# Revealing molecular orbital gating by transition-voltage spectroscopy\*

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# Abstract

Recently, Song et al [Nature 462, 1039 (2009)] employed transition-voltage spectroscopy to demonstrate that the energy  $\varepsilon_H$  of the highest occupied molecular orbital (HOMO) of single-molecule transistors can be controlled by a gate potential  $V_G$ . To demonstrate the linear dependence  $\varepsilon_H - V_G$ , the experimental data have been interpreted by modeling the molecule as an energy barrier spanning the spatial source-drain region of molecular junctions. Since, as shown in this work, that crude model cannot quantitatively describe the measured I-V-characteristics, it is important to get further support for the linear dependence of  $\varepsilon_H$  on  $V_G$ . The results presented here, which have been obtained within a model of a point-like molecule, confirm this linear dependence. Because the two models rely upon complementary descriptions, the present results indicate that the interpretation of the experimental results as evidence for a gate controlled HOMO is sufficiently general.

Keywords: molecular electronics, quantum transport, single-molecule transistors, transition-voltage spectroscopy, molecular orbital gating, Fowler-Nordheim transition

<sup>\*</sup> Dedicated to Professor Horst Köppel on the occasion of his 60<sup>th</sup> birthday

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#### I. INTRODUCTION

The practical realization of ever smaller transistors is of paramount importance for the future of nano- and molecular-electronic devices. Transistors of nanoscopic sizes fabricated by linking a lithographically defined semiconducting quantum dot to electrodes [1] are based on the Kondo effect. In even smaller transistors, the current flows through a single molecule. Besides the Kondo mechanism, the Coulomb blockade can also be used for achieving transistor functions with correlated single molecules [2–5]. For uncorrelated molecules, transistor-like I-V-characteristics can be obtained by modifying electrostatically the molecular orbital energies, a mechanism predicted theoretically [6] and realized in electrochemical environment [7, 8] as well in a beautiful recent experiment [9]. In all these (field-effect) transistors, the current I which flows due to a bias V applied between two electrodes (source and drain) is controlled by means of the voltage  $V_G$  applied on a third electrode (gate).

The very detailed characterization of the molecular devices of Ref. [9] has allowed to convincingly demonstrate that transistor functions can be achieved by means of single-molecule devices. In Sec. II, the experimental evidence on the molecular orbital gating obtained by transition-voltage spectroscopy will be reviewed. Importantly, as it will be shown there, the model used in Ref. [9] to describe the active molecules cannot quantitatively reproduce the I-V-curves measured experimentally. So, it is important to show that the linear dependence of the highest occupied molecular orbital (HOMO) energy  $\varepsilon_H$  on the gate potential  $V_G$ , a key feature demonstrating the HOMO-mediated transistor function, does not critically depend on the particular model assumed in Ref. [9]. To this aim, we shall consider in Sec. III a complementary model, namely a point-like molecule. As discussed in Sec. IV, this model reconfirms the aforementioned linear dependence. The conclusion of the present investigation, presented in Sec. V, is that the linear dependence of  $\varepsilon_H$  on  $V_G$  holds beyond the barrier model utilized in Ref. [9] and is therefore more general.

# II. REVIEW OF THE EXPERIMENTAL EVIDENCE ON THE MOLECULAR ORBITAL GATING

The *I-V*-curves measured in Ref. [9] for single-molecule transistors based on 1,8-octanedithiol (ODT) and 1,4-benzenedithiol (BDT) exhibit a sensitive dependence on the

gate potential (cf. Fig. 1) revealing thereby a clear transistor function. However these curves alone do not yet provide much insight into the underlying physical mechanism. Demonstrating that the current really flows through the molecule under consideration and ruling out spurious contributions from impurities and defects represent important challenges for molecular electronics altogether.

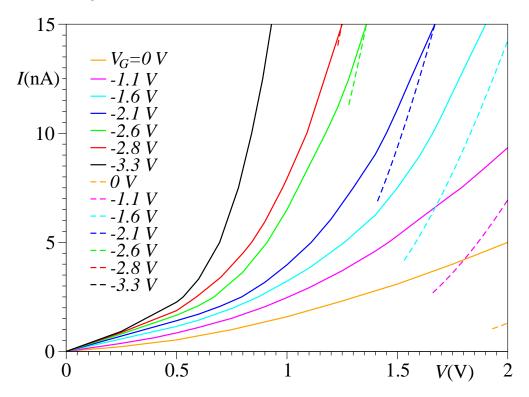


FIG. 1: Gate controlled I-V characteristics of the Au-ODT-Au molecular junctions of Ref. [9] for several gate potentials  $V_G$  given in the legend. The solid lines have been obtained by extracting the experimental data from Fig. 1a of Ref. [9] for ODT-based molecular transistors. The dashed lines, shown for voltages above the transition voltage ( $V > V_t^e$ ), should represent the high voltage approximation [Eq. (3)] of the experimental curves obtained by modeling the active molecule as a continuously expanded energy barrier, but, as visible in this figure, this approximation is very poor. See the main text for details.

A key issue is to provide direct evidence on the electrostatical modulation of the energy  $\varepsilon_0 (= \varepsilon_H \text{ or } \varepsilon_L)$  of the frontier molecular orbitals, i. e. the energy  $\varepsilon_H$  of the highest occupied molecular orbital (HOMO; p-type conduction) or the energy  $\varepsilon_L$  of the lowest unoccupied molecular orbital (LUMO; n-type conduction), depending on which of these molecular orbitals is the closest to the electrode Fermi energy  $\varepsilon_F$ . (Unless otherwise specified,  $\varepsilon_F$  is

chosen as zero of energy.) Is this the case, and does the device act indeed as a single-molecule transistor, the gate-controlled molecular energy  $\varepsilon_0$  should linearly depend on the gate potential

$$\varepsilon_0 = \varepsilon_0^0 + \alpha e V_G. \tag{1}$$

Here e > 0 is the elementary charge and  $\varepsilon_0^0$  the energy of the frontier molecular orbital without applied gate voltage. Similar to other cases encountered in nanotransport discussed recently in several papers coauthored by Köppel [10–13], unlike the gate voltage  $V_G$ , neither the level energy  $\varepsilon_0$  nor the conversion factor  $\alpha$  are directly accessible experimentally. So, a special procedure is required to verify the validity of Eq. (1).

To extract the energy  $\varepsilon_0$  from the measured I-V-curves, which further allowed to demonstrate the linear dependence  $\varepsilon_0 = \varepsilon_0(V_G)$ , Song et al [9] used the so-called transition-voltage spectroscopy [14–18]. This technique exploits the existence of two different regimes in the charge transport by tunneling through molecular junctions. The distinction between these two mechanisms was pointed out long time ago by means of semiclassical WKB calculations of the electric current between two metallic electrodes separated by a thin insulating film [19]. The latter was modeled as an energy barrier continuously filling the space between electrodes.

Without a source-drain bias (V = 0), the barrier can be assumed rectangular, with a certain height  $\varepsilon_B$  (Fig. 2a). A low bias  $(eV \ll \varepsilon_B)$  changes this rectangular barrier to a trapezoidal one (Fig. 2b) and yields an ohmic regime

$$I \simeq AV \exp\left(-\gamma \varepsilon_B^{1/2}\right).$$
 (2)

By sufficiently raising the bias  $(eV > \varepsilon_B)$ , the barrier becomes triangular. If the Fermi level of the drain lies below the bottom of the conduction band of the source (Fig. 2c) one arrives at a situation that resembles the field emission of electrons from a metallic electrode. In this regime (Fowler-Nordheim tunneling), the current can be expressed as

$$I \simeq \left(BV^2/\varepsilon_B\right) \exp\left(-\delta \varepsilon_B^{3/2}/V\right).$$
 (3)

Above, A,  $\gamma$ , B, and  $\delta$  are parameters that do not depend on V and  $\varepsilon_B$ .

The transition between these two regimes can be visualized with the aid of the so-called Fowler-Nordheim plot, which is the graph representing the quantity  $\log(I/V^2)$  as a function

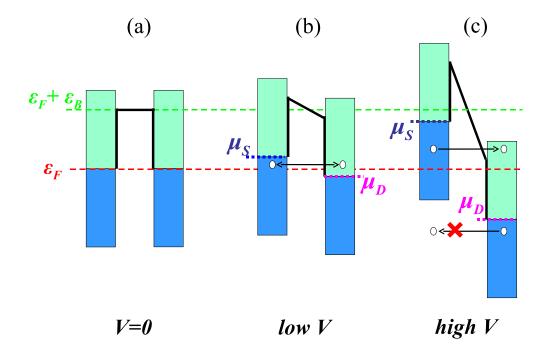


FIG. 2: Modeling a molecule spanning the region between the source (S) and the drain (D) of a molecular junction by a homogeneous energy barrier continuous in space whose shape is (a) rectangular, (b) trapezoidal, or (c) triangular, depending on the magnitude of the source-drain voltage V ( $\mu_{S,D} = \varepsilon_F \pm eV/2$ ). The situation depicted here (energy barrier for V = 0 above the electrodes' Fermi energy  $\varepsilon_F$ ) corresponds to a LUMO-mediated conduction.

of 1/V. As shown by Eqs. (2) and (3),  $\log(I/V^2)$  increases (logarithmically) with 1/V in the ohmic regime

$$\log(I/V^2) \simeq const + \log(1/V),\tag{4}$$

while it decreases (linearly) in the Fowler-Nordheim regime

$$\log(I/V^2) \simeq const - \delta \varepsilon_B^{3/2}(1/V). \tag{5}$$

In Ref. [14], the crossover between these two regimes has not been deduced from a specific analytic dependence I = I(V) but rather claimed in view a simple intuitive argument underlying the above analysis. Namely, it was specified by the point where the energy barrier changes from the trapezoidal shape to the triangular one. This condition defines a transition voltage  $V = V_t^e$  which can be expressed as [14]

$$eV_t^e = \varepsilon_B. (6)$$

Importantly, the transition voltage of Eq. (6) depends on the barrier height. Therefore  $\varepsilon_B$  can be estimated from  $V_t^e$ , because the latter can be deduced experimentally from the Fowler-Nordheim plot. On this basis, a number of recent experimental studies [14–17] succeeded to reveal a Fowler-Nordheim transition in molecular transport.

Basically, to produce a current through the molecule, the electrons have to overcome an energy barrier equal to the energy offset between the frontier molecular orbital ( $\varepsilon_0 = \varepsilon_H$  or  $\varepsilon_L$ ) and the electrode Fermi level  $\varepsilon_F$ , i. e.  $\varepsilon_B = \varepsilon_F - \varepsilon_H$  or  $\varepsilon_B = \varepsilon_L - \varepsilon_F$ . for p-type or n-type conduction, respectively. To reveal that the current through the molecules investigated in Ref. [9] was gated by the HOMO energy, transition-voltage spectroscopy turned out to be an essential tool. The more negative the applied gate potential  $V_G$ , the larger was the measured current through the molecular transistors of Ref. [9]. This indicates that the conduction is mediated by the HOMO and not by the LUMO; a negative gate potential pushes the HOMO energy  $\varepsilon_H$  upwards, and it becomes closer to the electrode's Fermi energy; thus, the energy barrier  $\varepsilon_B = \varepsilon_F - \varepsilon_H$  is reduced. Most important, the transition voltage  $V_t$  deduced experimentally from the minimum of the Fowler-Nordheim plot [20, 21] was found to linearly vary with the gate potential  $V_G$ , in agreement with Eqs. (6) and (1). The large conversion factors extracted in this way ( $\alpha = +0.25$  and  $\alpha = +0.22$  for the ODT and BDT molecules, respectively [9]) indicate a particularly strong coupling between the embedded molecules and the gate.

The experimental confirmation of the linear relationship  $V_t = f(V_G)$  represents a remarkable evidence of the fact that the current through the single-molecule transistors proceeds through the gate-controlled HOMO of the two molecules (ODT and BDT) investigated in Ref. [9]. However, further work has to be done for the quantitative description of the experimental data of Ref. [9].

One can easily show that Eqs. (2) and (3) cannot quantitatively reproduce the experimental I-V-characteristics. If Eq. (3) were applicable, for biases  $V > V_t^e$  the current at various gate voltages  $V_G$  ( $\varepsilon_B$ ) could be described by fitting the parameters B and  $\delta$ . To illustrate that this is not the case, in Fig. 1 the values of B and  $\delta$  have been adjusted to reproduce the points (I, V) of coordinates  $\approx$ (15.0 nA, 1.67 V) and  $\approx$ (15.0 nA, 1.36 V) at the ends of the experimental curves for  $V_G = -2.1$  V and  $V_G = -2.6$  V. The curves obtained from this fit, which are depicted by the dashed lines of Fig. 1, represent unsatisfactory approximations of the experimental ones.

#### III. FOWLER-NORDHEIM PLOTS FOR A POINT-LIKE MOLECULE

The field of molecular electric transport has long been plagued by notorious quantitative discrepancies between the current measured experimentally and computed theoretically. Until reaching the desirable agreement between them, it is important to demonstrate that the interpretation based on a gate controlled HOMO-mediated current holds beyond the model discussed in Sec. II.

Briefly, the model yielding the key Eq. (6) assumes an expanded molecule described by an energy barrier with a continuous spatial extension, which smoothly fills the source-drain space and has a position-dependent height linearly interpolated between the source and drain chemical potentials  $\mu_{S,D}$  (cf. Fig. 2). This is one extreme model of a molecule embedded into a junction. At the other extreme, one can model the active molecule as a point-like level of energy  $\varepsilon_0$ , from/to which the electrons are transferred to/from the electrodes. Let us assume that this point-like molecule is located symmetrically between the source and the drain [22], and that the bias is applied symmetrically, i. e.,  $\mu_{S,D} = \varepsilon_F \pm eV/2$ . Then, whether the potential V varies linearly between the source and the drain, or it sharply drops near electrodes and remains constant practically in the whole region between electrodes, the level energy  $\varepsilon_0$  does not depend on V (see Fig. 3). Within this picture there is no counterpart of the rectangular-, trapezoidal-, and triangular-shaped barriers of the extended molecule model discussed in Sec. II enabling to intuitively define a transition voltage. However, it is still possible to find an analogy between the two models and to introduce a transition voltage  $V_t^p$  for the point-like molecule as well.

Since electron correlations are neglected in both models, one can cast the electric current expressed by means of the Landauer formula (see, e. g. [23]) in the following form

$$I = I_{S} - I_{D},$$

$$I_{S} = 2\frac{e}{h} \int_{0}^{\infty} d\varepsilon T(\varepsilon, V) f(\varepsilon - \mu_{S}),$$

$$I_{D} = 2\frac{e}{h} \int_{0}^{\infty} d\varepsilon T(\varepsilon, V) f(\varepsilon - \mu_{D}),$$

$$(7)$$

where T and f denote the transmission and the Fermi distribution function, respectively, and h is Planck's constant. Above, the current I has been split into the contribution  $I_S$  of the electrons filling the levels in the source up to the energy  $\mu_S = \varepsilon_F + eV/2$  that tunnel into the empty drain, and the contribution  $I_D$  of the electrons filling the levels in the drain

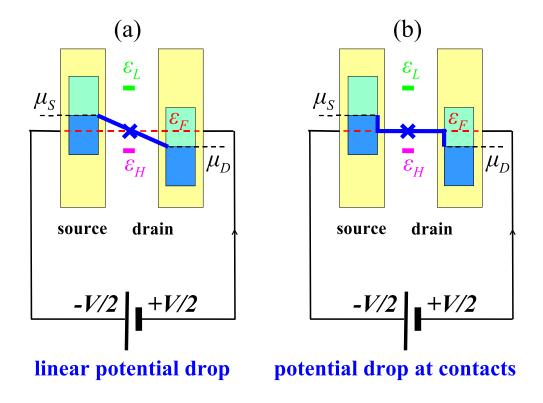


FIG. 3: Potential profile (blue line online) across the molecular junction: (a) linear variation between the source and the drain; (b) sharp potential drop at the two electrodes. In both cases, as visualized by the symbol × (blue online), the magnitude of the potential drop  $V = (\mu_S - \mu_D)/e$  does not affect the energy of the HOMO ( $\varepsilon_H$ ) and the LUMO ( $\varepsilon_L$ ) of a point-like molecule located symmetrically between the source and the drain.

up to the energy  $\mu_D = \varepsilon_F - eV/2$  that tunnel into the empty source.

At low source-drain voltages V (the trapezoidal barrier of Fig. 2b), both contributions  $I_S$  and  $I_D$  are important, and the small difference between them gives rise to a small ohmic current  $I \propto V$ . This mechanism is usually referred to as the direct tunneling [14, 16, 17], but perhaps the term (nearly symmetric) bidirectional tunneling would be more suggestive.

If the source-drain voltage becomes sufficiently high, one arrives at a situation (the triangular barrier of Fig. 2c) where the Fermi level of the drain lies below the bottom of the conduction band of the source. Then, the electrons can only tunnel from the source to the drain but not in the reverse direction, since there are no final states available. This is the so-called field emission mechanism (Fowler-Nordheim tunneling) [14–17], since it resembles the field emission of electrons from a metallic electrode. In fact, it is a unidirectional tunneling.

While the idea of a voltage-driven change in the shape of the barrier (rectangular  $\rightarrow$ 

trapezoidal  $\rightarrow$  triangular) cannot be generalized from the homogeneously expanded molecule of Fig. 2 to a point-like molecule, the notions of a tunneling that is symmetric or nearly bidirectional, highly asymmetric bidirectional or almost unidirectional, and completely unidirectional can be employed in both descriptions. This is illustrated in Fig. 4. Panels (a) and (b) of Fig. 4 shown for the case of a point-like molecule represent the counterpart of panels (b) and (c) of Fig. 2 for an extended molecule.

The intuitive considerations presented above suggest that a transition between two different tunneling mechanisms can also be expected for a molecule described within a point-like model. Within the common assumption of wide band electrodes, the current through a point-like level defined by the energy offset  $\varepsilon_B$  can be expressed in a simple analytical form (see e. g., [23, 24])

$$I = 2\frac{e\Gamma}{h} \left( \arctan \frac{eV - 2\varepsilon_B}{2\Gamma} + \arctan \frac{eV + 2\varepsilon_B}{2\Gamma} \right), \tag{8}$$

where  $\Gamma$  represents the finite width of the molecular level due to the molecule-electrode coupling. In all numerical calculations, we set e = h = 1 and the energy unit such that  $\Gamma = 0.08$ , but one should note that by using the reduced variables  $I/\Gamma$ ,  $V/\Gamma$ , and  $\varepsilon_B/\Gamma$ , the I-V-characteristics expressed by Eq. (8) are universal. By means of Eq. (8), one can straightforwardly obtain curves for  $\log(I/V^2)$  plotted versus versus 1/V for various  $\varepsilon_B$ . These (Fowler-Nordheim) plots, which are shown in Fig. 5, clearly reveal a crossover between two regimes corresponding to low and high biases, which also exist for the point-like model, in agreement with the foregoing qualitative analysis.

The Fowler-Nordheim transition line, which joins the minima [20] of the individual Fowler-Nordheim curves computed for various  $\varepsilon_B$ , is presented in Fig. 5. The abscissae of this transition line define the transition voltages  $V_t^p$  between the two tunneling regimes. The transition line of Fig. 5 shows the parametrical dependence of  $V_t^p$  on the energy offset  $\varepsilon_B$ . The curve expressing the explicit dependence  $V_t^p = f(\varepsilon_B)$  is depicted in Fig. 6. By inspecting this curve, one can conclude that this dependence is linear to a very good approximation

$$eV_t^p \simeq 1.15\,\varepsilon_B$$
 (9)

provided that the energy offset  $\varepsilon_B$  is sufficiently larger than the finite width  $\Gamma$  caused by the molecule-electrode couplings.

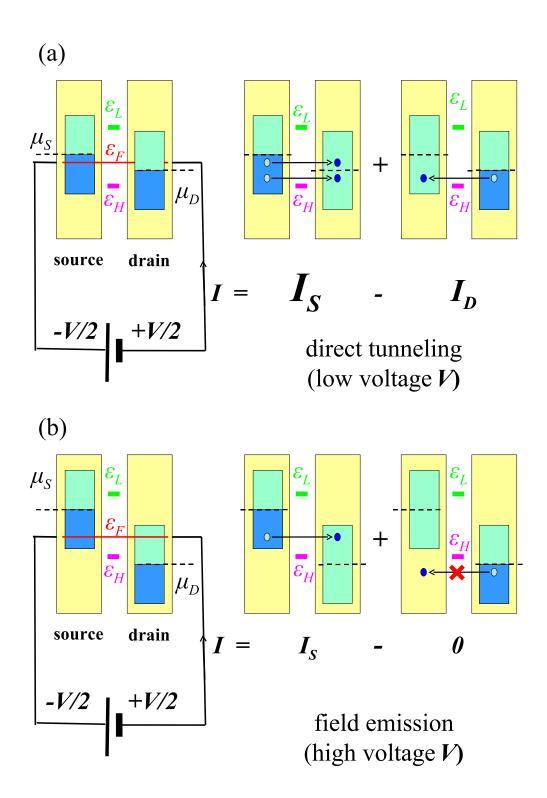


FIG. 4: The charge transfer mechanism is the bidirectional tunneling (direct tunneling) at lower source-drain voltages V and unidirectional tunneling (field emission) at higher voltages V.

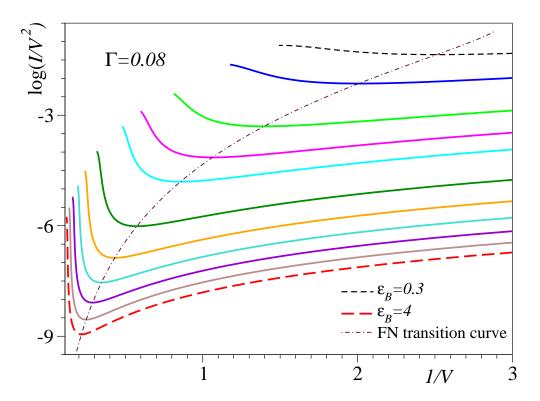


FIG. 5: Fowler-Nordheim plots deduced from Eq. (8) for the level energies  $\varepsilon_B = 0.3, 0.4, 0.6, 0.8, 1, 1.5, 2, 2.5, 3, 3.5, 4$  (values increase downwards). The dashed lines connecting the minima of the Fowler-Nordheim curves represents the Fowler-Nordheim transition line.

# IV. DISCUSSION

Following the previous Refs. [9, 14, 16, 17], I also employed above the notions of triangular barrier and field emission, but because they may be misleading, before discussing the aspects that are physically relevant, a few technical comments are in order.

In the case of electrons emitted from a metal into the vacuum due to a strong electric field, the triangular barrier to be overcome and unidirectional tunneling concomitantly exist. As discussed above, both for a point-like molecule (cf. Fig. 4) and for an extended energy barrier [19], the electron tunneling becomes unidirectional for rather high source-drain voltages, of the order of electrodes' bandwidth ( $eV \sim 2\varepsilon_F$ ). So, a transition from bidirectional tunneling to unidirectional tunneling occurs in both cases by sufficiently rising the voltage. The difference from the traditional vacuum electronics is that the "triangular" barrier regime encountered in molecular electronics does not necessarily refer to a situation where the backward tunneling is impossible but rather to situations where it is substantially inhibited.

As expressed by Eqs. (6) and (9), the system enters this regime at biases  $eV \sim \varepsilon_B$ , well in advance of reaching the "field emission" regime, because normally  $\varepsilon_B$  is substantially smaller than the electrodes' bandwidth. For example, for the ODT-based junctions of Ref. [9],  $\varepsilon_B \simeq 1 - 2 \,\mathrm{eV}$ , and for the BDT-based junctions  $\varepsilon_B \simeq 0.4 - 1.8 \,\mathrm{eV}$ , while for the utilized gold electrodes  $\varepsilon_F \simeq 5.6 \,\mathrm{eV}$ .

For practical realizations in molecular electronics, it is important that the values of the energy offset  $\varepsilon_B$  are sufficiently small, since too high values drastically suppress the current. So, for such situations of practical interest, the transition voltage is not too high and, as witnessed by experiments [9, 14–17], can be supported by already fabricated molecular junctions. In particular, this justifies the use of the wide band approximation assumed above in Eq. (8). Without this approximation the transmission function T entering the Landauer formula, Eq. (7), would exhibit a significant dependence on the applied bias V, and band edge effects could also become relevant even for a point-like molecule. Both these aspects have been discussed recently [24]. In fact, as illustrated in Figs. 3a, 3b, and 4b of Ref. [24], the results obtained for a point-like molecule within and without the wide band approximation practically coincide up to voltages  $eV \gtrsim 2\varepsilon_B$ .

As visible in the aforementioned figures of Ref. [24], the current rapidly increases at  $eV \simeq eV_s \equiv 2\varepsilon_B$ . The physical reason for this stepwise increase is that the frontier orbital becomes (nearly) resonant with the electrochemical potential of one electrode  $[\mu_S(V_s)] \equiv \varepsilon_F + eV_s/2 = \varepsilon_B + \varepsilon_F$  for the n-type conduction supposed in the present figures]. Similar to  $V_t$ , this voltage  $V_s$  is also straightforwardly related to the energy offset  $(eV_s = 2\varepsilon_B)$ ; it corresponds to an inflexion point of the I-V-characteristics [25]. This might suggest an alternative experimental procedure to determine  $\varepsilon_B$  from  $V_s$ . While this method poses no problems for theoretical calculations, it is unlikely that this method is experimentally viable: it is hardly conceivable that a molecular junction could support the high currents at voltages  $V = V_s \simeq 2V_t$  significantly higher than  $V \simeq V_t$ . By inspecting Fig. 1 and 2 of Ref. [9] as well as the present Fig. 1, one can remark that the high V-ranges sampled in the measurements comprise only small portions  $(V_s \gg V \gtrsim V_t)$  of the Fowler-Nordheim regime, (presumably) just because the currents become too high.

To conclude, what really happens at the transition voltage is that the frontier molecular orbital draws closer to the (electro)chemical potential of one electrode but still remains sufficiently distant from it. When the source-drain voltage is raised, the point  $V = V_t \approx \varepsilon_B$ 

is reached before reaching the point  $V = V_s \approx 2\varepsilon_B$ .

Switching now to the physical aspects, I note the following. The differences between the two models considered in Secs. II and III become notable only for nearly resonant frontier molecular orbitals  $\varepsilon_B \sim \Gamma$ . The fact that these differences are significant for  $\varepsilon_B \sim \Gamma$  can easily be understood if one bears in mind that the semiclassical (WKB) calculations related to the model of an extended molecule do not account for finite width effects, which are important for the tunneling through a barrier of small height.

Definitely, the condition  $\Gamma \ll \varepsilon_B$  holds in the experimental situation: by assuming a point-like molecule, from Fig. S6 of the supplementary material of Ref. [9] one can estimate  $\Gamma/\varepsilon_B = \sqrt{G/G_0} \sim 0.005$  for the ODT-based single molecule transistors, where G is the zero-bias conductance and  $G_0$  the conductance quantum. So, the result of Eq. (9), deduced for a point-like molecule, is not too much different from that obtained within the extended model of molecule, from the point where the barrier shape changes from trapezoidal to triangular, Eq. (6).

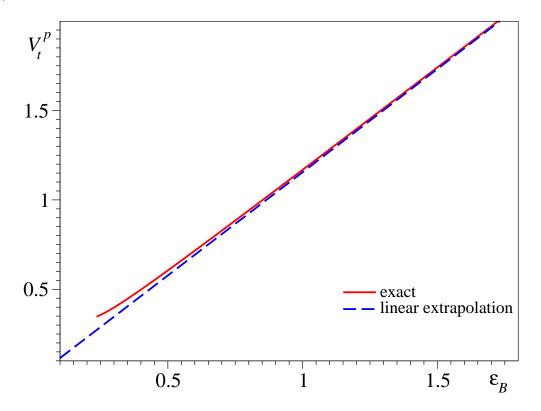


FIG. 6: The Fowler-Nordheim critical line, which expresses the dependence of the transition voltage on the energy offset  $\varepsilon_B$  of the frontier molecular orbital, for a point-like molecule, deduced from the minima of the Fowler-Nordheim plots of Fig. 5.

To summarize, for the realistic cases investigated in Ref. [9] and elsewhere, which are characterized by frontier molecular orbitals that are sufficiently away from resonance ( $\Gamma \ll$  $\varepsilon_B$ ), the dependence on the energy offset of the transition voltage of the point-like  $[V_t^p]$ Eq. (9)] and extended  $[V_t^e, \text{ Eq. (6)}]$  models of molecule is linear. Therefore, the linear dependence of the transition voltage (defined in conjunction with the Fowler-Nordheim plot) on the gate voltage found in the experimental curves for current of Ref. [9] provides a clear evidence for the charge transfer through the gated HOMO whatever the model (expanded or point-like molecule) used to interpret the measurements. Employing the point-like model instead of the expanded one to interpret the experimental findings on the transition voltage of Ref. [9] only results in a slightly weaker coupling between the molecules and the gate electrode: instead of the values  $\alpha = +0.25$  and  $\alpha = +0.22$  estimated in Ref. [9] for the ODT and BDT molecules, respectively, one obtains the slightly smaller conversion factors  $\alpha = +0.22$  and  $\alpha = +0.19$ , respectively. The estimates of the two models agree within  $\sim$  13%, which is quite satisfactory if one bear in mind that the employed models, which are rather crude, do not account for many effects that could be significant, e. g., possible potential drops at the contacts and charge image effects [19, 26], as already noted [14].

Interestingly, the dependence on  $\varepsilon_B$  of the transition voltage deduced from the Fowler-Nordheim plot is linear, despite the fact that the underlying I-V relationship of the two models [Eqs. (2) and (3) on one side, and Eq. (8) on the other side] are quite different. This suggests that the examination of the Fowler-Nordheim plots could also be useful in other situations wherein the charge transfer mechanisms at lower and higher biases are different from those considered here. It is also interesting to mention that, similar to other cases [16, 17, 21], the transition voltage can also be visible in  $\log I - \log V$  plots. This becomes visible if one inspects Fig. 7, where such plots are presented along with the Fowler-Nordheim transition line depicted in Figs. 5 and 6. Noteworthy, unlike the plots of Figs. 5 and 7, the I - V-characteristics represented in the usual linear scale do not exhibit any special feature at the transition voltage  $V = V_t$ , and therefore are not shown here.

# V. CONCLUSION

Remarkably, whether the molecule is modeled by a energy barrier continuously expanded in the space between the source and the drain, or by a point-like energy level, the transition

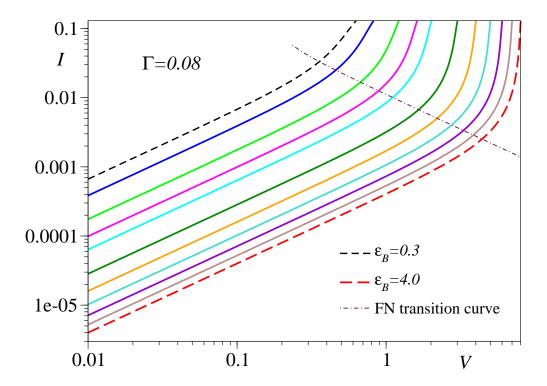


FIG. 7: The I-V-characteristics of a point-like molecule [Eq. (8)] plotted in logarithmic scale permit to evidence the crossover between two (low and high voltage) regimes and to relate it the Fowler-Nordheim transition line of Figs. 5 and 6.

voltage  $V_t$  extracted as described above exhibits a linear dependence on the energy offset between the frontier molecular orbital and the electrodes' Fermi energy. The difference between these two extreme descriptions, which only amounts  $\sim 13\%$  is quite reasonable in view of the fact that both descriptions represent rather crude approximations of a realistic molecular junction. Because it is plausible to assume that the potential profile in a real molecule corresponds to a situation, which lies between the situations described by these two extreme physical models, one can conclude that the evidence on molecular orbital gating reported in Ref. [9] is not restricted to the assumption made of the change in the barrier shape from trapezoidal to triangular and also holds in a model that is completely different.

Of course, the present work only represents a preliminary investigation of the molecular orbital gating, as it is based on a model, which is as oversimplified as the barrier model employed in Ref. [9]. To quantitatively reproduce the *I-V*-characteristics measured in the single-molecule transistors of Ref. [9] subsequent investigations should reliably account for effects that have to be considered in real systems. Open challenge for future investigations

are, e. g., the inclusion of the chemical information about the molecule, electron correlation effects, and selfconsistent determination of the potential distribution, as well as the numerous affinity and ionization levels of a real molecule, which should be used instead of the LUMO and the HOMO, respectively. The latter have been employed in the present paper to keep the discussion as simple as that of Ref. [9], but this should not create the wrong impression that a real experiment can actually be interpreted in terms of a single molecular orbital.

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