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a comparison of the Franz two-band model with exact results**

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## Tunneling through molecular wires: a comparison of the Franz two-band model with exact results

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### 1 Introduction

Despite a substantial effort that has been undertaken to relate the electron transmitting properties of molecular wires with their electronic structure [1–8], the use of phenomenological formulas dominates the electrical characterization of metal-molecule(s)-metal (MMM) contacts, see [9] and references therein. Here, under the term “molecular wires” we define organic oligomers as having the structure  $M-M-\dots-M = (M)_N$ , which can provide electrical contact between metal or semiconductor electrodes. Oligomers of polyene, alkane, and polyparaphenylene are one of many other molecules commonly used in MMMs.

Probably, the most simple and physically sound description of electron (or/and hole) tunneling through organic oligomers suggests the Franz two-band model [10]. It relates the electron imaginary wave vector  $i\kappa$  to electron energy  $E$  within the gap between the valence and conduction bands. It reads

$$\kappa^2 = \frac{2m^*}{\hbar^2} \frac{(E_b - E)(E - E_v)}{E_g} = \frac{2m^*}{\hbar^2} \Delta E \left( 1 - \frac{\Delta E}{E_g} \right), \quad (1)$$

where energy  $\Delta E = E_b - E$  is referenced to the conduction-band bottom  $E_b$  showing that in the vicinity of  $E_b$ , i.e., when  $\Delta E \ll E_g$ , the Franz model is practically equivalent to tunneling of a free particle with impulse  $\hbar k$  and mass  $m^*$  through a rectangular barrier. The same is true with respect to the holes, if the energy is close to the top of valence band, denoted as  $E_v$ .

According to Eq. (1), the WKB tunneling probability through a molecular wire with the band gap  $E_g$  and length  $d$  is given by  $T_{\text{WKB}}(E) = \exp[-2\kappa(E)d]$ . This translates into the ohmic tunnel current under

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the applied voltage  $V$ ,  $eV \ll \Phi$ , proportional to  $T_{\text{WKB}}(E = E_F) = \exp [(-2\kappa(E_F) d)]$  with the tunneling constant  $\kappa(E_F)$  defined as

$$\kappa^2(E_F) = \frac{2m^*}{\hbar^2} \Phi \left( 1 - \frac{\Phi}{E_g} \right), \quad (2)$$

where  $\Phi = E_b - E_F$  signifies the relative position of the Fermi energy  $E_F$  with respect to the conduction band bottom.  $\Phi$  is the potential barrier for electrons entering the molecule from contacting electrodes.

Few comments are in order. Although it was not explicitly stated by its inventor, formula (1) implies: (i) the quadratic dispersion relation for electrons in the conduction band and for holes in the valence band and (ii) equal effective masses of both types of charge carriers. These assumptions limit the applicability of the model but the actual restrictions have not been clarified. In this communication, we focus on the range of the applicability of dispersion relation (1) for MMM contacts. Specifically, we will show that the use of the Franz interpolation formula for a description of wide-gap tunnel contacts overestimates  $\kappa(E)$ , if  $E_g$  is of the order or larger than the conduction (valence) band width  $W$ . Also, the meaning of the apparent effective mass  $m^*$ , as it is inferred from measurements of  $\kappa(E_F)$ , will be specified in terms of the parameters of the molecular wires.

## 2 The Franz dispersion relation versus the exact dispersion relation

At zero voltages, the probability of tunneling through a molecular wire is governed by an exponential factor  $\exp [-2\delta(E) N]$ , where  $N$  is the number of monomers [for PE, AE, and PPP oligomers,  $N = N_C/2$ ,  $(N_C - 1)$ , and  $N_C/6$ ],  $\delta(E)$  is calculated from the electronic band structure [11]. In the tight-binding approximation, the interrelation between the electron energy and (dimensionless) wave vector is given by

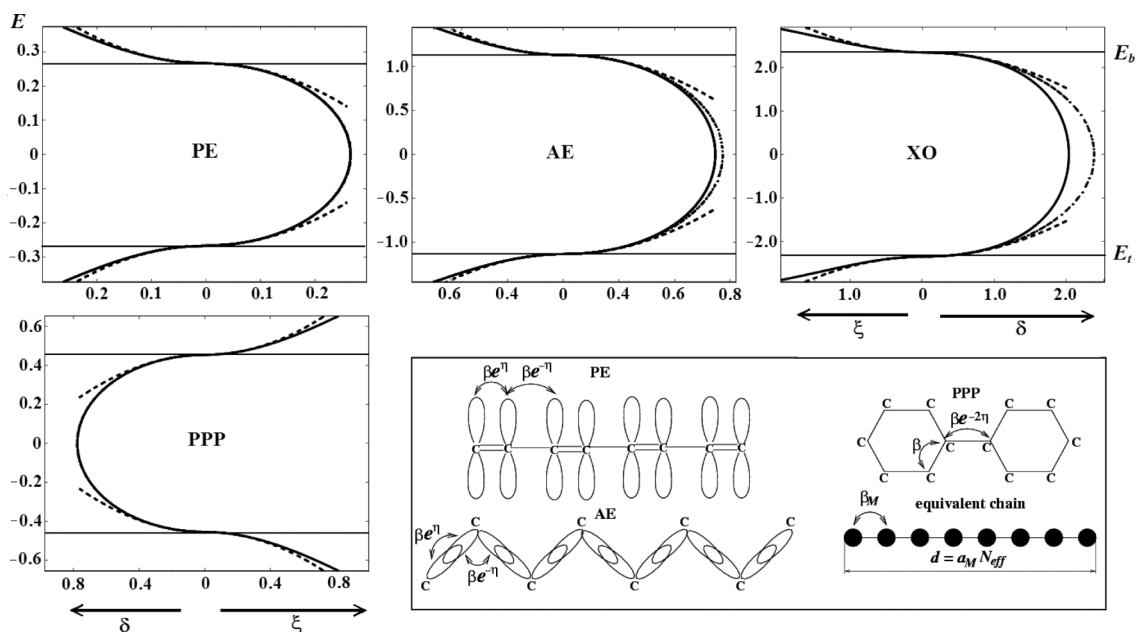
$$\cos \xi = f(E), \quad (3)$$

where  $f(E)$  is a certain functional of the monomer Green's function, and  $\xi$  takes real values from 0 to  $\pi$  within the bands, whereas in the band-gap energy intervals,  $\xi$  should be replaced by  $i\delta$  or  $\pi + i\delta$  [1]. Figure 1 represents the dispersion relation for a part of the valence and conduction bands, and the gap between them. In calculations, we have used the sets of tight-binding parameters which reasonably reproduce the  $\pi$  electronic structure of oligomers of polyene (PE), polyparaphenylene (PPP) [4], and two bands of extended  $\sigma$  states of alkane oligomers (AE) [5]. Solid lines correspond to the exact dependencies  $E(\xi)$  and  $E(\delta)$ , whereas dashed lines show parabolic approximations for  $E(\xi)$  and  $E(\delta)$  near the band edges. For example, near the conduction band bottom  $E = E_b + \beta_M \xi^2$  and  $E = E_b - \beta_M \delta^2$ . For each type of oligomers, the quadratic dispersion parameter  $\beta_M$  was determined from the best fit to the exact calculations; the obtained values of  $\beta_M$  are summarized in Table 1. With the use of this parameter and the lattice constant  $a_M$ , see Fig. 1, we can represent the Franz interpolation formulas (1) and (2) in the form

$$\delta_{\text{appr}}^2(E) = \frac{\Delta E}{\beta_M} \left( 1 - \frac{\Delta E}{E_g} \right) \Rightarrow \delta_{\text{appr}}^2(E_F) = \frac{\Phi}{\beta_M} \left( 1 - \frac{\Phi}{E_g} \right), \quad (4)$$

where, similarly to Eq. (2),  $\Phi = E_b - E_F$ . In Fig 1,  $\delta_{\text{appr}}(E)$  graphs are shown by dashed-dotted lines.

Equation (4) is in excellent agreement with the exact dispersion relation (3), if  $E_g$  is smaller than  $W$ . For PE and PPP oligomers, associated with narrow-gap ( $E_g/W \approx 0.3$ ) and mid-gap ( $E_g/W \approx 0.75$ ) semiconductors, see Table 1, approximate dependence of  $\delta(E)$  cannot be distinguished from the exact one in Fig. 1. For AE oligomer exemplifying wide-gap semiconductors ( $E_g/W \approx 2$ ), the difference between  $\delta_{\text{appr}}(E)$  and  $\delta(E)$  is noticeable only in the mid gap. Example of XO ( $E_g/W = 6.4$ ) is given to illustrate the tendency rather than to exemplify a real molecule. According to our estimates, for large-gap MMM contacts, maximal tunneling constant  $\delta_{\text{max}} \sim \ln(E_g/W)$  whereas Eq. (4) and Eq. (1) gives  $\delta_{\text{max}} \sim \sqrt{E_g/\beta_M}$ .



**Fig. 1** Dispersion relation (3) in and near the region of fundamental band gap is shown by solid lines; energy scale is in units of  $|\beta|$ , and the electron energy is referenced to the mid of the gap. Parabolic dashed curves  $E(\xi)$  and  $E(\delta)$  are determined by the values of (positive) parameter  $\beta_M/|\beta|$ , see text. Using these values,  $\delta(E)$  was calculated according Eq. (4) (dashed-dotted curves). Abbreviations PE =  $(\text{CH}=\text{CH})_N$  ( $N = N_C/2$ ), AE =  $(\text{CH}_2)_{N_C}$  ( $N = N_C - 1$ ), and PPP =  $(\text{C}_6\text{H}_4)_N$  ( $N = N_C/6$ ) stand for oligomers of polyene, alkane, and polyparaphenylene, respectively; XO =  $(\text{CH}_2)_{N_C}$  ( $N = N_C - 1$ ) signifies a hypothetical oligomer with a large-band-gap/band-width ratio. Inset: Schematic representation of PE, AE, and PPP oligomers with the same number of C atoms  $N_{\text{eff}}$  in row (eight). Hopping integrals between double and single C–C bonds (PE), between  $\text{sp}^3$  orbitals directed along the same and neighboring covalent bonds (AE), and between C atoms within the same benzene ring and the nearest-neighbor rings are denoted in such a way that  $\exp(-2\eta)$  determines the ratio of the inter-monomer to intra-monomer hopping integrals in the respective tight-binding Hamiltonians. *Equivalent chain* has the same length, as the respective oligomer with  $N_{\text{eff}}$  carbons in row, and the same dispersion relation near the band bottom (top), as the conduction (valence) band of the oligomer.

The observed regularities agree well with the following consideration. For  $\Delta E/W \ll 1$ , the behavior of  $\delta$  as a function of energy is controlled by the quadratic dispersion near the conduction band bottom. The same is true regarding dependence  $\delta(E)$  near the top of valence band, where it is controlled by the dispersion relation  $E = E_t - \beta_M \xi^2$ . Parabolic approximation is reasonable up to about half of the band width, which explains why we see divergence between approximate and exact values of  $\delta$  only for  $E_g/W > 1$ .

**Table 1** Interrelation between the electronic structure of molecular wires and the maximal tunneling constant, dimensionless  $\delta_{\text{max}}$  and dimensional  $\kappa_{\text{max}} = \delta_{\text{max}}/a_M$ , calculated with the tight binding parameters suggested in [4, 5].  $\exp(-2\eta)$  determines the ratio between smaller and larger energies of resonance electron transfer, see inset in Fig. 1. Other quantities are defined in the text. For shorter oligomers ( $N_C < 8$ ),  $a_M$  (and hence, the apparent effective mass  $m^* = \alpha m_e$ ) is a weakly varying function of molecular length.

	$e^{-2\eta}$	$E_g$ (eV)	$W$ (eV)	$\beta_M$ (eV)	$\delta_{\text{max}}$	$a_M$ (Å)	$\kappa_{\text{max}}$ (Å <sup>-1</sup> )	$m_M/m_e$	$\alpha$ ( $N \gg 1$ )
PE	0.77	2.00	6.58	7.04	0.27	1.24	0.22	0.35	0.30
PPP	0.92	3.42	4.56	1.42	0.78	1.06	0.74	2.39	0.39
AE	0.34	8.51	4.38	1.66	1.08	1.29	0.84	1.38	1.17
XO	0.14	17.66	2.76	0.80	2.00	1.29	1.55	2.86	1.69

### 3 What is the apparent effective mass?

Note, it is not the tunneling distance  $d$  but rather the number of monomers that appears in calculations of the probability of through molecule electron tunneling [11]. To make an instructive comparison of  $\delta_{\text{appr}}(E_{\text{F}})$  with  $\kappa(E_{\text{F}})$ , we introduce a lattice constant  $a_{\text{M}}$  such that  $d = a_{\text{M}} N_{\text{eff}}$ , see inset in Fig. 1. Under the *tunneling length* we understand the distance between the carbons at the molecule termini along the molecular axis. Calculated values of  $a_{\text{M}}$  (optimized molecular geometry was found with the use of BP86/6-31G\* method) are represented in Table 1. Obviously, the spectrum of a tight-binding chain with hopping integral  $-\beta_{\text{M}}$ , at the bottom and top of the band, has the same dispersion relation as that was found above for the oligomers. Using this equivalence, we can introduce electron effective mass  $m_{\text{M}}$  in oligomers using the standard relation between the effective mass and hopping integral in the tight-binding chain

$$m_{\text{M}} = \frac{\hbar^2}{2\beta_{\text{M}}a_{\text{M}}^2}. \quad (6)$$

Now, comparing  $\exp[-2\kappa(E)d]$  with  $\exp[-2\delta(E)N]$  and representing notation in Eq. (1) as  $m^* = \alpha^2 m_{\text{e}}$ , we can conclude that the coefficient in front of the free electron mass  $m_{\text{e}}$  can be calculated as

$$\alpha = \sqrt{\frac{m_{\text{M}}}{m_{\text{e}}} \frac{N}{N_{\text{eff}}}}, \quad (7)$$

where  $N_{\text{eff}} = 2N - 1$ ,  $N$ , and  $4N - 1$  for PE, AE (XO), and PPP oligomers, respectively.

It is worthwhile mentioning that the apparent effective mass does not repeat the trend of the  $m_{\text{M}}$ . For example, tunneling through PPP oligomers is more efficient, than tunneling through AE oligomers, because  $m^*$  of PPPs is smaller than that of AEs. However, the relation between the respective masses, which come out from the band structure calculations, is just the opposite,  $m_{\text{M}}(\text{PPP}) > m_{\text{M}}(\text{AE})$ .

In conclusion, we have suggested a scheme that allows one to classify molecular wires as electrical current conductors, by using only two inherent parameters of the wire: the lattice constant of the equivalent tight-binding chain  $a_{\text{M}}$  and the quadratic dispersion parameter  $\beta_{\text{M}}$ . These two parameters are needed to determine one phenomenological parameter  $m^*$  in the Franz formula. They can be found from the first principle calculations with any affordable accuracy. Applications of the scheme are limited to the case of equal effective masses of electrons and holes. A generalization that covers tunnel contacts with light and heavy charge carriers will be reported elsewhere.

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