

# Electronic supplementary information for Important issues facing model-based approaches to tunneling transport in molecular junctions

Ioan Bâldea \*  $a^\ddagger$

**Keywords:** molecular electronics; electron transport; single-molecule junctions; tunneling barrier; tight binding models; transition voltage spectroscopy

## Model Hamiltonians in second quantization

The second-quantized tight-binding Hamiltonian of model (iv) presented in the main text has the form

$$H_1 = \sum_{r=1}^N \underbrace{(\varepsilon_B - eV_r)}_{\varepsilon_B^r} c_r^\dagger c_r - t_h \sum_{r=1}^{N-1} (c_r^\dagger c_{r+1} + c_{r+1}^\dagger c_r) \quad (S1)$$

where  $c^\dagger$  and  $c$  are creation and annihilation operators for electrons whose spin is omitted for simplicity. It is schematically depicted in Fig. 2a of the main text.

To illustrate that model (iii) presented in the main text represents a limiting case of model (iv), we give below the transmission function computed exactly and within the sequential tunneling approximation for the case  $N = 2$

$$T_{\text{exact}}(\varepsilon) = \frac{\Gamma^2 t_h^2}{\left[ (\varepsilon - \varepsilon_B)^2 - t_h^2 - \Gamma^2/4 \right]^2 + \varepsilon_B^2 \Gamma^2}$$

$$\xrightarrow{t_h, \Gamma \ll \varepsilon_B} T_{\text{superexchange}}(\varepsilon) = \frac{\Gamma^2 t_h^{2(N-1)}}{(\varepsilon - \varepsilon_B)^{2N}} \Big|_{N=2} \quad (S2)$$

The second-quantized tight-binding Hamiltonian of model (v) described in the main text and schematically presented in Fig. 2b of the main text reads

$$H_2 = \varepsilon_B \sum_{r=1}^N \sum_{j=1}^6 c_{j,r}^\dagger c_{j,r} - t_i \sum_{r=1}^{N-1} \sum_{j=1}^6 (c_{j,r}^\dagger c_{j,r+1} + c_{j,r+1}^\dagger c_{j,r})$$

$$- t (c_{4,1}^\dagger c_{1,2} + c_{1,2}^\dagger c_{4,1} + c_{4,2}^\dagger c_{1,3} + c_{1,3}^\dagger c_{4,2} + \dots) \quad (S3)$$

where  $t_i$  and  $t$  stand for intra- and inter-ring hopping integrals, respectively.

<sup>a</sup> Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany.

<sup>‡</sup> E-mail: ioan.baldea@pci.uni-heidelberg.de. Also at National Institute for Lasers, Plasmas, and Radiation Physics, Institute of Space Sciences, RO 077125, Bucharest-Măgurele, Romania

## Analytical results for the case of a Gaussian transmission

The Gaussian transmission represents an important particular case ( $\delta = 2$ ) of the case of arbitrary  $\delta$  discussed in the main text

$$T_g(E) \equiv T_\delta(E)|_{\delta=2} = \exp \left[ -\frac{(E - \varepsilon_B)^2}{\Delta^2} \right] \quad (S4)$$

For this case, occasionally studied in the literature,<sup>1,2</sup> one gets

$$I(V) \stackrel{\Delta \ll \varepsilon_B}{\approx} I^{\text{approx}}(V) \equiv G \frac{\Delta^2}{e\varepsilon_B} \sinh \frac{eV\varepsilon_B}{\Delta^2} \quad (S5)$$

$$G = G_0 \exp \left( -\frac{\varepsilon_B^2}{\Delta^2} \right) \quad (S6)$$

$$V_t^{\text{approx}} = 1.91501 \frac{\Delta^2}{\varepsilon_B} \quad (S7)$$

$$c_2 = \frac{e^2}{12\Delta^2} \left( 2\frac{\varepsilon_B^2}{\Delta^2} - 1 \right) \stackrel{\Delta \ll \varepsilon_B}{\approx} c_2^{\text{approx}} \equiv \frac{e^2 \varepsilon_B^2}{6\Delta^4} \quad (S8)$$

$$c_4 = \frac{e^4}{480\Delta^4} \left( 4\frac{\varepsilon_B^4}{\Delta^4} - 12\frac{\varepsilon_B^2}{\Delta^2} + 3 \right)$$

$$\stackrel{\Delta \ll \varepsilon_B}{\approx} c_4^{\text{approx}} \equiv \frac{e^4 \varepsilon_B^4}{120\Delta^8} \stackrel{\Delta \ll \varepsilon_B}{\approx} \frac{3}{10} c_2^2 \quad (S9)$$

## Results for the off-resonant Newns-Anderson model

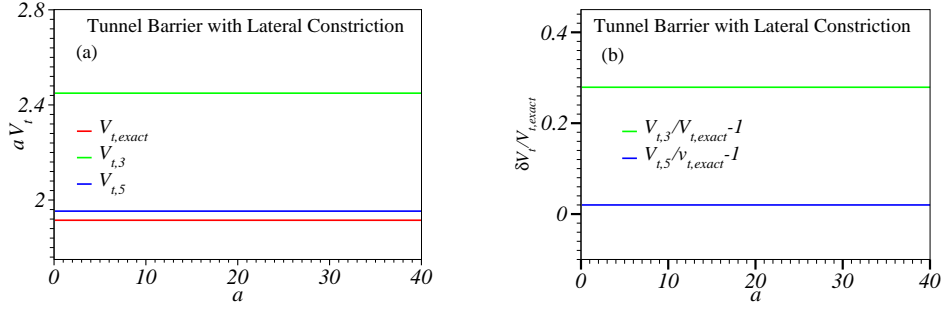
The current  $I$  and the transition voltages  $V_{t\pm}$  for positive and negative bias polarities have been deduced in ref. 3

$$I = I(V; \gamma) = GV \frac{\varepsilon_B^2}{(\varepsilon_B + \gamma eV)^2 - (eV/2)^2} \quad (S10)$$

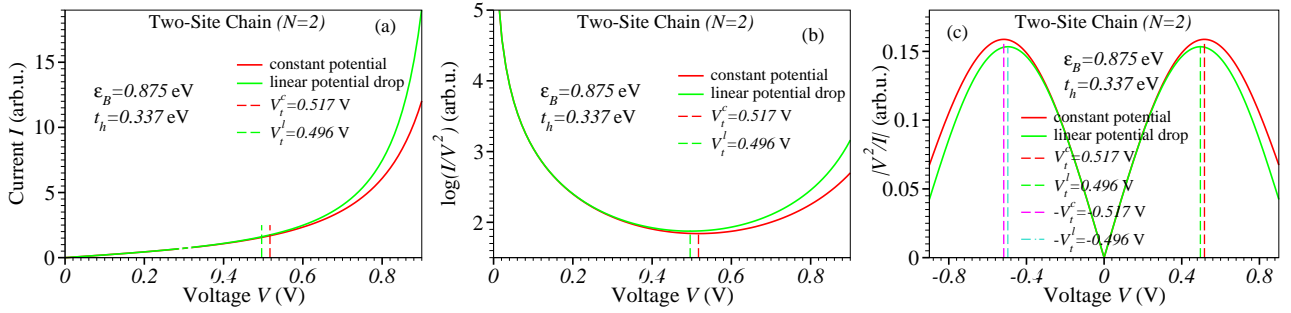
$$= -I(-V; -\gamma) \neq -I(-V; \gamma)$$

$$eV_{t+} = \frac{\varepsilon_B}{\sqrt{\gamma^2 + 3/4 - 2\gamma}}$$

$$eV_{t-} = -\frac{\varepsilon_B}{\sqrt{\gamma^2 + 3/4 + 2\gamma}} \quad (S11)$$



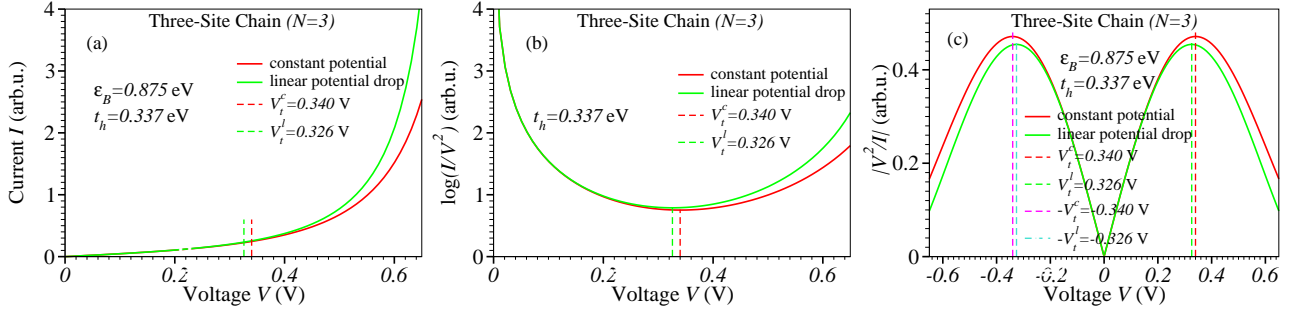
**Fig. S1** (a) The transition voltage  $V_{t,exact}$  computed from the current of eqn (14) of the main text due to laterally constricted electrons tunneling across an energy barrier [termed model (ii) above], along with the approximate estimates  $V_{t,3}$  and  $V_{t,5}$  obtained by inserting the expansion coefficients  $c_2$  and  $c_4$  of eqn (16) into eqn (5) and (6) of the main text (panel (a)). Panel (b) shows that  $V_{t,3}$  deviates from  $V_{t,exact}$  by 28% (larger than typical experimental uncertainties in  $V_t$  of  $\sim 10\%$ <sup>4,5</sup>), while  $V_{t,5}$  agrees with  $V_{t,exact}$  within 2%. Notice that the products  $aV_{t,3}$ , and  $aV_{t,5}$  do not depend on the parameter  $a \equiv \alpha de / (4\sqrt{\epsilon_B})$ .



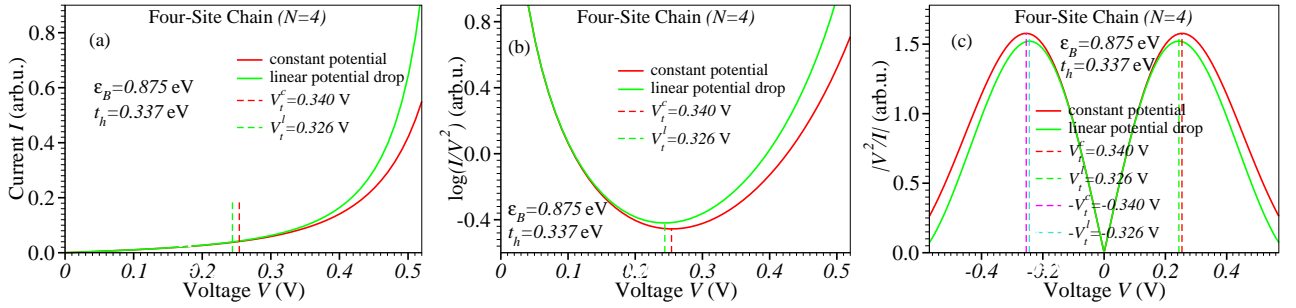
**Fig. S2** Results for chains with  $N = 2$  sites [termed model (iv) in the main text] computed by assuming a constant (Fig. 2c of the main text) and linearly varying (Fig. 2d of the main text) potential. Notice that the impact of the spatial potential profile is weak only at voltages not much higher than the transition voltage  $V_t$ .

## Notes and references

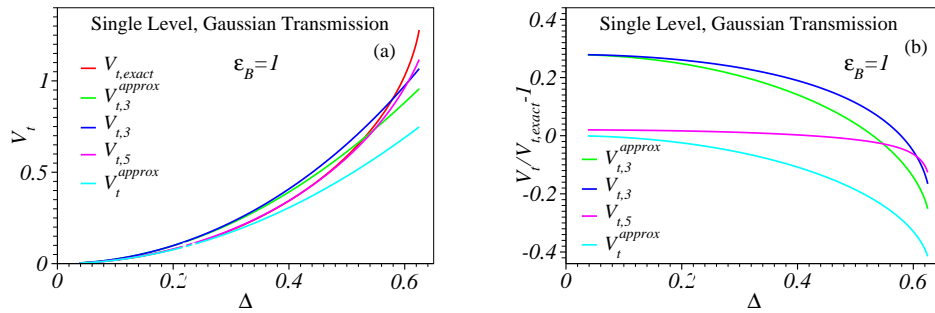
- 1 M. Araidai and M. Tsukada, *Phys. Rev. B*, 2010, **81**, 235114.
- 2 A. Vilan, D. Cahen and E. Kraissler, *ACS Nano*, 2013, **7**, 695–706.
- 3 I. Bâldea, *Phys. Rev. B*, 2012, **85**, 035442.
- 4 S. Guo, G. Zhou and N. Tao, *Nano Lett.*, 2013, **13**, 4326–4332.
- 5 The author thanks Dan Frisbie and Zuoti Xie for providing him the experimental data for CP-AFM Ag/OPDn/Ag junctions used in this work.



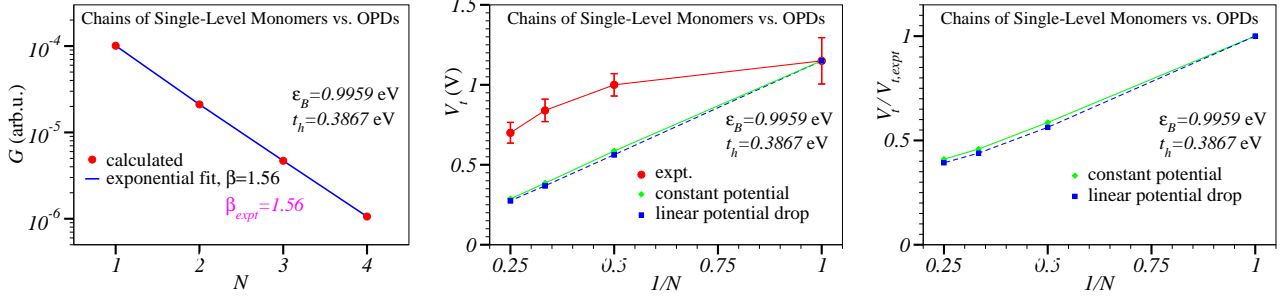
**Fig. S3** Results for chains with  $N = 3$  sites [termed model (iv) in the main text] computed by assuming a constant (Fig. 2c of the main text) and linearly varying (Fig. 2d of the main text) potential. Notice that the impact of the spatial potential profile is weak only at voltages not much higher than the transition voltage  $V_t$ .



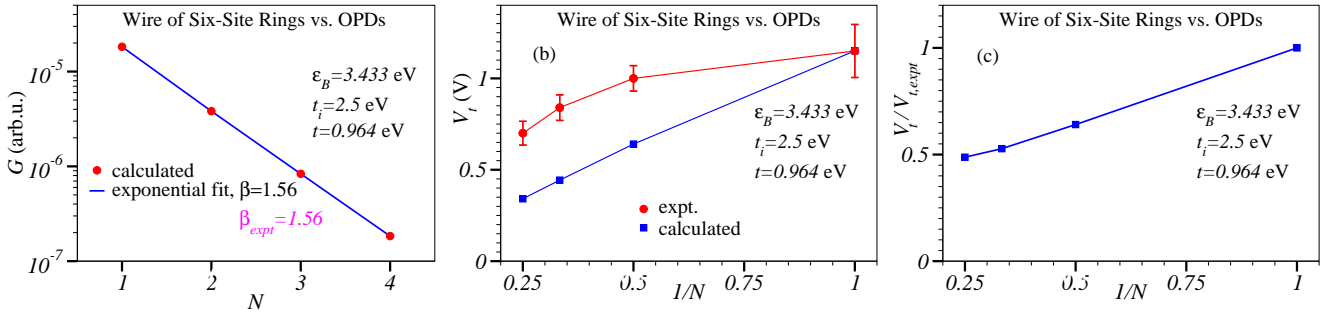
**Fig. S4** Results for chains with  $N = 4$  sites [termed model (iv) in the main text] computed by assuming a constant (Fig. 2c of the main text) and linearly varying (Fig. 2d of the main text) potential. Notice that the impact of the spatial potential profile is weak only at voltages not much higher than the transition voltage  $V_t$ .



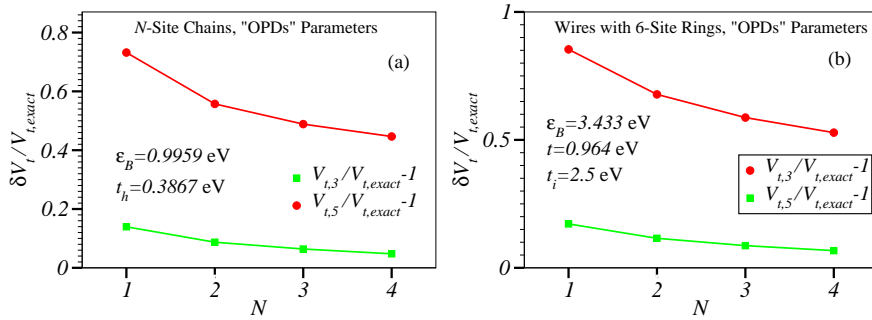
**Fig. S5** Results obtained using the Gaussian transmission of Eq. (S4) showing the dependence on  $\Delta$  of the transition voltage computed exactly ( $V_t$ ), and using its approximate estimates:  $V_{t,approx}$  of eqn (S7), and  $V_{t,3}^{approx}$ ,  $V_{t,3}$  and  $V_{t,5}$  obtained from eqn (5), (6), (S8) and (S9). Notice that both  $V_{t,approx}$  and  $V_{t,5}$  represent good approximations for large values of the ratio  $\epsilon_B/\Delta$ .



**Fig. S6** Results for model (iv) using  $\epsilon_B = 0.996$  eV, a value deduced from the experimental value  $V_t|_{N=1} \simeq 1.15$  V and  $t_h = 0.388$  eV, a value fitting the experimental conductance tunneling attenuation coefficient  $\beta = 1.56$  (panel (a)).<sup>5</sup> The calculated values  $V_t = f(N)$  (panel (b)) decrease substantially faster with the molecular size  $N$  than observed experimentally. The spatial potential profile across these junctions do not notably affect  $V_t$ , as illustrated by the results obtained for constant and linearly varying potentials (panel (c)). The points (panels (b) and (c)) and error bars (panel (b)) represent experimental results for CP-AFM Ag/OPDs/Ag junctions.<sup>5</sup>



**Fig. S7** Results for the conductance (panel (a)) and transition voltage (panel (b)) computed within model (v) using the value  $t_i = 2.5$  eV deduced ab initio as described in the main text and adjusting the parameters  $\epsilon_B = 3.433$  eV and  $t = 0.964$  eV to fit the experimental values  $\beta = 1.56$  and  $V_t|_{N=1} = 1.15$  V. Notice that the calculated dependence of  $V_t$  vs.  $1/N$  is significantly faster than observed experimentally. The points and error bars in panel (b) represent experimental results for CP-AFM Ag/OPDs/Ag junctions.<sup>5</sup>



**Fig. S8** The approximate estimates  $V_{t,3}$  and  $V_{t,5}$  computed numerically using the parameter values for model (iv) and (v) “best” adapted to OPDs junctions (cf. captions of Fig. S6 and S7, respectively) exhibit deviations from the  $V_t$ -values computed exactly similar to those shown in Fig. 3b, S1b and 4b, confirming thereby that a correct description of the transition voltage  $V_t$  needs expansions beyond the third-order.