Thesis Paper

Local Current Through Helical Orbitals

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Traditional chemical research has given great information about the physical properties of molecules. This research provides understanding of how molecules work in the classical ways, but the limit is reached when molecules are used in a non-traditional way. Now molecules can be inserted in molecular junctions, which makes it possible to examine molecules in new ways. Recent theoretical work has shown that some linear molecules can have helical orbitals. Here the question of interest is whether the current density around these particular molecules are affected by the helical orbitals and the coupling of the electrodes. We show that the helical orbitals in combination with the coupling of the electrodes, indeed has an impact on the current and that the orbitals contribute to a circular current around these linear molecules. As the understanding of the currents behavior around the molecules expand, it paves the way for new chemical questions about how we can control the current. For example, how helical current may induce magnetic properties in non-magnetic molecules, and how chemical substituent can be used to impact these effects.

1 Introduction

Molecular electronics have been of great interest in the field of chemistry and physics in the past few years. The possibilities associated with understanding how the molecules behave when introduced to new surroundings, e.g. when put in a junction, paves the way for new possibilities for using molecules in electronics.

Earlier studies have found that molecules can be used for electron transport, where the molecule is used as gate switches or other transport elements[1]. Though several things have an impact on how well the molecule conducts, a study found that electron transport across a molecule can go through-space and not only through-bond[2]. This indicates that there is still much to learn about how current travels across molecules. Apart from being used for electron transport, molecules can be used for spintronics, where the electron's spins is used to transfer information. Though this is a newer discovery and by now it is primarily associated with inorganic metals[3]. The interest lies in how the spin transport can be controlled by use of magnetic polarized electrodes or single-radical molecular junctions[4][5]. Another study found that molecules could be used as a field effect transistor made by using molecular orbitals, which suggests that the possibilities for using molecules for electronic devices only is limited to the current understanding of molecules[6]. Recent studies found that some linear molecules have helical orbitals[7][8], these molecules have recently been synthesized successfully[9]. Their ability to have helical orbitals paves the way for new chemical

questions, of how these orbitals can contribute to the current around these molecules, and whether these currents can be controlled.
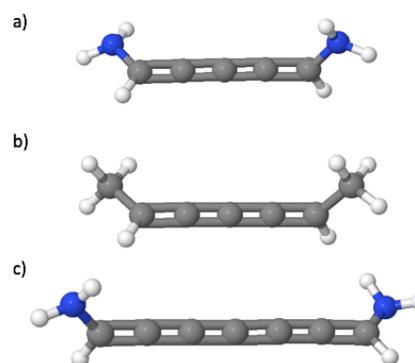

Fig. 1 The investigated molecules, a) (5)allene with amine as substituent, b) (5)allene with methyl as substituent, c) (7)allene with amine as substituent.

In this article, the focus is on how the helical orbitals affect the current around these linear molecules and how the coupling of electrodes to the molecule, changes the currents path across the molecule. The molecules were chosen based on examination of linear molecules with helical orbitals by Hendon *et al.*[8]. They use cumulene for linear molecules with an even number of double bound carbons,

and allene for linear molecules with an uneven number of double bound carbons. This nomenclature is adopted, as (n)allene, where n is the number of carbons. Hendon *et al.* found that the orbitals only twist in allene and not in cumulene. Therefore the focus in this article is on allene. The molecules chosen for this investigation are (5)allene and (7)allene with substituent groups replacing one of the hydrogens in each end of the carbon chain. The substituent groups for (5)allene is methyl and amine. For (7)allene the substituent group is amine, as seen in Figure 1.

The interest in these specific molecules lies in their ability to have helical orbitals. The twisting of the orbitals in (5)allene at the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are illustrated in Figure 2.
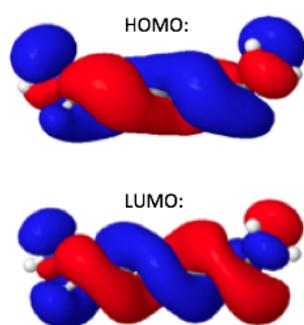

Fig. 2 Orbitals of (5)allene with amine as substituent. Here with HOMO top and LUMO bottom.

Aside from the orbitals' contribution, the placement of the electrodes is interesting in relation to which orbital the electrodes couple into. Figure 3 illustrates the coupling to the molecule. The black dot marks the position of the electrode. Here Figure 3a show the position of the electrode for the positive dihedral for amine (top) and methyl (bottom) and 3b shows the position of the electrode for the negative dihedral for amine (top) and methyl (bottom). The electrodes in each end can be either on the positive or negative dihedral. The electrodes placed at the positive dihedral will from now on be mentioned as p and the electrodes placed at the negative dihedral mentioned as m. If the electrodes are at the positive dihedral in each end, they will be mentioned as pp. If they are placed at the negative dihedral in each end, they will be mentioned as mm and if they are placed at the positive and negative dihedral, respectively, they will be mentioned as pm. The electrodes consist of dioxygen. These were chosen in order to overcome the limitations of using the Gaussian program, and the local current code. Additionally these electrodes make it easier to control the coupling to the molecule. Compared to a gold electrode, dioxygen provides the possibility of

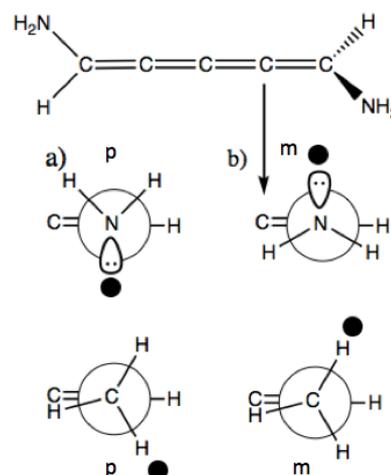choosing specific Fermi energies, and can be thought of as the tip of a gold electrode.

Fig. 3 A Newman projection illustrating the coupling of the electrode to the molecule. The black dot marks where the electrode is coupled. a) Illustrates the coupling to the positive dihedral for amine (top) and methyl (bottom). b) Illustrates the coupling to the negative dihedral for amine (top) and methyl (bottom).

To understand how the current is affected by the coupling of the electrodes into the molecule, the current density must be calculated. The current density is given by the following as they derive in Xue et al[10], with atomic units:

$$j(r) = \frac{1}{2} \cdot \sum_{ij} \left(\int dE \cdot G_{ij}^{<}(E) \right) \cdot dS_{ij}(r) \qquad (1)$$

where $dS_{ij}(r) = \phi_i(r) \cdot \nabla \phi_j(r) - \phi_j(r) \cdot \nabla \phi_i(r)$. Here ϕ_i and ϕ_j is the wave function and ∇ is the gradient to the wave function. The lesser Green's function ($G^{<}(E)$) is given by $G^{<}(E) = G^R \cdot \Sigma^{<} \cdot G^A$, where $G^R = [E \cdot S - H + \Sigma^R]^{-1}$. Here E is the energy, S is the overlap integral, H is the Hamiltonian and Σ^R is the self energy of the retarded Green's function(G^R) and $\Sigma^{<}$ is the self energy of the lesser Green's function[11][12][13]. In order to get $G^{<}$ and calculate the current density, a density functional theory (DFT) calculation of the molecule is necessary. From the output file of the DFT calculations, information for $G^{<}$ is given and thereby it is possible to calculate the current density. The DFT output file also gives information to the calculations of the orbitals as mentioned in SI.

2 Results and discussion

In order to explain how the current is affected by the orbitals and the position of the electrodes compared to the
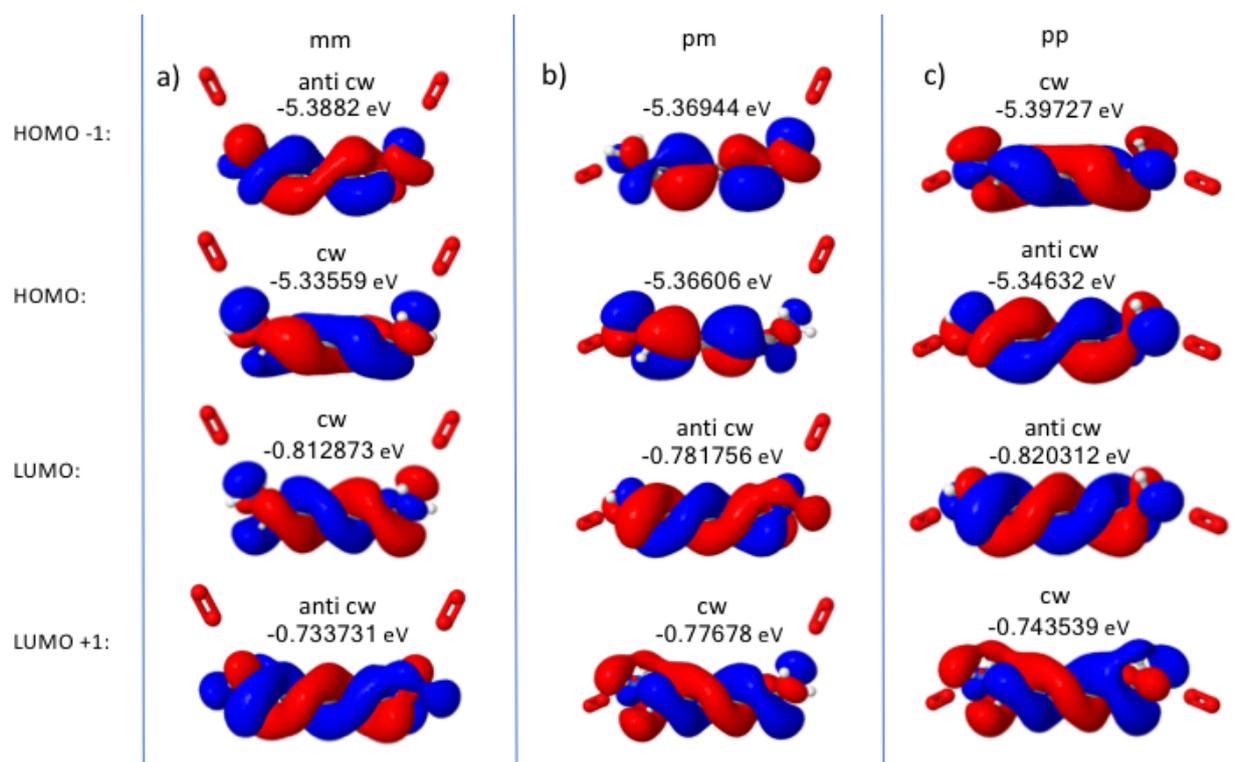
Fig. 4 Orbitals of (5)allene with amine as substituent. The HOMO-1, HOMO, LUMO and LUMO+1 orbitals are illustrated with their energies shown above. a) Electrodes placed at mm, b) Electrodes placed at pm, c) Electrodes placed at pp.

molecule, it is essential to see how the current density and the orbitals behave. Figure 4 illustrates the orbitals of (5)allene with amine as substituent. Here with the electrodes at mm (Figure 4a), pm (Figure 4b) and pp (Figure 4c). The orbitals are either clockwise (cw) or anti clockwise (anti cw) around the molecule. It is seen that with the electrodes at mm, for the HOMO-1 and the HOMO orbital, the twisting is anti cw and cw respectively. For the LUMO and the LUMO+1, the orbitals twist cw and anti cw. In contrast, when the electrodes are placed at pp the twisting is cw and anti cw for the HOMO-1 and the HOMO orbital and vice versa for LUMO and LUMO+1. Thus for the mm position of the electrodes the HOMO and the LUMO orbitals twist cw, where for pp position of the electrodes, the HOMO and the LUMO orbitals twists anti cw. The same effect is seen for (7)allene with amine as substituent (Figure S2). For (5)allene with methyl as substituent, the helical orbitals are mostly seen for the mm coupling (Figure S1). In general it is seen that the orbitals at the LUMO energy has one more node than the orbitals at the HOMO energy.

In Figure 5 the transmission and current density of (5)allene with amine as substituent is shown. Here the electrodes are at mm (5a), pm (5b) and pp (5c). From each of these electrode positions the current density is calcu-

lated at the HOMO energy (green), LUMO energy (blue) and a Fermi energy in between (red). Based on this, the current does not have helical behavior. Consequently no helical current is seen, though circular currents around the molecules are seen. The white and yellow arrows illustrates which way the current runs around the molecule. The white arrows indicate the current that circulates the molecule and the yellow, the current that runs along the molecule.

The pictures are difficult to interpret. The main current moves in the same direction as the voltage, still some currents seem to move in the opposite direction. Furthermore the pictures can not be compared to each other, only the direction of the circular currents around the molecules can be compared due to normalization. The question of quantifying what percentage of the current that flows linear and what flows circular is still unresolved. Moreover, it is relevant to have in mind whether this circular current contributes to the net current.

For (5)allene with amine as substituent a tendency is seen for the HOMO and the LUMO energies. Here the circular current runs the opposite direction of the orbitals at the HOMO energy, but in the same direction as the orbitals at the LUMO energy. The circular current seen around these molecules does not only differ in the the way
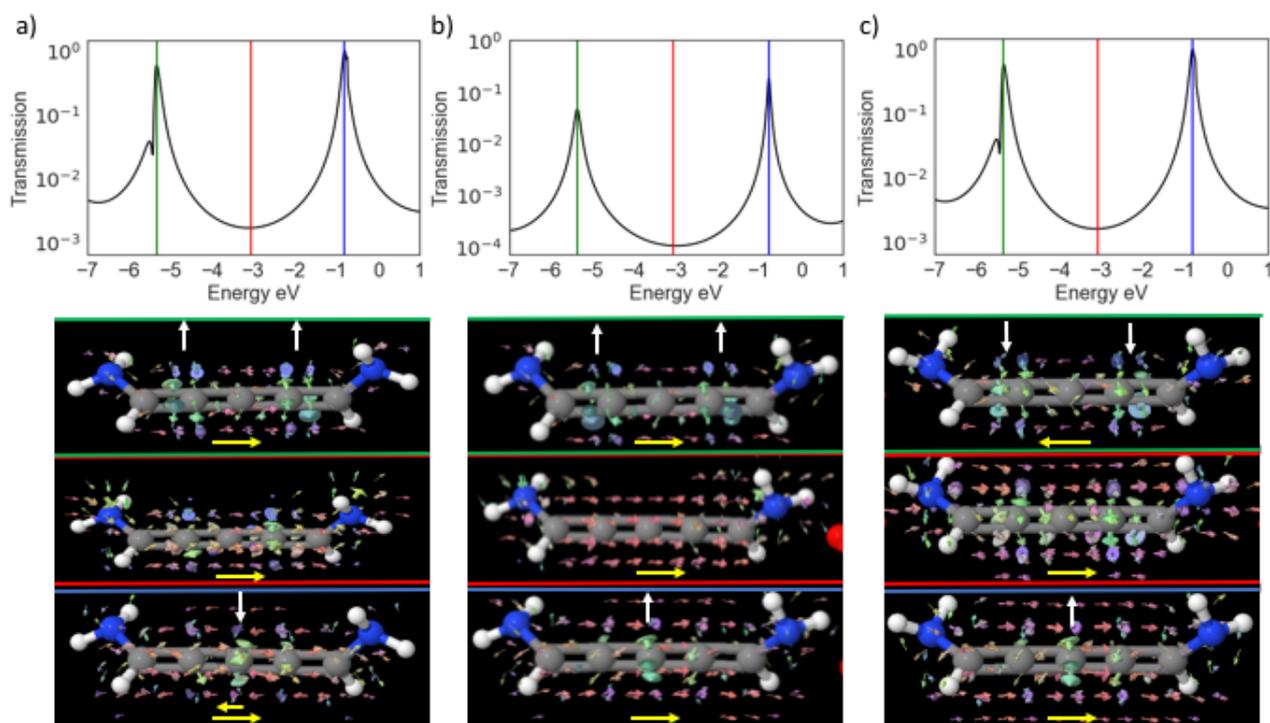
Fig. 5 Transmission and current density of (5)allene with amine as substituent. Here for three different energies, HOMO (green), LUMO (blue) and a Fermi energy in between (red). The green line on the graph correlates to the green box, and so forth. The yellow arrows illustrate the way the current runs along the molecule and the white arrows illustrate the way the circular current runs around the molecule. a) For (5)allene with the electrodes placed mm, with the HOMO energy at -5.33559 eV, the LUMO energy at -0.812873 eV and a Fermi energy at -3.0742315 eV. b) For (5)allene with the electrodes placed mp, with the HOMO energy at -5.36606 eV, the LUMO energy at -0.781756 eV and a Fermi energy at -3.073908 eV. c) For (5)allene with the electrodes placed pp, with the HOMO energy at -5.34632 eV, the LUMO energy at -0.820312 eV and a Fermi energy at -3.083316 eV. The arrows illustrating the current can only be compared at one energy and not at different energies due to the normalization, although the direction of the current can be compared.

they run around the molecule, they also differ in quantity and the distance between the circular currents. At the HOMO energy For (5)allene with amine as substituent (Figure 5), two circular currents are seen, where for the longer molecule (7)allene with amine as substituent three circular currents are seen (Figure 7). Both seem to have the same distance between the circular currents. For (5)allene with methyl as substituent (Figure 6), the circular currents for the HOMO energy and the LUMO energy have three circular currents, though for the LUMO energy the circular currents occur closer to each other. Apart from this the circular currents change direction, where the first circular current goes anti cw around the molecule, the second goes cw and the last anti cw. Furthermore, for (5)allene and (7)allene with amine as substituent it seems that the circular current prefers to go around an atom, where for (5)allene with methyl substituent the circular current is both around an atom and a bond.

At the Fermi energy in between the HOMO energy and the LUMO energy the current exhibits a mix of the HOMO and the LUMO current for all three molecules. They show no clear sign of a circular current at this energy, though (5)allene and (7)allene with amine as substituent (Figure 5 and 7) exhibit more affinity for circular current than (5)allene with methyl substituent (Figure 6) at this energy. Comparing the transmission of all three molecules, it is seen that the transmissions are lower when the electrodes are placed pm than when the electrodes are placed mm and pp. For all three molecules with the electrodes placed pm a cancellation of the current is seen, to varying degree, for the LUMO energy and the energy between the HOMO and LUMO energy. This cancellation causes the main current to be linear. The clearest cancellation is seen for (7)allene with amine (Figure 7), where both the current calculated at the LUMO energy and the Fermi energy in between the HOMO energy and LUMO energy is linear. This cancellation is due to coupling into both the negative and positive dihedral (coupling pm)[14].
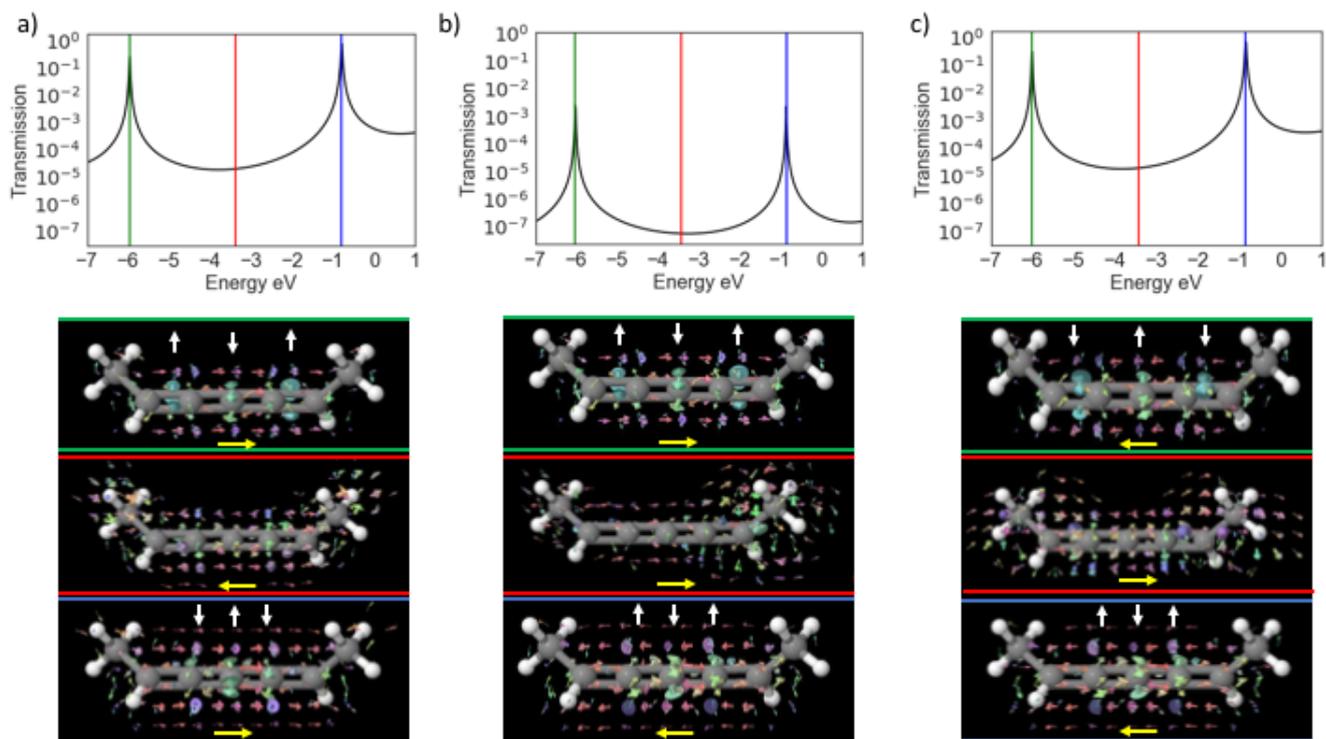
Fig. 6 Transmission and current density of (5)allene with methyl as substituent. Here for three different energies, HOMO (green), LUMO (blue) and a Fermi energy in between (red). The green line on the graph correlates to the green box, and so forth. The yellow arrows illustrates the way the current runs along the molecule and the white arrow illustrate the way the circular current runs around the molecule. a) For (5)allene with the electrodes placed mm, with the HOMO energy at -5.96372 eV, the LUMO energy at -0.795731 eV and a Fermi energy at -3.3797255 eV. b) For (5)allene with the electrodes placed mp, with the HOMO energy at -6.0237 eV, the LUMO energy at -0.859986 eV and a Fermi energy at -3.441843 eV. c) For (5)allene with the electrodes placed pp, with the HOMO energy at -6.00667 eV, the LUMO energy at -0.844707 eV and a Fermi energy at -3.4256885 eV. The arrows illustrating the current can only be compared at one energy and not at different energies due to the normalization, although the direction of the current can be compared.

At this point, no obvious correlation between the current and the orbitals is seen. It is not clear which orbital that contributes to the current at the HOMO energy and LUMO energy. For (5)allene with amine as substituent (Figure 5) the circular current at the LUMO energy runs in the same direction as the LUMO orbital, though this is only seen for this molecule. For (7)allene with amine as substituent (Figure 7) the opposite effect is seen.

A tendency for (5)allene and (7)allene with amine as substituent is observed for the circular current at the HOMO energy. The distance, direction and quantity of circular currents around these correlates with the length of the molecule. For (5)allene two circular currents for the HOMO energy were seen, where for (7)allene three circular currents were seen. The distance between the circular currents does not seem to be affected by the length of the molecule, only the quantity of circular currents seems to change. For both (7)allene and (5)allene all of the circular current turns in the same directions at each energy. At the

LUMO energy the same effect is seen. (5)allene has one clear circular current where (7)allene has two clear circular currents. (5)allene with methyl as substituent has, as mentioned, three circular currents at the HOMO energy, running different directions around the molecule. At the LUMO energy three circular currents are still seen, though each current has changed direction around the molecule and the circular currents has a decreased distance between each other.

Another way to find out if the helical orbitals gives helical current, is to look at the scattering states/eigenchannels[15]. If these have helical character, the helical orbitals do not give helical current but only the circular current, as seen. If the scattering state does not have helical character the question is still unresolved.

In summary circular current is seen for all three molecules. (5)allene and (7)allene with amine as substituent shows best examples of circular current. This could be explained by amine being more electron-
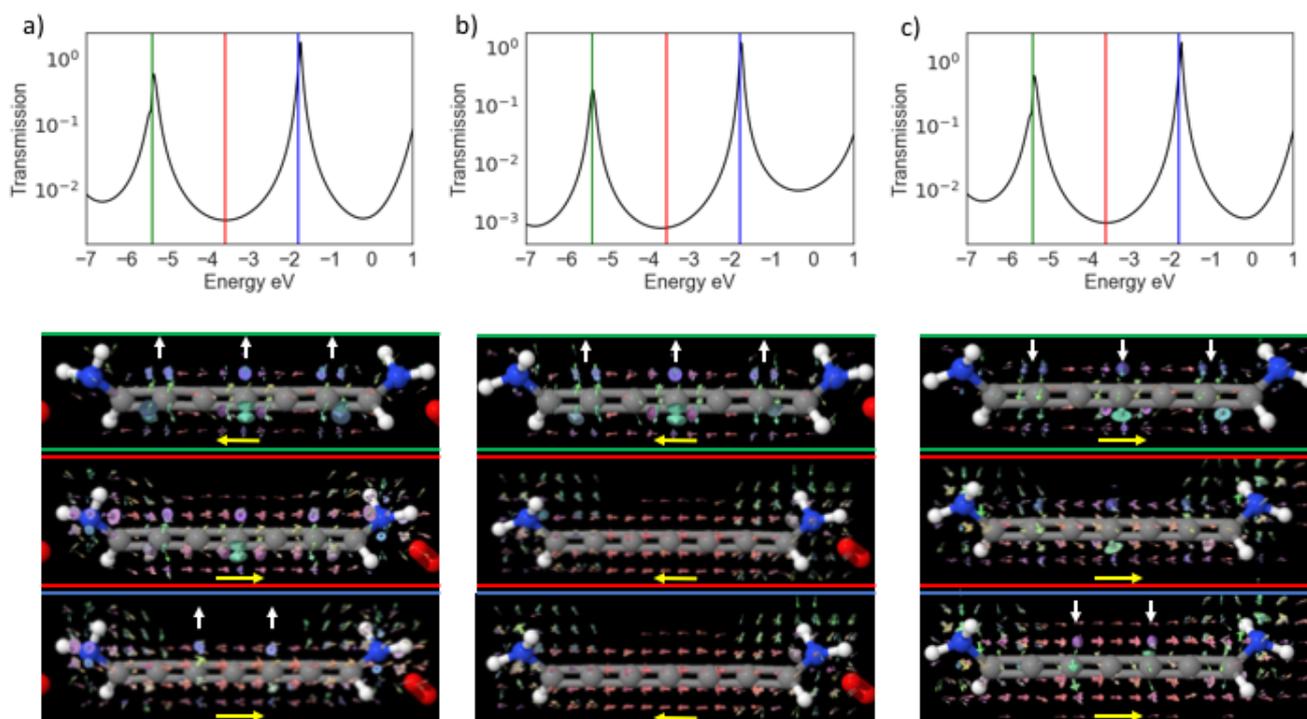
Fig. 7 Transmission and current density of (7)allene with amine as substituent. Here for three different energies, HOMO (green), LUMO (blue) and a Fermi energy in between (red). The green line on the graph correlates to the green box, and so forth. The yellow arrows illustrates the way the current runs along the molecule and the white arrow illustrate the way the circular current runs around the molecule. a) For (5)allene with the electrodes placed mm, with the HOMO energy at -5.37633 eV, the LUMO energy at -1.79429 eV and a Fermi energy at -3.58531 eV. b) For (5)allene with the electrodes placed mp, with the HOMO energy at -5.38005 eV, the LUMO energy at -1.76854 eV and a Fermi energy at -3.574295 eV. c) For (5)allene with the electrodes placed pp, with the HOMO energy at -5.37228 eV, the LUMO energy at -1.79072 eV and a Fermi energy at -3.5815 eV. The arrows illustrating the current can only be compared at one energy and not at different energies due to the normalization, although the direction of the current can be compared.

withdrawing compared to methyl, thereby contributing more to the splitting of the orbitals[16]. When the number of carbons in the chain increases, the number of circular currents increases. Furthermore, when going from the HOMO energy to the LUMO energy, the number of circular currents decreases by one for both (5)allene and (7)allene with amine as substituent. This could be due to the number of nodes increasing from the HOMO to the LUMO energy, indicating that the helical orbitals contributes to the current across the molecule, through the circular currents.

3 Methods

(5)allene and (7)allene were investigated using DFT and current density calculations. The substituent groups chosen were amine and methyl. Here only methyl for (5)allene and amine for both (5)allene and (7)allene. The molecules alone were optimized once, and a DFT calculation of the molecules with electrodes attached was done. The elec-

trodes consist of dioxygen, and were placed 3 Å from the molecules at each end at three different positions (mm, pm and pp). The optimization of (5)allene without electrodes was done using Gaussian with the following keywords: opt=verytight b3lyp/6-31g(d) int=ultrafine. The DFT calculation of (5)allene with the electrodes attached were done using, b3lyp/6-31g, int=ultrafine, nosymm, SCF (maxcyc=200, XQC) as keywords. For (7)allene the basis set was changed to 6-311g(d) and 6-311g for the optimization of the molecule and the DFT calculation with electrodes attached respectively, as described in SI. From the output obtained from Gaussian, the lesser Green's function ($G^<$) was calculated as mentioned earlier. From $G^<$ the current density and, by diagonalizing H_{ao}, the molecular orbitals, were calculated. The current was calculated at three chosen Fermi energies, the HOMO energy, the LUMO energy, and a Fermi energy in between the two. The placement of the HOMO energy and LUMO energy were obtained by getting the eigenenergies from

the output of Gaussian and finding the biggest gap.

4 Conclusion

(5)allene and (7)allene with methyl and amine as substituent groups, were investigated through DFT using the output to calculate the orbitals and current density around the molecules. From these calculations it is seen that the orbitals are helical both at the HOMO and the LUMO energy. The current around the molecules does not exhibit helical behavior, though circular current around the molecules is seen. Both linear and helical current are present. Furthermore depending on the energy at which the current is calculated, the current along the molecule changes direction. Circular current is seen at all three molecules, however, predominantly with amine as substituent, when the electrodes were placed mm and pp. Looking at the orbitals in relation to the current, when going from the HOMO energy to the LUMO energy, the number of nodes in the orbitals increase, whereas the number of circular currents seems to decrease. From this it can be concluded that even though there are circular currents around the molecules there are no clear signs that the orbitals match the current at the given energy. This investigation leads on to a deeper understanding of how the orbitals contribute to the circular current around the molecules and how this can be controlled.

5 Acknowledgements

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