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Electric current in star junctions of molecular wires

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There is an enormous amount of literature on molecular-size circuits. However, no common regularities have ever been reported regarding the embedding of Y-like or, more generally, starlike molecular junctions into circuits. At the same time, connections of several wires are unavoidable components of any circuit. We show that in star junctions of $\mathcal{N}$ identical molecular wires, which are equally coupled to the feeding leads, the branched current is inversely proportional to $\mathcal{N}^2$. It is also proved that, independently of molecular structure, the minimal resistance that is associated with the terminal-to-terminal current through such junctions is equal to $h\mathcal{N}^2/8e^2$. In words, it is divided by eight von Klitzing resistance times $\mathcal{N}^2$. These predictions rule the performance of quantum wire junctions and provide useful references for studies of complex multiterminal molecular devices. The current-voltage dependence predicted for the circuits that contain a star junction of molecular wires is compared with *I-V* characteristics of constructively similar junctions of conventional resistors, where the Ohm law prescribes the proportionality of branched current to $1/\mathcal{N}$. The newly derived basic formulas include the exact solution of Lippman-Schwinger equation for a general model of multiterminal, rigid (coherent) scatterer, and also, a new and general trace formula for multiterminal transmission.

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I. INTRODUCTION

Soon after great discoveries of integer and fractional quantum Hall effects,[1,2] and the conductance quantization,[3,4] it became commonly acknowledged that the combination of two fundamental constants, e^2/h, determines the maximal per-state conductance and its inverse—the minimal per-state resistance for any conductor.[5] As a consequence, in a perfect conductor possessing n current-carrying states within eU energy interval, the electric potential difference U along the conductor drives the current $\max\{I_q\} = (2e^2n/h)U$, $n = 1,2,\ldots$. The current is thus quantized. The observation of current quantization in experiments[3,4] was due to varying the number of current-carrying states in a constriction region of 2D degenerate electron gas.

Any contact of an ideal conductor with outer electrodes causes electron scattering on the way in and out of the conductor. The fundamental conclusion from the current-quantization law is immediate: in a two-terminal setup, the current through any conductor, or more generally, any rigid atomic system with n unfilled electron states within interval eU, cannot be larger than $\max\{I_q\}$. The remaining question is *what maximal current should we expect, if the scatterer is contacted by more than two probes?*

Over decades the source-to-drain quantum transport has been extensively investigated experimentally and theoretically. In contrast, the physics of multiterminal quantum conductors is still poorly understood. Not many studies are published where the basic quantities of the Landauer-Büttiker approach, the terminal-to-terminal transmission probabilities $T_{j'j}$ were calculated numerically.[6–11] To our knowledge, no analytical solution of the scattering problem for a physically sound model of multiterminal conductors has ever been reported until recently.

In Ref. 12, we have derived the exact formal expression for the reduced Green's function of a scatterer coupled to the external current sources and absorbers via feeding and withdrawing leads, Fig. 1 (see a general description of the model in Ref. 13). When used in an appropriate transmission trace formula, that expression has allowed us to obtain an analytical form that relates $T_{j'j}$ to the Green's functions of the decoupled scatterer and leads. The developed technique has been used to demonstrate the scaling of transmission probabilities by a factor $4/\mathcal{N}^2$, $\mathcal{N}$—the number of scatterer terminals.

Here, we discuss an important consequence of quoted result that reveals the principal difference between the currents governed by classic and quantum laws. We also consider a hypothetical but realistic experimental situation of current-voltage measurements to show that the branched current driven by the potential difference U through a star junction of $\mathcal{N}$ molecular wires is bounded from above as

$$I_q = \frac{(\mathcal{N}-1)U}{\mathcal{N}^2\mathcal{R}_*} \Rightarrow \max\{I_q\} = \frac{8e^2}{h}\frac{(\mathcal{N}-1)U}{\mathcal{N}^2}, \qquad (1)$$

provided that the wires within star junctions are identical and equally coupled to the feeding leads. The absence of integer n is explained by the transmitting ability of star junctions in focus, which are described in the tight-binding approximation, see Eq. (13) and following from it Eqs. (14)–(16). As known, this description, though limited, provides the basic understanding of electronic properties of conjugated and saturated hydrocarbons.[14] However, since this work contributes to the Landauer-Büttiker approach, which leaves out of focus the effects of electron-electron interaction,[15] a wealth of associated phenomena is beyond the scope. Their description, either approximate or based on postulated models, presents an appealing challenge that makes the elaboration of exact one-particle picture all the more important. From this perspective, Eq. (1) provides an important generalization of the well-known result for a two-terminal coherent conductor: $I_q = (2e/h)\int_{-\infty}^{\infty} T_{12}(E)[f_2(E) - f_1(E)]dE$, $\max\{I_q\} = 2e^2U/h$,

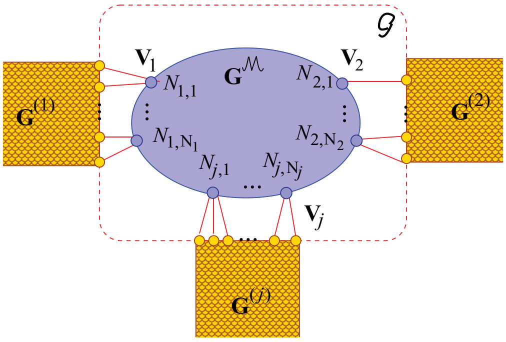

FIG. 1. (Color online) Formal description of scattering in an $\mathcal{N}$-terminal system in terms of reduced system Green's function $\mathcal{G}$ as a functional of reduced Green's function of scatterer $\mathcal{M}$, $\mathbf{G}^{\mathcal{M}}$ and lead Green's functions $\mathbf{G}^{(j)}$, $j = \overline{1,\mathcal{N}}$; $j = 1,2$ corresponds to two-terminal conductor. The model shown generalizes derivations,[16] where scatterer-lead coupling admits only pair-bond interaction and assumes all $\mathbf{V}_j$ square matrices of equal dimension.

where $f_j = [e^{(E-E_\mathrm{F}-eU_j)/k_\mathrm{B}T} + 1]^{-1}$ stands for the Fermi-Dirac distribution function.

II. BASICS

In accordance with the standard formulation, let the rigid atomic system (henceforth molecule $\mathcal{M}$) be in contact with $\mathcal{N}$ semi-infinite but otherwise perfect leads at terminals $j = 1, 2, \ldots, \mathcal{N}$, which deliver and withdraw electrons to and from scatterer $\mathcal{M}$. Then, in the absence of external magnetic field, the dc through-terminal currents are described by the set of $\mathcal{N}$ equations,[16]

$$I_j = \sum_{j'=1}^{\mathcal{N}} \mathcal{R}_{j'j}^{-1}(U_j - U_{j'}), \tag{2}$$

where $\mathcal{R}_{j'j} = [(2e^2/h)\bar{T}_{j'j}]^{-1}$ is a voltage dependent resistance of current path $j \to j'$, $e(U_j - U_{j'})\bar{T}_{j'j} = \int_{-\infty}^{\infty} T_{j'j}(E)[f_j(E) - f_{j'}(E)]dE$, and $T_{j'j}(E)$ is the probability that an electron entering lead j with kinetic energy E is transmitted into lead j'.

There are two conditions which are crucial for the validity of the equation above. The first is that a stationary state is maintained by external reservoirs of charge carriers. The second is that all leads are independent of each other. These, in combination with the assumption that electrons moving through the scattering region can experience only elastic scattering, define the model launched by Markus Büttiker.[13] Equation (2) represents a generalization of his equations for the nonlinear response.[16]

Thus defined, the electrical performance of any molecular device is fully determined by $\mathcal{N}(\mathcal{N}-1)/2$ transmission probabilities. The corresponding scattering problem is sketched in Fig. 1. As usual, the properties of the isolated scatterer (described by Hamiltonian $\mathbf{H}^{\mathcal{M}}$) and semi-infinite leads (described by Hamiltonians $\mathbf{H}^{(j)}$, $j = \overline{1,\mathcal{N}}$) are supposed to be known.

Calculations of $T_{j'j}$ can be performed with the use of Fisher-Lee-Datta trace formula,[16,17]

$$T_{j'j} = 4\mathrm{Tr}[(\mathrm{Im}\boldsymbol{\Sigma}_{j'})\mathbf{G}(\mathrm{Im}\boldsymbol{\Sigma}_j)\mathbf{G}^*]. \tag{3}$$

It suggests a scheme of direct calculations of transmission probabilities that implies the necessity of numerical inversion of matrix $\mathbf{G} = [E\mathbf{I} - \mathbf{H}^{\mathcal{M}} - \sum_{j=1}^{\mathcal{N}} \boldsymbol{\Sigma}_j]^{-1}$. The nonzero elements of self-energy matrix $\boldsymbol{\Sigma}_j$ coincide with matrix elements of $\mathbf{A}_j = \mathbf{V}_j^\mathrm{T}\mathbf{G}^{(j)}\mathbf{V}_j$, $\mathbf{G}^{(j)}$ is j-lead Green's function matrix, and $\mathbf{V}_j$ enters the matrix of lead-molecule interaction operator $\mathbf{V} = \sum_{j=1}^{\mathcal{N}} \mathbf{V}_j$. There are manifold implementations of this scheme. Yet, there is another path to choose.

We obtain the general exact solution of the scattering problem illustrated in Fig. 1, see Appendix A. We use it to derive a new trace formula (see Appendix B),

$$\begin{aligned} T_{j'j} &= 4\mathrm{Tr}[(\mathrm{Im}\mathbf{A}_j)\mathcal{G}_{j,j'}(\mathrm{Im}\mathbf{A}_{j'})\mathcal{G}^*_{j',j}], \\ j' &= 1,\ldots,j-1,j+1,\ldots,\mathcal{N} \equiv \{\tilde{j}\}. \end{aligned} \tag{4}$$

Equation (4) relates transmission probabilities $T_{j'j}$ to the entries into the off-diagonal member,

$$\mathcal{G}_{\{\tilde{j}\},j} = (\mathcal{G}_{1,j} \ldots \mathcal{G}_{j-1,j}\ \mathcal{G}_{j+1,j} \ldots \mathcal{G}_{\mathcal{N},j})^\mathrm{T}, \tag{5}$$

of the reduced Green's function $\mathcal{G} = \mathbf{G}^{\mathcal{M}} + \mathbf{G}^{\mathcal{M}}\mathbf{A}\mathcal{G}$, partitioned as

$$\mathcal{G} = \begin{pmatrix} \mathcal{G}_{j,j} & \mathcal{G}_{j,\{\tilde{j}\}} \\ \mathcal{G}_{\{\tilde{j}\},j} & \tilde{\mathcal{G}}_j \end{pmatrix}, \quad \mathbf{A} = \begin{pmatrix} \mathbf{A}_j & 0 \\ 0 & \tilde{\mathbf{A}}_j \end{pmatrix}. \tag{6}$$

This matrix describes a part of the whole system: a scatterer arbitrarily coupled to $\mathcal{N}$ semi-infinite leads, and refers exclusively to those molecular atoms that are involved in the interaction $\mathbf{V}$.

In general, nonsquare matrices $\mathcal{G}_{j',j}$ obey a set of $\mathcal{N}-1$ equations,[12]

$$\begin{aligned} &\big[\mathbf{I} - \tilde{\mathbf{G}}_j^{\mathcal{M}}\tilde{\mathbf{A}}_j - \mathbf{G}^{\mathcal{M}}_{\{\tilde{j}\},j}\mathbf{A}_j\big(\mathbf{I} - \mathbf{G}^{\mathcal{M}}_{j,j}\mathbf{A}_j\big)^{-1}\mathbf{G}^{\mathcal{M}}_{j,\{\tilde{j}\}}\tilde{\mathbf{A}}_j\big]\mathcal{G}_{\{\tilde{j}\},j} \\ &\quad = \mathbf{G}^{\mathcal{M}}_{\{\tilde{j}\},j}\big(\mathbf{I} - \mathbf{A}_j\mathbf{G}^{\mathcal{M}}_{j,j}\big)^{-1}, \end{aligned} \tag{7}$$

where the molecule Green's function

$$\mathbf{G}^{\mathcal{M}} = \begin{pmatrix} \mathbf{G}^{\mathcal{M}}_{j,j} & \mathbf{G}^{\mathcal{M}}_{j,\{\tilde{j}\}} \\ \mathbf{G}^{\mathcal{M}}_{\{\tilde{j}\},j} & \tilde{\mathbf{G}}^{\mathcal{M}}_j \end{pmatrix} \tag{8}$$

has the same partition as $\mathcal{G}$, whereas $\tilde{\mathbf{A}}_j$ is a block-diagonal matrix structured as

$$\tilde{\mathbf{A}}_j = \begin{pmatrix} \mathbf{A}_1 & \ldots & 0 \\ & \mathbf{A}_{j'\neq j} & \\ 0 & \ldots & \mathbf{A}_{\mathcal{N}} \end{pmatrix}. \tag{9}$$

Noteworthy, the commonly known and widely used formula (3) was derived in Ref. 16, assuming $\mathbf{V}_j$ square matrices of equal dimension. Moreover, each molecular atom was supposed to interact with only one nearest-neighbor atom from the respective lead. We are not aware of any more general derivation of Eq. (3). Free of the limitations just mentioned, our derivation of the alternative (4) is completely general, allows further analytical analysis in many actual cases, and suggests more efficient computation.

Finding $T_{j'j}$ with the usage of Eq. (7) for $(\mathcal{N}-1)$ $\mathrm{N}_{j'} \times \mathrm{N}_\mathrm{j}$ matrices $\mathcal{G}_{j',j}$ is, in general, a computational task. However, if molecule $\mathcal{M}$ is coupled to each of the leads via a single molecular atom, i.e., $\mathbf{A}_j = A_j$, the components of $\mathbf{G}^{\mathcal{M}}_{\{\tilde{j}\},j}$

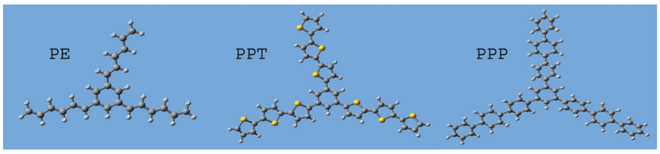

FIG. 2. (Color online) *Ab initio* optimized geometries of molecular wire Y connections which, with a sufficient accuracy, can be regarded as all-symmetric Y junctions, and where oligomers of polyene H(CH)$_n$H, polyparathiophene H(SC$_4$H$_2$)$_n$H, and polyparaphenylene H(C$_6$H$_4$)$_n$H play the role of semiconducting wires.[14,18–20] Benzene ring comes forward in the role of connector.

are just scalar functions of energy. Then, Eq. (7) can be simplified:

$$\begin{aligned}\big\{\big(1 - A_j G^{\mathcal{M}}_{j,j}\big)\big(\mathbf{I} - \tilde{\mathbf{G}}^{\mathcal{M}}_j \tilde{\mathbf{A}}_j\big)&\\ - A_j\big[G^{\mathcal{M}}_{j',j}\big]\big[G^{\mathcal{M}}_{j,j'}\big]\tilde{\mathbf{A}}_j\big\}[\mathcal{G}_{j',j}] &= \big[G^{\mathcal{M}}_{j',j}\big], \qquad (10)\end{aligned}$$

where $[\mathcal{G}_{j',j}]$ and $[G^{\mathcal{M}}_{j',j}]$ are column vectors and $[G^{\mathcal{M}}_{j,j'}]$ is a row vector. For all-symmetric junctions exemplified in Figs. 2 and 3, this equation can be solved analytically (see Appendix C) and ultimately leads to a closed explicit expression of $T_{j'j}$ as a function of energy and Hamiltonian parameters.

In what follows, we shall use this advantage to prove the central physical result of this article: the branched current in circuits incorporating star junctions $I_q/(\mathcal{N}-1)$ is inversely proportional to the squared number of wires. Thereby, the maximal conductance of terminal-to-terminal current path equals four times the spin-degenerate conductance quantum divided by the squared number of wires. The corresponding minimal resistance equals

$$\mathcal{R}_{j'j} = \mathcal{R}_*\mathcal{N}^2, \quad \min\{\mathcal{R}_*\} = \frac{h}{8e^2}. \qquad (11)$$

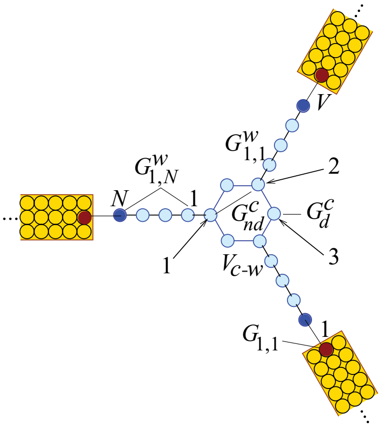

FIG. 3. (Color online) On the representation of transmission through star junctions as a functional of matrix elements of connector, wire, and lead Green's functions. In this example, three tight-binding chains (wires) are coupled to benzene ring (connector) and semi-infinite leads. V_{c-w} and V are connector-wire and wire-lead coupling constants. In Refs. 7 and 10, benzene carbon atoms indicated by arrows and labeled as 1, 2, and 3 are treated as scatterer terminals. Such a connection to leads does not satisfy the definition of all-symmetric junctions. The functioning of the molecular device studied in Refs. 7 and 10 is covered by Eqs. (D5)–(D7), but not by Eq. (12).

III. ALL-SYMMETRIC SCATTERERS

We define the all-symmetric scatterers as such, where $\mathbf{G}^{\mathcal{M}}_{j,j} = G^{\mathcal{M}}_d$ and $\mathbf{G}^{\mathcal{M}}_{j'\neq j,j} = G^{\mathcal{M}}_{nd}$. Then, the trace (4) is factorized as (see Appendix A)

$$T_{j'j} = \frac{4(\mathrm{Im}A_j)(\mathrm{Im}A_{j'})\big(G^{\mathcal{M}}_{nd}\big)^2}{\big|Q_j Q_{j'}\big[1 - G^{\mathcal{M}}_{nd}\sum_{j''=1}^{\mathcal{N}} A_{j''}Q^{-1}_{j''}\big]\big|^2}, \qquad (12)$$

where $Q_j \equiv 1 - A_j(G^{\mathcal{M}}_d - G^{\mathcal{M}}_{nd})$.

If the junction-lead coupling is equal at all terminals, $A_j = V^2 G_{1,1} \equiv A$ (see Fig. 3), all terminal-to-terminal transmission probabilities are also equal, $T_{j'j} = T_{\mathcal{N}}$, and take the form

$$T_{\mathcal{N}} = \frac{4V^4(\mathrm{Im}G_{1,1})^2\big(G^{\mathcal{M}}_{nd}\big)^2}{\big|1 - A\big(G^{\mathcal{M}}_d - G^{\mathcal{M}}_{nd}\big)\big|^2\big|1 - A\big[G^{\mathcal{M}}_d + (\mathcal{N}-1)G^{\mathcal{M}}_{nd}\big]\big|^2}. \qquad (13)$$

Furthermore, for this type of junctions, functional $T_{\mathcal{N}}(G^{\mathcal{M}}_d, G^{\mathcal{M}}_{nd})$ can be transformed into a functional of matrix elements of the connector, wire, and lead Green's functions, $T_{\mathcal{N}}(G^c_d, G^c_{nd}, G^w_{1,1}, G^w_{1,N}, G_{1,1})$.[12] The required entries into the functional were found earlier for a number of molecular wires and connectors.[14,18–20] Hence Eqs. (12) and (13) can be used in many straightforward applications (see, e.g., Ref. 21).

The shape of transmission spectrum $T_{\mathcal{N}}(E)$ is determined by the microscopic structure of the connector, wires, leads, and by the connector-wire and wire-lead interactions $V_{c-\mathrm{w}}$ and V. This information is compressed in the energy dependence of matrix elements $G^{\mathcal{M}}_d(E)$ and $G^{\mathcal{M}}_{nd}(E)$, and also, in the wire-lead coupling parameter V and LDOS at the lead binding atom, $\rho(E) = -\pi^{-1}\mathrm{Im}G_{1,1}(E)$. With the above expression at hand, the proof of Eq. (1) is as follows: if not constant, the LDOS is a function that has at least one maximum. In the vicinity of the maximum, LDOS can be approximated by a constant, $\rho(E_{\max}) = \alpha/(\pi V^2)$, $A = -i\alpha$, and $\mathrm{Re}G_{1,1} = 0$ due to the Kramers-Kronig relation. This limits the proof to small applied voltages.

The next two steps are crucial for the proof. The first is to express $G^{\mathcal{M}}_d$ and $G^{\mathcal{M}}_{nd}$ in terms of wire and connector Green's function matrix elements, which refer to the connector binding atoms (as in G^c_d, G^c_{nd}) and wire binding atoms from either the side of connector or lead (as in $G^w_{1,1}$, $G^w_{N,N}$), or from both sides (as in $G^w_{1,N}$). The corresponding expression has been obtained in Ref. 12. The second step is to transform Eq. (13) into a functional form:

$$T_{\mathcal{N}} = \frac{4}{\mathcal{N}^2}\frac{1}{1 + F^2\big(\alpha, \mathcal{N}, G^c_d, G^c_{nd}, G^w_{1,1}, G^w_{1,N}\big)}, \qquad (14)$$

where zeros of F as a function of energy are given by solutions of transcendent equation

$$\frac{\big(G^w_{1,1} - G^- G_\Delta\big)\big[G^w_{1,1} - G_\Delta\big(G^- + \mathcal{N}G^c_{nd}\big)\big]}{\big(1 - G^w_{1,1}G^-\big)\big[1 - G^w_{1,1}\big(G^- + \mathcal{N}G^c_{nd}\big)\big]} = -\frac{1}{\alpha^2}, \qquad (15)$$

$G^- = G^c_d - G^c_{nd}$, $G_\Delta = (G^w_{1,1})^2 - (G^w_{1,N})^2$. For simplicity, we assume that $G^w_{1,1} = G^w_{N,N}$ and $V = V_{c-w} = -t$, where t

(used as the energy unit) is the absolute value of the wire nearest-neighbor hopping integral.

A dense polelike structure of the left-hand side of Eq. (15) ensures that within the overlap of junction and lead energy spectra, solutions to this equation always exist. These solutions determine the energies at which $T_{\mathcal{N}} = \max\{T_{\mathcal{N}}\} = 4/\mathcal{N}^2$. Equation (1) is thus proved. A number of examples that illustrate the behavior of $T_{\mathcal{N}}(E)$ for different star junctions is given in Refs. 12 and 21. The calculations confirm that $\max\{T_{\mathcal{N}}\} = 4/\mathcal{N}^2$.

Thus the resistance $\mathcal{R}_*$ attains its minimal value, $\min\{\mathcal{R}_*\} = h/(8e^2)$, only if the molecular circuit is appropriately tuned. Otherwise, it is voltage-, material-, and wire-lead coupling dependent. Specifically, it depends on the junction electronic structure, i.e., which wires and wire connector form the junction. It is also important to notice that Eq. (1) refers to the case when $\mathcal{N} - 1$ terminals have equal electric potentials.

Obviously, the general regularity discussed above is just a reflection of that the transmission probability is proportional to the squared amplitude of the system wave function at the wire-lead interfaces. First, we have come to the result $T_{\mathcal{N}} \leqslant 4/\mathcal{N}^2$ considering a simple problem of transmission in a star junction of semi-infinite tight-binding chains via a carbon atom with (counted from zero) site energy ε_C. In this case, Eq. (13) can be transformed into[21]

$$T_{\mathcal{N}}(|E| \leqslant 2t) = \frac{4}{\mathcal{N}^2}\frac{t^2-(E/2)^2}{t^2-t^2V_C^{-2}(E-\varepsilon_C)\left[\mathcal{N}E-(E-\varepsilon_C)t^2V_C^{-2}\right]/\mathcal{N}^2}. \tag{16}$$

This equation will be discussed in Sec. IV.

The formulas presented above express the transmission probability in terms of connector Green's function, wire Green's function, and lead LDOS. In this context, it is worth emphasizing that the widely used WBL approximation $A = -i\alpha$[25] is applicable to the leads of any material and geometry as long as the lead LDOS has no or weak dependence on energy.

IV. GEDANKEN EXPERIMENT

The main experimentally sound result of this work, Eq. (1), suggests a number of unambiguous tests for the experimental verification of theoretical predictions. In particular, we propose to compare the performance of molecular wire Y junction with a constructively similar junction of conventional ohmic resistors R, see Fig. 4.

At first, the two-terminal resistance $const \times h/(2e^2)$ has to be measured for, e.g., alkane chain $(CH_2)_{2N+1}$. The resistance R can be chosen such as for a sequential connection of two resistors R, $I_q(\mathcal{N} = 2) = I_c(\mathcal{N} = 2)$, i.e., $R = const \times h/(4e^2)$. Then, I_c and I_q can be measured as shown in Fig. 4. The relation of currents $I_q(\mathcal{N} = 3)$ and $I_c(\mathcal{N} = 3)$, which are registered at the same voltage, is predicted to be $I_c/I_q = 3/2$. This is what tell us Eqs. (1) and (2) when the molecular circuit is tuned to $\max\{I_q\}$. The Y junction in our example can consist of any identical molecular wires which are attached to an all-symmetric connector that otherwise has an arbitrary structure. Also, the condition of equal wire-lead coupling must be fulfilled.

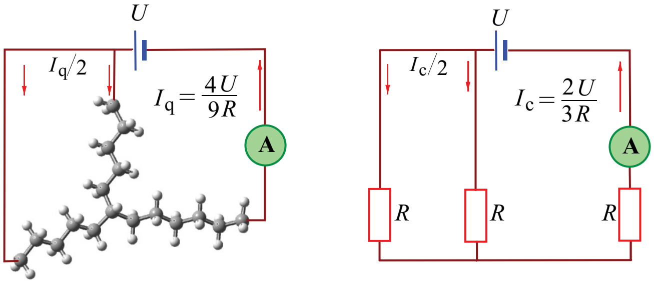

FIG. 4. (Color online) Circuits imbedding Y junctions of molecular wires (on the left) and conventional ohmic resistors R (on the right). If R is chosen as explained in the text, the currents measured by the left and right ammeters are related as $I_c/I_q = 3/2$.

The experimental realization of such measurements is really challenging. One of the expected difficulties is that a nonequal probing of Y junctions violates Eq. (1).[12,21] As a consequence, the number of unknown parameters to be determined in independent experiments increases. One of several ways to handle this problem is to measure currents I_q and I_c applying different voltages at all three terminals. This and other experimental difficulties may question the practical implementation of molecular dimension circuits but not the newly predicted law and its formal background. Recent advances in creating electric contacts with a single molecule,[22–24] where the use of wire chemical soldering[24] seems especially promising, strongly supports that an experimental verification of the predictions of this work and related to it work[21] might soon become the reality.

V. COMPARISON WITH OTHER STUDIES

As already mentioned, the results of this investigation provide useful references, not less for computational works. As an example, let us have a look at a paper of Cardamone *et al.*[7] and its near duplicate.[8] The calculations were claimed to refer to a three-terminal system of a type sketched in Fig. 3. The numbering of benzene carbon atoms is the same as in Ref. 7. In the quoted paper, the discussion of underlying physics is essentially based on an equation for an effective two-terminal transmission $T_{12}^{\rm eff} = T_{12} + T_{13}T_{32}/(T_{13} + T_{32})$, where (and only here in this paper) $T_{j'j} \equiv T_{j'j}(E_F)$, E_F is the Fermi energy. This borrowed from Ref. 26 equations is inconsistent with the exact expression for T_{12}, Appendix D, unless the coupling with the third lead is zero. The main results, represented in Figs. 4 and 5 in Ref. 7, are obtained for a negligible or zero coupling with the third lead. Specifically, the authors considered a current I_1 flowing between terminals 1 and 2. It was supposed to be controlled electrostatically. The part of Hamiltonian describing electrostatic coupling contains eighteen unknown capacitances plus an arbitrary value of reference potential U_2.[7] By varying these parameters, one can obtain a huge number of reasonable curves, which have a similar, as well as totally different shapes, if compared with *I-V* curves represented in Fig. 4 by Cardamone *et al.* Not remarkably, similar *I-V* curves can be simulated by exploiting Eqs. (2) and (B5). This can be done, for example, by prescribing proportionality of atom 3 site energy to the voltage U_3. We will not go further in this comparison because there is no chance to give a preference to one set of capacitances and disregard hundreds of other reasonable choices.

Another example concerns calculations of *I-V* characteristics of constructively the same benzene-based Y junction that is described by the single-particle tight-binding Hamiltonian.[10] We note first that this purely computational study was performed for the model that has an analytical solution (D5)–(D7). For the model, where the scatterer is a benzene ring coupled to semi-infinite tight-binding chains, $T_{j'j}$ has an explicit analytical expression.[12,21] Despite the simplifications mentioned, the author arrived at erroneous *I-V* curves. According to the exact solution of the problem, neither of curves $I_2(V_{23})$ shown in Figs. 8 and 9 in Ref. 10 can take the value $I_2(0) = 0$.

Finally, our expression (16) can be compared with a result for the star junction of four tight-binding chains, which was obtained in a recent study[29] and represented there in Sec. III and Appendix D. We rewrite Eq. (D22) for the case $V_i = 0$, $\phi_i = \phi$. Then, Eq. (D22) has to be equivalent to our Eq. (16) if $\varepsilon_C = 2t + \bar{V}_C$. Using a chain of definitions from Appendix D in Ref. 29 and preserving notations of quoted work (except that $\bar{V}_C$ stands for V_C in [29]), one can get

$$T_{ij} = 4\sin^2\phi|E/t - 2 - e^{-i\phi}|^{-2} \times |(E/t - \bar{V}_C/t - 4)(E/t - 2 - e^{-i\phi}) - 4|^{-2}, \quad (17)$$

where $2e^{i\phi} = E/t - 2 + i\sqrt{4 - (E - 2t)^2/t^2}$. This form is already suitable for the calculation of $T_{ij}(E/t)$, showing that $T_{ij}(E/t) = T_{\mathcal{N}=4}(E/t)$. However, it is only half way to a much more compact and easy readable form Eq. (16). Unlike Eq. (17), equation (16) makes obvious the transmission symmetry $T_{\mathcal{N}}(E) = T_{\mathcal{N}}(-E)$ and the independence of $T_{\mathcal{N}}$ of the sign of t. These properties are not at all evident from Eq. (17). In no way does Eq. (17) show the transmission dependence on E for the case of arbitrary $\mathcal{N}$, as Eq. (16) does. Furthermore, by no means the fact that the exact energy dependence (17), calculated for a single value of V_C, is nearly coincident with the CAP (complex absorbing potential) approximation can seriously be considered as a proof of general CAP applicability.

VI. CONCLUDING REMARKS

Being exact under the clearly specified model assumptions, the equations derived in this work provide the understanding of electric behavior of multiterminal systems at the level of single-particle Hamiltonian description. The only input required is the system Hamiltonian and a set of voltages applied to the terminals. Taking into account the approximate character of DFT and equivalent numerical calculations in the field of electron transport properties,[31] which thus far were almost exclusively addressed in two-terminal systems, makes the presented benchmark of exact results all the more important.

The above analysis of coherent transmission through all-symmetric starlike junctions of molecular wires has been performed on the basis of a pair of exact Eqs. (4) and (10), where the latter can be applied to a restricted class of models. Much more complex for the analytical as well as computational analysis is the pair of equations (4) and (7). As is proved here, it can be obtained either by starting from the Fisher-Lee-Datta trace formula and using a special partition technique, or by the direct solution of the Lippman-Schwinger equation. Both ways require finding matrix elements of operator $(E\mathbf{I} - \mathbf{H}^{\mathcal{M}})^{-1}$. If $\mathbf{H}^{\mathcal{M}}$ is not a single-particle operator, the validity of Eqs. (3) and (4) is seriously questioned.[15] Unfortunately, in some studies of electron-electron interaction effects, the transmission trace formula (3) is silently assumed to be applicable.

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APPENDIX A: GENERAL SOLUTION OF SCATTERING PROBLEM

As it can be seen in Fig. 5, to describe a multiterminal elastic scatterer, it is sufficient to consider an arbitrary molecular complex probed at two terminals, source ($j = s$) and drain ($j = d$). In this case, $\mathbf{V}$ is a block-diagonal matrix with two matrices $\mathbf{V}_s$ and $\mathbf{V}_d$ on the diagonal. Correspondingly, $\mathbf{A}_{j=s} = \mathbf{V}_s^{\mathrm{T}}\mathbf{G}^{(s)}\mathbf{V}_s$, $\tilde{\mathbf{A}}_{j=d} = \mathbf{A}_d = \mathbf{V}_d^{\mathrm{T}}\mathbf{G}^{(d)}\mathbf{V}_d$, and column vectors $\mathbf{G}^{\mathcal{M}}_{\{\tilde{j}\},j}$ and $\boldsymbol{\mathcal{G}}_{\{\tilde{j}\},j}$ are simply $[\mathrm{N}_d \times \mathrm{N}_s]$ matrices $\mathbf{G}^{\mathcal{M}}_{d,s}$ and $\boldsymbol{\mathcal{G}}_{d,s}$. As it comes out from these definitions, the generalization of two-terminal formulas to the case of multiterminal system is just another reading of matrices, column and row vectors in the forthcoming equations.

Any solution of stationary Schrödinger equation, which is subject to the boundary conditions for the scattering problem, obeys the Lippman-Schwinger equation,[30]

$$\mathbf{\Psi} = \mathbf{\Psi}^0 + \frac{\mathbf{I}}{E\mathbf{I} - \mathbf{H}^{\mathcal{M}} - \sum_{a=s,d}\mathbf{H}^{(a)}}\mathbf{V}\mathbf{\Psi}, \quad \text{(A1)}$$

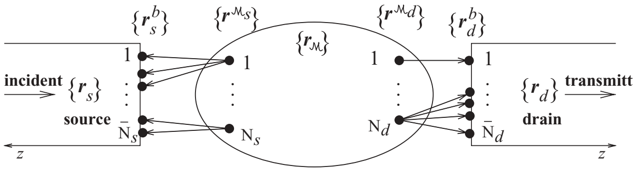

FIG. 5. Transmission through two-terminal conductor: particle incident from the left can be either reflected by molecule $\mathcal{M}$ back to the source or transmitted to drain. Each of source (drain) binding atoms 1, 2,. . . , $\bar{\mathrm{N}}_s$ ($\bar{\mathrm{N}}_d$) can interact with N_s (N_d) molecular binding atoms. Solving this problem and treating d terminal as $\mathcal{N}-1$ independent ways out, Eqs. (4) and (7) in the main text can be obtained by renaming indices, $s \rightarrow j$ and $d \rightarrow \{\tilde{j}\}$, and by the replacement $\mathbf{A}_d \rightarrow \tilde{\mathbf{A}}_j$.

where the system wave function can be represented as $\boldsymbol{\Psi} = \boldsymbol{\Psi}^{\mathcal{M}}(\mathbf{r}^{\mathcal{M}}) + \sum_{a=s,d} \boldsymbol{\Psi}^{(a)}(\mathbf{r}_a)$, and $\boldsymbol{\Psi}^0$ is the solution to equation $\mathbf{H}^{(s)}\boldsymbol{\Psi}^0 = E\boldsymbol{\Psi}^0$, which describes incident and reflected waves at the given energy $E = E_{\text{inc}}$ and wave vector k_{inc} in the isolated lead s, $\boldsymbol{\Psi}^0 = \boldsymbol{\Psi}^{\text{inc}}(E_{\text{inc}},k_{\text{inc}}) + \boldsymbol{\Psi}^{\text{refl}}(E_{\text{inc}},-k_{\text{inc}})$.

From now and on, we work with the basis set in the coordinate representation $|\{\mathbf{r}_a\}\rangle, |\{\mathbf{r}^{\mathcal{M}}\}\rangle$ divided into subspaces $\mathbf{r}_a \in \{\mathbf{r}_a^b\}$, $\mathbf{r}_a \notin \{\mathbf{r}_a^b\}$ and $\mathbf{r}^{\mathcal{M}} \in \{\mathbf{r}^{\mathcal{M}_a}\}$, $\mathbf{r}^{\mathcal{M}} \notin \{\mathbf{r}^{\mathcal{M}_a}\}$, $a = s,d$. The upper scripts b and $\mathcal{M}_a$ indicate that atom with such coordinates is involved into the molecule-lead interaction, see Fig. 5. That is to say, $\bar{\mathrm{N}}_s$ atoms $\{\mathbf{r}_s^b\}$ in lead s interact with N_s molecular atoms $\{\mathbf{r}^{\mathcal{M}_s}\}$, and $\bar{\mathrm{N}}_d$ atoms $\{\mathbf{r}_d^b\}$ from lead d interact with N_d molecular atoms $\{\mathbf{r}^{\mathcal{M}_d}\}$.

For vectors

$$\boldsymbol{\Psi}^0(\{\mathbf{r}_s^b\}) = \begin{pmatrix} \psi_1^0 \\ \cdots \\ \psi_{\bar{\mathrm{N}}_s}^0 \end{pmatrix}, \quad \boldsymbol{\Psi}^{(a)}(\{\mathbf{r}_a^b\}) = \begin{pmatrix} \psi_1^{(a)} \\ \cdots \\ \psi_{\bar{\mathrm{N}}_a}^{(a)} \end{pmatrix},$$

$$\boldsymbol{\Psi}^{\mathcal{M}_a}(\{\mathbf{r}^{\mathcal{M}_a}\}) = \begin{pmatrix} \psi_1^{\mathcal{M}_a} \\ \cdots \\ \psi_{\mathrm{N}_a}^{\mathcal{M}_a} \end{pmatrix}, \tag{A2}$$

we can write the following finite set of equations,

$$\begin{aligned} \boldsymbol{\Psi}^{(s)}(\{\mathbf{r}_s^b\}) &= \Psi^0(\{\mathbf{r}_s^b\}) + \mathbf{G}^{(s)}\mathbf{V}_s\boldsymbol{\Psi}^{\mathcal{M}_s}(\{\mathbf{r}^{\mathcal{M}_s}\}), \\ \boldsymbol{\Psi}^{(d)}(\{\mathbf{r}_d^b\}) &= \mathbf{G}^{(d)}\mathbf{V}_d\boldsymbol{\Psi}^{\mathcal{M}_d}(\{\mathbf{r}^{\mathcal{M}_d}\}), \\ \boldsymbol{\Psi}^{\mathcal{M}_s}(\{\mathbf{r}^{\mathcal{M}_s}\}) &= \mathbf{G}_{s,s}^{\mathcal{M}}\mathbf{V}_s^T\boldsymbol{\Psi}^{(s)}(\{\mathbf{r}_s^b\}) + \mathbf{G}_{s,d}^{\mathcal{M}}\mathbf{V}_d^T\boldsymbol{\Psi}^{(d)}(\{\mathbf{r}_d^b\}), \\ \boldsymbol{\Psi}^{\mathcal{M}_d}(\{\mathbf{r}^{\mathcal{M}_d}\}) &= \mathbf{G}_{d,s}^{\mathcal{M}}\mathbf{V}_s^T\boldsymbol{\Psi}^{(s)}(\{\mathbf{r}_s^b\}) + \mathbf{G}_{d,d}^{\mathcal{M}}\mathbf{V}_d^T\boldsymbol{\Psi}^{(d)}(\{\mathbf{r}_d^b\}), \end{aligned} \tag{A3}$$

where

$$\mathbf{G}^{(a)} = \begin{pmatrix} G_{1,1}^a & G_{1,2}^a & \cdots & G_{1,\bar{\mathrm{N}}_a}^a \\ \cdots & \cdots & \cdots & \cdots \\ G_{\bar{\mathrm{N}}_a,1}^a & G_{\bar{\mathrm{N}}_a,2}^a & \cdots & G_{\bar{\mathrm{N}}_a,\bar{\mathrm{N}}_a}^a \end{pmatrix}, \tag{A4}$$

$$\mathbf{V}_a = \begin{pmatrix} V_{1,1}^a & V_{1,2}^a & \cdots & V_{1,\mathrm{N}_a}^a \\ \cdots & \cdots & \cdots & \cdots \\ V_{\bar{\mathrm{N}}_a,1}^a & V_{\bar{\mathrm{N}}_a,2}^a & \cdots & V_{\bar{\mathrm{N}}_a,\mathrm{N}_a}^a \end{pmatrix}, \tag{A5}$$

and matrices $\mathbf{G}_{s,s}^{\mathcal{M}}$, $\mathbf{G}_{d,s}^{\mathcal{M}} = (\mathbf{G}_{s,d}^{\mathcal{M}})^{\mathrm{T}}$, and $\mathbf{G}_{d,d}^{\mathcal{M}}$ comprise the reduced matrix of molecule Green's function $\mathbf{G}^{\mathcal{M}} = \left(\begin{smallmatrix} \mathbf{G}_{s,s}^{\mathcal{M}} & \mathbf{G}_{s,d}^{\mathcal{M}} \\ \mathbf{G}_{d,s}^{\mathcal{M}} & \mathbf{G}_{d,d}^{\mathcal{M}} \end{smallmatrix}\right)$. The latter is defined on the manifold of matrix elements $\langle\mathbf{r}|[E\mathbf{I} - \mathbf{H}^{\mathcal{M}}]^{-1}|\mathbf{r}'\rangle$, $\mathbf{r},\mathbf{r}' \in \{\mathbf{r}^{\mathcal{M}_s},\mathbf{r}^{\mathcal{M}_d}\}$.

Obviously, the solution to the above set of equations determines all components of semi-infinite vectors $\boldsymbol{\Psi}^{(s)}$, $\boldsymbol{\Psi}^{(d)}$, and finite vector $\boldsymbol{\Psi}^{\mathcal{M}}$. Finding this solution is just a matter of matrix algebra that yields for $\boldsymbol{\Psi}^{(d)}$,

$$\boldsymbol{\Psi}^{(d)}(\{\mathbf{r}_d^b\}) = \mathbf{G}^{(d)}\mathbf{V}_d\boldsymbol{\mathcal{G}}_{d,s}\mathbf{V}_s^{\mathrm{T}}\boldsymbol{\Psi}^0(\{\mathbf{r}_s^b\}), \tag{A6}$$

where

$$\begin{aligned} \boldsymbol{\mathcal{G}}_{d,s} = {} & \big[\mathbf{I} - \mathbf{G}_{d,d}^{\mathcal{M}}\mathbf{A}_d - \mathbf{G}_{d,s}^{\mathcal{M}}\mathbf{A}_s(\mathbf{I} - \mathbf{G}_{s,s}^{\mathcal{M}}\mathbf{A}_s)^{-1}\mathbf{G}_{s,d}^{\mathcal{M}}\mathbf{A}_d\big]^{-1} \\ & \times \mathbf{G}_{d,s}^{\mathcal{M}}(\mathbf{I} - \mathbf{A}_s\mathbf{G}_{s,s}^{\mathcal{M}})^{-1}. \end{aligned} \tag{A7}$$

Notice that, (i) the permutation symmetry of $\boldsymbol{\mathcal{G}}_{d,s}$ can be proved for any Hermitian Hamiltonian, (ii) reading s as j, d as $\{\tilde{j}\}$, and $\mathbf{A}_d$ as $\tilde{\mathbf{A}}_j$ gives Eq. (7) in the main text, (iii) for any real system, the molecule-lead interaction satisfies the condition of convergence of von Neuman series for the corresponding inverse matrices.

APPENDIX B: TRANSMISSION TRACE FORMULA

Obtaining a compact expression for the transmission coefficient,[20]

$$T_{ds}(E) = \frac{\sum_{r_d^{\perp},\,\mathbf{r}_d \notin \{\mathbf{r}_d^b\}} (\partial E_d/\partial k_d)\boldsymbol{\Psi}^{(d)} \cdot \boldsymbol{\Psi}^{(d)*}}{\sum_{r_s^{\perp},\,\mathbf{r}_s \notin \{\mathbf{r}_s^b\}} (\partial E_s/\partial k_s)\boldsymbol{\Psi}^{\text{inc}} \cdot \boldsymbol{\Psi}^{\text{inc}*}}, \tag{B1}$$

$E = E_s(k_s{=}k_{\text{inc}}) = E_d(k_d)$, with the use of solution (A6), requires though cumbersome but straightforward algebra. It yields

$$T_{ds}(E) = 4\sum_{\mathrm{r}} \langle\mathbf{r}|(\mathrm{Im}\mathbf{A}_s)\boldsymbol{\mathcal{G}}_{s,d}(\mathrm{Im}\mathbf{A}_d)\boldsymbol{\mathcal{G}}_{ds}^*|\mathbf{r}\rangle, \tag{B2}$$

where $\mathbf{r} \in \{\mathbf{r}^{\mathcal{M}_s},\mathbf{r}^{\mathcal{M}_d}\}$ and matrix $\boldsymbol{\mathcal{G}}_{s,d}$ is defined in Eq. (A7). Equivalently,

$$T_{ds}(E) = 4\mathrm{Tr}[(\mathrm{Im}\mathbf{A}_s)\boldsymbol{\mathcal{G}}_{s,d}(\mathrm{Im}\mathbf{A}_d)\boldsymbol{\mathcal{G}}_{d,s}^*], \tag{B3}$$

where the trace operation is defined on s and d subspaces of binding molecular atoms.

To complete the framework of our methodology, we present the formal expression of $\boldsymbol{\mathcal{G}}_{d,s}$ for the case $\mathrm{N}_s = \mathrm{N}_d$. It reads

$$\boldsymbol{\mathcal{G}}_{d,s} = \big[(\mathbf{I} - \mathbf{A}_s\mathbf{G}_{s,s}^{\mathcal{M}})(\mathbf{G}_{d,s}^{\mathcal{M}})^{-1}(\mathbf{I} - \mathbf{G}_{d,d}^{\mathcal{M}}\mathbf{A}_d) - \mathbf{A}_s\mathbf{G}_{s,d}^{\mathcal{M}}\mathbf{A}_d\big]^{-1}, \tag{B4}$$

where $\mathbf{V}_s$ and $\mathbf{V}_d$ entering $\mathbf{A}_s$ and $\mathbf{A}_d$ can be square, as well as nonsquare matrices. Unlike Eq. (A7), which can acquire the form (B4), Eq. (7) in the main text remains unchanged even under the simplifying assumption $\mathrm{N}_j = \mathrm{N}_{j' \in \{\tilde{j}\}}$.

To further clarify the usage of the above equation, we note that if $\mathrm{N}_s = \mathrm{N}_d = 1$, i.e., $\{\mathbf{r}^{\mathcal{M}_a}\} = 1$ and hence, $\mathbf{A}_a = A_a$, Eqs. (B3) and (B4) can be combined into a closed analytical expression:[20,32]

$$T_{ds}(E) = \frac{4(\mathrm{Im}A_s)(\mathrm{Im}A_d)\big(G_{1_s,1_d}^{\mathcal{M}}\big)^2}{\big|(1 - A_sG_{1_s,1_s}^{\mathcal{M}})(1 - A_dG_{1_d,1_d}^{\mathcal{M}}) - A_sA_d\big(G_{1_s,1_d}^{\mathcal{M}}\big)^2\big|^2}, \tag{B5}$$

where

$$A_a = \sum_{\mathbf{r},\mathbf{r}' \in \{\mathbf{r}_a^b\}} V_{1,\mathbf{r}}^a G_{\mathbf{r},\mathbf{r}'}^a V_{\mathbf{r}',1}^a. \tag{B6}$$

where notation $\{\mathbf{r}_a^b\}$ refers to the coordinates of the manifold of binding atoms in lead $a = s$ and $a = d$.

Obtained for the first time in Ref. 32, formula (B5) gives probably the most compact explicit expression of the transmission coefficient for exactly solvable models described by tight-binding Hamiltonians. The use of N-long tight-binding chain to express $G_{1_s,1_s}^{\mathcal{M}} = G_{1_d,1_d}^{\mathcal{M}}$ and $G_{1_s,1_d}^{\mathcal{M}}$, and the same Hamiltonian for a semiinfinite chain to express A_s and A_d immediately gives an expression of $T_{ds}(E)$ that is equivalent to that pioneered by Mujica *et al.*[33] A number of other models of molecular wires has been specified by finding explicit expressions for matrix elements $G_{1_s,1_d}^{\mathcal{M}}$, $G_{1_a,1_a}^{\mathcal{M}}$, and $G_{\mathbf{r},\mathbf{r}'}^a$, see e.g., Refs. 14,18–20. Modified for a substrate-STM-tip arrangement of s and d contacts, Eq. (B5) has been used for the quantitative interpretation of *I*-*V* STM measurements performed on amine-terminated PPP oligomers.[34]

Later, a number of equivalent derivations have been published as, e.g., in Refs. 35–38. Some approximate schemes for the calculation of T_{ds}, such as the source-sink potential approach,[39–43] have also been developed and applied to the models, where the transmission is described exactly by the pair of Eqs. (B5) and (B6).

APPENDIX C: TRANSMISSION FOR ALL-SYMMETRIC SCATTERERS

Equation (10) can be written as

$$L(j)[\mathcal{G}_{j',j}] = \left[G^{\mathcal{M}}_{j',j}\right], \tag{C1}$$

where matrix $L(j)$ reads

$$\begin{aligned} L_{j',j''}(j) = {} & \left(1 - A_j G^{\mathcal{M}}_{j,j}\right)\left(\delta_{j',j''} - A_{j''} G^{\mathcal{M}}_{j',j''}\right) \\ & - A_j A_{j''} G^{\mathcal{M}}_{j,j'} G^{\mathcal{M}}_{j'',j}. \end{aligned} \tag{C2}$$

For all-symmetric scatterers, $\mathbf{G}^{\mathcal{M}}_{j,j} = G^{\mathcal{M}}_d$, $\mathbf{G}^{\mathcal{M}}_{j'\neq j,j} = G^{\mathcal{M}}_{nd}$, matrix elements $L_{j',j'}(j) \equiv L^d_{j'}$ and $L_{j',j''\neq j'}(j) \equiv L^{nd}_{j''}$, $j'' = 1,\ldots,j-1,j+1,\ldots,\mathcal{N} \equiv \{\tilde{j}\}$, take the form

$$\begin{aligned} L^d_{j'} &= \left(1 - A_j G^{\mathcal{M}}_d\right)\left(1 - A_{j'} G^{\mathcal{M}}_d\right) - A_j A_{j'}\left(G^{\mathcal{M}}_{nd}\right)^2, \\ L^{nd}_{j''} &= -A_{j''} G^{\mathcal{M}}_{nd}\left(1 - A_j G^{\mathcal{M}}_d\right) - A_j A_{j''}\left(G^{\mathcal{M}}_{nd}\right)^2. \end{aligned} \tag{C3}$$

In these notations, Eq. (C1) can be transformed into

$$\mathcal{G}_{j',j} = \left(L^d_{j'} - L^{nd}_{j'}\right)^{-1}\left(G^{\mathcal{M}}_{nd} - \sum_{\{\tilde{j}\}} L^{nd}_{j''}\mathcal{G}_{j'',j}\right). \tag{C4}$$

Multiplying both sides of the above equation by $L^{nd}_{j'}$ and summing over j', we arrive at

$$\mathcal{G}_{j',j} = \frac{G^{\mathcal{M}}_{nd}}{L^d_{j'} - L^{nd}_{j'}}\left[1 + \sum_{\{\tilde{j}\}} L^{nd}_{j''}\left(L^d_{j''} - L^{nd}_{j''}\right)^{-1}\right]^{-1}. \tag{C5}$$

Now, by noting that

$$L^d_{j'} - L^{nd}_{j'} = Q_{j'}\left(1 - A_j G^{\mathcal{M}}_d\right), \tag{C6}$$

where $Q_j \equiv 1 - A_j(G^{\mathcal{M}}_d - G^{\mathcal{M}}_{nd})$, it is easy to prove the equality

$$\mathcal{G}_{j',j} = G^{\mathcal{M}}_{nd} Q^{-1}_{j'}\left(1 - A_j G^{\mathcal{M}}_d + \sum_{\{\tilde{j}\}} L^{nd}_{j''} Q^{-1}_{j''}\right)^{-1}. \tag{C7}$$

Equivalently,

$$\mathcal{G}_{j',j} = G^{\mathcal{M}}_{nd} Q^{-1}_{j'} Q^{-1}_{j}\left(1 - G^{\mathcal{M}}_{nd}\sum_{j''=1}^{\mathcal{N}} A_{j''} Q^{-1}_{j''}\right)^{-1}. \tag{C8}$$

Substituting Eq. (C8) into Eq. (4), we arrive at Eq. (12).

APPENDIX D: EXPLICIT SOLUTION TO EQ. (7) FOR THREE-TERMINAL MOLECULAR DEVICES

For $\mathcal{N} = 3$ and $j = 3$, we have from Eq. (C2),

$$\begin{aligned} L_{1,1}(3) &= \left(1 - A_3 G^{\mathcal{M}}_{3,3}\right)\left(1 - A_1 G^{\mathcal{M}}_{1,1}\right) - A_1 A_3\left(G^{\mathcal{M}}_{1,3}\right)^2, \\ L_{2,2}(3) &= \left(1 - A_3 G^{\mathcal{M}}_{3,3}\right)\left(1 - A_2 G^{\mathcal{M}}_{2,2}\right) - A_2 A_3\left(G^{\mathcal{M}}_{2,3}\right)^2, \\ L_{1,2}(3) &= -A_2\left[\left(1 - A_3 G^{\mathcal{M}}_{3,3}\right) G^{\mathcal{M}}_{1,2} + A_3 G^{\mathcal{M}}_{1,3} G^{\mathcal{M}}_{2,3}\right], \\ L_{2,1}(3) &= A_1 L_{1,2}(3)/A_2. \end{aligned} \tag{D1}$$

For $j = 1$,

$$\begin{aligned} L_{3,3}(1) &= \left(1 - A_1 G^{\mathcal{M}}_{1,1}\right)\left(1 - A_3 G^{\mathcal{M}}_{3,3}\right) - A_1 A_3\left(G^{\mathcal{M}}_{1,3}\right)^2, \\ L_{2,2}(1) &= \left(1 - A_1 G^{\mathcal{M}}_{1,1}\right)\left(1 - A_2 G^{\mathcal{M}}_{2,2}\right) - A_1 A_2\left(G^{\mathcal{M}}_{1,2}\right)^2, \\ L_{3,2}(1) &= -A_2\left[\left(1 - A_1 G^{\mathcal{M}}_{1,1}\right) G^{\mathcal{M}}_{2,3} + A_1 G^{\mathcal{M}}_{1,3} G^{\mathcal{M}}_{1,2}\right], \\ L_{2,3}(1) &= A_3 L_{3,2}(1)/A_2. \end{aligned} \tag{D2}$$

Note that Eq. (D2) follows from Eq. (D1) under an interchange of indices 1 and 3, 1 ↔ 3.

Similarly, for $j = 2$ (interchange $2 \leftrightarrow 1$ in the last equation),

$$\begin{aligned} L_{1,1}(2) &= \left(1 - A_2 G^{\mathcal{M}}_{2,2}\right)\left(1 - A_1 G^{\mathcal{M}}_{1,1}\right) - A_1 A_2\left(G^{\mathcal{M}}_{1,2}\right)^2, \\ L_{3,3}(2) &= \left(1 - A_2 G^{\mathcal{M}}_{2,2}\right)\left(1 - A_3 G^{\mathcal{M}}_{3,3}\right) - A_2 A_3\left(G^{\mathcal{M}}_{2,3}\right)^2, \\ L_{1,3}(2) &= -A_3\left[\left(1 - A_2 G^{\mathcal{M}}_{2,2}\right) G^{\mathcal{M}}_{1,3} + A_2 G^{\mathcal{M}}_{1,2} G^{\mathcal{M}}_{2,3}\right], \\ L_{3,1}(2) &= A_1 L_{1,3}(2)/A_3. \end{aligned} \tag{D3}$$

The use of Eqs. (D1)– (D3) in the solution to Eq. (C2) for $\mathcal{N} = 3$ and then in the transmission formula,

$$T_{j'j} = 4\mathrm{Im}A_j\mathrm{Im}A_{j'}|\mathcal{G}_{j',j}|^2, \tag{D4}$$

yields

$$\begin{aligned} T_{1,3} &= \frac{4\mathrm{Im}A_1\mathrm{Im}A_3\left|G^{\mathcal{M}}_{1,3}L_{2,2}(3) - G^{\mathcal{M}}_{2,3}L_{1,2}(3)\right|^2}{\left|L_{1,1}(3)L_{2,2}(3) - L_{1,2}(3)L_{2,1}(3)\right|^2}, \\ T_{2,3} &= \frac{4\mathrm{Im}A_2\mathrm{Im}A_3\left|G^{\mathcal{M}}_{2,3}L_{1,1}(3) - G^{\mathcal{M}}_{1,3}L_{2,1}(3)\right|^2}{\left|L_{1,1}(3)L_{2,2}(3) - L_{1,2}(3)L_{2,1}(3)\right|^2}, \end{aligned} \tag{D5}$$

$$\begin{aligned} T_{3,1} &= \frac{4\mathrm{Im}A_1\mathrm{Im}A_3\left|G^{\mathcal{M}}_{1,3}L_{2,2}(1) - G^{\mathcal{M}}_{1,2}L_{3,2}(1)\right|^2}{\left|L_{3,3}(1)L_{2,2}(1) - L_{3,2}(1)L_{2,3}(1)\right|^2}, \\ T_{2,1} &= \frac{4\mathrm{Im}A_1\mathrm{Im}A_2\left|G^{\mathcal{M}}_{1,2}L_{3,3}(1) - G^{\mathcal{M}}_{1,3}L_{2,3}(1)\right|^2}{\left|L_{3,3}(1)L_{2,2}(1) - L_{3,2}(1)L_{2,3}(1)\right|^2}, \end{aligned} \tag{D6}$$

and

$$\begin{aligned} T_{1,2} &= \frac{4\mathrm{Im}A_1\mathrm{Im}A_2\left|G^{\mathcal{M}}_{1,2}L_{3,3}(2) - G^{\mathcal{M}}_{2,3}L_{1,3}(2)\right|^2}{\left|L_{1,1}(2)L_{3,3}(2) - L_{1,3}(2)L_{3,1}(2)\right|^2}, \\ T_{3,2} &= \frac{4\mathrm{Im}A_2\mathrm{Im}A_3\left|G^{\mathcal{M}}_{2,3}L_{1,1}(2) - G^{\mathcal{M}}_{1,2}L_{3,1}(2)\right|^2}{\left|L_{1,1}(2)L_{3,3}(2) - L_{1,3}(2)L_{3,1}(2)\right|^2}, \end{aligned} \tag{D7}$$

where $T_{j'j}(E) = T_{jj'}(E)$ for any scatterer that is described by a Hermitian Hamiltonian.

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