

Designing molecular devices by altering bond lengths

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Abstract The work focuses on a theoretical approach to investigating the electric field (EF) dependence of bond-length alternation, the geometric and electronic structures of molecular wires used in the design of molecular electronic devices, the EF dependence of SCF energy, and the spatial distribution of the frontier orbitals of the molecular wires. Just as the bond length is an important influence on the conductance of the molecular wire, the dependence of the conductance on the chain length was also studied. We have also investigated how the current–voltage (I–V) characteristics change with bond length, as the bond length plays an important role in determining the conductance of molecular wires.

Keywords Bond length · SCF · NEGF · Two-probe systems · Extended Hückel theory

Introduction

The development of molecular technology enables us to manipulate nanosized molecules [1, 2]. Molecules can be

used as active components in electronic devices such as rectifiers and switches. Since understanding electron transport through single molecules or chains of them is essential in molecular electronics, much work in this area has been reported [3–5]; I–V characteristics have been calculated which demonstrate that bond-length alternation plays an important role in determining the conductance of molecular wires. Charge transport across organic molecules as a function of molecular structure has previously been investigated with a variety of experimental approaches, including electrochemical [3], scanning probe [4], donor-bridge-acceptor [5], and mercury drop electrode [6] techniques, as well as theoretical calculations [7].

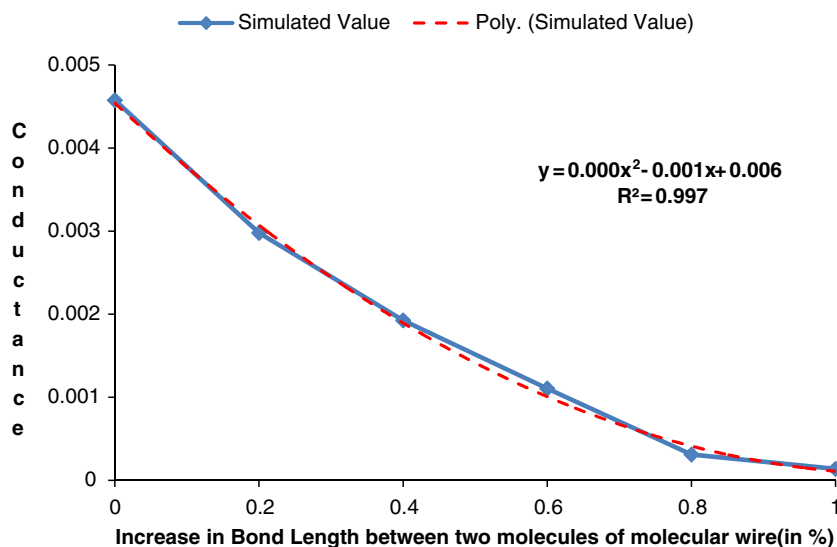
Two particular classes of molecular wires, oligo(phenylene ethylene) (OPE) and dithiole-benzene (DTB), have been the focus of our study. The theoretical calculations presented here highlight an important contribution to molecular wire conductance: the extent of the bond-length alternation along the δ -conjugated molecular backbone. To better understand the physical basis for the measurements, we calculated the I–V characteristics for the junctions studied using extended Hückel theory (EHT) and Green's functions (GF) under the approximation that the entire potential drop occurs at the metal–molecule interface. The details of the theoretical methods used here have been reported previously [7, 8]. Briefly, the EHT/GF treatment allows the calculation of the transmission function, which is then implemented within the Landauer–Buttiker formalism to calculate the I–V characteristics [8]. While we have found that junctions with asymmetric metal–molecule contacts can have unequal voltage drops at the two metal–molecule interfaces, resulting in asymmetric I–V characteristics, all of the junctions in this study have symmetric metal–molecule attachments, and thus the voltage drop is expected to be split equally at both interfaces.

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Fig. 1 Change in conductance the length of the bond between two molecules of a molecular wire is increased



Methods

We consider a 1,4-dithiole-benzene (DTB) molecular wire with a sulfur end group bonded to a gold probe. We use a double- ζ plus polarization basis set for the organic and a single- ζ polarized basis set for the s , p and d channels of the gold. The exchange-correlation potential is calculated using the local density approximation (LDA). The present work sheds new light on the conductance mechanisms of Au-DTB-Au molecular wires, which are very important in molecular electronics. Our findings also raise the prospect of bridging the gap that has persisted in this field between theory and experiment. The rest of this paper is organized as follows. We start with a brief description of the density functional based nonequilibrium Green's function method, before we present calculations of the (I-V) spectrum of a DTB molecule, together with an analysis of the molecular

levels that are important for electron transmission. Finally, the results will be summarized.

The calculations were performed using the Virtual Nano Lab package [9], which is based on the combination of DFT with the NEGF technique [10–14]. VNL is capable of fully and self-consistently modeling the electrical properties of a nanoscale device that consists of an atomic-scale system coupled to two semi-infinite electrodes. Such nanoscale devices are referred to as “two-probe systems,” and they are divided into three parts for theoretical calculations: the left and right electrodes and a central scattering region. The scattering region actually includes portions of the semi-infinite electrodes. The simulation procedure for such a two-probe system is described briefly below.

First, the electronic structures of the two electrodes are calculated to get a self-consistent potential. This potential

Fig. 2 Change in current when the length of the bond between two molecules of a molecular wire is increased

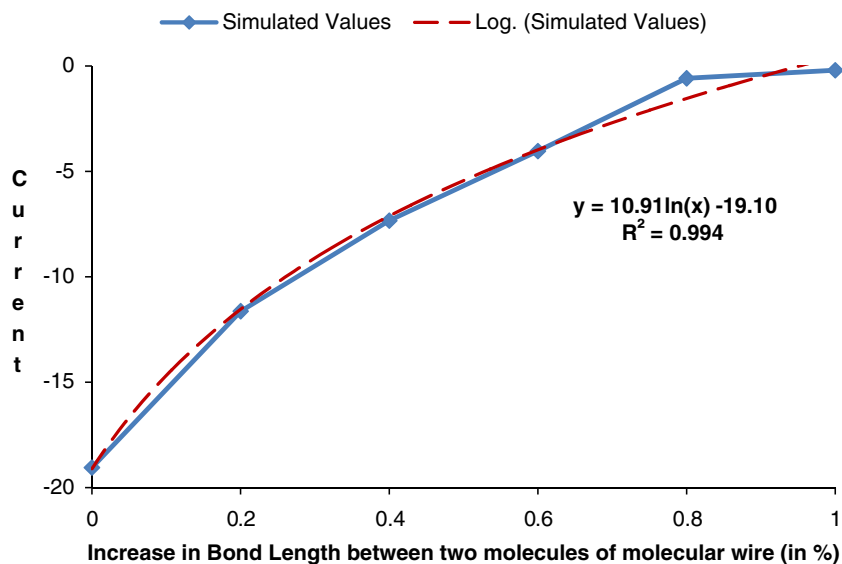
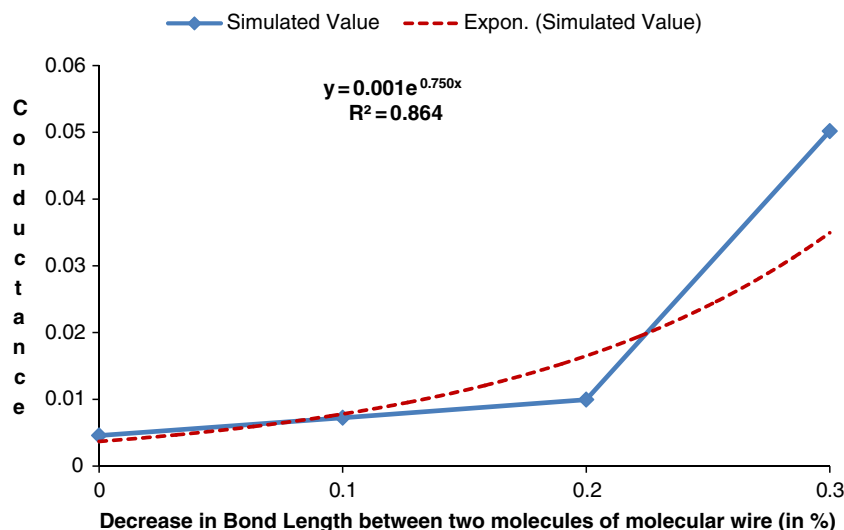


Fig. 3 Change in conductance when the length of the bond between two molecules of a molecular wire is decreased



will be shifted rigidly relative to each electrode by the external potential bias, and provides natural real-space boundary conditions for the Kohn–Sham (K-S) effective potential of the central scattering region. Then, from the Green's function of the central scattering region, the density matrix and thereby the electron density can be obtained. Once the electron density is known, the DFT Hamiltonian matrix, which is used to evaluate the Green's function, can be computed using the above boundary conditions by means of standard methods using the following equation:

$$G = \lim_{\delta \rightarrow 0} [(E + i\delta)S - H_{S|\rho}] - \Sigma_L - \Sigma_R]^{-1}. \quad (1)$$

Here, $H_{S|\rho}$ is the DFT Hamiltonian and Σ_L and Σ_R are the self-energies for the left and right electrodes, respectively. This procedure is iterated until self-consistency is achieved. Moreover, the current through the atomic-scale system can

be calculated from the corresponding Green's function and the self-energies using the Landauer–Buttiker formula [13].

$$I(V) = \frac{2e}{h} \int_{-\infty}^{+\infty} dE [f_L(E - \mu_L) - f_R(E - \mu_R)] T(E, V) \quad (2)$$

where μ_L and μ_R are the electrochemical potentials of the left and right electrodes, respectively, i.e.,

$$\mu_L - \mu_R = eV_b \quad (3)$$

and f_R and f_L are the corresponding electron distributions of the two electrodes. $T(E, V)$ is the transmission coefficient at energy E and bias voltage V , which will be calculated by

$$T(E, V) = Tr [\text{Im}\Sigma_L(E)G^R(E)\text{Im}\Sigma_R(E)G^A(E)] \quad (4)$$

where $G^R(E)$ and $G^A(E)$ are the retarded and advanced Green's functions of the central region. Based on the eigenchannel decomposition of the conductance, this total

Fig. 4 Change in current when the length of the bond between two molecules of a molecular wire is decreased

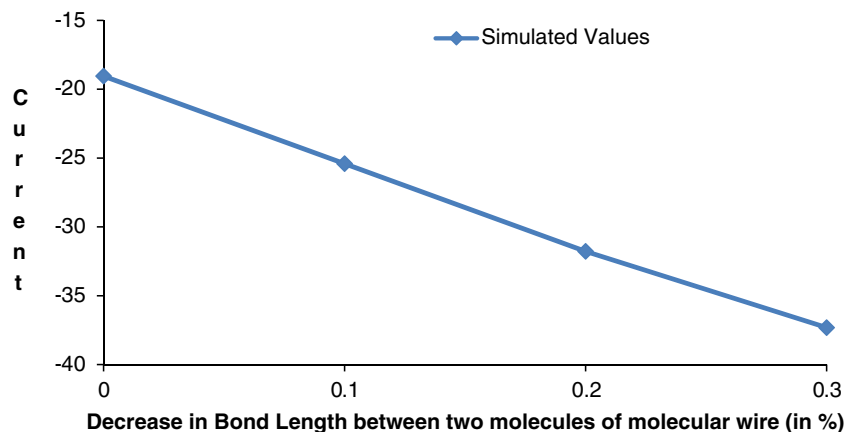
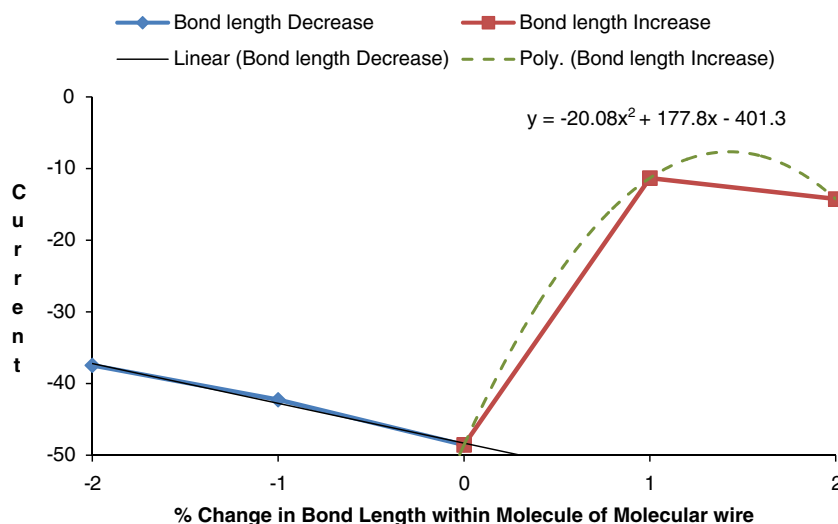


Fig. 5 Change in current when the length of a bond within a molecule in a molecular wire is varied



transmission $T(E)$ can be decomposed into the non-mixing eigenchannels $T_n(E)$ [14] as shown by

$$T(E) = \sum_n T_n(E) \quad (5)$$

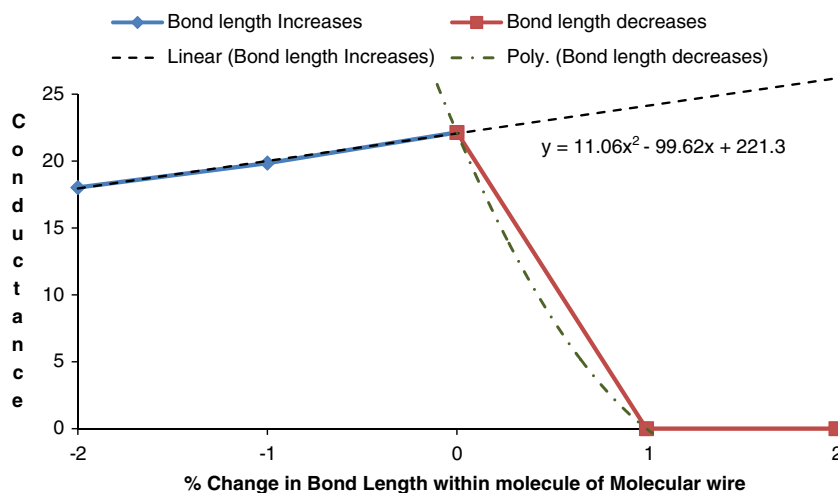
In our DFT calculation, the local-density approximation (LDA) to the exchange-correlation potential [15] is used. Only valence electrons are considered in the calculation, and the wavefunctions are expanded with localized numerical (pseudo)atom orbitals (PAOs) [16]. The atomic cores are described by norm-conserving pseudopotentials [17].

Results and conclusions

For a molecular wire, conductance decreases as the bond lengths between the molecules of the wire increase, and increases exponentially with decreasing bond length, as shown in Figs. 1–4. Because of the EF applied, the

molecular symmetry changes, although the coplanar conformation remains the same for the system we considered. When the EF increases, the carbon–carbon single bonds become shorter while the double bonds become longer, resulting in decreased bond length alternation (BLA). However, the EF dependence of the bond length is not the same for all of the bonds (meaning that we must study both bond and chain length to get a clear picture of the charge transport in this system). A simple quantitative relationship between single bond length and external EF was found after analyzing the data: single bond lengths increase linearly with EF to the power of R (R is non-integer), where R is the intermolecular distance in the nanowire and varies from 0.850 to 1.5. The nonlinearity between the length of single bonds and the square of EF also proves that the interaction between EF and the induced dipole moment predominates in the EF-induced molecular evolution. From Figs. 5 and 6, we found that stretching the individual molecules of the molecular wire causes the conductance to increase linearly

Fig. 6 Change in conductance when the length of a bond within a molecule in a molecular wire is varied



with the percentage increase in bond lengths within the molecule, and if the molecules are compressed the conductance decreases according to a second-order polynomial equation. This type of behavior can be explained by noting that the size of the energy gap between the highest occupied and lowest unoccupied molecular orbitals (the HOMO–LUMO gap) is directly related to the extent of bond-length alternation [18–21], and thus greater bond-length alternation causes a larger HOMO–LUMO gap, which affects the conductance and the electrical behavior of the molecules/molecular wire. We have simulated the I-V characteristics of two classes of molecules, and the simulated values for the I-V characteristics are in good agreement with the experimental values [19, 20]. The degree of bond-length alternation needs to be considered to fully understand the variations in charge transport across δ -conjugated molecular wires.

References

- Joachim C, Gimzewski JK, Aviram (2000) Electronics using hybrid-molecular and mono-molecular devices. *Nature* 408:541–548. doi:10.1038/35046000
- Carroll RL, Gorman C (2002) The genesis of molecular electronics. *Angew Chem Int Ed* 41:4378–4400. doi:10.1002/1521-3773(20021202)
- Nitzan A, Ratner MA (2003) Electron transport in molecular wire junctions. *Science* 300:1384–1389. doi:10.1126/science.1081572
- MAM R, Zhou C, Muller CJ, Burgin TP, Tour JM (1997) Conductance of a molecular junction. *Science* 278:252–254. doi:10.1126/science.278.5336.252
- Reichert J, Ochs R, Beckmann D, Weber HB, Mayor M, Lohneysen HV (2002) Driving current through single organic molecules. *Phys Rev Lett* 88:176804–176807. doi:10.1103/PhysRevLett.88.176804
- Weber HB, Reichert J, Ochs R, Beckmann D, Mayor M, Lohneysen HV (2003) Conductance properties of single-molecule junctions. *Phys E Low Dimens Syst Nanostruct* 18:231–232. doi:10.1016/S1386-9477(02)00986-4
- Bumm LA, Arnold JJ, Dunbar TD, Allara DL, Weiss PS (1999) Electron transfer through organic molecules. *J Phys Chem B* 103:8122–8127. doi:10.1021/jp9921699
- Cui XD, Primak A, Zarate X, Tomfohr J, Sankey OF, Moore AL, Moore TA, Gust D, Harris G, Lindsay SM (2001) Reproducible measurement of single-molecule conductivity. *Science* 294:571–574. doi:10.1126/science.1064354
- QuantumWise A/S (2008) Atomistix toolkit, 2008–10 student version. QuantumWise A/S, Copenhagen (see <http://www.quantumwise.com>)
- Wold DJ, Haag R, Rampi MA, Frisbie CD (2002) Distance dependence of electron tunneling through self-assembled monolayers measured by conducting probe atomic force microscopy: unsaturated versus saturated molecular junctions. *J Phys Chem B* 106:2813–2816. doi:10.1021/jp013476t
- Andergassen S, Meden V, Schoeller H, Splettstoesser J, Wegewijs MR (2010) Charge transport through single molecules, quantum dots and quantum wires. *Nanotechnology* 21:1–25. doi:10.1088/0957-4484/21/27/272001
- Bader RFW (1994) *Atoms in molecules: a quantum theory*. Oxford University Press, Oxford
- Datta S (2005) *Quantum transport: atom to transistor*. Cambridge University Press, Cambridge
- George CB, Ratner MA, Lambert JB (2009) Strong conductance variation in conformationally constrained oligosilane tunnel junctions. *J Phys Chem A* 113:3876–3880. doi:10.1021/jp809963r
- Zahid F, Paulsson M, Datta S (2003) Electrical conduction through molecules. In: Morkoc H (ed) *Advanced semiconductors and organic nanotechniques*. Academic, New York, pp 1–41
- González MT, Wu S, Huber R, Wolen SJVD, Schönenberger C, Calame M (2006) Electrical conductance of molecular junctions by a robust statistical analysis. *Nano Lett* 6:2238–2242. doi:10.1021/nl061581e
- Ulrich J, Esrail D, Pontius W, Venkataraman L, Millar D, Doerrer LH (2006) Variability of conductance in molecular junctions. *J Phys Chem B* 110:2462–2466. doi:10.1021/jp056455y
- Li C, Pobelov I, Wandlowski T, Bagrets A, Arnold A, Evers F (2008) Charge transport in single Au | alkanedithiol | Au junctions: coordination geometries and conformational degrees of freedom. *J Am Chem Soc* 130:318–326. doi:10.1021/ja0762386
- Haiss W, Martin S, Leary E, Zalinge VH, Higgins SJ, Bouffier L, Nichols RJ (2009) Impact of junction formation method and surface roughness on single molecule conductance. *J Phys Chem C* 113:5823–5833. doi:10.1021/jp811142d
- Kiguchi M, Miura S, Takahashi T, Hara K, Sawamura M, Murakoshi K (2008) Conductance of single 1,4-benzenediamine molecule bridging between Au and Pt electrodes. *J Phys Chem C* 112:13349–13352. doi:10.1021/jp806129u
- Lyshevski SE (2005) *Nano- and microelectromechanical systems: fundamentals of nano and microengineering*. CRC Press, Boca Raton