

# Conduction modulation of $\pi$ -stacked ethylbenzene wires on Si(100) with substituent groups

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**Abstract** For the realization of molecular electronics, one essential goal is the ability to systematically fabricate molecular functional components in a well-controlled manner. Experimental techniques have been developed such that  $\pi$ -stacked ethylbenzene molecules can now be routinely induced to self-assemble on an H-terminated Si(100) surface at precise locations and along precise directions. Electron transport calculations predict that such molecular wires could indeed carry an electrical current, but the Si substrate may play a considerable role as a competing pathway for conducting electrons. In this work, we investigate the effect of placing substituent groups of varying electron donating or withdrawing strengths on the ethylbenzene molecules to determine how they would affect the transport properties of such molecular wires. The systems consist of a line of  $\pi$ -stacked ethylbenzene molecules covalently bonded to a Si substrate. The ethylbenzene line is bridging two Al electrodes to model current through the molecular stack. For our transport calculations, we employ a first-principles technique where density functional theory (DFT) is used within

the non-equilibrium Green's function formalism (NEGF). The calculated density of states suggest that substituent groups are an effective way to shift molecular states relative to the electronic states associated with the Si substrate. The electron transmission spectra obtained from the NEGF–DFT calculations reveal that the transport properties could also be extensively modulated by changing substituent groups. For certain molecules, it is possible to have a transmission peak at the Fermi level of the electrodes, corresponding to high conduction through the molecular wire with essentially no leakage into the Si substrate.

**Keywords** Molecular wire · NEGF–DFT · Substituent group · Conductance modulation · Electron transport · Ethylbenzene wire

## 1 Introduction

The ability to control the properties of molecular wires is required if they are to be used in nanoelectronics. Advanced synthetic chemistry techniques can now be routinely applied to achieve very specific structures in high yields. One example is the self-directed line growth of styrene molecules on an H-terminated Si(111)– $2 \times 1$  surface, resulting in lines of  $\pi$ -stacked ethylbenzene molecules covalently bonded to the Si substrate [1]. During this reaction, a styrene molecule reacts with a dangling bond on the Si surface, forming a covalent C–Si bond, and also abstracting a H atom from a Si atom on the neighboring site. This leaves a dangling bond next to the attached molecule where another styrene molecule can attach and the process is repeated, resulting in self-assembled molecular wires on the Si surface. Experimental work by Piva et al. [2] on such systems showed that the tunneling current from an STM tip through an ethylbenzene

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molecule could be regulated by changing the charge state of a nearby dangling bond on the Si substrate, demonstrating field effect control. Basu et al. [3] have reported on the ability to control the extent of line growth using patterned TEMPO molecules on the surface. Work by Hossain et al. [4] showed the ability to grow molecular lines on H-Si(100) in the direction perpendicular to the dimer rows and then they reported line growth both perpendicular to and along dimer rows in the same sample [5], resulting in interconnected molecular lines. Subsequent work by Zikovskiy et al. [6] demonstrated the ability to control the direction of molecular line growth so that contiguous molecular lines having complex shapes could be grown on a Si surface.

Because there is  $\pi$ - $\pi$  overlap between the ethylbenzene molecules forming the lines in such structures, it is believed that they could perform as molecular wires if connected to electrodes. Due to experimental challenges involved in studying such a hypothesis, it has been investigated theoretically by several groups [7–11]. These studies agree that a line of  $\pi$ -stacked ethylbenzene molecules could indeed act as a molecular wire. However, because these structures exist chemisorbed to a Si surface, it has been suggested that the transport properties may be affected by the substrate [7, 10], and this was confirmed to be the case with transport calculations that explicitly include the Si substrate and treat all atoms on an equal footing [11]. Reference [11] revealed that the nearest transmission peak to the Fermi level ( $E_F$ ) of the electrodes was due to electron transport through the Si substrate, and this would dominate the low-bias conductance. Clearly, from the point of view of molecular conduction, it would be interesting to somehow alter the transmission spectrum for such a system to either increase transmission through the molecular wire near  $E_F$  or decrease transmission through the substrate. It is conceivable that the former could be achieved with substituent groups on the ethylbenzene molecules. It has been reported that lines composed of ethylbenzene substituted in the para

positions with  $-\text{CH}_3$ ,  $-\text{CF}_3$ , and  $-\text{OCH}_3$  have been grown experimentally [7, 12].

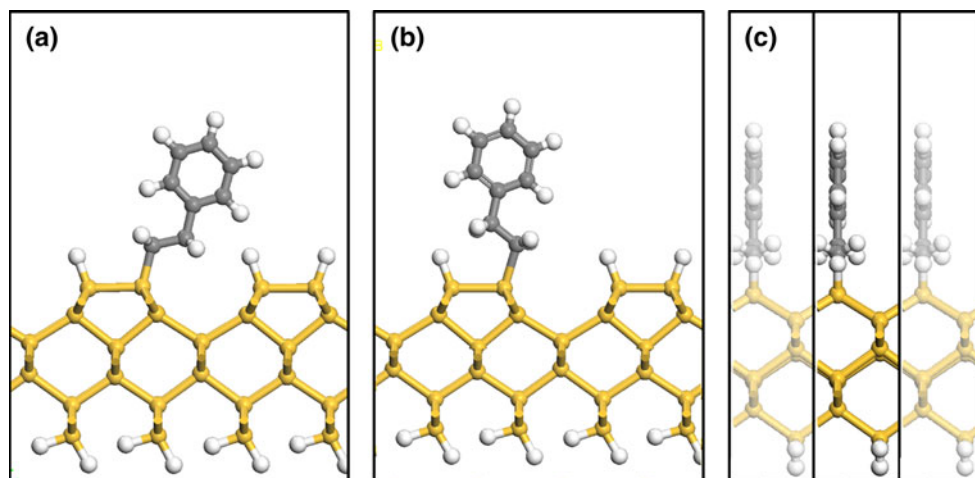
It is well known that substituent groups can have a profound effect on the energies of certain molecular energy levels. It has been shown that substituent groups could be used to modify the conductance properties of molecules such as benzene diamine [13] and benzenedithiol [14, 15]. Likewise, substituent groups could also alter the properties of a Si substrate. For example, Anagaw et al. [16] showed that the work function of a Si surface can be effectively tuned by chemisorbing substituted styrene molecules to it. In the present work, we investigate whether substituent groups can be used to modify the conductance properties of a molecular line composed of  $\pi$ -stacked ethylbenzene molecules bonded to a Si substrate. We employ density functional theory (DFT) combined with the non-equilibrium Green's function (NEGF) formalism for this study. This is an ab initio technique that treats all components of the system on an equal footing, including the molecules in the line, the Si substrate, and the electrodes connected to them.

## 2 Theoretical method

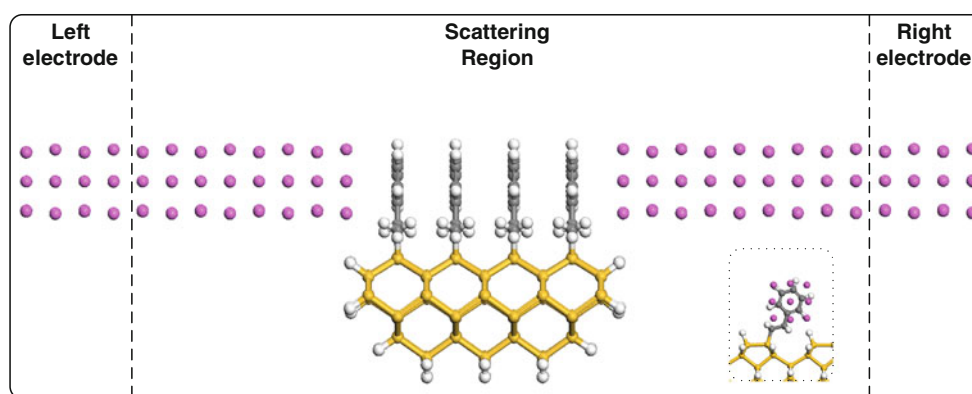
The systems studied consist of  $\pi$ -stacked aromatic rings bonded to a Si(100)- $2 \times 1$  surface via ethyl chains. The substrate is represented as a Si slab of six atomic layers in thickness, with H atoms used to cap dangling bonds, as shown in Fig. 1.

The structure relaxations were carried out using the Vienna ab initio simulation package (VASP) [17, 18] on a periodic (repeating) system consisting of one ethylbenzene molecule on the Si substrate. The substrate consists of two dimer rows, containing one dimer each, as shown in Fig. 1. The ethylbenzene molecule has  $\pi$ -stacking interactions with its images in the direction normal to the plane of the

**Fig. 1** Periodic structure of ethylbenzene bonded to a Si slab with six atomic layers. The front views show two possible conformations: **a** the molecule over the trench between dimer rows, **b** the molecule over a dimer row. The side view **c** shows one unit and its two images to illustrate the  $\pi$ -stacking arrangement



**Fig. 2** The two-probe system used for the transport calculations. *Inset* shows the alignment of the electrodes to the molecular wire from a different perspective



benzene ring, with a molecule–molecule separation of 3.867 Å, corresponding to the distance between two Si dimers on the same row, as shown in Fig. 1c. In the vertical direction (normal to the Si surface), at least 8 Å of vacuum space separated the top of the molecule from the lowest atom in the neighboring image so that there would be no interaction in between them.

The VASP calculations were carried out using the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE–GGA) for the exchange correlation energy [19] with a semi-empirical van der Waals (vdW) correction to account for dispersion interactions of the  $\pi$ -stacked rings [20].<sup>1</sup> A projector augmented wave method was used for the ionic potentials [21, 22], with a kinetic energy cutoff for the plane wave basis of 400 eV. During the structure relaxations, the lowest two layers of Si atoms were frozen to their bulk positions while all other atoms were relaxed until the net force was less than 0.02 eV Å. In the plane of the Si slab, the Brillouin zone was sampled with sufficient  $k$  points such that the energy was converged to less than 1 meV/atom.

It should be noted that there are two distinct possible conformations for the molecule bonded to the Si(100)– $2 \times 1$  surface. In one of them, the molecule is over the trench between two dimer rows (Fig. 1a), while in the other, it is over a dimer row (Fig. 1b). From our total energy calculations, we found that the arrangement over the trench is more energetically favorable, in agreement with the experiments of Lopinski et al. [1]. Therefore, this structure was used for all further calculations.

The relaxed structure from Fig. 1a, c is then used to build the two-probe structure for the transport calculations. The system is repeated to form a line of four ethylbenzene molecules, which are then connected to 1-D Al electrodes, as shown in Fig. 2. Note that the structure is

periodic in the direction normal to the page, as shown in Fig. 1a. It is also periodic in the vertical direction, but sufficient vacuum space separates the images so that there is no interaction between them. Along the direction of the electrodes, the scattering region is finite but the left and right electrode regions are periodic. The small cross-section of the electrodes was deliberately chosen to permit direct overlap with the  $\pi$ -stacked molecular wire, while limiting interaction with the Si substrate and the substituent groups on the molecules (see inset of Fig. 2). The electrodes used are 1-D Al(100) wires with cross-sectional area of  $3 \times 3$  units, as shown in Fig. 2. The electrodes were relaxed in VASP in the same manner as described above. For the electrode–molecule separation, VASP calculations determined the ideal distance to be 3.40 Å for the ethylbenzene molecule. The same approach was used to relax the substituted benzene systems and to set up their two-probe geometries. For consistency, the same electrode–molecule separation was used so that similar orbital overlap could be maintained between the molecular wire and the electrodes. In each system, the electrodes were aligned with the center of the benzene ring, as shown in the inset of Fig. 2.

To calculate the electron transport through the system, we used a computational quantum transport technique that is based on the real-space Keldysh NEGF formalism combined self-consistently with DFT [23, 24]. This has been packaged in the Nanodcal electron transport code.<sup>2</sup>

The idea behind this approach is to calculate the Hamiltonian and electronic structure of the two-probe transport structure by DFT and the non-equilibrium statistical properties (population of electronic levels) of the scattering region is done by NEGF. The transport boundary conditions are treated by real-space numerical procedures. Interested readers are referred to Refs. [23, 24] for details of the NEGF–DFT implementation.

<sup>1</sup> The van der Waals radius cutoff was set to 15.0 Å, so that the terms corresponding to interactions over distances greater than this value are assumed to be zero.

<sup>2</sup> <http://www.nanoacademic.ca>.

This procedure is summarized as follows. The retarded Green's function at energy  $E$  is obtained by inverting the Hamiltonian matrix,

$$G(E) = [(E + i\eta)S - H - \Sigma_1 - \Sigma_2]^{-1}, \quad (1)$$

where  $H$  and  $S$  are the Hamiltonian and overlap matrices for the central region determined with DFT [25].  $\eta$  is a positive infinitesimal and  $\Sigma_{1,2}$  are self-energies that include the effect of the left and right electrodes on the scattering region. The self-energy is calculated within the NEGF-DFT formalism by an iterative technique [26]. It is a complex quantity with its real part representing a shift of the energy levels and its imaginary part representing their broadening, which can be represented as the broadening matrix,  $\Gamma_{1,2} = i(\Sigma_{1,2} - \Sigma_{1,2}^\dagger)$ . The electronic density can be obtained from these quantities as,

$$\rho = (1/2\pi) \int_{-\infty}^{\infty} [f(E, \mu_1)G\Gamma_1G^\dagger + f(E, \mu_2)G\Gamma_2G^\dagger]dE, \quad (2)$$

where  $\mu_{1,2}$  are the electrochemical potentials of the left and right electrodes and  $f(E, \mu)$  is the Fermi-Dirac function that describes the population for a given energy and electrochemical potential. The density obtained is then used in a subsequent DFT iteration step, and the cycle is repeated until self-consistency is achieved. The transmission function is then calculated as

$$T(E) = \text{Tr}(\Gamma_1 G \Gamma_2 G^\dagger), \quad (3)$$

which represents the probability that an electron with a given energy  $E$  transmits from one electrode, through the scattering region, and into the other electrode. This quantity can then be used to calculate the electric current as,

$$I = 2e/h \int_{\mu_1}^{\mu_2} T(E)dE. \quad (4)$$

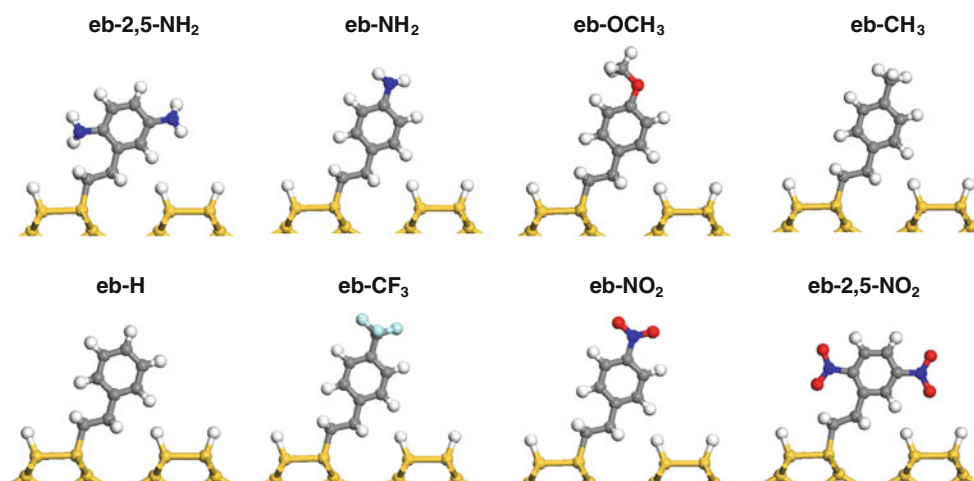
For the transport calculations, norm-conserving pseudopotentials [27] were used to describe the atomic cores, and double- $\zeta$  polarized (DZP) numerical orbitals for the valence electrons. The exchange-correlation was treated using the local density approximation (LDA).

### 3 Results and discussion

This work investigates the effect of different substituent groups on the electronic and transport properties of the ethylbenzene molecule in the molecular wires. The substituents are placed at the para position relative to the ethyl group attaching to the surface and include  $R = -\text{NH}_2$ ,  $-\text{OCH}_3$ ,  $-\text{CH}_3$ ,  $-\text{H}$ ,  $-\text{CF}_3$ , and  $-\text{NO}_2$ ; which are listed in order from strongest electron donating group (EDG) to strongest electron withdrawing group (EWG). To amplify the effect, di-substitution with the  $-\text{NH}_2$  and  $-\text{NO}_2$  groups at the 2,5-positions was also considered. The molecules are illustrated in Fig. 3.

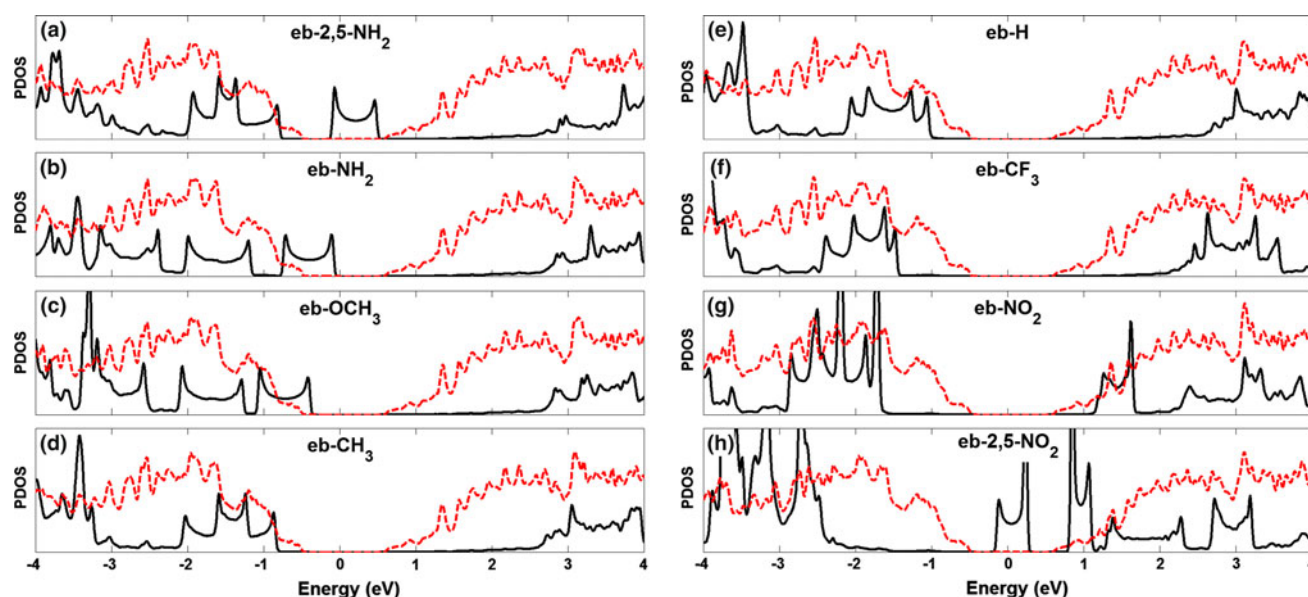
#### 3.1 Density of states

Plotting the density of states (DOS) is an effective way to compare the electronic structure for various systems. The DOS represents the proportion of electronic states as a function of energy. By projecting the DOS onto certain atoms, we can monitor which parts of a physical system contribute electronic states at certain energies. This analysis can be useful for interpreting the effect of substituent groups on the electronic structure of the different systems studied in this work. Note that the DOS calculations were



**Fig. 3** Set of substituted ethylbenzene molecules studied in this work





**Fig. 4** DOS projected onto atoms of substituted ethylbenzene molecules (solid black) and atoms of the Si substrate (dashed red)

carried out on the periodic systems shown in Fig. 1 with the Nanodcal code using LDA. Figure 4 shows DOS projected (PDOS) onto the atoms of the molecules (solid black plots) and the DOS projected onto the Si substrate (dashed red plots). The energy scale of the plots was shifted such that the valence and conduction bands of the Si would coincide in all systems for ease of comparison. In all cases, the Si PDOS look nearly identical showing only small differences in relative peak height. The top of the valence band is at  $-0.46$  eV while the bottom of the conduction band is at  $0.58$  eV, meaning that the bandgap of the Si  $1.04$  eV, which is close to the known experimental value of  $1.11$  eV. However, it should be pointed out that this is a fortuitous agreement due to the known tendency of LDA to underestimate the bandgap, and the fact that the Si in these calculations is not truly a bulk material but a slab of finite thickness (6 atomic layers). Nevertheless, the use of LDA and a finite slab have opposite effects on the bandgap, and this results in a value close to experiment.

Beginning with the eb-H system (Fig. 4e), the HOMO state is located near  $-1.1$  eV, HOMO-1 near  $-1.3$  eV, and so on; while the LUMO is near  $3.0$  eV.<sup>3</sup> This gives a HOMO–LUMO gap of ca.  $4.1$  eV, in agreement with our previous work [11], and also the work carried out by others [7, 10]. Note that for the eb-H system, there are no molecular states in the Si bandgap, i.e. in the range  $[-0.5, 0.6]$  eV. As expected, adding EDGs to the molecule shifts the electronic states to higher energies by an amount proportional to the strength of the substituent group. In

eb-CH<sub>3</sub>, the HOMO level is shifted up to  $-0.9$  eV; in eb-OCH<sub>3</sub> it is shifted to  $-0.4$  eV; in eb-NH<sub>2</sub> it is at  $-0.1$  eV; and with two -NH<sub>2</sub> substituents (Fig. 4a) it is at  $+0.5$  eV. For the three strongest EDG systems (Fig. 4a–c), the molecular states actually lie inside the Si bandgap.

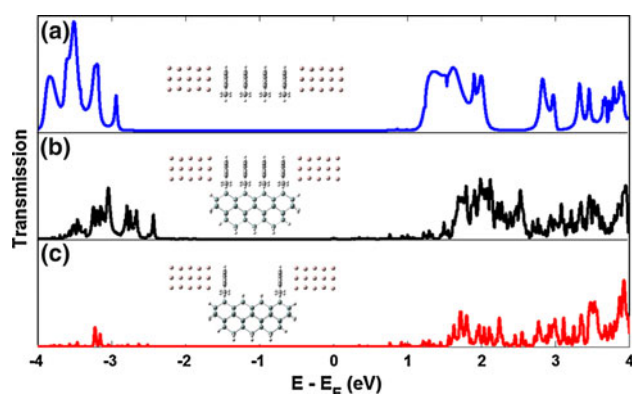
Conversely, the use of electron withdrawing groups has the opposite effect by shifting the molecular levels to lower energies. In this case, the LUMO level gets progressively closer to the Si bandgap for the eb-CF<sub>3</sub>, and eb-NO<sub>2</sub> systems, and finally it is inside the bandgap for the eb-2,5-NO<sub>2</sub> system. Therefore, we found that substituent groups could be used to very effectively shift the molecular levels relative to those of the substrate. This approach could even be used to select the type of orbital (occupied vs. unoccupied) that is desired for electron transport to occur through. Finally, this effect can be further amplified by using multiple substituent groups on the same molecule, as shown for the disubstituted -NH<sub>2</sub> and -NO<sub>2</sub> systems (Fig. 4a, h).

### 3.2 Transmission

The transmission spectrum of a two-probe system (Fig. 2) shows the probability that an electron with a given energy originating in the left electrode will transmit through the scattering region and into the right electrode. By comparing the transmission spectra for the various substituted ethylbenzene molecules, we can determine the effect of the different substituent groups on the conductance of the ethylbenzene molecular wire.

In Fig. 5, the transmission spectra of three related systems are compared. In the middle (Fig. 5b), the

<sup>3</sup> The reason these levels have finite broadening is because of the  $\pi$ -stacking interaction with molecules in neighboring images of the periodic system.



**Fig. 5** Transmission spectra for **a** four ethylbenzene molecules with no substrate, **b** four ethylbenzene molecules on top of Si, and **c** two molecules separated by a gap on Si

transmission through an ethylbenzene line on Si is plotted. At the top (Fig. 5a) is shown the transmission through an ethylbenzene stack with no underlying substrate, and at the bottom (Fig. 5c), there is a substrate but there is a gap in the molecular wire. For the system shown in Fig. 5a, clearly all of the transmission occurs through the molecules. The transmission peaks at  $-2.9$ ,  $-3.2$ ,  $-3.5$ , and  $-3.8$  eV are due to transport through the HOMO, HOMO-1, and so on, of the molecular stack. The peaks in the range  $[1, 2]$  eV and higher are due to transmission through the unoccupied states. For the system at the bottom (Fig. 5c), the transmission is only possible through the substrate since there is a gap in the molecular wire. The important result is that, even with a gap in the molecular line, some transmission peaks are present, which must represent transmission through the substrate. This phenomenon was previously reported for a similar system with a smaller Si substrate [11], but it is interesting that it remains very similar when a much larger substrate is included in the calculation.

The plot in the middle (Fig. 5b) shows the transmission through the intact eb-H wire on top of Si, where transmission is possible through either the molecular wire or the substrate. One way to determine the conduction pathway for this system is by comparing its transmission spectrum to the other two systems. For example, the peaks in the range  $[-3.5, -2.4]$  eV are due to transmission through the molecules since there are similar peaks near this region in Fig. 5a but not in Fig. 5c.<sup>4</sup> On the other end of the spectrum, near 2 eV, the transmission seems to be through a combination of the molecular wire and through the Si

substrate since there are substantial transmission peaks in both Fig. 5a and c.<sup>5</sup>

A subtle but important point is that there are some very small peaks at 0.35 and 0.77 eV for both systems containing the Si substrate (Fig. 5b, c), but these peaks are absent in the system without Si (Fig. 5a). It is significant because these peaks are the closest to the  $E_F$  of the electrodes, and therefore will play the most important role in the low-bias conductance properties. These transmission peaks represent current leakage into the substrate.

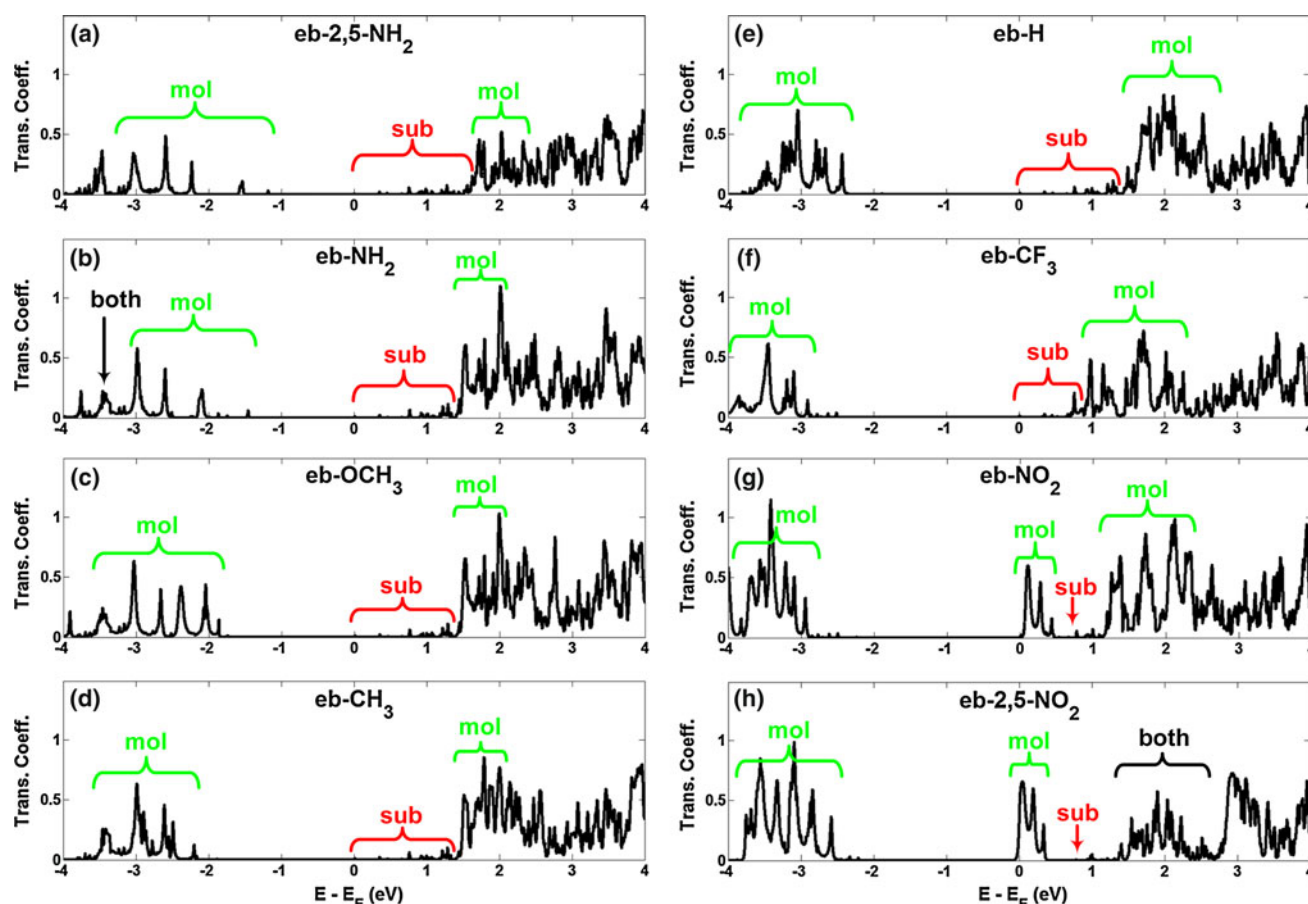
A more direct approach for assigning transmission peaks is by analyzing the scattering states associated with each peak. Scattering states are analogous to eigenstates, but they apply to open-boundary systems such as the two-probe geometries considered in this work. They can be plotted in real space and reveal the parts of the system that the electrons are transmitting through at a given energy [23]. Figure 6 shows the transmission spectra for molecular wires composed of the molecules shown in Fig. 3. Various peaks are labeled according to which part of the system the transmission is occurring through, such as the molecular wire (mol), the substrate (sub) or through both, as determined from a scattering state analysis (vide infra).

For the unsubstituted system eb-H (Fig. 6e), we can see that the scattering state analysis supports the conclusions reached from the comparison of Fig. 5. The peaks in the range  $[-4.0, -2.5]$  eV and those near  $[1.5, 2.5]$  eV are mainly due to transmission through the molecule, while those small peaks in the range  $[0.0, 1.5]$  eV are due to transmission through the substrate. As discussed in Sect. 3.1, adding EDG substituents to the molecular wire shifts the states up in energy, therefore these groups can be used to bring the transmission peaks due to occupied states closer to the  $E_F$  of the electrodes. This can be observed in Fig. 6a–d, the strongest effect being achieved with two  $-\text{NH}_2$  groups on each ethylbenzene molecule (Fig. 6a), where the peak due to transmission through the HOMO is at  $-1.2$  eV.

The use of EWGs as substituents has the opposite effect. It lowers the energy of the molecular states, bringing the peaks due to transmission through unoccupied states closer to the  $E_F$ , as can be seen in Fig. 6f–h. Substitution with one or two  $-\text{NO}_2$  groups actually brings the transmission peaks of the LUMO states near the  $E_F$  such that their tails spill over the  $E_F$ . In fact, were the LUMO states to be shifted below the  $E_F$ , these would, by definition, become occupied as electrons from the electrodes would fill them [28].

<sup>4</sup> Note that the effect of including the Si substrate is to shift the positions of the transmission peaks by ca. 0.5 eV and they become split due to hybridization with the Si states.

<sup>5</sup> Comparing the transmission peak positions in Fig. 5b to the PDOS positions in Fig. 4e, we see that they differ. This is because in position of the DOS peaks are relative to the Si substrate, while in the transmission spectrum they are relative to the  $E_F$  of the Al electrodes. In other words, the peaks in the transmission spectra are shifted (by ca.  $-1.5$  eV) relative to the PDOS plots.

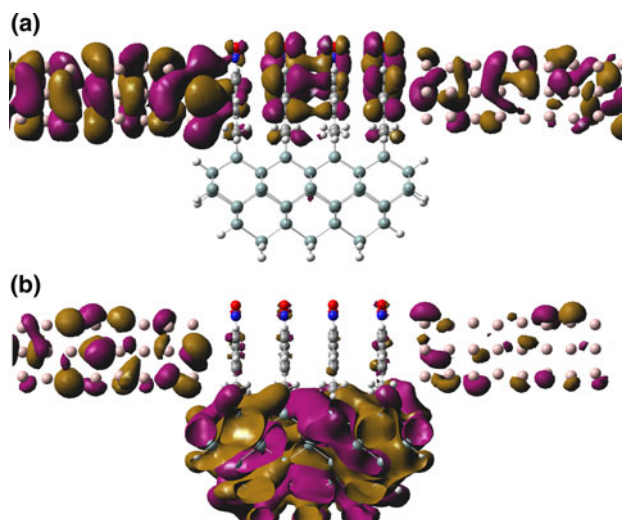


**Fig. 6** Transmission spectra for different substituted ethylbenzene molecules. Labels indicate whether transmission occurs through the molecular stack (mol), the substrate (sub), or through both

However, in Fig. 6g, h, only a small tail crosses the  $E_F$ , corresponding to a very small amount of charge transfer between the scattering region and the electrodes in these systems. The most important point is that in these cases (Fig. 6g, h), the transmission peak closest to the  $E_F$  is through a molecular state. Therefore, there would be negligible leakage into the substrate at low bias, and because of the height and width of these peaks, the eb- $\text{NO}_2$  and eb-2,5- $\text{NO}_2$  molecules would make excellent molecular wires.

To further support this point, Fig. 7 shows two scattering states for the eb- $\text{NO}_2$  system (Fig. 6g). Fig. 7a is the scattering state associated with the tall molecular peak at 0.11 eV, while Fig. 7b is the scattering state associated with the small substrate peak at 0.77 eV. Note that the scattering state through the molecular stack clearly shows transmission through the  $\pi$ -orbitals, as indicated by the nodal planes coinciding with the phenyl rings in Fig. 7a. This sort of analysis was carried out to assign all peaks in Fig. 6.

One interesting point about Fig. 6 is that the peaks in the range [0.0, 1.5] eV which are due to transmission through the substrate are not affected by the nature of the



**Fig. 7** Scattering states for the eb- $\text{NO}_2$  system. **a** is associated with transmission peak at 0.11 eV, and **b** is associated with transmission peak at 0.77 eV in Fig. 6g

substituent. In fact, the small peaks at 0.35 and 0.77 eV are present in all systems (presumably including the systems containing  $-\text{NO}_2$  groups, but buried underneath the tall

molecular peaks). This is in contrast to the results reported by Anagaw et al. [16] who showed that the work function of a similar system is affected by the nature of the substituents. At this time, it is not clear why this sort of effect is not evident in the transport features. It may be due to the fact that the Fermi level in our two-probe system is determined by the Al electrodes, which might align the Si states. Another possibility is that the Si peaks outside the [0.0, 1.5] eV range are affected, but they are difficult to identify and compare in the different systems (i.e., in the range of [1.5, 4.0] eV). In any case, our calculations show that molecular states are clearly affected by the presence of substituent groups, even though we have not observed an effect on the Si substrate in the energy range we considered.

#### 4 Summary

The electronic structure and transport properties were calculated for substituted ethylbenzene molecules that  $\pi$ -stack to form a wire on top of a Si substrate. The substituents varied from electron donating to electron withdrawing groups. In terms of the electronic structure, projected density of states revealed that molecular states could be tuned relative to the states of the Si substrate by judicious selection of the substituent groups. This degree of control was also reflected in the transmission spectra of such molecular wires when connected to Al electrodes. The low-bias transport mechanism can be changed from leakage into the Si substrate to high conductance through the molecular wire if the appropriate substituent groups are used.

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#### References

1. Lopinski GP, Wayner DDM, Wolkow RA (2000) *Nature* 406(6791):48
2. Piva PG, DiLabio GA, Pitters JL, Zikovsky J, Rezeq M, Dogel S, Hofer WA, Wolkow RA (2005) *Nature* 435(7042):658
3. Basu R, Guisinger NP, Greene ME, Hersam MC (2004) *Appl Phys Lett* 85(13):2619
4. Hossain MZ, Kato HS, Kawai M (2005) *J Am Chem Soc* 127(43):15030
5. Hossain MZ, Kato HS, Kawai M (2005) *J Phys Chem B* 109(49):23129
6. Zikovsky J, Dogel SA, Haider MB, DiLabio GA, Wolkow RA (2007) *J Phys Chem A* 111(49):12257
7. Kirczenow G, Piva PG, Wolkow RA (2005) *Phys Rev B* 72(24):245306
8. Liu XY, Reynolds JE, Wells C, Welch J, Cale TS (2005) *J Appl Phys* 98(3):033712
9. Rochefort A, Boyer P, Nacer B (2007) *Org Elect* 8(1):1
10. Geng WT, Oda M, Nara J, Kondo H, Ohno T (2008) *J Phys Chem B* 112(10):2795
11. Smeu M, Wolkow RA, Guo H (2009) *J Am Chem Soc* 131(31):11019
12. Kirczenow G, Piva PG, Wolkow RA (2009) *Phys Rev B* 80(3):035309
13. Venkataraman L, Park YS, Whalley AC, Nuckolls C, Hybertsen MS, Steigerwald ML (2007) *Nano Lett* 7(2):502
14. Smeu M, Wolkow RA, DiLabio GA (2008) *J Chem Phys* 129(3):034707
15. Jalili S, Ashrafi R (2011) *Physica E* 43(4):960
16. Anagaw AY, Wolkow RA, DiLabio GA (2008) *J Phys Chem C* 112(10):3780
17. Kresse G, Hafner J (1993) *Phys Rev B* 47(1):558
18. Kresse G, Furthmüller J (1996) *Phys Rev B* 54(16):11169
19. Perdew JP, Burke K, Ernzerhof M (1996) *Phys Rev Lett* 77(18):3865
20. Grimme S (2006) *J Comput Chem* 27(15):1787
21. Blöchl PE (1994) *Phys Rev B* 50(24):17953
22. Kresse G, Joubert D (1999) *Phys Rev B* 59(3):1758
23. Taylor J, Guo H, J. Wang (2001) *Phys Rev B* 63(24):245407
24. Waldron D, Haney P, Larade B, MacDonald A, Guo H (2006) *Phys Rev Lett* 96(16):166804
25. Datta S (1995) *Electronic transport in mesoscopic systems*. Cambridge University Press, Cambridge
26. Sancho MPL, Sancho JML, Rubio J (1984) *J Phys F: Met Phys* 14(5):1205
27. Troullier N, Martins JL (1991) *Phys Rev B* 43(3):1993
28. Smeu M, DiLabio GA (2010) *J Phys Chem C* 114(41):17874