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Spin resolved electronic transport through N@C_{20} fullerene molecule between Au electrodes: A first principles study

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ABSTRACT

Using first principles study, through Density Functional Theory combined with Non Equilibrium Green's Function Formalism, electronic properties of endohedral N@C_{20} fullerene molecule joining Au electrodes (Au-N@C_{20}) was addressed in the presence of spin property. The electronic transport behavior across the Au-N@C_{20} molecular junction was investigated by spin resolved transmission, density of states, molecular orbitals, differential conductance and current-voltage (*I-V*) characteristics. Spin asymmetric variation was clearly observed in the results due to single N atom encapsulated in the C_{20} fullerene cage, where the N atom played an essential role in the electronic behavior of Au-N@C_{20}. This N@C_{20} based molecular bridge, exhibiting a spin dependent *I-V* variation, revealed a metallic behavior within the bias range from −1 V to 1 V. The induced magnetic moment, spin polarization and other relevant quantities associated with the spin resolved transport were elucidated.

1. Introduction

Spin electronics has extensively been studied for a long time [1–3]. In this field, spin dependent electronic structure and transport properties of devices can be considered to reveal the envisaged technological applications. Hence, an analysis for the spin resolved behavior through the structure is essential. The analysis must exhibit novel results and be applicable in the field of spintronics. Spintronic devices, formed by a system between electrodes, rely on spin polarization (SP) which plays a key role in the spin resolved electronic transport. Molecular spintronics has also been drawing attention towards various applications in technology [4–11]. Using the spin property of electrons, the capability of a molecular device can further be improved to be employed in spintronics [12,13]. Organic molecules can be utilized to enhance the functionality and performance of molecular devices [4–6,12–17]. The potential spintronic applications of an efficient spin based molecular device require spin injection from the electrode and controllability of spins across the device [2].

Fullerene molecules, due to ample applications in technology, have been attained enormous consideration [18–27]. There have been many studies concerning their electronic and magnetic properties [20,23,25,26,28]. C_{60} fullerene molecule, which is a molecular allotrope of carbon, was discovered in 1985 [18]. After this discovery, many scientific works were addressed for this buckyball-shaped molecule and its derivatives [19–25]. Nitrogen (N) doped fullerenes were shown to be promising structures for the nanoelectronic devices [29]. Their derivatives were already synthesized [30], and theoretically studied [31,32]. Magnetic properties of fullerene molecules can be examined by encapsulation of atoms inside the fullerene cage (endohedral fullerene) [33–36]. Hence, an endohedral fullerene molecule can be harnessed in the field of spintronics. The emerging spin asymmetry in the electronic properties of such a fullerene molecule can be revealed by Density Functional Theory (DFT) through some approximations [37]. Endohedral fullerenes can be synthesized [38–41]. It was both experimentally and theoretically demonstrated that reactive atoms can be encapsulated inside the C_{60} fullerene molecule [42–45]. Reactive atoms, like N, can be stabilized inside the fullerene cage [33,45,46]. Thus, fullerene molecules can be employed as ideal containers for such reactive atoms [47,48]. For instance, the stability of an N based endohedral fullerene is due to dispersion interaction between N atom and fullerene cage [33]. The N atom encapsulated inside the C_{60} fullerene (N@C_{60}) is inert and retains in its atomic ground state ($^4S_{3/2}$ with electron spin $S = 3/2$) [46,48]. It was experimentally observed that N keeps the spherical symmetry [46]. Long spin relaxation time of the N atom and its stability have drawn great attention. Due to half-filled *p* orbitals, an N based endohedral fullerene is a potential structure in spin based quantum computation [46,49].

C_{20} fullerene, one of the derivatives of C_{60}, is especially attractive as it is the smallest fullerene molecule produced [23–27]. It was demonstrated that the lifetime of the C_{20} fullerene was long at room temperature [50]. Quantum transport properties of C_{20} were analyzed employing

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first principles calculations [23,25–27]. A pristine C_{20} molecule attached to the Au electrodes has recently been examined by M. Kaur et al. in Ref. [23], where (in the absence of spin property of the electrons) spin independent electronic transport behavior of C_{20} through the Au electrodes was investigated employing the DFT combined with Non Equilibrium Green's Function Formalism (NEGF). The present study was motivated by the work performed in Ref. [23]. In this work, an analysis was conducted to explore the spin resolved electronic transport of the N@C_{20} endohedral fullerene based molecular device. Such a molecular bridge is composed of two electrodes and a fullerene molecule attached to them. The electrode surfaces employed in a molecular junction are, in general, metallic such as Au, Ni, Al etc. In the present study, the molecular junction was produced by the Au electrodes between which N@C_{20} was inserted (Au-N@C_{20}). Hence, a C_{20} based organic molecular bridge was formed [4,15,23,51]. The spin dependent behavior and associated spin polarization were observed due to the N atom encapsulated inside the C_{20} cage. In order to reveal the spin dependent properties of Au-N@C_{20}, first principles calculations were performed through the DFT combined with NEGF using the software package Atomistix ToolKit (ATK) [52,53]. The effect of a single N atom within the C_{20} fullerene on the electronic transport across the molecular junction was mainly concentrated. To this end, spin dependent transmission ($T_{\uparrow\downarrow}$), device density of states ($\mathrm{DOS}_{\uparrow\downarrow}$), partial density of states ($\mathrm{PDOS}_{\uparrow\downarrow}$, projected onto the N atom and N@C_{20}), molecular orbitals, differential conductance ($G_{\uparrow\downarrow}$) and spin resolved current (I)-voltage (V) characteristics were exhibited. The magnetic property of the molecular device was addressed by the induced magnetic moment on the N@C_{20}, originating from the N atom. The coupling of N@C_{20} to the electrodes played a crucial role in the spin resolved electronic transport, as expected. An almost linear variation was observed in the *I-V* characteristics for both majority (spin up) and minority (spin down) spins. It was found that N@C_{20} based molecular bridge, exhibiting a spin dependent *I-V* variation, revealed a metallic behavior within the bias range from -1 V to 1 V. The model and the method are introduced in Section 2; Section 3 gives the numerical results and discussions; concluding remarks are presented in Section 4.

2. Method

The N@C_{20} endohedral fullerene was modeled and then inserted between the Au electrodes, through the ATK software. This molecular junction was formed by semi-infinite left and right electrodes (LE and RE, respectively) and a scattering region where the molecule was placed. A scattering region also comprises screening layers of LE and RE [52,53]. The molecular device was examined using the Au (100) electrodes (both LE and RE): LE-N@C_{20}-RE (Au-N@C_{20}). First, isolated N@C_{20} molecule was optimized. After the optimization, N@C_{20} was inserted between the LE and RE. Next, constraining the Au electrodes, Au-N@C_{20} was relaxed. The relaxation leads to optimized atomic distance between each electrode surface and the molecule. The lowest energy configuration for a molecular device corresponds to the optimum distance between the molecule and electrodes. This distance was measured as 2.185 Å for Au-N@C_{20}. During the relaxation, the force tolerance was set to $0.05\ \mathrm{eV}/\mathrm{\AA}$. Then, first principles calculations were carried out to expose the spin resolved electronic transport properties. In calculations, the exchange–correlation potential was approximated within the spin dependent generalized gradient approximation (SGGA) with Perdew-Burke-Ernzerhof (PBE) functional (SGGA.PBE) [54], for the exchange and correlation effects of the electrons. The software ATK employs the Troullier–Martins pseudopotentials [55] for the ion cores. A mesh cutoff energy of 150 Ry and (3,3,100) *k-point* mesh within the Monkhorst-Pack scheme [56] were utilized. In order to enhance the accuracy of the calculations, the double-zeta polarized basis set of local numerical orbitals was employed to represent the electronic structure of valence electrons of the atoms (C, N, Au) in the molecular junction. For the Au-N@C_{20} molecular junction schematically depicted in Fig. 1, the main goal is to reveal how a single N atom encapsulated by the C_{20} cage modifies the electronic transport across the Au surfaces.

3. Numerical results

The influence of the N atom inside the C_{20} fullerene on the spin dependent behavior was investigated. First principles calculations were performed on the spin resolved transmission, DOS and PDOS in the vicinity of the Fermi level (E_F, set to zero). Magnetic properties and the spin dependent electronic transport were elucidated by magnetic moment, $G_{\uparrow\downarrow}$ and *I-V* characteristics. First, local magnetic moment on the N atom and average magnetic moment per atom on the molecule for both isolated N@C_{20} molecule and Au-N@C_{20} device were calculated via Mulliken population [57]. The magnetic moments are listed in Table 1. The magnetic moment on the N atom was obtained as $1.108\,\mu_B$ and $0.625\,\mu_B$ for N@C_{20} and Au-N@C_{20}, respectively. While the average magnetic moment per atom on the isolated N@C_{20} cage was $0.238\,\mu_B$, it became $0.097\,\mu_B$ for the Au-N@C_{20} molecular bridge. Hence, introducing a single N atom within the C_{20} leads to an appreciable magnetic moment on the isolated N@C_{20}. It also induces a magnetic moment on the Au-N@C_{20} device, resulting in a spin resolved electronic behavior through this molecular junction. The induced spin dependent behavior is due to the half-filled *p* orbitals for an N based endohedral fullerene, where the N atom retains in its atomic ground state with electron spin $S = 3/2$. The average magnetic moment on the pristine C_{20} fullerene based molecular device (Au-C_{20}) was considered as well for the sake of comparison. It was almost zero, as expected. It implies that a spin dependent electronic transport does not manifest across the Au-C_{20} molecular junction. The Mulliken analysis yields the charge population in a system. In a molecular device a charge transfer exists between the molecule and the electrode surface, which is determined by the electrode structure and end atoms of the molecule. It is associated with the strength of molecule-electrode coupling and the electron transport from the molecule to the electrode. From the Mulliken analysis, the charge transfer across the Au-N@C_{20} was calculated as $0.0321|e|$. On the other hand, it was $0.0329|e|$ for the Au-C_{20} device. Hence, introducing an N atom in the fullerene caused no crucial change in the charge transfer. A significant change can be envisaged if the electrode structure is modified. An augmentation of the charge transfer implies more robust molecule-electrode coupling.

The transmission and DOS for the Au-C_{20} and Au-N@C_{20} molecular junctions in the presence of spin are illustrated in Fig. 2, where positive (negative) transmission and DOS denote the majority (minority) spins in the spectra. The electronic transport of a system is governed by the states in the vicinity of the E_F. The transmission spectra in Fig. 2a and b (where both the majority and minority transmission coefficients have certain values at the E_F for both Au-C_{20} and Au-N@C_{20}) indicate that the conductance through both C_{20} and N@C_{20} becomes nonzero at zero bias. On the other hand, the trend in the DOS spectra is consistent with that in

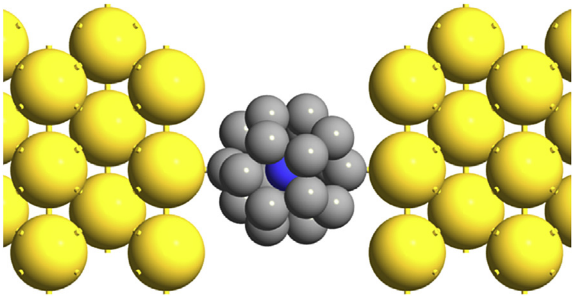

Fig. 1. Au-N@C_{20} molecular device composed of N@C_{20} and Au electrodes. Yellow spheres are Au atoms, grey spheres denote C atoms and blue sphere represents N atom. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)