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Controlling the conductance of molecular wires by defect engineering

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Abstract. Understanding the charge transport mechanisms in nanoscale structures is essential for the development of molecular electronic devices. Charge transport through one-dimensional (1D) molecular systems connected between two contacts is influenced by several parameters, such as the electronic structure of the molecule and the presence of disorder and defects. In this work, we have modeled 1D molecular wires connected between electrodes and systematically investigated the influence of both soliton formation and the presence of defects on properties such as conductance and the density of states. Our numerical calculations have shown that the transport properties are highly sensitive to the positions of both the solitons and the defects. Interestingly, the introduction of a single defect in the molecular wire that divides it into two fragments, both consisting of an odd number of sites, creates a new conduction channel at the center of the band gap, resulting in higher zero-bias conductance than for defect-free systems. This phenomenon suggests alternative routes for the engineering of molecular wires with enhanced conductance.

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1. Introduction

The investigation of quantum transport through molecular systems has become an important research field in the last few decades [1]. Progress in measuring and fabrication techniques [2] has led to the continuous miniaturization of electronic devices, which has reached the point where quantum effects are important. For example, semiconductor devices have been reduced in size to the nanoscale [3, 4] and even to the atomic scale [5, 6]. In addition to reports on metal atomic wires [7–11], stable and rigid carbon atomic chains have been reported recently [12, 13]. The key idea behind the advances in the understanding of charge transport through molecular systems is based on the view proposed by Landauer, ‘Conductance is transmission’ [14, 15].

Potential applications of molecular devices range from novel computer architectures [16, 17] to chemical sensors [18] and medical diagnostics [19]. Among the various molecular devices, one-dimensional (1D) conductors, such as molecular wires [20–23], have been considered to be one of the most fundamental components for nanotechnology. Due to the reduction in the dimensions of materials, 1D systems show sensitive response to external field or intrinsic characteristics, which can be exploited for the development of molecular devices, such as biological sensors [18] with high sensitivity.

Polymers are one of the most promising materials for acting as 1D conductors. Their applicability [24] ranges from displays [25–27] to thin film transistors [28], photovoltaics [29] and solar cells [30, 31]. The compatibility of polymer materials with light-weight, mechanically flexible plastic substrates and new fabrication methods makes them possible candidates for future electronic devices.

Intrinsic properties of molecules as well as external perturbations can strongly affect the transport properties of the resulting low-dimensional devices. For example, this is the case in carbon nano junctions [32]: the conductance of 1D polymers drastically depends on the concentration and position of impurities (dopant) [33, 34] or defects [35]. Other effects that are important include dimerization and the formation of solitonic defects. Hence, all of these properties should be considered in the design of 1D devices.
The on-site energy terms, $\alpha_n$, $n = 1, 2, \ldots, N$, L and R, are set to 0 for simplicity. The $\beta_{L/R}$ are hopping integrals for the left/right 1D electrode. $V_{L/R}$ and $V_{n,n+1}$, $n = 1, 2, \ldots, N-1$, are transfer integrals for the molecule/electrode interface on the left/right side and hopping integrals between nearest neighbors, respectively. The details of the theoretical framework are described in appendix A.

Therefore, in order to facilitate the design of controllable molecular devices, it is necessary to use a theoretical approach that simplifies the monitoring of how these intrinsic features affect their transport properties. Such an approach should allow one to gain understanding and deep insights into the physical origins of the behavior of these materials. The knowledge acquired through these models can be used for the interpretation and elucidation of experimental observations, as guidelines for the planning of experiments, as well as in the design of molecular devices.

In this paper, we model molecular junctions where a 1D molecular wire is connected between two electrodes using a tight-binding approach. Then we systematically investigate how the degree of dimerization and the position of solitonic and binding defects affect the transport properties of such 1D systems. We calculate the electronic density of states (DOS) and the conductance using the Landauer model in terms of the equilibrium Green functions [36].

This paper is organized as follows. Section 2 briefly presents the theoretical framework and section 3 presents the effect of solitonic and binding defects on quantum transport through molecular systems. Finally, section 4 summarizes this paper, stressing the importance of the defect position on the linear conductor.

2. Theoretical framework

We model a molecular junction by connecting a 1D molecular wire between two electrodes. We describe this molecular system using a standard tight-binding Hamiltonian $H_C$ [37–40] that considers only $\pi$ orbitals. Here, the dimerization is represented by a sequence of alternating weak and strong bonds, while the solitonic defect is described by a pair of consecutive weak bonds. For clarity, we model the electrodes as 1D wires with Hamiltonians $H_L$ and $H_R$, which result in a fair representation of infinite reservoirs. Figure 1 shows the molecular junction considered in this work. The tunneling between the central molecule and the left and right electrodes is represented by two matrix elements $V_L$ and $V_R$. Note that the electrode parameters and tunneling amplitude are reduced to two independent parameters $\Gamma_L$ and $\Gamma_R$, the escape rates to the left and the right electrode, respectively [41]. The details of the theoretical framework are described in appendix A.

In principle, we can expand this method to general molecular systems, which include any type of orbitals. In this work, we simplified the model Hamiltonian by only considering...
\( \pi \)-orbitals, since the contribution from other orbitals to the conductance near the Fermi energy is negligible in the sp\(^2\) carbon systems that we addressed. However, in the case of the molecular wires including metal atoms \([42, 43]\), where s-, p- and/or d-orbitals play a role in charge transport, those orbitals have to be taken into account.

3. Results and discussion

3.1. Influence of the position of soliton

Dimerization and soliton formation are closely related processes that have been extensively studied. Dimerization has been examined first in the context of the metal–insulator transition, where dimerization is known as Peierls distortion \([44]\), while soliton formation has been examined in the field of conducting 1D polymers \([45]\). These effects strongly modify the conductance and other electronic properties of 1D polymers. Thus, such effects on single molecular wires connected between contacts should also be considered.

In order to estimate the influence of solitons on transport, we modeled a 1D molecular system consisting of an odd number of sites coupled with electrodes and examined the dependence of the transmission spectra, total DOS (TDOS) and local DOS (LDOS) on the position of a soliton. For simplicity, we assumed that there is a single soliton on a molecular wire. However, this approach can also be applied to larger numbers of solitons on molecular wires.

Figure 2 shows modeled polyacetylene-based (PA-based) molecular wires consisting of 19 sites connected between 1D electrodes and allowing for possibly eight soliton positions along the molecular wires. Transfer integrals associated with double bonds and single bonds are, respectively, set as \( V_d = 1.164\beta \) and \( V_s = 0.836\beta \), such that the ratio between them is the same as in the literature \((V_d/V_s = 3.65 \text{ eV}/2.75 \text{ eV} = 1.33)\) \([46, 47]\). The two hopping parameters on either side of the soliton site are set between double bond \( V_d \) and single bond \( V_s \) to be \( 1.0\beta \). All on-site energies are set as \( \alpha_n = 0, n = 1, 2, \ldots, N \). The coupling constants to the electrodes are set as \( V_{L/R} = 0.88\beta \). The 1D electrodes are treated by the Newns–Anderson model \([47, 48]\) with \( \alpha_{L/R} = 0 \) and \( \beta_{L/R} = \beta \). The fermi energy is set as \( E_F = 0 \).

Before showing the results, we note that the details of the well-known oscillations of conductance and DOS for an odd versus an even number of sites are summarized in appendix B, and the effect of dimerization is summarized in appendix C. In addition, the relationship between dimerization and length dependence of conductance is summarized in appendix D.

Figure 3 shows calculated transmission spectra and TDOS of the 1D molecular systems with different soliton positions. Interestingly, depending on the position of the soliton, the transmission at the Fermi energy \((E = E_F)\) changes drastically (see animation in Supplemental Information, available from stacks.iop.org/NJP/12/063004/mmedia). When the soliton lies near an electrode, the resonances in the transmission spectra and TDOS at \( E = E_F \) broaden with lower peaks. In this case, in spite of having an odd number of sites, the features of the TDOS and transmission resemble those for the PA-based molecular junctions, which have an even number of sites (see figure C.2 in appendix C). On the other hand, when a soliton lies in the middle of the molecular wire, the resonances in the transmission spectra and TDOS sharpen and get narrower. The value of the transmission at \( E = E_F \) approaches its theoretical maximum of 1.0.

In order to elucidate the relationship between the positions of a soliton and sharpness of resonant peaks, the distribution of LDOS along the molecular framework was calculated.
Figure 2. Schematic description of PA-based molecular wires consisting of 19 sites, with a single solitonic defect, connected between two 1D electrodes. Depending on the position of the solitonic defect, eight cases can be considered. Transfer integrals for double bonds and single bonds are set as $V_d = 1.164\beta$ and $V_s = 0.836\beta$, respectively. Two hopping parameters near the solitonic defect are set as $1.0\beta$. Coupling constants are set as $V_{L/R}/\beta = 0.8\beta$. The left/right 1D electrodes are treated by the Newns–Anderson model [47, 48] with $\alpha_{L/R} = 0$ and $\beta_{L/R} = \beta$.

Figure 3. (a) Transmission spectra and (b) TDOS of the molecular wires consisting of 19 sites connected between two leads parameterized by the positions of a soliton.

We omit the results of cases 5–8 in figure 2 owing to their symmetries. Figure 4 shows the LDOS surface plot as a function of energy and site index. The LDOS surface plot has peaks near the Fermi energy ($E = E_F$) where the soliton is located. The LDOS peaks at $E = E_F$ broaden and reduce in height when the soliton is located at the terminal of the molecular wire (figures 2(a) and (h)), whereas the LDOS peaks at $E = E_F$ sharpen and narrow when the soliton is located.
in the middle of the molecule (figures 2(d) and (e)). This trend holds in the much longer 1D wires (see Supplemental Information B (available from stacks.iop.org/NJP/12/063004/mmedia) for the longer chain with \( N = 39 \)).

This feature can be explained as follows. When a soliton lies at the terminal of a molecular wire, the localized state on the molecular wire strongly interacts with surface states of the lead, broadening the LDOS peaks around \( E = E_F \). This means that an electron occupying the soliton state easily escapes back to the electrode where the electron was injected from, so that the probability of the electron traveling through to the other electrode is reduced, resulting in low transmission at \( E = E_F \). Additionally, we can see that the LDOS at the Fermi energy from the 8th to the 19th site in case 1 in figure 4(a) are suppressed. The conductance at the Fermi energy in case 1 in figure 3(a) is nearly the same as the conductance of the dimerized 1D wire, which consists of 12 sites (see Supplemental Information C, available from stacks.iop.org/NJP/12/063004/mmedia). This implies that a soliton provides electronic states near the Fermi energy only around the position of the soliton and that the other part of the wire far from the soliton behaves like a semiconducting wire. Meanwhile, when a soliton lies at the center of a molecular wire, the localized state of the molecular wires interacts symmetrically and weakly with surface states of the two leads, producing sharp LDOS peaks. The soliton distributes electronic states around the Fermi energy as if it works as a bridge for electron transport from one electrode to another.

This conclusion can also be understood in terms of the generalized symmetry condition [50–54]. The transmission peak close to the resonance is approximately described as
Figure 5. Schematic description of a non-dimerized 1D linear molecule consisting of six sites, with a single binding defect, connected between two electrodes. Depending on the positions of the binding defect, five cases can be considered (cases 1–5). Transfer integrals for nearest neighbors and coupling strength at the left/right interface are set to $V_{n,n+1} = 1.0\beta$, $n = 1, 2, \ldots, N - 1$, and $V_{L/R} = \beta/2$, respectively. The transfer integral corresponding to the position of the binding defect is reduced to $\beta/2$, i.e. $V_{n,n+1} = \beta/2$ in case $n = 1, 2, \ldots, 5$.

$$T_{\text{max}}(E \sim \tilde{E}_0) = 4\Gamma_L\Gamma_R/(\Gamma_L + \Gamma_R)^2,$$
where $\tilde{E}_0$ is the energy of the molecular orbital associated with the soliton. $\Gamma_{L/R}$ follows a simple relation, $\Gamma_{L/R} \propto |V_{L/R}||\Psi_{L/R}|^2$, where $\Psi_{L/R}$ is the orbital amplitude of the molecule at the left/right interface. Thus, symmetric coupling of the molecule to the two electrodes, $\Gamma_L = \Gamma_R$, which corresponds to the soliton localization at the center of the molecule in cases 4 and 5 in figure 2, gives optimal transmission probabilities, while asymmetric coupling, as can be seen in cases 1 and 8 in figure 2, gives lower transmission probabilities.

### 3.2. Creation of transmission channels by a defect

We have examined how the position of a soliton modifies the conductance of molecular wires and saw that the conductance is greatly reduced when the soliton lies near electrodes. Here, we investigate the influence of the defect and demonstrate the counter-intuitive result that the introduction of a defect satisfying special conditions creates a transmission channel leading to higher conductance than in defect-free systems.

In general, realistic molecular junctions will contain defects. The defects may induce disorder in the molecular framework. In the presence of defects, both the on-site energies and the hopping integrals are modified. Therefore, the transport properties of the molecular junctions will also be changed. Thus we need to consider the effect of defects on quantum transport. We will now examine the dependence of the transmission and DOS on the position of the defect. Here we only consider fluctuations in the hopping integrals and introduce a defect as a reduced transfer integral in a molecular system with an even number of sites. For simplicity we consider a single defect in the molecular system.

Figure 5 shows the schematic description of a 1D molecular wire consisting of six sites, with a single defect, coupled to two electrodes. Transfer integrals for nearest neighbors are set as $V_{n,n+1} = \beta$. Since the strong coupling at the left and right interfaces broadens the resonant peaks of the 1D wire, making the influence of the defect elusive, the coupling at the left/right interface is reduced to $V_{L/R} = \beta/2$. Although the reduction of the coupling at the interface changes the absolute value of the conductance, this setting changes neither the trend of transmission spectra nor the conclusion of this work (see Supplemental Information D (available from stacks.iop.org/NJP/12/063004/mmedia) for the stronger coupling at the interface $V_{L/R} = 0.8\beta$). The defect is introduced as a reduction of the transfer integral $V$ between the two sites on either side of the defect to a value of $\beta/2$. We considered five cases of different positions of a single...
defect on a molecular wire and investigated the position dependence of the transmission and DOS of the molecular wire.

Figure 6 shows the transmission spectra and TDOS of the molecular wires shown in figure 5. Depending on the position of the defect, the transport properties change dramatically, particularly around $E = E_F$. Figure 7 shows the $I–V$ curves of the molecular wire calculated in the linear response regime. Surprisingly, the transmission at $E = E_F$ for cases 1, 3 and 5 is higher than for defect-free systems (see figure 6).

In order to further analyze this behavior, we calculated the LDOS as a function of energy and site index. Figure 8 shows the surface plot of LDOS as a function of electronic energy and site index. The results for cases 4 and 5 are omitted because of their symmetries. The position of the defect is illustrated by changing the colour of the LDOS curve from red to blue on either side. When a defect is introduced such that the molecular wire is divided into two fragments that have an odd number of sites, for example $3 + 3$, the LDOS plot of each fragment, as shown...
Figure 8. Surface plot of LDOS of molecular wires with a single defect as shown in figure 5 as a function of energy and site index. In each case LDOS plots are depicted in different colors across a defect.

In figure 8(c), resembles that of a linear chain having three sites \((N = 3)\) without defects, as shown in figure B.2 in appendix B. The LDOS in figure 8(c) shows non-negligible split peaks around \(E = E_F\). Likewise, when a defect is introduced such that the molecular wire is divided into fragments containing \(1 + 5\) or \(5 + 1\) sites, the LDOS plot of the longer fragment resembles that of a linear chain having five sites \((N = 5)\) without defects, as can be seen in figure B.2(b) in appendix B. The LDOS in figure 8(a) shows non-negligible split peaks around \(E = E_F\). That is why, despite including the single defect, these cases lead to higher transmission probabilities and TDOS around \(E = E_F\) than the defect-free systems shown in figures 6 and 7.

On the other hand, when the defect is introduced such that the molecular wire is divided into two fragments, both having an even number of sites, for example \(2 + 4\), the LDOS plot of each fragment resembles that of a linear chain having an even number of sites without defects. The LDOS in figure 8(b) is small around \(E = E_F\). Thus, these cases lead to low transmission probabilities and TDOS around \(E = E_F\), as shown in figure 6.

Finally, to investigate the relationship between the degree of the binding defect and the modification of conductance, we calculated transmission spectra and TDOS with different strengths of coupling at the interfaces and at the binding defect. If the transfer integral across the binding defect is increased back to that of the defect-free system, the enhancements of the current in cases 1, 3 and 5 gradually decrease and disappear. Meanwhile, the reduced conductance in cases 2 and 4 gradually increases and recovers to the conductance of the defect-free system. It is interesting to note that, as long as a binding defect is introduced such that the number of sites in each divided fragment is odd as shown in cases 1, 3 and 5, the conductance
at the Fermi energy is higher than the defect-free system, independent of the strength of the binding defect and the coupling strength at the interfaces (see Supplemental Information D (available from stacks.iop.org/NJP/12/063004/mmedia) for the different parameters of the coupling strength and binding defect).

4. Conclusion

In summary, in order to elucidate the factors controlling charge transport through 1D molecules connected between electrodes, we have modeled molecular junctions using the tight-binding method. Then we calculated the influence of the parameters, including molecular lengths, degree of dimerization, odd–even effects, soliton formation and defects, on the transport properties of the molecular junctions at equilibrium using the Landauer approach combined with the Green’s function formalism.

The numerical calculations have shown that the transport properties at the Fermi energy ($E_F = 0$) dramatically change depending on the degree of dimerization and on whether the number of the sites is odd or even. It has been shown that dimerization of the molecular wires associated with Peierls distortion reduces the DOS at the Fermi energy, leading to exponential decay of the length dependence of conductance of the molecular wires. We also proved that the damping factor is closely related to the degree of dimerization of the molecular wires. Interestingly, the longer chain system without dimerization showed no decay in conductance at the Fermi energy. In the case of molecular wires with an odd number of sites, the extra non-bonding state appears in the middle of the band gap contributing to high conductance at low bias. Additionally, in the molecular wires with an odd number of sites, the conductance at the Fermi energy was independent of the length of the molecular wires.

Our calculations also demonstrate that the transport properties are highly sensitive to the position of solitons and defects. When a soliton lies near one electrode it strongly interacts with surface states of that electrode, giving rise to low, broad peaks in the zero-bias conductance, while when a soliton lies in the middle of the molecular wire, the interaction of the localized state with the electrodes is weaker, leading to high conductance at the Fermi energy with a sharp resonant peak. Concerning the calculation of the influence of defects, we obtained a counter-intuitive result that, in some cases, defects increase the zero-bias conductance. Our findings are that a defect that divides the molecular wire into two fragments both having an odd number of sites creates a new conduction channel and enhances the zero-bias conductance independent of the strength of the binding defect and the coupling strength at the interfaces. Since thermal fluctuation naturally changes transfer integrals and creates this type of defect that, at least for a while, strongly favors charge transfer, we might infer that this is one of the underlying mechanisms of transport at room temperature. We believe that the presented systematic study could be predictive for a wider range of materials (e.g. semiconductor/organic interfaces). Our results could guide the synthesis of novel molecular wires with enhanced conductors.

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Appendix A. Theoretical framework

We model a molecular junction by connecting a 1D molecular wire between two electrodes. For clarity, we model the electrodes as 1D wires. We describe this system using a tight-binding Hamiltonian, considering only $\pi$ orbitals. The tight-binding parameters used depend explicitly on the interatomic distances in real space. Thus, we can introduce defects or disorder by directly controlling on-site energies (diagonal elements) and hopping integrals (off-diagonal elements) of the electronic tight-binding Hamiltonian matrices.

Figure 1 shows the molecular junction considered in this work. Our starting point is to divide the entire 1D system into three regions: the left electrode, the right electrode and the central molecular region. We write the electronic Hamiltonian as

$$H = H_L + V_L + H_C + V_R + H_R,$$

where $H_{L/R}$, $H_C$ and $V_{L/R}$ are, respectively, the Hamiltonian matrices for the left/right electrodes, for the the central molecular region and the matrix representing the coupling between the central molecule and the left/right electrodes. In this case, we considered only nearest-neighbor interactions, so that the terms $V_{L/R}$ are scalar values. The matrix elements of $H_C$ are given by $[H_C]_{m,n} = \alpha_n \delta_{m,n} + V_{m,n} (1 - \delta_{m,n})$, where $\alpha_n$ and $V_{m,n}$ are on-site energies and hopping integral between the $m$th and the $n$th atomic orbitals, respectively. In this study, the electrodes are approximated as semi-infinite 1D chains with a single orbital per site; thus the Hamiltonians of the semi-infinite electrodes $H_{L/R}$ have similar forms to $H_C$. For simplicity, we only consider the interaction between nearest neighbors. The matrix elements of the left/right electrodes are given by $[H_{L/R}]_{n,m} = \alpha_{n/R} \delta_{m,n} + \beta_{L/R} (1 - \delta_{m,n})$. Hereafter we normalize all hopping integrals, $\beta_{L/R}$ and $V_{m,n}$, in terms of $\beta$ and we set all on-site energies as 0, $\alpha_n = 0$, $n = 1, 2, \ldots, N$, L and R.

In the orthogonal basis the retarded Green function is given by

$$G^R(E) = [(E + i\eta) I - H_C - \Sigma_L(E) - \Sigma_R(E)]^{-1},$$

where $I$, $\eta$ and $\Sigma_{L/R}(E)$ are the identity matrix, the positive infinitesimal and the self-energy in the left/right electrode, respectively. The self-energy term $\Sigma_{L/R}(E)$ is defined as $\Sigma_{L/R}(E) = V_{L/R} g_{L/R}(E) V_{L/R}^\dagger$, where $g_{L/R}(E)$ is the surface Green function of the left/right 1D electrode. The left/right electrode consists of equally spaced 1D sites, and coupling between nearest neighbors is set as $\beta_{L/R} = \beta$. The surface Green function of the electrode consisting of equally spaced 1D sites considering only nearest-neighbor interaction can be analytically described by the Newns–Anderson model [48, 49] as $g_{L/R}(E) = \exp(i k)/\beta_{L/R}$, whose derivation [55] is summarized in Supplemental Information.

The conductance of a molecular junction in a low bias is estimated from Landauer’s formula $G = G_0 T(E)$, where $G_0 = 2$ (for spin) $\frac{\pi}{e^2}$ is the conductance quantum and $T(E)$ is

the electronic transmission probability. $T(E)$ is obtained from the Fisher–Lee relation [56]:

$$T(E) = \text{Tr}[G^R(E)\Gamma_L(E)G^A(E)\Gamma_R(E)]$$

where $\Gamma_{L/R}(E)$ is the broadening function defined as $\Gamma_{L/R}(E) = i[\Sigma_{L/R}(E) - \Sigma_{L/R}^\dagger(E)]$. The DOS is calculated from the following equation:

$$\text{DOS}(E) = \frac{\text{Im}[G(E) - G^\dagger(E)]}{2\pi}.$$  

In this study, we only consider coherent transport and ignore internal scattering effects, such as inelastic transport or incoherent transport [57] associated with electron–phonon coupling [58, 59]. In addition, we neglect here the role of defects that are induced by the electrodes and the quality of topology in the contacts [60, 61].

Appendix B. Odd–even effect in non-dimerized molecular systems

Depending on whether the number of sites in the central molecule is even or odd, the molecular junctions can show quite different transport properties. Indeed, early numerical simulations have already hinted that electron transfer between electrodes depends on the parity of the bridging molecules [62, 63]. This is because effective coupling sign and strength depend on the DOS [64]. Here, we clarify how transport depends on the parity of molecular wires by modeling two types of non-dimerized 1D linear chains, having even and odd numbers of sites, embedded between two electrodes. Then we compare the transmission spectra, DOS and the length dependence of the conductance.

Figure B.1. (a) Transmission spectra and (b) DOS of non-dimerized even-membered 1D chain systems between 1D electrodes parameterized by the number of sites ($N$). (c) Transmission spectra and (d) DOS of non-dimerized even-membered 1D chain systems between 1D electrodes parameterized by the number of sites ($N$). The coupling constant is set as $V_{L/R} = \beta/2$. 

Figure B.2. LDOS plots for 1D linear chain systems having an odd number of sites: (a) \(N = 3\), (b) \(N = 5\), (c) \(N = 7\) and (d) \(N = 9\). The couplings are set as \(V_{L/R} = \beta/2\). There is no dimerization on the central molecular region \((V_{n,n+1} = 1.0\beta, n = 1, 2, \ldots, N - 1)\).

The on-site energies and transfer integrals are set as \(\alpha_n = 0, n = 1, 2, \ldots, N\) and \(V_{n,n+1} = \beta, n = 1, 2, \ldots, N - 1\), respectively. The coupling constants between the molecule and the electrodes are set as \(V_{L/R} = \beta/2\). The electrodes are treated by the Newns–Anderson model [48, 49] with \(\alpha_{L/R} = 0\) and \(\beta_{L/R} = \beta\). The fermi energy is set as \(E_F = 0\).

Figure B.1 shows the calculated transmission spectra and total TDOS for the 1D chains, having an even number of sites (figures B.1(a) and (b)) and an odd number of sites (figures B.1(c) and (d)), connected between two electrodes. All plots are parameterized by the length (the number of sites, \(N\)) of the 1D chains.

In the 1D chains having an even number of sites, the TDOS in figure B.1(b) contains resonant peaks originating from the eigenstates of the isolated 1D chains. The resonant peaks can be divided into two groups: valence states (with energy less than \(E = E_F\)) and conduction states (with energy more than \(E = E_F\)). The TDOS at the Fermi energy is small between these two peaks. The transmission spectra in figure B.1(a) also show resonant peaks consisting of valence and conduction states originating from eigenstates of isolated 1D chains.

Since the HOMO–LUMO gap decreases in longer 1D molecules indicating better achievement of 1D behavior [65], the energy gap in the TDOS plots (figure B.1(b)) between resonant peaks around the Fermi energy narrows as the 1D molecules get longer. Similar behavior also can be seen in the transmission spectra shown in figure B.1(a). Surprisingly the transmission at the Fermi energy does not decay in the longer 1D linear chains as long as the 1D chains do not dimerize.
Figure C.1. (a) A PA-based molecular wire and (b) a poly(ppv) (PPV)-based molecular wire connected between 1D electrodes.

In the 1D chains having an odd number of sites, we can see from both the transmission spectra (figure B.1(c)) and the TDOS plots (figure B.1(d)) that the additional states emerge at $E = E_F$ in the middle of the gap between the valence peaks and the conduction peaks. These peaks correspond to non-bonding states and contribute to the high conductance at $E = E_F$. In the case of odd sites, the transmission at the Fermi energy does not decay in longer 1D linear chains.

In order to investigate the distribution of non-bonding states along the molecular framework we have calculated the LDOS. Figure B.2 shows LDOS surface plots as a function of energy and site index. The LDOS at $E = E_F$ corresponding to non-bonding states has peaks only on the odd sites. These features resemble the non-bonding states of a polyacetylene (PA) fragment consisting of an odd number of carbon atoms [57, 66] or the localized states on the edge of zigzag graphite nanoribbons [67].

Appendix C. Effect on dimerization

It is known that the dimerization known as Peierls distortion [44] strongly modifies the electronic properties of conducting polymers. Since the hopping integrals explicitly depend on the distance between pairs of atomic orbitals, the displacement of atoms from their equilibrium positions due to the vibration of the molecular wires or excitation of phonon modes from electrodes will modify the tight-binding parameters of the molecules and hence their conductance. Here, we modeled two types of molecular junctions as shown in figure C.1: one based on (a) PA and the other based on (b) poly(p-phenylenevinylene) (PPV) [25]. For each junction, we calculated both the DOS and the transmission as a function of the degree of dimerization and analyzed the effect of dimerization on transport properties.

For this system, we used the simplest possible model, considering only a single $p_z$ orbital per single carbon atom perpendicular to the molecular plane. Additionally, we consider only the transfer integrals between nearest-neighbor sites. Since the hopping parameters explicitly depend on the displacement of atoms from their equilibrium positions, dimerization is introduced as bond alternations in the central molecular wires. The transfer integrals associated with double bond and single bond are set as $\beta_d = \beta + d$ and $\beta_s = \beta - d$, respectively. We use two values of $d = 0.1\beta$ and $d = 0.2\beta$ for the degree of dimerization. The 1D electrodes are treated by the Newns–Anderson model [48, 49] with $\alpha_{L/R} = 0$ and $\beta_{L/R} = \beta$.

Figure C.2 shows the transmission spectra and DOS of dimerized PAs connected between two electrodes with two different degrees of dimerization. The introduction of dimerization causes the energy gaps associated with Peierls distortion to appear in the DOS plots around $E = E_F$. In conjunction with the reduction of the DOS at $E = E_F$, the transmission at $E = E_F$ decays exponentially in the longer PA wires. When the degree of dimerization is increased from $d = 0.1\beta$ to $d = 0.2\beta$, the energy gaps at $E = E_F$ get larger and the exponential decay at
Figure C.2. Transmission spectra and DOS of PA-based molecular wires between 1D electrodes parameterized by the number of unit cells \((N)\). In (a) and (b), the degree of dimerization is set as \(d = 0.1\beta\). In (c) and (d), the dimerization is enhanced to \(d = 0.2\beta\). Coupling constants are set as \(V_{L/R} = 0.8\beta\).

\(E = E_F\) gets steeper. The steepness of the exponential decay is closely related to the degree of dimerization (bond alternation).

When bond alternation is introduced not only into the central molecules but also into the two 1D electrodes, the transport properties of the PA-based molecular junctions converge to that of dimerized infinite 1D linear chains. Figure C.3 shows the transport properties of the dimerized PAs connected between dimerized electrodes. The transmission spectra in figures C.3(a) and (c) form two rectangular-shaped ballistic conducting bands corresponding to valence and conduction states with energy gaps of \(2d\beta\). The conductance at the Fermi energy is completely suppressed due to the emergence of the forbidden band. The TDOS curves in figures C.3(b) and (d) also show two separated bands with energy gaps of \(2d\beta\). These TDOS curves obtained from the Green function approach are equivalent to the TDOS obtained from the band calculation of dimerized infinite 1D systems. The energy gaps seen in the transmission spectra and TDOS curves in figure C.3 obtained from the Green function approach match the Peierls gap \(E_g\) involved in the dimerization of an infinite 1D system given by 

\[
E_g = \sqrt{\beta_3^2 + \beta_5^2 + 2\beta_4\beta_5 \cos(ka)} = 2d\beta.
\]

These results imply the possibility of using 1D polymers to function as switching devices, turning from ON to OFF states or vice versa by controlling the degree of dimerization.

The transport properties of PPV-based molecular junctions (figure C.4) also show similar trends to PA-based molecular junctions [41]. The transmission at \(E = E_F\) decays exponentially.
and the decay gets steeper in strongly dimerized systems. One difference in transport properties between PA-based and PPV-based molecular junctions is that extra dips appear in the transmission spectra around $E = \pm 1.0\beta$ in PPV-based systems. This is due to the destructive interference between tunneling electrons traveling through two different paths: namely the upper and lower pathways in the phenyl ring (see figure C.1(b)). This is now known as anti-resonance [64, 68–70].

Appendix D. Length dependence of conductance

In general, the conductance of insulating or semi-conducting molecular wires connected between two electrodes is evaluated by the formula associated with the Simmons model [71, 72] in the low-bias regime: $G = G_0 \exp(-\beta_{\text{damp}}r)$, where $\beta_{\text{damp}}$ is the damping factor and $r$ is the distance between the electrodes. The value of $r$ is given by $r = r_{\text{unit}}N + c$, where $r_{\text{unit}}$, $N$ and $c$ are the length of a unit cell, the number of unit cells and the correction term associated with excess fragments and vacuum between the molecule and electrodes, respectively.

In figure D.1, we summarized the length dependence of conductance at equilibrium in PA-based and PPV-based molecular junctions parameterized by the degrees of dimerization. In both types of molecular wires the length dependence of conductance at $E = E_F$ decays

Figure C.3. Transmission spectra and DOS of dimerized PA-based molecular wires between dimerized 1D electrodes. In (a) and (b), the degree of dimerization is set as $d = 0.1\beta$. In (c) and (d), the dimerization is enhanced to $d = 0.2\beta$. The surface Green functions for dimerized 1D electrodes are calculated using the decimation technique [73].
Figure C.4. Transmission spectra and DOS of PPV-based molecular wires between 1D electrodes parameterized by the number of unit cells ($N$). In (a) and (b), the degree of dimerization is set as $d = 0.1\beta$. In (c) and (d), the dimerization is enhanced to $d = 0.2\beta$.

Figure D.1. Length dependence of conductance of (a) PE-based and (b) PPV-based molecular wires coupled to two 1D electrodes parameterized by the degree of dimerization.

exponentially in accordance with the Simmons formula shown above. Damping factors $\beta_{\text{damp}}$ get larger in the highly dimerized molecular wires. This is because stronger dimerization creates a larger energy gap and reduces the DOS around $E = E_F$, resulting in the coherent tunneling through the wires being suppressed.
Figure D.2 shows the relationship between the damping factor $\beta_{\text{damp}}$ and degree of dimerization of (a) PA-based and (b) PPV-based molecular wires, and the relationship between transmission at $E = E_F$. As can be seen from figure D.2, the damping factor is approximately linearly related to degree of dimerization. Therefore, knowing the degree of dimerization is key to evaluating the damping of tunneling electrons.

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