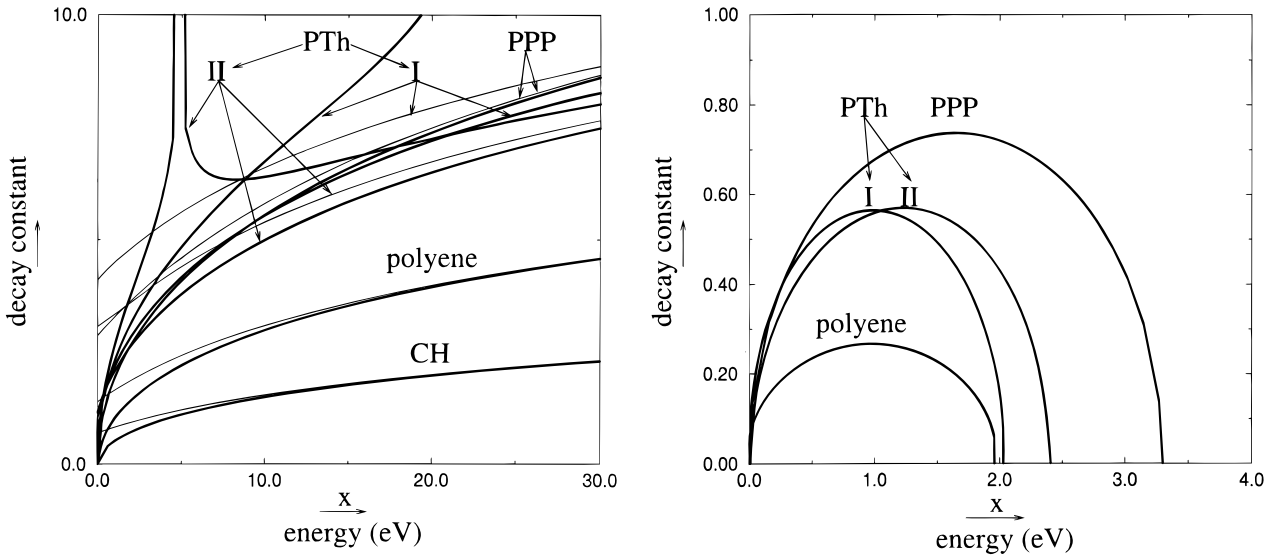

Figure 2. Decay constant $\delta(E)$ as a function of energy: **a** (to the left) above ($x = E - E_{\mathrm{upper}}^{\mathrm{edge}}$) and below ($x = |E - E_{\mathrm{lower}}^{\mathrm{edge}}|$) π electron spectrum; **b** (to the right) within HO−LU-band gap ($x = E_{\mathrm{LU}}^{\mathrm{edge}} - E$); $E_{\mathrm{upper}}^{\mathrm{edge}}$ ($E_{\mathrm{lower}}^{\mathrm{edge}}$) is the upper (lower) edge of the π electron spectrum, $E_{\mathrm{LU}}^{\mathrm{edge}}$ is the lower edge of the LU-band. Solid curves show asymptotics of decay constant defined in eqs 14 and 21. Bold-faced curves are calculated from eq 9, with parameters specified in the text.

$$E_{1,2} = -\frac{\mathrm{e}^{\eta}}{2\gamma_{\mathrm{X}}^{2}}\left(1 \pm \sqrt{1 + 4\gamma_{\mathrm{X}}^{2}\mathrm{e}^{-\eta}(\epsilon_{\mathrm{X}} + \gamma_{\mathrm{X}}^{2}\mathrm{e}^{-3\eta})}\right) \quad (22)$$

An exception is presented by the specific value of $\epsilon_{\mathrm{X}} = \mathrm{e}^{-\eta}$. In this case $G^{\mathrm{M}}_{\alpha_{\mathrm{l}},\alpha_{\mathrm{r}}}(E)$ is not equal to zero at $E = E_2 = e^{-\eta}$, so that $E_1 = -\mathrm{e}^{\eta}(\gamma_{\mathrm{X}}^{-2} + \mathrm{e}^{-2\eta})$ is the only energy at which eq 15 is fulfilled. It is interesting to note that, in heterocycles, where $\epsilon_{\mathrm{X}} = \mathrm{e}^{-\eta}$, the energy $E = E_2 = \mathrm{e}^{-\eta}$ corresponds to the monomer eigenstate with nodes at both monomer binding sites. This gives rise to an N-fold degenerate band. Nevertheless, at this particular energy the effective coupling is not equal to zero due to the contribution coming from nondegenerate π bands.

A review of literature data shows that the expected values of heteroatom parameters ϵ_{X} and γ_{X} place the solutions to eq 22 inside (E_1) and outside (E_2) of the π electron spectrum of heterocyclic oligomers. In these calculations we used two sets of sulfur parameters for thiophene ring suggested by Birnbaum et al.,[37] $\epsilon_{\mathrm{X}} = 0.25$, $\gamma_{\mathrm{X}} = 0.38$, and by Van-Catledge,[38] $\epsilon_{\mathrm{X}} = 1.11$, $\gamma_{\mathrm{X}} = 0.69$, and labeled in Figures 2 and 3 as I and II, respectively. We set $\eta = 0.1$ that is close to the experimental estimate of the C−C bond alternation parameter.[39] For parameters just specified the value of E_2 is above the upper conduction π band of polythiophene: $E_2 = -8$ [(-3.757) eV ≈ 30 eV] for $\epsilon_{\mathrm{X}} = 0.25$, $\gamma_{\mathrm{X}} = 0.38$, and $E_2 = -3.3$ [(-3.757) eV ≈ 12 eV] for $\epsilon_{\mathrm{X}} = 1.11$, $\gamma_{\mathrm{X}} = 0.69$. Though these values are far beyond the energies of experimental interest (the ionization potential of PTh is about 7 eV[40]), the singularity of the decay constant at E_2 affects the bridge mediated tunneling considerably not far from the upper edge of the π electron spectrum, see Figure 3a.

The singular-type dependence of δ and, correspondingly, antiresonance-type behavior of T_{DA} shown in Figure 2a and 3a, respectively, are in a sharp distinction with predictions of the McConnell model (curves labeled CH), as well as with the dependence of these same quantities on the electron energy in the case of polyene and PPP oligomers shown in the same figures.

For the parameters indicated above the energy of zero effective coupling E_1 is within the gap between the HO-1 and HO bands (HO: highest occupied) of polythiophene oligomers. This band gap is very narrow[24] and for this reason one can expect that near E_1 the switching ability of the kind illustrated in Figure 3a will be pronounced much more sharply. In the other words, zeros of effective coupling that are close to the oligomer electron carrying states can reveal themselves as antiresonances in, e.g., the conductance of molecular wires.

Unlike eq 15, eq 18 cannot be fulfilled for a five-membered heterocycle, as well as for vinylene group, and phenyl ring in the quinoid conformation. The calculation of bilinear combination 17 with the use of expressions 19 and 20 for phenyl ring in the case of aromatic geometry yields (for $\eta \neq 0$)

$$\beta^{2}_{\mathrm{C-C}}[G^{\mathrm{C6H4}}_{\alpha_{\mathrm{l}},\alpha_{\mathrm{l}}}(E)G^{\mathrm{C6H4}}_{\alpha_{\mathrm{r}},\alpha_{\mathrm{r}}}(E) - (G^{\mathrm{C6H4}}_{\alpha_{\mathrm{l}},\alpha_{\mathrm{r}}}(E))^{2}] = \frac{\gamma^{2}_{\mathrm{int}}(E^{2} - \mathrm{e}^{2\eta})(E^{2} - \mathrm{e}^{-2\eta})}{(E^{2} - 2\cosh(2\eta) + 1)^{2}(E^{2} - 4\cosh^{2}\eta)} \quad (23)$$

i.e., the solutions to eq 18 are given by

$$E'_{1,2} = \pm\sqrt{2\cosh(2\eta) - 1} \quad (24)$$

It is seen that the above energies coincide with poles of $G^{\mathrm{C_6H_4}}_{\alpha_{\mathrm{l}},\alpha_{\mathrm{r}}}(E)$. The monomer eigenstates with energies E'_1 and E'_2 are doubly degenerate and one of two states at each of these energies has a node at the monomer binding sites. Therefore, the Green function $G^{\mathrm{C_6H_4}}_{\alpha_{\mathrm{l}},\alpha_{\mathrm{r}}}(E)$ has only simple poles $E'_{1,2}$, see eq 19. The full monomer π electron spectrum containing six levels is restored by bilinear combination 23, where the poles at energies E'_1 and E'_2 are of the second order.

In accordance with eqs 9 and 10, if $N \neq 1$, the effective coupling falls to zero at energies 24 lying within very narrow gaps between HO-1 and HO bands, and LU and LU+1 bands (LU; lowest unoccupied). In the quinoid conformation of PPP oligomers these gaps are absent.[29]

Strictly speaking, the concept of effective coupling fails at energies which are close to the electron levels of bridging molecule. For PPP oligomers it suggests, in particular, that $T_{\mathrm{DA}} = 0$, if $E = E'_{1,2}$, at any length except $N = 1$. Such an exception is, of course, unphysical. Nevertheless, as mentioned above one can expect anomalies in observables related to zeros of effective coupling. For example, the strict nonperturbative

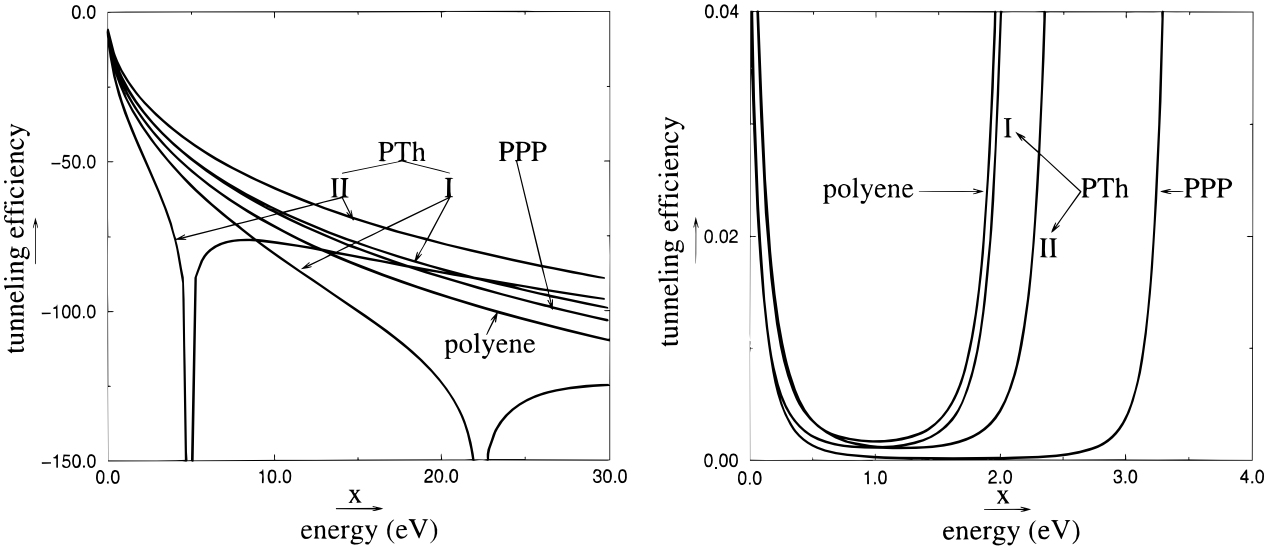

Figure 3. Through-bridge tunneling efficiency, $(\beta_{C-C}T_{DA}/\bar{\beta}^2)^2$, as a function of energy, calculated with the use of δ shown in Figures 2a and 2b, and $N = 24$ for CH chain (only in 3a], i.e., to the left); indistinguishable from polyene curve), $N = 12$ for polyene chain, and $N = 6$ for aromatic-ring chains of polyparaphenylene and polythiophene.

treatment of zero field conductance of PPP oligomer (in the aromatic conformation) which is spanned between metal electrodes predicts a sharp decrease of this quantity from nearly maximal to zero value at the Fermi energy close to values,[23] including the case of $N = 1$.

C. Through HO−LU-Band Gap Coupling. Here, we specify the expressions of effective coupling for energies within the gap between HO and LU bands.

The oligomers of polyene are the simplest stable of linear conjugated molecules. Their π electron spectrum contains only one gap between the valence (filled) and conduction (unfilled) bands. Defined in the limit $N \rightarrow \infty$ the HO−LU-band gap is of value 4 $\sinh|\eta|$ in units $|\beta|$.[41] It is symmetric with respect to $E = 0$, and hence, the ingap energies are $|E| < 2 \sinh |\eta|$.

With regard to the Green function matrix elements for the vinylene group given in eqs 19 and 20, expression 10 takes the form

$$T_{DA} = \frac{\bar{\beta}^2}{|\beta|}\frac{2 \sinh \delta}{|e^{-2\eta} - e^{\delta}|}e^{-\delta N} \tag{25}$$

where, according to eq 8,

$$\delta = \ln {}^1/_2(|2 \cosh(2\eta) - E^2| + \sqrt{[2 \cosh(2\eta) - E^2]^2 - 4}) \tag{26}$$

For $\eta > 0$, the above equations are valid for both ingap and out-of-π-band energies, provided the condition $e^{\delta N} \gg 1$ is satisfied. If $\eta < 0$ and $N > e^{2\eta}/(1 - e^{2\eta})$, there are two in-gap levels in the π electron spectrum of polyenes.[23] Therefore, for energies close to these levels, the preexponential factor in eq 25 has to be re-defined (in the particular context of the electron-transfer process), but an exponential dependence of the effective coupling on N with the decay constant defined in eq 26 is still applicable (see the discussion in section II).

For ingap energies, $|E| < 2 \sinh \eta$ and $\eta > 0$, the decay constant is a nonmonotonic function of energy that takes its maximal value δ_m in the middle of the gap and symmetrically decreases to zero value when the electron energy goes towards the conduction (valence) band boundary. Qualitatively, the preexponential factor T^0_{DA} exhibits the same dependence on energy with the maximal value $T^0_{DA}|_{max} = \bar{\beta}^2/|\beta|$ at $E = 0$.

Outside π bands, $|E| > 2 \cosh \eta$, and for both signs of the alternation parameter the preexponential factor saturates with the increase of energy at the value $\bar{\beta}^2/|\beta|$, while δ increases monotonously. The asymptotic behavior of T_{DA} for polyene bridges is the same as for nonalternated carbon chain, see eqs 14 and 21.

Qualitatively, the behavior of the decay constant and effective coupling within the HO−LU-band gap described above is identical for all alternant (all carbon) oligomers. The dependence of δ and T_{DA} on E for polyene and PPP oligomers is represented in Figures 2b and 3b. We set $\eta = 0.1333$ for polyenes,[38] and $\eta = 0.1$, $\gamma_{int} = 1.0$, for PPP oligomers assumed to be in an aromatic conformation.

Note that with $\beta = -3.757$ eV[39] used in our calculations, these parameters give a good agreement with the experimental estimates of HO−LU-band gaps in polyacetylene (1.8 eV[42]) and polyparaphenylene (3.4 eV[43]); just as parameters used above for polythiophene oligomers (also represented in Figures 2b and 3b) agree well with the observed value 2 eV.[44] Precisely, we obtain HO−LU-band gaps equal to 2, 3.3, 2.05 (I), and 2.38 (II) electron-volts for oligomers of polyene, polyparaphenylene, and polythiophene, respectively.

Furthermore, since for alternant oligomers $G^M_{\alpha_l,\alpha_l}(E)$ takes zero value in the middle of the HO−LU-band gap, for all such oligomers covered by the structural formula M−M−···−M we obtain $T^0_{DA}|_{max} = \bar{\beta}^2/|\beta|$ at $E = 0$, $e^{\delta m}|\beta_{C-C}G^M_{\alpha_l,\alpha_r}(0)|^{\pm 1}$, where sign "+" or "−" has to be taken depending on whether the value of $|\beta_{C-C}G^M_{\alpha_l,\alpha_r}(0)|$ is larger or smaller than unity. To recall, the case of the gap closing, $|\beta_{C-C}G^M_{\alpha_l,\alpha_r}(0)| = 1$, is out of the consideration.

We can prove that in any band gap of symmetric oligomers, $G^M_{\alpha_l,\alpha_l}(E) = G^M_{\alpha_r,\alpha_r}(E)$, at the energy satisfying equation

$$G^M_{\alpha_l,\alpha_l}(E) = 0 \tag{27}$$

the preexponential factor attains its maximum $\bar{\beta}^2/|\beta|$, whereas the decay constant takes the value $\ln|\beta_{C-C}G^M_{\alpha_l,\alpha_r}(E)|^{\pm 1}$. Thus,

$$T_{DA} = \frac{\bar{\beta}^2}{|\beta_{C-C}|}|\beta_{C-C}G^M_{\alpha_l,\alpha_r}(E)|^{\pm N} \tag{28}$$

where E is a solution to eq 27 in the given band gap, and "+" corresponds to $|\beta_{C-C}G^{M}_{\alpha l,\alpha r}(E)| < 1$, and "−" corresponds to $|\beta_{C-C}G^{M}_{\alpha l,\alpha r}(E)| > 1$. It is interesting to notice the formal similarity between the equation obtained and the asymptotic expression of the effective coupling, see discussion above eq 14.

Equations 27 and 28 give a useful estimate of the effective coupling. For the HO−LU-band gap of alternant oligomers, where the effective coupling as a function of energy is symmetric with respect to the middle of the gap, it corresponds to the minimal value of T_{DA}. In other cases it gives a value that is usually very close to the minimum of the effective coupling in the given gap, as, e.g., for the HO−LU-band gap of oligothiophenes shown in Figures 2b and 3b.

One can easily see from Figures 2b and 3b that in the middle of the gap the tunneling efficiency across polyene and polythiophene bridges with the same number of carbons in a row (N_C) is nearly identical, whereas it is lower for oligomers of polyparaphenylene, in clear correlation with the width of the band gap. (Different molecules of equal length is a kind of exotic. It is more informative therefore, to compare oligomers with equal N_C's. In the presented examples, such oligomers are close in their lengths.) The data on δ_m for these and a number of other oligomers are summarized in ref 18.

It is of interest to compare the above results with an estimate that can be obtained from the through-rectangular-barrier tunneling probability mentioned already in section II. For this purpose we replace the barrier hight V by the half-width of the HO−LU-band gap, $\Delta_{HL}/2$ (in units $|\beta|$), and the effective mass of electron m^* by $\hbar^2/(2|\beta|\alpha^2)$. The suggested replacement is natural and can be supported by strict arguments. In such a representation, the effective coupling takes the form

$$T_{DA} = e^{-\sqrt{(\Delta_{HL}/2 - E)}N} \tag{29}$$

where $0 \le E \le \Delta_{HL}/2$, and $E = 0$ corresponds to the middle of the gap.

With the parameters used in Figures 2b and 3b, eq 29 gives the following values of the decay constant $\delta_m = 0.516$, 0.663, and 0.510, 0.562 which are in a good agreement with the values $\delta_m = 0.533$, 0.737, and 0.564, 0.569 calculated from eq 10 for oligomers of polyene, polyparaphenylene, and polythiophene, models I and II, respectively.

It should be stressed, however, that eq 29 does not describe the above discussed anomalies of the effective coupling as a function of energy. The definition of the decay constant given in eq 29 is also incorrect in the case of the existence of in-gap states. So, in general, for the purpose of estimating the efficiency of through-molecule tunneling the model of rectangular barrier should be used with a good deal of precaution.

D. Discussion of Some Related Results. A number of advantages of the Green function approach to the description of the electron-transfer phenomena has been repeatedly emphasized in the literature.[5,6,11,14] However, in the present context this has been actually enjoyed only in the development and application of efficient computational schemes.[6,14,45] In relevant analytical treatments published thus far, the Green function technique has been used either in a perturbation-theory manner[46] or for a detailed analysis of the McConnell bridge model in various contexts.[2,6,11] The above discussion shows that the power of the Green function method can result in the exact and, importantly, easily handled analytical expressions for the effective coupling that take into account essentials of the π electronic structures.

In the particular case of polyene bridges, a complicated expression of the effective coupling which, however, can be transformed to eqs 25 and 26 was found earlier.[6]

We have noticed above that the tunnel conductance of a metal-molecular heterojunction is proportional to the square of effective coupling for the given molecule. The quantum conductance of the one-dimensional tight-binding model of molecular heterojunctions has been discussed by Joachim and Venuesa,[30] whose model was restricted to polyenes described by the same Hamiltonian as used here and in ref 6. They found: "In the homo-lumo gap, we find that the variation of $t(E_F)$ with N can be approximated for large N by an exponential law

$$t(E_F) = t_0 \exp[-\gamma(2N - 2)] \tag{5}$$

where t_0 is a function of β/a, β/h, α/β and γ is a function only of β'/β".

The correspondence with our notations is as follows: $t(E_F)$ is up to a factor $(T_{DA}/\beta_{C-C})^2$, $E_F \equiv |\beta|E$, $\beta' \equiv \beta \exp \eta$, $\beta \equiv \beta \exp(-\eta)$, $\alpha \equiv \bar{\beta}$, $\gamma \equiv \delta$, a is on-site electron energy at carbons, and parameter h represents a 1D electronic band used by Joachim and Vinuesa[30] to model the source and drain electrodes in molecular contacts. In a more general approach, ref 11 parameter h is known to enter the spectral density. The square of the spectral density is simply a factor in the expression of the tunnel conductance, see, e.g., ref 11.

Thus, eq 5 of ref 30 can be directly compared with our eq 25. Unlike the latter, neither the exponential decay constant nor the preexponential factor were defined in ref 30.

To avoid confusion, we note also: (i) the on-site energy a can be taken as the reference point of energy and consequently, it can be set equal to zero; thus, according to the above eq 5 the tunnel conductance depends on a parameter of infinite value; [in fact a enters the expression of $t(E_F)$ as $(E_F - a)$]; (ii) the most principal dependence of the tunnel conductance on the Fermi energy, i.e., the dependence of t_0 and γ on E_F was neither mentioned nor properly indicated in eq 5.

VI. Concluding Remarks

We have proved that tunneling across a chain of monomers of arbitrary complexity coupled to each other via the nearest-neighbor hopping integrals is described by an exponential law of exactly the same form as the handbook formula for the tunneling probability through a rectangular barrier. An important distinction, however, is that we find the modulus of imaginary part of the complex wave vector appearing in the exponent not from the effective-mass-type (parabolic) dispersion law with an ad hoc choice of the barrier hight but from the exact relation between the energy and wave vector for the given electronic structure of the molecule.

The tunneling efficiency is found to be dependent on the full spectrum of the oligomer one-electron states, and not only on the width of the particular band gap through which tunneling occur. Nevertheless, with the interrelation between the phenomenological parameters (barrier hight, effective mass, and lattice constant) and the parameters of Hamiltonian of the molecule, which are suggested in this work, the function 29 is shown to restore well the dependence of the effective coupling on energy, to the least in the examples given.

The dependence of the effective coupling and its exponent (decay constant) on the molecular electronic structure is illustrated for simple (polyenes) and more complex (oligophenylenes, oligothiophenes) linear molecules. Contrary to drastic

distinctions between the parabolic dispersion law and the band structure of real conjugated oligomers (consisting of a number of bands divided by band gaps) the above referred formula for the tunneling probability gives, as demonstrated, a good quantitative estimate of the decay constant of the through HO−LU-band gap effective coupling. At the same time, the barrier-type model does not really lead to the understanding of the relationship between the molecular electronic structure and through-molecule tunneling efficiency, and moreover, it is quite misleading in the case of the predicted anomalies of the effective coupling and when the π electron spectrum contains ingap states.

It is shown that for oligomers built up of monomers such that either eq 15 or eq 18, or both, are fulfilled, the decay constant of effective coupling in DBA systems is a singular function of energy. This implies that in addition to a smooth parabolic-type behavior of the effective coupling as a function of energy (as that illustrated here for the HO−LU-band gap) the conjugated oligomers consisting of the monomers, whose Green functions obey eqs 15 and 18, possess anomalous switching abilities. In the context of the molecular wire conductance, this leads to a conclusion that in response to changes of the Fermi energy within the π electron spectrum the ohmic conductance can drop to zero value at certain energies. The predicted variety of switching properties of conjugated oligomers and a comparative ease of their processing suggest a number of appealing applications in the field of molecular electronics. From this point of view an important message of the above analysis is that the effective coupling can be examined at the monomer level. Thus, the charge transfer properties of DBA and related systems can be overseen and designed essentially on the basis of the monomer electronic structure.

It must be stressed that the model adopted is restricted to the π electron subsystem of a rigid and regular carbon backbone. Certainly, as such it cannot pretend to give an accurate description of real molecules. However, since the results obtained are exact in the model sense, they indicate the basic trends of the nonadiabatic electron transfer across conjugated molecules that have to be elaborated further in a number of aspects. In particular, we expect that the inclusion of σ electron subsystem will result in negligible corrections to the value of the through HO−LU-band gap effective coupling. But for other band gaps, as well as outside one-particle π bands, the role of σ-states manifold in determining the effective coupling cannot be ignored.

Throughout all the above discussion we have extensively used the understanding of one-particle π electron spectra of conjugated oligomers developed in our previous analysis.[24,29] The results of the present work combined with findings of cited papers suggest a convenient tool for quick and reasonable evaluation of the quantity playing the basic role in the charge-transfer phenomena.

As was demonstrated in ref 24 and 29, see also references therein, the HO−LU-band gap of linear conjugated molecules, in particular, oligophenylenes and oligothiophenes, depends on the character of the carbon backbone geometry, aromatic or quinoid, with a pronounced tendency to a smaller band gap in conjugated oligomers with the quinoid structure. Also, it was shown that in the case of quinoid geometry the appearance of ingap states due to perturbation (say, by extra charging or excitation of the molecule) is more likely, than in the aromatic conformation of carbon backbone. For example, in polyenes with the reversed alternation of C−C bonds (quinoid conformation) and the number of double bonds larger, than $e^{2\eta}/(1 - e^{2\eta})$, $\eta < 0$, the π electron spectrum does contain two ingap states characterized by preferable distribution of the electron density near the chain ends.[23] The perturbation-induced HO−LU-band gap narrowing/closing and the appearance of ingap states are the likely mechanisms of a strong suppression/enhancement of the electron transfer across the molecule. These are readily foreseeable in the framework of the suggested approach by examining changes in the effective coupling in response to an appropriate modification of the molecular Hamiltonian.

In conclusion, on the basis of a tight-binding Hamiltonian known to give a reasonable description of conjugated systems and using the Green function technique we have derived the exact analytical expression of the through-bridge effective coupling for conjugated oligomers of the kind M−M−···−M, a wide class of organic molecules considered as perspective candidates to be used in molecular electronics. This is the central result of the work. It has been examined in many details: the asymptotics and zeros of through band-gap effective coupling have been found, as well as the expressions of this quantity for particular oligomers. It is also shown that for the Fermi energy in the middle of the HO−LU-band gap of alternant oligomers the effective coupling takes an especially simple form. New physics and some applied aspects of the results obtained have been discussed.

Acknowledgment. The authors are greatly indebted to Dr Lyuba Malysheva for careful reading the manuscript, valuable comments, and discussions. We thank Prof. Karl-Frederik Berggren for his encouraging interest to this work supported in part by the Royal Swedish Academy of Sciences and the Swiss National Science Foundation under the program CEEC/NIS.

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(33) It is instructive to note that this purely mathematical result, which places zeros of the Green function $G^{M}_{\alpha_l,\alpha_r}(E)$ of monomer M in the forbidden energy zones of the oligomer constructed of such monomers, tells us that if a bridge possesses the property of complete switching, it is "inherited" from monomers and can be expected only in a band gap of the oligomer.

(34) One of implications of zero effective coupling is that in such a case, the conductance of molecular wire in the quantum-point-contact arrangement will also be equal to zero. This is shown by calculations (to be published elsewhere) which rigorously take into account the oligomer-contact interaction within an approach similar to that used in refs 11, 14, 31.

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