

# When Current Does Not Follow Bonds: Current Density in Saturated Molecules

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## Abstract

The tools commonly used to understand structure-property relationships in molecular conductance, inter-atomic currents and conductance eigenchannels, generally give us a sense of familiarity, with the chemical bonding framework and molecular orbitals reflected in the current. Here we show that while this picture is true for conjugated molecules, it breaks down in saturated systems. We investigate the current density in saturated chains of alkanes, silanes and germanes and show that the current density does not follow the bonds, but rather the nuclei define the diameter of a pipe through which the current flows. We discuss how this picture of current density can be used to understand details about the electron transport properties of these molecules. Understanding the spatial distribution of current through molecules, rather than simply the magnitude, provides a powerful tool for chemical insight into physical properties of molecules that are related to current flow.

## Introduction

Structure-property relationships have long been the cornerstone of many areas of chemistry and are certainly a goal for understanding in many others. In molecular conductance, a field that has emerged relatively recently, understanding the link between chemical functionality and conductance properties has been an area of significant interest.<sup>1</sup> However, the measurable observables, for example current, conductance, thermopower, do not obviously lend themselves to chemical interpretation. Theoretical tools have therefore been developed that provide greater scope for chemical insight, alongside the methods to calculate these observables

Two popular methods are inter-atomic local currents<sup>2</sup> and conductance eigenchannels.<sup>3</sup> Both have been used successfully to understand interference effects<sup>2,4</sup> and inelastic electron tunnelling spectroscopy (IETS)<sup>5-7</sup> and part of their success comes from the extent to which they reinforce our pre-existing ideas about electronic structure. Local inter-atomic current

gives a map of the interactions within the molecule that mediate the tunnelling pathway and reinforces the idea of electronic coupling through-bond and through-space<sup>8</sup>. Eigenchannels show the decay characteristic of scattering states, but take the form of something very similar to the molecular orbitals at resonance. Both of these pictures undoubtedly provide additional information, but at the same time, give a sense that the knowledge we have about the isolated molecule in terms of chemical structure and that molecular orbitals are predictive of the pathway for the current.

At the same time, methods have been developed to calculate the current density through molecular junctions<sup>9-19</sup> a measure that gives spatial information about the pathway while being a much more direct tool for interpretation.<sup>20</sup> Here we probe what we can learn from the current density and show that, at least for saturated systems, it can depart significantly from any sense of the transport that the inter-atomic current or eigenchannel analysis would give us. Specifically, we show that the bonding topology and form of the molecular orbitals are not predictors of the form of the current density.

This paper proceeds as follows. We first outline the formal definition of the current density, with particular focus on the terms that are necessary to ensure current conservation and the choices made in our implementation. Then we compare inter-atomic current, eigenchannels and current density for conjugated and saturated molecules to illustrate when these three methods are providing complementary pictures of transport. Finally, we probe deeper into the nature of the current density through saturated chains looking at both conformational and chemical variation and how we can use this information to obtain physical insight.

# Method

## Formal definition

In the standard transport problem of a molecular junction we consider three regions: left electrode  $L$ , right electrode  $R$  and central region  $C$ . We can write the Hamiltonian in an orbital basis (on matrix form),

$$\mathbf{H} = \begin{bmatrix} \mathbf{H}_L & \mathbf{V}_L & 0 \\ \mathbf{V}_L^\dagger & \mathbf{H}_C & \mathbf{V}_R^\dagger \\ 0 & \mathbf{V}_R & \mathbf{H}_R \end{bmatrix}, \quad (1)$$

assuming there is no direct interaction between the left and the right electrode. The transport properties can be calculated with a combination of non-equilibrium Green's functions (NEGF) and non-interacting single particle states from density functional theory (DFT) or similar. In the NEGF formalism the current density in central region and in the absence of a magnetic field is defined as<sup>9</sup>

$$\mathbf{j}(\mathbf{r}) = \frac{e\hbar}{2m} \int \frac{dE}{2\pi} \lim_{\mathbf{r} \rightarrow \mathbf{r}'} (\nabla_{\mathbf{r}} - \nabla_{\mathbf{r}'}) G_C^<(E; \mathbf{r}, \mathbf{r}') \quad (2)$$

$$= \frac{e\hbar}{4m\pi} \sum_{i,j \in C} \int_{-\infty}^{\infty} dE G_{ij}^<(E) [\psi_i(\mathbf{r}) \nabla \psi_j(\mathbf{r}) - \psi_j(\mathbf{r}) \nabla \psi_i(\mathbf{r})]. \quad (3)$$

The central quantity here is the lesser Green's function,  $G^<(E; \mathbf{r}, \mathbf{r}') = \sum_{i,j} \psi_i^*(\mathbf{r}) G_{ij}^<(E) \psi_j(\mathbf{r}')$  which has been expanded into a standard non-orthogonal orbital basis  $\{\psi_i\}$ . In steady state conditions the lesser Green's function is defined as  $\mathbf{G}_C^<(E) = \mathbf{G}_C^r(E) \mathbf{\Sigma}^<(E) \mathbf{G}_C^a(E)$ . The retarded and advanced Green's functions of the central region are defined as  $\mathbf{G}_C^{r/a}(E) = [E\mathbf{S}_C - \mathbf{H}_C - \mathbf{\Sigma}^{r/a}(E)]^{-1}$  and the self-energy is defined in terms of the coupling between the left/right electrode and the central region  $\mathbf{V}_{L/R}$ ,  $\mathbf{\Sigma}^{r/a}(E) = \sum_{\alpha=L,R} \mathbf{V}_\alpha^\dagger \mathbf{g}_\alpha^{r/a}(E) \mathbf{V}_\alpha$  with the non-interacting Green's functions of the electrodes  $\mathbf{g}_\alpha^{r/a}(E) = [E\mathbf{S}_\alpha - \mathbf{H}_\alpha]^{-1}$ . The overlap matrix is given as  $S_{ij} = \langle \psi_i | \psi_j \rangle$ . The lesser self-energy is given as  $\mathbf{\Sigma}^<(E) =$

$i(\mathbf{\Gamma}_L(E)f_L(E) + \mathbf{\Gamma}_R(E)f_R(E))$  with the spectral densities  $\mathbf{\Gamma}_{L/R}(E) = i(\mathbf{\Sigma}_{L/R}^r(E) - \mathbf{\Sigma}_{L/R}^a(E))$  and Fermi functions  $f_{L/R}(E) = [e^{\frac{E-E_F}{k_B T}} + 1]^{-1}$  using the Fermi energy  $E_F$ , Boltzmann constant  $k_B$  and temperature  $T$ .

Here we only consider the case of zero temperature and small bias. In this limit, at energies between the chemical potentials of the two leads (ie. within the bias window),  $\mathbf{G}^<$  reduces to

$$\mathbf{G}^< = i\mathbf{G}^r\mathbf{\Gamma}_L\mathbf{G}^a. \quad (4)$$

We then define

$$\mathbf{G}^n = i\mathbf{G}^r\mathbf{\Gamma}_L\mathbf{G}^a\delta V \quad (5)$$

where  $\delta V = V_L - V_R$ , allowing us to write the current density as

$$\mathbf{j}(\mathbf{r}) = \frac{ie^2\hbar}{4m\pi} \sum_{i,j \in C} \int_{-\infty}^{\infty} dE G_{ij}^n(E) [\psi_i(\mathbf{r})\nabla\psi_j(\mathbf{r}) - \psi_j(\mathbf{r})\nabla\psi_i(\mathbf{r})]. \quad (6)$$

The total current can be found by integration over a cross section of the current density,

$$J = \int \mathbf{j}(\mathbf{r})d\mathbf{A}, \quad (7)$$

where  $d\mathbf{A} = dx dy$  if  $z$  is the transport direction. Another method for calculating the total current is through the standard Landauer Buttiker formula,

$$I = \frac{e\hbar}{2\pi} \int dE (f_L(E) - f_R(E)) \text{Tr}[\mathbf{G}_C^r(E)\mathbf{\Gamma}_L(E)\mathbf{G}_C^a(E)\mathbf{\Gamma}_R(E)]. \quad (8)$$

The two methods are equivalent  $J = I$ . However, numerical calculations integrating the current density using standard quantum chemistry basis sets can be difficult to converge to the values given by calculations of the total current, see SI for a discussion.

The two other methods applied here are: 1) the local inter-atomic current which can be found as<sup>2</sup>

$$I_{ij}(E_F) = \frac{2e}{h} \sum_{i \in k, j \in l} \text{Im} [H_{ij} G_{ji}^n(E_F)]. \quad (9)$$

where  $k$  and  $l$  are all orbitals on atom  $i$  and  $j$ , respectively.  $I_{ij}$  is thus the magnitude of the current at the Fermi energy between a specific pair of atoms,  $i$  and  $j$ . 2) The energy-normalised transmission eigenchannels are found through the method as prescribed by Paulsson and Brandbyge.<sup>3</sup>

The three common complementary methods applied to understand the structure-property relationship of molecular conductance each illustrate a unique perspective. The local inter-atomic current maps out the magnitude and direction of the current elements between pairs of atoms that mediate the total current. This method strictly distinguishes between through-bond and through-space transport. As the contributions from all atomic orbitals associated with each atom are summed, the method does not distinguish between current flowing through the  $\sigma$  or  $\pi$  systems without prior symmetry transformation. The interatomic currents are typically plotted as arrows overlaying the molecular structure, giving a sense of a spatial pathway, although this should be understood as an artificial construct rather than a real representation of the path.

The transmission eigenchannels give a spatial understanding of the pathway of the tunnelling electron in the form of a decaying wavefunction. The form of the eigenchannels is energy dependent, with each eigenchannel generally taking the form of the energetically proximate molecular orbitals, attenuated to a greater or lesser extent depending on how transmissive the molecule is (i.e. how fast the wave function decays within the molecule). The eigenchannel is the closest thing to a molecular orbital representation of the eigenstate responsible for carrying the current. While transport properties are frequently discussed as though a single orbital is responsible for the current, the reality is that many orbitals

participate. With some approximations, the magnitude of each orbital contribution can be shown to be directly proportional to the product of the orbital coefficients on the terminal atoms and inversely proportional to the energetic separation between the orbital and the Fermi energy, squared.<sup>21</sup> The eigenchannel thus provides a visual representation of this sum. At energies close to a resonance, the eigenchannel will generally take the form of the proximate molecular orbital, while off-resonance the channel will show the extent of the orbital mixing as its form varies continuously from one resonance to the next. The eigenchannel representation allows  $\sigma$  and  $\pi$  contributions to be distinguished as the  $\pi$  nodal structure is preserved in the eigenchannel when this is dominant for transport.

The current density maps the movement of the total charge density in real space. The otherwise useful distinction between through-space and through-bond current is thereby strictly lost, as the current density vector field shows the magnitude and direction of the current at a point in space without distinguishing which atoms mediate the current. On the other hand, the current density provides a direct representation of the path the current takes including the nodal planes reflecting the  $\sigma/\pi$  character of the eigenchannel.

## Practical Implementation

All calculations are carried out using DFT as implemented in GPAW<sup>22-24</sup> with PBE exchange and correlation functional.<sup>25</sup> The basis set is a linear combination of atomic orbitals, single- $\zeta$  with pseudo-potentials. The grid spacing was chosen to be 0.2 Å. The molecules were optimized in gas phase and the current density was calculated subsequently.

In the thiomethyl system we used artificial s-band electrodes (molecular hydrogen) at positions corresponding to a realistic geometry for coupling into the molecules.<sup>26-28</sup> The effect of the rest of the electrode was added as a constant  $\gamma = 1$  eV in the  $\mathbf{\Gamma}_{L/R}$  matrices. This is done in the end hydrogens of the artificial electrodes. The s-band electrodes provide a computationally effective junction-calculation which gives a transmission in qualitative agreement with that of a full metal-molecule-metal junction.<sup>29</sup> In the other calculations we

added  $\gamma$  to the H atom that continues the molecular chain. All calculations were done with a bias at  $V = 1\text{mV}$ .

## Results and discussion

In Figure 1 we show each of the three methods in the  $\pi$ -conjugated thio-methylated alkene to illustrate their relation to one another. In Figure 1 **A** the inter-atomic current suggests that the current is mediated by the chemical (bond) structure, that is, it is nearest neighbor interactions that dominate. In Figure 1 **B** the eigenchannel suggests a nodal plane in the current in the plane of the molecule although the channel does not resemble any molecular orbital of the system, but rather the sum of many orbital contributions, with density on every second atom. In Figure 1 **C** the current density reflects both the zigzag feature of the local current and the nodal feature of the eigenchannel. Note also the oscillations in the current density in the side view, reminiscent of the turbulence discussed in relation to the

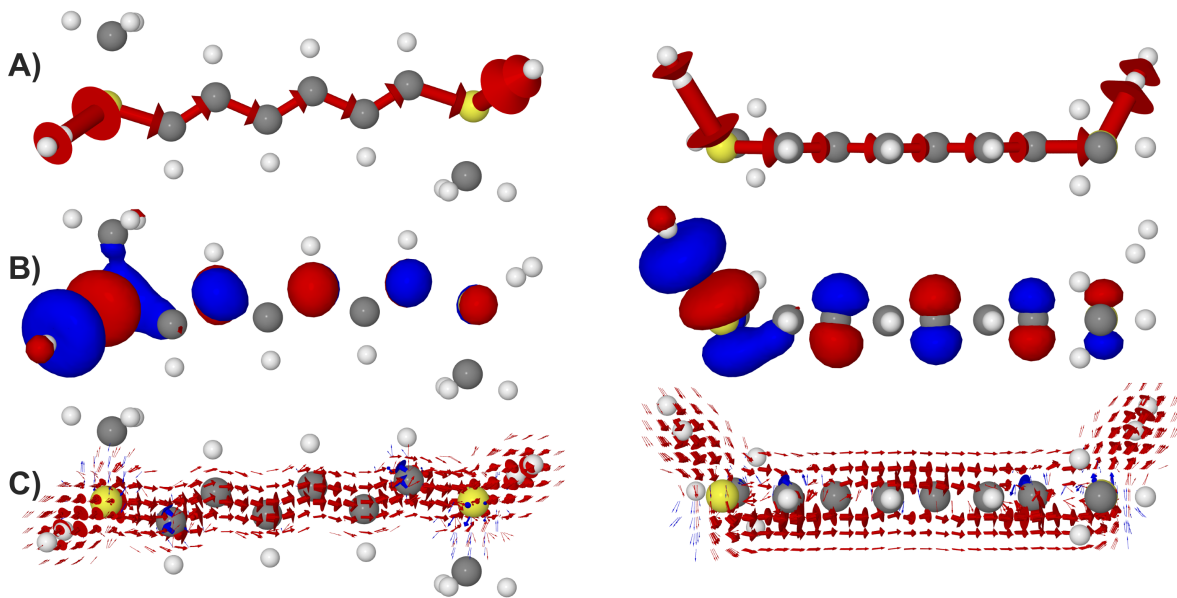


Figure 1: Top view (left) and side view (right) of three quantities used to understand the local/spatial transport properties of a alkene with thio-methyl binding groups. All properties here are at  $E_F = 0$  eV. **a)** Inter-atomic local current. **b)** The real part of the dominant eigenchannel. **c)** The current density.



fluid dynamics picture of current flow.<sup>30</sup>

There is clear agreement between of the predominantly “chemical” pictures in Figure 1 **A-B** and the current density in Figure 1 **C**. The ball-and-stick picture of molecules where the atoms are held together by chemical bonds is not only preserved in the inter-atomic local current (panel **A**), the through-bond zigzag pattern of the alkene is clearly retained in the current density (panel **C**). The nodal plane in the  $\pi$  eigenchannel (panel **B**) also remains in the current density (panel **C**), although the current density flows through atoms with and without eigenchannel density without distinguishing between the two. The chemical frameworks of inter-atomic currents and eigenchannels give a strong indication of the structure of the current density in a conjugated molecule, although neither gives the entire picture. The inter-atomic current gives not indication of the nodal plane and the eigenchannel does not suggest that each atom in the chain participates. The form we see for the current density agrees well with the literature on graphene,<sup>31</sup>  $C_{60}$ <sup>12</sup> and other  $\pi$ -conjugated systems.<sup>10,15–19</sup> The question is whether this is a general effect or simply a feature of  $\pi$ -conjugated molecules?

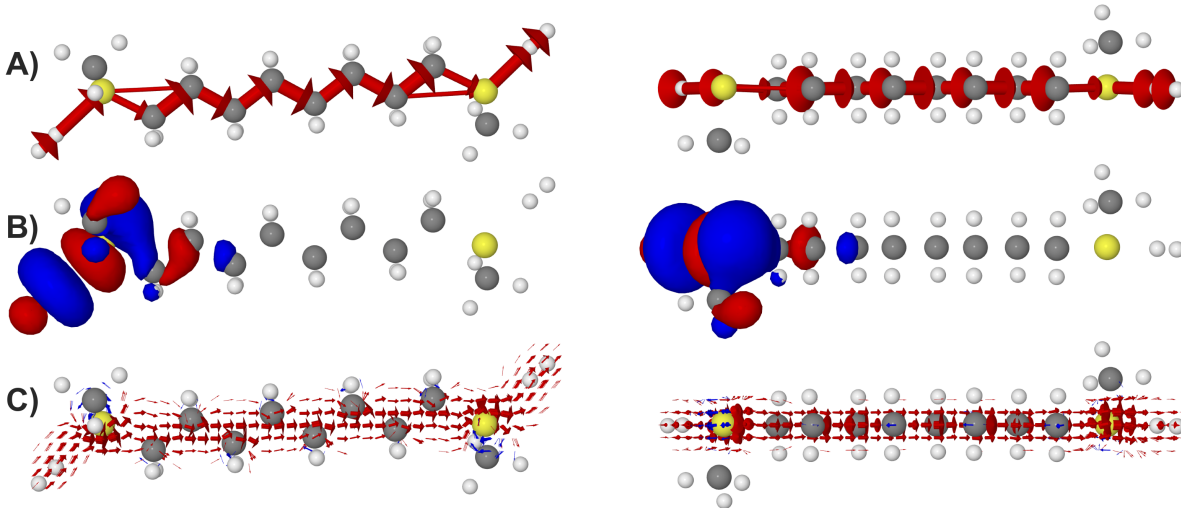


Figure 2: Top view (left) and side view (right) of three quantities used to understand the local/spatial transport properties of an alkene with thio-methyl binding groups. All properties here are at  $E_F = 0$  eV. **A**) inter-atomic local current. **B**) The real part of the dominant eigenchannel. **C**) The current density.

In Figure 2 we show the complementary methods for the saturated thiomethylated alkane. While the inter-atomic current in Figure 2 **A** still suggests a current pathway that follows the bonds, with nearest neighbor interactions dominating, there is no indication of the bonding topology in the current density in Figure 2 **C**. To a large extent, the current density indicates that the current simply takes the shortest straight path through the center of the linear molecule with the carbon atoms defining the diameter of a pipe. While some oscillations are evident in the current density, note that the current density appears to curve away from the carbon atoms, not towards them as it did in the alkene. In Figure 2 **B** the eigenchannel illustrates the much faster decay in the saturated system (by the limited spatial extent of the channel) but still the channel density extends into the  $\sigma$ -bonding orbitals in the backbone giving no suggestion of the pipe-like nature of the current density within the molecule.

The chemist’s picture of molecules and how current may flow through them appears to break down. The frameworks of local inter-atomic current and eigenchannels do not provide a picture that allows any prediction of the flow of current in real space for the case of alkanes. It is clear that molecular structure and molecular orbitals (and the corresponding eigenchannels) do not provide full insight into the structure-property relationship and caution should be employed when attempting to rationalize current pathways from these quantities.

## Inside the alkane

If we remove the thiomethyl binding groups and instead inject directly into an alkane, we can better investigate the role of the carbon backbone in controlling the nature of the current density, without variability from the binding groups. In Figure 3 **A** we plot the current density for octane with direct injection/absorption into the hydrogen atoms at each end. We observe the same pattern for the current density as was seen for the substituted system. In Figure 3 **B-D** we show three cross sections of the current density as indicated by the vertical line in Figure 3 **A**. In Figure 3 **B** we show a cross section right on top a  $\text{CH}_2$  plane. We see that the current density goes tightly over the C atoms and a weak backwards current goes

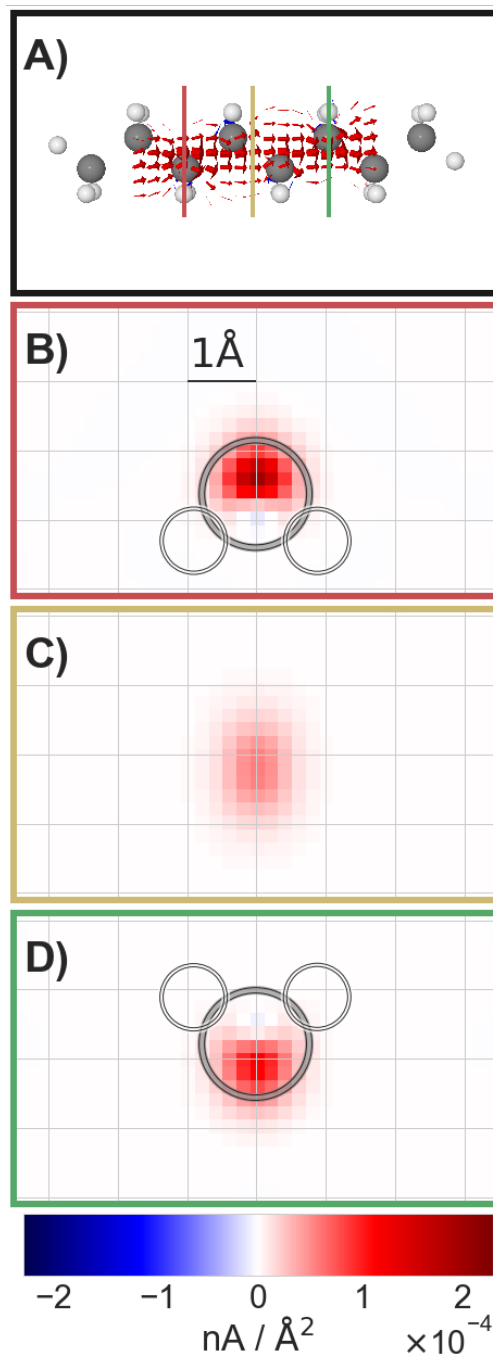


Figure 3: **A)** Sideview of octane and the current density for the converged region. Arrows smaller than 5% of the largest arrow are not shown. **B)-D)** Cross sections of the current density at chosen positions as illustrated in **A**.

underneath it. Compare this to Figure 3 **C** which shows the current density in the bonds. The current density is now elongated and more diffuse. The pipe is approximately 2 Å tall and 1 Å wide. In Figure 3 **D** we again show a cross section on top a CH<sub>2</sub> plane but here the majority of the current density goes underneath the C atom and with a small backwards current on top – the symmetry of the molecule appears preserved in the current density. In both Figure 3 **B** and **D**, the backward currents on the hydrogen-side of the carbon atoms seem to indicate a small ring current around these atoms.

The picture that emerges for the current density through the alkane has two characteristic (and arguably surprising) features. First, the direct flow of the current density through the molecule breaks from the intuition of chemical bonds and structure. The current density is not through-space in the sense commonly used by chemists, i.e. current running directly between non-bonded atoms. However, the current does not flow along the chemical bonds, there is no evidence of a zig-zag pattern, and as such the current density seems to ignore the perceived direction of the  $\sigma$ -bonds. Second, there are real-space ring currents around the carbon atoms.

## Why does the current flow through the center of an alkane?

A natural question to ask at this point is why does the current flows through the center of the alkane? The first point to note is that this is clearly the shortest path through the system, thus basic physics suggests that this would be the path taken through a conductor. This raises the alternate question of why the current density does not take a direct path through the alkane. In both cases, there is no indication from the inter-atomic currents or the eigenchannels/molecular orbitals that these two cases should be so different.

Beyond the inter-atomic current and eigenchannel pictures used to understand charge transport through molecules, orbital pathways analyses have also been developed to understand electron transfer<sup>32,33</sup> through alkane chains (amongst others).<sup>34,35</sup> We can ask the question of whether these orbital pathways provide insight into the form of the current den-

sity for alkanes? Some caution is required when making a direct comparison between electron transfer studies and electron transport as the choice of donor and acceptor need not allow for the same coupling into the alkane chain as the electrodes and binding group provide, for example the symmetry can differ. Further, the Fermi energy of the electrodes need not correspond to the energy range determined by the donor and acceptor, although this is not likely to be so significant in the case of the all-*trans* alkane as the transmission (and thus energy dependence of the coupling) is reasonably constant across a broad energy range around the Fermi energy. Nonetheless, this approach has been applied successfully to understand trends in charge transport experiments<sup>36</sup> we believe the orbital pathways provide a hint as to why the current density flows directly through the alkane.

In the orbital analyses, the coupling is decomposed into pathways involving interactions between pairs of C-C and C-H  $\sigma$ - and  $\sigma^*$ -orbitals along the chain. The details of the method (including the choice of basis set) are important for the details of the dominant pathways, but some broad conclusions are clear from these studies. Generally, the coupling through alkanes arises from contributions from multiple orbital paths and the dominant paths involve pairs of C-C orbitals that are non-nearest neighbors (i.e. the interactions “jump” over some C-C bonds). If we assume that the current density will flow through the center of these orbitals, then this result suggests that the current might simply flow through the center of the molecule. Indeed the “jumps” in the orbital interaction suggest that the zig-zag pattern of the bonding topology need not be reflected in the current as it is not nearest neighbor interactions that dominate.

While local descriptions of transport certainly provide an interesting visualization of current flow, we are left with the question of what physical insight we actually gain. In this case we ask: what properties of alkanes (transport or otherwise) might we be able to understand from the real-space picture of the current density? The pipe-like nature of the alkane suggests that the current flows through a region of the molecule that is effectively isolated by the surrounding nuclei. A suggestion that is reinforced by the comparison with the

$\pi$ -conjugated alkene system where the current flows above and below the plane of the nuclei. We speculate that this might offer some protection against environmental effects that may otherwise perturb the current. Indeed, calculations have suggested that alkanes are much less sensitive to the effect of close-packing in a monolayer than  $\pi$ -conjugated systems.<sup>37</sup>

## Structural dependence of the current density

In the previous section we examined the most commonly assumed all-*trans* conformation of the alkane. Let us now probe the effect of a gauche defect in the molecular backbone. These are known to reduce the conductance of saturated molecules due to destructive quantum interference.<sup>2,38-41</sup> It also changes the nature of the modes predicted for IETS and <sup>13</sup>C NMR.<sup>42,43</sup> How is the pipe-like current density of the alkane affected when the structure is perturbed?

In Figure 4 **A** we show the current density for the alkane where the central C-C-C-C dihedral angle is manipulated to 0°. The current density is significantly different from that of all-*trans* octane. Little of the pipe-like structure remains and we now see layers of forward and backward current through the center of the molecule. In Figure 4 **B-D** we again show three cross sections. In Figure 4 **C** shows how the current is stacked in three layers; strong forward current above the C atom, backwards current on top and finally a weak forward current. In Figure 4 **C** there are also three layers and the lower forward current is more diffuse than in panel **B**. In Figure 4 **D** a significant ring current appears around the the C atom, stronger than the forward current below it.

These large ring currents lead us to speculate as to whether this picture of current density could be reflecting an effect that would also be visible in NMR. At this stage it is simply a speculative question as the ring current picture of NMR<sup>45-48</sup> is not without controversy<sup>49</sup> and not normally applied to saturated systems. At the same time, there is theoretical evidence that the <sup>13</sup>C NMR is sensitive to these kinds of defects<sup>43</sup> so this may be related to the ring currents we see here. A further point to note is that of course our calculations are done at

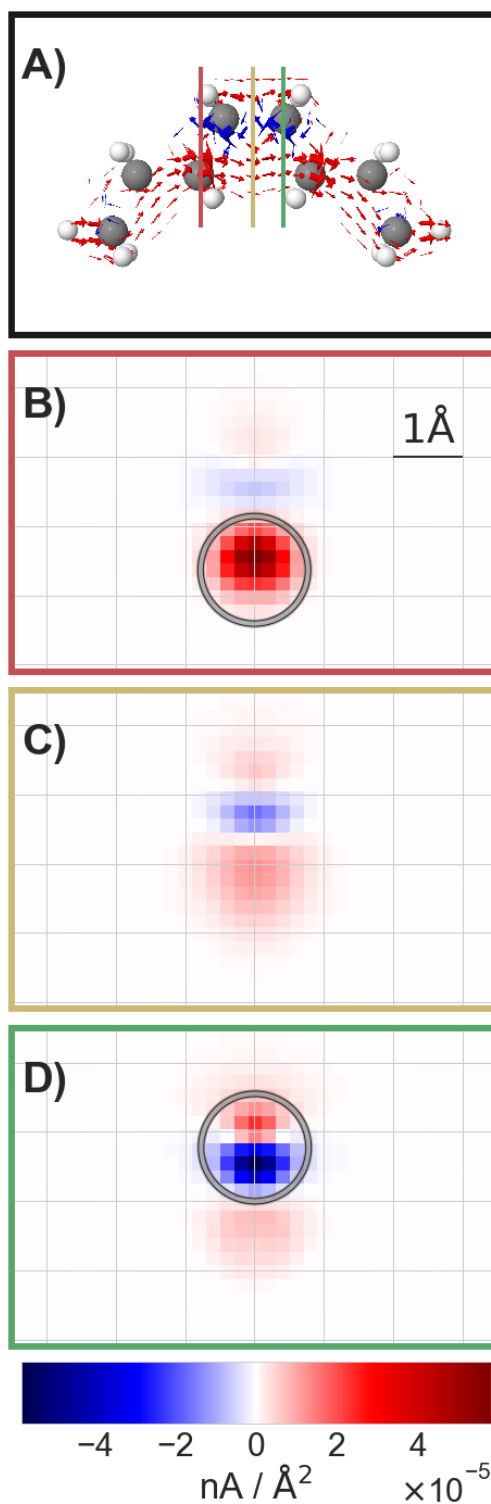


Figure 4: **A)** Sideview of octane with defect and the current density (2 and the Zhang method<sup>44</sup>) for the converged region. Arrows smaller than 5% of the largest arrow are not shown. **B)-D)** Cross sections of the current density at chosen positions as illustrated in **A)**.

finite bias, whereas NMR experiments are, of course, not performed under these conditions.

More closely related to transport, there are also calculations showing how the dominant peaks observed in IETS calculations can change under junction compression as defects are introduced.<sup>42</sup> In that case it was observed that the introduction of defects led a reduction in the intensity of the C-C stretch mode as well as new peaks in the IET spectra: notably a C-H stretch close to the defect as well as CH<sub>2</sub> rock and wag modes. In a picture of current flowing through bonds, the differences in these spectra are not easy to understand. However, when we consider the stark differences observed in the current density, we can question whether this picture might aid understanding of IETS. Certainly, the forward current that flows between carbon atom 3 and 6 near the defect is closer to the hydrogen atoms in this region, and similarly the large ring currents on carbon atoms 4 and 5 also interact with the hydrogen atoms. It remains an open question as to how exactly these effects result in the changing spectra, but it certainly points to the utility of a theory for inelastic scattering built on a real-space picture as a way to get further insight into these kinds of questions.

## Increasing $\sigma$ -conjugation

While the alkanes seem to offer the possibility of steric protection, they do not offer significant magnitude of the current. Moving down the group to Si and Ge is known to increase the conductance significantly,<sup>50-52</sup> so we compare the all-*trans* alkanes with the equivalent silane and germane in Figure 5. For comparable coupling into the molecules with the alkane, and comparability with the experimentally measured systems, the edge molecular units is -CH<sub>3</sub> in all systems.

In Figure 5 **A**, **D** and **G** the side views clearly show the direct flow through the molecules without following the bonds. The diameter of the region with significant current density also increases as the atom size increases. The cross sections on top of the atom shown in Figure 5 **B**, **E** and **F** show that the magnitude of the atomic ring currents or backward current is also increasing with the increase in the net current. The cross sections in the backbone bonds



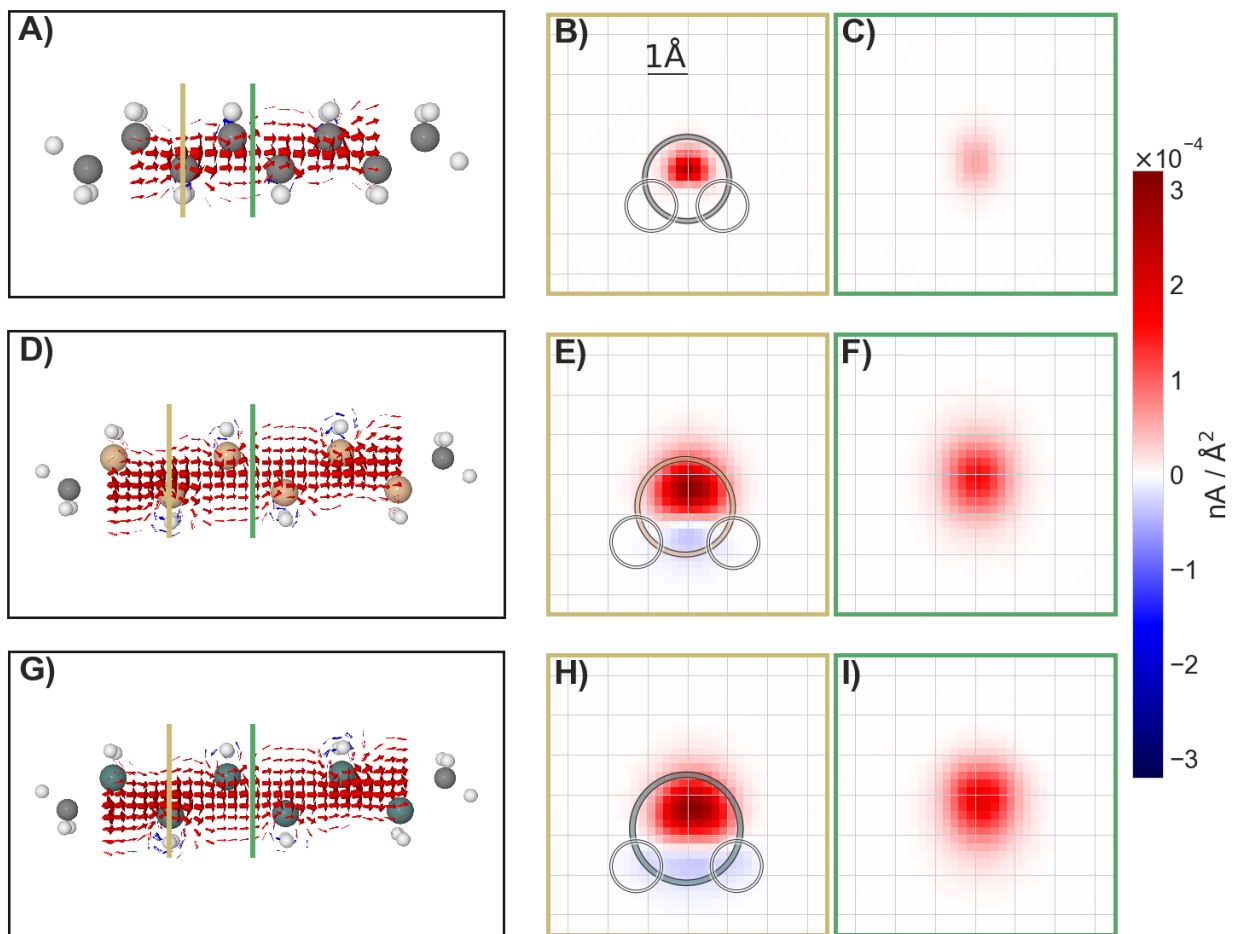


Figure 5: **A)** Sideview of octane **B)** Current density cross section on-top a C atom **C)** Current density cross section on-top in the C-C bond. **D)** Sideview of 1,6-dimethyl-hexasilane **E)** Current density cross section on-top a Si atom **F)** Current density cross section on-top in the Si-Si bond. **G)** Sideview of 1,6-dimethyl-hexagermane **H)** Current density cross section on-top a Ge atom **I)** Current density cross section on-top in the Ge-Ge bond.

(panels 5 **C**, **F** and **I**) show that the current density increases in size and the shape takes a more and more circular form as we go down the group. The total current through the silane and germane increases with a factor of  $\sim 5$  over the alkane in good agreement with STM break junction experiments.<sup>51</sup>

The difference in the electronic structure between alkanes and the more conductive silanes and germanes has been studied extensively. The increased  $\sigma$ -conjugation as one progress from carbon down group 14 is well-described theoretically<sup>53,54</sup> and experimentally,<sup>55,56</sup> and is in close agreement with the higher conductance of silanes and germanes compared to alkanes. From the theoretical models of  $\sigma$ -conjugation one expects the dominant electronic interactions through the linear backbone of the molecule to change from hyperconjugative interactions in carbon, to through-bond conjugative in germane.<sup>57</sup> This picture does not persist and the current density is uniform through the silane and germanes, like for alkanes. As the atoms become bigger and the orbitals more diffuse the “pipe” is larger and more current can flow.

While the increased spatial extent of the current density in the silane and germane might suggest these systems were less protected than the alkane, the molecules shown here are not stable at ambient conditions. Stable silanes and germanes are generally permethylated which adds a further layer of insulation; these are shown in the Supporting Information. Permethylated also induces a helical twist in the chain but this does not appear to change the nature of the current density.<sup>58,59</sup>

## Conclusion

To summarize, we have shown that while the chemical frameworks normally used to understand the structure-property relationships work well for conjugated molecules, they break down for saturated molecules. In alkanes, the current density showed a pipe-like character where the charge takes the shortest path possible and the nuclei define the diameter of

the pipe. In some sense this result should be entirely unsurprising. Basic physics tells us that current takes the shortest path through a conductor, yet chemical concepts lead us to different thinking. These ideas are resolved by appreciating that while we differentiate between through-bond and through-space interactions on the basis of where we draw chemical bonds, the pathway of the current does not necessarily reflect this distinction. Though the inter-atomic current in linear saturated systems is predominantly through-bond, the current density cannot be said to be clearly through-space or through-bond. The current density reflects an electronic structure in linear alkanes, silanes, and germanes that allows current to simply flow directly through the centre of the molecule, thus ignoring the zig-zag pattern of the  $\sigma$ -bonds. These protected cylinders of current density were preserved when moving down the group to silanes and germanes suggesting that these systems might offer the possibility of relatively high conductance systems that are (relatively) insensitive to their environment.

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## Supporting Information Available

Artificial electrodes and coupling; Current conservation; Alkane orbitals; Permethylated saturated chains.

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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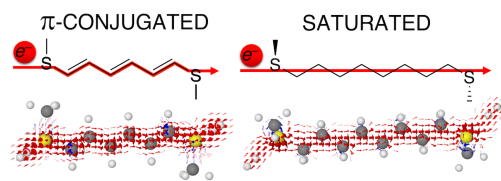
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