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We investigate inelastic cotunneling in a model system where the charging island is connected to the leads through molecules with energy-dependent transmission functions. To study this problem, we propose two different approaches. The first is a pragmatic approach that assumes Lorentzian-like transmission functions that determine the transmission probability to the island. Using this model, we calculate current versus voltage (IV) curves for increasing resonance level positions of the molecule. We find that shifting the resonance energy of the molecule away from the Fermi energy of the contacts leads to a decreased current at low bias, but as bias increases, this difference decreases and eventually inverses. This is markedly different from IV behavior outside the cotunneling regime. The second approach involves multiple cotunneling where also the molecules are considered to be in the Coulomb blockade regime. We find here that when $E_c \gg eV, k_B T$, the IV behavior approaches the original cotunneling behavior proposed by Averin and Nazarov [Phys. Rev. Lett. **65**, 2446–2449 (1990)]. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4975809]

## I. INTRODUCTION

Molecular electronics is inspired by the prospect of using molecular functionality for advanced nanodevices. Since the tantalizing concept of a molecular diode was first proposed in 1974,[2] research efforts have taken off on systems ranging from molecular wires and transistors[3] to switches.[4] Apart from these device concepts, however, molecular charge transport is of fundamental interest due to the quantum nature of the molecules and hence of their conductance properties, even at elevated temperatures.[4–6] Here, we focus on a specific regime of quantum transport that directly connects to a practical molecular device structure, i.e., inelastic cotunneling through hybrid molecule-nanoparticle junctions.

Initially, fabrication of molecular-scale electronic contacts proved a big problem. Nowadays, however, a wide range of methods for electrically connecting molecules exist.[7] One of these methods is interlinking nanoparticle networks with the molecule of interest.[8] At elevated temperatures, the nanoparticles behave as ordinary electrodes. However, if such a network is cooled down below a characteristic temperature (that depends on the nanoparticle size), the nanoparticles exhibit Coulomb blockade. Remarkably, current can still flow due to quantum fluctuations of charge on the nanoparticles. This process is called cotunneling.[1]

Specifically, in inelastic multiple cotunneling, the electrical current depends on the transmission probability of the interconnecting molecules raised to a power $N \geqslant 2$, with N related to the typical number of hops in the multiple cotunneling process.[9,10] Thus far, the resulting cotunneling current has only been calculated for systems in which the transmission probability is independent of energy. This assumption does not generally apply to molecules bridging between neighboring nanoparticles, however, as molecular transmission functions

can be strongly energy-dependent. Understanding the influence of the latter is not only of fundamental interest; it is also relevant for practical devices, since cotunneling can be utilized to enhance the signature of the molecules bridging.[11] If, for example, the bridges are formed by molecular switches, the ratio between the conductance in the "on" and the "off" state can be artificially increased. In this article, we study the effect of an energy-dependent transmission function on transport between nanoparticles in the Coulomb blockade regime. We propose two methods (outlined in Figs. 1(b) and 1(c)) to tackle this problem.

## II. THEORY OF COTUNNELING MECHANISMS

In this section we briefly review the mechanisms of inelastic cotunneling. Classically, when a system is Coulomb blockaded, no current is expected to flow. However, it was predicted[1] and found experimentally[13,14] that due to quantum corrections, this is not completely the case. The current flowing in the Coulomb blockade regime is due to the process of cotunneling.[1] Cotunneling is the simultaneous transfer of multiple electrons through energetically forbidden virtual states. The basic mechanism is as follows. Consider the device illustrated in Fig. 1(a). Two leads connect to a charging island from either side through a tunnel barrier. An electron can temporarily hop from the left lead onto the charging island. The resulting virtual charge state is energetically forbidden, but temporarily allowed by the Heisenberg uncertainty relation. In this time window, an electron already residing on the island may hop onto the right lead. If these two processes occur within this time window, an electron has effectively been transferred from the left to the right lead. The reverse process (i.e., to the right lead) is also possible, but the symmetry between these processes is broken by applying a voltage bias. The final charge state of the
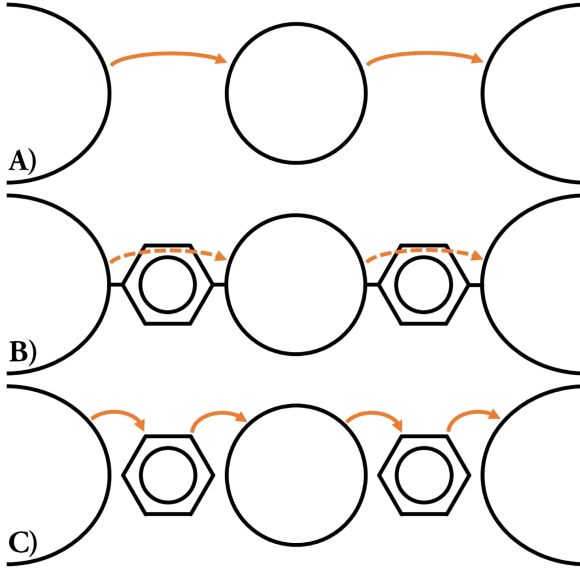
FIG. 1. Three approaches to the cotunneling problem. (a) The original method developed by Averin and Nazarov.[1] Here, the electrons tunnel through tunnel barriers with energy independent transmission probability in a single cotunneling process. (b) Electrons go from left to right via a single cotunneling process, but the transmission probability of the electrons depends on their incoming energy. (c) An adaptation of the multiple cotunneling model.[12] Electrons go from the left lead to the right lead via a multiple cotunneling process through various virtual states. Since the molecules are modeled as single levels as opposed to the leads and nanoparticle, cotunneling through the molecules is elastic, whereas tunneling through the nanoparticle is inelastic.

island is equal to the initial charge state, complying with total energy conservation.

There are two different types of cotunneling: elastic and inelastic. Elastic cotunneling can only be observed at sufficiently low bias and temperature,[13] compared to the quantum level spacing of the charging island. In an elastic cotunneling process, the electron hopping onto the charging island and the electron hopping off have the same energy. In inelastic cotunneling, this is not the case. This results in the charging island being left in an excited state after the process. The inelastic cotunneling current through a single junction as depicted in Fig. 1(a) can be written as[1]

$$I = \frac{1}{6\pi^2} G_0 \mathcal{T}^2 \frac{(eV)^2 + (2\pi k_B T)^2}{E_C^2} V, \qquad (1)$$

where $\mathcal{T}$ is the transmission probability of the tunnel barrier, $G_0 = {}^{2e^2}/_h$ is the conductance quantum, $E_C$ is the charging energy of the island, $T$ is the temperature, $k_B$ the Boltzmann constant, $e$ is the elementary charge, and $V$ is the voltage across the junction. Since two barrier transmissions are needed for transport to occur, it makes intuitive sense that $I \propto \mathcal{T}^2$. However, in the derivation of Eq. (1), it has been assumed that the transmission probability of the tunnel barriers is independent of energy. While this is normally a reasonable assumption, it is not always the case. In this article, we will explore the possibility of an energy-dependent transmission function. In Sec. III we consider the case where the two leads are connected to the nanoparticle through molecules, as seen in Fig. 1(b). The contact transmission is then expected to become dependent on electron energy, assuming a Lorentzian lineshape.

## III. APPROACH 1: LORENTZIAN TRANSMISSION

In this section, we will assume that each of the two molecules involved in the cotunneling problem can be represented by a single level, symmetrically connected to a lead and the central nanoparticle (see Fig. 1(b)). Furthermore, we will suppose that transport through each molecule is coherent, such that the transmission function becomes Lorentzian with a width determined by the lead-molecule coupling.[15] Still, inelastic cotunneling behavior in the full molecule-nanoparticle-molecule system is to be derived by allowing for virtual excitations. More specifically, an electron in the lead, with an energy $E_l$, will temporarily take up a different energy, $E_{s2}$, within the nanoparticle. As a result, the exact energy of electron transmission through the molecule is somewhat ill-defined. To circumvent this problem, we will assume that any change of energy, related to the formation of a virtual state, happens inside the nanoparticle. In that case, the molecular transmission function depends only on the energy of the incoming electron. Summarizing, we assume that all virtual processes take place within the charging island, while transmission through the molecules can still be described by the Lorentzian functions in Eq. (2),

$$\mathcal{T}_{M1}(E_l) = \frac{\Gamma^2}{(E_l - \epsilon_L - \eta_L eV)^2 + \Gamma^2},$$
$$\mathcal{T}_{M2}(E_{s1}) = \frac{\Gamma^2}{(E_{s1} - \epsilon_R - \eta_R eV)^2 + \Gamma^2}. \qquad (2)$$

Here $\Gamma$ is the half width half maximum of the Lorentzian which takes into account lead-molecule and molecule-nanoparticle coupling, $\epsilon_R$ and $\epsilon_L$ are the resonance energies of the molecular levels (we take $\epsilon_R = \epsilon_L$ in our calculations), $E_l$, $E_{s1}$ are the incoming electron energies and $\eta eV$ determines the shift of the level as an effect of the applied voltage. We take $\eta_{L(R)} = (-)^1/4$ in every calculation, implying an equal coupling to both the lead and the nanoparticle. Note that the maximum of the transmission function is taken to be unity.

To calculate the transition rate $R$ from the initial state $|i\rangle$ to the final state $|f\rangle$, the Fermi golden rule[16] can be expanded in order to sum over all virtual states $|v\rangle$. Within this perturbative approach, the small parameter is the coupling between the nanoparticle and the two leads:

$$R = \frac{2\pi}{\hbar} \sum_v \left| \frac{\langle i|H|v\rangle \langle v|H|f\rangle}{E_v - E_i} \right|^2 \delta(E_i - E_f), \qquad (3)$$

where the delta function ensures total energy conservation. $H$ is the same Hamiltonian as used by Averin and Nazarov, Eq. (1),[1] pragmatically extended to include energy-dependent transmission through the molecules. The initial, virtual, and final states are the unperturbed eigenstates of the molecule-nanoparticle-molecule system. The process amplitude should scale with the lifetime of the virtual state which is inversely proportional to the energy difference between the initial and virtual states: $E_i - E_v$. There are two different virtual states as can be seen in Fig. 2. Either an electron on the left lead tunnels through the molecule to the nanoparticle, or an electron first goes from the nanoparticle through the molecule to the right lead. These processes are complementary; if the former process causes the virtual state, the latter leads to the final state
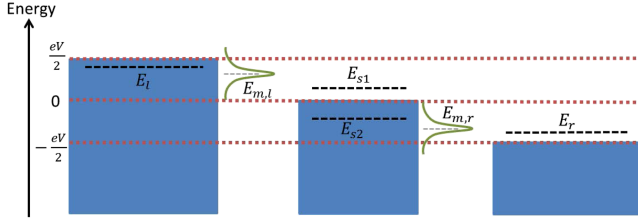
FIG. 2. Energy diagram of a charging island coupled to two leads with an applied bias voltage $V$. $E_l$ and $E_r$ are the electron energies of the left lead and the right lead, respectively. $E_{s1}$ and $E_{s2}$ are electron energies on the charging island.

and vice versa. For a system depicted in Fig. 2 the expression for the rate is given in the following equation:

$$R = \frac{2\pi}{\hbar} \int_E \mathcal{T}_{M1}(E_l)\mathcal{T}_{M2}(E_{s1}) \left[ \frac{1}{\Delta E_{v1}} + \frac{1}{\Delta E_{v2}} \right]^2$$
$$\times F_{FD}\delta(E_i - E_f)\, dE_l dE_r dE_{s1} dE_{s2}, \quad (4)$$

$$F_{FD} = f(E_l)[1 - f(E_{s2})]f(E_{s1})[1 - f(E_r)].$$

Here, the sum over virtual states has been replaced by an integral over all relevant energies. In Eq. (4), the matrix elements from Eq. (3) have been replaced by transmission probabilities $\mathcal{T}_{M1}(E_l)$ and $\mathcal{T}_{M2}(E_{s1})$ analogously to Averin and Nazarov,[1] depending on the incoming electron energies $E_l$ and $E_{s1}$. It should be noted that these transmission functions are chosen for their general applicability and ease of understanding. The model presented here is not limited to these Lorentzian-shaped transmission functions, however, and would work with other transmission functions as well. The energies $E_l$, $E_{s2}$, $E_r$, $E_{s1}$ are depicted in Fig. 2. The energies $\Delta E_{v1}$ and $\Delta E_{v2}$ are defined as the energy differences between the initial and the first and second virtual state, respectively. The occupation of states on the leads and nanoparticle is taken into account by their Fermi-Dirac distributions $f(E)$ (a derivation can be found in Appendix A).

Using Matlab we now calculate the cotunneling current $I(V)$ and differential conductance $dI/dV$ by solving Eq. (4) numerically for the system in Fig. 2. To test the validity of our approach, current versus voltage ($dI/dV$) was calculated for increasing coupling $\Gamma$ for resonant transport ($\epsilon = \epsilon_L = \epsilon_R = 0$). As the coupling increases, the width of the transmission function (as seen in Eq. (2)) increases. The consequence of this is that as $\Gamma$ becomes larger, the cotunneling current should approach the constant transmission case. This can indeed be seen in Fig. 3. Here, $\Gamma$ was varied from 3 meV to 1 eV and compared to the situation with constant transmission $\mathcal{T} = 1$, as derived by Averin and Nazarov.[1] In Fig. 3 it can also be seen that as the coupling increases, the voltage at which the current starts to deviate from the constant-transmission case increases as well, as expected.

Next, we study the effects of molecular gating on the cotunneling current. Gating shifts the resonance position ($\epsilon_L$ and $\epsilon_R$ in Eq. (2)) of the level. As a benchmark, let us first consider coherent transport through a single level connected to two leads, i.e., without Coulomb blockade. In that case, the maximal possible current can be calculated from the Landauer
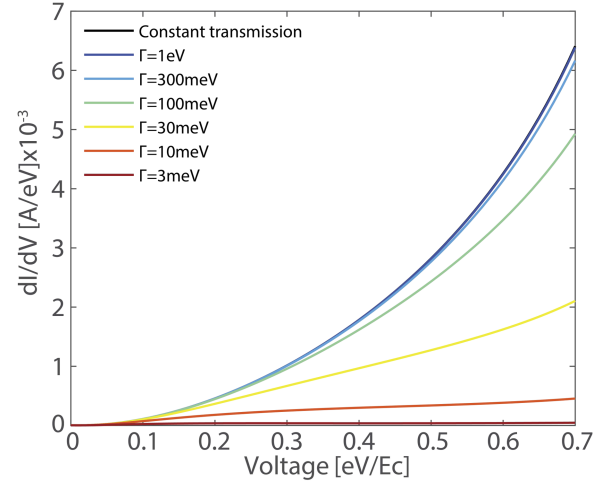


FIG. 3. Differential conductance ($dI/dV$) curves for the system in Fig. 2 with varying $\Gamma$. It can be seen that as the coupling increases, the current approaches the constant transmission case, as is expected. The temperature is 116 K (10 $^{meV}/_{k_B}$), the charging energy $E_C$ is 100 meV, and we take $\epsilon_L = \epsilon_R = 0$ to ensure resonant transport through the molecules. The maximum value of the transmission function is one in every case.

formula at 0 K,[17]

$$I = \frac{G_0}{e} \int_{-eV/2}^{eV/2} \mathcal{T}(E)dE. \quad (5)$$

Clearly, the maximum possible current is the integral over the transmission function as $V \to \infty$. This (finite) number does not change if the peak of the Lorentzian is shifted and/or if the temperature is changed to finite values. In the cotunneling regime, the situation is different, as can be seen in Fig. 4. At low bias (for example, at 0.2 $^{eV}/_{E_C}$), increasing $\epsilon = \epsilon_L = \epsilon_R$ away from zero results in a decrease of the current indeed. However, at larger bias (for example, at 0.45 $^{eV}/_{E_C}$), the current calculated for $\epsilon = 0$ meV is equal to the current found for $\epsilon = 5$ meV. In the $dI/dV$ (see Fig. 4(b)) at large bias (for example, 0.7 $^{eV}/_{E_C}$), it can be seen that the differential conductance is larger for larger $\epsilon$. This is never the case for systems without cotunneling, as the total current is only determined by the area of the transmission curve that is in the bias window. This suggests that cotunneling is selective for higher energy electrons, as long as the transmission function allows them to pass.

To explore possible explanations for this effect, we first note that the cotunneling current is inversely proportional to $(E_v - E_i)^2$ (or $\Delta E^2$), as can be seen in Eq. (3). Hence, electrons with a higher energy are energetically closer to the island charging energy. Thus, they have a lower $\Delta E$, increasing their transmission probability (see Eq. (4)). To test if this phenomenon could lead to the crossing of curves as found in Figs. 4(a) and 4(b), we have done a similar calculation but have replaced the $1/_{\Delta E^2}$ by $1/_{E_C^2}$. The results can be seen in Fig. 4(c). We find that even though the crossings from Figs. 4(c) and 4(d) have changed their position, they have not disappeared. We conclude that the $\Delta E^2$ in the denominator cannot be the principal source of the crossings.

A second explanation for the crossings can be seen in Eq. (4). Here, the electron energy not only appears due to the
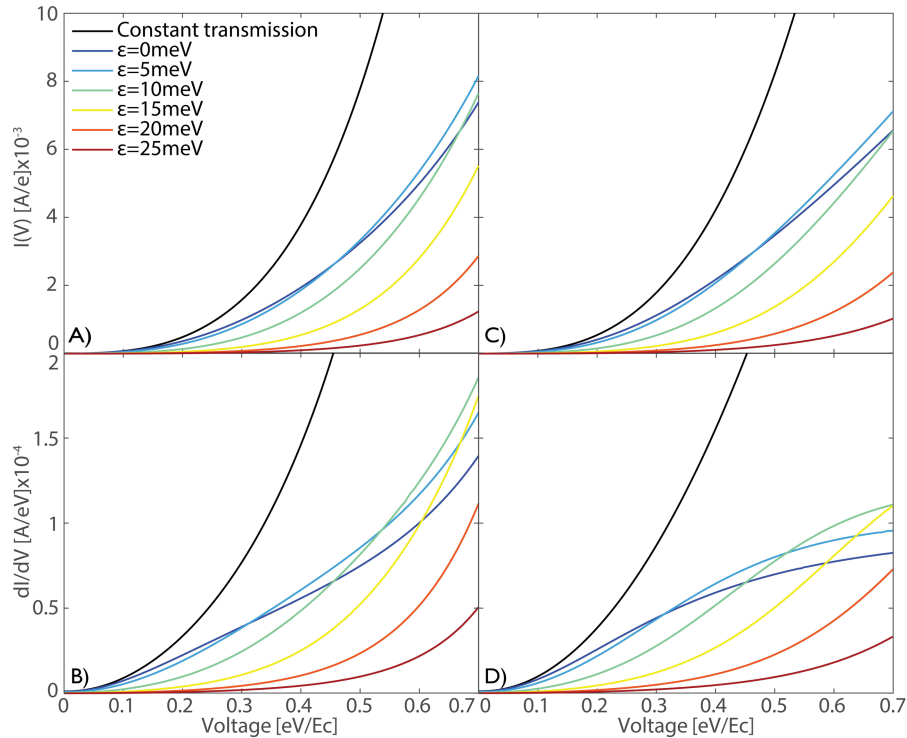
FIG. 4. Plots of current and differential conductance versus voltage for the system in Fig. 2, with $\epsilon$ varying from 0 to 25 meV (corresponding colors for all plots are denoted in (a)). The temperature is 12 K (1 $^{meV}/_{k_B}$), $\Gamma$ = 10 meV, and the charging energy $E_C$ is 100 meV. The maximum transmission is unity in every case. The constant transmission curve (black) is added for reference. (a) IV-plots. At low bias, the current decreases with increasing $\epsilon$. However, as the bias gets larger, the difference decreases. At 0.45 $^{eV}/_{E_C}$, the curve for $\epsilon$ = 0 meV crosses the curve for $\epsilon$ = 5 meV; it even crosses the curve for $\epsilon$ = 10 meV at 0.75 $^{eV}/_{E_C}$. (b) dI/dV-curves derived from (a), magnifying the trends observed in (a). It can be seen that at 0.7 $^{eV}/_{E_C}$ the current increases most rapidly for $\epsilon$ = 10 meV. (c) IV-curves calculated upon approximating the denominator of Eq. (4) by $E_C$. The crossings are still present, although somewhat shifted compared to (a). (d) dI/dV-curves derived from (c). Again, crossings are found, but the shape of the individual curves differs from (b). This can be expected, since the denominator of Eq. (4) as used in (a) and (b) diverges, in contrast to the case of (c) and (d).

Heisenberg uncertainty relation, but also in the overall conservation of energy. The delta function relating the initial and the final energy in Eq. (4) can be written as $\delta(E_r + E_{s1} - E_l - E_{s2} - eV)$. This means that as the voltage increases, more cotunneling pathways are opened to allow transport. If the peak of the transmission function is at this higher energy, these pathways can also tunnel through the molecule, increasing the total current. If the peak of the transmission function lies at a lower energy, the high energy pathways are blocked by the molecule and can therefore not contribute to the current.

To experimentally test the predictions made here, a device that can gate molecules selectively is required, as a back-gate would also gate the nanoparticle. This is non-trivial, however. Fortunately, it may also be possible to test our model using molecular switches.[18] Diarylethylene based switches, for example, do not only change their total transmission but also the position of the resonances.[19] Our predictions could be examined on nanoparticle arrays interlinked by molecular bridges, but this would also require our model to include percolation effects.[18] A more direct evaluation can be done on nanogap devices with a single nanoparticle placed in between the electrodes using dielectrophoresis.[20,21] The current within the Coulomb blockade regime should then be compared to the current outside of it for both states of the switch. This allows for a direct test of the validity of the model proposed above.

In this section, we have assumed that the molecular coupling to the leads and nanoparticle is strong. However, if

this coupling is weak, the charging energy of the molecule itself could start to play a role too.[22] In that case, elastic transmission through the molecule is no longer possible and the only allowed pathway from the left lead to the right is through multiple cotunneling. Sec. IV discusses this problem.

## IV. APPROACH 2: MULTIPLE COTUNNELING

In this section, we study the system depicted in Fig. 1(c) and introduce a charging energy to each (weakly coupled) molecule in order to shift transport across them to the Coulomb blockade regime. To study transport in this regime, we propose a second model based on higher order cotunneling. In Sec. III our model consisted of a second-order cotunneling event with coherent transport through the molecule. However, if the molecular energy levels are Coulomb blockaded, direct tunneling through the molecule is no longer allowed. Therefore, transport across the molecules will only occur through cotunneling. In the system depicted in Fig. 1(c), an electron can be transferred from the left lead to the right lead by a fourth-order cotunneling event, consisting of a collective hopping through four junctions: left lead-molecule, molecule-nanoparticle, nanoparticle-molecule, and molecule-right lead.

Transport across the nanoparticle is due to inelastic cotunneling. Since the molecules are modeled by a single level,
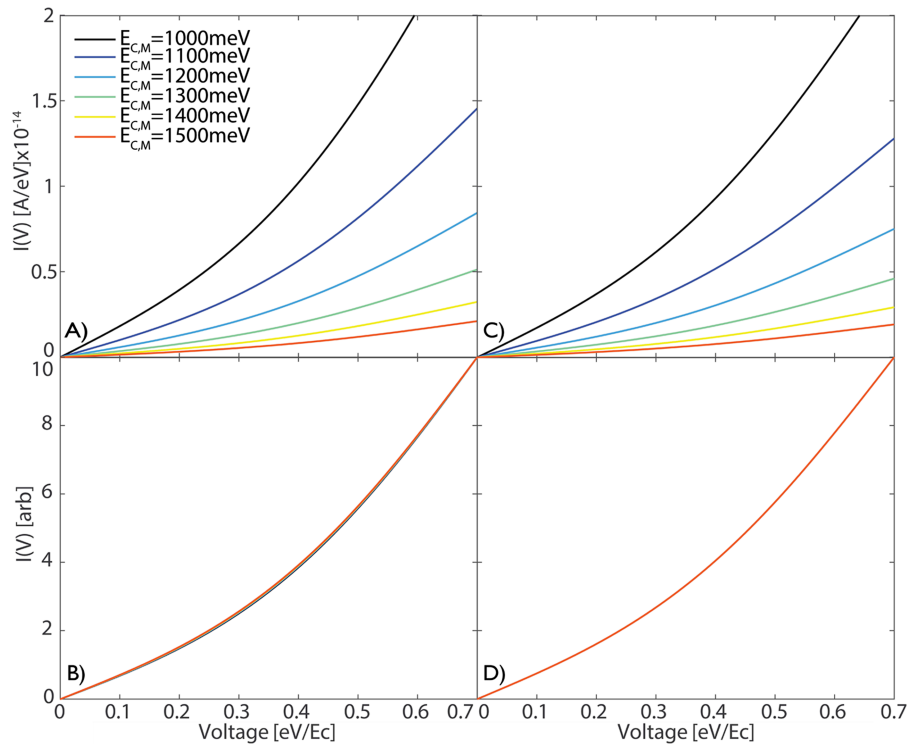
transport across the molecule occurs through elastic cotunneling. Therefore, cotunneling transport in our system is of the fourth-order and consists of a collective combination of two elastic and one inelastic cotunneling event. In a second-order cotunneling event there are two possible hop permutations with distinct virtual states, as stated in Sec. III. However, we now have four junctions, which means that there are 4! hop permutations, each with three virtual states. To calculate the total current in a four junction system, the contribution from each permutation needs to be taken into account. This can be done by considering the matrix elements from Eq. (3) as

$$M = \sum_{\{j_1, j_2, j_3, j_4\}} \prod_{k=1}^{3} \frac{\langle V_{k+1}| H |V_k\rangle}{E_{V_k} - E_i} \langle V_1| H |i\rangle, \quad (6)$$

which sums over all possible permutations of the electron hops that yield the transport of an electron from the left lead to the right lead, e.g., {3, 2, 1, 4} (see Fig. 5). The states



$|i\rangle$

$\epsilon_f$

$|V_1\rangle$

$\epsilon_f$

$|V_2\rangle$

$\epsilon_f$

$|V_3\rangle$

$\epsilon_f$

$|f\rangle$

$\epsilon_f$

FIG. 5. The permutation {3, 2, 1, 4} that contributes to the cotunneling current. Here, the process starts with an electron hopping from the nanoparticle to the right molecule, then from the left molecule to the nanoparticle, followed by an electron from the left lead to the left molecule, and is completed by a transfer from the right molecule to the right lead.

$|V_k\rangle$ are the corresponding virtual states analogously to those defined in approach 1, used during the cotunneling process of each permutation, of which there are three per permutation. The Hamiltonian in Eq. (6) is the same as the one in Eq. (1) of Ref. 1, with two additional terms describing the two molecules (see below). The unperturbed eigenstates of the central molecule-nanoparticle-molecule region are represented, analogously to Ref. 1, as $|n_{M1}, n_{NP}, n_{M2}\rangle$, with $n_i$ ($i = M1, NP, M2$) the number of electrons on molecule 1, the nanoparticle, and molecule 2. The tunnel couplings between the left lead and left molecule, left molecule and nanoparticle, nanoparticle and right molecule, and finally right molecule and right lead are the small parameters in this perturbative approach.

We model each molecule as a singly occupied energy level at the initial state as depicted in Fig. 5. This approximation is valid for a small bias if the energy level is in the Coulomb blockade regime, namely $\epsilon = -\frac{1}{2}E_{C,M}$, where $E_{C,M}$ is the Coulomb charging energy of the molecules. For the situation in Fig. 5, the initial energy for every permutation is $E_i = E_L + {}^V/_2 + 2\epsilon + E_{S2}$, and the final energy for every permutation is $E_f = 2\epsilon + E_{S1} + E_R - {}^V/_2$. We can then write the total rate as a contribution of all possible initial and final energies, the sum of Eq. (3) for every set of energies, $E_L$, $E_R$, $E_{S1}$ and $E_{S2}$. By converting the sum into an integral and the matrix elements $\langle V_{k+1}| H |V_k\rangle$ in Eq. (6) into tunneling rates, we write an explicit equation to calculate the cotunneling rate in our system[1,23] (see Appendix B for details):

$$R = \frac{\hbar^3}{8\pi^3} \mathcal{T}_M^4 \int_{\mathbf{E}} \left| \sum_{\{j_1, j_2, j_3, j_4\}} \prod_{k=1}^{3} \frac{1}{E_{V_k} - E_i} \right|^2 \quad (7)$$

$$\times F_{FD} \delta(E_i - E_f) dE_l dE_r dE_{S1} dE_{S2}.$$

The Fermi distribution functions have been added to Eq. (7) to account for the probability of a state being empty or occupied, accordingly. The conservation of energy is taken into account by $\delta(E_f - E_i)$. $\mathcal{T}_M$ is the transmission probability for an electron going out of or into the molecule, $\mathcal{T}_M$ takes the same role as $\mathcal{T}_{M1}$ and $\mathcal{T}_{M2}$ in Eq. (2), except that it is now assumed to be a constant (set to 1) independent of electron energy.

Moreover, the matrix element from Eq. (6) can be further simplified if we assume that the charging energy of the molecule and of the nanoparticle is larger than all other energies in the system. Interestingly, the energy independence of the matrix element results in the multiple cotunneling behavior of the system reducing to singular cotunneling. This matrix element then becomes

$$M = \frac{T_1^\dagger T_2^\dagger}{E_S}, \quad (8)$$

with $T_1^\dagger, T_2^\dagger$ taking into account the transmission probability to and from the molecules and $E_S$ is a function of the charging energies of the molecules and nanoparticle. A complete derivation can be found in Appendix B.

Using Matlab, we now calculate the cotunneling current ($I(V)$) by solving Eq. (7) numerically (see Fig. 6). We take the charging energy of the molecule to be ten times larger than the charging energy of the nanoparticle, $E_{C,M} = 10E_C$, together

FIG. 6. IV curves for varying $E_{C,M}$, calculated using Eq. (7). The temperature is set to 11.6 K, we take $E_C$ = 100 meV, and $E_{C,M}$ is varied between 1 and 1.5 eV (see legend of (a) for the color coding, holding for all panels). (a) IV-curves calculated. It can be seen that as $E_{C,M}$ increases, the current decreases, as expected. (b) Normalized IV-curves using the same parameters as in (a), i.e., the current at $^{eV}/_{E_C}$ = 0.7 has been set to unity for every curve. It can be seen that this normalization corrects for most of the differences due to variations in $E_{C,M}$. However, it does not fully remove the variation between the curves. (c) IV-curves calculated for varying $E_{C,M}$, where all terms in the denominator other than the charging energies have been neglected. The result of this is that the sum over all virtual states is now a constant, independent of voltage. It can be seen that the total current is lower than in (a). (d) Normalized IV-curves using the same parameters as in (c) (normalization at $^{eV}/_{E_C}$ = 0.7 again). Now the curves, calculated for different $E_{C,M}$, lie exactly on top of one another.

with a small bias voltage and $\epsilon = -\frac{1}{2}E_{C,M}$ ensures Coulomb blockade in the molecule and single occupancy. Analogously to our calculations in Sec. III, we first calculate the current for varying molecular charging energies ($E_{C,M}$). From Eq. (7), we expect the current to decrease as the molecular charging energy increases. This can be seen in Fig. 6(a).

Since the amplitude of each pathway scales inversely with the product of all three energy differences $\Delta E_i$, it can be expected that the total current should decrease with increasing molecular charging energy $E_{C,M}$. Furthermore, if the charging energies of the molecules and nanoparticle are much larger than both the electrostatic and thermal energies in the system, the shape of the I-V curves should not change when changing the charging energy. In Fig. 6(b) we have normalized each curve by the current at 70 meV. It can be seen that this moves the curves very close together, confirming our expectations. However, the rescaled curves are still not precisely identical.

If we now remove any thermal and electrostatic energy from the energy differences in the virtual pathways, we expect the IV-curves to fully overlap. Removing all energies except the charging energies in our calculation of the energy differences, we get the results shown in Fig. 6(c). After normalization, these curves, displayed in Fig. 6(d), lie fully on top of each other, as expected.

Interestingly, the calculations in this section predict that when a charging island is coupled to leads through Coulomb blockaded single levels, it is not possible to distinguish between

multiple cotunneling and inelastic cotunneling with a constant transmission function (as derived by Averin and Nazarov[1]). This holds for any system where transport across the system is through two instances of elastic cotunneling and one instance of inelastic cotunneling.

## V. CONCLUSION

We have explored two approaches to calculate inelastic cotunneling through a nanoparticle connected to two leads through molecules with energy-dependent transmission functions. In the first approach, the molecules are modeled as having single-level Lorentzian transmission functions. Interestingly, we find that at large applied bias, the current for systems with the molecular levels slightly off-resonant can be higher than for the case of resonant molecular levels. This remarkable behavior is a direct consequence of transport taking place via cotunneling. To test this prediction, a nanoparticle covered with molecules could be trapped in a nanogap using dielectrophoresis. Cotunneling transport in such a system is expected to deviate from results derived by Averin and Nazarov[1]. In the second approach we model the molecules as Coulomb blockaded, so that transport across the molecules takes place through elastic cotunneling. We show that at low temperature and bias, the multiple cotunneling current should approach the expression for regular cotunneling. Our calculations support this by showing that the IV-curves are identical when normalized.

## APPENDIX A: THEORETICAL BACKGROUND OF APPROACH 1

Starting from Eq. (3), we first take a look at one of the two possible virtual states. The first virtual state is where an electron from the left lead tunnels through the left molecule onto the nanoparticle. This pathway is finalized by an electron from the nanoparticle that tunnels through the right molecule to the right lead. The matrix element for this state is as follows:

$$\frac{\langle i|H|v_1\rangle\langle v_1|H|f\rangle}{E_{v_1} - E_i} = \frac{T_{m,1}T_{m,2}}{E_l - E_{s1} + E_C + eV_l}. \quad \text{(A1)}$$

For the other virtual state, an electron first goes from the nanoparticle through the right molecule to the right lead and is then followed by an electron from the left lead that goes through the molecule onto the nanoparticle. The expression for this process is as follows:

$$\frac{\langle i|H|v_2\rangle\langle v_2|H|f\rangle}{E_{v_2} - E_i} = \frac{T_{m,2}T_{m,1}}{E_{s2} - E_r + E_C - eV_r}. \quad \text{(A2)}$$

The initial, virtual, and final states are the unperturbed eigenstates of the molecule-nanoparticle-molecule system, defined analogously to the definition used by Averin and Nazarov.[1] Substituting this back into Eq. (A1), we have to take the occupation of states into account to change the sum over states to a sum over energies. Also rewriting the delta function in terms of the energies in the system, we obtain

$$R = \frac{2\pi}{\hbar} \sum_{E_l,E_r,E_{s1},E_{s2}} |T_{m,1}|^2|T_{m,2}|^2$$

$$\times \left| \frac{1}{E_l - E_{s1} + E_C + eV_l} + \frac{1}{E_{s2} - E_r + E_C - eV_r} \right|^2 \quad \text{(A3)}$$

$$\times f(E_l)[1 - f(E_r)]f(E_{S2})[1 - f(E_{S1})]$$

$$\times \delta(E_r + E_{s1} - E_l - E_{s2} - eV).$$

We change the sum for an integral and pragmatically assume $|T_{m,1}|^2|T_{m,2}|^2 = \mathcal{T}_{M1}(E_l)\mathcal{T}_{M2}(E_{s2})$ to obtain Eq. (4). This is done analogously to a previous work[1] where these matrix elements are replaced by constants. To solve this integral numerically, we use the delta function to relate $E_r$ to the other energies ($E_r = E_l - E_{s1} + E_{s2} + eV$) and replace the four dimensional integral by a three dimensional one. We also calculated the current by relating $E_l$ to the other energies ($E_l = E_r + E_{s1} - E_{s2} - eV$) and found no difference between results.

## APPENDIX B: EQUIVALENCE OF MULTIPLE COTUNNELING MODEL TO SECOND ORDER COTUNNELING

We start with the Fermi golden rule, just as with normal cotunneling,

$$R_{E_f,E_i} = \frac{2\pi}{\hbar}|M|^2\delta(E_f - E_i), \quad \text{(B1)}$$

where $E_i$ and $E_f$ are the initial energy and final energy of the system, respectively, and $M$ the matrix element for a fourth order cotunneling event. For the model considered by Averin and Nazarov,[1] this matrix element can be written as

$$M = \sum_v \frac{\langle i|H|v\rangle\langle v|H|f\rangle}{E_v - E_i}. \quad \text{(B2)}$$

Whereas for the fourth order cotunneling event, $M$ can be written as

$$M = \sum_{\{j_1,j_2,j_3,j_4\}} \prod_{k=1}^{3} \frac{\langle V_{k+1}|H|V_k\rangle}{E_{V_k} - E_i} \langle V_1|H|i\rangle. \quad \text{(B3)}$$

The summation is now over 4! virtual states, and the product is over the whole sequence of cotunneling events. In other words, this product can be written as

$$\prod_{k=1}^{3} \frac{\langle V_{k+1}|H|V_k\rangle}{E_{V_k} - E_i} \langle V_1|H|i\rangle$$

$$= \frac{\langle i|H|V_1\rangle\langle V_1|H|V_2\rangle\langle V_2|H|V_3\rangle\langle V_3|H|f\rangle}{\Delta E_1 \Delta E_2 \Delta E_3}, \quad \text{(B4)}$$

where the energy differences of the Heisenberg uncertainty relation are taken into account by the $\Delta E_i$ in the denominator. Following the derivation in Ref. 23, we can replace the matrix elements by transmission constants. The previous equation then becomes

$$\prod_{k=1}^{3} \frac{\langle V_{k+1}|H|V_k\rangle}{E_{V_k} - E_i} \langle V_1|H|i\rangle = \frac{T_1 T_2 T_3 T_4}{\Delta E_{v1} \Delta E_{v2} \Delta E_{v3}}. \quad \text{(B5)}$$

Since the result of multiplication does not depend on the order of multiplication, we can simply write the transmission coefficients as follows:

$$T_1 T_2 T_3 T_4 = T_{l,m1}T_{m1,NP}T_{NP,m2}T_{m2,r}, \quad \text{(B6)}$$

where the transmission coefficients here are respectively from the left lead to the first molecule, from the first molecule to the charging island, from the charging island to the second molecule, and from the second molecule to the right lead.

If we assume that the energy differences $\Delta E_i$ are dominated by the charging energies of the nanoparticle and molecules, all other energies can be ignored. This means that the sum over all virtual pathways becomes a constant which only depends on the charging energies of the molecules and nanoparticle,

$$\sum_n \frac{T_1 T_2 T_3 T_4}{\Delta E_1 \Delta E_2 \Delta E_3} = \frac{T_{l,m1}T_{m1,NP}T_{NP,m2}T_{m2,r}}{E_S(E_{C,m1}E_C, E_{C,m2})},$$

$$E_S(E_{C,m1}E_C, E_{C,m2}) = \left( \sum_v \frac{1}{\Delta E_{v1} \Delta E_{v2} \Delta E_{v3}} \right)^{-1}. \quad \text{(B7)}$$

If we now define $T_1^\dagger = T_{l,m1}T_{m1,NP}$ and $T_2^\dagger = T_{NP,m2}T_{m2,r}$, we have

$$M = \frac{T_1^\dagger T_2^\dagger}{E_S}, \quad \text{(B8)}$$

which is equal to the matrix element in cotunneling derived in Ref. 23. This therefore means that our fourth order cotunneling event will resemble the already familiar cotunneling, with a

transmission function that decreases with increasing Coulomb charging energy. This in turn means that even if there are single levels in between the charging island and the leads, the transmission probability of these levels will be constants.

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