Theory and Modelling of Electronic Properties of Molecular-Scale Systems

By

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Ph.D. Thesis in Materials Science



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This thesis is submitted in partial fulfilment for the degree of Doctor of Philosophy

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Declaration

This thesis is the main researcher's study and research for the award of the PhD degree at Lancaster University, and nowhere else. The thesis documents are studies and research from Oct 2021 to Jan 2025 under the supervision of Prof. Colin J. Lambert and Dr. Songjun Hou at the Department of Physics, Lancaster University, United Kingdom, and funded by the Ministry of Education and King Faisal University Scholarship, Saudi Arabia.

Abdulrahman Aljasim January 2025

Dedication

This work is dedicated to my beloved mother and father, Aesha Alefhaid and Othman Aljasim and my dear wife, Anfal Aldihnayn and my beloved kids, Othman and Aesha for their sacrifices, prayers, big support, and love

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Abstract

Single-molecule junctions (SMJs) provide an excellent platform for understanding charge transfer (CT) in molecular-scale structures and are a crucial building block for investigating electronic devices. Over the past two decades, numerous efforts have been focused on studying electron transport in molecular systems. The aim is vital for synthesising stable molecules and designing highly efficient energy devices. Furthermore, explorations of electronic and thermoelectric properties of single-molecule junctions have established the validity of applying quantum tools to molecular systems. This thesis addresses theoretical simulations for electric and thermoelectric transport properties such as transmission coefficient T(E), Seebeck coefficient S, and electrical conductance G. The charge transfer (CT) in single-molecule junctions can tune their thermoelectric properties. Particularly, CT complexes such as chlorine perylene bisimide (Cl-PBIs) combined with tetracyanoethylene (TCNE) and tetrathiafulvalene (TTF) can exhibit distinct electron transport behaviours due to donor-acceptor interactions and also molecular-orbital hybridisation. Furthermore, porphyrin-based wires incorporating hexafluorophosphate $[PF_6]^-$ counterions can influence redox activity through electrostatic gating. Thus, theoretical tools are employed to explain many phenomena, including quantum interference effects, rectification, switching, and transistor effects. In Chapter 2, density functional theory (DFT) is implemented within the SIESTA code. In Chapter 3, Green's function methods and thermoelectric coefficients are addressed. In Chapter 4, I investigated charge transfer complexes of chlorine perylene bisimide (Cl-PBI) with TCNE as a pendant molecule in SMJs. In Chapter 5, thermoelectric properties are explored in the chlorine perylene bisimide (Cl-PBI) with a TTF as a pendant molecule, which affects an electron transport behaviour close to the Fermi energy E_F at room temperature (\sim 300K). In Chapter 6, I focused on tuning the thermoelectric properties of single-porphyrin wires by studying various scenarios.

Chapter 1	13
Introduction to Molecular-Scale Systems	13
1.1 Introduction	13
1.2 Molecular Electronics Modelling	15
1.3 Perylene Bisimide (PBI)	16
1.4 Porphyrin Molecule	17
1.5 Outline of Thesis	18
Bibliography	20
Chapter 2	28
The Density Functional Theory (DFT)	28
2.1 Introduction	28
2.2 Many-Body Problem	30
2.3 Born-Oppenheimer Approximation	31
2.4 Hohenberg-Kohn Theorems	32
2.5 Kohn-Sham Method and Self-Consistent Field	35
2.6 The Exchange-Correlation Functionals	38
2.7 SIESTA	38
2.8.1 Local Density Approximation (LDA)	41
2.10 Counterpoise Correction Method	42
Bibliography	44
Chapter 3	50
Quantum Theory of a Single-Particle Transport	50
3.1 Introduction	50
3.2 Green's Function Method	50
3.3 A One-Dimensional Scattering System	52
3.4 An Infinite Periodic System	54
3.5 A Semi-Infinite Periodic System	59
3.6 Transmission Coefficient of a Scattering Region	61
3.7 Landauer Formula	65
3.8 Thermoelectric Coefficients	67
Bibliography	73
Chapter 4	76
Charge Transfer Complexes of Chlorine Perylene Bisimide with the Presence of TCNE in Single- Molecule Junctions	- 76
4.1 Introduction	77

Contents

4.2 Computational Techniques	78
4.3 Electronic Structure Simulations	78
4.4 Frontier-Molecular Orbitals (FMO)	79
4.5 Binding Energy Between Anchor Groups and Gold Electrodes	81
4.6 Molecular Complexes of Cl-PBI with TCNE	84
4.6.1 Frontier-Molecular Orbitals of TCNE	85
4.6.2 Binding Energy Between Cl-PBI and TCNE	86
4.6.3 Frontier-Molecular Orbitals of Cl-PBIs with Presence of TCNE	90
4.8. Results and Discussion	92
4.7.1 Transmission Coefficient and Electrical Conductance of Bare Junctions	93
4.7.2 Transmission Coefficient and Electrical Conductance of Cl-PBI_Py + TCNE	94
4.7.3 Transmission Coefficient and Electrical Conductance of Cl-PBI_SMe + TCNE	96
4.7.4 Comparison of Transmission Coefficient and Electrical Conductance of Cl-PBIs and	ГСNE 98
4.7.5 Comparison of Seebeck Coefficient S of Cl-PBIs	100
4.7 Summary	101
Bibliography	102
Chapter 5	106
Exploring Charge Transfer Complexes of Chlorine Perylene Bisimide with the Presence of TTF	in
Single-Molecule Junctions	106
5.1 Introduction	106
5.2 Molecular Complexes between Cl-PBI and the Presence of TTF	107
5.2.1 Frontier-Molecular Orbitals of TTF	107
5.2.2 Binding Energy Between Cl-PBI and TTF	108
5.2.3 Frontier-Molecular Orbitals of Cl-PBIs with the Presence of TTF	112
5.3 Results and Discussion	113
5.2.3 Comparison of Transmission Coefficient and Electrical Conductance of Cl-PBIs and	ГТF 117
5.2.3 Comparison of Seebeck Coefficient S of Cl-PBIs with TTF	120
5.4 Summary	121
Bibliography	123
Chapter 6	125
Tuning The Thermoelectric Properties of Single-Porphyrin Molecules in Single-Molecule Wires	125
6.1 Motivation	125
6.2 Introduction	126
6.3 Results and Discussion	127
6.3.1 Impact of Side Groups on Thermoelectric Performance of Free-Base Porphyrins	128

	$6.3.2$ Thermoelectric Calculations of Free-base Porphyrin with Side Groups of C_3N_2	129
	6.3.3 Thermoelectric Calculations of Free-base Porphyrin with Side Groups of [Pyridine R CH ₃]	Lings + 132
	6.3.4 Comparisons of Thermoelectric Calculations for Both Free-base Porphyrins	136
	6.3.5 Tuning Thermoelectric Properties of Metalloporphyrin Wires	138
	6.3.6 Thermoelectric Calculations of Ni-Porphyrin	140
	6.3.7 Thermoelectric Calculations of Zn-Porphyrin	142
	6.3.8 Thermoelectric Calculations of Mg-Porphyrin	145
	6.3.9 Thermoelectric Calculations of Co-Porphyrin	148
	6.3.10 Comparisons of Thermoelectric Calculations	151
	6.3.11 Comparisons of Electrical Conductance <i>G</i> Between Theoretical Calculations and Experimental Measurements	156
	6.3.12 Transmission Coefficients of Porphyrin Molecules in the Presence of Hexafluorophosphate [PF 6] ⁻	158
	6.3.13 Comparisons of Transmission Coefficient Calculations	164
(6.4 Summary	166
]	Bibliography	167
Ch	apter 7	173
Co	onclusions and Future Works	173
,	7.1. Conclusions	173
,	7.2. Future Works	175
]	Bibliography	177

List of Publications

Xiaohang Qiao, Richard Nichols, Andrea Vezzoli, Simon Higgins, Jonathan Ward, Colin Lambert, Songjun Hou, <u>Abdulrahman Aljasim</u>. <u>Soft Electrochemical Gating of Charge</u> <u>Transport Across Phenothiazine Molecular Wires.</u>

List of Abbreviations

ME	Molecular Electronics
QI	Quantum Interference
CMOS	Complementary Metal-Oxide Semiconductor
DFT	Density Functional Theory
LDA	Local Density Approximation
GGA	Generalized Gradient Approximation
SCF	Self-Consistent Field
CQI	Constrictive Quantum Interference
DQI	Distractive Quantum Interference
SIESTA	Spanish Initiative for Electronic Simulations with Thousands of Atoms
LCAO	Linear Combination of Atomic Orbitals
SMJ	Single-Molecule Junction
STM-BJ	Scanning Tunnelling Microscopy Break Junctions
SAM	Self-Assembled Monolayer
HEG	Homogeneous Electron Gas
НОМО	Highest Occupied Molecular Orbital

LUMO	Lowest Unoccupied Molecular Orbital
DZ	Double-ξ
DZP	Double- ξ Polarised
BSSE	Basis Set Superposition Error
СТ	Charge Transfer
FMO	Frontier Molecular Orbitals
ТВ	Tight Binding
BE	Binding Energy
T(E)	Transmission Coefficient
G	Electrical Conductance
G_0	Quantum Conductance
S	Seebeck Coefficient
${ m E}_{ m F}^{ m DFT}$	DFT-Predicted Fermi Energy
ZTe	Electric Figure of Merit
κ _e	Thermal Electric Conductance

Chapter 1 Introduction to Molecular-Scale Systems

1.1 Introduction

Electronic components, such as semiconductors, have become smaller and smaller at an exponential rate, according to a historical tendency that Gordon Moore predicted in 1965. Many investigations have been carried out to discover ways that can continue this historical trend, and these investigations are now approaching the nano- or molecular scale [1]. At the nanoscale, a range of device concepts have been proposed, and used to demonstrate fundamental phenomena associated with electron transport, including nanoscale superconducting devices [2-6], devices based on carbon nanotubes [7-9], and sensors based on nanopores in graphene [10-12] or silicone [13]. Many of these concepts carry over to molecular-scale structures.

Molecular electronics (ME) is the field of science that analyses the electrical and thermal transport properties of circuits constructed with individual molecules (or groups of them) as their fundamental components. In 1974, Aviram and Ratner provided the initial concept for the molecular current rectifier [14]. Since that time, a range of single-molecule electrical devices have been proposed as transistors [15], rectifiers [16,17] and switches [18, 19] and a variety of methods for controlling electron transport through molecules have been proposed, including governing their molecular conformation [20], orientation within a junction [21], and frontier-orbital energy levels relative to the Fermi energy of electrodes [22].

In a single-molecule junction, electron transport can be controlled by varying the anchor groups, the molecular core, and attaching pendant groups to the core besides the linkages to the anchor groups. In contrast with the 1974 work of Aviram and Ratner [14], which assumed

that electron transport through single molecules incoherently takes place, one of the great discoveries during the past decade or so is that electron transport through single molecules can remain phase coherent, even at room temperature. This phase coherence means that a range of quantum interference effects are possible and that these can be used to control the electrical and thermal transport properties of molecular junctions. Manifestations of such interference effects include conductance oscillations in atomic wires [23] and Seebeck oscillations in π -stacked molecular junctions [24]. In addition, since molecules can be attached to electrodes via anchor groups, and the anchor groups can be connected to a molecular core with atomic accuracy, a range of connectivity-dependent quantum interference (QI) effects can be observed [25-27]. This ability to control connectivity to electrodes is a unique feature of single-molecule junctions, which distinguishes them from artificial quantum dots, where the connectivity to electrodes is poorly defined at an atomic scale.

In the simplest configuration, a molecule can be anchored to a gold electrode via direct carbongold bonds. Many other anchor groups have been tested in the literature, and correlations between the binding energy of the anchor to the electrodes and the magnitude of the electrical conductance have been demonstrated [28,29]. Gold is the most commonly used electrode material, but since it is not a complementary metal-oxide semiconductor (CMOS) like other electrode materials such as graphene [30-32].

Remarkably, many of the quantum interference effects discovered in single-molecule junctions have been shown to persist in materials formed from self-assembled molecular layers [33,34]. This is important because organic molecules can be utilised in scalable devices, such as crossbar architectures. The finite cross-section electrodes will inevitably make contact with a film of many molecules in parallel. It is also worth noting that the above interference effects derive from the wave nature of electrons passing through a molecule from one electrode to another. Since heat is mediated by vibrational waves and minimisation of thermal conductance is highly desirable for thermoelectric applications, it is of interest to determine phonon interference effects can be used to control thermal conductance. This question has been explored by adapting techniques originally developed to model lattice dynamics in nanostructures [35] to model phonon transport through single-molecule junctions [36,37].

1.2 Molecular Electronics Modelling

In molecular-scale structures, calculating the electronic properties of an isolated molecule is the first step in understanding electron transport. After solving the Schrödinger equation to find eigenvalues, eigenvectors, and the self-consistent Hamiltonian of these systems, one can then calculate the Green's function and scattering matrix. In the case of many-body problems, it is very difficult to provide an exact solution, therefore, some approximate methods must be applied to decrease the complexities of such interactions. There are two approaches to deal with such systems. The first involves semi-empirical techniques, which require different parameters to be fitted to experimental data. The second is a first-principles 'ab initio' approach, which I shall use in this thesis [38-41] to provide a systematic way to understand electronic structure without recourse to experimental data.

As an implementation of the 'ab initio' method, density functional theory (DFT) is a convenient way to calculate the electronic features of molecular-structure systems consisting of hundreds of atoms. Even though it is an approximate approach, DFT often provides good agreement with experimental data [42], although in some cases, it shows significant differences. In this thesis, I shall mainly utilise the DFT-SIESTA code, which allows eigenvalues and eigenfunctions to be obtained using computational methods. In the next chapters, I shall explain how density functional theory (DFT) can be combined with a Green's function scattering method to calculate the electronic properties of molecular junctions.

1.3 Perylene Bisimide (PBI)

Currently, silicon applications are a well-known field of research and have many industrial investigations [43,44]. Hence, the interest in discovering new features and understanding properties of charge transport in molecular junctions has been increasing in the past two decades [45-49]. Here, I introduce organic molecules and investigate their electric properties by studying various molecular structures in single-molecule junctions in the next chapters. I shall start my investigation with chlorine perylene bisimide (Cl-PBI), which is classified as an organic molecular group with unique electrical properties and innovations in sensors and fluorescence [45,46.50-54]. Generally, PBIs are extended π -systems, which can provide more π -orbital overlap and π - π interactions with other molecular derivatives [54-57] in Figure 1.1 below the core of the perylene bisimide PBI molecule. Moreover, they have valuable properties such as thermal and chemical stability, larger electron mobility, and high electron affinity [65,68].



Figure 1.1. a) The chemical structure of perylene bisimide (PBI). b) The molecular configuration of PBI, where atoms are nitrogen (blue), oxygen (red), carbon (grey), and hydrogen (white).

1.4 Porphyrin Molecule

As a continuous work in this thesis, I shall address the porphyrin molecule, which contains two different side groups on its backbone, and then add metal atoms [M =Ni, Zn, Mg, and Co], which are centred at their backbone to tune thermoelectric behaviours. Porphyrins are regarded as high-potential building blocks in molecular devices, due to their unique properties such as emission, absorption behaviours, and stability features [58] as shown in Figure 1.2. Given the rich chemical redox of porphyrin molecules, I shall proceed to investigate the porphyrin molecule, including the role of charged pendant groups of $[PF_6]^-$ anions, which deforms a dimer system to study the charge transport complexes in such metal-molecule-metal wires and understand their charged states which can be interesting in memory device applications.



Figure 1.2. a) The chemical structure of the porphyrin molecule core (left) and metalloporphyrin core (right). b) The molecular configuration of the porphyrin molecule core.

1.5 Outline of Thesis

This thesis reports calculations and predictions of electric and thermoelectric properties of organic molecules. Consequently, I shall study electron transfer through metal-molecule-metal systems and then expand my work to investigate charge transfer complexes of organic molecules by constructing a dimer system with pendant group molecules. Additionally, the results will describe electric and thermoelectric behaviour in single-molecule junctions. In the thermoelectrical process, a temperature difference causes an electrical voltage to appear across the system, which can cause charge to move from a hot side to a cold one. As a potential application, this phenomenon enables the generation of electrical current in a system from

waste heat. More generally, thermoelectric effects encompass three crucial principles, which include the Seebeck effect, the Peltier effect, and the Thomson effect.

As the building up of this thesis in Chapter 2, I shall introduce some fundamental principles of the density functional theory (DFT) and the SIESTA code by outlining the formalism, which allows us to treat many-body problems and apply the exchange-correlation technique. In Chapter 3, I shall illustrate the Green's function method, used for quantum transport calculations, and introduce the electric properties of single-molecule junctions. In Chapters 4 and 5, I aim to study the electric properties of chlorine perylene bisimide (Cl-PBI) as a main candidate for single-molecule junctions by varying its anchor groups for pyridine and a methyl thioether (SMe), which are symmetrically linked at opposite ends. I investigate further the charge transfer (CT) complexes by adding extra pendant molecules in the system of Cl-PBI and creating dimer systems which consist of pendant groups of tetracyanoethylene (TCNE) and tetrathiafulvalene (TTF). In Chapter 6, I shall show my results of studying the porphyrin molecules and modifying its bay area with different scenarios by including various side groups $(X = C_3N_2)$, $(X = pyridine rings plus CH_3)$, centred atoms (M= Ni, Zn, Mg, and Co), and the pendant anions [PF6]⁻ which can form a dimer system to study the charge transport complexes and redox-active interaction in nano-wires. Finally, in Chapter 7, I shall summarise my findings and calculations and provide some ideas for my future projects.

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Chapter 2

The Density Functional Theory (DFT)

In this chapter, the formalism of density functional theory (DFT) implemented with the SIESTA code will be introduced, which is employed for single-molecule calculations in this thesis. The first step in solving the electron transport mechanism of molecules is to apply DFT to obtain a mean-field Hamiltonian. I shall present computational methods in electronic molecular calculations. I shall begin with a general description of a many-body problem consisting of electrons and nuclei. The next sections will describe with Born-Oppenheimer Approximation, the Hohenberg-Kohn Theorems, and the Kohn-Sham Method. Then shall present Exchange-Correlation functionals and SIESTA formalisms in the following sections. Finally, the counterpoise correction method will be addressed.

2.1 Introduction

Density Functional Theory (DFT) is a crucial computational approach that scientists use to study the electronic properties of atoms, molecules, and lattice systems. Indeed, this method is a powerful tool to investigate and predict the ground-state properties of interacting many-particle systems. It is constructed to solve many-body problem systems that consist of many interacting particles. These physical properties can be calculated by considering a function of the ground-state density of many-body interacting systems [1,2]. Thus, the DFT is a dependable approach utilised on a wide range of molecular systems since numerous papers and literature offer in-depth explanations of the principles of DFT and how it is used [1-6]. The significance of DFT was underscored in 1998 by the Nobel Prize in Chemistry being granted to Walter Kohn [4] for developing density functional theory. The inception of DFT traces back to the Thomas-Fermi model from the 1920s, offering initial steps toward deriving the density functional for

total energy based on wavefunctions [1,6-8]. Progress was subsequently made by Hartree, Dirac, Fock, and Slater, nearly forty years following the work of Thomas-Fermi. The Hohenberg-Kohn theorems and Kohn-Sham method further cemented the foundations [5,33-37].

This chapter provides an overview of DFT, illustrating its primary formalism as a means of understanding how electrons are transported in organic molecular junctions begins with comprehending the electronic characteristics of an individual junction. This process involves solving the complex interacting many-body Schrödinger equation to identify eigenvalues, eigenvectors, Hamiltonian, and overlap matrices, which are then utilised to compute the electron scattering matrix. Unfortunately, solving this equation becomes impractical with numerous interacting electrons and particles. Nonetheless, various alternative methods exist to simplify the issue, such as employing 'ab initio' techniques rooted in theoretical principles or semi-empirical methods involving parameter fitting to experimental data [12-15].

This thesis opts for the former approach to offer a consistent and systematic method of determining electronic structure, eliminating the need for experimental measurements. An illustration of an 'ab initio' method is Density Functional Theory (DFT), commonly used in computing the electronic attributes of complicated molecules containing thousands of electrons. Despite being an approximation, DFT frequently yields accurate properties, though differences can arise in some instances [16]. Given the focus on molecules with extensive electron populations, employing DFT is a practical choice for efficiently deriving eigenvalues and transfer integrals, providing computational capabilities.

2.2 Many-Body Problem

A molecule consisting of many atoms can be considered a good example of a many-body system. For a system that exhibits one or two particles, numerical techniques can be applied to solve the system with a higher order of complexity. However, the mathematics tools of many-body quantum mechanics for large systems are difficult to solve since the computational time is expensive and requires memory storage to apply for realistic calculations. The DFT can provide an accurate description of a charged system surrounded by electrons. In quantum theory, we can describe a system consisting of electrons and nuclei by expressing the Schrödinger equation as:

$$H\Psi(\boldsymbol{r}_i, \boldsymbol{R}_I) = E\Psi(\boldsymbol{r}_i, \boldsymbol{R}_I) \tag{2.1}$$

where *H* represents the Hamiltonian operator for a system with *M* nuclei and *N* electrons, r_i is the position of the *i*-th electron, and R_I is the position of the *I*-th nucleus.

Solve the Schrödinger equation by applying this Hamiltonian would be exceedingly difficult since the complexity of interactions between particles in the system. Hamiltonian can be illustrated by the general equation (2.2) of many body-Hamiltonian of a system containing N interacting electrons and M Nucleons as:

$$H = \sum_{i=1}^{N} -\frac{\hbar^{2}}{2m_{i}} \nabla_{i}^{2} + \sum_{I=1}^{M} -\frac{\hbar^{2}}{2M_{I}} \nabla_{I}^{2} + \frac{1}{2} \sum_{i\neq j}^{N} \frac{v_{ee}}{4\pi\epsilon_{0} |\mathbf{r}_{i} - \mathbf{r}_{j}|} + \frac{1}{2} \sum_{i\neq j}^{N} \frac{e^{2}}{4\pi\epsilon_{0} |\mathbf{r}_{i} - \mathbf{r}_{j}|} - \sum_{i=1}^{N} \frac{v_{en}}{4\pi\epsilon_{0} |\mathbf{r}_{i} - \mathbf{R}_{I}|}$$
(2.2)

The first two terms in equation (2.2) represent the kinetic energies of electrons and nucleons respectively, the third one is the electron-electron interactions, while the fourth term is the

nucleon-nucleon interactions, and the last one is the electron-nucleon interactions. Solving the Schrödinger equation by applying this Hamiltonian would be exceedingly difficult because of the complexity of interactions between particles in the system. Therefore, to find a solution for the system, an approximation is required to be applied to decrease the size of the problem and ignore the electron-nucleon interactions to increase the degree of freedom, which is treated by the Born-Oppenheimer approximation in the next section.

2.3 Born-Oppenheimer Approximation

To find a solution to the Schrödinger equation (2.1), there is a wavefunction that contains the coordinates of all the nucleons and electrons of the system as 3N + 3M components. Thus, Born and Oppenheimer came up with an efficient approach to solve a wavefunction by separating the Hamiltonian into effective electron and nucleon parts, which can be calculated individually. The nucleon is considered to be a stationary object compared with the electron due to their size, and the relaxation time of the electron is much faster to reach the ground state, so the nucleon is assumed to be fixed and independent of the positions of the electron. The equation (2.1) can be presented as the product of an independent nucleon wavefunction Θ and the electron wavefunction Φ as:

$$\Psi(\boldsymbol{r}_{i},\boldsymbol{R}_{l}) = \Theta(\boldsymbol{R}_{l})\Phi(\boldsymbol{r}_{i},\boldsymbol{R}_{l})$$
(2.3)

It can be considered that the function of nucleon positions is considered to be zero as the nucleons are assumed to be fixed within the relaxation time of the electrons whereas the electron-phonon interaction can be omitted by considering low temperatures while it can take a phonon self-energy which can be presented in Green's function calculations and Dyson's equations [17].

Hence, we can write an electron Hamiltonian within an effective Schrödinger equation of an electron as:

$$H_e \varphi = E_e \varphi \tag{2.4}$$

It presents the motion of an electron in a fixed positive potential field due to the stable nuclei. Hence, the Hamiltonian of electron can be written as:

$$H_{e} = \sum_{i} -\frac{\hbar^{2}}{2m_{i}} \nabla_{i}^{2} + \frac{1}{2} \sum_{i \neq j} \frac{e^{2}}{4\pi\epsilon_{0} |\mathbf{r}_{i} - \mathbf{r}_{j}|} - \sum_{iI} \frac{Z_{I}e^{2}}{4\pi\epsilon_{0} |\mathbf{R}_{I} - \mathbf{r}_{i}|}$$
(2.5)

Therefore, the Hamiltonian of nucleon includes only the kinetic and interaction terms of the nucleons and can be written as:

$$H_n = \sum_{I} -\frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 |\mathbf{R}_I - \mathbf{R}_J|}$$
(2.6)

Thus, the Born-Oppenheimer approximation can apply the degree of freedom to solve the Schrödinger equation by separating electrons and nucleons.

2.4 Hohenberg-Kohn Theorems

The first and second Hohenberg-Kohn theorems are fundamental concepts in density functional theory (DFT), which play an essential role in solving the ground-state of the effective electron Schrödinger equation. These theorems present the ground-state properties of a system n_0 corresponding to a minimum total energy functional [18]. The Hohenberg-Kohn theorem describes a system of interacting particles within an external potential field V(r)[10]. Thus, the density functional is applied to minimise the functional of total energy, whereas the global minimum presents the ground state density. The external potential is described by the ground-

state density n_0 of a particle; however, it is not applied for a constant potential. Furthermore, Levy and Leib have provided other methods to have the same calculations as the previous theorems do with a restriction for a non-degenerate system [19-23]. In one method, there are two Hamiltonians H_1 and H_2 with two external potentials V_1 and V_2 , which lead to the same ground-state density n_0 , so the Schrödinger equations can be written as:

$$H_1 \varphi_1 = E_1 \varphi_1$$

$$H_2 \varphi_2 = E_2 \varphi_2 \tag{2.7}$$

For non-degenerate systems, the wavefunction φ_2 is not the ground state of H_1 and it can be shown:

$$\langle \varphi_1 | H_1 | \varphi_1 \rangle < \langle \varphi_2 | H_1 | \varphi_2 \rangle \tag{2.8}$$

We can expand the right side of (2.8) producing eigenvalues E_2 of H_2 and the external potentials V_1 and V_2 .

$$\langle \varphi_2 | H_1 | \varphi_2 \rangle = \langle \varphi_2 | H_2 | \varphi_2 \rangle + \langle \varphi_2 | H_1 - H_2 | \varphi_2 \rangle$$
$$= E_2 + \int [V_1(\mathbf{r}) - V_2(\mathbf{r})] n_0(\mathbf{r}) d^3 \mathbf{r}$$
(2.9)

Again, we do the same procedure with $\langle \varphi_2 | H_2 | \varphi_2 \rangle$ and then substitute them back in equation (2.8) to get:

$$E_{1} < E_{2} + \int [V_{1}(\mathbf{r}) - V_{2}(\mathbf{r})]n_{0}(\mathbf{r})d^{3}\mathbf{r}$$

$$E_{2} < E_{1} + \int [V_{2}(\mathbf{r}) - V_{1}(\mathbf{r})]n_{0}(\mathbf{r})d^{3}\mathbf{r}$$
(2.10)

By summing the final expressions of (2.10), we are going to have contradicting inequality $E_1 + E_2 < E_1 + E_2$ which illustrates that there are no external potentials with various values for no

more than only one constant. Thus, we will have the same non-degenerate ground-state value of the density, and the external potentials are determined by a unique ground-state density.

Then the second method can be described as the previous one that corresponds to the minimization of a total energy functional [24]. Thus, a functional E[n(r)] is defined to be a way of mapping a function n(r) into a single value E [25]. As it has been described before, the density can uniquely present the external potential that corresponds to the Hamiltonian, which is applied to the wavefunction to solve the Schrödinger equation of the system. Thus, the wavefunction is a functional of the density, which leads to defining the expectation value E of the Hamiltonian is also to be a functional of the density.

$$\langle \Psi[\mathbf{n}]|H_e|\Psi[\mathbf{n}]\rangle = \langle \Psi[\mathbf{n}]|T|\Psi[\mathbf{n}]\rangle + \langle \Psi[\mathbf{n}]|V_{int}|\Psi[\mathbf{n}]\rangle$$
(2.11)

Hence, the variational principle can be applied to find the ground-state energy and to minimise the expected value of the effective electron Hamiltonian H_e with the wavefunctions that can be written as:

$$E[n] = (\langle \Psi | H_e | \Psi \rangle)_{min_{\Psi}}$$

$$= \left(\langle \Psi | T | \Psi \rangle + \langle \Psi | V_{int} | \Psi \rangle + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d^3 \mathbf{r} \right)_{min_{n}|\Psi}$$
$$= \left(T[n] + E_{int}[n] + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d^3 \mathbf{r} \right)_{min_{n}|\Psi}$$
$$= (E[n])_{min_{n}|\Psi}$$
(2.12)

The first two terms in equation (2.12) consist of the kinetic energy T[n] and the electronelectron interaction energy functional $E_{int}[n]$. Therefore, the density of the system is considered to reach a minimum, which is equivalent to the wavefunction Ψ in the system. In other words, if the density functional does not approach the ground-state, then the wavefunction cannot be the ground-state wavefunction and the expectation value is not considered to be corresponding to the ground-state energy of the system.

2.5 Kohn-Sham Method and Self-Consistent Field

The density functional theory (DFT) is based on the Kohn-Sham formalism [31], which involves an effective potential $V_{eff}(r)$ that plays an important role in solving a non-interacting system. We can represent the energy functional of a non-interacting system by introducing the non-interacting kinetic energy functional $T_{KS}[n]$. Thus, the non-interacting system energy functional can be written as:

$$E_{non}[n(\mathbf{r})] = T_{KS}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d^3\mathbf{r}$$
(2.13)

The main purpose is to reach the minimum energy functional of the ground-state density, as the Hohenberg-Kohn theories predict that the functional $E_{non}[n(\mathbf{r})]$ is zero when it is derived over the state density $\delta/\delta n(\mathbf{r})$ [26]. To be able to minimise the equation (2.13), the density functional needs to be normalized to the number of electrons under the extra constraint as:

$$N = \int n(\mathbf{r}) d^3 \mathbf{r} \tag{2.14}$$

To write the full energy functional of the ansatz Kohn-Sham $E_{KS}[n]$ of the whole interacting system that contains the kinetic energy functional of the non-interacting system and the electron-electron interaction term, which are the Hartree functional E_H , and the exchangecorrelation functional E_{xc} which can be expressed as:

$$E_{KS}[n] = T_{KS}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d^{3}\mathbf{r} + E_{H}[n] + E_{xc}[n]$$
(2.15)

The Hartree functional $E_H[n]$ represents the electron self-interaction of the Hartree potential:

$$E_{H}[n] = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{4\pi\epsilon_{0}|\mathbf{r} - \mathbf{r}'|} d^{3}\mathbf{r} d^{3}\mathbf{r}'$$
(2.16)

The functional of exchange-correlation $E_{xc}[n]$ contains the interacting kinetic energy for many-body interactions, and it can be reduced for non-interacting systems. We can minimise the functional by taking the derivative of alternative functionals that contain many-body interactions as written:

$$E_{xc}[n] = (T[n] - T_{KS}[n]) + (E_{int}[n] - E_H[n])$$
(2.17)

The Kohn-Sham potential V_{KS} can be presented as non-interacting system and can be written as:

$$V_{KS}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}' + V_{xc}(\mathbf{r}) + V_{ext}(\mathbf{r})$$
(2.18)

In addition, the single electron potential is affected by the many-body interactions. By understanding the Kohn-Sham formalism with the exact known of the exchange-correlation functional can lead us for the ground-state density as a result of the Hohenberg-Kohn theorems. Therefore, the previous prosses can be illustrated by the use of the self-consistent cycle in Figure 2.1.


Figure 2.1 A schematic of the DFT self-consistent cycle.

As a condition of solving the total energy functional, the density has to be known, in addition to the Hamiltonian of the electron. Hence, by diagonalising the Hamiltonian, we can solve the eigenvectors of the system, which can be turned back to solve the density. Therefore, we can simplify the problem of many-body systems into non-interacting systems by involving the Kohn-Sham method and also knowing the functional of exchange-correlation. The accuracy of the calculations appears only in finding the eigenfunctions and ground states of energies and densities.

2.6 The Exchange-Correlation Functionals

The exchange-correlation functional $E_{xc}[n]$ Includes all the interactions of many-body electrons and potentials in the calculations and provides an accurate approximation that reasonably describes the empirical data. There are a variety of approximations, that can be used for different purposes in molecular calculations as a fruitful choice for accuracy such as the local density approximation (LDA) and the generalized gradient approximation (GGA) where the exchange-correlation functional lies only on the density at the former and depends on the gradient and also density at the latter with some degrees of differences in the accuracy [26-29].

The exchange-correlation functional can be expressed as:

$$E_{xc}[n] = \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \frac{1}{2} \frac{n(\mathbf{r}) \bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
(2.19)

The exchange-correlation energy arises from the electrostatic interaction between every electron and the coupling constant of the averaged exchange-correlation hole located around it. We mean the hole because it is generated by three factors:

- I) Pauli exclusion principle.
- II) The unphysical self-interaction correction since an electron cannot interact with itself.
- III) Coulomb repulsion.

The first two effects contribute to the exchange, while the third one deals with the correction.

2.7 SIESTA

In this thesis, my calculations are based on applying Spanish Initiative for Electronic Simulation with Thousands of Atoms (SIESTA) [35], which is a numerical code used to compute various electronic structures. SIESTA can be applied to simulate a large system

consisting of thousands of atoms and perform many methods and parameters, such as normconserving pseudopotentials, a linear combination of atomic orbitals (LCAO) basis, and a periodic supercell.

The SIESTA code allows us to apply different types of basis set functions in computational calculations. Thus, the self-consistent cycle optimises the basis set and requires the Hamiltonian to be diagonalized to generate the wavefunctions of the system. A single- ξ (SZ) basis set is the simplest set in the SEISTA code for calculating a single basis function $\varphi_{nlm}(\mathbf{r})$ per electron orbital in an atom. In this thesis, I have mainly applied the double- ξ polarised (DZP) basis set along with double- ξ (DZ) basis set for the electrodes [43,44].

2.9 Pseudopotentials

Pseudopotentials play a significant role in removing the effect of core electrons from atoms. The first introduction of pseudopotentials was established by Fermi in 1934, and then they have been applied in methods to generate non-realistic experimental pseudopotentials to create realistic ab initio pseudopotentials [36-39]. Typically, electrons are considered to be core electrons and valence electrons, where the core ones are located in the shells of atoms, and the valence electrons lie on the partially filled orbitals of atoms. Thus, the valence electron states can make an overlap as atoms become close together, and they correspond to the formation of the molecular orbitals between atoms, whereas the core electrons are localised around the nucleus. By applying a pseudopotential, the core electron can be considered replaced, and the valence electrons can test the same charge of the nucleon. All of that will assist us in decreasing the number of electrons included in the system to reduce the required time and memory for calculations.

The SIESTA code consists of an ab initio pseudopotential, which is called a 'norm-conserving pseudopotential' to study the properties of molecules [40]. Hence, to start with, wavefunctions of all electrons (AE) in the valence levels of isolated atoms are written as a product of the radial and spherical wavefunctions $\varphi_{nlm}^{AE}(\mathbf{r}) = R_{nl}^{AE}(\mathbf{r})Y_{lm}(\mathbf{r})$ respectively. The solution of the radial Schrödinger equation is the radial wavefunction R_{nl}^{AE} which includes 'All-Electron' (AE) potential V_{nl}^{AE} which consists of all electron interactions in the atom. SIESTA uses the Troullier-Martins method to define the pseudo-wavefunction [41,42].

Thus, five rules are controlled by the radial pseudo-wavefunction due to classifying the resulting pseudopotential as a norm-conserving:

1. For larger values of the cut-off radius (r_c) all-electron (AE) wavefunctions and the pseudo-wavefunction (PP) have to be equal as:

$$R_{nl}^{PP}(r > r_c) = R_{nl}^{AE}(r > r_c)$$
(2.20)

- 2. To generate a smooth pseudopotential, the pseudo-wavefunction is required to be nodeless and smooth so that it can be produced as R_{nl}^{PP} and the first four derivatives of it should be continuous at the cut-off radius r_c .
- 3. The eigenvalues of the pseudo-wavefunction and all-electron wavefunctions have to be identical as:

$$\varepsilon_{nl}^{PP} = \varepsilon_{nl}^{AE} \tag{2.21}$$

4. For the norm conservation, the total charge which is enclosed inside the range of the cut-off radius (r_c) has to be equivalent for both pseudo-wavefunctions (PP) and all-electron (AE) wavefunctions as:

$$\int_{0}^{r_{c}} |R_{nl}^{PP}(r)|^{2} r^{2} dr = \int_{0}^{r_{c}} |R_{nl}^{AE}(r)|^{2} r^{2} dr$$
(2.22)

If the previous conditions are applied and satisfied, the resulting pseudopotential 'the screened pseudopotential' will be nodeless and smooth in order to get convergence of calculations [42].

2.8.1 Local Density Approximation (LDA)

This approximation of the exchange-correlation was presented by Kohn-Sham [31]. Since the relatively slow change in the density of the exchange-correlation hole, it can be approximated by depending only on the local density $n(\mathbf{r})$. Therefore, the functional can be defined as the energy functional per electron in a homogeneous electron gas (HEG) $\epsilon_{xc}[n(\mathbf{r})]$ with a local density $n(\mathbf{r})$.

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int n(\mathbf{r})\epsilon_{xc}^{LDA}[n(\mathbf{r})]d^3\mathbf{r}$$
(2.23)

Where ϵ_{xc} is a sum of the exchange ϵ_x and the correlation ϵ_c energies [32].

The correlation functional needed to be parametrised first and then applied to the Monte-Carlo simulations for various densities. The well-known accurate results are presented by the Ceperley-Ander [33] and Perdew-Zunger [34] parameterisations. LDA has a disadvantage, which is the self-interaction error due to the one-electron self-interacting term that is partially cancelled, so it is not like the Hartree-Fock theory, where the electron self-potential is cancelled out in the calculations.

2.8.2 Generalized Gradient Approximation (GGA)

By constructing a gradient expansion, considering isotropy conditions, and ensuring that the exchange-correlation holes are controlled by their respective normalised conditions, this approach has been undertaken by various research groups, with notable functionals developed by Perdew in 1986 [51,52], and Wang in 1991 [53]. These exchange-correlation functionals fall under the category of generalized gradient approximations (GGAs).

Essentially, GGA enhances the treatment of quantities already well-handled by LDA, such as total energies, binding energies, and geometries of the system. In general, Kohn-Sham ionization energies are comparable between GGA and LDA. In common, LDA overestimates correlation energy and underestimates exchange energy, whereas GGA illustrates these differences to a specific limit. However, since these corrections have opposing effects, the overall impact is not remarkably valuable [54-56].

$$E_{xc}^{GGA}[n(\mathbf{r})] = \int n(\mathbf{r})\epsilon_{xc}^{GGA}[n(\mathbf{r}), |\nabla n(\mathbf{r})|]d^3\mathbf{r}$$
(2.24)

2.10 Counterpoise Correction Method

SIESTA code provides a basis set superposition error (BSSE) due to the localised basis sets, as quantum chemistry computations can apply finite basis sets that are volatile to BSSE. The overlap occurs when molecule atoms interact with each other through the system, which allows their basis set functions to interact. The accuracy of the calculations increases when molecules reach their minimum energy related to their geometry optimisations. However, involving a long-range energy with a short-range energy can produce an error in calculations.

For the BSSE to be corrected in the SIESTA code, the counterpoise correction method is involved, which was investigated by Boys and Bernardi in 1970 [45,46]. This technique utilises the total interaction energy of the molecular system and subtracts its contribution from the basis set overlaps. By considering two molecular systems A and B interacting and separated by a distance r. Thus, the total energy of the combined system can be written as [47]:

$$\Delta E_{total}^{AB}\left(\boldsymbol{r}\right) = E_{AB}^{AB} - E_{AB}^{A} - E_{AB}^{B} \tag{2.25}$$

Where E_{AB}^{AB} is the energy of the combined molecules and E_{AB}^{A} and E_{AB}^{B} are the energies of the isolated molecules. Hence, we can express the binding energy (BE) of this system as [50]:

$$BE = E_{AB}^{AB} - (E_{AB}^{A} + E_{AB}^{B})$$
(2.26)



Figure 2.3. A schematic configuration of the counterpoise correction (CP) method to find the binding energy (BE), where (I) displays the basis function of the entire system. (II) and (III) represent the basis functions for the individual system. Meanwhile, parts (IV) and (V) illustrate the ghost states (blue atoms) by applying the counterpoise correction, where every single molecule is involved for the same basis functions of the total system in part (I) [48].

Figure 2.3 shows the five parts of the interactions between basis sets of molecules by presenting the ghost atoms whose basis set functions do not include electrons or protons in the simulations. The counterpoise correction technique can improve the accuracy of the basis set functions by decreasing the basis set superposition error (BSSE) in the computational systems [46-49].

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Chapter 3

Quantum Theory of a Single-Particle Transport

3.1 Introduction

In the previous chapter, I introduced the density functional theory (DFT) and the SIESTA code as the first step to calculating the electronic properties of an isolated molecular system. To solve the Schrödinger equation for an open system connected to semi-infinite electrodes, I shall now discuss Green's function scattering formalism, which is utilised in later calculations. To illustrate the formalism of the fundamental concepts, I shall illustrate Green's function of a one-dimensional tight-binding (TB) chain and show how scattering arises in a one-dimensional chain whose periodicity is broken by a single defect. Then, I shall show the surface Green's function for infinite and finite periodic systems and introduce the idea of the transmission coefficient associated with a scattering region. Lastly, the Landauer Formula for electrical conductance and thermoelectric coefficients will be addressed.

3.2 Green's Function Method

To illustrate the Green's function formalism, first of all, I shall provide a simple example of a doubly infinite one-dimensional chain, with identical on-site energies ε_0 and coupling parameters $-\gamma$ between them as shown in Figure 3.1.



Figure 3.1. A doubly infinite one-dimensional (1D) chain of identical sites ε_0 linked with identical couplings $-\gamma$.

The Schrödinger equation is:

$$H|\Phi\rangle = E|\Phi\rangle$$

(E - H)| $\Phi\rangle = 0$ (3.1)

where the tight-binding (TB) Hamiltonian H of the system can be expressed as:

$$H = \begin{pmatrix} \ddots & -\gamma & 0 & 0\\ -\gamma & \varepsilon_0 & -\gamma & 0\\ 0 & -\gamma & \varepsilon_0 & -\gamma\\ 0 & 0 & -\gamma & \ddots \end{pmatrix}$$
(3.2)

Thus, the Schrödinger equation (3.1) can be expanded for the site z in terms of the energy E and wavefunction $|\Phi_z\rangle$ as:

$$\varepsilon_0 |\Phi_z\rangle - \gamma |\Phi_{z-1}\rangle - \gamma |\Phi_{z+1}\rangle = E |\Phi_z\rangle \tag{3.3}$$

Therefore, the wavefunction can be written in the Bloch state for a perfect system as:

$$|\Phi_z\rangle = \frac{1}{\sqrt{\nu}} e^{ikz} |z\rangle \tag{3.4}$$

where v is the group velocity, and k is a wavenumber. If we insert (3.4) into the equation (3.3), we obtain the following 'dispersion relation'.

$$E = \varepsilon_0 - 2\gamma \cos\left(k\right) \tag{3.5}$$

In contrast with (3.1), the retarded Green's function g(z, z') is defined to satisfy:

$$(E - H)g(z, z') = \delta_{z, z'} , \qquad \delta_{z, z'} = \begin{cases} 1 & \text{if } z = z' \\ 0 & \text{if } z \neq z' \end{cases}$$
(3.6)

where $\delta_{z,z'}$ is the Kronecker delta.

The retarded Green's function g(z, z') provides a wave function at z direction and caused by an excitation state at a point z'. One finds that the retarded Green's function for the infinite one-dimensional chain can be written as [1]:

$$g(z,z') = \frac{1}{i\hbar\nu} e^{ik|z-z'|}$$
(3.7)

where the group velocity v can be obtained from the dispersion equation (3.3) as:

$$v = \frac{1}{\hbar} \frac{\partial E(k)}{\partial k} = 2\gamma \sin(k)$$
(3.8)

From (3.5), we also note that the energies of electrons in the one-dimensional chain are restricted to the energy bands $\varepsilon_0 - 2\gamma$ and $\varepsilon_0 + 2\gamma$.

3.3 A One-Dimensional Scattering System

In this section, to find the entire Green's function for a system that consists of a double-infinite one-dimensional chain, with an impurity coupling energy $(-\Gamma)$ and identical on-site energies (ε_0) , and hopping elements $(-\gamma)$ that appear in Figure 3.2 below.



Figure 3.2. A double-infinite one-dimensional (1D) chain with identical on-site energies ε_0 and couplings $-\gamma$, and an impurity coupling energy $-\Gamma$.

The Hamiltonian of this infinite system can be written as:

$$H = \begin{pmatrix} \ddots & \ddots & 0 & 0 & 0 & 0 \\ \ddots & \varepsilon_0 & -\gamma & 0 & 0 & 0 \\ 0 & -\gamma & \varepsilon_0 & -\Gamma & 0 & 0 \\ 0 & 0 & -\Gamma & \varepsilon_0 & -\gamma & 0 \\ 0 & 0 & 0 & -\gamma & \varepsilon_0 & \ddots \\ 0 & 0 & 0 & 0 & \ddots & \ddots \end{pmatrix} = \begin{pmatrix} H_L & V_c \\ V_c^{\dagger} & H_R \end{pmatrix}$$
(3.9)

Where H_L and H_R are the Hamiltonians of the left and right electrodes, and the coupling is V_c . Therefore, to obtain the Green's function of this system:

$$G = (E - H)^{-1} \tag{3.10}$$

Now, for the case of decoupled electrodes ($-\Gamma = 0$), the new Green's function of both sides of semi-infinite electrodes is found by the decoupled Green's function *g* of the infinite 1-D chain in a matrix as:

$$g = \begin{pmatrix} g_L & 0\\ 0 & g_R \end{pmatrix} = \begin{pmatrix} -\frac{e^{ik}}{\gamma} & 0\\ 0 & -\frac{e^{ik}}{\gamma} \end{pmatrix}$$
(3.11)

By turning on the interaction, the Green's function for the coupled electrodes with the utility of Dyson's equation as:

$$G = (g^{-1} - V)^{-1} \tag{3.12}$$

The perturbation operator V is expressed as:

$$V = \begin{pmatrix} 0 & -\Gamma \\ -\Gamma & 0 \end{pmatrix}$$
(3.13)

By the utility of Dyson's equation, we can find the Green's function of this system:

$$G = \frac{1}{\gamma^2 e^{-2ik} - \Gamma^2} \begin{pmatrix} \gamma e^{-ik} & \Gamma \\ \Gamma & \gamma e^{-ik} \end{pmatrix}$$
(3.14)

The next step is to calculate the transmission (t') and the reflection (r') coefficients of a scattering region, the Fisher-Lee relations are employed. Hence, we can yield the reflection (r) the transmission (t) amplitudes respectively as:

$$r = i\hbar v G(0,0) - 1 \tag{3.15}$$

$$t = i\hbar v G(0, N+1)e^{ik}$$
(3.16)

However, the quantities r and t are not considered observable due to the complex values. Therefore, by taking the modulus squared of both r and t, we can find the observable coefficients $R = |r|^2$ and $T = |t|^2$. For instance, in a system consisting of a single channel, there are probabilities $T \le 1$ and $R \ge 0$ that are defined in the unitary S-matrix condition as [2]:

$$T + R = 1 \tag{3.17}$$

3.4 An Infinite Periodic System

In this section, I shall describe a general infinite periodic electrode by modelling a tight-binding (TB) method, which can be extended periodically along the *z* direction containing two parts of the intra-Hamiltonian H_0 and inter-Hamiltonian H_1 elements as shown in Figure 3.3.



Figure 3.3. A schematic configuration of an infinite periodic electrode consists of intra-Hamiltonian H_0 and inter-Hamiltonian H_1 elements.

In this case, the total Hamiltonian of the infinite periodic system can be illustrated as a blocktridiagonal matrix *H* by considering only the neighbour interactions between cells.

$$H = \begin{pmatrix} \ddots & \ddots & 0 & 0 & 0 & 0 \\ \ddots & H_0 & H_1 & 0 & 0 & 0 \\ 0 & H_1^{\dagger} & H_0 & H_1 & 0 & 0 \\ 0 & 0 & H_1^{\dagger} & H_0 & H_1 & 0 \\ 0 & 0 & 0 & H_1^{\dagger} & H_0 & \ddots \\ 0 & 0 & 0 & 0 & \ddots & \ddots \end{pmatrix}$$
(3.19)

Then we can write the Schrödinger equation in terms of the energy and the wavefunction of the system:

$$H_0|\Phi_z\rangle + H_1|\Phi_{z+1}\rangle + H_1^{\dagger}|\Phi_{z-1}\rangle = E|\Phi_z\rangle$$
(3.20)

The considered system is finite in both x and y directions except the z direction, which is the only infinitely periodic. Thus, the on-site wavefunction $|\Phi_z\rangle$ can be written in Bloch's state, which is the product of a propagating plane wave and a wavefunction $|\phi_k\rangle$ in the perpendicular movement to pass. The wavefunction $|\phi_k\rangle$ is a normalised m-component column vector consisting of *m* degree of freedom and corresponding to a $1 \times J$ dimensional vector.

$$|\Phi_z\rangle = \frac{1}{\sqrt{v_k}} e^{ikz} |\varphi_k\rangle \tag{3.21}$$

By substituting equation (3.20) into (3.21), the Schrödinger equation can be modified and left with $\xi = e^{ik}$ since the dependence on z position vanishes.

$$\left(H_0 + H_1 \xi + H_1^{\dagger} \xi^{-1}\right) |\varphi_k\rangle = E |\varphi_k\rangle \tag{3.22}$$

For the band-theory structure, the Hamiltonian on the left-hand side of (3.22) is diagonalised for provided values of k to obtain m number of energy eigenvalues E(k) and the corresponding set of eigenvectors $\{|\varphi_k\rangle\}$. We can rewrite the equation (3.22) in a new form by applying an opposite method for a given value of E(k) and all the complex values of k will be determined and the values of ξ will be found.

$$\left[-H_{1}^{-1}(H_{0}-E)-\xi-H_{1}^{-1}H_{1}^{\dagger}\xi^{-1}\right]|\phi_{k}\rangle = \xi|\phi_{k}\rangle$$
(3.23)

We can assume that $|\Omega_k\rangle = \xi^{-1} |\varphi_k\rangle$ and substitute it into equation (3.23) to be an equivalent eigenvalue as:

$$\begin{pmatrix} -H_1^{-1}(H_0 - E) & -H_1^{-1}H_1^{\dagger} \\ I & 0 \end{pmatrix} \begin{pmatrix} |\varphi_k\rangle \\ |\Omega_k\rangle \end{pmatrix} = \xi \begin{pmatrix} |\varphi_k\rangle \\ |\Omega_k\rangle \end{pmatrix}$$
(3.24)

The solution of equation (3.24) provides a set of 2*J* eigenvalues and the identified wavefunctions $|\varphi_k\rangle$ which are considered as the top *J* components of eigenvectors.

For the Hermitian matrix H_0 , we can describe the eigenvalues for four cases of two sets: the first set is right-moving and decaying plane waves as $z \to \infty$ and the second set is left-moving and decaying plane waves as $z \to -\infty$. Consequently, the left and right-moving states depend on the real values of k, whereas the decaying states relate to the complex values of k for $z \to \pm \infty$. For the real values of k, two solutions correspond to the right k and left \tilde{k} propagating states which either take a positive v_+ or negative v_- group velocities respectively. The real k-vectors describe open scattering channels, as in the case when $k = -\tilde{k}$. Hence, the channel velocities can be written as:

$$v_{+} = \frac{1}{\hbar} \frac{\partial E(k)}{\partial k} > 0 \tag{3.25}$$

$$v_{-} = \frac{1}{\hbar} \frac{\partial E(\tilde{k})}{\partial \tilde{k}} < 0 \tag{3.26}$$

For the complex solutions of k, we can consider two pairs of solutions k and also k^* , whereas there are two possible sets of $\{k_R\}$, and $\{\tilde{k}_L\}$ representing the right or left moving/decaying states respectively.

Now, we can define a general Green's function for the infinitely periodic system as:

$$g(z, z') = \begin{cases} \sum_{l=1}^{J} |\varphi_{k_l}\rangle e^{ik_l(z-z')} \langle M_{k_l}| & z \ge z' \\ \sum_{l=1}^{J} |\varphi_{\tilde{k}_l}\rangle e^{i\tilde{k}_l(z-z')} \langle M_{\tilde{k}_l}| & z \le z' \end{cases}$$
(3.27)

The equation (3.36) represents Green's function, which corresponds to the wavefunction of the system, where its vectors are $\langle M_{k_l} |$, and $\langle M_{\tilde{k}_l} |$ which must be determined. At the point z = z' the Green's function is continuous, which leads us to the continuity condition as:

$$\sum_{l=1}^{J} |\varphi_{k_l}\rangle \langle \mathsf{M}_{k_l}| = \sum_{l=1}^{J} |\varphi_{\tilde{k}_l}\rangle \langle M_{\tilde{k}_l}|$$
(3.28)

We can introduce the defined equation of Green's function for the closest cell where interactions take place at a point z to be written as:

$$(E - H_0)g(z, z') + H_1g(z, z+1) + H_1^{\dagger}g(z, z-1) = I$$
(3.29)

$$\sum_{l=1}^{J} \left[(E - H_0) |\varphi_{k_l}\rangle \langle M_{k_l}| + H_1 |\varphi_{k_l}\rangle e^{ik_l} \langle M_{k_l}| + H_1^{\dagger} |\varphi_{\tilde{k}_l}\rangle e^{-i\tilde{k}_l} \langle M_{\tilde{k}_l}| \right] = I$$
(3.30)

In the normal band structure calculations, the wavefunctions are chosen to be functions of k and are orthogonal to each other. Nevertheless, the wavefunctions linked to different selections of wavevectors k cannot always be orthogonal because the operator on the left side of equation (3.22) does not interact with itself for different values of ξ . Subsequently, to find the solutions of (3.24) for a fixed energy, we need to choose various nonorthogonal wavevectors k. Thus, a dual basis set can be applied $\{|\tilde{\varphi}_{k_l}\rangle\}$ which is orthogonal to the basis $\{|\varphi_{k_l}\rangle\}$ and they both form a complete basis in the Hilbert space.

$$\left\langle \varphi_{\tilde{k}_{l}} \middle| \tilde{\varphi}_{\tilde{k}_{j}} \right\rangle = \delta_{\tilde{k}_{l}\tilde{k}_{j}}, \quad \sum_{l=1}^{J} |\varphi_{\tilde{k}_{l}}\rangle \left\langle \tilde{\varphi}_{\tilde{k}_{l}} \right| = I$$

$$\left\langle \varphi_{k_{l}} \middle| \tilde{\varphi}_{k_{j}} \right\rangle = \delta_{k_{l}k_{j}}, \quad \sum_{l=1}^{J} |\varphi_{k_{l}}\rangle \left\langle \tilde{\varphi}_{k_{l}} \right| = I$$

$$(3.31)$$

We can define the dual basis and then express the vectors $\langle M_{k_l} |$, and $\langle M_{\tilde{k}_l} |$ as a superposition of each other as:

$$\langle M_{k_l}| = \sum_{j=1}^{J} \left\langle \tilde{\varphi}_{k_l} \middle| \varphi_{\tilde{k}_j} \right\rangle \left\langle M_{\tilde{k}_j} \right|$$
(3.33)

$$\left\langle M_{\tilde{k}_{l}}\right| = \sum_{j=1}^{J} \left\langle \tilde{\varphi}_{\tilde{k}_{l}} \middle| \varphi_{k_{j}} \right\rangle \left\langle M_{k_{j}}\right|$$
(3.34)

We then substitute the previous equations into (3.30), and then simplify it to be able to represent both vectors $\langle M_{k_l} |$, and $\langle M_{\tilde{k}_l} |$ in terms of the basis set and the dual basis functions.

$$\left\langle M_{k_{l}}\right| = \sum_{j=1}^{J} \left\langle \tilde{\varphi}_{k_{j}} \right| \Lambda^{-1}$$
(3.35)

$$\langle M_{\tilde{k}_l} | = \sum_{j=1}^J \left\langle \tilde{\varphi}_{\tilde{k}_j} \right| \Lambda^{-1}$$
(3.36)

Where Λ^{-1} is expressed as:

$$\Lambda^{-1} = \sum_{l=1}^{J} H_{1}^{-1} \left(\left| \varphi_{k_{l}} \right\rangle e^{-ik_{l}} \left\langle \tilde{\varphi}_{k_{l}} \right| - \left| \varphi_{\tilde{k}_{l}} \right\rangle e^{-i\tilde{k}_{l}} \left\langle \tilde{\varphi}_{\tilde{k}_{l}} \right| \right)$$
(3.37)

By substituting the vectors $|M\rangle$ back into the equation (3.27), then we can rewrite the Green's function of the infinite periodic system as:

$$g(z,z') = \begin{cases} \sum_{l=1}^{J} |\varphi_{k_l}\rangle e^{ik_l(z-z')} \langle \tilde{\varphi}_{k_l} | \Lambda^{-1} & z \ge z' \\ \sum_{l=1}^{J} |\varphi_{\tilde{k}_l}\rangle e^{i\tilde{k}_l(z-z')} \langle \tilde{\varphi}_{\tilde{k}_l} | \Lambda^{-1} & z \le z' \end{cases}$$
(3.38)

3.5 A Semi-Infinite Periodic System

In this section, the construction of Green's function of the left and right semi-infinite periodic systems will be presented. We can derive the one-dimensional semi-infinite Green's function from the infinite Green's function system. First, the left electrode is defined to be a periodic system from the extended value $z = -\infty$ to the last Hamiltonian cell at $z = z_0 - 1$ whereas the right electrode is defined as the extending periodic system from $z = +\infty$ to the last Hamiltonian cell at $z = z_0 + 1$ as shown in Figure 3.4 below. Therefore, these boundary conditions constrain the left and right electrodes Green's function to be zero at the point $z = z_0$ as:

$$g_L(z_0, z_0) = g_R(z_0, z_0) = 0$$
(3.39)

For the previous constraints to be obeyed, a wavefunction is added to the Green's function g (3.38).



Figure 3.4. A schematic configuration of a periodic system consists of intra-Hamiltonian H_0 and inter-Hamiltonian H_1 elements.

To start with the left electrode, we assume adding a left-moving wavefunction of the amplitude $\Upsilon_L(z', z_0)$.

$$g_{L}(z,z') = g(z,z') + \sum_{l=1}^{J} |\varphi_{\tilde{k}_{l}}\rangle e^{i\tilde{k}_{l}z} \Upsilon_{L}(z',z_{0})$$
(3.40)

Then we can find the amplitude when the constraint (3.39) is applied at the point $z = z_0$.

$$\sum_{l=1}^{J} |\varphi_{k_l}\rangle e^{i\tilde{k}_l(z_0 - z')} \langle \tilde{\varphi}_{k_l} | \Lambda^{-1} + \sum_{l=1}^{J} |\varphi_{\tilde{k}_l}\rangle e^{i\tilde{k}_l z} \Upsilon_L = 0$$
(3.41)

Hence,

$$\Upsilon_{L} = -\sum_{j=1}^{J} e^{-i\tilde{k}_{l}z_{0}} \left\langle \tilde{\varphi}_{\tilde{k}_{j}} \middle| \varphi_{k_{l}} \right\rangle e^{ik_{l}(z_{0}-z')} \left\langle \tilde{\varphi}_{k_{l}} \middle| \Lambda^{-1} \right\rangle$$
(3.42)

Therefore, we can substitute (3.42) into equation (3.40) to obtain the Green's function of the left semi-infinite electrode as:

$$g_{L}(z,z') = \left[\sum_{l=1}^{J} |\varphi_{k_{l}}\rangle e^{ik_{l}(z-z')} \langle \tilde{\varphi}_{k_{l}} | -\sum_{l,j}^{J} |\varphi_{\tilde{k}_{l}}\rangle e^{i\tilde{k}_{l}(z-z_{0})} \langle \tilde{\varphi}_{\tilde{k}_{j}} | \varphi_{k_{l}} \rangle e^{ik_{l}(z_{0}-z')} \langle \tilde{\varphi}_{k_{l}} | \right] \Lambda^{-1}$$
(3.43)

Now, we can do the same process for the right electrode by applying the right-moving wavefunction to get the Green's function as:

$$g_{R}(z,z') = \left[\sum_{l=1}^{J} |\varphi_{\tilde{k}_{l}}\rangle e^{i\tilde{k}_{l}(z-z')} \langle \tilde{\varphi}_{\tilde{k}_{l}} | -\sum_{l,j}^{J} |\varphi_{k_{l}}\rangle e^{ik_{l}(z-z_{0})} \langle \tilde{\varphi}_{k_{j}} | \varphi_{\tilde{k}_{l}} \rangle e^{i\tilde{k}_{l}(z_{0}-z')} \langle \tilde{\varphi}_{\tilde{k}_{l}} | \right] \Lambda^{-1}$$
(3.44)

To introduce the evaluated surface Green's function for every endpoint ($z_0 = z = z'$) of both side electrodes, the completeness relations (3.31) and (3.32) are applied.

$$g_{L}^{S} = \left(I - \sum_{l,j}^{J} |\varphi_{\tilde{k}_{j}}\rangle e^{-i\tilde{k}_{j}} \langle \tilde{\varphi}_{\tilde{k}_{j}} ||\varphi_{k_{l}}\rangle e^{ik_{l}} \langle \tilde{\varphi}_{k_{l}} |\right) \Lambda^{-1}$$
(3.45)

$$g_R^S = \left(I - \sum_{l,j}^J |\varphi_{k_j}\rangle e^{ik_j} \langle \tilde{\varphi}_{k_j} | |\varphi_{\tilde{k}_l}\rangle e^{-i\tilde{k}_l} \langle \tilde{\varphi}_{\tilde{k}_l} | \right) \Lambda^{-1}$$
(3.46)

Finally, we have a convenient way of applying the numerical method in equation (3.33) in order to calculate the surface Green's functions in equations (3.43) and (3.44) for a semi-infinite system. In the next section, we will apply the same technique for treating a scattering problem to calculate the transmission coefficient T(E).

3.6 Transmission Coefficient of a Scattering Region

Now we can define a structure of the scattering region, as we have already illustrated the semiinfinite Green's functions. Let us consider a scattering region which is defined by the Hamiltonian H_{Sc} , and also linked to a left electrode by a coupling energy Γ_L , and connected at the right electrode by a coupling energy Γ_R , as shown in Figure 3.5.



Figure 3.5. A sketch of two semi-infinite periodic electrodes which consist of intra-Hamiltonian H_0 and inter-Hamiltonian H_1 elements and coupled to a scattering region with a scattering Hamiltonian H_{Sc} which coupled with coupling energies Γ_L , Γ_R .

By assuming zero values of the couplings Γ_L and Γ_R , the surface Green's function can be written as:

$$g = \begin{pmatrix} g_L^S & 0 & 0\\ 0 & (EI - H_{Sc})^{-1} & 0\\ 0 & 0 & g_R^S \end{pmatrix}$$
(3.47)

The Green's function of the isolated scatterer can be calculated by solving the Green's equation $(EI - H_{Sc})g_{Sc} = I$ and also, we can introduce the perturbation Γ which is related to the couplings to the scattering region:

$$\Gamma = \begin{pmatrix} 0 & \Gamma_L & 0\\ \Gamma_L^{\dagger} & 0 & \Gamma_R\\ 0 & \Gamma_R^{\dagger} & 0 \end{pmatrix}$$
(3.48)

Hence, we can include both equations (3.47) and (3.48) in Dyson's equation to computationally calculate the new Green's function *G* as [3]:

$$G = (g^{-1} - \Gamma^{-1})^{-1} \tag{3.49}$$

$$G = \begin{pmatrix} G_{00} & G_{0S} & G_{0N} \\ G_{S0} & G_{SS} & G_{SN} \\ G_{N0} & G_{NS} & G_{NN} \end{pmatrix}$$
(3.50)

The next process is to calculate the transmission t and reflection r coefficients by employing a projector operator $P_l(z')$ which projects the Green's function of the infinite periodic electrode (3.39) onto a normalised plane-wave moving along a channel l with k-value k_l .

$$\left[\sum_{j=1}^{J} |\varphi_{k_j}\rangle e^{ik_j(z-z')} \left\langle \tilde{\varphi}_{k_j} | \Lambda^{-1} \right] P_l(z') = \frac{1}{\sqrt{\nu_{k_l}}} |\varphi_{k_l}\rangle e^{ikz} \qquad z > z'$$
(3.51)

By employing the orthogonality of the dual basis from (3.31) and (3.32), the projector $P_l(z')$ can be written as:

$$P_{l}(z') = \begin{cases} \frac{1}{\sqrt{\nu_{l}}} \Lambda |\varphi_{k_{l}}\rangle e^{ik_{l}z'} & z > z' \\ \frac{1}{\sqrt{\nu_{l}}} \Lambda |\varphi_{\tilde{k}_{l}}\rangle e^{i\tilde{k}_{l}z'} & z < z' \end{cases}$$
(3.52)

The projector can produce a wavefunction from the Green's function G of the general scatterer in (3.50). The wavefunction on either side of the scattering region is complicated because the incident wave in the channel k_l can be transmitted or reflected in various channels $\{k_j\}$ and $\{\tilde{k}_j\}$ respectively. Thus, the wavefunction of the system can be obtained as:

$$|\Phi(z)\rangle = \begin{cases} \frac{1}{\sqrt{v_l}} |\varphi_{k_l}\rangle e^{ik_l z} + \sum_j \frac{r_{lj}}{\sqrt{v}} e^{i\tilde{k}_j z} |\varphi_{\tilde{k}_j}\rangle & z \le 0\\ \sum_j \frac{t_{lj}}{\sqrt{v_j}} e^{ik_j z} |\varphi_{k_j}\rangle & z \ge N \end{cases}$$
(3.53)

Now, from the equations (3.52) and (3.53), we can express the transmission and reflection coefficients in terms of the surface Green's function components (3.50).

$$t_{lj} = \sqrt{\frac{\nu_j}{\nu_l}} \left\langle \tilde{\varphi}_{k_j} \left| G_{0N} \Lambda \right| \varphi_{k_l} \right\rangle e^{-ik_j N}$$
(3.54)

$$r_{lj} = \sqrt{\frac{v_j}{v_l}} \left\langle \tilde{\varphi}_{\tilde{k}_j} \left| G_{00} \Lambda - \mathbf{I} \right| \tilde{\varphi}_{k_l} \right\rangle$$
(3.55)

Where the transmission coefficient t_{lj} describes a wave which scatters from a channel l with k-vector k_l to a right-moving channel j with k-vector k_j , and the reflection coefficient r_{lj} represents a wave which scatters from a channel l with k-vector k_l to a left-moving channel j with k-vector \tilde{k}_j . Thus, to calculate the transmission coefficient is to apply the appropriate projector to the total surface Green's function. Eventually, the crucial portion of our interest is the total observable transmission coefficient, which is the sum over all channels, as it can be written in terms of the trace of the transmission t [4]. Thus, we can write the transmission coefficient T(E).

$$T = \sum_{lj}^{J} |t_{lj}|^{2}$$
$$= \sum_{lj} t_{lj} t_{jl}^{*}$$
$$= Tr(tt^{\dagger})$$
(3.56)

Finally, we can sum up the key steps to calculate the transmission coefficient T(E):

- Using the SIESTA code to relax and optimise the geometry and energy of the isolated molecule.
- 2. Construct an extended molecule system and apply the SIESTA code to run DFT calculations to solve the Hamiltonian of the system.
- 3. Define the boundary layers of the scarring region and then extract the H_0 and H_1 of the electrodes to solve the left and right surface Green's function of the electrodes.

4. Connect the reduced extended molecule system to the surface Green's function by using Dyson's equation, then compute the transmission coefficients via the GOLLUM code.

In conclusion, this is the explanation of Green's function method, which is applied to calculate the transmission coefficients of a single-molecule junction in this thesis. Computationally, applying Green's function scattering approach with the potentially infinitely sized system can assist in reducing the complexity of the problem to a finite-sized system which can be calculated [5].

3.7 Landauer Formula

The Landauer formula provides an important relation between the transmission coefficient T(E)and the electrical current passing in a single-molecule system through the scattering region, as shown in Figure 3.6 [6]. The moving wavefunction is defined by a state of energy corresponding to the Fermi energy E_F^L of the left electrode at zero temperature. Furthermore, the right-moving current is described by many states with different energies defined by the Fermi distribution function $f_L(E - E_F^L)$, and also the same case with the right-moving current defined by the Fermi distribution function $f_R(E - E_F^R)$ at a finite temperature. According to Landauer, the electrical conductance G can be described in terms of a Fermi distribution function, which is defined by a common Fermi energy E_F , and the transmission coefficient T(E) in a low-bias regime [7-9].



Figure 3.6. An electron passing through an electrode-molecule-electrode junction at the Fermi energy E_F .

Thus, the current flowing from the left electrode to the right one is written as:

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} T(E) \left[f_L(E) - f_R(E) \right] dE$$
(3.57)

where e is electron charge, h is Planck's constant. The Fermi distribution f(E) is defined as:

$$f_{L,R}(E) = \frac{1}{[e^{(E-\mu_{L,R})/k_BT} + 1]}$$
(3.58)

where $\mu_{L,R}$ are the chemical potentials of the left and right reservoirs and the Boltzmann constant is $k_B = 8.62 \times 10^{-5} \ eV/K$, and *T* is the temperature. Hence, when the voltage is symmetrically employed, the chemical potentials are $\mu_L = E_F + \frac{eV}{2}$ and $\mu_R = E_F - \frac{eV}{2}$ respectively and then I = 0 as $f_L(E) = f_R(E)$. Thus, at finite voltage and absolute zero temperature, the current can be expressed as:

$$I = \frac{2e}{h} \int_{E_F - \frac{eV}{2}}^{E_F + \frac{eV}{2}} T(E) dE$$
(3.59)

The electrical conductance G at zero voltage and an ambient finite temperature range of $(k_b T \approx 25 \text{ meV})$ can be expressed as:

$$G = \frac{I}{V} = \frac{2e^2}{h} \int_{-\infty}^{\infty} T(E) \left(-\frac{\partial f(E)}{\partial E} \right) dE$$
(3.60)

where $\frac{\partial f(E)}{\partial E} = -\delta(E - E_F)$ is defined in the bias regime at zero temperature and represents a normalised probability distribution with a width close to $k_b T$. Thus, we can define the zero-bias conductance at the Fermi energy as:

$$G(E_F) = \left(\frac{2e^2}{h}\right)T(E_F) = G_0T(E_F)$$
(3.61)

where $G_0 \approx 77.5 \ \mu S$ is the quantum conductance. Employing a high bias on the system might alter the geometrical structures and energy levels of molecules. Thus, the systems I investigate are set to be in equilibrium conditions and equilibrium Green's function formalism, which are applied to my calculations via the GOLLUM code. For high-bias calculations, we can apply numerical codes such as SMEAGOL and TranSiesta, which contain the non-equilibrium Green's function formalism, which is not of interest [10-14].

3.8 Thermoelectric Coefficients

The thermoelectric properties depend on common physical quantities, i.e. heat, current, voltage and temperature, which are represented by the Thompson [15,16], Peltier effects [17], and Seebeck effects [18]. Since the 19th century, these effects have remained significant for describing the electrical currents. The Seebeck effect involves voltage generation due to a temperature difference across a conductor. In contrast, the Peltier effect causes heating or cooling with an electric current, and the Thomson effect deals with the change of heat through a conductor.

Now, we will show the relationship between the electrical conductance G, which depends on the applied electrical bias on the system, as my calculations are set up for a small potential across the system of interest. A general view can be presented since there is a temperature difference ΔT and a potential drop ΔV through the system, as shown in Figure 3.11. Consequently, this will allow the current *I* and the heat current \dot{Q} to flow across the system. These currents are linearly related to the temperature and potential differences as the thermoelectric coefficients *G*, *L*, *M*, and *K* take place as [19,20]:



Figure 3.11. A schematic structure of the thermopower effect due to an applied temperature difference $(T_{Hot} - T_{Cold})$ in a metal-molecule-metal junction.

$$\begin{pmatrix} I\\\dot{Q} \end{pmatrix} = \begin{pmatrix} G & L\\ M & K \end{pmatrix} \begin{pmatrix} \Delta V\\ \Delta T \end{pmatrix}$$
(3.62)

We can express the previous equation further to demonstrate the current in terms of thermoelectric coefficients:

$$\begin{pmatrix} \Delta V \\ \dot{Q} \end{pmatrix} = \begin{pmatrix} \frac{1}{G} & -\frac{L}{G} \\ \frac{M}{G} & K - \frac{LM}{G} \end{pmatrix} \begin{pmatrix} I \\ \Delta T \end{pmatrix}$$
$$= \begin{pmatrix} R & S \\ \Pi & \kappa \end{pmatrix} \begin{pmatrix} I \\ \Delta T \end{pmatrix}$$
(3.63)

Where *R* is the electrical resistance, the thermopower is *S*, Peltier coefficient is Π and the thermal conductance is κ . The ratio represents the electrical conductance $G = I/\Delta V$, whereas at $\Delta T = 0$ it can be expressed as:

$$G = G_0 L_0 \tag{3.64}$$

where G_0 is the quantum conductance and L_0 is the Lorenz number.

$$L_n = \int_{-\infty}^{\infty} (E - E_F)^n \left(-\frac{\partial f(E)}{\partial E} \right) T(E) dE$$
(3.65)

The thermopower depends on the potential corresponding to the temperature difference, as the electrical current is not represented.

$$S \equiv -\left(\frac{\Delta V}{\Delta T}\right)_{I=0} = -\frac{L_1}{eTL_0} \tag{3.66}$$

The Peltier coefficient Π is obtained by the heat transfer because of the charge current, in the absence of a temperature difference.

$$\Pi \equiv -\left(\frac{\dot{Q}}{I}\right)_{\Delta T=0}$$
$$= \frac{M}{G}$$
$$= -ST \qquad (3.67)$$

Consequently, S and Π coefficients provide information on the electric device's actions through the heating or cooling mechanism. Furthermore, a crucial parameter known as the dimensionless number thermoelectric figure of merit ZT is used to measure the thermoelectric efficiency of a system for energy conversion [21-23].

$$ZT = \frac{S^2 GT}{\kappa}$$
(3.68)

From a classical electronics perspective, the figure of merit ZT originated by determining the highest temperature variation when producing electrical current, where the Joule heating effects are present. For a current-conducting material attached with two heat reservoirs at temperatures T1 and T2, and electrical potentials V1 and V2, respectively. The thermoelectric figure of merit ZT is attained by quantifying the peak temperature difference generated by the electrical current flowing through a conductor.

By defining \dot{Q} as the obtained amount of heat from reservoir 1 to reservoir 2, we can express the transferred heat using the measurable thermoelectric coefficients.

$$\dot{Q} = \Pi I - \kappa \Delta T \tag{3.69}$$

This transferred heat will result cooling from one reservoir and heating from the other reservoir, increasing ΔT . The Joule heating in the conductor is expressed as $\dot{Q}_J = RI^2$ which is directly proportional to the electrical resistance and the square of the current, and also this Joule heating influences the temperature difference which induced by the transferred heat. Subsequently, for a stable situation, we can write the temperature difference as:

$$\Pi I - \kappa \Delta T = \frac{RI^2}{2} \tag{3.70}$$

$$\Delta T = \frac{1}{\kappa} \left(\Pi I - \frac{RI^2}{2} \right) \tag{3.71}$$

Therefore, we now possess an equation indicating how the temperature difference varies with the electrical current and determine the maximum temperature difference which involves differentiating (3.79) and solving for ΔT as:

$$\frac{\partial \Delta T}{\partial I} = \frac{\Pi - IR}{\kappa} \tag{3.72}$$

Now, we apply the current $I = \Pi/R$ and then substitute the equation (3.67) into the equation (3.72) to yield the maximum temperature difference as:

$$(\Delta T)_{max} = \frac{\Pi^2}{2\kappa R} = \frac{S^2 T^2 G}{2\kappa}$$
(3.73)

Hence,

$$\frac{(\Delta T)_{max}}{T} = \frac{S^2 GT}{2\kappa} = \frac{1}{2}ZT \tag{3.74}$$

In the case of the thermal conductance due to electrons can be expressed as:

$$\kappa_e = K_e - S^2 GT \tag{3.75}$$

At $\Delta T = 0$,

$$\kappa_e = \frac{2}{hT} \left(L_2 - \frac{(L_1)^2}{L_0} \right)$$
(3.76)

The electric contribution figure of merit describes the property of electrons expressed as:

$$ZT_e = \frac{S^2 GT}{\kappa_e} = \left(\frac{(L_1)^2}{L_0 L_2 - (L_1)^2}\right)$$
(3.77)

where,

$$L_{0} \approx T(E_{F})$$

$$L_{1} \approx (eT)^{2} \alpha \left(\frac{dT(E)}{dE}\right)_{E=E_{F}}$$

$$L_{2} \approx (eT)^{2} \alpha T(E_{F})$$
(3.78)

where α is the Lorentz number ($\alpha = 2.44 \times 10^{-8} W \cdot \Omega \cdot K^{-2}$), so the thermal electric conductance can take the form:

$$\kappa_e \approx \alpha GT$$
(3.79)

The equation (3.79) is well-known as the Wiedemann-Franz law, which indicates that the electric thermal conductance is proportional to *G* as the transmission coefficient $T(E_F)$ differs slowly with the range of k_bT .

Also, the Seebeck coefficient can take the form at this limit as:

$$S(E_F) = eT\alpha \left(\frac{dln[T(E)]}{dE}\right)_{E=E_F}$$
(3.80)

The equation (3.80) shows that the sign of the Seebeck coefficient depends on the slope of the transmission coefficient T(E). Hence, according to Wiedemann-Franz law the expression of the electric thermal conductance κ_e can lead to the form of electric figure of merit as:

$$ZT_e = \frac{S^2}{\alpha} \tag{3.81}$$

To attain $ZT_e > 1$, the condition $S^2 > \alpha$ must be met, and the Seebeck coefficient should exceed approximately $150 \,\mu V K^{-1}[3]$.
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Chapter 4

Charge Transfer Complexes of Chlorine Perylene Bisimide with the Presence of TCNE in Single-Molecule Junctions

In this chapter, I shall illustrate the first primary outputs of my research by studying charge transfer (CT) complexes in single-molecule junctions (SMJs). This theoretical study of electric and thermoelectric properties of chlorine perylene bisimide (Cl-PBI) molecules is partially motivated by experimental research by Prof. Thomas Wandlowski's group at the University of Ben [1] and also the prior related theoretical study entitled "Exploiting the extended p-system of perylene bisimide for label-free single-molecule sensing" Journal of Materials Chemistry C, 3(9), 2101-2106, 2015 [2]. Hence, I shall specifically focus on studying the electron transport properties of chlorine perylene bisimide (Cl-PBI) molecule linked with two different anchor groups pyridine (pyridyl) and a methyl thioether (SMe). Additionally, I shall involve tetracyanoethylene (TCNE) as a pendant group in the junctions, which is well-known as an acceptor to discover its effect on quantum transport. To enhance the development of functional advanced organic materials, I shall focus on functionalising chlorine perylene bisimide (Cl-PBIs) molecules as organic building blocks and study their thermoelectric properties. I shall also investigate charge transport complexes exhibiting electron transport through a donor/acceptor system.

4.1 Introduction

There are many theoretical studies of the physical properties of molecular systems and many of them are based on organic materials [3-7,30-33]. Related experimental studies have investigated a variety of thermoelectric properties of molecular systems [8]. The increasing demand for highly efficient energy of nano-structure devices motivates us to synthesise organic materials to reach discoveries in this area of research. PBI molecules are unique organic molecules due to their large chemical and thermal stability and provide strong absorption through the electromagnetic spectrum. Furthermore, they can form self-assemble in molecular-scale devices and have interesting synthesis possibilities and applications in exhibiting fluorescence and dyes [9,10]. It is also possible to tune their electrical conductance G of electrode-molecule-electrode systems by employing various anchor groups such as pyridine (pyridyl) and SMe anchor groups.

Experimentally it is a challenging task to control the connection between anchor groups linked with molecules and electrodes. However, numerically it is possible to control geometrical configurations to have realistic systems of general connections. In addition, introducing a tunnelling barrier on any side of the electrodes can affect on conductance [11]. Thus, potentially studying the thermoelectric properties at the room temperature (\sim 300*K*) lead us to solutions for many applications, such as power generation, waste heat efficiency, and cooling systems. findings of this research provide some theoretical predictions of thermoelectric properties of single-molecule junctions, which assist experimental and theoretical scientists focusing on electron transport behaviours.

4.2 Computational Techniques

To reach the optimum ground state geometry of molecules, I used density functional theory (DFT) within the SIESTA code, which is based on the unitised Troullier-Martins pseudopotentials and a local atomic orbital basis (LAOB) [12,13]. I used a double-zeta polarised (DZP) basis set defined by a confining cut-off of 0.003 Ry, norm-conserving pseudopotentials, an energy cut-off of 150 Ry and the generalized gradient approximation (GGA) method [14] to describe the exchange-correlation functionals [14,15]. All forces on atoms were relaxed to a force tolerance of 0.01 eV/Å to allow isolated molecules to reach their optimum geometries. By choosing a basis set at a cut-off value of 0.003 Ry, we can control the position of the Fermi energy E_F within the HOMO-LUMO gap. Hence, all of these previous parameters were applied through this thesis.

4.3 Electronic Structure Simulations

The systems studied in this chapter consist of two molecules forming metal-molecule-metal junctions, one constructed of Cl-PBIs molecules linked with pyridine (Py) anchor groups and the other with methyl thioether (SMe) anchor groups, as shown in Table 4.1. Later in this chapter, I shall report thermoelectric calculations of Cl-PBIs combined with the tetracyanoethylene (TCNE) molecule, forming a donor-acceptor system that possibly can enhance charge transfer (CT) complexes. Firstly, the studied molecules are optimised until they reach their ground-state geometries, as shown in Table 4.1.

Table.4.1 Chemical structures and molecular configurations of chlorine perylene bisimide (Cl-PBI) backbone linked with pyridine (Py) anchor groups and SMe anchor groups, where the atoms are nitrogen (blue), chlorine (green), oxygen (red), carbon (grey), and hydrogen (white).

Molecules	Chemical Structures	Molecular Configurations	
Chlorine Perylene Bisimide (Cl-PBI) _Pyridine		KHKKKK	
Chlorine Perylene Bisimide (Cl-PBI_SMe)		to the total	

4.4 Frontier-Molecular Orbitals (FMO)

Molecular orbitals are essential for understanding electron interactions and regions where they can be found at the atomic level. When molecular orbitals overlap, quantum constructive interference (QCI) or quantum destructive interference (QDI) can occur. In molecular junctions, electron transport is partly determined by how close the HOMO and LUMO are to the Fermi energy E_F of the electrodes [16-18].

The first three frontier molecular orbitals (FMO) of Cl-PBI_Py and Cl-PBI_SMe are shown in Tables 4.2 and 4.3 respectively, where the highest occupied molecular orbitals (HOMO), HOMO-1, HOMO-2, and also the lowest unoccupied molecular orbitals (LUMO), LUMO+1, and LUMO+2 are presented. The blue and red colours represent negative and positive amplitudes of the regions along the molecules.

Table 4.2 The HOMO-LUMO wavefunctions of Cl-PBI_Pyridine, where the negative orbitals are blue, and the positive ones are red.



Table 4.3 The HOMO-LUMO wavefunctions of Cl-PBI_SMe, where the negative orbitals are blue and the positive ones are red.

LUMO= - 3.53 eV	LUMO+1= - 2.55 eV	LUMO+2= - 2.40 eV	
~\\$- \$\$ -\$\$	૾ૺૢ૽ૺૺ૽૾ૢૺ૽૾ૢૺ૽૾ૺૺ૽૾ૺૺ૽૾ૺ	~~ <u>`</u> }- ``` }	
HOMO= - 4.28 eV	HOMO-1= - 4.31 eV	HOMO-2= - 4.99 eV	
314	6 1)-}}}}		

Due to the electrostatic factors, Cl-PBI molecules are twisted in their bay area, which reduces the probability of π - π interactions with nearby molecules and allows the formation of singlemolecule junctions [19]. Thus, the results of relaxing Cl-PBIs molecules show that the twisted backbones are due to the repulsive forces of chlorine atoms on both edges of the bay area. For Cl-PBI_Py, there is a torsion angle of 23⁰, whereas for Cl-PBI_SMe, the torsion angle is 29⁰. Table 4.4 summarises the Kohn-Sham (K-S) calculations of the HOMO and LUMO eigenvalues, the Fermi energy, the energy gap (Eg).

Table.4.4 The Kohn-Sham calculations.

Component	HOMO (eV)	LUMO (eV)	$E_F(eV)$	Energy gap
				(eV)
Cl-PBI_Py	- 4.72	- 3.88	- 4.29	0.84
Cl-PBI_SMe	- 4.28	- 3.53	- 3.90	0.75

4.5 Binding Energy Between Anchor Groups and Gold Electrodes

In the following molecular electronic calculations, the single-molecule junctions are built of a single molecule attached to two identical gold electrodes, which are a face-centred unit cell of (111). Every electrode is constructed from 5 periodic principle layers, each consisting of 25 gold atoms, where the terminated surface is arranged in a triangular pyramidal shape containing 11 atoms. To calculate their binding energies to a gold electrode, I set up Cl-PBIs molecules to be constructed with either pyridine (Py) anchor groups, as in Figure 4.1 (a) or methyl thioether

(SMe) anchors, as in Figure 4.2 (a). Both are attached with the gold electrodes, and the distance varies to obtain the favourable optimum energetic states.

I first constructed the system by positioning the isolated molecule to be connected symmetrically with the gold electrodes at a separation distance d between the N and the apex Au atom or the S and the apex gold atom of the electrode pyramid. Then I calculate the binding energy E_b as a function of the separation distance d between N-Au and S-Au atoms.

I calculated using the local density approximation (LDA) to reach the expected minimum energy between two systems. Then, I employ a counterpoise method as a localised basis set is applied to avoid the basis set superposition errors (BSSE). The ghost states were presented for calculating the binding energy E_b by using the following equation [20,21]:

$$E_b = E_{AB}^{AB} - (E_A^{AB} + E_B^{AB})$$
(4.1)

where E_{AB}^{AB} is the ground state energy of the entire system, whereas E_A^{AB} and E_B^{AB} are energies in systems A and B, respectively.

Figure 4.3 (b) and Figure 4.4 (b) show the binding energy E_b as a function of a separation distance *d* between the isolated molecule and the gold electrode. The results show that the bond length between N-Au atoms is approximately $d \approx 1.7$ Å as shown in Figure 4.1 (b), and the corresponding value of the binding energy is $E_b = -1 eV$. Similarly, the optimum distances for the connection between the bond length between S-Au atoms are approximately $d \approx 2.62$ Å in Figure 4.2 (b), the value of the binding energy is found to be $E_b = -0.39 eV$ Since nitrogen

atoms have higher electronegativity than sulphur atoms, the N-Au bond length is stronger than the S-Au bond, and the N atom sits closer to the gold surface of the electrodes.



Figure 4.1 a) Molecular configuration where the Au-N bonded atoms. b) The binding energy E_b as a function of distance *d* between Au-N atoms.



Figure 4.2 a) Molecular configuration where the Au-S bonded atoms. b) The binding energy E_b as a function of distance d between Au-S atoms.

4.6 Molecular Complexes of Cl-PBI with TCNE

As mentioned above, PBI molecules possess intriguing structural characteristics associated with the twisted π -system that shows conformational flexibility [22]. Additionally, the twisting of the π -system is due to repulsive interactions, which can vary by considering the size of the

bay-substituents [23]. This section provides a deeper scope of the impact of the studied substituent with its bay position of Cl-PBIs backbones by considering the presence of the organic pendant-group tetracyanoethylene (TCNE) molecule. The TCNE has been widely utilised in donor-acceptor studies, and therefore, it is of my interest to determine how it binds differently with Cl-PBI molecules. Figure 4.3 illustrates the mechanism of charge transfer (CT) complexes, which occur when an electron moves through a donor/acceptor system.



Figure 4.3 A sketch of charge transfer (CT) complexes through a donor-acceptor system consists of a molecular backbone coupled to left (source) and right (drain) electrodes by hopping elements $-\Gamma$ and a pendant molecule.

4.6.1 Frontier-Molecular Orbitals of TCNE

Table 4.5 shows the frontier orbitals and their corresponding energy values for the isolated TCNE molecule. The Fermi energy E_F is - 6.59 eV, and the energy gap E_g is 2.62 eV.



Table 4.5 The frontier molecular orbitals of TCNE, where the negative amplitudes are blue and the positive ones are red.

4.6.2 Binding Energy Between Cl-PBI and TCNE

In this section, I calculated the binding energy E_b between the extended π -system of the Cl-PBIs and the pendant electron acceptor tetracyanoethylene (TCNE) [24]. By applying the LDA method to find the minimum binding energy E_b and the most favourable location between the Cl-PBI backbone and the TCNE, the TCNE molecule is simulated to be moved along the Δx and Δy directions, with a fixed distance $\Delta z \approx 3\text{Å}$ on Cl-PBI_Py and then Cl-PBI_SMe, as demonstrated in Figure 4.4 below. Plot (a) in Figure 4.4 below shows the binding energy (BE) of the combined system Cl-PBI + TCNE for various locations. Thus, the favourable location is determined at the minimum binding energy of the combined

system is -0.36 eV. Plot (b) shows the fruitful position to set the TCNE on the Cl-PBI_SMe molecule, which is found to be at the minimum binding energy of -0.5 eV.



Figure 4.4. a) The binding energy between the CI-PBI_Py with the presence of the TCNE pendant molecule at various locations. b) The binding energy of CI-PBI_SMe with the presence of the TCNE pendant molecule at various locations.

In Figure 4.5, I calculated the binding energy again as a function of distance along z-direction for Cl-PBI_Py + TCNE, where I found the minimum $E_b = -0.36$ eV at $d_z = 3.26$ Å. In Figure 4.6, I calculated the binding energy again as a function of distance along the z-direction for Cl-PBI_SMe + TCNE where the minimum binding energy is found $E_b = -0.7$ eV at a separation distance $d_z = 3.26$ Å from the Cl-PB backbone.



Figure 4.5. a) Molecular configuration of CI-PBI_Py and TCNE molecules. b) The binding energy E_b as a function of the separation distance d_z .



Figure 4.6. a) Molecular configuration of CI-PBI_SMe and TCNE molecules. b) The binding energy E_b as a function of the separation distance d_z .

Now, some population analysis is needed to understand how the TCNE pendant molecule tends to accept an electron from the backbone of Cl-PBI molecules. I calculated the total net charge ΔQ of the TCNE as demonstrated in Table 4.6.



Table.4.6 The combined molecular systems configurations and calculations of population analysis of the TCNE.

4.6.3 Frontier-Molecular Orbitals of Cl-PBIs with Presence of TCNE

The frontier molecular orbitals and HOMO-LUMO energy levels were calculated for the combined systems. The interactions of the combined systems are responsible for affecting electric and thermoelectric features, which can be discriminated between. Table 4.7 illustrates the FMO of the investigated combined systems of the Cl-PBIs with TCNE linked with pyridine and SMe anchor groups, respectively. where for Cl-PBI_Py with TCNE the HOMO level is

delocalised across the backbone, whereas the LUMO is more localised in the core of portion of Cl-PBI and has significant overlap with the TCNE. In this case, the energy gap E_g is 0.22 eV. For Cl-PBI_SMe with the TCNE, the HOMO is also delocalised and the LUMO is located in the core of portion of Cl-PBI. Clearly, there is again a significant overlap with orbitals on the TCNE. In this case the energy gap E_g is 0.16 eV. My results of the population methods indicate that the TCNE molecule tends to gain an electron from the Cl-PBI molecule, forming an acceptor/donor structure.

In the following section, I shall discuss electron transport calculations computed by the utility combination of DFT-SIESTA code [3] and Green's function method via GOLLUM code [27] which can potentially provide attractive findings of electronic properties that can be applied in various fields such dyes, fluorophores, and solar technologies [25,26].

Table 4.7 HOMO-LUMO frontier molecular orbitals of the combined systems for Cl-PBI_Py with TCNE and Cl-PBI_SMe with TCNE.



4.8. Results and Discussion

In this section, density functional theory (DFT) as utilised in the SIESTA code and the equilibrium Green's function transport code of GOLLUM [27] are employed in the calculations. First, I compute the scattering region of bare Cl-PBIs junctions to find their electric properties under zero bias. In the following discussion, I use a double-zeta polarised (DZP) basis set for all atoms except the gold atoms of the electrodes, which are set to be a double-zeta (DZ) due to stability and to avoid artificial noise and the generalised gradient approximation (GGA) for the exchange-correlation functionals. To calculate the electric properties of the studied molecules, I start by calculating the transmission coefficients T(E), and electrical conductance *G* of bare Cl-PBI molecules, which are linked to Au (111) electrodes by pyridine (pyridyl) and SMe. The Hamiltonian defining the system is extracted by using the SIESTA code.

The transmission coefficient describes the probability of electron transport through singlemolecule systems and provides a crucial tool for understanding electron transport behaviour in a junction. Additionally, the transmission coefficient T(E) can significantly impact electrical conductance G, with more variations occurring closely at the Fermi energy E_F . Hence, by the Landauer formula, we can express the relation between the transmission and electrical conductance where the energy range is close to the Fermi energy E_F [28,29].

4.7.1 Transmission Coefficient and Electrical Conductance of Bare Junctions

Now, I shall calculate the transmission coefficient for both the bare junctions of Cl-PBI_Py and Cl-PBI_SMe for an electron passing from the left to the right electrode through the scatterer. The strength of the coupling between the anchor groups and electrodes can broaden the transmission curve and shift down the energy because of the electrodes' self-energy, hence increasing the electron transport passing the scattering region.



Figure.4.7 Chemical configurations of Au-Cl-PBIs-Au junctions. a) Bare junction of Cl-PBI_Py. b) Bare junction of Cl-PBI_SMe.

In Figure 4.8 Breit-Wigner resonances appear for the HOMO and LUMO levels in the energy window, and the Fermi E_F energy is located within the HOMO-LUMO gap. In addition to the effect of the strength of the coupling between the Au-Cl-PBIs-Au, the shape of the Breit-Wigner can be changed by the presence of more than one orbital. For Figure 4.8 (a) the

transmission curve (blue) for Cl-PBI_Py shows LUMO-dominant transport close to Fermi energy, with a narrower energy gap, whereas the Cl-PBI_SMe shows a tunnelling behaviour 'silent resonance' (orange) with wider energy gap E_g .



Figure 4.8. a) Comparison between transmission coefficients T(E) as a function of energy E (left panel) for both bare Cl-PBI_Py (blue) and Cl-PBI_SMe (orange) junctions. b) Comparison between transmission Electrical conductance *G* (right panel) for both bare Cl-PBI_Py (blue) and Cl-PBI_SMe (orange) junctions.

4.7.2 Transmission Coefficient and Electrical Conductance of Cl-PBI_Py + TCNE

In this section, I present the effect of the TCNE pendant group complexed with the Cl-PBI_Py junction to observe the electric properties of the combined system, as shown in Figure 4.9. below.



Figure.4.9 Chemical configurations of Au-Cl-PBIs-Au junctions. a) Bare junction of Cl-PBI_Py. b) junction of Cl-PBI_Py+ TCNE.



Figure 4.10. a) The two views of the configuration structure of the combined system Cl-PBI_Py with TCNE. b) Comparison of the transmission coefficients T(E) (left panel). c) the corresponding electrical conductance G (right panel).

Figure 4.10. b) shows the transmission coefficients T(E) as a function of energy for two cases of Cl-PBI_Py junctions, and reveals that transport is LUMO-dominated in both cases. In the presence of TCNE (red curve) an extra resonance appears near the LUMO level, and a shift of the HOMO-LUMO resonances occurred, whereas the bare junction shows only two resonances close to the Fermi energy E_F . Plot (c) shows the corresponding room-temperature electrical conductance of both junctions. For the bare junction (blue curve) $log (G/G_0) = -4.4$ whereas the combined system of Cl-PBI with TCNE (red curve) has a value $log (G/G_0) = -4.3$ at the DFT-predicted Fermi energy at $(E_F - E_F^{DFT} = 0)$.

4.7.3 Transmission Coefficient and Electrical Conductance of Cl-PBI SMe + TCNE

Figure 4.12 b) shows the transmission coefficient for the TCNE-Cl-PBI_SMe. This is a tunnelling behaviour occurring with a wide energy gap, but with a 'silent resonance' (green curve) which indicates a $\pi - \pi$ stacking feature. Plot (c) (right panel) in Figure 4.12 shows that the electrical conductance *G* for the bare junction (orange curve) is around $log (G/G_0) = -7.2$ and the combined Cl-PBI_SMe + TCNE system (green curve) is about $log (G/G_0) = -7.47$ at the DFT-predicted Fermi energy.



Figure.4.11. Chemical configurations of Au-Cl-PBIs-Au junctions. a) Bare junction of Cl-PBI_SMe. b) junction of Cl-PBI_SMe + TCNE.



Figure 4.12. a) The two views of the configuration structure of the combined system Cl-PBI_SMe with TCNE. b) Comparison of the transmission coefficients T(E) (leftpanel). c) The corresponding electrical conductance G (right panel).

4.7.4 Comparison of Transmission Coefficient and Electrical Conductance of Cl-PBIs and TCNE

Overall, the presence of the TCNE pendant group does not significantly affect the roomtemperature conductance compared to the difference that occurs when the anchor groups are changed from Py to SMe. Figures 4.13, 4.14, and Table 4.7 compare junction properties of the two anchor groups, with and without TCNE. For the Cl-PBI_Py junctions, the LUMO resonances appear to be positioned closer to $E - E_F^{DFT}$ as the influence of these bridges on the conjugated nature [4]. Subsequently, results of T(E) indicate that the group connections of Cl-PBI with pyridine anchor groups exhibit a narrower HOMO-LUMO gap than group connections Cl-PBI with SMe anchor groups because the coupling strengths are affected by the binding energies to the electrodes.



Figure 4.13. a) Comparisons between Transmission coefficients for Cl-PBIs junctions (left panel). b) Comparisons between the electrical conductance G of all Cl-PBIs molecules with varying anchor groups (pyridine and SMe) with the presence of the pendant groups (TCNE) and with bare junctions. (right panel).

$\log(G/G_0)$	
$(E_F - E_F^{DFT} = 0 \ eV)$	
-4.4	
-4.3	
-7.2	
-7.47	

Table.4.8 The averaged values of electrical conductance G at the Fermi energy.



Figure 4.14. The average electrical conductance *G* at room temperature based on Cl-PBI linked via the pyridine anchor groups attached to gold electrodes.

Table 4.8 illustrates logarithmic values of the electrical conductance G calculations of two groups of Cl-PBIs molecules by varying their anchor groups and adding TCNE pendant molecules. Figure 4.14 above represents theoretical calculations of these molecules' electrical conductance G values as a function of energy for the energy window at room temperature (300K). The results show the values of electrical conductance G from the greatest to the smallest values as follows: Cl-PBI_Py + TCNE > Cl-PBI_Py > Cl-PBI_SMe > Cl-PBI_SMe + TCNE, as the DFT-SIESTA calculations demonstrate at the Fermi energy E_F of the electrodes.

4.7.5 Comparison of Seebeck Coefficient S of Cl-PBIs

The Seebeck coefficient *S* can take a positive or negative sign corresponding to the sign of the slope of the transmission function at the Fermi energy. Figure 4.15 illustrates Seebeck coefficients (thermopower) for a general comparison of the four cases of Cl-PBIs with pyridine anchor groups, where the calculated values of the Seebeck coefficient *S* are at the DFT-predicted Fermi energy. Table 4.9 addresses the values of the Seebeck coefficient *S* at the energy window $(E_F - E_F^{DFT})$.



Figure 4.15. Comparison of Seebeck coefficients S of CI-PBIs junctions with the presence of TCNE and without TCNE.

Component	$S(\mu V/K)$
Cl-PBI_Py	7.98
Cl-PBI_Py + TCNE	-9.24
Cl-PBI_SMe	-42.55
Cl-PBI_SMe + TCNE	-1.23

Table 4.9 The values of the Thermopower effect (Seebeck coefficient S) at $(E_F - E_F^{DFT} = 0)$.

4.7 Summary

In conclusion, the above calculations indicate that with both anchor groups (pyridine and SMe), Cl-PBIs combined with the TCNE, they tend to have similar behaviours as the bare junctions. The transmission coefficients of single-molecule junctions are mainly influenced by the anchor groups, which affect molecular electronic structures and the coupling at the molecule-electrode interfaces. The transmission coefficient T(E) as a function of energy illustrate the electron tunnelling behaviours, as HOMO-LUMO resonances occur far from the Fermi energy for both bare Cl-PBI_Py, Cl-PBI_SMe, Cl-PBIs + TCNE, and Cl-PBI_SMe + TCNE junctions.

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Chapter 5

Exploring Charge Transfer Complexes of Chlorine Perylene Bisimide with the Presence of TTF in Single-Molecule Junctions

Investigating charge transfer complexes between chlorine perylene bisimide (Cl-PBI) and tetrathiafulvalene (TTF) exhibits significant promise for molecular devices [1]. The charge transfer occurs through interactions between electron donors and acceptors with unique electronic features. Since PBIs can work as electron acceptors while TTF is well-known as a good donor of electrons, I shall explore the CT by combining Cl-PBI and TTF in a single-molecule junction to enhance CT interactions and tune electron transport behaviour. Thus, introducing TTF as a pendant molecule in SMJs can lead us to the discovery of thermoelectric properties.

5.1 Introduction

The research on charge transfer (CT) complexes, specifically involving perylene bisimide (PBI) molecules and tetrathiafulvalene (TTF), is interesting due to their unique electronic and photonic applications. These organic molecules can play essential roles in molecular devices, since the perylene bisimides are excellent candidates for their light absorption, photostability, and fluorescence features [4-7]. These properties can enable CT complexes, when combined with TTF as an electron-donating molecule, to exhibit new electronic characteristics in SMJs.

These combined systems are crucial for designing applications, e.g., light-emitting diodes [2], photovoltaics [3], and switches [13-15].

5.2 Molecular Complexes between Cl-PBI and the Presence of TTF

In this section, chlorine perylene bisimides (Cl-PBIs) and tetrathiafulvalene (TTF) are analysed to reveal transport mechanisms through these charge transfer (CT) complexes. Since TTF has a conjugated π -electron system, their combined systems exhibit electron-accepting features of Cl-PBIs and electron-donating features of TTF [12].

5.2.1 Frontier-Molecular Orbitals of TTF

In this section, I calculated the frontier molecular orbitals of TTF. Table 5.1 shows the HOMO-LUMO levels of the optimised TTF molecule. It shows that all its wavefunctions are delocalised over the TTF. The Fermi energy E_F is - 2.61 eV, and the energy gap E_g is 1.94 eV.

Table 5.1 the frontier molecular orbitals of TTF, where the negative orbitals are blue and the positive ones are red.



5.2.2 Binding Energy Between Cl-PBI and TTF

Now, I computed the binding energy (BE) between the extended. π -system of the Cl-PBI_Py, Cl-PBI_SMe, and the pendant molecule TTF, which is considered electrondonating. To achieve this goal, I keep the Cl-PBIs stationary, and the TTF is moved on top along Δx and Δy directions with a fixed position $\Delta z \approx 3\text{\AA}$, as shown in Figure 5.1 (a) and (b) [16,17]. Plot (a) illustrates the BE of Cl-PBI_Py + TTF for various locations, where the favourable location for the combined system is at the binding energy of -0.14 eV. Plot (b) shows the BE of Cl-PBI_SMe + TTF, where the favourable location for the combined system is at the binding energy of -0.53 eV.


Figure 5.1. a) The binding energy between the CI-PBI_Py with the presence of the TTF pendant molecule at various locations. b) The binding energy of CI-PBI_SMe with the presence of the TTF pendant molecule at various locations.

In further steps, I calculated the binding energy E_b as a function of the distance d_z of the dimer molecules as shown in Figure 5.2 (a). The result shows that the minimum binding energy between Cl-PBI_Py and TTF is close to -0.53 eV at the equilibrium distance $d_z = 3.06$ Å in Figure 5.2 (b).



Figure 5.2. a) Molecular configuration of CI-PBI_Py and TTF molecules. b) The binding energy E_b as a function of the separation distance d_z .

Then, I used the same process of computing the minimum binding energy between Cl-PBIs and TTF along the z direction as the chemical configuration is illustrated in Figure 5.3 (a). I found the optimum binding energy $E_b = -0.61$ eV at the equilibrium distance $d_z = 3.2$ Å shown in Figure 5.3 (b).



Figure 5.3. a) Molecular configuration of CI-PBI_SMe and TTF molecules. b) The binding energy E_b as a function of the separation distance d_z .

I carried out the population methods to determine the electronic charge distribution of TTF. The calculations are performed using the local density approximation (LDA). Three population analysis methods, the Mulliken, Hirshfeld, and Voronoi populations, are applied to gain insights into the distribution of electrons on the atomic structure of the molecule. Indeed, the findings show that the TTF tends to donate an electron to the Cl-PBIs molecules, as shown in Table 5.2 below.



Table.5.2 The combined molecular systems configurations and population analysis of TTF.

5.2.3 Frontier-Molecular Orbitals of Cl-PBIs with the Presence of TTF

The wavefunctions distribution of the combined system Cl-PBIs + TTF using two different pyridine and SMe anchor groups, the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) are computed. Table 5.3 illustrates the FMO of the investigated combined systems of Cl-PBIs + TTF for HOMOs-LUMOs, where the red regions are positive and the blue ones are negative, where for Cl-PBI_Py with TTF the HOMO level is localised with overlap orbitals and LUMO level there are a clear overlap between TTF

and the core of Cl-PBI orbitals with energy gaps E_g of 0.13 eV, whereas for Cl-PBI_SMe + TTF, the HOMO level is delocalised and LUMO level there are overlap orbitals between TTF and the core of Cl-PBI with energy gap E_g of 0.23 eV.

Table 5.3 HOMO-LUMO frontier molecular orbitals of the combined molecules for Cl-PBI_Py with TTF and Cl-PBI_SMe with TTF.



5.3 Results and Discussion

Transmission coefficient T(E) and the electrical conductance *G* are computed employing the quantum transport theory via the GOLLUM code [7]. I applied DFT-SIESTA calculations to study CT complexes in dimer molecular systems of Cl-PBIs + TTF, where I investigated them in the TTF pendant group to observe their thermoelectric features.

5.3.1. Transmission Coefficient and Electrical Conductance of Cl-PBI_Py + TTF



Figure.5.4 Chemical configurations of Au-Cl-PBIs-Au junctions. a) Bare junction of Cl-PBI_Py. b) junction of Cl-PBI_Py+ TTF.

Figure 5.4 shows the investigated SMJs of my interest. Figure 5.5 (b) shows the transmission coefficient T(E) as a function of energy E for the bare-Cl-PBI_Py (blue) and in the presence of TTF (black), both LUMO-dominant close to E_F. It can be seen from plot (b) that a Fanoresonance occurs close to E_F, which indicates that the TTF pendant group interacts electronically with the backbone molecule. Figure 5.5 (c) shows the corresponding room-temperature electrical conductance *G* for the bare-Cl-PBI_Py and Cl-PBI+TTF. Plot (c) illustrates the corresponding electrical conductance *G* of both junctions, where bare-Cl-PBI_Py (blue curve) is $log (G/G_0) = -4.4$ whereas the combined molecules of Cl-PBI_Py with TTF (black curve) have a value of $log (G/G_0) = -3.67$ at the DFT-predicted Fermi energy.



Figure 5.5 a) The two views of the configuration structure of the combined system Cl-PBI_SMe with TTF. b) Comparison of the transmission coefficients T(E) (leftpanel). c) the corresponding electrical conductance G (right panel).

5.3.2 Transmission Coefficient and Electrical Conductance of Cl-PBI_SMe + TTF

In this section, I compared the bare Cl-PBI_SMe with Cl-PBI-SMe + TTF, as shown in Figure 5.6.



Figure.5.6 Chemical configurations of Au-Cl-PBIs-Au junctions. a) Bare junction of Cl-PBI_SMe. b) junction of Cl-PBI_SMe + TTF.

In Figure 5.7 (b) the transmission coefficient T(E) as a function of energy E shows the bare-Cl-PBI_Py (blue) and the presence of TTF (black), both LUMO-dominant close to E_F. It can be seen from plot (b) that a Fano resonance occurs close to E_F, which indicates that a CT complex has formed. Figure 5.7 (c) below represents logarithmic values of the electrical conductance *G* for the bare-Cl-PBI_Py and Cl-PBI+TTF. Plot (c) illustrates the corresponding electrical conductance *G* of both junctions, where for bare-Cl-PBI_SMe (orange curve) is $log (G/G_0) = -7.2$ whereas the combined molecules of Cl-PBI_SMe with TTF (pink curve) have a value of $log (G/G_0) = -7.93$ at DFT-predicted ($E - E_F^{DFT} = 0$).



Figure 5.7 a) The two views of the configuration structure of the combined system Cl-PBI_SMe with TTF. b) Comparison of the transmission coefficients T(E) (leftpanel). c) the corresponding electrical conductance *G* (right panel).

5.2.3 Comparison of Transmission Coefficient and Electrical Conductance of Cl-PBIs and TTF

In this section, I compare the previous results for transmission coefficients T(E) and electrical conductance *G* with the two different anchor groups for both bare-Cl-PBIs junctions and in the presence of TTF. From Figure 5.8 (a) it can be seen clearly that Fano-resonance appears for both cases with the presence of TTF demonstrating that a charge transfer (CT) occurs. Figure 5.8 (b) illustrates the room-temperature electrical conductance *G* for the studied junctions of Cl-PBIs with TTF pendant group.



Figure 5.8 a) Comparisons between Transmission coefficients for Cl-PBIs junctions (left panel) with TTF and without the pendant group. b) Comparisons between the electrical conductance G (right panel) of Cl-PBIs molecules with varying anchor groups (pyridine and SMe) with the presence of the TTF pendant group and the bare junctions.

Table.5.4 The averaged values of electrical conductance G at

Component	$\log(G/G_0)$
Cl-PBI_Py	-4.4
Cl-PBI_Py + TTF	-3.67
Cl-PBI_SMe	-7.2
Cl-PBI_SMe + TTF	-7.93

$$(E_F - E_F^{DFT} = 0 \ eV).$$



Figure 5.9 The averaged electrical conductance *G* at room temperature based on Cl-PBI linked via the pyridine anchor groups attached to gold electrodes.

Table 5.4 shows logarithmic values of the electrical conductance *G* calculations of two groups of Cl-PBIs molecules with different anchor groups (Pyridine and SMe) and in the presence of TTF pendant molecules. Figure 5.9 above represents theoretical calculations of the electrical conductance *G* values of these molecules as a function of energy for the energy window at room temperature (300K). My findings show the values of electrical conductance *G* from the greatest to the smallest values as follows: Cl-PBI_Py > Cl-PBI_Py + TTF > Cl-PBI_SMe > Cl-PBI_SMe + TTF as the DFT-SIESTA calculations demonstrate at the Fermi energy ($E_F - E_F^{DFT} = 0 \ eV$) of the electrodes.

5.2.3 Comparison of Seebeck Coefficient *S* of Cl-PBIs with TTF

Figure 5.10 illustrates the Seebeck coefficients S for a general comparison of the four cases of Cl-PBIs where the calculated values of the Seebeck coefficient S are at the DFT-predicted Fermi energy.



Figure 5.10. Comparison of Seebeck coefficients *S* of Cl-PBIs junctions with the presence of TTF and the bare-Cl-PBIs.

Component	$S(\mu V/K)$
Cl-PBI_Py	7.98
Cl-PBI_Py + TTF	15.64
Cl-PBI_SMe	-42.55
Cl-PBI_SMe + TTF	11.03

Table.5.5 The values of the Seebeck coefficient S at $(E_F - E_F^{DFT} = 0 \ eV)$.

5.4 Summary

To sum up, through chapters 4 and 5, I have presented a new investigation of the electrical and thermoelectrical properties of single-molecule junctions formed from charge transfer complexes in six cases of Cl-PBIs, including two different anchoring groups (Pyridine, SMe) and also combined with two pendant groups (TCNE [acceptor] and TTF [donor]). In the beginning, I started optimising isolated molecules, then I computed their minimum binding energy between their dimer systems to find a favourable position to observe new electric features in SMJs. After that, Fano resonances were found close to the Fermi energy in the system where Cl-PBI+TTF combined with the pendant groups TTF, with both Pyridine and SMe anchors. In contrast, the Cl-PBIs +TCNE complexes show general Breit-Wigner behaviour in HOMO-LUMO gaps and only a very narrow Fano resonance, which is called 'silent', because it has a negligible effect on the electrical conductance.

By understanding these aspects theoretically and synthesising chemically the organic molecules, they can be controlled and expanded for self-assembled monolayer study. With the

variety of methods to measure the electrical properties of single-molecule junctions (SMJs), there are challenges in controlling the molecule connection geometries to achieve precise efficiency in molecular devices. Thus, all of that can lead us to remarkable results in the field of nanotechnologies and their applications, i.e. molecular rectifiers [8], switches [9], and sensors [10].

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Chapter 6

Tuning The Thermoelectric Properties of Single-Porphyrin Molecules in Single-Molecule Wires

In chapters 4 and 5, I investigated the neutral pendant molecules 'side groups', formed by charge transfer complexation to a conjugated backbone. In this chapter, I shall examine the effects of charged pendant groups covalently bonded to a backbone. This work is stimulated by a collaborative project between our theory group at Lancaster University, Prof. Harry Anderson's group at the University of Oxford, which specialises in the synthesis of porphyrin molecules and Prof. Richard Nichol's group at the University of Liverpool, which can measure single-molecule conductances. Thus, I shall investigate porphyrin molecules linked with SMe anchor groups to discover the effect of side groups on charge transport. In this chapter, I shall focus on studying the electric and thermoelectric properties of porphyrin molecules, which are varied by attaching different side groups and involve a charged pendant molecule.

6.1 Motivation

Since the beginning of the 19th century, the interest in attempts to create energy from a temperature gradient has increased rapidly [1]. The Seebeck effect can convert waste heat from industry to electricity, and the inverse process (Peltier effect) can be employed in cooling electronic components [2-5]. Recently, the aim has been to find high-efficiency materials by attempting to parameterise factors that affect the thermoelectric properties of nano-structured

materials [6-12]. My findings will reveal some essential features affecting the thermoelectric properties of nanostructures.

Studying porphyrin molecules provides many advantages in nanostructure applications as they possess unique features and characteristics, including high chemical stability and conjugated structures. Furthermore, they can form metalloporphyrin molecules by inserting a metal ion into their aromatic backbones [13-17]. Furthermore, porphyrin is a building block for constructing self-assembled arrays in molecular-scale devices.

6.2 Introduction

In this chapter, I shall illustrate the charge transport properties of a two-terminal device formed from metallic electrodes attached to porphyrin molecules, which can allow electron transport resonances to occur close to the Fermi energy E_F . By studying the thermoelectric properties at room temperature (~300*K*) I aim to develop a fundamental understanding of various applications, such as power generation, waste heat efficiency, and cooling systems. I shall address a theoretical study of various scenarios of side groups linked to porphyrin molecules with centrally coordinated metal ions and demonstrate their electric features in single-molecule wires.

Since porphyrin molecules are building blocks in nano-structure devices, they possess key features such as being rigid, stable, and conjugated. Porphyrins can accommodate various metallic ions [18-26]. Due to their rich chemical redox activity, I shall investigate porphyrin molecules in the presence of $[PF_6]^-$ anion. Thus, from the electric and thermoelectric features perspective, single-molecule wires made from porphyrins are intriguing. Therefore, applying

the same computational methods is worth investigating the porphyrin molecules and metalloporphyrins, which can affect thermoelectric phenomena in nano-scale devices [27-30].

6.3 Results and Discussion

Figure 6.1. The below shows a porphyrin molecule attached to two gold electrodes. The Hamiltonian is extracted for the extended molecular system via the SIESTA code. In what follows, I set up the isolated molecules to be attached to two gold electrodes as the favourable optimum energetic states. Generally, I attempt to position the molecules to be connected perpendicularly with two identical gold electrodes at a minimum separation binding energy E_b . Therefore, the favourable position is the distance. d = 2.6 Å and the angle $\theta \approx 122.6^{\circ}$ Between the sulphur atom and the gold atom of each tip of the electrodes. In my charge transfer (CT) calculations.



Figure 6.1. An Au-porphyrin-Au wire configuration of electrons passes from a source through a porphyrin molecule into a drain.

6.3.1 Impact of Side Groups on Thermoelectric Performance of Free-Base Porphyrins

Side groups can play a crucial role in the functionality and electronic properties of porphyrin molecules. Altering the side groups can affect porphyrins' chemical stability and binding interactions [31] and impact their redox-activity behaviours by changing electron-donating/accepting duality [32]. In Figure 6.2 below, there are two free-base porphyrin molecules consisting of an inner ring. π -systems with varying side groups. I shall consider the cases where porphyrin 1 possesses two side groups of (X = C₃N₂), whereas free-base porphyrin 2 possesses two side groups of (X = Pyridine rings + CH₃) on each edge of its backbone. Both porphyrins have SMe anchor groups. Thus, my aim in the following sections is to explore how changing the side groups can affect the thermoelectric properties of free-base porphyrins in molecular wires.



Figure 6.2. Chemical structures of porphyrins with different side groups. (a) free-base porphyrin molecule. (b) Porphyrin 1 (P1) consists of side groups of $(X = C_3N_2)$, (c) Porphyrin 2 (P2) consists of the side groups of [Pyridine rings + CH₃].

6.3.2 Thermoelectric Calculations of Free-base Porphyrin with Side Groups of C_3N_2

In this section, I shall demonstrate the thermoelectric properties of porphyrin molecule P1, which possesses side groups C_3N_2 as shown in Figure 6.3. Table 6.1 shows the spin-up/down frontier orbitals of P1, and the HOMO-LUMO levels expose identical localised states all over the molecule.



Figure 6.3. (a) The chemical structure of the free-base porphyrin 1, (b) The optimised free-base porphyrin P1 consists of the side groups of $[X = C_3N_2]$.

Table 6.1 The spin-up/down frontier molecular orbitals of porphyrin P1 with the positive (red) and negative (blue) orbitals.

MOL.	Conf.	HOMO-1	НОМО	LUMO	LUMO+1
		611-32 -110	÷()-2-()-	54100 00 00 00 00 00 00 00 00 00 00 00 00	1.1.2 × 1.1.
P1	E _F = -4.22 eV	Spin up	Spin up	Spin up	Spin up
	и-0-={+ + -, -, -, -,	611- 5 6-116	÷()-	64100 00 00 00 00 00 00 00 00 00 00 00 00	100 2 2 000
	E _g = 1 eV	Spin down	Spin down	Spin down	Spin down

Figure 6.4. (a) shows the free-base porphyrin P1 molecule attached symmetrically to two gold electrodes linked with SMe anchor groups. Figure 6.4. (b) shows the spin-dependence of the transmission coefficient T(E) as a function of energy E. The figure presents the spin-dependent and total transmission coefficient of the free-base P1 and shows that Fano resonances occur close to the HOMO level, whereas the transport is LUMO-dominated at the DFT-predicted Fermi energy E_F . Figure 6.5. (a) shows the room-temperature electrical conductance G for P1. Figure 6.5. (b) shows the Seebeck coefficient *S*, which is boosted by increasing the slope of

transmission coefficients T(E). Thus, the zero-bias conductance for the provided geometries are affected by the different connection geometries. The electric thermal conductance κ_e values are shown in Figure 6.6. (c) and the electric Figure of merit ZT_e values shown in Figure 6.5. (d).



Figure 6.4. (a) The electrode-molecule-electrode structure. (b) The total transmission as a function of energy T(E) (black curve) whereas the spin-dependent is illustrated as spin up (dashed red curve) and the spin down (dashed blue curve)



Figure 6.5. Thermoelectric calculations. (a) the electrical conductance G. (b) the Seebeck Coefficient S. (c) the electric thermal conductance κ_e . (d) the electric figure of merit ZT_e .

6.3.3 Thermoelectric Calculations of Free-base Porphyrin with Side Groups of [Pyridine Rings + CH₃]

In this section, I shall alter the side groups of the free-base porphyrin backbone by adding pyridine rings + CH₃ on both edges as shown in Figure 6.6, to yield molecule P2.



Figure 6.6. (a) The chemical structure of the free-base porphyrin (P2), (b) The optimised free-base porphyrin 2 consists of the side groups of [Pyridine rings + CH₃].

In Table 6.2 the spin up/down frontier molecular orbitals of porphyrin P2 with the positive (red) and negative (blue) orbitals for P2 the HOMO levels expose localised states on the molecule whereas the LUMO levels exhibit a delocalised state on the backbone for the first level and a localised all over the molecule for LUMO+1.

Table 6.2 The spin-up/down frontier molecular orbitals of porphyrin 2 with the positive (red) and negative (blue) orbitals.

MOLECULE	Conf.	HOMO-1	НОМО	LUMO	LUMO+1
	1443 X	610-20-55-616	611-) <u>//</u> [-1]6	14- 35 -54	\$()=
P2	E _F = -4.97 eV	Spin up	Spin up	Spin up	Spin up
	••-○ ={;;; ;; ;; ;; ;; ;; ;; ;; ;; ;; ;;	610-3 ¹⁶ 5-416	611-)))(I-1)6	14- 2 -41	5(1-5
	E _g = 0.21eV	Spin down	Spin down	Spin down	Spin down

In Figure 6.7 (a), the studied system consists of a free-base porphyrin molecule that forms a metal-molecule-metal junction. Plot (b) illustrates the transmission coefficient T as a function of E, which presents the spin-dependent and total transmission coefficient of the free-base P2. Fano-resonances occur close to the DFT-predicted Fermi energy E_F as the transport is considered to be LUMO-dominated.



Figure 6.7. (a) The electrode-molecule-electrode structure. (b) The total transmission as a function of energy T(E) (black curve) whereas the spin-dependent is illustrated as spin up (dashed red curve) and the spin down (dashed blue curve).

Figure 6.8 shows the thermoelectric properties of P2 attached symmetrically to two gold electrodes linked with SMe anchor groups. Plot (a) shows the room-temperature electrical conductance G for P1. Plot (b) shows the Seebeck effect S is boosted by increasing the slope of transmission coefficients T(E). Thus, the zero-bias conductance G for the provided

geometry is affected by the different connection geometries. The electric thermal conductance κ_e values are shown in Figure 6.8. (c) and the electric Figure of merit ZT_e values shown in panel (d).



Figure 6.8. Thermoelectric calculations. (a) the electrical conductance G. (b) the Seebeck Coefficient S. (c) the electric thermal conductance κ_e . (d) the electric figure of merit ZT_e .

6.3.4 Comparisons of Thermoelectric Calculations for Both Free-base Porphyrins

Now, I shall compare thermoelectric calculations between the free-base porphyrins to highlight their differences. In Table 6.3, some electronic structure calculations of P1 and P2 are shown.

Molecule	HOMO (eV)	LUMO (eV)	$E_F(eV)$	Eg (eV)
P 1	- 4.72	- 3.72	-4.22	1
P 2	- 5.08	- 4.87	-4.97	0.21

Table 6.3. The electronic structure calculations of the isolated free-base porphyrins.

Figure 6.9. shows compares results for the thermoelectric properties for P1 and P2. The transmission coefficient T (E) as a function of energy E is shown in Figure 6.9. a, along with the electrical conductance G (Figure 6.9. b), the Seebeck Coefficient S (Figure 6.9. c). and (d) the electric thermal conductance κ_e and (e) the electric figure of merit ZT_e due to electrons. Hence, these findings reveal the values of electrical properties as follows: G2 < G1 and the $ZT_e \ 1 < ZT_e \ 2$ as shown in Table 6.2. I observe that Seebeck coefficients *S* (thermopower) has larger value $S1 \approx -141 \ \mu V/K$ for the free-base porphyrin 1 whereas for free-base porphyrin 2 has a smaller value $S2 \approx -21.19 \ \mu V/K$ as shown in Figure 6.2.



Figure 6.9. Comparisons of thermoelectric calculations for both free-base porphyrins. (a) Transmission coefficient T(E) as a function of energy E. (b) the electrical conductance G. (c) the Seebeck Coefficient S. (d) the electric thermal conductance κ_e . (e) electric figure of merit ZT_e .

Table 6.4	Thermoelectric	properties cale	culations of	the studied	free-base an	d metalloporphyrir
molecule	s.					

Molecule	$Log(G/G_0)$	S (μV K ⁻¹)	Log κ _e (pW/K)	ZT _e
P1	-2.36	-141	12.55	0.2
P2	-2.84	-21.19	12.22	0.52

6.3.5 Tuning Thermoelectric Properties of Metalloporphyrin Wires

Porphyrins are regarded as high-potential building blocks in molecular devices due to their unique properties such as emission, absorption behaviours, and stability [33]. In this section, I shall address some metalloporphyrin molecules that generally contain metal atoms at the centre of their backbones, as shown in Figure 6.8. Therefore, metal atoms of Ni, Zn, Mg, and Co are embedded in the core of porphyrin molecules that will be studied due to their electronic features for enhancing electron transport through π -systems as shown in Figure 6.9. The aim is to study the thermoelectric properties of these single-molecule wires. By altering the metal atoms of the core of porphyrins, there is a possibility to adjust the HOMO-LUMO energy levels to be closer to the Fermi energy E_F of the electrodes, where electron transport is expected to occur. To start modelling, I tested the charge transfer and spin states for the isolated metalloporphyrin molecules.



Figure 6.8. Molecular structure of metalloporphyrin.

The isolated metalloporphyrins with all metal atoms [M=Ni, Zn, Mg, and Co] are twisted after making geometry optimisation as shown in Figure 6.9 below. Then I attached each metalloporphyrin molecule between two gold electrodes, where the equilibrium bond length between SMe and the gold atom of the tip is found to be 2.6 Å.



Figure 6.9. Molecular Configurations of four metalloporphyrins. (a) Nickel porphyrin (Ni-P). (b) Zinc porphyrin (Zn-P). (c) Magnesium porphyrin (Mg-P). (d) Cobalt porphyrin (Co-P).

6.3.6 Thermoelectric Calculations of Ni-Porphyrin

The wavefunctions of HOMO-LUMO levels are calculated as shown in Table 6.3 below for both the Ni-porphyrin. In Table 6.3 for the Ni-P molecule, the HOMOs are positioned between -3.53 eV to -2.38 eV and the LUMOs are positioned between -2.2 eV to -1.93 eV.

MOLECULE	Conf.	HOMO-1	HOMO	LUMO	LUMO+1
		611-0 00 -011-0	14 -	\$ \$	
Ni-P	E _F = -2.21 eV	Spin up	Spin up	Spin up	Spin up
		142- 1 22-124	*******		******
	E _g = 0.18 eV	Spin down	Spin down	Spin down	Spin down

Table 6.3. The spin up/down and HOMO-LUMO energy levels are calculated for Ni-porphyrin.

In Figure 6.10 (a), the studied system consists of a metal atom of Ni centred on a porphyrin core that forms an Au-molecule-Au wire where the electron transfer occurs from the left side of the electrode to the right side. Plot (b) illustrates the transmission coefficient T as a function of E, which represents the spin-dependent and total transmission coefficient of the Ni-P, where Fano-resonances occurred close to the DFT-predicted Fermi energy E_F as the transport is LUMO-dominated.



Figure 6.10. (a) Electrode-Nickel-porphyrin-electrode structure (left), (b) logarithmic transmission coefficient T(E) (right).

Figure 6.11 illustrates the thermoelectric properties of Ni-P that is attached symmetrically to two gold electrodes linked with SMe anchor groups. Plot (a) shows the room-temperature electrical conductance G for Ni-P. Plot (b) shows the Seebeck effect S is boosted by increasing the slope of transmission coefficients T(E). Thus, the zero-bias conductance G for the provided geometry is affected by the different connection geometries. The electric thermal conductance κ_e values are shown in plot (c) and the electric Figure of merit ZT_e values shown in panel (d).



Figure 6.11. Thermoelectric calculations. (a) the electrical conductance G. (b) the Seebeck Coefficient S. (c) the electric thermal conductance κ_e . (d) the electric figure of merit ZT_e .

6.3.7 Thermoelectric Calculations of Zn-Porphyrin

Here, I alter the central atom by inserting Zn in the centre of the porphyrin molecule, to determine if the chemical features of this metal produce new features in thermoelectric properties in such nanowires. Table 6.4 shows the spin up/down frontier molecular orbitals of Zn-P wire where the HOMOs of all Zn-porphyrin are located between about -3.43 eV to -2.43 eV and the LUMOs are located between about -1.99 eV to -1.92 eV.

MOLECULE	Conf.	HOMO-1	HOME	LUMO	LUMO+1
75 0	1,4 →	6()= 	14- 2 -21	· *****	
211-P	Lr- 2.21 CV	Spin up	Spin up	Spin up	Spin up
	E 0.44-14	ét]=	14- 8 -41	*****	
	E _g = 0.44eV	Spin down	Spin down	Spin down	Spin down

Table 6.4. The spin-up/down and HOMO-LUMO energy levels are calculated for Zn-porphyrin.

In Figure 6.12 (a), the studied system consists of a metal atom of Zn centred on a porphyrin core that forms an Au-Zn-P-Au wire where the electron transfer occurs from the left side of the electrode to the right side. Plot (b) illustrates the transmission coefficient T as a function of E, which represents the spin-dependent and total transmission coefficient of the Zn-P. Fanoresonances occur close to the DFT-predicted Fermi energy E_F as the transport is considered to be LUMO-dominated.



Figure 6.12. (a) Electrode-Zinc-porphyrin-electrode structure (left), (b) logarithmic transmission coefficient T(E) (right).

Figure 6.14 demonstrates the thermoelectric properties of Zn-P attached symmetrically to two gold electrodes linked with SMe anchor groups. Plot (a) shows the room-temperature electrical conductance G for Zn-P. Plot (b) shows the Seebeck effect S is boosted by increasing the slope of transmission coefficients T(E). Thus, the zero-bias conductance G for the provided geometry is affected by the different connection geometries. The electric thermal conductance κ_e values are shown in plot (c) and the electric Figure of merit ZT_e values shown in panel (d).


Figure 6.13. Thermoelectric calculations. (a) the electrical conductance G. (b) the Seebeck Coefficient S. (c) the electric thermal conductance κ_e . (d) the electric figure of merit ZT_e .

6.3.8 Thermoelectric Calculations of Mg-Porphyrin

To continue this study of a series of metalloporphyrins, I replaced the central atom of the backbone of the porphyrin's ring and added a magnesium Mg atom to observe the change in the thermoelectric properties. First, I optimised the isolated molecule and calculated its electronic structure. Table 6.5 shows the spin-up/down molecular orbitals of Mg-P and its

corresponding HOMO-LUMO energy levels, where HOMO-LUMO energies range approximately between -3.48 to -1.92 eV.

MOLECULE	Conf.	HOMO-1	HOMO	LUMO	LUMO+1
	*******	•11-1 <mark>3</mark> 	¥X-	**************************************	*** * **
Mg-P	E _F = -2.21 eV	Spin up	Spin up	Spin up	Spin up
		+11-1 2 	¹ X-	*****	
	E _g = 0.44eV	Spin down	Spin down	Spin down	Spin down

Table 6.5. The spin up/down and HOMO-LUMO energy levels are calculated for the Mg-P molecule.

In Figure 6.14 (a), the nano-structure shows a metal atom of Mg centred on a porphyrin core that forms an Au-Mg-P-Au wire. Right panel (b) illustrates the transmission coefficient T as a function of E, which represents the spin-dependent and total transmission coefficient of the Mg-P, where Fano-resonances occurred close to the DFT-predicted Fermi energy E_F as the transport is considered to be LUMO-dominated.



Figure 6.14. (a) Electrode-Magnesium-porphyrin-electrode structure (left), (b) logarithmic transmission coefficient T(E) (right).

Figure 6.15 shows the thermoelectric properties of Mg-P that is attached symmetrically to two gold electrodes. Plot (a) shows the room-temperature electrical conductance G for Mg-P. Plot (b) shows the Seebeck effect S which corresponds to the slope of transmission coefficients T(E). Thus, the zero-bias conductance G for the provided geometry is affected by the different connection geometries. The electric thermal conductance κ_e values are shown in plot (c) and the electric Figure of merit ZT_e values shown in panel (d).



Figure 6.15. Thermoelectric calculations. (a) the electrical conductance G. (b) the Seebeck Coefficient S. (c) the electric thermal conductance κ_e . (d) the electric figure of merit ZT_e .

6.3.9 Thermoelectric Calculations of Co-Porphyrin

In this section, I alter the metallic atom by cobalt Co, which is centred on the core of the porphyrin. Table 6.6 represents the spin-up/down molecular orbitals and their HOMO-LUMO energies, which range between -2.76 to -1.88 eV. It can be seen clearly that spin-up molecular orbitals vary from spin-down orbitals due to the spin-splitting behaviour in electron transport.



Table 6.6. The spin-up/down orbitals and HOMO-LUMO energy levels are calculated for the Co-P molecule.

In Figure 6.16 (a), the studied system consists of a metal atom of Co centred on a porphyrin core that forms an Au-Co-P-Au wire where the electron transfer occurs from the left side of the electrode to the right side. Plot (b) illustrates the transmission coefficient T as a function of E, which represents the spin-dependent and total transmission coefficient of the Co-P. Fanoresonances occur close to the DFT-predicted Fermi energy E_F as the transport is considered to be LUMO-dominated.



Figure 6.16. (a) Electrode-Cobalt-porphyrin-electrode structure (left), (b) logarithmic transmission coefficient T(E) (right).

Figure 6.17 shows the thermoelectric properties of Co-P that is attached symmetrically to two gold electrodes. Plot (a) shows the room-temperature electrical conductance G for Co-P. Plot (b) shows the Seebeck effect S which corresponds to the slope of transmission coefficients T(E). Thus, the zero-bias conductance G for the provided geometry is affected by the different connection geometries. The electric thermal conductance κ_e values are shown in plot (c) and the electric Figure of merit ZT_e values shown in panel (d).



Figure 6.17. Thermoelectric calculations. (a) the electrical conductance G. (b) the Seebeck Coefficient S. (c) the electric thermal conductance κ_e . (d) the electric figure of merit ZT_e .

6.3.10 Comparisons of Thermoelectric Calculations

Based on the DFT-SIESTA code and GOLLUM code, I calculate the electric and thermoelectric properties of molecular wires [34] and compare the results of the porphyrins to distinguish clear observations on the charge transfer behaviours. Table 6.7 illustrates electronic structure calculations of the isolated free-base and metalloporphyrins. Based on the spin-polarisation method for accuracy, the transmission functions are represented for five scenarios of porphyrin molecules using the DFT-SIESTA code predicted for the Fermi energy E_F. The thermoelectric

properties are calculated including electrical conductance (*G*), Seebeck coefficient (*S*), electric thermal conductance (κ_e), and electric figure of merit (*ZT_e*).

Porphyrins	E _F (eV)	E _g (eV)
Free-base-P (Bare-P)	-4.97	0.21
Ni-P	-2.21	0.18
Zn-P	-2.21	0.44
Mg-P	-2.21	0.44
Co-P	-2.29	0.55

Table 6.7. The electronic structure calculations of the isolated porphyrins.

Figure 6.18 shows comparisons of thermoelectric properties for the free-base and metalloporphyrin wires. Plot (a) illustrates the transmission coefficients, and there are HOMO-LUMO resonances located close E_F . Generally, there are Fano resonances that appear near $(E - E_F^{DFT} = 0)$.



Figure 6.18. Comparisons of thermoelectric properties of the free-base porphyrin (Bare) and metalloporphyrins [M= Ni, Zn, Mg, and Co] at room temperature (\sim 300K). (a) Transmission coefficient *T* (*E*) as a function of energy E. (b) the electrical conductance G. (c) the Seebeck Coefficient S. (d) the electric thermal conductance κ_e . (e) the electric figure of merit ZT_e .

Junction	$Log(G/G_0)$	S (μV K ⁻¹)	Log κ _e (pW/K)	ZT _e
Free-base (Bare)	-2.84	-141	12.22	0.2
Ni-P	-2	-122.26	12.44	4.97
Zn-P	-1.79	-100.5	12.49	4.88
Mg-P	-1.78	-101.16	12.52	4.72
Co-P	-2.27	-129.27	12.14	6

Table 6.8 Thermoelectric properties calculations of the studied free-base and porphyrins.

Table 6.8 above demonstrates the thermoelectric properties calculations of G, S, κ_e , and ZT_e . The calculated values of Seebeck coefficient S are $S_{bare} > S_{Co} > S_{Ni} > S_{Mg} > S_{Zn}$ at the DFTpredicted Fermi energy in Table 6.8. In comparison, Figure 6.19 shows in plot (a) the electrical conductance *G* values of these studied molecules as a function of energy at the roomtemperature (\sim 300K), showing results from large to small as follows: Mg-P > Zn-P > Ni-P > Co-P > bare. For plot (b), the values of the electronic contribution to the thermal conductance κ_e are as following: Mg-P > Zn-P > Ni-P > bare > Co-P. For plot (c), the values of the electric figure of merit ZT_e are as following: Co-P > Ni-P > Zn-P > Mg-P > bare at the DFT-predicted Fermi energy (E_F = 0 eV).



Figure 6.19. (a) The room-temperature electrical conductance G for the free-base porphyrin (Bare, Ni-P, Zn-P, Mg-P, and Co-P, respectively, where the quantum conductance is $G_0 = 2e^2/h = 77\mu S$. (b) the electric thermal conductance κ_e .(c) the electric figure of merit ZT_e .

6.3.11 Comparisons of Electrical Conductance *G* Between Theoretical Calculations and Experimental Measurements

Now, I shall compare my DFT calculations with recent experimental measurements to provide more insights into the values of electrical conductance (*G*). For comparisons, there are two experimental groups that I compare my results with because of some common conditions with my simulations. The experimental measurements of Group 1 are based on the STM-BJ method and investigate two metalloporphyrins of Au-NiP1-Au and Au-ZnP1-Au linked to various anchor groups [43], whereas the measurements of Group 2, which also utilised the STM-BJ technique, focus on porphyrins such as Au-TPP-Au and Au-CoTPP-Au terminated with a one-sided amino group and the other with a porphyrin ring [44]. Table 6.9 shows a comparison between my theoretical values of electrical conductance and experimental measurements of group 1 and group 2, respectively. Figure 6.20 shows a comparison between DFT calculations (red circles) and experimental measurements of Group 1 (blue triangles) and Group 2 (green stars). Up to this point, my DFT-predicted calculations show excellent agreement with STM-BJ measurements of free-base-porphyrin, Ni-P, Zn-P, and Co-P.

Molecule	Theo. (DFT) Log(G/G ₀)	Exp. (Group1) Log(G/G ₀)	Exp. (Group2) Log(G/G ₀)
Free-base (Bare)	-2.84		-2.49
Ni-P	-2	-2.2	
Zn-P	-1.79	-2	
Mg-P	-1.78		
Co-P	-2.27		-2.58

Table 6.9 The electrical conductance G calculations of the studied free-base and metalloporphyrin molecules.

Note: (--) NO experimental measurements are available.



Figure 6.20. Comparisons of the electrical conductance (*G*) between Thermotical DFT calculations (red) of free-base-porphyrins (Bare) and metalloporphyrins (M= Ni, Zn, Mg, Co) and the excremental group 1 measurement (blue) and the excremental group 2 measurements.

6.3.12 Transmission Coefficients of Porphyrin Molecules in the Presence of Hexafluorophosphate $[PF_6]^{-1}$

Many researchers have investigated redox properties [34,35] and the photovoltaic features of metalloporphyrins [36]. In this section, I am interested in investigating porphyrin molecules which exhibit paramagnetic behaviour (H=1) [37,38] in the presence of [PF $_6$] ⁻ anions. If the results of calculating transmission coefficients close to the Fermi energy show unique behaviours as I modify the metalloporphyrin backbones, these will lead us to explore the possibility of tuning the redox activity and charge transfer (CT) complexation in porphyrin nano-wires. Hence, I shall examine the charge transfer (CT) of free-base porphyrin and metalloporphyrin molecules [M= Ni, Zn, Mg, and Co] with the presence of hexafluorophosphate [PF $_6$]⁻. Here, I position two [PF $_6$] ⁻ anions located on top of the methyl (CH₃) on the edges of the porphyrin's ring by attempting to study electron transport through the combined systems formed from the porphyrins and the hexafluorophosphate. Hence, an oxidation state can occur when an interaction can take place in dimer systems where the [PF $_6$] ⁻ anion molecule can be attractive for forming the charge transfer complexes.

Now, the combination of the free-base-P with the presence of $[PF_6]^-$ anions is shown in Figure 6.21 below, which shows two views of the molecular configuration of the combination of free-base-P plus PF_6^- anions. In Figure 6.22, the spin-up/down orbitals for the HOMO-LUMO energy levels are computed.



Figure 6.21. Two views configuration of free-base porphyrin with the presence of two $[PF_6]^-$ anions.



Figure 6.22. The spin up/down orbitals of HOMO-LUMO for free-base-porphyrin + edged [PF₆⁻]₂.

Next, I formed the combination of Ni-P with the presence of $[PF_6]^-$ anions, as shown in Figure 6.23 below for two views of the molecular configuration of the combination of Ni-P with edged

 PF_{6}^{-} anions. In Figure 6.24, the spin-up/down orbitals of the HOMO-LUMO energy levels are computed.



Figure 6.23. Two views configuration complex of Ni-porphyrin with [PF₆]⁻ anions



Figure 6.24. The spin up/down orbitals and HOMO-LUMO levels for Ni-porphyrin + edged [PF₆⁻]₂.

Figure 6.25 shows two views of the molecular configuration of the combination of Zn-P with edged PF_6^- anions on top of the methyl (CH₃). In Figure 6.26, the spin-up/down orbitals and the HOMO-LUMO energy levels are computed.



Figure 6.25. Two views configuration complex of Zn-porphyrin with $[PF_6]_2$ anions.



Figure 6.26. The spin up/down orbitals and HOMO-LUMO levels for Zn-porphyrin + edged [PF₆]⁻₂.

Then, the combination of Mg-P with the presence of two $[PF_6]^-$ anions is illustrated in Figure 6.27, which shows two views of the molecular configuration of the combination of Mg-P with PF6⁻ anions on top of the methyl (CH₃). In Figure 6.28, the spin-up/down orbitals of the HOMO-LUMO energy levels are computed.



Figure 6.27. Two views configuration complex of Mg-porphyrin with [PF₆]⁻ anions.



Figure 6.28. The spin up/down orbitals and HOMO-LUMO levels for Mg-porphyrin + edged [PF₆⁻]₂.

Here, I combined the Co-P with the presence of $[PF_6]^-$ anions, as shown in Figure 6.29, which shows two views of the molecular configuration of the combination of Co-P with edged $PF_6^$ anions on top of the methyl (CH₃). In Figure 6.30, the spin-up/down orbitals of the HOMO-LUMO energy levels are computed.



Figure 6.29. Two views configuration complex of Co-porphyrin with [PF₆]⁻ anions.



Figure 6.30. The spin up/down orbitals and HOMO-LUMO levels for Co-porphyrin + edged [PF₆⁻]₂.

6.3.13 Comparisons of Transmission Coefficient Calculations

For comparison, Table 6.10 shows the electronic structure calculations of Fermi energies E_F and energy gaps E_g of the studied molecules, obtained from DFT-SIESTA calculations for various scenarios of porphyrins. It can be observed that the range of the Fermi energy E_g is between -3.89 eV to -1.09 eV, and the range of energy gap E_g is between 0.09 eV to 1.33 eV.

Complexes	$E_F(eV)$	E_g (eV)
Free-base-P +	-3.98	0.93
[PF ₆] ⁻ 2		
$Ni-P + [PF_6]^{-2}$	-1.09	0.31
$Zn-P + [PF_6]^2$	-1.23	0.09
$Mg-P + [PF_6]^2$	-1.16	1.33
$\text{Co-P} + [\text{PF}_6]^2$	-1.46	0.3

Table 6.10. The electronic structure calculations of the isolated free-base porphyrins and metalloporphyrins.

The transmission coefficients in Figure 6.31 demonstrate that the presence of the anions $[PF_6]^$ on top of porphyrins junctions affects the electron transport behaviours. By comparing the transmission curves corresponding to free-base and metalloporphyrin wires with (red curves) / without (blue curves) anions $[PF_6]^-$ at room temperature. Fano-resonances occur for each scenario due to charge transfer on the porphyrin's backbone, and PF_6^- anions influence charge transfer behaviours of porphyrin wires [40,41]. As a result, the transmission coefficients show LUMO-dominant behaviours close to the DFT-predicted Fermi energy for all scenarios. Hence, the transmission coefficients T(E) as energy functions are calculated to distinguish unique features in single-molecule wires at room temperature.



Figure 6.31 Comparison of the transmission coefficient functions for porphyrin junctions with (blue curves) vs without (red curves) the anions $[PF_6]^-$. (a) T(E) of Free-base porphyrin (Bare-P) junctions. (b) T(E) of Ni-porphyrins. (c) T(E) of Zn-porphyrins. (d) T(E) of Mg-porphyrins. (e) T(E) of Co-porphyrins.

6.4 Summary

Finally, in this effort, I have investigated a new work to study thermoelectric properties in molecular wires and to discover the electron transfer in porphyrin molecules and their electronic structures. I started by altering the side groups of the free-base porphyrin backbone for two cases, the first is with $(X = C_3N_2)$ and the second case is with [X = pyridine rings plus]the methyl (CH₃)]. Then I introduce a centre metallic ion M into the core of the porphyrins for the series (M = Ni, Zn, Mg, and Co), and the side groups are [X = pyridine rings plus the methyl group (CH₃)]. For the free-base porphyrin and all metalloporphyrins, I studied their effects on the thermoelectric behaviours through molecular wires. Metalloporphyrin molecules are unique organic molecules due to their large chemical and thermal stability, and provide strong absorption through the electromagnetic spectrum. As I previously illustrated the results, my investigations in using functionalised metal-centred candidates Ni, Zn, Mg, and Co, embodied in the centre of the porphyrin core. I can adjust the molecular energy states related to the Fermi energy of the electrodes. Next, I combined the porphyrin molecule with the presence of two hexafluorophosphate [PF₆]⁻ anions located on top of the methyl (CH₃) of the porphyrin backbone. Moreover, different scenarios of porphyrin candidates are combined with two anions [PF₆] seeking confirmation of the oxidation state. The resulting values of thermoelectric properties show a significant range of values, depending on the metal. I demonstrated in this chapter significant calculations which show results of conductance in single-molecule wires as follows: **Mg-P > Zn-P > Ni-P > Co > bare**.

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Chapter 7 Conclusions and Future Works

7.1. Conclusions

In this thesis, I have presented fundamental aspects of quantum transport by first illustrating computational methods, which are widely used for nano-structure systems. My interest in these synthesised systems is motivated by the possibility of controlling the unique features which occur close to the Fermi energy E_F of the electrodes. To explore this possibility, this thesis explores the electric and thermoelectric properties of various molecular systems by using the density functional theory (DFT), the Green's function method in detail. In Chapter 2, I introduced the formulation of the density functional theory (DFT), particularly with local density approximations for the exchange-correlation and the pseudopotentials used in the SIESTA code. Furthermore, the Klein-Bylander method was illustrated. In Chapter 3, the Green's function method was addressed, and the Landauer formula was explained, along with important features in the transmission coefficients, including resonances and thermoelectric properties.

In Chapters 4 and 5, detailed simulations focused on charge transport (CT) complexes based on π -conjugated chlorine bisimide perylene (Cl-PBI) molecular junctions linked with various anchor groups (pyridine and SMe). In particular, the effects of pendant groups of tetracyanoethylene (TCNE) and then tetrathiafulvalene (TTF) were investigated. I also applied the DFT-SIESTA method to calculate thermoelectric properties. The studied molecules offer advantages for on/off molecular switching and sensing applications. Moreover, I showed the relationship between the transmission coefficient as a function of energy and the thermopower effect at the DFT-predicted Fermi energy E_F . My results suggested that the dimer combinations between the Cl-PBIs and the TTF show a Fano resonance feature close to the Fermi energy of gold electrodes, whereas the combinations of Cl-PBIs and the acceptor TCNE show normal tunnelling behaviour as for the bare junctions, with two Breit-Wigner resonances associated with the HOMO-LUMO levels.

I demonstrated that varying the anchor groups (Pyridine and SMe) symmetrically connected to both sides of chlorine bisimide perylene Cl-PBIs and linked to two gold electrodes can affect the physical properties in single-molecule junctions SMJs. Furthermore, introducing the charge transfer (CT) complexes using the pendant molecules TCNE and TTF can provide a means to adjust the electron transport behaviour. It was shown that the combined system consisting of Cl-PBI + TTF produces Fano resonance close to Fermi energy for different anchor groups pyridine and SMe. Additionally, using pyridine anchor groups leads to magnitudes of Seebeck coefficients S ranging between [-366 to +354 μ V/K] and provides higher electrical conductance log (G/G₀) ranging between [-4.4 to -3.67]. On the other hand, SMe anchor groups lead to magnitudes of Seebeck coefficients *S* ranging between [-345 to +408 μ V/K] and also provide smaller electrical conductance G/G₀ ranging between [-7.93 to -7.2].

In Chapter 6, I examined the thermoelectric properties of porphyrin molecules attached to gold electrodes and examined the properties of a series of metalloporphyrins, obtained by inserting metal atoms Ni, Zn, Mg, and Co into the core of porphyrin. In this way, I examined the thermoelectric properties of a variety of metalloporphyrin derivatives. In these molecules, different ions are coordinated in the centre of the porphyrin core. At room temperature, I attempted to enable the tuning of the electric and thermal features by varying the side groups

of the bay area on the backbone of free-base porphyrin molecules. Next, I investigated the effect of introducing PF_6^- anions on top of the methyl (CH₃) along the porphyrins. I found that the electrical conductance G increases due to the presence of these ions.

In conclusion, I illustrated the main concepts of my work starting with theoretical formalisms and then computational calculations at single-molecule levels. Density functional theory is the foundation of my calculations to study quantum transport behaviours and to investigate the electric and thermoelectric properties in molecular systems. I have concentrated on the charge transfer complex in single-molecule junctions.

7.2. Future Works

I shall expand my current work further by including more derivatives of perylene bisimides (PBIs), which contain different bay-area substituents. A family consists of four symmetric PBIs derivatives, such as thiobutyl (S-PBI), pyrrolidinyl (Py-PBI), and tert-butyl-phenoxy (T-PBI, P-PBI) and also one unsymmetric derivative, such as (aPy-PBI), which are linked by thiol anchor groups to study their thermoelectric properties. As a next step, I shall combine the previous molecules with TCNE and TTF to observe any unique features in charge transfer complexes.

and introducing new anchor groups (i.e., Thiol: [-SH], and Amine: [-NH₂]), and varying electrode materials (i.e., Graphene, and Silicon [Si]) and multi-terminals, shapes and also including effected quantities on the single-molecule junctions such as electric and thermal conductance and how the effective mass can play a role in phononic calculations. Furthermore, I am also interested in involving different electrodes and anchor groups and how they can affect changing electric and thermoelectric properties in SMJs. I shall introduce more theoretical

analysis techniques for future projects, such as increasing my understanding of analytical and physical concepts of quantum transport systems and expanding our studies for more thermoelectric properties.

For future studies, I shall focus on enhancing the thermoelectric figure of merit ZT either by increasing the thermopower effect or reducing the relative contribution of phononic thermal conductance compared to electric thermal conductance from the ratio of κ_{ph}/κ_e as a function of the temperature T and current-voltage (I/V) calculations. I shall involve more computational techniques, i.e., Gaussian 16, and VASP and cooperate with theoretical and experimental groups. One of my interesting plans is to investigate larger and stronger coupling to pendant groups to exploit new features by studying the CT with various donors/acceptors (i.e., *Dibenzotetrathiafulvalene* (DBTTF), *Bis(ethylenedithio)tetrathiafulvalene* (BEDT-TTF)

Tetracyanoquinodimethane (TCNQ), and F₄TCNQ.

The phononic contributions can play an essential role in the thermal conductance and affect the magnitude of the full figure of merit (ZT) at room temperature. Phonons represent atomic vibrations; thus, I shall elaborate on studying how electron-phonon interaction affects molecular device efficiency at room temperature. Thermal transport is controlled by vibrational behaviours of phonons in single-molecule junctions [1]. The thermal conductance can be varied for more rigorous calculations due to phonon interactions along a metal-molecule-metal junction. I can use the density functional theory (DFT) approach to calculate the phononic thermal properties for single-molecule junctions. Theoretical studies of thermal transport in nano-scale systems can provide a deep scope of understanding thermal features, which leads to improving thermoelectric applications. There are many opportunities for applying thermal features in various fields, i.e. heat pumps/ratchets [2,3], thermal modulators/rectifiers/ transistors [4-7].

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