Chapter 4

Silver Electrodes

There is currently strong interest in the preparation of atomic-scale devices and in the understanding of their electronic and transport properties. Techniques to form short and thick metal-atom wires has been discovered time ago\textsuperscript{97} and this has given great stimuli to their detailed study. However at the present there exist only three metals that are known to form atomic chains: Au, Pt and Ir\textsuperscript{98}. A good alternative is provided by carbon-based wires, such as nanotubes or graphene nanoribbons, covalently bound to metallic electrodes. Within this class, the simplest wires are linear carbon polymers, namely polyynes and cumulenes. In such molecules the cylindrical electronic delocalization along the conjugate backbone makes the electronic transport independent on the rotation around the single bond, which is a limitation often found in other aromatic oligomers.

The metal-chain-metal systems have been extensively studied, and a large number of papers theoretically address their geometrical, electronic and transport properties when contacted to metallic and carbon-based electrodes, often introducing linking atoms to enhance the stability of the contact, showing a number of nonlinear properties such as conductance switching and negative differential resistance\textsuperscript{11,21,99}.

However, experimentally it is difficult to precisely manipulate these systems or even measure their structure and transport properties. Therefore neither the influence of the atomic structure of the molecule-electrode contacts on electron transport through the device, nor a systematic way to improve their performances is clear.

Recently the first experimental transport measurements in monoatomic carbon chains have been reported, for both metal-metal\textsuperscript{75} and graphene-metal contacts\textsuperscript{77}. Measured conductances have been found to be much lower than the theoretically predicted ones and it has been argued that, in the carbon-graphene contact case, this is a consequence
of the residual strain in the chain which increases the bond length alternation, hence the bandgap. However it is worth underlying that the most common calculation method used to determine the conductance properties – the Non-Equilibrium Green’s Function method with Density Functional Theory hamiltonian (NEGF-DFT) – strongly underestimates the bandgap, resulting in an overestimation of the current.

Although several important issues have already been investigated, informations are very scattered and a well-rounded perspective of the key aspects affecting the electron transport is missing. This work represents one attempt to fill this gap first in the case of metal-chain-metal devices, then in the case of graphene-chain-graphene systems (see chapter 5).

First, we studied the binding properties of a number of one-side H-terminated molecules adsorbed on the Ag(100) surface, which we have chosen as electrode for the subsequent transport calculations.

Next, we investigated ballistic electronic transport for carbon chains of different length contacted to Ag(100) electrodes in the three high symmetry sites of the surface (top, bridge and hollow). In particular we will show that the Ag-C junction plays a central role in determining the strength of the electrode-chain coupling as well as the resonances position in the conductance spectrum. In fact qualitative different transport properties have been found depending on the chain adsorption site, while results show only a weak dependence on the chain length, for all but the smallest molecule considered (C$_2$) for which the transport occurs mainly by direct tunneling between the two electrodes. We will also show that the above results can be extended to ”tip-like” contacts, mimicking a more realistic electrodic surface.

Next, we also investigated the electronic and transport properties of the sulfur and silicon capped C$_4$ chain, chosen as representative of polyyne species, showing that the capping species strongly influence the conductance.

We further demonstrated that the vibrational motion of the atoms has negligible effects on the transport properties for a very large range of temperature, as a consequence of the stiffness of polyynes.

At last we also critically discuss the reliability of our results using the optical properties of the free molecules to benchmark the adopted functional.
4.1 Computational setup

Electronic structure calculations were performed at the Density Functional Theory (DFT) level, using the periodic, pseudopotential, self-consistent method implemented in the SIESTA package and the Perdew-Burke-Ernzerhof (PBE) functional to handle exchange-correlation effects. Core electrons were described by separable, norm-conserving pseudopotentials and a double-$\zeta$ plus polarization (DZP) set of atomic orbitals was used to expand the wavefunction.

Cut-off radii of the atomic orbitals were determined by setting the confinement energy to 0.02 Ry and an energy cutoff of 300 Ry was adopted for the real-space integration of the electron density.

A $2 \times 2$ supercell was chosen along the Ag(100) surface and Brillouin zone sampling was performed following the Monkhorst-Pack scheme using a $5 \times 5$ $k$-mesh for the self-consistent steps which was later increased to $10 \times 10$ for the determination of the transmission probabilities in the transport calculations.

In order to investigate the binding of carbon chains, a 4-layer Ag(100) slab was chosen to represent the silver surface. The two topmost layers were let free to optimize and a large vacuum layer ($\sim 15$ Å) was introduced along the surface normal between the free-end of the molecule and the repeated image of the slab in order to avoid interaction between the free termination of the chain and the image.

Geometry optimizations of chains connected to Ag(100) surface at both ends, were performed on a 9-layer Ag(100) slab, as shown in fig. 4.1. In this case, only the electrode layers (two for each electrode) and an additional buffer layer, introduced to ensure proper boundary conditions, were kept frozen in the optimization step.

Transport calculations were performed self-consistently using the TranSIESTA code which exploits the Non-Equilibrium Green’s Function approach to the open-system transport problem (explained in details in chapter 3).

FIGURE 4.1: Supercell used in transport calculations. The buffer Ag layer added in optimization calculations to ensure proper periodicity of the cell is shown in light grey, the electrode layers in dark grey and the two topmost layers included in the scattering region in intermediate grey.
Spatial features of electron transport were analyzed with the help of transmission eigen-channels, \( i.e. \) the eigenvectors of the current operator in the scattering-region subspace of the left-incoming scattering states, calculated by means of the INELASTICA package\(^{101-103}\). Eigenchannels are a very useful tool providing an intuitive understanding of the electron transport, since they allow to obtain a spatially resolved picture of the molecular orbitals extended on the whole scattering region which hold the transport process.

Moreover, Crystal Orbital Hamiltonian Population (COHP) and Crystal Orbital Overlap Population analysis (COOP) have been used in order to better understand the electronic structure of the systems investigated. COHP/COOP\(^{104}\) are valuable tools to obtain information difficult to extract from density of states (DOS) and projected density of states (PDOS). Both COOP and COHP are partitioning methods for analyzing the (\(k\)-dependent) wavefunction. While COOP partitions the electron number, COHP partitions the band structure energy in orbital-pair interactions, allowing to determine their bonding or antibonding contribution. As a consequence, integration of a COOP curve allows to obtain a number of electrons (like in the Mulliken scheme), while integration of a COHP curve allows to get an energy values that hints toward the bond strength.

### 4.2 Adsorption on Ag(100) surface

We first investigated the adsorption of \(-\text{C}_n\), \(-\text{C}_n\text{H}\) and \(-\text{C}_n\text{H}_2\) radical species on the ideal Ag(100) surface (see fig. 4.2), that has been used as electrodic surface in the transport calculations.

We computed the binding energies, defined as:

\[
E_b = E_C + E_M - E_{MC}
\]  \hspace{1cm} (4.1)

where \(E_C\), \(E_M\) and \(E_{MC}\) are the energies of the radical, of the clean metal surface and of the adsorbed chain-surface system, respectively, for chains of several length adsorbed in the three highest symmetry sites of the silver surface, namely the top, the hollow and the bridge (shown in fig. 4.2). Vibrational analysis performed on a few selected cases showed that the hollow, bridge and top structures have zero, one and two imaginary frequencies, as expected. Hence, the hollow site results a stable position on the potential energy surface, while the bridge and top turn out to be a first- and a second-order saddle point, respectively.
The computed binding energies, shown in fig. 4.3, evidence a larger stability of the hollow adsorbed chains, followed by the bridge and the top ones, for all the molecular species considered. This strongly correlates with the coordination number between the terminal carbon atom of the chain and the surface (i.e. with the number of Ag-C bonds, 1, 2 and 4 for the top, bridge and hollow cases, respectively): the higher the coordination number the more stable the chain adsorbed system.

The high values of the binding energies are typical of formation of a localized $\sigma$ (covalent) bond between the ending C atom of the chain and the metal and, accordingly,
Figure 4.4: Left panel: bond length alternation of gas-phase \(-\text{C}_{11}, \ -\text{C}_{11}\text{H}, \ -\text{C}_{11}\text{H}_2\) and and \(\text{HC}_{11}\text{H}\). Right panel: as left panel for gas-phase \(-\text{C}_{12}, \ -\text{C}_{12}\text{H}, \ -\text{C}_{12}\text{H}_2\) and \(\text{HC}_{12}\text{H}\).

Figure 4.5: Bond length alternation of \(-\text{C}_{12}\text{H}\) adsorbed on top, hollow and bridge site and of the gas-phase \(\text{HC}_{12}\text{H}\) molecule.
depend only weakly on the chain length.
Furthermore we found that at the most stable hollow adsorption site all radicals show binding energies of similar magnitude and a significative odd-even atom number oscillatory behavior. -C\(_n\)H\(_2\) species are on average ~0.5 eV less stable than -C\(_n\)H ones, with an opposite alternating trend in the length dependence (that is, with odd chains favored over even ones), whereas -C\(_n\) species show a trend similar to -C\(_n\)H ones and a more marked alternation.
An accurate examination of the electronic structure reveals that these binding properties are strictly related to the gas-phase structure of the molecules. To better explain the results it is useful to introduce the bond length alternation parameter, BLA\(_k\), defined as the difference between the lengths (\(d\)) of two consecutive bonds \(k\) and \(k - 1\):

\[
BLA_k = |d_k - d_{k-1}|
\]

The BLA of C\(_{11}\) and C\(_{12}\) radicals along with the BLA of both-ends H-terminated chains are shown in fig. 4.4. As is evident, even HC\(_n\)H molecules turn out to be polyynic, with a more marked cumulenic character towards the center of the molecule due to the reduced influence of the terminations. Similar behavior features odd chains, but with a more marked cumulenic character (lower BLA). All the radicalic species show a more marked cumulenic character, compared with such molecules, especially in even members.

From the analysis of the electronic structure, it turns out that odd C\(_n\) chains couple the unpaired electrons in lone pairs on the terminal carbons of the chain (\(\vdash C = C = C = C = C\vdash\)), while even C\(_n\) localizes one unpaired electron on each ending-C resulting in undercoordinated terminal carbons (\(\vdash C - C \equiv C - C\vdash\)) and in a more polyynic BLA, but inverted with respect to HC\(_n\)H. This explains the higher stability of odd C\(_n\) chains in the gas phase, i. e. the lower binding energies.

Even -C\(_n\)H chains show a lower stability in the gas phase with respect to the odd members, as a consequence of the lower capability to delocalize the unpaired electrons throughout the backbone. In fact even chains feature cumulenic BLA at the non-hydrogenated end that rapidly evolves into polyynic after two bonds, suggesting a structure like :C = C = C\(\equiv\)C - C \equiv C - H, whereas odd chains become polyynic more slowly.

Opposite is the behavior of C\(_n\)H\(_2\), showing a more cumulenic BLA for even members (\(\vdash C = C = C = CH_2\)), while the more polyynic character of odd chains suggests that the unpaired electrons are more localized on the chain end. Thus, in this case, the adsorption of the less stable odd chains results favored.
The formation of the metal-carbon bond strongly influences the structure of the chain, giving it a more cumulenic character at its contacted end. The BLA of the \(-\text{C}_{12}\text{H}\) chain adsorbed on the three above mentioned sites is shown in fig. 4.5. The BLA of the gas-phase H-terminated \(\text{HC}_{12}\text{H}\) molecule is also reported for comparison. As is evident from this figure, in the gas-phase molecule the BLA decreases (the cumulenic character increases) from the molecule ends to the middle, whereas the BLA progressively decreases from the H-terminated to the opposite end when a metal-carbon contact is formed. The BLA also shows an increasing polyyenic behavior (higher BLA) in the sequence hollow < bridge < top.

The strength of the chain-surface coupling is determined by two contrasting effects: the number of Ag atoms coordinating the ending carbon of the chain and the C-Ag bond length. The number of C-Ag bonds decrease in the order hollow > bridge > top, while the bond length increases in the reverse order (2.01 Å for top, 2.13 Å for bridge and 2.31 Å for hollow). However, in the next section it will be shown that the chain-silver coupling mainly relates to the coordination number. This establishes an important relation between the structure of the chain and the binding energies, as well as it plays a central role in determining the transport properties.

### 4.3 Adsorption process of \(\cdot\text{C}_8\text{H}\)

In this section we describe more in details the adsorption process of one-end H-terminated chains on the Ag surface, focusing on the evolution of the electronic energy levels and of the metal-molecule interactions as well as eventual electron transfer between the radical and the surface. To this end we studied the changes of the electronic structure of \(-\text{C}_8\text{H}\) species, taken as a representative member of the \(-\text{C}_{2m}\) chains, along an adsorption path. Few changes in the computational setup have been necessary in order to correctly describe the systems at large molecule-surface separation. In particular, for the calculations described in this section, we used (i) a cell with an increased vacuum region above the Ag surface (40 Å), (ii) the self-consistent dipole correction and (iii) an additional layer of Ag atoms. Such expedients prevent artificial charge transfer to occur at large molecule-surface distances.

The \(\text{C}_8\text{H}\) molecule has been moved at different heights \(\Delta z\) (1, 2 and 3 Å) above the surface and the geometry has been relaxed keeping fixed the position of the chain atom closest to the surface only. A summary of the changes in the electronic structure accompanying adsorption at a hollow site is shown by Fig. 4.6, which compares the
Figure 4.6: Evolution of the Ag-C₈H electronic structure along an adsorption path to the stable hollow position. From bottom to top results refer to the optimized structure, and to structures which are shifted upwards by Δz = 1, 2 and 3 Å. Left panels: PDOS (per atom) on the surface Ag(4d) and Ag(5s) orbitals, on the π orbitals of the chain and on the σ orbital of its unsaturated C end. Results have been vertically shifted for clarity and portrayed for spin majority (upper curves) and spin minority (lower curves) components as usual. Middle panels: COHP curves for the interaction between the σ orbital of the unsaturated C-end of the chain and the 5s and 4d orbitals of the Ag(100) surface. Right: same as in the middle panel for the π orbitals of the chain.

Projected Density of States (PDOS) and the Crystal Orbital Hamiltonian Population (COHP) curves, from bottom to top for increasing height of the molecule above the surface. PDOS (per atom) are given in the left panel for the top-most Ag atoms closest to the molecule, and both for the σ (i.e. C(2s,2p_z)) orbital of the ending binding carbon and for the π orbitals of the chain.

Well above the surface, the molecular energy levels closely resemble those of the isolated radical species and feature four, doubly degenerate π states below the Fermi level describing the occupied π orbitals (see fig. 4.8). With the same token, in the energy range displayed in Fig. 4.6, only a sharp σ peak appears, ~0.6 eV below the Fermi
level, which should represent the partially occupied $\sigma$ state hosting the unpaired electron. A number of peaks appear at much lower energies ($\lesssim -10$ eV) arising from the other $\sigma$ states which spread over the chain.

Integration of the PDOS up to the Fermi level, though, reveals that when the molecule is far from the surface one electron is transferred from the $\pi$ orbitals to the $\sigma$ one, confirming the results described in the previous section from BLA analysis. Indeed the DOS projected on the $\sigma$ orbitals of the terminal C atom integrates to three electrons (one more than expected for a radical with an unpaired electron in a $\sigma(sp)$ state and a $\sigma$ bond with the neighboring C atom), whereas the projection on the $\pi$ states of the whole chain integrates to 15 electrons.

When the molecule gets closer to the surface the energy level broadens and shift downwards in energy because of hybridization with Ag orbitals. Such hybridization is particularly relevant for the $\sigma$ state, as expected, but is substantial also for the $\pi$ states. The latters, of course, are those involved in charge transport, hence $\pi$-hybridization, even
though less dramatic than its $\sigma$ case, has a major effect in the transport properties of the junction. The changes in the electronic structure of the surface closely parallel the above results. In particular, the Ag(5s) peak (the projection of the $s$ band on the surface atoms) widens and finally disappears when the metal-molecule bond is formed, but also the Ag(4d) projection broadens and shifts downwards in energy, indicating a favorable interaction with the molecular levels.

To better detail the hybridization process, we analyzed four different kinds of COHP curves: $C(\sigma)/\text{Ag}(5s)$, $C(\sigma)/\text{Ag}(4d)$, $C(\pi)/\text{Ag}(5s)$ and $C(\pi)/\text{Ag}(4d)$, where only the carbon atom involved in the bond formation process has been considered. The middle and right panels of fig. 4.6 show, respectively, that hybridization is strongly bonding for $E \lesssim -4$ eV for both the $\sigma$ and the $\pi$ orbitals of the C atom at the chain end, and moderately antibonding at higher energies, due mainly to the antibonding hybridization with Ag(4d) orbitals established by both $\sigma$ and $\pi$ states.

We performed a similar analysis for adsorption of C$_8$H at bridge and top sites. A comparison of the electronic structures obtained is reported in fig. 4.7 (hollow, bridge and top binding from bottom to top). The PDOS reported on the left panels clearly indicate an increasing interaction ($i.e.$ broadening and shifting of the molecular resonances) in the order top < bridge < hollow while the COHP curves (middle and the right panels) make evident that, while hybridization of the $\sigma$ orbitals in similar in the three cases, hybridization of the $\pi$ states is of increasing magnitude along the same sequence. Specifically the antibonding $C(\pi)$-Ag(5s) interaction, which is maximum for adsorption at the hollow site and vanishes for adsorption in top, mainly determines the different behavior for the three adsorption sites.

![Figure 4.8: Electronic structure of $\pi$ orbitals of gas-phase even polyyne (left), odd polyyne (right)]
4.4 Zero-bias properties

We computed the zero-bias transmission function for chains from $C_2$ to $C_{12}$ contacted with silver electrodes and adsorbed in the top, hollow and bridge sites. These results are plotted in fig. 4.9 (hollow) and 4.10 (top and bridge). All transmission spectra show a number of resonances, each one describing the transmission of electrons through a specific electronic states of the electrode-chain-electrode device. Consequently the transmission closely resembles the Density of States (DOS) and in the following we implicitly assume a relationship between the resonances in the transmission spectrum and the electronic states provided by the DOS. These electronic states derive from the hybridization of the molecular orbitals of the chain with the electronic bands of the metal, thus are delocalized on the whole junction and can act as conduction channels.

With the assumption (justified a posteriori) that the coupling with the leads is strong enough to make coherent transport regime adequate to describe the electron transport, but not so strong to lose the identity of the molecular orbital originating the conducting state in the DOS, the above mentioned electronic states can be nicely related to the energy levels of gas-phase $HC_nH$ molecule. Of course the coupling with the electrodes deeply affects these energy levels, that are broadened and shifted downwards in energy as the molecule gets closer to the Ag(100) surface along an adsorption path. The natural consequence is that the transmission function strongly depends on the adsorption site, thus the electrode-chain junction plays a key role in determining the transport properties.

In particular it appears evident that the magnitude of the broadening of the resonances increases in the order top $< \text{bridge} < \text{hollow}$ (from about 0.2 eV to about 1 eV for $C_{12}$), suggesting that the chain-electrode coupling is related to the coordination number of the terminal carbon of the chain. This also confirms that the Ag-C bond strength increases in the same order, despite of the bond length reduction. In the previous section we have shown that an accurate analysis of the electronic structure revealed that the broadening of the $\pi$ resonances has two contributions, one almost site-independent due to $C(\pi)$-Ag(4d) interactions and one due to $C(\pi)$-Ag(5s) hybridization which markedly decreases in the order hollow $> \text{bridge} > \text{top}$, and which is therefore responsible of the different behavior of the adsorption sites.

Another important quantity influencing the transport properties is the charge transfer between the chain and the electrode that results in a doping effect, increasing or decreasing the carrier density of the chain. In our case, only a little charge-transfer occurs when
establishing the contact. Mulliken population analysis shows that electronic charge is transferred from the leads to the molecule and is of the order 0.2-0.3 $|e|$ for top and bridge geometries and $\sim$0.5 $|e|$ for adsorption in hollow position. Such excess charge however does not spread uniformly over the molecule and mainly locates at the contact atoms, which become slightly negatively charged (0.1-0.2 $|e|$ each), generating a small Schottky barrier at the junctions.

The transmission at the maxima of the resonances approaches the maximum value allowed by a $\pi$-conjugated wire with cylindrical symmetry (4, due to degeneracy of $\pi$ states and the spin), indicating that the degeneracy of the $\pi$ states is effectively preserved in the metal-molecule system. An exception is the bridge case, where a reduction of the symmetry (from $D_{4h}$ for hollow and top to $D_{2h}$) implies that the two $\pi$ states differently interact with the electrode, resulting in a slight splitting and in the consequent decreasing in magnitude of the resonances.

From the analysis of the eigenchannels, i. e. the “extended molecular orbitals” of conduction, we can unambiguously confirm that the peaks in the transmission spectra correspond to the molecular orbitals of the polyyne coupled with the electrodes. In particular, for all chains, those closer to Fermi level can be assigned to the HOMO (Highest Occupied Molecular Orbital) and the LUMO (Lowest Unoccupied Molecular Orbital) of the isolated molecule. For hollow-adsorbed C$_4$ chain, these two states strongly overlap, leading to high transmission values across the Fermi level region, whereas with the increasing of the chain length, and the consequent narrowing of the resonances, the transmission at the Fermi level decreases. From C$_8$ chain, also the $HOMO_{-1}$ and the $LUMO_{+1}$ peaks are clearly visible in the transmission spectra in the energy regions [-2, -3] eV and [2, 3] eV, respectively.

The eigenchannels of the hollow-adsorbed C$_{12}$ and and the corresponding molecular orbitals of gas-phase HC$_{12}$H are shown in fig. 4.9. From low to high energies these correspond to $HOMO_{-1}$, $HOMO$, LUMO and $LUMO_{+1}$.

Concerning the chain length dependence, the transport properties are similar for all even chains but the shortest (C$_2$), for which the transport is mainly dominated by direct tunneling between the electrodes, as a consequence of their closeness. This point will be investigated in details in the next section.

For C$_4$-$C_{12}$ chains the width of the resonances decreases when increasing the chain length, especially for the lowest energy one above the Fermi level. This effect is more

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*A good way to compare the eigenchannels with the molecular orbitals of the free molecule is to count the number of nodes along the chains. In general for a chain of $N$ atoms, the HOMO shows $(N/2) - 1$ nodes for even chains and $(N - 1)/2$ for odd chains. The LUMO features $N/2$ nodes for even chains and $(N + 1)/2$ for odd chains.*
Figure 4.9: Transmission function for even chains from \( C_4 \) to \( C_{12} \) in a hollow site. Above the plot, the eigenchannels (black boxes) of the \( HOMO_{-1} \), \( HOMO \), \( LUMO \) and \( LUMO_{+1} \) resonances for \( C_{12} \) chain and the corresponding molecular orbitals (red boxes) for the gas-phase \( HC_{12}H \) chain are reported.

Evident for short chains and is due to the decreasing amplitude of the molecular orbital on the wire ends when increasing the chain length. For instance this is particularly clear for the \( LUMO \) resonance of hollow-bound chains, whose width decreases from \( \sim 2.2 \) eV (at half maximum) for \( C_4 \) to \( \sim 0.8 \) eV for \( C_{12} \). In top and bridge cases, the reduction of the resonance widths by increasing the chain length is less marked due to the weaker
Figure 4.10: Transmission function for even chains from C₄ to C₁₂ in a top (top plot) and bridge (bottom plot) site chain-electrode coupling.

The resonances also slowly approach the Fermi level, as a consequence of the reduction of the \textit{HOMO} – \textit{LUMO} gap, due to the increased delocalization (\(\pi\) conjugation) of the
chain, much like in the gas-phase HC\textsubscript{n}H molecules. This is particularly evident for the LUMO resonance of top-bound chains, shifting from $\sim$3.5 eV for C\textsubscript{4} to $\sim$1.8 eV for C\textsubscript{8}.

Completely different is the behavior of odd chains. We computed the transmission of C\textsubscript{5} molecule, chosen as representative member of the series, as shown in fig. 4.11. The H-terminated gas-phase molecule is a radical and the two unpaired electrons half occupy the HOMO $\pi$ pair (see fig. 4.8). This gives rise to a resonance at the Fermi level in the transmission spectrum, slightly shifted downwards in energy in the hollow and bridge cases as a consequence of a significative charge transfer (about 0.4 and 0.2 |e| respectively) from the electrode to the chain, partially filling the HOMO energy level. As a consequence of the higher DOS at the Fermi level we expect that odd chains give higher currents with respect to even chains for reasonable small bias.

As in even chains, this resonance is differently broadened depending on the adsorption site, in the order top $<$ bridge $<$ hollow, but results significantly wider ($\sim$0.5 eV in top and bridge and $\sim$1 eV in hollow) with respect to the corresponding HOMO resonance of C\textsubscript{4} or C\textsubscript{6}. This is a direct consequence of the increased amplitude of the HOMO orbital at the C\textsubscript{5} chain ends, where the unpaired electrons are mainly located. Less clear is the behavior of HOMO\textsubscript{−1} (between -2 and -3 eV) and LUMO (between 2.3 and 3.3 eV for bridge and hollow cases) that result largely narrowed if compared to the corresponding ones of even chain with similar number of atoms.

At considerably small bias voltage applied, different transport mechanism can be predicted from the transmission spectra depending on the adsorption site and the parity of atom number. Odd chains necessarily features a mixed (both $p$- and $n$-type) mechanism, as a consequence of the partially empty state at the Fermi level, for all adsorption sites.
In even top- and bridge-bound chains the main mechanism is of \( p \)-type (the HOMO is closer to the Fermi level than the LUMO), while for hollow-bound ones of \( n \)-type.

### 4.5 Through-space tunneling

The transmission for the \( \text{C}_2 \) chain adsorbed in the hollow, top and bridge site is shown in Fig. 4.12. It can be easily noticed that, especially in the hollow site, the transmission is one order of magnitude larger than that found for longer chains, thus much higher than the maximum allowed values predicted for polyynes. This suggests that a different transport mechanism takes place in this case. In fact \( \text{C}_2 \) is sufficiently small that direct tunneling between the two electrodes can occur. In this “through space” conduction (as opposite to “through molecule”) the chain mainly acts as a spacer between the electrodes, controlling the width of the tunneling barrier, hence the conductance.

In order to confirm this transport mechanism we performed transport calculations similar to those mentioned above but without the chain, for several values of the distance between the electrodes (defined from the position of the atoms in the top-most layers). The results of such calculations are reported in Fig. 4.13, along with the results for \( \text{C}_2 \) adsorbed in hollow, bridge and top positions. As can be seen from that figure, \( \text{C}_2 \) introduces small modifications in the transport properties of the “empty” junction. The conductance mainly depends on the distance between the electrodes and is larger for \( \text{C}_2 \)
adsorbed at hollow sites because of closeness of the electrodes allowed by this configuration. Notice that at the distance of \( \sim 3.2 \, \text{Å} \), as appropriate for hollow-adsorbed \( \text{C}_2 \), the conductance is about 4 for the \( 2 \times 2 \) electrode configuration considered in the simulation cell, i.e. almost twice the maximum value expected for a degenerate conduction channel due to the chain but consistent with one non-perfectly conducting channel per Ag atom of the leads.

Notice also that tunneling effects occurs up to a distance of 5.7 Å, thus also conduction of top- and bridge-bound \( \text{C}_2 \) is slightly affected by this transport mechanism \( (d \sim 5.3 \, \text{Å}) \). This can also be observed in fig. 4.12, where the magnitude of the top \textit{HOMO} resonance is higher than 4 (for bridge case the effect of the tunneling is “hidden” by the slight splitting of such resonance). The shape of the curve in fig. 4.13, however, does not show the exponential decay of the transmission probability between the surfaces expected in common tunneling models\(^8\). In particular, at the shortest distance, the tunneling is slightly reduced by the hybridization of the valence orbitals of the leads (the equilibrium Ag-Ag distance in bulk Ag computed with our set-up is 2.92 Å).

An accurate analysis of the electronic structure suggests that the small decrease of the conductance in the presence of the chain is due to the reduction of the contribution of the Ag orbitals involved in the formation of the Ag-C bond.

The tunneling also affects, to a lesser degree, the transmission of hollow-bound \( \text{C}_3 \), where the electrode are distanced by \( \sim 4.6 \, \text{Å} \), featuring a transmission value at the Fermi level of about 5.

![Figure 4.13: Zero bias conductance (in units of \( G_0 = 2|e|^2/h \)) in the absence of any molecular linker as a function of the distance between the electrodes. Also shown for comparison the zero-bias conductance for \( \text{C}_2 \) bound in a top, hollow and bridge site.](image-url)
4.6 I-V characteristics

In this section we examine the results of the non-equilibrium transport calculations whereby the carbon chain is contacted with two electrodes at different chemical potentials. In principle, the transmission function depends on the bias applied, but in practice we found a negligible dependence, as shown in fig. 4.14, featuring the transmission functions for hollow adsorbed C\textsubscript{12} chain for biases in the range 0-2 V. Specifically we observed only a general slight shift of the resonances at higher energies and a reduction of the magnitude of the \textit{LUMO}+1 peak (at \~{}2 eV) for the highest bias considered. For this reason the current necessarily increases (or, at most, remains constant) by increasing the bias voltage.

We further calculated the differential conductance, defined as the (discrete) derivative of the current with respect to the bias:

\[ G(V_{SD}) = \frac{\Delta I}{\Delta V_{SD}} \]  

(4.3)

A comparison of the I-V characteristics of C\textsubscript{12} at top, hollow and bridge sites and the corresponding differential conductances are shown in fig. 4.15, while I-V characteristics and conductances for hollow-adsorbed chains of several lengths are reported in fig. 4.16.

The results obtained for the different adsorption sites reflect the transmission function reported in figg. 4.10 and 4.9, with the hollow-adsorbed C\textsubscript{12} providing the highest current.
and conductance, whereas similar values are obtained for top and bridge cases. We found a linear (Ohmic) behaviour, thus a nearly constant differential conductance, in a rather large voltage window, say up to $\sim 1.5$ V, for $C_{12}$ adsorbed at the hollow, bridge and top sites. For higher bias top and bridge currents start deviating from the linearity since the $HOMO$ resonance starts being included in the bias window, while in the hollow case such resonance is farther from the Fermi level, resulting in an Ohmic behavior also above 1.5 V. The current for chains adsorbed at the stable hollow position
again linearly increases as a function of the chain length in the whole bias window considered, showing only a little dependence on the chain length. In particular the current slightly decreases from C_4 to C_{12}, as a consequence of the narrowing of the resonances with the increasing of the chain length. However at higher bias (> 2 V) the current is expected to increase in the opposite sequence, as a consequence of the reduction of the gap between HOMO and LUMO resonances. The C_2 case is clearly at odds with the general behavior of even-numbered chains. As discussed at length in the previous section, the transport is dominated by tunneling effects, providing a current about 3-4 times larger than C_8. Finally, the results of C_5 are also reported in fig. 4.16. As previously discussed the transmission function features a peak close to the Fermi level due to the approximate electron-hole symmetry of the junction (i.e. a partially filled electronic state) and this results in a conductance sensibly higher than that found for even-numbered chain. The same holds for any odd-numbered chain and gives rise to an odd-even parity oscillation of the conductance. Such behavior does not depend on the polyynic or cumulenic character of the chain, even though in our calculations results particularly marked because the chains turn out to be polyynic for n even and cumulenic for n odd.

### 4.7 Anchoring groups

In this section we will show that the conductance of a carbon chain connected with the electrodes by means of anchoring groups is fundamentally different with respect to that of a direct chain-electrode contact.

Of course, the choice of the anchoring group, often dictated by practical reasons, such as ease of chemical synthesis or junction stability, strongly affects the coupling strength (i.e. the degree of the hybridization) between the molecule and the leads. This in turn crucially modifies the chemical stability of the device as well as its transport properties by influencing the amount of charge transfer at the junction and the final energy level alignment, i.e. the relative positions of the electronic states with respect to the Fermi level.
One of the most common chemical anchoring species is thiol, which is known to readily bind gold and silver surfaces. In particular one-side sulfur ending organic and bioorganic molecules find applications in many areas of nanoscale research especially for their ability to form ordered self-assembled monolayers, but their potential use in molecular electronics has also been investigated. For example several experimental studies\textsuperscript{105–108} on 1,6hexandithiol and 1,8octanedithiol reported conductance values in the ranges $[1.2 \cdot 10^{-3}, 3.2 \cdot 10^{-5}] G_0$ and $[1.3 \cdot 10^{-5}, 2.5 \cdot 10^{-4}] G_0$, respectively, although the details of the junction geometry and mainly the number of wired molecules are not clear.

Recent developments have also explored the possibility of binding directly a carbon backbone to gold electrodes\textsuperscript{109}, effectively forming an Au–C bond at each end. Different backbones have been tested, the first being a series of alkanes ranging from buthane to dodecane, showing conductance values significantly higher than the corresponding thiol or amine terminated alkanes with an identical number of CH\textsubscript{2} units. Also comparing wires with the same number of atoms\textsuperscript{110} (\textit{i.e.} considering the terminal carbons as...
anchoring atoms), thiols show a conductance 3-4 times lower than the directly bound alkene.

Here, we considered two different kinds of capping atoms: sulphur, because of its well-known affinity with many transition metal surfaces, and silicon, because of its formal similarity to carbon and its widespread use in much of the nanotechnology devices.

We investigated only capped C₄ chain (see fig. 4.17), chosen as representative member, since we expect a behavior similar to that of sulfur-capped chains contacted with gold electrodes as a function of the chain length, already reported in literature. Specifically, calculations of the conductance of S-capped cumulenes highlighted an even-odd oscillation between constant value characteristic of odd and even number of atoms of the chain. As opposite, no odd-even oscillations and conductance values of one order of magnitude higher than any other conducting polymers have been found for S-capped polyynes.

In the presence of the above mentioned capping species, the hollow position remains the most stable site for adsorption. For S-C₄-S, adsorption at a hollow site is about 1.9 (1.6) eV more stable than at a top (bridge) position, while with silicon the corresponding energies are ~1.7 and ~3.7 eV, respectively.

The transmission spectra of S-capped C₄ adsorbed on the top, bridge and hollow position of the ideal Ag(100) electrode surface are shown in fig. 4.20 along with the results of C₄ without capping species.

The presence of the sulfur atom at the ends of the chain has dramatic effects on the transmission. The top SC₄S spectrum features four sharp resonances, the closest to the Fermi level at -1.9 and -0.06 eV, while the bridge-bound chains three well-separated resonances at -1.8, -0.9 and -0.05 eV. The hollow spectrum shows two relevant resonances at -2 and -0.55 eV, partially overlapping as a consequence of the broadening.

As is evident, the general effect of the linking atom is to considerably narrow the resonance peaks, especially for adsorption at the top and bridge sites, and to reduce the effect of the adsorption site, as can be seen by the close similarity of the transmission functions for both-end S-capped C₄. Remarkably, the resonance peaks shift and get closer to the Fermi level, analogously to what happens for S-capped polyyynes contacted with gold electrodes. However the width of the resonances (and then the coupling) reflects the results of C₄ without capping, increasing in the order top<bridge<hollow both for the increasing of the coordination number and the decreasing of the S-Ag bond length (see fig. 4.18).

A closer look at the optimized structures also reveals that SC₄S adsorbed in top or in

---

In sect. 4.10 we will show that results with Ag and Au electrodes are almost qualitatively comparable.
bridge position has a reduced BLA between C atoms matching that found for C₄ adsorbed in hollow position (~3 pm). On the other hand, such BLA is smaller than that found in SC₄S adsorbed at the hollow sites and in C₄ adsorbed either in a top or a bridge position (~ 10 pm). This suggests that when S binds either on a top or on a bridge site the S-C bond is close to be double (~ 1.61 Å vs ~ 1.69 Å for hollow) justifying the increased cumulenic character of the chain.

An accurate electronic structure analysis of the capped and the uncapped chain shows that additional π peaks appear in the DOS of the capped molecule, confirming that sulphur atoms effectively increase the length of the conjugated chain. Nominally, each sulphur adds four π electrons to the system, that are expected to fill two π states. Instead, integration of the sulphur PDOS reveals that the σ states host three electrons, i.e. one more than expected for a thiole-like atom Ag-S-C-. This is not due to the hybridization being different from sp, because the molecule remains linear in these structures and the σ – π orbitals are well defined. Rather, this is due to a charge transfer from the π to the σ states, which makes sulphur to behave as Ag :S-C-. leaving a hole (for each sulfur) in one of π states. This generates an electron-hole symmetry in the electronic structure, giving rise to the resonance at the Fermi level.

Analysis of the Mulliken population shows that a small charge transfer occurs from the electrodes to the S atoms, becoming slightly negatively charged (~0.1 |e| each) while the carbon chain is essentially neutral. Thus the charge transfer does not play an important role in determining the position of the resonance in the spectrum.

Since the current flowing at small biases is essentially determined by the density of states around the Fermi level, we expect a current increasing in the sequence top-bridge-hollow, as opposite of C₄ without capping. Moreover, we expect I-V characteristics showing large plateau alternated with rigid steps, each one deriving by the inclusion of one electronic state within the source-drain bias window.

We also considered the case of the one-end sulfur capped C₄ adsorbed in the hollow position, whose transmission spectrum is shown in fig. 4.20. As expected C₄S shows intermediate properties between C₄ and SC₄S both concerning the geometry (S-Ag and C-Ag bond lengths are very close to those of SC₄S and C₄ adsorbed in the same position) and the transport properties. Indeed the transmission spectrum features a narrowing and a shift of the resonances upwards in energy not marked as in SC₄S. We also computed the I-V characteristics of C₄S. A comparison with the C₄ one is reported in fig. 4.19 and shows a reduction of the current of about 60% for the S-capped C₄, as a consequence of the overall reduction of the transmission probabilities, in good agreement with the previous mentioned results for gold electrodes appeared in literature.
Chapter 4. *Silver Electrodes*

At last we studied the transport properties of Si-capped C₄ chain at the top, hollow and bridge sites, whose transmission spectra are reported in fig. 4.21.

In this case the results are less clear, apart from a general broadening of the resonances, which is mainly related to a sizeable antibonding interaction between the Si(\(\pi\)) orbitals and the 4d orbitals of the metal, with an additional, significant bonding contribution from Ag(5s) orbitals when adsorption proceeds in a hollow site.

Also in this case the hollow SiC₄Si spectrum shows the wider resonances, in particular a large peak in the Fermi level region (containing contributions from both the *HOMO* and the *LUMO* of the molecule, from eigenchannels analysis) merges with another resonance at 2.5 eV (due to the *LUMO*\(_{+1}\)), forming a high transmission region from -1 to 3 eV. The top case spectrum features the same (better resolved) resonances in such energy range. Particularly unclear is the behavior of bridge-bound SiC₄Si, showing not well recognizable resonances above -1 eV, other than a sharp resonance at about -2.2 eV originating by *HOMO*\(_{-1}\) state (also found in hollow and top spectra at similar energies).

The optimized structures show an increased cumulenic character in the sequence hollow-bridge-top (see fig. 4.18), with a BLA between C atoms of the order 8-4-1 pm, respectively.

Analysis of the Mulliken populations reveals a little overall charge transfer from the leads to the molecule (\(-0.1|e|\)) which however is unequally shared between the anchoring groups and the molecule: the first gain 0.3-0.4 \(|e|\) per atom and the latter is slightly positively charged (\(-0.5|e|\)). Thus silicon-capped chains are expected to show higher values of Schottky barriers with respect to sulfur, *i.e.* to cause a more rapid potential drop at the junctions.
Figure 4.20: Transmission function of C₄ with and without sulfur linking atoms.
4.8 Tips

In the previous sections we considered carbon chains adsorbed on the ideal Ag(100) surface, used as a rather simplified model for the electrodes. A more realistic Ag electrode is never perfectly flat, but always features local surfaces discontinuities, such as line defects, pores, terraces or tips, that can alter the transport properties of the device. Moreover such defects are in general more reactive than the clean Ag(100) surface, then can be expected to be the preferential sites for adsorption of molecules.

In particular in this section we consider different “tip-like” contacts, showing that the results obtained so far can be, almost qualitatively, translated to more realistic junction geometries.
We investigated the transport properties of C₄ chain contacted with the four different tips shown in fig. 4.22. Two of these feature a top-like contact, whereby the chain binds to a Ag atom placed on a hollow site, either on the ideal (100) surface (A) or on four-atom “terrace” (B), forming a 5 Ag atoms tip. The remaining exhibit binding to either at the center of a four-atom cluster terrace (C), mimicking the binding in a hollow site, or a Ag dimer (D), mimicking a bridge-like contact, both deposited on the flat (100) surface.

The results of these calculations are shown in fig. 4.23, also compared with the results of the ideal electrodes, namely top-adsorbed C₄ for cases (a) and (b), bridge for (c) and hollow for (d).

As is evident from fig. 4.23 the tip geometry have no dramatic effect on the overall appearance of the transmission spectra, but minor influences on the position and the width of the resonances. The geometrical characteristics of the chain and of the Ag-C bonds result almost unchanged for all tips, with respect to binding on Ag(100) surface, thus modifications of the transmission are due only to the tip geometry.

First, the spectra feature a general narrowing of the resonances, particularly for tip (B), due to some “incomplete” binding to the leads occurring in tip-like contacts, compared to the ideal case. However HOMO and LUMO resonances show contrasting behaviors for bridge- and hollow-like tips, the first narrowing, the second widening probably as a consequence of an increased hybridization between the LUMO of the chain and the orbitals of the Ag atoms of the tip, with respect to the ideal surface binding.

Second, the resonances are shifted upwards in energy in top-like tips, especially for case (B), approaching the Fermi level, while opposite shift occurs for (C) and (D). Furthermore the tip-like geometry can change the local symmetry of the metal-molecule contact and may enhance the symmetry breaking. This is evident for instance in case...
Figure 4.23: Transmission function of C₄ contacted with tips and on the ideal Ag(100) surface
(D) where the chain binds to a Ag dimer and splitting of the HOMO resonance is complete.

In conclusion, the geometry of the electrode has important influences on the transmission probabilities, but the overall transport properties are mainly determined by the characteristics of the Ag-C bonds (i.e. bond length and coordination number).

4.9 Phonons

In this section we focus on the effects the vibrational motion of the atoms have on the transport properties, showing that temperature does not significatively affects the conductance, as a consequence of the stiffness of polyynes.

To this aim we first performed a vibrational study of the hollow-adsorbed \( \text{C}_8 \) contacted with Ag(100) electrodes at both ends, computing the dynamical matrix by shifting only the carbon atoms of the chain and keeping fixed the position of the metal atoms.

Fig. 4.26 and 4.27 feature the atomic displacements for many vibrational modes. We found that the three lowest-frequency modes are related to the translational degree of freedom, involving the motion of the whole system in the x, y and z directions. These are followed by the two lowest-frequency and essentially doubly degenerate bending modes at 141 cm\(^{-1}\) and 185 cm\(^{-1}\) causing atomic displacements orthogonal to the molecular axis. The frequency region up to \( \sim 500 \text{ cm}^{-1} \) is dominated by other bending modes with an increasing number of nodes along the chain.

At about 545 cm\(^{-1}\) the first longitudinal mode appears, involving the simmetric stretching of chain, followed by a number of modes involving different stretching of the single bonds. These stretching modes dominate the high frequency region which extends up to 2059 cm\(^{-1}\), the frequency value for the stretching of triple bonds. In general, the computed frequencies compare favorably with those calculated for \( \text{C}_8 \) between Ag(111) electrodes\(^{114}\). Moreover including Ag atoms in the dynamical matrix modifies only the low frequency region of the phonon spectrum (\( \omega \leq 300 \text{ cm}^{-1} \)) and introduces a longitudinal mode for block oscillations of the chain along the surface normal at \( \sim 240 \text{ cm}^{-1} \) (i.e. related to the stretching of the Ag-C bonds).

In order to understand the effect that geometrical displacements of the chain atoms may have on the transport properties, we calculated the maximum displacement allowed for several temperatures up to 500 K.
As well known, phonons obey the Bose-Einstein distribution function, and the occupation of the vibrational levels follows the relation:

\[
\langle n_k \rangle = \frac{1}{\exp\left(\frac{\hbar \omega_k}{K_B T}\right) - 1}
\]  \hspace{1cm} (4.4)

where \( n_k \) is the occupation number, \( \omega_k \) the frequency of the \( k \)-th vibrational mode, \( K_B \) the Boltzmann constant and \( T \) the temperature.

According to this distribution, the maximum displacement \( \Delta r \) of the atom \( \alpha \) along the direction \( s \) can be calculated as:

\[
\langle \Delta r_{\alpha,s}^k \rangle = \left( \sqrt{\frac{\hbar}{M_\alpha \omega_k}} \left( \langle n_k \rangle + \frac{1}{2} \right) \right) Q_{k,s}
\]  \hspace{1cm} (4.5)

where \( M_\alpha \) is the mass of the \( \alpha \)-th atom and \( Q_{k,s} \) the eigenvector of the \( k \)-th mode along \( s \). The calculated displacements are shown in fig. 4.26 and 4.27 for several vibrational modes at 0 K and 300K. As is evident, such displacements are very small for both temperatures with highest value ranging from \( \sim 3 \) (3) pm for the stretching of triple bonds to \( \sim 6 \) (9) pm for the low-frequency bending at 0 (300) K. Specifically all the stretching modes are not significatively affected by temperature.

We computed the transmission (not shown) for \( C_8 \) adsorbed in the stable hollow sites distorting the chain along a bending and a stretching mode (see fig. 4.24), as representative of a low- and a high- frequency molecular motion, according to the average displacement allowed for a (quantum) harmonic oscillator at 300 K. No significative differences has been found in the transport properties with respect to the undisplaced geometry. We thus conclude that the computed properties are rather robust with respect to (small) displacement of the carbon atoms out of their equilibrium position. It is worth underlining that these calculations were only exploratory and are not representative of the possible coupling between vibrational and electronic degrees of freedom.

We further considered the progressive stretching of the central single bond of hollow-bound \( C_8 \), keeping fixed all the other bond lengths, in order to simulate the chain breaking experimentally seen in TEM experiments. The evolution of the transmission as a function of the C-C distance is shown in fig. 4.25. The case of the (equilibrium) bond length of 1.325 \( \text{Å} \) has been previously discussed. Upon stretching of about 30%, \( (d = 1.737 \text{Å}) \) the transmission features significative changes in the positions of the resonances. Specifically the \( HOMO_{-1} \) and the \( HOMO \) resonances shift close to each other,
overlapping, as well as the \textit{LUMO} and the \textit{LUMO}$_{+1}$ ones, as a consequence of the reduction of the conjugation of the chain. Such resonances further merge upon subsequent stretching of 30\%, becoming no longer resolved. Despite of the narrowing of the transmission peaks, due to the progressive decoupling of the C atoms, the magnitude of the resonances remains close to 4, indicating that all the four channels are still conductive. Notice also that a weak resonance appears right at the Fermi level as a consequence of the residual hybridization between the $\sigma$ orbitals hosting the (now unpaired) bond electrons. Upon further distancing of the resulting C$_4$ chains ($d = 2.562$ Å) the magnitude of the resonances drastically drops, almost disappearing for $d = 2.975$ Å.
Figure 4.26: Maximum displacements of atoms of C$_8$ at 0 K (blue) and 300 K (red). The internuclear axis of the molecule is directed along the z direction.
Figure 4.27: Maximum displacements of atoms of C₈ at 0 K (blue) and 300 K (red). The internuclear axis of the molecule is directed along the z direction.
4.10 Gold electrodes

Gold is one of the most common metals used as electrode in nanodevices for its capabilities to readily bind a wide variety of molecules, especially sulfur capped species. Recently the first electrical characterization of carbon chains between gold electrodes has been reported\textsuperscript{115}, showing that dihydrobenzothiophene is one of the most promising capping groups allowing to form a stable chain-electrode contact.

Bulk gold features geometrical characteristics similar to Ag, in particular has the same structure (face centered cubic), and almost the same cell constant (4.16 Å for Ag and 4.29 Å for Au).

We computed the transmission for the C\textsubscript{4} chain adsorbed on Au(100) surface. The hollow case is shown in fig. 4.28, featuring little differences with respect to the same binding on Ag(100) electrode (top and bridge behave similarly). Specifically the resonances are lightly shifted at higher energies, and, mainly, the transmission across the Fermi level region is reduced by 3-4 times. Analysing the optimized geometry it appears clear that this is due to an increased Au-C bond length with respect to Ag contacts, reducing the coupling with the electrodes and in turn the broadening of the resonances. For instance, the hollow Au-C bond is longer by \( \sim 0.4 \) Å (\( \sim 0.1 \) Å for top and bridge sites) compared with the Ag-C bond.

However, these results allow a qualitative comparison between gold and silver contacts, in addition to provide further confirmation that transport properties are primarily determined by the characteristics of the junction (\( i.e. \) the metal-chain bond) rather than by electrode itself.

![Figure 4.28: Transmission of C\textsubscript{4} chain at a hollow site on Ag(100) and Au(100) electrodic surfaces.](image)
4.11 Reliability of results

As well known, DFT represents a true improvement over semiempirical approaches for describing the binding to the electrodes, providing correct calculations of lattice constants and energies, but the bandgaps turn out to be considerably underestimated. Then the application of more advanced and, accordingly, computationally more expensive simulation techniques, such as many-body perturbation theory (MBPT) in the GW approximation, are required to increase the accuracy of quasi-particle spectrum calculations. Clearly, such limitation of DFT also reflects on the calculation of the transport properties.

Recently, La Torre et al.\textsuperscript{77} reported the synthesis and the characterization of different carbon-metal nanocontacts, specifically a graphene ribbon, an irregular nanotube-like object and a monoatomic carbon chain contacted to Fe/graphite electrodes. They found that the monoatomic chain gives a current of the order $\sim 0.2\,nA$ for a bias $\sim 0.1\,V$, i.e. $4 - 5$ orders of magnitude smaller than the value we find theoretically ($\sim 10\,\mu A$ for the same bias). Even though the chain length and the exact nature of the contacts remain unknown, such a large discrepancy cannot be related to different electrodes only, but appears to be a limitation of the DFT-NEGF approach adopted here which relates to the well-known gap problem of current density functionals. This causes the gap between the resonances closest to the Fermi level to be largely underestimated, and the transmission probability at the Fermi level – due to the tails of the broadened resonances – turns out to be much larger than the actual one.

In the following we try to provide an estimation of the typical error expected for such band-gap with the theory level adopted in our calculations.

To this aim we first investigated the dependence of the BLA on the chain length, using the both-ends hydrogen-terminated molecular species $\text{HC}_{2m}\text{H}$ as a benchmark. We optimized the geometry of a large number of molecules ($n = 2m = 4 - 100$) performing all-electron DFT calculations as implemented in the Gaussian quantum chemistry code\textsuperscript{116}, testing several functionals with the standard 6-31++G** Pople’s basis set. The results of such calculations are shown in fig. 4.29 where the BLA of the central bonds of the molecule is reported as a function of the inverse number of C atoms in the chain $1/n$.

It is evident that the choice of the exchange-correlation functional strongly affects the BLA, with the lowest values provided by PBE, the highest by adding the long-range correction of such functional. Intermediate values result from the hybrid B3LYP, with
Figure 4.29: Bond length alternation of even HC\textsubscript{n}H molecules computed at their center at different theory levels.

The BLA being increased by on average \( \sim 3 \text{ pm} \) when the long-range correction is included. Notice, also, that the adopted setup in SIESTA calculations (pseudopotential approach with a DZP basis-set) favorably compare with the Gaussian one (all-electrons with Pople’s basis set).

As it is well known in literature CAM-B3LYP is the most accurate functional for such systems, since it provides values bracketed (for small \( n \)) by coupled-cluster and MP2 results\textsuperscript{118}, thus it turns out that PBE severely underestimate the BLA (and in turn the band gap, strictly related to the BLA) by about three times (for the infinite chain we extrapolate \( \sim 4 \text{ pm} \) for PBE and \( \sim 13 \text{ pm} \) for CAM-B3LYP) and that similar results hold also when contacting the molecule to a metal surface.

Unfortunately, since hybrid functionals do not generally represent a good solution for metals\textsuperscript{119}, it is not currently possible to solve this issue for the transport problem, but we can only critically assess the reliability of our results.

The second step to this end, is the calculation of the optical properties of several gas-phase polyynes HC\textsubscript{n}H, as obtained by linear-response TD-DFT (Casida) method\textsuperscript{120} testing different functionals.

As a consequence of the cylindrical symmetry of the molecules (and the consequent arrangement of the \( \pi \) electrons in degenerate orbital pairs) the promotion of one electron from the \textit{HOMO} to the \textit{LUMO} results in the transition to four possible electronic
excited states (the second is degenerate):

\[
A \ 1\Sigma_u^- \leftarrow X \ 1\Sigma_g^+ \\
B \ 1\Delta_u \leftarrow X \ 1\Sigma_g^+ \\
C \ 1\Sigma_u^+ \leftarrow X \ 1\Sigma_g^+ 
\]

(4.6)  (4.7)  (4.8)

Such transitions were computed for molecular geometries optimized at the same level of theory and the energies of the lowest-energy dipole-allowed transition \((C \ 1\Sigma_u^+ \leftarrow X \ 1\Sigma_g^+)\) for which experimental data are available are reported in fig. 4.30. It can be observed that accurate results can be obtained with long-range corrected functionals over a wide range of molecular sizes. In particular the CAM-B3LYP functional provides results in very good agreement with the experimental ones\(^{117}\), with a maximum deviation less than 0.1 eV for the molecules considered. We thus take the CAM-B3LYP results as a reference for computing the gap most relevant for transport, namely the energy of the lowest energy dipole-forbidden \(A \ 1\Sigma_u^- \leftarrow X \ 1\Sigma_g^+\) transition.

Before proceeding with further analysis, it is essential to compare the results of such

\[^{117}\]In this case the selection rules read as:

\[
\Sigma \rightarrow \Sigma \quad \text{+} \rightarrow \text{+} \quad g \rightarrow u 
\]

(4.9)
transition at PBE theory level with the HOMO-LUMO gaps obtained in the PBE-NEGF transport calculations. These are obtained calculating the energy gap between the maxima of the resonances closer to the Fermi level in the transmission spectra of hollow- and top-bound chains (for bridge case the slight splitting of the resonances prevent us to perform this symple analysis) and are shown in fig 4.31. Despite of these gaps refer to very different physical situations, for the top case they compare quantitatively with the gas-phase values at the same level of theory whereas for the hollow case they are considerably smaller because of the higher coupling with the electrode and hence the increased effective delocalization.

The above-mentioned transition energies are reported in fig. 4.32 for the same functionals used to compute the dipole-allowed one. It appears evident that PBE provides a much smaller gap than the “correct” CAM-B3LYP one, even with long-range correction. The infinite-chain CAM-B3LYP extrapolated value is found to be 2.19 eV, in reasonable agreement with the non-self-consistent GW result of 2.58 eV obtained at a HSE06 optimized geometry (BLA~9 pm)\textsuperscript{121}. The differences between the gaps calculated with PBE and CAM-B3LYP increase as a function of the chain length, ranging from \(~0.7\) eV for \(C_6\) to \(~1.7\) eV for \(C_{50}\). We expect this causes a reduction of the current of 2-3 order of magnitude.

Even though not enough to explain the 4–5 order of magnitude discrepancy mentioned
above, the results presented here show that the gap-problem of DFT is likely the main source of disagreement with experiments. Other significative effects causing differences between theory and experiments are certainly the different electrodes and structure of the junctions as well as a possible strain of the chain due to the experimental procedure.