

Breakdown of Ohm's Law in Molecular Junctions with Electrodes of Single-Layer Graphene

Ioan Bâldea,* Yuhong Chen, Miao Zhang, Na Xin, Yunxia Feng, Jiajun Feng, Chuancheng Jia, Xuefeng Guo,* and Zuoti Xie*



O hm's law,¹ historically the first mathematical relation of paramount importance for electric circuits, states that the current I through a macroscopic material is proportional to the applied bias voltage V. It is experimentally supported by empirical measurements for currents and length scales varying over many orders of magnitude and holds for the vast majority of materials.

Considering the acceleration induced by an applied electric field on electrons in random zigzag motion due to rapid scattering by atoms or ions within the framework of classical mechanics, the Drude model² succeeded to unravel a net electron drift with an average velocity proportional to the field and thence the first microscopic justification of Ohm's law. Accounting for Fermi statistics in a free electron model, Sommerfeld³ was able to give the first quantum mechanical justification of Ohm's law in metals. Quantum theory of solids relates differences between the ohmic conductance of various macroscopic solids to the (non)existence of the band gaps characterizing the specific energy band structures.⁴ Depending on the presence and/or the magnitude of the band gaps, calculations within the linear Kubo response theory^{5,6} explicitly accounting for the actual band structure allows to estimate the ohmic (also referred to as zero-bias or linear) conductance G and provides the microscopic rationale why some materials are conductors, some semiconductors, and some insulators.

In the 1920s, on the eve of quantum mechanics, there was a renewed interest in the Ohm's law, which was thought to fail at the atomic scale.⁷ Electrons' motion over short distances is coherent, contrasting the incoherent electron collisions occurring in macroscopic materials that give rise to Joule

dissipation. For adequately assessing the importance of the finding reported below, it is of paramount importance to emphasize that the "failure" of Ohm's law meant in the above context did not refer to the proportionality between current and voltage I = V/R. Rather, this "failure" was merely understood as the breakdown of the proportionality between resistance R and *length L*, a relationship that holds true for macroscopic samples. Albeit certainly significant, it is not the latter proportionality (R ~ L) but rather the former proportionality $(I \sim V)$ that represents the primary message conveyed by Ohm's law. With the advent of nanoscience, the possibility to address experimentally the implicit question envisaged above (namely: is R proportional to L or not?) became reality. Plenty of experiments on molecular tunnel junctions fabricated with various homologous molecular series (alkanes,⁸⁻¹⁰ oligophenyls,^{11–13} oligoacenes,¹⁴ oligothiophens^{15,16}) and all common platforms (MC-BJ,^{17,18} STM-BJ,^{19,20} CP-AFM,^{8,21} EGaIn^{22,23}) performed over more than the last two decades confirmed this expected "failure", and this result belongs to textbook's wisdom:^{24,25} at the nanoscale, R does not grow linearly but rather exponentially with L ($R \sim \exp(\beta L)$).

"Ohm's Law Survives to the Atomic Scale" is the title of a report published more than a decade ago.²⁶ While undoubtedly

Received:February 5, 2024Revised:March 11, 2024Accepted:March 12, 2024Published:March 15, 2024





pubs.acs.org/JPCL



Figure 1. Schematic representation of the charge transport in molecular junctions with metal electrodes. (a) Metal electrodes possess a nonvanishing density of states, which is almost energy independent around the Fermi energy E_{F^*} (b) At zero temperature, the (nonvanishing) ohmic conductance is the result of the elastic tunneling (depicted by the solid brown horizontal arrow) mediated by the closest molecular orbital (illustrated by the dashed brown arrows) involving the occupied electron states in the left electrode and the empty states in the right electrode (depicted as orange rectangle) in a tiny Fermi energy window ($E_F - eV/2 < E < E_F + eV/2$, $V \ge 0$). (c) Measured I-V curves invariably possess a nonvanishing slope at zero bias which defines the (linear) conductance $G (\neq 0)$ at low bias.

a remarkable result from the above perspective,⁷ one should note that ref 26 confirmed Ohm's law only in the above sense $(R \sim L)$. That is, ref 26 experimentally demonstrated "ohmic" scaling of the electric resistance, namely that atomic-scale nanowires of phosphorus in silicon have electrical resistance depending linearly upon lengths down to ~1 nm. Whether *I* is proportional to *V*, which is our main concern in the present study, was not an issue addressed in ref 26.

Returning to our concern (namely: is *I* proportional to *V* or not?), the fundamental question is not whether the dependence of *I* on *V* is linear in general at an arbitrary bias. It is well-known that, whether for conventional solids (let them be metals, semiconductors, or dielectrics) or plasmas, deviations from the linear relationship ("nonohmic behavior") become significant at sufficiently large biases, eventually at the breakdown electric field which characterizes any real material. But even the nonohmic materials, so important in electrical engineering,²⁷ do possess a certain range of low biases, wherein the *I*–*V* dependence is linear to a good approximation; the tangent of the *I*–*V* curve at origin (*V* = 0) does have a nonvanishing slope. A nonlinear dependence of *I* on *V* sets in only at sufficiently large biases.

To the best of our knowledge, at least for molecular junctions, all I-V curves measured so far possess tangents having a slope at origin (V = 0), which clearly differs from zero within experimental accuracy.²⁸ This slope defines the low (zero-) bias conductance (Figure 1c)

$$G = \frac{I}{V}\Big|_{V \to 0} = \frac{\partial I}{\partial V}\Big|_{V \to 0} \neq 0$$
⁽¹⁾

In molecular junctions fabricated with short molecular species, charge transport proceeds via tunneling.^{21,29} Neglecting manybody electron correlation effects, the tunneling current dominated by a single energy level (molecular orbital MO) can be computed as integral over transmission *T* weighted by the difference of the electrodes' Fermi distribution f^{30}

$$I = \frac{G_0}{e} \int_{-\infty}^{\infty} \frac{\frac{\Gamma_s(\varepsilon)\Gamma_d(\varepsilon)}{(\varepsilon - \varepsilon_0)^2 + \left[\frac{\Gamma_s(\varepsilon) + \Gamma_d(\varepsilon)}{2}\right]^2}}{[f(\varepsilon - eV/2) - f(\varepsilon + eV/2)]d\varepsilon}$$
(2)

Noteworthily, eq 2 follows from the general Keldysh formalism applied to nonlinear transport (e.g., ref 30) as opposed to the

generic Landauer approach ubiquitously utilized. The zero-bias (ohmic) conductance at zero temperature is expressed by

$$\frac{G}{G_0}\Big|_{T \to 0} = T(\varepsilon)|_{\varepsilon \to 0} = \frac{\Gamma_{\varepsilon}(0)\Gamma_d(0)}{\varepsilon_0^2 + \left[\frac{\Gamma_{\varepsilon}(0) + \Gamma_d(0)}{2}\right]^2}$$
(3)

where *e* and $G_0 = 2e^2/\hbar = 77.48 \ \mu\text{S}$ are the absolute electron charge and the universal conductance quantum, respectively, ε_0 = $E_{MO} - E_F$ is the MO energy offset relative to the electrodes' Fermi level ($E_F = 0$), and Γ_s and Γ_d are MO electronic couplings to the two (source and drain) electrodes.

"Conductance is transmission" (cf. eq 3), the very popular Landauer paradigm,^{31–34} is exemplarily substantiated by the resonant level ($\varepsilon_0 = 0$) symmetrically coupled electrodes having wide, flat conduction bands (energy independent $\Gamma_s = \Gamma_d$)

$$G = 1, G = G_0$$
 (4)

Its strictly linear response at zero temperature (T)

$$I|_{T \to 0} = \frac{G_0}{e} \int_{-\epsilon V/2}^{\epsilon V/2} T d\epsilon = G_0 V$$
(5)

is par excellence ohmic.

In more physical terms, the ohmic conductance of eq 3 is the result of the fact that (say) the negative electrode (source, label s) injects electrons from occupied single-particle states slightly above the equilibrium Fermi level E_F (= 0) that tunnel through the molecule and finally land on empty single-particle states of the positive electrode (drain, label d). This rather trivial narrative implicitly assumes electrodes possessing nonvanishing densities of states at the Fermi level $\rho_{s,d}(0) \neq 0$. Mathematically, this is embodied in the proportionality relationship $\Gamma_{s,d} \propto \rho_{s,d}$.³⁰

The aforementioned condition is trivially fulfilled by conventional metal electrodes, which possess flat conduction bands around E_F (Figure 1a). However, this does not hold for the presently considered graphene electrodes (Figure 2). What makes the single-layer graphene^{37,38} completely different from a conventional metal is its band structure.^{35,36,39} The planar honeycomb structure (Figure 2a) with two atoms per unit cell gives rise to two conduction and valence π bands touching the corners of the hexagonal Brillouin zone (six Dirac points). Near the Dirac points, the exact V-shaped density of states emerging from tight-binding band structure calculations³⁹ expressed in terms of the complete elliptic integral of the first kind³⁵ can reasonably be described within the linear approximation $\rho(\varepsilon) \propto$



Figure 2. Charge transport through molecular junctions with electrodes consisting of single-layer graphene. (a) A single-layer graphene with its characteristic honeycomb structure. (b) The V-shaped density of states (DOS) computed exactly^{35,36} (red line) exhibits van Hove singularities characteristic for two-dimensional systems and vanishes approximately linearly with energy (purple line) at the Dirac point depicted as energy zero. Energies are scaled by the tight-binding transfer integral ($t \approx 2.8eV$). (c) Within the aforementioned linear approximation, the dependence on the two-dimensional wave vector $K_{\parallel} \equiv (k_{xx}k_{y})$ of electron energy (dispersion relation) is depicted by the (blue and red) Dirac cones, which are shifted by an applied bias *V*. (d) The orange triangles, which depict the electrodes' electronic states in the Fermi energy window contributing to charge transport via elastic tunneling (depicted by the solid brown horizontal arrow) mediated by a single level (illustrated by the dashed brown arrows), aim at intuitively illustrating what makes conduction through junctions with graphene electrodes different from that with conventional metals (Figure 1b). Because each leg of these triangles scales with *V*, their area $A \propto V^2$ at $V \rightarrow 0$ decreases faster with *V* that the area of the orange rectangles of Figure 1b, and this behavior makes ohmic conduction impossible. (e,f) Numerical simulations using the model parameters and equations indicated in the legend confirm quantitatively the absence of the linear (ohmic) regime for molecular junctions with graphene electrodes (additional simulations in Figure S1).

 $|\varepsilon - E_D|$ (Figure 2b). The latter is the consequence of the approximate linear dispersion relation $E \rightarrow E_{K_{\parallel}} \approx \hbar \nu_F K_{\parallel}$, where the wave vector K_{\parallel} is measured relative to the Brillouin zone vertex, which makes electrons in graphene resemble massless Fermions of relativistic quantum field theory, obeying an equation similar to Dirac equation of quantum electrodynamics wherein the speed of light $c = 3 \times 10^8 m/s$ is replaced by the smaller Fermi velocity $\nu_F \approx 10^6 m/s \approx c/300.^{38}$

Because the band of the pristine single-layer graphene is exactly half-filled (semimetallic character), the Fermi surface is point-like (Figure 2c). In the absence of doping and gate potential (as assumed throughout unless otherwise specified), the energy of the Dirac points coincides with the Fermi energy $E_D = E_F$ (= 0). This gives rise to a vanishing DOS at the Fermi energy $\rho(E - E_F) \sim |E - E_F|$

$$\rho_{s,d}(0) = 0 \to \Gamma_{s,d}(0) = 0 \tag{6}$$

Then, eq 3 implies $G \equiv 0$. This means that the ohmic regime is absent in molecular junctions with graphene electrodes.

In general, the MO electronic couplings to graphene layers $(\Gamma_{s,d} \propto \rho_{s,d})$ under a nonvanishing bias can be expressed as

$$\Gamma_{s,d}(\varepsilon) = \overline{\Gamma}_{s,d}|\varepsilon \mp eV/2| \tag{7}$$

where $\overline{\Gamma}_{s,d}$ are dimensionless MO-electrode electronic couplings. Full I-V curves at arbitrary biases and temperatures can be computed via numerical integration by combining eqs 2 and 7. A general formula to express the current of eq 2 at arbitrary temperatures in closed analytic form cannot be deduced, but the approximate expression valid at $T \rightarrow 0$ and lower biases ($\lfloor eV \rfloor \leq |\varepsilon_0|$) presented below



Figure 3. Schematic representation of single-molecule DAE junctions with electrodes of single-layer graphene. (a) Fabrication of graphene nanogap. (b) Strictly, the electrodes' density of states $\rho(E_r)$ vanishes only in molecular junctions with infinite periodic graphene layers. (c) In real junctions, an absent ohmic regime can be expected for graphene electrodes having sufficiently extended defect-free periodicity in the transverse direction on either side of the contacted molecule. (d,e) Possible departures from periodicity in real single-layer graphene electrodes that give rise to a nonvanishing graphene's DOS, thereby preventing Ohm's law breakdown.

$$I \approx I_3 = G_0 \overline{\Gamma}_s \overline{\Gamma}_d \frac{e^2}{6\varepsilon_0^2} V^3 \propto V^3$$
(8)

turns out to be useful for the analysis that follows.

A numerical simulation using the exact eqs 2 and 7 at T = 0 along with the approximate eq 8 depicts that, rather than being proportional to *V* (as would be the case if the ohmic regime existed), the current is proportional to V^3 at low bias (Figure 2e,f). Additional numerical simulations emphasize this aspect (Figure S1).

Expressed in intuitive physical terms, the current I in an "ordinary" junction with metal electrodes is due to charge transfer between the occupied electronic states in the left electrode and the empty electronic states in the right electrodes. At low temperatures and biases, they are depicted as tiny rectangles defined by the Fermi energy window (Figure 1b). Because the rectangles have a constant length ($\Gamma_{s,d} \propto \rho_{s,d}$ do not depend on energy) and height proportional to V, their area, which quantifies the number of these states, is proportional to V $(A \propto V)$. At low biases, the MO density of states in the Fermi window negligibly varies with energy, and this gives rise to a current $I \simeq GV$ proportional to V. At infinitesimally small biases $V \rightarrow 0$, the area becomes infinitesimally small, $A \propto V \rightarrow 0$, but the ratio remains finite $(A/V \neq 0)$, and this translates into a nonvanishing linear conductance $G = I/V \neq 0$. This picture contrasts with the left and right orange triangles in the Fermi energy window of Figure 2d. Because both triangle legs are proportional to V, their area, which quantifies the number of states that contribute to transport, vanishes faster than $V(A \propto V^2)$. By virtue of eq 2, this results in the cubic dependence of I on V(cf. eq 8) and in the absence of the ohmic regime associated with it.

We emphasize that both the theoretical formula expressing the current through a junction with electrodes of single-layer graphene at arbitrary bias and temperature (eqs 2 + 7) and its particular case (eq 8, valid at T = 0 and low bias) are direct consequences of the general Keldysh formalism; except for the assumption of a dominant MO, no other special assumption on the active molecule is needed in the mathematical deduction.

To interrogate the above theoretical predictions experimentally, we fabricated single-molecule junctions with diarylethene (DAE) sandwiched between electrodes consisting of graphene monolayers (Figure 3). Our experimental approach junctions followed that utilized in our previous studies.^{40,41} More details can be found in the Supporting Information.

To be sure, the theoretical results presented above refer to single-molecule junctions having ideal, defect-free electrodes consisting of periodic single-layer graphene with infinite lengths and widths (Figure 3b). On the other side, the foregoing description of manufacturing the real graphene-based junctions used in experiments should make it clear that "good" junctions that can be fabricated as delineated above resemble at best a junction having a sufficiently extended periodicity in the transverse direction (Figure 3c). Inherent limitations of atomic

Letter



Figure 4. Demonstrating the breakdown of Ohm's law in single-molecule junctions with electrodes of single-layer graphene. (a) Schematic diagram of the DAE single-molecule junction. (b-g) *I*–*V* curves measured at various temperatures indicated in the legend for a given junction fabricated with an open DAE molecule are accurately described by the general model defined by eqs 2 and 7, which predicts that the ohmic regime is absent in molecular junctions having graphene single layers as electrodes. Enlarged diagrams that better illustrate the absence of an ohmic regime hardly visible in panels (b–g) are shown in Figure S6.

level precision of the cutting procedure in achieving a nanogap matching the (DAE) molecule size and defined by linear contact edges parallel to each other, each comprising a "reasonable" large number of periodic, defect-free graphene units on either side of the contact (as opposed to the situation depicted in Figure 3c) make the experimental task a formidable challenge. It should therefore be understandable why most of the real junctions that can be fabricated (Figure 3d,e) depart from this "ideal" structure achievable in the laboratory (Figure 3c).

Notwithstanding these tremendous difficulties, we were able to experimentally fabricate junctions that demonstrate the breakdown of Ohm's law predicted theoretically above and, more generally, to validate the present model defined by eqs 2 and 7 Our key results are collected in Figures 4, S4, and S5. Along with experimental I-V curves (black lines), in all the aforementioned figures, we show best fitting curves (red lines) obtained via the exact eqs 2 and 7. These I-V curves are indeed ohmic-free curves. Notice that there is no significant qualitative difference between the I-V curves computed at temperatures up to T = 195 K (Figure 4g) and the simulations at T = 0 (Figure 2e,f). This should not be surprising. The temperature dependence of the tunneling current is significant only close to resonant tunneling.⁴²⁻⁴⁴ In off-resonant situations like those presently envisaged, the tunneling current is only weakly temperature dependent, which makes it possible to quantitatively interpret transport data measured at room temperature⁴⁵ using theoretical formulas for current deduced for $T = 0.^{46}$

The foregoing analysis made it clear that the absence of the ohmic regime is intimately connected to the vanishing DOS at the Dirac points. Therefore, although it may sound paradoxical for the molecular electronics community, the active molecule plays only a secondary role here. To emphasize this aspect, along

3271

with the I-V curves measured for the open DAE isomer (Figures 4 and S4), we also present results for the closed DAE molecule (Figure S5).

With regard to our specific choice of the active (DAE) molecule, we have to note the pronounced structural difference between open and closed DAE (Figure S7) reflects itself in the values of the pertaining currents that differ from each other up to 2 orders of magnitude; compare Figure 4 with Figure S5. These differences are much larger than differences between consecutive members of homologous series utilized to fabricate molecular junctions, such as oligoacenes,⁴⁷ alkyls,⁴⁸ oligophenyls,¹¹ and oligophenylene dimethanethiols.⁴⁹ They are also much larger than those caused by changing the anchoring group, e.g., thiols versus alkynes.^{9,50,51}

Intentionally or not, this graphene's salient feature can be destroyed:

A gate voltage (V_G) shifts the Dirac point energy and creates an imbalance $E_F \neq E_D$.⁵² Then, ohmic conduction becomes possible, because the DOS ceases to vanish at the Fermi energy $(\rho_{s,d}(E_F) \neq 0)$. A nonvanishing DOS at the Fermi energy means that charge carriers (electrons or holes) can be transferred at infinitesimal biases ($|V| \gtrsim 0$) between electrodes and molecule (Figure S8a). To exemplify this effect, we refer to the I-V curve measured experimentally at various gate voltage values $V_G \neq 0$ (Figure 3 in ref 53).Their slopes do no longer vanish at V = 0; that is, $G \neq 0$ and a linear (ohmic) regime at low V does exist for gated junctions.

In doped graphene single layers (Figure S8b), the alignment between the Dirac energy and the Fermi energy is also broken.^{52,54} This is indeed a very challenging difficulty that we had to overcome in experimentally demonstrating the absence of the ohmic regime in molecular junctions having graphene sheets as electrodes. Saying this, we do not refer to intentional doping, which is absent in the presently considered junctions. Unintentional (unwanted) doping can mean, e.g., charge transfer induced by etching, graphene's vulnerability to chemical surface and environmental contamination.55,56 Even the junction manufacturing process itself can give rise to a nonvanishing DOS at the interface. "Invasive", strong covalent bonds between the molecule's anchoring group and the graphene sheet edge distort the local charge distribution at contact ("unintentional local doping") and can have thereby a local impact on graphene similar to defects/impurities.⁵⁷ These can significantly alter graphene's DOS in the vicinity of the Fermi energy,⁵⁷ which ultimately yields a nonvanishing ohmic conductance ($G \neq 0$).

To better assess the meaning of the present finding ($G \equiv 0$), one should remind that, contrary to expectations, as the density of electrons and holes vanishes $(n \rightarrow 0, \text{ neutrality point})$, the conductivity of the single-layer graphene does not vanish but approaches a value that remains finite $(\sigma_{2D} \approx e^2/h \neq 0)$ down to liquid helium^{38,58} (Recall that in two dimensions $\sigma_{2D} = G \times$ width/length is expressed in siemens (S) and not in S/m as in three dimensions). This is but a single illustration of the fact that electrons in graphene represent an intriguing system; as if it consisted of independent particle moving relativistically (massless Fermions obeying a Dirac-type equation with $v_F \neq$ c) but strongly interacting nonrelativistically (because $v_F \approx c/$ $300 \ll c$).³⁸ The latter feature traces back to graphene's effective fine structure constant $\alpha_G \equiv e^2/\hbar v_F = \alpha(c/v_F) \approx 300\alpha$ much larger than the fine structure constant $\alpha = e^2/\hbar c \approx 1/137$, which implies screening effects much weaker than in ordinary metals and stronger electron correlations.

If significant for the present molecular junctions with graphene electrodes, electron correlations would renormalize the single-particle Fermi distributions and the electrodes' (electro)chemical potential ($\mu_{s,d} = \pm eV/2$), invalidating thereby the present theory based on eq 2 that holds for uncorrelated transport. Definitely, the overall good agreement between experiment and theory (Figures 4, S4, and S5) rules out this possibility.

Returning to the junctions investigated in our experiments, we wish to add two remarks.

- (i) Noteworthily, we have used experimental setups having single-layer graphene as electrodes. We do have electrodes of graphene monolayers; we do not only use graphene monolayers, e.g., to coat metal electrodes. The twodimensional in-plane motion of electrons in our electrodes makes the DOS $\rho(E - E_F) \sim |E - E_F|$ vanishing at the Dirac (Fermi) point (Figure 2b) and justifies utilization of eq 7 in calculating the current (eq 2). Our graphene-based molecular junctions are qualitatively different from molecular junctions wherein graphene monolayers are merely used for coating metal electrodes. In the latter case, the charge transport is determined by electrons traveling across the graphene monolayer and not by the two-dimensional in-plane motion of electrons; for those junctions, neither the relationship $\rho(E - E_F) \sim |E - E_F|$ nor the ubiquitously drawn Dirac cones (Figure 2c,d) or eq 7 related to it can be justified to compute the current.
- (ii) Ordinary molecular junctions having metal electrodes often possess practically symmetric I-V curves (i.e., I(-V) = -I(V) even if they are fabricated with noncentrosymmetric molecules. Therefore, the fact that, albeit nonspectacular, our I-V curves systematically exhibit a certain asymmetry upon bias reversal appears to be a conundrum; both open and closed DAE are centrosymmetric (Figure S7), and both electrodes consist of single-layer graphene. The formula used to compute the current, the analysis presented above, and the fitting parameter values allow us to solve this conundrum: notwithstanding the fact that both the molecule and the electrodes are chemically symmetric, the moleculeelectrode electronic couplings are different (the values of $\overline{\Gamma}_s$ and of $\overline{\Gamma}_d$ are substantially different from each other, see the legends of Figures 4, S4, and S5), and this makes eqs 2 + 7 noninvariant under bias reversal. This is why in molecular junctions with electrodes of single-layer graphene the asymmetric MO couplings to electrodes yield asymmetric I-V curves (current rectification). Recall that this is not the case in molecular junctions having electrodes of ordinary, wide-band metals.44,59-62

In closing, we predicted theoretically and demonstrated that when adequately fabricated experimentally to comply with theoretical modeling, molecular junctions using single-layer graphene as electrodes do not exhibit ohmic charge transport. The absence of the ohmic regime is the direct consequence of the vanishing density of states at the Dirac energy, which inhibits the transfer of electrons (or holes) between the active molecule and electrodes consisting of undoped single-layer graphene. Formulating alternatively, the breakdown of Ohm's law is merely due to this unique property of the pristine single-layer graphene. Paradoxically, it is by no means related to the "active" molecule, unlike in most molecular electronic devices, where it plays a paramount importance in achieving the desired functionality. Our present choice (namely open and closed DAE, a molecule species extensively and intensively investigated by us in the past^{41,53,63,64} and for which we achieved a remarkable high control) is merely motivated by the enormous difficulty to strictly meeting experimentally the challenging conditions wherein the theoretical prediction applies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.4c00387.

Experimental and theoretical details; supplementary figures (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Ioan Bâldea Department of Materials Science and Engineering, MATEC, Guangdong Technion - Israel Institute of Technology, Shantou, Guangdong 515063, P. R. China; Theoretische Chemie, Universität Heidelberg, D-69120 Heidelberg, Germany; orcid.org/0000-0003-4860-5757; Email: ioan.baldea@pci.uni-heidelberg.de
- Xuefeng Guo Center of Single-Molecule Sciences, Institute of Modern Optics, Frontiers Science Center for New Organic Matter, Tianjin Key Laboratory of Micro-scale Optical Information Science and Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300350, P. R. China; Beijing National Laboratory for Molecular Sciences, National Biomedical Imaging Center, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China; o orcid.org/0000-0001-5723-8528; Email: guoxf@pku.edu.cn
- Zuoti Xie Department of Materials Science and Engineering, MATEC, Guangdong Technion - Israel Institute of Technology, Shantou, Guangdong 515063, P. R. China; Quantum Science Center of Guangdong-Hong Kong-Macao Greater Bay Area (Guangdong), Shenzhen-Hong Kong International Science and Technology Park, Shenzhen, Guangdong 518000, P. R. China; ◎ orcid.org/0000-0002-1828-0122; Email: zuoti.xie@gtiit.edu.cn

Authors

- Yuhong Chen Department of Materials Science and Engineering, MATEC, Guangdong Technion - Israel Institute of Technology, Shantou, Guangdong 515063, P. R. China; orcid.org/0009-0004-6855-8788
- Miao Zhang Center of Single-Molecule Sciences, Institute of Modern Optics, Frontiers Science Center for New Organic Matter, Tianjin Key Laboratory of Micro-scale Optical Information Science and Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300350, P. R. China
- Na Xin Beijing National Laboratory for Molecular Sciences, National Biomedical Imaging Center, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China
- Yunxia Feng Department of Materials Science and Engineering, MATEC, Guangdong Technion - Israel Institute of Technology, Shantou, Guangdong 515063, P. R. China
- Jiajun Feng Department of Materials Science and Engineering, MATEC, Guangdong Technion - Israel Institute of Technology, Shantou, Guangdong 515063, P. R. China

Chuancheng Jia – Center of Single-Molecule Sciences, Institute of Modern Optics, Frontiers Science Center for New Organic Matter, Tianjin Key Laboratory of Micro-scale Optical Information Science and Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300350, P. R. China; Beijing National Laboratory for Molecular Sciences, National Biomedical Imaging Center, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpclett.4c00387

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

X.G. acknowledges primary financial supports from the National Key R&D Program of China (2021YFA1200101 and 2022YFE0128700) and the National Natural Science Foundation of China (22150013, 21727806 and 21933001). Z.X. acknowledges financial supports from the National Natural Science Foundation of China (22373026) and Guangdong Science and Technology Department (2021B0301030005, 2022A1515011843, STKJ2021169, and 2021QN02X538) and Strategic Special Project of Guangdong Province (GDZX2304005). In the initial stage, I.B. was funded by the German Research Foundation (DFG grant BA 1799/3-2), who also acknowledges computational support from the state of Baden-Württemberg through bwHPC and the German Research Foundation through Grant No. INST 40/575-1 FUGG (bwUniCluster 2.0, bwForCluster/MLS&WISO 2.0/ HELIX, and JUSTUS 2.0 cluster).

REFERENCES

(1) Ohm, G. S. Die Galvanische Kette, Mathematisch Bearbeitet; T. H. Riemann: Berlin, 1827.

(2) Drude, P. Zur Elektronentheorie Der Metalle. Ann. Phys. 1900, 306, 566.

(3) Sommerfeld, A.; Bethe, H. *Handbuch Der Physik*; Julius - Springer - Verlag: Berlin, 1933.

(4) Ashcroft, N. W.; Mermin, N. D. Solid State Physics; Cengage Learning: New York, 1976.

(5) Kubo, R. Statistical-Mechanical Theory of Irreversible Processes. I. General Theory and Simple Applications to Magnetic and Conduction Problems. J. Phys. Soc. Jpn. **1957**, *12*, 570.

(6) Mahan, G. D. Many-Particle Physics; Plenum Press: New York, 1990.

(7) Ferry, D. K. Ohm's Law in a Quantum World. *Science* **2012**, *335*, 45–46.

(8) Engelkes, V. B.; Beebe, J. M.; Frisbie, C. D. Length-Dependent Transport in Molecular Junctions Based on SAMs of Alkanethiols and Alkanedithiols: Effect of Metal Work Function and Applied Bias on Tunneling Efficiency and Contact Resistance. J. Am. Chem. Soc. 2004, 126, 14287–14296.

(9) Bowers, C. M.; Liao, K. C.; Zaba, T.; Rappoport, D.; Baghbanzadeh, M.; Breiten, B.; Krzykawska, A.; Cyganik, P.; Whitesides, G. M. Characterizing the Metal-SAM Interface in Tunneling Junctions. *ACS Nano* **2015**, *9*, 1471–1477.

(10) Wang, W.; Lee, T.; Reed, A. Mechanism of Electron Conduction in Self-Assembled Alkanethiol Monolayer Devices. *Phys. Rev. B* 2003, 68, No. 035416.

(11) Xie, Z.; Bâldea, I.; Frisbie, C. D. Determination of Energy-Level Alignment in Molecular Tunnel Junctions by Transport and Spectroscopy: Self-Consistency for the Case of Oligophenylene Thiols and Dithiols on Ag, Au, and Pt Electrodes. J. Am. Chem. Soc. 2019, 141, 3670-3681.

(12) Quek, S. Y.; Choi, H. J.; Louie, S. G.; Neaton, J. B. Length Dependence of Conductance in Aromatic Single-Molecule Junctions. *Nano Lett.* **2009**, *9*, 3949–3953.

(13) Malen, J. A.; Doak, P.; Baheti, K.; Tilley, T. D.; Segalman, R. A.; Majumdar, A. Identifying the Length Dependence of Orbital Alignment and Contact Coupling in Molecular Heterojunctions. *Nano Lett.* **2009**, *9*, 1164–1169.

(14) Kim, B.; Choi, S. H.; Zhu, X. Y.; Frisbie, C. D. Molecular Tunnel Junctions Based on π -Conjugated Oligoacene Thiols and Dithiols between Ag, Au, and Pt Contacts: Effect of Surface Linking Group and Metal Work Function. *J. Am. Chem. Soc.* **2011**, *133*, 19864–19877.

(15) Capozzi, B.; Dell, E. J.; Berkelbach, T. C.; Reichman, D. R.; Venkataraman, L.; Campos, L. M. Length-Dependent Conductance of Oligothiophenes. J. Am. Chem. Soc. **2014**, 136, 10486–10492.

(16) Smith, C. E.; Odoh, S. O.; Ghosh, S.; Gagliardi, L.; Cramer, C. J.; Frisbie, C. D. Length-Dependent Nanotransport and Charge Hopping Bottlenecks in Long Thiophene-Containing π -Conjugated Molecular Wires. *J. Am. Chem. Soc.* **2015**, *137*, 15732–15741.

(17) Hong, W.; Li, H.; Liu, S. X.; Fu, Y.; Li, J.; Kaliginedi, V.; Decurtins, S.; Wandlowski, T. Trimethylsilyl-Terminated Oligo-(Phenylene Ethynylene)s: An Approach to Single-Molecule Junctions with Covalent Au-C σ -Bonds. *J. Am. Chem. Soc.* **2012**, *134*, 19425–19431.

(18) Kaliginedi, V.; Moreno-García, P.; Valkenier, H.; Hong, W.; García-Suárez, V. M.; Buiter, P.; Otten, J. L. H.; Hummelen, J. C.; Lambert, C. J.; Wandlowski, T. Correlations between Molecular Structure and Single-Junction Conductance: A Case Study with Oligo(Phenylene-Ethynylene)-Type Wires. J. Am. Chem. Soc. 2012, 134, 5262–5275.

(19) Garner, M. H.; Li, H.; Chen, Y.; Su, T. A.; Shangguan, Z.; Paley, D. W.; Liu, T.; Ng, F.; Li, H.; Xiao, S.; Nuckolls, C.; Venkataraman, L.; Solomon, G. C. Comprehensive Suppression of Single-Molecule Conductance Using Destructive σ -Interference. *Nature* **2018**, *558*, 415–419.

(20) Li, Y.; Xiang, L.; Palma, J. L.; Asai, Y.; Tao, N. Thermoelectric Effect and Its Dependence on Molecular Length and Sequence in Single DNA Molecules. *Nat. Commun.* **2016**, *7*, 11294.

(21) Ho Choi, S.; Kim, B. S.; Frisbie, C. D. Electrical Resistance of Long Conjugated Molecular Wires. *Science* **2008**, *320*, 1482–1486.

(22) Nijhuis, C. A.; Reus, W. F.; Whitesides, G. M. Molecular Rectification in Metal-SAM-Metal Oxide-Metal Junctions. *J. Am. Chem. Soc.* **2009**, *131*, 17814–17827.

(23) Sangeeth, C. S. S.; Demissie, A. T.; Yuan, L.; Wang, T.; Frisbie, C. D.; Nijhuis, C. A. Comparison of DC and AC Transport in 1.5–7.5 nm Oligophenylene Imine Molecular Wires across Two Junction Platforms: Eutectic Ga-In versus Conducting Probe Atomic Force Microscope Junctions. J. Am. Chem. Soc. **2016**, *138*, 7305–7314.

(24) Cuevas, J. C.; Scheer, E. Molecular Electronics An Introduction to Theory and Experiment; World Scientific, 2017.

(25) Datta, S. Quantum Transport: Atom to Transistor; Cambridge Univ. Press, 2005.

(26) Weber, B.; Mahapatra, S.; Ryu, H.; Lee, S.; Fuhrer, A.; Reusch, T. C. G.; Thompson, D. L.; Lee, W. C. T.; Klimeck, G.; Hollenberg, L. C. L.; Simmons, M. Y. Ohm's Law Survives to the Atomic Scale. *Science* **2012**, 335, 64–67.

(27) Purcell, E. M.; Morin, D. J. *Electricity and Magnetism*; McGraw-Hill, 1985.

(28) Guo, S.; Zhou, G.; Tao, N. Single Molecule Conductance, Thermopower, and Transition Voltage. *Nano Lett.* **2013**, *13*, 4326– 4332.

(29) Hines, T.; Diez-Perez, I.; Hihath, J.; Liu, H.; Wang, Z. S.; Zhao, J.; Zhou, G.; Müllen, K.; Tao, N. Transition from Tunneling to Hopping in Single Molecular Junctions by Measuring Length and Temperature Dependence. J. Am. Chem. Soc. **2010**, *132*, 11658–11664.

(30) Haug, H.; Jauho, A.-P. Quantum Kinetics in Transport and Optics of Semiconductors, 2nd ed.; Springer-Verlag Berlin Heidelberg, 2008.

(31) Landauer, R. Spatial Variation of Currents and Fields Due to Localized Scatterers in Metallic Conduction. *IBM J. Res. Dev.* **1957**, *1*, 223–231.

(32) Landauer, R. Conductance Determined by Transmission: Probes and Quantised Constriction Resistance. J. Phys.: Condens. Matter **1989**, 1, 8099.

(33) Imry, Y. Physics of Mesoscopic Systems. *Directions in Condensed Matter Physics* **1986**, *1*, 101–163.

(34) van Houten, H.; Beenakker, C. Quantum Point Contacts. *Phys. Today* **1996**, *49*, 22.

(35) Hobson, J. P.; Nierenberg, W. A. The Statistics of a Two-Dimensional, Hexagonal Net. *Phys. Rev.* **1953**, *89*, 662.

(36) Horiguchi, T. Lattice Green's Functions for the Triangular and Honeycomb Lattices. J. Math. Phys. **1972**, 13, 1411–1419.

(37) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.

(38) Geim, A. K.; Novoselov, K. S. The Rise of Graphene. *Nat. Mater.* **2007**, *6*, 183–191.

(39) Wallace, P. R. The Band Theory of Graphite. *Phys. Rev.* **1947**, *71*, 622.

(40) Cao, Y.; Dong, S.; Liu, S.; He, L.; Gan, L.; Yu, X.; Steigerwald, M. L.; Wu, X.; Liu, Z.; Guo, X. Building High-Throughput Molecular Junctions Using Indented Graphene Point Contacts. *Angew. Chemie Int. Ed.* **2012**, *51*, 12228.

(41) Jia, C.; Migliore, A.; Xin, N.; Huang, S.; Wang, J.; Yang, Q.; Wang, S.; Chen, H.; Wang, D.; Feng, B.; Liu, Z.; Zhang, G.; Qu, D.-H.; Tian, H.; Ratner, M. A.; Xu, H. Q.; Nitzan, A.; Guo, X. Covalently Bonded Single-Molecule Junctions with Stable and Reversible Photoswitched Conductivity. *Science* **2016**, *352*, 1443–1445.

(42) Sedghi, G.; García-Suárez, V. M.; Esdaile, L. J.; Anderson, H. L.; Lambert, C. J.; Martín, S.; Bethell, D.; Higgins, S. J.; Elliott, M.; Bennett, N.; Macdonald, J. E.; Nichols, R. J. Long-Range Electron Tunnelling in Oligo-Porphyrin Molecular Wires. *Nat. Nanotechnol.* **2011**, *6*, 517.

(43) Poot, M.; Osorio, E.; O'Neill, K.; Thijssen, J. M.; Vanmaekelbergh, D.; Van Walree, C. A.; Jenneskens, L. W.; Van Der Zant, H. S. J. Temperature Dependence of Three-Terminal Molecular Junctions with Sulfur End-Functionalized Tercyclohexylidenes. *Nano Lett.* **2006**, *6*, 1031–1035.

(44) Bâldea, I. Protocol for Disentangling the Thermally Activated Contribution to the Tunneling-Assisted Charge Transport. Analytical Results and Experimental Relevance. *Phys. Chem. Chem. Phys.* **2017**, *19*, 11759–11770.

(45) Bâldea, I. Can Room-Temperature Data for Tunneling Molecular Junctions Be Analyzed within a Theoretical Framework Assuming Zero Temperature? *Phys. Chem. Chem. Phys.* **2023**, *25*, 19750.

(46) Bâldea, I. Can Tunneling Current in Molecular Junctions Be so Strongly Temperature Dependent to Challenge a Hopping Mechanism? Analytical Formulas Answer This Question and Provide Important Insight into Large Area Junctions. *Phys. Chem. Chem. Phys.* **2024**, *26*, 6540.

(47) Kim, B.; Choi, S. H.; Zhu, X.-Y.; Frisbie, C. D. Molecular Tunnel Junctions Based on π -Conjugated Oligoacene Thiols and Dithiols between Ag, Au, and Pt Contacts: Effect of Surface Linking Group and Metal Work Function. *J. Am. Chem. Soc.* **2011**, *133*, 19864–19877.

(48) Xie, Z.; Baldea, I.; Frisbie, C. D. Energy Level Alignment in Molecular Tunnel Junctions by Transport and Spectroscopy: Self-Consistency for the Case of Alkyl Thiols and Dithiols on Ag, Au, and Pt Electrodes. J. Am. Chem. Soc. **2019**, *141*, 18182–18192.

(49) Van Nguyen, Q.; Xie, Z.; Frisbie, C. D. Quantifying Molecular Structure-Tunneling Conductance Relationships: Oligophenylene Dimethanethiol vs Oligophenylene Dithiol Molecular Junctions. *J. Phys. Chem. C* 2021, 125, 4292–4298.

(50) Fracasso, D.; Kumar, S.; Rudolf, P.; Chiechi, R. C. Self-Assembled Monolayers of Terminal Acetylenes as Replacements for Thiols in Bottom-up Tunneling Junctions. *RSC Adv.* **2014**, *4*, 56026–56030.

(51) Chen, Y.; Bâldea, I.; Yu, Y.; Liang, Z.; Li, M.-D.; Koren, E.; Xie, Z. CP-AFM Molecular Tunnel Junctions with Alkyl Backbones Anchored Using Alkynyl and Thiol Groups: Microscopically Different Despite Phenomenological Similarity. *Langmuir* **2024**, *40*, 4410.

(52) Solís-Fernández, P.; Okada, S.; Sato, T.; Tsuji, M.; Ago, H. Gate-Tunable Dirac Point of Molecular Doped Graphene. *ACS Nano* **2016**, *10*, 2930–2939.

(53) Meng, L.; Xin, N.; Hu, C.; Sabea, H. Al; Zhang, M.; Jiang, H.; Ji, Y.; Jia, C.; Yan, Z.; Zhang, Q.; Gu, L.; He, X.; Selvanathan, P.; Norel, L.; Rigaut, S.; Guo, H.; Meng, S.; Guo, X. Dual-Gated Single-Molecule Field-Effect Transistors beyond Moore's Law. *Nat. Commun.* **2022**, *13*, 1410.

(54) Joucken, F.; Tison, Y.; Lagoute, J.; Dumont, J.; Cabosart, D.; Zheng, B.; Repain, V.; Chacon, C.; Girard, Y.; Botello-Méndez, A. R.; Rousset, S.; Sporken, R.; Charlier, J. C.; Henrard, L. Localized State and Charge Transfer in Nitrogen-Doped Graphene. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2012**, *85*, No. 161408.

(55) Hess, L. H.; Jansen, M.; Maybeck, V.; Hauf, M. V.; Seifert, M.; Stutzmann, M.; Sharp, I. D.; Offenhäusser, A.; Garrido, J. A. Graphene Transistor Arrays for Recording Action Potentials from Electrogenic Cells. *Adv. Mater.* **2011**, *23*, 5045–5049.

(56) Jiang, L.; Fu, W.; Birdja, Y. Y.; Koper, M. T. M.; Schneider, G. F. Quantum and Electrochemical Interplays in Hydrogenated Graphene. *Nat. Commun.* **2018**, *9*, 793.

(57) Bena, C.; Kivelson, S. A. Quasiparticle Scattering and Local Density of States in Graphite. *Phys. Rev. B* 2005, *72*, No. 125432.

(58) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-Dimensional Gas of Massless Dirac Fermions in Graphene. *Nature* **2005**, 438, 197–200.

(59) Kitagawa, T.; Berg, E.; Rudner, M.; Demler, E. Topological Characterization of Periodically Driven Quantum Systems. *Phys. Rev. B* **2010**, *82*, No. 235114.

(60) Zhang, G.; Ratner, M. A.; Reuter, M. G. Is Molecular Rectification Caused by Asymmetric Electrode Couplings or by a Molecular Bias Drop? J. Phys. Chem. C 2015, 119, 6254–6260.

(61) Bâldea, I. Why Asymmetric Molecular Coupling to Electrodes Cannot Be at Work in Real Molecular Rectifiers. *Phys. Rev. B* 2021, *103*, No. 195408.

(62) Peterson, I. R.; Vuillaume, D.; Metzger, R. M. Analytical Model for Molecular-Scale Charge Transport. J. Phys. Chem. A 2001, 105, 4702–4707.

(63) Jia, C.; Wang, J.; Yao, C.; Cao, Y.; Zhong, Y.; Liu, Z.; Liu, Z.; Guo, X. Conductance Switching and Mechanisms in Single-Molecule Junctions. *Angew. Chemie - Int. Ed.* **2013**, *52*, 8666–8670.

(64) Xin, N.; Hu, C.; Al Sabea, H.; Zhang, M.; Zhou, C.; Meng, L.; Jia, C.; Gong, Y.; Li, Y.; Ke, G.; He, X.; Selvanathan, P.; Norel, L.; Ratner, M. A.; Liu, Z.; Xiao, S.; Rigaut, S.; Guo, H.; Guo, X. Tunable Symmetry-Breaking-Induced Dual Functions in Stable and Photoswitched Single-Molecule Junctions. *J. Am. Chem. Soc.* **2021**, *143*, 20811–20817.