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Symmetry-controlled negative differential resistance effect in a triangular molecule

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We consider, within the Hubbard model, nonequilibrium transport through a triangular molecule [or, equivalently, triple quantum dot system (3QD)], weakly coupled to electrodes. The exact solution of the eigenproblem for the isolated 3QD is used for computation of the current-voltage (*I*-*V*) characteristics of the device in the sequential tunneling limit. We analyze the effects of symmetry perturbation of the device and show that local energy perturbation at one of the sites coupled to the electrodes can lead to a negative differential resistance as well as rectifying properties of the device.

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I. INTRODUCTION

One of the main goals of the molecular electronics is understanding the relation between a chemical structure of a molecular bridge and a desired transport characteristic of the device. In this respect, so-called Tour wires which exhibit a prominent negative differential resistance behavior[1] as well as asymmetric *I*-*V* characteristics attracted much attention recently. The existing theoretical explanations put emphasis on the asymmetry in chemical bonding to the electrodes,[2] role of Coulomb correlations in the current collapse,[3] or polaronic origin of the negative differential resistance (NDR) behavior.[4,5] So far, however, one does not know a simple recipe for obtaining the NDR characteristics of the molecular junction in a general case.

In this paper, we consider possible dependence of the NDR effect on symmetry of a molecule and a proper selection of the molecular levels active in transport. For this purpose we study a model of an abstract triangular molecule. Within the applied model this molecule is equivalent to a system of three coherently coupled quantum dots studied by Gaudreau *et al.*[6] They were mainly interested in complex charge and spin arrangements of this artificial molecule, which can be understood within a set of topological Hund's rules (see also the following papers[7–9]). Emary[10] showed that in such a system, a destructive interference can lead to the effect of coherent population trapping at a so-called dark state, which can have asymmetric coupling with the electrodes. A magnetic flux penetrating the system can alter interference conditions and give rise to large oscillations in the current (see also Ref. 7, in which an evolution of many-electron states of the triangular system in the magnetic field was studied). Here we analyze a problem of rotational symmetry breaking of the molecule and investigate conditions for appearance of the dark states.

The problem of dark states in molecular junctions was also considered from the point of view of *ab initio* approach[11] as well as the model calculation.[3,12] Hettler *et al.*[3] showed that the dark state can occur in a molecular junction with the benzene molecule. Due to symmetry of molecular orbitals, such a state is uncoupled from both the electrodes and, in general, it does not participate in charge transport. However, when a radiative relaxation inside the molecule is allowed, an electron can be transferred to this state from an excited molecular state. The electron can not be transmitted to the electrodes, it is trapped at this state and blocks tunneling current through the molecule.

Our choice of the triangular molecule is dictated mainly by the fact that it is the simplest possible planar molecule, being able to mimic a behavior of typical molecules used in molecular electronics. Its simplicity gives us an opportunity to obtain some analytical results, with an exact account for electron correlations within the molecule, illustrating principle of work in a general case. Here, we are concerned mainly with effects of symmetry breaking by a local perturbation at one of the sites of the triangle. We show how the perturbation of the symmetry influences the current-voltage characteristics and we determine conditions; under which it can lead to the NDR effect as well as rectifying properties of the device.

II. SEQUENTIAL TUNNELING APPROACH FOR TRIPLE QUANTUM DOT

We describe the molecule using the Hubbard Hamiltonian,

$$\mathcal{H} = t\sum_{\sigma} (d^{\dagger}_{1\sigma}d_{2\sigma} + d^{\dagger}_{2\sigma}d_{3\sigma} + d^{\dagger}_{3\sigma}d_{1\sigma} + \text{H.c.}) + \sum_{j=1,2,3} U_j n_{j\uparrow}n_{j\downarrow} + \sum_{\sigma,j=1,2,3} E_j n_{j\sigma}. \tag{1}$$

In Eq. (1), we consider the electron repulsion U_j and the local energy E_j to be site-dependent quantities, while the hopping parameter t is treated as bond independent. Hamiltonian (1) may also be interpreted as a simplified model for a triple quantum dot (3QD) system, the stability diagram of which was recently studied both experimentally and theoretically.[6] The site dependence of the parameters of the Hamiltonian may account for the chemical variation in the molecule components or the local electrostatic potential fields due to a voltage gate in the case of the system of quantum dots; both types of effects perturbing the initial ideal symmetry of the triangle. The complete model of the device includes the terms describing coupling to the electrodes,

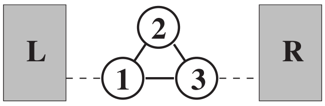

FIG. 1. A schematic view of the triangular molecule weakly coupled to the electrodes.

$$\mathcal{H}_T = \sum_{\mathbf{k}} v^L_{\mathbf{k}}(c^\dagger_{L\mathbf{k}\sigma}d_{1\sigma} + \text{H.c.}) + \sum_{\mathbf{k}} v^R_{\mathbf{k}}(c^\dagger_{R\mathbf{k}\sigma}d_{3\sigma} + \text{H.c.}), \quad (2)$$

as well as the terms $\mathcal{H}_\ell = \Sigma_{\mathbf{k}}\varepsilon_{\ell\mathbf{k}}c^\dagger_{\ell\mathbf{k}\sigma}c_{\ell\mathbf{k}\sigma}$ describing electrodes, treated here in the independent-particle approximation with a quasiparticle energy $\varepsilon_{\ell\mathbf{k}}$. In Eq. (2) the left $\ell = L$ (right $\ell = R$) electrode couples directly to the first (third) atom of the molecule and the second atom is uncoupled from the electrodes (see Fig. 1).

Here we assume that the coupling $v^\ell_{\mathbf{k}}$ to the electrodes is weak enough to be treated within the perturbation approach. This is a common situation of the molecules which are physisorbed rather than chemisorbed to a metal surface[13,14] or which are bound to the surface with an insulating alkane linking chain.[15] In this limit, the standard quasiparticle approach[2] may be questionable and the perturbation method is a useful alternative.[16] Consequently, we confine our studies to the lowest order of the coupling parameter and apply the formalism of the sequential tunneling theory[17–19] based on the solution of the master equation to find the occupation probability of the molecular eigenstates and electric current flowing through the device in the steady limit. The system of master equations can be written in the following form:

$$\begin{aligned}\frac{dP_{n,\mu}}{dt} &= \sum_{\ell,\lambda} W^{(\ell)}_{n-1,\lambda\to n,\mu}P_{n-1,\lambda} + \sum_{\ell,\nu} W^{(\ell)}_{n+1,\nu\to n,\mu}P_{n+1,\nu},\\ &- P_{n,\mu}\left(\sum_{\ell,\lambda} W^{(\ell)}_{n,\mu\to n-1,\lambda} + \sum_{\ell,\nu} W^{(\ell)}_{n,\mu\to n+1,\nu}\right),\\ &\text{for } 0 < n < N. \qquad (3)\end{aligned}$$

In Eq. (3) $P_{n,\mu}$ denotes probability of occupation of molecular state $|n,\mu\rangle$ with n electrons at the molecule. $W^{(\ell)}_{n,\mu\to n',\mu'}$ denotes a transfer rate for the process in which the molecular state changes from $|n,\mu\rangle$ with n electrons to $|n',\mu'\rangle$ with n' electrons, by a hopping of an electron from or to the electrode ℓ, for $n' > n$ and $n' < n$, respectively. Above, we explicitly indicated that the molecule in question may exist in several different quantum states for a given charging state. Corresponding equations for the empty molecule ($n=0$) and the fully occupied molecule ($n=N$) are different from Eq. (3) by skipping contributions from $n-1$ and $n+1$ components, respectively. We are interested here in the steady-state solution of Eq. (3) with $dP_{n,\mu}/dt=0$. In this case, the current flowing through the device reads as

$$I = e\sum_{n,\mu,n'\mu'}(\delta_{n',n+1} - \delta_{n',n-1})W^{(L)}_{n,\mu\to n',\mu'}P_{n\mu}. \qquad (4)$$

All the information about the molecular electronic structure and the positions of electrochemical potential in the electrodes V_ℓ is supplied to Eqs. (3) and (4) via the transfer rate $W^{(\ell)}_{n,\mu\to n',\mu'}$, which is given by

$$\begin{aligned}W^{(L)}_{n,\mu\to n',\mu'} &= \Gamma_L\sum_\sigma |\langle n',\mu'|d^\dagger_{1\sigma}|n,\mu\rangle|^2 f(E_{n'\mu'} - E_{n\mu} - \mu_L)\\ &+ \Gamma_L\sum_\sigma |\langle n',\mu'|d_{1\sigma}|n,\mu\rangle|^2\\ &\times[1 - f(E_{n\mu} - E_{n'\mu'} - \mu_L)], \qquad (5)\end{aligned}$$

where $\Gamma_L = 2\pi\Sigma_{\mathbf{k}}|v^L_{\mathbf{k}}|^2\delta(E-\varepsilon_{L\mathbf{k}})$ is a parameter describing coupling between the molecule and the electrode, assumed here to be an energy-independent quantity, f denotes the Fermi distribution function, the chemical potential is $\mu_L = E_F + eV_L$, E_F denotes the Fermi energy, and V_L is an applied potential. Analogous formula holds for the transfer rate $W^{(R)}_{n,\mu\to n',\mu'}$ from the right electrode with $d^{(\dagger)}_{3\sigma}$ substituting $d^{(\dagger)}_{1\sigma}$.

III. SYMMETRY-DEPENDENT EFFECTS IN *I-V* CHARACTERISTICS

At moderate temperature and voltage values, transport behavior of the system is principally dependent on the symmetry of the solutions. For the most symmetric case $U_j = U$ and $E_j = E$ and for the analysis of the solutions of the isolated molecule, it is convenient to chose the eigenstates of $\mathcal{H}$ to be simultaneously the eigenstates of symmetry operations of the triangle. A rotation with respect to the center of the triangle $\hat{\mathcal{O}}$ has three eigenvalues: $q=1$, $\exp(\pm 2\pi i/3)$, and all the eigenstates corresponding to $q=\exp(\pm 2\pi i/3)$ are degenerate in energy. The finite coupling to the electrodes breaks the perfect rotational symmetry of the triangle. For this case it may be more appropriate to choose the Hamiltonian eigenfunctions as the eigenfunctions of the mirror reflection of the whole junction $\hat{\mathcal{R}}$. The two symmetry operations commute with the symmetric Hamiltonian but do not commute with themselves. Note that the transfer rates computed from Eq. (5) as well as the solutions of the master equations depend on the particular choice of the symmetry of the eigenstates. Another effect which spoils the perfect rotational symmetry, as well as the degeneracy of the Hamiltonian eigenvalues, is due to the potential ramp for finite bias voltage. In what follows we assume that the effect of finite bias voltage as well as other local energy perturbations dominates over the symmetry-breaking effects due to coupling to electrodes, which is consistent with the weak-coupling limit.

Qualitatively, the symmetry-breaking effects are most significant, when the eigenstates originating from the eigenvalues $q=\exp(\pm 2\pi i/3)$ of $\hat{\mathcal{O}}$ enter the source-drain voltage window and simultaneously the symmetry of the perturbation is different from the reflection symmetry of the whole junction. To illustrate this point we consider a symmetry-breaking perturbation localized at site 1, which is in direct contact with the left electrode. The perturbation represented by the operator $\hat{\Delta}_1$ may be related to an increase in one of the energy parameters: E and U (or both) at this particular site, while the sites 2 and 3 are energetically equivalent. Let us assume that the perturbation $\hat{\Delta}_1$ is much greater than the coupling to the electrodes. At not too high voltage and small temperature, only the lowest-energy states of the system are important for the transport.

For definiteness we consider a specific range of the parameters E, U, and $t>0$, for which a singlet state with $n=4$ electrons $|4,S_0(+)\rangle$ is the lowest-energy solution of the unperturbed fully symmetric 3QD. The ground state is also the eigenstate of $q=1$ eigenvalue of $\hat{\mathcal{O}}$. It is as well the symmetric eigenstate of the reflection operator $\hat{\mathcal{R}}_{23}$, transforming site 2 to site 3 and vice versa, and leaving site 1 unchanged. Note that the perturbation $\hat{\Delta}_1$ is an invariant of $\hat{\mathcal{R}}_{23}$, i.e., $[\hat{\mathcal{R}}_{23},\hat{\Delta}_1]=0$.

Let us assume that a symmetric potential difference is applied to the electrodes ($V_L=V/2$ and $V_R=-V/2$). Current flowing through the junction in this parameter range is exponentially small up to the point when for some threshold voltage one of the eigenstates from the $n=4\pm 1$ subspace enters the voltage window. The lowest-energy state from $n=3$ subspace $|3,[q=\exp(\pm 2\pi i/3)]_\sigma\rangle$ is double degenerate orbitally for the fully symmetric 3QD. In the presence of the symmetry-breaking perturbation $\hat{\Delta}_1$, the energetic degeneracy of the orbital doublet $|3,[q=\exp(\pm 2\pi i/3)]_\sigma\rangle$ is removed and the resulting two eigenstates are the eigenstates of $\hat{\mathcal{R}}_{23}$: one symmetric state $|3,(+)_\sigma\rangle$ and the other antisymmetric one $|3,(-)_\sigma\rangle$ (see the Appendix),

$$\hat{\mathcal{R}}_{23}|3,(r)_\sigma\rangle = r|3,(r)_\sigma\rangle.$$

The significance of this splitting for the transport is that the matrix element of the electron operator $d_{1\sigma}^{(\dagger)}$ which determines the transfer rate between the molecular eigenstates vanishes between states of different reflectional symmetry,

$$\langle 4,S_0(+)|d^{\dagger}_{1,-\sigma}|3,(-)_\sigma\rangle = 0, \quad \langle 4,S_0(+)|d^{\dagger}_{1,-\sigma}|3,(+)_\sigma\rangle \neq 0,$$

because $d_{1\sigma}^{(\dagger)}$ is also invariant with respect to $\hat{\mathcal{R}}_{23}$. In result, a process in which an electron hops from the 3QD being in $|4,S_0(+)\rangle$ state to the left electrode and leaves an antisymmetric state $|3,(-)_\sigma\rangle$ behind is forbidden by the symmetry. At the same time, a corresponding hopping to the right electrode is still possible provided only that it is allowed by the energy conservation and the position of the electrochemical potential in the right electrode.

Let us consider the voltage evolution of the occupations of the relevant eigenstates as well as the current on the basis of the approximate solution of the system of master equations. In the solution we restrict our basis to five states: $|4,S_0(+)\rangle$ and $|3,(r)_\sigma\rangle$, where: $r=\pm 1$, $\sigma=\uparrow,\downarrow$. In this approximation the solutions of the master equations read as

$$P_r = 2\frac{W_{S,r}}{W_{r,S}}P_S, \quad P_S = 1 \Bigg/ \left(1 + 2\frac{W_{S,+}}{W_{+,S}} + 2\frac{W_{S,-}}{W_{-,S}}\right), \tag{6}$$

where P_S, P_+, P_- denote the probabilities of occupation of the singlet state, symmetric doublet, and antisymmetric doublet ($P_r \equiv P_{3(r)\uparrow}+P_{3(r)\downarrow}$), respectively. The corresponding transfer rates are given by

$$W_{S,r} \equiv W^{(L)}_{4S_0\to 3(r)_\sigma} + W^{(R)}_{4S_0\to 3(r)_\sigma} = \gamma_L(r) f\left(\frac{e(V_r+V)}{2}\right) + \gamma_R(r) f\left(\frac{e(V_r-V)}{2}\right),$$

$$W_{r,S} \equiv W^{(L)}_{3(r)_\sigma\to 4S_0} + W^{(R)}_{3(r)_\sigma\to 4S_0} = \gamma_L(r) f\left(-\frac{e(V_r+V)}{2}\right) + \gamma_R(r) f\left(-\frac{e(V_r-V)}{2}\right),$$

$$\gamma_L(r) = \Gamma_L |\langle 4,S_0(+)|d^{\dagger}_{1,-\sigma}|3,(r)_\sigma\rangle|^2,$$

$$\gamma_R(r) = \Gamma_R |\langle 4,S_0(+)|d^{\dagger}_{3,-\sigma}|3,(r)_\sigma\rangle|^2. \tag{7}$$

Above we assumed the Fermi energy at $E_F=0$ and $V_r \equiv 2\Delta E_{3(r),4S_0}/e = 2(E_{3(r)}-E_{4S_0})/e>0$.

Let us assume that the symmetric spin doublet $|3,(+)_\sigma\rangle$ has lower energy than the asymmetric one $|3,(-)_\sigma\rangle$, i.e., $E_{3(+)}<E_{3(-)}$ and $V_+<V_-$. For $\mu_L>\mu_R$, small temperatures, $\Gamma_\ell < k_B T \ll eV_r$, we have the following ranges of voltage dependence of current:

(1) $V<V_+$: transition rates are approximately given by

$$W_{S,r} \sim [\gamma_L(r)+\gamma_R(r)]e^{-\beta e(V_r+V)}, \quad W_{r,S} \sim [\gamma_L(r)+\gamma_R(r)].$$

From Eq. (6) it follows that only the ground state $|4,S_0(+)\rangle$ is appreciably occupied, $P_S \sim 1$. Here the chemical potentials μ_ℓ of the electrodes lie in the gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital. Since the other charge states need thermal excitations: $P_r \sim 2e^{-\beta e(V_r+V)}$, current is exponentially small in this region. It is a typical feature of the Coulomb blockade effect seen in systems of quantum dots.

(2) $V_+<V<V_-$: approximate transfer rates read as

$$W_{S,+} \sim \gamma_R(+), \quad W_{+,S} \sim \gamma_L(+),$$

$$W_{S,-} \sim \gamma_R(-)e^{-\beta e(V_- - V)/2}, \quad W_{-,S} \sim \gamma_R(-),$$

and both $|4,S_0(+)\rangle$ and doublet $|3,(+)_\sigma\rangle$ are in the voltage window. These states are predominantly occupied,

$$P_S \sim 1/[1+2\gamma_R(+)/\gamma_L(+)],$$

$$P_+ \sim 2\frac{\gamma_R(+)}{\gamma_L(+)}P_S \gg P_- = 2e^{-\beta e(V_- - V)/2}P_S,$$

and participate in electron transfer between the electrodes. This is the conducting region, in which the current is approximately constant, dependent on the transfer rates $W_{S,+}$ and $W_{+,S}$.

(3) $V_-<V$: the transfer rates are

$$W_{S,r} \sim \gamma_R(r), \quad W_{+,S} \sim \gamma_L(+), \quad W_{-,S} \sim \gamma_R(-)e^{-\beta e(V-V_-)/2}.$$

Now the voltage window includes additionally the state $|3,(-)_\sigma\rangle$. Usually opening a new conducting channel leads to an increase in current. However, in the present case the transfer rate $W_{-,S}$ becomes exponentially small because of the symmetry reasons $\gamma_L(-)=0$. When the molecule is in the ground state $|4,S_0(+)\rangle$, an electron can hop to the right (i.e., drain) electrode, leaving either state $|3,(+)_\sigma\rangle$ or state $|3,(-)_\sigma\rangle$ behind. In the former case, the molecule can accept

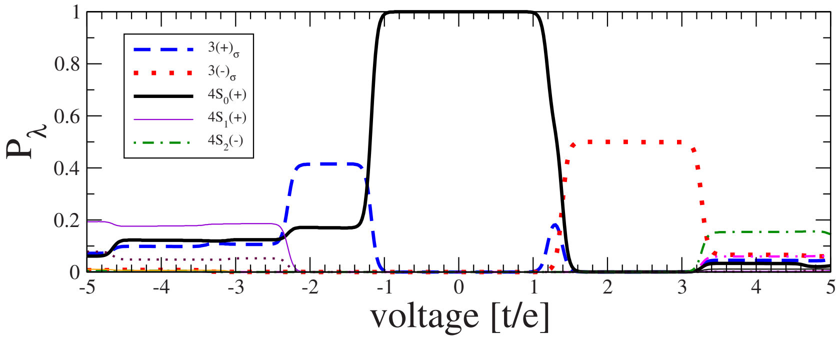

FIG. 2. (Color online) Probability occupations for several most important states as a function of bias voltage V for local energies $E_1 = E+1$ and $E_2 = E_3 = E = -4$. Other parameters are $U_j = 5$, $\Gamma_L = \Gamma_R = 0.01$, and $k_B T = 0.02$ and parameter of potential ramp $\eta = 0.1$. Here and in the other figures $t = 1$ is our energy unit and energies are taken relatively to $E_F = 0$.

an electron from the left (i.e., source) electrode going back to the $|4, S_0(+)\rangle$ state. In the latter case, the molecule cannot accept any more electrons from the left electrode because $\gamma_L(-) = 0$. Above behavior bears a resemblance of a dark state, which is well known in optics and Bose condensations of atoms (as coherent populating trapping)[20,21] and recently also studied in quantum dots.[9,10,22–24] Here, however, the state $|3, (-)_\sigma\rangle$ is uncoupled with the left electrode, but it is still coupled with the right electrode. The antisymmetric doublet $|3, (-)_\sigma\rangle$ becomes a dominating state at the cost of quickly decreasing occupation of both singlet $|4, S_0(+)\rangle$ and the symmetric doublet $|3, (+)_\sigma\rangle$,

$$P_S \sim \frac{1}{2} e^{-\beta e (V - V_-)/2}, \quad P_+ \sim \frac{\gamma_R(+)}{\gamma_L(+)} e^{-\beta e (V - V_-)/2}, \quad P_- \sim 1.$$

Since the molecule in $|3, (-)_\sigma\rangle$ state cannot release an electron to the right electrode and states from $n = 2$ subspace are still beyond the scope of the voltage window, the molecule is kept in this state exponentially long. Moreover, the electronic transfer through the state $|3, (+)_\sigma\rangle$ is blocked; therefore the total tunneling current collapses. It is a manifestation of a dynamical interchannel Coulomb blockade—the effect predicted in a multichannel transmission through quantum dots.[25–29]

With further increase in the voltage for $V \sim V_T$, the states from $n = 2$ subspace and the excited states from $n = 4$ subspace finally enter the play. Some of them are antisymmetric with respect to the reflection and therefore have nonzero matrix elements with $|3, (-)_\sigma\rangle$ state for $d_{1\sigma}$ (corresponding transfer rates are nonzero). These antisymmetric states unlock the $|3, (-)_\sigma\rangle$ state, resulting in a rapid rise of the current. The phenomenon of dynamical channel Coulomb blockade is observed here for $V_- < V < V_T$. The width of the NDR peak is equal to the energy splitting between antisymmetric doublet and the symmetric one $E_{3(-)} - E_{3(+)} \sim \|\hat{\Delta}_1\|$.

IV. RESULTS AND DISCUSSION

Results of exact numerical computations including all 64 basis states of 3QD are presented in Figs. 2–4 for the case when the local energy at site 1, $E_1 = E + \Delta E_1$, is enhanced with respect to the local energies $E_2 = E_3 = E$. Here we included also the finite effect of the potential ramp, assuming the voltage dependence of local energy parameters on the voltage in the form: $E_1(V) = E_1 + \frac{1}{6}\eta e V$, $E_2(V) = E_2$, and

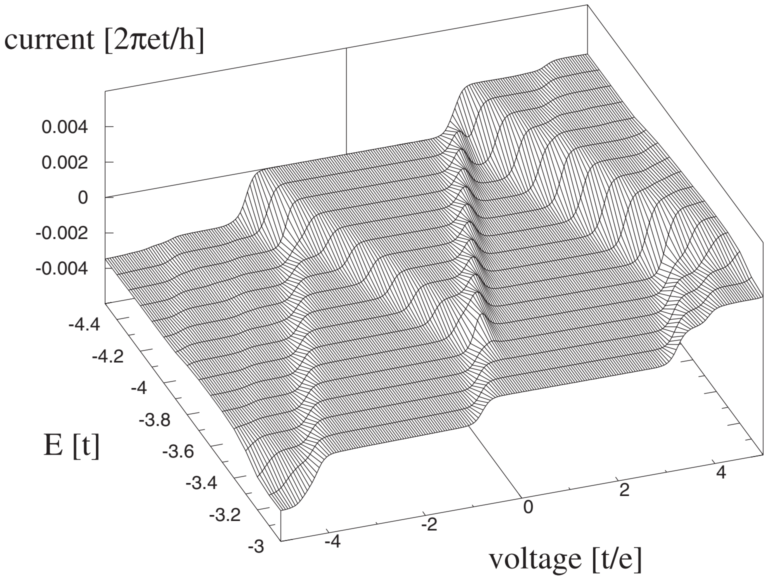

FIG. 3. I-V characteristics for $E_1 = E+1$, $E_2 = E_3 = E$, $U_j = 5$, $\Gamma_L = \Gamma_R = 0.01$, $k_B T = 0.04$ ($t = 1$), and $\eta = 0.1$, in the range of E where the NDR effect is found. For the case $E \approx -3.3$, I-V shows substantial asymmetry but no NDR effect.

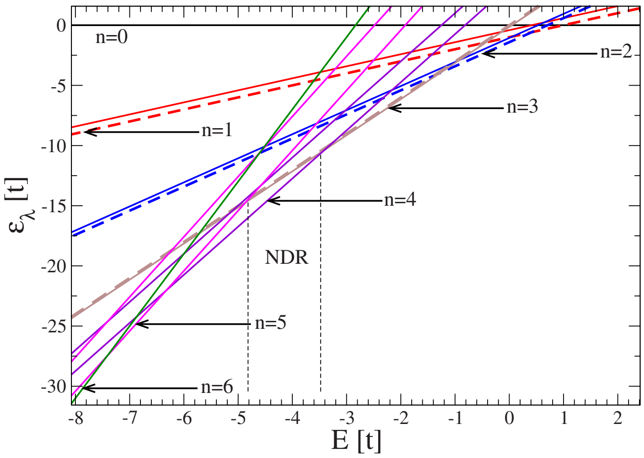

FIG. 4. (Color online) Eigenvalues of the 3QD versus E for $E_1=E+1$, $E_2=E_3=E$, and $U=5$. We show only the ground state for each electron occupation (pointed with an arrow) and the lowest-excited state for the same occupation: the line of the same slope as the ground-state line but shifted upward. The states symmetric with respect to the reflection $\hat{\mathcal{R}}_{23}$ are shown with solid lines; the antisymmetric ones with the broken lines. The range of E for which NDR effect can be found is located between the vertical broken lines. The effect of the potential ramp is not included here.

$E_3(V)=E_3-1/6\eta eV$ for $\eta=0.1$. Including the ramp mimics the effects of actual connection with the electrodes, which breaks the perfect symmetry of the triangle. From the numerical computation, it follows that the effect of the ramp does not modify much the results obtained for sufficiently large $\hat{\Delta}_1$, when the effect of the symmetry breaking due to the perturbation is dominating.

In Fig. 3 we show the evolution of the *I*-*V* characteristics and the NDR peak with a change in the reference local energy E. Here we can see the NDR peak emerging near $V=0$ for $E\approx-3.4$ t. With the decrease in the local energy E, the peak moves steadily to the higher voltage region. The peak finally merges with the continuum of *I*-*V* dependence near $E\approx-4.5$ t. Note that, except the existence of the NDR peak, the *I*-*V* dependence shows a considerable rectification ratio for any voltage between the peak and the *I*-*V* continuum.

The appearance of NDR effect in the *I*-*V* dependence can be related to the peak of occupation of the symmetric $|3,(+)_\sigma\rangle$ state at about $V\approx1.3$ seen in Fig. 2. The sudden drop of the occupation of $|3,(+)_\sigma\rangle$ state is accompanied by a simultaneous rise of occupation of $|3,(-)_\sigma\rangle$ which begins to dominate the behavior of the system and blocks the transport until the first antisymmetric excited state enters the voltage window. In the case presented in Fig. 2, it is the second-excited state of $n=4$ subspace $|4,S_2(-)\rangle$ which finally unlocks the current. Since this state possesses the same symmetry as $|3,(-)_\sigma\rangle$ state with respect to the reflection, matrix element $\langle 4,S_2(-)|d^\dagger_{1,-\sigma}|3,(-)_\sigma\rangle$ and the corresponding transfer rates $W^{(L)}_{3(-)_\sigma\to4S_2(-)}$ are nonzero. Note that the threshold voltage $V_T>0$ for which the current begins to rise again is determined by the eigenvalue of the antisymmetric-excited state, even if the symmetric-excited state from $n=4$ subspace $|4,S_1(+)\rangle$ has lower energy than $|4,S_2(-)\rangle$ state.

In Fig. 4 we show the dependence of the lowest-energy state and the first-excited state for each electron occupation as a function of local energy E. The range of existence of the NDR peak shown in Fig. 3 can be related to the region where symmetric singlet state $|4,S_0(+)\rangle$ is the ground state of the molecule, the symmetric spin doublet $|3,(+)_\sigma\rangle$ is the lowest-excited state, and the second-excited state is the antisymmetric spin doublet $|3,(-)_\sigma\rangle$ (see the energy interval limited by the vertical broken lines Fig. 4). Here the scenario for the appearance of the NDR effect discussed in Sec. III can be realized due to the sufficient energy separation of $|3,(-)_\sigma\rangle$ state from other antisymmetric-excited states of 3QD (see also Fig. 2).

The possibility of appearance of NDR effect is also suggested by the sequence of the ground state and the excited ones for $E>1$. Here the 3QD is empty in the ground state and the lowest-excited states originate from the $|1,[q]_\sigma\rangle$ orbital doublet split by the perturbation. However for $\Delta E_1>0$, the lowest-energy state from $n=1$ subspace $|1,(-)_\sigma\rangle$ is antisymmetric rather than symmetric with respect to the $\hat{\mathcal{R}}_{23}$ reflection. The matrix element $\langle 0|d_{1\sigma}|1,(-)_\sigma\rangle$ as well as the corresponding transfer rate $W^{(L)}_{0,-}$ vanishes and the transport is suppressed until the symmetric state $|1,(+)_\sigma\rangle$ gets into the voltage window. In result the NDR effect is not present in this parameter region.

The symmetric and antisymmetric states originating from the orbital doublets interchange in energy scale if we reverse sign of ΔE_1. For $\Delta E_1<0$ we no longer find the NDR effect for the region where $|4,S_0(+)\rangle$ is the ground state of the system. The transport is suppressed until $|3,(+)_\sigma\rangle$ state (being the second-excited state for $\Delta E_1<0$) enters the voltage window. The negative sign of ΔE_1 by itself still does not make possible the NDR effect to appear for $E>1$. This is due to energetic proximity of excited triplet states from $n=2$ subspace $|2,T(-)_{2\sigma,0}\rangle$ to state $|1,(-)_\sigma\rangle$. The energy distance between the triplet states of $n=2$ subspace and $|1,(-)_\sigma\rangle$ state is equal to the distance between $|1,(-)_\sigma\rangle$ state and the empty state [cf. Appendix, Eq. (A2)]. In result the triplet states appear in the voltage window simultaneously with $|1,(-)_\sigma\rangle$ state and unlock the current.

The triplet states of $n=2$ subspace as well as the states of $n=1$ subspace do not depend on the Coulomb on-site repulsion, but their relative position in the energy scale can be changed by including in the Hamiltonian intersite repulsion. This term pushes up the two-electron states beyond the voltage window and makes possible to observe the NDR effect in the region where the empty state is the ground state of the molecule.

V. SUMMARY

Summarizing, we present studies of sequential electronic transport through a molecule with the triangular symmetry. The eigenproblem for the molecule has been solved analytically for any number of electrons, also for the case of broken rotational symmetry (details are presented in the Appendix). Analyzing the perturbation of the local symmetry, we found conditions for the half-dark states. In contrast to the dark states discussed in other works,[9,10,22–24] these states are uncoupled from one of the electrodes only. A finite coupling with the second electrode enables injection of a charge to the half-dark state, which leads to the dynamical interchannel Coulomb blockade[25–29] and the NDR effect.[3] In the considered detail example of four electrons at the molecule, the ground state is symmetric singlet state $|4,S_0(+)\rangle$; whereas the lowest-excited states form the split doublets: $|3,(+)_\sigma\rangle$ and $|3,(-)_\sigma\rangle$, the second one being the half-dark state. When the voltage bias increases, first $|3,(+)_\sigma\rangle$ participates in electronic transfer through the molecule, which is seen in an abrupt increase in the current. For a little bit larger voltage $|3,(-)_\sigma\rangle$ enters the play. Its coupling with the electrodes is very asymmetric, $\gamma_L(-)=0$ and $\gamma_R(-)\neq 0$, due to symmetry of the local potential which breaks the rotational symmetry; but it keeps the reflection symmetry. For this situation, an electron can be pushed from the right electrode to this state and accumulated at the molecule for a long time. The transfer channel through the state $|3,(+)_\sigma\rangle$ becomes blocked due to joint effect of Coulomb interactions and the symmetry perturbation, which result in the current collapse. The position of the half-dark state depends on a sign of the local potential $\hat{\Delta}_1$ [see the Appendix and Eqs. (A16) and (A17)], and it can be the ground state as well. For such situation, the Coulomb blockade gap is much larger and the NDR peak is not seen.

Our results suggest possibility of finding the NDR effect due to symmetry reasons in other molecules as well provided that the following sufficient conditions are fulfilled. (i) The ground state $|n,(s)\rangle$ and the first-excited state $|n+1,(s)\rangle$ of a molecule should correspond to the same eigenvalue s of a molecular symmetry $\mathcal{S}$. (The conditions are identical if the excited state belongs to $n-1$ subspace). This condition provides nonzero transfer rates $W^{(\ell)}_{n(s)\to n+1(s)}$ and $W^{(\ell)}_{n+1,(s)\to n,(s)}$ and a finite tunneling current through the molecule. (ii) The second-excited state $|n+1,(s')\rangle$ should correspond to another eigenvalue $s'\neq s$ of symmetry $\mathcal{S}$ and at the same time the coupling between one of the leads and the molecule should be invariant with respect to the symmetry $\mathcal{S}$. Due to symmetry reasons, one of the transfer rates $W^{(\ell)}_{n,(s)\to n+1,(s')}=0$ (or $W^{(\ell)}_{n+1,(s')\to n,(s)}=0$) and the state $|n+1,(s')\rangle$ is then decoupled from one of the electrodes. If this condition is fulfilled, a charge can be trapped at this excited state, which leads to interchannel Coulomb blockade with a collapse of the current. (iii) All other excited states should be well separated in energy from both the ground state and the first two-excited states.

The above conditions as well as most of the quantitative results of our paper hold provided that the coupling to the electrodes and the effect of the potential ramp is weak enough to be treated as only minor perturbations of symmetry $\mathcal{S}$. It would be interesting to extend the present studies for coherent tunneling processes, e.g., to include cotunneling processes for the stronger coupling. The higher-order tunneling modifies little the molecular spectrum, but their role is relevant in electronic transport. One can expect that calculations of various cotunneling terms will show different contributions of many electronic states (also the Kondo states) to transport.[30] Such studies can also provide information on decoherence processes and leakage currents,[31] which are important for coherent manipulation of entangled molecular states.[32]

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APPENDIX: EIGENSOLUTIONS OF THE TRIANGULAR DOT AND THEIR SYMMETRIES

In this section, we gather relevant explicit results for the energy eigenvalues and the eigenstates of the isolated triangular molecule. We discuss below the cases with $n=1,2,3$ electrons in the 3QD; the solutions from subspaces with $n=4,5$ can be obtained from the presented ones by means of an electron-hole transformation with a change $t\to -t$. We summarize first the fully symmetric case ($E_j=E$, $U_j=U$); next we consider the effect of the symmetry perturbation.

1. Fully symmetric case

n=1 *subspace*. The explicit eigensolutions are given by

$$|1,[q]_\sigma\rangle = d^\dagger_{q\sigma}|0\rangle = \frac{1}{\sqrt{3}}(d^\dagger_{1\sigma}+q^* d^\dagger_{2\sigma}+q d^\dagger_{3\sigma})|0\rangle,$$

$$\varepsilon_{1q}=E+2t\cos(\eta),\quad q=e^{i\eta},\quad \eta=0,\pm\frac{2\pi}{3},\qquad \text{(A1)}$$

where q is a corresponding eigenvalue of the rotation operator $\hat{\mathcal{O}}$. The ground state is nondegenerate for the $t<0$, but it is double degenerate for $t>0$.

n=2 *subspace*. This subspace splits into three other subspaces corresponding to the eigenvalues of the z component of spin operator $\hat{S}_z$, $S_z=\pm 1,0$. The eigenstates and the eigenvalues from the $S_z=\pm 1$ subspaces belong to one of three triplet families and can be directly obtained using single-particle solutions defined in Eq. (A1),

$$|2,T[q\cdot q']_{2\sigma}\rangle = d^\dagger_{q\sigma}d^\dagger_{q'\sigma}|0\rangle,\quad (q\neq q'),\qquad \text{(A2)}$$

$$\varepsilon_{2T,qq'}=2E+\varepsilon_{1q}+\varepsilon_{1q'}.$$

The eigenstates from the $S_z=0$ subspace can be written in terms of an orthonormal basis,

$$|2^s_{ij}\rangle = \frac{1}{\sqrt{2}}(d^\dagger_{i\uparrow}d^\dagger_{j\downarrow}+s d^\dagger_{j\uparrow}d^\dagger_{i\downarrow})|0\rangle \qquad \text{(A3)}$$

$$\text{for:}\;\; i\neq j,\text{and}\;:\quad |2_{ii}\rangle = d^\dagger_{i\uparrow}d^\dagger_{i\downarrow}|0\rangle,$$

Solutions are

$$|2,T[q]_0\rangle = \frac{1}{\sqrt{3}}(|2^-_{12}\rangle + q^*|2^-_{23}\rangle + q|2^-_{31}\rangle)$$

$$|2,[q]_0\rangle = \alpha_q(|2_{11}\rangle + q^*|2_{22}\rangle + q|2_{33}\rangle) + \beta_q(|2^+_{12}\rangle + q^*|2^+_{23}\rangle + q|2^+_{31}\rangle). \quad \text{(A4)}$$

The solutions including $|2^-_{ij}\rangle$ states belong to one of the triplet families. The eigenvalues of the solutions with $|2^+_{ij}\rangle$ states read as

$$\varepsilon^{(\pm)}_{2q} = 2E + \frac{2t\cos\eta + U}{2} \pm \frac{1}{2}\sqrt{(U - 2t\cos\eta)^2 + 32t^2\cos^2(\eta/2)}. \quad \text{(A5)}$$

The ground state for $t<0$ is a symmetric singlet $q=1$ state from $S_z=0$ subspace, whereas for $t>0$ the ground state is the triplet state. Note that the eigenstates of the rotation operator corresponding to eigenvalues q and q^* are energetically degenerate.

$n=3$ *subspace*. This subspace splits into four subspaces with respect to the corresponding eigenvalue of $\hat{S}_z$: $S_z = \pm 3/2, \pm 1/2$. In the $S_z = \pm 3/2$ subspace the eigensolution is

$$|3_{3\sigma}\rangle = d^\dagger_{1\sigma}d^\dagger_{2\sigma}d^\dagger_{3\sigma}|0\rangle, \quad \varepsilon_3 = 3E. \quad \text{(A6)}$$

In $S_z = \pm 1/2$ subspace the eigenstates of the rotation operator can be chosen as

$$|3(0,q)_\sigma\rangle = \frac{1}{\sqrt{3}}(d^\dagger_{1\bar{\sigma}}d^\dagger_{2\sigma}d^\dagger_{3\sigma} + q^* d^\dagger_{2\bar{\sigma}}d^\dagger_{3\sigma}d^\dagger_{1\sigma} + q d^\dagger_{3\bar{\sigma}}d^\dagger_{1\sigma}d^\dagger_{2\sigma})|0\rangle,$$

$$|3^s(1,q)_\sigma\rangle = \frac{1}{\sqrt{6}}[(b^\dagger_2 + sb^\dagger_3)d^\dagger_{1\sigma} + q^*(b^\dagger_3 + sb^\dagger_1)d^\dagger_{2\sigma} + q(b^\dagger_1 + sb^\dagger_2)d^\dagger_{3\sigma}]|0\rangle, \quad \text{(A7)}$$

where $s=\pm$ and $b^\dagger_\ell = d^\dagger_{\ell\uparrow}d^\dagger_{\ell\downarrow}$ creates a double-occupied site. The states $|3(0,q)_\sigma\rangle$ and $|3^s(1,q)_\sigma\rangle$ belong to different subspaces concerning the total number of double-occupied sites (0 and 1, respectively). The eigenstates of the 3QD Hamiltonian, being also the eigenstates of the rotation operator, can be written as

$$|3,[q]_\sigma\rangle = \alpha_q|3^+(1,q)_\sigma\rangle + \beta_q|3^-(1,q)_\sigma\rangle + \gamma_q|3(0,q)_\sigma\rangle, \quad \text{(A8)}$$

where for $q \neq 1$ we can choose $\alpha_q = -\alpha_{q^*}$, $\beta_q = \beta_{q^*}$, and $\gamma_q = \gamma_{q^*}$. The eigenvalues for $q \neq 1$ read as

$$\varepsilon_{3\lambda} = 3E + t\lambda, \quad \lambda^3 - \lambda^2(2U/t) + \lambda[(U/t)^2 - 9] + 6(U/t) = 0. \quad \text{(A9)}$$

For $q=1$ we obtain the eigenvalues $3E+U$ (double degenerate) and $3E$.

2. Effects of a weak perturbation of the symmetry

In the presence of the considered symmetry perturbation, i.e., the energetic inequivalence of a vertex No.1 of the triangle, the eigenstates of the rotation operator are no longer exact eigenstates of the system. Since the system is still symmetric with respect to the reflection $\hat{\mathcal{R}}_{23}$, the eigenstates of $\mathcal{H}$ can be classified according to their symmetry with respect to the reflection. Below we present the eigenstates of the perturbed Hamiltonian exact up to the first order of the perturbation theory. This classification is helpful in determining which matrix elements of the electron operator $d_{1\sigma}$, $\langle n,(r)|d_{1\sigma}|n+1,(r')\rangle$, and consequently the corresponding transfer rates $W^{(L)}_{n(r),n+1(r')}$ vanish for reasons of symmetry.

$n=1$ *subspace*. The eigenstates of the reflection $\hat{\mathcal{R}}_{23}$ obtained from the eigenstates (A1) of the fully symmetric Hamiltonian read as

$$|1,(r)_\sigma\rangle = \frac{1}{\sqrt{2}}[|1,[q]_\sigma\rangle + r|1,[q^*]_\sigma\rangle], \quad \text{(A10)}$$

for $q \neq 1$ whereas $q=1$ eigenstate (A1) is symmetric with respect to the reflection ($r=+1$).

$n=2$ *subspace*. From the triplet states (A2) and (A4) one can form the eigenstates of the reflection as follows:

$$|2,T(r)_0\rangle = \frac{1}{\sqrt{2}}[q|2,T[q]_0\rangle - rq^*|2,T[q^*]_0\rangle]$$

$$|2,T(r)_{2\sigma}\rangle = \frac{1}{\sqrt{2}}[|2,T[q]_{2\sigma}\rangle + r|2,T[q^*]_{2\sigma}\rangle], \quad \text{(A11)}$$

whereas $q=1$ triplet states $|2,T[1]_0\rangle$ and $|2,T[1]_{2\sigma}\rangle$ are antisymmetric eigenstates of $\hat{\mathcal{R}}_{23}$. The eigenstates of the orbital doublet for $q \neq 0$ can be combined to make the eigenstates of $\hat{\mathcal{R}}_{23}$ as follows:

$$|2,(r)_0\rangle = \frac{1}{\sqrt{2}}[|2,[q]_0\rangle + r|2,[q^*]_0\rangle] \quad \text{(A12)}$$

and $q=1$ singlet state (A4) is the symmetric eigenstate of $\hat{\mathcal{R}}_{23}$.

$n=3$ *subspace*. State (A6) and $q=1$ state (A7) are also the eigenstates of the reflection operator; whereas $q \neq 1$ state (A8) can be used to form the eigenstates of $\hat{\mathcal{R}}_{23}$ as follows:

$$|3,(r)_\sigma\rangle = \frac{1}{\sqrt{2}}(|3,[q]_\sigma\rangle - r|3,[q^*]_\sigma\rangle). \quad \text{(A13)}$$

The width of the NDR peak depends on the perturbation-dependent splitting of the lowest-energy states. Up to the first order in the perturbation, the energy eigenvalues are generally given by

$$\varepsilon_r \to \varepsilon_r + \Delta\varepsilon_r, \quad \Delta\varepsilon_r = \langle 3,(r)_\sigma|\hat{\Delta}_1|3,(r)_\sigma\rangle. \quad \text{(A14)}$$

We consider now separately perturbations due to the modified local energy at site 1 or the modified Coulomb repulsion, i.e.,

$$\hat{\Delta}_1 = \hat{\Delta}_E = \Delta E_1 \sum_\sigma \hat{n}_{1\sigma}, \quad \text{or:} \quad \hat{\Delta}_1 = \hat{\Delta}_U = \Delta U_1 \hat{n}_{1\uparrow}\hat{n}_{1\downarrow}. \quad \text{(A15)}$$

In the case of the modified local energy at site 1, we get

$$\Delta\varepsilon_r = \Delta E_1\left[1 + r\frac{2\alpha_q\beta_q}{3}(q^* - q)\right] = \Delta E_1\left(1 + r\frac{2|\alpha_q|^2}{\lambda - U/t}\right). \tag{A16}$$

In the case of the modified Coulomb repulsion at site 1, we get

$$\begin{aligned}\Delta\varepsilon_+ &= \frac{\Delta U_1}{6}|(q + q^*)\alpha_q + (q - q^*)\beta_q|^2\\ &= \frac{\Delta U_1}{6}|\alpha_q|^2\left(1 - \frac{3}{U/t - \lambda}\right)^2\end{aligned}$$

$$\begin{aligned}\Delta\varepsilon_- &= \frac{\Delta U_1}{6}|(q - q^*)\alpha_q + (q + q^*)\beta_q|^2\\ &= \frac{\Delta U_1}{2}|\alpha_q|^2\left(1 + \frac{1}{U/t - \lambda}\right)^2.\end{aligned} \tag{A17}$$

In Eqs. (A16) and (A17) λ is a solution of Eq. (A9) and

$$|\alpha_q| = \frac{1}{\sqrt{1 + 6/\lambda^2 + 3/(\lambda - U/t)^2}}. \tag{A18}$$

The smallest solution of Eq. (A9) is smaller than U/t and it approaches $-3|t|/U$ in the large U limit. Therefore in both cases an enhancement of the energy parameter at site 1, making this site less favorable for the electrons, produces proportional increase in the energy of the antisymmetric state ($r = -1$) with respect to the symmetric state ($r = +1$). Note also that in both cases the splitting between the antisymmetric level and the symmetric one decreases with increase in the Hubbard repulsion U.

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