Connectivity-dependent Wigner delay times in molecular-scale nanostructures

By

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Declaration

I hereby declare that the thesis is my own work and effort and has not been submitted in substantially the same form for the award of a higher degree elsewhere. Where other sources of information have been used, they have been acknowledged.

Except where stated otherwise, this thesis is a result of the author's original work and has not been submitted in whole or in part for the award of a higher degree elsewhere. This thesis documents work carried out between October 2014 and September 2016 at Lancaster University, UK, under the supervision of Prof. Colin J. Lambert.

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Abstract

This thesis addresses the question of the time spent by a transmitted wave packet within a scattering region. The study involves mathematical aspects of solving the Schrodinger equation in open systems with a view to developing new conceptual approaches to scattering theory. Efficient schemes to obtain scattering matrices from mean-field Hamiltonians are developed and these are implemented in new numerical codes. The relationship between the phase of S-matrix elements and Wigner delay times is also elucidated.

I consider the scattering problem in a tight-binding lattice, as a simple way to understand the relation between M-functions and Greens functions and to investigate the connectivity dependence of Wigner delay times. To analyse delay times in bipartite lattices, tight binding calculations are used and a new computer code is developed to verify analytical predictions. In particular, Green's functions and a mid-gap theory are used to calculate Wigner delay times for different connectivities in graphene like molecules. One interesting and counterintuitive result is that in the weak coupling limit at the middle of HOMO and LUMO gap, the Wigner delay time does not depend on the distance between the connections to external reservoirs.

Acknowledgements

*" Above all, my great thanks to **ALLAH** for his mercy and blessing "*

I would like to dedicate my thesis to my father and mother

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Chapter 1

Introduction

1.1   Molecular scale electronics

In recent years much emphasis has been given to understanding the electronic structure and uncovering the properties of single molecules [1]. This has led to the possibility of utilising a few or single molecules as building blocks in a nanoscale device with the aim of miniaturizing electronic circuits and producing systems such as atomic scale sensors and thermoelectric devices. The advantage of single molecules lies in the ability to be able to chemically design and synthesise molecules with targeted functionality and this is an area where theory can help by predicting the optimum behaviour before synthesis. [2].

In the present study the molecular system is used for investigating significant characteristics of electron propagation such as the group velocity of electrons, energy bands, density of states and transmission coefficient that are defined as function of energy. Tight binding model has been used for investigating transmission coefficients.

Greens function plays a significant role in determining the transmissions coefficients. The study presents the Landauer formula and greens function approach for analysing the scattering processes [3-5] in a system attached to infinite one-dimensional leads. The study involves the calculation of the retarded greens' function in which the simple formula of a one-dimensional tight binding chain in presented. The periodicity of the

lattice is also broken at a single connection for showing the green's function associated with the transmission coefficient along the scattering region.

1.2 The concept of the Wigner delay time

The concept of time delay was primarily introduced by using the explanation of a scattering process. If the transmission amplitude is $t = |t|\exp(i\theta)$, then the time delay is usually represented as $\hbar \frac{d\theta}{dE}$, and describes the amount of time spent by a wave packet passing through the scattering region. I present a theoretical and analytical study of this Wigner delay time in graphene-like cores by using a tight-binding calculation as a tool to achieve analytic and numerical solutions.

1.3 Thesis outline

Following this chapter, the overview of the thesis as follows:

1. In the second chapter following I will present a simplest description of retarded Green's function. First I consider a perfect one-dimensional tight binding chain, and then I break the periodicity at a single connection and show how the Green's function is related to the transmission coefficient through the scattering region. Then I will introduce another method to calculate the transmission coefficient from the wave function starting with the Schrodinger equation. Finally, I will show the relation between the green's function and mid-gap transport for molecule structures such as bipartite lattices which their HOMO is

completely filled and $E_{HL}=0$ where it is analytic everywhere unlike G which includes poles at the eigenvalues E_n of H.

2. In chapter three I will introduce the analytical formula of Wigner delay time starting with the time dependent Schrodinger equation and by applying it to a scattering problem [6]. Then, I will relate this concept to the M-function and connectivities[7-9] to investigate Wigner delay time in graphene-like molecules using tight-binding calculations when the coupling to the molecule is very weak and the Fermi energy coincides with the center of the HOMO-LUMO gap. Finally, I will present and discuss my results related to the Wigner delay time.

3. Chapter four is the last chapter. It will contain a summary of the outcomes of this work and the possible applications that could arise from this work in future.

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Chapter 2

Quantum transport

2.1 Introduction

The theory of single particle transport is introduced as the main numerical tool for studying a range of molecular geometrics and involves detailed investigation of electronic properties. Molecular electronics is focused on understanding the electrical properties of molecular junctions where a molecule is attached between electrodes and the ballistic transport is occurring through energy levels of the molecules. The coupling strength existing between lead and molecules is considered to be small in comparison to intra- electrode and inter molecular binding strengths. A scattered process is also involved in the movement from electrode to molecule and then from molecule to electrode. The scattering process from electrode junction and molecular bridge can be understood following a general approach of the green's function formalism helps in achieving this process. In the beginning of this chapter I introduce a simple formula of a retarded green's function has been explained for one dimensional tight binding chain. Then by breaking the periodicity of this lattice at a single connection, the green's function directly related to transmission coefficient through the scatting region is obtained.

2.2 Theory of electron transport

To have a good understanding of electron transport we should know about the transmission probability (T) which is related to the conductance G at Fermi energy E_F by the Landauer formula [1, 2]:

$$\sigma(E) = G_o T(E) \tag{2.2.1}$$

Where the electrical conductance is $\sigma(E)$ as a function of energy and the quantum conductance is represented by $G_o = \frac{2e^2}{h}$ where 'e' is the electron charge and h is the Planck's constant. $T(E)$ has denotes the transmission coefficient as a function of energy, and is the probability that an electron with energy E can transfer from one electrode to the other.

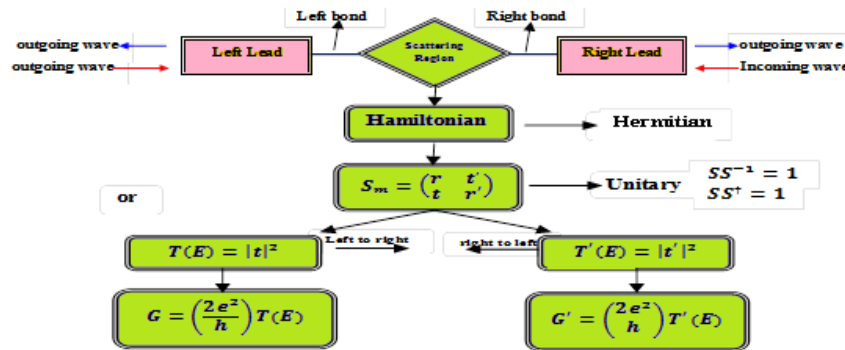This leads us to the scattering formalism shown schematically below:

Diagram 1.The transport mechanism where it is combination of mathematical and physical structures.

The transport mechanism is composed of two types of probabilities as probability of $R(E)$ and probability of $T(E)$

$$|t|^2 + |r|^2 = 1 \;\; \rightarrow T(E) + R(E) = 1$$

Where r and t are the amplitudes of reflection and transmission respectively.

2.3 Green's functions in one-dimension

2.3.1 Perfect one-dimensional lattice

It is helpful to calculate the scattering matrix for a simple one dimensional structure before representing a generalized methodology. I use the green's function approach for the derivation and a later stage the scattering matrix of one dimensional scatter is calculated. In this section, a simple infinite one dimensional chain having on-site energies (ε_o) along with hopping elements$(-\gamma)$ as shown in figure (2.3.1) is discussed for green's functions.
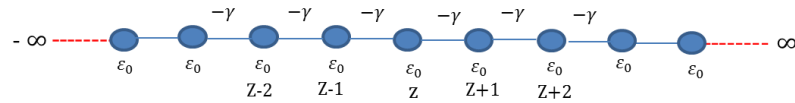
Figure 2.3.1.The tight-binding model of a one-dimensional periodic lattice with energy site ε_o and hopping elements$(-\gamma)$.

For obtaining z row of Hamiltonian the Schrödinger equation is represented as;

$$-\gamma\Psi_{(z-1)} + (E - \varepsilon_o)\Psi_{(z)} - \gamma\Psi_{(z+1)} = 0 \qquad (2.3.1)$$

For any function $\Psi_{(z)}$ that has to be a wave function, it only needs to satisfy criteria of the Schrodinger equation (2.3.1)

It is assumed that $\gamma = \gamma *$ and substituting a plane wave into equation (2.3.1) leads to the dispersion relation (2.3.2).

$$E = \varepsilon_o - 2\gamma \cos k \qquad\qquad (2.3.2)$$

The wave number is commonly represented by the quantum number (k) and the wave function is linked to the retarded green's function represented as $g(z, z')$. This equation is very similar to the Schrödinger equation;

$$\left.\begin{array}{c} (E - H)\, g(z, z') = \delta_{(z,z')} \\ -\gamma g(z - 1, z') + (E - \varepsilon_o)\, g(z, z') - \gamma\, g(z + 1, z') = \delta_{(z,z')} \end{array}\right\} \qquad (2.3.3)$$

Where

$$\delta_{(z,z')} = 1, \qquad if\ z = z'$$

And

$$\delta_{(z,z')} = 0, \qquad if\ z \neq z'$$

Physically, the response of a system is defined at point z described under retarded green's function $g(z, z')$ resulting from excitation at point z'. We expect two waves traveling outward from the excitation point with amplitude B and D as represented in figure (2.3.2).
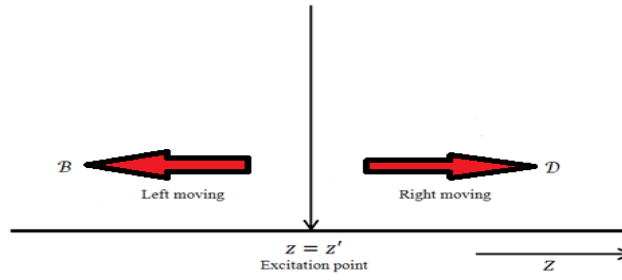
Figure 2.3.2.The structure of retarded Green's function having an infinite one dimensional lattice. The wave is propagated towards the left and right sides through excitation at $z = z'$ with amplitude B and D respectively.

These waves can be simply expressed as:

$$g(z,z') = \begin{cases} De^{ikz}, & z \geq z' \\ Be^{-ikz}, & z \leq z' \end{cases}$$ (2.3.4)

This expression satisfies equation (2.3.3) at every point, while the condition $z = z'$ is not satisfied where the green's function must be continuous at $z = z'$.

$$[g(z,z')]_{Left} = [g(z,z')]_{Right}$$ (2.3.5)

$$Be^{-ikz'} = De^{ikz'}$$ (2.3.6)

$$B = De^{2ikz'}$$ (2.3.7)

So I find that,

$$g(z,z') = \begin{cases} D\,e^{ikz} & = D\,e^{ikz'}\,e^{ik(z-z')} & z \geq z' \\ De^{2ikz'}e^{-ikz} = De^{ikz'}e^{ik(z'-z)} = D\,e^{ikz'}\,e^{ik(z'-z)} & z \leq z' \end{cases}$$ (2.3.8)

We know that, the power of the complex exponent has to be always positive and the simplified form of latter equation is represented as;

$$g(z, z') = De^{ikz'}e^{ik|z'-z|}, \qquad \forall z \qquad\qquad (2.3.9)$$

Secondly, this expression must satisfy the green's equation, $(E - H)g(z, z') = \delta_{z,z'}$:

$$\delta_{z,z'} = Eg(z, z') - \varepsilon_0 g(z, z') + \gamma g(z+1, z') + \gamma g(z-1, z') \qquad\qquad (2.3.10)$$

I find the solution at $z = z'$:

$$1 = (E - \varepsilon_0)g(z, z) + \gamma g(z+1, z) + \gamma g(z-1, z)$$

$$= D\,e^{ikz'}[(E - \varepsilon_0)e^{ik|z-z'|} + \gamma e^{ik|z+1-z'|} + \gamma e^{ik|z-1-z'|}] \qquad (2.3.11)$$

solving for $D\,e^{ikz'}$:

$$\frac{1}{D\,e^{ikz'}} = (E - \varepsilon_0) + \gamma e^{ik} + \gamma e^{ik}$$

$$= (E - \varepsilon_0) + \gamma e^{ik} + \gamma e^{ik} + \gamma e^{-ik} - \gamma e^{-ik}$$

$$= \gamma e^{ik} - \gamma e^{-ik}$$

$$= 2i\gamma sink \;\rightarrow D\,e^{ikz'} = \frac{1}{2i\gamma sink} \qquad\qquad (2.3.12)$$

Since we know that from the Schrödinger equation, the group velocity $hv_g = 2\gamma \sin k$,

and the green's function for a one-dimensional chain can be written as:

$$g^R(z, z') = \frac{1}{ihv_g}\,e^{ik|z-z'|} \qquad\qquad (2.3.13)$$

There are more solutions that can be found for this problem in the literature [3,4,5]. In above equation, I have shown the retarded green's function $g^R(z, z')$. On the other hand the advanced green's function $g^A(z, z')$ is an equally valid solution;

$$g^A(z, z') = \frac{-1}{i\hbar v_g} e^{-ik|z-z'|} = \frac{i}{\hbar v_g} e^{-ik|z-z'|} \qquad (2.3.14)$$

The retarded green's function describes outgoing waves from an excitation point $(z = z')$, but the advanced green's function is describing two incoming waves that vanish at the excitation point. From here I will use the retarded green's function and for the sake of simplicity, drop the R from its representation. So $g(z, z') = g^R(z, z')$.

2.3.2   Semi-infinite one-dimensional lattice
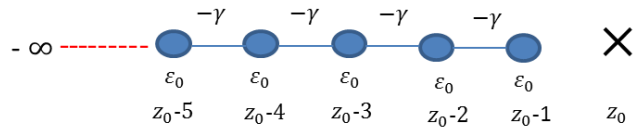
Figure 2.3.3.The tight-binding model of a semi-infinite one-dimensional lattice with energy site ε_o and hopping elements $(-\gamma)$.

I introduce another plane wave component with a new amplitude:

$$g(z, z') = \frac{1}{i\hbar v_g} e^{ik|z-z'|} + A\, e^{-ik|z-z'|} \qquad (2.3.15)$$

To satisfy the boundary condition, we expect that a source at z_0 when $z' = z_0$- doesn't have any effect on the chain. In other words from this condition $g(z, z_0) = 0$, $z \le z'$, we find:

$$g(z, z_0) = \frac{1}{i\hbar v_g} e^{ik(z_0-z)} + A\, e^{-ik(z_0-z)}$$

$$A = -\frac{1}{i\hbar v_g} e^{2ik(z_0-z)} \qquad (2.3.16)$$

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By substituting this back into the green's function, I find:

$$g(z, z') = \frac{1}{ihv_g} e^{ik(z\prime - z)} - \frac{1}{ihv_g} e^{2ik(z_0 - z)} e^{-ik(z\prime - z)}$$

$$g(z, z') = \frac{1}{ihv_g} \left[e^{ik(z\prime - z)} - e^{ik(2z_0 - z - z\prime)} \right] \qquad (2.3.17)$$

The second condition is that, any point beyond $z_0 - 1$ does not have effect from a source in the chain. So if $z \geq z'$ and $z = z_0$, we expect $g(z_0, z) = 0$ so from this condition, I find:

$$g(z_0, z) = \frac{1}{ihv_g} e^{ik(z_0 - z\prime)} + A\, e^{-ik(z_0 - z\prime)}$$

$$A = -\frac{1}{ihv_g} e^{2ik(z_0 - z\prime)} \qquad (2.3.18)$$

By substituting this back into the green's function, I find:

$$g(z, z') = \frac{1}{ihv_g} e^{ik(z - z\prime)} - \frac{1}{ihv_g} e^{2ik(z_0 - z\prime)} e^{-ik(z - z\prime)}$$

$$g(z, z') = \frac{1}{ihv_g} \left[e^{ik(z - z\prime)} - e^{ik(2z_0 - z - z\prime)} \right] \qquad (2.3.19)$$

By summarizing these two results I find:

$$\begin{cases} \frac{1}{ihv_g} \left[e^{ik(z - z')} - e^{ik(2z_0 - z - z')} \right], & z \geq z' \\ \frac{1}{ihv_g} \left[e^{ik(z' - z)} - e^{ik(2z_0 - z - z')} \right], & z \leq z' \end{cases} \qquad (2.3.20)$$

The above result can be written as:

$$g(z, z') = \frac{1}{ihv_g} \left[e^{ik|z - z\prime|} - e^{ik(2z_0 - z - z\prime)} \right] = g_{z,z\prime}^{\infty} + \Psi_{z,z\prime}^{z_0} \qquad (2.3.21)$$

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2.3.3 Surface Green's function

In this case the surface Green's function is evaluated with the site energy at point

$z_0 - 1$. So the surface Green's function is:

$$g(z_0 - 1, z_0 - 1) = \frac{1}{ihv_g} \left[e^{ik|z_0-1-z_0+1|} - e^{ik(2z_0-z_0+1-z_0+1)} \right] \quad (2.3.22)$$

Then we end with the simple form;

$$g(z_0 - 1, z_0 - 1) = \frac{1}{ihv_g}(-2isink)\, e^{ik} \quad (2.3.23)$$

$$g(z_0 - 1, z_0 - 1) = -\frac{2isink}{2i\gamma sink}\, e^{ik} = -\frac{e^{ik}}{\gamma} \quad (2.3.24)$$

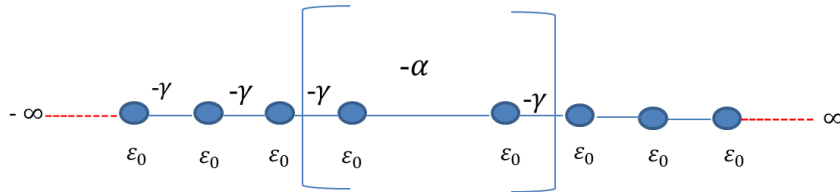### 2.3.4 One-dimensional Scattering Using green's functions

Figure 2.3.4.The tight binding model of two semi-infinite leads with one site energies ε_0 and couplings $-\gamma$, coupled by hopping element $-\alpha$.

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I consider two semi-infinite one-dimensional leads coupled by hopping element α.
The total green's function is obtained in the case of decoupled leads $(\alpha = 0)$ and it is
represented by;

$$g = \begin{pmatrix} -\dfrac{e^{ik}}{\gamma} & 0 \\ 0 & -\dfrac{e^{ik}}{\gamma} \end{pmatrix} = \begin{pmatrix} g_L & 0 \\ 0 & g_R \end{pmatrix} \qquad (2.3.25)$$

This green's function represents two decoupled semi-infinite leads , $g = (E - h_1)^{-1}$
where h_1 is the Hamiltonian of two decoupled semi-infinite leads and by defining
an infinite matrix this Hamiltonian will be;

$$h_1 = \begin{pmatrix} \ddots & \ddots & 0 & 0 & 0 & 0 & 0 & 0 \\ \ddots & \ddots & -\gamma & 0 & 0 & 0 & 0 & 0 \\ 0 & -\gamma & \varepsilon_o & -\gamma & 0 & 0 & 0 & 0 \\ 0 & 0 & -\gamma & \varepsilon_o & -\gamma & 0 & 0 & 0 \\ 0 & 0 & 0 & -\gamma & \varepsilon_o & -\gamma & 0 & 0 \\ 0 & 0 & 0 & 0 & -\gamma & \varepsilon_o & -\gamma & 0 \\ 0 & 0 & 0 & 0 & 0 & -\gamma & \ddots & \ddots \\ 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots \end{pmatrix} \qquad (2.3.26)$$

By connecting this two leads by hopping element α , and the Hamiltonian for whole
system or coupled system in figure(2.3.4) becomes $H = h_1 + h_0$ where h_0 contains
the coupling parameters

$$h_0 = \begin{pmatrix} 0 & \alpha \\ \alpha & 0 \end{pmatrix} \qquad (2.3.27)$$

The green's function obtained for coupled system will be found by using Dyson's
equation as follows;

$$G = (E - H)^{-1} = (E - h_1 - h_0)^{-1} \qquad (2.3.28)$$

$$G = (g^{-1} - h_0)^{-1} \qquad (2.3.29)$$

The solution, in this case, will be:

$$G = \left(\left(\begin{matrix} -\dfrac{e^{ik}}{\gamma} & 0 \\ 0 & -\dfrac{e^{ik}}{\gamma} \end{matrix} \right)^{-1} - \begin{pmatrix} 0 & \alpha \\ \alpha & 0 \end{pmatrix} \right)^{-1} \qquad (2.3.30)$$

$$G = \dfrac{1}{\gamma^2 e^{-2ik} - \alpha^2} \begin{pmatrix} -\gamma e^{-ik} & \alpha \\ \alpha^* & -\gamma e^{-ik} \end{pmatrix} \qquad (2.3.31)$$

In order to calculate the transmission $\vec{t}$ and the reflection $\overleftarrow{r}$ amplitudes, we use the greens' function presented in equation (2.3.31) and apply them to the Fisher Lee relation which calculates the scattering amplitudes of the scattering problem by relating it to the green's function of the same problem [3,6].

Since we know the green's function components from equation (2.3.31), then we can define the transmission and reflection coefficients. The source from the excitation point sends two waves travelling outwards, one away from the scatter and one towards the scatter with amplitude B and D respectively. So the green's function contains information about two waves, left wave or a reflected wave $(D\,e^{-ik|z-z'|} + Bre^{ik|z-z'|})$ and the transmitted right wave $(Bte^{ik|z-z'|}))$. Here we use symbol $\vec{t}$ for

transmitted right wave and $\check{r}$ for reflected wave where arrows are pointing directions of amplitudes.

$$1 + r = -ihv_g \frac{\gamma \, e^{-ik}}{\gamma^2 e^{-2ik} - \alpha^2} \qquad (2.3.32)$$

$$t = ihv_g \frac{\alpha \, e^{ik}}{\gamma^2 e^{-2ik} - \alpha^2} \qquad (2.3.33)$$

To calculate the transmission and reflection probabilities we use these coefficients as follows;

$$T = |t|^2 \qquad and \qquad R = |r|^2$$

So, by using the Landauer formula represented in equation (2.2.1) we can also calculate the conductance of the system.

2.4 More general method to calculate the transmission from a wave function

In this chapter I discuss the relationship between a wave function and green's function in more detail and present a more general method for computing the transmission amplitude of an arbitrary scattering region connected to one-dimensional leads.
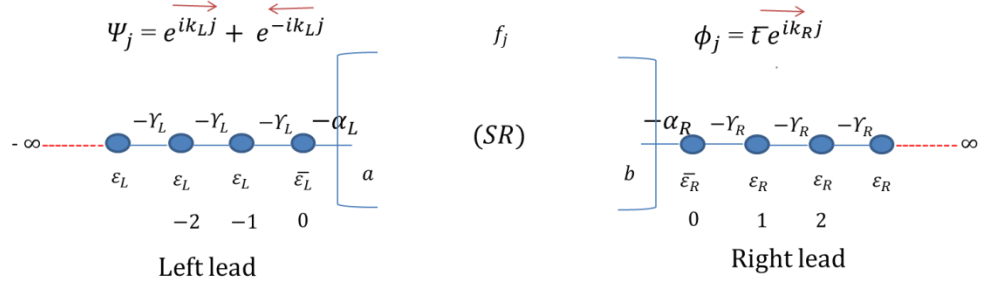
Figure 2.4.1.A simple tight binding model having two different infinite leads that are connected with independent scattering regions via hoping elements $(-\alpha_L)$ and $(-\alpha_R)$.

The structure presented in figure (2.4.1) can be described in details that will provide a clear picture of the methodology used. We have two different leads one of them called the left lead and another one the right lead. The left lead is a one-dimensional periodic lattice constructed with site energies ε_L and coupling $-\gamma_L$ and in the same for the right lead just the values of the site energies are ε_R and the coupling $-\gamma_R$. The hopping elements $-\alpha_L$ and $-\alpha_R$ are used for connecting the infinite leads with independent scattering regions. In this section, I will use the form of green's function to solve the problem and calculate the transmission coefficient as a function of energy.

2.4.1 Schrödinger equation representation

The problem is solved by considering the Schrödinger equation for the current system. The equation is represented below:

$$H|\Psi\rangle = E|\Psi\rangle \tag{2.4.1}$$

The Hamiltonian of the scattering region is represented by H that will be used for describing the current system. The eigenvalues are represented by E of the Hamiltonian H and are used to present the wave function of the whole system and developing the equation.

$$H \begin{pmatrix} \vdots \\ \Psi_{-2} \\ \Psi_{-1} \\ \Psi_0 \\ f_a \\ \vdots \\ f_b \\ \phi_0 \\ \phi_1 \\ \phi_2 \\ \vdots \end{pmatrix} = E \begin{pmatrix} \vdots \\ \Psi_{-2} \\ \Psi_{-1} \\ \Psi_0 \\ f_a \\ \vdots \\ f_b \\ \phi_0 \\ \phi_1 \\ \phi_2 \\ \vdots \end{pmatrix} \qquad (2.4.2)$$

The Schrödinger equation is derived as;

$$\bar{\varepsilon}_L \Psi_0 - \gamma_L \Psi_{-1} - \alpha_L f_a = E\, \Psi_0 \qquad (2.4.3)$$

$$\bar{\varepsilon}_R \phi_0 - \gamma_R \phi_{+1} - \alpha_R f_b = E\phi_0 \qquad (2.4.4)$$

$$\therefore (\bar{\varepsilon}_L - \varepsilon_L)\Psi_0 + \gamma_L \Psi_1 = \alpha_L f_a \qquad (2.4.5)$$

$$(\bar{\varepsilon}_R - \varepsilon_R)\phi_0 + \gamma_R \phi_{-1} = \alpha_R f_b \qquad (2.4.6)$$

From the physical structure:

$$\Psi_1 = e^{ik} + r\, e^{-ik}$$

While

$$\Psi_0 = 1 + r$$

A new equation is obtained

$$\Psi_1 = 2i \sin k_L + \Psi_0 e^{-ik_L} \tag{2.4.7}$$

Where

$$\phi_{-1} = \phi_0 e^{-ik_R} \qquad \text{and} \qquad \phi_0 = \overline{t}$$

So,

$$t = \left(\frac{v_R}{v_L}\right)^{1/2} \times \overline{t} \tag{2.4.8}$$

So, the aim here is to write Ψ_1 and ϕ_{-1} in terms of Ψ_0 and ϕ_0 to make the problem easier where ($\vec{t}$) is the transmission amplitude and ($\tilde{r}$) is the reflection amplitude.

An appropriate boundary condition has been introduced in order to derive the green's function for an infinite leads and the system will be represented as;

$$f_a = \frac{\gamma_L}{\alpha_L} \Psi_1 \tag{2.4.9}$$

$$f_b = \frac{\gamma_R}{\alpha_R} \phi_{-1} \tag{2.4.10}$$

Hence; we know that from the general Schrödinger equation:

$$H|f_j\rangle = E|f_j\rangle + |S\rangle \tag{2.4.11}$$

Also,

$$\sum_{j=1}^{N} H_{ij} f_j = E f_i + \alpha_L \Psi_0 \delta_i + \alpha_R \phi_0 \delta_i$$

$$\left(E - H\right)|f\rangle = -\,|S\rangle \quad \text{where,} \quad |S\rangle = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ -\alpha_L \Psi_0 \\ 0 \\ 0 \\ \vdots \\ -\alpha_R \phi_0 \\ \vdots \end{pmatrix} \tag{2.4.12}$$

So, the above equation is transformed as:

$$|f\rangle = -\,g(E)\,|S\rangle \tag{2.4.13}$$

The problem can be solved after calculating the green's function of the normal form and it can be written as;

$$g(E) = (E - H)^{-1} \tag{2.4.14}$$

So,

$$\begin{pmatrix} f_a \\ f_b \end{pmatrix} = -\begin{pmatrix} g_{aa} & g_{ab} \\ g_{ba} & g_{bb} \end{pmatrix}\begin{pmatrix} -\alpha_L \Psi_0 \\ -\alpha_R \phi_0 \end{pmatrix} \tag{2.4.15}$$

This yields to:

$$-\begin{pmatrix} g_{aa}\,\alpha_L + \frac{\gamma_L}{\alpha_L}\,e^{-ik_L} & g_{ab}\,\alpha_R \\ g_{ba}\,\alpha_L & g_{bb}\,\alpha_R + \frac{\gamma_R}{\alpha_R}\,e^{-ik_R} \end{pmatrix}\begin{pmatrix} \Psi_0 \\ \phi_0 \end{pmatrix} + \frac{\gamma_L}{\alpha_L}\,2i\sin k_L\begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{2.4.16}$$

I want to calculate the transmission coefficient and it's comes from ϕ_0

So,

$$\begin{pmatrix} \Psi_0 \\ \phi_0 \end{pmatrix} = -g^{-1} \times \begin{pmatrix} 1 \\ 0 \end{pmatrix}\frac{\gamma_L}{\alpha_L}\,2i\sin k_L \tag{2.4.17}$$

$$\begin{pmatrix} \Psi_0 \\ \phi_0 \end{pmatrix} = \frac{1}{detg} \begin{pmatrix} g_{aa}\,\alpha_L + \frac{\gamma_L}{\alpha_L}\,e^{-ik_L} \\ g_{ba}\,\alpha_L \end{pmatrix} \times \frac{\gamma_L}{\alpha_L}\ 2i\sin k_L \qquad (2.4.18)$$

I calculate the determinant of g and find

$$det\, g = \frac{\gamma_L\,\gamma_R}{\alpha_L\,\alpha_R}\,e^{-i(k_L+k_R)}\,[1 + g_{aa}\,\frac{\alpha_L{}^2}{\gamma_L}\,e^{ik_L} + g_{bb}\,\frac{\alpha_R{}^2}{\gamma_R}\,e^{ik_R} + (g_{aa}\,g_{bb} - g_{ba}\,g_{ab})$$
$$\frac{\alpha_L{}^2\,\alpha_R{}^2}{\gamma_L\,\gamma_R}\ e^{i(k_L+k_R)} \qquad (2.4.19)$$

So,

$$\phi_0 = \overline{t} = \frac{g_{ba}\alpha_L}{detg} \times \frac{\gamma_L}{\alpha_L}\ 2i\sin k_L \qquad (2.4.20)$$

Where,

$$\phi_0 = \overline{t} = \frac{\alpha_L\,\alpha_R}{\gamma_L\,\gamma_R} \times e^{i(k_L+k_R)} \times \frac{g_{ba}}{detg} \times \gamma_L\,2i\sin k_L \qquad (2.4.21)$$

So, by using equation (2.4.8) we obtain:

$$t = \frac{i\,(v_R\,v_L)^{1/2}}{\alpha_L\,\alpha_R} \times \frac{g_{ba}}{detg} \times e^{i(k_L+k_R)} \qquad (2.4.22)$$

Where $v_L = 2\gamma_L \sin k_L$ is the group velocity of the left lead.

From this, the transmission coefficient T is obtained from

$$T = |t|^2 \qquad (2.4.23)$$

2.5 Molecules and Quantum dot

If we have a closed system with discrete energy levels then for molecules the energy level spacing will be much larger than that found in a quantum dotard for the molecule the chemist can control their connectivity as shown in figure (2.5.1). In the case of the quantum dot, where the object is very small, the connectivity is problematical. Working with molecules therefore gives us a much wider scope to study the effect of these connectivities. Polyaromatic hydrocarbons PAHs are a class of molecules which I will concentrate on in this thesis as their connectivities can be carefully controlled. In particular I will study how the Wigner delay time depends upon the connectivity. I will introduce a simple method to understand how the electron interference effects due to the connectivity can influence the Wigner delay time.
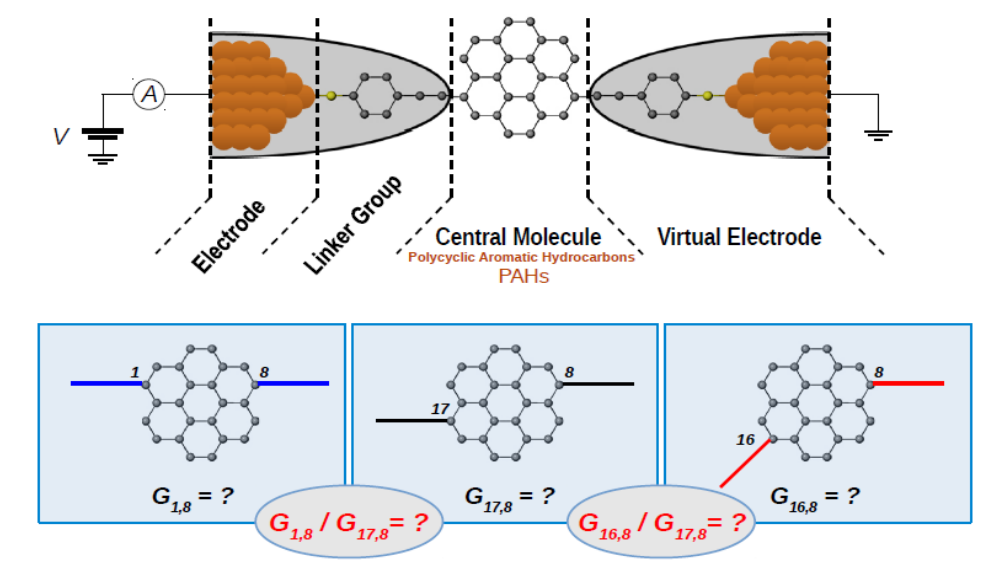

Figure 2.5.1.The figure illustrates the connectivity set up across a PAH, in this case coranine. The connectivities are labelled by numbering the atoms as shown.

The connectivity dependence of the conductance has already been published [7], but here I'm going to highlight the main points and give an overview about what is in the literature.

To study the effect of the connectivity on the conductance we should know how we connect a molecule, by looking at figure (2.5.1) a linker group has been used to connect the molecule between two gold electrodes.Therefore to model the single electron transport across the PAH with different connectivities the effective scattering region now includes both linker group and PAH. To simplify the study and results I introduced the three different examples of connectivity as shown in the lower three illustrations in figure (2.5.1). Initially I can calculate the electrical conductance to find which connectivity gives the highest conductance or which one gives the lowest conductance. A simple way to answer of all these questions uses the magic ratio rule which is explained in the following section.

2.6 Mathematics underpinning the magic ratio rule
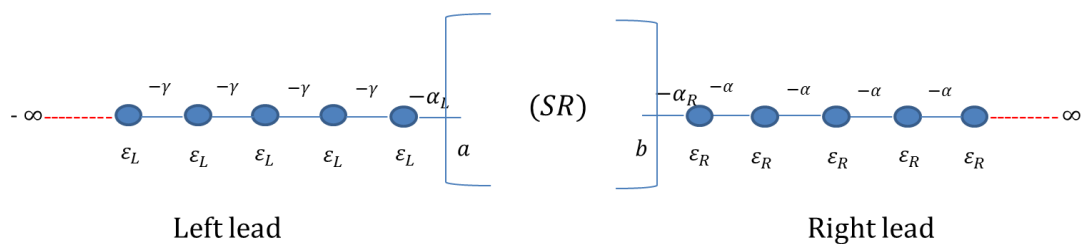

Figure 2.6.1.A simple tight binding model having two different infinite leads that are connected with independent scattering region via hoping elements $(-\alpha_L)$ and $(-\alpha_R)$.

We calculate the electrical conductance by using Landauer formula which is given by this relation:

$$\sigma(E) = G_0\, T(E) \tag{2.6.1}$$

In order to obtain the electrical conductance we calculate the transmission coefficient by using a green's function method by following relation:

$$T(E) = \hbar\, v_L \hbar\, v_R \times |G_{ab}|^2 \times \frac{\alpha_L{}^2}{\gamma^2} \times \frac{\alpha_R{}^2}{\alpha^2} \tag{2.6.2}$$

I'm trying to solve the green's function of an open system and I found that, the green's function of an open system is related to the green's function of a close system via this relation:

$$G_{ab}(\mathrm{E}) = \frac{g_{ab}(E)}{\Delta} \tag{2.6.3}$$

Where

$$\Delta = 1 + \frac{\alpha_L{}^2}{\gamma}\, g_{aa}\, e^{ik_L} + \frac{\alpha_R{}^2}{\alpha}\, g_{bb}\, e^{ik_R} + \frac{\alpha_L{}^2}{\gamma}\frac{\alpha_R{}^2}{\alpha}\big(g_{aa} \times g_{bb} - g_{ab} \times g_{ba}\big) \tag{2.6.4}$$

$$\times\, e^{(ik_L + ik_R)}$$

If α_L and α_R are zero then the green's function of an open system is equal to the green's function of a close system but if α_L and α_R are very weak and much less than one then Δ could be negligible just if the energy of electron is not go inside any one of the eigenvalues of the isolated molecule then in this case;

$$G_{ab}(\mathrm{E}) \approx g_{ab}(E) \quad , \text{then} \quad T_{ab}(E) \propto |g_{ab}(E)|^2 \tag{2.6.5}$$

And the ratio of the two transmission coefficient is given by the following weakly coupled ratio rule (WRR):

$$\frac{T_{ab}(E)}{T_{lm}(E)} = \frac{|g_{ab}(E)|^2}{|g_{lm}(E)|^2}$$

(2.6.6)

Finally, if $E = E_F = 0$ which located at the center of the H-L gap and for PAHs which have identical site that is described by a tight-binding model

$$g_{ab}(E_F) = (E_F - H)^{-1} = (-H)^{-1} = (C)^{-1}$$

(2.6.7)

$$g_{ab}(0) = -\frac{1}{d} M_{ab}(0)$$

(2.6.8)

Then the ratio of the two transmission coefficient for two different connectivities a,b and l,m is given by the following magic ratio rule (MRR):

$$\frac{T_{ab}(0)}{T_{lm}(0)} = \frac{(M_{ab})^2}{(M_{lm})^2}$$

(2.6.9)

2.6.1 Relationship between Green's functions and M-functions

From the above analysis, if the Green's function g of the isolated scattering region is known (ie when $\alpha_L = \alpha_R = 0$), then t is determined.

In the study of graphene-like molecules described in reference [7] a description of mid-gap transport was obtained in which the Hamiltonian describing the molecular core was simply a tight binding Hamiltonian, with zeroes for on-site energies and -1 for nearest neighbour couplings. If the energy E of electrons passing through the core

is equated to the middle of the HOMO-LUMO gap E_{HL}, then a simple and parameter free theory is obtained which describes how the transmission coefficient at the gap centre depends on the connectivity a, b (ie on the atoms a, b of the core which connect to the external leads). In the following we look at the relation between mid-gap transport theory and Greens function.

To obtain the simplest-possible theory of transport, for electrons of energy E near the middle of the HOMO-LUMO gap of a molecule, it is convenient to introduce M-functions, which are related to the Green's function $G(E)$ of the isolated molecule by $M(E) = D(E)G(E)$, where $D(E)$ is chosen to cancel any divergences in $G(E)$. If the Hamiltonian describing the isolated molecule is H, then the isolated-molecule Greens function is defined by $(E - H)G = 1$. ie $G(E) = F(E)/det(E - H)$, where $F(E)$ is the transpose of the cofactor matrix of $(E - H)$. Hence if $D(E)$ is chosen to be proportional to $det(E - H)$ then $M(E)$ is proportional to the well-behaved matrix $F(E)$. The main reason for using $M(E)$, rather than $G(E)$ is that for molecular cores described by bipartite lattices, $M(E_{HL})$ can be chosen to be a matrix of integers, which makes the connectivity dependence of conductances easy to understand.

If $H|\varphi_n\rangle = E_n|\varphi_n\rangle$, then $(E) = \sum_n \frac{|\varphi_n\rangle\langle\varphi_n|}{E - E_n}$, $det(E - H) = \prod_n (E - E_n)$ and $F(E) = G(E)\, det(E - H)$ and is analytic everywhere unlike G which contains poles at the eigenvalues E_n of H. We therefore choose $M(E) = aF(E)$, where the choice of the scalar a is arbitrary. This is equivalent to choosing $M(E) = D(E)G(E)$, where $D(E) = a\, det(E - H)$. Such a choice yields M-functions which are analytic everywhere and inside the range $E_H < E < E_L$ (where E_H is the HOMO energy and E_L is the LUMO energy) and they can be approximated by low-order polynomials in E_M.

In bipartite lattices describing molecules with a filled HOMO and $E_{HL}=(E_H + E_L)/2$ $=0$, then the M-functions $M_{a,b}(E)$ are either odd or even functions of E. For the former, $M_{a,b}(0)=0$, whereas for the latter $M_{a,b}(0)$ is an integer.

The crucial observation is that when the linker groups are very weak, and the Fermi energy E_F is located at the mid-gap $E= E_{HL}$, then the denominator in equation 2.6.4 can be approximated by unity, because E_{HL} is far from the poles of the Greens function in the denominator of 2.4.6. Consequently the low-temperature electrical conductance $\sigma_{a,b} \sim [M_{a,b}(E_{HL})]^2$.

Hence the ratio of two conductances linked to (a and b or l and m) is given by the mid-gap M-ratio rule:

$$\sigma_{a,b}/\sigma_{l,m} = \left[M_{a,b}(E_{HL})/M_{l,m}(E_{HL})\right]^2 \qquad (2.6.10)$$

More generally, the ratio of two conductances $\sigma_{a,b}$ for arbitrary E_F in the vicinity of the mid-gap is given by:

$$\sigma_{a,b}/\sigma_{l,m} = \left[M_{a,b}(E_F)/M_{l,m}(E_F)\right]^2 \qquad (2.6.11)$$

If the coupling from the molecule to the electrodes are very weak via atomic orbitals a and b, then the transmission coefficient is proportional to 'isolated-core transmission coefficient' $T_{a,b}(E)$, where;

$$T_{a,b}(E) = (M_{a,b}(E)/ D(E))^2 = (G_{a,b}(E))^2 \qquad (2.6.12)$$

Comparing the plots of $T_{a,b}(E)$ versus E with other theories of electron transmission may be of interest , but it is much more complicated with the plotting of $M_{a,b}(E)$, because of the presence of the denominator $D(E)$.

2.6.2 Taylor expansions of M-functions, Green's functions and core transmission functions

Later we shall be interested in Taylor expansions of Green's functions and M-functions, which we now examine for subsequent use.

In terms of the mid-gap energy E_{HL},

$$G(E) = (E - H)^{-1} = (E_{HL} - H)^{-1}[1 + (E - E_{HL})(E_{HL} - H)^{-1}]^{-1} = (E_{HL} - H)^{-1}\sum_{n=0}^{\infty}(E_{HL} - H)^{-n}[-(E - E_{HL})]^n = G(E_{HL})\sum_{n=0}^{\infty}G(E_{HL})^{-n}[-(E - E_{HL})]^n$$

$$(2.6.13)$$

Hence to order $(E - E_{HL})^2$,

$$G(E) = G(E_{HL}) + (E_{HL} - E)G^2(E_{HL}) + (E_{HL} - E)^2 G^3(E_{HL}) \qquad (2.6.14)$$

The above equation allows us to generate a low-order power series for M-functions, Since $M(E) = D(E)G(E)$, and it will be convenient to define $\boldsymbol{\varepsilon} = (E - E_{HL})/D(E_{HL})$ and therefore to order $\boldsymbol{\varepsilon^2}$,

$$G(E) = G(E_{HL})[1 - \varepsilon M(E_{HL}) + \varepsilon^2 M^2(E_{HL})] + \ldots \qquad (2.6.15)$$

And

$$M(E) = D(E)G(E_{HL})[1 - \varepsilon M(E_{HL}) + \varepsilon^2 M^2(E_{HL})] + \ldots \qquad (2.6.16)$$

Here , $D(E) = a \, det(E - H)/P(E)$, where $P(E)$ cancels degeneracies.

The M-function can be represented by a low-order polynomials in E_M in contrast with a Green's function. In what follows, we shall generate low-order Taylor expansions in E_M of the form:

$$M_{ab}(E) = M_{ab}(E_{HL}) + M_{ab}^{(1)}E_M + M_{ab}^{(2)}E_M^2 + \cdots \qquad (2.6.17)$$

Where $E_{HL} = 0$, $M^{(3)} = -1/2I$ (I is the unit matrix) and $M^{(1)}$, $M^{(2)}$ can be constructed from a knowledge of $M(E_{HL})$ alone. So $M^{(1)} = \frac{1}{2} M^2(E_{HL})$ and $M^{(2)} = M(E_{HL}) \{\frac{1}{4} [M^2(E_{HL}) - 5]\}$.

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Chapter 3

Wigner delay time in graphene-like molecules.

3.1 Introduction

The Wigner delay time function was proposed by Wigner in 1955 for a single scattering channel and was first derived from a Hermitian operator based on the scattering amplitude and then generalized by Smith in 1960 to the multichannel scattering matrices[1, 2].

Wigner delay time is a measure of time spent by the electron within a scatter, as it passes from one electrode to another through the scattering region [1]**.** Scattering processes are common in many areas of physics, and therefore many systems are candidates for the measurement of this time delay [3].

In this chapter, I will discuss the concept of Wigner delay time with a quick summary of the most fundamental properties. I consider a molecule as a scattering region which is described by the Hamiltonian, and I'm interesting to see how much time the electron spends when it comes from one lead through the molecule to another lead. In this chapter I focus on the analytical formula to have a clear understanding for the derivation of Wigner delay time in graphene like molecules. In the beginning, I will introduce the solution of the time dependent

Schrödinger equation for Wigner delay time by using a scattering problem as a simple model leading to understand the concept of time delay. Then, I present a simple tight-binding model of two identical (1-D) infinite leads connected with an independent scattering region by hopping elements $(-\alpha_L)$ and $(-\alpha_R)$ to have a clear picture about the phase and their relation with time delay. This scattering problem allows us to describe the phase difference between a scattered wave and a freely propagating one by using Wigner delay time[2]

3.2 Analytical formula of Wigner delay time in graphene-like molecules.

In the following sections I will derive the analytical formula for the Wigner delay time.

3.2.1 Solution of time dependent Schrödinger equation for Wigner delay time

First, I consider the Schrödinger equation in a one-dimensional system with no scattering:

$$H(x)\,\Psi(x) = E\,\Psi(x) \qquad (3.2.1)$$

Where $\qquad H(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \quad,\quad \Psi(x) = e^{ikx} \quad$ and $\quad E = \frac{\hbar^2 k^2}{2m}$

To solve

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = H(x)\,\Psi(x,t) \tag{3.2.2}$$

We write;

$$\Psi(x,t) = e^{ikx}\,e^{-i\omega t} \tag{3.2.3}$$

Since

$$\frac{\partial}{\partial t}\Psi = -i\omega\Psi \tag{3.2.4}$$

$$\frac{-\partial^2}{\partial x^2}\Psi = k^2\Psi \tag{3.2.5}$$

By putting equation (3.2.4) and (3.2.5) into (3.2.2) we get:

$$\hbar\omega\Psi = \frac{\hbar^2 k^2}{2m}\Psi \tag{3.2.6}$$

So that, $\hbar\omega = \frac{\hbar^2 k^2}{2m}$

More generally an electron wave packet moving in one dimension is:

$$\Psi(x,t) = \int dk\, a_k\, e^{i(k_x - \omega_k t)} \tag{3.2.7}$$

If the time $t = 0$ then;

$$\Psi(x,0) = \int dk\, a_k\, e^{ik(x - x_0)} \tag{3.2.8}$$

If this initial wave packet has a maximum at x_0, and if a_k has a maximum at $E_0 = \hbar\omega_0$ then at a later time t , the wave packet will have a maximum at

$$x_t = x_0 + vt$$

$$v = \frac{\partial \omega}{\partial k}, \quad \hbar v = \frac{\partial E}{\partial k} \quad \text{where,} \quad E = E_0 = \hbar\omega_0$$

If such a wave passes through a scatter, then the transmitted wave packet will have the form;

$$\Psi_T(x,t) \int dk\, a_k\, t_{(\omega_k)}\, e^{i(x - \omega_k t)} \tag{3.2.9}$$

Where

$$t_{(\omega_k)} = |t_{(\omega_k)}|e^{i\theta(\omega_0)}e^{i[\theta(\omega_k) - \theta(\omega_0)]} \tag{3.2.10}$$

Assuming $|t_{(\omega_k)}|$ is approximately constant $|t_{(\omega_0)}|$ on the scale of the width in energy

of the amplitudes a_k yields

$$\Psi_T(x,t) \approx t_{(\omega_0)} \int dk \; a_k \; e^{i[\theta(\omega_k) - \theta(\omega_0)]} \; e^{i(x - \omega_k t)}$$

Writing
$$\theta(\omega_k) \approx \theta(\omega_0) + \frac{\partial \theta(\omega_0)}{\partial \omega_0}(\omega_k - \omega_0) \tag{3.2.11}$$

yields

$$\Psi_T(x,t) = t_{(\omega_0)} \int dk \; a_k \; e^{i\beta(\omega_k - \omega_0)} \; e^{i(x_k - \omega_k t)} \tag{3.2.12}$$

ie $\quad \Psi_T(x,t) = t_{(\omega_0)} \; e^{-i\beta(\omega_0)} \int dk \; a_k \; e^{ikx} \; e^{-i\omega_k(t - \beta)} \tag{3.2.13}$

Where $\beta = \frac{\partial \theta(\omega_0)}{\partial \omega_0}$.

The modulus squared of the transmitted wave is exactly the same the wave without a

scattering region but multiplied by $t_{(\omega_0)}{}^2$, but t is shifted by β so this β is a delay

time.

In what follows, we show that when the coupling to the molecule is very weak and the

Fermi energy of the molecule is at the centre of the HOMO-LUMO gap, the Wigner

delay time of graphene-like molecules between two atoms a, b depends on the value
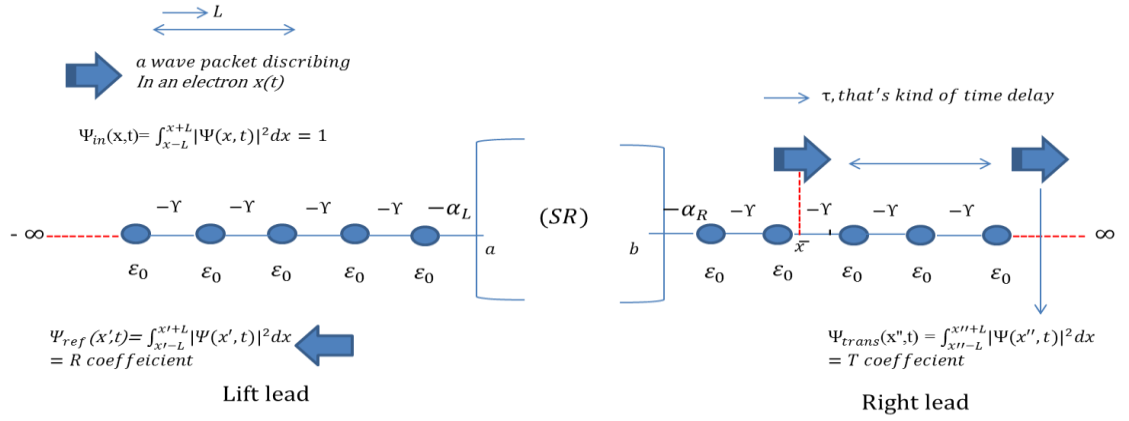
of M-functions at each site (M_{aa}, M_{bb})[4].

Figure 3.2.1.The simple tight-binding model of two identical (1-D) infinite leads connected with an independent scattering region by hopping elements $(-\alpha_L)$ and $(-\alpha_R)$.

In particular, the tight-binding model related to the Wigner delay time for scattering theory of molecules represented by lattices shown in figure (3.5.1) model are reviewed in this study. In the paradigm example of a tight-binding model figure (3.2.1) where there are two identical (1-D) infinite leads connected with an independent scattering region in the limit of weakly coupling by $(-\alpha_L)$ and $(-\alpha_R)$. When the electron comes from one lead and passes through the molecule to the other lead, the associated dispersive behavior leads to the time delay.

Therefore, we know that each particular wave component of a transmitted wave packet has following form of the transmission coefficient:

$$T(E) = |t(E)|^2 \qquad (3.2.14)$$

The transmission amplitude contains the magnitude and the phase

$$t(E) = |t(E)| \times e^{i\theta(E)} \qquad (3.2.15)$$

The corresponding Wigner delay time τ_w is defined by:

$$\tau_w = \frac{d\theta}{d\omega} = \hbar \frac{d\theta}{dE} \qquad (3.2.16)$$

For a molecule which is weakly coupled to electrodes, shall I now prove that the delay time takes the form ;

$$\theta(E) = \tan^{-1}\left(\frac{\Delta_2}{1+\Delta_1}\right) \qquad (3.2.17)$$

From the previous chapter I introduced a method to calculate a transmission coefficient using wave functions and we end with equation (2.4.22) where in this equation the transmission amplitude for a scattering problem connected with two identical leads as shown in figure (3.2.1) is given by:

$$t = 2i \sin k \times e^{2ik} \times \left(\frac{\alpha_L \times \alpha_R}{\gamma}\right) \times \frac{g_{ab}}{\Delta} \qquad (3.2.18)$$

In this equation, α_L , α_R in figure (3.2.1) are the coupling between molecule and the left and right lead respectively , γ is the coupling of the atoms in the leads. g_{ab} is the green's function of site element 'a' and 'b' when the electron comes from 'a' site and passes from 'b' site , which is a property of the core molecule where $g = (E - H)^{-1}$ and H is the Hamiltonian describing the isolated core. So when H is real, the Green's function is real. Δ is a complex because it contains a real part and an imaginary part and we are interested in Wigner delay time which is a derivation of the phase, and the phase here is a contribution of e^{2ik} and also from an imaginary part of Δ. But in e^{2ik} the phase is zero where i is a phase of $\pi/2$ this is not going to change anything in the delay time and k which is a property of the lead does change, but only very slowly with energy because the barriers in the leads are not big. So the only parameter which is changed by energy is the phase of Δ and then when we differentiate the phase of Δ with different energy we end with

$$\Delta = 1 + \frac{\alpha_L{}^2}{\gamma}\, g_{aa}\, e^{ik} + \frac{\alpha_R{}^2}{\gamma}\, g_{bb}\, e^{ik} + \frac{\alpha_L{}^2 \times \alpha_R{}^2}{\gamma^2} \left(g_{aa} \times g_{bb} - g_{ab} \times g_{ba} \right) \quad (3.2.19)$$

$$\times \; e^{2ik}$$

Where,
$$\Delta = 1 + \Delta_1 + i\Delta_2 \qquad\qquad (3.2.20)$$

$$\Delta_1 = \alpha \cos k + \beta \cos 2k \qquad\qquad (3.2.21)$$

$$\Delta_2 = \alpha \sin k + \beta \sin 2k \qquad\qquad (3.2.22)$$

And

$$\alpha = \frac{1}{\gamma} \times \left(g_{aa} \times \alpha_L{}^2 + g_{bb} \times \alpha_R{}^2 \right) \qquad\qquad (3.2.23)$$

$$\beta = \left(g_{aa} \times g_{bb} - g_{ab} \times g_{ba} \right) \times \left(\frac{\alpha_L{}^2 \times \alpha_R{}^2}{\gamma^2} \right) \qquad (3.2.24)$$

In the weak coupling limit;

$$\theta = \frac{\pi}{2} + 2k + S\pi - \phi \qquad \text{where} \qquad S = 0 \text{ if } g_{ab} > 0$$

$$= 1 \text{ if } \; g_{ab} < 0$$

$$\tan\phi = \left(\frac{\Delta_2}{1 + \Delta_1} \right) \qquad\qquad (3.2.25)$$

$$\frac{d\tan\phi}{dE} = \frac{d\tan\phi}{d\phi} \times \frac{d\phi}{dE} = (1 + \tan^2\phi) \times \frac{d\phi}{dE} = \frac{\frac{d\Delta_2}{dE}}{1+\Delta_1} \times \frac{\Delta_2 \times \frac{d\Delta_1}{dE}}{(1+\Delta_1)^2}$$

$$\frac{d\phi}{dE} = \frac{(1 + \Delta_1)\,\dot{\Delta}_2 - \Delta_2\,\dot{\Delta}_1}{(1+\Delta_1)^2} \qquad\qquad (3.2.26)$$

In the weak coupling limit;

$$\frac{d\phi}{dE} \approx \dot{\Delta}_2 \approx \dot{\alpha}\sin k + \dot{\beta}\sin 2k \qquad (3.2.27)$$

In the limit of weakly coupling to the electrodes, $\beta \ll \alpha$

$$\tau_{ab} \approx \hbar\frac{d\phi}{dE} \approx \frac{\hbar}{\gamma}(\dot{g}_{bb}\alpha_R{}^2 + \dot{g}_{aa}\alpha_L{}^2) \qquad (3.2.28)$$

Where we have defined an intrinsic core delay time to be

$$\tau_{aa} = \frac{dg_{aa}}{dE} = \dot{g}_{aa} \qquad (3.2.29)$$

This equation shows that the total delay time is a sum of independent times due to each contact and is of the form:

$$\tau_{ab} \approx \frac{\hbar}{\gamma}(\tau_{bb}\alpha_R{}^2 + \tau_{aa}\alpha_L{}^2) \qquad (3.2.30)$$

Which is independent of the coupling to the leads.

3.3   M-function, relation between connectivities and Wigner delay time

I predict that when the coupling to the molecule is very weak and the Fermi energy coincides with the center of the HOMO-LUMO gap, the contribution to the delay time due a lead connected to site 'a' is τ_{aa} , which I have found to be proportional to $\dot{g}_{aa}$. Now I use this expression to compute Wigner delay times in graphene-like cores which can be represented by lattices of identical sites whose Hamiltonian H is simply proportional to a parameter-free connectivity matrix C. In this case for electrons of energy E entering the core at site a and exiting at site b, then I obtain the delay time

from the M-function $M_{ab}(E)$, which is parameter-free and depends on connectivity

alone.

3.4 Properties of the intrinsic core delay time τ_{aa}.

As I discussed in chapter 2, M-functions are related to the green's function of a core by:

$$M(E) = \det(E - H) \times g(E) \tag{3.4.1}$$

From equation (2.6.14) to order $(E - E_{HL})^2$

$$G(E) = G(E_{HL}) + (E_{HL} - E)G^2(E_{HL})$$

Therefore

$$\dot{G}(E_{HL}) = -G^2(E_{HL}) = -M^2(E_{HL})/A^2 \tag{3.4.2}$$

Where $= \det(E_{HL} - H)$.

So the Wigner delay time of intrinsic core is given by:

$$\tau_{aa} = -(M_0{}^2)_{aa}/A^2 \tag{3.4.3}$$

Where $M_0 = M(E_{HL})$ and $(M_0{}^2)_{aa}$ is the aa elements of the squared

matrix $M^2(E_{HL})$.

Therefore, by just looking at the table of $(M_0{}^2)$ we obtain the connectivity

dependence of the Wigner delay time of a given PAH core.

3.5 Results and discussion

Consider the graphene-like molecules shown in figure (3.5.1) in which (a) represents a benzene ring, (b) Naphthalene, (c) Anthracene, (d) Tetracene, (e) Pentacene, (f) Pyrene, (g) Anthanthrene and (k) Azulene, all of which are bipartite lattices except azulene which is a non-bipartite lattice. I predict that when the coupling to the molecule is weak and the Fermi energy coincides with the center of the HOMO-LUMO gap the delay time of the intrinsic core for example of site 'a' is proportional to τ_{aa} which is equal to $\dot{g}_{aa}$. Here I use a minimal tight-binding description where only pi orbitals were taken into account and without losing any generality, the Hamiltonian constructed by considering site energies to be 0 and coupling between connected sites to be -1.
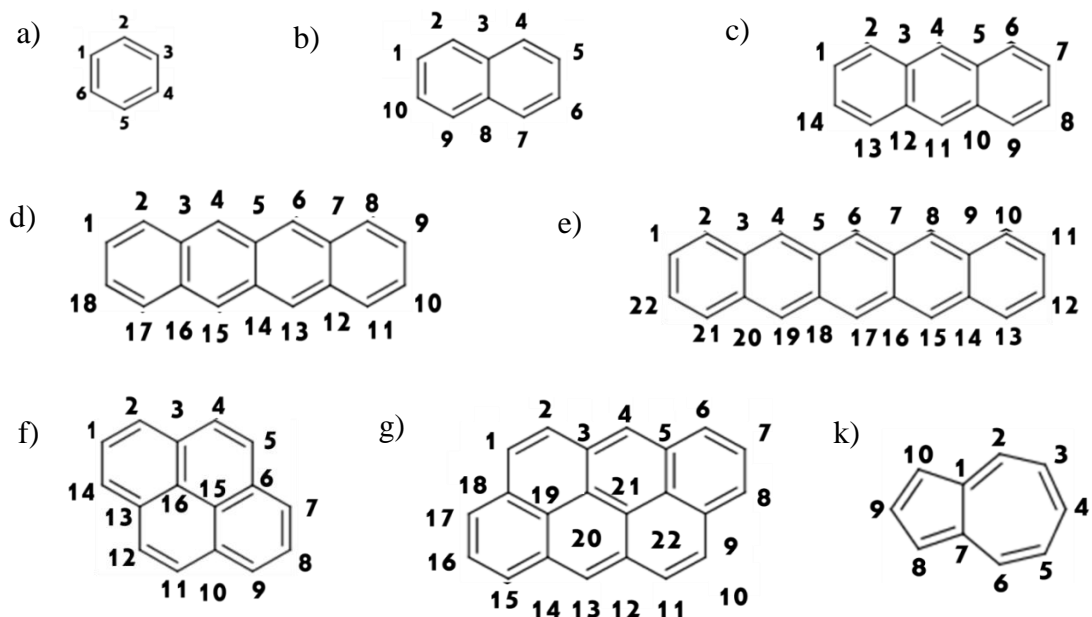

Figure 3.5.1.Molecular structure of substituted a) benzene ring, b) naphthalene, c) anthracene, d) 4-ring, e) 5-ring, f) pyrene, g) anthanthrene and k) Azulene.

We now examine three examples:

Example 1

Consider a naphthalene core shown in figure (3.5.2,a) the Wigner delay time for the connectivity with equal M-number is equal. So, for those connectivities where $M_{aa} = M_{bb}$ then $\tau_{aa} = \tau_{bb}$. For example as shown in the table of figure (3.5.2,c) for sites 1 and 6 where their M-number are equal figure(3.5.2,b) then $\tau_{11} = \tau_{66}$ whereas for those connectivity that the M-numbers are different the τ's are different (if the $M_{aa} \neq M_{bb}$ then $\tau_{aa} \neq \tau_{bb}$, for example $\tau_{11} \neq \tau_{99}$). From equation (3.2.30) it is apparent that the Wigner delay time from site 'a' to 'b' (τ_{ab}) could be obtained by having τ_{aa} and τ_{bb}. The table of figure (3.5.2,c) describes the Wigner delay time in the middle of HOMO-LUMO gap. To obtain the Wigner delay time for other reference energies, one needs to use the M-function.

a)   b)   c)

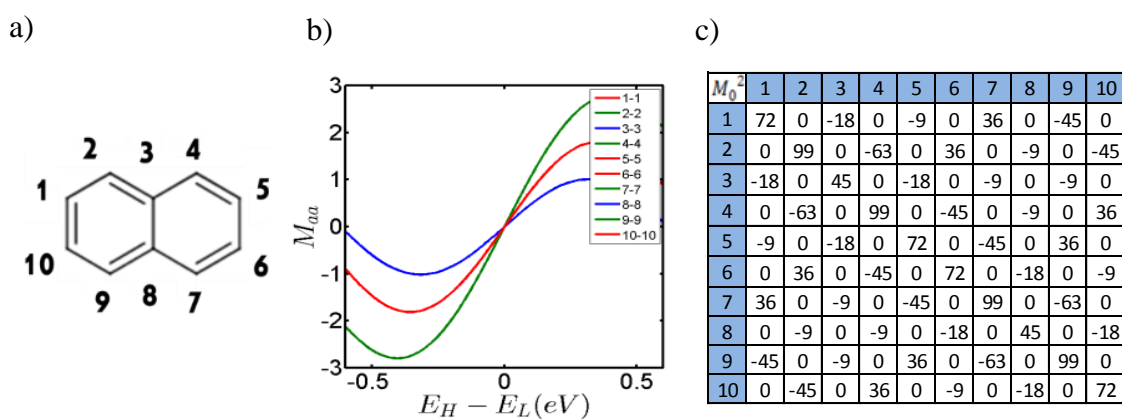| M_0^2	1	2	3	4	5	6	7	8	9	10
1	72	0	-18	0	-9	0	36	0	-45	0
2	0	99	0	-63	0	36	0	-9	0	-45
3	-18	0	45	0	-18	0	-9	0	-9	0
4	0	-63	0	99	0	-45	0	-9	0	36
5	-9	0	-18	0	72	0	-45	0	36	0
6	0	36	0	-45	0	72	0	-18	0	-9
7	36	0	-9	0	-45	0	99	0	-63	0
8	0	-9	0	-9	0	-18	0	45	0	-18
9	-45	0	-9	0	36	0	-63	0	99	0
10	0	-45	0	36	0	-9	0	-18	0	72

Figure 3.5.2.a) The molecule structure of naphthalene with numbering. b) Energy-dependent M-functions of naphthalene. c) M_0^2 table of naphthalene.

Example 2

Consider a benzene ring, as shown in figure (3.5.3,a) where M-function for all sites are the same then Wigner delay time of all connectivities is equal as shown in figure (3.4.3,b and c).
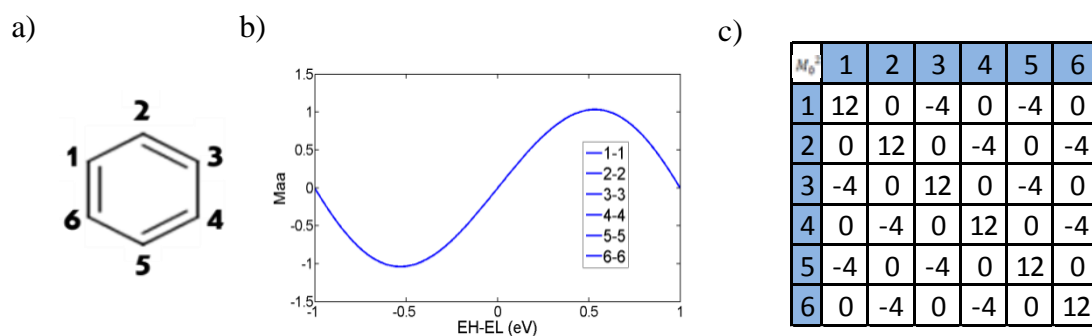
a)   b)   c)

M_0^2	1	2	3	4	5	6
1	12	0	-4	0	-4	0
2	0	12	0	-4	0	-4
3	-4	0	12	0	-4	0
4	0	-4	0	12	0	-4
5	-4	0	-4	0	12	0
6	0	-4	0	-4	0	12

Figure 3.5.3.a)The molecule structure of benzene with numbering. b) Energy-dependent M-functions of benzene. c) M_0^2 table of benzene.

Example 3

Consider an azulene as shown in figure (3.5.4,a) and we found from M_0^2 table and M-function in figure (4.5.4,b and c) $M_{33} = M_{55}$ then $\tau_{33} = \tau_{55}$ also $M_{66} \neq M_{99}$ then $\tau_{66} \neq \tau_{99}$.
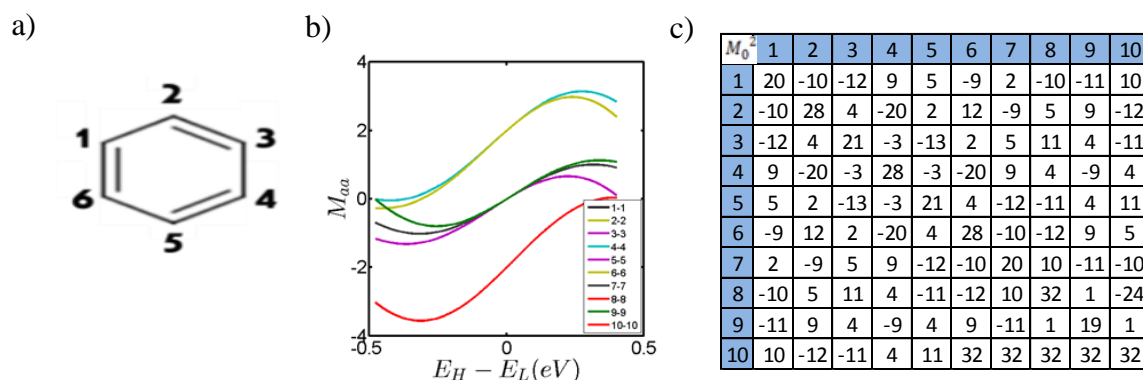
a)

b)

c)

M_0^2	1	2	3	4	5	6	7	8	9	10
1	20	-10	-12	9	5	-9	2	-10	-11	10
2	-10	28	4	-20	2	12	-9	5	9	-12
3	-12	4	21	-3	-13	2	5	11	4	-11
4	9	-20	-3	28	-3	-20	9	4	-9	4
5	5	2	-13	-3	21	4	-12	-11	4	11
6	-9	12	2	-20	4	28	-10	-12	9	5
7	2	-9	5	9	-12	-10	20	10	-11	-10
8	-10	5	11	4	-11	-12	10	32	1	-24
9	-11	9	4	-9	4	9	-11	1	19	1
10	10	-12	-11	4	11	32	32	32	32	32

Figure 4.5.4.a) The molecule structure of azulene with numbering. b) Energy-dependent M-functions of azulene. c) M_0^2 table of azulene.

Note that the Wigner delay time is independent on the distance between atoms, for example the Wigner delay time of connectivy 1 and 10 (short distance) is equal to the Wigner delay time of connectivy 1 and 6 (long distance) in figure (3.5.2,a and c). So, this is due to the equality of the M-function.

To demonstrate how the Wigner delay time changes with the number of rings in series, I calculate the maximum and minimum values of τ as a function of the number of rings in structures in figure (3.5.5). Then I plotted the envelope of the maximum and minimum of the Wigner delay time as shown in figure (3.5.6) and from this figure it is apparent that by increasing the number of N-rings for the PAH molecules shown in figure (3.5.5) τ also is increased.

For benzene all the Wigner delay times are equal whereas for other molecules shown in figure (3.5.5) we have different delay times, the maximum is shown in red and the minimum in blue. For example in naphthalene the maximum delay time corresponds to atoms number 2, 4, 9, 7 and atoms 3 and 8 have the minimum value.
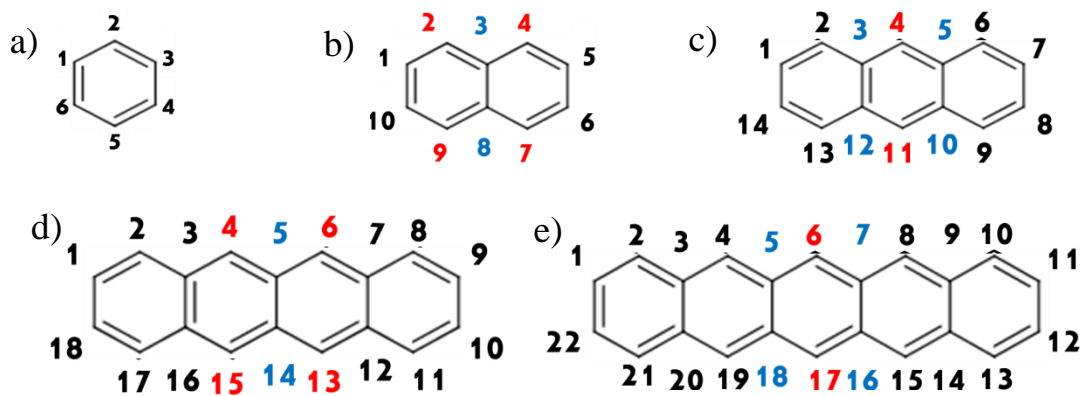
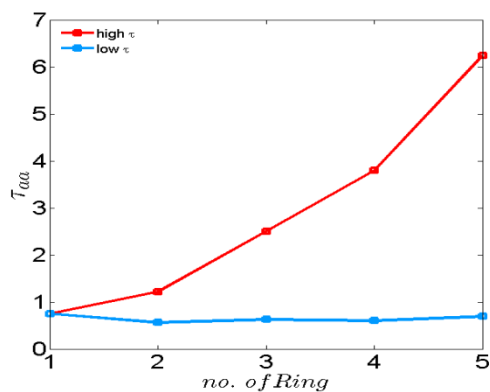Figure 3.5.5.The molecules structure by increasing the number of rings.

Figure 3.5.6.Graph of max −min τ_{aa} by increasing number of rings.

It is interesting to note that the maximum and minimum Wigner delay time τ_{aa} of the PAH core molecules shown in figure (3.5.5) are located at the center of the molecule as shown with blue (minimum) and red (maximum) in the figure.

Now I examine the relation between Wigner delay time τ_{aa} and the local density of states η_{aa}, which allows us to compare with results obtained from density functional theory calculations. If ς is a small positive number, then

$$g = \sum_n \frac{|\Psi_n\rangle \langle \Psi_n|}{E - E_n + i\varsigma} \tag{3.5.1}$$

$$g = \sum_n \frac{|\Psi_n\rangle \langle \Psi_n|}{(E - E_n)^2 + (E - E_n - i\varsigma)} \tag{3.5.2}$$

Hence

$$Im \ g = \sum_n \frac{\varsigma \ |\Psi_n\rangle \langle \Psi_n|}{(E - E_n)^2 + \varsigma^2} \tag{3.5.3}$$

Also

$$(g^2)_{ab} = \sum_n \frac{\langle a|\Psi_n\rangle \langle \Psi_n|b\rangle}{(E - E_n)^2} \tag{3.5.4}$$

Therefore

$$\eta_{aa} = -Im \ (g_{aa})/\pi = \varsigma \ (g^2)_{aa}/\pi \tag{3.5.5}$$

This means that for those connectivities which the core wave-function is more localized, the Wigner delay time is higher, as shown in figure (3.5.7). For example for naphthalene the M-table predicts the maximum Wigner delay time is for connectivity 2,4,7,9 whereas the minim delay is for 3,8 and for the LDOS calculation of figure (3.5.7) it is clear that there is more weight on sites 2, 4, 7, and 9 but there is no weight on sites 3 and 8.
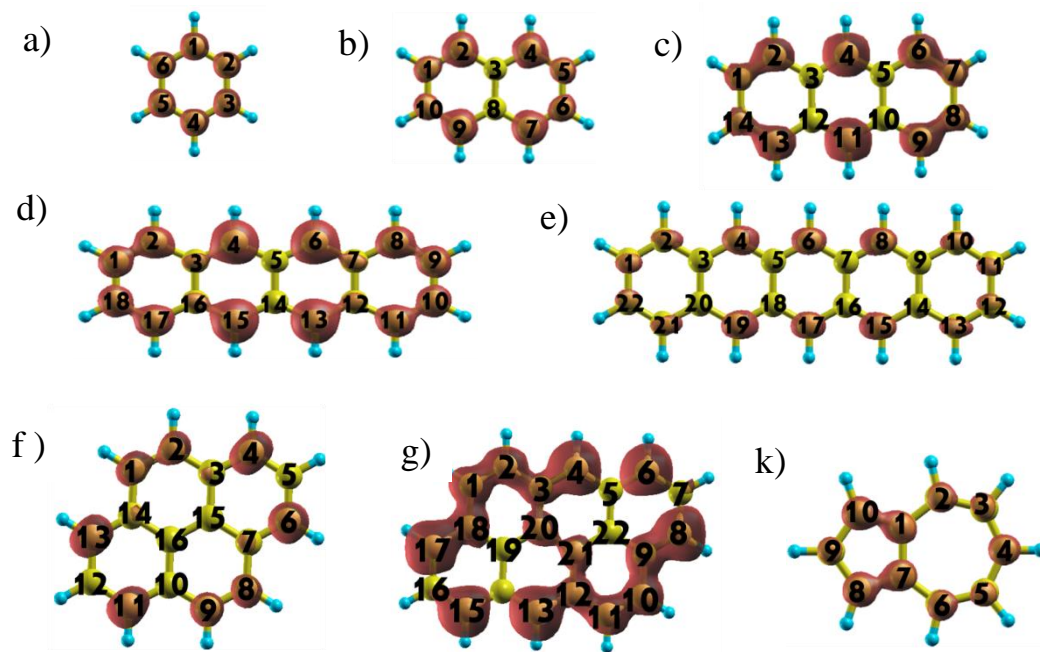
Figure 3.5.7. LDOS of molecules obtained from the DFT code SIESTA.

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Chapter 4

Conclusion and future work

4.1 Summary

This Thesis has focused on the following:

1) Green's functions based calculations of electronic transmission in quantum transport have been carried out. The study involved the calculation of the retarded Greens' function in which simple formula of one-dimensional tight binding chain in presented and by breaking the periodicity of the lattice at a single connection it was shown that the Greens' function is associated with transmission coefficient along the scattering region.

2) Investigation of the Wigner delay time in graphene-like molecules has been studied and the solution of the analytical formula for the Wigner delay time shows that when the coupling to the molecule is very weak and the Fermi energy of the molecule is at the centre of the HOMO-LUMO gap the Wigner delay time of graphene-like molecules between two atoms a, b just depend on the value of M-functions at each site (M_{aa}, M_{bb}). Also when the M-functions of two connectivities are the same then the Wigner delay time of those connectivities are equal.

4.2 Future Work

In this thesis, I have concentrated on the connectivity-dependence of Wigner delay times for electrons. For the future it would of interest to examine the connectivity-dependence of delay tames for phonons [1,2] and quasi-particles associated with superconducting leads [3] , spin-dependent delay times in the presence of ferromagnetic leads or more complex metals[4,5], combinations of superconducting and ferromagnetic leads [6,7] and the connectivity dependence of current-induced forces [8]. In practice, for such complex structures, it may not be possible to obtain simple analytic results. Nevertheless such problems could be investigated numerically, using quantum transport codes such as the multiple-scattering code Gollum [9].

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