Ab initio correlation effects on the electronic and transport properties of metal(II)-phthalocyanine-based devices

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Abstract
Using first-principles calculations in the framework of density functional theory, we investigated the electronic and transport properties of metal(II)-phthalocyanine (M(II)Pc) systems, both in a single-molecule configuration and in a model device geometry. In particular, using copper(II)-Pc and manganese(II)-Pc as prototypical examples, we studied how electronic correlations on the central metal ion influence the analysis of the electronic structure of the system and we demonstrated that the choice of the exchange–correlation functional, also beyond the standard local or gradient corrected level, is of crucial importance for a correct interpretation of the data. Finally, our electronic transport simulations have shown that M(II)Pc-based devices can act selectively as molecular conductors, as in the case of copper, or as spin valves, as in the case of manganese, demonstrating once more the great potential of these systems for molecular nanoelectronics applications.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Metal(II)-phthalocyanines (MPcs) have attracted a growing interest in view of their potential for nanoscale applications, such as light-emitting diodes, field-effect transistors, photovoltaic cells and single-molecule devices [1]. In particular, metal(II)-phthalocyanines are considered prototypical organic semiconductor materials, and their properties have been widely investigated in a variety of experimental conditions. The characteristics of the Mpc/substrate interactions [2–5], the effects of doping [6–8], and the adsorption of additional small molecules [9] have been investigated with techniques such as photoemission spectroscopy [10–13], scanning tunnelling spectroscopy (STS) [14–16] and microscopy [17–19], electronic paramagnetic resonance [20], nuclear magnetic resonance [21], gas-phase electron diffraction [22], etc. However, it is not infrequent that different experiments produce somewhat contradicting results [6, 10, 11, 23–25], and a careful interpretation of these data in terms of a robust theoretical analysis has become mandatory.

An accurate theoretical determination of the electronic structure of the single molecule is the first step towards a meaningful interpretation of these complex systems: understanding the sequence of the frontier molecular orbitals along with their spin order is of paramount importance for the analysis of photoemission, optical and transport experiments.

Phthalocyanines (Pcs) are planar organic macrocycles that can host a central metal ion (typically a 3d transition metal), as shown in figure 1. Because of the relatively large size of the molecule, the use of \textit{ab initio} approaches [26–33] to investigate the complex metal–ligand coupling has become viable only recently. However, different electronic structures

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic representation of a metal phthalocyanine molecule.}
\end{figure}
response approach proposed by Cococcioni and De Gironcoli shown in figure 1. This system has been recently proposed as gold atoms in a typical lead/conductor/lead configuration, as an M(II)Pc molecule bridged between two atomic chains of data. Moreover, we have analysed the effects of the electron is of crucial importance for a correct interpretation of the demonstrated that the choice of the exchange–correlation (XC) functional theory calculations, as implemented in the PW SCF approximation (LSDA) [35] and the generalized gradient correlation functional is evaluated within the local spin density code [34]. At the standard level, the exchange and ab initio DFT calculations, with the Landauer approach to describe transport properties of extended systems [41, 42]. The connection is realized by transforming the Bloch orbitals into maximally localized Wannier functions [43, 44]. This representation naturally introduces the ground-state electronic structure into the real-space Green’s function scheme, which is our tool for the evaluation of the Landauer quantum conductance.

The transport properties of the system have been computed in a lead/molecule/lead geometry using the fully first-principles approach implemented in the WAnT code [39, 40]. The method combines an accurate description of the electronic ground state, provided by ab initio DFT calculations, with the Landauer approach to describe transport properties of the system has been computed in a lead/molecule/lead geometry using the fully first-principles approach implemented in the WAnT code [39, 40]. The method combines an accurate description of the electronic ground state, provided by ab initio DFT calculations, with the Landauer approach to describe transport properties of extended systems [41, 42]. The connection is realized by transforming the Bloch orbitals into maximally localized Wannier functions [43, 44].

3. Results and discussions

3.1. Copper(II)-phthalocyanine systems

3.1.1. Single molecule. The single-particle orbitals of the planar CuPc molecules can be classified according to the irreducible representation of the D_{6h} group. In this representation the 3d orbitals split into a_{1g} (d_{x^2−y^2}), b_{1g} (d_{xy}, d_{x^2−y^2}), c_{g} (d_{xz}, d_{yz}) and b_{2g} (d_{yz}, d_{xz}) orbitals. One of the open problems in the interpretation of the experimental data is the energy position of the b_{1g} orbital with respect to the a_{1g} and 2e_{g} states, which are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the Pc rings, respectively. The b_{1g} orbital has a σ character and is localized on the copper ion, whereas the a_{1g} and 2e_{g} are singly and doubly degenerate π-like states, delocalized over the entire Pc macrocycles (see figure 2(a)).

In order to clarify the issue, we have calculated the electronic structure of the isolated CuPc molecule by using two different XC correlation functionals, namely LDA and PBE. The resulting densities of states are reported in figures 2(b) and (c). The analysis of the electronic structure shows the presence of mixed metal–ligand states in the low-energy part of the spectrum, especially between the copper ion and the pyrrole rings, the fingerprint of a direct interaction between the two subsystems. In figure 2, we show the b_{1g}, a_{1g} and 2e_{g} states that are the frontier orbitals of the overall CuPc molecule. In both LDA and PBE cases, the a_{1g} and the 2e_{g} states are spin degenerate (i.e. have the same energy for both spin components), and the corresponding energy differences

![Figure 1. Atomic structure of a generic metal(II)-phthalocyanine (MPC) bridged between two one-dimensional gold chains in a lead/conductor/lead geometry. The circle marks the phthalocyanine molecule. Different colours identify different chemical species: grey = C, white = H, cyan = N, gold = Au, yellow = S, green = M; M stands for either copper or manganese. In the single-molecule configuration the Au chains are absent and the two S atoms are replaced by H atoms.](image-url)
The total magnetization of the XC functional, the CuPc molecule has a resulting result is not biased by the choice of the basis set used in the calculations. We calculated the electronic structure of the molecule also using a localized atom-centred numeric basis set (figure 2(a)).

In our DFT calculations the net charge transfer from the Cu atom to the rest of the environment is symmetric and smaller than the formal one: the analysis of the Löwdin charges indicates that the copper atom is positively charged, $\delta q_{\text{Cu}} = +1.02e$, and the 3d shell hosts $\sim 9.4$ electrons. Even though the calculated values are smaller than the formal ones, the correlation effects, due to the opening of the 3d shell, must be taken carefully into account, especially if one attempts to use the ground-state structure as the basis for the interpretation of effects (such as doping) that imply the variation of the oxidation/reduction state of the central ion.

In order to gain further insights on this issue, we introduced electronic correlation effects beyond standard DFT by including a local Hubbard $U$ term on the Cu ion. We tested several values of the $U$ parameter ($U = 0.5$, $2.0$, $3.0$, $4.0$, $6.0$ eV); the results for $U = 3$ eV are shown in figure 2(d). The Hubbard term operates mainly on the energy of the ion-centred states, leaving the Pce ones unchanged. We note a downward (upward) shift of the $b_{1g}$ state for the spin-up (spin-down) component, respectively. The net effect is the opening of the SOMO–LUMO gap. By increasing the value of the Hubbard $U$, the shift of the $b_{1g}$ peak increases accordingly. In particular, for $U = 0.5$ and 2.0 eV, both DOSs resemble the LDA spectra of figure 2(b). For $U = 3.0$ eV, even though $b_{1g}$ is still the SOMO, it is almost degenerate with the spin-up $a_{1u}$ state (figure 2(d)). This effective degeneracy is observed also for the other two values of the Hubbard parameter ($U = 4.0$, 6.0 eV) that we considered.

By further increasing $U$, we observe a slight shift of the $b_{1g}$ peak, that leads to an inversion of the $b_{1g}$ and $a_{1u}$ states for $U = 6.0$ eV (see inset of figure 2(d)). This trend confirms how the order of the single-particle states is strongly related to the specific treatment of the electron–electron correlation. However, an on-site correlation parameter $U = 6.0$ eV is a rather high value, greater than any of those experimentally...
calculated the ground-state electronic structure using the LDA. On the basis of the results for a single molecule, we have simulated an open device where the Au wires constitute the semi-infinite leads and the CuPc acts as the conductor. (a) Spin-polarized DOS of the periodic \((\text{Au}_5\text{S})\text{CuPc}\) system. The shaded area (thick line) is the projection on the CuPc (S–Au) atomic states. (b) Mean field (shaded area) and correlated (straight and dashed lines) two-terminal transmittance of an open CuPc-based device, spin resolved. The zero energy references are set to the Fermi level of the periodic \((\text{Au}_5\text{S})\text{CuPc}\) system.

measured for similar systems\(^5\). Thus, it is reasonable to conclude that the LDA order of the states is the correct one, while the exact position of the \(b_{1g}\) peak with respect to the \(\text{Pc}\)’s states depends on the correct value of the electron correlation. From our calculations it results also that in the case of CuPc the PBE XC functional overestimates the e–e correlation, as if a strong Hubbard potential were applied\(^6\).

3.1.2. Device configuration. The system we studied is inspired by a prototypical one-dimensional single-molecule device originally proposed by Nazin et al [14]. The original system was realized placing a CuPc molecule between two short chains of gold atoms, deposited on a NiAl substrate. The electronic structure was then characterized by STS measurements. The metallic character of the substrate prevented the direct measurement of current–voltage \((I–V)\) characteristics through the double interface. The coherent transport properties of the open device have been calculated previously by Tada and co-workers [32], who found a quantum conductance of the order of \(G = 3 \times 10^{-4} e^2/h\). This value, smaller than the typical ones \((G = 0.01 e^2/h)\) observed for aromatic molecules [51], is mostly due to the weak gold/CuPc interaction, i.e. to the absence of a direct chemical bond. For these reasons we slightly modified the geometry of the system, connecting the molecule and the leads through a sulfur bridge (figure 1). The choice of the sulfur functionalization is justified by the well-known ability of thiol groups to anchor molecules to gold electrodes [52].

Following the method [40] described in section 2, we have simulated an open device where the Au wires constitute the semi-infinite leads and the CuPc acts as the conductor. On the basis of the results for a single molecule, we calculated the ground-state electronic structure using the LDA XC functional. The spin-resolved electronic structure of the periodic \((\text{Au}_5\text{S})\text{CuPc}\) building block (figure 3(a)) is characterized by a finite density of states at the Fermi level \((E_F = 0 \text{ eV})\); while the formation of the nanojunction induces a realignment of the molecular and gold orbitals, the CuPc molecule perturbs the pure one-dimensional features of the infinite Au chain, such as the van Hove singularities, and the dispersive sd band crossing the Fermi level [53, 54]. As expected, the presence of the thiol bridge at the metal/molecule interface favours the mixing of the molecular orbitals. Indeed, the overall SOMO for the spin-up component is the result of the hybridization of the delocalized sd-like states of the pristine chain and the \(b_{1g}\) state of the CuPc molecule. Other hybridized orbitals, which also involve the \(\text{a}_{1u}\) state of the molecule, are recognizable in the energy range from \(E = −0.5 \text{ eV}\) to the Fermi level. The \((\text{Au}_5\text{S})\text{CuPc}\) system maintains a global magnetic polarization of \(1.0 \mu_B\), due to the single occupation of the \(b_{1g}\) state derived from the isolated molecule. However, the effect of this imbalance on the overall transmission is reduced by the spin-unpolarized density of states of the gold wire.

As a starting point, we calculated the electronic transport at the mean field level: we treated the electron correlation within DFT (LDA), by using the Landauer formula [42]. In particular, we focused on the zero bias regime; in this case the quantity to be calculated is the quantum transmittance \(T(E)\). The value of the transmittance at the Fermi level gives the quantum conductance.

The results for the spin-up and spin-down components of the quantum transmittance (logarithmic scale) are shown in figure 3(b). The corresponding quantum conductances are \(G_{\text{up}} = 0.059 e^2/h\) and \(G_{\text{dw}} = 0.064 e^2/h\). These values are reasonably high, when compared with those calculated for the unbound system [32] or with the gold chain [55] (which gives almost \(G = 1.0 e^2/h\) for each spin channel). This is due to the important mixing of the CuPc orbitals with the sd bands of the gold wire. In other energy regions, such as in the range \(E \in [−2.0, −0.5] \text{ eV}\), that corresponds to the 5d band of the Au wire, the orbital mixing is very small, leading to a localization of the electronic states and a corresponding reduction of the transmittance.

As a further test, we calculated the transport properties starting from PBE DFT calculations. In that case the inversion of the CuPc states near the Fermi level is almost irrelevant, due to the same coupling with the unpolarized sd manifold of the gold wire.

\(^5\) The screened value of the local Hubbard potential may be evaluated in the self consistent calculation as the derivative of the total energy with respect to the number of electrons, as described in [38]. However this goes beyond the aim of the present work. Here, we are not interested in the exact evaluation of the e–e interaction, but in the qualitative description of the effects of the electron correlation.

\(^6\) We observed this effect in this specific CuPc molecular structure, thus this conclusions can not be straightforwardly extended to other copper-based system, without deep further analysis.
In order to take into account the effect of the electron correlation, we evaluated the additional e–e self-energy operator $\Sigma_{\text{e-e}}(\omega)$. The latter is calculated in the framework of the so-called 3BS formalism [48, 49]. 3BS treats the electron correlation in a full many-body approach beyond the single-particle approximation. The resulting self-energy is non-Hermitian and frequency dependent, and the inclusion of this quantity in the evaluation of quantum transmittance may introduce incoherent and dynamical effects on transport that are not accessible [46] within mean-field techniques, like for example DFT + $U$.

The 3BS scheme requires the inclusion of an on-site Hubbard-like term $U$ for the Cu ions. We looked at the effects induced by two values of the parameter, $U = 3.0$ and $U = 6.0$ eV. The results are summarized in figure 3(b). Similar to the single-molecule case, the effect of correlation does not radically change the character of the up and down transmittance spectra. This is in agreement with the absence of Cu$_{3d}$-derived states close to the Fermi level. The displacement of the b$_{1g}$ state is not sufficient to modify the conduction properties of the device. The main differences are in the region $E \in [-2.0, -0.5]$ eV, where an enhancement of the transmittance is observed. This is mainly due to the real part of the e–e self-energy, which shifts the molecular orbitals, leading a higher alignment with the lead states. The amount of such realignment depends on the value of the selected Hubbard $U$ term, and it is not strictly related to a further hybridization of the conductor/lead molecular orbitals.

### 3.2. Manganese(II)-phthalocyanine systems

#### 3.2.1. Single molecule

Let us now consider how the electronic structure of the molecule is modified by the presence of a highly correlated Mn central cation that substitutes the original copper. Due to the half occupation of the strongly localized 3d shell, the LDA is expected to fail in the description of the electronic structure of the manganese atom. Therefore, we followed previous theoretical calculations [33] in using a gradient-corrected (PBE) XC functional.

The relaxed MnPc molecule still exhibits a planar square-like geometry, as in the case of CuPc, and we can still label the single-molecular orbitals according to the D$_{4h}$ symmetry. However, due to different ionic radius and different metal d-orbital occupancy, we observe a contraction (\(~1.5\%) of the Mn–N bond length and a reduction of the metal–ligand ionicity, resulting in a stronger metal–molecule coupling. The spin-resolved density of states of the isolated MnPc molecule is displayed in figure 4(a). For the spin-up channel $a_{1u}$ and $2e_g$ states are singly occupied HOMO$_{\text{Up}}$ and LUMO$_{\text{Up}}$ respectively, while the $b_{1g}$ orbital is empty. The energy difference $\Delta E = E(2e_g) - E(\text{HOMO}) = 1.41$ eV is very similar to the CuPc case. In contrast, the spin-down $a_{1u}$ state corresponds to the HOMO-1. The spin-down HOMO and LUMO are given by the almost degenerate (\(\Delta E = 0.16\) eV) couple of states $e_{1g}$ (one state occupied, one empty). These are $\pi$-like orbitals extended over both the Mn ion and the Pc rings. The corresponding spin-up states are instead completely occupied; the double degenerate $2e_g$ peak is shifted at higher energy and split into two single peaks, separated by (\(\Delta E = 0.07\) eV). Furthermore, they both exhibit a large 3d Mn component. It is worth noticing that between the $e_{1g}$ and the $2e_g$ duplets there are two other empty states, $b_{2g}$ and $a_{1g}$, fully occupied in the spin-up spectrum, that are $\sigma$-like orbitals localized on the central ion. Finally, the $b_{1g}$ peak is more than 3 eV above the spin-down HOMO. The MnPc molecule has a total magnetization of 3.0 $\mu_B$, resulting from the unbalancing of three orbitals ($e_{1g}$, $b_{2g}$ and $a_{1g}$) between the up and down components.

The small SOMO–LUMO gap, along with the presence in the same energy region of several molecular orbitals mostly localized on the metallic site, deserves further investigation in view of the strongly correlated character of the manganese atom. To this end, we improved the description of the electronic structure by including a Hubbard $U$ term on the central ion (DFT + $U$). We considered two cases, $U = 2.0$ and 3.0 eV; the results for the latter value are shown in figure 4(b). Due to stronger correlations effects, even the presence of small Hubbard potential strongly modifies the electronic properties of the system. We observe a general downward (upward) shift of the occupied (empty) Mn components in the density of states. The effect of the correlation is weaker for spin-up states, since the frontier orbitals have a predominant Pc character. In contrast, in the spin-down case the on-site e–e correlation increases the SOMO–LUMO gap, splitting the almost degenerate $e_{1g}$ peak with an energy separation that is a function of the applied $U$: $\Delta E = 0.39$ eV and 0.46 eV for $U = 2.0$ eV and 3.0 eV, respectively. The $2e_g$ duplet also splits into two separate contributions, as shown in figure 4(b).
The effect of the correlation on the $2e_g$ states is more relevant for the minority spin, because it includes a greater metallic contribution. The $b_{1g}$ and $a_{1g}$ states migrate towards higher energies, between the split $2e_g$ fork, changing the global order of the MnPc orbitals. Higher values of the local Hubbard term ($U > 3.0$ eV) do not lead to stable (converged) electronic structures, confirming that the results are very sensitive to the electron correlation model.

3.2.2. Device configuration. We modelled the double interface (Au$_5$S$_2$)MnPc as before in the case of the CuPc. The relaxed geometry does not present any new characteristics, while the DFT electronic structure (figure 5(a)) is more complex, due to the greater complexity of the MnPc molecule. While the Au component of the spectra is not particularly affected by the change of the metal atom, the molecular states display a complex reorganization. In the spin-up component, the molecule/metal coupling induces a broadening of the $a_{1u}$ state with the sd gold band in the energy range $E = [-1.0, -0.25]$ eV, and the splitting of the pristine doubly degenerate $2e_g$ peak into a molecular doublet, close to the empty $b_{1g}$ state. The spin-up HOMO and LUMO both have an sd character, derived from the gold chain, and are separated by an energy gap $\Delta E = 0.43$ eV, higher than the corresponding Cu case. The analysis of the single-particle orbitals shows that the spin-down HOMO has also a pure Au character, while the spin-down LUMO is a hybrid state, stemming from the mixing of the sd gold band and the $a_{1u}$ state of the phthalocyanine. The spin-down HOMO and LUMO are almost degenerate in energy, with a gap $\Delta E = 74$ meV (figure 5(a)). In the range $E \in [0.1, 0.5]$ eV we observe a manifold of states, which includes the two $e_{1g}$, the $b_{2g}$ and the $a_{1g}$ orbitals, each partially hybridized with the gold states. The split $2e_g$ and $b_{1g}$ peaks are recognizable at higher energies. The depletion of the spin-down $a_{1u}$ and $e_{1g}$ states, occupied in the gas phase (figure 4), leads to a further imbalance of $\sim 2$ electrons between the up and down components, with respect to the isolated molecule. This enhances the total magnetization up to $\mu = 4.79$ Bohr mag/cell, which may be justified in terms of charge transfer at the interface from the molecule towards the gold chain for the spin-down component.

This marked spin asymmetry is reflected in the transmittance spectra, as shown in figure 5(b). At the mean-field level, the spin-up component behaves as a semiconductor with a vanishing conductance at zero bias. In contrast, the non-negligible density of states at the Fermi energy (zero of the energy scale) in the spin-down component leads to a finite conductance $G_{dw} = 0.12 e^2/h$. If we compare the cases of Cu-Pc and Mn-Pc, we observe a distinctly different behaviour: in the case of copper the reduced spin imbalance modifies only slightly the almost degenerate conduction properties of the gold wires, leading to a better conductor (higher conductance) for both the spin channels, while for manganese the spin asymmetry along with an enhanced molecule/lead coupling changes the conduction properties of the Au wire as a function of the spin. This is a very remarkable result that suggests that the MnPc molecular device could work as a spin valve. If confirmed by experiments, this would open the way to a new generation of devices for molecular spintronics applications.

We have studied the correlated transmittance of the MnPc two-terminal device for two values of the Hubbard $U$ parameter ($U = 2.0, 3.0$ eV) in our 3BS scheme. The results for the correlated transport (straight and dashed lines in figure 5(b)) clearly show that in the region near the Fermi energy the transmittance is almost insensitive to the inclusion of the electron–electron correlation. In particular, the spin valve behaviour of the MnPc-based device is stable upon the inclusion of the e–e coupling, and only minor modifications at $E \in [-2.0, -1.0]$ eV are induced by the realignment of the lower-energy molecular orbitals, as in the case of CuPc system.

This result can be understood in terms of the electronic structure (figure 5(a)). The strong molecule/gold bonding leads to a removal of the Mn$_{14}$ states from the Fermi level to higher energies, while the only molecular components close to $E = 0$ eV are related to the aromatic Pc rings ($a_{1u}$), only slightly affected by the electron correlation. In other words, the short-range electron correlation truly affects transport when the simultaneous mixing of the delocalized states of the leads and the partially occupied states of the correlated conductor occurs at the Fermi energy [45, 46]. As a consequence, both Cu-Pc and Mn-Pc transmittances are almost unaffected by the e–e correlation.

4. Conclusions

In conclusion, we have demonstrated that a proper inclusion of electronic correlation effects is essential to develop a complete...
understanding of the electronic and transport properties of phthalocyanine-based nanostructures. Considering different forms for the exchange–correlation functional (LDA, PBE, DFT + U) in the standard DFT, as well as the inclusion of on-site correlation beyond DFT (3BS), we have proved that the inclusion of correlation reproduces the correct orbital sequence in CuPc, as observed in experiments. We should stress that our results are valid for the molecule in its ground state, so a comparison with experiments involving oxidized or reduced states of the molecule is not physically meaningful. Moreover, electronic correlations have clearly an even greater effect in the MnPc molecule, due to the open 3d shell of the manganese ion. We also do not exclude that other kinds of effect, such as those related to the Jahn–Teller distortions, might play an important role in the electronic properties of these systems, as proposed in the case of alkali-doped MPC crystals [56].

The transport properties of these M(II)Pc-based devices are less sensitive to the inclusion of electron correlation effects than the corresponding single-molecule electronic structures. The e–e interaction seems in fact to be partially quenched by the strong coupling with the uncorrelated gold leads. This might be important in other device configurations, where the molecule/lead coupling is different.

Finally, our electronic transport simulations have shown (irrespective of the details of the calculations) that M(II)Pc-based devices can act selectively as molecular conductors, as proposed (irrespective of the details of the calculations) that M(II)Pc-based devices can act selectively as molecular conductors, as proposed
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