Study of ballistic transport in molecular junctions based on H2O@C60, B40 and phenalenyl-based molecule

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Study of ballistic transport in molecular junctions based on $\text{H}_2\text{O}@\text{C}_{60}$, $\text{B}_{40}$ and phenalenyl-based molecule

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"This thesis is presented as part of the requirements for the award of the Degree of the University of Wollongong"

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DECLARATION

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Wollongong and where applicable, any partner institution responsible for the joint-award of this degree.

Chengbo Zhu
2014
This thesis is dedicated to my mother, Yang Tao,
for her endless love, support
and encouragement.
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Molecular electronics has been an attractive area for the past two decades. New concepts, with no classical analogues, have been inspired by nanoscale devices. As electronic devices are scaled down to nanometer dimensions, their operation depends on the detailed atomic structure. Recently, more and more attention has been paid to the physical properties of metal–molecule–metal junctions that go beyond electronic transport characterizations.

In this thesis, a short history and the latest progress on molecular electronics are introduced. Then, we briefly describe the theory and simulation methods.

First, the transport properties of $\text{H}_2\text{O}@\text{C}_{60}$-based nanostructures sandwiched between electrodes have been calculated. We find that, unlike the single endohedral fullerene molecule in electrostatic field, such nanostructures can no longer act as a Faraday cage under voltage bias. The screening effect disappears completely. In addition, the disappearance of the screening effect is water-position-independent. Nevertheless, the conductance of the junction is water-position-dependent. When the encapsulated water molecule moves towards the centre of the C$_{60}$, the conductance of the molecular junction decreases, and vice versa. For this highly symmetric dipolar molecule, with the same contact geometry, its transport properties can be manipulated by controlling the encapsulated water molecule.

Secondly, the conductance of two $\text{H}_2\text{O}@\text{C}_{60}$ molecules in series order is reported, as well as how the number of encapsulated water molecules influences the transport properties of the junction. Encapsulating an H$_2$O molecule in one of the C$_{60}$ cages increases the conductance of the dimer. Negative differential resistance is found in the dimer systems, and its peak-to-valley current ratio depends on the number of encapsulated H$_2$O molecules. The conductance of the C$_{60}$ dimer and the H$_2$O@C$_{60}$ dimer is two orders of magnitude smaller than that of the C$_{60}$ monomer. Furthermore, we demonstrate that the conductance of the molecular junctions based on the H$_2$O@C$_{60}$ dimer can be tuned by moving the encapsulated H$_2$O molecules. The conductance is H$_2$O-position dependent. Our findings indicate that the H$_2$O@C$_{60}$ can be used as a building block in C$_{60}$-based molecular electronic devices and sensors.

Thirdly, the transport properties and thermopower of individual B$_{40}$ molecules are calculated. Our study suggests that B$_{40}$ is a highly conductive molecule...
compared with C$_{60}$. The conductance of Au-B$_{40}$-Au junctions can be as high as several times that of Au-C$_{60}$-Au junctions with similar contact geometries. As a rule of thumb, in single-molecule junctions based on $\pi$-conjugated molecules or C$_{60}$ fullerene, the number of conduction channels usually equals the number of C atoms in contact with the electrode. However, the number of conduction channels in a B$_{40}$-molecule junction is less than the number of B atoms in direct contact with the electrode, due to the unique electronic structure of B$_{40}$. Moreover, we have found that the thermopower of B$_{40}$ with gold electrodes is dramatically smaller than that of the Au-C$_{60}$-Au junction and is negative, except for one configuration, due to the fact that the lowest unoccupied molecular orbital dominates the charge transport. There is reason to believe that chemical modification and functionalization of the B$_{40}$ are possible. This may lead to finding molecules with higher conductance after doping. The B$_{40}$ fullerene is a new platform for highly conductive single-molecule junctions for future molecular circuits.

Fourthly, we propose a way of connecting phenalenyl-based molecules to gold electrodes with their spin-polarized state preserved. As a result, spin-polarized transmission is found in the phenalenyl (C$_{13}$H$_9$) molecular junction. Remarkably, the peak positions for both spins are found to differ by more than 0.5 eV. The spin-polarized transmission is suppressed or enhanced by replacing two carbon atoms of phenalenyl with boron or nitrogen atoms. The current of the nitrogen-doped junction is spin-balanced at low bias but spin-polarized at finite bias. This leads to a device that can generate spin-polarized current at the desired bias by doping. By B-doping, the spin-polarized transmission is enhanced, as the orbitals in one spin channel resonate with the electrons on the electrodes, indicating its potential application in making spin filter devices.
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Chapter 1

Introduction

1.1 Molecular electronics

Over the past two decades, experimental and theoretical investigations of single-molecule junctions have become a robust area for researchers [1] because of their promising application in future molecular electronics. According to Moore’s law [2], the number of transistors in a dense integrated circuit doubles approximately every two years. To survive in a competitive market, the industry is constantly pushed to look for new materials and technologies for manufacturing smaller, faster, and more energy-efficient devices. Today’s electronics industry is based on the silicon metal-oxide-semiconductor field-effect transistor (MOSFET) technology, where a severe limitation is going to be encountered – to the miniaturization of the transistors. One of the solutions is to look for new materials beyond silicon, such as single-molecule transistors. It is difficult for single-molecule devices to replace the MOSFET technology in the foreseeable future, but it is believed that the studies of the molecular devices will eventually lead to novel applications in the industry.

Molecular electronics offers a platform where the devices are built in the size of individual molecule. The idea of utilizing the intrinsic properties of molecules for electronics was proposed in the early 1970s by A. Aviram and M. Ratner [3]. They suggested that a rectifier could be made of single molecule. Other than providing the opportunity for building devices at atomic size, single- or multi-molecular devices exhibit many characteristics that cannot be achieved otherwise [4]. In molecular devices,
for example, identical building blocks can be replicated; control of electronic devices at atomic level is available [5]; and spin quantum effects at room temperature have been observed [6]. Nevertheless, our understanding of molecules is just beginning, and their potential applications extend far beyond their utility as electronic elements [7]. At the present, there are still many practical obstacles to be overcome: reproducibility of the results, stability of the contacts, capability for mass production, etc. Therefore, the development of molecular electronics technology requires multidisciplinary efforts and cooperation from physicists, chemists, surface scientists, and electrical engineers.

1.2 Electron transport in molecular devices

The single-molecule junction gives us a window to understand fundamental physical phenomena at the atomic level. It was an experimental challenge, however, before the development of the scanning tunnelling microscope (STM) and later the atomic force microscope (AFM), which were invented by Gerd Binnig and Heinrich Rohrer at IBM laboratories in Zurich. These tools were soon found to be useful for measuring electronic transport in molecular junctions.

Since quantitative measurement of the conductance of a single-molecule junction was no longer a problem experimentally, it led to a broader interest in molecular electronics [8]. Yet single-molecule electronics are unable to replace the silicon-based semiconductor industry at present. The biggest challenge that prohibits the molecular devices from commercial application is the contact stability and reproducibility of the results. When the size of the devices is reduced down to the molecular level, the coupling between the single molecule and the metallic electrodes dominates the transport properties, indicating that the conductance of the junction is very sensitive to the contact geometry between the molecules and electrodes.
To produce reliable experimental data, many types of electrodes composed of different elements have been tried [9-12]. Gold, the most common material used for the electrodes in molecular junctions so far, has been studied extensively [13-21]. In addition, other materials, such as platinum, aluminium, silver, and alkali metals (Na, K, etc.) are also used for electrodes. On the other hand, different atomic configurations on electrode surfaces may result in distinctive transport properties [22-25]. The control of crucial atoms in the junction is still an experimental challenge.

Another aspect that has influence on the electronic transport in molecular junctions is the link group between the molecules and electrodes. Many chemical link groups are used to bind molecules to metal electrodes in single-molecule junctions. They control both the physical structure and the electronic coupling at the interface. How the discrete molecular energy levels of the molecule align with the Fermi level of the electrodes is another crucial factor for understanding the transport properties of the junction.

Thiol links are usually preferred when the junctions are formed using gold metallic electrodes [8, 10, 26-39]. It is easy to form Au-S bonds when the molecule approaches the gold substrate due to the strong bonding force between them [40]. Xu and Tao formed N-alkanedithiol-gold junctions by repeatedly moving a gold scanning tunnelling microscope (STM) tip into and out of contact with a gold substrate in a solution containing the sample molecules [26], where \( N \) was the number of carbon atoms along the tunnelling pathway, as shown in Fig. 1.1. They measured the resistance of each sample and determined the tunnelling decay constant. In addition, the thiol link group of a single molecule can be coupled to control break-junction electrodes mechanically [28]. While the authors measured the current-voltage characteristics (\( IV \) characteristics) of the metal-molecule-metal system, an interesting property of the molecule was identified: its
symmetry. Asymmetrical shapes of molecules may result in asymmetrical IV characteristics. This is ideal for making rectifier devices. Since then, searching for a large rectification ratio has become an intriguing task for searchers using molecules with asymmetric structures [41, 42]. Phenalenyl-based molecules with different contact geometries have different rectification ratios [41]. With the same electrodes, the rectification ratio is dependent on the number of thiol groups used in the junction [42]. Furthermore, using different link groups at the two terminals of the molecule can also lead to the rectification phenomenon in the molecular junction [43].

On the other hand, the disadvantage of the thiol links is that the conductance of \( \pi \)-conjugated molecules is strongly influenced by the orientation of the \( \pi \) system relative to the Au-S bond [44], although this can be exploited to enlarge the conductance of the junction by aligning the orientations of \( \pi \) electrons on the molecule and the orientation of the Au-S bond [45]. The strength of the Au-S bond is larger than that of the Au-Au bond, which means the Au-S bond is more difficult to break [46, 47]. This strong bond sometimes makes the interpretation of single-molecule measurements more complicated [48]. A theoretical study showed that gold-gold bonds could be broken by pulling a single thiolate molecule that is anchored on a stepped gold surface, so that a monoatomic gold nanowire was formed [47]. Other link groups were also studied on gold electrodes, such as amines (-NH\(_2\)) [11, 45, 49-53], methyl sulfide (-SMe) [54], dimethyl phosphine (-PMe\(_2\)) [54], cyanide (-CN) [55], pyridyl [17], thiocyanate (-SCN) [56], and isothiocyanate (-NCS) [57-59].

Recently, direct metal–carbon couplings were also formed to achieve high conductance [50, 60-66]. The benzene molecule is the most common molecule selected to form a direct carbon-metal bond [63]. M. Kiguchi et al. formed a junction where the benzene molecule was bonded directly to Pt leads, and they demonstrated that this
configuration was stable [61]. Its transmission could be tuned by varying the inter-electrode distance and the molecule’s orientation. The conductance of the junction was as high as 1 \( G_0 \), where \( G_0 \) is the conductance quantum. The benzene-silver bond was also formed experimentally, exhibiting a fixed conductance value of 0.24 \( G_0 \) [62].

Figure 1.1 Conductance of a gold contact formed between a gold STM tip and a gold substrate decreases in quantum steps near multiples of \( G_0 \) as the tip is pulled away from the substrate. (A) shows well-defined peaks near 1 \( G_0 \), 2 \( G_0 \), and 3 \( G_0 \) due to conductance quantization. (B) When the contact shown in (A) is completely broken, corresponding to the collapse of the last quantum step, a new series of conductance steps appears if molecules such as 4,4-bipyridine are present in the solution. These steps are due to the formation of a stable molecular junction between the tip and the substrate.
electrodes. (C) In the absence of molecules, no such steps or peaks are observed within the same conductance range [26].

Furthermore, molecular chains were used to form Au-C bonds [60]. A series of SnMe$_3$-terminated polymethylene chains with 4–12 carbons were synthesized, and molecular junctions based on these molecules were created. Due to the covalent Au–C σ bond, high conductances were achieved. The conductance decreases exponentially with increasing number of carbon atoms in the molecule. A decay constant of 0.97 is found in theoretical calculations.

Along with the technical progress in experimentation, our theoretical understanding of single-molecule junction was developed in 1990s. The transmission formalism was established to describe the mesoscopic transport. The conductance of the junction was explained very well by the development of the non-equilibrium Green’s function approach [67]. Since then, research that is beyond simple charge transport has emerged and a number of articles have been published with exciting discoveries.

1.3 Molecular junctions beyond electronic transport

In the study of metal-molecule-metal junctions, researchers have exploited different methods such as mechanical, optical and thermoelectric methods to measure and manipulate the electronic transport in molecular junctions [68]. This research went beyond electronic transport characterization, enhancing our basic understanding and heralding new device concepts with no classical analogues.

Simultaneous mechanical and electronic measurements are able to determine the structure of atomic-size junctions, which cannot be obtained from measurements of electronic properties of nanoscale and molecular junctions [69]. This was done first by
Rubio et al. [46]. They measured the mechanical properties of atomic-sized gold contacts at room temperature and their relationship to electrical properties. Stepwise variation of the conductance was observed due to the atomic rearrangements in the contact. The experiments were performed at room temperature in a solution of molecules, analogous to the STM-based break-junction method that has now been widely adopted to perform conductance measurements [26]. The relationship between the measured current and the force is the most basic information from simultaneous measurements of force and conductance in metal contacts. Ternes et al. analysed experimentally and theoretically the relationship between the chemical force and the tunnelling current during bond formation in atom-scale metallic junctions [70]. They found that the short-range force and the conductance in metal junctions depended exponentially on the distance and that they have essentially the same exponents.

Another dynamic area with a potentially important application of molecular electronics is ‘molecular optoelectronics’. It has already achieved success in commercial applications with organic light-emitting diodes (OLEDs). Recently, G. Reecht et al. studied the electroluminescence of a polythiophene wire suspended between a metallic surface and the tip of a scanning tunnelling microscope [71]. The emission mechanism and polarity dependence were similar to what occurs in OLEDs, but at the level of a single molecular wire. As this model shows, there are two prerequisites for a junction to be luminescent: (1) the asymmetric position of the highest occupied molecular orbital – lowest unoccupied molecular orbital (HOMO-LUMO) gap with respect to the Fermi level at zero bias; (2) asymmetric voltage drop repartition at the interfaces [72, 73]. Raman spectroscopy combined with the STM-based break-junction technique was also employed for measuring single-molecule junctions formed between an Au STM tip and an Au (111) substrate [74]. The measurement allows mutually verifiable single-molecule
conductance and Raman signals with single-molecule contributions to be acquired simultaneously at room temperature. This will lead to a better understanding of electron-transport processes in molecular junctions. Beyond measurements of the Raman spectra of molecular junctions, light could be used to control transport in junctions formed with photochromic molecular backbones that occur in two (or more) stable and optically accessible states. A number of compounds, such as azobenzene derivatives, can be switched between a conducting conjugated form and a non-conducting cross-conjugated form [75].

In addition to mechanics and optics, the molecular junction is also an intriguing area for thermoelectronics. A decade ago, researchers were focusing on searching for more efficient thermoelectric nanoscale devices [76, 77]. This requires a fundamental understanding of thermoelectrics at the single-molecule level [78]. The Seebeck coefficient at zero voltage is related to the derivative of the transmission probability at the metal Fermi energy (in the off-resonance limit):

$$S = -\frac{\pi^2 k_B^2 T}{3e} \frac{\partial \ln [T(E)]}{\partial E},$$

where $k_B$ is the Boltzmann constant, $e$ is the charge of the electron, $T(E)$ is the energy-dependent transmission function, and $E_F$ is the Fermi energy. Ludoph et al. first measured the Seebeck coefficient and conductance in atomic-size metallic contacts [79]. Their work offered a way to achieve thermoelectric characterization of molecular junctions. Afterwards, the thermoelectric characteristics of fullerene molecules (i.e., C$_{60}$ and C$_{70}$) were studied by trapping the molecule between metallic electrodes (i.e., Pt, Au, Ag) [80]. The measurement setup is shown in Fig. 1.2. The electronic conductance depends on the multiple orientations and the electrode coupling of molecules between the junctions. The thermopower is predictable from the molecular energy level.
alignment based on the work function of the electrodes. Their work demonstrated that organic dopants at inorganic interfaces could lead to further enhancements of thermoelectric efficiency.

Figure 1.2 Measurement set-up. Schematic illustration of the experimental setup for measuring conductance and thermopower with a modified (STM) break junction. For conductance, a voltage bias is applied between the tip and the substrate, and the conductance is determined using a current amplifier. The STM tip approaches the substrate and traps fullerene molecules. For thermopower, fullerene molecules are trapped between the STM tip held at ambient temperature and a heated Au substrate held at $\Delta T$ above the ambient temperature. As the STM tip approaches, a voltage bias is applied between the tip and the substrate, and the conductance is monitored. Once a threshold conductance is reached, indicating formation of a molecular junction, the tip is withdrawn. During the withdrawal sequence, a switch disconnects the voltage bias and current amplifier in favour of a voltage amplifier. The induced thermoelectric voltage $V$ is measured as the tip withdraws but before the junction breaks [80].

There is another area for molecular electronics that has no classic analogues: quantum interference, which arises due to the wave nature of electrons and has an
influence on the transport in molecular junctions. Electronic transport at the molecular level is not a simple extension of the Aharonov–Bohm effect in metal rings [81]. The conductance of a cross-conjugated molecule can be lowered significantly by the quantum interference effects [82, 83]. The anti-resonance in the transmission probability through the junction is the typical signature of destructive interference in molecular junctions. C. Guédon et al. were able to show evidence of transmission anti-resonance in a junction composed of about 100 molecules [37].

Quantum interference effects can also cause the conductance of two parallel benzene molecules to be larger than twice that of each single molecule [84]. According to Kirchhoff’s circuit laws, the net conductance of two parallel components in an electronic circuit is the sum of the individual conductances. On other hand, in quantum theory, the resulting conductance influenced by quantum constructive interference should increase by four times or more [85].

Figure 1.3 Schematic representation of (a) junctions with one (top) and two (bottom) molecular backbones (M) connected in parallel through common links L. (b) Chemical structures of exemplary molecules with single- (1) and double- (2) backbone molecules [84].
It was a formidable challenge to form such junction with multiple conductive backbones. H. Vazquez et al. were successful in forming a parallel backbone junction as depicted in Fig. 1.3 [84]. The authors demonstrated that the conductance of the parallel backbones is enhanced by a factor of ~3. Their study was a vivid example, illustrating that molecular junctions cannot simply be treated as a scaled down version of mesoscopic devices.

When the degree of freedom of spin was introduced in single-molecule junctions, a new category of materials named molecular spintronics emerged [86]. Spin-filter effects had been found in two-layer organic molecules adsorbed on ferromagnetic surfaces due to the hybridization and magnetic exchange between the molecules and the surface of a ferromagnet [86-88]. Theoretical calculations showed that giant magnetoresistance (GMR) could be found in spin-crossover molecules [89, 90]. The GMR ratio could reach as high as 3000%. Spin-crossover molecules are ideal candidates for future production of small spin devices at the molecular level.

In organic molecules, it is easier to control and manipulate their properties by changing their composition and molecular structure than in the case of inorganic materials. Also, the longer spin lifetime in organic molecules makes them even more attractive materials for building spintronic devices. C. Barraud and co-workers developed a spin transport model that describes the role of interfacial spin-dependent metal/molecule hybridization in the effective polarization [91]. They fabricated nanometre-scale (La, Sr)MnO$_3$/Al$_3$/Co magnetic tunnel junctions which exhibited a magnetoresistive response of up to 300%. The results of this study suggested that chemical bonds between the organic molecules and the magnetic electrodes govern the
tunnelling of spins across the interface. A simplified description of the spin-filtering mechanism at an organic/inorganic hybrid interface is shown in Fig. 1.4.

Figure 1.4 Schematic illustration of the spin-filtering mechanism at an organic/inorganic hybrid interface. (a) When the magnetic metal (left) and the molecule (right) are well separated, the overall DOS is simply the superposition of the individual DOS of the two spin components (where blue represents the spin-up DOS and red the spin-down DOS) — that is, a broad spin-polarized DOS for the metal and a series of discrete energy levels for the molecule (with only the HOMO represented here). In this case, the DOS of the metal alone determines the spin-polarization of the tunneling current. (b), (c), When the molecule is brought into contact with the metal, the DOS is modified into two ways: the energy levels broaden (b) and their position shifts in energy (c). In both cases, new peaks in the DOS might appear at the Fermi energy \( E_F \) of the electrodes, arising from new hybrid interfacial states. It is this new DOS that determines the spin-polarization of the injected current, which can be dramatically different, and even reversed, compared with the polarization of the electrodes (as in (b)) [92].
It is helpful to consider what happens to the density of states (DOS) of a magnetic metal and an organic molecule as they are brought into contact [92]. The spin-split electronic structure of the metallic lead is broad, whereas the counterpart for the molecule is discrete. Assuming that only the HOMO is near enough to the electrodes’ $E_F$ to contribute to the current, as the two materials are brought together, the DOS of the molecule becomes modified in one of two ways. The DOS of the molecule is either broadened or shifted.

In general, it is difficult to transfer spins between two materials with very different conductivities. Metal ions and nitroxy radicals are usually the spin carriers in molecular materials due to their stability [93]. The unpaired electrons in such compounds do not communicate much with each other because they are largely localized [94]. As a result, the manipulation of quantum information and spin-based magnetic properties by chemical modification is severely limited.

On the contrary, delocalized radicals, which are furthermore readily amenable to chemical modification, provide a promising future method to form building blocks for the construction of materials in which the electrons’ spins serve as information carriers. Many techniques, such as continuous-wave, pulsed electron spin resonance (ESR), or electron nuclear double resonance, can be employed to measure the spin distribution in open-shell systems. These techniques allow the identification of important magnetic properties of the system, such as the spin multiplicity, the $g$ factors, the hyperfine interactions, zero-field splitting parameters/tensors, and exchange interactions. One of the most fundamental delocalized neutral radicals is phenalenyl and its derivatives, which can be viewed as fragments of graphene, as shown in Fig. 1.5. Phenalenyl has fascinated researchers for a long time because of its simple and highly symmetric
structure, as well as its intriguing properties in solution and in the crystalline state [95]. Theoretical studies show that the spin density of an individual π-extended phenalenyl molecule mainly resides on the edges of the molecule, which are more exposed than the core, although the spin density is delocalized over the entire molecule [96-101]. Fig. 1.6 shows the spin density distributions of 1) tri-\(t\)-butyl-phenalenyl, 2) tri-\(t\)-butyl-1,3-diazaphenalenyl, 3) 1,9-dithiophenalenyl, and 4) and tri-\(t\)-butyl-6-oxophenalenoxyl. Those molecules are easy to dimerize and react with oxygen because of the kinetic instability caused by the presence of unpaired electron density at the edges. Nevertheless, the phenalenyl-based radicals are promising for designing novel molecular functionalities with their tunable spin structures [102-107].

Figure 1.5 Triangular motifs and π-extended phenalenyl radicals, shown with their spin
densities, can be interpreted as triangular fragments of graphene. These systems are termed open-shell graphene fragments [93].

Another intriguing molecular device is the $C_{60}$-based molecular junction. The reason is that $C_{60}$ is thought to be a good candidate to build highly conductive single-molecule junctions owing to the delocalization of its frontier orbitals. The $C_{60}$-based molecule can be a component of molecular electronics devices, e.g., electrical amplifiers, single-molecule transistors, and molecular switches [108-110]. Studies of the interactions and geometry of $C_{60}$ on electrode surfaces help us understand the fundamental electronic properties at the interface. N. Néel et al investigated various contact distances to a $C_{60}$ molecule on Cu (100) [111]. They used the tip of a low-temperature STM approaching a $C_{60}$ molecule to form a tip-molecule contact. The measured conductance $G$ in term of tip displacement $\Delta z$ is shown in Fig. 1.7.

Figure 1.6 Spin density distributions of 1) tri-$t$-butyl-phenalenyl, 2) tri-$t$-butyl-1,3-diazaphenalenyl, 3) 1,9-dithiophenalenyl, and 4) tri-$t$-butyl-6-oxophenalenoxyl [93].

There are three regimes when the tip approaches to $C_{60}$ molecule. When the tip
starts approaching the $C_{60}$ molecule, the conductance increases exponentially from $10^{-4} G_0$ to $\approx 0.025 G_0$. The contact distance is between 0-1.6 Å. This is the tunneling regime.

The next is the transition regime, where $-1.6 \text{ Å} < \Delta z < -2.0 \text{ Å}$. A drastic increase in the conductance is observed in this regime. The conductance increases slightly when the tip-molecule distance is further decreased. This study showed how contact distance influenced the conductance. G. Schull et al. measured the conductance of $C_{60}$-$C_{60}$. They found that the conductance of the $C_{60}$-$C_{60}$ contact was lower by 2 orders of magnitude [112].

The impact of the electrode material on the electron transport at the metal – $sp^2$ carbon interface was investigated [113]. The results revealed that the charge transfer between the metallic lead and the edge C atoms of the $C_{60}$ molecule modified the positions of the molecular resonances to some extent and thus affected the conductance of the atomic-scale contact. G. Schull presented a method for probing the current through a single $C_{60}$ molecule while changing, one by one, the number of atoms in the electrode that were in contact with the molecule [114]. The results showed that the contact geometry had a strong influence on the conductance.

Figure 1.7 Conductance ($G$) in units of $G_0$ vs. tip displacement $\Delta z$. Zero displacement corresponds to the tip position before freezing the feedback loop at $V = 300 \text{ mV}$ and $I =$
3 nA. Experimental data appears as a line due to the high data point density, calculated data are depicted as squares. Upper right inset: set-up for calculations. Lower left inset: single conductance curve revealing a discontinuity at $\Delta z = -3.3$ Å [111].

Different contact geometries and the distance of the Au-$C_{60}$-Au junction were also investigated theoretically [22, 23, 115-122]. Theoretical studies on $C_{60}$/metal interfaces are mostly based on density-functional theory within the local density approximation (LDA) or the generalized gradient approximation (GGA), and have been used successfully to describe several $C_{60}$/metal interfaces. The transmission functions of top geometry and hollow geometry, and their channel decompositions have been calculated [23]. It is obvious that the conductance of the molecular junction is influenced and modified by the contact geometry.

In addition, $C_{60}$ is considered a good candidate as an anchoring group owing to the $C_{60}$ molecule’s highly symmetric structure [23]. Its unique structure provides a large contact area, which may reduce the spread of conductance values [50]. Due to their outstanding physical and chemical properties, fullerene dimers have been attractive organic compounds in various fields, such as nonlinear optics, organic materials, biology, and medicine [123]. T. Ono and K. Hirose studied the electronic transport of the lithium-doped $C_{60}$ dimer. The conductivity of the doped $C_{60}$ dimer was significantly improved by inserting Li atoms into the cages [119]. Negative differential resistance (NDR) was observed in the $C_{60}$ dimer system, and the peak-to-valley ratio (PVR) as well as the transport properties could be tailored by doping too [124-127].

alto sum up, molecular electronics is a rapidly growing research field where we haven’t yet really made the most out of the molecules’ potential and specificity [4]. There is still a long way to go to transform molecular electronics from a nanoscience to a
nanotechnology, although the unique properties of molecular junctions, which have no analogues in bulk materials, have shown a promising future for semiconductor industry.

### 1.4 Role of computation in the research on molecular electronics

*Prediction is very difficult, especially about the future.* --Niels Bohr

Theoretical and computational study based on *ab initio* calculations plays a critical role in modern chemistry and has become a useful way to investigate materials that are too difficult to find or too expensive to purchase. Theoretical calculation is the application of physical, chemical, mathematical, and computing skills to the solution of interesting materials problems. It uses computers to generate information such as band structures or total energies of materials, or simulated experimental results. It also helps scientists make predictions before running the actual experiments so that they can be better prepared for making observations. In all cases the computer time and other resources (such as memory and disk space) increase rapidly with the size of the system being studied.

The term "*ab initio*" is Latin for "from the beginning". This indicates that the computations are derived directly from theoretical principles, with no inclusion of experimental data. Alternatively, calculations based on density functional theory (DFT), which makes approximations in the calculations, are more popular and efficient in modern chemistry computation.

Although there still are issues and problems waiting to be solved, computation has become a very powerful tool in chemistry.

Some properties obtainable from DFT calculations:

- Geometrical structures (rotational spectra)
• Rovibrational energy levels (infrared and Raman spectra)
• Electronic energy levels (ultraviolet and visible spectra)
• Ionization potentials (photoelectron and X-ray spectra)
• Dipole moments
• Polarizabilities
• Electron density maps and population analyses
• Magnetic shielding tensors and nuclear magnetic resonance (NMR) spectra

1.5 Outline of the thesis

The purpose of this thesis is to investigate the electronic transport properties of molecular electronic devices. The computational framework is based on non-equilibrium Green’s function (NEGF) formalism combined with DFT. The outline of this thesis is as follows:

Chapter 2: the theoretical framework used in the calculation is introduced. In addition, I describe the software used in this thesis.

Chapter 3: The transport properties of H₂O@C₆₀-based nanostructures sandwiched between electrodes are studied. The results show that, unlike the single endohedral fullerene molecule in electrostatic field, H₂O@C₆₀-based junction cannot act as a Faraday cage anymore when there is voltage bias. The screening effect disappears completely. The disappearance of the screening effect is water-position-independent. Significantly, the encapsulated water’s position and its dipole direction have an effect on the conductance of the molecular junction. For this highly symmetric dipolar molecule, with the same contact geometry, its transport properties can be tuned by controlling the encapsulated water molecule.
Chapter 4: The electrical transport properties of the endohedral complex H$_2$O@C$_{60}$ dimer are studied. Encapsulating an H$_2$O molecule in one of the C$_{60}$ cages increases the conductance of the dimer. Negative differential resistance is found in the dimer systems, and its peak-to-valley current ratio depends on the number of encapsulated H$_2$O molecules. The conductance of the C$_{60}$ dimer and the H$_2$O@C$_{60}$ dimer is two orders of magnitude smaller than that of the C$_{60}$ monomer. Furthermore, we demonstrate that the conductance of the molecular junctions based on the H$_2$O@C$_{60}$ dimer can be tuned by moving the encapsulated H$_2$O molecules. The conductance is H$_2$O-position dependent. Our findings indicate that the H$_2$O@C$_{60}$ can be used as a building block in C$_{60}$-based molecular electronic devices and sensors.

Chapter 5: the transport properties and thermopower of individual B$_{40}$ molecules are calculated. The results show that the conductance of single-molecule junctions based on a newly discovered molecule, borospherene (B$_{40}$), is comparable to that for the C$_{60}$-based junction with its more delocalized $\pi$ electrons. The charge injection efficiency in the B$_{40}$-based junction is improved, as up to 7 atoms in direct contact with the electrode are possible in the Au-B$_{40}$-Au junction. Interestingly, a higher number of atoms in direct contact with the electrode does not result in a higher number of conduction channels because of the unique chemical bonding in the B$_{40}$ molecule, without two-centre two-electron bonds. The transport properties of Au-B$_{40}$-Au junctions can be proved by doping. With a Ca, Sr, or Y atom encapsulated into the B$_{40}$ cage, the conductance at zero bias increases significantly. Moreover, our calculations show that the lowest unoccupied molecular orbital dominates the low-bias transport, as the thermopower in these junctions is negative. Our study indicates that B$_{40}$ is an attractive new platform for designing highly conductive single-molecule junctions for future molecular circuits.
Chapter 6: Calculations of spin-resolved transport for phenalenyl-based molecules have been performed. Spin-polarized transmission is found in the phenalenyl (C$_{13}$H$_9$) molecular junction. Remarkably, the peak positions for both spins are found to differ by more than 0.5 eV. The spin-polarized transmission is suppressed or enhanced by replacing two carbon atoms of phenalenyl with boron or nitrogen atoms. The transmission of the nitrogen-doped junction is spin-polarized when the bias is increased. This leads to a device that is able to generate spin-polarized current at the desired bias. By B-doping, the spin-polarized transmission is enhanced, as the orbitals in one spin channel resonate with the electrons on electrodes, indicating its potential application in making spin filter devices.

Chapter 7: Conclusions and outlook.

1.6 References


Chapter 2

Computational methods and tools

2.1 Density functional theory

2.1.1 Many-body system

Density functional theory (DFT) is one of popular quantum mechanical approaches that have been applied successfully in many fields, such as physics, chemistry and material science. It has become a standard tool for explaining and analysing experimental phenomena and predicting the atomic structure and electron structure of new materials.

The goal of this approach is to solve the time-independent, non-relativistic Schrödinger equation [1]:

\[
\left[ \sum_{\ell} \frac{p_{\ell}^2}{2m} - V(\mathbf{r}_i - \mathbf{R}_i) + \sum_{i<j} U(\mathbf{r}_i, \mathbf{r}_j) \right] \Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N),
\]  

(2.1)

where \( N \) is the number of electrons;

\[
V(\mathbf{r}_i - \mathbf{R}_i) = \sum_{i,l} \frac{Z_i q_l^2}{|r_i - R_l|}
\]  

(2.2)

is the interaction between nuclei and electrons, and \( Z_{\ell} \) the atomic numbers of the nuclei; \( \mathbf{r}_i \) and \( \mathbf{R}_i \) are the positions of the electrons and nuclei; \( m \) and \( q \) are the conventional fundamental constants; and \( U(\mathbf{r}_i, \mathbf{r}_j) \) is the electron-electron interaction. For a Coulomb system, the \( U(\mathbf{r}_i, \mathbf{r}_j) \) is given by

\[
U = \sum_{i<j} U(\mathbf{r}_i, \mathbf{r}_j) = \sum_{i<j} \frac{q^2}{|r_i - r_j|},
\]  

(2.3)

If there are enough single-electron functions used in the calculation, one can approximate any multi-electron wave function to arbitrarily high accuracy. This will cause the amount of calculation to be too big to solve in practice, however. Therefore,
using the absolute minimum can reduce the cost of calculation. In this case, the wave function is approximated as the antisymmetrized product of \( N \) orthonormal spin orbitals \( \psi_i(r_i) \), and the wave function is written as a single Slater determinant:

\[
\Psi(r_1, r_2, \ldots, r_N) \approx \Psi_{HF} = \frac{a}{\sqrt{N!}} \begin{vmatrix}
\psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_N(r_1) \\
\psi_1(r_2) & \psi_2(r_2) & \cdots & \psi_N(r_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(r_N) & \psi_2(r_N) & \cdots & \psi_N(r_N)
\end{vmatrix},
\tag{2.4}
\]

where \( a \) is a constant. With the normalization condition \( \int \psi_i^*(r)\psi_j(r) dr = \delta_{ij} \), the orthogonal wave function can be determined approximately by minimizing the energy for the determinantal form of \( \Psi \). This is the Hartree-Fock approximation [2].

In general, it is unrealistic to solve the many-body Schrödinger equation in such a way because the cost of calculation scales exponentially with the number of electrons in the system and is intractable for all but the smallest of systems. Apparently, another approximation is needed to deal with this problem.

### 2.1.2 Born-Oppenheimer approximation

The Born-Oppenheimer approximation simplifies the task of computing the energy and the wave function of an average-size model. This approximation was proposed in 1927 [3], and it states that the nuclei can be considered to be static at their equilibrium position and interact with the electrons via an external potential. Because the masses of the nuclei are much greater than the mass of the electrons, the motion of the electrons can be separated from that of the nuclei. The wave function for the molecule thus becomes:

\[
\Psi_{\text{total}} = \psi_{\text{electron}}\psi_{\text{nuclear}}. \tag{2.5}
\]

The electronic wavefunction depends upon the nuclear positions but not upon their velocities, and the nuclear motion (e.g., rotation, vibration) sees a smeared out potential from the speedy electrons.
2.1.3 The Hohenberg-Kohn theorems

The expectation value of the Hamiltonian operator with $\Psi_{HF}$ is given by

$$E = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle. \quad (2.6)$$

In 1964, Hohenberg and Kohn [4] first proposed that trial electron densities instead of trial wave functions could be used to solve this equation. Every trial function $\Psi$ corresponds to a trial density $\rho(r)$, which is obtained by integrating $\Psi^* \Psi$ over all variables except the first and multiplying by $N$. The electron density is given by

$$\rho(r) = N \int d^3 r_2 \int d^3 r_3 \cdots \int d^3 r_N \Psi^*(r, r_2, \cdots, r_N) \Psi(r, r_2, \cdots, r_N). \quad (2.7)$$

Theorem 1: the ground state density $\rho(r)$ of a bound system of interacting electrons in some external potential $\nu_{ext}(r)$ determines this potential uniquely. This is also applied for a degenerate ground state, where any ground state density $\rho(r)$ is referred. Then the energy minimum is defined as

$$E[\rho(r)] = \min \langle \Psi | \hat{H} | \Psi \rangle = \int \nu(r)\rho(r)dr + F[\rho(r)], \quad (2.8)$$

where

$$F[\rho(r)] \equiv \min \langle \Psi | T + U | \Psi \rangle. \quad (2.9)$$

$F[\rho(r)]$ is called the Hohenberg-Kohn (HK) function and requires no explicit knowledge of $\nu_{ext}(r)$. It is a universal functional of the density $\rho(r)$.

Proof:

Given two different external potentials, $\nu_{ext,1}(r)$ and $\nu_{ext,2}(r)$, they result in the same density $\rho(r)$. Therefore, the associated Hamiltonians $\hat{H}_1$ and $\hat{H}_2$, will have different groundstate wavefunctions, $\Psi_1$ and $\Psi_2$, that each yield $\rho_0(r)$. Employing the variational principle, together with Eq. (2.9) yields,

$$E_1^0 < \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle = \langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \rangle$$

$$= E_2^0 + \int \rho_0(r) \left[ \nu_{ext,1}(r) - \nu_{ext,2}(r) \right] dr, \quad (2.10)$$
where $E_1^0$ and $E_2^0$ are the ground-state energies of $\tilde{H}_1$ and $\tilde{H}_2$, respectively. Eq. (2.10) leads to

$$E_1^0 + E_2^0 < E_2^0 + E_1^0,$$

which is a contradiction. As a result, the external potential $\nu_{\text{ext}}(r)$ is uniquely determined by the ground-state density.

**Theorem 2:** For any positive integer $N$ and potential $\nu_{\text{ext}}(r)$, there exists a density functional $F[\rho(r)]$ such that $E[\rho(r)] = \int \nu_{\text{ext}}(r)\rho(r)dr + F[\rho(r)]$ obtains its minimal value at the ground-state density of $N$ electrons in the potential at $(r)$. The minimal value of $E_{0,N}[\rho(r)]$ is then the ground state energy of this system.

**Proof:**

Assume that there is a trial density $\rho(r)$, which defines its own Hamiltonian and thus its own wave function. We take this trial wave function to the Hamiltonian with true external potential $\nu_{\text{ext}}(r)$, and then we have

$$\langle \Psi | \mathcal{H} | \Psi \rangle = T[\rho(r)] + U[\rho(r)] + \int \rho_0(r)\nu_{\text{ext}}(r)dr$$

$$= E[\rho(r)] \geq E_0[\rho(r)] = \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle.$$

(2.12)

In practice, the two theorems do not provide a way of computing the ground-state density of a system. The explicit form of the functional $F[\rho(r)]$ is the major challenge of DFT.

### 2.1.4 Kohn-Sham equations

Kohn and Sham [5] proposed an approach to find the ground-state density by solving the $N$ one-electron Schrödinger equations

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}\right] \varphi_j(r) = \varepsilon_j \varphi_j(r),$$

(2.13)

where

$$v_{\text{eff}} = V(r) + V_H(r) + V_{xc}(r).$$

(2.14)
The first term $V(r)$ is, according to Born–Oppenheimer approximation, the static external potential generated by the position-fixed nuclei in the system. The second term $V_H(r) = \int \frac{\rho(r')}{|r-r'|} dr'$ is the so-called Hartree term that describes the electron-electron Coulomb repulsion. The last term $V_{xc}(r) = \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)}$ describes the exchange-correlation potential.

The usual way of solving the equations is to start with an initial guess for $\rho(r)$, calculate the corresponding $v_{\text{eff}}$, and then solve the differential Eq. (2.13) for the $\varphi_j$. From these one calculates a new density, using

$$\rho(r) = \sum^N f_i |\varphi_i(r)|^2,$$

and starts again. The process is repeated until it converges. One iteration of this is called the ‘self-consistency cycle’. Various algorithms have been implemented into computational software to accelerate the convergence. Once the calculation is convergent, the ground-state energy can be calculated by the converged solution $\rho(r)$ [6]

$$E = \sum_j \varepsilon_j + E_{xc}[\rho(r)] - \int V_{xc}(r)\rho(r) dV - \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|}.$$

It is clear from the Eq. (2.16) that the ground-state energy is not simply the sum of all $\varepsilon_j$. As shown in Eq. (2.15), the $\varepsilon_j$ are the eigenvalues of an auxiliary single body equation whose eigenfunctions (orbitals) yield the correct density. In fact, only this density has strict physical meaning in the Kohn-Sham (KS) equations. The KS eigenvalues, on the other hand, in general bear only a semi-quantitative resemblance to the true energy spectrum [7]. Therefore, attention must be paid when calculating the band structures in solid-state physics because most of the calculations actually compute the KS eigenvalues. In this process, the auxiliary single-body equation (KS) is calculated instead of the many-body Schrödinger equation. This simplification is proved
successfully to predict band structures for many materials.

Another key to solve Kohn-Sham equations is to find appropriate approximations for the functionals $E_{xc}$ and $V_{xc}$ that are sufficiently simple and sufficiently accurate at the same time.

2.1.5 The exchange-correlation functionals

If we know the exact forms of $E_{xc}$ and $V_{xc}$, then the Kohn-Sham equation can be solved exactly. Unfortunately, it is almost impossible because it is difficult to find the exact form of $V_{xc}$, although certain physical quantities can be derived accurately from the DFT calculations by taking approximations.

Local-density approximation (LDA):

Historically, the simplest, and at the same time, the most important approximation for $E_{xc}$ is the local-density approximation (LDA) [8-10]. The exchange-correlation energy for the local-density approximation is written as

$$E_{xc}^{LDA} = \int e_{xc}[\rho(r)]\rho(r)d\mathbf{r},$$  \hspace{1cm} (2.17)

where $e_{xc}[\rho(r)]$ is the exchange-correlation energy per particle of a uniform electron gas of density $\rho(r)$ [8]. The exchange-correlation energy is then decomposed into exchange and correlation terms linearly,

$$E_{xc}^{LDA} = E_x + E_c.$$  \hspace{1cm} (2.18)

The exchange part is elementary and given, in atomic units, by

$$E_x \equiv -\frac{0.458}{r_s},$$  \hspace{1cm} (2.19)

where $r_s$ is the radius of a sphere containing one electron and given by

$$\left(\frac{4\pi}{3}\right)r_s^3 = \rho^{-1}.$$  \hspace{1cm} (2.20)

Many efforts have been made to estimate the correlation part [9, 11, 12]. This approximation for $E_{xc}$ has proved amazingly successful when applied to a homogeneous
electron gas (HEG) model. Experience shows that the LDA could deliver fair accuracy for ionization energies of atoms, dissociation energies of molecules, and cohesive energies. The LDA approximation works well for solid systems and has become a common choice in solid state calculations for many years. The LDA has a notorious tendency to over-bind, however, and fails to predict the geometries of molecules.

Generalized gradient approximation (GGA):

LDA works excellently for a uniform electron gas, but any real system is spatially inhomogeneous. The first attempt to deal with this is the so-called gradient-expansion approximation (GEA). In a GEA approximation, gradient-corrections of the form \(|\nabla \rho(r)|, |\nabla^2 \rho(r)|\), etc., to the LDA are calculated. A famous example is the lowest-order gradient correction to the Thomas-Fermi approximation. In application to real systems, however, this expansion has generally been disappointing, and indeed, has often worsened the results of the LDA [6]. In the early 1980s, researchers realized that general functions of \(\rho(r)\) and \(\nabla \rho(r)\) need not proceed order by order. Such functionals, of the general form

\[
E_{xc}^{GGA} = \int f[\rho(r), |\nabla \rho(r)|] \rho(r) dr,
\]

have become known as generalized-gradient approximations (GGAs) [13-15]. Depending on the method of construction employed for obtaining \(f[\rho(r), |\nabla \rho(r)|]\), different forms of \(f[\rho(r), |\nabla \rho(r)|]\) lead to different result.

Current GGAs seem to give reliable results for all the main types of chemical bonds. The total energies [17], atomization energies [16-18], energy barriers, and structural energy differences [19-22] have been improved by comparing GGA with LDA [14]. In this thesis, the Perdew-Burke-Ernzerhof (PBE)-GGA (a functional proposed in 1996 by Perdew, Burke and Ernzerhof) is used in the calculations [14].
2.2 Two-probe system and Non-equilibrium Green’s function

2.2.1 Two-probe system

Kirchhoff’s circuit laws fail to predict the transport properties of systems whose size dimensions are comparable to the electronic phase coherence length because quantum interference effects play an important role. Small conductors whose dimensions are intermediate between the microscopic and the macroscopic are called mesoscopic. Transport models have been established to predict the charge transport and current in the mesoscopic and microscopic regimes [23, 24]. The method used in the field of electron transport is different from that used in DFT calculations, mainly in two aspects: a) the geometry of the system studied is either finite or periodic, and b) the electronic system must be in equilibrium. The system of interest has two electrodes in the z direction, which is the current direction, as shown in Fig. 2.1. The transport properties are calculated by taking into account the effects of two semi-infinite electrodes.

Figure 2.1 Typical configuration of two-probe transport system, which is a combination of three parts: the left electrode, the central region, and the right electrode. The
electrodes are periodic in the current direction, and they are semi-infinite. The bridged conductor is finite.

For a traditional conductor, where the conductor is stretched between two large contact leads, as shown in Fig. 2.1, its conductance is given by $G = \sigma W/L$, where the $W$ is the width of the conductor, $L$ is the length and $\sigma$ is conductivity, which is independent of the material’s dimensions. When the conductor is reduced to a size comparable to the mean free path, however, the conductance approaches a limiting value. The resistance should be zero in such a ballistic conductor, because the electrons in the conductor can travel freely from one lead to another without scattering. Actually, the resistance arises from the interface between the conductor and the contact leads. For the model depicted in Fig. 2.1, the contact leads are assumed to be ‘reflectionless’. With this assumption, electrons can enter contact leads from the conductor without suffering reflection. A theoretical study has shown that the probability of reflection is negligible so long as the energy of an electron is not too close to the bottom of the band [25]. As a result, in 'reflectionless' contacts, electrons originating in the left contact occupy the whole of the $+k$ states in the conductor, while electrons originating in the right contact only occupy $-k$ states. Therefore, the quasi-Fermi level $F^+$ ($F$) for the $+k$ ($-k$) states is always equal to the chemical potential $\mu_L$ ($\mu_R$) of the left (right) lead, even when a bias is applied. Then, the current of a conductor with length $L$ for a single $k$ state is expressed as

$$I^+ = \frac{e}{L} \sum_k \nu f^+(E) = \frac{e}{Lh} \sum_k \frac{dE}{dk} f^+(E),$$

(2.22)

where $\nu$ is the group velocity of the conducting electrons and $h$ is the Planck’s constant. Summing over $k$, the current becomes

$$I^+ = \frac{2e}{h} \int_{\epsilon}^{\infty} f^+(E) dE,$$

(2.23)

where $\epsilon$ is the cut-off energy of the transverse mode. In the energy range $\mu_L > E > \mu_R$, the current is written as
\[ I = \frac{2e^2}{h} M \frac{\mu_L - \mu_R}{e}, \quad (2.24) \]

where \( M \) is the number of the transverse mode. Then, the contact conductance is given by

\[ G_c = \frac{2e^2}{h} M. \quad (2.25) \]

So, the contact resistance is

\[ G_c^{-1} = \frac{(\mu_L - \mu_R)/e}{I} = \frac{h}{2e^2 M} \approx \frac{12.9}{M}. \quad (2.26) \]

For a single-mode conductor, the resistance is \( \sim 12.9 \, \text{k}\Omega \).

### 2.2.2 Landauer-Büttiker formalism

The maximum conductance for one conduction channel is \( G_0 = \frac{2e^2}{h} \). The conductance for the general system is

\[ G = \frac{2e^2}{h} T, \quad (2.27) \]

where the \( T \) represents the sum of the probabilities of all the paths that electrons take in transmission from one lead to the other [7]. Here, we assume that the current is carried by a single energy channel around the Fermi energy. For a non-zero bias system, the current can be written as

\[ I = \frac{2e}{h} T [\mu_L - \mu_R], \quad (2.28) \]

where \( T \) represents the product of the number of the transverse mode \( M \) and the transmission probability per mode \( T \) at the Fermi energy over the energy range \( \mu_L > \mu_R \) at zero temperature. If the transport is in the coherent regime, for a multi-energy-channel conductor at non-zero bias, the current can be calculated from the Landauer-Büttiker formalism

\[ I(V_{bias}) = \frac{2e}{h} \int_{-\infty}^{\infty} T(E, V_{bias}) [f_L(E - \mu_L) - f_R(E - \mu_R)] \, dE, \quad (2.29) \]

where \( f_{L/R} \) is the Fermi-Dirac distribution function for the left/right electrode and
\( T(E, V_{bias}) \) is the transmission function at a given bias voltage \( V_{bias} \).

### 2.2.3 Non-equilibrium Green’s function (NEGF)

The non-equilibrium Green’s function (NEGF) formalism is a powerful tool that provides a computational framework for treating quantum transport in nanodevices. It goes beyond the Landauer approach for ballistic, non-interacting electronics to include inelastic scattering and strong correlation effects at an atomistic level. Hence, we are able to calculate the behavior of electrodes with a realistic atomic structure and a more complicated electronic structure that is beyond that of the jellium electrodes.

The retarded Green’s function \( G^R \) is defined as

\[
[E I - H_c - \Sigma^R] G^R = I,
\]

then

\[
G^R = [E I - H_c - \Sigma^R]^{-1},
\]

where \( I \) is the identity matrix, \( H_c \) is the Hamiltonian for a finite-sized isolated conductor. \( \Sigma^R \) is the self-energy function and is non-zero only for the points on the conductor that are adjacent to a lead.

As shown in Fig. 2.1, there are three parts in the system, the right lead (L), the central portion (C), and the right lead (R). The density matrix of interest is

\[
\begin{pmatrix}
H_L + \Sigma_L & V_L & 0 \\
V_L^+ & H_C & V_R \\
0 & V_R^+ & H_R + \Sigma_R
\end{pmatrix},
\]

where \( H_L, H_C, \) and \( H_R \) are the Hamiltonian matrices of the left lead, the central portion, and the right lead, respectively, and \( V_L \) (\( V_R \)) is the interaction between the left (right) lead and the central portion. \( \Sigma_L \) and \( \Sigma_R \) are the self-energies due to coupling to the left and right leads. The L-C-R region has to be large enough to include all the screening inside of it. The density matrix can be calculated based on Green’s function,
the electron density is expressed by
\[ \rho(r) = \sum_{\mu, \nu} \phi_{\mu}(r) D_{\mu\nu} \phi_{\nu}(r), \]  
where \( \phi_{\mu(\nu)}(r) \) is localized atomic basis orbital. Eq. (2.34) allows us to calculate the DFT Hamiltonian elements \( H \).

After a convergence criterion is achieve in the calculation, the spin-resolved transmission function is given by
\[ T_{\sigma}(E, V) = \text{Tr}\{ \Gamma_{\sigma}^R(E) G_{\sigma}^R \Gamma_{\sigma}^L(E) G_{\sigma}^L \}, \]
where
\[ \Gamma_{\sigma}^{L(R)}(E) = i[\Sigma_{\sigma}^{L(R)}(E) - \Sigma_{\sigma}^{L(R)}(E)^+], \]
\( \Sigma_{\sigma}^{L(R)}(E) \) is the retarded self-energy of the semi-infinite electrode, and \( \sigma \) represents the majority or minority spin channel, respectively. If the calculation is not spin-polarized, then the total transmission is the sum for each spin channel. The current through the system is calculated from Eq. (2.29).

### 2.3 Computational software

#### 2.3.1 SIESTA and TRANSIESTA

Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) is a DFT implementation for performing electronic structure calculations [26]. Based on a flexible linear combination of atomic orbitals (LCAO) basis set, high accuracy can be achieved from the calculations performed by SIESTA. The Kohn-Sham self-consistent density functional method in the local density or the local spin density (LDA-LSDA), or generalized gradient (GGA) approximations has been implemented with norm-conserving pseudopotentials in their fully nonlocal (Kleinman-Bylander) form. SIESTA uses atomic orbitals as a basis set. The electron wave functions and density are projected
onto a real-grid. Siesta-3.2 is used for the studies of molecular junctions based on H$_2$O@C$_{60}$, H$_2$O@C$_{60}$ dimers, and B$_{40}$ molecules in this thesis.

Electronic transport properties are calculated using TRANSIESTA, which is part of the SIESTA package. TranSIESTA solves the electronic density from the DFT Hamiltonian using Green's function techniques to derive the electronic structure of an open system – two-probe system, where a finite structure is sandwiched between two semi-infinite electrodes.

### 2.3.2 Atomistix ToolKit (ATK)

ATK is a commercial software package developed by QuantumWise [27]. It is known as an effective way to study the transport properties of nano-electronic devices, employing DFT combined with NEGFs. The norm-conserving pseudopotentials are used in ATK too. ATK is now being updated in order to obtain more accurate and reliable outcomes in the calculations. A number of pre-built basis sets for each elements are provided, and both LDA and GGA are implemented in ATK, plus meta-generalized GGA (meta-GGA), offering a much more accurate description of the band gap of semiconductors. ATK is used for the study of transport properties of molecular junctions based on phenalenyl molecules in this thesis.

### 2.3 References

Chapter 3

Electronic transport in molecular junctions based-on H$_2$O@C$_{60}$.

3.1 Introduction

The emerging field of molecular electronics (ME) based on single molecules offers a platform for miniaturization of devices which are able to respond to various external excitations [1]. Thus, molecular electronic systems are ideal for the study of charge transport on the single molecule scale [2-8]. The drive to design functional molecular devices has pushed the study of metal-molecule-metal junctions beyond electronic transport characterization [9]. Single-molecule junctions have been investigated under a variety of physical stimuli, such as mechanical force, optical illumination, and thermal gradients. In addition, spin- and quantum interference play important roles in ME [10-14].

It should be pointed out that the change in conductance of single-molecule junctions in response to various external stimuli is at the focus of studies of single-molecule electronic devices with multiple functionalities. It is well known that, in addition to doping [15-17], a system’s electrical conductance or resistivity does not change unless there are variations in its shape, size, and composition due to some external influence. Here, we propose the concept that the conductance of molecular systems can be tuned from inside, which offers a new degree of freedom for changes of conductance without changes in their physical appearance.
The systems which show such an effect should be cavity-like and able to encapsulate objects with freedom of motion inside the cavity. This is absent in any classical material. In addition, the effect breaks down for metallic cavities due to the screening effect. Systems showing this internal influence effect could be possible, however, in some single-molecule systems. It has come to our attention that the recently synthesized molecular systems with H₂O encapsulated into C₆₀, H₂O@C₆₀, meets this criterion perfectly.

Encapsulating a single water molecule in the most common fullerene, C₆₀, has been successfully accomplished by Kurotobi and Murata [18]. They created an elegant way of opening up the outer surface of the C₆₀ cage to entrap the water molecule and then closing the cage. The synthesized molecule, H₂O@C₆₀, has fascinated many researchers. It provides a platform where the water molecule is isolated and prevented from forming any hydrogen bonding to another organic molecule or metal [19]. It is a remarkable molecule that combines an encapsulated polar molecule with a highly symmetric and nonpolar cage. For H₂O@C₆₀, the polarity is no longer associated with its external shape. A number of studies have been carried out to predict the dipole of the molecule [20 - 22]. Kurotobi and Murata suggest that the dipole moment of H₂O@C₆₀ is almost the same as that of a single water molecule, which is in disagreement with many other calculations [20, 23]. Recent simulations show that the dipole of H₂O@C₆₀ is smaller than that of a single water molecule. The significant reduction in dipole moment is due to the screening effect generated by the fullerene [20, 24]. Table 3.1 shows the calculated dipoles for both H₂O@C₆₀ and C₆₀. As can be seen from the table, the magnitudes of the dipoles are very controversial. A molecular dynamic simulation shows that the encapsulated polar H₂O molecule can be manipulated by an external electric field [25]. The electrons on the C₆₀ cage are redistributed when the water molecule is
encapsulated. The cage generates an electrostatic field inside the cage, compensating the electric field induced by the water molecule. As a result, the total dipole is reduced significantly. Since the calculated dipole moments of the molecule are still controversial, experimental data are required to clarify this question.

Table 3.1 Literature values for the dipole moment (in units of Debye).

<table>
<thead>
<tr>
<th>Ref.</th>
<th>25</th>
<th>30</th>
<th>29</th>
<th>31</th>
<th>28</th>
<th>27</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O@C₆₀</td>
<td>2.03</td>
<td>2.0</td>
<td>0.54</td>
<td>0.61</td>
<td>1.5</td>
<td>0.59</td>
</tr>
<tr>
<td>C₆₀</td>
<td>2.02</td>
<td>1.86</td>
<td>2.5</td>
<td>1.94</td>
<td>2.02</td>
<td>2.16</td>
</tr>
</tbody>
</table>

The fullerene can act as a small Faraday cage to screen out the most of the external field (75%) when a lithium atom is inside the C₆₀ [26]. Note that a Faraday cage is an enclosure formed by conducting materials so that it can exclude electrostatic and electromagnetic influences. This is because the delocalized π electrons in hexagonal rings on the C₆₀ make the fullerene an ideal molecule to isolate the encapsulated atom or molecule, protecting it from electrical noise and other external perturbations. If the screening effect no longer exists in H₂O@C₆₀ when it is sandwiched between metallic electrodes, then the encapsulated water molecule is able to feel and respond to an external perturbation by moving around inside the cage. In principle, we can control the water molecule inside by applying external stimuli outside the cage. When the water molecule moves inside the cage, there is a possibility that the carbon atoms in a certain area that the water molecule is approaching will change their molecular energy levels, and thus the conductance of the junction is changed by the external stimuli. In such a case, the H₂O@C₆₀ is the ideal candidate as a sensor for detecting the external stimuli.
In this chapter, the transport properties of the H$_2$O@C$_{60}$-based nanostructure sandwiched between electrodes are studied, as shown in Fig. 3.1. We demonstrate that, without changing the contact distance, the conductance of the H$_2$O@C$_{60}$-molecule junction is dependent on the position and the dipole direction of the encapsulated H$_2$O molecule. Our study indicates that the H$_2$O@C$_{60}$ is a unique cage molecule for potential applications in ME and sensors.

Figure 3.1 Schematic representation of a molecular junction containing H$_2$O@C$_{60}$, as is used in the transport calculations. Red atom: O, grey: C, golden: Au.

### 3.2 Computational details

The density functional theory (DFT)-based non-equilibrium Green’s function (NEGF) formalism has been employed to calculate the transport properties [27]. The model calculated is shown in Fig. 3.1. The single molecule is first optimized using SIESTA [28]. Then, the molecular junctions are constructed by placing the relaxed molecule between two Au tips in a 5×5 Au (111) unit cell. The H$_2$O@C$_{60}$ molecule is connected to the electrodes with 6:6 double bonds [29]. The initial Au-C distance is set to 2.45Å.
The new structure is optimized again until the forces on all the molecule atoms are smaller than 0.03 eV/Å. The GGA (PBE) approximation is used for exchange-correlation [30]. Au atomic orbitals are described using single-zeta polarized orbitals, and molecular atoms are described by double-zeta polarized orbitals. Real-space grid integrations were carried out using a 300 Ry energy cut-off. The k points of the electrodes are set to a Monkhorst-Pack grid of $1 \times 1 \times 50$. The electric current $I$ under bias voltage $V$ is calculated using the Landauer-Büttiker formula [31]. Local current is calculated under finite bias following the formalism in refs. [32, 33].

### 3.3 Screening effect in H$_2$O@C$_{60}$-based junction.

The significant reduction in dipole moment upon H$_2$O encapsulation can be described by the screening effect of the cage [34], which is controlled by the electrical and dipolar polarizations [35-37].

To see if the screening effect exists in the junction, we first determine the current density between the encapsulated water molecule and the carbon atoms on the cage. Surprisingly, our calculations show that there is current flowing through the encapsulated water molecule, indicating that the Faraday cage no longer exists when the H$_2$O@C$_{60}$ molecule is sandwiched between electrodes under voltage bias. The current flows mainly through the carbon bonds on the cage. There are still possibilities for electron scattering from the carbon atoms to water the molecule, however, although it is very weak, being 1 per cent of the magnitude of the current flowing between the carbon bonds. Fig. 3.2 shows the current density between the carbon atoms and the water molecule. The radius of the cylinder is proportional to the current density. Green currents represent the positive transport direction (along the z direction), and blue currents represent the negative direction (along the $-z$ direction). The currents are
calculated at 0.5 V. As can be seen, all the positive currents first flow onto the O atom, then flow out of water molecule from the two H atoms. The negative currents do the opposite. They first flow onto the two H atoms, then go through the O atom to the C atoms on the cage. Interestingly, the current paths are symmetrical with respect to the y-z plane.

Figure 3.2 Local currents between the carbon atoms and the water molecule, where the radius of the cylinder is proportional to the current density. Green currents represent the positive transport direction (along the +z direction), and blue currents represent the negative direction (along the −z direction). The currents are calculated at 0.5 V. It is obvious that the C<sub>60</sub> molecule cannot act as a Faraday cage because there are a number of current channels between the encapsulated water molecule and the C atoms.

To make the junction more conductive, we shorten the contact distance between the H<sub>2</sub>O@C<sub>60</sub> molecule and the electrodes to 3.2 a.u. (~1.69 Å) [29]. The contact
distance between the edge of the molecule and the surface of the electrode increases after relaxation, in agreement with ref. [29]. The junction is very conductive, and the conductance is as high as 3.3 G$_0$. In such a highly conductive junction, the current still flows through the encapsulated water molecule. Therefore, the C$_{60}$ molecule cannot be a Faraday cage in the bridged junction.

### 3.4 Electronic transport of H$_2$O@C$_{60}$ junction

We calculate the conductance and total energy for the H$_2$O@C$_{60}$ junction with the water molecule at different positions, as shown in Fig. 3.3. From the relaxed position, the water molecule is moved left 1.0 Å (L1.0), up 1.0 Å (U1.0), right 0.5 Å (R0.5), and right 1.0 Å (R1.0), while the dipole direction remains constant. Also, the conductance is calculated when the dipole direction is rotated 180 degrees around the x-axis after the encapsulated water molecule is moved 1.0 Å to the right (RR). We will refer to these possibilities as the L1.0-, U1.0-, R0.5-, R1.0-, and RR-junctions. During the calculation, the position of the H$_2$O molecule is constrained. The conductances, their change ratios, and the total energies are plotted in Fig. 3.3(b). When the encapsulated water molecule moves right 0.5 Å, the distance between it and the centre of the C$_{60}$ cage is shorter than that between its relaxed position and the centre of the C$_{60}$ cage. It can be seen from Fig. 3.3(a) and (b) that when the water molecule moves toward the centre of the C$_{60}$ cage, the conductance of the junction decreases.

Remarkably, our calculations demonstrate that the transport properties of the H$_2$O@C$_{60}$ molecular junction can be tuned by manipulating the encapsulated water molecule without changing the contact geometry. Also, the results show that the disappearance of the screening effect is independent of the position of the water molecule. As the water molecule moves further right to the position of R1.0, the
conductance increases to 0.575 $G_0$, almost the same as for the $\text{H}_2\text{O}@\text{C}_{60}$ junction when the water molecule is at its relaxed position. Surprisingly, the conductance of the R1.0-junction increases when the dipole direction flips.

Figure 3.3 (a) and (b) The conductance, its change ratio, and the total energy for $\text{H}_2\text{O}@\text{C}_{60}$ junctions with the encapsulated water molecule at different positions with the dipole direction remaining unchanged; (c) and (d) the conductance, its change ratio, and the total energy for $\text{H}_2\text{O}@\text{C}_{60}$ junctions with the dipole of the water molecule pointing in different directions. All conductance changes and total energies shown are relative to those of the $\text{H}_2\text{O}@\text{C}_{60}$ junction with the water molecule at the relaxed position. It is clear that, with the same contact geometry, the conductance is dependent not only on the
position of the encapsulated water molecule, but also on the dipole direction of the water molecule.

As can be seen from Fig. 3.3(b), the total energy of the RR-junction is much lower than that of the R1.0-junction, suggesting that the water molecule would change its dipole direction if it moved to the position of R1.0. The water molecule does not necessarily change its dipole direction by 180 degrees, as only two dipole directions are calculated.

It is apparent that not only can the position of the molecule affect the conductance, but also the dipole direction of the water molecule can influence the conductance and the local currents. We therefore calculate the conductances and total energies for H$_2$O@C$_{60}$ junctions with the dipoles of the encapsulated water molecule pointing in different directions, as shown in Fig. 3.3(c) and (d). During the calculation, the oxygen atom is fixed at its relaxed position. Z, –Z, X, –X, Y, and –Y indicate the dipole direction of the water molecule. We will refer to these possibilities as Z-, –Z-, X-, –X-, Y-, and –Y-junctions. The Z-junction is the H$_2$O@C$_{60}$ junction with the water molecule at its relaxed position. As can be seen from Fig. 3.3(c), the conductance is clearly dependent on the dipole direction. When the dipole direction of the water molecule is along the –Z direction, the conductance is reduced. When the dipole points along Y or –Y, the conductance of the junction is larger. The total energy of the Y-junction is much higher than that of the –Y-junction. The conductances of the X-junction and –X-junction are both lower than that of the Z-junction. It is well known that the electrons of the fullerene are reorganized with respect to the dipole direction in which the encapsulated H$_2$O molecule points. The carbon atoms on the fullerene cage near the oxygen atom of the water molecule are slightly positively charged, while those near the
hydrogen atoms become slightly negatively charged [14,18]. Thus, the conductance can be tuned by rotating the encapsulated water molecule.

There are many methods to tune the position and orientation of the H$_2$O molecule inside the cage such as light irradiation, electric fields, heating, etc. All these external stimuli can ‘communicate’ with the water molecule, causing it to adjust its location, which, in turn, changes the conductance of the H$_2$O@C$_{60}$ junction. Our study paves a way for the H$_2$O@C$_{60}$ molecule to act as a new platform for novel molecule-based electronics and sensors.

### 3.5 Conclusion

In conclusion, we have theoretically investigated the transport properties of the H$_2$O@C$_{60}$ junction. The screening effect disappears completely when the H$_2$O@C$_{60}$ molecule is sandwiched between electrodes. At high bias, the H$_2$O@C$_{60}$ junction is more conductive, whilst the C$_{60}$ junction is more conductive in the low bias range. H$_2$O@C$_{60}$ is a remarkable dipolar molecule with a highly symmetrical structure. We demonstrate that, without changing the contact distance, the transport properties of the H$_2$O@C$_{60}$ junction are dependent on the position and dipole direction of the encapsulated water molecule. If we find a way to control the water molecule’s position and its dipole direction, then the electronic transport can be tuned by external stimuli. Trapping a water molecule inside fullerene is a fascinating area. Our study paves a way to use its intrinsic properties for future molecular electronic devices.

### 3.6 References

Chapter 4

Transport properties of the
\( \text{H}_2\text{O}@\text{C}_{60}\text{-dimer-based junction} \)

4.1 Introduction

Since the first experiment on individual \( \text{C}_{60} \) molecules was conducted with a scanning tunnelling microscope, fullerene has attracted much attention because it is thought to be a good candidate for building highly conductive molecular junctions [1-6]. The fullerenes have a number of potential applications in molecular electronic devices, such as electrical amplifiers [7], single-molecule transistors [8], and molecular switches [9]. Also, the transport of \( \text{C}_{60} \)-based junctions becomes versatile after doping [10-13]. On the other hand, devices that require efficient long-distance electron transfer have aroused new interest in intermolecular charge transport [14,15]. Understanding and controlling charge transfer from a single molecule to another one is a prerequisite for building such devices. Based on the recently synthesized \( \text{H}_2\text{O}@\text{C}_{60} \) molecule [16], the goal of this present work is to theoretically study the transport properties of the \( \text{H}_2\text{O}-\text{doped-}\text{C}_{60}\)-dimer junction.

It is expected that molecular electronic devices will play an important role in the semiconductor industry in the future. Among the huge number of molecules, \( \text{C}_{60} \) is undoubtedly one of the most attractive candidates. Various contact geometries, such as the ideal surface, the hollow position, pyramid-shaped clusters with 3 atoms in the first layer, or adatoms, have been studied theoretically and experimentally [11, 17-35]. The
conductance of Au-C$_60$-Au junctions can be more than 1 G$_0$ [10, 31-33], which is very high compared with those of other organic molecules of similar length. The charge efficiency can be improved when a higher number of atoms on the electrode are in direct contact with the molecule [33-35]. Also, electrodes made of different metals have been employed in these studies, which show that the electronic structure at the interface is another essential factor that dominates the performance of nanodevices [17-19]. Those previous studies indicate that the interface between the single C$_{60}$ molecule and the surface of a metallic electrode plays a critical role in the transport properties of the system. The conductance of the junction is very sensitive to the interface [23]. With the same interface, the transport properties of a fullerene junction can be modified by encapsulation of an atom or molecule in the hollow cage [36,37]. For example, the conductance of the fullerene is increased dramatically by entrapping a lithium atom in the molecule [10]. Lithium atoms have also been enclosed in fullerene dimers, resulting in a much larger negative differential resistance (NDR) at much lower bias [11]. Therefore, searching for new endohedral fullerene molecules that are potentially useful in molecular electronics is still fascinating.

Recently, the H$_2$O molecule was first encapsulated in C$_{60}$ [16]. This ‘wet fullerene’ has become an intriguing topic of research [38-41]. It is a remarkable molecule that consists of a polar molecule encapsulated in a highly symmetric and nonpolar cage. For H$_2$O@C$_{60}$, the polarity is no longer associated with its external shape. This provides a way to manipulate the transport properties without changing the junction’s contact geometry. The transport properties of Li@C$_{60}$ dimer have been previously studied [10, 11]. How the encapsulated dipolar molecule influences the conductance of the two C$_{60}$ cages is still elusive.
Figure 4.1 Schematic illustration of the unit cell containing two H$_2$O@C$_{60}$ molecules that is used in the transport calculations. The transport direction is along the z axis.

In this chapter, our aim is to study the transport properties of the H$_2$O@C$_{60}$ dimer, as shown in Fig. 4.1. The transport properties of the C$_{60}$ dimer, the H$_2$O@C$_{60}$ dimer, and the C$_{60}$ dimer with one water molecule encapsulated in the left cage have been calculated. For simplicity, in the following discussion, the three molecular junctions will be referred as (C$_{60}$)$_2$, (H$_2$O@C$_{60}$)$_2$, and (H$_2$O@C$_{60}$)C$_{60}$ junctions, respectively. Our calculations show that the conductance of the (H$_2$O@C$_{60}$)$_2$ molecule is much smaller than the conductance of the H$_2$O@C$_{60}$ monomer by about two orders of magnitude. NDR is found in the three junctions. Furthermore, the conductance of the (H$_2$O@C$_{60}$)$_2$ junction can be tuned by moving the encapsulated H$_2$O molecule.

### 4.2 Computational details

The density functional theory (DFT)-based non-equilibrium Green’s function (NEGF) formalism has been employed to calculate the transport properties of the above junctions [42]. The systems studied can be divided into three regions: the central region, the left electrode, and the right electrode. The electronic structure for the central region was calculated using SIESTA [43]. Each of the free molecules was relaxed first. Then, the molecular junctions were constructed, using structures comprising a 6-layer slab of Au
(111) in a 5×5 representation and the relaxed free molecule. The \( \text{H}_2\text{O}@\text{C}_{60} \) molecule is connected to the electrodes with 6:6 double bonds, and the initial distance between the edge atoms of the inserted molecules and the Au (111) atomic plane in the electrode is set at 3.20 au [10]. The distance increases after the structural optimization of the molecules, in agreement with Ref. 5. The new structure is optimized again until the forces on all the atoms of the bridging molecule(s) are smaller than 0.03 eV/Å. The generalized gradient (GGA) Perdew-Burke-Ernzerhof (PBE) approximation was used for exchange-correlation [44]. A single-zeta plus polarization basis set for Au atoms and a double-zeta plus polarization basis set for molecules were employed. The mesh cut-off was chosen as 300 Ry. In our calculations, the \( \text{C}_{60} \) dimer is connected to two Au (111) surfaces. Results from both experiments [45] and calculations [46] show that the Au-\( \text{C}_{60} \) bond is covalent with ionic character. The effect of van der Waals interactions between the \( \text{H}_2\text{O}@\text{C}_{60} \) dimer and Au on binding is thus limited, and the bonding should be well described with standard DFT in the GGA. The subsequent transport calculations were performed using TRANSIESTA [42]. A 1×1×50 Monkhorst-Pack k-mesh was used. The zero-bias conductance \( G \) is calculated by [47]

\[
G = G_0 T(E),
\]

where \( T(E) \) is the transmission function, and \( G_0 = 2e^2/h \). The structure of the junction is constrained while calculating the current under finite bias. The individual transmission coefficients were calculated using Inelastica [48, 49].

### 4.3 Transport properties of junctions based on \( \text{C}_{60} \) dimer and its complex endohedrals

After relaxation, the oxygen atom in the \( (\text{H}_2\text{O}@\text{C}_{60})\text{C}_{60} \) junction is offset to the left from the centre of the left cage. The off-centre distance is 0.37 Å. After another water
molecule is entrapped in the right cage, the oxygen atom in the left cage moves to the left by another 0.095 Å, being 0.465 Å off the centre. The oxygen atom in the right cage is 0.3 Å away from the centre, moving towards the left cage.

Figure 4.2 Conductances of C₆₀, H₂O@C₆₀, (C₆₀)₂, (H₂O@C₆₀)₂, and (H₂O@C₆₀)C₆₀ junctions, respectively. The conductance is in units of G₀ and calculated at zero bias.

Fig. 4.2 shows the conductance of five junctions at zero bias: single C₆₀, H₂O@C₆₀, (C₆₀)₂, (H₂O@C₆₀)₂, and (H₂O@C₆₀)C₆₀ junctions, respectively. The conductances of the three dimer junctions are 0.0275 G₀, 0.033 G₀, and 0.03 G₀ for the (C₆₀)₂, (H₂O@C₆₀)C₆₀, and (H₂O@C₆₀)₂ junctions, respectively, similar to the reported conductance of dumbbell-shaped dimers,²⁷ where G₀ = 2e²/h. The (H₂O@C₆₀)C₆₀ junction has the largest conductance at low bias. Encapsulating another water molecule in the other empty cage reduces the conductance of the junction, but still, it is larger than that in the (C₆₀)₂ junction.

With the same contact geometry of the junctions in our calculations, the conductance of the single-H₂O@C₆₀ junction is 2.96 G₀. It is apparent that the
The conductance of the \((\text{H}_2\text{O} @ \text{C}_{60})_2\) junction is two orders of magnitude smaller than that of the \(\text{H}_2\text{O} @ \text{C}_{60}\) monomer junction, similar to the decrease in conductance of the \((\text{C}_{60})_2\) junction compared with that of the \(\text{C}_{60}\) monomer junction [32].

The current-voltage \((I-V)\) curves for \(\text{C}_{60}\)-based junctions are depicted in Fig. 4.3(a) and (b). From Fig. 4.3(a), the current of the \(\text{H}_2\text{O} @ \text{C}_{60}\)-monomer junction increases monotonically with the bias voltage, while the current for each of the three junctions based on the \(\text{C}_{60}\) dimer is significantly smaller. It is clearer to show the details of the \(I-V\) curves for the three dimer junctions independently, as in Fig. 4.3(b). For all three junctions, the currents approach their largest at 0.4 V. The current becomes larger after one water molecule is encapsulated in one of the \(\text{C}_{60}\)-dimer cages. At low bias, molecular junctions with water molecule(s) encapsulated are more conductive, although the curve for the \((\text{C}_{60})_2\) junction and the curve for the \((\text{H}_2\text{O} @ \text{C}_{60})_2\) junction have a crossover between 0.3 V and 0.4 V. In the high bias range, the current in the \((\text{H}_2\text{O} @ \text{C}_{60})_2\) junction becomes lower than that in the \((\text{C}_{60})_2\) junction. It is apparent that, for the three molecular junctions studied, the transport properties are dependent upon the number of encapsulated water molecules. NDR is found in the \(\text{C}_{60}\)-dimer junction. Clearly, encapsulating a water molecule inside the \(\text{C}_{60}\) cage changes the peak-to-valley current ratio (PVCR), while no NDR is found in the \(\text{H}_2\text{O} @ \text{C}_{60}\)-monomer junction in our calculations.

The PVCRs are 3.28, 3.5, and 3.6 for the \((\text{C}_{60})_2\), \((\text{H}_2\text{O} @ \text{C}_{60})\text{C}_{60}\), and \((\text{H}_2\text{O} @ \text{C}_{60})_2\) junctions, respectively. The more water molecules that are encapsulated, the larger the PVCR that the junction can achieve. The NDR can be explained by the transmission spectra, which are shown as a function of electron energy and bias voltage in Fig. 4.3(c-f).
Figure 4.3 (a) The calculated $I$-$V$ curves of the three dimer junctions and the H$_2$O@C$_{60}$ monomer junction. (b) The calculated $I$-$V$ curves of the three dimer junctions with an enlarged current scale. The transmission spectra of (c) the H$_2$O@C$_{60}$ monomer junction, (d) the (C$_{60}$)$_2$ junction, (e) the (H$_2$O@C$_{60}$)C$_{60}$ junction, and (f) the (H$_2$O@C$_{60}$)$_2$ junction as functions of the electron energy $E$ and the bias voltage. The downward-pointing triangle shown in (c), (d), (e) and (f) by two intersecting solid straight lines is the bias window which sets the boundaries for transmission that contributes to the current at a given bias voltage.
The two solid straight lines intersecting at the origin in the spectra indicate the bias window, which sets boundaries for the transmission that contributes to the current at a given bias voltage. As can be seen, the height of peaks in the transmission in Fig. 4.3(c) is nearly one order of magnitude higher than those in Fig. 4.3(d), (e), or (f). Also, the non-zero area for the H$_2$O@C$_{60}$-monomer junction in the bias window grows constantly with the increasing bias voltage. As a result, the $I$-$V$ curve increases almost linearly, and the current is larger than those in the dimer junctions. In the (H$_2$O@C$_{60}$)$_2$ junction, the non-zero area in transmission increases before the bias approaches around 0.4 V, whereas it becomes smaller after the bias is larger than 0.4 V, resulting in decreased current in the junction. The transmission spectra for the (H$_2$O@C$_{60}$)C$_{60}$ junction and the (C$_{60}$)$_2$ junction are similar. The zero area (blue area), however, in the transmission spectrum of the (H$_2$O@C$_{60}$)$_2$ junction is larger within the bias range from 0.5 V to 1.5 V, leading to smaller current in that bias range.

4.4 Tuning the conductance by moving the encapsulated H$_2$O molecule

H$_2$O@C$_{60}$ is remarkable because it is a dipolar molecule [41]. Unlike other atoms/molecules that are able to move freely inside the C$_{60}$ cage [50], the encapsulated water molecule can respond to an external stimulus, such as an electrostatic field [40]. Therefore, if a way can be found to “communicate” with the H$_2$O molecule after it is encapsulated, then the conductances of the junctions are still tunable without changing their contact geometries.

From our calculations, the transport properties of the molecular junction based on the H$_2$O@C$_{60}$ dimer can be tuned by moving the encapsulated water molecule. Fig. 4.4(a) shows the conductance of the (H$_2$O@C$_{60}$)$_2$ junction as a function of distance, $r$, of
H$_2$O from its relaxed position. The encapsulated water molecules are moved left ("-") and right ("+") stepwise (in steps of ~ 0.2 Å), whereas all the other geometric parameters are kept constrained. Clearly, the conductance becomes largest when the H$_2$O molecules move 1.2 Å to the left from their relaxed position. It reaches a minimum at 0.4 Å, which is near the centre of the C$_{60}$ cage, because the relaxed position of each water molecule is off-centre by 0.37 Å to the left. The conductance and the corresponding force on the encapsulated H$_2$O molecule increase as the distance between the H$_2$O molecule and the cage centre increases, and they decrease as the distance decreases. Fig. 4.4(b) shows the conductance of the (H$_2$O@C$_{60}$)$_2$ junction with opposite dipole orientation as a function of the distance of the encapsulated water molecule from its relaxed position. The black squares (red dots) represent the dipole orientation pointing along the +Z (-Z) direction. In the calculations, the encapsulated H$_2$O molecules were flipped and their dipole orientation pointed along the opposite direction (from the +Z direction to –Z direction). The conductance as a function of the distance of the encapsulated water molecule from its relaxed position is shown in Fig. 4.4(b). As can be seen, the dipole orientation has a significant influence on the conductance of the junction. The conductance increases when the H$_2$O molecules move towards the C$_{60}$ cage wall.

The transmission spectrum of the (H$_2$O@C$_{60}$)$_2$ junction as a function of electron energy $E$ and distance $r$ is plotted in Fig. 4.5. As can be seen from Fig. 4.5(a), the height of the peaks for transmission is different when the H$_2$O molecule moves inside the C$_{60}$ cage. From Fig. 4.5(b), the peaks become broader and the pseudo-gaps between two peaks become narrower when the H$_2$O molecules move towards the C$_{60}$ cage wall. The broadening for $r = -1.2$ Å may simply be explained by a stronger coupling between the H$_2$O@C$_{60}$ dimer and the Au electrodes.
Figure 4.4 (a) The conductance and the corresponding force on the left/right H\textsubscript{2}O molecule of the (H\textsubscript{2}O@C\textsubscript{60})\textsubscript{2} junction as a function of the distance of the encapsulated water molecule from its relaxed position; (b) the conductance of the (H\textsubscript{2}O@C\textsubscript{60})\textsubscript{2} junction with opposite dipole orientation as a function of the distance of the encapsulated water molecule from its relaxed position. Black squares (red dots) represent the dipole orientation pointing along the +Z (−Z) direction, (c) and (d) show the (H\textsubscript{2}O@C\textsubscript{60})\textsubscript{2} molecule with the H\textsubscript{2}O molecules pointing in different directions: +Z and −Z.

When the encapsulated H\textsubscript{2}O molecules move inside the cages, the dipolar molecules have an influence on the distribution of electrons on the C\textsubscript{60} cages, and hence affect the coupling at the contact interface. We first turn to Mulliken analysis to see the change in the distribution of the electrons on the C\textsubscript{60} cage wall after the H\textsubscript{2}O molecules are encapsulated. Fig. 4.6(a) shows the difference in the Mulliken population (M)
between the \((\text{H}_2\text{O}@\text{C}_{60})_2\) junction and the \((\text{C}_{60})_2\) junction. Red (blue) indicates that the Mulliken charges decrease (increase) on the C atoms after the H\(_2\)O molecules are encapsulated. The red spots occupy most of the C atoms on the left-hand sides of the two C\(_{60}\) cages, while blue spots dominate the right-hand sides of the C\(_{60}\) cages. The H\(_2\)O molecule is dipolar and its dipole moment almost points towards the Z direction for its relaxed position.

![Graph](image)

**Figure 4.5** Transmission spectrum of \((\text{H}_2\text{O}@\text{C}_{60})_2\) junction as a function of electron energy \(E\) above the Fermi energy \(E_F\) and distance \(r\).

The electrons on the left-hand side of C\(_{60}\) cage feel a repulsive force from the electronegative part (O atom) of the H\(_2\)O molecule and tend to move to the other side of the C\(_{60}\) cage. Therefore, the left-hand sides of the C\(_{60}\) cages become more electropositive, and the right-hand sides of the C\(_{60}\) cages become more electronegative, compared with the C\(_{60}\) dimer without any H\(_2\)O molecules encapsulated. It is this redistribution of electrons on the C\(_{60}\) cages that changes the electrostatic potential of the \((\text{H}_2\text{O}@\text{C}_{60})_2\) junction, resulting in the changes in conductance.
Figure 4.6 Mulliken population on each C atom of (a) \((C_{60})_2\), (b) \((H_2O@C_{60})C_{60}\), (c) \((H_2O@C_{60})_2\). Red (blue) indicates the Mulliken charges gained (lost) after the dimer is sandwiched between the electrodes. Electrodes and encapsulated \(H_2O\) molecule(s) are not plotted. (d) and (e) show the difference in the Mulliken charges between \((H_2O@C_{60})C_{60}\) and \((C_{60})_2\), and \((H_2O@C_{60})_2\) and \((C_{60})_2\), respectively. Violet-red (slate blue) indicates that the number of electrons on the C atom increases (decreases) after the \(H_2O\) molecule(s) are encapsulated.

When the encapsulated \(H_2O\) molecules move inside their cages, the dipolar molecules have an influence on the distribution of electrons on the \(C_{60}\) cages, and hence affect the coupling at the contact interface. We first turn to the Mulliken analysis to see the distribution of electrons on the \(C_{60}\) cage wall and its changes after the \(H_2O\) molecules
are encapsulated. Fig. 4.6(a), (b), and (c) show the Mulliken population on each C atom of (C$_{60}$)$_2$, (H$_2$O@C$_{60}$)C$_{60}$, and (H$_2$O@C$_{60}$)$_2$, respectively. Red (blue) indicates the Mulliken charges gained (lost) after the dimer is sandwiched between the electrodes. As can be seen, it is easy to gain or lose more electrons for the C atoms on the two sides of the C$_{60}$ molecules which are used to connect with the other molecule or electrodes: the C atoms gain electrons when they are connected with the electrodes, and lose electrons when they are connected to the other C$_{60}$ molecule. Comparing the three figures, the electron distribution is clearly changed by encapsulating H$_2$O molecule(s). It is straightforward to see the changes in Fig. 4.6(d) and (e), where the differences in the Mulliken population between (H$_2$O@C$_{60}$)C$_{60}$ and (C$_{60}$)$_2$, and (H$_2$O@C$_{60}$)$_2$ and (C$_{60}$)$_2$ are plotted, respectively. The difference in the Mulliken population on each C atom is calculated by

$$Mulliken[A] - Mulliken[(C_{60})_2]$$

where A represents the (H$_2$O@C$_{60}$)C$_{60}$ or (H$_2$O@C$_{60}$)$_2$ molecule in the junction. Violet-red (slate blue) indicates that the electrons on the C atom have increased (decreased) after the H$_2$O molecule is encapsulated. From Fig. 4.6(d), electrons on the left (right)-hand side of the left C$_{60}$ molecule increase (decrease), while the electron distribution on the right C$_{60}$ molecule remains almost the same. This is the direct result of encapsulating an H$_2$O molecule inside the C$_{60}$ cage. The electrons on the left-hand side of the C$_{60}$ cage feel a repulsive force from electronegative part (O atom) of the H$_2$O molecule and tend to move to the other side of the C$_{60}$ cage. Therefore, the left-hand sides of the C$_{60}$ cages become more electropositive, and the right-hand sides of the C$_{60}$ cages become more electronegative. In Fig. 4.6(e), the violet-red spots occupy most of the C atoms on the left-hand sides of the two C$_{60}$ cages, while the slate-blue spots dominate the right-hand sides of the two C$_{60}$ cages. It is this redistribution of electrons on the C$_{60}$ cages that
affects the coupling between the electrodes and the dimer molecule, resulting in the changes in conductance.

Figure 4.7 Visualization of the eigenchannel wave functions (incoming from the left electrode) at the Fermi energy for the \((\text{H}_2\text{O}@\text{C}_{60})_2\) junctions with the H\(_2\)O molecules (a) being in their relaxed position and (b) after moving 1.2 Å to the left at zero bias. The isosurfaces of the eigenchannel wave function are coloured according to the phase and sign, with the positive/negative real part being coloured in red/blue, respectively. The junctions are plotted with the same isovalues to make them comparable.

Fig. 4.7 illustrates the eigenchannel wave functions at the Fermi level of the \((\text{H}_2\text{O}@\text{C}_{60})_2\) junctions with the H\(_2\)O molecules (a) in their relaxed positions and (b) after moving 1.2 Å to the left at zero bias. To make them comparable, the isovalues of the wave functions are set to be the same. As can be seen, most of the orbital densities are
delocalized on the left cage. For the right cage, the orbital density becomes more delocalized when the water molecules move left, resulting in higher conductance.

4.5 Conclusion

In conclusion, without changing the interface between the molecule and the metallic electrode, the transport properties of a $C_{60}$ single molecule or dimer junction can be modified by encapsulating one or two water molecules inside the $C_{60}$ cages. From our calculations, for two molecules in series, the conductance of the $C_{60}$ dimer or its endohedral complex $H_2O@C_{60}$ dimer is two orders of magnitude smaller than that of the $C_{60}$ monomer. NDR is found in the dimer systems, and its PVCR is influenced by the encapsulated water molecule(s). Furthermore, we theoretically demonstrate that the conductance of the molecular junctions based on the $H_2O@C_{60}$ dimer can be tuned by moving the encapsulated $H_2O$ molecules. Our findings indicate that $H_2O@C_{60}$ can be used as a building block in $C_{60}$-based molecular electronic devices and sensors.

4.6 References

Chapter 5

Transport properties of $B_{40}$-based single-molecule junction

5.1 Introduction

Allotropy, where the atoms of an element are bonded together in different manners, can lead to distinctive electronic properties from the different atomic structures. The most famous example is Carbon, which has many allotropes, from 3-dimensional diamond and graphite to 0-dimensional buckminsterfullerene [1]. While diamond is an electrical insulator, buckminsterfullerene is conductive and can become a superconductor after doping [2-7]. Although buckminsterfullerene was discovered in 1985, its properties are still being intensively studied because of its promising applications in molecular electronics [8-24]. Meanwhile, searching for fullerenes made of materials other than Carbon has been an intriguing topic for researchers [25]. The natural place to look is at the adjacent element to Carbon in the periodic table, Boron. There have been various theoretical works predicting the existence of all-boron fullerene [26-38]. Recently, the first all-boron fullerene-like cage cluster molecule, $B_{40}$, was observed experimentally [39]. It is well known that pure Boron is an electrical insulator at room temperature, so the question of whether this newly discovered all-boron fullerene molecule exhibits exotic electronic properties on the mesoscopic scale and has potential applications in the field of molecular electronics remains elusive. Furthermore, can the electronic properties of $B_{40}$ be tuned? The goal of this work is to study these two questions from a theoretical point of view.
A number of C-based materials, such as carbon nanotubes, graphene sheets, and carbon nanoribbons, are promising components for future nanoelectronics [40] due to their unique transport properties. While the injection and the collection of charges between these graphitic structures and external metallic leads are controllable [41-43], it is more challenging to form a stable contact in single-molecule junctions. For C\textsubscript{60}-based junctions, various contact geometries have been proposed and studied both theoretically and experimentally [10-22]. Understanding the transport characteristics of C\textsubscript{60} fullerene bonded between metal electrodes is of fundamental importance, because it is thought to be a good candidate to build highly conductive single-molecule junctions. Based on scanning tunnelling microscopy (STM), different contact geometries and electrode materials have been constructed and used to measure the conductance of C\textsubscript{60} fullerene [9-13,15,44]. Together with the theoretical calculations, the reported values for the conductance vary between \(~10^{-4}\) \(G_0\) and \(1 \ G_0\) [16-19,22,45,46]. These values are scattered over more than 3 orders of magnitude. Searching for highly conductive single-molecule junctions with stable contacts remains a challenge.

Recently, the first all-boron fullerene-like cage cluster molecule, B\textsubscript{40}, with an extremely low electron binding energy has been observed experimentally [39]. Interest in the novel properties of the B\textsubscript{40} molecule and its endohedral metallaborospherenes [47,48] has been growing. This has encouraged the further exploration of B\textsubscript{40}’s potential application in molecular electronics. There is an urgent need for investigations to demonstrate if the junctions based on B\textsubscript{40} have advantages over C\textsubscript{60}-based junctions and, in turn, make B\textsubscript{40} a good candidate for future molecule-based electronics.

The contact geometry of the B\textsubscript{40}-based junction is expected to be more stable than that of the C\textsubscript{60}-based junction, owing to the atomic structure of the B\textsubscript{40} molecule. It is easy to form a contact between one of the hexagonal or heptagonal faces of the
molecule and the electrode. Six or seven boron atoms would form a direct contact with the metallic electrode, leading to a higher injection rate of charges.

Furthermore, unlike the C$_{60}$ molecule, there is no localized two-center two-electron bond (2c-2e) on the B$_{40}$ molecule. It is well known that the degree of delocalization of the π electrons plays an important role in the electrical conduction in the C$_{60}$-based molecular junction. All of the π electrons on the B$_{40}$ molecule are 5c-2e, 6c-2e, or 7c-2e bonds [39]. With more delocalized electrons, B$_{40}$ as a highly conductive molecule is an ideal candidate. So far, the transport properties of the B$_{40}$ molecular junction have not been studied.

In this chapter, our aim is to study the transport properties of single-molecule junctions based on the B$_{40}$ molecule and its endohedral borospherenes. Gold electrodes have been used in our calculations. The results show that the conductance of the Au-B$_{40}$-Au junction is comparable to that of the Au-C$_{60}$-Au junction. Two contact geometries have been simulated: one is formed by using the hexagonal faces to couple with the electrodes; and the other is formed by using the heptagonal faces to couple with the electrodes. In the contact regime, the B$_{40}$ molecular junction is more conductive when the heptagonal face is used to couple the electrodes, because of the greater number of B atoms in direct contact with the electrodes. Furthermore, we have studied the thermopower of the B$_{40}$ molecule. It is found that the low-bias transport is mainly dominated by the lowest unoccupied molecular orbital (LUMO) of the molecule. Also, the doping effect is significant in tuning the transport properties. Our results reveal that B$_{40}$ provides a new platform for designing highly conductive single-molecule junctions for future molecular circuits.
5.2 Computational details

The density functional theory (DFT)-based non-equilibrium Green’s function (NEGF) formalism has been employed to calculate the transport properties [49].

The systems studied can be divided into three regions: the central region, the left electrode, and the right electrode, as shown in Fig. 5.1 (a) and (b). The electronic structure for the central region was calculated using SIESTA [50]. The single B40 molecule was relaxed first. Then, the molecular junctions were constructed by structures comprising an 8-layer slab of Au (111) in a 4×4 representation and the relaxed B40 molecule. A 1×1×100 Monkhorst-Pack k-point mesh was used. The B40 molecule, which was sandwiched in the junction with 4 Au layers on each side was optimized again until the forces on all the B40 atoms were smaller than 0.03 eV/Å. The subsequent transmission calculations were carried out using TranSIESTA [49]. The zero-bias conductance $G$ can be expressed as [51]

$$G = G_0 T(E),$$

(1)

where $T(E)$ is the transmission function, $G_0 = 2e^2/h$.

The generalized gradient (GGA) Perdew-Burke-Ernzerhof (PBE) approximation was used for exchange-correlation [52]. A single-zeta plus polarization basis set for Au atoms and double-zeta plus polarization basis set for B$_{40}$ atoms were employed. The mesh cut-off was chosen as 300 Ry. The individual transmission coefficients were calculated using Inelastica [53, 54].

To simulate the stretching of the contacts, we started with a geometry in which the molecule is positioned between two gold electrodes with flat surfaces. Due to the atomic structure of the B40 molecule, two contact geometries can be formed: with two hexagonal or two heptagonal faces being coupled with the electrodes. In the following,
we refer to the two types of junctions as hex/hep-junctions, in which the hexagonal/heptagonal face is used to couple with the electrodes, respectively. The original distance between the surface of a gold electrode and the nearest edge atoms (atoms in the hep/hex face) of the inserted B40 molecule was set to 1.7 Å. The hex-junction and the hep-junction studied in our calculations are shown in Fig. 5.1 (a) and (b). Then, the gold electrodes were separated stepwise from the molecule (in steps of ~0.5 Å), and the junction geometry was relaxed at every step. This protocol was repeated until the junction was broken and the molecule lost contact with the electrodes. During the stretching of the contact, the B$_{40}$ molecule moves up and down to form a stable geometry.

In this work, the binding energy, $E_b$, is calculated by using Eq. (2),

$$E_b = E_T(B_{40} + Au) - [E_T(B_{40}) + E_T(Au)],$$

(2)

where $E_T$ is the total electronic energy, (B40+Au) represents the B40-based junction, (B40) represents a single B40 molecule, and (Au) in Equation (5) represents the junction without the B$_{40}$ molecule inserted. A negative binding energy thus corresponds to a stable system.

Another transport property of interest in this work is the thermopower ($S$; also known as the Seebeck coefficient). At zero applied bias voltage, $S$ can be calculated by

$$S = -\frac{\pi^2 k_B T}{3e} \frac{T'(E_F)}{T(E_F)},$$

(3)

where $T(E_F)$ is the transmission function at the Fermi level ($E_F$), and the prime denotes the derivative with respect to energy, $k_B$ is the Boltzmann constant, $T$ is the temperature ($T = 300$ K in our calculations), and $e$ is the charge of the electron. The sign of $S$ can be used to deduce the nature of the charge carriers in molecular junctions: a positive $S$ results from hole transport through the highest occupied molecular orbital (HOMO),
whereas a negative $S$ indicates electron transport through the lowest unoccupied molecular orbital (LUMO) [51].

### 5.3 Transport properties of single-molecule junctions based on $B_{40}$

To achieve as many conductive channels as possible, two electrodes with ideal surfaces were considered in our calculations. The transmission for the two types of the junctions with various B-Au distances is depicted in Fig. 5.1 (c) and (d). For the two types of junctions, the zero-bias conductance, which is determined by the transmission at the $E_F$, increases exponentially while the B-Au distance decreases. When the B-Au distance is larger than 3.2 Å, the transmission shows peaks related to the molecular energy levels of the $B_{40}$’s orbitals. The closer the B-Au distance is, the smaller the HOMO-LUMO gap will be, as the coupling between the molecule and the electrodes becomes stronger. When the B-Au distance is smaller than 2.7 Å, however, the coupling between the electrodes and the molecule is so strong that the HOMO and LUMO peaks are broadened significantly, resulting in transmission without pronounced peaks around the $E_F$.

The zero-bias conductance of the $B_{40}$-juntion with B-Au distance of 2.2 Å is 4.86 $G_0$ and 3.31 $G_0$ for the hep-junction and hex-junction, respectively; with B-Au distance of 2.7 Å, the zero-bias conductance is 3.9 $G_0$ and 2.92 $G_0$ for the hep-junction and hex-junction, respectively. Conductances above 1 $G_0$ have been reported in theoretical studies of $C_{60}$ junctions with Al [18, 55], Au [19,22], and Cu [21] electrodes, when the leads are similar to ideal surfaces, i.e., with high Au-$C_{60}$ coordination. For $C_{60}$ junctions with different contact geometries where the electrodes are made of Au, the relaxed C-Au distances fall between 2.15-2.45 Å [20,22,56]. It is clear that the conductance of a $B_{40}$-
based junction is comparable to that of a C\textsubscript{60}-based junction with similar molecule-electrode distances.

Figure 5.1 Au-B\textsubscript{40}-Au junctions with different surface coupling to the electrodes viewed from different angles: (a) hex-junction (hexagonal faces pointed at electrodes) and (b) hep-junction (heptagonal faces pointed at electrodes). Transmission as a function of energy at zero bias for the two geometries: (c) hex-junction, and (d) hep-junction, with different B-Au distances from 2.2 Å to 4.2 Å.
The conductance is mainly dependent on two factors, the charge injection rate and the ability to scatter electrons [13]. The first factor is generally dependent upon the contact geometry. Since electrodes with ideal surfaces are used in our calculations, the charge injection rate is maximized: for hep (hex)-junctions, 7 (6) B atoms would have direct contact with the metallic electrode. The bottleneck is therefore the intrinsic ability to scatter electrons.

The conductance of a molecular junction is dependent on the molecular length [57-59], and it usually decreases exponentially as the molecular length increases. The tunneling decay constant of a series of alkane diamines, for example, is 0.91 ±0.03 per methylene group [59]. The nucleus-to-nucleus diameter of C\textsubscript{60} is ~7 Å. The B\textsubscript{40} molecule has 20 fewer atoms than the C\textsubscript{60} molecule, and thus, it has a smaller diameter. The distance between the two furthest atoms on opposite heptagonal faces of a single B\textsubscript{40} molecule, according to the results of our calculation, is ~5.57 Å; the distance between the two furthest atoms on the opposite hexagonal faces is ~5.2 Å. With a larger charge injection rate and smaller diameter, however, the conductance of a B\textsubscript{40}-based junction is not remarkably higher than that of a C\textsubscript{60}-based junction.

To explain this, the transmission curves of Au-B\textsubscript{40}-Au junctions for the two geometries at the B-Au distance of 3.2 Å and their channel decompositions are shown in Fig. 5.2. (Transmission curves of Au-B\textsubscript{40}-Au junctions with individual conduction channels at different B-Au distances are shown in Supplementary Fig. 5.3-5.20) As can be seen from Fig. 5.2, the number of conduction channels which contribute significantly to the conductance is smaller than the number of B atoms in direct contact with the electrode. For a single-molecule junction based on a π-conjugated molecule or C\textsubscript{60} fullerene, the number of conduction channels is generally given by the number of C atoms bonded to the surface of the electrode, because each C atom provides one π-
channel. In the B₄₀ junction, even when the B-Au distance is as close as 1.7 Å, the contributions to the total transmission from the fifth and sixth conduction channels are negligible (Fig. 5.3-5.20). This is due to the unique chemical bonding in the all-boron fullerene: on average, each boron atom contributes 0.6 electrons to the π bonding [39], which is responsible for the conductance in the B₄₀-molecule junction.

Figure 5.2 Transmission as a function of energy for a B-Au distance of 3.2 Å for the two geometries: (a) hex-junction and (b) hep-junction. The solid black line corresponds to the total transmission, while the other lines correspond to the contributions of the individual transmission coefficients as functions of energy.

Still, with a similar molecule-electrode contact distance, the B₄₀-based junction is more conductive compared with the C₆₀-based junction. The conductance can be further improved by doping.
Figure 5.3 The total transmission and individual transmission coefficients of hep-junction with B-Au distance 1.7 Å.

Figure 5.4 The total transmission and individual transmission coefficients of hep-junction with B-Au distance 2.2 Å.
Figure 5.5 The total transmission and individual transmission coefficients of hep-junction with B-Au distance 2.7 Å.

Figure 5.6 The total transmission and individual transmission coefficients of hep-junction with B-Au distance 3.7 Å.
Figure 5.7 The total transmission and individual transmission coefficients of hep-junction with B-Au distance 4.2 Å.

Figure 5.8 The total transmission and individual transmission coefficients of hep-junction with B-Au distance 4.7 Å.
Figure 5.9 The total transmission and individual transmission coefficients of hep-junction with B-Au distance 5.2 Å.

Figure 5.10 The total transmission and individual transmission coefficients of hep-junction with B-Au distance 5.7 Å.
Figure 5.11 The total transmission and individual transmission coefficients of hep-junction with B-Au distance 6.2 Å.

Figure 5.12 The total transmission and individual transmission coefficients of hex-junction with B-Au distance 1.7 Å.
Figure 5.13 The total transmission and individual transmission coefficients of hex-junction with B-Au distance 2.2 Å.

Figure 5.14 The total transmission and individual transmission coefficients of hex-junction with B-Au distance 2.7 Å.
Figure 5.15 The total transmission and individual transmission coefficients of hex-junction with B-Au distance 3.7 Å.

Figure 5.16 The total transmission and individual transmission coefficients of hex-junction with B-Au distance 4.2 Å.
Figure 5.17 The total transmission and individual transmission coefficients of hex-junction with B-Au distance 4.7 Å.

Figure 5.18 The total transmission and individual transmission coefficients of hex-junction with B-Au distance 5.2 Å.
Figure 5.19 The total transmission and individual transmission coefficients of hex-junction with B-Au distance 5.7 Å.

Figure 5.20 The total transmission and individual transmission coefficients of hex-junction with B-Au distance 6.2 Å.
To characterize the junction during the stretching process, various quantities other than conductance were calculated, such as the binding energy, Mulliken charges, and Seebeck coefficient, as shown in Fig. 5.21. As can be seen from Fig. 5.21 (c) and (d), the conductance drops exponentially during the stretching process. It is more straightforward to see the trend in Fig. 5.21 (a), which shows the transmission as a function of the B\textsubscript{40}-Au distance for both hex- and hep-junctions.

Figure 5.21 (a) Conductance of the two types of Au-B-Au junctions, (b) binding energy of the junctions, (c) Mulliken charge on the B\textsubscript{40} molecule, and (d) Seebeck coefficient (S) at room temperature, all as functions of the B\textsubscript{40}-Au distance during the stretching process. Black squares represent the hex-junction, while red circles represent the hep-junction.
Figure 5.22 (a) Conductance of the $B_{40}$ junctions (b) binding energy of the junctions, (c) charge on the $B_{40}$ molecule, (d) thermopower at room temperature during the stretching process where the B-Au distance is between 1.7 and 2.7 Å (in steps of 0.1 Å). Black squares represent hex-junctions, while red circles represent hep-junctions.

In the B-Au distance range of 1.7-2.7 Å, where the binding energy is lower than -5.5 eV, the conductance exhibits a “plateau”, with values between 2.91-5.98 $G_0$. The plateau indicates that a chemical bond between the electrodes and the $B_{40}$ molecule is formed. This is the contact regime [10, 22]. During the stretching process, the contact
breaks at the B-Au distance of \(~3.7\) Å, as suggested by the evolution of the binding energy and the exponential drop in conductance. This is the tunnelling regime.

The distance between two heptagonal faces of a single B\(_{40}\) molecule is \(~0.37\) Å longer than the distance between two hexagonal faces. With the same B-Au distance, the distance between electrodes is smaller for the hex-junction, and it is easier for electrons to tunnel through. Interestingly, in the contact regime, the conductance of the hept-junction is higher than that of the hex-junction (Fig. 5.22). This is simply a matter of competition between two factors as to which one dominates the transport: the charge injection rate or the molecule’s ability to scatter electrons. In spite of the longer tunnelling distance, the charge injection has more influence on the transport in the contact regime, leading to higher conductance in the hep-junction, as one more B atom on each side of the B\(_{40}\) molecule is in direct contact with the electrodes. In the tunnelling regime, however, the conductance of the hep-junction is lower. This is because the rate at which the electrons tunnel through from the electrodes decays less between two hexagonal faces (smaller diameter) on the B\(_{40}\) molecule, resulting in higher conductance for the hex-junction in the tunnelling regime.

The Au-B distance of 3.7 Å is not only a point which defines the transition from contact to tunneling, but also a crossover point from the regime in which the transport is dominated by charge injection at contact to the regime in which the transport is dominated by the scattering at the molecule.

The binding energies of the junctions corresponding to the B-Au distances are shown in Fig. 5.21 (b). The binding energy reaches its minimum at the B-Au distance of 2.2 Å for both types of junction. (A higher resolution of the binding energy between the B-Au distances of 1.7 Å and 2.7 Å is shown in Fig. 5.22) The energetically preferred B-Au distance for the hex-junction is 2.0 Å, and for the hep-junction, it is 2.2 Å. At such a
B-Au distance, the conductance is 4.59 $G_0$ and 4.86 $G_0$ for the hex-junction and the hep-junction, respectively. As the $B_{40}$-Au distance is shorter than 3.2 Å, the binding energies for both types of junction approach around -5.5 eV and below, indicating that the couplings between the $B_{40}$ molecule and the electrodes have become stronger. The transmission without pronounced peaks in the vicinity of $E_F$ is the direct result of such strong coupling.

Mulliken charges on the $B_{40}$ molecule are shown in Fig. 5.21 (c). During the stretching process, the Mulliken charges and binding energy approach zero when the B-Au distance becomes larger. The Mulliken analysis shows that both types of junction are positively charged unless the B-Au distance is very close.

The Seebeck coefficient is shown in Fig. 5.21 (d). Except for the hep-junction at the B-Au distance of 3.2 Å, the $S$ is negative at all stages of the elongation process, indicating that the low-bias transport is dominated by the LUMO of the molecule at these B-Au distances. It is worth mentioning that the $S$ of $B_{40}$ is 2–3 orders of magnitude smaller than that of $C_{60}$ fullerene \[22, 23\], and not as sensitive to the contact distance.

### 5.4 Tuning the transport properties of the $B_{40}$-based junction

The conductance of a $C_{60}$-based junction can be tuned by trapping a single atom inside the C cage. The transport properties of molecular junctions based-on endohedral borospherenes: $M@B_{40}$ ($M = Ca, Sr, Y, H_2O$) with B-Au distance of 3.2 Å were also studied. The structures of single endohedral molecules were optimized first. The total energy of the $H_2O@B_{40}$ molecule is 0.596 eV lower than the sum of energies of the free $H_2O$ molecule and the $B_{40}$ molecule, indicating that the $H_2O@B_{40}$ molecule is a stable molecule. Then, the optimized molecules are bridged between two Au electrodes. The
double-zeta plus polarization basis set for dopant atoms was used. The rest of the parameters in the calculations remained the same.

![Graph and captions](image)

Figure 5.23 (a) Conductance for $\text{B}_40^-$, $\text{Ca@B}_40^-$, $\text{Sr@B}_40^-$, $\text{Y@B}_40^-$, and $\text{H}_2\text{O@B}_40$-based junctions with two coupling geometries: the hex-junction (black squares) and the hep-junction (red circles); (b) and (c) transmission as a function of energy at zero bias for the doped junctions with the two types of coupling geometry. Black, red, blue, cyan and orange represent transmission of $\text{B}_40^-$, $\text{Ca@B}_40^-$, $\text{Sr@B}_40^-$, $\text{Y@B}_40^-$, and $\text{H}_2\text{O@B}_40$-based junctions, respectively.

The conductance of a $\text{B}_40^-$-based junction is dependent upon the species inside the molecule and the coupling geometry. It increases after metallic doping and changes slightly after $\text{H}_2\text{O}$ molecule doping, as shown in Fig. 5.23 (a).
From Fig. 5.23 (b) and (c), the transmission of an H$_2$O@B$_{40}$ junction is similar to that of a B$_{40}$ junction for the two types of contact geometry. For the doped hep-junction, however, it is obvious that the transmission peaks shift downwards after metallic doping (Ca, Sr, and Y). Also, the doping results in a broadening of the LUMO. The Y@B$_{40}$ junction has the highest LUMO peak, while the one for the Ca@B$_{40}$ junction is broadened and spreads over the vicinity of $E_F$, resulting in the highest conductance among the doped junctions. Interestingly, the HOMO splits into two peaks after Sr doping. As can be seen, the broadened HOMO for the Sr@B$_{40}$ junction partially lies on the $E_F$, making it the only metal-doped junction with hole transport at low bias. For the metal-doped hex-junction, the transmission peaks shift downwards without HOMO splitting. All the LUMOs are broadened, with the one for Y@B$_{40}$ being the highest at $E_F$, leading to the conductance of Y@B$_{40}$ being the highest for a doped hex-junction.

To understand the evolution of the conductance with doping, the HOMOs and LUMOs of the five single molecules were calculated. The HOMO-LUMO gap for a single B$_{40}$ molecule is 1.76 eV, in agreement with the 1.77 eV in ref. [48]. The HOMOs and LUMOs are more delocalized after metallic doping and change slightly after H$_2$O doping, suggesting that the metal-doped molecules tend to be more conductive in molecular junctions.

With the electrodes present in the junction, it is useful to visualize the scattering states at $E_F$ that are transmitted through the junction. The scattering states are eigenstates (eigenchannels) of the transmission matrix in Eq. (2). These states characterize the electron transport through the transmission eigenchannels$^{31}$. The charge transfer effects are included, and this information would not be available in the calculations of the free molecule without the Au electrodes. At zero bias, the sum of eigenvalues for each eigenchannel at $E_F$ is the conductance of the junction. For the doped junctions studied, 3
eigenchannels dominate the transport properties, and the corresponding scattering states are plotted in Fig. 5.24. Only the scattering states projected onto the bridged molecule are plotted. It can be seen that the molecular scattering states are separately distributed on part of the B atoms. After H$_2$O doping, the changes in molecular scattering states are negligible. This is why the conductance of the H$_2$O@B$_{40}$ junction is not changed too much after doping. After Ca, Sr, and Y doping, however, the scattering states change significantly. They are more delocalized, at least in one eigenchannel that was plotted, being almost distributed over the whole bridged molecule in that eigenchannel(s), leading to higher conductance.

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<th>hep-junction</th>
<th>B$_{40}$</th>
<th>Ca@B$_{40}$</th>
<th>Sr@B$_{40}$</th>
<th>Y@B$_{40}$</th>
<th>H$<em>2$O@B$</em>{40}$</th>
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<th>Ca@B$_{40}$</th>
<th>Sr@B$_{40}$</th>
<th>Y@B$_{40}$</th>
<th>H$<em>2$O@B$</em>{40}$</th>
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Figure 5.24 Visualization of the three most transmissive eigenchannels (incoming from the left electrode) at the $E_F$ for the B$_{40}$, Ca@B$_{40}$, Sr@B$_{40}$, Y@B$_{40}$, and H$_2$O@B$_{40}$-based junctions. Electrodes are not plotted. The isosurfaces of the eigenchannels are colored according to the phase and sign, with the positive/negative real part being colored in red/blue. The scattering states are plotted with the same iso-value to make them comparable.

Comparing the scattering states in the three different eigenchannels in the Ca@B$_{40}$ hep-junction and hex-junction, those in the second and third eigenchannels are
comparable, while the scattering states on the first eigenchannel are more delocalized in the hep-junction. Therefore, the hep-junction has higher conductance. This is not the case in the Sr@B\(_{40}\) and Y@B\(_{40}\) junctions. From Fig. 5.24, in the Sr-doped junctions, there is only one eigenchannel with the scattering states distributed over the whole molecule in the hep-junction, while there are two eigenchannels with the scattering states distributed over the whole molecule in the hex-junction. In the Y-doped junctions, although there are two eigenchannels with the scattering states distributed over the whole molecule, they are less delocalized compared with the first and third eigenchannels in the hep-junction. As a result, after Sr or Y doping, the hex-junction is more conductive than the hep-junction at the B-Au distance of 3.2 Å.

### 5.5 Conclusions

In conclusion, we theoretically demonstrate that the B\(_{40}\)-based junction is highly conductive compared to the C\(_{60}\)-based junction. For the energetically preferred geometries, the conductance of Au-B\(_{40}\)-Au junctions can be as high as several times that of comparable Au-C\(_{60}\)-Au junctions. This is another material where a low-dimensional allotrope reveals distinctive electronic properties from those of the pure bulk. Pure Boron in bulk form is an electrical insulator at room temperature. Unlike single-molecule junctions based on π-conjugated molecules or C\(_{60}\) fullerene, the number of conduction channels in a B\(_{40}\)-molecule junction is less than the number of B atoms in direct contact with the electrode, due to the unique electronic structure of B\(_{40}\). Moreover, we have found that the thermopower of B\(_{40}\) with gold electrodes is dramatically smaller than that of the Au-C\(_{60}\)-Au junction. The transport properties of Au-B\(_{40}\)-Au junctions can be tuned by doping. With a Ca, Sr, or Y atom encapsulated in the B\(_{40}\) cage, the conductance at zero bias increases significantly. Our study indicates that the B\(_{40}\)
fullerene is a new platform for highly conductive single-molecule junctions for future molecular circuits.

5.6 References

Chapter 6

Spin current in phenalenyl-based molecular junction

6.1 Introduction

The idea of designing novel nanoscale electronic devices and quantum information processing systems based on molecular materials can be traced back to the early 1970s [1, 2]. The progress of research in this area was not very great, however, until several advanced devices could be used for measuring single-molecule transport in the past two decades.

During the past few years, studies beyond simple charge transport have been conducted extensively. The results suggest that the metal-molecule interfaces play an important role in understanding the physics involved in molecular junctions. There are two ways to vary the bridging structure between the single molecule and metallic electrode: (1) using different chemical link groups such as thiols or amines, or even forming straight covalent Au-C sigma bonds [3-8]; and (2) varying the connected sites on the bridged molecule [9, 10].

In addition to designing and forming new kinds of contact geometry, researchers have focused on interesting organic molecules. Recently, magnetoresistance of up to 300% has been measured in a magnetic tunnel junction made of magnetic metal and non-magnetic organic molecules [11]. The spin-polarization of the current in the junction is determined and can be manipulated by the chemical bonds between the
organic molecule and the metallic electrode [12]. Theoretical calculations show that the magnetoresistance of a nanoscale junction incorporating spin-cross molecules can increase up to 3000% at finite bias [13]. Thus, searching for interesting organic molecules that have promising potential for applications has become an intriguing task.

Phenalenyl and its derivatives, which can be viewed as open-shell graphene fragments, have attracted much attention because of their highly symmetric structure, unique electronic properties, and promising potential applications [10, 14-19].

When the phenalenyl and its triangular motifs are bridged between two metallic electrodes, interesting properties, such as negative differential resistance and rectification, are observed [10, 15, 16]. Both experimental and computational studies have shown that the spin density of the triangular graphene fragments resides mainly on the edges of the molecule, making them unstable with respect to external perturbation [14, 20-22]. Several contact interfaces of phenalenyl-based molecular junctions have been studied by connecting different sites of the molecule to electrodes [15, 17]. Fig. 6.1 shows the structure of the phenalenyl-based molecular bridge. Electronic transport of two connecting sites, σ and β (shown in Fig. 6.1 b), are studied. When the σ sites are connected to the electrodes, no spin-polarized transmission is observed for any of the three junctions. When the β sites are connected to the electrodes, transmission function for no doping junction is slight spin-polarized and transmission functions for the other two doping junctions are spin-unpolarized. H. Liu et al calculated the transmission function and current of triangular graphene fragments with different contact geometries. They find the significant rectification with a favorite electron transfer direction from the vertex to the right edge. However, no spin-polarized current is observed in those models [15], as shown in Fig. 6.2.
Similar rectification can be observed in smaller triangular graphene fragment - phenalenyl-based molecule. The rectification ratio is different by using different electrodes [16].

The previous works show that although the single piece of ribbon has a net magnetic moment, the transport properties are not affected significantly by the magnetic state. This is because spin majority states are disturbed by the electrode wave function, as some of them are distributed on those atoms at the edges that are connected with the electrodes [17]. Although spin-polarized transmission spectra are spotted when the spin minority sites are used to connect the electrodes, the difference in energy between the spin majority and spin minority peak positions is very small: 0.02 eV [17].

These studies indicate that the spin polarization state can easily be eliminated or significantly suppressed by the bridging effect due to the sensitivity of the wave function residing on the edge of the molecule. As a result, the molecule’s spin distribution, which is determined by the molecular structure, is crucial when maintaining the spin polarized states in the molecular junction.

Figure 6.1 (a) Structure of the phenalenyl-based molecular bridge. The label X is doping site. (b) Spin-density distribution of the isolated phenalenyl molecule. Orange and Blue correspond to the up (majority) and down (minority) spin densities, respectively [17].
Figure 6.2 (a) The structure of the triangular graphene fragments together with the addressed question that current from two directions is asymmetric ($I_L \neq I_R$). (b) The molecular junction, including three parts: the left electrode, the scattering region, and the right region. The arrow denotes the positive bias with a direction from the left vertex to the right edge. (c) Chemical structures of graphene fragments. The dashed lines represent electron transport pathways where $P_C$ is the central pathway, and $P_S$ shows the side pathways. The probable pathways of $P_C$ and $P_S$ marked by bold lines in M3 consist of 11 C-C bonds from the injecting point to the ejecting site, that is, $L(P_C)=L(P_S)=11R_{CC}$ [15].

Therefore, it is a great challenge to preserve the molecule’s spin-polarized states when it is bridged between the electrodes. If the spin-polarized states are not destroyed, another question arises: is there any other factor that is able to have a notable influence on the spin-polarized states?

A very recent proposal has come to our attention. When a non-magnetic organic molecule and magnetic electrodes are brought together, the interface between them affects the spin-polarization of the density of states (DOS) of the molecules at the Fermi level ($E_F$), as the molecular energy levels can shift due to the coupling between the
molecule and the electrodes [12]. The shifting of the spin-polarized frontier orbital to $E_F$ allows the injected spin-polarized electrons with the corresponding direction to flow through the junction. In the phenalenyl-based molecular junction, where the magnetic organic molecule is connected to non-magnetic electrodes, the energy levels of the molecular orbitals (MO) may also shift, but the scenario is not the same because the spin-polarized electrons are not injected by a magnetic electrode.

It is well known that the presence of an unpaired $\pi$-electron is responsible for the spin-polarized states in the phenalenyl molecule. When the MO of the $\pi$-electron is at the $E_F$ of the junction, the electrons injected from the non-magnetic electrode are selected to pass through the junction in terms of their spin direction. Therefore, the spin-polarized states may be retained when the MO of the $\pi$-electron moves toward the $E_F$, or they may be destroyed when the MO of the $\pi$-electron moves away from the $E_F$. As the wave function on the edge of the phenalenyl molecule is very sensitive to external perturbation, the spin-polarized state may also disappear if the coupling between the molecule and the electrode is too strong.

The molecular energy level of phenalenyl ($C_{13}H_{9}$) can be shifted by doping without changing the contact interface [17]. As shown in Fig. 6.3, when the two carbon atoms on doping sites are replaced by nitrogen atoms, the spin-polarized state still exists [14, 17]. This leads to another potential application in which we can have spin-polarized current at the desired bias, as the MO of the $\pi$-electron of the molecule can be tuned to a specific energy level by doping.
Figure 6.3 Structure of the type-C molecular junction. Type-N and type-B junctions have the same contact geometry but different atoms on the two doping sites.

### 6.2 Computational details

In our study, the ab initio transport calculations are carried out within the framework of density-functional theory (DFT) combined with the non-equilibrium Green’s function method (NEGF), as implemented in the ATOMISTIX TOOLKIT (ATK) package (version 13.8.0) [23, 24]. The three molecules were each sandwiched between two Au (111)-(4×4) surfaces via terminal thiol groups. S-Au bonds are thus formed and set to 2.5 Å. For simplicity, in the following discussion we will refer to the molecular junctions with X = C, B, and N as type-C, type-B, and type-N molecular junctions, respectively. The geometry of the type-C molecular junction studied is shown in Fig. 6.3. Type-B and type-N molecular junctions are those in which carbon atoms on doping sites are replaced by B and N, respectively. The generalized gradient approximation (GGA) is adopted for exchange-correlation functional [25]. The single-zeta plus polarization basis set for gold atoms and the double-zeta plus polarization basis
set for other atoms are used for electron wave functions. A cutoff energy of 150 Ry is used in the transport calculations. The \( k \) points of the electrodes are set to Monkhorst-Pack \( 1 \times 1 \times 50 \). Before calculating the transport properties, the geometries are optimized until the maximum ionic forces are smaller than 0.03 eV/\( \text{Å} \). Transport properties can be understood in terms of the transmission spectrum. In the coherent transport regime, the spin-resolved transmission function is given by

\[
T_{\sigma}(E, V) = \text{Tr}\{\Gamma_{\sigma}^R(E)G_{\sigma}^{\text{ret}}(E)G_{\sigma}^{\text{ret}}\},
\]

where \( \Gamma_{\sigma}^{L(R)}(E) = i[\Sigma_{\sigma}^{L(R)}(E) - \Sigma_{\sigma}^{L(R)^\dagger}(E)] \) and \( \Sigma_{\sigma}^{L(R)}(E) \) is the retarded self-energy of the semi-infinite electrode, \( G_{\sigma} \) is the retarded Green’s function, and \( \sigma \) represents the majority or minority spin channel, respectively [26].

### 6.3 Spin-polarized transport

Fig. 6.4 shows the current-voltage (I–V) curve of the magnetic molecular junction for each junction and their spin filter efficiencies. The total current for the three junctions at same bias are different. The current increases significantly after B-doping and decreases after N-doping, compared with that in type-C junction. Fig. 6.4 (a), (b), and (c) also display the currents for spin-up and spin-down channels for the three junctions. For the type-B junction, the spin-down current is suppressed at low bias range. When the bias voltage is larger than 0.5 V, the suppressed current increases rapidly, becoming comparable to the current of spin-up channel. The trend is similar for the current of the type-C junction. However, current in the type-N junction is spin-balanced at low bias range, and then becomes spin-polarized when the bias voltage is larger than 0.4 V. The spin filter efficiency (SFE) defined as \( \eta = (I_\uparrow - I_\downarrow)/(I_\uparrow + I_\downarrow) \) is depicted in Fig. 6.4 (d). As can be seen, the SFE of the type-B junction reaches its maximum at 0.1 V, being more than 80%, then decreases and approaches around zero at 0.6 V. The curve
of SFE for the type-C junction has similar shape but its SFE is much smaller than that of the type-B junction. In the type-N junction, the SFE is zero at low bias range. It becomes finite when the bias voltage increases to 0.5 V. Fig. 6.4 shows that the phenalenyl-based molecules have the potentiality for making spin filter device by employing their intrinsic properties.

Figure 6.4 Transmission spectra for (a) type-C junction, (b) type-N junction, and (c) type-B junction. Black and red curves are transmission spectra for spin-up and spin-down channels, respectively. The gold-sulfur gateway states for the type-C junction and MOs are marked.

It is well known that a nitrogen (boron) atom contributes one more electron (hole) to the molecular junction when replacing a carbon atom in the molecule, and thus
the conductance of the type-N (B) junction is expected to be larger than that of the type-C junction due to the extra carrier introduced into the system, while the DOS of the bridged molecule is expected to be similar with a shifted-downward (shifted-upward) version of that of the undoped molecule, which is not the case in our calculations. The spin-resolved projected density-of-states (PDOS) for the three junctions is shown in Fig. 6.5. The peaks around $E_F$ are not similar as expected after doping, except those broad peaks below $E_F$. They recede deeper in energy after N doping because of the extra electrons introduced into the system, and move toward $E_F$ after B doping. The broad peaks are formed due to the coupling between the molecule and gateway states (the states on the sulfur–gold links to the electrodes). The couplings have significant influence on the frontier orbital, dominating the transport properties of the junction. The conductance of type-C, B, and N junctions is $0.057\ G_0$, $0.1\ G_0$ and $0.041\ G_0$, respectively. The conductance decreases 28 per cent after N doping.

Figure 6.5 Spin-resolved PDOS for the three molecular junctions. Black, blue, and pink curves correspond to the PDOS of type-C, type-N, and type-B junctions, respectively.
To further explore the underlying mechanisms of the spin filter effect, the spin-polarized transmission functions at zero bias for the three molecular junctions and molecular projected self-consistent Hamiltonian states (MPSHs) are depicted in Fig. 6.6. It can be seen from Fig. 6.6 (b) that for the type-C junction, the transmission is spin-polarized. Remarkably, the energy difference between single occupied molecular orbital (SOMO) and single unoccupied molecular orbital (SUMO) of the type-C junction is about 0.665 eV. The SOMO and SUMO have the same patterns to those of a”₁ in ref [17] and only reside on the spin majority sites except the central site of the molecule, indicating that, by connecting the spin minority sites directly to metallic electrodes via thiol group, the frontier orbitals are not disturbed remarkably by electrodes wave functions. Therefore, the transmission preserves spin-polarized.

Fig. 6.6 Transmission and MPSH for (a) type-B junction (b) type-C junction, and (c) type-N junction at zero bias. Black and red curves are transmissions for spin-up and spin-down channels. All energies are relative to the Fermi energy of the Au electrode.
The spin-polarized states can be destroyed by doping. However, for the case of type-B junction in Fig. 6.6 (a), only one significant peak (around 0.015 eV) for spin-up channel exists in the very vicinity of the Fermi level, resulting in the large SFE at low bias, as shown in Fig. 6.4 (a). For SUMO in type-B junction, the orbitals are distributed on part of spin majority site, so the spin-polarized state of the molecular junction does not disappear. In transmission, the peak of SUMO in type-B junction is broader than the SOMO in type-C junction. Also, the SOMO and SOMO-1 in type-B junction are broadened because of the coupling between the doped molecule and electrodes, as electrons are distributed on S atoms. The broadening in transmission indicates that the coupling between the molecule and Au electrodes is stronger in the type-B junction. As a result, the current in the type-B junction at low bias is larger than that in the type-C junction.

Fig. 6.7 Transmission of the type-N junction at (a) 0.4 V and (b) 0.5 V. Black and red curves are transmissions for spin-up and spin-down channels. Dotted line indicates the Fermi level. Between the two dashed lines is bias window.
For the type-N junction in our calculations, the transmission spectrum is completely spin-balanced at zero bias; even the single N-doped molecule is spin-polarized. The peak above Fermi level resides at 0.087 eV. Electrons distributions on FOs in type-N junction are shown in Fig. 6.6 (c).

The transmission for type-N junction at 0.4 V and 0.5 V are depicted in Fig. 6.7. As the bias continues to increase, the transmission of type-N junction becomes spin-polarized when bias voltage approaches to 0.5 V. Therefore, the current of type-N junction becomes spin-polarized at high bias range.

### 6.4 Conclusion

We have studied the spin-resolved transport properties for the three junctions based on DFT calculations combined with the NEGF method. From our calculations, we confirm that, to preserve the spin-polarized states on the molecule, connections on spin-minority sites are a preferred, although connections between spin-minority sites and electrodes do not assure spin-polarized transmission as in the type-N junction in our calculations. On the other hand, spin-polarized current in type-N junction are expected at finite bias when the π-electron orbitals enter in the bias window. In the type-B junction, due to the resonance between the MPSH states on the molecule and the gateway states, only one single sharp peak is left in the vicinity of the Fermi level, making the type-B junction a good candidate for a spin filter device. This paves the way to finding and designing spin filters by employing the gateway states to disturb the orbitals for one spin channel.

### 6.5 References

Chapter 7

Summary

Molecular electronics is promising for future electronic device and offers an opportunity to control electronic functions in molecular junctions. No need to set up large junctions in molecular devices, and the limitations arising from the energy-level misalignment are easy to control. Also, experimental demonstrations of quantum interference and the manipulation of electronic and nuclear spins in single-molecule circuits are heralding new device concepts with no classical analogues. So far, no ‘molecular electronics’ devices are manufactured commercially, which is probably because we haven’t yet really made the most of the molecules’ potential and specificity. Therefore, further understanding in this intriguing area is still required.

This thesis has been focused on the electronic transport of molecular junctions and on how to manipulate the electronic transport. The non-equilibrium Green’s function method (NEGF) combined with density functional theory (DFT) has been used to investigate the electrical conduction properties of nanoscale systems at an atomistic level. A method has been provided tune the electronic transport of the molecular junction without changing its interface. There are many methods to tune the position and orientation of the H$_2$O molecule inside the cage such as light irradiation, electric fields, heating, etc. All these external stimuli can ‘communicate’ with the water molecule, causing it to adjust its location, which, in turn, changes the conductance of the H$_2$O@C$_{60}$ junction. How to manipulate the encapsulated water molecule could be next direction for how to exploit the unique property of H$_2$O@C$_{60}$ in molecular junction. It has been theoretically demonstrated that B$_{40}$ is a highly conductive molecule compared with C$_{60}$. 
In addition, a model to generate the spin-polarized current using the molecule’s intrinsic properties is proposed. This paves the way to the fabrication of devices that generate spin-polarized current at finite bias. The Heisenberg model has been employed to study the spin waves in the surface and edges of a bulk material.

Overall, tremendous progress has been made in molecular electronics. Nowadays, researchers are study aspects of the molecular junctions beyond simple electronic transport. Molecular electronics is an area that involves multidisciplinary efforts and cooperation between physicists, chemists, surface scientists and electrical engineers. With such efforts, it is likely that the molecular devices could be eventually commercialized.