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NANOSCIENCE AND NANOTECHNOLOGY

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DOTTORATO DI RICERCA

TIME DEPENDENT DFT INVESTIGATION OF
OPTICAL PROPERTIES AND CHARGE DYNAMICS
IN LIGHT-HARVESTING ASSEMBLIES

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As far as the laws of mathematics refer to reality, they are not certain; and as far as they are certain, they do not refer to reality.

<table>
<thead>
<tr>
<th>5.3 Conclusions</th>
<th>44</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 Charge Transfer Dynamics</td>
<td>47</td>
</tr>
<tr>
<td>6.1 Photo-induced Charge Separation Mechanism</td>
<td>48</td>
</tr>
<tr>
<td>6.2 Methods</td>
<td>50</td>
</tr>
<tr>
<td>6.3 Results</td>
<td>51</td>
</tr>
<tr>
<td>6.4 Conclusions and Work in Progress</td>
<td>54</td>
</tr>
</tbody>
</table>

| Bibliography | 62 |
Chapter 1

Introduction

The quest for efficient ways to exploit renewable energy sources has become one of the key problems of our times. The idea of a solid-state device capable of transforming solar light energy into electric potential energy is quite old, and enormous progress has been made in optimizing traditional junction-based devices with respect to their thermodynamical efficiency and production cost [1].

Figure 1.1 shows the energy band diagram of a standard p–n junction

Figure 1.1: Energy band diagram of a p–n junction with energy conversion loss processes.
Chapter 1. Introduction

solar cell. The right-hand side of the figure represent the n-type region of the device where a semiconductor is doped by adding some amount of an element with more valence electrons than the semiconductor element. The left-hand side represent a p-type region obtained by doping the same semiconductor with an element with less valence electrons. When these two types of doped semiconductors are in contact, once reached the equilibrium, we have the so-called p–n junction useful in solar cells. The necessary condition is that the valence band of a side of the junction falls into the band gap of the other side. As shown in Figure 1.1 an hypothetical photoexcited electron in the p side of the junction is under the influence of an electrochemical potential gradient that moves the electron to the n side. The n-type region is well predisposed to accept electrons due to the presence of the dopant that yields a conduction band where electrons can flow easily to and from cells contacts. This high mobility of the charge carriers produce the current flow.

Recently with the coming of the nanotechnology, the study of the control of matter on an atomic and molecular scale (generally structures of the size 100 nanometers or smaller), entirely new classes of materials have been proposed as building blocks for next-generation solar cells. Among these nanostructured semiconductors, organic-inorganic hybrid and supramolecular assemblies appear to be the most promising.

The problems concerning the manipulation of matter at nano size was first illustrated by the physicist Richard Feynman in the famous lecture “There’s Plenty of Room at the Bottom” at an American Physical Society meeting at Caltech on December 29, 1959. He pointed that as the sizes got smaller, we would have to reconsider the physics of the system because the relative strength of various forces would change. Gravity would become less important, surface tension would become more important, Van der Waals attraction would become important, etc. This opened the doors to a new science dedicated at the study of the “nano-world”, the nanoscience.

1.1 Third Generation Photovoltaics

In green plants photosynthesis light-harvesting complexes, systems that absorb the photons with very high effectiveness, are able to capture the solar
energy and to store it in a charge-separated state. The solar energy is first used to create an excited state of the molecule, and it is later transferred in a reaction center. This reaction center is composed by several electron acceptor molecules disposed like a chain, where the first molecule transfers its excited electron to the next creating an electron transport chain. The solar energy is thus converted into potential energy in terms of charge-separation.

**Organic-Inorganic Hybrid Assemblies**

Organized organic-inorganic nanohybrids can be developed by mimicking the photoinduced electron-transfer process of natural photosynthesis, tailoring the optoelectronic properties of metal nanoparticles. This nanohybrids are made by assembling monolayers of organic molecules containing functional groups, such as amines, thiols, isothiocynate, and silanes, on to three-dimensional surface of metal nanoparticles, such as gold nanoparticles. Such monolayer protects the metal cluster and can be functionalized with a chromophore monolayer. This type of spherical shape hybrid clusters exhibits efficient light-harvesting capability and suppresses undesirable energy transfer quenching of singlet-excited-state of the chromophores due to the fact that they are densely packed on metal nanoparticle surfaces (Figure 1.2(a)).
The nonmetallic property of metal nanoparticles can also be utilized to accept and then to transfer the electrons from an excited sensitizer to another acceptor molecule bound to the surface [4]. For example, a gold-nanoparticle could bridge for a chromophore and a TiO\(_2\) surface, in which a bifunctional surface-linking molecule such as mercaptopropionic acid was used to link the gold nanoparticle to the TiO\(_2\) surface (thiol group to gold and carboxylic group to TiO\(_2\)) (Figure 1.2(b)).

**Semiconductor/Metal Nanocomposites**

Of particular interest is the use of semiconductor nanostructures for solar hydrogen production by the photocatalytic splitting of water. An example are the TiO\(_2\)–Gold composite nanoparticles [4], where the gold nanoparticles capped with organic molecules exhibit unusual redox activity by readily accepting electrons from the charged semiconductor TiO\(_2\) nanostructure. The Au-mediated electron transfer to an electron acceptor, such as C\(_{60}\), can be followed by introducing Au nanoparticles to UV-irradiated TiO\(_2\) suspension (Figure 1.3(a)).

This type of coupled metal–semiconductor structure is obtained by exposing both metal and oxide surfaces to reactants, products, and the medium. Corrosion or dissolution of the noble metal particles during the operation of photocatalytic reaction is problematic. A better synthetic design would be
to employ the metal as a core and a semiconductor photocatalyst as a shell. For example, the Ag@TiO$_2$ core–shell clusters are able to store electrons under UV irradiation and discharge them on demand in the dark (Figure 1.3(b)).

Photoinduced charge separation in a semiconductor nanoparticle can be greatly improved by coupling it with another semiconductor particle having favorable energetics. By selecting a short band gap semiconductor, one can also harvest photon in the visible, and by controlling the particle size of quantum dots, one can vary the energetics of the particles. Opportunities exist to develop ordered assemblies of short and large band gap semiconductors and harvest photons over a wide spectral range of the visible and infrared light with better charge separation.

Dye-Sensitized Solar Cells

The first example of solar cells in which the units responsible of the photoexcitation and of the charge collection are separated, are the so-called dye-sensitized (or Grätzel) solar cells (Figure 1.4(a)). The dye-modified semiconductor films provide an efficient method to mimic the photosynthetic process. The charge separation in this case is facilitated by a semiconductor particle. In this devices the nanostructured TiO$_2$ films modified with a ruthenium complex (Figure 1.4(b)) exhibit photoconversion efficiencies in the range of 11%, which is comparable to that of amorphous silicon-based photovoltaic cells. When the electrode is illuminated with visible light, the sensitizer molecules absorb light and inject electrons into the semiconductor particles. These electrons are then collected at the conducting glass surface to generate anodic photocurrent. The charge injection from excited sensitizer into semiconductor nanoparticles is an ultrafast process occurring on the time scale of femtoseconds to nanoseconds. The redox couple (e.g., I$_3^-$/$I^-$) present in the electrolyte quickly regenerates the sensitizer. The iodide is regenerated in turn by the reduction of triiodide at the counter-electrode the circuit being completed via electron migration through the external load. The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte.
Chapter 1. Introduction

Figure 1.4: (a) Schematic of operation of a dye-sensitized electrochemical photovoltaic cell (from Ref. [7]). (b) Ru-complex adsorbed on TiO$_2$ nanoparticle (from Ref. [8]).

Overall the device generates electric power from light without suffering any permanent chemical transformation.

Recently this type of cells are been subject of several studies toward fine-tuning the performance of electrode structure, pretreatment of TiO$_2$ surface, modification of ruthenium bipyridyl complex with a variety of functional groups, regenerative redox couples, and electrolyte medium. Despite this large body of work, the maximum attainable efficiency has remained in the range of 10-11%.

Donor-Acceptor Assemblies

In the class of supra-molecular assemblies the donor-acceptor dyads and triads are objects of careful experimental study. In fact they are considered an ideal mimic for the primary photo-synthetic process, which basically consists of a photo-excitation followed by a charge-transfer between the component units [9]. The research for ideal components of light-harvesting dyads has led to porphyrin-C$_{60}$ assemblies [10] (Figure 1.5).

Porphyrin molecules show extensive absorption of visible light, and an optical gap of approximately 2 eV and are therefore ideal photo-reaction
centers and electron donors. \( C_{60} \), on its side, is the ideal electron acceptor. It has a particularly deep triply degenerate LUMO at approximately \(-4.3\) eV vs vacuum, capable of accommodating six electrons from neighboring molecules. Moreover the highly conjugated nature of its bonds, together with a cage radius of 3.45 Å, stabilizes the extra charges in a very efficient way, so that little repulsive forces are felt by the excess electrons. A further step toward solar cells based on these components consisted in transforming the donor-acceptor unit into a donor-bridge-acceptor unit. This change has the main purpose of obtaining a better charge separation and a longer life time of the final (excited) state.

Figure 1.5: Porphyrin-\( C_{60} \) dyad (from Ref. [9]).
Chapter 2

Time-Dependent Density Functional Theory

The aim of this chapter is to introduce the basic formalism of the Density Functional Theory (DFT) and its time-dependent extension (TDDFT). We start in the section 2.1 with the statement of two important theorem that are the foundation of the DFT. In section 2.2 we illustrate how to extend the basic idea of DFT to time-dependent phenomena.

2.1 An introduction on DFT

The problem of the determination of ground state properties of a many-body system in Quantum Mechanics is formulated in terms of the solution of the statical Schrödinger equation. This procedure is well applicable only for small systems. As pointed by W. Kohn in his Nobel Lecture, in January 28 1999, for systems with a number of interacting electrons $N > O(10)$, we have a so call “exponential wall” that makes unfeasable the traditional wavefunction method, that provide the “required” chemical accuracy.

The aim of the DFT is to replace the many-body wave-function, a very complex mathematical object, that depends on $3N$ variable, with a simple function, the charge density, that depends solely on the three spatial coordinates. The advantage is clear in particular from a computational point of view. In this section we illustrate the scheme proposed by Kohn and Sham.
that is based on the Hohenberg-Kohn theorem.

### 2.1.1 The Hohenberg-Kohn Theorem

The Hohenberg-Kohn (HK) theorem states that the ground state expectation value of any observable $\hat{O}$ is a unique functional of the exact ground state density $n(r)$

$$\langle \Psi[n]|\hat{O}|\Psi[n]\rangle = O[n] .$$

To prove the HK theorem we start considering a many-fermion system characterized by a non-relativistic time-independent Hamiltonian $\hat{H}$, composed by a kinetic contribution $\hat{T}$, a Coulomb (two-particle interaction) contribution $\hat{W}$, and an external potential $\hat{V}$ that belongs to a set $\mathcal{V}$ of local one-particle potentials

$$\hat{H}\Psi = (\hat{T} + \hat{W} + \hat{V})\Psi = E_{gs}|\Psi\rangle , \quad \hat{V} \in \mathcal{V} . \quad (2.1)$$

The states $|\Psi\rangle$ are collected in a set $\Psi$ of antisymmetric ground state wavefunctions, that solves the fermions eigenvalue problem, and defines the surjective map

$$C : \mathcal{V} \rightarrow \Psi .$$

Calculating the ground state density

$$n(r) = N \sum_{\sigma_2...\sigma_N} \int dr_2... \int dr_N |\Psi(r_\sigma, r_2\sigma_2, ..., r_N\sigma_N)|^2 ,$$

where $N$ is the number of fermions

$$N = \sum_\sigma \int d^3r n_\sigma(r) ,$$

another surjective map is generated collecting the ground state densities in the set $\mathcal{N}$

$$D : \Psi \rightarrow \mathcal{N} .$$
2.1. An introduction on DFT

Now we demonstrate that the maps $C$ and $D$ are also injective. For the map $C$ we consider the eigenvalue problem of a ground state $|\Psi'\rangle$

$$
\hat{H}'|\Psi'\rangle = (\hat{T} + \hat{W} + \hat{V}')|\Psi'\rangle = E_{gs}'|\Psi'\rangle , \quad \hat{V}' \in \mathcal{V} ,
$$

(2.2)

where the Hamiltonian differ by the one in (2.1) only by the external potential. With the assumption $|\Psi\rangle = |\Psi'\rangle$ and subtracting the two Schrödinger equations (2.1) and (2.2) we obtain

$$(\hat{V} - \hat{V}')|\Psi\rangle = (E_{gs} - E_{gs}')|\Psi'\rangle ,$$

and

$$\hat{V} = \hat{V}' + (E_{gs} - E_{gs}') .$$

(2.3)

The last equation shows that the potentials differ by only an additive constant, thus they are equivalent. For the map $D$ we start to calculate the ground state energy as the expectation value of the Hamiltonian, and for $|\Psi\rangle \neq |\Psi'\rangle$ we get

$$E_{gs} = \langle \Psi | \hat{H} | \Psi \rangle < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' + \hat{V} + \hat{V}' | \Psi' \rangle$$

then

$$E_{gs} < E_{gs}' + \int n'(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]d^3r .$$

A similar procedure for $E_{gs}'$ leads to

$$E_{gs}' < E_{gs} + \int n(\mathbf{r})[v'(\mathbf{r}) - v(\mathbf{r})]d^3r ,$$

and additioning the last two inequalities with the assumption $n(\mathbf{r}) = n'(\mathbf{r})$ we obtain

$$E_{gs} + E_{gs}' < E_{gs} + E_{gs}' .$$

(2.4)

The contradictions (2.3) and (2.4) proves that the maps $C$ and $D$ are also injective and thus bijective. In particular the unique inversion of the map $D$

$$D^{-1} : n(\mathbf{r}) \rightarrow |\Psi[n]\rangle$$
proofs the Hohenberg-Kohn (HK) theorem.

In particular, if our observables are the kinetic contribution and the two-particle interaction, we can define the functional

$$ F_{HK}[n] = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle $$

that is an universal functional, i.e., valid for any number of fermions and does not depend on the one-particle external potential. The energy functional now can be written as

$$ E_{v_0}[n] = \langle \Psi[n] | \hat{T} + \hat{W} + \hat{V}_0 | \Psi[n] \rangle = F_{HK}[n] + \int d^3rv_0(r)n(r) $$

(2.5)

and another important statement, of the HK theorem, shows its variational character: the exact ground state density can be determined by minimization of the energy functional

$$ E_0 = \min_{n \in \mathcal{N}} E_{v_0}[n] $$

(2.6)

### 2.1.2 Degenerate Ground States and $v$-Representability

In the case of a system with degenerate ground states we can define a subset $\Psi_V$ as a linear combination of the states that solve the eigenvalue problem (2.1), related to a potential $V \in \mathcal{V}$, where the union of all subset gives the set $\Psi$. It is also possible to define a subset $\mathcal{N}_V$ that groups all the ground state densities related to a potential $V \in \mathcal{V}$, where the union of all subset gives the set $\mathcal{N}$.

In this case the relation $C$ could not be considered a map, because one potential now is associated with more then one ground state. Moreover the map $D$ is now not invertible.

We can overcome the problem proving that $(CD)$ is a proper map and it is invertible. Kohn [12] showed that the ground state energy corresponding to the unique external potential $\hat{V}[n]$ of a given density $n(r)$ is the same for all the degenerate ground states $|\Psi_i\rangle \in \Psi_V$

$$ \langle \Psi_i | \hat{T} + \hat{W} + \hat{V}[n] | \Psi_i \rangle = \langle \Psi_j | \hat{T} + \hat{W} + \hat{V}[n] | \Psi_j \rangle \equiv E $$
Thus

\[ F_{HK}[n] = E - \int n(r)v([n]; r)d^3r \]

is an unique functional of the density and the relations (2.5) and (2.6) are conserved.

A function \( n(r) \) is termed pure-state \( v \)-representable if it is the density of a (possibly degenerate) ground state of the Hamiltonian in the (2.1) with some suitably chosen local external potential \( v(r) \) (the number of particles, \( N \), and their mutual interaction \( w(r, r') \) being specified). But not all “reasonably well behaved” non-negative functions are pure-state \( v \)-representable. A first extension of the domain of the functional \( F_{HK}[n] \) was proposed by Levy and further investigated by Lieb [13] and Levy [14]. The functional is defined as

\[ F_{LL}[n] = \inf_{\Psi \rightarrow n} \langle \Psi|\hat{T} + \hat{W}|\Psi \rangle , \]

where the notation \( \Psi \rightarrow n \) indicates that the infimum be searched over all antisymmetric, normalized \( N \)-particle functions \( \Psi(r_1\sigma_1, \ldots, r_N\sigma_N) \) whose density equals the prescribed function \( n(r) \). As consequence of the Rayleigh-Ritz principle \( F_{LL}[n] = F_{HK}[n] \) for all pure-state \( v \)-representable functions \( n(r) \), thus

\[ E_{v_0}[n] = F_{LL}[n] + \int n(r)v_0(r)d^3r . \]

### 2.1.3 The Kohn-Sham Equations

The HK theorem establishes a one-to-one correspondence between a given local external potential \( v(r) \) and the ground state density \( n(r) \) of a \( N \)-fermionic system. Now we need a scheme to make the theorem suitable for solving actual quantum-mechanical problems.

To achieve this Kohn and Sham introduce and auxiliary system of \( N \) non-interacting particles denoted with the letter “\( s \)” and described by the same density as the interacting one \( n(r) = n_s(r) \).

Following the HK theorem there exists a potential \( v_s(r) \) generated by a given density \( n(r) \), thus the single-particle orbital obtained by solving the Schrödinger equation

\[ \left( -\frac{\hbar^2}{2m} \nabla^2 + v_s(r) \right) \varphi_i(r) = \varepsilon_i\varphi_i(r) \] (2.7)
with
\[ n(r) = \sum_{i=1}^{N} |\varphi_i(r)|^2, \] (2.8)
are unique functional of the density, \( \varphi_i(r) = \varphi_i([n]; r) \) as well as the non-interacting kinetic energy
\[ T_s[n] = \sum_{i=1}^{N} \int \varphi_i^*(r) \left( -\frac{\hbar^2}{2m} \nabla^2 + v_s(r) \right) \varphi_i(r) d^3r. \]

Now considering an interacting system, with external potential \( v_0(r) \) and ground state density \( n_0(r) \), we can rewrite its total energy functional in terms of the non-interacting system
\[ E_{v_0}[n] = T_s[n] + \int d^3r v_0(r) n(r) + \frac{1}{2} \int d^3r d^3r' n(r) w(r, r') n(r') + E_{xc}[n], \]
where the exchange-correlation (xc) functional is defined as
\[ E_{xc}[n] = F_{HK}[n] - \frac{1}{2} \int d^3r d^3r' n(r) w(r, r') n(r') - T_s[n]. \]

Defining the xc potential as
\[ v_{xc}([n_0]; r) = \frac{\delta E_{xc}[n]}{\delta n(r)} \bigg|_{n_0} \]
we can obtain the auxiliary potential, the so called Kohn-Sham potential,
\[ v_{s,0}(r) = v_0(r) + \int d^3r' w(r, r') n_0(r') + v_{xc}([n_0]; r). \] (2.9)

The equations (2.8) (2.7) and (2.9) allow us to apply the Kohn-Sham theorem: the exact ground state density \( n(r) \) of an arbitrary interacting system can be obtained by the self-consistent solution of the following set of equations
\[ \left( -\frac{\hbar^2}{2m} \nabla^2 + v(r) + \int d^3r' w(r, r') n(r') + v_{xc}([n]; r) \right) \varphi_i(r) = \varepsilon_i \varphi_i(r). \] (2.10)
with

\[ n(r) = \sum_{i=1}^{N} |\varphi_i(r)|^2. \]

Finally the ground state total energy of the interacting system is given by

\[
E_0 = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \int \int d^3r d^3r' n(r) w(r, r') n(r') + E_{xc}[n] - \int v_{xc}(n; r) n(r) d^3r.  
\]

\[ \text{2.2 Excited States} \]

This section is dedicated to the study of excited states. The simplest approximation in the calculation of the excited energies is to take the differences between the ground state KS eigenvalues. However, it is important to emphasize that the KS eigenvalues, obtained from (2.10), do not have a physical meaning, thus this procedure is not entirely justifiable. In particular, as mentioned in section 2.1, with DFT we have a scheme to obtain the expectation value of a ground state observable as a functional of the ground state density. Thus we are not able to predict correctly the expectation value of a time dependent observable only with the stationary density. Several techniques have been proposed to overcome this problem, and one of the most successful for the calculation of excitations in finite system is the TDDFT. In this section we state the fundamental theorem of TDDFT, and outline a procedure to extract absorption spectra from the solution of TDDFT equations. Application to a real-world system is presented in Chapter 5.

\[ \text{2.2.1 The Runge-Gross Theorem} \]

The Runge-Gross (RG) theorem [15] is the time dependent extension of the HK theorem. It states that, given the initial state of a many-fermionic sys-
Chapter 2. Time-Dependent Density Functional Theory

tem, there is a one-to-one correspondence between the time dependent external potential and the time dependent density

\[ v(r, t) \leftrightarrow n(r, t) . \]

There are some important differences between the statical and the dynamical problems. The first is that, for time dependent systems, there isn’t a variational principle on the basis of the total energy. Moreover, as mentioned in the statement, there is a dependence on a fixed initial state of the system.

The proof of the RG theorem, that we will not examine, requires the demonstration that if two potentials, \( v(r, t) \) and \( v'(r, t) \), differ by more than a purely time dependent function \( c(t) \), they cannot produce the same time dependent density \( n(r, t) \).

As well as the statical case now we need a scheme to make the theorem suitable for solving actual time dependent quantum-mechanical problems.

2.2.2 Time Dependent Kohn-Sham Equations

In order to remark that the TDDFT is the extension of the DFT to time dependent phenomena, now we introduce the time dependent KS equations that are an exact reformulation of the time dependent Schrödinger equation

\[ i \frac{\partial}{\partial t} \varphi_i(r, t) = \left[ -\frac{\nabla^2}{2} + v_{KS}(r, t) \right] \varphi_i(r, t) , \tag{2.11} \]

where \( v_{KS}(r, t) \) is the potential operating on an auxiliary system of non-interacting fermions, and the density of the interacting system is obtained from the KS orbitals

\[ n(r, t) = \sum_{i}^{occ} |\varphi_i(r, t)|^2 . \tag{2.12} \]

We can rewrite the KS potential as the sum of three terms

\[ v_{KS} = v_{ext}(r, t) + v_H(r, t) + v_{xc}(r, t) , \]
2.3. Photo-absorption Spectra

where, $v_{\text{ext}}(r, t)$ is the external potential, $v_H(r, t)$ is the classical electrostatic interaction, the so called Hartree potential, and $v_{xc}(r, t)$ is the Exchange and Correlation potential.

This last term in DFT is obtained as functional derivative of the Exchange and Correlation energy. However, we don’t known its exact expression, thus we are obliged to introduce approximations.

**Adiabatic Local Density Approximation**

In the present thesis we used the local density approximation (LDA) to solve the DFT calculations. It is based on the concept that the electron density in considered locally constant, thus the xc energy is approximated as

$$E_{xc}^{LDA} = \int d^3r \frac{\delta}{\delta n} \varepsilon_{\text{HEG}}(n)|_{n=n(r)} ,$$

where $\varepsilon_{\text{HEG}}(n)$ is the xc energy per unit volume of the homogeneous electron gas. From this the expression of the xc potential follows

$$v_{xc}^{LDA}(r) = \frac{\delta}{\delta n} \varepsilon_{\text{HEG}}(n)|_{n=n(r)} .$$

Despite the main problem of this approximation, i.e. the exact xc potential decay as $-1/r$, while the LDA xc potential falls off exponentially, it works very well, in particular for finite systems, and is one of the most widely used xc functional as basis for time dependent approximations.

In fact we can obtain the time dependent xc potential using the so called adiabatic LDA (ALDA), that considers the xc potential as a functional local in time

$$v_{xc}^{ALDA}(r, t) = v_{xc}^{LDA}[n](r)|_{n=n(r, t)} .$$

Obviously the ALDA retains all merits and defects already present in the LDA.

2.3 Photo-absorption Spectra

We conclude this chapter showing how the TDDFT allows us to obtain photo-absorption spectra by simplifying the perturbation theory or by propagating in real-time the time dependent KS equations.
Linear Response Theory

From perturbation theory the quantity that allows us to calculate the optical absorption spectrum is the linear change of the density, i.e., the response of the system when perturbed by a weak time dependent external electric potential $\delta v_{\text{ext}}(r,t)$. We know that the time dependent perturbation of the density is related to the perturbing potential. In frequency space it reads

$$\delta n(r,\omega) = \int dr' \chi(r,r',\omega) \delta v_{\text{ext}}(r',\omega),$$

where $\chi(r,r',\omega)$ is the linear density-density response function of the system. Unfortunately, the evaluation of $\chi$ through perturbation theory is a very demanding task. TDDFT is able to simplify this process calculating the induced density using the KS auxiliary system

$$\delta n(r,\omega) = \int dr' \chi_{\text{KS}}(r,r',\omega) \delta v_{\text{KS}}(r',\omega),$$

where $\chi_{\text{KS}}(r,r',\omega)$ is the density-density response function of a system of non-interacting electrons. Thus applying first order perturbation theory to KS equations (2.10), $\chi_{\text{KS}}$ can be expressed in term of the ground state KS eigenvalues $\varepsilon_i$ and eigenfunctions $\varphi_i$

$$\chi_{\text{KS}}(r,r',\omega) = \sum_{ij} (f_i - f_j) \frac{\varphi_i^*(r) \varphi_j^*(r') \varphi_j(r') \varphi_i(r')}{\omega - (\varepsilon_i - \varepsilon_j) + i\eta},$$

where $f_i$ is the occupation number of the KS orbitals.

We can now define the dynamical polarizability in terms of the linear response function as

$$\alpha_{ij} = -\int \int dr dr' x_i \chi_{\text{KS}}(r,r',\omega)x_j.$$

Finally the photo-absorption cross-section is proportional to the imaginary part of the dynamical polarizability averaged over the three spatial directions

$$\sigma(\omega) = \frac{4\pi\omega}{c} \frac{1}{3} \Im[Tr\alpha(\omega)], \quad (2.13)$$

where $c$ is the velocity of light.
Full solution of the KS equations

If we don’t want to limitate the perturbation at a weak field, or if we want to study both linear and non-linear functions of finite systems, a very efficient method consist in the direct solution of the time dependent KS equations (2.11). In Quantum Mechanics a time dependent problem is mathematically defined as an initial value problem. Using as starting point the KS ground state, obtained from a DFT calculation, we can perturb it with an instantaneous electric field $\delta v_{ext} = -k_0 x_\nu \delta(t)$, where $x_\nu = x, y, z$. All frequencies of the system are excited with equal weight, and at time $t = 0^+$ we have

$$\varphi_i(r, t_0^+) = e^{i k_0 x_\nu} \tilde{\varphi}_i(r),$$

where $\tilde{\varphi}_i(r)$ are the KS ground state wave-functions. Now the orbitals are propagated in time using the time-evolution operator $\hat{U}$

$$\varphi_i(r, t_f) = \hat{U}(t_f, t_0^+)\varphi_i(r, t_0^+) = \hat{T} \exp \left[ -i \int_{t_0^+}^{t_f} d\tau \hat{H}_{KS}(\tau) \right]\varphi_i(r, t_0^+). (2.14)$$

Once reached the desired propagation we can obtain the change of the density through equation (2.12) as

$$\delta n(r, t) = n(r, t) - \tilde{n}(r), \quad (2.15)$$

in real-time space, where $\tilde{n}(r)$ is the ground state density of the system. With a Fourier transformation in frequency space of the induced density the dynamical polarizability can be obtained directly from

$$\alpha_{\nu\nu}(\omega) = -\frac{1}{k_0} \int d^3 x_\nu \delta n(r, \omega),$$

Finally the photo-absorption cross-section can be calculated by equation (2.13).
Chapter 3

Carotenoid-Porphyrin-C$_{60}$ Molecular Triad

In this thesis we study the electronic structure, absorption spectrum, and charge dynamics of the Carotenoid-Porphyrin-C$_{60}$ supra-molecular triad (abbreviated hereafter as triad or C-P-C$_{60}$), depicted in Figure 3.1.

Figure 3.1: Structure formula for C-P-C$_{60}$.

As mentioned in Chapter 1, this type of systems are considered an ideal mimic for the primary photosynthetic process, that occurs in green plant and bacterial photosynthetic membrane. The membrane is composed by a lipid bilayer containing several protein components, each of which has a specific role in the photo-induced process. An antenna component capture the solar photon energy. The photo-excitation in the antenna migrates to a reaction center where it is converted to chemical energy in the form charge separation across the bilayer in a series of steps involving several donor-acceptor interactions.
cofactors. Skipping the following steps of the process, the photosynthesis culminates in the production of ATP, the natural energy storage. Thus the question is: what are the design requirement for an artificial antenna plus reactor center? A minimal design includes an electron donor chromophore that absorbs visible light, and an electron acceptor. In this molecular assembly triad a covalent bond joins a diaryl-porphyrin, the donor chromophore, with a pyrrole-C$_{60}$, the acceptor, and provides electronic coupling that allows photoinduced electron transfer. The β-carotenoid is an additional electron donor moiety and it is joined to the diaryl-porphyrin by an amide connector. The role of the β-carotenoid is to prolong the lifetime of the charge separated final state by taking the hole from the porphyrin.

### 3.1 Photochemistry of Carotenoporphyrin-Fullerene Triads

The observed absorption spectrum of a similar triad in toluene is shown in Figure 3.2. Superimposed on the bands at 629, 576, and 411 nm that are characteristic of the porphyrin is the broad carotene absorption with maxima at 509, 477, and 448 nm. The weak fullerene absorption throughout the visible with a long-wavelength maximum at 705 nm is also present, but the amplitude is too low to see in the figure. The absorption spectrum is essentially a linear combination of the spectra of porphyrin, carotenoid, and fullerene compounds. Thus, electronic interaction among the chromophores is too weak to cause significant spectral perturbations. In fact, D. Kuciauskas et al. [16] have observed in benzonitrile and 2-methyltetrahydrofuran small ($\leq 3$ nm) spectral shifts to longer wavelengths.

Steady-state fluorescence emission studies of a triad in polar solvents, with excitation at wavelengths where the porphyrin and fullerene absorb, demonstrated very strong quenching of the emission from both the porphyrin and fullerene chromophores. This is ascribed to rapid photoinduced electron transfer involving either excited state. Excitation of the carotenoid moiety did not lead to the observation of any carotenoid fluorescence, as the fluorescence quantum yields of carotenoids of this type are $\leq 10^{-4}$. Studies of
3.1. Photochemistry of Carotenoporphyrin-Fullerene Triads

![Absorption spectra](image)

Figure 3.2: Absorption spectra in toluene solution at 292 K of a triad [16] (—), and a model porphyrin (− − −), carotenoid (− · − · −), and fullerene (− · · − · · −). Also shown is a linear combination of the spectra of the model compounds that approximates the spectrum of the triad (⋯).

carotenoporphyrin molecules have shown that singlet-singlet energy transfer from the carotenoid to the porphyrin is negligible, and that charge-separated species that might be generated by carotenoid excitation are not observed. Thus, the carotenoid is photochemically inert in the singlet manifold of the triad.

Transient absorption experiments were undertaken to learn more about electron-transfer processes in a P-C\textsubscript{60} dyad and a C-P-C\textsubscript{60} triad by Kuciauskas et al. [16]. The samples were excited at 590 nm with 200-fs laser pulses. Their conclusion were that the first excited singlet state of the porphyrin moiety in the dyad, \(^1\)P-C\textsubscript{60}, decays at least in part by photoinduced electron transfer to yield the P\(^+\)-C\textsubscript{60}\textsuperscript{−} charge-separated state. The same results was obtained for the triad and, after the formation of C-P\(^+\)-C\textsubscript{60}\textsuperscript{−}, the transient absorption experiments revealed a strong new absorption assigned to the carotenoidal radical cation of the C\(^+\)-P-C\textsubscript{60}\textsuperscript{−} charge-separated state.
Figure 3.3: Relevant transient species created after excitation of triad 2 and interconversion pathways. The energies of the charge-separated states are estimated from the cyclic voltammetric data obtained in polar solvents, as reported in Ref. [16].

The electron-transfer events leading to the final state in the triad are shown in Figure 3.3. Excitation at 590 nm yields mostly C-1-P-C60, which decays by step 3 to yield C-P+C60\(^-\). The fullerene excited singlet state also undergoes photoinduced electron transfer to give the same species. Electron transfer from the carotenoid (step 4) gives the final C\(^+\)-P-C60\(^-\) state. Kuci- auskas et al. have observed the formation of the carotenoid radical cation as a function of time measured at 970 nm in 2-methyltetrahydrofuran at 292, 200, 120, and 77 K. They relate formation time constants of 59 ps (292 K), 90 ps (200 K), 247 ps (120 K), and 615 ps (77 K).

The time-scale of the transient absorption experiments discussed above is too short to allow observation of the decay of the C\(^+\)-P-C60\(^-\) state. Therefore, transient absorption spectroscopy on the nanosecond time-scale was employed by Kodis et al. [17] for investigation of the long-lived state. The decay of the absorption maximum at \(\sim980\) nm is fitted by an exponential function with a time constant of 57 ns. The decay is accompanied by a complemen-
tary exponential rise (fitted by an exponential function with a 57 nm time constant) of absorbance at 550 nm. Absorbance at this wavelength is due to the carotenoid triplet state, and its rise indicates the formation of $^{3}\text{C-P-C}_{60}^{0}$ by charge-recombination of $\text{C}^+\text{-P-C}_{60}^-$. The decay of this absorbance can be observed on an even longer time-scale, and has a time constant of 4.9 $\mu$s in absence of oxygen.

3.2 Why TDDFT?

While many experimental properties of porphyrin-$\text{C}_{60}$ based dyads and triads are known, less is known from an ab-initio theoretical point of view. The main reason is that the large size of the systems yields traditional accurate quantum-chemistry methods such Configuration Interaction (CI) impractical or infeasible. Less accurate but computationally efficient methods such as Density Functional Theory (DFT) have successfully been employed to describe the ground state of such compounds [18], but unfortunately, the prediction of excited state properties, like the optical absorption spectrum, from the ground state Kohn-Sham orbitals and eigenvalues usually leads to results that are in disagreement with the observed spectra. In particular the role of the interfaces between different parts of the triad and between the molecule and the solvent are not understood in spite of the fact that they are of paramount relevance to the problem of improving the energy conversion efficiency of next generation solar cells.

Time Dependent Density Functional Theory (TDDFT) is a rigorous and in principle exact method that allows the calculation of excited-states through an extension of DFT to the domain of time-dependent external potentials [15].
Chapter 4

Ground State

Our first goal was to study the ground state properties of the molecule, and compare the electronic structure to the electronic structure of the separated components. For all our calculations we used an optimized geometry obtained by Baruah et al. [18]. In this structure the molecule can be entirely embedded in a box approximately $55 \times 16 \times 20$ Å wide, the longest side being along the $x$ axis. As it is also clear following a steric argument, the porphyrin ring is perpendicular to the aryl rings, which, in turn, are coplanar with the carotenoid. The optimized geometry shows a slight bent in the carotene chain (see Figure 4.1). In the calculations of the separated moieties the same geometries used in the triad were employed.

4.1 Geometry Optimization

The C-P-C$_{60}$ system is composed by 207 atoms with 632 valence electrons. Its structure corresponds to the formula C$_{132}$H$_{68}$N$_6$O. The geometry optimization was carried out, using the LBFGS scheme [19] [20], by Baruah et al. [18]. Initially the geometries of the separate units were optimized before constructing the triad. After forming the composite molecular triad, its geometry was optimized again. Since the molecule has a quite floppy structure, two different geometries were optimized. In the first geometry, the three subunits were attached in such a way that the resultant triad has an elbow shape structure. Its energy after optimization turned out to be higher
by about 0.6 eV and also the dipole moment for the final charge separated structure is much smaller. The linear geometry as shown in Figure 4.1 was found to be lower in energy and all subsequent calculations were carried out on this geometry. In the optimization stage, the process was carried out until the smallest force was 0.003 eV/Å and RMS force was 0.076 eV/Å. It can be pointed out here that NMR studies on carotenoid-porphyrin dyad shows a structure similar to the linear structure [21]. Similar structure was found by Smirnov et al. as the lowest energy structure based on a molecular mechanics level calculation [22]. We would like to point out that the molecule has a long
4.2 Preliminary Tests

In a real-space based approach the choice of the grid mesh is a critical parameter, and the consistency of the calculations must be checked with a careful set of convergence tests. A cartesian grid was chosen with uniform spacing of the mesh. We analyze the convergence of the eigenvalues, of the last 6 occupied states and of the first 4 unoccupied states as a function of the distance between grid points.

The first test was performed to determine the volume necessary to enclose the states of the molecules. In the open source code octopus [23, 24] is possible to choose a particular box shape that is composed putting a sphere of radius $R$ over all the atoms. The union of all these spheres makes the box shape that enclose the molecule. As boundary conditions we imposed the wave-functions to be zero at the surface of the volume. This approximation keeps the consistency only if the surface of the box is far enough from the system, because if the box is too small the wave-functions will be forced to go to zero unnaturally. Moreover if the box is too large, will be increased the memory requirement and the computational time because of the large number of grid points. The test analyze the convergence of the states changing the values of radius sphere, and for all the moieties was observed a good convergence for value of $R \geq 4.0$ Å.

The second test was performed analyzing the energy of the states changing the value of the mesh spacing. This test allow us to find out the largest value of spacing for which ground state quantities are expect to converge. Figure 4.2 shows that the convergence of the systems was maintained until a spacing of 0.26 Å.
Figure 4.2: Plots of the last six occupied orbitals (red lines) and first four unoccupied orbitals (green-dashed lines) for the three moieties of the triad at different values of spacing.
4.3 Results

We have thus performed a plain DFT calculation at the LDA level, using the Perdew-Zunger correlation functional \[25\]. The core electrons were represented via Troullier-Martins pseudo-potentials \[26\], and the Interpolating Scaling Functions method \[27\] was used to efficiently solve the Poisson’s equation in the calculation of the Hartree potential. All the simulations in the present work, a part from the geometry optimization, were performed using the open source code octopus on a Linux cluster (IBM BCX/5120) composed on Opteron Dual Core 2.6 GHz processors, maintained by CINECA Bologna. All the quantities were discretized in real-space using a uniform mesh with 0.2 Å spacing that guarantees the convergence of the total energy of the system \[24\]. This value of spacing, couple with a radius \( R = 4.0 \) Å of the atomic spheres that compose the simulation box, gives 862,017 points on the inner mesh, and 1,287,768 points adding the boundary mesh.

In Table 4.1 we report the ground state energies of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) for the isolated moieties and for the full triad. The detailed energy levels for other orbitals are depicted in Figure 4.3.

Comparing the values of the HOMO and LUMO energies of the triad with those of the isolated moieties we notice that the energy of the HOMO in the triad and in the isolated \( \beta \)-carotenoid differ by only 40 meV, as well as the energy of the LUMO in the triad and in the isolated \( C_{60} \). Moreover, looking at Figure 4.4 and 4.5 we observe that it is possible to find a close correspondence between many of the orbitals localized on each molecule,

<table>
<thead>
<tr>
<th>molecules</th>
<th>( \epsilon_{HOMO} ) (eV)</th>
<th>( \epsilon_{LUMO} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta )-carotenoid</td>
<td>-4.47</td>
<td>-3.49</td>
</tr>
<tr>
<td>Diaryl-porphyrin</td>
<td>-5.15</td>
<td>-3.31</td>
</tr>
<tr>
<td>pyrrole-C( _{60} )</td>
<td>-5.89</td>
<td>-4.42</td>
</tr>
<tr>
<td>Triad</td>
<td>-4.51</td>
<td>-4.38</td>
</tr>
</tbody>
</table>

Table 4.1: Energy of HOMO and LUMO respectively for \( \beta \)-carotenoid, Diaryl-porphyrin, pyrrole-C\( _{60} \) and the whole triad.
Chapter 4. Ground State

Figure 4.3: Ground state energy levels of the triad and of the separated moieties: $\beta$-carotenoid ($\beta$car), Diaryl-porphyrin (Dpor), and Pyrrole-C$_{60}$ (pyr-C$_{60}$).

and orbitals of the full triad. In particular the HOMO wave-function of the triad is localized on the carotenoid, and it corresponds to the HOMO of the isolated $\beta$-carotenoid, while the LUMO of the triad is fully localized on the C$_{60}$ and it corresponds to the LUMO of the C$_{60}$ alone. The same is for the HOMO-2 and LUMO+4 of triad that correspond respectively to the HOMO and LUMO of the isolated Diaryl-porphyrin.

In some other cases the correspondence between the localization of orbitals remains, but some degeneracies are lifted, for example the triply degenerate C$_{60}$ LUMO is split into three separate levels in the triad. Finally some orbitals present a clear mixed character (Figure 4.3), such as the LUMO+5, LUMO+6, LUMO+7 with mixed P-C$_{60}$ character, or HOMO-6, with mixed C-P character. These orbitals however do not appear to have a major role.
4.4 Conclusions

From the latter results we conclude that the electronic structure of the ground state of the triad is well approximated by the overlap of the electronic structures of the isolate molecules (Figure 4.3). It is a noteworthy fact that this property is not an artefact of the local density approximation adopted here, but it is also an experimentally observed property of the system \[^17\]. This point becomes more clear with the analysis of the excited-state properties in Chapter 5.

In Chapter 11 we illustrate the basic working of a single-junction cell, and
Figure 4.5: Ground state energy levels of the triad. Some orbitals of the triad are depicted.

we said that the necessary condition for the electrons migration is that the valence band of a side of the junction falls into the band gap of the other side. All the examples of third-generation solar devices presented in the Chapter are based on the same idea, where the sides of the junction are replaced by electron donor/acceptor moieties creating assemblies. In the triad presented here the porphyrin is the donor moiety and the fullerene is the acceptor moiety.

There are two reason because this type of assembly is considered a good candidate for third-generation photovoltaics. The first could be detected only looking the electronic structures of the electron donor, the dyaril-porphyrin, and of the electron acceptor, the Fullerene. In Figure we can notice
the same type of structure of the p–n junction, where the HOMO of the porphyrin, at -5.15 eV, falls into the HOMO-LUMO gap of the fullerene. Gap of about 1.81 eV, from the HOMO at -6.14 eV to the LUMO at -4.33 eV. Then it is present the necessary condition because the photoexcited electron could migrate to the almost degenerate LUMO of the C$_{60}$.

The second important consideration is the presence of mixed P-C$_{60}$ character orbitals in the triad at energy close to the LUMO+4 at -3.39 eV (see Figure 4.5). This is the state supposed to be the end point of the photoexcitation, and it corresponds to the LUMO of the porphyrin moiety. For example, the shape of the LUMO+5 and LUMO+6, respectively at only 28 meV and 64 meV above the LUMO+4, suggests the possibility that the electron migration could be made easier by the presence of these mixed orbitals.

As mentioned above, the β-carotenoid is an additional electron donor moiety. His role will be better explained in the Chapter 6.
Chapter 5

Excited States

In this Chapter we show the application of TDDFT for the calculation of the optical absorption spectra of the triad and of its components. The method used, illustrated in Section 2.3, is recalled and deepened before the results are analysed.

5.1 Propagation Scheme

Starting from the ground state Kohn-Sham orbitals $\tilde{\varphi}_j$, the system is instantaneously perturbed by a weak external electric potential of magnitude $k_0$ along the principal cartesian direction (i.e. by applying the external potential $\delta v_{\text{ext}}(r, t) = -k_0 x_\nu \delta(t)$). The magnitude of the perturbation is kept small in order to keep the dipolar response linear \cite{24}. In this way all the frequencies of the system are excited with the same weight. The initially perturbed states therefore become

$$\varphi_i(r, t_{0^+}) = e^{ik_0 x_\nu} \tilde{\varphi}_i(r).$$

Now the orbitals are propagated in time using the time-evolution operator $\hat{U}$ (see equation (2.14)), and the new wave-functions are used to solve the time dependent KS equations

$$i \frac{\partial}{\partial t} \varphi_i(r, t) = \left[ -\frac{\nabla^2}{2} + v_{KS}(r, t) \right] \varphi_i(r, t).$$
In order to reduce the error in propagation from \( t_0 \) to \( t_f \), the time interval is splitted into smaller sub-intervals of duration \( \Delta t \). The orbitals are then propagated from \( t_n \) to \( t_n + \Delta t \), step by step, until to reach \( t_f \). The simplest approximation to the time-evolution operator \( \hat{U} \) is a direct expansion of the exponential in a power series of \( \Delta t \)

\[
\hat{U}(t + \Delta t, t) \approx \sum_{l=0}^{k} \left[ -i\hat{H}(t + \Delta t/2)\Delta t \right]^l l! + \hat{O}(\Delta t^{k+1}) .
\]  

(5.1)

Unfortunately, this expression does not retain the unitarity of the operator. To correct this it is possibile to use the enforced time-reversal symmetry method [28]. This procedure relies on the fact that we can obtain the state at time \( t + \Delta t/2 \) either by forward propagating the state at \( t \) by \( \Delta t/2 \), or by backward propagating the state at \( t + \Delta t \). In fact we can write

\[
\varphi(t + \Delta t/2) = \hat{U}(t + \Delta t/2, t)\varphi(t) = \hat{U}(t - \Delta t/2, t + \Delta t)\varphi(t + \Delta t) ,
\]

that imposing the inverse relation \( \hat{U}^{-1}(t + \Delta t, t) = \hat{U}(t - \Delta t, t) \) becomes

\[
\varphi(t + \Delta t) = \hat{U}(t + \Delta t/2, t + \Delta t)\hat{U}(t + \Delta t/2, t)\varphi(t) .
\]  

(5.2)

The whole procedure amounts to the following steps: i) obtain an estimate of KS wave -functions at time \( t + \Delta t \) using a “low quality” formula (for example the expression (5.1) expanded to third or forth order); ii) construct an approximation to \( \hat{H}(t + \Delta t) \) and \( \hat{U}(t + \Delta t/2, t + \Delta t) \); iii) apply the equation (5.2). By enforcing the time-reversal symmetry in the approximate operator, and splitting the interval \( \Delta t \) in two halves, we recover the unitarity of the original time-evolution operator. This procedure leads to a very stable propagation.

The numerical discretization of the propagation equations requires that a finite difference equation is defined on a discretized grid in both space and time. This lead to a dependency of the time step on the size of space meshing. In addition the time-step depends on the method used to numerically calculate the exponential of the Hamiltonian in the propagation operator. For the triad we used a fourth order Taylor expansion that forces us to use
5.2. Results

a small time-step (1.69 as). For the isolated molecules we use the Lanczos method \[29\] that is compatible with a larger time-step (7.89 as), resulting in a window of approximately 8 eV for the described spectral range. The KS orbitals were propagated for 15 fs in total, that corresponds to a spectral resolution of about 0.15 eV.

Finally the dynamical polarizability, is obtained from

\[
\alpha_{\nu\nu}(\omega) = -\frac{1}{k_0} \int dx_{\nu} \delta n(r, \omega),
\]

where \(\delta n(r, \omega)\) is the Fourier transform of \(n(r, t) - n(r, t = 0)\). The photo-absorption cross section is related to the imaginary part of the polarizability through the expression

\[
\sigma(\omega) = \frac{4\pi\omega}{c} \frac{1}{3} \text{Im}[\text{Tr}(\alpha(\omega))].
\]

5.2 Results

We start our description of the optical properties of the system analyzing the absorption spectra of the separated parts of the triad. In Figure 5.1 it is reported the comparison between theoretical optical absorption in diarylporphyrin and observed optical absorption in a free-base porphyrin. The TDDFT spectra is obtained with a real time propagation, and the observed absorption as reported in Ref. \[30\]. In order to get a plausible attribution of the single-excitation states involved in the process of photo-excitation, we have also performed a linear response calculation \[31, 32\] of the absorption spectrum on the diaryl-porphyrin moiety.

The spectra obtained by the two methods are quite similar, even if it is not expected that they are identical. In particular the analysis of the absorption of the diaryl-porphyrin allows us to clarify that, even if an intense shoulder only appears in the UV region around 3.3 eV, the so called B-band of the porphyrin, the actual very weak onset of absorption, the Soret Q-band, is in the orange-yellow visible region at approximately 2.2 eV. In the inset of Figure 5.1 that magnifies the region between 2.0 to 2.4 eV, are reported the transition energies obtained by linear response calculation. The excitation named “a” at 2.14 eV is composed at 60% by the transition
Figure 5.1: Comparison between theoretical TDDFT optical absorption in diaryl-porphyrin and observed free-base porphyrin absorption as in [30]. In the inset the region between 2.0 to 2.4 eV is magnified, and the vertical lines are the transition energies obtained by linear-response calculations.

HOMO→LUMO+1 and at 38% by HOMO-1→LUMO. The excitation “b” at 2.32 eV is composed at 56% by the transition HOMO→LUMO and at 42% by HOMO-1→LUMO+1. The remaining 2% for both the excitation is due to other transition with a not relevant weight. These two transitions were observed also in the spectra obtained by time propagation (thick line). The non-symmetric shape of the large peak at about 2.2 eV suggest that a longer propagation could resolve two peaks.

In Figure 5.2 left, it is shown the comparison between theoretical TDDFT optical and observed absorption for fullerene as in [33]. In these spectra we can notice a good correspondence of the peaks, provided a mean red-shift of about 0.28 eV is taken into account. The right plot shows the comparison between the β-carotenoid main absorbance peak as observed in [34], at
Figure 5.2: Left: comparison between theoretical TDDFT optical and observed absorption for fullerene as in [33]. Right: comparison between the β-carotenoid main absorbance peak as observed in [34] and the calculated one.

approximately 1.24 eV and the calculated one. Here is visible a blue-shift of about 0.47 eV. For an in depth discussion about the effect of exciton confinement in molecular chains see also Ref. [35].

The TDDFT photo-absorption cross-section of the triad and of the separated molecules is shown in Figure 5.3. We can easily distinguish one dominant peak at 1.7 eV, several small features between 2.0 and 3.0 eV, another peak at 3.3 with a shoulder at 3.6 eV, and a group of peaks between 4.0 and 8.0 eV.

The decomposition of the spectrum into optical densities of the isolated moieties clearly shows again that the total spectrum is very well approximated by the sum of the spectra of the parts. In particular the main feature at 1.7 eV appears to be entirely originated by the β-carotenoid, which has
Chapter 5. Excited States

Figure 5.3: Calculated absorption spectrum of the triad, and the isolated pyrrole-C$_{60}$, Diaryl-porphyrin and β-carotenoid.

a weak contribution on the rest of the spectral range, apart from a small feature at 2.3 eV that partially obscures the weak Soret Q-band of the diarylporphyrin. The B-band of the diaryl-porphyrin is the main contribution at 3.2 eV, and the diaryl-porphyrin has another prominent peak in the ultraviolet region at 6.6 eV. The contribution of pyrrole-C$_{60}$ counts many peaks, notably two isolated at 5.3 and 5.9 eV, and several more from 4.0 to 5.0 eV.

The comparison of our calculations with the experimentally observed absorption in similar triads clearly shows that TDDFT improves on DFT in describing the main features of the spectra. In Figure 5.4 we compare our data to the absorption reported in Ref. [17], that refers to a triad in 2-methyltetrahydrofuran solution. We observe a good one-to-one correspondence between the calculated and the observed peaks, whose positions appear overestimated in the calculation by an overall rigid shift of about 0.3 eV. We do not investigate here the possible role of the environment, that
5.2. Results

Figure 5.4: Comparison between theoretical and observed optical absorption for the full C-P-C₆₀. DFT is the calculated spectrum as in [18]. TDDFT present work. EXP depicts the observed spectrum as reported in [17].

might well be responsible for the rigid shift, but is unlikely to qualitatively change the shape of the spectrum. In fact triads made of slightly different components, or immersed in different solvents, often have very similar spectra (see Ref. [36]). In particular the prominent porphyrin peak around 3 eV and the wide band between 2.0 and 3.0 eV seem to be common features in all the experimental data. The transitions approximately at 2.0 eV corresponds to the calculated transitions in the diaryl-porphyrin alone, and they are also responsible for the optical excitation of the triad as a whole.

Also notice that, despite the apparent superposition of the main experimental peak to a peak in the DFT calculation, the nature of the latter is predicted to be of C₆₀ character, while the corresponding TDDFT feature at 3.5 eV correctly is attributed to the porphyrin (see decomposition in Figure 5.3). The experimental data range in Refs. [17, 36] are limited above approx-
imately 2.0 eV, but as mentioned above, the \( \beta \)-carotenoid absorption does not appear to be relevant for the photo-conversion in the triad.

5.3 Conclusions

In summary, we have addressed the fundamental problem of describing the creation of electron-hole pairs and the efficient charge separation in a supramolecular assembly of interest for third generation solar devices. Since not all the effects leading to the final-state charge separation are fully known the accurate description of the excited states of such an object is a crucial step in order to understand the details of the photo-absorption and charge-transfer processes occurring in the system.

We have calculated the optical absorption cross section of such a large system using TDDFT as a rigorous ground for the excited states dynamics. In addition to the computational challenge, our calculations demonstrate that the simple ground-state DFT description of the system is not able to capture the correct shape of the photo-absorption spectrum. In contrast we have shown that the main features of the TDDFT spectrum are in good agreement with the experimental data, and the analysis of the total absorption in terms of the absorption of the isolated moieties indicates that even at the TDDFT level (at least in the weak field limit) the component molecules in the triad do not appear to strongly interact.

Finally, in Figure 4.5 we have shown the energy levels for the ground state of the full triad, and we have emphasized the two orbitals, HOMO-2 and LUMO+4, localized on the porphyrin moiety. From the analysis of the electronic structures we supposed that these two orbitals are responsible for the optical excitation. From the analysis of the spectra of the porphyrin we find that the orbitals that could be involved in the photo-excitation process are the HOMO-1, HOMO, LUMO and LUMO+1 of the moiety. This allow us to think that also in the triad there are other orbitals involved in the photo-excitation, in particular considering the presence of the orbitals with mixed P-C\(_{60}\) character. As concluding remarks we must recall that the 15 \( fs \) time span of our simulation is unlikely to account for the complete charge transfer process, that occurs on a different time scale, but it is able to accurately
describe the photo-excitation of the molecule. Nevertheless we have been able to get a valuable insight about the charge transfer from the careful examination of the energy levels and of the calculated absorption spectrum of the system.
Chapter 6

Charge Transfer Dynamics

In Chapters 4 and 5 we have analyzed respectively the theoretical ground state and optical properties of the triad and of its parts. In this chapter we address the charge transfer dynamics in the whole triad.

The charge transfer dynamics is a crucial step in the realization of third-generation photovoltaics devices such as Grätzel or donor-acceptor based systems, and it happen in a subsequent step respect to the photo-excitation process. Also the time scales are different.

We want to stress the needed features of a good candidate for third-generation photovoltaics. It should be composed at minimum by two units each with a different role in the photo-induced charge separation mechanism. The first unit is a chromophore that absorbs in visible light and the second unit is an electron acceptor capable to provide electronic coupling that allows the photo-induced electron transfer. The central idea is to separate the light absorption process from the charge collection process, mimicking natural light harvesting procedures in photosynthesis. In order to make solar cells efficient, intense visible absorption in addition to rapid charge transfer are required. The efficiency is determined by two main factors: i) the maximum photocurrent density, related to the charge transferred rate from the chromophore (donor) HOMO to the acceptor unoccupied orbitals (probably the LUMO), and ii) the open circuit potential, related to the energy difference between the HOMO of the electron donor to the LUMO of the acceptor. In addition to those, other two features could increase the efficiency,
a long mean lifetime of the charge separated state and good photochemistry stability.

All the properties described above are present in the Carotenoid-Porphyrin-
$C_{60}$ triad, where an additional unit take the role of second electron donor. 
The function of the carotene is described in the next sections.

6.1 Photo-induced Charge Separation 
Mechanism

Resting on the careful examination of the structure, levels, and orbital local-
ization we concluded that the triad have the perfect electronic configuration 
for a photo-induced charge separation. This thanks to the fact that the HOM-
MOs and LUMOs of the moieties are localized in the respective sub-molecule, 
and right positioned. In particular the HOMO of the porphyrin falls into the 
HOMO-LUMO gap of the fullerene, and the presence of mixed P-C60 char-
acter orbitals in the triad at energy close to the LUMO of the porphyrin, 
that could made easier the electron migration.

We are now able to achieve a theoretically motivated view of the photo-
excitation process, and of the subsequent charge-transfer that can be sum-
marized in the following chain of steps:

\[
C-P-C_{60} + h\nu \rightarrow C-P^{*-}C_{60}^{*}
\]
\[
C-P^{*-}C_{60}^{*} \rightarrow C-P^{+}-C_{60}^{-} \rightarrow C^{+}-P-C_{60}^{-}
\]

The first step corresponds to the optical transition from HOMO-2 to 
an orbital between LUMO+4 and LUMO+7. We call this excited state 
$C-P^{*-}C_{60}^{*}$. The electron in a previously unoccupied orbital on the porphyrin 
is now under the influence of the high affinity of the $C_{60}$, and it is easily 
accommodated on the almost-degenerate orbitals LUMO+1, LUMO+2 at 
0.14 eV above LUMO localized on the $C_{60}$. In the assembled triad the three-
fold degeneracy of the $C_{60} T_{1u}$ LUMO is broken due to the presence of the 
Pyrrrole and the LUMO of the triad is a singlet state. We have then reached 
a configuration $C-P^{+}-C_{60}^{-}$. The last step consists in a hole delocalization
6.1. Photo-induced Charge Separation

The scheme shows the photo-excitation step and the two steps representing the electron and hole migration.
from the Porphyrin HOMO to the Carotenoid HOMO to give the final state $C^+{-}P-C_{60}^-$. Obviously only the study of the full dynamics of the whole process can support the latter two steps interpretation, which is inferred here on the basis of the analysis of the energy levels in Figure 6.1 and on the electrochemical properties of the moieties. Despite the fact that the lifetime of the final state is estimated to be in the order of tens of $ns$, it is possible to get an accurate description of the photo-excitation, and possibly charge-transfer processes that occur on a much faster time-scale.

As we have already stressed, it is the almost non-interacting character of the moieties, demonstrated by the shape of the absorption spectrum, and the nature of the molecular orbitals, that makes it possible to describe this process in terms of orbitals localized on each component. In fact the charge-transfer states associated with this molecule are not dipole allowed transitions due to the fact that the hole on the (donor) carotene and the particle-state on the $C_{60}$ (acceptor) molecule are essentially non overlapping.

### 6.2 Methods

In order to focus on the charge transfer process we have chosen as the initial state for the propagation a single-particle state, presumably close to the real excited state after a photon absorption. Namely the state obtained by occupying the LUMO+4 of the triad with one electron, taken from the state HOMO-2. As mentioned above these two orbitals are almost fully localized on the porphyrin. This excitation corresponds to an increase of about 1.85 eV to the ground state energy.

To decrease the computational time for this demanding task, we decided to use a mesh spacing of 0.24 Å, an acceptable value that guarantees the convergence of the total energy of the system (see Section 4.2 about the tests performed to obtain a good simulation grid). In addition we increase the radii, of the spheres that compose the volume of the simulation box, from 4.0 Å to 5.0 Å. This to be sure to contain the orbitals also for long time propagations.

We have performed calculations both with clamped and mobile ions, in order to investigate the role of ion-electron dynamics coupling in the charge-
6.3 Results

In order to obtain evidence of the charge-transfer process we have partitioned the simulation box into three regions matching the moieties boundaries along the longitudinal axis of the molecule. Figure 6.2 shows the evolution of the excess electronic charge contained in the volume including the pyrrole-C$_{60}$ and in the remaining part of the molecule. The black line represents the fraction of electronic charge transferred into a volume that contain the pyrrole-C$_{60}$ moiety as function of time. From this plot is easy to see that there is an increase of the electronic charge into this volume, which corresponds to a transfer process. In the mobile case we have assigned random velocities to the atoms following a Boltzmann distribution with a temperature of 300 K.

Figure 6.2: Fraction of electrons transferred to the pyrrole-C$_{60}$ part (black line) from the Carotenoid-Porphyrin part (cyan line) of the triad as a function of time after excitation.
decrease of electronic charge into the volume containing the carotenoid and the porphyrin. Less than 70 fs are needed to transfer 0.9 e to the fullerene.

The fact that the charge transfer is tied to the dynamics of the ions is visible in the Figure 6.3. The solid line shows the charge transferred to fullerene when the ions are allowed to move freely, while the dashed line shows the charge transfer if the triad’s ions are held fixed. In the last case the fraction of electron transferred into the fullerene volume after 17 fs is too small to be considered a trend rather than a fluctuation. This plot clearly shows that the energy recombination due to a rearrangement of the ions plays a major role in the process.

In Figure 6.4 we can see the time dependent perturbation of the density $\delta n(r, t)$ at different values of the time propagation. The pictures are snapshots of an animation visible following the link:
6.3. Results

(a) time = 9.31 fs

(b) time = 17.69 fs

(c) time = 41.74 fs

(d) time = 68.15 fs

Figure 6.4: Plots of the time dependent perturbation of the density $\delta n(r, t)$ (see equation (2.15)) at different values of time. The letters “a”, “b”, “c”, and “d” are referred at the points of the Figure 6.2.
It is obtained by computing the difference between the charge density at time $t$ and the density of the KS ground state (see equation (2.15)). The magenta isosurface corresponds to a positive difference and the green to a negative difference. In the figure it is evident an increase of the magenta color during the time evolution on the fullerene region. It means an increase of charge density in this region. From Figure 6.4(a) to Figure 6.4(b) it is also possible to notice a decrease of the charge density on the porphyrin region in terms of increase of the green isosurface. From Figure 6.4(c) to Figure 6.4(d) is visible a charge polarization, that starts at about 40 fs, where in the region between the fullerene and the porphyrin is observable an emptying of charge. Since we know from Figure 6.2 that a net charge is transfered from the porphyrin to the fullerene, we interpreted these changes of signs as a local polarization of the moieties.

6.4 Conclusions and Work in Progress

In order to clarify the spectral weight of different excitations in the charge fluctuations, we have performed a Fourier analysis of the charge variation on the fixed volumes. We have decomposed the charge density $\rho(t)$ into a linear term and an oscillating term

$$\rho(t) \rightarrow A t + B + f(t).$$

Then we have performed a Discrete Fourier Transform of the oscillating term alone

$$f(t) \rightarrow \text{dft}[f(t)] = F(\omega_n).$$

The functions in the frequency space are plotted in Figure 6.5. In all the three regions is possible to see frequencies of relevant amplitude in the energy region until 1 eV. These small energetic frequencies could be associated to vibrational modes of the molecule. In addition, in the fullerene and carotene regions are also present relevant frequencies from 3.0 to 3.5 eV that could be assigned at electronic modes. As an assessment of our procedure in Figure
6.4. Conclusions and Work in Progress

Figure 6.5: Discrete Fourier transform of the excess of electronic charge contained in the volumes matching the moieties. In the vertical axis is reported the amplitude of the Fourier coefficients.

In section 6.6 we have reconstructed the signal back to the time domain. Using only the first 10 frequencies we are able to obtain a good matching with the main features of the original function. Moreover we needed the first 50 frequencies to reproduce properly also the small fluctuations visible in the inset of the fullerene plot in the Figure 6.6.
Figure 6.6: Harmonic reconstruction of the excess of electronic charge contained in the volumes matching the moieties.

The next step in the study of the charge transfer dynamics is the attribution of the frequencies used for the reconstruction at the mode (rotational, vibrational, electronic, etc...) of the molecule. This could help us to better understand the role of the ions dynamic in the charge transfer process. Some of these mode are visibly indispensable for the charge transfer (see...
Figure 6.3 and non influential in the photo-excitation process, probably due to the different time scale in which these process are brought to completion.

In addition, with a single-particle excitation in a single state (the LUMO+4 of the triad), probably we have provided the amount of energy necessary for the excitation of other transitions. In the Figure 6.6 the plot concerning the carotene shows an increase of charge comparable with that on the fullerene. This could be due to the excitation of some transitions that involve the orbitals localized on the carotene. For this reason a next calculation could be done performing an excitation with partial occupation of the states with mixed P-C$_{60}$ character.
Bibliography


