Symmetry-induced quantum interference effects in metalloporphyrin wires

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Abstract

We calculate the electronic and transport properties of a series of metalloporphyrin molecules sandwiched between gold electrodes using a combination of density functional theory and scattering theory. The impact of strong correlations at the central metallic atom is gauged by comparing our results obtained using conventional DFT and DFT + U approaches. The zero- and finite-bias transport properties may or may not show spin-filtering behavior, depending on the nature of the d state closest to the Fermi energy. The type of d state depends on the metallic atom and gives rise to interference effects that produce different Fano features. The inclusion of the U term opens a gap between the d states and changes the conductance and spin-filtering behavior qualitatively in some of the molecules. We explain the origin of the quantum interference effects found as due to the symmetry-dependent coupling between the d states and other molecular orbitals and propose the use of these systems as nanoscale chemical sensors. We also demonstrate that an adequate treatment of strong correlations is really necessary to correctly describe the transport properties of metalloporphyrins and similar molecular magnets.

(Some figures may appear in colour only in the online journal)

1. Introduction

A key issue in the field of molecular electronics is the search for molecular compounds that give rise to new or improved functionalities. Compounds that include quantum interference (QI) effects [1] are specially appealing due to the large variation of conductance that such phenomena generate [2]. Porphyrin molecules constitute in this respect promising candidates due to the presence of Fano-like [3] resonances that can greatly affect their transport properties, and are as such receiving increasing attention. These molecules play an essential role in many biological processes such as electron transfer, oxygen transport, photosynthetic processes and catalytic substrate oxidation [4]. Porphyrins have been extensively studied in the past by biologists and chemists [5–8]. However, an increasing number of theoretical [3, 9–11] and experimental [12, 13] physics studies have appeared in the past few years. Progress in the design of supramolecular structures involving porphyrin molecules has also been rather spectacular [14].

Porphyrins are cyclic conjugate molecules. Their parent form is the porphin, which is made of four pyrrole groups joined by carbon bridges and has a nearly planar D4h symmetry [15]. The alternating single and double bonds in its structure, make this molecule chemically very stable. In addition, the macrocycle can accommodate inside a metallic atom, such as Fe (which is the base of the hemoglobin in mammals), Cu (hemolymph in invertebrates), Mg (chlorophyll in plants), etc, which gives rise to metalloporphyrins. Large porphyrin systems can undergo certain ruffling distortions because of its peripheral ligands, its metallic atom inside or the environment [16]. It is precisely the large number of possible configurations, which give rise to a wide variety of interesting properties that make these molecules very attractive for molecular-scale technological applications.
Figure 1. Schematic view of a Fe-porphyrin molecule between gold leads. Yellow, dark yellow, gray, black, blue, and magenta represent gold, sulfur, hydrogen, carbon, nitrogen and iron, respectively.

From the electronic point of view, metalloporphyrins have frontier states (HOMO, LUMO) that extend across the whole molecule, owing to their conjugate character. The inclusion of metallic atoms with d states that couple to such frontier states can give rise to quantum interference effects due to the presence of an additional path through the metallic center [3]. It is not clear however how this additional path affects the electronic structure and generates different transport resonances for different metallic atoms. The combination of extended frontier orbitals and localized spin-polarized d states makes these systems promising for the exploitation of quantum properties in nanoelectronics, since large changes in the conductance are expected when spin-polarized d-generated resonances cross the Fermi level due to e.g. the influence of gate potentials or the attachment to the metallic center of other atoms or molecules.

In this work, we present a simple model that can describe an array of Fano-like quantum interference effects in molecular electronics systems. In such a model an isolated molecular orbital can be coupled differently to the leads and to other molecular orbitals, which may result in different features in the transmission. We apply this model to metalloporphyrin systems, where we find an excellent agreement with ab-initio results based on density functional theory (DFT) [17]. The systems under study are made of metalloporphyrins with different metallic atoms sandwiched between gold electrodes. The porphyrin molecule is attached to the gold surface by a thiol group and oriented perpendicular to it, as sketched in figure 1. The metallic atom placed inside can be Fe, Co, Ni, Cu and Zn, so that the metalloporphyrins are denoted FeP, CoP, NiP, CuP and ZnP, respectively. For the sake of comparison, we have also studied the porphin compound, which has no metallic atom. Since DFT fails to describe correctly transition metal (TM) elements in correlated configurations, we have also adopted a DFT + U approach. We show that the inclusion of strong correlations, necessary to accurately characterize compounds with TM, does not destroy completely the features of the transmission found with DFT.

The outline of the article is as follows: in section 2 we show the simple model that we use to understand the origin of the interference effects and the evolution of the conductance as a function of the position of the d levels of the metallic atom. Then we turn to our DFT calculations. In section 3 we describe our DFT methodology and provide a short description of our DFT + U approach. We then go on to describe in section 4 the most relevant bits of the electronic structure on the molecules contacted with gold metal electrodes. In section 5 we present and discuss the transport properties of the junctions obtained from first principles. The conclusions are written in section 6. Finally, more extended descriptions of the DFT + U approach and the electronic structure of metalloporphyrins in the gas phase are relegated to the appendices.

2. Simple model for Fano-like quantum interference in molecule electronic systems

We first introduce a simple model that describes quantum interference effects arising from Fano resonances [18, 19] in single-molecule junctions, where a metallic atom with localized d orbitals resides in the backbone of the molecule. The existence or not of Fano resonances in a given junction can be elucidated by looking at the energy dependence of the transmission coefficient $T(E)$. The hallmark for a Fano resonance is the appearance of a sharp peak followed by a strong dip (or the reverse) in $T(E)$. However, these features might be masked by neighboring Breit–Wigner resonances. Our model can be thought of as the minimal model that describes the masking or smoothing of Fano resonances inside the HOMO–LUMO gap. In this model, the leads are featureless, meaning that they are treated in the wide-band approximation. We then consider only those molecular orbitals in the neighborhood of the Fermi level which have the strongest coupling to the leads. Specifically, the model includes three molecular levels: a $\sigma$ level below the HOMO, one level (S) associated mainly to the linker
atoms (sulfurs) that represents the HOMO and a π level which represents the LUMO. Finally, the model includes a single d orbital with no direct coupling to the electrodes, but coupled instead to either the σ or the π levels, depending on the symmetry of the molecule. The model and its two possible couplings is sketched in figures 2(a) and (b), respectively. The Hamiltonian is diagonal, except for the coupling between the d state and the isolated level. We also choose diagonal and identical 0 matrices, that couple the molecule to the leads:

\[ \hat{H} = \begin{pmatrix} \epsilon_\sigma & t_\sigma & 0 \\ 0 & \epsilon_S & 0 \\ t_\sigma^* & 0 & \epsilon_d \\ 0 & 0 & t_\pi \end{pmatrix}, \]

\[ \hat{\Gamma}_L = \hat{\Gamma}_R = \begin{pmatrix} \Gamma_\sigma & 0 & 0 & 0 \\ 0 & \Gamma_S & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \Gamma_\pi \end{pmatrix}. \]

To facilitate the comparison with the ab-initio results in next sections we have chosen the following values for the on-site energies and the couplings: \( \epsilon_\sigma = -2, \epsilon_S = -1, \epsilon_d = 0, \epsilon_\pi = 0.6, \Gamma_\sigma = 0.04, \Gamma_S = 0.06, \) and \( \Gamma_\pi = 0.06, \) where all energies are measured in eV. For model (a), we choose \( t_\sigma = -0.4 \) and \( t_\pi = 0, \) while for model (b) we choose \( t_\sigma = 0 \) and \( t_\pi = -0.2. \) From the Hamiltonian and the Γ matrices it is easy to calculate the retarded Green’s function and the transmission, which are given by

\[ \hat{G}^R(E) = [E\hat{I} - \hat{H} - i\hat{\Gamma}]^{-1} \]

\[ T(E) = \text{Tr}[\hat{\Gamma}\hat{G}^R(E)\hat{\Gamma}\hat{G}^R(E)]. \]

We show in figure 3 the transmissions obtained for models (a) and (b). The solid lines represents the transmission calculated with the full model. The dashed line in figure 3(a) shows the transmission when the HOMO (S) and π orbitals in model (a) are dropped and only the d and σ orbitals are considered. This is to show that a clear-cut Fano resonance emerges at the d level on-site energy. Such resonance is masked when the HOMO (S) and π orbitals are re-integrated back into the calculation because the additional transmission hides the dip. This leaves what looks at first sight a conventional and very narrow Breit–Wigner resonance. The transmission of the full model in figure 3(b), however, features a clearer Fano resonance. In this case, the dip of the resonance is not washed out, because the transmission of the σ and
HOMO (S) resonances (dashed line) cannot completely mask the drop in transmission at higher energies. Therefore, when a localized d level is present in a molecule and coupled to one molecular orbital, quantum interference may appear in two different ways: like a narrow peak close to the d level on-site energy (a masked Fano resonance) or like a clear Fano resonance (resonance followed by antiresonance, only partially masked by other molecular resonances). Notice that by looking at the parity of the clear Fano resonance (resonance–antiresonance, or vice versa) it is possible to determine to which molecular orbital it is coupled. If the molecular orbital is lower in energy then the antiresonance appears first (see the dashed line in figure 3(a)), whereas if the molecular orbital is higher in energy the resonance comes first.

3. Computational method

We have performed the electronic structure calculations in this article using the DFT code SIESTA [20], which uses norm conserving pseudopotentials and a basis set of pseudoatomic orbitals to span the valence states. For the exchange and correlation potential, we have used both the local density approximation (LDA), as parameterized by Ceperley and Adler [21], and the generalized gradient approximation (GGA), as parameterized by Perdew, Burke and Ernzerhof [22]. SIESTA parameterizes the pseudopotentials according to the Troullier and Martins [23] prescription and factorizes them following Kleinman and Bylander [24]. We have included non-linear core corrections in the transition metal pseudopotentials to correctly take into account the overlap between the valence and the core charges [25]. We have also used small non-linear core corrections in all the other elements to get rid of the small peak in the pseudopotential close to the nucleus when using the GGA approximation.

We have placed explicitly the s and d orbitals of gold as valence orbitals and employed a single-ζ basis (SZ) to describe them. We have used a double-ζ polarized basis (DZP) for all the other elements (H, C, O, N, S and TM). We have computed the density, Hamiltonian, overlap and the matrix elements in a real-space grid defined with an energy cutoff of 400 Ryd. We have used a single k-point when performing the structural relaxations and transport calculations, which is enough to relax the coordinates and correctly compute the transmission around the Fermi level in the case of gold electrodes. We have relaxed the coordinates until all forces were smaller than 0.01 eV Å⁻¹. We have varied the U-parameter and the radii of the U-projectors and compared the results with experiments or previous simulations of the molecules (see below).

Figure 1 shows the central part of the extended molecule in a gold–FeP–gold junction. The gold electrodes have been grown in the (001) direction, which we have taken as the z axis. The sulfur atoms have been contacted to the gold surfaces in the hollow position. We have carried out a study of the most stable position and distance and have found, both in GGA and LDA, that the hollow configuration is more stable than the top and bottom sites, in agreement with previous results obtained for other molecules. The most stable distances are 1.6 Å and 1.8 Å for LDA and GGA, respectively. We have finally chosen a distance of 1.8 Å for all cases in order to make a systematic study of geometrically identical systems.

We have performed the transport calculations using the GOLLUM code, a newly developed and efficient quantum transport code [26]. According to the transport formalism the junctions have been divided in three parts: left and right leads and extended molecule (EM). The EM block includes the central part of the junction (molecule attached to the gold surfaces) and also some layers of the gold leads to make sure that the electronic structure was converged to the bulk electronic structure. The same general parameters as in the bulk simulation (real-space grid, perpendicular k-points, temperature, etc) and also the same parameters for the gold electrodes (bulk coordinates along x and y and basis set) have been used in the transport simulation.

The DFT + U functional can be written as

\[ E_{\text{DFT+U}} = E_{\text{DFT}} + \frac{U_{\text{eff}}}{2} \sum_{m,\sigma} n_{m,\sigma} (1 - n_{m,\sigma}) \]  

where \( U_{\text{eff}} = U - J \), and where the correction term depends on the occupation number matrix. This matrix is not well defined because the total density charge cannot be broken down unambiguously into simple atomic contributions. Therefore, many different definitions of the occupation number matrix may be defined [34]; in our case we have evaluated it by introducing projection operators as follows:

\[ n_{mn}(\sigma) = \sum_{j} q_{j}^{(\sigma)} (\psi_{j}^{(\sigma)}|\hat{P}_{mn}^{(\sigma)}|\psi_{j}^{(\sigma)}) \]  

where \( \psi_{j}^{(\sigma)} \) are the Kohn–Sham eigenvectors for the j state with spin index \( \sigma \) and \( q_{j}^{(\sigma)} \) are their occupations. The choice of the projection operators \( \hat{P}_{mn}^{(\sigma)} \) is crucial, because due to the non-orthogonal basis set different projection operators give different occupation number matrices. In our case, we have chosen to use the so-called full representation. Here, the selected operator is

\[ \hat{P}_{mn}^{(\sigma)} = |\chi_{m}|\langle \chi_{m}| \]  

where \( |\chi_{m}\rangle \) and \( \langle \chi_{m}| \) are the atomic orbitals of the strongly correlated electrons. Introducing this projector in (6), we get:

\[ n_{\sigma}^{\text{full}} = S D_{\sigma} S \]  

with \( S \) and \( D_{\sigma} \) the overlap matrix and the density matrix of the system.

In order to determine the influence of different U’s and cutoff radii and see how the results compare to previous experiments and calculations we studied first the case of the bulk iron oxide FeO (wustite) [35], where DFT is known to give qualitatively different behavior (metallic instead of insulating character) [36]. We performed calculations with \( U = 4 \) eV and \( U = 4.5 \) eV, which is the range of values most used in the literature for iron [36], and used projectors with different radii (see appendix A). We found that the results
were very sensitive to such radii, i.e. the FeO gap was only reproduced for radii larger than 2.5 Bohr. The parameters that best fitted the experiments and previous calculations for FeO were $U = 4.5$ eV and $r_c = 5.5$ Bohr, which gave a gap of 2.5 eV (2.4 eV in [35]).

To reproduce previous theoretical results for the iron metalloporphyrin [10, 37], we had to choose $r_{cut} = 1.5$ Bohr, which is smaller than the values used for FeO. This is possibly justified by the fact that the values of $U$ and the projectors radii depend on the environment where the strongly correlated atom is located. In case of the other transition metals (Co, Ni, Cu and Zn), $U$ is expected to increase towards Zn but still be similar [30]. The same can be said when the metalloporphyrins are coupled between gold electrodes. We therefore used the same parameters for all metalloporphyrins, which also simplified the comparison between different cases and made the study more systematic.

The use of slightly different $U$’s for different elements does not affect qualitatively and quantitatively the transport results, (only slight movements of some resonances around the Fermi level) and therefore we can be confident the study remains valid with the choice of the same $U$ for all cases.

4. Electronic structure of metalloporphyrins molecules

We have analyzed the electronic structure of FeP, CoP, NiP, CuP and ZnP, both in isolation (see appendix B) and contacted by (001) gold electrodes. The ground-state electronic configuration of the metallic atom, which reflects the crystalline field generated in the molecules, is shown in table 1. Notice that we have laid down the molecules on the XZ plane.

The molecular orbitals of the porphyrins are broadened when the molecules are contacted by the gold electrodes. This broadening is however minimal for the d orbitals of the transition metal atom, because of their small coupling to the rest of the molecule. Even so, a small broadening can be appreciated in figures 4 and 5 for FeP and CoP, respectively.

Panel (b) of figure 4 shows the PDOS projected on the orbital $d_{yz}$ of iron, which is spread and reduced. This indicates a larger delocalization of this state as a consequence of its coupling to other molecular states that hybridize with the gold states. Something similar happens to the $d_{xz}$ and, to a lesser extent, to the other d orbitals. This effect is maintained when the $U$-term is included. Also, as a consequence of

![Figure 4. PDOS projected on the Fe d states (a) $d_{xy}$, (b) $d_{yz}$, (c) $d_{z^2}$, (d) $d_{xz}$ and (e) $d_{x^2-y^2}$ of a contacted FeP molecule, computed with spin-polarized GGA. Positive and negative values represent spin up and spin down electrons. The blue ellipse in the (b) $d_{yz}$ and the green ellipse in the (d) $d_{xz}$ panels indicate states giving rise to Fano resonances in the transmission coefficients.](image-url)
hybridization and charge transfer the total spin of the molecule is reduced by more than a half as compared to the isolated molecule (from 2 µB to 1.07 µB and 1.34 µB, for GGA and GGA + U, respectively). This reduction comes mainly from the d_{yz} state, which crosses the Fermi level as a consequence of the spreading.

In molecules other than FeP and CoP, the broadening of resonances is not so clear, because the d states become more localized when the atomic number increases. The case of Ni, shown in figure 6, is striking because the differences between the isolated and contacted molecules are not only quantitative but qualitative (the spin calculated with U decreases from 2 µB to 0 µB). This can be explained by taking into account that electrons in the d_{xz} and d_{x^2−y^2} can be more delocalized in the contacted molecule, which decreases the effect of Hund’s interaction. As a consequence, the contacted molecule loses its magnetism (even after including the U-term).

5. Transport properties of metalloporphyrins between gold electrodes

5.1. Zero-bias

We start discussing the impact of the U-term on the transport properties of the junctions. We have found that the impact is largest in FeP and CoP because they have the strongest electron correlations. The zero-bias transmission coefficients T(E) are shown in figure 7, computed using spin-polarized GGA. Both systems present Fano-like resonances close to the Fermi level that move upwards (Fe) or downwards (Co) when U = 4.5 eV is included. The Fano resonance in FeP (no U) is spin-polarized, leading to a strong spin-filtering behavior. However, including the U-term kills the resonance as a consequence of changes in the coupling between the d-state and the molecular orbitals. For CoP, including the U-term reduces the spin polarization and moves several of the sharp resonances (in particular the clear Fano resonances appearing at about −0.7 eV, which is moved to −1.6 eV).

From these results it is clear that accounting for strong correlations is necessary to accurately describe these systems. We will therefore discuss from now on the results obtained using spin-polarized GGA + U.

The zero-bias transmission T(E) of all the molecules is shown in figure 8. As can be seen, four very broad Breit–Wigner resonances appear at energies about −1.4, −1.0, 0.5 and 1.5 eV (HOMO-1, HOMO, LUMO and LUMO+1). Resonances with the same shape at the same energy appear in the transmission coefficients of the contacted porphin molecule, which has no metallic atom. They therefore correspond to the conjugated molecular orbitals of the porphyrins, associated mainly to the sulfurs (HOMO) and the carbons and nitrogens (HOMO-1, LUMO and LUMO+1).

Superposed to them, there appear a number of sharp peaks, which we find to be either sharp Breit–Wigner of Fano resonances. Notice that the sharp peak at 0.3–0.5 eV marked by a red ellipse remains at the same position for all the
Figure 6. PDOS projected on the Ni d states (a) $d_{xy}$, (b) $d_{yz}$, (c) $d_{z^2}$, (d) $d_{xz}$ and (e) $d_{x^2−y^2}$ of a contacted NiP molecule, computed with spin-polarized GGA. Positive and negative values represent spin up and spin down electrons. The green ellipse in the (d) $d_{xz}$ panels indicate a state giving rise to a Fano resonance in the transmission coefficients.

Figure 7. Transmission coefficients of a FeP (a) and a CoP (b) contacted by gold electrodes, computed with spin-polarized GGA. Left (1) and right (2) columns correspond to calculations with $U = 0$ eV and $U = 4.5$ eV. Continuous and dashed lines represent spin up and spin down electrons.

A clear Fano resonance marked by a blue ellipse can be seen for the FeP and CoP junctions at $\sim-1.5$ eV. This resonance moves down and disappears from the energy window in the following junctions.

porphyrins. This peak also appears in the porphin junction. It corresponds to a sharp Breit–Wigner resonance associated to a weakly coupled molecular orbital with weight in the carbon and nitrogen atoms.

A clear Fano resonance marked by a blue ellipse can be seen for the FeP and CoP junctions at $\sim-1.5$ eV. This resonance moves down and disappears from the energy window in the following junctions.
Figure 8. Transmission coefficients of (a) FeP, (b) CoP, (c) NiP, (d) CuP and (e) ZnP molecules contacted by gold electrodes, computed with spin-polarized GGA and $U = 4.5$ eV. Continuous and dashed lines represent spin up and spin down electrons. The red ellipse circles a sharp Breit–Wigner resonance. The blue ellipse signals a Fano resonance. The green ellipse indicates a masked Fano resonance.

Figure 9. (a) Transmission coefficients and (b) PDOS around a Breit–Wigner-like resonance (1) and a Fano resonance (2), calculated on a gold–CoP junction and computed with spin-polarized GGA. Positive and negative values in the lower panels represent spin up and spin down electrons.

In contrast, the sharp resonance marked by a green ellipse which looks like a sharp Breit–Wigner resonance is actually a masked Fano resonance. Notice that it changes its energy position from FeP to ZnP, starting at $\sim 1.4$ eV for FeP, moving down in energy from FeP to CuP, appearing very close to the Fermi level on CuP, and disappearing for ZnP. Notice that it is spin-polarized except in the NiP junction.

We stress that these three resonances appear regardless of the kind of calculation (GGA and LDA, no-$U$ and $U$, paramagnetic and spin-polarized), as discussed in appendix C.
The Fano and masked Fano resonances (blue and green ellipses in figure 8) must come from the d orbitals of the transition metal atom, for two reasons: first, they do not appear in the transmission $T(E)$ when a porphin instead of a porphyrin is contacted; second, they shift in energy when the metallic atom is changed. Notice their correspondence with some of the features inside similar ellipses in figures 4–6. In the FeP case the Fano resonance is not clearly seen because its peak is located at high energies but its effect on the down spin transmission is rather large. To gain more knowledge on their origin we look at the PDOS projected onto the d levels and the surrounding atoms at the energies where these resonances happen. This is shown in figure 9 for CoP, computed with GGA and without $U$, which is the case where different Fano interference effects from different atoms can be seen most clearly. We find that the spin down d states that are closest to the energy of the resonance are the $d_{xz}$ for the masked Fano and the $d_{yz}$ for the clear-cut Fano resonances. For the first resonance the PDOS shows a rather strong hybridization between the $d_{xz}$ level and the nitrogen atoms. For the Fano resonance, however, the $d_{xz}$ hybridizes much more with the carbon atoms. This is in agreement with the LDOS of figure 10, which shows that the $d_{xz}$ hybridizes with the nitrogens and the $d_{yz}$ with the carbons (see appendix B for more details).

Taking into account the previous data and the simple model that was presented in section 2, it is possible to explain the behavior of these junctions as follows. The d orbitals are localized states that couple to certain molecular states. Such configurations are similar to those where a side state couples to a molecular backbone, which produce Fano resonances in the transmission coefficients. The d orbitals generate therefore Fano resonances associated to one or several molecular states. If, for example, the molecular state is the LUMO and the d orbital is in the HOMO–LUMO gap, the effect of the Fano resonance is clearly seen because it affects the transmission in the gap, which has a large weight from the LUMO. The Fano resonance does not go to zero, however, because of the tails of the transmission of other molecular states. If, on the other hand, the d orbital couples to a state below the HOMO or above the LUMO, the effect of the Fano resonance turns out to be much smaller because the transmission of such state does not affect too much the transmission in the HOMO–LUMO gap.

We stress that these features, specially the sharp resonances, appear in all cases, with and without $U$, and are a general feature of these molecules. The main effect of increasing the intra-atomic repulsion, produced by the $U$, is a shift of the resonances and sometimes a change in their width.

### 5.2. Finite bias

From the zero-bias transmission coefficients it is not clear whether the sharp resonances associated to the d levels can give rise to distinctive features or even survive when a finite bias is applied. To clarify that, we have applied a finite bias by using an approximation that includes non-equilibrium effects by shifting differently the levels associated to the electrodes and the molecule [27]. We focused on the CuP (GGA $+ U$), which has a spin-polarized resonance very close to the Fermi level, and compared it to the ZnP, which has no sharp resonances coming from the d levels. We applied a small bias, enough to cover the resonance with the integration window. The resonance, however, does not remain static but moves to lower energies, as can be seen in figure 11(a). To further enhance the effect of the resonance we also applied a gate.
Figure 11. Spin down transmission coefficients around the Fermi level for CuP (GGA + U) under different bias voltages and a gate voltage of 0 V (a) and 3 V (b).

![Graph showing spin down transmission coefficients around the Fermi level for CuP (GGA + U) under different bias voltages and a gate voltage of 0 V (a) and 3 V (b).](image)

Figure 12. Total current (a) and its derivative (b) for ZnP and CuP porphyrins. A gate voltage of 3 V in the central part of the junction is also included in the CuP case.

![Graph showing total current (a) and its derivative (b) for ZnP and CuP porphyrins. A gate voltage of 3 V in the central part of the junction is also included in the CuP case.](image)

The $I$$-$$V$ characteristics calculated with the resonance differ from those obtained without it (ZnP), as can be seen in figure 12. These differences become much more evident when the derivative of the current is taken. Without gate, the resonance produces a peak when the bias reaches it, at approximately 0.065 V. When the gate is included the peak develops at zero voltage. The resonance produce therefore different $I$$-$$V$ characteristics and can increase the total value of the conductance by a factor larger than 2 at the peak maxima. Notice however that these values are masked by the spin up conductance, which is the same for all cases. If only the spin down conductance is taken into account the changes are larger. These results also prove that a spin-polarized current can be generated under finite bias since the peaks are only associated to the spin down component.

6. Conclusions

We have studied the electronic and transport properties of metalloporphyrins between gold electrodes and proposed a simple model that can explain the main features of the...
zero-bias transmission. We found that the coupling to the electrodes changes only slightly the electronic properties but the magnetic moments decrease as a consequence of charge transfer and hybridization with the electrodes. We have found two types of features in the transport properties, which are shown to be Fano resonances by the use of the simple model. We have also computed the $I-V$ characteristics and shown that the presence such resonances can significantly change the value of the finite-bias conductance.

Based on these results and in particular on the evolution of the resonances as a function of the degree of freedom that the choice of different 3d atoms provides to position the relevant d levels and the intra-atomic potential, we propose that metalloporphyrin-based junctions are an excellent playground for the control and exploitation of Quantum Interference in functional molecular electronics devices. Whenever a given atom or molecule couples either to the metallic atom or to other parts of the molecular backbone the changes in the metallic d states affect the Fano resonances. This mechanism can generate sharp increases or decreases in the zero-bias conductance. Differences between spin up and spin down transmissions, which are specially important in the cases of iron, cobalt and copper, can also give rise to spin-filtering behavior.

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**Appendix A. Details of the DFT + $U$ approach**

DFT has emerged as the tool of choice for the simulation of a wide array of materials and nanostructures. However, the theory fails to describe strongly correlated electron systems, such as embedded 3d transition metal or 4f rare earth elements. Apart from the fact that even exact DFT cannot describe all excited states [28], the approximations included in the exchange–correlation potential induce qualitative errors in correlated systems. There have been many attempts to fix these problems. These include generating exchange–correlation functionals specifically tailored to the system under investigation, but those are frequently not transferable. Another attempt is based on removing the electronic self-interactions introduced by the approximate treatment of exchange in DFT [29]. This unphysical self-interaction is a significant source of errors when electrons are localized. However it is not clear that just by removing the self-interaction error the physical description will be qualitatively correct. We used in this article the DFT + $U$ approach, a mean-field way to correct for strong correlations in systems with transition metals or rare earth compounds, developed by Anisimov and co-workers, which produces qualitatively correct results in a large number of systems [30–32].

The DFT + $U$ method assumes that electrons can be split into two subsystems: delocalized electrons, that can be treated with traditional DFT, and localized electrons (3d or 4f), which must be handled using a generalized Hubbard model Hamiltonian with orbital-dependent local electron–electron interactions. The DFT + $U$ functional is defined then as:

$$
E_{\text{DFT}+U}^{\text{eff}}[\rho^\sigma(\vec{r}), \{n^\sigma\}] = E_{\text{DFT}}^{\text{eff}}[\rho^\sigma(\vec{r})] + U \sum_{\alpha \neq \beta} n_{\alpha \sigma} n_{\beta \sigma},
$$

(A.1)

where $E_{\text{DFT}}$ is the standard DFT functional; $\rho^\sigma(\vec{r})$ is the $\sigma$-spin charge density; $E_{\text{Hub}}$ is the on-site coulomb correction; $E_{\text{DC}}$ is the double counting correction, which is necessary to avoid including twice the average electron–electron interaction, that appears also in $E_{\text{DFT}}$; and $\{n^\sigma\}$ are the atomic orbital occupations corresponding to the orbitals that need to be corrected.

The generalized Hubbard Hamiltonian is written as

$$
\hat{H}_{\text{int}} = \frac{U}{2} \sum_{m \neq m', \sigma} \hat{n}_{m \sigma} \hat{n}_{m' \sigma}^\dagger + \frac{U-J}{2} \sum_{m \neq m', \sigma} \hat{n}_{m \sigma} \hat{n}_{m', \sigma}^\dagger.
$$

(A.2)

Following [33], we take the atomic limit of the above Hamiltonian where the number of strongly correlated electrons $N_{\sigma} = \sum n_{m \sigma}$ is an integer and write:

$$
E_{\text{DC}} = \langle \text{integer } N_{\sigma} | \hat{H}_{\text{int}} | \text{integer } N_{\sigma} \rangle
$$

$$
= \frac{U}{2} \sum_{\sigma} N_{\sigma} N_{\sigma} - \frac{U-J}{2} \sum_{\sigma} N_{\sigma} (N_{\sigma} - 1).
$$

(A.3)

In contrast, for a noninteger occupation number, corresponding to an ion embedded in a larger system, we write:

$$
E_{\text{Hub}} = \langle \text{noninteger } N_{\sigma} | \hat{H}_{\text{int}} | \text{noninteger } N_{\sigma} \rangle
$$

$$
= \frac{U}{2} \sum_{m \neq m', \sigma} n_{m \sigma} n_{m' \sigma}^\dagger + \frac{U-J}{2} \sum_{m \neq m', \sigma} n_{m \sigma} n_{m' \sigma}^\dagger.
$$

(A.4)

The above two equations can be merged and, after some algebra, the DFT + $U$ functional can be written as

$$
E_{\text{DFT}+U} = E_{\text{DFT}} + \frac{U_{\text{eff}}}{2} \sum_{m \sigma} n_{m \sigma} (1 - n_{m \sigma})
$$

(A.5)

where $U_{\text{eff}} = U - J$.

It has to be noted that the correction term depends on the occupation number matrix. This matrix, which is a centerpiece of the DFT + $U$ approach, is not well defined, because the total density charge cannot be broken down into simple atomic contributions. Since the appearance of the DFT + $U$ approach, there have been many different definitions of the occupation number matrix [34]; in our case we evaluate it by introducing projection operators in the following way [34]:

$$
n_{mm'}^{\sigma} = \sum_j q_j^{\sigma} (\langle \psi_j^{\sigma} | \hat{p}_{mm'}^{\sigma} | \psi_j^{\sigma} \rangle)
$$

(A.6)
where $\psi_{j}^{(\sigma)}$ are the Kohn–Sham eigenvectors for the $j$ state with spin index $\sigma$ and $\psi_{j}^{(\sigma)}$ are their occupations. The choice of the projection operators $\hat{P}_{nm}$ is crucial, because due to the non-orthogonal basis set different projection operators give different occupation number matrices. In our case, the choice corresponds to so-called full representation. Here, the selected operator is

$$\hat{P}_{nm} = |\chi_{m}\rangle \langle \chi_{m}|$$

where $|\chi_{m}\rangle$ and $\langle \chi_{m}|$ are the atomic orbitals of the strongly correlated electrons. Introducing this projector in (A.6), we get:

$$n_{\sigma}^{\text{full}} = SD_{\sigma}S$$

where $S$ is the overlap matrix and $D_{\sigma}$ is the density matrix of the system.

### Appendix B. Electronic structure of isolated molecules and comparison between different functionals

The atomic configurations, which determine in turn the total spin and magnetic moment of the molecules, are shown in table B.1. Table B.2 shows the HOMO/LUMO gaps of the molecules.

#### B.1. Isolated FeP

The crystalline field in FeP forces the $d_{xz}$ orbital of Fe to move above the Fermi level. The molecule displays as a consequence an intermediate spin configuration, $S = 1$, which is in agreement with experimental results [38]. The density of states projected (PDOS) onto the iron $d$ states calculated with GGA and GGA + $U$ is shown in figure B.1 for spin-up and -down electrons. As can be seen the closest orbitals to the Fermi level are the spin down $d_{xy}$ and $d_{yz}$. The states that are not completely filled and contribute to the magnetic moment of the molecule are the $d_{x}$ and the $d_{x^2−y^2}$, whereas the $d_{z}$ is completely empty. The $d_{z}$ shows also a strong hybridization. When the $U$ is included all gaps increase as a consequence of the movement of the filled orbitals to lower energies and the empty orbitals to higher energies. From here it is already possible to get an idea of the effect of the Fe $d$-states on the transport properties of the molecule: those with large hybridization with other molecular states, such as the $d_{z}$, are expected to give rise to relatively broad Breit–Wigner transmission resonances, whereas those with a small hybridization such as the $(d_{x^2} + d_{y^2})$ are expected to produce either very thin Breit–Wigner resonances, or Fano resonances as explained in the main text.

The amount of hybridization can also be seen by plotting the PDOS on the different atoms of FeP, as shown in figure B.2 for GGA (left panel) and GGA + $U$ (right panel). Notice some Fe $d$-states that do not hybridize with the rest of the molecule, whereas other Fe $d$-states do hybridize producing extended molecular orbitals. We discuss first the PDOS calculated with plain GGA. The HOMO and LUMO orbitals have Fe and C contributions. In the HOMO, the contribution of Fe is bigger but in the LUMO both Fe and C contribute equally. Specifically, the Fe contribution to the HOMO (LUMO) comes from 3$d_{z}$ and 3$d_{x^2}$ orbitals; in addition, Fe contributes to the HOMO-1 with the 3$d_{x^2}$ and a small part of the 3$d_{z^2}$-$2p_{z}$. In the case of carbon the state that contributes to both the HOMO and LUMO is the $2p_{z}$. Note that there are also sulfur states around the Fermi level, which we do not show. By switching on the $U$-term, a partial rearrangement is seen. The states that most contribute to HOMO are still Fe $3d_{z}$, but the C $2p_{y}$ states are the most important in the LUMO; this latter orbital has also a small contribution from N $2p_{y}$. Even though the $U$ term acts only on the iron atom, the C $2p_{y}$ states are indirectly affected, i.e. the C $2p_{y}$ states, located around $−1$ eV and 1 eV, lower their energy as a consequence of the changes on the iron states.

By using the spatial projection of the density of states (local density of states, LDOS) it is also possible to understand where a particular molecular state is located. In figure 10 we show the LDOS projected on the molecular states associated to the $d_{yz}$ (a) and $d_{xz}$ (b) spin down states (with an isosurface value of $0.001 \text{eV} \AA^{-3}$), i.e. those peaks in the density of states where the weight of these $d$ orbitals for spin down is largest, calculated with GGA. These states are located at $E − E_{F} = 0.3 \text{eV (}yz\text{)}$ and $2.3 \text{eV (}xz\text{)}$ and move across the Fermi level when the atomic charge of the metal increases towards the Zn. Notice that in the $d_{xz}$ case, due to the strong hybridization, the $d$ peak splits in two and therefore the choice is ambiguous. The spatial distribution of each peak is similar however. On each $d$ state it is possible to see the typical shape associated to it, i.e. four lobes on the diagonals of the YZ or XZ planes, plus some charge on other atoms of the molecule due to hybridization with other molecular

| Molecule | GGA | GGA + $U$ | LDA | LDA + $U$ |
|----------|-----|----------|-----|---------|
| FeP      | 2.00| 2.00     | 2.00| 2.00    |
| CoP      | 1.00| 1.00     | 1.00| 1.00    |
| NiP      | 0.00| 2.00     | 0.00| 2.00    |
| CuP      | 1.00| 1.00     | 1.00| 1.00    |
| ZnP      | 0.00| 0.00     | 0.00| 0.00    |
| Au–FeP–Au| 1.07| 1.34     | 1.14| 1.32    |
| Au–CoP–Au| 0.83| 1.08     | 0.62| 1.07    |
| Au–NiP–Au| 0.00| 0.00     | 0.00| 0.00    |
| Au–CuP–Au| 0.80| 0.98     | 0.84| 0.97    |
| Au–ZnP–Au| 0.02| 0.00     | 0.02| 0.00    |

| Molecule | GGA | GGA + $U$ | LDA | LDA + $U$ |
|----------|-----|----------|-----|---------|
| FeP      | 0.48| 1.10     | 0.10| 0.85    |
| CoP      | 0.90| 1.80     | 0.27| 1.80    |
| NiP      | 1.50| 1.60     | 1.55| 1.65    |
| CuP      | 0.75| 1.40     | 0.85| 1.40    |
| ZnP      | 1.60| 1.60     | 1.60| 1.60    |
Figure B.1. PDOS projected on $-d_{xy}$ (a), $d_{yz}$ (b), $d_{z^2}$ (c), $d_{xz}$ (d) and $d_{x^2-y^2}$ (e)—for an isolated FeP molecule, computed with spin-polarized GGA. The left (1) and right (2) columns correspond to calculations without $U$ and with $U = 4.5$ eV, respectively. Positive and negative values represent spin up and spin down electrons.

Figure B.2. PDOS projected on the atoms (a) Fe; (b) N; and (c) C in an isolated FeP molecule. Details are as in figure B.1.

Orbitals. Notice that the $d_{yz}$ state does not interact too much with the nitrogens but rather with the carbons, specially with those located closest to the sulfur atoms. This produces an hybridization between this orbital and the carbon $\pi$ states, as can be clearly seen in figure 10(a) where the charge on the carbon atoms is mainly located on top of them. On the other
hand, in the $d_{xz}$ case, the lobes are directed exactly towards the nitrogen atoms and therefore this state interacts strongly with them. This interaction is $\sigma$-like, which is the type of interaction that nitrogen forms with the adjacent atoms, and therefore localizes the charge between atoms. The differences between the $d_{xz}$ and $d_{yz}$ orbitals and their coupling to different...
Figure C.1. Transmission coefficients of (a) FeP, (b) CoP, (c) NiP, (d) CuP and (e) ZnP molecules contacted by gold electrodes, computed with spin-polarized LDA. Left (1) and right (2) columns correspond to calculations without $U$ and with $U = 4.5$ eV. Continuous and dashed lines represent spin up and spin down electrons.

molecular states has a direct impact on the transport properties of some of these molecules, as explained in the main text. We comment new that LDA (and LDA + $U$) produces slightly different PDOS.

B.2. Isolated CoP

Our electronic configuration for CoP, shown in table 1, has $S_z = 1/2$ in agreement with previous results [10]. With GGA, the HOMO is made of Co 3d$_{zy}$ and 3d$_{xy}$ states, C2p$_y$ states and small fraction of N 2p$_y$ states. The LUMO is made only of Co3d$_{z^2}$ and a small fraction of 3d$_{x^2-y^2}$. We the $U$-term in turned on all states in Co and C tend to lower their energy. Now the HOMO and LUMO are formed by C2p$_y$ and N and C2p$_y$ states and have a small contribution of Co3d$_{xz}$ states; LDA results are similar.

B.3. Isolated NiP

Unlike the FeP and CoP cases, the electronic configurations of NiP changes when the $U$-term is included from $\ldots$(d$_{xy}$)$^2$(d$_{z^2}$)$^2$(d$_{xy}$)$^2$(d$_{x^2-y^2}$)$^2$ ($S_z = 0$) to $\ldots$(d$_{xy}$)$^2$(d$_{z^2}$)$^2$(d$_{xy}$)$^2$(d$_{x^2-y^2}$)$^2$(d$_{yz}$)$^2$ ($S_z = 1$). This change is generated by the transfer of one electron from the 3d$_{x^2-y^2}$ to the 3d$_{xz}$ orbital. This can be clearly seen in figure B.3, where both spin up and spin down 3d$_{xz}$ states are above the Fermi level without $U$ (panel (d1)), whereas both 3d$_{x^2-y^2}$ are below the Fermi level (panel (e1)). However, when $U$ is introduced one of the 3d$_{xz}$ moves downwards and one of the 3d$_{x^2-y^2}$ moves upwards, each of them crossing the Fermi level.

In CuP, the 3d orbitals have closed shells, except the 3d$_{xz}$, which loses a bit of charge. The total spin of the molecule is $S_z = 1/2$, which comes mainly from the Cu 4s and 3d$_{xz}$ orbitals. Furthermore, the magnetism is not strictly localized in the Cu atom, but extends a little to the nitrogens. The PDOS projected on the atoms Cu, C and N with GGA shows that the HOMO comes from C and N2p$_y$ states. The Cu states are present in the HOMO-1, which is made of Cu 3d$_{xz}$ and has small contributions from N and C2p$_x$ and 2p$_z$ states. The LUMO is made of Cu3d$_{xz}$ and N2p$_y$ states. With GGA + $U$, the HOMO remains the same, but the previous HOMO-1 moves to lower energies and the new HOMO-1 has
C and N2p_y character. Although the LUMO is still formed by the same type of orbitals (i.e. Cu3d_{xz} and N2p_y) now changes its spin polarization and becomes populated by spin down electrons, unlike GGA.

B.5. Isolated ZnP

The lowest energy electronic structure for ZnP is a close-shell electronic configuration Therefore the U correction does not affect to electronic configuration of this molecule. By analyzing the PDOS for the atoms Zn, C and N we find that the HOMO and LUMO come from N and C2p states. The energy gaps in all cases are about 1.60 eV. The only difference between LDA (LDA + U) and GGA (GGA + U) is the energy position of the levels, which is slightly different.

Appendix C. Additional transport results

The transmission coefficients for FeP, CoP, NiP, CuP and ZnP single-molecule junctions, computed with spin-polarized LDA and paramagnetic GGA are shown in figures C.1 and C.2, respectively. The results with spin polarization are qualitatively very similar to those calculated with the GGA functional, excluding some changes in the position of the Fano resonances in the Fe and Co cases with and without U. The results without spin polarization follow also a similar pattern and are analogous to those obtained by Wang et al [3].

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