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Electron Transport in Boron Fullerenes

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Abstract- The electron transport properties of B\textsubscript{80} fullerene is studied using first-principles density functional theory in conjunction with the Landauer-Büttiker quantum transport formalism. The electron transmission in B\textsubscript{80} fullerene is calculated to be much higher than that in C\textsubscript{60} fullerene in the Fermi-level region. The enhanced transmission in the B\textsubscript{80} fullerene is attributed to its spatially extended charge distribution in delocalized bonds.

I. INTRODUCTION

The carbon fullerenes have shown a great potential in applications such as field effect transistors [1], spin valves [2], [3], electro-mechanic amplifiers [4], high temperature superconductors [5], to name just a few. By far the most common one is the buckminster fullerene, C\textsubscript{60}, which has been shown to act as a semiconductor quantum dot [4]. Recently, boron related nanostructures have been the subject of several theoretical and experimental studies. Despite its preference to the three-dimensional (3D) structural motifs in natural structures, boron is shown to have planar or quasi-planar structures in small clusters [6], [7]. Theoretical studies have also shown the existence of two-dimensional (2D) boron sheets [8]-[10]. First principles calculations have predicted the most stable boron sheets and the corresponding single-walled nanotubes to be metallic [11], [12], in contrast to the diverse nature of single-walled carbon nanotubes ranging from metallic to semiconducting depending upon their chirality and diameter. The metallic nature of boron sheets and nanotubes is due to the unique bonding features of boron in forming multi-center bonds and having high coordination numbers [6], [7], [13]. Boron nanostructures are therefore expected to provide an alternative to carbon nanostructures for novel nanoscale devices.

Similar to carbon, boron fullerenes can be constructed from 2D boron sheet by following the isolated pentagon rule [14]. In addition, the hexagon rings prefer to have an extra boron atom at the center, following the Aufbau principle [6]. Just like in carbon, boron fullerene structures are predicted to be relatively more stable at certain “magic” numbers, such as B\textsubscript{80} [15]. The goal of this paper is to explore the electronic and transport properties of boron fullerenes, namely B\textsubscript{80}. The calculated results are compared with those of C\textsubscript{60} fullerene to reveal differences, if any, between boron and carbon fullerenes.

II. COMPUTATIONAL DETAILS

The symmetry-constrained geometry optimization calculations were performed using Gaussian03 electronic structure program package [16] for B and C fullerenes considered using B3LYP functional form [17], [18] in the framework of density functional theory. The geometry of the two fullerenes were optimized with the use of STO-3G basis set. The choice of a relatively small basis set was made due to the computational requirements for large clusters. The bond lengths after relaxation are in good agreement with the previous theoretical study [15]. Finally single-point calculations at the optimized geometry were performed with a larger polarized basis set, 6-31G*. Table I lists the energies obtained using the 6-31G* set. The electronic transport calculations on the fullerenes coupled to semi-infinite Au electrodes (Fig. 1) were performed following the Landauer-Büttiker formalism [19]-[21]. The core scattering region was simulated by the extended molecular complex, Au-fullerene-Au where atomic scale contacts were used for the fullerene molecule. The LanL2DZ basis sets for boron and gold atoms were used for transport calculations.

The total current in the Au-fullerene-Au device can be obtained by the following equation

\[ I = \frac{2e}{h} \int dE T(E,V) \left[ f(E - \mu_1) - f(E - \mu_2) \right] \]

where, \( \mu_1 \) and \( \mu_2 \) are the electrochemical potentials in the two contacts under an external bias \( V \), \( f(E) \) is the Fermi-Dirac distribution function. \( T(E,V) \) is the electron transmission function which can be calculated from a knowledge of the molecular energy levels and their coupling to the metallic contacts. Additional details of the calculations can be found elsewhere [3], [22].

In the scattering region, the point contacts of the gold leads were represented by a single atom [3], [23], and the bulk effect was implicitly included by the self-energy term \( \Sigma \). The bridge site between two six-membered rings of the fullerene was taken to be the binding site of the metallic contact atom [3].
with the bond distances of 2.2 Å and 2.4 Å, Au-B and Au-C were kept at, respectively.

III. RESULTS AND DISCUSSION

A. Electronic Structure

The optimized structure of B\textsubscript{80} fullerene is shown in Fig. 1 together with the contact Au atoms. Symmetries, binding energies $E_b$, and the frontier orbital gaps, obtained as the energy difference between the highest occupied (HO) and the lowest unoccupied (LU) molecular orbitals (MOs) of the fullerene molecules C\textsubscript{60} and B\textsubscript{80} are listed in Table I. The B\textsubscript{80} molecule can be viewed as a derivative of C\textsubscript{60}-like structure by adding extra atoms at the center of all hexagons [15]. It consists of 12 pentagons and 20 centered-hexagons holding $I_h$ symmetry. The centered-hexagons are cross-linked through the global molecule. The bond lengths after relaxation are in good agreement with the previous theoretical study (using PBE/plane-wave basis sets, ultrasoft pseudopotentials) [15].

<table>
<thead>
<tr>
<th>fullerene</th>
<th>Symmetry</th>
<th>$E_b$ (eV/atom)</th>
<th>HOMO-LUMO Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B\textsubscript{80}</td>
<td>$I_h$</td>
<td>5.17</td>
<td>2.12</td>
</tr>
<tr>
<td>C\textsubscript{60}</td>
<td>$I_h$</td>
<td>6.97</td>
<td>2.74</td>
</tr>
</tbody>
</table>

B. Electron Transport

The calculated transmission functions and currents of B\textsubscript{80} along with that of C\textsubscript{60} are shown in Fig. 2 and Fig. 3 respectively. The transmission function, in general, reflects the intrinsic transmission characteristics of the fullerene molecule. The large HOMO-LUMO gap of the isolated C\textsubscript{60} molecule reflects itself in a vanishing transmission gap in the near-Fermi region [23]. The closest transmission peaks at ~0.7 eV (labeled by * in Fig. 2) are due to LUMO-derived states, i.e. two pure C\textsubscript{60}-LUMO states and one hybrid state of C\textsubscript{60}-LUMO and Au (note that the isolated C\textsubscript{60} has 3-fold degenerate LUMOs). These results are consistent with an earlier theoretical study using the non-equilibrium Green’s function (NEGF) method [24], except the shift in peak position about 0.6 eV towards higher energy. It should also be pointed out that the previous study [24] utilized Au(100) surface to model the metal electrode. A higher charge transfer of 0.7 e from Au to C\textsubscript{60} was predicted there as compared to the current value of 0.22 e, which indicates a higher population of C\textsubscript{60} LUMO states.

The B\textsubscript{80} fullerene system has a non-negligible transmission at the zero injection energy, which arises from the diffusive transmission peaks due to the Au-molecule hybrid states in the near-Fermi region. The gap in the transmission due to the HOMO-LUMO gap is still tractable for B\textsubscript{80}. Within the gap, there are two metal induced gap states (MIGS) for the B\textsubscript{80} extended molecule. They arise from the hybridization of Au 6s and B\textsubscript{80} states located mainly on the B-B bridge sites binding to Au contacts, which, however, do not show any close affinity to any of the isolated B\textsubscript{80} molecular states near the pseudo Fermi level $E_F$. The HOMO state is shown to be rather delocalized, leading to a very diffusive transmission without showing a distinguishable peak. The LUMO state of the system, which is more localized at the two Au-bonding region, accounts for the sharper transmission peak shown at ~0.2 eV (labeled by ^ in Fig. 2) for B\textsubscript{80}. The charge transfer from Au to B\textsubscript{80} is about the same as to C\textsubscript{60}.

IV. SUMMARY

In summary, the boron family of engineered nanomaterials has appeared to have unique chemical bonding and electronic properties. In this work, we have studied the electron transport properties of one of the most stable boron fullerenes, B\textsubscript{80}. The calculated results reveal a substantially enhanced transmission as well as tunneling current for B\textsubscript{80} as compared to C\textsubscript{60}. In the case of the former, a non-vanishing transmission near $E_F$ is observed, while in the latter case a large gap in transmission near $E_F$ is observed, resulting from its semiconducting property.
ACKNOWLEDGMENT

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