MASTER THESIS
Optical properties of pentacene and picene

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14 September 2011
Acknowledgement

I would like to express my gratitude to all those who gave me the possibility to complete this thesis. This work would not have been possible without the support from Prof. Dr. Angel Rubio under whose guidance I chose this topic. I would like to gratefully acknowledge the supervision of my advisor, Dr. Matteo Gatti, who has been abundantly helpful and has assisted me in numerous ways. I specially thank him for his infinite patience. The discussions I had with him were invaluable. I would like to say a big thanks to Dr. Pierluigi Cudazzo, who helped me a lot.
I would like to thank Donostia International Physics Center and the University of the Basque Country for financial supports.
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Chapter 1

Introduction

Organic molecular solids have attracted considerable interest for both fundamental reasons and possible technological applications. In fact they are very promising materials for a wide range of applications [1], as their properties can be efficiently tailored for their use in (opto)electronic devices [2] such as field-effect transistor [3], light-emitting diodes [4][5], photovoltaic cells [6][7], etc. Among the different classes of organic molecular solids, the most studied one in the last years is probably that of the aromatic molecules. The interest for this class of molecular crystals recently increased after the discovery of superconductivity in potassium doped picene and potassium doped coronene at critical temperature \( T_c = 18 \text{ K} \) [8] and 15 K respectively [9].

Since the constituents of molecular solids are molecular units interacting through weak Van der Waals forces their physical properties, as for example dynamical, electronic and optical properties, are to a large extent governed by the individual molecular units [10]. Thus, in principle, by studying the isolated molecule we have access also to the corresponding condensed states.

In this work we present a first-principles study based on density functional theory of the electronic and optical properties of two aromatic molecules namely picene and pentacene. This will be a good starting point for the understanding of the electronic and optical properties of the related molecular crystals.

Aromatic molecules are obtained by combining benzene rings in different ways. In particular picene and pentacene both with molecular formula \( C_{22}H_{14} \) consist of five benzene rings in two different configurations. In pentacene the benzene rings are arranged in a linear manner (Fig. 3.7(a)) while in picene they are arranged in a zigzag manner (Fig. 3.7(b)). Since C atoms present 4 valence electrons (2 in the 2s state and 2 in the 2p state) they form 4 covalent bonds while H atoms only one bond involving their 1s electron. Due to the planar structure in picene and pentacene as well as in benzene, for each carbon atom the s orbital combines with two \( p (p_x, p_y) \) orbitals. The resulting three hybrid orbitals are oriented at 120° angles to each other.
These orbitals are called $sp^2$ hybrid orbitals because they are composed of one $s$ and two $p$ orbitals. If the $sp^2$ orbitals of different C atoms overlap in phase between them or with the H $s$ orbital they interact constructively to form a bonding molecular orbitals. The corresponding electron density results centred along the line connecting the atomic nuclei. This type of bond is called a $\sigma$ bond. When they interact out of phase they give rise to anti-bonding states called $\sigma^*$ state. The remain $p_z$ orbitals (one for each C atoms) combine among them giving the so called $\pi$ bond. The $\pi$ bond is parallel to the line connecting the C nuclei and the related electron density is localized above and below the line connecting the nuclei. The corresponding antibonding states are called $\pi^*$ states. Since the overlap between in-plane atomic orbitals is larger than that between out of plane atomic orbitals, $\sigma$ bonds result stronger than the $\pi$ ones [11]. Thus the electronic structure of picene and pentacene can be described in terms of $\sigma$ states responsible for in plane C-C and C-H bonds and $\pi$ states responsible for out of plane C-C bonds. However being the $\pi$ bonds the weakest, the chemical and optical properties of these molecules are set mainly by $\pi$ and $\pi^*$ states.

The present work is organized as follows: in chapter one we discuss the theoretical tools used in this thesis, namely DFT and TDDFT while in the second chapter we present our results. Here, first we address the structural and electronic properties of picene and pentacene then we focus on their optical properties evaluating the absorption spectra with two different method: performing time propagation and solving the Casida equation. The last chapter is devoted to our conclusions.
Chapter 2

Theory

2.1 DFT

The first goal is to find the ground state of the molecules. In fact, by knowing
the ground state we can obtain the atomic structure of the molecules, and the
electronic properties (the orbital wavefunctions and energies). Moreover, the
ground state of the system will be the starting point to employ perturbation
theory (see sec. (2.2.5)) to study the optical response.

In order to find the ground state of a system of M atoms (with N elec-
trons), one has to solve the Schrödinger equation:

\[ H \Psi(r_1, \ldots, r_N, R_1, \ldots, R_M) = E \Psi(r_1, \ldots, r_N, R_1, \ldots, R_M), \quad (2.1) \]

and obtain the eigenstate \( \Psi_0 \) corresponding to the lowest eigenvalue \( E_0 \). In
atomic units (\( e = m = \hbar = 1 \)), the non-relativistic Hamiltonian for the
electrons and the nuclei of mass \( M_I \), is:

\[
H = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \frac{1}{2} \sum_{I=1}^{M} \nabla_I^2 + \frac{1}{2} \sum_{i\neq j=1}^{N} \frac{1}{|r_i - r_j|} \\
- \sum_{iI} \frac{Z_I}{|r_i - R_I|} + \frac{1}{2} \sum_{I\neq J} \frac{Z_I Z_J}{|R_I - R_J|}, \quad (2.2)
\]

where the index \( i \) runs over electrons and \( I \) runs over nuclei. These are just
the kinetic terms of nuclei and electrons, plus the instantaneous Coulomb
interaction between all pairs of bodies.

One of the first proposal to solve Eq. (2.1) was published in 1927 by
Max Born and Julius Robert Oppenheimer. They observed that the nuclei
in the system move much slower than the electrons because they are more
massive [12]. From this, they assumed that the electrons are following the
slow motion of the nuclei. For each fixed ionic configuration, they are in
their ground state. The total wavefunction \( \Psi(r_1, \ldots, r_N, R_1, \ldots, R_M) \) is
decoupled in the product of an electronic wavefunction and a ionic wavefunction. The ionic coordinates appear as given parameters in the electronic Hamiltonian. Thus, the electronic Hamiltonian reduces to [13]

\[
H = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j=1}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{iL} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}.
\] (2.3)

Even in the Born-Oppenheimer approximation, solving the electronic problem (2.3) remains a formidable task. A possible strategy of solution is to formulate a trial wavefunction and solve the Hamiltonian (2.3) with this trial wavefunction.

In 1928, the british physicist Douglas Rayner Hartree proposed a product of the single-electron wavefunctions as the solution of the many-body Hamiltonian in a self-consistent way. This method is known as Hartree approximation [14]. The wave function in Hartree approximation is simply:

\[
\Psi_{\text{Hartree}}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\cdots\psi_N(\mathbf{r}_N) \quad \text{(2.4)}
\]

Two years later the russian physicist Vladimir Aleksandrovich Fock modified the Hartree’s method by allowing the wavefunction to be represented by a Slater determinant [15]. This approach is commonly known as the Hartree-Fock method (HF). The trial wavefunction \(\Psi_{HF}\) is antisymmetric with respect to the interchange of both spin and space coordinates of any two electrons.

\[
\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \cdots & \psi_N(\mathbf{r}_1) \\
\psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \cdots & \psi_N(\mathbf{r}_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(\mathbf{r}_N) & \psi_2(\mathbf{r}_N) & \cdots & \psi_N(\mathbf{r}_N)
\end{vmatrix} \quad \text{(2.5)}
\]

In the Slater determinant, exchanging the coordinates of two electrons is the same as exchanging two rows, with a resulting change in the sign. Because of this property of a Slater determinant, the basic antisymmetric property of the wavefunction related with its fermionic nature is conserved.

The introduction of the antisymmetric principle in the wavefunction allowed an improved description of the total electronic energy, because the exchange energy effect is considered. However, in many problems in physics this term is not enough to predict the properties of a electronic system. This method does not take in account the fact that the motion of a single electron affects the motion of all other electrons in the system. The missed term in the total energy is called as correlation energy. A way of taking into account correlation effects is called configuration interaction, in which
2.1. DFT

the many body wavefunction is expressed as a linear combination of Slater determinants.

These approaches are all based upon improving the trial wavefunctions. In the configuration interaction method, the combination of wavefunctions soon becomes very complicated, resulting in severe limiting of the size of problems, that can be treated.

Another and very different approach called the density functional theory (DFT) has been proposed. DFT is the practical first-principles scheme that is employed in the calculation of the ground-state properties. DFT is a minimum-information theory. Instead of dealing with the many-body wavefunction \( \Psi(r_1, ..., r_N) \), DFT leads to calculate directly the simplest quantity, i.e. the electronic density, that one needs in order to have access to the ground-state properties. The correlation effect is taken into account, and the size of the system which can be handled is far larger. Since 1980, this method has established a position as one of the main tools of calculating the properties of solid and molecules.

2.1.1 The Hohenberg-Kohn theorems

Density-functional theory is based upon two theorems first proved by Hohenburg and Kohn in 1964. The Hohenberg and Kohn theorems prove that, for a system with a nondegenerate ground state [16], the ground-state energy of electrons is a unique functional of the electron density. Furthermore, given an external potential, it is shown that the ground-state energy can be obtained by minimizing the energy functional, with respect to the electron density. When the density is the true ground-state electron density, this minimizes the energy functional. Their results can be summarized as follows:

- The first theorem states that, for a system with a nondegenerate ground state, there exists a one-to-one correspondence, up to an additive constant, between the ground-state density and the static external potential \( V_{\text{ext}}(r) \). Since there is also a one-to-one correspondence between the external potential and the ground-state many-body wavefunction \( \Psi \), \( \Psi \) can be written as a function of the density \( \Psi[n(r)] \).

- The second theorem states that a universal functional for energy \( E[n] \) in terms of the density \( n(r) \) can be defined, valid for any external potential \( V_{\text{ext}}(r) \). For any particular \( V_{\text{ext}}(r) \), the exact ground state energy of the system is the global minimum value of this functional, and the density \( n(r) \) that minimizes the functional is the exact ground state density \( n_0(r) \).

The functional \( E[n] \) alone is sufficient to determine the exact ground state energy and density. In general, excited states of the electrons must be determined by other means.
The Hohenberg-Kohn theorem is valid only for the densities that are the ground state of some potential. These densities are called $V$-representable. While the $V$-representability condition assesses the existence of the one-to-one mapping between density and $V_{\text{ext}}$, the Hohenberg-Kohn theorem establishes its uniqueness. In the worst case, the potential has degenerate ground states such that the given density is representable as a linear combination of the degenerate ground-state densities (the density is then called ensemble-$V$-representable) \cite{17}.

The Hohenberg-Kohn theorem has been then generalized in many ways: to cases where the ground states is degenerate, or where the system is spin-polarized, to relativistic DFT \cite{18}, to multicomponent DFT, to DFT for superconductors \cite{19}, and so on.

### 2.1.2 The Kohn-Sham method

In a subsequent paper by Kohn and Sham \cite{20}, it is shown that the energy functional can be recast by using one particle orbitals as $E_{\text{KS}}[\{\Phi_i\}]$. The one-electron wavefunctions $\Phi_i(r)$ are moreover subjected to the orthogonalization condition.

\[
E_{\text{KS}}(\{\Phi_i\}) = -\frac{1}{2} \sum_i k_i \int \Phi_i(r) \nabla^2 \Phi_i(r) d^3r + \int n(r) V_{\text{ion-electron}} d^3r + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' + \epsilon_{\text{xc}}[n(r)] \tag{2.6} \]

where the $i$-summation takes over all one-electron orbitals, $k_i$ is the number of occupations in $i$-state, $E_{\text{xc}}$ the exchange energy, and $n(r)$ is the electronic density. It is given by

\[
n(r) = \sum_{i}^{\text{occ}} |\Phi_i(r)|^2. \tag{2.7} \]

The wavefunctions $\Phi_i$ which minimize the Kohn-Sham functional energy in Eq. (2.6) satisfy the following eigenvalue equations,

\[
H_{\text{KS}} \Phi_i(r) = \epsilon_i \Phi_i(r), \tag{2.8} \]

where $H_{\text{KS}}$ is Kohn-Sham Hamiltonian,

\[
H_{\text{KS}} = -\frac{1}{2} \nabla^2 + V_{\text{ion-electron}}(r) + V_H(r) + V_{\text{xc}}(r). \tag{2.9} \]

Here, $V_H(r)$ is the Hartree potential

\[
V_H(r) = \int \frac{n(r')}{|r-r'|} d^3r', \tag{2.10} \]
2.1. **DFT**

$V_{xc}(\mathbf{r})$ is the exchange correlation potential

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}, \quad (2.11)$$

and

$$V_{\text{electron-ion}}(\mathbf{r}) = \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \quad (2.12)$$

is the electron-ion interaction (see Eq. (2.3)). $\varepsilon_i$ and $\Phi_i$ denote the eigenvalues and eigenfunctions of the Kohn-Sham equation, respectively. The wavefunctions calculated by Eq. (2.8) yield the charge density by Eq. (2.7). Hence, the Kohn-Sham equation must be solved self-consistently. It seems that Eq. (2.8) plays a role of Schrödinger equation of one-electron wavefunction, but the idea underlying these equation is quite different. While in Hartree, Hartree-Fock, or configuration interaction the key variable is the many body wavefunction $\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$ and the ground-state is found by solving the many body Hamiltonian (2.3), in DFT the key variable is the much simpler electronic density $n(\mathbf{r})$ and the ground-state energy is found by minimizing the energy functional or, equivalently, by solving the Kohn-Sham equations. However, the Kohn-Sham orbitals and energies do not have a physical meaning. The Slater determinant obtained using Kohn-Sham orbitals is different from the Slater determinant that is the solution of the Hartree-Fock equations.

### 2.1.3 Local Density Approximation

A price of mathematical simplification of the density functional method, which replaces the many-electronic problem by one-electron problem is paid by introducing an unknown functional of exchange and correlation $E_{xc}$ of the charge density. Fortunately, there is a simple approximation for $E_{xc}$. The most widely used form of $E_{xc}$ is the so-called local density approximation (LDA). The true system is locally (that is for every point $\mathbf{r}$) approximated by a homogeneous electron gas of density $n = n(\mathbf{r})$. Thus the exchange-correlation energy becomes:

$$E_{xc}^{\text{LDA}}[n] = \int n(\mathbf{r}) \varepsilon_{xc}^{\text{HEG}}(n(\mathbf{r})) d^3 \mathbf{r}, \quad (2.13)$$

where $\varepsilon_{xc}^{\text{HEG}}(n(\mathbf{r}))$ is the exchange-correlation energy per electron in a homogeneous electron gas of density $n$ [20]. This equation is, by construction, exact for the homogeneous electron gas and we can expect it to work well for systems where the density has small spatial variations, or where the electron-electron interaction is well-screened.

The domain of applicability of LDA has been unexpectedly found to go much beyond the nearly-free electron gas and accurate results can be obtained for inhomogeneous systems like atoms or molecules.
2.1.4 Pseudopotential approximation

In order to solve the Kohn-Sham equations on a computer, a possibility is to represent them on a discrete grid of points in space. A limitation to this approach is given by the fact that the electron-ion interaction Eq. (2.12) is rapidly varying on a very short scale length. These rapid variations are mostly due to the interactions with core electrons, which are more tightly bound to the ionic cores than valence electrons. Fortunately, the physical and chemical characteristics of many materials are governed by the valence electrons which extend to more wide region, and the core states are insensitive to those properties. Then, we can make an approximation by using valence electrons solely in describing the chemical combining characters of materials. Therefore, needed potentials have relatively slowly varying characters. The electron-ion interaction is then expressed by means of slowly varying “pseudopotentials”. In the norm-conserving pseudopotential formalism, the corresponding valence wavefunctions (called “pseudowavefunctions”) match the true all electron ones outside a cutoff radius $R_c$. The process is sketched in Fig. (2.1).
2.2 Time Dependent Density Functional Theory

As I said before, with DFT we can calculate the ground-state properties of a system. However, to simulate absorption, we need to deal with time-dependent external potentials. The description of time-dependent phenomena was incorporated properly into a density functional framework by Runge and Gross, who generalized the Hohenberg-Kohn theorem to time-dependent densities and potentials, establishing the time dependent density functional theory (TDDFT) [21].

Now we should solve the time-dependent Schrödinger equation

\[ \frac{i}{\partial t} \Psi(r_1, \ldots, r_N, t) = H(r_1, \ldots, r_N, t) \Psi(r_1, \ldots, r_N, t). \]  

(2.14)

The only difference between the Hamiltonian in Eq. (2.3) is that we have time-dependent external potential \( V_{\text{ext}}(r, t) \) in the Hamiltonian. The time-dependent Schrödinger equation is a first order differential equation in time, therefore, the initial value \( \Psi(r, t_0) \) must be given. In the present case, it will always be the ground-state.

2.2.1 The Runge-Gross theorem

The theorem was published by Erich Runge and Eberhard K. U. Gross in 1984 [22]. It states that two densities \( n(r, t) \) and \( n'(r', t') \) evolving from a common initial state \( \Psi(r, t_0) \) under the influence of two potentials \( V_{\text{ext}}(r, t) \) and \( V'_{\text{ext}}(r, t) \), both Taylor-expandable about the initial time \( t_0 \), eventually differ if the potentials differ by more than a purely time-dependent function, \( V_{\text{ext}}(r, t) - V'_{\text{ext}}(r, t) \neq C(t) \). So, there is a one to one correspondence between the time-dependent external potential, \( V_{\text{ext}}(r, t) \), and the time-dependent electron density, \( n(r, t) \) for a fixed initial state [22] [21].

2.2.2 Time-Dependent Kohn-Sham Theory

According to the Runge-Gross theorem there is a one to one correspondence between the potential and the density. This can be seen as a generalization of the Hohenberg-Kohn theorem for electronic ground states. The density of the interacting system can be reproduced by the non-interacting time-dependent Kohn-Sham orbitals

\[ n(r, t) = \sum_{\text{occ}} |\Phi_i(r, t)|^2, \]  

(2.15)

where the orbitals \( \Phi_i(r) \) satisfy the time-dependent Kohn-Sham equations

\[ i \frac{\partial}{\partial t} \Phi_i(r, t) = \left[ -\frac{\nabla^2}{2} + V_{\text{KS}}[n](r, t) \right] \Phi_i(r, t). \]  

(2.16)
The Kohn-Sham potential is conventionally separated in the following way

\[ V_{KS}[n](r,t) = V_{ext}(r,t) + V_{Hartree}[n](r,t) + V_{xc}[n](r,t). \] (2.17)

With respect to Kohn-Sham DFT, all the potentials become here time-dependent. The potential \( V_{xc} \) is a functional of the density \( n(r,t) \). This means that in principle to obtain \( V_{xc} \) at given \( \bar{r} \) and \( \bar{t} \) one needs to know the density at all the points \( r \) and times \( t < \bar{t} \). The exact expression of \( V_{xc} \) as a functional of the density is unknown. At this point we are obliged to perform an approximation [21][23][24].

2.2.3 xc functionals

**Adiabatic approximations** In adiabatic approximations, we neglect the dependence on the past. The approximate \( V_{xc}(r,t) \) only depend on the density at time \( t \). We can use \( V_{xc}^{\text{static}}[n](r) \) evaluated at \( n = n(r,t) \) to obtain \( V_{xc}^{\text{adiabatic}}(r,t) \).

By inserting the LDA functional in \( V_{xc}^{\text{adiabatic}}(r,t) \) we obtain the so-called adiabatic local density approximation (ALDA)

\[ V_{xc}^{ALDA}(r,t) = V_{xc}^{\text{HEG}}(n)|_{n=n(r,t)}. \] (2.18)

The ALDA assumes that the xc potential at the point \( r \), and time \( t \) is equal to the xc potential of a (static) homogeneous-electron gas (HEG) of density \( n(r,t) \).

2.2.4 DFT vs TDDFT

We now compare DFT with TDDFT:

1. DFT is based on the Hohenberg-Kohn theorem while, TDDFT is based on the Runge-Gross theorem. They both establish a one-to-one correspondence between densities and external potentials. The key variable is in both cases the density. Additionally, in TDDFT the initial conditions must be given.

2. In DFT, the ground-state of the system can be determined through the minimization of the total energy functional

\[ \langle \Phi | \hat{H} | \Phi \rangle = E[n]. \] (2.19)

In TDDFT, there is no variational principle on the basis of the total energy for it is not a conserved quantity. There exists the quantum
2.2. TIME DEPENDENT DENSITY FUNCTIONAL THEORY

mechanical action

\[
\int_{t_0}^{t_1} dt \langle \Phi(t)|i\partial_t - \hat{H}(t)|\Phi(t)\rangle = A[n]. \tag{2.20}
\]

Equating the functional derivative of Eq. (2.20) in terms of \(n(r,t)\) to zero we arrive at the time-dependent Schrödinger equation. We can therefore solve the time-dependent problem by calculating the stationary point of the functional \(A[n]\).

In DFT, equating the functional derivative of Eq. (2.19) in terms of \(n(r)\) to zero we arrive at the minimum of \(E[n]\). In TDDFT, there is no “minimum principle”, but only a “stationary principle”.

3. In DFT, the density just depends on the space coordinate \(n(r) = \sum_{i=1}^{N} |\Phi_{KS}i(r)|^2\). In TDDFT, the density depends on the time and space coordinates \(n(r,t) = \sum_{i=1}^{N} |\Phi_{KS}i(r,t)|^2\).

The same difference holds for the potentials. \(V_{KS}\) in DFT

\[
V_{KS}(r) = V_{ext}(r) + \int dr' \frac{n(r')}{|r-r'|} + \frac{\delta E_{xc}[n]}{\delta n(r)}, \tag{2.21}
\]

while in TDDFT

\[
V_{KS}(r,t) = V_{ext}(r,t) + \int dr' n(r',t) \frac{1}{|r-r'|} + \frac{\delta A_{xc}[n]}{\delta n(r,t)}. \tag{2.22}
\]

4. In DFT, the static Schrödinger equation is a second order differential equation in the space coordinates. It can be formulated as an eigenvalue problem.

\[
H_{KS}(r)\Phi_{KS}i(r) = \varepsilon_{KS}i\Phi_{KS}i(r). \tag{2.23}
\]

In contrast, in TDDFT, the time-dependent Schrödinger equation is a first-order differential equation in the time coordinate. The wavefunction (or the density) thus depends on the initial state, which implies that the Runge-Gross theorem can only hold for a fixed initial state (and that the xc potential depends on that state) [25][23]. In our case, we will neglect this initial state dependence, because the initial state will always be the ground state.

2.2.5 Linear response theory

We are interested in calculating electronic excitations of our system. Two regimes can be observed: If the time-dependent potential in respect to the internal interactions is weak, it is sufficient to resort to linear-response theory to study the system. In this way it is possible to calculate, e.g. optical absorption spectra. On the other hand, if the time-dependent potential is
strong, a full solution of the Kohn-Sham equations is required. A canonical example of this regime is the treatment of atoms or molecules in strong laser fields. In this case, TDDFT is able to describe nonlinear phenomena like high-harmonic generation, or multi-photon ionization. Here I will limit the discussion to the linear response aspect, the particular focus being on electronic excitation [23]. Where the external time-dependent potential is weak, perturbation theory may prove sufficient to determine the behaviour of the system. We will focus on the linear change of the density, that allows us to calculate, e.g., the optical absorption spectrum.

We start with a system in its ground state and assume that for \( t < t_0 \) the time-dependent potential is zero. At \( t_0 \) add a small perturbation \( \delta V_{\text{ext}} \). Due to this perturbation the density of the system evolves differently than in the unperturbed system which would remain unchanged. Since the perturbation is small the change in the density is also small

\[
n(r, t) = n_{gs}(r) + \delta n(r, t)
\]  

(2.24)

The first order variation of the density in frequency space is

\[
\delta n(r, \omega) = \int \frac{\delta n(r, \omega)}{\delta V_{\text{ext}}(r', \omega)} |_{n_{gs}} \frac{\delta V_{\text{ext}}(r', \omega)}{\chi(r, r', \omega)}.
\]  

(2.25)

The quantity \( \chi \) is the linear density-density response function of the system.

We recall that in the time-dependent Kohn-Sham framework, the density of the interacting system of electrons is obtained from a fictitious system of non-interacting electrons. The Kohn-Sham system has to produce the same change in the density by changing the Kohn-Sham potential, i.e.

\[
\delta n(r, \omega) = \int \frac{\delta n(r, \omega)}{\delta V_{\text{Kohn-Sham}}(r', \omega)} |_{n_{gs}} \frac{\delta V_{\text{Kohn-Sham}}(r', \omega)}{\chi_{\text{Kohn-Sham}}(r, r', \omega)}.
\]  

(2.26)

Note that the response function that enters Eq. (2.26), \( \chi_{\text{Kohn-Sham}} \), is the density response function of a system of non-interacting electrons and is, consequently, much easier to calculate than the full interacting \( \chi \). In terms of the unperturbed stationary Kohn-Sham orbitals it reads :

\[
\chi_{\text{Kohn-Sham}}(r, r', \omega) = \lim_{\eta \to 0^+} \sum_{jk} \frac{\Phi_j(r)\Phi_j^*(r')\Phi_k(r')\Phi_k^*(r)}{\omega - (\epsilon_j - \epsilon_k) + i\eta},
\]  

(2.27)

where \( f_m \) is the occupation number of the m orbital in the Kohn-Sham ground-state. The \( \delta V_{\text{Kohn-Sham}} \) that enters Eq. (2.26) can be calculated explicitly from the definition of the Kohn-Sham potential

\[
\delta V_{\text{Kohn-Sham}}(r, t) = \delta V_{\text{ext}}(r, t) + \delta V_{\text{Hartree}}(r, t) + \delta V_{\text{xc}}(r, t).
\]  

(2.28)
It is useful to introduce the exchange-correlation kernel, \( f_{xc} \), defined by
\[
f_{xc}(r, r', \omega) = \frac{\delta V_{xc}(r, \omega)}{\delta n(r', \omega)}, \tag{2.29}
\]
and to remind that
\[
\delta V_{\text{Hartree}}(r, \omega) = \int dr' \frac{1}{|r - r'|} \delta n(r', \omega). \tag{2.30}
\]

Combining the previous results, in frequency space we arrive at:
\[
\delta n(r, \omega) = \int d^3r' \chi_{KS}(r, r', \omega) \delta V_{\text{ext}}(r', \omega) \\
+ \int d^3r_1 d^3r' \chi_{KS}(r, r_1, \omega) \left[ \frac{1}{|r_1 - r'|} + f_{xc}(r_1, r', \omega) \right] \delta n(r', \omega). \tag{2.31}
\]

From Eq. (2.25) and Eq. (2.31) follows the relation
\[
\chi(r, r', \omega) = \chi_{KS}(r, r', \omega) + \\
\int d^3r_1 \int d^3r_2 \chi_{KS}(r, r_1, \omega) \left[ \frac{1}{|r_1 - r_2|} + f_{xc}(r_1, r_2, \omega) \right] \chi(r_2, r', \omega). \tag{2.32}
\]

This equation is a formally exact representation of the linear density response in the sense that, if we possessed the exact \( f_{xc} \) a solution of (2.32) would yield the response function, \( \chi \), of the interacting system. If \( \omega \) is equal to a transition frequency of our system the change in the density is dramatic and \( \chi \) has a pole. \( \chi_{KS} \) has its instead poles at the transition frequencies of the KS system.

The main ingredient in linear response theory is the xc kernel. \( f_{xc} \) as expected, is a very complex quantity that includes - or, in other words, hides - all non-trivial many-body effects. Many approximate xc kernels have been proposed in the literature over the past years. The most ancient, and certainly the simplest is the ALDA kernel
\[
f_{xc}^{\text{ALDA}}(rt, r't') = \delta(r - r') \delta(t - t') f_{xc}^{\text{HEG}}(n)|_{n=n(r)}, \tag{2.33}
\]
where
\[
f_{xc}^{\text{HEG}}(n) = \frac{d}{dn} \chi_{xc}^{\text{HEG}}(n) \tag{2.34}
\]
is just the derivative of the xc potential of the homogeneous electron gas. The ALDA kernel is local both in the space and time coordinates [23].
2.2.6 Casida’s equations

Casida has reformulated the calculation of the poles (namely the transition energies) of the response function $\chi$ into a generalized Hermitian eigenvalue problem [26]. Casida showed that, for real orbitals, finding the poles of $\chi$ is equivalent to solving the eigenvalue problem:

$$
\sum_{q'} \tilde{\Omega}_{qq'}(\omega)V_{q'} = \tilde{\omega}_q^2 V_q,
$$

(2.35)

where $q$ is a double index, representing a transition from occupied KS orbital $j$ to unoccupied KS orbital $k$, $\omega_q = \varepsilon_k - \varepsilon_j$, and $\varphi_q(r) = \Phi_j(r)\Phi_k(r)$. The matrix is

$$
\tilde{\Omega}_{qq'}(\omega) = \delta_{qq'}\omega_q^2 + 2\sqrt{\omega_q\omega_{q'}}\langle q|f_{Hxc}(\omega)|q' \rangle,
$$

(2.36)

where

$$
\langle q|f_{Hxc}(\omega)|q' \rangle = \int d^3r \int d^3r' \varphi_q(r)f_{Hxc}(r,r',\omega)\varphi_{q'}(r').
$$

(2.37)

In this equation, $f_{Hxc}$ is the Hartree-exchange-correlation kernel, $1/|r - r'| + f_{xc}(r,r',\omega)$. In the special case of an adiabatic approximation, these equations are a straightforward matrix equation [27].

The eigenvalues $\tilde{\omega}_q$ of Eq. (2.35) yields the excitation energies and the eigenvectors of the Casida’s equation $V_q$ can be used to extract the strength of the response to the external field and to obtain the cross-section tensor, which is proportional to imaginary part of polarizability:

$$
\sigma(\omega) = \frac{4\pi\omega}{c} \text{Im} \alpha(\omega).
$$

(2.38)

And finally the optical absorption spectrum can be given as the “strength function”, which is [28]:

$$
S(\omega) = \frac{c\sigma(\omega)}{2\pi^2}.
$$

(2.39)

2.2.7 Electronic excitations by means of time-propagation

Equivalently, the calculation of the electronic excitations such as the dynamical polarizability can be performed by propagating in real time the Kohn-Sham equation. This methodology does not require the calculation of unoccupied KS states, and scales well with the size of the system, and is thus our preferred scheme for large systems. Let us recall the essentials of this formulation. We will restrict hereafter to electrical dipole perturbations:

$$
\delta V_{ext}(r,\omega) = -x_jk(\omega).
$$

(2.40)
This defines an electrical perturbation polarized in the direction $j$: $\delta E(\omega) = k(\omega) \hat{e}_j$. The response of the system dipole moment in the $i$ direction

$$\delta \langle \hat{X}_i \rangle(\omega) = \int d^3 r x_i \delta n(r, \omega)$$

(2.41)

is then given by:

$$\delta \langle \hat{X}_i \rangle(\omega) = -k(\omega) \int d^3 r \int d^3 r' x_i \chi(r, r', \omega) x'_j.$$  

(2.42)

We may define the dynamical dipole polarizability $\alpha_{ij}(\omega)$ as the quotient of the induced dipole moment in the direction $i$ with the applied external electrical field in the direction $j$, which yields:

$$\alpha_{ij} = -\int d^3 r \int d^3 r' x_i \chi(r, r', \omega) x'_j.$$  

(2.43)

The dynamical polarizability elements may then be arranged to form a second-rank symmetric tensor, $\alpha(\omega)$. The cross-section tensor is proportional to its imaginary part:

$$\sigma(\omega) = \frac{4\pi\omega}{c} \Im \alpha(\omega).$$  

(2.44)

We consider a sudden external perturbation at $t = 0$ (delta function in time), which means $k(\omega) = k$, equal for all frequencies. This perturbation is applied along a given polarization direction, say $\hat{e}_j$. By propagating the time-dependent Kohn-Sham equations, we obtain the density $\delta n(r, \omega)$ and $\delta \langle \hat{X}_i \rangle(\omega)$ through Eq. (2.41). The polarizability element $\alpha_{ij}$ may then be calculated via [29]:

$$\alpha_{ij} = -\frac{\delta \langle \hat{X}_i \rangle(\omega)}{k} = -\frac{1}{k} \int d^3 r x_i \delta n(r, \omega).$$  

(2.45)
Chapter 3

Results

3.1 Ground state properties

3.1.1 Convergence study

We want to solve Kohn-Sham equation (2.8)

\[-\frac{1}{2}\nabla^2 + V_{\text{ion-electron}}(r) + V_H(r) + V_{xc}(r)\] \(\Phi_i(r) = \epsilon_i \Phi_i(r). \quad (3.1)\]

In principle the quantities that appear in Eq. (3.1) are defined for a continuous set of infinite points. However, we cannot deal with an infinite number of points on a computer. To implement Eq. (3.1) on a computer we have two possibilities. We can either expand the functions on a basis and truncate the expansion in a finite number of basis elements.

Or we can represent the wavefunction on a discrete and finite grid of points. In both cases we introduce an error which we can control by doing a convergence analysis. Octopus uses the grid representation. So we need to check that the grid is accurate with respect to its spacing and its extension, and at the same time we should balance the accuracy with the time that the calculation takes to run.

So we have to study the convergence of the results with respect to two parameters: first the grid spacing (i.e. the distance between mesh points) and second the radius of the simulation box that contains the molecule.

Convergence with respect to grid spacing

As I said before, we need to check that the grid is accurate for the spacing. And here spacing means the spacing between the points in the mesh.

We run the Octopus for different spacing and for each of them we calculate the total energy of the molecules.

For pentacene we have the results in Fig. (3.1). We can see that for spacings smaller than 0.12 Å, we have very small error. For example the
difference between 0.12 Å and 0.10 Å spacing is about 0.18 eV. It is very small with respect the energy: only 0.005% of the energy. And in addition, the time of the calculation is important. So, we choose 0.12 Å spacing for calculation of pentacene.

We do the same calculation for picene. We can see the result in Fig. (3.2). We can see that the suitable spacing for picene is the same as for pentacene.

We can compare the results for picene and pentacene in Fig. (3.3). The spacing just depends on a type of atoms that compose the molecules. In fact it depends on the pseudopotential. So for picene and pentacene we have the same suitable spacing that is equal to 0.12 Å.
Convergence with respect to box radius

For our calculation we need a finite space around the molecule, for this we choose a box and we should sure that the size of the box is suitable. So, we should try to do the calculation and try to converge with respect to radius of the simulation box.

We run the Octopus for different size of the simulation box and for each of them we calculate the total energy of the molecules. For pentacene we have the results in Fig. (3.4). We can see that for radius bigger than 4 Å, we have very small error. For example the difference between 4 Å and 5 Å radius is about 0.01 eV. It is very small with respect the energy: only $3 \times 10^{-4}$% of the energy. And in addition, the time of the calculation is important. So, we choose 4 Å radius for the calculation on pentacene.
CHAPTER 3. RESULTS

We do the same calculation for picene. We can see the result in Fig. (3.5). We can see that the suitable radius for picene is the same as for pentacene.

![Figure 3.5: Convergence with radius of box for picene](image)

We can compare the results for picene and pentacene in Fig. (3.6). The radius of the simulation box just depends on the type of atoms that compose the molecules. In fact it depends on the pseudopotential. So for picene and pentacene we have the same suitable radius that is equal to 4 Å.

3.1.2 Structural optimisation

First of all I obtained the molecular structures of picene and pentacene by assembling 5 benzene rings, in a zigzag and a linear configuration, respectively. I tried to optimise these structures to find the ground state.

As I said before in section (2.1), in order to find the ground state of a system we should solve the Schrödinger equation (2.1). According to the
3.1. GROUND STATE PROPERTIES

Born-Oppenheimer approximation, for each fixed ionic configuration, electrons are in their ground state. Within the DFT framework we can calculate the ground-state electronic energy $E(R_1, \ldots, R_M)$, where the ionic positions appear as parameters. We want to minimize $E$ as a function of ionic positions in order to find the ground-state geometry of the molecules. Different algorithms exist to find the minimum of $E(R_1, \ldots, R_M)$.

I found that the minimisation was very slow. For this reason, we decided to use the structures that appear in the (American) National Institute of Standard and Technology (NIST) website. From (http://webbook.nist.gov/cgi/cbook.cgi?Str3File=C135488) for pentacene and for picene from (http://webbook.nist.gov/cgi/cbook.cgi?ID=213-46-7).

In Fig. (3.7(a)) and Fig. (3.7(b)) we show the optimisation structures of pentacene and picene. As can be inferred from Fig. (3.7(a)), pentacene is symmetric with respect

![Figure 3.7: Optimisation structure (a) optimisation structure of pentacene (b) optimisation structure of picene (c) structure of benzene](image-url)
to the $xy$, $xz$, and $yz$ planes. While picene (see Fig. 3.7(b)) is symmetric only with respect to the $yz$ and $xy$ plane. Thus picene has fewer symmetries than pentacene.

Now, we compare C–C and C–H bond lengths in pentacene, picene, and benzene. All C–H bond lengths in picene, pentacene, and benzene are equal to 1.10 Å. All C–C bond lengths in benzene are equal to 1.40 Å, but in picene and pentacene we can see different bond lengths. For instance, we compare the C–C bond lengths in the middle rings for pentacene and picene. One could expect that the bond lengths of C–C atoms 6–7 in picene is equal to 7–16 in pentacene, we can see the bond length of 6–7 in picene is equal to 1.36 Å but 7–16 in pentacene is equal to 1.43 Å. Another example is bond length of C atoms 5–6 in picene and 7–6 in pentacene. We can see the bond length of 5–6 in picene is equal to 1.42 Å and 7–6 in pentacene is equal to 1.40 Å. So, we can see that we have different bond lengths in pentacene and picene.

### 3.1.3 Kohn-Sham orbitals and energy levels

We know that we have 22 Carbon atoms and 14 Hydrogen atoms in both picene and pentacene. Each Carbon atom has 4 valence electrons and each Hydrogen atom has one valence electron. So we have 102 valence electrons. According to the Pauli exclusion principle, in each state we have 2 electrons. So, we have 51 occupied orbitals. Since π states are linear combinations of $p_z$ atomic orbitals, their number is set by the number of carbon atoms. So that for the two molecules we have 11 π states. The other 40 states present σ character. We know that σ states have lower energy than π states. We write the results of the energy of some states in Table (3.1). From $i = 1$ to $i = 40$ we have the σ states, from $i = 41$ to $i = 51$ we have π states, from $i = 52$ to $i = 62$ we have π* states, and the others are σ* states.

In Table (3.2) we write the energy width of the Kohn-Sham levels that belong to each group of states. While the σ states have the different energy width (13.58 eV in pentacene and 13.92 eV in picene), the σ* states present smaller and different energy width (4.25 eV in pentacene and 4.42 eV in picene). The energy width of π states is larger for pentacene than for picene. It is 3.71 eV for π states and 3.95 eV for π* states in pentacene, while it is 2.76 eV for π states and 4.42 eV for π* states in picene.

In Table (3.3) we compare the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in picene and pentacene. In our calculation the HOMO–LUMO energy gap for pentacene is 1.13 eV. We compare it with the data that we find in literature.
### Table 3.1: The Energy of some states of pentacene and picene

<table>
<thead>
<tr>
<th>States</th>
<th>Energy of pentacene (eV)</th>
<th>Energy of picene (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i=1</td>
<td>-22.20</td>
<td>-22.32</td>
</tr>
<tr>
<td>i=40</td>
<td>-8.62</td>
<td>-8.40</td>
</tr>
<tr>
<td>i=41</td>
<td>-8.34</td>
<td>-8.30</td>
</tr>
<tr>
<td>i=50</td>
<td>-5.75</td>
<td>-5.73</td>
</tr>
<tr>
<td>i=51</td>
<td>-4.63</td>
<td>-5.54</td>
</tr>
<tr>
<td>i=52</td>
<td>-3.51</td>
<td>-2.45</td>
</tr>
<tr>
<td>i=53</td>
<td>-2.28</td>
<td>-2.41</td>
</tr>
<tr>
<td>i=61</td>
<td>0.13</td>
<td>0.52</td>
</tr>
<tr>
<td>i=62</td>
<td>0.44</td>
<td>0.53</td>
</tr>
<tr>
<td>i=63</td>
<td>0.49</td>
<td>0.53</td>
</tr>
<tr>
<td>i=64</td>
<td>0.88</td>
<td>0.56</td>
</tr>
<tr>
<td>i=102</td>
<td>4.74</td>
<td>4.95</td>
</tr>
</tbody>
</table>

### Table 3.2: The Energy band of $\sigma$, $\sigma^*$, $\pi$, and $\pi^*$ state

<table>
<thead>
<tr>
<th></th>
<th>Pentacene</th>
<th>Picene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$ band(eV)</td>
<td>13.58</td>
<td>13.92</td>
</tr>
<tr>
<td>$\pi$ band(eV)</td>
<td>3.71</td>
<td>2.76</td>
</tr>
<tr>
<td>$\pi^*$ band(eV)</td>
<td>3.95</td>
<td>2.98</td>
</tr>
<tr>
<td>$\sigma^*$ band(eV)</td>
<td>4.25</td>
<td>4.42</td>
</tr>
</tbody>
</table>

### Table 3.3: HOMO–LUMO energy gap for pentacene and picene

<table>
<thead>
<tr>
<th></th>
<th>Pentacene</th>
<th>Picene</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO–LUMO energy gap (eV)</td>
<td>1.13</td>
<td>3.09</td>
</tr>
</tbody>
</table>
CHAPTER 3. RESULTS

The agreement with other calculations is very good: in Ref. [30] the authors find 1.1 eV and in Ref. [31] they find 1.12 eV. From this comparison, we understand that our calculation is correct.

But when we compare this value with experimental data, we see that this value is about 80% smaller than the experimental value, 5.22 eV [30]. The underestimation of the energy gap is due to two reasons. First, because the Kohn-Sham orbitals have no physical meaning. Second, because when we model $E_{xc}$ using a local density approximation where the system is locally approximated by the homogeneous electron gas of density $n = n(r)$.

The same observation holds for picene. For picene in our calculation the HOMO–LUMO energy gap is 3.09 eV. In Ref. [31] the authors report a value of 2.96 eV. So, again, we conclude that our calculation is correct.

Even though the Kohn-Sham HOMO–LUMO energy gaps underestimate the experimental ones, we can use these results to compare picene with pentacene. Here we can see that the picene HOMO–LUMO gap is much larger than in pentacene.

We show the Kohn-Sham HOMO and LUMO orbital isosurfaces for picene and pentacene in Fig. (3.8(a), 3.8(b), 3.9(a), 3.9(b)), where we take only the positive region of the wavefunctions. From the shape of the wavefunctions we note that the corresponding charge is localized out of the plane of the molecules. This means that these states present π character and are responsible for the out-of-plane C–C bonds. In particular comparing Figs. (3.8(a)) and (3.9(a)) with Figs. (3.8(b)) and (3.9(b)) we clearly identified the HOMO and LUMO orbitals as bonding π states and anti-bonding π* states respectively.

The higher symmetry of the pentacene molecule clearly reflects on the shape of the wave functions. In fact, comparing Fig. (3.9(a)) with Fig. (3.9(b)) we find that in pentacene both HOMO and LUMO orbitals are symmetric with respect to the $yz$ plane while respect to the $xz$ plane they are anti-symmetric and symmetric respectively. On the other hand, for picene (see Fig. (3.8(a)) and (3.8(b))) the HOMO and LUMO orbitals are symmetric and anti-symmetric with respect to the $yz$ plane respectively but they do not have any symmetry respect to the $xz$ plane. Moreover being the HOMO (LUMO) orbitals as well as all the $\pi$ ($\pi^*$) states linear combinations of $p_z$ atomic orbitals they are anti-symmetric respect to the plane of the molecule ($xy$ plane) in both picene and pentacene.

We show in Figs. ((3.9(c)), (3.8(c)), (3.9(d)), (3.8(d))) the orbital isosurface (positive region) for the highest occupied $\sigma$ state and the lowest unoccupied $\sigma^*$ state for both picene and pentacene. Being these states related to the $s$, $p_x$ and $p_y$ atomic orbitals, their charge distribution is strongly localized on the plane of the molecules resulting in the formation of strong C-H bonds and in-plane C-C bonds. A comparison of Fig. (3.8(c)) and (3.9(c)) with Fig. (3.9(d)) and (3.8(d)) clearly reveal the bonding (anti-
bonding) character of the $\sigma$ ($\sigma^*$) states. Finally, contrarily to the $\pi$ ($\pi^*$) states, $\sigma$ ($\sigma^*$) states are symmetric respect the molecular plane.

Figure 3.8: Kohn-Sham orbital for picene (a) Kohn-Sham orbital of the HOMO (b) Kohn-Sham orbital of the LUMO (c) Kohn-Sham orbital of the last $\sigma$ state (d) Kohn-Sham orbital of the first $\sigma^*$ state
Figure 3.9: Kohn-Sham orbital for pentacene (a) Kohn-Sham orbital of the HOMO (b) Kohn-Sham orbital of the LUMO (c) Kohn-Sham orbital of the last $\sigma$ state (d) Kohn-Sham orbital of the first $\sigma^*$ state
3.2 Absorption spectra from time propagation

According to the section (2.2.5), we know that if the time-dependent potential is weak with respect to the internal interactions, we are in the regime of the linear-response approximation.

As we said before in section (2.2.7), our time-dependent external potential is a sudden external perturbation at $t = 0$ (delta function in time). So, first of all we should check the strength of the delta perturbation to be sure that it is not too strong and we can use the linear-response approximation. We call the strength of the delta perturbation TDDeltaStrength. We do the calculation for the TDDeltaStrength is equal to 0.005 (1/Å) and 0.01 (1/Å) for pentacene in one direction. We show the results in Fig. (3.10). We see that both of them have the same absorption spectrum, so we decided to use 0.01 (1/Å) strength.

![Absorption spectrum of pentacene](image)

Figure 3.10: The absorption spectrum for pentacene in one direction for TDDeltaStrength = 0.005 (1/Å) and TDDeltaStrength = 0.01 (1/Å)

3.2.1 Convergence study

We try to converge the absorption spectrum with respect to the calculation parameters. Here we have two important parameters: the first is the time-step for the time propagation (TDTimeStep) while the second one is the number of time-propagation steps (TDMaximumIter). TDMaximumIter is equal to the ratio between the total propagation time (T) and TDTimeStep. So, we need to converge the absorption spectrum with respect to the TDTimeStep and total propagation time.
Convergence with respect to time step

We should choose the suitable length of each time step. Longer time steps are desirable to assure a shorten computational propagation time, but they limits to the maximum frequency we will able to observe. So, we should find the largest value that it is possible without the evolution becomes unstable. For this purpose, we should run the calculation just with the time-evolution of the system, departing from the ground-state, under the influence of no external perturbation. As a consequence if the time step is correct, the electronic system evolve in such a way that the total energy does not change. We do this calculation with the total time propagation equal to 0.1 \( (\hbar/eV) \) and time step equal to 0.002 \( (\hbar/eV) \), 0.0015 \( (\hbar/eV) \), and 0.001 \( (\hbar/eV) \). We found that the total energy of the system is conserved just for the time step equal to 0.001 \( (\hbar/eV) \). So, we chose the time step equal to 0.001 \( (\hbar/eV) \) for our calculation.

For checking that this time step is correct, we did the calculation also in presence of an external perturbation. We did the calculation with external perturbation in one direction with total time propagation equal to 15 \( (\hbar/eV) \), and compare the result for time step equal to 0.001 \( (\hbar/eV) \) with that for time step equal to 0.0005 \( (\hbar/eV) \). In Fig. (3.11) we can see the absorption spectrum for two time steps for pentacene and in Fig. (3.12) for picene. In these two figures, we plot the strength function Eq. (2.39). We can see that we have the same results for both time steps. From these results, we understand that our time step is correct.
3.2. ABSORPTION SPECTRA FROM TIME PROPAGATION

![Absorption spectrum of picene](image)

**Figure 3.12:** The absorption spectrum for two time step (TDTimeStep=0.0005 \((\hbar/eV)\) and TDTimeStep=0.001 \((\hbar/eV)\)) for picene

**Convergence with respect to total propagation time**

Increasing the total propagation time (T) reduces the width of the peaks. We do the calculation for time step equal to 0.001 \((\hbar/eV)\) and \(T=10\) \((\hbar/eV)\), \(T=20\) \((\hbar/eV)\), \(T=25\) \((\hbar/eV)\), \(T=30\) \((\hbar/eV)\), \(T=35\) \((\hbar/eV)\), and \(T=40\) \((\hbar/eV)\). In Fig. (3.13) for pentacene and in Fig. (3.14) for picene, we plot the average absorption coefficient \(Tr \sigma/3\) for these different total propagation time. As we can see, when we increase the total propagation time, the width of the peaks reduces. Moreover the increase of total propagation time causes the appearance of new structures in the spectra indicating that we are not in convergence up to about \(T=40\) \((\hbar/eV)\). We checked that above this value the spectra does not change any more.

Thus, we find the suitable total propagation time equal to 40 \((\hbar/eV)\).

**Analysis of the absorption spectra from time propagation**

We do the calculation with total propagation time equal to 40 \((\hbar/eV)\) and the time step equal to 0.001 \((\hbar/eV)\) and we applied the external perturbation in three directions \((x, y, \text{and } z)\). According to the section (2.2.7) by propagating the time-dependent Kohn-Sham equations, we obtained the density \(\delta n(r, \omega)\) and \(\delta \langle \hat{X}_i \rangle(\omega)\) through Eq. (2.41) and finally we obtained the spectra.

First we start with the analysis of the pentacene spectrum. In Fig. (3.15(a)) we show the absorption spectrum for pentacene obtained plotting the average absorption coefficient while in Fig. (3.15(b)) we show the absorption spectrum for three different direction of polarizations obtained from the
According with the distribution of the Kohn-Sham energy levels shown in Table (3.2) and Table (3.3) we can distinguish two main energy windows in the absorption spectra: a low energy region between 0 eV and 4.84 eV where only $\pi - \pi^*$ transitions are allowed by energy conservation and a higher energy one (above 4.84 eV) involving both $\pi - \pi^*$ and $\pi - \sigma^*$ ($\sigma - \pi^*$) transitions. As can be inferred from Fig. (3.15(b)) the lower energy region of the spectrum is dominated by electronic transitions induced by in-plane dipole moment, in particular in the $x$ direction. While the out-of-plane component ($z$ component) of the dipole moment gives a remarkably contribution only at energy higher than 10 eV where only $\pi - \sigma^*$ ($\sigma - \pi^*$) transitions are involved. This behaviour can be explained in terms of the symmetry properties of the electronic wave functions discussed in the previous section. In fact as we have seen previously $\pi$ ($\pi^*$) and $\sigma$ ($\sigma^*$) states are respectively antisymmetric and symmetric respect to the $xy$ plane. This means that the only allowed electronic transitions in the dipole approximation are $\pi - \pi^*$ and $\sigma - \sigma^*$ for polarization direction belonging to the plane of the molecule and $\pi - \sigma^*$ and $\sigma - \pi^*$ for the direction perpendicular to the plane. Interestingly, we note that, although the main contribution to the lower energy region of the spectrum arises from the $x$ component of the polarization (see for example the feature at 3.98 eV), the onset of the absorption (1.58 eV) involving mainly HOMO-LUMO transition is related only to the $y$ component. In fact being HOMO and LUMO orbitals both symmetric respect to the $yz$ plane, the HOMO-LUMO transition is forbidden for dipole moment along the $x$ axis. On the other hand it is allowed for dipole along the $y$ axis being HOMO and LUMO orbitals respectively antisymmetric and symmetric respect to the $xz$ plane.
In the following we focus on picene. In Fig. (3.16(a)) we see the absorption spectrum for picene obtained evaluating the average absorption coefficient while in Fig. (3.16(b)) we see the absorption spectrum for three different directions of polarizations obtained from the strength function.

As for pentacene, also for picene, according to the results shown in Table (3.2) and Table (3.3), we can identify two main energy windows in the absorption spectrum: a lower energy region between 0 eV and 5.85 eV related to \(\pi - \pi^*\) transitions and a higher energy region (above 5.85 eV) involving both \(\pi - \pi^*\) and \(\pi - \sigma^*\) \((\sigma - \pi^*)\) transitions. As for pentacene the symmetry of the electronic wave functions reflects on the structure of the absorption spectrum, so that the lower energy region of the spectrum is mainly related to the in plane component of the polarization while the higher energy one to the \(z\) component. Contrarily to what happens in pentacene, we find that for picene the onset of the absorption (3.4 eV) presents contributions from both the \(x\) component and the \(y\) component of the dipole moment. In fact, in the case of picene the HOMO and LUMO orbitals are respectively symmetric and antisymmetric respect to the \(yz\) plane so that HOMO-LUMO transitions are allowed in dipole approximation for dipole moment along the \(x\) axis. Moreover since for picene the \(xz\) plane is not a symmetry plane we do not have any restriction imposed by the symmetry on the transitions induced by the dipole moment oriented along the \(y\) axis.
3.3 Absorption spectra from Casida equation

Convergence study

We have to converge the absorption spectrum with respect to the calculation parameters. According to the section (2.2.6) we know that the most important parameter that we have here is the number of unoccupied states. So, we have to increase the number of unoccupied states until our absorption spectrum is in convergence. We performed the Casida calculation for pentacene with the number of unoccupied states equal to 51, 100, 150, and 200. We show the results for pentacene in Fig. (3.17). As we can see the spectra for the number of unoccupied states equal to 150 and 200 are exactly the same. So in order to have a shorter calculation we chose to do the calculation with a number of unoccupied states equal to 150.

For picene we performed the calculation for the number of unoccupied states equal to 51, 100, and 150. We show the results for picene in Fig. (3.18). As for pentacene we decided to do the calculation with a number of unoccupied states equal to 150.

Analysis of the casida spectra

As discussed in section (2.2.6), we can obtain the absorption spectra by solving the eigenvalue problem in Eq. (2.35) (Casida equation). As we know the eigenvalues of the Casida equation yield the excitation energies while the corresponding eigenvectors yield the weight of the different electron-hole pairs contributing to that excitations. In an independent particle picture (i.e. when $f_{Hxc} = 0$) the Casida equation is already in the diagonal form.
in the basis of electron-hole Kohn-Sham wave functions so that it exists a one to one correspondence between excitation energies and the energies of the electron-hole pairs. However when $f_{Hxc} \neq 0$ the Casida equation is no more diagonal in this basis since the Hartree and the exchange-correlation terms cause a mixing of electron-hole transitions. Thus, solving Eq. (2.35) not only gives access to the absorption spectra but also allows to understand the nature of the different excitations.

We can see the absorption spectrum with the number of unoccupied states equal to 150 for pentacene in Fig. (3.19(a)) and picene in Fig. (3.20(a)).

In Fig. (3.19) and Fig. (3.20) we compare the spectra from Casida with that obtained from time propagation and we find that they are in good agreement between them.

To understand the role played by the exchange-correlation effects we compare in Fig.(3.22) and Fig.(3.21) the spectra evaluated with and without $f_{xc}$. We see that the effect of $f_{xc}$ is negligible in the first region of the spectra and causes only a small red shift of the spectra of about 0.1 eV in both picene (Fig. (3.22)) and pentacene (Fig.(3.21)) at high energy. This means that in these systems the mixing of electron-hole transitions is mainly related to the Hartree term.

Thus in the following we focus on the analysis of the main features of the spectra looking to the eigenstates of the Casida equation solved neglecting the $f_{xc}$ term. First we analyse the results for pentacene.

As I said before the onset of the absorption is at about 1.58 eV. We find from the solution of Casida equation that this excitation is related to the mixing of two transitions: the dominant contribution arises from HOMO-LUMO transition with energy difference of about 1.13 eV while the other one is related to the transition from the level 50 to the level 53 with energy
CHAPTER 3. RESULTS

Figure 3.17: The absorption spectrum for Casida equation with the number of unoccupied states are equal to 51, 100, 150, and 200 for pentacene.

Figure 3.18: The absorption spectrum for Casida equation with the number of unoccupied states are equal to 51, 100, and 150 for picene.

difference of about 3.47 eV. Thus the Hartree term causes a red shift of the onset of about 0.45 eV respect to the value set by the HOMO-LUMO gap.

The dominant peak at 3.98 eV is related to the mixing of transitions with energy from 2.899 eV to 4.98 eV revealing a strong effects of the Hartree term.

Now we focus on picene. The onset of the absorption is at about 3.4 eV. We find from the solution of Casida equation that this excitation is related to the mixing of transitions with energy from 3.09 eV to 4.184 eV. Thus the Hartree term causes a red shift of the onset of about 0.31 eV respect to the value set by the HOMO-LUMO gap (3.09 eV).

The dominant peak at 4.39 eV is related to the mixing of transitions with
3.3. ABSORPTION SPECTRA FROM CASIDA EQUATION

Figure 3.19: The absorption spectrum for pentacene (a) absorption spectrum from Casida (b) the absorption spectrum from time propagation energy from 3.09 eV to 6.06 eV. Even in this case the mixing of transitions due to the Hartree term is very strong.
CHAPTER 3. RESULTS

Figure 3.20: The absorption spectrum for picene (a) absorption spectrum from Casida (b) the absorption spectrum from time propagation

Figure 3.21: The absorption spectrum for Casida equation with $f_{xc}$ and without $f_{xc}$ of pentacene
Figure 3.22: The absorption spectrum for Casida equation with \( f_{xc} \) and without \( f_{xc} \) of picene
Chapter 4

Conclusion

In this work I studied the optical properties of two aromatic molecules: pentacene and picene. They are both made of 5 benzene rings. While in pentacene they are in a linear configuration, in picene they have a zigzag configuration, as we can see in Fig. (3.7(a) and 3.7(b)). Picene has fewer symmetries than pentacene.

I used the Octopus code in the framework of density functional theory for the ground state and time-dependent density functional theory for the absorption spectra. The first step has been the calculation of the Kohn-Sham orbitals and their energy levels. We have 11 $\pi$ ($\pi^*$) states and 40 $\sigma$ ($\sigma^*$) states. According to the Table (3.2) we see the $\sigma$ states have the different energy width (13.58 eV in pentacene and 13.92 eV in picene), the $\sigma^*$ states present smaller and different energy width (4.25 eV in pentacene and 4.42 eV in picene). The energy width of $\pi$ states is larger for pentacene than for picene. It is 3.71 eV for $\pi$ states and 3.95 eV for $\pi^*$ states in pentacene, while it is 2.76 eV for $\pi$ states and 4.42 eV for $\pi^*$ states in picene.

In our calculation the HOMO–LUMO energy gap for pentacene is 1.13 eV, and when compare it with the data that we find in literature we understand that our calculation is correct. But when we compare this value with experimental data, we see that this value is about 80% smaller than the experimental value, 5.22 eV. For picene in our calculation the HOMO–LUMO energy gap is 3.09 eV. And when compare it with the data of literature, again, we conclude that our calculation is correct.

We see that the picene HOMO–LUMO gap is much larger than in pentacene.

In Fig. (3.8(a),3.8(b),3.9(a),3.9(b)) we show the Kohn-Sham HOMO and LUMO orbital isosurfaces for picene and pentacene. The higher symmetry of the pentacene molecule clearly reflects on the shape of the wave functions. In fact, comparing Fig. (3.9(a)) with Fig. (3.9(b)) we find that in pentacene
both HOMO and LUMO orbitals are symmetric respect to the $yz$ plane while respect to the $xz$ plane they are anti-symmetric and symmetric respectively. On the other hand, for picene (see Fig. (3.8(a)) and (3.8(b))) the HOMO and LUMO orbitals are symmetric and anti-symmetric respect to the $yz$ plane respectively but they do not have any symmetry respect to the $xz$ plane. Moreover being the HOMO (LUMO) orbitals as well as all the $\pi$ ($\pi^*$) states linear combinations of $p_z$ atomic orbitals they are anti-symmetric respect to the plane of the molecule ($xy$ plane) in both picene and pentacene. In Fig. (3.8(c)) and (3.9(c)) with Fig. (3.9(d)) and (3.8(d)) we see $\sigma$ and $\sigma^*$ states that they are symmetric respect the molecular plane.

Then we find the absorption spectrum with two ways: first from time propagation and second from Casida equation. In the spectra that we obtained from time propagation for pentacene (Fig. (3.15)) and for picene (Fig. (3.16)) we have two main energy windows: a low energy region between 0 eV and 4.84 eV for pentacene and for picene between 0 eV and 5.85 eV where only $\pi - \pi^*$ transitions are allowed by energy conservation and a higher energy one (above 4.84 eV for pentacene and for picene above 5.85 eV) involving both $\pi - \pi^*$ and $\pi - \sigma^*$ ($\sigma - \pi^*$) transitions. The lower energy region of the spectrum is dominated by electronic transitions induced by in-plane dipole moment. The main contribution to the lower energy region of the spectrum arises from the $x$ component of the polarization for picene and pentacene. The onset of the absorption for pentacene involving mainly HOMO-LUMO transition is related only to the $y$ component, but for picene the onset of the absorption presents contributions from both the $x$ component and the $y$ component of the dipole moment.

We see the spectra from Casida with that obtained from time propagation are in good agreement. We see that the effect of $f_{xc}$ is negligible in the first region of the spectra and causes only a small red shift of the spectra of about 0.1 eV in both picene (Fig. (3.22)) and pentacene (Fig.(3.21)) at high energy. This means that in these systems the mixing of electron-hole transitions is mainly related to the Hartree term.
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