jz-2021-03769g.R1

Name: Peer Review Information for "Electronic Conduction Through Monolayer Amorphous Carbon Nano-Junctions"

First Round of Reviewer Comments

Reviewer: 1

Comments to the Author

In this work, the authors studied transport properties through an ensemble of monolayer amorphous carbon (MAC) nano junctions. The structures were obtained using Monte Carlo simulations, and the electronic structure was determined at the Pariser-Parr-Pople (PPP) level. The transport was computed using the Landauer formula, with the coupling matrices (\Gamma_L and \Gamma_R) modeled using the wide-band approximation. The analysis of the result is reasonable, which showed the relation between edge localization and energy/coupling of the states. The results were further compared to graphene nano-flake.

The combination of Monte Carlo calculations with subsequent electronic structure and transport calculations for an ensemble of systems is an advance in this paper, which demonstrated the variation of properties within the ensemble. The comparison between MAC and graphene nano-flakes is important, directing future studies in carbon-based materials. I therefore recommend publication in J. Phys. Chem. Lett.

I only have one comment for the authors to consider: in graphene nanoribbons, previous literature showed that although the material only consists of carbon, complicated spin properties could arise. See, e.g., Nature 514, 608-611 (2014), and Phys. Rev. Lett. 97, 216803 (2006). In this work, the authors did not mention the spin properties at all. I was wondering, for these MAC structures, especially those with defects (such as those five- or seven-member rings shown in Fig. 1), could exotic spin properties emerge, and if so, how do those phenomena affect the analysis and the conclusions?

Reviewer :2

Comments to the Author

1) The discussion of MCOs does not cite Gemma Solomon's early work, which is where the idea for the Q-matrix is from. Solomon et al, J. Chem. Phys., 2008 should be cited when introducing the concept of MCOs.

2) In Figure 1c, there are no units or values for the DOS on the y-axis. In Figure 1d, it is unclear if the difference plot is generated by taking the difference of the ensemble T(E) and the ensemble DOS presented in Figures 1b and 1c, respectively, or the difference between the T(E) and DOS for each of the 413 samples and then averaged. The authors don't explain how they calculate the DOS. Based on Figure S1c, it appears that they are binning the energy levels in a histogram. Instead, they should be using the spectral function (i.e., DOS = Tr[Im[G(E)]]), which would produce a continuous function much like T(E) in Figure S1b. Plotting DOS - T(E) in Figure 1d seems. I think there are better ways to demonstrate the points the authors are trying to make with Figure 1d.

• If they want to show QI, instead of the DOS they should use Tr[Q(E)], which is the noninterfering part of the Q matrix. So, Figure 1d could be a plot T(E)-Tr[Q(E)], which would show the net QI as a function of energy.

• If they want to show localization, they could consider the imaginary part of the virtual levels (i.e., lambda in Eq. 2), which represents the coupling to the leads. They could produce a plot like Figure 5g of our QI paper, showing coupling as a function of energy. Localized states would have low coupling.

3) The authors argue that the constructive interference between the HOMO and LUMO is due to the partial spatial overlap between these two states at the edges, as shown in Figure 4c and 4d. However, the images shown in Figure 4c and 4d are not strong evidence. The electron density of the HOMO looks to be a little lower than the electron density of the LUMO. Maybe it's due to the color scheme? Also, this representation of the HOMO and LUMO does not illustrate the phase.

4) Minor comment: Values and units should be separated by a space, e.g., it should be "2 nm" not "2nm" throughout the manuscript.

5) This is more of a question than a comment: The authors use channel interchangeably with level throughout the manuscript. In our lab, we use "channel" when referring to the number of atoms in a contact and use "level" to refer to molecular orbitals. We usually say the number of channels determines the integer value of G0 we measure, and we usually say the spatial distribution of a molecular orbital dictates how well a level will couple to the leads. Is there a meaningful difference between channel and level? Part of the reason I'm asking is because in Figure S1a, the transmission

function goes above 1 several times. The authors state that the "T(ε) remains greater than 1 within the nano-fragment's HOMO-LUMO gap, despite the absence of channels in this range of energies." I am not sure what this means.

6) there are many typos in the Si.

Author's Response to Peer Review Comments:

# Response to reviewers

December 23, 2021

Dear Editor,

We would like to convey our appreciation for the fast and clear handling of this manuscript. Furthermore, we would like to thank the reviewers for thoughtful comments that helped improve the manuscript. The response is structured as follows: we quote reviewers' comments centered and italicized, then present our response, and finally we list the changes we have made to the text.

## Notes from reviewer 1

**Note 1**

*In graphene nanoribbons, previous literature showed that although the material only consists of carbon, complicated spin properties could arise. See, e.g., Nature 514, 608-611 (2014), and Phys. Rev. Lett. 97,*

*216803 (2006). In this work, the authors did not mention the spin properties at all. I was wondering, for these MAC structures, especially those with defects (such as those with five- or seven-member rings shown in Fig. 1), could exotic spin properties emerge, and if so, how do those phenomena affect the analysis and the*

*conclusions?*

**Response:** We intentionally kept our model simple as we were looking for very crude and basic ways to characterize some of the electronic properties of an ensemble of disordered structures of amorphous graphene nano-fragments. Our model does not include spin but we are curious to see whether effects introduced by including spin and also treating some of the defects more carefully are significant - this is difficult to predict, at least for us, without doing the calculation and we leave this to future work. It is not difficult, however, to make the case for why our current conclusions are not likely to change qualitatively, that is to say - new features may appear, but features we describe in this manuscript will not likely disappear. We still expect to see 'phase-separation' of insulating states because the reason we see it is in the fact that when interior states and edge-like states are close to each other in energy a small perturbation will mix them turning the insulating interior state into a perturbed edge-like state and the only way for interior states to appear is as a cluster within the spectrum, in our case the cluster appears close to band edges. We do not see at this time a reason for this behavior to change regardless of whether the spin degree of freedom is included in the calculation or not. Similar logic applies to other energy-localization relationships. Quantum interference (QI) is a weak effect in our current report and we point QI out predominantly as a curiosity - the fact that it survives averaging in a large ensemble is interesting, but it is not a very strong effect. It is difficult for us to formulate a strong position regarding what we expect from a spin-full model and QI, we would need to perform the calculation and learn more. The outcomes may show more interesting features than what we show but there is no reason to expect that the QI would disappear entirely because we have included the spin and in that case our analysis and conclusions simply present a stripped down simpler version of the phenomenon, something that is often useful in its own right.

**Changes to text:** We have added the following sentences and the relevant citations to the end of the paragraph starting with "We employ the semi-empirical Pariser-Parr-Pople (PPP) Hamiltonian...", on page 4 of the revised manuscript:

Our model does not account for the effect of electron spin on the electronic structure of MAC nano-fragments and the molecular orbitals we obtain are spin-degenerate. Exploring the spin properties of MAC nano-fragments motivated by the intricate magnetic properties reported for graphene nanoribbons with defects is left to future work.

# Notes from reviewer 2

## Note 1

*The discussion of MCOs does not cite Gemma Solomon's early work, which is where the idea for the Q-matrix is from. Solomon et al, J. Chem. Phys., 2008 should be cited when introducing the concept of MCOs.*

**Response:** We apologise for this oversight.

**Changes to text:** Citations of Solomon *et al., J. Chem. Phys.* 2008 have been added when the text first mentions molecular conductance orbitals (MCOs) and when the $Q$ matrix is introduced. We also cite Solomon *et al., Nano Lett.*, 2006 (which, to the authors' knowledge, originally introduced MCOs) at the paper's first mention of MCOs. All added citations are on page 5 of the revised text.

## Note 2

*In Figure 1c, there are no units or values for the DOS on the y-axis. In Figure 1d, it is unclear if the difference plot is generated by taking the difference of the ensemble* T (*E*) *and the ensemble DOS presented in Figures 1b and 1c, respectively, or the difference between the* T (*E*) *and DOS for each of the 413 samples and then averaged. The authors don't explain how they calculate the DOS. Based on Figure S1c, it appears that they are binning the energy levels in a histogram. Instead, they should be using the spectral function (i.e., DOS* $= Tr[\mathrm{Im}G_s(E)]$*), which would produce a continuous function much like* T (*E*) *in Figure S1b. Plotting DOS −* T (*E*) *in Figure 1d seems. I think there are better ways to demonstrate the points the authors are trying to make with Figure 1d.*

- *If they want to show QI, instead of the DOS they should use* $Tr[Q(E)]$*, which is the noninterfering part of the Q matrix. So, Figure 1d could be a plot* T (*E*)$-Tr[Q(E)]$*, which would show the net QI as a function of energy.*
- *If they want to show localization, they could consider the imaginary part of the virtual levels (i.e.,* $\lambda$ *in Eq. 2), which represents the coupling to the leads. They could produce a plot like Figure 5g of our paper, showing coupling as a function of energy. Localized states would have low coupling.*

**Response:** This note raises a number of issues, which we address individually below.

1) We have added units to our density of states (DOS) plots (i.e. Figs. 1c and S1c).
2) The difference plot in Fig. 1d was generated by evaluating the difference between the ensemble-averaged transmission coefficient $\langle T(\varepsilon)\rangle$ (plotted in Fig. 1b) and the aggregate DOS of all structures in our ensemble plotted in Fig. 1c). Given that our plot of $\langle T(\varepsilon)\rangle$ in Fig. 1b is resolved on a much finer

energy grid ($\delta\varepsilon_{\mathrm{T}} \simeq 8 \cdot 10^{4}$ eV) than the DOS ($\delta\varepsilon_{\mathrm{DOS}} \simeq 0.05$eV), $\langle \mathrm{T}(\varepsilon) \rangle$ was sampled at the DOS bin centers before evaluating its difference with the DOS.

3) We acknowledge that obtaining the DOS from the spectral function DOS($\varepsilon$) = $\rho(\varepsilon)$ = $-\mathrm{Tr}[\mathrm{Im}\mathbb{G}(\varepsilon)]/\pi$ is more rigorous and in better keeping with the Green's function formalism used in this work. However, our implementation of this calculation encountered minor numerical instabilities making it impossible to include the outcomes in the main text while meeting the manuscript revision deadline. We will include our results here instead and try to convince the reviewer that the outcome is close to being equivalent to the calculation reported in the main text.

For each structure, we evaluate:

$$\rho(\varepsilon) = -\frac{1}{\pi} \sum_{n} \frac{\gamma_n}{(\varepsilon - \varepsilon_n)^2 + \gamma_n^2}$$

where $\varepsilon_n$ and $\gamma_n$ respectively denote the real and imaginary parts of the eigenvalue associated with the MAC

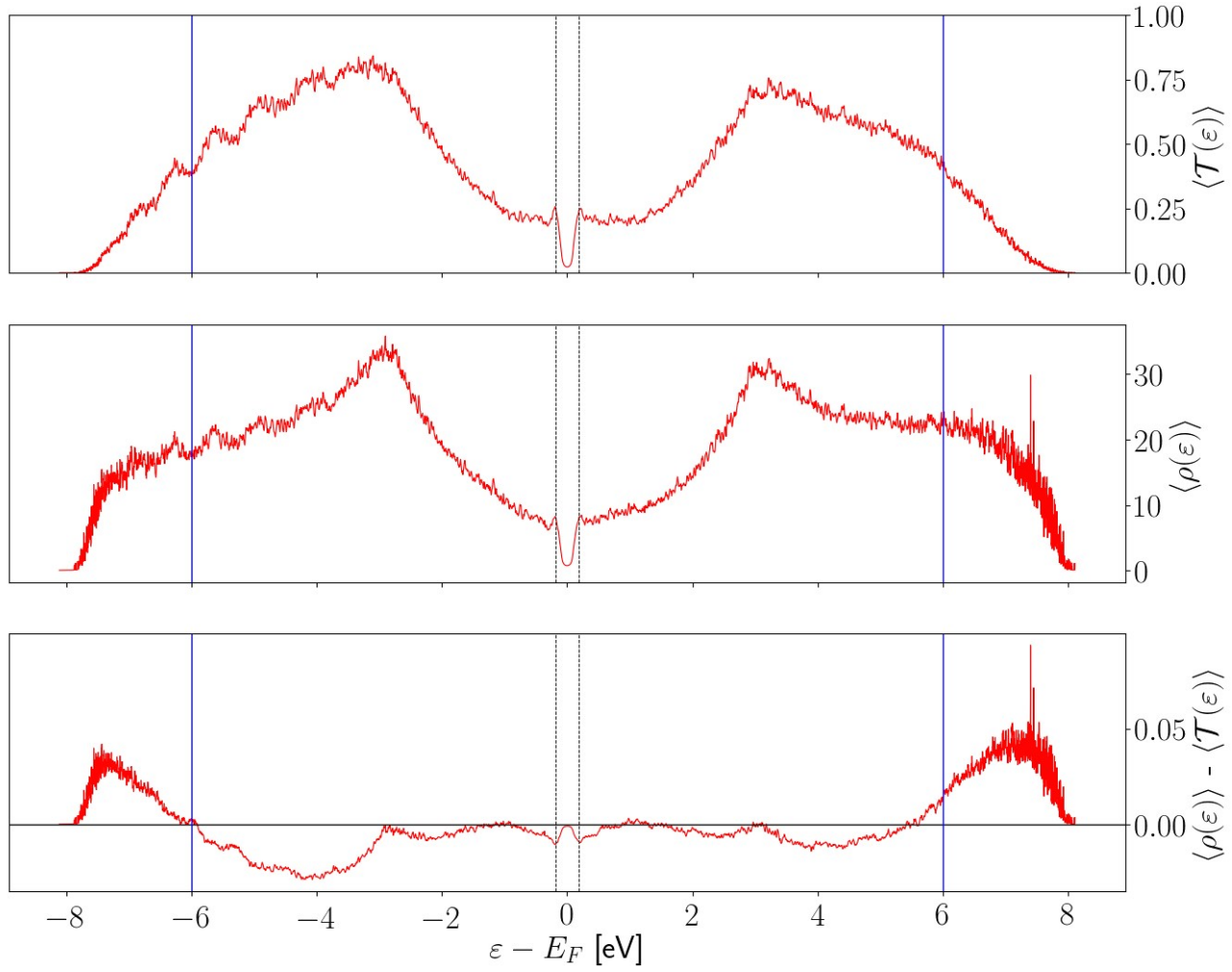


Figure R1: **(a)** Ensemble averaged transmission function of MAC nano-fragments (413 samples were used). **(b)** Ensemble-averaged spectral function of the 413 MAC nano-fragments used in our paper. The vertical dashed lines are placed at $\varepsilon = \pm\langle\Delta\varepsilon\rangle/2$, where $\langle\Delta\varepsilon\rangle$ denotes the average bandgap of the ensemble of MAC structures. Verticle solid lines are placed around ±6eV to indicate separation of insulating states from conducting states. **(c)** Difference plot between the spectral function and transmission function computed following normalization by the area under their respective curves.

fragment's $n^{\text{th}}$ MCO (which we evaluate using SciPy's linalg.eig function), and $\varepsilon$ is sampled from the same energy grid as the one used to evaluate T ($\varepsilon$). We then average the spectral function over all fragments to obtain $\langle\rho(\varepsilon)\rangle$, and we evaluate the difference $\langle\rho(\varepsilon)\rangle - \langle$T ($\varepsilon$)$\rangle$. We plot our results in Figure R1. Examining this plot, we can see the curves on figure R1b and R1c exhibit odd noise at the higher energies in the spectrum. We had very little time to identify the origins of this noise but it is likely something trivial. Unfortunately all authors at this time are scattered around the world for the winter break and their minds are somewhat distracted from this particular problem. Given the circumstances and the instabilities, we elect to keep our plot as is. While our original method of evaluating the DOS is more primitive, it exhibits less risk for numerical error and we therefore have greater confidence in its result.

4) While the reviewer is correct in noting that the difference between the ensemble's aggregate DOS and $\langle T(\varepsilon)\rangle$ is an imperfect way of showing QI or MCO localisation, our intent behind Figure 1d is to highlight regions of energy spectrum over which MAC exhibits non-trivial transmission properties (i.e. a much greater/lower transmission than one would expect from the number of states in such regions). In other words, Figure 1d represents our attempt at qualitatively capturing both QI and MCO localisation simultaneously. The disagreements between $\langle T(\varepsilon)\rangle$ and the DOS then motivate further examination into both QI and localisation deeper in the text. The figures that follow are then focused on one or the other; Figures 2 and 3 focus on MCO geometry and localisation,

while Figure 4 focuses on QI.

5) We follow the reviewer's suggestion by adding a scatter plot of the MAC ensemble's MCOs in $(\varepsilon,\gamma,1/\text{IPR})$ space to the Supporting Information (this plot is also shown in Figure R2 of this response). Interestingly, this plot reveals that the most strongly coupled MCOs tend to be the ones that are localised on the fewest sites. Producing the same plot for a graphene nanoribbon of similar size produces very similar results. The comparison of both plots strongly suggests that graphene's well-known edge states are robust to the introduction of significant disorder at the edges and in the bulk of the carbon network. We discuss this in some detail in the Supporting Information.

6) Finally, noting that the spectral function remains finite inside of the ensemble's bandgap, we relax our language concerning the connection between QI and the nonzero transmission in the bandgap: our revised draft now states that the constructive QI between MAC's frontier orbitals is one of the contributing factors to finite transmission at $E_F$.

**Changes to text:**

- We added units to the DOS plots on Figures 1c and S1c. We also added a clearer explanation of how the DOS and difference plot were obtained:

We evaluate the DOS by binning the real parts of the MCO eigenvalues (i.e. the MCO energies) $\varepsilon_j = \text{Re}\lambda_j$

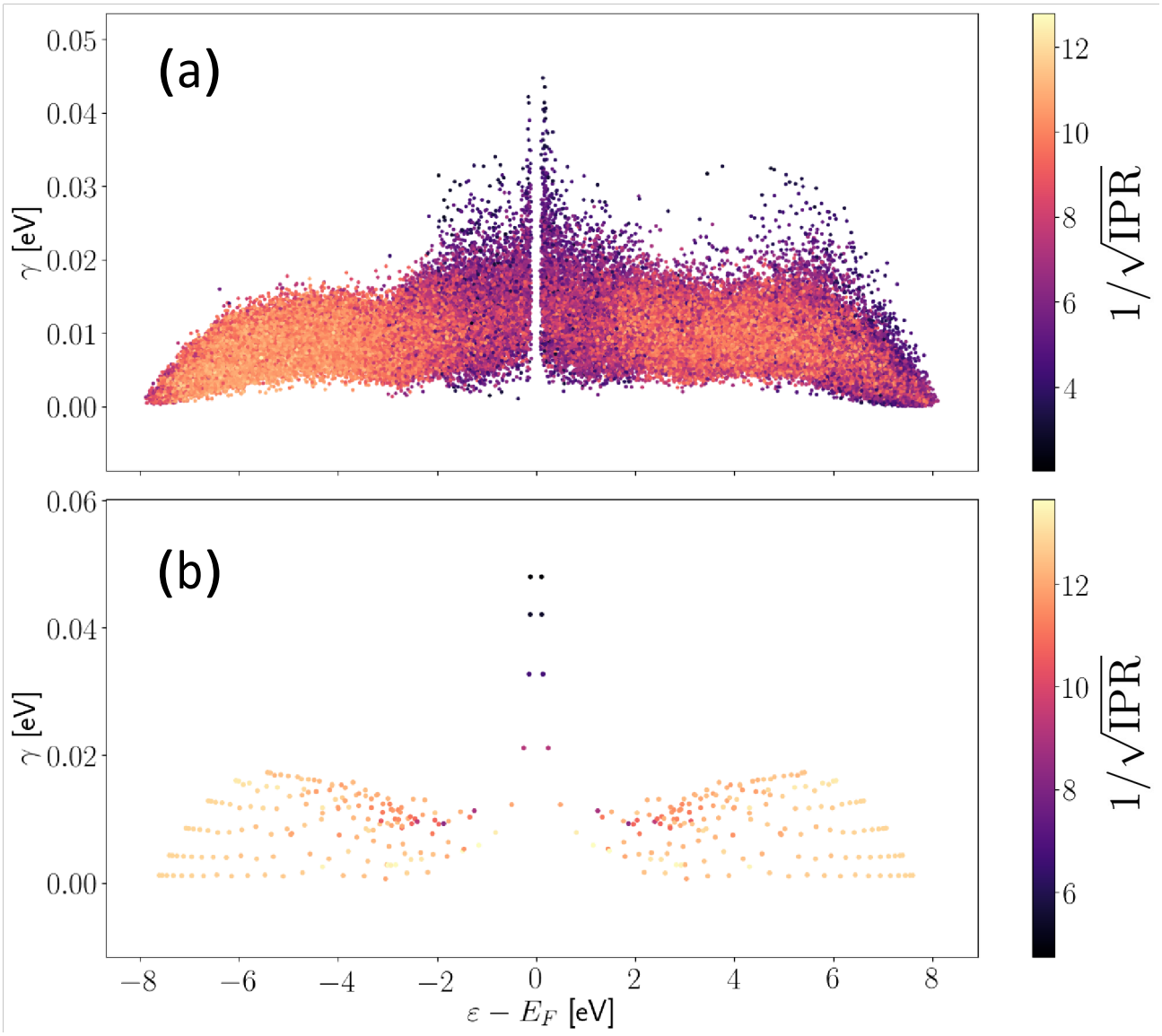


Figure R2: Energy dependence of MCO-lead coupling in **(a)** the MAC nano-fragment ensemble, and **(b)** the graphene nano-fragment discussed in section S4 of the SI (see Figure S1a therein). The colour bars of both subplots corresponds to the MCOs' IPR-derived localisation metric (defined in the paper).

in 300 bins of width $\delta\varepsilon_{\mathrm{DOS}} \simeq 0.05$eV, and normalising the resulting histogram by its total area.

- We also added the following footnote in the second sentence of the the paragraph starting with "The agreements and the disagreements between the transmission and the DOS..." which reads:

Given that our plot of $\langle \mathrm{T}(\varepsilon) \rangle$ in Fig. 1b is resolved on a much finer energy grid ($\delta\varepsilon_{\mathrm{T}} \simeq 8 \cdot 10^{-4}$ eV) than the DOS plotted on Fig. 1c, $\langle \mathrm{T}(\varepsilon) \rangle$ was sampled at the DOS bin centers before evaluating its difference with the DOS.

- We added section S5 to the SI, which discusses Fig. R2 and the robustness of edge states.

- We replaced "...which suggests that finite transmission within a given sample's bandgap is due to constructive QI." on pages 11-12 of our original draft with "which suggests that constructive QI contributes to the finite transmission within a given sample's bandgap." on page 13 of the revised manuscript.

## Note 3

*The authors argue that the constructive interference between the HOMO and LUMO is due to the partial spatial overlap between these two states at the edges, as shown in Figure 4c and 4d. However, the images shown in Figure 4c and 4d are not strong evidence. The electron density of the HOMO looks to be a little lower than the electron density of the LUMO. Maybe it's due to the color scheme? Also, this representation of the HOMO and LUMO does not illustrate the phase.*

**Response:** We agree that the point we were trying to make was not well illustrated by Figures 4c-d. We have therefore made a few adjustments to the figures and to the text to rectify this.

**Changes to text:**

- We modified Figures 4c and 4d to show the probability amplitude (i.e. $\langle\varphi_n|\psi\rangle$) associated with the HOMO and LUMO site-space wavefunctions, instead of the probabilities ($|\langle\varphi_n|\psi\rangle|^2$) associated with them. The revised figures now convey phase information and more clearly depict the sites on which both the HOMO and LUMO overlap (some of the sites that weakly contribute to a given state were less visible on the original figure since $|\langle\varphi_n|\psi\rangle|^2 < |\langle\varphi_n|\psi\rangle|$).

- We also added the following paragraph (footnote included) to further highlight the importance of edge-site overlap in QI between two MCOs, on page 13 of our revised manuscript:

  Figures 4c-d depict the frontier conducting orbitals of this MAC structure. The interference between these two states is explained by their partial spatial overlap at the edges of the fragment. This can be clearly shown by expanding Equation (**??**) in the basis of atomic orbitals $\{|\varphi_j\rangle\}$ and exploiting the diagonal structure of the $\Gamma_L$ and $\Gamma_R$ matrices in this basis. Letting $\{|l_m\rangle\}$ and $\{|r_n\rangle\}$

denote the set of atomic orbitals centered on sites at the left and right edges of a given fragment, we have:

$$Q_{jk}(\varepsilon) \propto \sum_{mn} \langle \psi_j | l_m \rangle \langle l_m | \psi_k \rangle \, \langle \bar{\psi}_k | r_n \rangle \langle r_n | \bar{\psi}_j \rangle$$

The expression of $Q_{jk}(\varepsilon)$ (for the derivation see Section S6 in the Supporting Information) shows that a pair of MCOs ($j \neq k$) can only interfere if they have nonzero spatial overlap at the left edge of the fragment, and their duals overlap on the right edge. We note that a state's amplitude at the edges of the fragment is the main aspect of its spatial distribution which determines its transmission properties; the state's amplitude in the bulk of the structure is of lesser importance. It is worth noting that the MCOs depicted on Figures 4c-d bear no visible differences to their respective duals[1].

- We added section S6 to the SI, which justifies equation (R1) in some detail.

## Note 4

*Minor comment: Values and units should be separated by a space, e.g., it should be "2 nm" not "2nm" throughout the manuscript.*

**Changes to text:** We have rectified this error wherever we have spotted it in the text and SI.

## Note 5

*This is more of a question than a comment: The authors use channel interchangeably with level throughout the manuscript. In our lab, we use "channel" when referring to the number of atoms in a contact and use "level" to refer to molecular orbitals. We usually say the number of channels determines the integer value of $G_0$ we measure, and we usually say the spatial distribution of a molecular orbital dictates how well a level will couple to the leads. Is there a meaningful difference between channel and level? Part of the reason I'm asking is because in Figure S1a, the transmission*

[1] For the HOMO, we have: $\max_j \left| \langle \varphi_j | \psi_{\text{HOMO}} \rangle - \langle \varphi_j | \bar{\psi}_{\text{HOMO}} \rangle \right| \simeq 0.007$ (idem for the LUMO). This difference is much smaller than the relevant contributions to the site-space wavefunctions of either the HOMO-LUMO (cf. the colour bar on Figures 4c-d).

*function goes above 1 several times. The authors state that the "*T (*ε*) *remains greater than 1 within the nano-fragment's HOMO-LUMO gap, despite the absence of channels in this range of energies." I am not sure what this means.*

**Response:** We thank the reviewer for catching this, our interchangeable use of "channel" with "level" was merely a naive stylistic choice to avoid repeating "level" or "orbital" too many times in the same sentence, we did not intend to imply that there were technical differences. In order to avoid confusion we have replaced all references to 'channels' with more accurate alternatives.

**Changes to text:** All instances of the word "channel(s)" within the manuscript were replaced with "level", or "orbital", or "MCO".

## Note 6

*There are many typos in the SI.*

**Changes to text:** We have fixed all of the typos that we have encountered in the SI. There were indeed more than we thought.

Sincerely,

Lena Simine and Nicolas Gastellu