

Transport properties of molecular junctions from many-body perturbation theoryT. Rangel,^{1,2} A. Ferretti,^{1,3,4} P. E. Trevisanutto,^{1,5,6} V. Olevano,^{1,6} and G.-M. Rignanesi^{1,2}¹*European Theoretical Spectroscopy Facility (ETSF)*²*Institute of Condensed Matter and Nanosciences (IMCN), Université Catholique de Louvain, Place Croix du Sud 1 bte 3, BE-1348 Louvain-la Neuve Belgium*³*Department of Materials, University of Oxford, Oxford, United Kingdom*⁴*CNR-INFM S3 and Dipartimento di Fisica, Università di Modena e Reggio Emilia, Modena, Italy*⁵*Max-Planck Institut für Mikrostrukturphysik, Halle/Saale, Germany*⁶*Institut Néel, CNRS and UJF, Grenoble, France*

(Received 9 February 2011; revised manuscript received 26 May 2011; published 13 July 2011)

The conductance of single molecule junctions is calculated using a Landauer approach combined with many-body perturbation theory to account for electron correlation. Contrary to intuition, a mere correction of the density-functional theory eigenvalues is found *not to affect* noticeably the zero-bias conductance. To improve the agreement with experiments, it is necessary to go beyond this standard procedure by also updating the wave functions. This leads to both the reduction of the molecular character and the increase of the $e_g(d_{z^2})$ character on gold atoms around the Fermi energy.

DOI: [10.1103/PhysRevB.84.045426](https://doi.org/10.1103/PhysRevB.84.045426)

PACS number(s): 85.65.+h, 71.10.-w, 72.10.-d, 73.40.-c

I. INTRODUCTION

Most recent theoretical studies of coherent transport in nanojunctions are based on a Landauer approach¹ in which the electron interactions are treated at a simplified mean-field level using density-functional theory (DFT). While this approach has proven quite successful for systems having a strong coupling between the molecule and the metallic leads,^{2,3} it overestimates the zero-bias conductance of weakly coupled systems compared to experimental measurements.⁴⁻⁶ Many explanations have been proposed for such a discrepancy. For example, arguing an uncertainty over the experimental junction structure, the sensitiveness to the contact geometry was investigated.^{7,8}

More fundamentally, it has been found that the zero-bias conductances may vary by several orders of magnitude when using different exchange-correlation (XC) energy functionals.^{9,10} Moreover, the DFT lack of derivative discontinuity was shown to be a source of significant errors in weakly coupled systems.¹¹ In fact, the validity of using DFT to treat electron interactions in the Landauer formalism has also been questioned.¹² It is believed that a many-body theory should be better suited.¹³ Indeed, the DFT eigenstates do not have a formal direct connection to the quasiparticle (QP) states.

Recently, many-body perturbation theory (MBPT) calculations¹⁴ have been used in combination with the Landauer formalism to study the conductance of a simple gold monoatomic chain.¹⁵ The applicability of this method to more complex systems, such as realistic three dimensional junctions, is extremely difficult and hence very limited especially when using plane-waves. Therefore, a simpler approach relying on a model self-energy,^{5,16,17} based on projectors onto molecular orbitals, has been applied to molecular junctions with some success. Nevertheless, a formal justification of this model is still lacking.

In this work, the effect of electron-electron interactions on the zero-bias conductance is investigated for the benzene diamine (BDA) and benzene dithiol (BDT) molecules attached to gold electrodes. The QP electronic structure, calculated

using different approximations for the MBPT self-energy, is used in the Landauer formalism. It is found that correcting only the eigenenergies has no or little effect on the conductance. To improve the agreement with the experiment, it is thus crucial to update also the wave functions by taking into account the off-diagonal self-energy matrix elements. A comparison of the original and the updated LDOS at the Fermi level shows that both the molecule and the gold regions are affected. In particular, it is found that the change of the zero-bias conductance is triggered by a decrease of the molecular character and an increase of the $e_g(d_{z^2})$ character of the wave functions on the gold atoms. Finally, our results are compared to those provided by the molecular-projectors model proposed in Refs. 5 and 16.

The paper is organized as follows. Section II is devoted to the presentation of the technical details of the calculations. In Sec. III, the different methods used in this work are introduced and commented. Our results are discussed in Sec. IV. Finally, some conclusions are drawn and possible perspectives are indicated.

II. TECHNICAL DETAILS

The DFT and MBPT calculations are performed using the ABINIT package.¹⁸ The XC energy is approximated by the Perdew-Burke-Ernzerhof functional.¹⁹ Norm-conserving pseudopotentials²⁰ are used. For gold, these include the 5s and 5p semicore states, which are crucial for the MBPT calculations.²¹ The wave functions are expanded on a plane-wave basis set up to kinetic energy cutoff of 30 Ha. The corresponding maximally localized Wannier functions (MLWFs)²² are obtained following the procedure of Ref. 23. These are used in the transport calculations, which are performed with the WANT package.²⁴

Two systems are considered: BDA and BDT attached to gold electrodes.²⁵ For the atomic relaxation, a 2×2 surface cell is adopted for the Au (111) surface with seven atomic layers in the electrodes. The relaxed geometries agree with previous theoretical predictions.^{8,16,26} For the MBPT

calculations, three gold layers are removed. This guarantees an affordable computational cost without compromising the calculated conductance²⁷ despite the rather packed geometry (with ~ 3.1 Å between the repeated images of the molecules). All the parameters of the calculations are converged to ensure an error smaller than $0.001 \mathcal{G}_0$ on the zero-bias conductance $\mathcal{G}(E = 0)$. Hence, a $8 \times 8 \times 3$ grid of \mathbf{k} points is adopted to sample the Brillouin zone. The QP corrections are calculated explicitly for 210 bands at 96 irreducible \mathbf{k} -points including ~ 300 bands in the calculations.

III. METHODOLOGY

For the MBPT calculations, the GW approximation is adopted for the self-energy Σ , neglecting vertex corrections.¹⁴ In principle, Σ is a nonhermitean, nonlocal and frequency-dependent operator. The nonhermitian part of Σ is ignored, assuming infinite QP lifetimes, while the nonlocality is fully taken into account. Different flavors are then considered for the GW self-energy. In the standard single-shot G_0W_0 approach, the self-energy is approximated using the DFT electronic structure, and the QP corrections to the DFT eigenvalues are determined using first-order perturbation theory considering only the diagonal elements of Σ in the space of the DFT orbitals ϕ_i^{sys} of the contact-molecule system. The frequency dependence is obtained using a plasmon pole model.²⁸ In order to calculate the first-order correction to the DFT wave functions, the off-diagonal elements of Σ would also be needed. Currently, such calculations are out of reach for the systems considered here. Nevertheless, a full diagonalization can be performed if a further simplified self-energy is considered. For this purpose, the Coulomb-hole screened-exchange (CHSX) approach,²⁹ which is a static approximation to the GW self-energy, is adopted here. For the sake of comparison, both the full ($\overline{\text{CHSX}}$) and diagonal (CHSX) forms of this self-energy are considered. Finally, the molecular-projectors model (MPM) proposed in Refs. 5 and 16 is also used for the self-energy:

$$\Sigma = \sum_m \text{sgn}(E_m^{\text{mol}} - E_F) \Delta |\phi_m^{\text{mol}}\rangle \langle \phi_m^{\text{mol}}|, \quad (1)$$

where m runs over the DFT orbitals of the isolated molecule (E_m^{mol} and ϕ_m^{mol} being the corresponding wave functions and energies, respectively), E_F is the Fermi energy, and Δ is the scissor-operator shift to be applied. Its value is obtained in a two-step procedure. First, the correction to the DFT HOMO-LUMO gap of the molecule in the gas phase is computed either from a delta self-consistent field calculation or, more simply, by matching the experimental value. Second, the presence of the metallic surface is taken into account through a classical image-charge model leading to a reduction of Δ compared to the gas phase, as calculated using the G_0W_0 approximation.^{30,31} This self-energy operator is nondiagonal in the space of the DFT orbitals ϕ_i^{sys} . Its diagonal form (MPM) is also considered.

IV. RESULTS AND DISCUSSION

The values of the zero-bias conductance $\mathcal{G}(E = 0)$ calculated with these different approaches are reported in Table I for

TABLE I. Zero-bias conductance $\mathcal{G}(E = 0)$ in \mathcal{G}_0 units calculated with different approaches (see text) for the two systems.

	DFT	G_0W_0	CHSX	$\overline{\text{CHSX}}$	MPM	$\overline{\text{MPM}}$	Expt.
BDA	0.018	0.019	0.019	0.013	0.017	0.004	0.006 ^a
BDT	0.034	0.036	0.037	0.020	0.027	0.004	0.011 ^b

^aRefs. 5 and 32.

^bRefs. 33 and 34.

BDA and BDT. For the latter, the complete energy dependence of the conductance $\mathcal{G}(E)$ is also given in Fig. 1. The DFT results are in good agreement with previous calculations.^{4–6,8,26} Quite surprisingly, the G_0W_0 results for $\mathcal{G}(E = 0)$ are almost identical to the DFT ones despite the changes in the curve $\mathcal{G}(E)$.

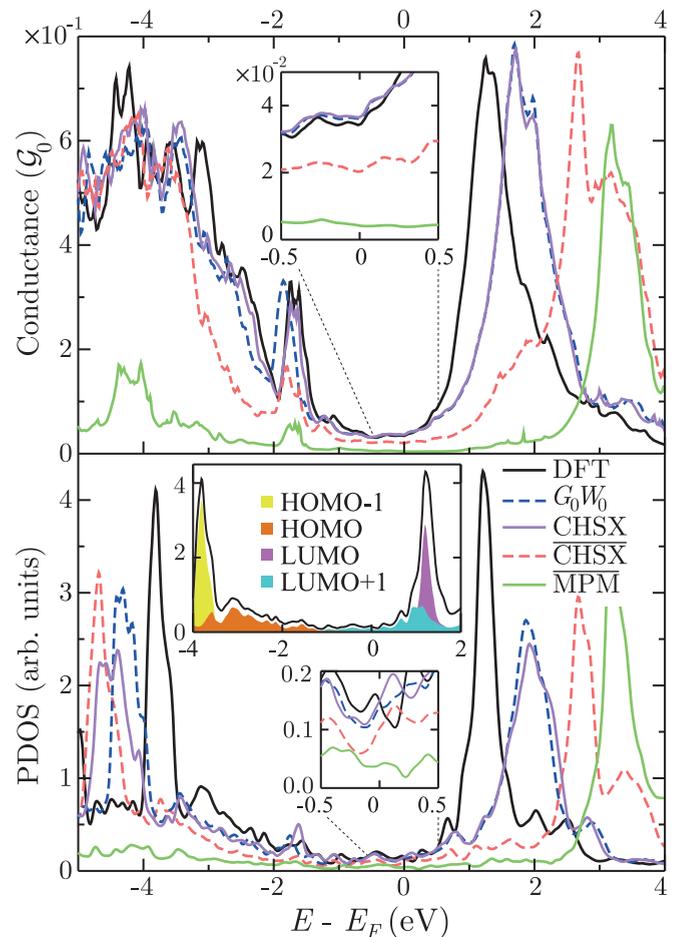


FIG. 1. (Color online) Conductance (top) and PDOS on the molecule (bottom) as a function of the energy (the Fermi energy E_F is set to zero) for the BDT junction. Different approaches are considered: DFT (solid black), G_0W_0 [dashed black (blue)], CHSX [solid gray (purple)], $\overline{\text{CHSX}}$ [dashed gray (red)], and $\overline{\text{MPM}}$ [solid light gray (green)]. For each panel, an inset provides a zoom around E_F . In the bottom panel, a second inset shows the total PDOS on the molecule computed in DFT (black line), and the corresponding contributions of the HOMO-1 [in very light gray (yellow)], the HOMO [in dark gray (orange)], the LUMO [in medium gray (purple)], and the LUMO+1 [in light gray (cyan)].

In order to understand this finding, the projected density of states (PDOS) on the molecule is computed as reported in the bottom panel of Fig. 1 for BDT. In particular, an inset shows a decomposition of the total PDOS on the molecule calculated within DFT in terms of the contributions of the different molecular orbitals close to the Fermi level. The HOMO-1 and LUMO (in yellow and purple [very light and medium gray], respectively) lead to very sharp peaks in the PDOS. In fact, these states are very localized on the molecule and present very little hybridization with the leads. Hence, they do not play an important role on $\mathcal{G}(E = 0)$. The latter is thus mainly driven by the HOMO and LUMO+1 (in orange and cyan [dark and light gray], respectively) in agreement with the findings of Ref. 26.

As expected, the G_0W_0 corrections to the DFT eigenvalues open the gap between the occupied and unoccupied molecular-like levels, as can be seen by the displacement of the peaks in the PDOS (bottom panel) and in the conductance (top panel) in Fig. 1. But, contrary to intuition, this opening of the gap does not lead to a reduction of $\mathcal{G}(E = 0)$. In fact, the QP corrections depend on the weights of the different states of the system on the molecular orbitals, $w_i = |\langle \phi_i^{\text{sys}} | \phi_m^{\text{mol}} \rangle|^2$, and hence on the DFT wavefunctions. In particular, these weights are quite small around the Fermi level for the very hybridized HOMO and LUMO+1, which drive the zero-bias conductance. Hence, if the DFT wavefunctions are not updated, the resulting G_0W_0 zero-bias conductance will be very close to the DFT one. In contrast, the values of w_i are higher for the more localized LUMO and HOMO-1, which influence the conductance at larger biases. Thus the effect of the QP corrections on the energies is mostly visible for $\mathcal{G}(E \neq 0)$. Similar results are observed for BDA.

As a confirmation, the CHSX approximation also does not modify $\mathcal{G}(E = 0)$ despite the fact that it usually leads to bigger gaps than those obtained with the G_0W_0 approach. This points to the importance of the quality of the wavefunctions around E_F .

When updating not only the eigenenergies but also the wave functions by the $\overline{\text{CHSX}}$ approximation, $\mathcal{G}(E = 0)$ is reduced by a factor 1.4 (1.7) in the direction of the experimental value reaching 0.013 (0.020) \mathcal{G}_0 for BDA (BDT). The agreement with experiments would probably be further improved if one could afford to perform calculations with (i) more realistic geometries, such as those depicted in Ref. 5, and (ii) a higher number of gold layers entering the Landauer formula. Furthermore, the results depend somehow on the flavor of the GW self-energy and on the degree of self-consistency adopted, as very recently observed in Ref. 35. In that work, both self-consistent \overline{GW} and non-self consistent $\overline{G_0W_0}$ (including off-diagonal elements for the self-energy) calculations have been performed also on the BDA and BDT junctions. A direct comparison with our results is not straightforward since the packing regimes, contact geometries, and methodologies used in both studies are slightly different.³⁶ The most meaningful comparison is between their $\overline{G_0W_0}$ results and our findings for $\overline{\text{CHSX}}$. It turns out that they observe a reduction of the conductance by a factor 2.6 (3.4) for BDA (BDT) with respect to DFT, while the reduction is 1.4 (1.7) in our case.

The PDOS on the molecule (Fig. 1) shows that $\overline{\text{CHSX}}$ corrections contribute to further separate the unoccupied and

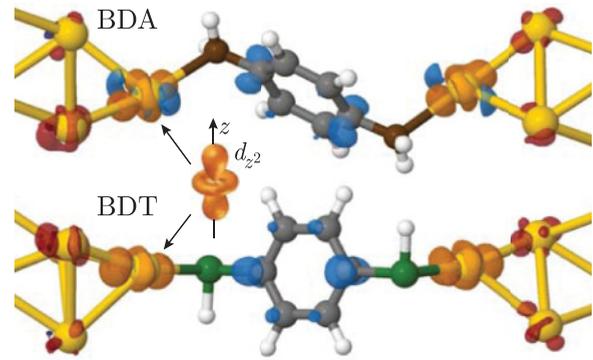


FIG. 2. (Color online) Difference between the $\overline{\text{CHSX}}$ and CHSX LDOS calculated in an energy window of 0.8 eV around E_F for BDA (top) and BDT (bottom). Four isovalues are shown: $+4\rho$ in light gray (orange), $+1\rho$ in dark gray (dark red), -1ρ in black (dark blue), and -4ρ in medium gray (light blue) with $\rho = 4 \times 10^{-4}$ (6×10^{-4}) $e^-/\text{\AA}^3$ in BDA (BDT). The Au, C, N, S, and H atoms are represented by light gray, medium gray, black, dark grey, and white (yellow, gray, brown, green, and white) spheres, respectively.

occupied molecular-like orbitals. Since the eigenenergies are only affected at the second order compared to CHSX, this increased opening of the gap is to be attributed to modifications of the metal-molecule hybridizations. To gain more insight on the changes of the wave functions, the LDOS is computed in an energy window of 0.8 eV around the Fermi level E_F :

$$\text{LDOS}(\mathbf{r}) = \int_{E_F-0.4\text{eV}}^{E_F+0.4\text{eV}} \sum_i |\phi_i^{\text{sys}}(\mathbf{r})|^2 \delta(E - E_i) dE. \quad (2)$$

The effect of the off-diagonal elements of Σ can be analyzed by plotting the difference between the $\overline{\text{CHSX}}$ and CHSX LDOS, as shown in Fig. 2. Two main changes can be identified. First, the molecular character is reduced (see the p -like blue lobes on the carbon atoms). Second, the d_{z^2} character increases on gold atoms (see the typical torus with pear-shaped lobes in orange on the gold add-atoms³⁷). Since the net spatial charge transfer from the molecule to the gold leads is negligible (less than $0.02e^-$), the effect of the off-diagonal elements of Σ is to be interpreted as a transfer in energy. The molecular orbitals are shifted away from E_F (see the PDOS in Fig. 1), while gold orbitals with d_{z^2} character are transferred from lower energies to the E_F region.

Finally, the self-energy is also modeled by the $\overline{\text{MPM}}$,^{5,16} which includes off-diagonal elements, using $\Delta = 2$ eV. The $\overline{\text{MPM}}$ leads to an effective opening of the gap between the unoccupied and occupied molecular-like orbitals, which is much bigger (~ 4 eV) than the one obtained with the $\overline{\text{CHSX}}$ approximation (~ 2 eV). As a result, the $\overline{\text{MPM}}$ conductance is much lower than in any of the fully *ab initio* approaches. This discrepancy can be attributed to some limitations in both the fully *ab initio* calculations and the model ones. On the one hand, the use of highly packed geometries considerably increases the screening and reduces the size of the corrections obtained within the fully *ab initio* calculations. Nevertheless, the use of the $\overline{\text{CHSX}}$ approximation, which is known to overestimate the experimental gaps, may partially compensate this reduction. On the other hand, three main drawbacks can be pointed out for the model calculations: (i) the classical

image-charge model is not always appropriate in predicting the individual shifts,³¹ (ii) many-body effects on the gold region are not negligible as observed in our $\overline{\text{CHSX}}$ calculations, and (iii) the molecular projectors might not be sufficient to describe the changes of the wave functions on the molecule.

V. CONCLUSIONS

In summary, we have demonstrated that a self-energy operator leading to the mere correction of the eigenenergies (such as the diagonal G_0W_0 or CHSX approximations) is not enough to change the initial DFT zero-bias conductance despite the opening of the gap that it induces between the occupied and unoccupied molecular-like levels. In contrast, when updating also the wave functions within the $\overline{\text{CHSX}}$ approximation, the conductance is reduced, improving the agreement with the experiment. This conductance change can be attributed to both the reduction of the molecular character and the increase of the d_{z^2} gold character. Finally, when using

the MPM approach, the conductance is sensibly lower than in any of our *ab initio* calculations (whose accuracy is only limited by the available computational time). This might be due to an overestimation of the scissor-operator shift Δ but, more importantly, our results point out the role of the wave-function changes on both the gold atoms and the molecule. The model might thus be improved by including a proper treatment of the gold/molecule interface, providing a good compromise between accuracy and speed of the calculations.

ACKNOWLEDGMENTS

This work was supported by the EU FP7 through the ETSF I3 e-Infrastructure (Agreement 211956) and the project FRFC No. 2.4502.05. T.R. and G.M.R. are grateful to the French Community of Belgium for funding via the Concerted Research Action ARC NANHYMO (Convention 07/12-003). A.F. thanks Italian MIUR for support through Grant "EC_SPECTRA" PRFR08F0AL_001.

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³⁶Regarding the packing regimes, our plane-wave calculations only allow us to use a 2×2 surface unit cell while it is a 4×4 cell in Ref. 35. Regarding the contact geometries, in the present work, the attachment of the molecule to the leads is modeled by an add-atom connected to a flat surface, whereas pyramid-like tips are adopted in Ref. 35. Regarding the methodologies, both the self-energy and the polarizability extend over the whole junction (molecule and

leads) in our calculations, while they are limited to the molecule and a few atoms of the leads in Ref. 35. Finally, our wave functions are expanded on a plane-wave basis-set, while a localized basis-set is used in Ref. 35.

³⁷For the gold add-atoms, the z direction of the $e_g(d_{z^2})$ orbital (see inset in Fig. 2) is oriented along the Au-N bonding direction. For the gold atoms of the following layers, the z direction changes though; it is still conditioned by the Au-N direction.