Comparative Study of Symmetrical And Asymmetrical B₄₀ Molecular Junctions

Harleen Kaur

Guru Nanak Dev University

Jupinder Kaur (✉ jupinderece.rsh@gndu.ac.in)

Guru Nanak Dev University <https://orcid.org/0000-0001-9214-8130>

Ravinder Kumar

Guru Nanak Dev University

Rajan Vohra

Guru Nanak Dev University

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Abstract

The quantum transport in symmetric and asymmetric borospherene based molecular junction with adenine has been probed. Adenine is a nucleobase of DNA among the four nucleobases of DNA, adenine is selected because of its excellent transport properties. The DFT-NEGF mathematical approach has been utilized. This was further used to calculate quantum transport parameters such as the I-V curve, transmission spectra, highest occupied molecular orbital (HOMO)- lowest occupied molecular orbital (LUMO) gap (HLG), differential conductance, and transmission pathways. From our research work we have noticed that both symmetric and asymmetric devices exhibit non-linear behavior thus leading to non-differential resistance (NDR). Also symmetric B₄₀ molecular device has reduced HLG in contrast to asymmetric B₄₀ molecular device. This drop-in HLG is due to a reduction in electron density. A high rectification ratio for the devices is observed at 0.2V. Hence symmetric and asymmetric B₄₀ molecular junction is the potential candidates that can be utilized in future nano-scale devices.

Introduction

In the last four decades, uprising change in the field of science and technology has completely changed the industry. "There is plenty of room at the bottom" an acclaimed lecture by Richard P. Feynman has paved the way for nanotechnology and many researchers have shown their curiosity in this field [1]. So over the years in the field of electronics, researchers have investigated the use of single molecules in devices. There have been many kinds of research related to single molecular devices but utilization of B₄₀ with DNA is another promising candidate for molecular electronic applications.

Deoxyribonucleic Acid (DNA) was first scrutinized by Frederich Miescher in 1869 but its value for electronic applications was not anticipated for many years. Extensive research has shown that DNA exhibits good conductivity and researchers have researched how the charge is transferred [2]. It is composed of a long wire-like structure formed by four nucleobases i.e adenine (A), guanine (G), thymine (T), and cytosine (C). Furthermore, it has been proved that by changing the length of DNA its conductance can be varied. In addition, while formulating devices using DNA; electrode material, nucleotide content, and miler indices orientation has stern effects on the properties of the device [3–5]. The DNA molecule has the unique equity of duplicating itself that makes it applicable to form molecular electronic devices. Cytosine and guanine nucleobases of DNA have been also examined individually [6]. The comparative study of both the nucleobases depicts excellent conductive properties in the case of cytosine whereas guanine exhibits exceptional NDR. Borospherene (B₄₀) is another emerging material in the field of molecular electronics. In 2014 Zahi et. al discovered a highly stable B₄₀ molecule [7]. A comparative study was conducted by He et. al between B₄₀ and other boron clusters and it was deduced that B₄₀ exhibits strong absorbing capability [r]. Further research revealed that the borospherene cage encompasses two hexagons, one at the top and the other at the bottom alongside four heptagons positioned at the sides [8]. Wang et. al analyzed the properties of B₄₀ by positioning the transition metals inside the fullerene cage. Mn, Fe, Co, and Ni were encapsulated and it was scrutinized that M@B₄₀ (M = Fe and Mn) were spin-

polarized whereas Ni encapsulated fullerene remained unpolarized [9]. Borospherene has shown its capabilities as a sensor for the detection of various toxic gases due to the presence of both acidic and basic sites [10]. Kaur et. al utilized the chalcogen family elements with B₄₀ to investigate its electronic transport properties [11]. Maniei et. al used a lithium doped variant in B₄₀ fullerene which they used to capture NO₂ [12]. Plenty of research has already been conducted in the field of molecular electronics based on borospherene (B₄₀) and DNA, yet both the materials have not been investigated in a single molecular device as symmetrical and asymmetrical junctions.

In the present research work, transport properties of symmetric and asymmetric B₄₀ molecular junctions are studied. Adenine (A) (C₅H₅N₅) is used due to its excellent properties in comparison to other nucleobases of DNA [13]. Adenine with B₄₀ is used in the molecular junction. We aim to study various properties of B₄₀ fullerene with adenine. Transmission spectra, electron density, HLG, and transmission pathways were examined. Figure 1 depicts both asymmetrical and symmetrical devices, where blue atoms are nitrogen atoms, grey atoms are carbon atoms, white atoms are hydrogen atoms and yellow atoms are sulfur atoms that act as linkers.

Methodology

DNA is a nano-molecule acclaimed material to be used as molecular wire. It is an organic molecule that has the characteristics of self-replication. Thus, it becomes necessary to individually study the bases of DNA and in this paper, we focus on Adenine. The investigation was done by forming asymmetrical and symmetrical devices. For the first case, an asymmetrical device was formed with adenine and B₄₀, whereas a symmetrical device was formed by placing adenine on both sides of B₄₀ fullerene. For the formation of the device, the adenine and B₄₀ are sandwiched between two gold (Au) electrodes with sulfur as linker atoms [14].

To implement all the modeling and simulations Atomistix Toolkit interface VNL software has been used [15]. The density functional theory in association with non-equilibrium green's function (NEGF) was employed [16–19]. Gold is the most favorable material for electrodes because of its high stability at room temperature. The assembled device constitutes three regions the left electrode, right electrode, and scattering region. Double-zeta polarized basis set (DZPS) is employed for both the devices and Perdew-Burke-Ernzerhof's generalized gradient approximation (GGA) was selected as a correlational function [20]. The orientation of the electrode was chosen to be < 1,1,1 > and the length of the electrode was taken as 7 Å [21–22]

The I-V (current-voltage) curve can be determined by imposing Landauer-Buttiker formalism [r]. The formalism anticipates the relation between applied voltage and current, with the help of transmission probability [T(E, V)] [23]:

$$I(V) = 2 \frac{e}{h} \int_{\mu_L}^{\mu_R} T(E, V) [f(E - \mu_L) - f(E - \mu_R)] dE \quad (1)$$

In Eq. 1, $T(E, V)$ demonstrates transmission function and μ_L/μ_R represents the electrochemical potential of the left and right electrodes. The transmission function can be perceived from the information about the portion of coupling between the electrodes and the molecule and the molecular energy level. The transmission was envisaged similarly [24]:

$$T^k(E, V) = T_r [\Gamma_1^k(E, V) G_M^k(E, V) \Gamma_2^k(E, V) G_M^{k'}(E, V)] \quad (2)$$

In the above Eq. 2, $\Gamma(E)$ demonstrates the coupling function which adequately gives the information about the type of contact between the molecule and electrodes and $G_M(E, V)$ represents Green's function. Suppose that energy levels of the molecule are susceptible to float towards a higher level with a value eV_{mol} which is relatively proportionate to the molecule's electrostatic potential. To persuade, it can be supposed that energy levels of molecules are fixed, while the substrate is susceptible to float towards a lower level by an amount eV_{mol} . Hence, for both the metallic electrodes electrostatic potentials can be represented as [25]:

$$\mu_L = E_F - eV_{mol} = E_F - \eta eV \quad (3)$$

$$\mu_R = E_F - eV + eV_{mol} = E_F + (1-\eta)eV \quad (4)$$

In Eq. 3 and Eq. 4, E_F demonstrates the equilibrium Fermi energy, e denotes electron charge, and η denotes the distribution of the potential difference between the electrodes. It can be defined as $\eta = V_{mol}/V$ [24–25].

The transmission pathways can be utilized to investigate the flow of electrons in molecular junctions. It divides the transmission coefficient into local bond contribution, T_{ij} . The pathways have the ability that splits the system into two parts (A, B), then pathways all over the boundary between A and B sum up to the total transmission coefficient [26]

$$T(E) = \sum_{i \in A, j \in B} T_{ij}(E) \quad (5)$$

In the above Eq. 5 T_{ij} , demonstrates local bond contribution and it can be positive and negative. A positive value of T_{ij} is visualized in red color as an arrow from i to j while a negative value is visualized in blue color as an arrow from j to i i.e in opposite direction. Thus it signifies that the direction of arrows shows the flow of electrons.

Results And Discussion

QUANTUM TRANSPORT UNDER EQUILIBRIUM

The transmission spectra at 0V are analyzed for both the adenine-based molecular junctions. The arrangement of molecular orbitals along with the extent of coupling between the metallic leads is

examined by exploring transmission spectra at equilibrium. The transmission spectra explain which molecular orbitals are responsible for transmission along with the HOMO-LUMO gap. From the Fig. 2, it is anticipated that for Adenine-B40-Adenine peak is closer to the Fermi level for negative bias voltages, signifying the dominance of HOMO orbitals in transmission. In the case of Adenine-B40, peaks are closer to E_F for positive bias, signifying the dominance of LUMO orbitals in transmission.

Furthermore, the molecular energy spectrum of both devices at 0V is considered. The HOMO, LUMO, and HLG (HOMO-LUMO gap) devices are as tabulated in Table 1. From the table, it can be deduced that for the device in which adenine is placed on both sides of the borospherene the HLG gap reduces in comparison to the device in which adenine is placed only on one side of the borospherene. HLG gap for Adinine-B40 is 0.804 eV, whereas for Adenine-B40-Adenine it is 0.470 eV.

Table 1
HOMO. LUMO and HLG

Device	HOMO	LUMO	HLG
A-B40	-0.6881377	0.1159547	0.8040924
A-B40-A	-0.2107773	0.2594467	0.470224

QUANTUM TRANSPORT UNDER NON-EQUILIBRIUM TRANSPORT

To further investigate the quantum transport for adenine-based molecular junction, transport properties under non-equilibrium conditions were determined. In this context, transmission spectra were analyzed at various biases ranging from $-1V$ to $+1V$ with a step size of $0.2V$. Figure 3. depicts comparative graphs for both the devices. In the case of Adenine-B40 intensity of peaks is higher and in close proximity to the Fermi level, depicting the effortless flow of electrons from the left to the right electrode. For Adenine-B40-Adenine, also a large number of peaks can be seen, but with lower intensity and having sharpness in the peaks which reveal lesser transmission between electrodes. Also, with the variation in applied bias there is shifting of peaks, thus implying that with change in bias, the states engaging in conduction also change.

Also from Fig. 3, a comparison is done between transmission at all the negative and positive biases. For the transmission spectra at $-1V$ Adenine-B₄₀ device has more peaks which depict more transmission and the Adenine-B₄₀-Adenine less and sharp peaks which depict lesser transmission. Whereas for the positive bias at $+1V$ the intensity of transmission further reduces for both the devices. When the rest of the biases are compared for the negative bias transmission is more than the transmission at positive bias, which corresponds to the results of transmission spectra at $-1V$ and $+1V$.

Along with other parameters, the current-voltage (I-V) curve was investigated. From Fig. 4, it is anticipated that for Adenine-B40-Adenine the current is lesser in contrast to the Adenine-B40 device. Adenine-B40 shows symmetrical behavior for both positive and negative bias. Also, the current depicts the non-linear behavior for both devices. The negative differential resistance (NDR) is distinguishable in the case of

Adenine-B40-Adenine in the positive bias range. It signifies that there will be a decrease in current with an increase in bias voltage.

Now the question arises, why current is lesser in Adenine-B40-Adenine based molecular junction, even though HOMO-LUMO gap (HLG) is lesser. This is due to the weak bonding of electrodes to the molecule, which corresponds to the lesser value of the current. To probe this further, we assimilated the electron density for both devices. From Fig. 5 it can be seen that for the Adenine-B40 device, electron-cloud is more oriented around all the nitrogen atoms in adenine, as compared to Adenine-B40-Adenine. This is why although HLG is less for Adenine-B40-Adenine, still they have less current because of lower electron density and larger value of work function. Also, adenine has nitrogen atoms which pose high electro-negativity which hold more number free electrons hence reduction in the flow of current.

The rectification ratio (RR) can be calculated as $R = [I(V)/I(-V)]$. The graph shows the rectification ratio for both devices. The calculated values of the rectification ratio as shown in Table 2 present a clear picture of minor variations in RR values with an increase in bias. The Adenine-B40 device shows a maximum RR of 2.11 at 0.2V, whereas Adenine-B40-Adenine shows a maximum RR of 1.25 at 0.2V. The rectification ratio for both devices decreases with an increase in bias voltage. The devices depicting prominent NDR and good RR are good candidates for tunnel diodes with vital relevance in high-speed logic circuits.

Table 2
for rectification ratio

Voltage	A-B40	A-B40-A
0	0	0
0.2	2.11	1.25
0.4	1.645	0.3
0.6	0.97	0.35
0.8	0.713	0
1	0.588	0.28

To further understand how the current flow in the central scattering region of molecular junction, we have analyzed transmission pathways. The transmission pathways are also known as local currents, which are represented by arrows that superimpose on molecular geometry. The red arrow exhibits the transmission that is in direction of the net current, whereas the blue arrow shows components in opposite direction, thereby reducing the net current. Figure 6 shows the local currents of Adenine-B40 and Adenine-B40-Adenine. It is visible that for Adenine-B40 the current flows along the spherical surface, not directly through the cage, and has more number channels, thus increasing the conductance. On the other hand for Adenine-B40-Adenine the flow of current is also along the spherical surface of the cage, but it has fewer channels in comparison with the first device.

Conclusion

The electron transport properties of borospherene in the asymmetric and asymmetric molecular junction have been elucidated with adenine. The density functional theory with non-equilibrium function (NEGF) duo has been used in ATK-VNL software. The various transport parameters are investigated such as transmission spectra, HLG, electron density, conductance, I-V curve, and transmission pathways. By analyzing transmission spectra at equilibrium, it is inferred that LUMO orbitals play the dominant role in transmission for asymmetrical devices whereas for symmetrical devices HOMO is dominant. Symmetrical junctions have reduced HLG due to lower electron density as nitrogen has high electro-negativity which holds more number of free electrons. The highest value of current is observed for asymmetrical junctions in contrast to symmetrical junctions. Non-linear behavior is observed for both the devices due to which NDR comes into the picture. The highest rectification ratio for both the devices is observed at 0.2V which is 2.11 for asymmetrical devices and 1.25 for the symmetrical device. Thus borospherene based symmetric and asymmetric molecular junctions are the potential candidates that can be utilized in future nano-scale devices.

Declarations

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Figures

Figure 1

Pictorial representation of (a) Adenine-B40 (b) Adenine-B40-Adenine

Figure 2

Transmission Spectra at 0V

Figure 3

Transmission Spectra at various voltages

Figure 4

I-V curve for (a) Adenine-B40 (b) Adenine-B40-Adenine

Figure 5

Figure 6

Rectification Ratio

Figure 7

Transmission Pathways (a) Adenine-B40 (b) Adenine-B40-Adenine