Revisiting the Calculation of I/V Profiles in Molecular Junctions Using the Uncertainty Principle

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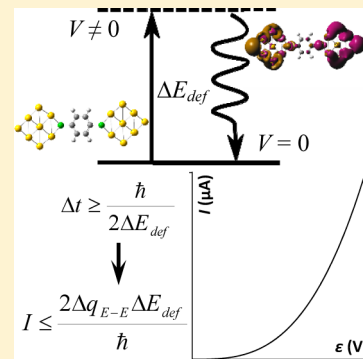
Revisiting the Calculation of *I/V* Profiles in Molecular Junctions Using the Uncertainty Principle

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ABSTRACT: Ortiz and Seminario (*J. Chem. Phys.* **2007**, *127*, 111106/1−3) proposed some years ago a simple and direct approach to obtain *I/V* profiles from the combination of ab initio equilibrium electronic structure calculations and the uncertainty principle as an alternative or complementary tool to more sophisticated nonequilibrium Green's functions methods. In this work, we revisit the fundamentals of this approach and reformulate accordingly the expression of the electric current. By analogy to the spontaneous electron decay process in electron transitions, in our revision, the current is calculated upon the relaxing process from the "polarized" state induced by the external electric field to the electronic ground state. The electric current is obtained from the total charge transferred through the molecule and the corresponding electronic energy relaxation. The electric current expression proposed is more general compared with the previous expression employed by Ortiz and Seminario, where the charge variation must be tested among different slabs of atoms at the contact. This new approach has been tested on benzene-1,4-dithiolate attached to different gold clusters that represent the contact with the electrodes. Analysis of the total electron deformation density induced by the external electric voltage and properties associated with the electron deformation orbitals supports the conclusions obtained from the *I/V* profiles.

$$V \neq 0$$
$$\Delta E_{def}$$
$$V = 0$$
$$\Delta t \geq \frac{\hbar}{2\Delta E_{def}}$$
$$I \leq \frac{2\Delta q_{E-E}\Delta E_{def}}{\hbar}$$
$$I\,(\mu A)$$
$$\varepsilon\,(V)$$

■ INTRODUCTION

Since the calculation of the electric conductance of a single molecule in 1997,[1] the field of molecular electronics has experienced continuous growth.[2−5] The investigation of different molecular electron carriers in electric contact with two electrodes is currently being addressed either experimentally or theoretically. Whereas experiments are mainly orientated to the search of efficient and reproducible processes of synthesis of molecular electronic junctions,[6−22] theoretical efforts are focused on the development of suitable theoretical methods for the estimation of the electron transport through a single molecule in a ballistic regime.[23−52] Despite the technological limitations in the fabrication of single-molecule junctions, experimental efforts were focused on the direct observation of charge transport through benzene-1,4-dithiolate in contact with gold electrodes, the first system to which experimental current/voltage measurements was possible.[1]

Recent progress in nanotechnology has enabled the formation of different chemical links between a single molecule and an electrode beyond conventional linkers such as thiols or amines.[20,21] This has allowed expanding the kind of considered single molecular junctions to π-conjugated systems.[53,54] However, the current theoretical approximations are not able to provide systemically concordant results with experiments.[12,35,52] Therefore, the challenge of developing proper theoretical approaches able to integrate adequately the electronic structure of the molecular conductor and the effect of the molecule-electrode interface is still in progress.

The most widespread approximation tackles the conductance and current/voltage profiles combining the nonequilibrium Green's function formalism of quantum transport and the density functional theory (DFT) of electronic structure.[55] However, in an alternative method proposed by Ortiz and Seminario,[56] the current/voltage profiles can be obtained from direct electronic structure calculations. In their method, nonequilibrium electron transport approaches are not employed, but only equilibrium electronic structure calculations in electrically perturbed and unperturbed systems are required. Only the calculation of the atomic charge variations induced by the external voltage at a given time, the latter indirectly calculated with the uncertainty principle,[57] is required for the calculations of the current. This method avoids the problems raised from a poor atomic-scale description of the device electronic structure when it is subjected to a bias voltage and the delimitation of the "extended molecule" and semi-infinite bulk electrodes. However, the most attractive point of this approach is, undoubtedly, its simplicity.

Although the method previously described may present a priori some advantages due to the inequality given by the uncertainty relation, this approach leads as much to an upper bound limit to the current intensity.[56,58] Despite this important limitation, the calculation of the electron transport through the uncertainty relation still remains interesting due to its computational simplicity and first-principles foundation. However, it demands a further analysis and an extensive revision of its theoretical grounds. We revisit the applicability of the uncertainty relation to the calculation of the electron

transport and propose a new expression for the electron current in molecular devices.

Considering that the electron transport across a single molecule depends strongly on the type of junction between the molecule and the electrodes and the molecular orientation, these factors were previously investigated for terminal linker groups such as thiols[1,11,13] and amines.[14,17] A single benzene-1,4-dithiolate attached to gold electrodes has been the main reference model in the field of molecular electronics over the last decades.[1,12,25,30,31,35,40] Although this molecular junction has been extensively studied using different theoretical approximations,[25,30,31,35,52] its conductance and molecular adsorption preferences are still a matter of controversy.

Herein, we analyze the I/V profiles obtained for a single benzene-1,4-dithiolate attached to different gold clusters, which represent different descriptions of the molecule−electrode junction.[12,40] The electric response is also analyzed by means of the electron deformation orbitals (EDOs) and their associated properties such the electron polarization and the occupied-virtual electron transfer, which have been shown to be simple and useful tools to understand the electron transport in single molecules.[54,59] This way, we establish a connection between the electric response of the system and the electrical conductance obtained with the revisited approach.

■ THEORETICAL DEVELOPMENTS

In our approach, the conducting properties of the molecule are calculated upon the relaxing process of the system from the "polarized" state to the ground state. During this process, some electron charge crosses the molecule from the positive to the negative electrode. The magnitude of this charge and the time involved in the process determines the current intensity. Notice that relaxation occurs when the external potential drops to zero, so that the Hamiltonian governing the process corresponds to the unperturbed Hamiltonian and the energy change is given by

$$\Delta E_{def} = \langle \Psi | H_0 | \Psi \rangle - \langle \Psi_0 | H_0 | \Psi_0 \rangle \qquad (1)$$

where Ψ_0 and Ψ are the wave functions for the ground and "polarized" states, respectively. We will denote the energy relaxation involved in the process as deformation energy by analogy to the deformation energy in perturbation theory.

The uncertainty relation (eq 2) is applied, for instance, in spectroscopy to determine the natural lifetime of an electronic excited state.

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2} \qquad (2)$$

Introducing the uncertainty relation to measure the lifetime of the "polarized" state, one obtains an expression of the current intensity in terms of the electron charge transferred during the process and the corresponding deformation energy.

$$I \leq \frac{2 \Delta q_{E-E} \Delta E_{def}}{\hbar} \qquad (3)$$

Δq_{E-E} is given by the lowest value of the charge transferred from or to the molecule at the right or left contacts; the difference between both values just represent electron charge accumulation/depletion in the molecule. In homogeneous conductors, charge accumulation/depletion must be zero along the conducting section. Our definition therefore avoids the arbitrariness of selecting small charge variations at different slabs taken from either side of the system as proposed in the

original expression of the current intensity given by Ortiz and Seminario.[56] We will show later how the picture of the electron charge deformation induced by the external electric perturbation and the concept of bond electron transfer may help us to understand the essential differences between good and poor molecular conductors.

It is important to remark that ΔE_{def} is related to the total energy change, ΔE, employed by Ortiz and Seminario in their original expression of the current in nonpolar molecules. Then, ΔE results from the addition of two energy terms: the energy associated with the "deformation" of the wave function (ΔE_{def}) and the electrostatic interaction energy between the external electric field and the "polarized" state of the molecule (ΔE_{elec}).

$$\Delta E = \Delta E_{def} + \Delta E_{elec} \qquad (4)$$

Using the Rayleigh−Schrödinger perturbation theory (RSPT) up to second order, one arrives to the following relation between the deformation energy and the second-order correction to the expectation value of the perturbation operator.

$$\Delta E_{def}^{(2)} = -\frac{1}{2} \Delta E_{elec}^{(2)} \qquad (5)$$

The electrostatic energy in eq 5 also contains the first-order correction to the energy

$$E^{(1)} = \langle \Psi_0 | \hat{V} | \Psi_0 \rangle \qquad (6)$$

but it is straightforward to show that this term is zero in nonpolar systems. Then, in the case of nonpolar or slightly polar molecules, as those considered in this work, and for small perturbations where second order correction is sufficient, substituting eq 5 in eq 4 one arrives to

$$\Delta E = -\Delta E_{def} \qquad (7)$$

showing how substitution of ΔE_{def} by ΔE in the current expression leads to equivalent results, at least for small external voltages.

On the contrary, in the case of polar systems, the first-order correction to the energy (eq 6) may lead to significant differences between ΔE and ΔE_{def}. This energy term is associated with the ground ("unperturbed") state wave function and so it does not carry direct information on the response of the system to the external voltage, which is reflected on properties such as polarizability or electric conductivity. As an example, a highly polar poor-conducting (weakly polarizable) molecule may display large ΔE values, which would contribute artificially to increase the electric current in the original expression of ref 56. On the contrary, the deformation energy must be small, leading to lower values of the current in eq 3, as would be expected.

■ COMPUTATIONAL DETAILS

The geometries and wave functions were obtained with the DFT at the B3PW91/LANLD2Z level using the 6-31G(d) basis set for the atoms carbon, hydrogen, and sulfur. Calculations were done with Gaussian09 program.[60] Previous works have demonstrated the efficiency of this level of theory in theoretical computations of molecular conductance.[25,43] We have performed full geometry optimizations and electronic structure calculations for benzene-1,4-dithiolate covalently bonded to one or two atoms of clusters containing up to eight gold atoms per side. These gold clusters are necessary to

account for the junction conductance and the effects of the covalent contacts with the gold electrodes on the electronic structure of the molecule. As pointed out in ref 58, the inclusion of these clusters in the calculations may come with other problems associated with the large polarizability of the metal, which causes the gold clusters to dominate the properties of the system and the measured conductance. Thus, it is expected that increasing the number of gold atoms in the clusters will increase the current in our approach. For that reason, we have limited the number of metal atoms at the contacts to just eight.
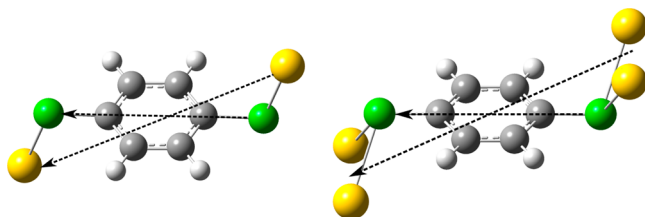
All calculations including the external voltage were performed at the same level of theory. We have varied this voltage from 0 to 2.5 V by applying a constant electric field of proper intensity. We have analyzed the influence of the electric field direction only for the smallest systems, those where the electrodes are described only by the gold atoms directly attached to the molecule. The molecular geometries employed for these calculations were those obtained at 0 V because we have confirmed that the effect of the electric field on the geometry is negligible within this range.

I/V profiles have been obtained with (eq 3). As previously discussed, we have replaced the total energy difference by the deformation energy in the calculation of the current intensity. These deformation energies (eq 4) together with the perturbation terms up to second-order correction (eq 5) are calculated using an own Fortran code, which reads one-electron integral information from the Gaussian09 output files.
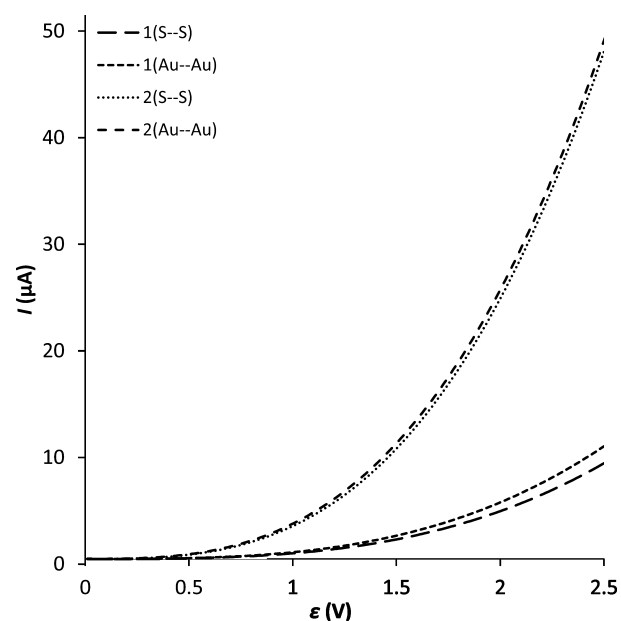
The electron polarization was analyzed with the help of the electron deformation densities, which are defined as the difference between the electron densities computed with and without the external electric perturbation. Furthermore, in connection with the band model of conductivity, we have delved into the part of the electron deformation density associated with an effective electron transfer from occupied to virtual orbitals. To do so, we have employed EDOs, which are obtained by diagonalization of the deformation density matrix. The EDOs pair off, displaying the same eigenvalue but opposite sign. Each pair represents an amount of accumulation/depletion of electron charge at different molecular regions. For more details about this procedure, see ref 59 and references therein. Deformation densities were plotted with the help of the graphical interface program Gaussview.[61]
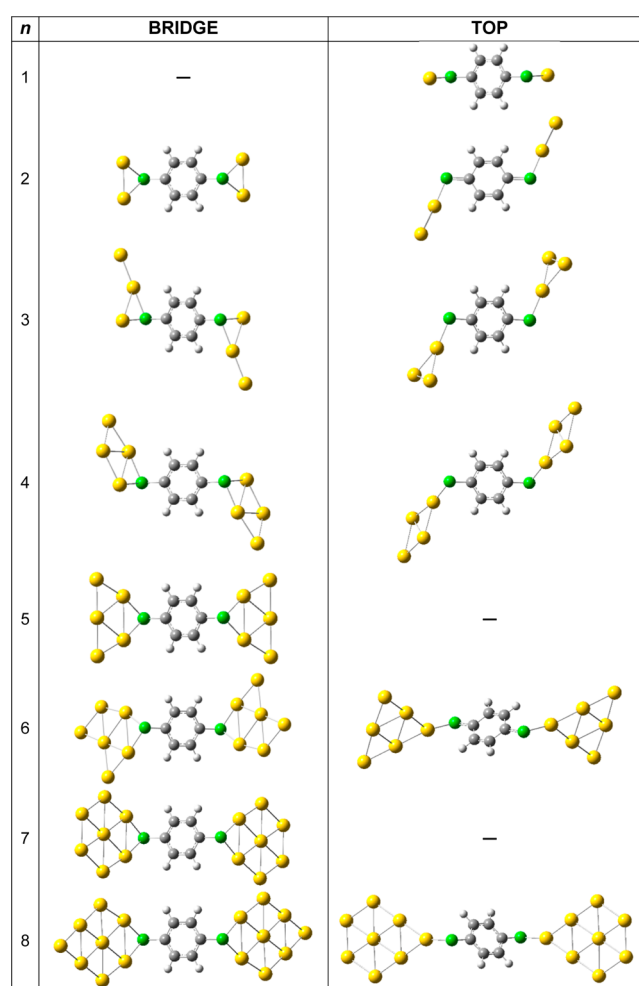
■ RESULTS AND DISCUSSION

One of the main problems to tackle when theoretical methods are applied for the calculations of the conductance in benzene-1,4-dithiolate molecule is the lack of experimental information about the type of molecule−electrode junction and about the
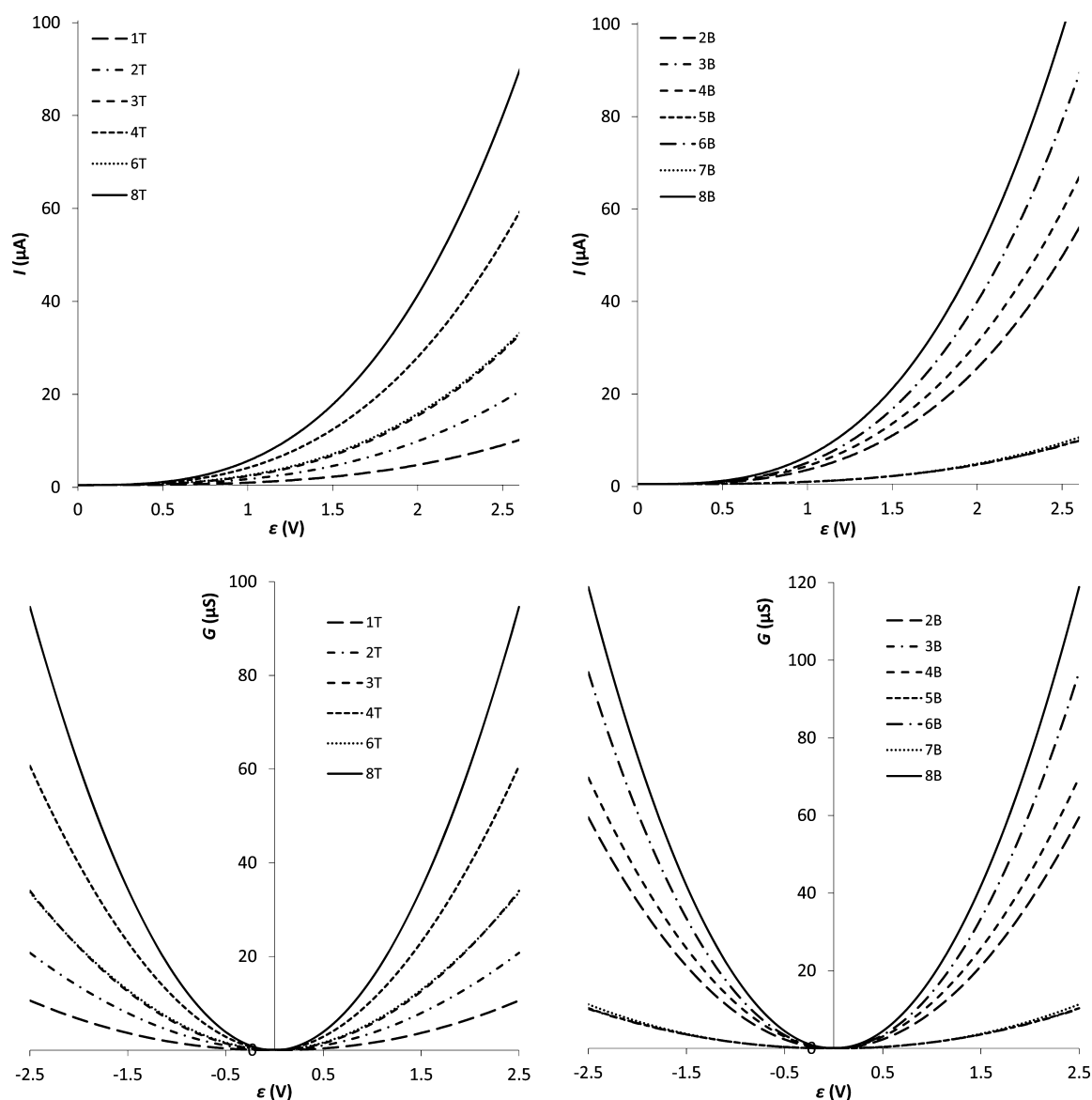

Figure 2. I/V profiles at different field directions for Au-S-(p-C$_6$H$_4$)−S-Au and (Au)$_2$-S-(p-C$_6$H$_4$)-S-(Au)$_2$.

Figure 3. Optimized structures for "top" (right) and "bridge" (left) conformations.

Figure 1. Optimized structures Au-S-(p-C$_6$H$_4$)-S-Au and (Au)$_2$-S-(p-C$_6$H$_4$)-S-(Au)$_2$ upon the electric perturbation at different field directions (parallel to the imaginary lines that connect S⋯S atoms and Au⋯Au atoms).

Figure 4. I/V and G/V profiles obtained for "top" (left) and "bridge" (right) conformations.

orientation of the molecule. The possibilities of adsorption sites of the benzene-1,4-dithiolate on gold surfaces include on-top, bridge, and hollow sites. The most accepted binding sites for Au (111) surfaces are the benzene-1,4-dithiolate directly bonded to one or two gold atoms. Both possibilities were taken into account by Seminario et al, who extended the number of gold atoms at the contacts assuming these binding situations. Even though they concluded that on-top sites are better conductors than the bridge sites, the I/V profiles obtained for bridge sites fitted better with the experiment results. For the sake of comparison, we have also considered both binding situations in our work. Hollow sites were also initially considered; however, all geometries tended toward bridge orientation in the optimization calculations.

As in Seminario's work, we have also determined the current−voltage characteristics of benzene rings connected via thiols to gold electrodes $(Au)_n$-S-$(p$-C$_6$H$_4)$-S-$(Au)_n$ $(1 \leq n \leq 8)$. As an initial step, we have studied the electric response of the system considering only the gold atoms in direct contact with the molecule. In addition, we have changed the electric field orientation to evaluate its effect on the I/V profiles, a point

that was not clear in the original work of Ortiz and Seminario. Thus, Figure 1 shows the optimized structures upon the electric perturbation at different field directions (parallel to the imaginary lines that connect S⋯S atoms or Au⋯Au atoms).

The profiles shown in Figure 2 demonstrate that electric field orientation is a minor effect, especially in the case of "bridge" conformation. Therefore, the results provided by this approach do not depend much on how the electric field direction is defined in the calculations. Thus, considering that our purpose is to investigate the electron transport through the single molecule, the most suitable direction is that with the electric field orientation parallel to the imaginary S⋯S line.

All optimized structures are shown in Figure 3. Besides the studied structures in Ortiz and Seminario's work, we have considered some additional structures that were missing in their previous work. In doing so, we have included all structures from one to eight gold atoms per contact for both "top" and "bridge" conformations. However, the "top" conformations with five and seven gold atoms were not characterized as energy minima and were omitted in the subsequent calculations, in contrast with bridge conformations, where all the structures were confirmed
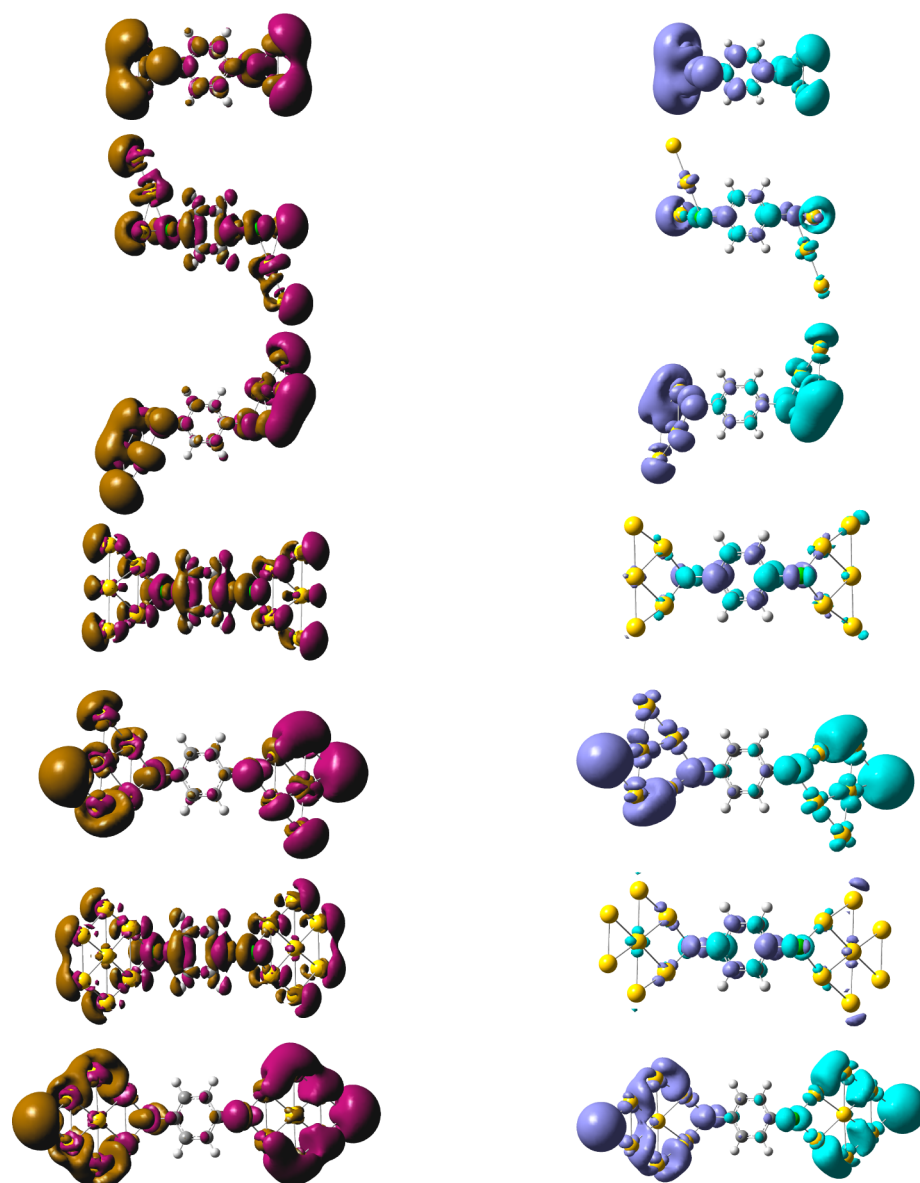
Figure 5. Representation of the total electron deformation density (left side) and the electron density of the main pair of EDOs (right side) induced by an external potential of 2.5 V for the "bridge" conformations. Isosurface value corresponds to 4×10^{-4} au. Positive density (negative charge) is represented by magenta (left side) and lilac (right side) colors, whereas negative density (positive charge) is represented by light-brown (left side) and light-blue (right side) colors.

to be energy minima. Furthermore, electronic structure calculations evidenced a greater stability of "bridge" conformations.

The I/V and G/V profiles obtained for both conformations are shown in Figure 4. In "bridge" conformation, one can clearly distinguish two different behaviors. Thus, the current intensity is significantly larger when the contact is built with an even number of gold atoms and increases proportionally with the number of atoms. These intensities are also larger than their corresponding "top" counterparts. On the contrary, for an odd number of gold atoms, the intensity is quite similar among all "bridge" conformations and smaller than their corresponding "top". It is worth remarking that such distinction between "odd" and "even" structures cannot be applied to the "top" conformations, where the current intensity increases proportionally with the number of atoms with the exception of the structure with four gold atoms. This structure deviates from the

general trend, showing an exceptionally high conductance similar to that of the corresponding "bridge" conformation.

In view of the results previously expounded, we can conclude that "bridge" conformations are more stable and better conductors than the corresponding "top". Therefore, we have focused the study of the electron deformation density and the EDOs on the "bridge" structures. This may serve to reinforce the results obtained for the I/V and G/V profiles with a completely different tool grounded on the band model of conductivity.

The total electron deformation densities and those corresponding to the main EDOs are represented in Figure 5 for the "bridge" conformations. These plots represent the electron polarization induced by an external electric voltage of 2.5 V applied between the electrodes. The electron deformation density (left side of Figure 5) clearly reflects the differences between "even" and "odd" structures. Thus, the electron
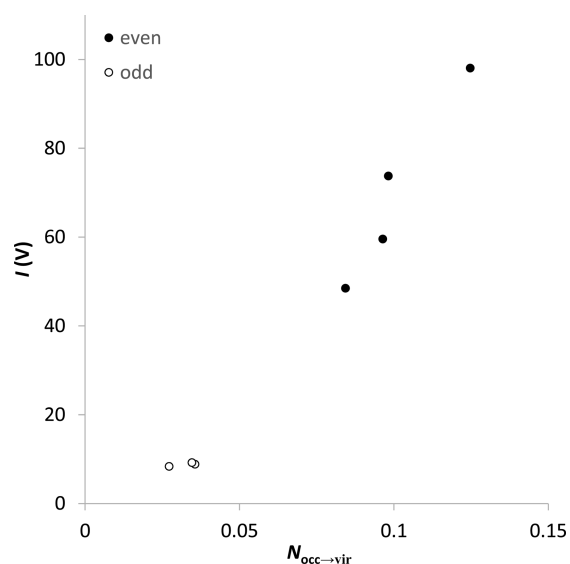
Figure 6. Current intensity, I, versus the occupied-virtual electron transfer, $N_{occ \rightarrow vir}$, for the "bridge" conformations.

Table 1. Six-Center Delocalization Indices Calculated for the "Bridge" Conformations upon External Voltages of 0 and 2.5 V

	6-DI		
number of gold atoms per contact	0 V	2.5 V	diff
2	0.0227	0.0236	0.0009
3	0.0375	0.0364	−0.0011
4	0.0277	0.0283	0.0006
5	0.0392	0.0383	−0.0008
6	0.0329	0.0326	0.0003
7	0.0385	0.0376	−0.0009
8	0.0344	0.0347	0.0003

through the molecule in "even" structures. It is also more evident looking at the EDOs that in the "odd" structures the deformation density is accumulated at the benzene rings.

Another magnitude that can be calculated from the EDOs is the electron population transferred from occupied to virtual orbitals. This magnitude gives us an idea of the overlapping between these two bands induced by the external voltage, which is expected to be significant in good conductors. According to our results, this occupied-virtual electron transfer is about three or four times larger in "even" structures than in "odd" structures. Moreover, as reflected in Figure 6, there exists a quite good correlation between the intensity current and the electron transfer. This good correspondence is in line with the results obtained in ref 59 for oligophenyl chains.

Finally, we have also investigated the role played by the benzene ring aromaticity in the electric conductance of the different structures. The effect of the aromaticity on the electric conductance of oligophenyl chains was previously analyzed theoretically by our group,[54] concluding that disruption of aromaticity provoked by the external voltage decreases the electric conductance, whereas enhancement of the aromatic character increases it. Very recently, experimental determinations of the electric conductance in single molecules containing five-membered aromatic rings confirmed that the more aromatic the ring is, the worse conductor the molecule is.[22] To measure the aromaticity of the benzene rings at different external voltages, we have calculated the six-center delocalization indices. The results obtained at 0 and 2.5 V are collected in Table 1 and reflect a slight increase in aromaticity under the external voltage in "even" structures and a decrease in the "odd" ones. According to ref 54, increase in the aromatic stabilization of the benzene ring upon the external voltage may favor the electron transfer through the benzene-1,4-dithiolate; the contrary should happen for a decrease in aromaticity. Moreover, the six-center delocalization indices and then the aromaticity at 0 V are significantly larger for the "even" structures than for the "odd" ones. This result is also supported by the experimental work published in ref 22.

■ CONCLUSIONS

In this work, we have revisited the application of the uncertainty relation to the determination of I/V profiles in single molecular conductors. A new expression of the electric current is proposed where the total energy variation in the original expression is replaced by the deformation energy and the charge is taken as the total electron charge transferred between the electrodes under the action of an external electric voltage.

For the sake of comparison with previous works, the new expression has been applied on the benzene-1,4-dithiolate molecule attached to gold clusters containing from one to eight atoms. The electric voltage was modulated from 0 to 2.5 V. We have considered in this work two kinds of molecule−electrode contacts, "top" and "bridge". The most stable and most conducting structures were found to be those established through bridge contacts. Significant differences were found between those structures formed with an even and an odd number of gold atoms. Whereas in "even" structures the electric conductance increases with the gold cluster size, in "odd" structures, the conductance is smaller and does not change significantly.

Determination of the total electron polarization and analysis of properties derived from EDOs support the results obtained

deformation plots for "even" structures show an effective electron transfer between the electrodes with opposite charges concentrated at the electrode-contact regions. On the contrary, "odd" structures display a remarked electron polarization within the benzene ring, which opposes the external voltage and hinders the electron transfer. Moreover, it is noticeable how the residual small polarization at the benzene rings existing in "even" structures decreases with the number of gold atoms. This can explain the trends followed by the current intensity in terms of the resistance to the electron transport exerted by the benzene ring. A similar behavior was found in the oligophenyl chains investigated in ref 54, which differed in the type of contact with gold. In that case, differences were qualitatively explained in terms of the number of Kekule polarized valence bond structures and confirmed by measures of ring electron delocalization. Similar measures of the benzene ring electron delocalization have been determined for benzene-1,4-dithiolate in this work and will be discussed at the end of this section.

Furthermore, the electron densities of the main pair of EDOs are shown at the right side of Figure 5. These plots represent the sum of the electron density deformation given by the eigenvectors with the largest positive/negative eigenvalue pair (with the largest occupation). The main EDOs support the conclusions extracted from the total electron density deformation plots and highlight the accumulation of opposite charge at the electrodes representing the electron transfer

and conclusion achieved with the I/V profiles. Moreover, aromaticity measures indicate that the electric conductance decreases with the benzene ring aromaticity. Also, the "even" structures present an increase in the aromaticity when the external voltage is applied, contrary to that found in "odd" structures. These results are in agreement with recently published theoretical and experimental results.[22,54]

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Notes
The authors declare no competing financial interest.

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