



# Diverse electron transfer behavior through saturated molecular chains: From molecular insulator to semiconductor

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## ARTICLE INFO

### Keywords:

Molecular wire  
 $\sigma$ -conjugation  
 Electron transport  
 Polysilane  
 Polygermane

## ABSTRACT

The electron transfer behavior through a series of  $\sigma$ -bonded molecular wires has been studied with density functional theory together with non-equilibrium Green's function method, for the potential utility in molecular device. Depending upon the interaction between the adjacent  $\sigma$ -bonds, the electron transfer behavior appears diverse, ranging from insulator to semiconductor. For the carbon-based wires in which there is lack of the interaction between the  $\sigma$ -bonds, the attenuation factors, i.e.,  $\beta$  values, are 0.83 and  $0.77 \text{ \AA}^{-1}$ , for perfluoroalkyl and alkyl chains, respectively. The large  $\beta$  value indicates the insulative behavior of the carbon-based molecular wires. However, while the skeleton silicon or germanium atoms are constructed in the molecular wires, the strong interaction between the adjacent  $\sigma$ -bonds forms the  $\sigma$ -conjugation and facilitates the electron transfer, resulting in a much reduced  $\beta$  value. In particular, the attenuation factors are 0.30 and  $0.24 \text{ \AA}^{-1}$ , for polysilane and polygermane, respectively, suggesting a semi-conductive feature.

## 1. Introduction

Understanding of electron transfer in a single molecule bridged between two metallic electrodes is paramount to the goal of fabricating electronic devices from single molecules and also relevant to the phenomena of electron transfer in many chemical and biological systems [1,2]. Among the electronic components, molecular resistor is of fundamental importance as it may block the current flow, adjust the signal levels, divide voltages, bias active elements, as well as assist other components to realize more complex functions [3–7]. Unlike traditional resistors, the molecular resistors typically have nonlinear current-voltage characteristics, and do not behave ohmically [8]. The electron transfer through a molecular resistor usually obeys a coherent tunneling mechanism [9]. The molecular conductance is reduced exponentially with increasing the molecule length as given by the following equation,

$$G = G_0 \exp(-\beta \cdot d) \quad (1)$$

where  $G_0$  is the contact conductance of the junction,  $\beta$  is the attenuation factor, and  $d$  is the molecular length.

The attenuation factor,  $\beta$  in  $\text{\AA}^{-1}$ , is directly correlated to the properties of the molecular bridge, especially the mean barrier height,  $\phi$  in electronvolts, via the following relation [10,11],

$$\beta = 1.025 \sqrt{\phi} \quad (2)$$

The mean barrier height of electron tunneling is a kind of apparent

physical quality, which can be obtained by the theoretical computation fitting to the experimentally measured current-bias data. Alternatively, a more feasible approach to the determination of the  $\beta$  value can be considered from the correlation with the HOMO-LUMO gap, i.e., the energy gap as shown in the following empirical relation [12,13],

$$\beta = -0.19 + 0.32 \sqrt{(E_g)_\infty} \quad (3)$$

where  $(E_g)_\infty$  is the energy gap of an infinite chain length obtained by extrapolation of  $E_g$  vs. the reciprocal of chain length. The direct correlation between  $\beta$  and  $E_g$  gives the possibility to estimate the attenuation factor as well as the mean electron tunneling barrier height,  $\phi$ , from quantum chemistry calculation.

The saturated alkyl chain has a large energy gap, and a large attenuation factor as well [14–24]. It is usually considered as molecular resistor in the concept of molecular device. On the contrary, the conjugated molecule has a narrow energy gap, and is, therefore, treated as conducting wire [12,13]. Between these two categories, the molecular wires with semiconducting feature are of great importance in theoretical consideration. The  $\sigma$ -bonded main chains made up entirely of Si or Ge atoms are promising candidates for this purpose. Many properties of these polymers are different significantly from analogous carbon-based systems such as polyethylene. They resemble rather more closely the fully  $\pi$ -conjugated systems such as polyacetylene and its analogues [25–27].

So far, tremendous efforts have been made to characterize the  $\beta$

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values of the saturated molecular resistors by either theoretical calculations [4,24,28–30] or experimental measurements [14–24]. In particular, recent studies have examined the physical tunnel junctions in which alkanes of varying lengths are bonded between gold electrodes via amine or thiol linkers [25,31,32]. Tao et al. demonstrated that the prefactor of the exponential decay function is highly sensitive to the end group, but the decay constant is weakly dependent on it [22]. Kaun et al. [4] and Basch et al. [28] found that the decay constants of the alkane dithiol systems are 0.95 and  $1.0 \text{ \AA}^{-1}$  respectively by the NEGF/DFT method, which are in good agreement with the measurements made for these tunnel junctions [22,24,32,33].

Other  $\sigma$ -bonded molecular wires, especially, polysilane [31] and polygermane [34–36] have been synthesized and characterized widely. In an early work, by using the Slater-Koster linear combination of atomic orbitals (LCAO) method, the electronic structure for the ideal polysilane chain was calculated. The results proved that the chainlike polysilane is a semiconductor having a wide direct band gap [37]. Ab initio calculation was performed for the hexagermane with side substitution [38]. It showed that the polygermane is a quasi-one-dimensional semiconductor with a direct band gap, and its valence and conduction bands are mainly contributed by the skeletal Ge atoms. In another theoretical work, Michl et al. proved that the  $\sigma$ -bonds in polysilane and polygermane have more pronounced delocalization nature of the  $\sigma$ -electrons compared with the carbon-based chains [39]. George et al. used DFT/NEGF and many-electron correlated scattering (MECS) formalism to calculate the electronic transport properties of alkane and silane chains with anchoring groups of dithiol and diamine. They found that silane-bridged junctions have larger conductance values compared with the alkane-bridged ones [25].

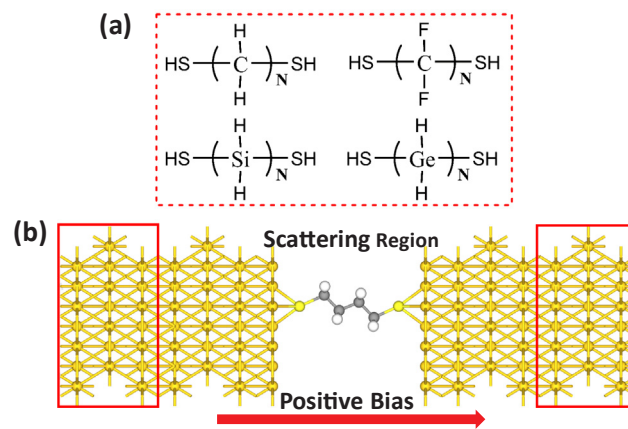
Experimentally, Su et al. demonstrated that  $\text{SiSbndSi}$  and  $\text{GeSbndGe}$   $\sigma$ -bonds are more conductive than the analogous  $\text{CSbndC}$   $\sigma$ -bonds using a scanning tunneling microscopy-based break-junction (STM-BJ) technique to measure conductance [26]. They found that the decay constant of oligogermanes ( $\beta_{\text{Ge}} = 0.36 \text{ \AA}^{-1}$ ) is very similar to that of oligosilanes ( $\beta_{\text{Si}} = 0.39 \text{ \AA}^{-1}$ ), but much shallower than that of alkanes ( $\beta_{\text{C}} = 0.74 \text{ \AA}^{-1}$ ). In a very recent work, they found that the conductance decay of Si- and Ge-based wires is similar in magnitude to those from  $\pi$ -based molecular wires such as para-phenylenes, and greatly affected by the linkers which attach molecular wires to the electrodes [5]. These experimental and theoretical investigations indicate that the Si- and Ge-based molecular wires more likely behave as a semiconducting molecular wires in electron transfer.

Though significant progress has been made, molecular details of the electron transfer through the  $\sigma$ -bonded molecular wires are not clear thoroughly. In the present study, by investigating a series of  $\sigma$ -bonded molecular wires, we aim to elucidate how the  $\sigma$ -electron delocalization occurring along the uninterrupted runs of the skeleton Si or Ge atoms contributes to the efficient electron transfer.

## 2. Methodology

### 2.1. Modelling and geometric optimization of the molecular wires

Scheme 1 illustrates the model molecular wires as well as the junction structure. In order to gain a stable molecular structure, the systems were fully optimized at the B3LYP level, with a LANL2DZ basis set for all the atoms, using the Gaussian 09 program [40]. Each model was then sandwiched between two equilateral triangular gold clusters with a gold bond length of  $2.88 \text{ \AA}$ , for further geometric optimization at the same level of theory. The triangular gold clusters properly simulate the electrode effect on the central molecule, therefore, the energy convergence can be accelerated. Finally, the molecule was inserted into a split gold junction.



**Scheme 1.** (a) The structures of all model molecular wires. (b) Schematic representation of the molecular junction, in which takes  $\text{sbn}(\text{CH}_2)_4\text{sbn}$  as an example.

### 2.2. Modelling of the molecular junction and the electron transfer characterization

The sophisticated molecular junction was divided into three parts: left electrode, scattering region, and right electrode. Each gold contact with (111) facet was constructed using a  $3 \times 3$  cell with a periodic boundary condition and a supercell consisting of 4 layers of 36 Au atoms in total. In our early publications, it has been reported that taking 4 layers of Au in the self-consistent cycle is enough to avoid the finite size effect [12]. The relative positions of Au atoms were frozen in space, but the configuration of central molecule together with the distance between the Au slabs was fully optimized again with a convergence criterion of  $0.05 \text{ eV/\AA}$ , by using the Atomistix Toolkit (ATK) software [40], which was based on first-principles DFT combined with the NEGF formalism [41]. The exchange-correlation potential was described by the Perdew-Burke-Ernzerh (PBE) with generalized gradient approximation (GGA) exchange-correlation functional. A double- $\zeta$  plus polarization basis set (DZP) was adopted for all atoms except Au atoms, for which single- $\zeta$  plus the polarization basis set (SZP) was used to achieve a balance between calculation efficiency and accuracy. The energy cutoff for the real space mesh was 300 Ry.

## 3. Results and discussion

### 3.1. Properties of molecular orbitals

To give insight into the molecular nature in the  $\sigma$ -bonded molecular wires, we systematically investigated the electronic structures and the electron transfer behaviors. The spatial distribution of molecular orbitals, especially, those of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are good indicators of a set of molecular properties. Fig. 1 compares the spatial distributions of HOMO and LUMO that are projected onto the molecular bridge with the interaction of the metallic electrode. In general, HOMO shows a more localized feature as compared to LUMO. This character is especially obvious for those insulative molecular wires. As presented in the alkyl and perfluoroalkyl chains, HOMOs are localized on the terminal sulfur groups. This character is ubiquitous for all of alkyl and perfluoroalkyl chains regardless of chain length. The localization of HOMO together with the low molecular orbital energy (around  $-2.0 \pm 0.2 \text{ eV}$  for all samples) indicates that the generation of cation on the molecular bridge is hard as compared to the  $\pi$ -conjugated wires [42,43]. Therefore, the alkyl and perfluoroalkyl series behave in an excellent insulative manner. On the contrary, polysilane has a distributed HOMO, supposing that it possesses better conductivity. Further analysis of the coefficient of HOMO proved that the HOMO state is composed of the 3p

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