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Conduction of molecular electronic devices: Hückel implementation of the source-and-sink potential method and qualitative insights through atom-atom polarizabilities

Graduation thesis submitted in partial fulfillment of the
requirements for the degree of master in chemistry

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JUNE 2014

Acknowledgements

I would like to thank my promotors Dr. S. Fias, Prof. Dr. Paul Geerlings and Prof. Dr. Frank De Proft. Because of their support and constructive criticism, I was challenged to give the best of myself while working on this thesis. I also want to thank them for investing so much time in my work, reading and rereading the numerous versions and ideas I put forward and for critically evaluating them.

Special thanks goes to Dr. S. Fias for his continuous assistance throughout every step of my research. He was always prepared to listen even to the most odd questions or ideas I put forward and respond to them properly. Without his support and knowledge this thesis would never have been accomplished.

I would also like to thank my parents for their financial and emotional support and for giving me the ability to pursue my dreams. I would also like to devote some words to my friends. There is a time and place for everything, and so next to working hard to make this thesis as good as possible, I also took some time to enjoy my last year on campus as a student. Taking a break from work now and then allowed me to free my mind, stay motivated and look at things from a different perspective. For all the memorable times and their support I would like to thank them.

Contents

Chapter 1

Introduction

Conventional electronic devices are made from bulk materials. A lot of different electronic components exist, ranging from simple wires to rectifiers and transistors. Especially transistors are of huge importance in modern technology, since they are the main building block of integrated circuits, which are responsible for the computational power in all computers, mobile phones, etc.[1]

As the computing force of an integrated circuit increases with the amount of transistors, scientists and engineers all over the world have tried to minimize the size of the electronic components which make up these circuits, so that as much computational power as possible can be concentrated on a surface as small as possible. However, this miniaturization effort is approaching its limit under the current manufacturing technology, which starts from bulk semiconducting materials.[2]

This evolution has sparked an interest in so called 'molecular scale electronics'. Molecular scale electronics is a branch of nanotechnology which uses single molecules or assemblies of molecules as electronic components. These components are then called molecular electronic devices (MED). As single molecules are the smallest stable structures possible, MED are the ultimate endpoint of the miniaturization attempt which started more than 60 years ago when the first transistors were developed and applied in computers. Although practical applications for these devices are still far away, a lot of effort is put in trying to understand the behavior of these devices as they do not behave in the same way as ordinary electronic components.

What makes the study of these devices very challenging is that the electronic properties not only depend on the considered molecule, but also on the choice of the contact atoms at which the molecule is integrated into the electrical circuit.[1][3][4] Rationalizing the influence of the contact positions has proven to be a big challenge.[5][6][7] That is why in this study, an attempt is made to get some qualitative insight in these phenomena based on a chemical concept named the atom-atom polarizability.[8][9][10]

In order to study MED, the considered molecule is usually connected to two semi-infinite bulk contacts and the current is measured as a function of the applied voltage.[11]

Differentiating the current (I) versus voltage (V) curve, the primary property used to characterize a molecular conductor, the differential conductance g=dI/dV, is obtained. The conductance of a molecule can be linked to its transmission probability through the Landauer formula

$$g(E,V) = \frac{e^2}{h}T(E,V) \tag{1.1}$$

For a device with one conduction channel, the transmission probability can range between 0 and 1. Integration of this expression between the boundaries set by the applied voltage V leads to the actual current I flowing through the molecule.

Traditionally, physicists make use of Green's function approach to predict the transmission through molecular electronic devices.[12][13] While this method can give accurate results, it does not allow chemical insight into the influence of the molecular structure on the transmission probability. A more simple approach to look at transmission, the source and sink potential (SSP) method, has recently been introduced by Ernzerhof et al.[11] In this new framework, Fowler et al. proposed a selection rule for transmission at the Fermi-level in Hückel level of theory.[6]

Next to this rule, other selection rules have been introduced too.[7] These selection rules are respectively based on bond orders, Kekulé counts[14] or frontier orbitals.[5] While each of these selection rules allow to make a qualitative statement about the transmission in carbon based devices in Hückel level of theory, none of them has been expanded to higher levels of theory.

In this work, the use of atom-atom polarizabilities to get qualitative insight into the transmission probability will be explored. The atom-atom polarizability of molecules is a concept introduced by Coulson et al. in 1947.[8] What makes the atom-atom polarizability especially interesting is that it is the Hückel-level analogue of the linear response in conceptual density functional theory (DFT), as currently under development in ALGC.[15][16][17] Thus, qualitative insight in transmission through the atom-atom polarizability might be translated to a higher level of theory, making it possible to study molecules which cannot be studied in Hückel theory.

Chapter 2

Objectives

The main objective of this work is to get some qualitative insight into the influence that the positioning of the contacts on molecules has on the transmission probability close to the Fermi level through consideration of the atom-atom polarizability.

The main reason why we focus specifically on the atom-atom polarizability is that this property (as well as its density functional theory analogue 'the linear response') is a measure for how a perturbation is handed on throughout a molecule. More exactly, the mathematical definition for the linear response, which will be discussed more extensively later on, reads

$$\chi(\mathbf{r},\mathbf{r}') = \left(\frac{\delta\rho(\mathbf{r})}{\delta v(\mathbf{r}')}\right)_N = \left(\frac{\delta^2 E}{\delta v(\mathbf{r})\delta v(\mathbf{r}')}\right)_N \tag{2.1}$$

which shows that the linear response can be defined as the change in the electron density at a point **r** due to a perturbation in point **r'**.[15]

Looking at transmission, one can say that when a bias is applied to a MED, perturbations are applied to the contact atoms and these perturbations cause a current to flow through the molecule between these contacts. So, the current flow, evidently related to a change in electron density, can be interpreted as a response of the system to the perturbations at the contacts.

This rationale shows that one can intuitively expect these two measures to be somehow connected physically. Another argument for our decision to focus on the atom-atom polarizability is that there is a striking similarity between the expression for the transmission probability in the SSP method at Hückel level of theory in the wide band limit as it was established by Fowler et al.[4]

$$T_{WBL}(E) = \frac{4(\tilde{\Delta}_{r,r}\tilde{\Delta}_{s,s} - \tilde{\Delta}\tilde{\Delta}_{rs,rs})}{(\tilde{\Delta} - \tilde{\Delta}_{rs,rs})^2 + (\tilde{\Delta}_{r,r} + \tilde{\Delta}_{s,s})^2} \tag{2.2}$$

and the expression for the atom-atom polarizability, derived by Coulson et al.[8]

$$\pi_{r,s} = -\frac{1}{\pi i}\int_{-\infty i}^{\infty i} \frac{\Delta\Delta_{rs,rs} - \Delta_{r,r}\Delta_{s,s}}{\Delta^2} dz \tag{2.3}$$

A more profound look at these two expressions will be given in the next chapter.

Both the atom-atom polarizability and the transmission probability have been implemented in computer programs during this work and these programs have been used to study the series of polycyclic rings: benzene, naphthalene, anthracene, tetracene, pentacene. Next to an ordinary program to calculate the transmission probability in one chosen configuration of the contacts on the molecule, another program was developed which is able to calculate all possible configurations at once. This method, which was suggested by Fowler but has not yet been published, had never been implemented or tested before. Based on the results of these calculations, which will be presented in chapter 5, an attempt will be made to establish a formal link between the two quantities and we will try to propose a selection rule for transmission.

Next to programs to calculate the atom-atom polarizability and the transmission probability, a program capable of calculating the linear response current (not to be confused with the chemical concept 'linear response') has been developed. This linear response current makes it possible to determine whether a molecule will act as a conductor or as an insulator when a relatively small bias is applied. In section 5.5 we will illustrate that, just as is the case with the transmission probability spectra, the IV-curves are influenced by the positioning of the contact atoms.

As all calculations in this work are done at the Hückel level of theory, an introduction to this computational method will be given in the next chapter. Another section of the next chapter will be devoted to conceptual density functional theory and the linear response. This is done in order to show where our interest in the linear response (and equivalently the atom-atom polarizability) comes from. But first off, a small introduction to quantum chemistry and a general overview of the problem involving transmission calculations through molecules will be given.

Chapter 3

Theoretical background

3.1 Introduction to quantum chemistry and overview of the problem

Quantum chemistry is the study of the electronical structure of molecules and the properties which emerge from this characteristic structure. The principal tool to calculate the electronic structure of a molecule is the determination of the electronic wave function by solving the time independent Schrödinger equation.[18]

$$\hat{H}_{el}\Psi_{el} = E_{el}\Psi_{el} \tag{3.1}$$

Several strategies exist to solve this equation, but most ab initio methods share the same characteristic procedure. They start by separating the N-electron wave function in several 1-electron functions, molecular spin orbitals (MSOs) $\chi_k(i)$, which can further be separated in spatial functions, the molecular orbitals (MO) $\psi_a(r_i)$, and spin functions $\alpha(\sigma_i)$ or $\beta(\sigma_i)$

$$\chi_k(i) = \chi_k(r_i, \sigma_i) = \psi_a(r_i)\left\{\begin{array}{c}\alpha(\sigma_i)\\ \beta(\sigma_i)\end{array}\right. \tag{3.2}$$

The MOs are then usually defined in a basis (consisting of a set of n basis functions ϕ_r).

$$\psi_j = \sum_{r=1}^{n} c_{rj}\phi_r \tag{3.3}$$

Another general characteristic shared by most (single determinantal) quantum mechanical methods is the use of the variational theorem to determine both the energy

E and the coefficients c_r of each MO. The procedure according to which these parameters are determined is called optimization. Practically, during optimization the coefficients and the energy E are determined by minimizing the latter with respect to the former

$$\frac{\partial E}{\partial c_r} = 0 \ (r = 1, 2, ..., n) \tag{3.4}$$

$$E = \frac{\int \psi^* H \psi dv}{\int \psi^* \psi dv} \tag{3.5}$$

A side effect of introducing a basis is that the Hamiltonian operator can be written in matrix form. In this matrix, the diagonal elements contain the Hamiltonian associated to the individual basis functions while the other elements contain the interaction terms between the respective basis functions. Sometimes the eigenfunctions of a system can be divided into several groups, corresponding to specific parts of the system which can be distinguished from each other. The Hamiltonian matrix can then be written more compactly by considering the partial Hamiltonians associated to the different parts which together constitute the system.

Molecular electronic devices for example are systems which consist of 3 parts, 2 semi-infinite contacts (L and R) on both sides of a central supermolecule (M). For such a system the Hamiltonian matrix becomes[4]

$$H = \begin{pmatrix} H_L & M_{L,M} & 0 \\ M_{L,M}^+ & H_M & M_{M,R} \\ 0 & M_{M,R}^+ & H_R \end{pmatrix} \tag{3.6}$$

A remark to be made is that $M_{L,R}$ and $M_{R,L}$ aren't exactly zero, but, as they are spatially separated, these coupling terms are so small that they can be approximated by zero.

In order to calculate the transmission through the central molecule, a voltage between the 2 contacts has to be applied which is kept constant long enough such that a stationary state is obtained. This applied potential influences the Hamiltonian matrix and insertion in the Schrödinger equation leads to a very complicated expression which is not easy to solve due to several reasons.[19]

A first reason for this is that the Hamiltonian matrix gets very large (actually infinite due to the contacts being made of bulk material).[13] A second reason is that eigenvectors of all 3 parts of the system take part in the eigenvalue equation.

$$H \begin{pmatrix} C_L \\ C_M \\ C_R \end{pmatrix} = E \begin{pmatrix} C_L \\ C_M \\ C_R \end{pmatrix} \tag{3.7}$$

And last but not least, since the potential is not homogeneous along the system (as is usually the case when solving the Schrödinger equation in quantum chemistry), the equation becomes a linear inhomogeneous differential equation with 2-point boundary conditions.[11]

The boundary conditions are the following:

- in the left contact there is an incoming Bloch wave with a normalized amplitude as well as a reflected wave that has been scattered off the molecule
- in the right contact there is only an outgoing Bloch wave

Such differential equations are, as has been said before, usually solved by Green's function approach. This method, which won't be elaborated on here, enables one to express the transmission probability in a single equation. This equation however cannot be interpreted intuitively and as such gives no qualitative insight in the mechanism of ballistic transport.

A much more intuitive way of analyzing ballistic transport is achieved in the Source and Sink Potential method (SSP method). In this method, the molecular electronic device is partitioned such that the supermolecule contains a sufficiently large part of the contacts to take on its asymptotic behavior (the behavior described by the Bloch waves in the contacts). Introducing a source and a sink potential in terms of the incoming and outgoing Bloch wave, the problem is reduced to finding the reflection coefficient which leads to the considered stationary state.

Both the SSP as the Green's function method start by describing the Hamiltonian matrix in the same form as it was expressed in equation (3.7). However, one should note that in the SSP method a part of the contacts is assigned to the molecular part of the Hamiltonian.

3.2 The Hückel method

In this study all calculations will be done at the Hückel level of theory.[20][21] Application of this theory, which is restricted to planar unsaturated molecules, allows the determination of a very crude approximation of the electronic structure of an unsaturated system. The obtained numerical results are often far from accurate but the method is still used frequently because it enables a physical interpretation of a lot of chemical concepts.

In what follows, the rationale behind the method will be shown through consideration of an example system, the ethene molecule.

For ethene, the following bonding pattern is obtained

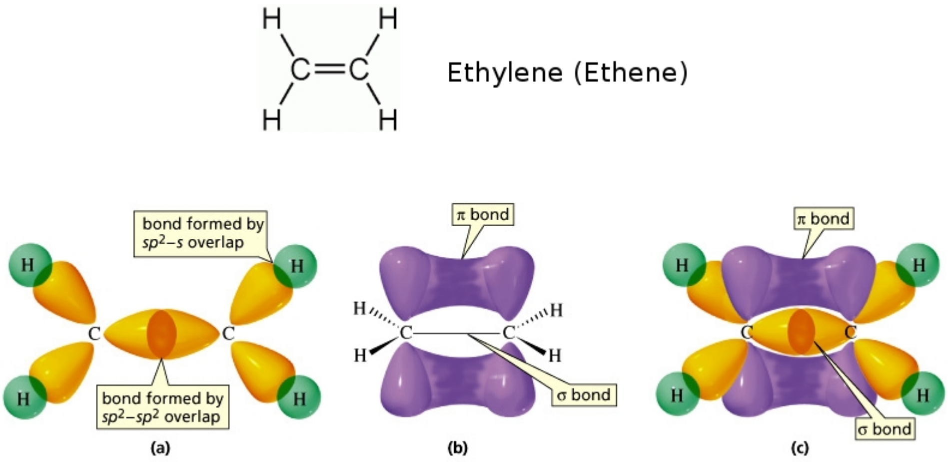

Figure 3.1: bonding pattern ethene[22]

- a σ-bond is formed between atoms C_1 and C_2 from two sp^2-hybrids (one on each C atom) with directional overlap
- σ-bonds are formed between the two remaining sp^2-hybrids on each C-atom and H 1s-orbitals
- a $C_1 - C_2$ π-bond arises form the non-directional (parallel) overlap of the p_z-orbitals. The electrons in these orbitals are the mobile electrons and the part of the molecule in which they move is called the conjugated system.

In Hückel method, the σ-electrons of the system are not considered, only the π-electrons lying in a common plane are taken into account. As such, the σ- and

π-electrons of the system are separated.

So the Hückel method only considers the conjugated system, as the electrons that move in the conjugated system are the ones that cause all effects that depend on conjugation, such as resonance energies and variations in bond orders and electron densities.

The N-electron function Ψ_π can be constructed from one electron functions, namely the π molecular spin orbitals (MSO) χ_i. In the Hückel method, these MSO are separated into MO ψ_j and spin functions α or β. In a first approximation, the Hartree-product can be written as

$$\Psi_i = \prod_i \chi_i(i) \tag{3.8}$$

The N-electron wave function can be connected to a total Hamiltonian H_π. This total Hamiltonian can now be written as a sum of one particle Hamiltonians

$$H_\pi = \sum_{i=1}^{n} h_i(\pi) \tag{3.9}$$

where h_i^π comprises the kinetic energy operator of electron *i*, the attraction towards the nuclei of the π-electrons, the interaction of these π-electron *i* with the σ-electrons and the 'inner shell' electrons and, finally, the (average) interaction with the other π-electrons.

Unlike most more advanced quantum mechanical methods, Hückel method does not require the derivation of an analytical expression for operator h_i^π. Combination of equation (3.8) and (3.9) leads to an expression for the time independent Schrödinger equation for the π-system

$$H_\pi \Psi_\pi = E_\pi \Psi_\pi \tag{3.10}$$

$$\Rightarrow \left(\sum_i h_i^{(\pi)}\right)\left(\prod_j \chi_j\right) = E_\pi \left(\prod_j \chi_j\right) \tag{3.11}$$

Dividing the left and right hand side of this last equation by $\prod_j \chi_j(j)$ gives

$$\sum_i \left\{1/\chi_i(i)\right\} h_i^{(\pi)} \chi_i = E_\pi \tag{3.12}$$

The total energy on the right hand side of equation (3.12) can be written as a sum of one-electron contributions of the form

$$E_\pi = \sum_j \epsilon_j^\pi \tag{3.13}$$

The summation runs over the different MO's present in equation (3.8) leading to

$$E_\pi = \sum_j n_j \epsilon_j^\pi \tag{3.14}$$

where n_j is the occupancy of the orbital.

The combination of equations (3.12) and (3.14) enables one to split the N-electron equation (3.10)

$$h_i^\pi \chi_i(i) = \epsilon_i^{(\pi)} \chi_i(i) \tag{3.15}$$

or, after division by the spin functions

$$h_i^\pi \psi_i(i) = \epsilon_i^{(\pi)} \psi_i(i) \tag{3.16}$$

where $\epsilon_i^{(\pi)}$ represents the energy of the considered MO. When the unsaturated system is oriented in the (x,y)-plane, the π-MSO χ_i, or the π-MO ψ_j can be constructed by making use of the p_z-AO (ϕ_r) of the atoms that are part of the unsaturated system due to symmetry reasons. The constructed MO ψ_j can then be written as a linear combination of the considered p_z-orbitals, analogously to equation (3.3).

Combination of equations (3.3) and (3.16) leads to

$$h_i^\pi \sum_r c_{ri}\phi_r = \epsilon_i^\pi \sum_r c_{ri}\phi_r \tag{3.17}$$

After multiplication with $\phi_s^\star$ and integration, the following expression is obtained

$$\sum_r c_{ri} \int \phi_s^\star h_i^\pi \phi_r d\tau = \epsilon_i^\pi \sum_r c_{ri} \int \phi_s^\star \phi_r d\tau \tag{3.18}$$

The integral on the left hand side of this equation can be defined as $(h_i^\pi)_{rs}$ and the integral on the right hand side (the overlap integral) can be defined as S_{rs}. Under these conventions, a final expression can be obtained

$$\sum_r c_{ri}[(h_i^\pi)_{rs} - \epsilon_i^\pi S_{rs}] = 0 \quad (s = 1, 2, ..., m) \tag{3.19}$$

This equation can be written for every value of *s*. This set of equations (3.19) only has a non-trivial solution if

$$det|\mathbf{H}^\pi - \epsilon^\pi \mathbf{S}| = 0 \tag{3.20}$$

where $\mathbf{H}^\pi$ stands for the matrix of the π-hamiltonian and **S** denotes the overlap matrix.

A final obstacle for solving the time independent Schrödinger is the construction of $\mathbf{H}^\pi$ and **S**. This can be tackled as follows.

Assuming orthonormality of the basis, the elements S_{rs} are equal to δ_{rs}.

The elements of $\mathbf{H}^\pi$ are defined without defining the effective hamiltonian h^π:

- All the matrix-diagonal elements h_{rr}^π are considered to be equal to each other and are written as α. The meaning of this parameter follows from the equation

  $$h_i^\pi \psi_i = \epsilon_i^\pi \; or \; \int \psi_i^\star h_i^\pi \psi_i d\tau = \epsilon_i^\pi \tag{3.21}$$

  If $\psi_i = \phi_r$ (which means that the MO ϕ_i is located on a single atom, atom *r*), this gives

  $$h_{rr}^\pi = \epsilon_i^\pi = \alpha_i \tag{3.22}$$

  which shows that that the diagonal element of **H** can be interpreted as the energy associated to the electron *i* in the p_z-orbital of the C-atom r. This integral is generally called the Coulomb integral.

  An important note is that no numerical value is assigned to α, it will remain a reference energy level for the π-system.

- The non-diagonal elements h^{π}_{rs} $(r \neq s)$ are also approximated. In order to understand the rationale behind the approximation, a molecule consisting of a π-system stretching over 2 atoms *r* and *s* has to be considered. For this π-system, the MO $\psi_i = 1/\sqrt{2}(\phi_r + \phi_s)$ can be constructed. Introducing this MO in equation (3.21) leads to

  $$\epsilon_i = \alpha + h^{(\pi)}_{rs} \tag{3.23}$$

  As the electron now has extra delocalization possibilities over 2 atoms and a favorable interaction is established with 2 nuclei instead of with 1, it can be expected intuitively that ϵ_i decreases (becomes more negative) compared to α. As the atoms *r* and *s* are positioned closer to each other, the importance of this stabilizing term is expected to increase.

  In a first approximation, the 'nearest neighbor approximation' can be used in molecules. This approximation states that the h^{π}_{rs} $(r \neq s)$ terms can be neglected when *r* and *s* are not direct neighbors since the interaction between these 2 atoms is very small compared to the interactions between nearest neighbors. The h^{π}_{rs} that are retained are denoted as β_{rs}. When all atoms in the molecule are equal, these remaining terms are also equal, allowing β_{rs} to be set equal to β. The quantity β is then called the nearest neighbor hopping parameter.[11] Sometimes however, this last approximation is not made when constructing the secular determinant. The non-diagonal elements are then denoted by β_{rs}.

Neglecting the nearest hopping parameter approximation, equation (3.20) leads to the condition that the following secular determinant

$$\Delta(\epsilon) = \begin{vmatrix} \alpha_1 - \epsilon & \beta_{12} & \beta_{13} & \dots & \dots \\ \beta_{21} & \alpha_2 - \epsilon & \beta_{23} & \dots & \dots \\ \beta_{31} & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \alpha_n - \epsilon \end{vmatrix} \tag{3.24}$$

should be equal to zero

$$\Delta(\epsilon) = 0 \tag{3.25}$$

This so called "secular equation" has n roots ϵ_j. The corresponding sets of expansion coefficients can be found by substituting these roots into the secular equations and by considering the normalization condition

$$c_{1j}^2 + c_{2j}^2 + c_{3j}^2 + ... + c_{nj}^2 = 1 \tag{3.26}$$

The electronic ground state of the π-electron system can be constructed through application of the Aufbau principle. The total energy of the π-system can then be calculated by applying equation (3.14).

Taking the nearest hopping parameter approximation into account, the Hückel Hamiltonian for the π-system of the considered molecule can be written more compactly as

$$\mathbf{H}^M = \alpha\mathbf{1} + \beta\mathbf{A} \tag{3.27}$$

where **A** is the so called adjacency matrix.

Sometimes, the carbon atoms of a hydrocarbon can be divided into 2 sets as in the example below, where the atoms of set 1 are denoted by $\star$ and the atoms of set 2 by 0.

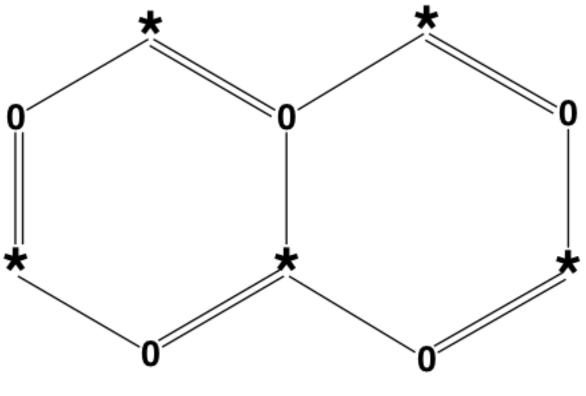

Figure 3.2: example of an alternating hydrocarbon

It can be seen from the example that atoms with a $\star$ are never situated next to an atom of the same set and vice versa; these hydrocarbons are alternating and their graphs are called bipartite. For alternating hydrocarbons, the energy levels exist in pairs and are symmetrical with respect to the Fermi level of the isolated molecule. This property will be of vital importance further on in this work.

In the final paragraphs of this section an expression for Bloch waves in Hückel theory is derived. The contacts that are used in MED are metal crystals (periodic solids). As only one atom connects the contact with the molecule, the approximation can be made that the entire contact can be represented by a chain of atoms with nearest neighbor hopping parameter β, and α set to zero.[11] This way, a one dimensional crystal is obtained. Due to translational symmetry in the infinite crystal, any observable property has to be the same at each atom in the solid. The probability to find an electron at atom *n* is $|\Psi(n)|^2$. Symmetry then requires that[23]

$$|\Psi(n)|^2 = |\Psi(n+m)|^2 \tag{3.28}$$

where n is an integer number. The condition stated in equation (3.28) can only be satisfied if $|\Psi(n)|^2$ and $|\Psi(n+m)|^2$ differ only by a phase factor. It is reasonable to expect the phase factor to depend only on the separation between the points (*m*), leading to

$$\Psi(n+m) = e^{i\phi_m}\Psi(n) \tag{3.29}$$

where ϕ_m is the phase factor. In Hückel theory, the wave function $\Psi(n) = \langle n|\Psi\rangle$ is expressed in terms of the atomic orbitals $\langle n|j\rangle$

$$\Psi(n) = \sum_j c_j \langle n|j\rangle \tag{3.30}$$

For $\Psi(n+m)$ one obtains

$$\Psi(n+m) = \sum_j c_j \langle n+m|j\rangle \tag{3.31}$$

$\langle n+m|j\rangle$ can be rewritten as $\langle n|j-m\rangle$. Equation (3.31) can then be restated as

$$\Psi(n+m) = \sum_j c_{j+m} \langle n|j\rangle \tag{3.32}$$

Comparing equations (3.30) and (3.32), it is evident that equation (3.28) can only be satisfied if

$$\frac{c_{j+m}}{c_j} = e^{i\phi_m} \tag{3.33}$$

This relation has to be true for any *j* and *m*, and since the right hand side only depends on *m*, c_j has to have the following form

$$c_j = Ae^{iqj} \tag{3.34}$$

where *A* is an arbitrary constant and *q* is any real number. *A* is determined from the normalization condition and is equal to $\frac{1}{\sqrt{N}}$. This finally leads to the expression for a Bloch wave in Hückel theory

$$\Psi(n+m) = e^{iqm}\Psi(n) \tag{3.35}$$

Solving equation (3.35) for $\Psi(n)$, the simplest solution possible is

$$\Psi(n) = e^{iqn} \tag{3.36}$$

where we note that, as the spatial form of the orbitals is not exploited in the Hückel method, the function describing the form of the orbitals, which is usually present in the expression of a Bloch wave, can be set to unity. So, $\Psi(n)$ has the form of a plane wave where *q* is called the wave vector. This expression for the Bloch wave will be used later on in this work. For a chain with periodic boundary conditions, the Hamiltonian acquires the same form as a ring with an infinite number of atoms

$$H = \begin{pmatrix} \alpha & \beta & 0 & ... & ... & 0 & \beta \\ \beta & \alpha & \beta & 0 & ... & ... & 0 \\ 0 & \beta & \alpha & \beta & 0 & ... & 0 \\ ... & ... & ... & ... & ... & ... & ... \\ 0 & ... & ... & 0 & \beta & \alpha & \beta \\ \beta & 0 & ... & ... & 0 & \beta & \alpha \end{pmatrix} \tag{3.37}$$

The eigenvalues of such a matrix are given by[23]

$$E(q) = \alpha + 2\beta cos(q) \tag{3.38}$$

As α is set to 0 in this work, equation (3.38) can be rewritten as

$$q = arccos\left(\frac{E}{2\beta}\right) \tag{3.39}$$

This expression is known as the dispersion relationship.

3.3 The SSP method

As has already been mentioned in section (3.1), the transmission through molecules in MED is usually calculated through application of the Green's function method. Recently however, Ernzerhof et al. developed a new method to get some qualitative insight in the mechanism of ballistic transport.[11] In this method, the central part of the MED, the supermolecule, contains a sufficiently large part of the contacts to take on its asymptotic behavior which can be described by Bloch waves.

In the left contact, the wave function (C_L) is a combination of a forward (C_L^+) and backward (C_L^-) going Bloch wave

$$C_L = C_L^+ + rC_L^- \tag{3.40}$$

where *r* is the reflection coefficient.

In order to normalize the coefficients in this equation, C_L^+ has been set equal to 1. In the right contact R, the boundary conditions dictate that the wave function is an outgoing Bloch wave

$$C_R = tC_R^+ \tag{3.41}$$

where *t* is the transmission amplitude and can be related to the transmission probability through following expression

$$T(E) = |t(E)|^2 \tag{3.42}$$

where E is the energy of the considered electron that enters the molecule. The reflection coefficient *r* can now be related to T(E) as

$$T(E) = 1 - |r(E)|^2 \tag{3.43}$$

In the SSP method, the fact is exploited that, apart from *r* and *t*, the wave function in the contacts is known. This is the main difference with the Green's function approach. Taking a look at the part of the eigenvalue equation (3.7) that involves C_L, C_M and C_R simultaneously, the following equation is obtained

$$M_{L,M}^+ C_L + H_M C_M + M_{M,R} C_R = EC_M \tag{3.44}$$

In this equation, all eigenvectors of the system are still present. In order to get rid of the eigenvectors of the contacts, an artificial source-sink potential is introduced

$$\Sigma = \Sigma_L + \Sigma_R \tag{3.45}$$

$$M^{+}_{L,M} C_L = \Sigma_L C_M \tag{3.46}$$

$$M_{M,R} C_R = \Sigma_R C_M \tag{3.47}$$

These artificial potentials can be interpreted as the projection of the interaction-potential between the molecule and the contacts on the basis of the supermolecule.

To further simplify, an additional condition is set on $\Sigma_{L(R)}$, requiring that these matrices are diagonal in the basis C_M. Σ_L and Σ_R can be determined for each basis function *k* by manipulating these equations

$$\Sigma_{L_{kk}} = \frac{(M^{+}_{L,M} C_L)_k}{C_{M_k}} \tag{3.48}$$

and

$$\Sigma_{R_{kk}} = \frac{(M_{R,M} C_R)_k}{C_{M_k}} \tag{3.49}$$

From these expressions it can evidently be concluded that solutions for $\Sigma_{L_{kk}}$ and $\Sigma_{R_{kk}}$ can always be found except when C_{M_k}=0. In the case that C_{M_k} does equal 0, the system can be perturbed slightly, leading to $C_{M_k} \neq 0$, which enables the calculation of the desired SSP matrix element even in these cases.

By introducing the SSP, equation (3.44) can be rewritten compactly as

$$H^{SSP}(E, r) C_M = E C_M \tag{3.50}$$

with

$$H^{SSP}(E, r) C_M = H_M + \Sigma_L(E, r) + \Sigma_R(E) \tag{3.51}$$

This last expression is relatively simple, as the contacts have been eliminated compared to the initial equation. Another advantage is that the potential Σ is defined in terms of Bloch waves which automatically introduce the boundary conditions into the SSP Hamiltonian $H^{SSP}(E, r)$. Note that $\Sigma_R(E)$ is independent of *t*. The reason for this can be easily understood when taking a look at the expression for the sink potential as it will be presented in equation (3.53).

The SSP method allows a great reduction of the complexity of the calculus required to solve these kinds of problems. An extra level of simplification can be introduced by using a Hückel approximation. At this level of theory, the equations of the SSP method become fairly easy to interpret, and qualitative insight in the transmission can be obtained for small molecules.

In this approximation, the nearest neighbor hopping parameter is denoted by β and diagonal matrix elements are set equal to zero (the energy origin is chosen so that α=0). The resonance integrals in the contacts, denoted as β_L and β_R, are expressed as multiples of β.

In a contact, the wave functions are, as was already mentioned before, combinations of plane waves e^{iqn} and e^{-iqn}, where the index n corresponds to the number of atoms. The expression for Σ_L at the boundary between the supermolecule and the left contact then becomes

$$\Sigma_{L_{nn}}(E(q), r) = \beta \frac{C_{n-1}}{C_n} = \beta \frac{e^{iq(n-1)} + re^{-iq(n-1)}}{e^{iqn} + re^{-iqn}} = \beta \frac{e^{-iq} + \tilde{r}e^{iq}}{1 + \tilde{r}} \tag{3.52}$$

In this equation $\tilde{r}$ is defined by $\tilde{r} = re^{-2iqn}$, where the exponential is simply a phase factor. So it is clear that r and $\tilde{r}$ differ only by a certain phase which does not influence the final value of T(E) (see equation (3.43)). As such, no distinction is made between r and $\tilde{r}$ in the remainder of this discussion.

The expression for Σ_R then becomes

$$\Sigma_{R_{nn}}(E(q)) = \beta \frac{C_{n+1}}{C_n} = \beta \frac{te^{iq(n+1)}}{te^{iqn}} = \beta e^{iq} \tag{3.53}$$

Considering a concrete system, the isolated molecule can be represented by graphs with vertices for atoms and edges for σ-bonds. This way, the Hamiltonian for the π-electrons of the isolated molecule can be expressed as

$$\mathbf{H}^M = \beta \mathbf{A} \tag{3.54}$$

where **A** is the adjacency matrix of the considered graph. The SSP Hamiltonian for the whole system is now constructed by adding to the graph and the resulting Hamiltonian the contact atoms L and R, assigned vertex numbers n+1 (for source vertex L) and n+2 (for sink vertex R). Both of these vertices bear their respective potentials as described above. The molecular vertices to which the external vertices are connected will be denoted as *s* and *r* respectively. Taking these conventions into account, the Hamiltonian matrix becomes

$$\mathbf{H} = \begin{pmatrix} \mathbf{A} & \beta_{sL} e_s & \beta_{rR} e_r \\ \beta_{sL} e_s^+ & a_{LL} & 0 \\ \beta_{rR} e_r^+ & 0 & a_{RR} \end{pmatrix} \tag{3.55}$$

which is a block partition into the internal, left-contact, and right-contact subspaces of the total supermolecule space. The vectors in the contact subspaces are unit vectors given by

$$(e_s)_i = \delta_{si} \tag{3.56}$$

$$(e_r)_i = \delta_{ri} \tag{3.57}$$

which represent the two connections, limited to one single edge each, between the external and internal contact vertices. The contact matrix elements consist of an intrinsic energy value for the respective contact and the respective source-sink potential (see equations (3.52) and (3.53))

$$a_{RR} = \alpha_R + \beta_R e^{iq_R} \tag{3.58}$$

$$a_{LL} = \alpha_L + \beta_L \frac{e^{-iq_L} + r e^{iq_L}}{1 + r} \tag{3.59}$$

As a_{LL} contains the reflection parameter *r*, the SSP Schrödinger equation for the system, which can be expressed as

$$(E\mathbf{1} - \mathbf{H}^{SSP})c = 0 \tag{3.60}$$

implicitly contains *r* too. As there is a solution for every E within the transparency region, the secular equation has to fulfill the following condition

$$det(E\mathbf{1} - \mathbf{H}^{SSP}) = 0 \tag{3.61}$$

This condition can then be used to determine *r*(E) at each fixed value of E, and hence eigenvector **c**. To achieve this, the secular determinant is expanded along the columns and rows of the border, leading to the following cofactor

$$(E-a_{LL})(E-a_{RR})\Delta+\beta_{sL}^2\beta_{rR}^2\Delta_{rs,rs}-\beta_{sL}^2(E-a_{RR})\Delta_{s,s}-\beta_{rR}^2(E-a_{LL})\Delta_{r,r}=0 \tag{3.62}$$

with

$$\Delta(E) = det(E\mathbf{1} - \mathbf{A}) \tag{3.63}$$

$$\Delta_{s,s}(E) = det(E\mathbf{1} - \mathbf{A})^{s,s} \tag{3.64}$$

$$\Delta_{r,r}(E) = det(E\mathbf{1} - \mathbf{A})^{r,r} \tag{3.65}$$

$$\Delta_{rs,rs}(E) = det(E\mathbf{1} - \mathbf{A})^{rs,rs} \tag{3.66}$$

It can be seen easily that $\Delta(E)$ is the minor obtained when the original determinant is expanded along a_{LL} and a_{RR}. $\Delta_{s,s}(E)$ is the result of expansion, first along a_{RR}, secondly along $\beta_{sL}e_s$ and thirdly along $\beta_{sL}e_s^+$. This result is equivalent to the adjacency matrix of the graph in which the vertex, linked to the left contact, is deleted. $\Delta_{r,r}(E)$ and $\Delta_{rs,rs}(E)$ are obtained analogously, respectively deleting the vertex linked to the right contact, and both the vertices, linked to either the right or left contact.

Equation (3.62) can be written more compactly by replacing the minors by the following scaled polynomials

$$\tilde{\Delta} = \Delta \qquad \tilde{\Delta}_{s,s} = \tilde{\beta}_L\Delta_{s,s} \qquad \tilde{\Delta}_{r,r} = \tilde{\beta}_R\Delta_{r,r} \qquad \tilde{\Delta}_{rs,rs} = \tilde{\beta}_L\tilde{\beta}_R\Delta_{rs,rs} \tag{3.67}$$

where

$$\tilde{\beta}_L = \frac{\beta_{sL}^2}{\beta_L} \qquad \tilde{\beta}_R = \frac{\beta_{rR}^2}{\beta_R} \tag{3.68}$$

These factors express how the strengths of the bonds between and within the molecule are related to each other.

Replacing a_{LL} and a_{RR} in equation (3.62) by the expressions in equations (3.58) and (3.59), leads, after some calculus (see appendix A), to the following expression for the transmission probability T(E)

$$T(E) = \frac{4 \sin q_L \sin q_R (\tilde{\Delta}_{r,r} \tilde{\Delta}_{s,s} - \tilde{\Delta} \tilde{\Delta}_{rs,rs})}{|e^{-i(q_L+q_R)} \tilde{\Delta} - e^{-iq_R} \tilde{\Delta}_{s,s} - e^{-iq_L} \tilde{\Delta}_{r,r} + \tilde{\Delta}_{rs,rs}|^2} \tag{3.69}$$

In the case of ipso connection (both left and right contact linked to the same atom), expansion of the characteristic determinant leads to a minor with a column containing only zeros for $\Delta_{rs,rs}$(E), resulting in this secular determinant always being zero, independently of the value for E. In this case, $\Delta_{s,s}$(E) and $\Delta_{r,r}$(E) also become equal to each other.

Taking a look now at the factor $(\tilde{\Delta}_{r,r} \tilde{\Delta}_{s,s} - \tilde{\Delta} \tilde{\Delta}_{rs,rs})$ in the numerator of equation (3.69), one can write this as the square of one single determinant by applying the Jacobi/Sylvester determinant identity to the unscaled polynomials,

$$\tilde{\beta}_L \tilde{\beta}_R (\Delta_{r,r} \Delta_{s,s} - \Delta \Delta_{rs,rs}) = \tilde{\beta}_L \tilde{\beta}_R \Delta_{r,s}^2 = \tilde{\Delta}_{r,s}^2 \tag{3.70}$$

This factor $\Delta_{r,s}^2$ play an important role further on (see equation (3.76)).

In the final expression for T(E), $4 \sin q_L \sin q_R$ in the numerator acts as a 'band-pass' filter, which cuts off transmission at the ends of the range defined by the intersection of left and right conduction bands. If the band of energy range of the molecular states is much smaller than that of the energy bands of the semi-infinite wires, the wide band limit (WBL) is approached. The expression for the transmission probability is found by letting the resonance parameters β_L, β_{sL} and β_R, β_{rR} all approach infinity while keeping $\tilde{\beta}_L$ and $\tilde{\beta}_R$ constant. In the limit, equation (3.68) then becomes

$$\tilde{\beta}_L = \tilde{\beta}_R = k \tag{3.71}$$

where *k* is a constant. In such case, it becomes clear from equation (3.39) that q_L and q_R can be set equal to $\pi/2$, greatly simplifying the final expression for T(E)

$$T_{WBL}(E) = \frac{4(\tilde{\Delta}_{r,r}\tilde{\Delta}_{s,s} - \tilde{\Delta}\tilde{\Delta}_{rs,rs})}{(\tilde{\Delta} - \tilde{\Delta}_{rs,rs})^2 + (\tilde{\Delta}_{r,r} + \tilde{\Delta}_{s,s})^2} \tag{3.72}$$

Conceptually, the final equation is quite easy to solve for concrete systems. However, it still requires quite some calculus to find all the characteristic polynomials. To avoid this time-consuming process, some transformations can be performed in equation (3.72). In linear algebra, the relationship between the elements of an inverse matrix (a_{ij}^{-1}) and the original matrix A is given by Cramer's rule[24]

$$a_{ij}^{-1} = \frac{\tilde{a}_{ij}}{det[A]} \tag{3.73}$$

where $\tilde{a}_{ij}$ the cofactor of the element ij of A. The cofactor of element ij is obtained by multiplying the minor of entry ij with a factor $(-1)^{i+j}$. Applying this rule to the matrix Δ, introduced in equation (3.63), gives for the diagonal elements

$$\frac{\Delta_{s,s}}{\Delta} = \frac{det(E\mathbf{1} - \mathbf{A})^{s,s}}{det(E\mathbf{1} - \mathbf{A})} = [E\mathbf{1} - \mathbf{A}]^{-1}_{s,s} \tag{3.74}$$

$$\frac{\Delta_{r,r}}{\Delta} = [E\mathbf{1} - \mathbf{A}]^{-1}_{r,r} \tag{3.75}$$

For the non-diagonal elements, two possibilities arise. Either r+s is even, leading to

$$\frac{\Delta_{r,s}}{\Delta} = [E\mathbf{1} - \mathbf{A}]^{-1}_{r,s} \tag{3.76}$$

or, if r+s is odd, then

$$\frac{\Delta_{r,s}}{\Delta} = -[E\mathbf{1} - \mathbf{A}]^{-1}_{r,s} \tag{3.77}$$

So the sign of $\Delta_{r,s}$ depends on the choice of r and s. However, $\Delta_{r,s}^2$ will always be positive. As in the remainder of this work $\Delta_{r,s}$ only appears as a square (vide infra), the specific sign plays no role in what follows.

Using the Jacobi/Sylvester determinant identity, $\Delta_{rs,rs}$ can be written as

$$\Delta_{rs,rs} = \frac{\Delta_{r,r}\Delta_{s,s} - \Delta^2_{r,s}}{\Delta} \tag{3.78}$$

where $\Delta^2_{r,s}$ was defined in equation (3.70). These equations can be introduced into equation (3.72) by dividing both numerator and denominator by Δ^2

$$T_{WBL}(E) = \frac{4\tilde{\beta}_L\tilde{\beta}_R(\frac{\Delta_{r,r}}{\Delta}\frac{\Delta_{s,s}}{\Delta} - \frac{\Delta_{rs,rs}}{\Delta})}{(1 - \tilde{\beta}_L\tilde{\beta}_R\frac{\Delta_{rs,rs}}{\Delta})^2 + (\tilde{\beta}_R\frac{\Delta_{r,r}}{\Delta} + \tilde{\beta}_L\frac{\Delta_{s,s}}{\Delta})^2} \tag{3.79}$$

This way, equation (3.72) can be solved for any system just by inverting the adjacency matrix, with the energy values as its diagonal elements. After the inversion, the respective values for the elements of the resulting matrix have to be selected and put into equation (3.79) to find T_{WBL} for a certain energy. Interestingly, T_{WBL} can now be calculated for every possible configuration of the contacts simultaneously, meaning that inversion of the matrix for benzene for example immediately leads to the transmission probability for both the ipso, ortho, meta and para case.

3.4 Conceptual DFT and the linear response

Although all calculations and derivations in this study are done in Hückel theory, the most used ab initio method nowadays is Density Functional Theory (DFT).[25] This theory distinguishes itself from the other ab initio methods in the fact that it makes use of functionals of the electron density instead of the wave function to determine the properties of the system.[26] The main advantage of this approach is that by considering the electron density, only 3 variables are necessary to characterize an N-electron system, while the wave function depends on 4N variables.

Even though in DFT the goal is to determine the electron density, this does not mean that wave functions can be omitted entirely from this method; the only way to retrieve the main part of the kinetic energy of the system is by introduction of the so-called 'Kohn-Sham'-orbitals ψ_i.[27] These orbitals can be determined by solving the Kohn-Sham equation

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_j(\mathbf{r}) + v_{XC}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \tag{3.80}$$

where $-\frac{1}{2}\nabla^2$ denotes the kinetic energy operator, $v(\mathbf{r})$ the nucleus-electron attraction operator and $v_j(\mathbf{r})$ is called the Coulomb-operator, which arises due to the electron-electronrepulsion. The final operator is the exchange-correlation operator.

For each of the energy terms associated to one of the operators in equation (3.80), an expression is known, except for the exchange-correlation operator. However, as the exchange-correlation energy is known to be very small, good computational results can already be obtained by making very crude approximations of this energy. Various, more elaborate, approximations for this operator have been proposed, enabling very accurate results to be computed, but these won't be discussed here since they exceed the scope of this work and are of little interest for what follows.

Next to a purely computational tool, DFT can also be used to define a theory of chemical reactivity. In this domain of DFT, called conceptual DFT, reactivity indices are introduced which correspond to the response of a system to perturbations.[28] In conceptual DFT, all perturbations on the system are written in terms of perturbations in the number of electrons and/or the external potential. The change in the energy due to a change in these variables can be expressed by the following equation

$$dE[v(\mathbf{r});N] = \left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})} dN + \int \left(\frac{\partial E}{\delta v(\mathbf{r})}\right)_N \delta v(\mathbf{r}) d\mathbf{r} \tag{3.81}$$

The coefficient of dN is called the electronic potential, by analogy with classical thermodynamics

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})} \tag{3.82}$$

The coefficient of $\delta v(\mathbf{r})$ is nothing else than the electron density itself

$$\rho(\mathbf{r}) = \left(\frac{\partial E}{\delta v(\mathbf{r})}\right)_N \tag{3.83}$$

The chemical potential and the electron density on their own are again dependent on the number of electrons and the external potential

$$d\mu = \left(\frac{\partial \mu}{\partial N}\right)_{v(\mathbf{r})} dN + \int \left(\frac{\partial \mu}{\delta v(\mathbf{r})}\right)_N \delta v(\mathbf{r}) d\mathbf{r} \tag{3.84}$$

$$d\rho(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})} dN + \int \left(\frac{\partial \rho(\mathbf{r})}{\delta v(\mathbf{r}')}\right)_N \delta v(\mathbf{r}') d\mathbf{r}' \tag{3.85}$$

The two point (nonlocal) reactivity indicator in this last equation is called the linear response function[15]

$$\chi(\mathbf{r},\mathbf{r}) = \left(\frac{\delta \rho(\mathbf{r})}{\delta v(\mathbf{r}')}\right) = \left(\frac{\delta^2 E}{\delta v(\mathbf{r}) \delta v(\mathbf{r}')}\right)_N \tag{3.86}$$

This nonlocal reactivity indicator has an analogue in Hückel theory, where it is called the 'atom-atom polarizability'. In the next chapter, an expression for this quantity will be derived.

3.5 The atom-atom polarizability

In 1947 Coulson and Longuet-Higgins wrote an article in which they developed a general theory for the electronic structure of conjugated systems at the Hückel level of theory.[8] [9] [10] In this article they derived expressions for some of the properties and concepts that are also studied in DFT. One of the featured properties is the mutual polarizability of atoms, which is a nonlocal response kernel, equivalent to the linear response kernel in DFT.[26]

Their rationale starts from the secular determinant defined in equation (3.37).

Since the matrix of Δ (see equation (3.37)) is Hermitian, the ϵ_j are all real, and Coulson and Longuet-Higgins assumed that they are all distinct, which is true most of the time and is especially convenient in the derivation that follows.

As was mentioned before in the chapter about Hückel theory, determination of the eigenvalues from the secular determinant allows the derivation of the respective eigenvectors. From these eigenvectors, an equation that expresses the total density of π-electrons around atom *r* can be established

$$q_r = 2\sum_{j=1}^{m} c_{rj}^2 \tag{3.87}$$

In this form, q_r is given as a sum over the occupied MO. Equation (3.87) is the most often used expression for the electron density in Hückel theory.[20]

Coulson and Longuet-Higgins argued however that electron densities could also be determined directly from the secular determinant. In this form, important deductions can be made concerning both their absolute magnitudes and their variations with changes in α and β, which wasn't possible through the former expression (3.87).

Their rationale continued by considering equations (3.5) and (3.17) and the definitions of α_r and β_{rs} and an orbital energy ϵ, leading to the following expression for ϵ

$$\epsilon = (\sum_{r} c_r^2\alpha_r + 2\sum_{r<}\sum_{s} c_r c_s \beta_{rs})/\sum_{t} c_t^2 \tag{3.88}$$

which is then differentiated, leading to

$$\delta\epsilon = \sum_r \{\frac{c_r^2}{\sum_t c_t^2}\}\delta\alpha_r + \sum_{r<}\sum_s \{\frac{2c_r c_s}{\sum_t c_t^2}\}\delta\beta_{rs} + \sum_r \delta c_r \frac{\partial\epsilon}{\delta c_r} \quad (3.89)$$

But due to the variational principle and the normalization condition, which give

$$\partial\epsilon/\partial c_r = 0 \qquad \sum_t c_t^2 = 1 \quad (3.90)$$

this equation can be be simplified to

$$\delta\epsilon = \sum_r c_r^2 \delta\alpha_r + \sum_{r<}\sum_s 2c_r c_s \delta\beta_{rs} \quad (3.91)$$

for small changes in α_r, β_{rs} and c_r. Taking the partial derivative of this equation respectively with respect to α_r and β_{rs} at $\Delta = 0$ (the necessary condition for obtaining solutions to the minimization problem), the following expressions for $(\frac{\partial\epsilon}{\partial\alpha_r})_{\Delta=0}$ and $(\frac{\partial\epsilon}{\partial\beta_rs})_{\Delta=0}$ are obtained

$$(\frac{\partial\epsilon}{\partial\alpha_r})_{\Delta=0} = c_r^2 \qquad (\frac{\partial\epsilon}{\partial\beta_{rs}})_{\Delta=0} = 2c_r c_s \quad (3.92)$$

which, after summation over the occupied MO, gives a new expression for the electron density, as it was defined in equation (3.87)

$$q_r = 2\sum_{j=1}^{m} c_{rj}^2 = 2\sum_{j=1}^{m}(\frac{\partial\epsilon_j}{\partial\alpha_r})_{\Delta=0} = (\frac{\partial\varepsilon}{\partial\alpha_r})_{\Delta=0} \quad (3.93)$$

In this expression ε denotes the sum of the π-electron energies, i.e.

$$\varepsilon = \sum_{j=1}^{m} 2\epsilon_j \quad (3.94)$$

In a next step of the derivation, they proposed rewriting the partial derivative as follows

$$(\frac{\partial\epsilon_j}{\partial\alpha_r})_{\Delta=0} = -(\frac{\partial\Delta}{\partial\alpha_r})/(\frac{\partial\Delta}{\partial\epsilon}) \quad (3.95)$$

In which, after differentiation of the characteristic polynomial, ϵ is given the value ϵ_j. And

$$\frac{\partial \Delta}{\partial \alpha_r} = \Delta_{r,r} \tag{3.96}$$

where $\Delta_{r,r}$ is the determinant obtained by deleting from Δ the *r*th row and *r*th column and $\Delta_{r,s}$ is obtained by deleting the *r*th row and *s*th column. These last equations finally lead to the following expression for the electron density

$$q_r = -2 \sum_{j=1}^{m} \frac{\Delta_{r,r}(\epsilon_j)}{\Delta'(\epsilon_j)} \tag{3.97}$$

where $\Delta'(\epsilon_j)$ denotes $[\frac{\partial \Delta(\epsilon)}{\partial \epsilon}]_{\epsilon=\epsilon_j}$

Calculating the electron density through equation (3.97) is very challenging. However, the authors came up with a method to avoid this difficult calculus. In complex analysis, a theorem exists which allows the construction of a complex function which has residues that exactly correspond to the sum in equation (3.97)[29]

$$f(z) = \frac{\Delta_{r,r}(z)}{\Delta(z)} \tag{3.98}$$

According to the residue theorem in complex analysis, the residues of this complex function can be determined by calculating a contour integral around them. Taking into account that only filled orbitals contribute to the electron density, only the poles of f(z), i.e. the solutions of $\Delta(z) = 0$ (the orbital energies), on the negative part of the real axis have to be considered. This explains why the authors limited their contour to the semicircle confined to the left part of the complex plane, as is shown in the figure below.

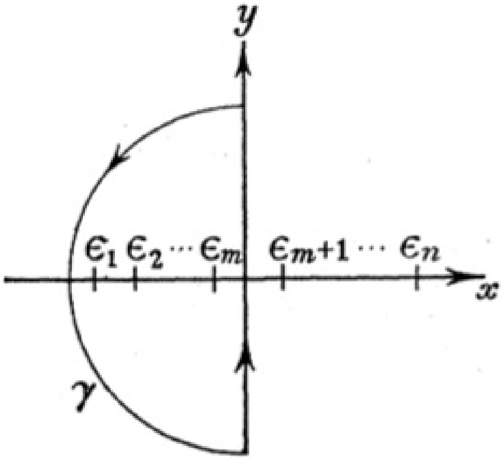

Figure 3.3: contour integral used for the evaluation of equation (3.97), ϵ_1 stands for the lowest, ϵ_m stands for the highest occupied orbital[8]

It should also be noted that no pole will be found at the origin because the origin of the considered energy axis can be explicitly forced to comply with this condition as the choice for this origin is completely arbitrary. A final remark to be made is that the roots of the secular determinant (ϵ_j) are all on the real axis as the corresponding matrix is Hermitian and as such, these points are the only poles of the complex function located inside the contour.

Thus, if the semicircle depicted in figure (3.3) is taken sufficiently large so that all ϵ_j are included, the following line integral over the semicircle of the complex function can be considered

$$\frac{1}{2\pi i}\int_{\gamma}\frac{\Delta_{r,r}(z)}{\Delta(z)}dz \tag{3.99}$$

Now, at large distance from the origin the integrand tends to -1/z. So calculation of the line integral over the infinite semicircle leads to -1/2. The part of the contour integral that still remains is the integral over the imaginary axis. As such, the last expression can be rewritten as

$$\frac{1}{2\pi i}\int_{-\infty i}^{\infty i}\frac{\Delta_{r,r}(z)}{\Delta(z)}dz - \frac{1}{2} \tag{3.100}$$

Summarizing all this, the Cauchy theorem allows the following equation to be written

$$\frac{1}{2\pi i}\int_{-\infty i}^{\infty i}\frac{\Delta_r,r(z)}{\Delta(z)}dz-\frac{1}{2}=\sum_{j=1}^{m}\frac{\Delta_{r,r}(\epsilon_j)}{\Delta'(\epsilon_j)} \tag{3.101}$$

Replacing the sum over the residues in equation (3.97) by the corresponding integral gives

$$q_r=1-\frac{1}{\pi i}\int_{-\infty i}^{\infty i}\frac{\Delta_{r,r}(z)}{\Delta(z)}dz \tag{3.102}$$

Now that an integral expression for q_r has been established, the authors derived a way to express the mutual polarizability of atoms as a function of the electron density (very reminiscent of the conceptual DFT-relationships), after which they substituted q_r by the integral expression derived above.

Their derivation of this formula starts with the idea that one is able to alter the energy integral α_r of an atom to a slightly different value $\alpha+\delta\alpha$. As a result of this change in α_r the electron densities around all the nuclei will change. The change of the electron density on atom *s* (δq_s) can be treated as the response to a perturbation applied to atom *r*. This consideration leads to the following expression for δq_s

$$\delta q_s=\frac{\partial q_s}{\partial\alpha_r}\delta\alpha_r=\pi_{s,r}\delta\alpha_r \tag{3.103}$$

Coulson and Longuet-Higgins rewrote this equation according to equation (3.93), leading to

$$\pi_{s,r}=\frac{\partial q_s}{\partial\alpha_r}=\frac{\partial^2\varepsilon}{\partial\alpha_r\partial\alpha_s}=\frac{\partial^2\varepsilon}{\partial\alpha_s\partial\alpha_r}=\frac{\partial q_r}{\partial\alpha_s}=\pi_{r,s} \tag{3.104}$$

which resembles a lot the definition of the linear response in DFT. The symmetry that is evident in this last expression motivated the authors to call this quantity the *mutual* polarizability of atoms *r* and *s*.

Substitution of q_r by its integral form in equation (3.102) permitted them to write the mutual polarizability in an integral form

$$\pi_{r,s}=-\frac{1}{\pi i}\int_{-\infty i}^{\infty i}\frac{\partial}{\partial\alpha_s}\frac{\Delta_{r,r}(z)}{\Delta(z)}dz \tag{3.105}$$

or

$$\pi_{r,s} = -\frac{1}{\pi i}\int_{-\infty i}^{\infty i} \frac{\Delta\Delta_{rs,rs} - \Delta_{r,r}\Delta_{s,s}}{\Delta^2} dz \tag{3.106}$$

where the letters before and after the comma in each suffix denote respectively the row and the column omitted from Δ.

Next to the derivation of an integral formula for the atom-atom polarizability, Coulson and Longuet-Higgins also came up with a formula in terms of the MO coefficients. The derivation of this formula is based on first-order perturbation theory.

Consider a molecule with occupied MO $\psi_1, \psi_2, ..., \psi_m$ and unoccupied MO ψ_{m+1}, ..., ψ_n, constructed from the component atomic orbitals $\phi_1, ..., \phi_n$. According to first order perturbation theory, the change in the MO when the coulomb integral α_r is increased by a small amount $\delta\alpha_r$ can be expressed as

$$\psi_j + \psi_j' = \psi_j + \sum_{k=1}^{n} \left\{ \frac{\int \psi_j H' \psi_k dv}{\epsilon_j - \epsilon_k} \right\} \psi_k \tag{3.107}$$

$$\Leftrightarrow \psi_j + \psi_j' = \psi_j + \sum_{k=1}^{n} \frac{c_{rj} c_{rk} \delta\alpha_r}{\epsilon_j - \epsilon_k} \psi_k \tag{3.108}$$

Since

$$\psi_j = \sum_{s=1}^{n} c_{sj}\phi_s \;\; and \;\; \int \phi_r H' \phi_r dv = \delta\alpha_r \tag{3.109}$$

This allows the change in the MO to be written as

$$\psi_j' = \delta\alpha_r \sum_{k=1}^{n} \left\{ \frac{c_{rj} c_{rk}}{\epsilon_j - \epsilon_k} \sum_{s=1}^{n} c_{sk}\phi_s \right\} = \sum_{s=1}^{n} c_{sj}' \phi_s \tag{3.110}$$

where

$$c_{sj}' = \delta\alpha_r c_{rj} \sum_{k=1}^{n} \frac{c_{rk} c_{sk}}{\epsilon_j - \epsilon_k} \tag{3.111}$$

Keeping in mind the fact that the occupied orbitals are those for which $1 \leq j \leq m$, the change in electron density at atom *s* can be expressed as

$$\delta q_s = 2\sum_{j=1}^{m}\{(c_{sj}+c'_{sj})^2 - c_{sj}^2\} = 4\sum_{j=1}^{m} c_{sj}c'_{sj} \tag{3.112}$$

since c'_{sj} is small. Thus

$$\delta q_s = 4\delta\alpha_r \sum_{j=1}^{m}\sum_{k=1}^{n} \frac{c_{rj}c_{sj}c_{rk}c_{sk}}{\epsilon_j - \epsilon_k} \tag{3.113}$$

This last equation leads to an expression for $\pi_{s,r}$

$$\pi_{s,r} = \frac{\partial q_s}{\partial \alpha_r} = 4\sum_{j=1}^{m}\sum_{k=1}^{n} \frac{c_{rj}c_{sj}c_{rk}c_{sk}}{\epsilon_j - \epsilon_k} \tag{3.114}$$

But the summand here is antisymmetric in *j* and *k* so that $\sum_{j=1}^{m}\sum_{k=1}^{m}$=0. Taking this into account, the expression for the atom-atom polarizability can finally be written as

$$\pi_{s,r} = -4\sum_{j=1}^{m}\sum_{k=m+1}^{n} \frac{c_{rj}c_{sj}c_{rk}c_{sk}}{\epsilon_k - \epsilon_j} \tag{3.115}$$

This expression is the equation that was used in the computational part of this study to calculate the atom-atom polarizability of the considered molecules. This equation is also analogous to the expression for the calculation of the linear response in DFT.[15]

3.6 The linear response current

Up until now, the transmission spectrum in the case where no voltage is applied has been the main focus of this work. In the following paragraphs, the calculation of the current flow which results from the application of a small bias will be discussed.

The transmission spectrum gives the probability for an incident electron with a certain energy to go through the molecule unscattered. As the electrons originate from the reservoirs, their energy can not be higher than the Fermi level of these reservoirs. As long as no voltage is applied, the Fermi levels of the reservoirs are equal, and so is the rate of electron transfer from one reservoir to the other through the molecule (each incident electron has a counterpart in the other reservoir).[13] As a bias is applied, more energy levels are filled in one reservoir while in the other one less energy levels are filled. This means that some electrons in one reservoir no longer have a counterpart of the same energy in the other reservoir, leading to a net current. According to the Bütticker-Landau equation, this current can be expressed as[30]

$$I = \frac{2e}{h} \int_{E_{F_1}}^{E_{F_2}} g(E,V) dE \tag{3.116}$$

where E_{F_1} and E_{F_2} are the energy levels of the 2 reservoirs. g(E,V) can be retrieved from the transmission probability through application of equation (1.1).

An important note to be made about equation (3.116) is that g is dependent of the applied voltage. This is obviously also true for the transmission probability; the transmission spectrum changes as the applied voltage changes.[31] So, in order to calculate the change in current with respect to the applied voltage, one has to calculate the transmission probability at every bias and integrate the resulting transmission spectrum between the boundaries set by the applied voltage. However, at low bias, one can make the assumption that the transmission spectrum has not changed much and so it is sufficient to integrate the zero-bias transmission spectrum.[32] The resulting current versus applied voltage graph is called the linear response current.

The linear response current can be used qualitatively to predict the conducting properties of the molecule at small bias but at bigger bias this method of calculation breaks down completely. For instance, in this method the current can only increase as the bias window opens up as the transmission probability is never negative, which does not comply with the image one gets when taking the more elaborate approach of calculating the transmission spectrum at every bias where negative differential conductances do arise.

Chapter 4

Methodology

As a first step in our research, computer programs were developed, written in the FORTRAN programming language, which are capable of calculating the transmission probability and the atom-atom polarizability. The codes of these programs have been added as an appendix to this work. Some of the used subroutines were adapted from a handbook listing the most frequently used numerical methods in FORTRAN.[33]

The program capable of calculating the transmission probability has actually been programmed in threefold. First, the initial formula put forward by Fowler et al. to calculate the transmission, as it was given in equation (3.69), was implemented. The T(E) curves which were obtained through this program were compared to the results found in literature to test whether our program works correctly. Next, the same program was written again, but this time in the wide band limit as it was given in equation (3.72). As can be seen in section 5.1, close to the Fermi-level these 2 programs give the same results. This result has also been backed up for a lot of molecule-contact combinations at higher level in literature.[34] As this part of the curves is our main region of interest in this study, the decision was made to keep working in the wide band limit, as the formula in that case is a lot more straightforward than the original one, and the resemblance to the expression for the atom-atom polarizability is more evident. Next to the wide band limit, further restrictions have been put forward on the studied systems. In this research only symmetric connections with $\alpha_L = \alpha_R = 0, \beta_{sL} = \beta_{rR} = \beta$ and $\beta_L = \beta_R = \beta_C = 1.4\beta$ have been considered. Thirdly, equation (3.79) was implemented, as with this method, it becomes possible to calculate the transmission probability for all combinations of contacts simultaneously. The validity of this method was confirmed by comparing the resulting graphs with the curves obtained from the second program.

For the program capable of calculating the atom-atom polarizability, expression (3.115) was used. In order to obtain the linear response current, a program was written which numerically integrates the transmission expression in equation (3.79).

Next, the final programs for the the calculation of the atom-atom polarizability and transmission probability have been applied to a series of polycyclic aromatic hydrocarbons: benzene, naphthalene, anthracene, tetracene and pentacene.

As input, the considered systems were numbered as follows:

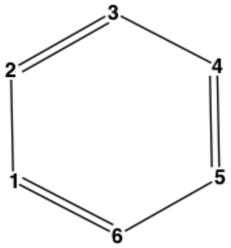

Figure 4.1: benzene

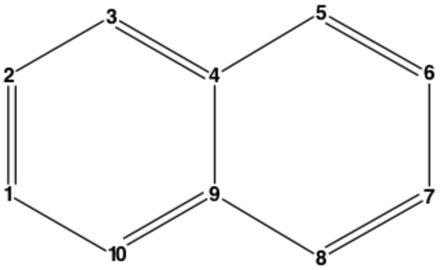

Figure 4.2: naphthalene

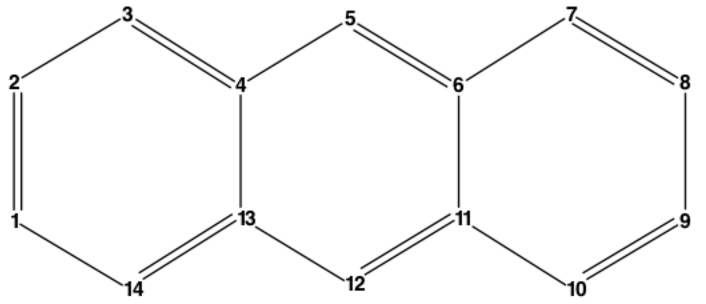

Figure 4.3: anthracene

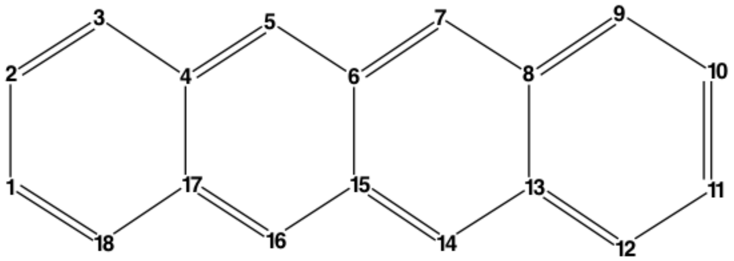

Figure 4.4: tetracene

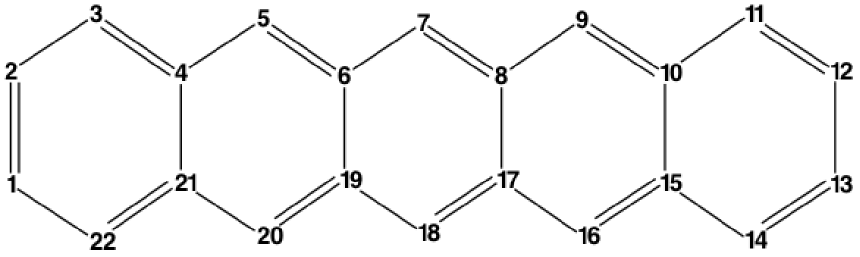

Figure 4.5: pentacene

This add hoc numbering, which does not coincide with the IUPAC numbering rules, was merely chosen because of practical considerations.

In a first set of calculations, a reference atom (the left contact atom) was kept fixed at a certain position in the first ring (atom 1) when going through the series of considered hydrocarbons. The results of these calculations will be presented in section 5.2. A next set of calculations involved the variation of the choice of the reference atom for anthracene. These results are presented in section 5.3. Finally, some calculations were performed on pentacene to reinforce the conclusions drawn in section 5.3 (see section 5.4). In all of these sections, the results are presented graphically. These graphical representations were produced by a script, written in FORTRAN, which produces POSTSCRIPT files.[35]

In a final section, section 5.5, the linear response current was calculated for every possible configuration of the contacts of benzene, naphthalene and anthracene when one contact is kept fixed at atom 1.

Based on all these results, combined with theoretical considerations, a formal link between the atom-atom polarizability and the transmission probability has been derived and a selection rule has been put forward. The rationale behind this link will be presented in section 5.6.

Chapter 5

Results and discussion

5.1 Validation of the method for the transmission probability calculation

In a first section, the transmission curves for benzene are presented, both in the wide band limit and not in the wide band limit. Each configuration is denoted by the numbering of the contact atoms, as it was introduced in figure 4.1. The energy of the incident electron is scaled to β (the nearest hopping parameter) and the Fermi level of the molecule is taken as the origin of the energy axis.

We will first focus on the calculations when the wide band limit is not applied, as these results can be compared to results in literature. The implemented program gave rise to the following curves:

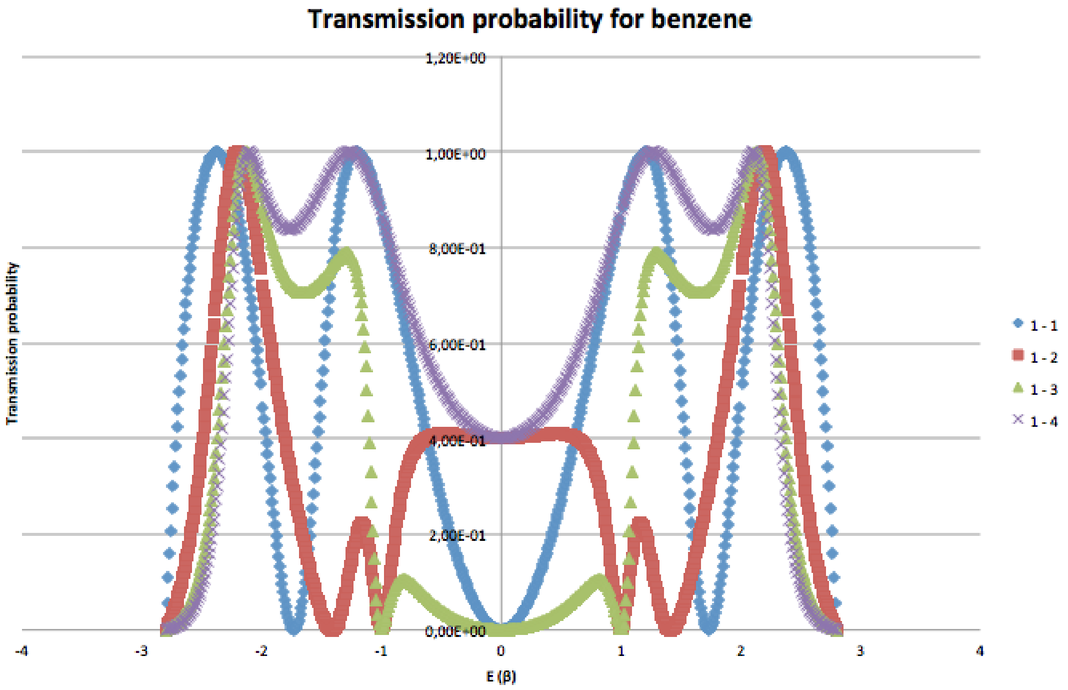

Figure 5.1: transmission probability for benzene (no wide band limit)

From these results it can be concluded that at the Fermi level, ipso and meta configurations of the contacts lead to no transmission. For both ortho and para configurations, a transmission probability of 0,4 is obtained. Further away from the Fermi level, the transmission probability of the para configuration increases even more while it remains constant for the ortho configuration for quite a while. The transmission probability of meta configurations remains relatively flat when moving away from the Fermi level. Only starting from energies of the incident electron of $-\beta$ or β, transmission becomes significant. For ipso connection, the transmission probability rises more quickly. A remark to be made is that all of the curves depicted above are perfectly symmetrical. This is due to the fact that the studied system, just as all the other ones in this work, is bipartite.

Fowler et al. obtained the following results for benzene[4]

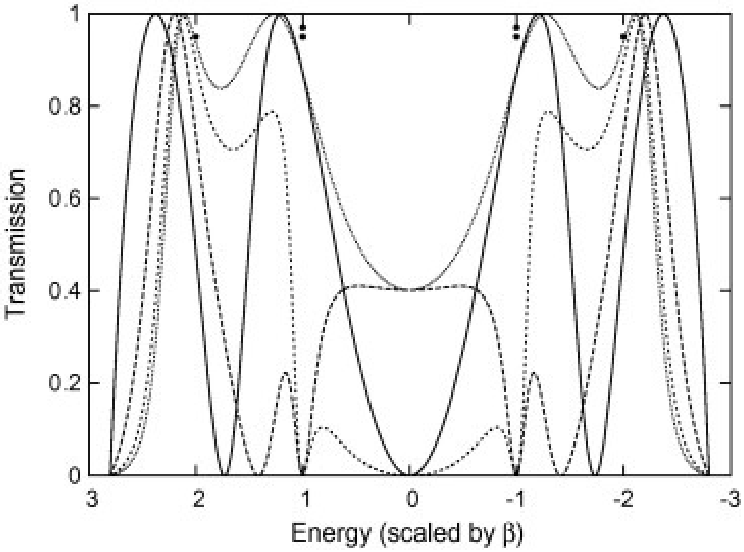

Figure 5.2: transmission probability for benzene (no wide band limit), according to Fowler et al.

Comparison of figure 5.1 with figure 5.2 leads to the conclusion that our program produces accurate results.

The program for the calculation of the transmission probability in the wide band limit led to the following results for benzene

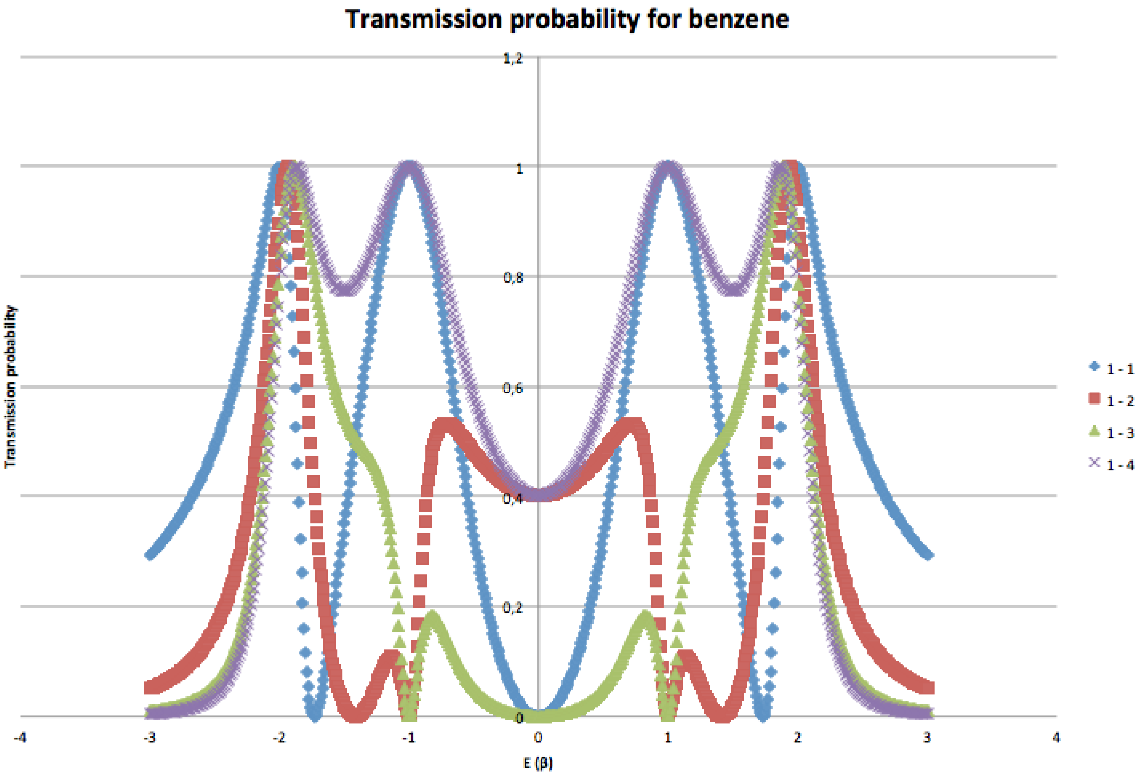

Figure 5.3: transmission probability for benzene in the wide band limit

Comparing this graph with graph 5.1, one can clearly see that the two graphs give qualitatively the same trend. However, at the Fermi level, they agree exactly. As the goal of this study is to inquire the transmission behavior of molecules close to the Fermi level, the wide band limit has been used for all the other calculations, as the equations are much easier in this case.

Similar graphs have been produced for the other studied systems. However, as one can already notice for the case of benzene depicted above, these graphs become too complex very quickly when the number of possible configurations of the contacts rises. As our only region of interest in these graphs is the behavior of the transmission close to the Fermi level, we made the decision not to add a similar graph like the one above for every system studied. The choice was made to depict the transmission probability close to the Fermi level in a graphical way, as will be explained in the next section.

5.2 Comparison between the atom-atom polarizability and the transmission probability for one fixed reference atom

In this section both the atom-atom polarizability and the transmission probability are depicted for each of the studied systems in a graphical way. Throughout this section, the ad hoc numbering introduced in chapter 4 has been used. Only one reference atom (atom 1) was considered, as this allows us to study the way these properties change when more aromatic rings are added to the system. For the atom-atom polarizability, the reference atom is denoted by a green sphere, where the area of the sphere is proportional to the self-polarizability of that atom. One should keep in mind that self-polarizabilities are always negative. The black spheres and red spheres denote the amount of atom-atom polarizability caused by a perturbation to the reference atom on the considered atom. The black spheres correspond to a positive atom-atom polarizability and the red ones to a negative atom-atom polarizability. Again, the area of the spheres is proportional to the value for the atom-atom polarizability.

For the transmission probability in the wide band limit at the Fermi level, the same approach is taken as above. The green sphere denotes the reference case where both contacts are placed on the reference atom. As in this case, transmission at the Fermi level is always zero, the sphere was emptied. Since the transmission probability can only range between 0 and 1, no red spheres will arise. The black spheres on the atoms denote the amount of transmission in the case where the contacts are respectively placed on reference atom and the atom on which the sphere is drawn.

Next to these graphical representations, tables were also added to allow numerical verification of the results presented in these figures. These tables can be found in appendix B.

First we will focus on benzene.

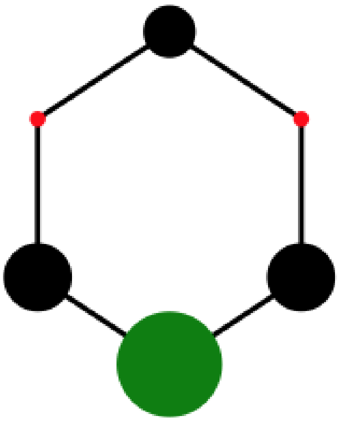

Figure 5.4: atom-atom polarizability of benzene

It can be seen from this figure that only atoms in ortho and para positions exhibit a positive atom-atom polarizability with the reference atom. Normally, one would expect that the atom-atom polarizability decreases with the distance, but here this is not the case as the atom in para position exhibits a higher atom-atom polarizability than the atoms in meta position.

This apparently odd result can however be rationalized. First off, it is possible to draw a resonance structure of benzene where a para bond is present. Due to valence bond theory, this resonance structure, often (incorrectly) called ”Dewar benzene”,[36] contributes to a minor extent to the overall description of benzene,[37] thus enforcing the para bond slightly compared to the meta bond, leading to a positive atom-atom polarizability. Another way to rationalize this is to draw the mesomeric structures for benzene when an electron donor is placed on the ring system.[38] This shows that the negative charge can only be placed on the ortho and para positions and not on the meta positions, in compliance with the atom-atom polarizability picture obtained from figure 5.4.

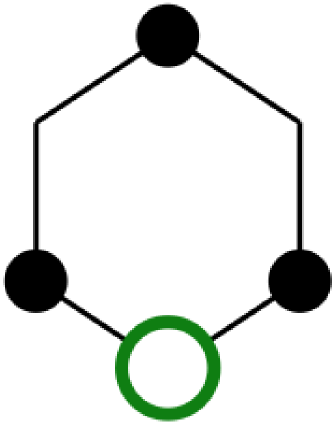

Figure 5.5: transmission probability in the wide band limit for benzene at the Fermi-level

Comparison of figure 5.4 with 5.5, leads to the conclusion that black spheres for the atom-atom polarizability coincide with black spheres for the transmission probability. The atoms which show a red sphere for the atom-atom polarizability show no sphere for the transmission probability. In other words, it seems that in order to have transmission for a certain configuration of the contacts on the molecule, one needs a positive atom-atom polarizability between the 2 contact atoms.

Now turning to naphthalene, the following results are obtained.

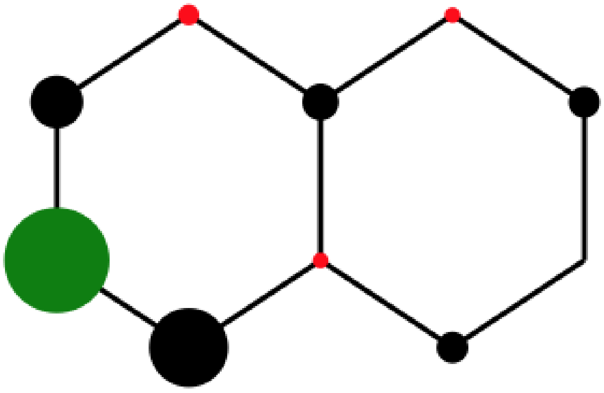

Figure 5.6: atom-atom polarizability of naphthalene

Figure 5.6 leads to the conclusion that the the atom-atom polarizability is highest between atom 1 and 10. This can be rationalized by drawing all the possible resonance structures of naphthalene, leading to a higher bond order between these two atoms compared to the bond order between atom 1 and 2, which consequently leads to a higher atom-atom polarizability. Experimentally, this is reflected in a decreased bond length between these atoms.[39]

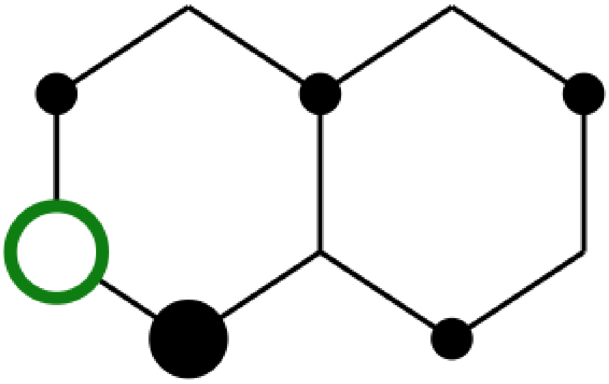

Figure 5.7: transmission probability in the wide band limit for naphthalene at the Fermi-level

Again there seems to be a correspondence between the atom-atom polarizability (figure 5.6) and the transmission probability (figure 5.7), the same conclusions can be drawn as for benzene. It can also be observed that the atom with the highest atom-atom polarizability leads to the highest transmission probability when the second contact is placed on this atom.

Next, the atom-atom polarizability and transmission probability for anthracene, tetracene and pentacene are presented and discussed all at once.

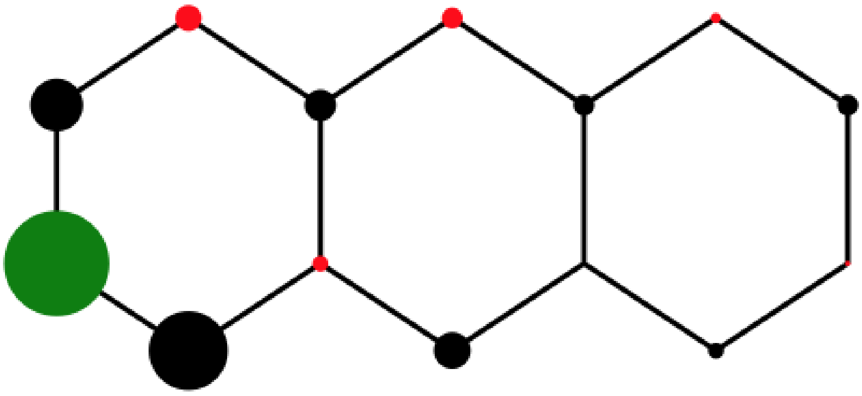

Figure 5.8: atom-atom polarizability of anthracene

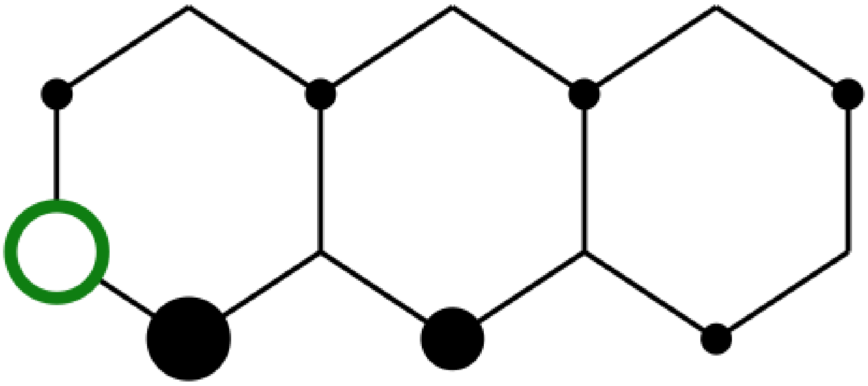

Figure 5.9: transmission probability in the wide band limit for anthracene at the Fermi-level

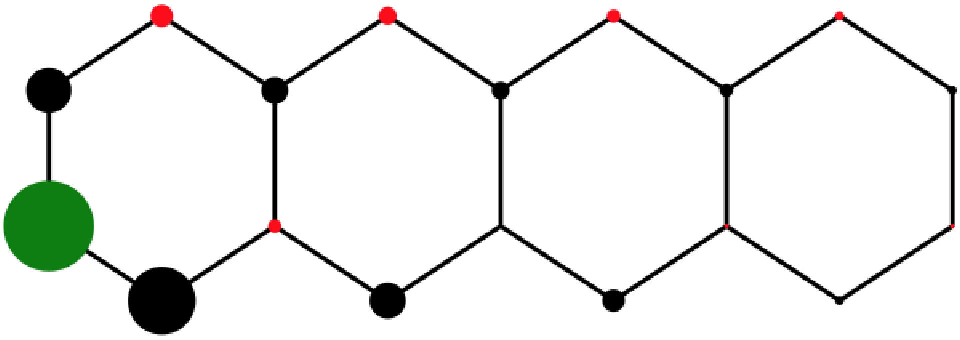

Figure 5.10: atom-atom polarizability of tetracene

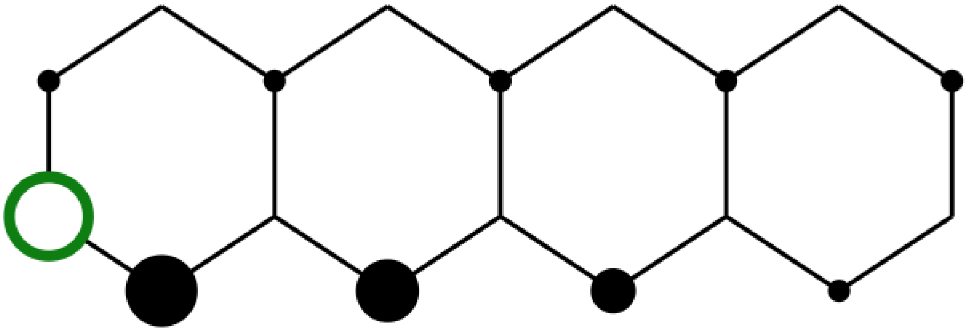

Figure 5.11: transmission probability in the wide band limit for tetracene at the Fermi-level

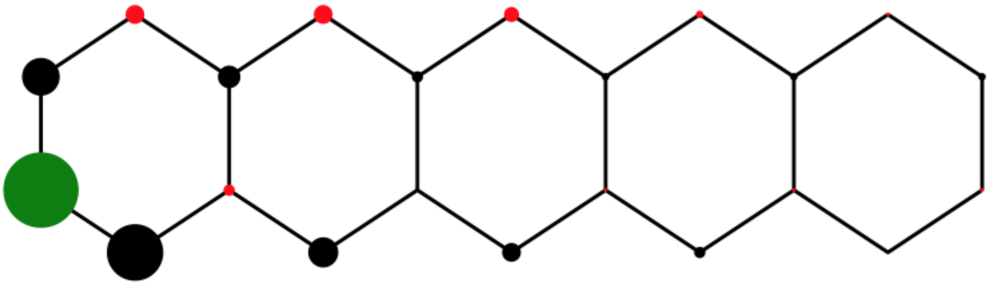

Figure 5.12: atom-atom polarizability of pentacene

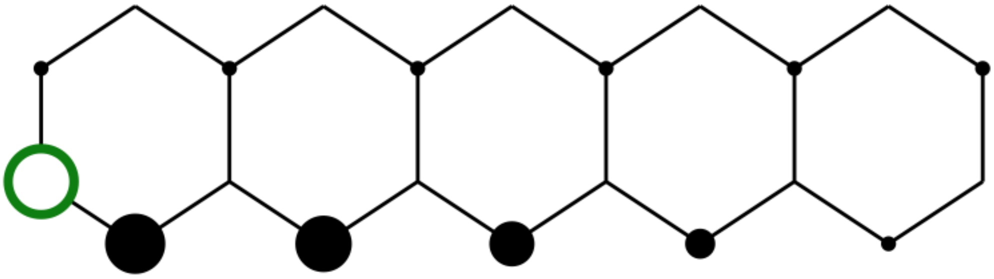

Figure 5.13: transmission probability in the wide band limit for pentacene at the Fermi-level

For each of these systems, the same conclusions can be drawn as above. Transmission only takes place when the second contact is placed on an atom which exhibits a positive atom-atom polarizability and the atom with the highest atom-atom polarizability always leads to the highest transmission probability when the second contact is placed on this atom.

Putting all these results together, the idea that a positive atom-atom polarizability is a necessary condition in order to have transmission for a certain configuration of the contacts on the molecule is reinforced. As the atom-atom polarizability is a measure for electronic delocalization, these empirical results give rise to the picture that delocalization should be a necessary condition for transmission.

Considering now the area of the spheres, one can conclude that there is no exact proportionality between the value for the atom-atom polarizability and the value for the transmission probability at the Fermi level. However, one can clearly observe that when the atoms are numbered across the ring, starting in the direction where the atom with the highest atom-atom polarizability is situated, the transmission probability at the Fermi level drops monotonously when going down this ranking. So it seems that the atom with the highest atom-atom polarizability acquires the highest transmission probability when the second contact is placed on that atom, and the position of this atom relative to the first contact determines the sense in which the transmission probability drops. From then on, the probability decreases along the chain independently of the amount of atom-atom polarizability between the reference atom and the other atoms.

For each of the systems presented above, the reference atom remained constant. In the next section, this reference atom will be varied for anthracene, allowing us to verify the observations made above and to get an indication of the importance of the position of this reference atom.

5.3 The variation of the atom-atom polarizability and transmission probability for anthracene when the reference atom is altered

In the previous section the reference atom was kept constant for all of the studied systems. In this section, the influence of the choice of the reference atom will be examined for anthracene. Throughout this section, the ad hoc numbering introduced in chapter 4 has again been used. Due to symmetry reasons, only 3 distinct choices for the reference atom exist. One of these choices has already been presented in section 5.2. The other two will be listed below.

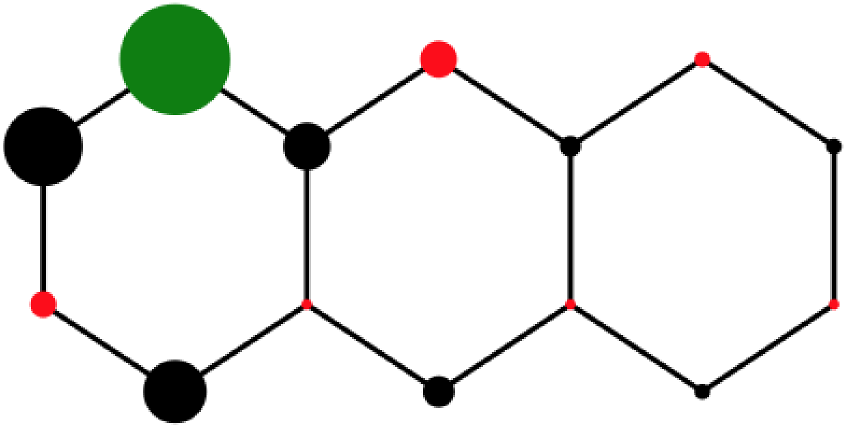

Figure 5.14: atom-atom polarizability of anthracene for reference atom 3

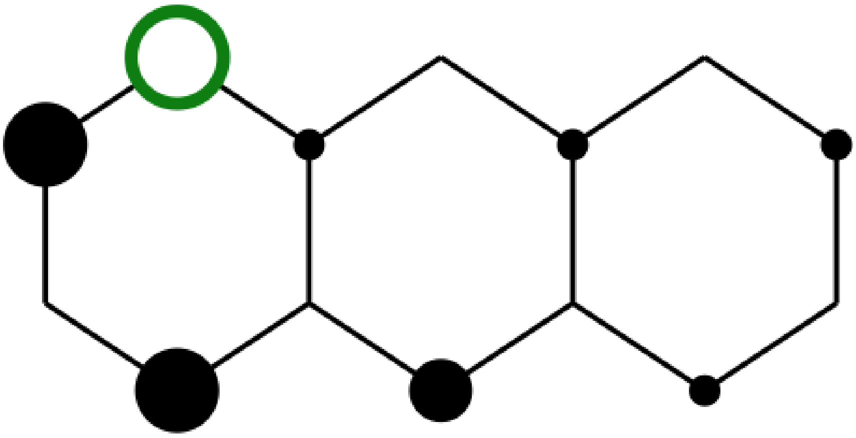

Figure 5.15: transmission probability in the wide band limit for anthracene at the Fermi-level for reference atom 3

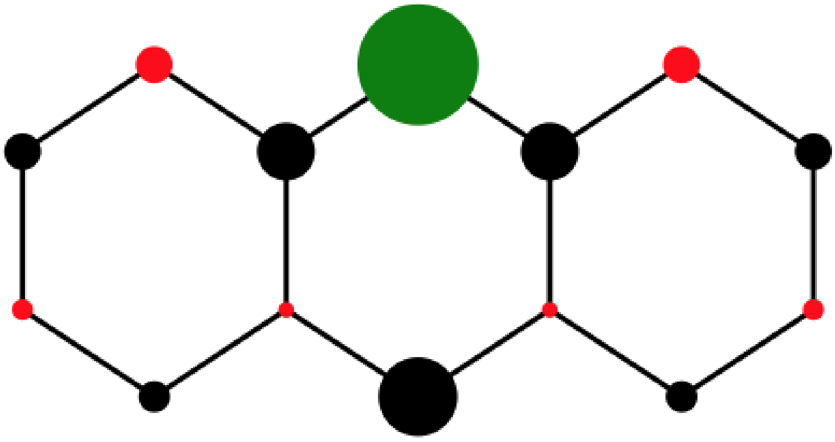

Figure 5.16: atom-atom polarizability of anthracene for reference atom 5

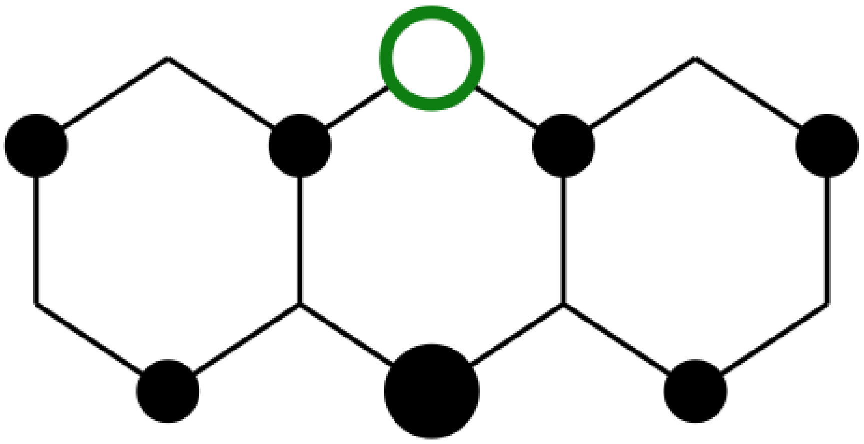

Figure 5.17: transmission probability in the wide band limit for anthracene at the Fermi-level for reference atom 5

These results demonstrate that the choice of the reference atom is indeed important for the transmission probability. For example, when atom 3 is chosen as a first contact instead of atom 1, the transmission probability at the Fermi level becomes as high in the 3-14 configuration of the contacts as for the 2-3 configuration. More remarkable, if atom 5 is chosen as a first contact, the monotonous drop of the transmission probability across the ring is no longer observed. In this case, the atom at the opposite position on the central ring shows the highest transmission probability. Across the entire system, the transmission probabilities are elevated compared to the other situations.

Comparing these results for the transmission probability with the results for the atom-atom polarizability, it can be seen that, for reference atom 3, the same phenomena as in the previous section take place. For the choice of atom 5 as reference atom, the system becomes symmetrical and now the atom-atom polarizability is equal at both sides of the reference atom. The highest atom-atom polarizability in this case can be observed at the opposite side of the molecule, and this configuration also shows the highest transmission probability.

These observations reinforce the idea put forward in section 5.2 that a positive atom-atom polarizability is a necessary condition for transmission to take place. The second proposed rule that the relative position of the atom with largest atom-atom polarizability, compared to the reference atom, determines the direction in which the transmission probability decreases, appears to be more subtle according to figure 5.17. In the next section, a few configurations of contacts for pentacene will be studied in order to allow this second rule to be rephrased so that it becomes applicable to all possible configurations of the contacts.

5.4 The variation of the atom-atom polarizability and transmission probability for pentacene when the reference atom is switched from one ring to another

In this section, the influence of the change of the reference atom was studied for pentacene. As too many configurations of the contacts are possible for this system to list them all here, the decision was made to consider only reference atoms 3, 5 and 7. The results for reference atom 1 have already been presented in section 5.2.

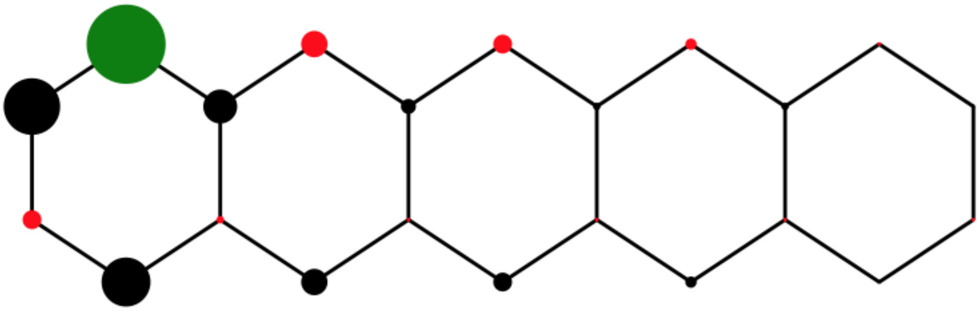

Figure 5.18: atom-atom polarizability of pentacene for reference atom 3

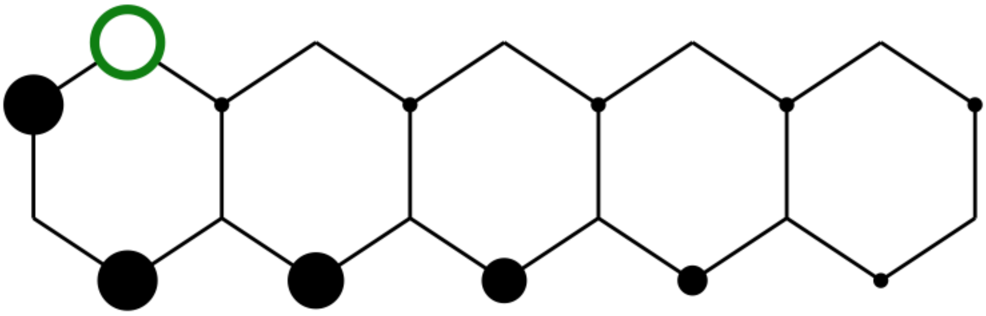

Figure 5.19: transmission probability in the wide band limit for pentacene at the Fermi-level for reference atom 3

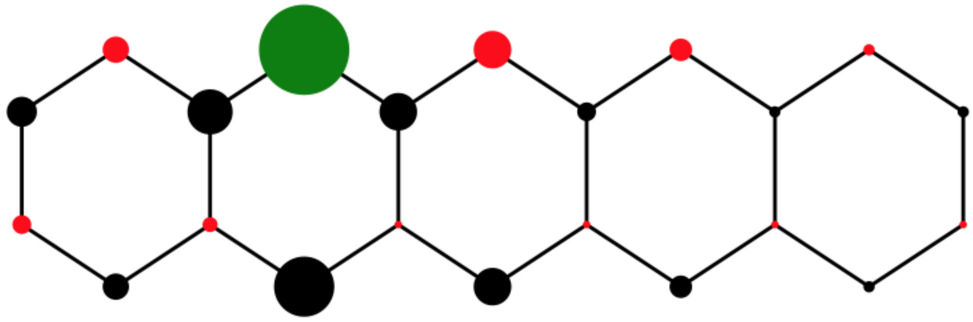

Figure 5.20: atom-atom polarizability of pentacene for reference atom 5

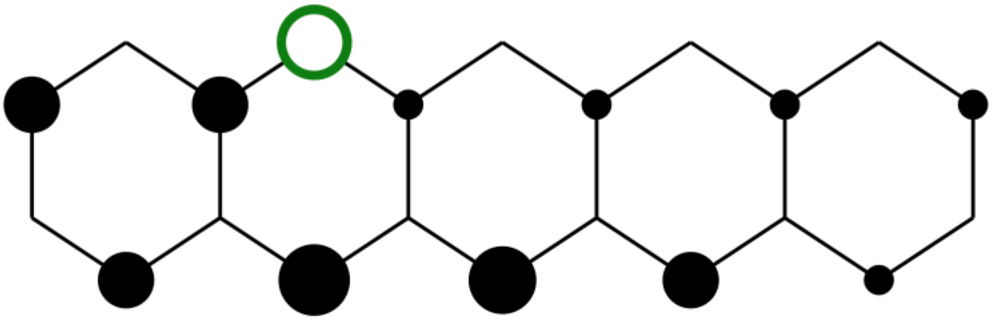

Figure 5.21: transmission probability in the wide band limit for pentacene at the Fermi-level for reference atom 5

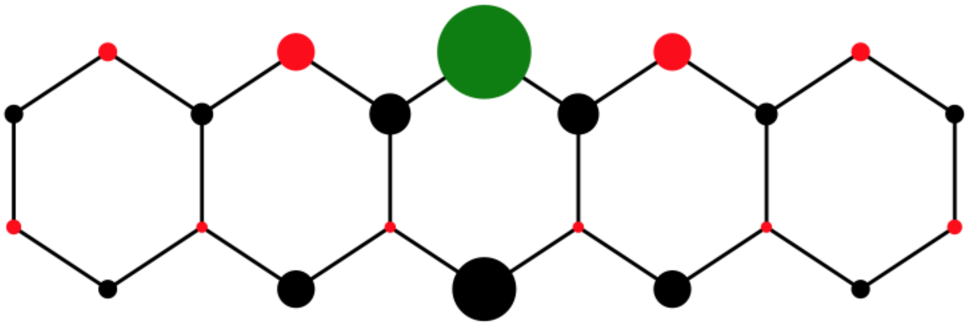

Figure 5.22: atom-atom polarizability of pentacene for reference atom 7

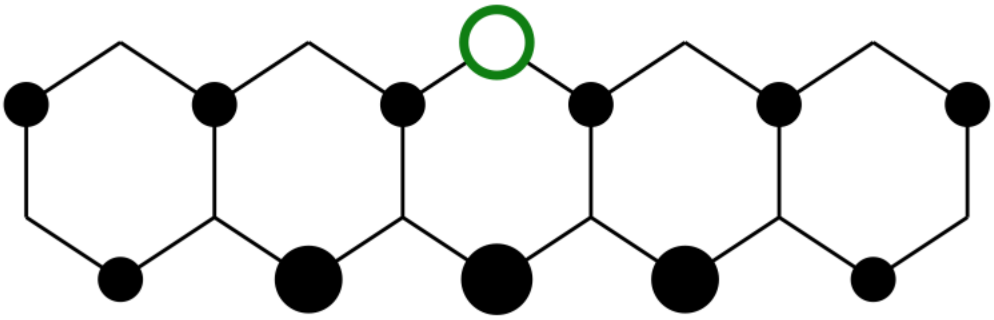

Figure 5.23: transmission probability in the wide band limit for pentacene at the Fermi-level for reference atom 7

For reference atoms 3 and 7, exactly the same conclusions can be drawn as in sections 5.2 and 5.3. For reference atom 5, the picture becomes more complicated. As is the case for reference atom 7, the opposite atom again shows the highest transmission probability. To the right of the line through these 2 atoms, the behavior is exactly the same as before; the transmission probability drops monotonously in the direction of the atom with the highest atom-atom polarizability. In the leftmost ring, the transmission probabilities are all equal.

The reason for this apparent complication is the fact that in the case of reference atom 5, just as is the case for reference atom 7 for pentacene and reference atom 5 for anthracene, the atom with the highest atom-atom polarizability is no longer adjacent to the reference atom. In each of these cases this atom was the atom with the highest transmission probability, and starting from this atom, the transmission probability decreases monotonously in either direction away from this atom. The direction of the sharpest decline was the direction in which the atom with the lowest relative atom-atom polarizability (adjacent to the atom which exhibits the highest transmission probability) is located.

This rule is generally applicable to all systems considered before, and can thus be interpreted as a more general and more precise rule than the one put forward earlier on about the variation of the amount of atom-atom polarizability across the system.

5.5 The linear response current

In this section, the linear response currents were plotted for benzene, naphthalene and anthracene. As the applied voltage is expressed in terms of β, the unit of the resulting current is ill defined. As such, we decided to drop the factor present in front of the integral in equation (3.116) and to not take into account the β factor in the integration boundaries. This leads to a value for the current which has no standard units and can only be used relatively, to compare the linear response currents between the different configurations of the same system. These currents have no absolute quantitative significance.

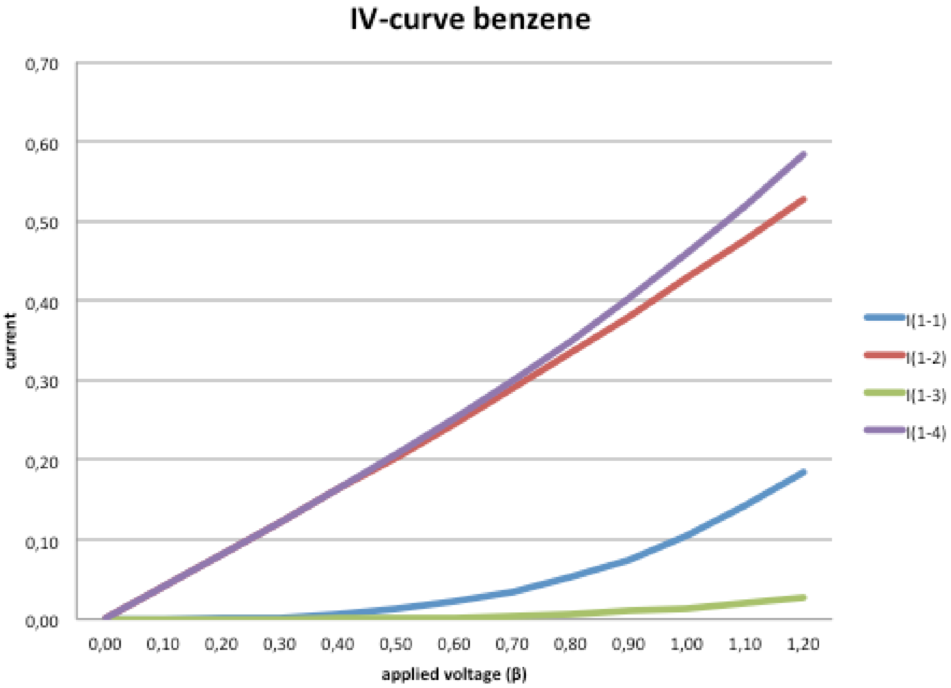

Figure 5.24: IV-curve benzene in the linear response current regime

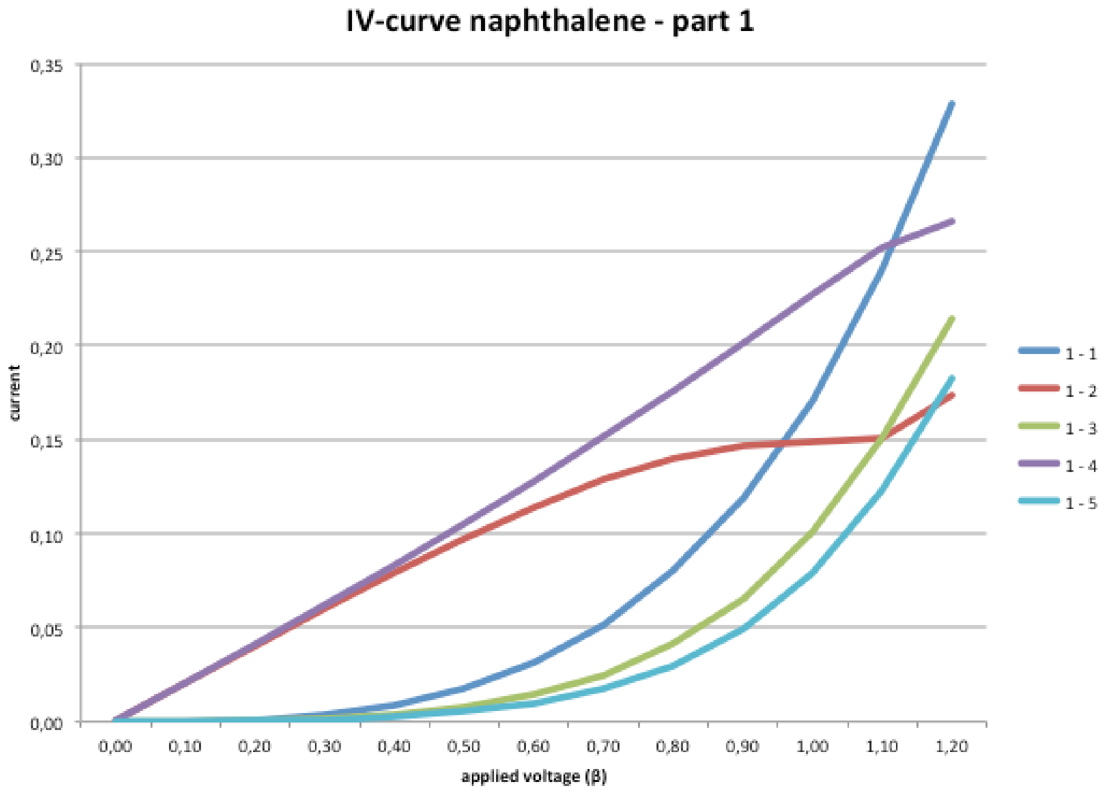

Figure 5.25: IV-curve naphthalene in the linear response current regime - part 1

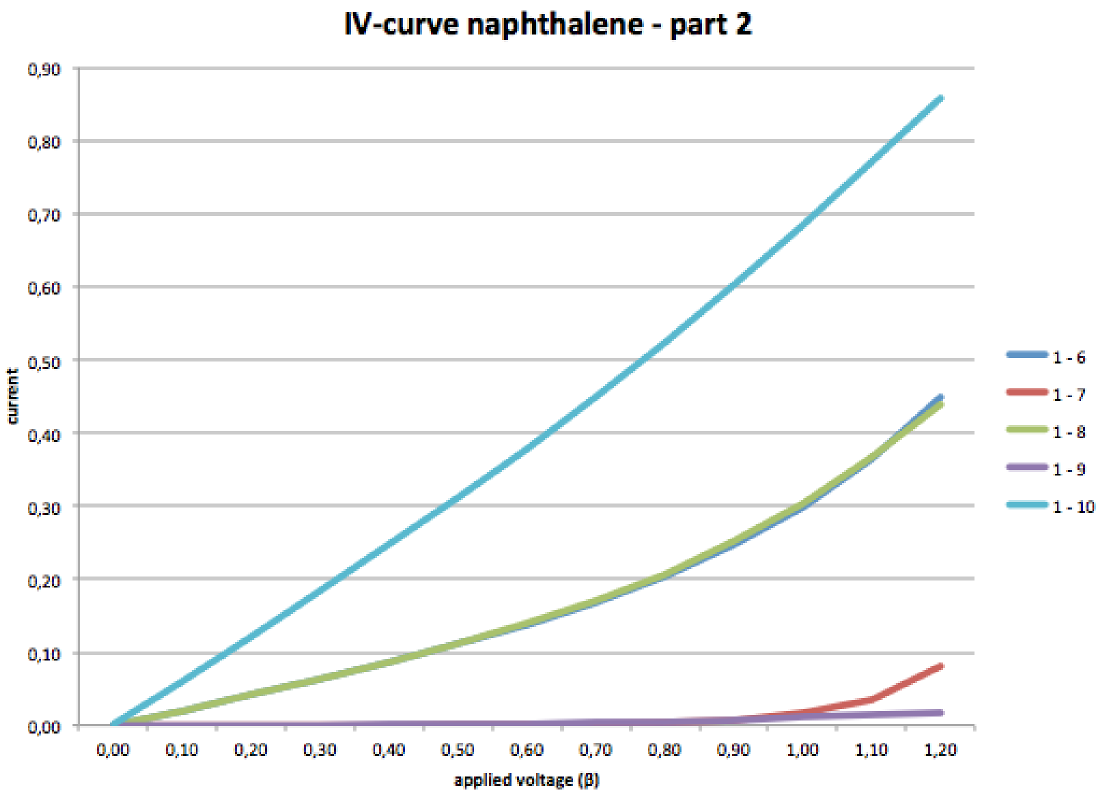

Figure 5.26: IV-curve naphthalene in the linear response current regime - part 2

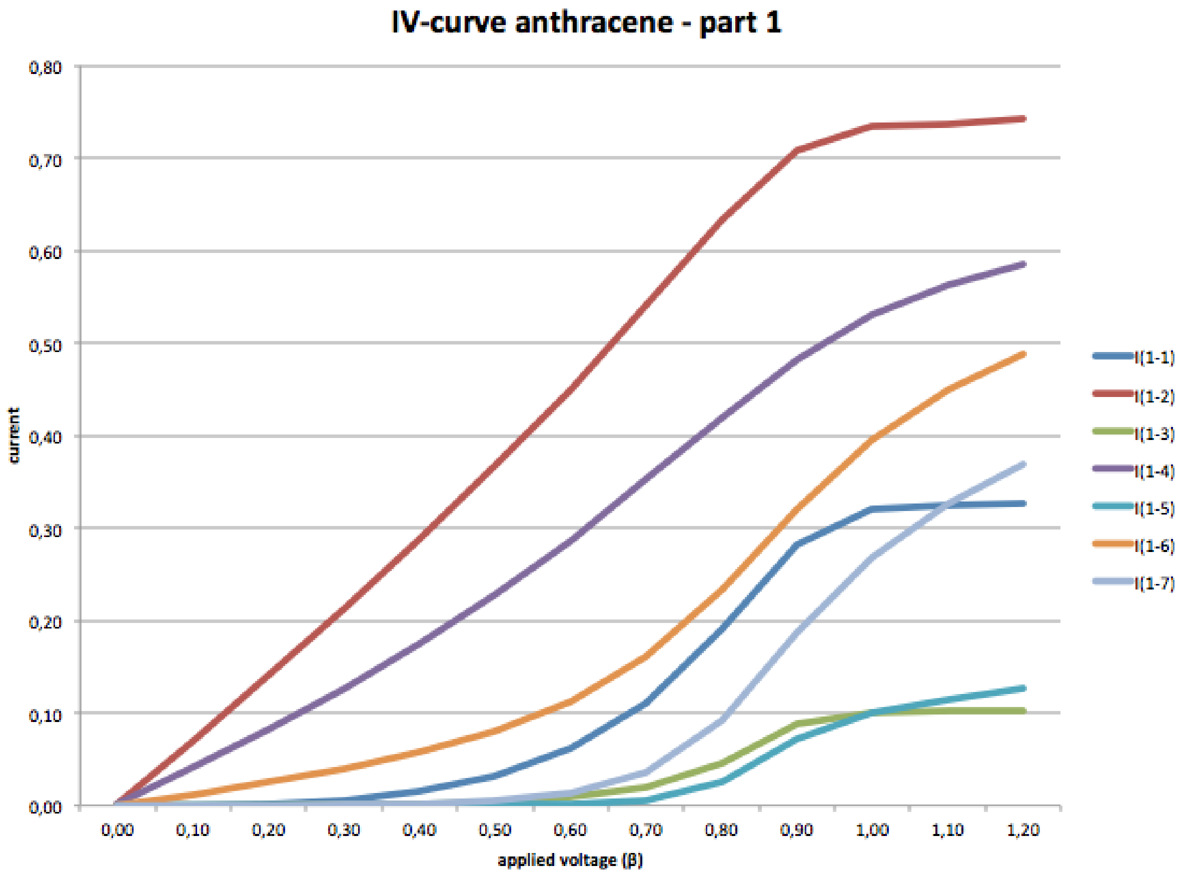

Figure 5.27: IV-curve anthracene in the linear response current regime - part 1

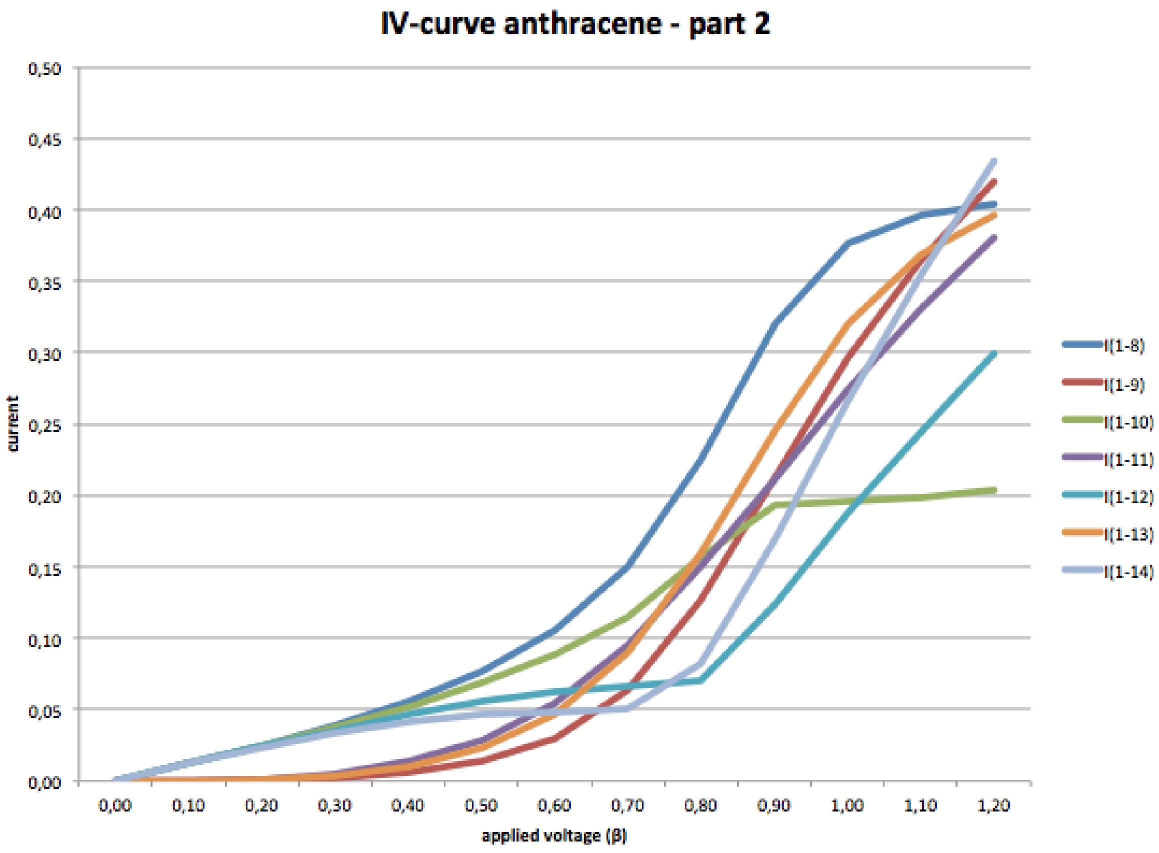

Figure 5.28: IV-curve anthracene in the linear response current regime - part 2

By comparing these curves with the results obtained in section 5.2, it can be seen that a high transmission probability leads to a high linear response current (conducting behavior) and low transmission probability leads to a low linear response current (insulating behavior). Again, we note that these curves are only valid at very low bias, already at a bias of 0,4V the linear response current can deviate from the actual current.[32]

5.6 The link between the transmission probability and the atom-atom polarizability

From the observations put forward in the discussion of the results presented previously in this chapter, it is evident that some link seems to exist between the transmission probability at the Fermi level and the atom-atom polarizability. In this section, the expressions of these two quantities will be examined in order to derive a mathematical relationship between them.

Recall the expression for the transmission in the SSP method[4] and consider symmetric systems ($\tilde{\beta}_L = \tilde{\beta}_R$):

$$T(E) = \frac{4\sin^2 q(\Delta_{r,r}\Delta_{s,s} - \Delta\Delta_{rs,rs})\tilde{\beta}^2}{|e^{-2iq}\Delta - e^{-iq}(\Delta_{s,s} + \Delta_{r,r})\tilde{\beta} + \Delta_{rs,rs}\tilde{\beta}^2|^2} \tag{5.1}$$

Taking now the limit of this expression as $E \to 0$ (transmission at the Fermi level) and $\tilde{\beta} \to 0$ (corresponding to weak coupling systems where there is no chemical bonding between the molecule and the electrodes)

$$T(E) = 4\tilde{\beta}^2 \frac{(\Delta_{r,r}\Delta_{s,s} - \Delta\Delta_{rs,rs})}{\Delta^2} \tag{5.2}$$

When this last expression is compared with the expression for the atom-atom polarizability

$$\pi_{r,s} = -\frac{1}{\pi i}\int_{-\infty i}^{\infty i} \frac{\Delta\Delta_{rs,rs} - \Delta_{r,r}\Delta_{s,s}}{\Delta^2} dz \tag{5.3}$$

$$= \frac{1}{\pi i}\int_{-\infty i}^{\infty i} \frac{\Delta_{r,r}\Delta_{s,s} - \Delta\Delta_{rs,rs}}{\Delta^2} dz \tag{5.4}$$

It becomes evident that for weak coupling systems the expression for the transmission can be identified with the integrand in the expression for the atom-atom polarizability, multiplied with a constant.

In other words, one can conclude that, for the considered systems, a complex function exists which couples the atom-atom polarizability with the transmission at E=0. For a fixed energy value (usually E=0, the Fermi-level), the atom-atom polarizability can be calculated by integrating the function over the imaginary axis.

The value of the function at this point is the transmission probability at E=0. This function has the form

$$X = \frac{\Delta_{r,r}\Delta_{s,s} - \Delta\Delta_{rs,rs}}{\Delta^2} \tag{5.5}$$

or more compactly (see earlier)

$$X = \frac{\Delta_{r,s}^2}{\Delta^2} \tag{5.6}$$

From the properties of this complex function, a selection rule can be established for alternant hydrocarbons with no energy level situated at the Fermi level. The rationale behind this selection rule is based for a large part on the proof of the law of alternating polarity as it was provided by Coulson et al.[10]

Coulson suggested to separate the 2 sets of atoms in the considered alternant hydrocarbon into 2 separate secular equations. If the atoms of one set are numbered from *1* to *h*, and all the atoms of the other set from *h+1* to *n*, the secular equations become

$$-\epsilon c_r + \sum_{s=h+1}^{n} \beta_{rs} c_s = 0 \qquad (r = 1, 2, ..., h) \tag{5.7}$$

$$-\epsilon c_r + \sum_{s=1}^{h} \beta_{rs} c_s = 0 \qquad (r = h+1, h+2, ..., n) \tag{5.8}$$

The secular determinant for an alternant hydrocarbon can then be written in its most general form as

$$\Delta(z) = \begin{vmatrix}
-\epsilon & 0 & 0 & \cdots & \cdots & \beta_{1,h+1} & \beta_{1,h+2} & \cdots & \cdots \\
0 & -\epsilon & 0 & \cdots & \cdots & \beta_{2,h+1} & \beta_{2,h+2} & \cdots & \cdots \\
0 & 0 & -\epsilon & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\cdots & \cdots & \cdots & \cdots & -\epsilon & \cdots & \cdots & \cdots & \beta_{h,n} \\
\beta_{1,h+1} & \beta_{2,h+1} & \beta_{3,h+1} & \cdots & \cdots & -\epsilon & 0 & \cdots & \cdots \\
\beta_{1,h+2} & \beta_{2,h+2} & \beta_{3,h+2} & \cdots & \cdots & 0 & -\epsilon & \cdots & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\cdots & \cdots & \cdots & \cdots & \beta_{h,n} & \cdots & \cdots & \cdots & -\epsilon
\end{vmatrix} \tag{5.9}$$

The first *h* rows and columns refer to the atoms of one set, while the other *n-h* rows and columns refer to the atoms of the other set. This determinant can be written more compactly as

$$\Delta(z) = \begin{vmatrix} -zI & A \\ \bar{A} & -zJ \end{vmatrix} \tag{5.10}$$

where *I* and *J* are unit matrix respectively of orders *h* and *n-h* and A and $\bar{A}$ are the two blocks of resonance integrals β_{rs}. Note also that ϵ is replaced by the complex number z.

In a next step, Coulson et al. showed that this determinant is either even or odd, depending on the number of atoms in the alternant hydrocarbon. Multiplication of the first *h* rows of $\Delta(\epsilon)$ by -1 and then of the last (*n-h*) columns, leads to the following identity

$$\begin{aligned} \Delta(z) &= \begin{vmatrix} -zI & A \\ \bar{A} & -zJ \end{vmatrix} && (5.11) \\ &= (-)^h \begin{vmatrix} zI & -A \\ \bar{A} & -zJ \end{vmatrix} && (5.12) \\ &= (-)^n \begin{vmatrix} zI & A \\ \bar{A} & zJ \end{vmatrix} && (5.13) \\ &= (-)^n \Delta(-z) && (5.14) \end{aligned}$$

Expansion of this determinant leads to the polynomial in z. So if *n* is even, only even powers of z occur in the polynomial, whereas if *n* is odd, only odd powers occur.

In the remainder of this rationale, the focus is placed on the case where *n* is even as we focus here on alternant hydrocarbons with an even number of carbon atoms (no energy level located at the Fermi level). As the polynomial is even, it contains no terms with odd powers. So in general, an even polynomial can be represented as

$$f(z) = a_0 z^{2n} + a_1 z^{2(n-1)} + ... + a_{n-1} z^2 + a_n \tag{5.15}$$

where $a_0, a_1, ..., a_n$ are the coefficients. Consider now the case that all the coefficients are real. On the imaginary axis, *z* can be replaced by *iy*, leading to

$$f(iy) = a_0(-y)^n + a_1(-y)^{n-1} + ... + a_{n-1}(-y) + a^n \tag{5.16}$$

So it is clear that on the imaginary axis, the image of every even polynomial with real coefficients is entirely real. As Δ is the expansion of a determinant with only real elements, its characteristic polynomial is also entirely real. Hence, the image of Δ on the imaginary axis is entirely real. The image of Δ^2 is then evidently entirely real and positive on the imaginary axis.

A next step is to consider the determinant $\Delta_{r,s}$. Looking at equation (5.11) one can see that if atoms *r* and *s* are in the same set or are identical (ergo $r, s \leq h$), then $\Delta_{r,s}$ becomes

$$\Delta_{r,s}(z) = \begin{vmatrix} -zI_{r,s} & A_{r,0} \\ \bar{A}_{0,s} & -zJ \end{vmatrix} \tag{5.17}$$

where letters before and after the comma in a suffix denote respectively rows and columns struck out (for example: $A_{r,0}$ denotes *A* with the *r*th row struck out but no column deleted). Multiplication of the first $h-1$ rows and the last $n-h$ columns by -1 leads to the following identity

$$\Delta_{r,s}(z) = (-)^{n-1}\Delta_{r,s}(-z) \tag{5.18}$$

Therefore as n is even, $\Delta_{r,s}(z)$ is a sum of odd powers of *z*. On the other hand, if atoms *r* and *s* are in different sets (ergo $r \leq h < s$), then $\Delta_{r,s}$ becomes

$$\Delta_{r,s}(z) = \begin{vmatrix} -zI_{r,0} & A_{r,s} \\ \bar{A} & -zJ_{0,s} \end{vmatrix} \tag{5.19}$$

Multiplication of the first $h-1$ rows and the last $n-h-1$ columns by -1 then leads to the following identity

$$\Delta_{r,s}(z) = (-)^{n-2}\Delta_{r,s}(-z) \tag{5.20}$$

So in this case, as n is even, $\Delta_{r,s}(z)$ is a sum of even powers of *z*.

So one can state that, if r and s are from the same set, Δ is even and $\Delta_{r,s}$ is odd. Odd polynomials with real coefficients lead to an image on the imaginary axis which is entirely imaginary. This can be demonstrated by taking a look at the general representation of an odd polynomial

$$f(z) = a_0 z^{2n+1} + a_1 z^{2(n-1)+1} + ... + a_{n-1} z^3 + a_n z \tag{5.21}$$

where $a_0, a_1, ..., a_n$ are the coefficients. Now one can write

$$f(z) = z(a_0 z^{2n} + a_1 z^{2(n-1)} + ... + a_{n-1} z^2 + a_n) = z * f'(z) \tag{5.22}$$

where $f'(z)$ is a general even polynomial. On the imaginary axis, z can be replaced by iy. As all coefficients are real, $f'(iy)$ will produce an entirely real image. Taking this into account it becomes clear from equation (5.22) that the image of an odd polynomial with real coefficients is indeed entirely imaginary on the imaginary axis. As Δ is even and its image is entirely real on the imaginary axis, $\frac{\Delta_{r,s}}{\Delta}$ will evidently be odd and its image will be entirely imaginary too. It is now evident from equation (5.6) that the square of this function is nothing else than X.

Taking the square of the odd polynomial $\frac{\Delta_{r,s}}{\Delta}$, an entirely real and negative image is obtained on the imaginary axis. Integration over the imaginary axis in this case leads to a negative atom-atom polarizability. As $\frac{\Delta_{r,s}}{\Delta}$ is odd, its image at the origin is 0, and this is evidently also true for its square $\left(\frac{\Delta_{r,s}^2}{\Delta^2}\right)$. So negative atom-atom polarizabilities for alternant hydrocarbons with an even number of atoms can be connected to cases of no transmission (X=0).

On the other hand, if r and s belong to different sets, Δ and $\Delta_{r,s}$ are both even. This leads to $\frac{\Delta_{r,s}}{\Delta}$ being even too. On the imaginary axis, the image of even polynomials with real coefficients is entirely real. The square of this entirely real image is entirely real and positive. Integration over the imaginary axis in this case leads to a positive atom-atom polarizability. For even functions, the image at the origin is not forced to be 0. So X can differ from 0, leading to transmission. So positive atom-atom polarizabilities for alternant hydrocarbons with an even number of carbon atoms can be connected to transmission taking place.

To summarize, for alternant hydrocarbons with an even number of carbon atoms:

- Transmission is allowed when the atom-atom polarizability between the two contact atoms is positive
- Transmission is not allowed when the atom-atom polarizability between the two contact atoms is negative

For a given reference reference atom, a positive atom-atom polarizability is obtained for atoms of a different set and negative atom-atom polarizability is obtained for atoms of the same set.

It is now also clear that no systems can be considered which have energy levels at the origin, since in this case, X has a pole at the origin and so the image is not defined at this point.

The constraint of a weak coupling system is logic, as strong chemical bonding between the molecule and the contacts would perturb the electron density of the considered molecule, leading to a change in its properties (see Hohenberg-Kohn theorems).[25] The atom-atom polarizability is a property of the isolated molecule which allows the determination of the transmission probability through this molecule, but once it is firmly bonded in an electrical circuit, its properties change and thus also its transmission probability. However, as long as the bonding of the molecule is weak, the transmission probability of the bonded molecule can be approximated by the transmission probability of the isolated molecule.

Until now, only weak coupling systems were considered. However, the proposed selection rule for transmission based on the atom-atom polarizability has a wider applicability, as will be shown next.

In the chapter about transmission in the SSP method, the wide band limit was introduced. This limit is approached when the molecule is weakly coupled to the contacts or when the bonding in the metal contacts is strong. The wide band limit can be seen as a more general regime compared to the weak coupling systems considered above.

Moreover, at the Fermi level, the general equation for the transmission probability in the SSP method becomes equal to the expression for the transmission probability in the wide band limit (3.72) as q then becomes equal to $\pi/2$. This can be seen easily by comparing equation (5.1) with the expression for the transmission probability in the wide band limit

$$T_{WBL}(E) = \frac{4(\tilde{\Delta}_{r,r}\tilde{\Delta}_{s,s} - \tilde{\Delta}\tilde{\Delta}_{rs,rs})}{(\tilde{\Delta} - \tilde{\Delta}_{rs,rs})^2 + (\tilde{\Delta}_{r,r} + \tilde{\Delta}_{s,s})^2} \tag{5.23}$$

It is now possible to rewrite equation (5.23) as

$$T_{WBL}(E) = 4\tilde{\beta}^2 \frac{\Delta_{r,r}\Delta_{s,s} - \Delta\Delta_{rs,rs}}{\Delta^2} \frac{1}{(1 - \tilde{\beta}^2 \frac{\Delta_{rs,rs}}{\Delta})^2 + (\tilde{\beta}\frac{\Delta_{r,r}}{\Delta} + \tilde{\beta}\frac{\Delta_{s,s}}{\Delta})^2} \tag{5.24}$$

According to equation (3.78), the numerator of the first factor in equation (5.24) can be written more compactly, leading to

$$T_{WBL}(E) = 4\tilde{\beta}^2 \frac{\Delta_{r,s}^2}{\Delta^2} \frac{1}{(1 - \tilde{\beta}^2 \frac{\Delta_{rs,rs}}{\Delta})^2 + (\tilde{\beta} \frac{\Delta_{r,r}}{\Delta} + \tilde{\beta} \frac{\Delta_{s,s}}{\Delta})^2} \tag{5.25}$$

Taking the limit of $\tilde{\beta} \rightarrow 0$ in this equation, one can see that the denominator of the second term becomes one, leaving only the first term and so equation (5.2) is retrieved, showing that the weak coupling limit is a special case of the wide band limit.

Equation (5.25) can be simplified by taking the first part of this section into consideration. For alternant hydrocarbons with an even number of carbon atoms, $\Delta_{r,r}$ and $\Delta_{s,s}$ are odd polynomials and so are $\frac{\Delta_{r,r}}{\Delta}$ and $\frac{\Delta_{s,s}}{\Delta}$. The image of odd polynomials at the origin is per definition zero. So for these systems, equation (5.25) can, at the Fermi level, be rewritten as

$$T_{WBL}(0) = 4\tilde{\beta}^2 \frac{\Delta_{r,s}^2}{\Delta^2} \frac{1}{(1 - \tilde{\beta}^2 \frac{\Delta_{rs,rs}}{\Delta})^2} \tag{5.26}$$

Again according to equation (3.78) one can write

$$\frac{\Delta_{rs,rs}}{\Delta} = \frac{\Delta_{s,s}}{\Delta} \frac{\Delta_{r,r}}{\Delta} - \frac{\Delta_{r,s}^2}{\Delta^2} \tag{5.27}$$

leading to

$$T_{WBL}(0) = 4\tilde{\beta}^2 \frac{\Delta_{r,s}^2}{\Delta^2} \frac{1}{(1 + \tilde{\beta}^2 \frac{\Delta_{r,s}^2}{\Delta^2} - \beta^2 \frac{\Delta_{r,r}}{\Delta} \frac{\Delta_{s,s}}{\Delta})^2} \tag{5.28}$$

Once more, $\frac{\Delta_{r,r}}{\Delta}$ and $\frac{\Delta_{s,s}}{\Delta}$ are zero. Equation (5.28) then becomes

$$T_{WBL}(0) = 4\tilde{\beta}^2 \frac{\Delta_{r,s}^2}{\Delta^2} \frac{1}{(1 + \tilde{\beta}^2 \frac{\Delta_{r,s}^2}{\Delta^2})^2} \tag{5.29}$$

In both this equation and the more general equation (5.25), the first factor of the product is exactly the same as the expression for the transmission probability in the weak coupling systems and can again be identified with the integrand in the expression for the atom-atom polarizability. This leads to the same selection rule as derived before. As we already noted, this selection rule is not restricted to the wide-band limit, but is generally applicable at the Fermi level.

Note that in equation (5.29) the denominator in the second factor can never be zero, since $\tilde{\beta}^2\frac{\Delta^2_{r,s}}{\Delta^2}$ is always positive. As such, the transmission probability is always defined for bipartite systems with no energy level located at the Fermi level. In the more general equation (5.25), which is valid for all non-bipartite (planar) systems, it can be possible that the denominator in the second factor becomes zero. More research is needed to identify in which cases this happens. But, since for bipartite systems with no energy level situated at the origin, equation (5.29) is always valid, the systems studied in this work pose no problem. The proposed selection rule is generally applicable to these systems.

Now that a relationship between transmission and atom-atom polarizability has been established, the next part of this section will be used to validate the integral calculation of the atom-atom polarizability through consideration of an example. This graphical example also allows to get a better grasp of the proposed selection rule.

For benzene, application of the program which is capable of calculating the atom-atom polarizability leads to the following table

Table 5.1: atom-atom polarizability for benzene

	1	2	3	4	5	6
1	-0.3981	0.1574	-0.0093	0.1019	-0.0093	0.1574
2	0.1574	-0.3981	0.1574	-0.0093	0.1019	-0.0093
3	-0.0093	0.1574	-0.3981	0.1574	-0.0093	0.1019
4	0.1019	-0.0093	0.1574	-0.3981	0.1574	-0.0093
5	-0.0093	0.1019	-0.0093	0.1574	-0.3981	0.1574
6	0.1574	-0.0093	0.1019	-0.0093	0.1574	-0.3981

Now returning to function X, for atoms in meta positions in benzene, the curve of this function has the following form on the real axis

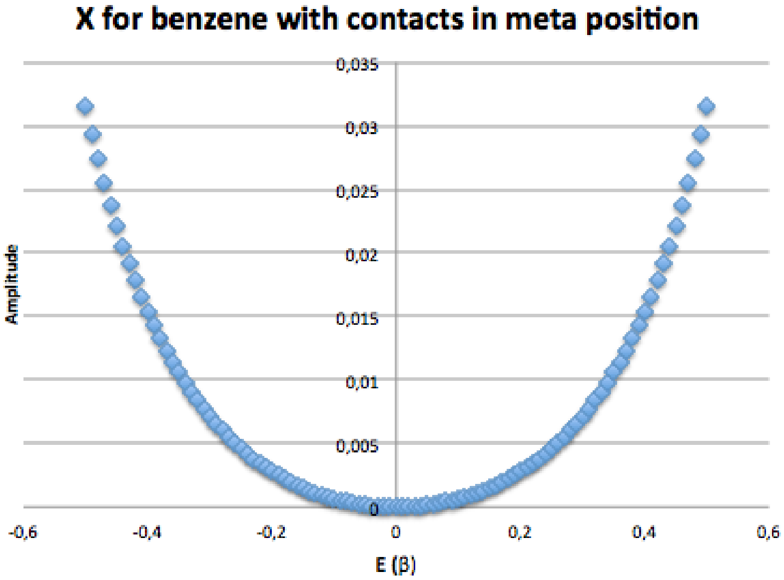

Figure 5.29: X for meta positions real axis

On the imaginary axis, the curve has the following form

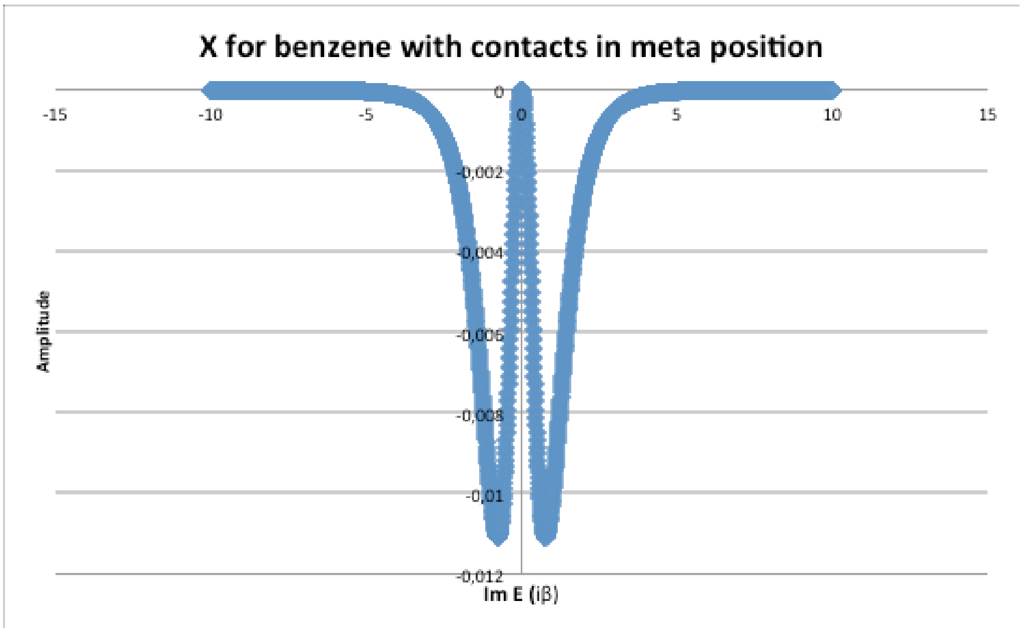

Figure 5.30: X for meta positions imaginary axis

Numerical integration over this curve gives -0,0093 as a value, corresponding exactly to the value found in the table above. One can clearly see in this figure that the image of X on the imaginary axis is always negative and reaches zero at the origin.

For atoms in para positions in benzene, the curve has the following form on the real axis

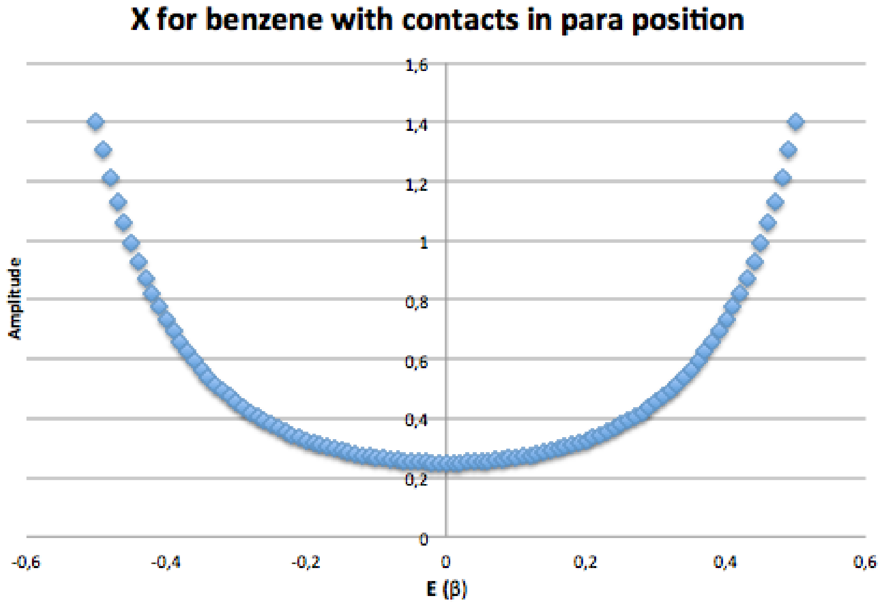

Figure 5.31: X for para postions real axis

On the imaginary axis, the curve has the following form

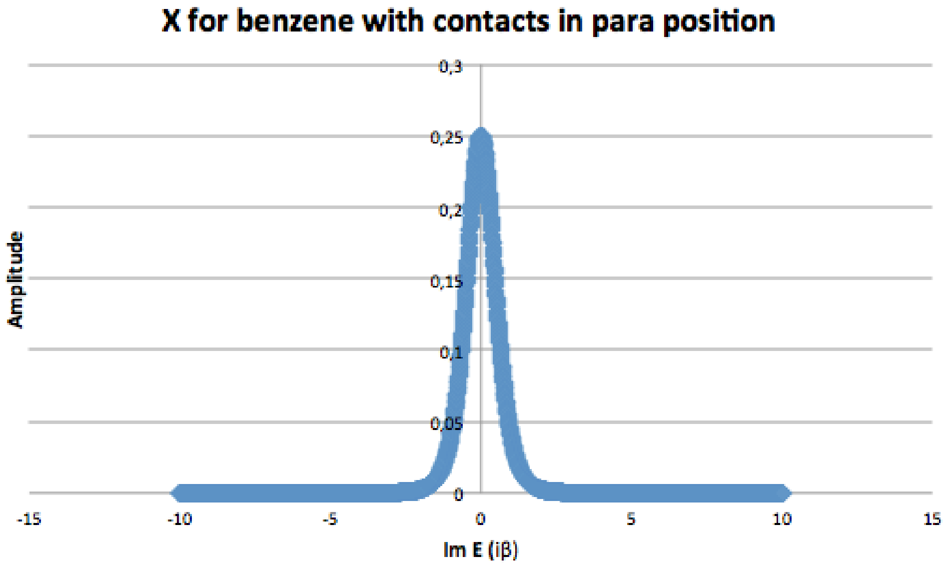

Figure 5.32: X for para positions imaginary axis

Numerical integration over this curve gives 0,1019 as a value, corresponding to the value found in the table above. This time, the image of the function is always positive, and differs from zero at the origin. Taking the value of X at the origin and plugging it into equation (5.29) leads to a transmission probability of 0,3951 at the origin, which corresponds closely to the value calculated by our program (see appendix B) and the results presented by Fowler et al.[4]

Chapter 6

Conclusions

In this study, programs for the calculation of the transmission probability, the atom-atom polarizability and the linear response current at the Hückel level of theory have been implemented successfully. An alternative version of the program capable of calculating the transmission probability has been developed for the first time which enables the calculation of all possible configurations of contacts simultaneously.

With these tools at our disposal, a series of polycyclic aromatic hydrocarbons has been studied. Analysis of the results revealed that a positive atom-atom polarizability between the contact atoms is a necessary condition for transmission to take place at the Fermi level. This selection rule has been proven theoretically to be valid for all bipartite systems with no energy level situated at the origin of the energy axis in Hückel theory.

Moreover it seems that, for a fixed first contact, the atom which possesses the highest atom-atom polarizability with this contact atom will facilitate the highest transmission probability when the second contact is located at this position. From this atom on, the transmission probability decreases monotonously in either direction away from this atom. The direction of the sharpest decline in transmission probability is the direction of that neighbor of the atom with the highest transmission probability, which exhibits relatively the lowest atom-atom polarizability.

We also showed that configurations that exhibit a high transmission probability at the Fermi level also exhibit a high linear response current and thus become relatively conducting at low bias. Configurations that exhibit a low transmission probability act as relative insulators when a low bias is applied.

Chapter 7

Outlook

In this final chapter, a few possible future research topics are explored. In a first section, the possibility to expand the selection rule for transmission based on the atom-atom polarizability to non-bipartite systems is explored. This is done in a mere theoretical way, as time constraints made it impossible to back this up with actual calculations.

Another section is devoted to the exploration of a possible physical interpretation of the link between the transmission probability and the atom-atom polarizability. In this section, some indications are presented that would allow the identification of X with the square of the unperturbed Green's function of the molecule. Although these indications come across as quite convincing, our understanding of Green's functions is very limited, encouraging us to remain very cautious not to make premature assertions. As will be noted in the specific section, a lot of work is still needed to fully grasp all aspects of Green's functions.

A final topic that could be explored is whether the selection rule can be expanded to higher levels of theory, for example Hartree-Fock or DFT. This expansion would allow the application of our selection rule to general molecules which can not be studied in Hückel theory. However, no work has been done on this already, so we won't elaborate on such an expansion in this chapter.

7.1 Expansion of the proposed selection rule to non-bipartite systems

In section 5.6 a selection rule for the transmission has been proposed for alternant hydrocarbons with no energy levels situated at the origin. Now, one can start to think about expanding this rule to more general classes of molecules, like non bipartite planar systems. Such an expansion would also make it possible to study molecules with heteroatoms.

For planar systems it is still possible to construct and diagonalize the H^π matrix to obtain π-electron levels and wave functions. The resulting diagonalized matrix contains all the roots of the characteristic polynomial. With these roots, the factorized form of the characteristic polynomial (Δ) can be constructed

$$\Delta = (z - a_1)(z - a_2)...(z - a_n) \tag{7.1}$$

where $a_1, a_2, ..., a_n$ are the roots of the characteristic polynomial.

Taking the square of this polynomial leads to Δ^2, which is the denominator of X. For general planar systems, one can not assume that Δ is even or odd, so generally the image of Δ^2 will contain a real and an imaginary part on the imaginary axis. It is however convenient, when working with rational functions, to have a completely real denominator. The image of Δ^2 can be made entirely real by multiplying Δ^2 with the square of the following factorized polynomial

$$\Delta^+ = (z + a_1)(z + a_2)...(z + a_n) \tag{7.2}$$

where $-a_1, -a_2, ..., -a_n$ are the roots of the characteristic polynomial. This way, $\Delta^2 * (\Delta^+)^2$ will be completely real. This can be demonstrated easily. One can generally write that

$$\Delta^2 * (\Delta^+)^2 = (z^2 - a_1^2)^2(z^2 - a_2^2)^2 \;...\; (z^2 - a_n^2)^2 \tag{7.3}$$

On the imaginary axis, z can be replaced with iy, leading to

$$\Delta^2 * (\Delta^+)^2 = (-y^2 - a_1^2)^2(-y^2 - a_2^2)^2 \;...\; (-y^2 - a_n^2)^2 \tag{7.4}$$

which shows that the image of this polynomial on the imaginary axis is entirely real.

It now becomes possible to write X in such a way that its denominator becomes real

$$X = \frac{\Delta_{r,s}^2}{\Delta^2} = \frac{\Delta_{r,s}^2}{\Delta^2} * \frac{(\Delta^+)^2}{(\Delta^+)^2} = \frac{\Delta_{r,s}^2 * (\Delta^+)^2}{\Delta^2 * (\Delta^+)^2} \tag{7.5}$$

As the factorized polynomial of $\Delta_{r,s}$ can, analogously to the construction of Δ, be constructed through diagonalization of $H_{r,s}^{\pi}$, it becomes possible to write the numerator of X as a factorized polynomial. From the factorized form, the general expression for the resulting polynomial can be obtained

$$\Delta_{r,s}^2 * (\Delta^+)^2 = a_0(z)^n + a_1(z)^{n-1} + ... + a_{n-1}(z) + a_n \tag{7.6}$$

Such a general polynomial contains both terms of even and odd power. In section 5.6 it was demonstrated that on the imaginary axis, terms of odd power lead to an entirely imaginary image, while terms of even power lead to an entirely real image. If one separates the terms of even powers from the ones of odd power, one can write the complex polynomial as as the sum of a real and an imaginary part of the form $u + iv$, where u is a real and even function and v is a real and odd function. As the the image of the denominator of X is entirely real on the imaginary axis and never changes signs (all roots are situated on the real axis), X as a whole can also be separated in a real and odd part on the imaginary axis, leading to

$$X(iy) = u(iy) + iv(iy) \tag{7.7}$$

Calculating the atom-atom polarizability involves integration of X over the imaginary axis. As $v(iy)$ is odd, its integral over the imaginary axis is zero. This leads to the conclusion that the atom-atom polarizability is always real and never has an imaginary part. This result agrees with what one would expect. As $u(iy)$ is even, its integral over the imaginary usually differs from zero.

Consider now the case where $\Delta_{r,s}$ has no roots on the imaginary axis, except for the origin potentialy. As all roots of Δ were situated on the real axis, so will all the roots of $(\Delta^+)^2$. So it becomes evident that in this case, the numerator of X ($\Delta_{r,s}^2 * (\Delta^+)^2$) has no roots on the imaginary axis and neither does the denominator. So, in this case, X is either positive or negative on the imaginary axis but can not change signs. This leads to 2 possible situations

- The atom-atom polarizability is positive. This means that the image of X on the imaginary axis is positive all the time. As was already mentioned, the image of the function is always positive on the real axis, so no restrictions are posed on the image at the origin. The image at the origin will be positive and can be reached in a continuous way across both axes.
- The atom-atom polarizability is negative. This means that the image of the function on the imaginary axis is negative all the time. As the image of X is always positive on the real axis (a sum of squares is always real when no imaginary coefficients are present), a restriction is posed on the image at the origin. In order for the function to be continuous at this point, the image at this point has to be reached in a continuous way both on the real and imaginary axis; the image has to be part of both $\mathbb{R}^+$ and $\mathbb{R}^-$. The only number which belongs to both sets is zero. When X is zero at the origin, no transmission will take place (see equation (5.25)).

This analysis clearly shows that theoretically, it is possible to expand the earlier proposed selection rule to other classes of systems. The only conditions that have to be fulfilled are that no pole can be situated at the origin and that $\Delta_{r,s}$ can not have any roots on the imaginary axis except for the origin itself. Some calculations will have to be performed in order to confirm the theoretical expansion of this selection rule.

As of this moment, we also do not know for which classes of systems this requirement is fulfilled and for which it is not, but identifying these classes of systems would allow us to apply the earlier proposed selection rule to a lot more systems than the ones discussed in this work.

A remark to be made is that by multiplying Δ^2 with $(\Delta^+)^2$, the situation of alternant hydrocarbons with an even number of carbon atoms is 'mimicked': the roots of $(\Delta^+)^2$ are the counterparts of the roots of Δ^2, leading to a final polynomial (the denominator in X) which roots are all paired on the real axis.

7.2 Can the link between the transmission probability and the atom-atom polarizability be interpreted physically?

In section 5.6, a mathematical relationship between the transmission probability and the atom-atom polarizability was established. Based on the behavior of the underlying X function, selection rules for transmission were proposed. This way, the objectives of this thesis were met. One can however now start to think about the meaning of this underlying X function which links both quantities. In this final section a first attempt will be made to find a proper interpretation for this function.

As a start, we would like to focus on the final expression for X in equation (5.6). The numerator of X involves the characteristic polynomial $\Delta_{r,s}$. Fowler et al. already mentioned that this polynomial links their expressions with the Green's function formalism, as it was introduced by Mujica et al.[13] Taking a look at their work on Green's functions, the expression on which the assertion of Fowler et al. is based states that

$$G_{rs} = \frac{|\tilde{\mathbf{h}}_M(r|s)|}{|\tilde{\mathbf{h}}_M|} \tag{7.8}$$

where G_{rs} is the Green's function between contact atoms *r* and *s*, $|\tilde{\mathbf{h}}_M|$ denotes the determinant of Hamiltonian $\tilde{\mathbf{h}}_M$ and $\tilde{\mathbf{h}}_M(i|j)$ the cofactor of the element (ij) of $\tilde{\mathbf{h}}_M$.

Although the structure of this expression is the same as the expression for $\sqrt{X}$, these two expressions are not entirely the same. The reason for this is that the Hamiltonian matrix connected to equation (7.8) differs from the Hamiltonian used in equation (5.6). This difference is caused by the interaction between the reservoirs and the molecule. This interaction causes so called 'self-energy'-terms to arise in the Hamiltonian matrix elements corresponding to the contact atoms. The precise meaning of these self-energies and the derivation and meaning of the Green's function formalism will not be discussed here (for more information see Mujica et al.),[13] but what is important to know is that when there is a strong interaction between the reservoirs and the molecule, these terms will be big, and when the interaction is weak, these terms will be small.

So, in the limit of no interaction, the following relationship is valid

$$X = \frac{\Delta_{r,s}^2}{\Delta^2} = |G_{rs}^0(0)|^2 \tag{7.9}$$

This argument about the meaning of X can be backed up by considering the research done by Yoshizawa et al.[5] In their work, a selection rule for transmission through molecules was derived based on the unperturbed Green's functions. What is interesting is that Yoshizawa used a MO expansion coefficient expression of the unperturbed Green's function

$$G_{rs}^{(0)}(E) = \sum_k \frac{C_{rk}C_{sk}^\star}{E - \epsilon_k \pm i\eta} \tag{7.10}$$

Or, as $\eta \to 0$ and focussing on the Green's function at the Fermi level (E=0)

$$G_{rs}^{(0)}(0) = -\sum_k \frac{C_{rk}C_{sk}^\star}{\epsilon_k} \tag{7.11}$$

This expansion coefficient expression is related to the expression of the characteristic polynomials in the same way as the expressions for the atom-atom polarizability in equations (3.115) and (3.106) are related. So, if our assertion in equation (7.9) were correct, then it should be possible to obtain the same transmission probability results with the unperturbed Green's functions instead of X, independent of whether $\frac{\Delta_{r,s}^2}{\Delta^2}$ or $\sum_k \sum_j \frac{C_{rk}C_{sk}^\star C_{rj}C_{sj}^\star}{\epsilon_k * \epsilon_j}$ is used. This statement was tested for the systems that were studied in this work in the wide band limit, leading to the following results

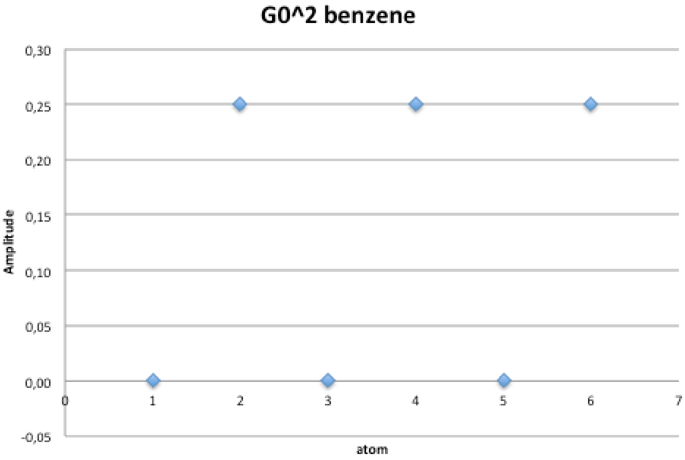

Figure 7.1: $|G^0_{1N}(0)|^2$ for benzene

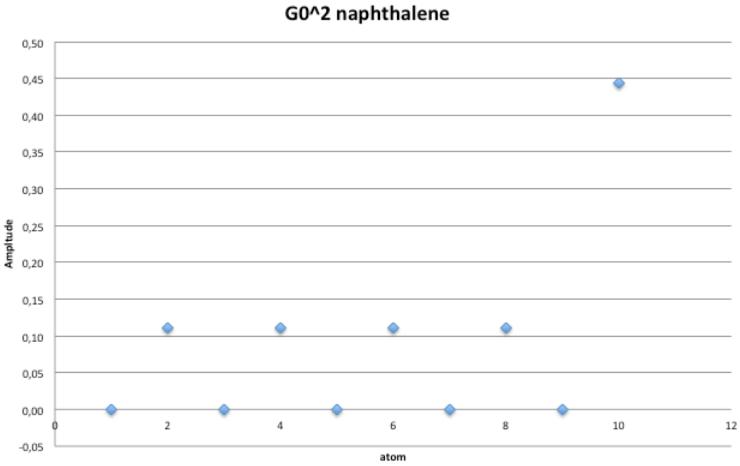

Figure 7.2: $|G^0_{1N}(0)|^2$ for naphthalene

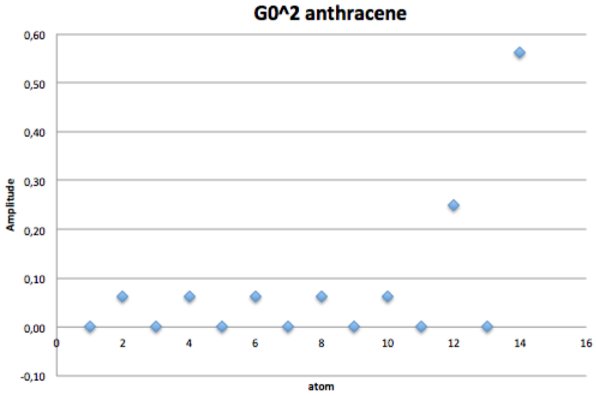

Figure 7.3: $|G^0_{1N}(0)|^2$ for anthracene

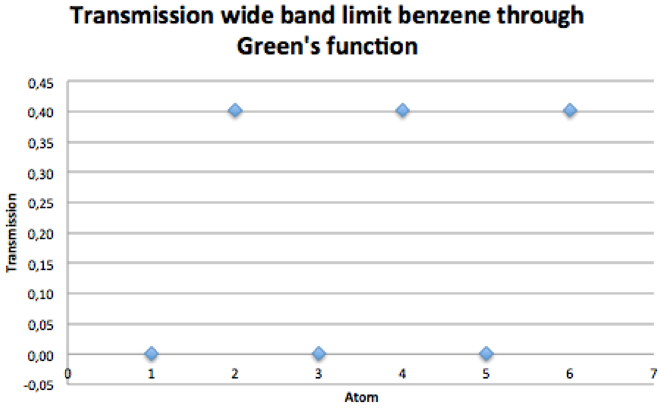

Figure 7.4: Transmission probability at the Fermi level for benzene, calculated through $|G^0_{1N}(0)|^2$

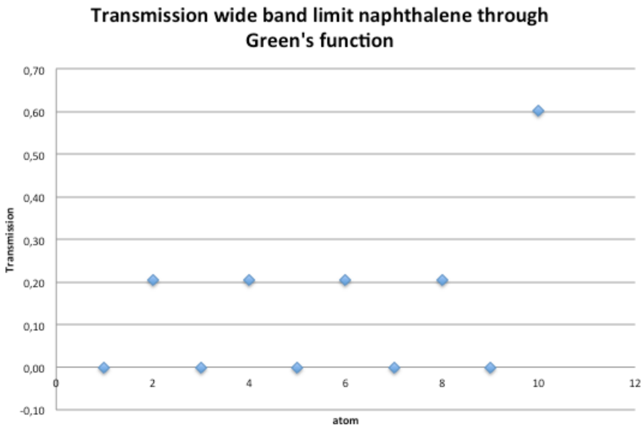

Figure 7.5: Transmission probability at the Fermi level for naphthalene, calculated through $|G_{1N}^{0}(0)|^{2}$

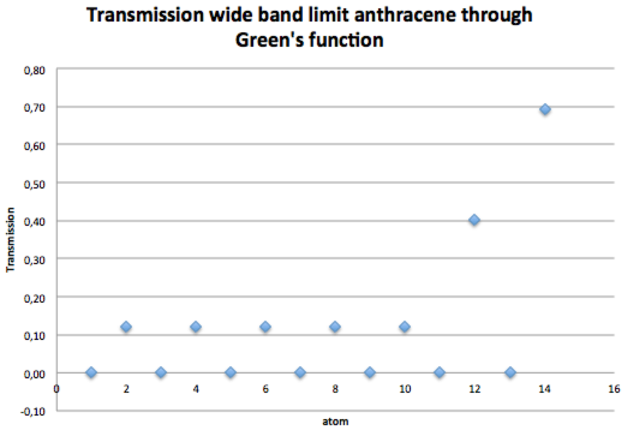

Figure 7.6: Transmission probability at the Fermi level for anthracene, calculated through $|G_{1N}^{0}(0)|^{2}$

The code for the program which was used for these calculations has been added as an appendix (see appendix C).

These last 3 graphs completely agree with the transmission probability at the Fermi level in the SSP method as they were presented before. So it seems that X can indeed be connected to $|G_{rs}^{0}(0)|^{2}$. This would lead to the conclusion that the atom-atom polarizability is the integral over the imaginary axis of the unperturbed Green's function.

In order to be able to fully interpret what this integral over the imaginary axis of the Green's function means physically, full understanding of all the aspects of Green' functions first has to be achieved. A final note is that Green's functions can be considered to be the impulse response (output) of of a linear system with zero initial conditions and a unit impulse function as the input.[40] This is a clear indication that unperturbed Green's functions should indeed somehow be physically connected to the atom-atom polarizability/linear response. More research will be necessary to work out further this relationship.

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Appendix A

Derivation of the expression for the transmission probability in the SSP method

Taking a look at equation (3.62), and separating the r-dependent factors from the r-independent factors, the following equation can be obtained

$$(E - a_{LL})[(E - a_{RR})\Delta - \beta_{rR}^2 \Delta_{r,r}] = -\beta_{sL}^2 \beta_{rR}^2 \Delta_{rs,rs} + \beta_{sL}^2 (E - a_{RR})\Delta_{s,s} \quad \text{(A.1)}$$

a_{RR} and a_{LL} can now be replaced, according to equation (3.58) and equation(3.59)

$$a_{RR} = \alpha_R + \beta_R e^{iq_R} \quad \text{(A.2)}$$

$$a_{LL} = \alpha_L + \beta_L \frac{e^{-iq_L} + r e^{iq_L}}{1 + r} \quad \text{(A.3)}$$

Taking into account now that the energy is conserved as an electron moves from the left contact, through the molecule, into the right contact, the three wave-vectors can now be related to each other.

$$E = \alpha_L + 2\beta_L \cos q_L = \alpha + 2\beta \cos q = \alpha_R + 2\beta_R \cos q_R \quad \text{(A.4)}$$

This enables a substitution of E in the terms $(E - a_{LL})$ and $(E - a_{RR})$ from equation (A.1)

$$(E - a_{LL}) = 2\beta_L \cos q_L - \beta_L \frac{e^{-iq_L} + re^{iq_L}}{1+r} \tag{A.5}$$

$$\begin{aligned}(E - a_{RR}) &= 2\beta_R \cos q_R - \beta_R e^{iq_R} \\ &= 2\beta_R \cos q_R - \beta_R \cos q_R - i\beta_R \sin q_R \\ &= \beta_R e^{-iq_R}\end{aligned} \tag{A.6}$$

Substitution in equation (A.1) leads to the following expression, after division of the righthand side of the equation by the term put between brackets, of the lefthand side,

$$2\beta_L \cos q_L - \beta_L \frac{e^{-iq_L} + re^{iq_L}}{1+r} = \frac{-\beta_{sL}^2 \beta_{rR}^2 \Delta_{rs,rs} + \beta_{sL}^2 \beta_R e^{-iq_R} \Delta_{s,s}}{\beta_R e^{-iq_R} - \beta_{rR}^2 \Delta_{r,r}} \tag{A.7}$$

Dividing both numerator and denominator of the righthand side by β_R, applying the same denominator to the entire lefthand side of the equation and applying Euler's formula, the former expression can be transformed to

$$\begin{gathered}\frac{-\tilde{\Delta}_{rs,rs} + e^{-iq_R}\tilde{\Delta}_{s,s}}{e^{-iq_R}\tilde{\Delta} - \tilde{\Delta}_{r,r}} = \\ \frac{2\cos q_L + 2r\cos q_L - \cos q_L + i\sin q_L - r\cos q_L - ir\sin q_L}{1+r}\end{gathered} \tag{A.8}$$

Which can be simplified to

$$\frac{e^{iq_L} + re^{-iq_L}}{1+r} = \frac{-\tilde{\Delta}_{rs,rs} + e^{-iq_R}\tilde{\Delta}_{s,s}}{e^{-iq_R}\tilde{\Delta} - \tilde{\Delta}_{r,r}} \tag{A.9}$$

applying distributivity leads to

$$\begin{gathered}e^{iq_L}e^{-iq_R}\tilde{\Delta} - e^{iq_L}\tilde{\Delta}_{r,r} + re^{-iq_L}e^{-iq_R}\tilde{\Delta} - re^{-iq_L}\tilde{\Delta}_{r,r} = \\ -\tilde{\Delta}_{rs,rs} + e^{-iq_R}\tilde{\Delta}_{s,s} - r\tilde{\Delta}_{rs,rs} + re^{-iq_R}\tilde{\Delta}_{s,s}\end{gathered} \tag{A.10}$$

separating all r-dependent terms from all r-independent terms leads to the following expression

$$r(\tilde{\Delta}_{rs,rs} - e^{-iq_R}\tilde{\Delta}_{s,s} + e^{-iq_L}e^{-iq_R}\tilde{\Delta} - e^{-iq_L}\tilde{\Delta}_{r,r}) = \tag{A.11}$$

$$- e^{iq_L}e^{-iq_R}\tilde{\Delta} + e^{iq_L}\tilde{\Delta}_{r,r} - \tilde{\Delta}_{rs,rs} + e^{-iq_R}\tilde{\Delta}_{s,s} \tag{A.12}$$

It can be seen easily that this expression leads to the following equation

$$r = -\frac{e^{iq_L}(e^{-iq_R}\tilde{\Delta} - \tilde{\Delta}_{r,r}) - (e^{-iq_R}\tilde{\Delta}_{s,s} - \tilde{\Delta}_{rs,rs})}{e^{-iq_L}(e^{-iq_R}\tilde{\Delta} - \tilde{\Delta}_{r,r}) - (e^{-iq_R}\tilde{\Delta}_{s,s} - \tilde{\Delta}_{rs,rs})} = \frac{e^{iq_L}F - G}{e^{-iq_L}F - G} \tag{A.13}$$

where

$$F = e^{-iq_R}\tilde{\Delta} - \tilde{\Delta}_{r,r} \qquad G = e^{-iq_R}\tilde{\Delta}_{s,s} - \tilde{\Delta}_{rs,rs} \tag{A.14}$$

Substituting this equation into the expression for T(E) leads to the following final equation for the transmission probability

$$T(E) = \frac{4\sin q_L \sin q_R(\tilde{\Delta}_{r,r}\tilde{\Delta}_{s,s} - \tilde{\Delta}\tilde{\Delta}_{rs,rs})}{|e^{-i(q_L+q_R)}\tilde{\Delta} - e^{-iq_R}\tilde{\Delta}_{s,s} - e^{-iq_L}\tilde{\Delta}_{r,r} + \tilde{\Delta}_{rs,rs}|^2} \tag{A.15}$$

Appendix B

Numerical results for the performed calculations

B.1 The atom-atom polarizability

Table B.1: atom-atom polarizability for benzene

	1	2	3	4	5	6
1	-0.3981	0.1574	-0.0093	0.1019	-0.0093	0.1574
2	0.1574	-0.3981	0.1574	-0.0093	0.1019	-0.0093
3	-0.0093	0.1574	-0.3981	0.1574	-0.0093	0.1019
4	0.1019	-0.0093	0.1574	-0.3981	0.1574	-0.0093
5	-0.0093	0.1019	-0.0093	0.1574	-0.3981	0.1574
6	0.1574	-0.0093	0.1019	-0.0093	0.1574	-0.3981

Table B.2: atom-atom polarizability for naphthalene

	1	2	3	4	5	6	7	8	9	10
1	-0.405	0.110	-0.018	0.049	-0.006	0.033	0.000	0.032	-0.007	0.213
2	0.110	-0.405	0.213	-0.007	0.032	0.000	0.033	-0.006	0.049	-0.018
3	-0.018	0.213	-0.443	0.089	-0.027	0.032	-0.006	0.023	-0.004	0.139
4	0.049	-0.007	0.089	-0.330	0.089	-0.007	0.049	-0.004	0.077	-0.004
5	-0.006	0.032	-0.027	0.089	-0.443	0.213	-0.018	0.139	-0.004	0.023
6	0.033	0.000	0.032	-0.007	0.213	-0.405	0.110	-0.018	0.049	-0.006
7	0.000	0.033	-0.006	0.049	-0.018	0.110	-0.405	0.213	-0.007	0.032
8	0.032	-0.006	0.023	-0.004	0.139	-0.018	0.213	-0.443	0.089	-0.027
9	-0.007	0.049	-0.004	0.077	-0.004	0.049	-0.007	0.089	-0.330	0.089
10	0.213	-0.018	0.139	-0.004	0.023	-0.006	0.032	-0.027	0.089	-0.443

Table B.3: atom-atom polarizability for anthracene

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	-0.411	0.099	-0.022	0.036	-0.014	0.018	-0.004	0.012	-0.001	0.011	0.000	0.054	-0.009	0.231
2	0.099	-0.411	0.231	-0.009	0.054	0.000	0.011	-0.001	0.012	-0.004	0.018	-0.014	0.036	-0.022
3	-0.022	0.231	-0.454	0.078	-0.043	0.018	-0.008	0.011	-0.004	0.008	-0.003	0.040	-0.003	0.151
4	0.036	-0.009	0.078	-0.331	0.125	-0.005	0.018	0.000	0.018	-0.003	0.026	-0.009	0.059	-0.003
5	-0.014	0.054	-0.043	0.125	-0.526	0.125	-0.043	0.054	-0.014	0.040	-0.009	0.217	-0.009	0.040
6	0.018	0.000	0.018	-0.005	0.125	-0.331	0.078	-0.009	0.036	-0.003	0.059	-0.009	0.026	-0.003
7	-0.004	0.011	-0.008	0.018	-0.043	0.078	-0.454	0.231	-0.022	0.151	-0.003	0.040	-0.003	0.008
8	0.012	-0.001	0.011	0.000	0.054	-0.009	0.231	-0.411	0.099	-0.022	0.036	-0.014	0.018	-0.004
9	-0.001	0.012	-0.004	0.018	-0.014	0.036	-0.022	0.099	-0.411	0.231	-0.009	0.054	0.000	0.011
10	0.011	-0.004	0.008	-0.003	0.040	-0.003	0.151	-0.022	0.231	-0.454	0.078	-0.043	0.018	-0.008
11	0.000	0.018	-0.003	0.026	-0.009	0.059	-0.003	0.036	-0.009	0.078	-0.331	0.125	-0.005	0.018
12	0.054	-0.014	0.040	-0.009	0.217	-0.009	0.040	-0.014	0.054	-0.043	0.125	-0.526	0.125	-0.043
13	-0.009	0.036	-0.003	0.059	-0.009	0.026	-0.003	0.018	0.000	0.018	-0.005	0.125	-0.331	0.078
14	0.231	-0.022	0.151	-0.003	0.040	-0.003	0.008	-0.004	0.011	-0.008	0.018	-0.043	0.078	-0.454

Table B.4: atom-atom polarizability for tetracene

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	-0.414	0.096	-0.024	0.033	-0.019	0.013	-0.009	0.007	-0.002	0.005	-0.001	0.004	-0.001	0.020	0.000	0.064	-0.010	0.237
2	0.096	-0.414	0.237	-0.010	0.064	0.000	0.020	-0.001	0.004	-0.001	0.005	-0.002	0.007	-0.009	0.013	-0.019	0.033	-0.024
3	-0.024	0.237	-0.458	0.075	-0.050	0.014	-0.016	0.006	-0.004	0.004	-0.002	0.004	-0.002	0.017	-0.002	0.048	-0.003	0.155
4	0.033	-0.010	0.075	-0.334	0.138	-0.006	0.031	0.000	0.006	-0.001	0.007	-0.002	0.010	-0.008	0.020	-0.012	0.055	-0.003
5	-0.019	0.064	-0.050	0.138	-0.556	0.107	-0.077	0.031	-0.016	0.020	-0.009	0.017	-0.008	0.077	-0.005	0.250	-0.012	0.048
6	0.013	0.000	0.014	-0.006	0.107	-0.331	0.107	-0.006	0.014	0.000	0.013	-0.002	0.020	-0.005	0.048	-0.005	0.020	-0.002
7	-0.009	0.020	-0.016	0.031	-0.077	0.107	-0.556	0.138	-0.050	0.064	-0.019	0.048	-0.012	0.250	-0.005	0.077	-0.008	0.017
8	0.007	-0.001	0.006	0.000	0.031	-0.006	0.138	-0.334	0.075	-0.010	0.033	-0.003	0.055	-0.012	0.020	-0.008	0.010	-0.002
9	-0.002	0.004	-0.004	0.006	-0.016	0.014	-0.050	0.075	-0.458	0.237	-0.024	0.155	-0.003	0.048	-0.002	0.017	-0.002	0.004
10	0.005	-0.001	0.004	-0.001	0.020	0.000	0.064	-0.010	0.237	-0.414	0.096	-0.024	0.033	-0.019	0.013	-0.009	0.007	-0.002
11	-0.001	0.005	-0.002	0.007	-0.009	0.013	-0.019	0.033	-0.024	0.096	-0.414	0.237	-0.010	0.064	0.000	0.020	-0.001	0.004
12	0.004	-0.002	0.004	-0.002	0.017	-0.002	0.048	-0.003	0.155	-0.024	0.237	-0.458	0.075	-0.050	0.014	-0.016	0.006	-0.004
13	-0.001	0.007	-0.002	0.010	-0.008	0.020	-0.012	0.055	-0.003	0.033	-0.010	0.075	-0.334	0.138	-0.006	0.031	0.000	0.006
14	0.020	-0.009	0.017	-0.008	0.077	-0.005	0.250	-0.012	0.048	-0.019	0.064	-0.050	0.138	-0.556	0.107	-0.077	0.031	-0.016
15	0.000	0.013	-0.002	0.020	-0.005	0.048	-0.005	0.020	-0.002	0.013	0.000	0.014	-0.006	0.107	-0.331	0.107	-0.006	0.014
16	0.064	-0.019	0.048	-0.012	0.250	-0.005	0.077	-0.008	0.017	-0.009	0.020	-0.016	0.031	-0.077	0.107	-0.556	0.138	-0.050
17	-0.010	0.033	-0.003	0.055	-0.012	0.020	-0.008	0.010	-0.002	0.007	-0.001	0.006	0.000	0.031	-0.006	0.138	-0.334	0.075
18	0.237	-0.024	0.155	-0.003	0.048	-0.002	0.017	-0.002	0.004	-0.002	0.004	-0.004	0.006	-0.016	0.014	-0.050	0.075	-0.458

Table B.5: atom-atom polarizability for pentacene - part 1

	1	2	3	4	5	6	7	8	9	10	11	12
1	-0.415	0.096	-0.025	0.032	-0.022	0.012	-0.013	0.005	-0.006	0.003	-0.002	0.002
2	0.096	-0.415	0.239	-0.010	0.068	0.000	0.026	0.000	0.009	-0.001	0.002	-0.001
3	-0.025	0.239	-0.459	0.075	-0.053	0.013	-0.020	0.005	-0.008	0.003	-0.002	0.002
4	0.032	-0.010	0.075	-0.335	0.143	-0.006	0.037	0.000	0.012	0.000	0.003	-0.001
5	-0.022	0.068	-0.053	0.143	-0.569	0.103	-0.096	0.024	-0.034	0.012	-0.008	0.009
6	0.012	0.000	0.013	-0.006	0.103	-0.333	0.117	-0.006	0.024	0.000	0.005	0.000
7	-0.013	0.026	-0.020	0.037	-0.096	0.117	-0.601	0.117	-0.096	0.037	-0.020	0.026
8	0.005	0.000	0.005	0.000	0.024	-0.006	0.117	-0.333	0.103	-0.006	0.013	0.000
9	-0.006	0.009	-0.008	0.012	-0.034	0.024	-0.096	0.103	-0.569	0.143	-0.053	0.068
10	0.003	-0.001	0.003	0.000	0.012	0.000	0.037	-0.006	0.143	-0.335	0.075	-0.010
11	-0.002	0.002	-0.002	0.003	-0.008	0.005	-0.020	0.013	-0.053	0.075	-0.459	0.239
12	0.002	-0.001	0.002	-0.001	0.009	0.000	0.026	0.000	0.068	-0.010	0.239	-0.415
13	-0.001	0.002	-0.002	0.003	-0.006	0.005	-0.013	0.012	-0.022	0.032	-0.025	0.096
14	0.002	-0.002	0.002	-0.002	0.008	-0.002	0.022	-0.002	0.052	-0.003	0.157	-0.025
15	-0.001	0.003	-0.002	0.004	-0.006	0.008	-0.012	0.018	-0.014	0.054	-0.003	0.032
16	0.009	-0.006	0.008	-0.006	0.036	-0.005	0.097	-0.005	0.265	-0.014	0.052	-0.022
17	0.000	0.005	-0.002	0.008	-0.005	0.016	-0.008	0.045	-0.005	0.018	-0.002	0.012
18	0.026	-0.013	0.022	-0.012	0.097	-0.008	0.299	-0.008	0.097	-0.012	0.022	-0.013
19	0.000	0.012	-0.002	0.018	-0.005	0.045	-0.008	0.016	-0.005	0.008	-0.002	0.005
20	0.068	-0.022	0.052	-0.014	0.265	-0.005	0.097	-0.005	0.036	-0.006	0.008	-0.006
21	-0.010	0.032	-0.003	0.054	-0.014	0.018	-0.012	0.008	-0.006	0.004	-0.002	0.003
22	0.239	-0.025	0.157	-0.003	0.052	-0.002	0.022	-0.002	0.008	-0.002	0.002	-0.002

Table B.6: atom-atom polarizability pentacene - part 2

	13	14	15	16	17	18	19	20	21	22
1	-0.001	0.002	-0.001	0.009	0.000	0.026	0.000	0.068	-0.010	0.239
2	0.002	-0.002	0.003	-0.006	0.005	-0.013	0.012	-0.022	0.032	-0.025
3	-0.002	0.002	-0.002	0.008	-0.002	0.022	-0.002	0.052	-0.003	0.157
4	0.003	-0.002	0.004	-0.006	0.008	-0.012	0.018	-0.014	0.054	-0.003
5	-0.006	0.008	-0.006	0.036	-0.005	0.097	-0.005	0.265	-0.014	0.052
6	0.005	-0.002	0.008	-0.005	0.016	-0.008	0.045	-0.005	0.018	-0.002
7	-0.013	0.022	-0.012	0.097	-0.008	0.299	-0.008	0.097	-0.012	0.022
8	0.012	-0.002	0.018	-0.005	0.045	-0.008	0.016	-0.005	0.008	-0.002
9	-0.022	0.052	-0.014	0.265	-0.005	0.097	-0.005	0.036	-0.006	0.008
10	0.032	-0.003	0.054	-0.014	0.018	-0.012	0.008	-0.006	0.004	-0.002
11	-0.025	0.157	-0.003	0.052	-0.002	0.022	-0.002	0.008	-0.002	0.002
12	0.096	-0.025	0.032	-0.022	0.012	-0.013	0.005	-0.006	0.003	-0.002
13	-0.415	0.239	-0.010	0.068	0.000	0.026	0.000	0.009	-0.001	0.002
14	0.239	-0.459	0.075	-0.053	0.013	-0.020	0.005	-0.008	0.003	-0.002
15	-0.010	0.075	-0.335	0.143	-0.006	0.037	0.000	0.012	0.000	0.003
16	0.068	-0.053	0.143	-0.569	0.103	-0.096	0.024	-0.034	0.012	-0.008
17	0.000	0.013	-0.006	0.103	-0.333	0.117	-0.006	0.024	0.000	0.005
18	0.026	-0.020	0.037	-0.096	0.117	-0.601	0.117	-0.096	0.037	-0.020
19	0.000	0.005	0.000	0.024	-0.006	0.117	-0.333	0.103	-0.006	0.013
20	0.009	-0.008	0.012	-0.034	0.024	-0.096	0.103	-0.569	0.143	-0.053
21	-0.001	0.003	0.000	0.012	0.000	0.037	-0.006	0.143	-0.335	0.075
22	0.002	-0.002	0.003	-0.008	0.005	-0.020	0.013	-0.053	0.075	-0.459

B.2 The transmission probability

Table B.7: Transmission probability for benzene at the Fermi level

	1	2	3	4	5	6
1	0.000	0.401	0.000	0.401	0.000	0.401
2	0.401	0.000	0.401	0.000	0.401	0.000
3	0.000	0.401	0.000	0.401	0.000	0.401
4	0.401	0.000	0.401	0.000	0.401	0.000
5	0.000	0.401	0.000	0.401	0.000	0.401
6	0.401	0.000	0.401	0.000	0.401	0.000

Table B.8: Transmission probability for naphthalene at the Fermi level

	1	2	3	4	5	6	7	8	9	10
1	0.000	0.203	0.000	0.203	0.000	0.203	0.000	0.203	0.000	0.603
2	0.203	0.000	0.603	0.000	0.203	0.000	0.203	0.000	0.203	0.000
3	0.000	0.603	0.000	0.203	0.000	0.203	0.000	0.203	0.000	0.603
4	0.203	0.000	0.203	0.000	0.203	0.000	0.203	0.000	0.203	0.000
5	0.000	0.203	0.000	0.203	0.000	0.603	0.000	0.603	0.000	0.203
6	0.203	0.000	0.203	0.000	0.603	0.000	0.203	0.000	0.203	0.000
7	0.000	0.203	0.000	0.203	0.000	0.203	0.000	0.603	0.000	0.203
8	0.203	0.000	0.203	0.000	0.603	0.000	0.603	0.000	0.203	0.000
9	0.000	0.203	0.000	0.203	0.000	0.203	0.000	0.203	0.000	0.203
10	0.603	0.000	0.603	0.000	0.203	0.000	0.203	0.000	0.203	0.000

Table B.9: Transmission probability for anthracene at the Fermi level

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.401	0.000	0.693
2	0.120	0.000	0.693	0.000	0.401	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.120	0.000
3	0.000	0.693	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.401	0.000	0.693
4	0.120	0.000	0.120	0.000	0.401	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.120	0.000
5	0.000	0.401	0.000	0.401	0.000	0.401	0.000	0.401	0.000	0.401	0.000	0.895	0.000	0.401
6	0.120	0.000	0.120	0.000	0.401	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.120	0.000
7	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.693	0.000	0.693	0.000	0.401	0.000	0.120
8	0.120	0.000	0.120	0.000	0.401	0.000	0.693	0.000	0.120	0.000	0.120	0.000	0.120	0.000
9	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.693	0.000	0.401	0.000	0.120
10	0.120	0.000	0.120	0.000	0.401	0.000	0.693	0.000	0.693	0.000	0.120	0.000	0.120	0.000
11	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.401	0.000	0.120
12	0.401	0.000	0.401	0.000	0.895	0.000	0.401	0.000	0.401	0.000	0.401	0.000	0.401	0.000
13	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.401	0.000	0.120
14	0.693	0.000	0.693	0.000	0.401	0.000	0.120	0.000	0.120	0.000	0.120	0.000	0.120	0.000

Table B.10: Transmission probability for tetracene at the Fermi level

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.279	0.000	0.524	0.000	0.742
2	0.078	0.000	0.742	0.000	0.524	0.000	0.279	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000
3	0.000	0.742	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.279	0.000	0.524	0.000	0.742
4	0.078	0.000	0.078	0.000	0.524	0.000	0.279	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000
5	0.000	0.524	0.000	0.524	0.000	0.279	0.000	0.279	0.000	0.279	0.000	0.279	0.000	0.742	0.000	0.977	0.000	0.524
6	0.078	0.000	0.078	0.000	0.279	0.000	0.279	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000
7	0.000	0.279	0.000	0.279	0.000	0.279	0.000	0.524	0.000	0.524	0.000	0.524	0.000	0.977	0.000	0.742	0.000	0.279
8	0.078	0.000	0.078	0.000	0.279	0.000	0.524	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000
9	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.742	0.000	0.742	0.000	0.524	0.000	0.279	0.000	0.078
10	0.078	0.000	0.078	0.000	0.279	0.000	0.524	0.000	0.742	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000
11	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.742	0.000	0.524	0.000	0.279	0.000	0.078
12	0.078	0.000	0.078	0.000	0.279	0.000	0.524	0.000	0.742	0.000	0.742	0.000	0.078	0.000	0.078	0.000	0.078	0.000
13	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.524	0.000	0.279	0.000	0.078
14	0.279	0.000	0.279	0.000	0.742	0.000	0.977	0.000	0.524	0.000	0.524	0.000	0.524	0.000	0.279	0.000	0.279	0.000
15	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.279	0.000	0.279	0.000	0.078
16	0.524	0.000	0.524	0.000	0.977	0.000	0.742	0.000	0.279	0.000	0.279	0.000	0.279	0.000	0.279	0.000	0.524	0.000
17	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.279	0.000	0.524	0.000	0.078
18	0.742	0.000	0.742	0.000	0.524	0.000	0.279	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000	0.078	0.000

Table B.11: Transmission probability for pentacene at the Fermi level - part 1

	1	2	3	4	5	6	7	8	9	10	11	12
1	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055
2	0.055	0.000	0.773	0.000	0.603	0.000	0.401	0.000	0.203	0.000	0.055	0.000
3	0.000	0.773	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055
4	0.055	0.000	0.055	0.000	0.603	0.000	0.401	0.000	0.203	0.000	0.055	0.000
5	0.000	0.603	0.000	0.603	0.000	0.203	0.000	0.203	0.000	0.203	0.000	0.203
6	0.055	0.000	0.055	0.000	0.203	0.000	0.401	0.000	0.203	0.000	0.055	0.000
7	0.000	0.401	0.000	0.401	0.000	0.401	0.000	0.401	0.000	0.401	0.000	0.401
8	0.055	0.000	0.055	0.000	0.203	0.000	0.401	0.000	0.203	0.000	0.055	0.000
9	0.000	0.203	0.000	0.203	0.000	0.203	0.000	0.203	0.000	0.603	0.000	0.603
10	0.055	0.000	0.055	0.000	0.203	0.000	0.401	0.000	0.603	0.000	0.055	0.000
11	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.773
12	0.055	0.000	0.055	0.000	0.203	0.000	0.401	0.000	0.603	0.000	0.773	0.000
13	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055
14	0.055	0.000	0.055	0.000	0.203	0.000	0.401	0.000	0.603	0.000	0.773	0.000
15	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055
16	0.203	0.000	0.203	0.000	0.603	0.000	0.895	0.000	0.998	0.000	0.603	0.000
17	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055
18	0.401	0.000	0.401	0.000	0.895	0.000	0.995	0.000	0.895	0.000	0.401	0.000
19	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055
20	0.603	0.000	0.603	0.000	0.998	0.000	0.895	0.000	0.603	0.000	0.203	0.000
21	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055
22	0.773	0.000	0.773	0.000	0.603	0.000	0.401	0.000	0.203	0.000	0.055	0.000

Table B.12: Transmission probability for pentacene at the Fermi level - part 2

	13	14	15	16	17	18	19	20	21	22
1	0.000	0.055	0.000	0.203	0.000	0.401	0.000	0.603	0.000	0.773
2	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000
3	0.000	0.055	0.000	0.203	0.000	0.401	0.000	0.603	0.000	0.773
4	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000
5	0.000	0.203	0.000	0.603	0.000	0.895	0.000	0.998	0.000	0.603
6	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000
7	0.000	0.401	0.000	0.895	0.000	0.995	0.000	0.895	0.000	0.401
8	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000
9	0.000	0.603	0.000	0.998	0.000	0.895	0.000	0.603	0.000	0.203
10	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000
11	0.000	0.773	0.000	0.603	0.000	0.401	0.000	0.203	0.000	0.055
12	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000
13	0.000	0.773	0.000	0.603	0.000	0.401	0.000	0.203	0.000	0.055
14	0.773	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000
15	0.000	0.055	0.000	0.603	0.000	0.401	0.000	0.203	0.000	0.055
16	0.603	0.000	0.603	0.000	0.203	0.000	0.203	0.000	0.203	0.000
17	0.000	0.055	0.000	0.203	0.000	0.401	0.000	0.203	0.000	0.055
18	0.401	0.000	0.401	0.000	0.401	0.000	0.401	0.000	0.401	0.000
19	0.000	0.055	0.000	0.203	0.000	0.401	0.000	0.203	0.000	0.055
20	0.203	0.000	0.203	0.000	0.203	0.000	0.203	0.000	0.603	0.000
21	0.000	0.055	0.000	0.203	0.000	0.401	0.000	0.603	0.000	0.055
22	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000	0.055	0.000

B.3 The linear response current

Table B.13: IV benzene

V (β)	I(1-1)	I(1-2)	I(1-3)	I(1-4)
0.00	1.15E-13	4.01E-04	1.28E-14	4.01E-04
0.10	9.87E-05	4.06E-02	1.10E-05	4.06E-02
0.20	7.80E-04	8.09E-02	8.73E-05	8.11E-02
0.30	2.63E-03	1.21E-01	2.97E-04	1.22E-01
0.40	6.27E-03	1.63E-01	7.17E-04	1.64E-01
0.50	1.23E-02	2.04E-01	1.43E-03	2.08E-01
0.60	2.15E-02	2.47E-01	2.55E-03	2.53E-01
0.70	3.45E-02	2.90E-01	4.21E-03	3.00E-01
0.80	5.22E-02	3.35E-01	6.55E-03	3.50E-01
0.90	7.53E-02	3.81E-01	9.78E-03	4.02E-01
1.00	1.05E-01	4.28E-01	1.41E-02	4.58E-01
1.10	1.41E-01	4.77E-01	1.99E-02	5.19E-01
1.20	1.86E-01	5.27E-01	2.75E-02	5.83E-01

Table B.14: IV naphtalene

V (β)	I(1-1)	I(1-2)	I(1-3)	I(1-4)	I(1-5)	I(1-6)	I(1-7)	I(1-8)	I(1-9)	I(1-10)
0.00	1.61E-13	2.03E-04	6.30E-14	2.03E-04	4.03E-14	2.03E-04	2.52E-15	2.03E-04	1.01E-14	6.03E-04
0.10	1.39E-04	2.05E-02	5.44E-05	2.05E-02	3.49E-05	2.06E-02	2.20E-06	2.06E-02	8.68E-06	6.09E-02
0.20	1.10E-03	4.06E-02	4.37E-04	4.10E-02	2.82E-04	4.13E-02	1.82E-05	4.14E-02	6.90E-05	1.22E-01
0.30	3.74E-03	6.03E-02	1.51E-03	6.18E-02	9.84E-04	6.29E-02	6.64E-05	6.30E-02	2.35E-04	1.83E-01
0.40	8.98E-03	7.94E-02	3.74E-03	8.31E-02	2.46E-03	8.57E-02	1.77E-04	8.60E-02	5.67E-04	2.46E-01
0.50	1.79E-02	9.75E-02	7.73E-03	1.05E-01	5.17E-03	1.10E-01	4.04E-04	1.11E-01	1.14E-03	3.11E-01
0.60	3.16E-02	1.14E-01	1.43E-02	1.28E-01	9.80E-03	1.38E-01	8.54E-04	1.39E-01	2.02E-03	3.79E-01
0.70	5.17E-02	1.29E-01	2.48E-02	1.51E-01	1.74E-02	1.68E-01	1.74E-03	1.70E-01	3.33E-03	4.49E-01
0.80	8.00E-02	1.40E-01	4.09E-02	1.76E-01	2.96E-02	2.04E-01	3.54E-03	2.07E-01	5.17E-03	5.23E-01
0.90	1.19E-01	1.47E-01	6.52E-02	2.02E-01	4.89E-02	2.46E-01	7.33E-03	2.51E-01	7.66E-03	6.01E-01
1.00	1.71E-01	1.49E-01	1.01E-01	2.28E-01	7.88E-02	2.99E-01	1.58E-02	3.04E-01	1.09E-02	6.84E-01
1.10	2.40E-01	1.51E-01	1.51E-01	2.52E-01	1.23E-01	3.65E-01	3.59E-02	3.67E-01	1.45E-02	7.71E-01
1.20	3.29E-01	1.74E-01	2.15E-01	2.67E-01	1.83E-01	4.50E-01	8.17E-02	4.39E-01	1.71E-02	8.57E-01

Table B.15: IV anthracene

V (β)	I(1-1)	I(1-2)	I(1-3)	I(1-4)	I(1-5)	I(1-6)	I(1-7)	I(1-8)	I(1-9)	I(1-10)	I(1-11)	I(1-12)	I(1-13)	I(1-14)
0.00	2.58E-13	6.93E-04	2.87E-14	4.01E-04	3.19E-15	1.20E-04	2.87E-14	1.20E-04	7.97E-14	1.20E-04	2.04E-13	1.20E-04	1.56E-13	1.20E-04
0.10	2.23E-04	7.01E-02	2.49E-05	4.07E-02	2.82E-06	1.22E-02	2.52E-05	1.22E-02	6.97E-05	1.22E-02	1.77E-04	1.21E-02	1.36E-04	1.20E-02
0.20	1.79E-03	1.40E-01	2.03E-04	8.23E-02	2.42E-05	2.51E-02	2.13E-04	2.49E-02	5.81E-04	2.45E-02	1.45E-03	2.39E-02	1.11E-03	2.33E-02
0.30	6.22E-03	2.12E-01	7.23E-04	1.26E-01	9.45E-05	3.96E-02	8.05E-04	3.89E-02	2.14E-03	3.76E-02	5.18E-03	3.54E-02	3.98E-03	3.34E-02
0.40	1.54E-02	2.87E-01	1.87E-03	1.74E-01	2.80E-04	5.72E-02	2.27E-03	5.54E-02	5.82E-03	5.19E-02	1.33E-02	4.62E-02	1.03E-02	4.15E-02
0.50	3.22E-02	3.66E-01	4.16E-03	2.27E-01	7.52E-04	8.01E-02	5.70E-03	7.63E-02	1.37E-02	6.83E-02	2.87E-02	5.58E-02	2.29E-02	4.65E-02
0.60	6.11E-02	4.50E-01	8.72E-03	2.87E-01	2.04E-03	1.12E-01	1.39E-02	1.05E-01	3.02E-02	8.82E-02	5.50E-02	6.30E-02	4.65E-02	4.79E-02
0.70	1.10E-01	5.41E-01	1.87E-02	3.52E-01	6.27E-03	1.61E-01	3.53E-02	1.50E-01	6.41E-02	1.15E-01	9.57E-02	6.60E-02	8.92E-02	5.01E-02
0.80	1.91E-01	6.34E-01	4.54E-02	4.20E-01	2.49E-02	2.33E-01	9.14E-02	2.24E-01	1.27E-01	1.57E-01	1.50E-01	7.08E-02	1.59E-01	8.18E-02
0.90	2.83E-01	7.08E-01	8.78E-02	4.81E-01	7.15E-02	3.20E-01	1.87E-01	3.20E-01	2.12E-01	1.94E-01	2.12E-01	1.24E-01	2.46E-01	1.69E-01
1.00	3.20E-01	7.34E-01	1.00E-01	5.30E-01	9.93E-02	3.95E-01	2.68E-01	3.76E-01	2.96E-01	1.96E-01	2.74E-01	1.88E-01	3.20E-01	2.67E-01
1.10	3.24E-01	7.36E-01	1.02E-01	5.63E-01	1.15E-01	4.49E-01	3.26E-01	3.97E-01	3.64E-01	1.98E-01	3.30E-01	2.44E-01	3.68E-01	3.54E-01
1.20	3.26E-01	7.42E-01	1.02E-01	5.84E-01	1.26E-01	4.87E-01	3.70E-01	4.04E-01	4.20E-01	2.04E-01	3.80E-01	2.99E-01	3.96E-01	4.34E-01

Appendix C

Code of the implemented programs

C.1 Program to calculate the transmission probability

```
program alttransmissionall
implicit none
integer :: n,i,j,r,E
real :: w,x,y,z,T,betal,betar
real*8, pointer :: A(:,:), C(:,:),temp(:,:),K(:), Tr(:,:)

print *, ' '
!read size of matrix A
print *, 'What is the dimension of the square matrix?'
read *, n

!allocate memory for A and C
allocate(A(1:n,1:n))
allocate(C(1:n,1:n))
allocate(temp(1:n,1:n))
allocate(K(1:n))
allocate(Tr(1:n,1:n))

!read connectivity matrix A
open(12,file='input tetracene.txt')
do i=1,n
read(12,*) (A(i,j), j=1, N)
end do
```

```
call outputra(n,A)

!save A before inversion
temp=A

!create transmission output file for plotting T curve
!redefine diagonal elements, make a list of all E-values
open(13,file='invoutput.txt')
do E=-300,300
do i=1,n
temp(i,i)=E/100.0
end do
A=temp

call inverse(A,C,n)

do r=1,n

!define w as $\frac{\Delta_{s,s}}{\Delta}$, x as $\frac{\Delta_{r,r}}{\Delta}$, y as $\frac{\Delta_{r,s}}{\Delta}$ and z as $\frac{\Delta_{rs,rs}}{\Delta}$
w=C(1,1)
x=C(r,r)
y=C(1,r)
z=(x*w-y**2)
betal=1/1.4
betar=1/1.4

!calculate the transmission
T=(4*(betar*x*betal*w-betal*betar*z)
/((1-betal*betar*z)**2+(betar*x+betar*w)**2))
!store T in a matrix for each value of r
K(r)=T
end do
write(13,*) E/100.0, (K(r),r=1,n)
end do

!create postscript input
open(14, file='Toutput.txt')

do i=1,n
temp(i,i)=0.000001
end do
```

```
A=temp

call inverse(A,C,n)

do r=1,n

!define w as $\frac{\Delta_{s,s}}{\Delta}$, x as $\frac{\Delta_{r,r}}{\Delta}$, y as $\frac{\Delta_{r,s}}{\Delta}$ and z as $\frac{\Delta_{rs,rs}}{\Delta}$
w=C(7,7)
x=C(r,r)
y=C(7,r)
z=(x*w-y**2)
betal=1/1.4
betar=1/1.4

!calculate the transmission
T=(4*(betar*x*betal*w-betal*betar*z)
/((1-betal*betar*z)**2+(betar*x+betar*w)**2))
!store T in a matrix for each value of r
write(14,*) T
end do

!create table with numerical results
open(14, file='Ttetracenetable.txt')

do i=1,n
temp(i,i)=0.000001
end do
A=temp

call inverse(A,C,n)

do i=1,n
do r=1,n

!define w as $\frac{\Delta_{s,s}}{\Delta}$, x as $\frac{\Delta_{r,r}}{\Delta}$, y as $\frac{\Delta_{r,s}}{\Delta}$ and z as $\frac{\Delta_{rs,rs}}{\Delta}$
w=C(i,i)
x=C(r,r)
y=C(i,r)
z=(x*w-y**2)
betal=1/1.4
betar=1/1.4
```

```
!calculate the transmission
Tr(i,r)=(4*(betar*x*betal*w-betal*betar*z)
/((1-betal*betar*z)**2+(betar*x+betar*w)**2))
!store T in a matrix for each value of r
end do
write(14,*) (Tr(i,r),r=1,n)
end do

end program
!++++++++++++++++++++++++++++++++++++++++++
subroutine inverse(A,C,n)
! adapted from 'Numerical Recipes in Fortran 90, Second Edition (1996)'
implicit none
integer n
double precision A(n,n), C(n,n)
double precision L(n,n), U(n,n), b(n), d(n), x(n)
double precision coeff
integer i, j, k

! step 0: initialization for matrices L and U and b
! Fortran 90/95 allows such operations on matrices
L=0.0
U=0.0
b=0.0

! step 1: forward elimination
do k=1, n-1
do i=k+1,n
coeff=A(i,k)/A(k,k)
L(i,k) = coeff
do j=k+1,n
A(i,j) = A(i,j)-coeff*A(k,j)
end do
end do
end do

! Step 2: prepare L and U matrices
! L matrix is a matrix of the elimination coefficient
! + the diagonal elements are 1.0
do i=1,n
```

```
L(i,i) = 1.0
end do
! U matrix is the upper triangular part of A
do j=1,n
do i=1,j
U(i,j) = A(i,j)
end do
end do

! Step 3: compute columns of the inverse matrix C
do k=1,n
b(k)=1.0
d(1) = b(1)
! Step 3a: Solve Ld=b using the forward substitution
do i=2,n
d(i)=b(i)
do j=1,i-1
d(i) = d(i) - L(i,j)*d(j)
end do
end do
! Step 3b: Solve Ux=d using the back substitution
x(n)=d(n)/U(n,n)
do i = n-1,1,-1
x(i) = d(i)
do j=n,i+1,-1
x(i)=x(i)-U(i,j)*x(j)
end do
x(i) = x(i)/u(i,i)
end do
! Step 3c: fill the solutions x(n) into column k of C
do i=1,n
C(i,k) = x(i)
end do
b(k)=0.0
end do
end subroutine inverse
!++++++++++++++++++++++++++++++++
subroutine outputra(n,A)
implicit none
integer :: n,row,col
real*8 A(n,n)
```

```
character :: reply*1
do row =1,n
write(*,11) (A(row,col),col=1,n)
11 format(100f10.5)
end do
print*,' '
print*,'Hit a key and press enter to continue'
read *,reply
end subroutine outputra
```

C.2 Program to calculate the atom-atom polarizability

```
Program aapolarizability
implicit none
integer ialloc, k,n, NROT,i,E,j,c,b
real :: pi
real*8, pointer :: A(:,:),X(:,:),V(:,:),D(:),Z(:),P(:,:),wksp(:)
integer, pointer :: iwksp(:)

print *,' '
!read size of matrix A
print *, 'what is the dimension of the square matrix?'
read *, n

!allocate memory for A and P
allocate(A(1:n,1:n))
allocate(X(1:n,1:n))
allocate(V(1:n,1:n))
allocate(D(1:n))
allocate(P(1:n,1:n))
allocate(iwksp(1:n))
allocate(wksp(1:n))

!read connectivity matrix A
open(12,file='input pentacene.txt')
do i=1,n
read(12,*) (A(i,j), j=1, N)
end do

call outputra(n,A)

!diagonalization
call Jacobi(A,N,D,V,NROT)
do i=1,n
print *, i,D(i)
end do

call outputra(n,V)
```

```
!sorting of eigenvalues and eigenvectors from low to high value
call sort(n,D,V,wksp,iwksp)

do i=1,n
print *, D(i)
end do

call outputra(n,V)

!writing of output
open(11, file='aapoutput.txt')
do c=1,n
do b=1,n
pi=0.0
do j=1,n/2
do k=(n/2)+1,n
pi=pi-((4*(V(c,j)*V(c,k))*(V(b,j)*V(b,k)))/(D(k)-D(j)))
end do
end do
P(c,b)=pi
print *, c,b,P(c,b)
end do
end do

call outputra(n,P)

do c=1,n
write(11,*) (P(c,b),b=1,n)
11 format(100f10.5)
end do
flush(11)

open(12, file='aappentacene.txt')
do b=1,n
do c=1,n
write(12,*) P(c,b)
end do
end do

END
!+++++++++++++++++++++++++++++++
```

```
!output of matrix A
subroutine outputra(n,A)
implicit none
integer :: n,row,col
real*8 A(n,n)
character :: reply*1
do row =1,n
write(*,11) (A(row,col),col=1,n)
11 format(100f10.5)
end do
print*,’ ’
print*,’Hit a key and press enter to continue’
read *,reply
end subroutine outputra
!++++++++++++++++++++++++++++++++
!diagonalisation through jacobi rotations
! adapted from ’Numerical Recipes in Fortran 90, Second Edition (1996)’
Subroutine Jacobi(A,N,D,V,NROT)
integer N,NROT
real*8 A(1:N,1:N),D(1:N),V(1:N,1:N)
real*8, pointer :: B(:), Z(:)
real*8 c,g,h,s,sm,t,tau,theta,tresh

allocate(B(1:100),stat=ialloc)
allocate(Z(1:100),stat=ialloc)

do ip=1, N !initialize V to identity matrix
do iq=1, N
V(ip,iq)=0.d0
end do
V(ip,ip)=1.d0
end do
do ip=1, N
B(ip)=A(ip,ip)
D(ip)=B(ip)
Z(ip)=0.d0
end do
NROT=0
do i=1, 50
sm=0.d0
do ip=1, N-1 !sum off-diagonal elements
```

```
do iq=ip+1, N
sm=sm+DABS(A(ip,iq))
end do
end do
if(sm==0.d0) return !normal return
if(i.lt.4) then
tresh=0.2d0*sm/n**2
else
tresh=0.d0
end if
do ip=1, N-1
do iq=ip+1, N
g=100.d0*DABS(A(ip,iq))
! after 4 sweeps, skip the rotation if the off-diagonal element is small
if((i.gt.4).and.(DABS(D(ip))+g.eq.DABS(D(ip))) &
.and.(DABS(D(iq))+g.eq.DABS(D(iq)))) then
A(ip,iq)=0.d0
else
if(DABS(A(ip,iq)).gt.tresh) then
h=D(iq)-D(ip)
if(DABS(h)+g.eq.DABS(h)) then
t=A(ip,iq)/h
else
theta=0.5d0*h/A(ip,iq)
t=1.d0/(DABS(theta)+DSQRT(1.d0+theta**2))
if(theta.lt.0.d0) t=-t
end if
c=1.d0/DSQRT(1.d0+t**2)
s=t*c
tau=s/(1.d0+c)
h=t*A(ip,iq)
Z(ip)=Z(ip)-h
Z(iq)=Z(iq)+h
D(ip)=D(ip)-h
D(iq)=D(iq)+h
A(ip,iq)=0.d0
do j=1, ip-1
g=A(j,ip)
h=A(j,iq)
A(j,ip)=g-s*(h+g*tau)
A(j,iq)=h+s*(g-h*tau)
```

```
end do
do j=ip+1, iq-1
g=A(ip,j)
h=A(j,iq)
A(ip,j)=g-s*(h+g*tau)
A(j,iq)=h+s*(g-h*tau)
end do
do j=iq+1, N
g=A(ip,j)
h=A(iq,j)
A(ip,j)=g-s*(h+g*tau)
A(iq,j)=h+s*(g-h*tau)
end do
do j=1, N
g=V(j,ip)
h=V(j,iq)
V(j,ip)=g-s*(h+g*tau)
V(j,iq)=h+s*(g-h*tau)
end do
NROT=NROT+1
end if !if ((i.gt.4)...
end if
end do !main iq loop
end do !main ip loop
do ip=1, N
B(ip)=B(ip)+Z(ip)
D(ip)=B(ip)
Z(ip)=0.d0
end do
end do !main i loop
stop ' 50 iterations !'
return
END
!++++++++++++++++++++++++++++++++++
!creation of an index
! adapted from 'Numerical Recipes in Fortran 90, Second Edition (1996)'
Subroutine indexx(n,arr,indx)
integer :: n,indx(n),M,NSTACK
real*8 arr(n)
parameter (M=25,NSTACK=50)
integer :: i,indxt,ir,itemp,j,jstack,k,l,istack(NSTACK)
```

```
real :: e
do j=1,n
indx(j)=j
end do
jstack=0
l=1
ir=n
1 if(ir-l.lt.M) then
do j=l+1,ir
indxt=indx(j)
e=arr(indxt)
do i=j-1,l,-1
if(arr(indx(i)).le.e)goto 2
indx(i+1)=indx(i)
end do
i=l-1
2 indx(i+1)=indxt
end do
if(jstack.eq.0)return
ir=istack(jstack)
l=istack(jstack-1)
jstack=jstack-2
else
k=(l+ir)/2
itemp=indx(k)
indx(k)=indx(l+1)
indx(l+1)=itemp
if(arr(indx(l)).gt.arr(indx(ir))) then
itemp=indx(l)
indx(l)=indx(ir)
indx(ir)=itemp
end if
if(arr(indx(l+1)).gt.arr(indx(ir))) then
itemp=indx(l+1)
indx(l)=indx(l+1)
indx(ir)=itemp
end if
if(arr(indx(l)).gt.arr(indx(l+1))) then
itemp=indx(l)
indx(l)=indx(l+1)
indx(l+1)=itemp
```

```
end if
i=l+1
j=ir
indxt=indx(l+1)
e=arr(indxt)
3 continue
i=i+1
if(arr(indx(i)).lt.e) goto 3
4 continue
j=j-1
if(arr(indx(j)).gt.e) goto 4
if(j.lt.i) goto 5
itemp=indx(i)
indx(i)=indx(j)
indx(j)=itemp
goto 3
5 indx(l+1)=indx(j)
indx(j)=indxt
jstack=jstack+2
if(jstack.gt.NSTACK) stop 'NSTACK too small in indexx'
if(ir-i+1.ge.j-1)then
istack(jstack)=ir
istack(jstack-1)=i
ir=j-1
else
istack(jstack)=j-1
istack(jstack-1)=1
l=1
end if
end if
goto 1
end Subroutine
!+++++++++++++++++++++++++++++++++
!sorting
! adapted from 'Numerical Recipes in Fortran 90, Second Edition (1996)'
subroutine sort(n,ra,V,wksp,iwksp)
integer :: n,iwksp(n)
real*8 ra(n),rb(n),rc(n),wksp(n),V(n,n),D(n)
integer :: j
call indexx(n,ra,iwksp)
do j=1,n
```

```
wksp(j)=ra(j)
print *, ra(j), iwksp(j)
print *, ’ ’
end do
do j=1,n
ra(j)=wksp(iwksp(j))
end do
do i=1,n
do j=1,n
wksp(j)=V(i,j)
end do
do j=1,n
V(i,j)=wksp(iwksp(j))
end do
end do
return
end subroutine
```

C.3 Program to calculate the linear response current

```
program IVall
implicit none
integer :: n,i,j,r,E,delta
real :: w,x,y,z,T,betal,betar
real*8, pointer :: A(:,:), C(:,:),temp(:,:),K(:)

print *, ’ ’
!read size of matrix A
print *, ’What is the dimension of the square matrix?’
read *, n

!allocate memory for A and C
allocate(A(1:n,1:n))
allocate(C(1:n,1:n))
allocate(temp(1:n,1:n))
allocate(K(1:n))

!read connectivity matrix A
open(12,file=’input anthracene.txt’)
do i=1,n
do j=1,n
read(12,*) A(i,j)
end do
end do

call outputra(n,A)

!save A before inversion
temp=A

open(13,file=’IVoutput.txt’)

do r=1,n
K(r)=0
end do

do delta=0,60
```

```
!set all K(r) to zero
do r=1,n
K(r)=0
end do
!redefine diagonal elements, make a list of all E-values
do E=-delta*50,delta*50
do i=1,n
!scale the energy to beta, just as the other elements of the matrix
temp(i,i)=(E/1000.0)+1.0e-5
end do
A=temp

call inverse(A,C,n)

do r=1,n

!define w as $\frac{\Delta_{s,s}}{\Delta}$, x as $\frac{\Delta_{r,r}}{\Delta}$, y as $\frac{\Delta_{r,s}}{\Delta}$ and z as $\frac{\Delta_{rs,rs}}{\Delta}$
w=C(1,1)
x=C(r,r)
y=C(1,r)
z=(x*w-y**2)
betal=1/1.4
betar=1/1.4
!calculate the transmission
T=(4*(betar*x*betal*w-betal*betar*z)/((1-betal*betar*z)**2+(betar*x+betar*w)**2))
!store T in a matrix for each value of r
K(r)=K(r)+T*0.001
end do
end do
write(13,*) delta/10.0, (K(r),r=1,n)
end do

do r=1,n
print *, r, K(r)
end do

end program
!++++++++++++++++++++++++++++++++++++++++++
subroutine inverse(A,C,n)
! adapted from 'Numerical Recipes in Fortran 90, Second Edition (1996)'
implicit none
```

```
integer n
double precision A(n,n), C(n,n)
double precision L(n,n), U(n,n), b(n), d(n), x(n)
double precision coeff
integer i, j, k

! step 0: initialization for matrices L and U and b
! Fortran 90/95 allows such operations on matrices
L=0.0
U=0.0
b=0.0

! step 1: forward elimination
do k=1, n-1
do i=k+1,n
coeff=A(i,k)/A(k,k)
L(i,k) = coeff
do j=k+1,n
A(i,j) = A(i,j)-coeff*A(k,j)
end do
end do
end do

! Step 2: prepare L and U matrices
! L matrix is a matrix of the elimination coefficient
! + the diagonal elements are 1.0
do i=1,n
L(i,i) = 1.0
end do
! U matrix is the upper triangular part of A
do j=1,n
do i=1,j
U(i,j) = A(i,j)
end do
end do

! Step 3: compute columns of the inverse matrix C
do k=1,n
b(k)=1.0
d(1) = b(1)
! Step 3a: Solve Ld=b using the forward substitution
```

```
do i=2,n
d(i)=b(i)
do j=1,i-1
d(i) = d(i) - L(i,j)*d(j)
end do
end do
! Step 3b: Solve Ux=d using the back substitution
x(n)=d(n)/U(n,n)
do i = n-1,1,-1
x(i) = d(i)
do j=n,i+1,-1
x(i)=x(i)-U(i,j)*x(j)
end do
x(i) = x(i)/u(i,i)
end do
! Step 3c: fill the solutions x(n) into column k of C
do i=1,n
C(i,k) = x(i)
end do
b(k)=0.0
end do
end subroutine inverse
!++++++++++++++++++++++++++++++++
subroutine outputra(n,A)
implicit none
integer :: n,row,col
real*8 A(n,n)
character :: reply*1
do row =1,n
write(*,11) (A(row,col),col=1,n)
11 format(100f10.5)
end do
print*,' '
print*,'Hit a key and press enter to continue'
read *,reply
end subroutine outputra
```

C.4 Program to calculate the unperturbed Green's function

The program that was used to calculate the unperturbed Green's function is exactly the same as the one used to calculate the atom-atom polarizability except for the part where the output is written:

```
...

!writing of output
open(11, file='aapoutput.txt')
do c=1,n
do b=1,n
G0=0.0
do j=1,n
do k=1,n
G0=G0+(V(c,j)*V(c,k)*V(b,j)*V(b,k))/(D(k)*D(j))
end do
end do
P(c,b)=G0
print *, c,b,P(c,b)
end do
end do

call outputra(n,P)

do c=1,n
write(11,*) (P(c,b),b=1,n)
11 format(100f10.5)
end do
flush(11)

END

...
```