

Electronic supplementary information for Protocol for disentangling the thermally activated contribution to the tunneling-assisted charge cransport. Analytical results and experi- mental relevance

Ioan Bâldea * ^{a‡}

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S1 Results for various forms of transmission

We present below a few special cases of the transmission function expressed by eq 12 in the main text:

(c) Gaussian transmission ($\delta = 2$ in eq 12)

$$\begin{aligned}\mathcal{T}(E; E_{MO}; \Delta) &= \exp\left(-\frac{|E - E_{MO}|^2}{\Delta^2}\right) \\ \frac{G}{G_0} &= \underbrace{\exp\left(-\frac{|\epsilon_0|^2}{\Delta^2}\right)}_{G_{0K}/G_0} + \underbrace{\frac{\sqrt{\pi}}{2} \frac{\Delta}{2k_B T} \text{sech}^2\left(\frac{\epsilon_0}{2k_B T}\right)}_{G_T/G_0} \\ \frac{G_T}{G_{0K}} &= \frac{\sqrt{\pi}}{2} \frac{\Delta}{|\epsilon_0|} \exp\left(\frac{|\epsilon_0|^2}{\Delta^2}\right) \frac{|\epsilon_0|}{2k_B T} \text{sech}^2\left(\frac{\epsilon_0}{2k_B T}\right) \quad (\text{S1})\end{aligned}$$

(d) Exponential transmission ($\delta = 1$ in eq 12)

$$\begin{aligned}\mathcal{T}(E; E_{MO}; \Delta) &= \exp\left(-\frac{|E - E_{MO}|}{\Delta}\right) \\ \frac{G}{G_0} &= \underbrace{\exp\left(-\frac{|\epsilon_0|}{\Delta}\right)}_{G_{0K}/G_0} + \underbrace{\frac{\Delta}{2k_B T} \text{sech}^2\left(\frac{\epsilon_0}{2k_B T}\right)}_{G_T/G_0} \\ \frac{G_T}{G_{0K}} &= \frac{\Delta}{|\epsilon_0|} \exp\left(\frac{|\epsilon_0|}{\Delta}\right) \frac{|\epsilon_0|}{2k_B T} \text{sech}^2\left(\frac{\epsilon_0}{2k_B T}\right) \quad (\text{S2})\end{aligned}$$

(e) WKB-like transmission ($\delta = 1/2$ in eq 12)

$$\begin{aligned}\mathcal{T}(E; E_{MO}; \Delta) &= \exp\left(-\sqrt{\frac{|E - E_{MO}|}{\Delta}}\right) \\ \frac{G}{G_0} &= \underbrace{\exp\left(-\sqrt{\frac{|\epsilon_0|}{\Delta}}\right)}_{G_{0K}/G_0} + \underbrace{\frac{\Delta}{k_B T} \text{sech}^2\left(\frac{\epsilon_0}{2k_B T}\right)}_{G_T/G_0} \\ \frac{G_T}{G_{0K}} &= \frac{2\Delta}{|\epsilon_0|} \exp\left(\sqrt{\frac{|\epsilon_0|}{\Delta}}\right) \frac{|\epsilon_0|}{2k_B T} \text{sech}^2\left(\frac{\epsilon_0}{2k_B T}\right) \quad (\text{S3})\end{aligned}$$

S2 Crossover between lower and higher temperature regimes

Figures S1, S2, S3, S4, S5, S6, and S7 depict results for the crossover temperature T_c for generalized exponential transmission functions characterized by several values of the exponent δ .

S3 Supplementary results on the accuracy of the analytical interpolation formula

As noted in Section 4, eq 4 (alternatively, eq 9) represents an approximation of the exact zero bias conductance expressed by eq 2. In addition to Figure 1 of the main text, which refers to the case of a Lorentzian transmission, the example presented in Figure S8 illustrates that also in the case of a generalized exponential transmission this approximation represents a reasonable interpolation between the zero temperature and the high temperature limit. Noteworthy, the parameters chosen in Figure S8 represents a model calculation corresponding to the *smallest* energy offset ($\epsilon_0 = 43.14$ meV) of Figure 11, which is only moderately larger than the thermal energy at room temperature ($k_B T_{RT} = 25.6$ meV), and one may suspect that the two peaks of the integrand of equation 2 are not enough separated, which is detrimental for the approximation expressed by equation 3 underlying eq 9. However, as visible in Figure S8,

^a Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany.

[‡] 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

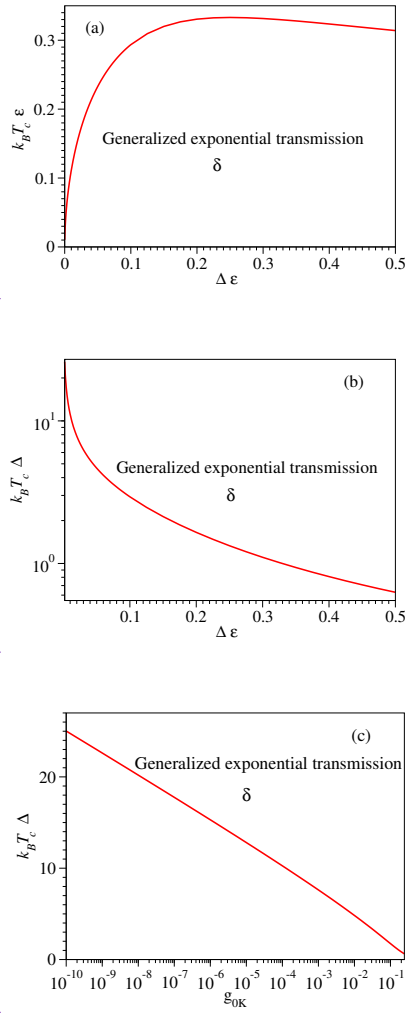


Fig. S1 Results for the crossover temperature T_c in case of a generalized exponential transmission of exponent $\delta = 0.5$.

the interpolation formula, eq 9, is reasonable accurate even in such cases.

S4 Remark on experimental data for single-molecule junctions based on Zn-porphyrin

Figure S9 depicts experimental conductance data at variable temperature in single molecule junctions studied in ref. 1. They were obtained by digitizing the information presented in Figure S12 of that work. Notice that because the temperature range sampled in experiment was not broad enough, both in logarithmic y-scale scale (panel a) and in linear y-scale the

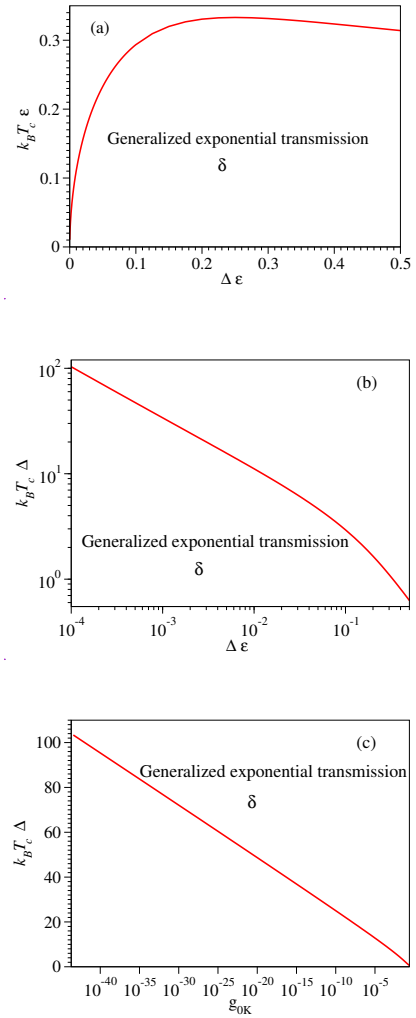


Fig. S2 Results for the crossover temperature T_c in case of a generalized exponential transmission of exponent $\delta = 0.5$. The difference from Figure S1 is that the range of g_{0K} shown here is broader.

data exhibit a roughly linear dependence. As discussed in the main text, this makes impossible a reliable extraction of the model parameters ϵ_0 and Δ (or g_{0K}).

S5 Results for the fluorine atom

To demonstrate that the accurate determination of MO energy offset values $\epsilon_0 \sim 0.1$ eV of interest in the context of the present paper is a formidably challenging task of theory, we will briefly discuss below the very simple case of a single flu-

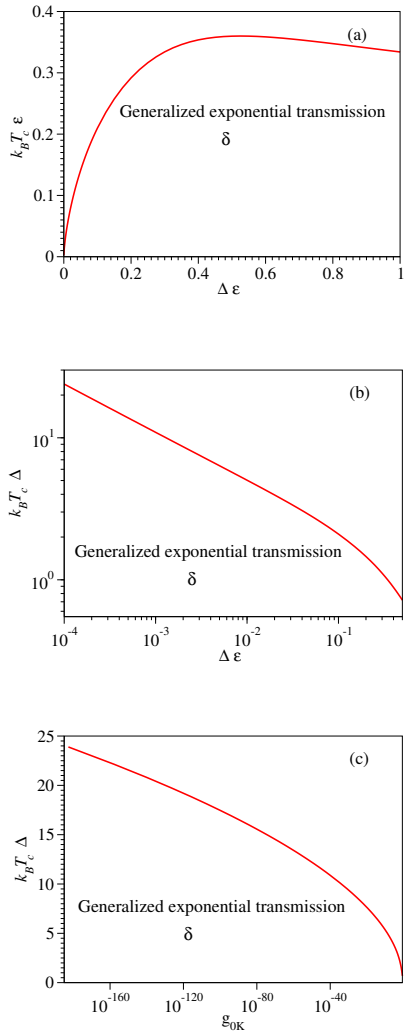


Fig. S3 Results for the crossover temperature T_c in case of a generalized exponential transmission of exponent $\delta = 0.656$. The difference from Figure 4 is that the range of g_{0K} shown here is broader.

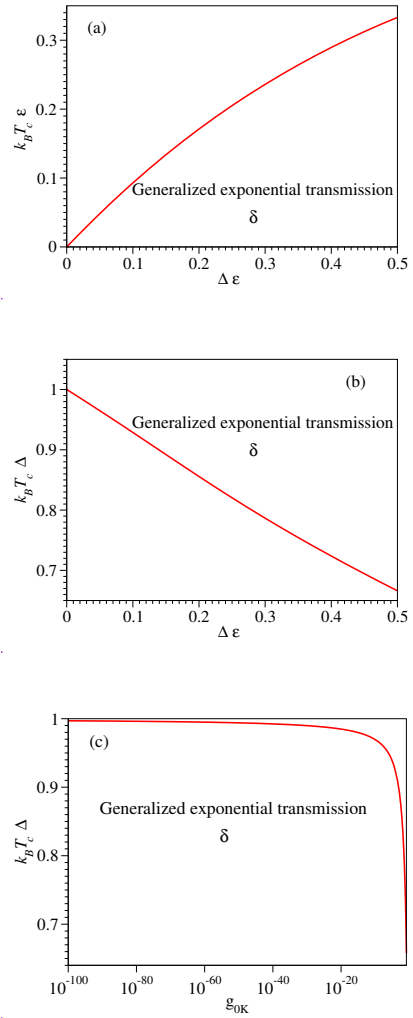


Fig. S4 Results for the crossover temperature T_c in case of a generalized exponential transmission of exponent $\delta = 1$. The difference from Figure 5 is that the range of g_{0K} shown here is broader.

orine atom. Experimental and theoretical results for the lowest ionization potential $IP \rightarrow -E_{HOMO}$ and lowest electron affinity $EA \rightarrow -E_{LUMO}$ are collected in Table S1. Along with DFT-values computed *via* the Kohn-Sham (KS) HOMO and LUMO energies, we present theoretical estimates obtained with two methods representing the state-of-the-art of quantum chemistry: coupled cluster (CC) expansions at CCSD level²⁻⁴ and outer valence Green's functions (OVGF)^{5,6}. In addition to the polarized double zeta (DZP) basis set (GAUSSIAN 09⁷ keyword D95V) — which represents the highest level for DFT

transport calculations done in conjunction with nonequilibrium Green's functions (NEGF) —, very high quality basis sets were utilized (GAUSSIAN 09 keywords in parentheses) to compile Table S1: augmented correlation-consistent Dunning basis sets of triple (aug-cc-pvtz) and quadruple (aug-cc-pvqz) zeta quality as well as the Pople's highest quality basis set (6-311++g(3d, 3p)).

The DFT calculations were done with the LDA and GGA-PBE exchange correlation functionals used in refs. 1 and 8, respectively (GAUSSIAN 09⁷ keywords SVWNS and

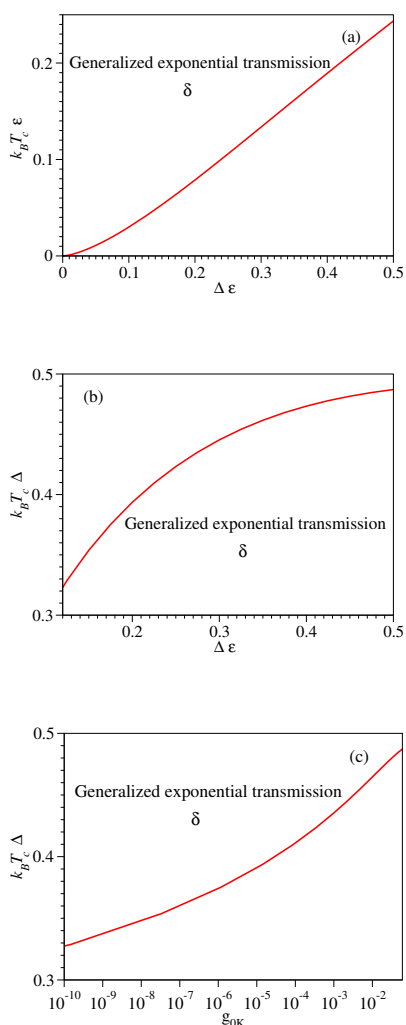


Fig. S5 Results for the crossover temperature T_c in case of a generalized exponential transmission of exponent $\delta = 1.5$.

PBEPBE, respectively).

By inspecting Table S1 one can conclude that, as well known,⁹ DFT KS-energies represent totally unsatisfactory estimates for the experimental values. Although much better, CCSD and OVGf estimates using polarized double zeta functions are far from being acceptable quantitatively. To obtain reasonable estimates of the energies of the frontier molecular orbitals, very quality basis sets are needed, which are much too demanding computationally when used in calculations for molecules linked to electrodes.

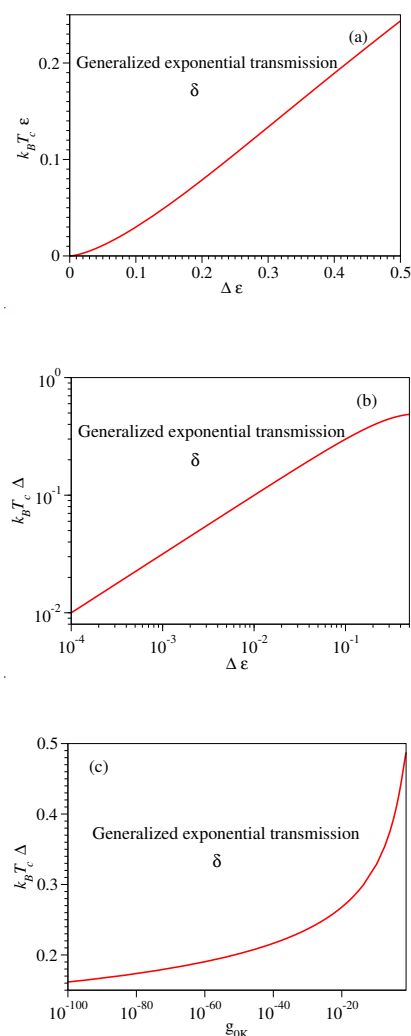


Fig. S6 Results for the crossover temperature T_c in case of a generalized exponential transmission of exponent $\delta = 1.5$. The difference from Figure S5 is that the range of g_{0K} shown here is broader.

Notes and references

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Method	Basis set	$IP \rightarrow -E_{HOMO}$ (eV)	$EA \rightarrow -E_{LUMO}$ (eV)
Exp.		17.44	3.40
DFT/GGA-PBE	D95V (DZP)	11.17 ($-E_{KS-HOMO}$)	< 0 (unstable anion!)
DFT/LDA	D95V (DZP)	12.69 ($-E_{KS-HOMO}$)	< 0 (unstable anion!)
CCSD	D95V (DZP)	16.72	1.76
OVGF	D95V (DZP)	16.88	1.46
CCSD	aug-cc-pvtz	17.21	3.15
OVGF	aug-cc-pvtz	17.34	1.91
CCSD	aug-cc-pvqz	17.28	3.21
OVGF	aug-cc-pvqz	17.39	1.90
CCSD	6-311++g(3d, 3p)	17.08	3.06
OVGF	6-311++g(3d, 3p)	17.24	2.01

Table S1 Experimental and computed values of the lowest ionization potential (IP) and electron attachment energy (EA) of the fluorine atom.

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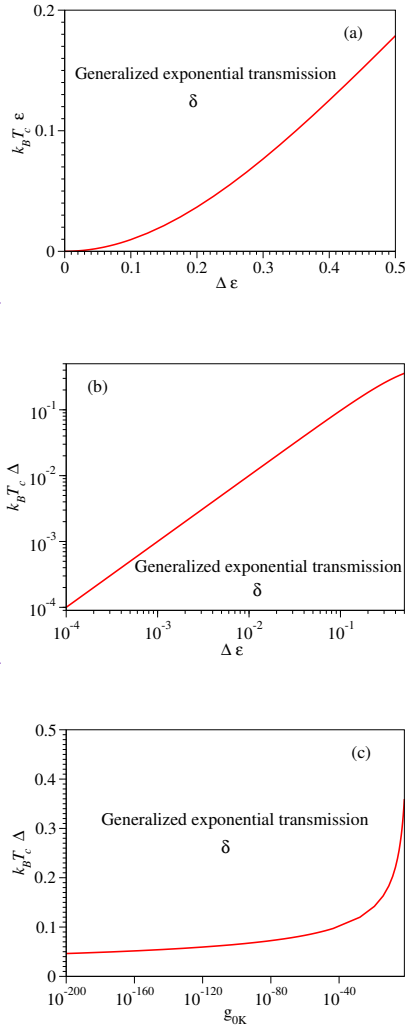


Fig. S7 Results for the crossover temperature T_c in case of a generalized exponential transmission of exponent $\delta = 2$. The difference from Figure 6 is that the range of g_{0K} shown here is broader.

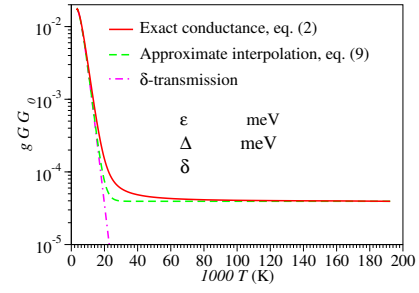


Fig. S8 The green line shown in this figure, obtained *via* eq 9 represents the interpolation of the exact curve (red line) for conductance computed from eq 2 for a transmission expressed by 12 having the smallest exponent ($\delta = 0.656$) shown in Figure 11.

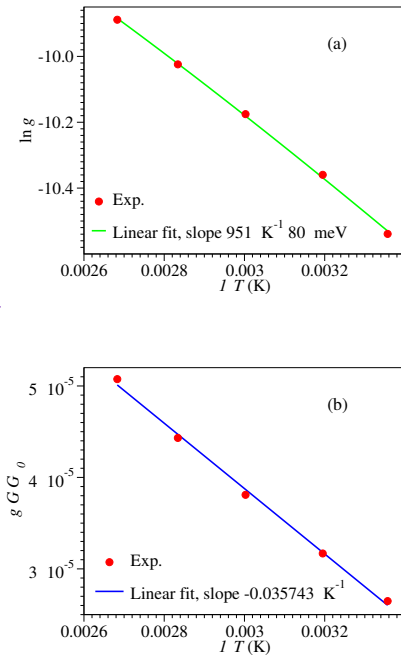


Fig. S9 Experimental conductance data (red points) on molecular junctions based on Zn-porphyrin monomers obtained by digitizing Figure S12 of ref.¹ depicted as $\ln g$ vs $1/T$ (panel a) and as g vs $1/T$ (panel b). Notice the almost linear dependence in both panels; a consequence of the fact that the T -range sampled in experiment is too narrow for the present purposes.