Physica E 42 (2010) 2026–2032

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe

First principle conductance calculation of zigzag, armchair and mixed geometries of S–6C–4H–S structures

S.K. Ambavale*, A.C. Sharma

Physics Department, Faculty of Science, The M. S. University of Baroda, Vadodara-390002, India

ARTICLE INFO

Article history:
Received 10 February 2010
Received in revised form
9 March 2010
Accepted 10 March 2010
Available online 18 March 2010

Keywords:
Ballistic transport
Ab-initio calculation
Molecular electronics

ABSTRACT

We investigated ballistic transport properties of armchair (AC), zigzag (ZZ), mixed, rotated-AC and rotated-ZZ geometries of small molecules made of 2S, 6C & 4H atoms which exhibit sp–sp^2 hybridization. Well-tested first principle scattering states formalism implemented in Quantum Espresso package has been employed to perform the calculations. The chains made of 6C-atoms with 1S-atom at each end and 4H-atoms attached to different C-atoms have been relaxed. This resulted in AC, ZZ, mixed geometry structures. Differences in transmission coefficient (T) curves of AC, ZZ and mixed molecules suggest geometry dependence of conductance and are in accordance with the previously reported results for AC and ZZ nanoribbons. In addition, our computed results for rotated-AC and rotated-ZZ suggest that the angle between electrode surface layers and molecular axis plays dominant role, compared to the role of angle between S–C bond and electrode surface layers, in determining conduction through the structure. The structures with molecular axis perpendicular to electrode surface layers yield higher conductance values.

1. Introduction

Molecular electronics is an emerging field of research that seeks to utilize individual molecules to perform functions of electronic circuitry. The molecular conductance has been measured employing experimental techniques such as scanning tunnelling microscopy [1], atomic force microscopy [2], break junctions [3], and monolayer evaporation [4]. Simultaneously, a rapid advancement is also taking place in computational methods, such as those based on density functional theory (DFT), that enable to reproduce and predict the nature of the molecular systems.

Due to their potential use in molecular electronic devices, electronic transport in organic molecules is one of the few fields that has been pursued immensely both experimentally and computationally, in recent years [5]. Graphene sheets and nanoribbons are strong candidates for futuristic molecular electronics due to their tunable and controllable properties that depend on its shape, surface termination, and applied field or pressure [6]. The exceptionally attractive features of their electronic and mechanical properties mainly depend on their electronic structure and geometry. In nanographenes, peripheral edges strongly affect the electronic states [7]. The sp–sp^2 hybridization present in these edge structures results in delocalized states across the whole molecule and opens a channel for transport [8]. We were motivated to investigate the geometry-dependent transport properties of structures made of 6C-atoms, 2S-atoms at two ends, and 4H-atoms joined to four different C-atoms where sp–sp^2 hybridization is present. These chain structures arising from basic building block (namely benzene ring) of graphene and of nanoribbon have sp^2 bonding for middle C-atoms and sp bonding for terminal C atoms. Benzenedithiolate is a very well-studied structure, which can give common platform to the studies related to molecular conductance. This motivated us to choose chain structures made from 2S, 6C and 4H atoms. Each of the studied structures initially comprised of straight chain of 6C atoms with 4H atoms attached to four different C-atoms, and one S-atom at each end has been relaxed to get minimum energy structure. At the end of relaxation process, we get AC, ZZ and mixed (combination of AC and ZZ) geometries depending on initial positions of H–C bonding in the chain. Resultant geometries have energies very close to that of a benzene molecule. These chain structures are reproducibly synthesizable through computer simulation and have potential advantage over other nanoelectronic systems with tailored atomic configuration.

The substitution of S-atom at both ends of a chain has distinct effects. (a) It introduces new molecular states that are thiol (S) end-group related. (b) Conductance behaviour of different chain geometries is comparable, without concerning much about their mechanical properties, as thiol-electrode chemistry mainly

---

* Corresponding author.
E-mail address: sagarambavale@yahoo.co.in (S.K. Ambavale).

1386-9477/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.physe.2010.03.016

determines the mechanical properties of junctions and is weakly dependent on the actual molecule between the electrodes [9]. (c) The sulphur forms a strong chemisorption bond with noble metal surfaces. We selected Al-nanorod as an electrode in place of widely used gold-nanorod. Gold has been suggested as one of the worst possible choices for high-conductance molecular nanowires as in the gold case the DOS of the leads does not penetrate into the molecule and electrons have to tunnel between both surfaces, which produces a very small zero-bias conductance [10]. The Al is a noble metal having high conductivity and has been used in many prior performed benchmark calculations [8,11].

Three basic electronic processes in metal- molecule- metal junctions are; (a) charge transfer between the metals and the molecules, (b) change of the electrostatic potential and (c) modification of the molecular geometry and electronic states. The nature of these processes under both zero and nonzero bias determines the electrical characteristics of the molecular junction. In our case, device is at equilibrium and therefore the linear dc-transport properties of molecular device probes the equilibrium charge distribution of molecular junction established by adsorption of chains onto the electrodes. Therefore, there appears a need to determine the appropriate geometry of molecular junction and the resulting line-up of the molecular levels relative to the metal Fermi level, and modification of the molecular states. Solving of adsorption-induced conformation change requires an accurate knowledge of surface lattice structure at the atomic scale for devices, which is not known in typical molecular transport measurement. Hence, one has to examine the effects that different adsorption and molecular geometries may have on the device characteristics. In view of this, we also computed conductance properties of rotated molecules with respect to electrode surface layers. The paper is organized in IV sections. Computational details are reported in Section 2. Discussion on results is given in Section 3 and the final Section 4 concludes the work.

2. Computational procedure

Transport properties of molecular devices have been investigated with the use of several theoretical methods in which determination of the electronic structure is a key element. Particularly, the relative position of the frontier (highest occupied and lowest unoccupied) molecular orbitals and the Fermi level of the metallic electrodes are of utmost importance. Among the various approaches, DFT-based methodologies provide better results on electronic structure calculations with an acceptable computational cost. Due to nanometric dimensions, electron transport in atomic-sized nanocontacts is essentially ballistic [12]. One therefore assumes that the electron moves ballistically in a potential caused by scattering region and electrodes. Moreover, at molecular level, the adsorption-induced modification of molecular states is larger than the field-induced effect, unless there is large bias. Therefore, accurate modelling of the electronic processes at equilibrium is critical for determining low-bias transport characteristics. In view of this, we studied ballistic conductance properties in a linear regime with zero applied bias and neglected the field-induced effects. PWSCF of Quantum Espresso package, which uses plane wave formulism, has been used to perform ground state DFT calculations [13]. The scattering-based approach of PWCOND code of Quantum Espresso package is used to compute conductance.

The exchange-correlation energy is evaluated within Perdew and Zunger formula for local density approximation, which works relatively good in case of organic molecules, noble metals and alkali metals. Only valence electrons are explicitly considered using norm-conserving pseudopotentials to account for core-valence interactions [14]. For all chains made of 6C, 2S and 4H atoms, we first performed structural optimization by relaxing them until the forces become less than 0.025 eV/Å. Different chains are prepared by taking into consideration possible permutations of attaching 4H to 6C atoms. The geometry of a relaxed chain structure depends on to which C-atoms H-atoms are attached in the starting chain geometry. Accordingly, we get final geometries as armchair (AC), zigzag (ZZ) and mixed structures, as can be seen from Fig. 1a to c. The relaxed chain geometries resemble with isomers of well-known conjugated π-electron polymer, polyacetylene. The AC geometry resembles with *cis*, ZZ geometry resembles with *trans* and MIXED geometry resembles with *trans–cisoid* isomers of polyacetylene. Our computed S–C, C–C and C–H bond lengths for all chains are given in Table 1. Computed values of C–C bond length are in good agreement with those measured experimentally in polyacetylene [15] and with those calculated with density functional crystal orbital method using B3LYP functional [16]. In the final relaxed geometries, H atoms prefer to be in radial position irrespective of whether H-atoms in initial geometry are at bridge positions or at radial position. We also computed transmission co-efficient of benzene which is a cyclic trimmer of acetylene.

A two-probe system is made of a central scattering region (also known as extended molecule) coupled with two atomic-scale Al [1 0 0] electrodes, which extend to reservoirs at ± ∞ where the

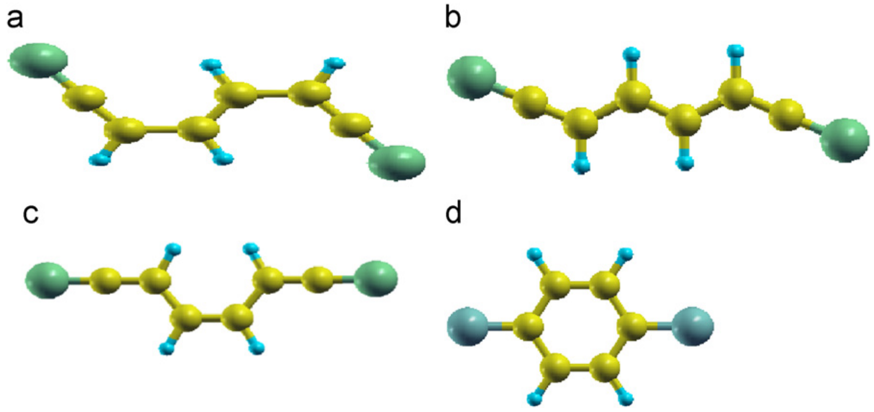

Fig. 1. (a) The relaxed final geometry comprising of 6C (yellow), 2S (green) and 4H (blue) atoms, which looks like AC geometry. (b) The relaxed final geometry resembling to ZZ geometry. (c) The relaxed final geometry that looks like combination of armchair and zigzag geometry. It is named as mixed geometry. (d) The relaxed final geometry of benzene, which is cyclic trimer of acetylene.