First Principles Modeling of Soft X-ray Spectroscopy of Complex Systems

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Abstract

The electronic structures of complex systems have been studied by theoretical calculations of soft x-ray spectroscopies like x-ray photoelectron spectroscopy, near edge x-ray absorption fine structure, and x-ray emission spectroscopies. A new approach based on time dependent density functional theory has been developed for the calculation of shake-up satellites associated with photoelectron spectra. This method has been applied to the phthalocyanine molecule, describing in detail its electronic structure, and revealing the origin of controversial experimental features. It is illustrated in this thesis that the theoretical interpretation plays a fundamental role in the full understanding of experimental spectra of large and complex molecular systems. Soft x-ray spectroscopies and valence band photoelectron spectroscopies have proved to be powerful tools for isomer identification, in the study of newly synthesized fullerene molecules, the azafullerene C_{48}N_{12} and the C_{50}Cl_{10} molecule, as well as for the determination of the conformational changes in the polymeric chain of poly(ethylene oxide). The dynamics of the core excitation process, revealed by the vibrational fine structure of the absorption resonances, has been studied by means of density functional and transition state theory approaches.
List of Publications


VIII. Characterization of the electronic structure of C_{50}Cl_{10} by means of soft x-ray spectroscopies, B. Brena and Y. Luo, *Manuscript*.

IX. Molecular ordering in isonicotinic acid on rutile TiO$_2$(110) investigated with valence band photoemission, J. O’Shea,


**XI. Electronic and geometrical structures of the N1s⁻¹3π excited states in the N₂O molecule**, B. Brena, S. Carniato and Y. Luo, *Manuscript*. 

ii
Comments on my own participation

I have been responsible for all the theoretical calculations in PAPERS I to IX, and for the preparation of all the manuscripts in which I am the first author. I have performed most of the calculations for PAPER XI. I have contributed to the discussion and the manuscript writing of PAPER X.
Contents

1 Introduction 1

2 Soft x-ray spectroscopies 5
  2.1 Adsorption of radiation 6
  2.2 X-ray photoelectron spectroscopy 9
    2.2.1 The shake-up process 10
  2.3 Near edge x-ray absorption fine structure 12
    2.3.1 Selection rules 13
    2.3.2 Polarization dependence 14
  2.4 Decay of the core excited state 16

3 Theoretical methods 21
  3.1 The Born-Oppenheimer approximation 21
  3.2 The Slater determinant 23
  3.3 Solving the Schrödinger equation: Hartree-Fock 23
  3.4 Koopmans’ theorem 25
  3.5 Density functional theory 26
    3.5.1 Exchange and correlation functionals 29
  3.6 Time dependent density functional theory 30

4 Calculation of spectroscopies 33
  4.1 Electron transitions 34
    4.1.1 Ionization potentials: ΔKS approach 34
    4.1.2 Absorption spectra 34
    4.1.3 Emission spectra 36
  4.2 The Franck-Condon principle 37
    4.2.1 The linear coupling model 39
CONTENTS

5 Phthalocyanines and shake-up calculations 41
  5.1 C1s shake-up of phthalocyanines .................. 44
  5.2 Orientation of phthalocyanine films ................. 49

6 Soft x-ray spectroscopy of large molecules 53
  6.1 The conformation of poly(ethylene oxide) .......... 53
      6.1.1 The calculated electronic structure ........... 55
  6.2 Fullerenes ........................................... 57
      6.2.1 Two isomers of C_{48}N_{12} .................... 58
      6.2.2 The electronic structure of C_{50}Cl_{10} ........ 60

7 Vibrational profiles of absorption resonances 63
  7.1 The Renner-Teller effect on the N_{2}O 1s \rightarrow 3\pi^* excitation 64
  7.2 Vibrational analysis of the 1s\rightarrow \pi^* excitation in acetonitrile 66

References 69

Acknowledgments 75
1

Introduction

The development of x-ray spectroscopies constitutes one of the most important achievements in fundamental science of the last century, as they are outstanding tools for the detailed study of electronic and morphological structures at the atomic level. The working principle of these techniques is based on the interaction of electromagnetic radiation with matter. The physical processes governing the absorption and emission of soft x-rays in matter constitute not only an extremely fascinating field of research in itself, but, moreover, they are used to extract unique information at a fundamental level on specimens of relevance for plenty of scientific branches. Applications range from material science to biological, medical, and environmental research.

X-ray spectroscopies and their theoretical interpretation find their origin in some of the milestones of modern physics. Fundamental works, at the basis of the spectroscopical methods used in this thesis, are, for example, the discovery of x-rays, operated by Wilhelm Conrad Röntgen in 1895\(^1\) and the interpretation of the photoelectric effect by Albert Einstein in 1905, which followed the introduction of the quantization of electromagnetic radiation by Max Planck in 1900. The quantized model of the hydrogen atom was proposed by Niels Bohr in a paper in 1913, and the Schrödinger equation was formulated in 1925.\(^2\) More recently, with relevance to this thesis, the Nobel Prize in Physics in 1981 was awarded to

\(^1\)W.C. Röntgen was awarded the first Nobel Prize in Physics in 1901 due to his discovery of the x-rays, whose name was chosen to indicate that their nature was initially unknown.

\(^2\)It is needless to underline the importance of these works in the development of modern physics, and this list has no ambition of being exhaustive. The Nobel Prizes
1 Introduction

Kai M. Siegbahn, for the development of high resolution photo-electron spectroscopy, and in Chemistry in 1998 to John A. Pople and Walter Kohn, for the development of important quantum chemical methods.

It is a great advantage for this research field that theory and experiment have the possibility to strictly interplay. This close collaboration made it possible to successfully shed light on many aspects of the inner shell processes. The progress in the experimental and theoretical branches occurs almost simultaneously, taking advantage on the newest and most advanced technologies. Nowadays, the best laboratories to provide suitable radiation sources are the synchrotron facilities, that are located, and still being built, in many parts of the world\textsuperscript{3}. Some characteristics of synchrotron radiation are high resolution, high brilliance, possibility to tune the photon energy and to select the radiation polarization. These are exploited in sophisticated experimental methods. From the theoretical side, modelling based on quantum mechanical theories like the Hartree Fock (HF) and the density functional theories (DFT), have been developed and successfully applied in solid state as well as in atomic and molecular physics and chemistry. The rapid development in computer technology has led to more and more powerful computing resources. On one hand, the focus of this research is now moving towards larger and more complex systems, like for instance big molecules of technological and biological relevance. On the other hand, there is an interest in understanding the fine structure revealed by the high resolution spectra, that leads to a deeper comprehension of the inner shell phenomena. In both these types of development, the theoretical description is necessary to extract useful information from the experimental results. This represents a big challenge for the theory, because often, to handle new problems, the established methods need to be modified, or even completely new approaches must be developed.

This thesis is mostly dedicated to the theoretical simulation of soft x-ray spectroscopies applied to large molecules. A part of the work is devoted to the interpretation of the spectral fine structure. The methods employed and the results are described in the next chapters. In the second chapter some soft x-ray spectroscopies are introduced. The focus is turned to those techniques that have been employed in the papers.

\textsuperscript{3}In recent years, Free Electron Lasers are being built, as the 'next step' of light generation sources.
The third chapter is dedicated to some of the theoretical methods that have been developed to solve the Schrödinger equation for molecular and atomic systems, in particular to the HF and DFT theories. These theories have further been implemented in order to obtain an interpretation of the soft x-ray spectroscopies, as is discussed in chapter 4. In the final chapters we report a survey of the results obtained and presented in the papers included in this thesis. Chapter 5 deals with the study of the phthalocyanines. This is done through the calculation of the shake-up states associated to x-ray photoelectron spectroscopy, presented in PAPERS I, II and IV, and through the characterization of phthalocyanine films via the study of the electronic structure (PAPERS III and V). In chapter 6 the analysis carried out for the characterization of large molecules is described. The structure of a large polymer, poly(ethylene oxide) (PEO), has been determined by spectroscopic methods (PAPER VI). The geometrical and electronic structures of recently synthesized molecules of the fullerene family have been studied in PAPERS VII and VIII, and the structure of a isonicotinic acid layer has been analysed in PAPER IX. The calculation of vibrational profiles in near edge x-ray absorption fine structure (NEXAFS) spectra as implemented and shown in PAPERS X and XI is presented in chapter 7. In this context it has been chosen to study two small molecules: acetonitrile (PAPER X) and dinitrogen oxide (PAPER XI).
Soft x-ray spectroscopies

Soft x-rays provide an optimal mean to explore atomic and molecular inner shell processes. In the electromagnetic spectrum, the energies of soft x-rays cover a region between about one hundred to a few thousand of eV\(^{1}\), which coincides with plenty of electronic transition energies of the most abundant elements. This fact has large scientific and technological implications. Atomic resonances and spectral edges of elements with low or intermediate atomic numbers (Z) fall in this spectral region. The absorption edge is the energy needed to extract an electron of a core level by photoabsorption, and the \(K\) and \(L\) edges refer to core electrons with fundamental quantum number \(n\) equal to 1 and 2, respectively. The \(K\) edge of many important elements are below 1000 eV, like Be (112eV), C (284 eV), N (410eV) and O (536eV), as well as the \(L\) edges of Al (73eV), Si (99eV), S (163eV), Ca (346eV), Fe (707eV), Ni (853eV) and Cu (933eV)[1]. Soft x-rays therefore provide a unique and sensitive instrument for elemental characterization. Since they are to a large degree absorbed in many materials, unlike electromagnetic radiation with lower and higher energy, they are difficult to handle, and many experiments need conditions of *ultra high vacuum* (UHV) to be performed. At the synchrotron radiation laboratories plenty of soft x-rays spectroscopies have been developed, using synchrotron radiation as excitation source. These techniques are employed on a variety of specimens ranging from atoms

\(^{1}\)The x-ray region comprises soft and hard x-rays, and extends into the wavelengths between \(10^{-8}\) and \(10^{-11}\) m, corresponding to energies of the order of 100 to \(10^{5}\) eV. Soft x-rays have lower energy (below about 2000 eV) and wavelengths above about 0.1 nm. Hard x-rays correspond to the shorter wavelengths and higher energies.
2 Soft x-ray spectroscopies

![Figure 2.1: Schematic representation of the adsorption of soft x-rays in an atom or in a molecule. The core (c), valence (v) and unoccupied (u) electronic states are indicated, and $\hbar \omega$ is the photon energy. In A, a core electron is photo-ionized into the continuum, leaving an ionized atom (as in XPS spectroscopy); in B an electron is photo-excited into an unoccupied level, leaving the atom in an excited state (as in NEXAFS spectroscopy). The processes illustrated here are simple one-electron pictures.](image)

and molecules in gas and liquid phases, to solid materials like metals, semiconductors and insulators, just to mention a few. The presentation of the experimental techniques and of the theoretical methods in this and in the next chapters will be dedicated to the study of molecules, which is the subject of this work. The interaction of electromagnetic radiation with matter is the physical process at the basis of the spectroscopies we have studied, and which are introduced in the following sections.

### 2.1 Adsorption of radiation

The photoabsorption processes at the electronic level are represented in Figure 2.1, with the expulsion (part A) or excitation (part B) of an electron. If the photon energy, $\hbar \omega$, is higher than the ionization potential (IP)\textsuperscript{2} of the electron, the latter gets excited into the continuum, i.e. ionized: this is the photoelectric effect\textsuperscript{3} (Figure 2.1 part A). If the photon energy matches the energy difference between an occupied and an unoccu-

\textsuperscript{2}The IP is the minimum energy required to extract completely an electron from its orbital.

\textsuperscript{3}When the incoming radiation has an energy of about 0.5 MeV or higher, the photoelectric process is substituted by the Compton effect, which becomes the dominant process at high photon energy. It consists of radiation scattering by individual electrons.
pied electronic level, there is a probability of having an electron transition between these two states. This process is shown in Figure 2.1, part B. In general, the probability per unit time of a transition between an initial state $\Phi_i$ and a final state $\Phi_f$ is given by the Fermi Golden Rule:

$$\Gamma_{i\rightarrow f} = \frac{2\pi}{\hbar} |<\Phi_f|\nabla|\Phi_i>|^2 \delta(E_i - E_f + \hbar\omega)$$ (2.1)

where $\nabla$ is the operator describing the interaction between radiation and matter and $E_i$ and $E_f$ are the electron energies in the initial and final states. The argument of the $\delta$ function derives from the conservation of energy, and tells that this is an absorption process, such that the excitation energy $\hbar\omega$ equals the difference: $E_f - E_i$. It is interesting to observe that the minus sign in front of the photon energy $\hbar\omega$ in the above expression, would have indicated an emission process, in which an electron decays into a level with higher binding energy: the radiative decay and the connected spectroscopies are discussed in the last section of the present chapter. In the case of the photoelectric effect, the final state corresponds to an outgoing free electron, and the argument of the $\delta$ function turns into:

$$\delta(E_i - E_f + \hbar\omega) = \delta(\hbar\omega - E_B - \frac{p_e^2}{2m_e})$$ (2.2)

where $m_e$ is the electron mass, $p_e$ the electron momentum, and $E_B$ is the magnitude of the binding energy of the electron.

The interaction of an electron in a static potential $\phi(r)$ with an electromagnetic field is expressed by the Hamiltonian:

$$H = \frac{\mathbf{p}^2}{2m_e} + e\phi(r) - \frac{e}{m_ec} \mathbf{A} \cdot \mathbf{p}$$ (2.3)

where $\mathbf{A}$ is the vector potential. The vector potential of a monochromatic plane wave has the form:

$$\mathbf{A}(r,t) = A_0 \hat{\mathbf{e}}(e^{i(kr - \omega t)} + e^{-i(kr + \omega t)})$$ (2.4)

Electron transitions can be induced not only by electromagnetic radiation, but, for instance, also by using an electron beam as excitation source. Many laboratories are equipped with electron beam sources, and carry out experiments comparable to some soft x-rays spectroscopies. One example is the electron energy loss spectroscopy (EELS) that provides information similar to the NEXAFS (see next sections) but with different selection rules.

Equation 2.3 is formulated for the classical radiation field after dropping the $\mathbf{A}^2$ term, and specifying the gauge relation $\nabla \cdot \mathbf{A}(r,t) = 0$.\textsuperscript{[2]}
where $\hat{e}$ is the polarization unit vector of the photon electric field. From this expression, and by applying the time dependent perturbation theory, one can obtain a formulation for the harmonic potential $\mathbf{V}$ that represents the transition operator for the absorption (or emission) of a single photon \[3\]. Its expression is:

$$\mathbf{V} = e^{-i\mathbf{k}\mathbf{r}} \cdot \mathbf{p}$$

(2.5)

Since in an atomic transition the wavelength of the radiation is larger than the atomic dimensions, the exponential term can be approximated by a series expansion that can be truncated at the first term (dipole approximation):

$$e^{-i\mathbf{k}\mathbf{r}} = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} (\mathbf{k} \cdot \mathbf{r})^n \approx 1$$

(2.6)

The inclusion in this expression of higher order terms, corresponds to considering multipole transitions. The dipole approximation leads to a simplified formula for the operator $\mathbf{V}$, and the transition matrix ($d_{\mathbf{n}}$) becomes:

$$d_{\mathbf{n}} = \langle \Phi_f | \hat{\mathbf{e}} \cdot \mathbf{p} | \Phi_i \rangle$$

(2.7)

in the momentum operator representation, and:

$$d_{\mathbf{n}} = im\hat{\epsilon} \omega \langle \Phi_f | \mathbf{r} | \Phi_i \rangle$$

(2.8)

in the position operator representation. The resulting expression for the transition probability is:

$$\Gamma_{i\rightarrow f} = \frac{2\pi}{\hbar} | \hat{\epsilon} \langle \Phi_f | \mathbf{r} | \Phi_i \rangle |^2 \delta(E_i - E_f + \hbar\omega)$$

(2.9)

where the transition operator (or dipole operator) is simply $\mathbf{r}$, which is accepted in a large number of cases as a good operative approximation for the description of one-electron transitions in the spectroscopies. There are many situations, however, when a description beyond the dipole approximation is desired.

An important quantity related to photo-absorption is the cross section ($\sigma$), that is a measure of the number of electrons excited/ionized per unit time, divided by the number of impinging photons per unit area and per unit time.\[6\]

---

\[6\]The absorption cross section is usually expressed in cm$^2$ or in barn (1 barn = $10^{-24}$cm$^2$).
Within the dipole approximation, the absorption cross section takes the form\[2]:

\[
\sigma = 4\pi^2 \alpha \omega \hbar \left| < \Phi_f | r | \Phi_i > \right|^2 \delta(E_i - E_f + \hbar \omega)
\] (2.10)

The \(\delta\) function, in general, has a peak when the photon energy \(\hbar \omega\) coincides with an electron transition energy.

In the photoelectric effect, one can calculate the differential cross section for the transition of an electron from a bonded state to a continuum state. The free electron is usually described by a plane wave. One can consider the same absorption cross section as in the transition between two bonded states, but one has moreover to integrate over the density of final states. One obtains, within certain approximations\(^7\), the following expression for the photoelectric differential cross section\[3\]:

\[
\frac{d\sigma}{d\Omega} = 2\sqrt{2}Z^5 \alpha^2 \frac{a_0^2}{a} \left( \frac{E}{mc^2} \right)^{-\frac{7}{2}} \frac{\sin^2 \theta}{(1 - \frac{v}{c} \cos \theta)^4}
\] (2.11)

where \(d\Omega\) is the solid angle into which the electron momentum vector points, and \(\theta\) defines the angle between the electron momentum and the vector \(\hat{e}\). At relativistic energies, or when the photon energy is very close to the electron’s IP (the resonant condition), more complex calculations need to be performed, and the above approximation is no longer valid. After integrating \(d\sigma/d\Omega\) one can introduce a quantity called the mass absorption coefficient, \(N\sigma/\rho\), where \(N\) is the number of atoms per \(\text{cm}^3\), and \(\rho\) is the density in \(\text{g per cm}^3\). Expressed as a function of the photon wave length, the mass absorption coefficient presents a series of edges that correspond to the K, L etc, absorption edges.

### 2.2 X-ray photoelectron spectroscopy

X-ray photo-electron spectroscopy (XPS, often referred to as PES) is based on the photoelectric effect described in the previous paragraph, in which a core electron is photoionized. The process is sketched in figure 2.1, part A. A diagram of the kinetic energy distribution of the emitted electrons (the spectrum) is collected during the experiment. In a

\[^7\]This expression is derived for hydrogen-like atoms, with non-polarized photons in the case of non-relativistic photoelectrons with kinetic energy well above absorption threshold and for light elements.
schematic one-electron picture, which means that the interaction of the photoelectron with the remaining electrons of the system is neglected, the process can be described by the following relation that derives from the energy conservation:

\[ E_B^i = h\omega - E_K^i - \Phi \]  

(2.12)

where \( E_B^i \) is the binding energy of the electron in the initial electronic level \( i \), \( h\omega \) is the photon energy, \( E_K^i \) is the kinetic energy of the photoemitted electron, and \( \Phi \) is the work function, which is a property of the sample. With a good approximation, this formula gives the binding energy of the emitted electron, and allows the XPS technique to be used as a probe to identify the chemical elements present in the sample. The binding energy varies, however, even for electrons in a same core level, since it is considerably influenced by factors like the local chemical and physical environment. These modifications are known as chemical shifts, and provide the XPS technique the ability to distinguish atoms of the same species in different environments, which constitutes the property of atomic selectivity. Photoelectron spectroscopy of the valence electrons can be used to determine the orientation of molecules, due to the directional character of the molecular orbitals. This feature has been exploited in PAPER IV to study the orientation of isonicotinic acid molecules on the rutile TiO_2(110) surface, and in PAPER IX to determine the stacking direction of the molecules of an iron phthalocyanine (FePc) film with respect to the silicon Si(100) substrate.

### 2.2.1 The shake-up process

So far, a simplified picture of the photo-ionization has been discussed, in which the rest of the system is thought to be unaffected by the emission of the electron, and is treated as frozen (unchanged). This description, although very useful for the immediate interpretation of the main spectral lines, does not account for the complexity of the XPS satellite lines and spectral shapes, which are found in the experiments.

A more detailed understanding of the photoemission process requires the consideration of the remaining electrons of the system. In fact, elec-
2.2 X-ray photoelectron spectroscopy

Figure 2.2: A scheme of the shake-up process for the case of two electrons. The excitation of a valence electron takes place in association with a core ionization.

electron correlation and relaxation have considerable effects on the photoelectron spectra like, for example, asymmetry of the shape of the peaks due to post collision interaction (PCI) or extra features close to the spectroscopical main lines (shake-up, shake-off). The shake processes are due to the ionization of valence electrons associated to the photo-ionization (Shake-off) or to their excitation into unoccupied states (Shake-up). The shake-up excitations are experimentally observable as satellite lines, lying at higher binding energies than the main peak. The shake-up phenomenon is schematically shown in figure 2.2.

According to a simplified two electron scheme, there are two transitions that take place: the photo-ionization (for example: $1s \rightarrow \Psi_k$, where $\Psi_k$ indicates a free electron) plus a valence electron excitation into an unoccupied level ($\Psi_i \rightarrow \Psi_{\nu}$, where $\Psi_i$ indicates a valence level and $\Psi_{\nu}$ an initially unoccupied level). A more complete view should involve a larger number of valence electrons and a more complex scheme of transitions. Back to the two-electron picture, the wave functions for the ground state $\Psi_0$ and final state $\Psi_F$ can be built as antisymmetric combinations of the considered electronic levels:

$$\Psi_0 = \frac{1}{\sqrt{2}} [1s(1)\Psi_i(2) - 1s(2)\Psi_i(1)], \Psi_F = \frac{1}{\sqrt{2}} [\Psi_k(1)\Psi_{\nu}(2) - \Psi_k(2)\Psi_{\nu}(1)]$$

(2.13)

where 1 and 2 are the electrons involved. The dipole transition matrix element between these two states may be approximated as:

---

9This effect is related to the electronic screening.
2 Soft x-ray spectroscopies

\[ \langle F|\mathbf{r}|\Psi_0 \rangle \approx \langle \Psi_k|1s \rangle \langle \Psi_\nu|\Psi_i \rangle \quad (2.14) \]

For high energy photoelectrons, the \( \langle \Psi_k|1s \rangle \) varies slowly with \( k \) [4], and one obtains the relation:

\[ \langle F|\mathbf{r}|\Psi_0 \rangle \approx \langle \Psi_\nu|\Psi_i \rangle \quad (2.15) \]

The probability for a shake-up process is:

\[ P_{\text{shake-up}} = |\langle \Psi_\nu|\Psi_i \rangle|^2 \quad (2.16) \]

The transition is possible because of the relaxation of the unoccupied valence orbital in the field of the core hole. This causes the product \( \langle \Psi_\nu|\Psi_i \rangle \) (or, the overlap between the two orbitals \( \Psi_\nu \) and \( \Psi_i \)) to be in general different from zero. One way to understand this is provided by the Sudden approximation [4]. It states that when the photo-ionized electron has high enough kinetic energy, the core electron ionization is rapid compared to the time needed by the rest of the electrons to fully relax in the new configuration, i.e. the orbital \( \Psi_i \) is still the eigenstate of the initial \( N \) electron Hamiltonian. The final orbital \( \Psi_\nu \) is, however, the eigenstate of the relaxed (\( N-1 \)) electron Hamiltonian. The two electronic levels \( \Psi_i \) and \( \Psi_\nu \) are not eigenfunctions of the same Hamiltonian, and therefore not necessarily orthonormal functions. It should also be mentioned that in the calculations presented in this thesis the doubly occupied valence orbitals are assumed to be unchanged upon the ionization and excitation.

2.3 Near edge x-ray absorption fine structure

The near edge x-ray absorption fine structure (NEXAFS) is dedicated to the study of the near edge region of the absorption spectra. It is an important probe for the unoccupied energy levels, and provides information on the chemical bonding, as well as on the geometrical orientation of a molecule. The measurements are performed by scanning the photon energy in an interval ranging, usually, from a few eV below a certain ionization threshold of a chosen element, to about thirty or forty eV above. Figure 2.3 shows schematic pictures of the various regions in a NEXAFS spectrum of an atom and of a molecule. The peaks below the IP in the spectra derive from the excitation of the selected core electron into the unoccupied atomic/molecular levels. In a molecular spectrum, the first
2.3 Near edge x-ray absorption fine structure

Figure 2.3: Scheme of NEXAFS spectra for an atom and a molecule. In the upper part of the figure, the spectra for an atom A and for a diatomic molecule B are shown. The corresponding energy levels are sketched in the lower part of the illustration.

peak corresponds in general to the lowest unoccupied molecular orbital (LUMO), and the Rydberg states lie closer to the IP. Near the IP and slightly above, instead of peak like features, an edge (similar to a step) is generated, and, at higher energies, the electrons are free in the continuum. Also the continuum region of the spectra of molecules shows some structures, like for instance shape resonances (see Figure 2.3).

2.3.1 Selection rules

The dipole approximation introduces restrictions about which transitions are allowed for the atomic/molecular electrons. Let’s consider the azimuthal (l) and magnetic (m) quantum numbers for the atomic electrons. If \( \Delta m = m_f - m_i \) and \( \Delta l = l_f - l_i \), where i and f indicate the initial and final state electronic quantum numbers, then only the transitions that satisfy the following relations are possible:

\[
\Delta l = \pm 1, \Delta m = 0, \pm 1
\]  

\[\text{(2.17)}\]

\(^{10}\)The shape resonance is explained in two different ways: either by multiple scattering of the photoelectron within the molecule, or by a quasi bonded electronic state due to the potential barrier, as sketched in Figure 2.3 [5].
2 Soft x-ray spectroscopies

One can enunciate the selection rules according to a group theory perspective: a transition is allowed if the direct product of the irreducible representations of the initial and final states contains or coincides with the irreducible representation to which the dipole operator belongs. Symmetry considerations and quantum number selection rules are extremely useful for the interpretation of spectra. Of course, deviations from the symmetry, or the necessity to go beyond the simple dipole approximation, need to be treated in a more detailed way, and lead to the breakdown of the clear selection rules described.

The intensity of the resonances in NEXAFS is expressed by the oscillator strength, \( f \), that is the energy integral of the absorption cross section. \( f \) is defined as:

\[
\begin{align*}
    f_{f,i} &= \frac{2}{m \hbar \omega} | < \Phi_f | \hat{\epsilon} \cdot \mathbf{p} | \Phi_i > |^2 \\
    &= \frac{2m\omega}{\hbar} | \hat{\epsilon} < \Phi_f | \mathbf{r} | \Phi_i > |^2
\end{align*}
\]

(2.18)

or, in the position operator reference system:

\[ f_{f,i} = \frac{2m\omega}{\hbar} | \hat{\epsilon} < \Phi_f | \mathbf{r} | \Phi_i > |^2 \]  

(2.19)

The total oscillator strengths for all the possible transitions for one electron, in an atom or a molecule, sum to one: thus, the sum extended to all the electrons gives \( N \), the total number of electrons (Thomas-Reiche-Kuhn sum rule)\(^{11}\). The sum rule allows to establish a correspondence between the total calculated oscillator strengths and the experimental peak area.

2.3.2 Polarization dependence

One important property of the NEXAFS technique is the polarization dependence, which is commonly exploited to determine the orientation of ordered molecules. The angular dependency is contained in the dipole transition matrix. The molecular and atomic electrons are described by wave functions that are characterized by a well defined spatial orientation. The orientation of the transition matrix element depends on the relative orientations of the electronic wavefunctions. The intensity of a particular resonance depends on the relative orientations of the matrix element with respect to the polarization vector of the photon electric field, \( \hat{\epsilon} \).

\(^{11}\)This sum rule holds in the dipole approximation. Taking into account higher order corrections to the dipole approximation, would break the sum rule. In general, within the approximations described, the oscillator strength obeys several sum rules [5].
2.3 Near edge x-ray absorption fine structure

As an example, one can consider the 1s excitation of a second row atom (like for instance carbon) into a molecular electronic level described as a linear combination of 2s and 2p wave functions, according to the Linear Combination of Atomic Orbitals (LCAO) method. In this case, the x-rays are assumed linearly polarized. The resulting vector matrix element in this K-edge spectrum, is dominated by the highly oriented 2p components, and has a maximum amplitude along the direction determined by the composition of these levels (let’s call it \( \mathbf{O} \)). The polarization dependence can be expressed as a function of the angle \( \delta \) between the direction of maximum amplitude of the resulting vector matrix here discussed, and the polarization vector of the photons.

The transition intensity, \( \mathbb{I}_{f,i} \), is proportional to the oscillator strength, and consequently to the squared cosine of \( \delta \):

\[
\mathbb{I}_{f,i} \propto |\hat{e} < \Phi_f | r | \Phi_i > |^2 \propto |\hat{e} \cdot \mathbf{O}|^2 \propto \cos^2 \delta \quad (2.20)
\]

An immediate view of this result is offered by a case that is rather often encountered with molecules of the second row: a double or triple bond composed by the \( \pi^* \) and \( \sigma^* \) type molecular orbitals. If the molecular internuclear axis lies along, say, the \( z \) Cartesian coordinate of a reference system, then the \( \sigma^* \) bond is also aligned along the \( z \) coordinate. The \( \pi^* \) bonds are aligned in two orthogonal directions perpendicular to \( z \) that we choose as \( x \) and \( y \) of the resulting Cartesian system. The resonance intensities for the transition from the 1s to the \( \sigma^* \) and, respectively, \( \pi^* \) levels are:

\[
\begin{align*}
\mathbb{I}_{f,i}(\sigma) & \propto |\hat{e} \cdot \hat{\mathbf{z}}|^2 \propto \cos^2 \theta \\
\mathbb{I}_{f,i}(\pi) & \propto |\hat{e} \cdot \hat{x}|^2 + |\hat{e} \cdot \hat{y}|^2 \propto \sin^2 \theta
\end{align*} \quad (2.21)
\]

where \( \theta \) is the polar angle between \( \hat{e} \) and the internuclear axis (along \( z \)), and \( \phi \) between the projection of \( \mathbf{O} \) in the \( xy \) plane, and \( x \). The polarization dependences for \( \pi^* \) and \( \sigma^* \) have opposite behaviour. \( \mathbb{I}_{f,i}(\sigma) \) is at its maximum when the polarization vector is aligned with the internuclear axis, while \( \mathbb{I}_{f,i}(\pi) \) reaches its maximum when the polarization vector is normal to the internuclear direction. This offers a very useful and simple thumb rule for the determination of molecular orientations and also for the study of the molecular bonds. This method has been used in PAPERS III and V.
2 Soft x-ray spectroscopies

![Diagram](image)

**Figure 2.4:** The non resonant (XES) (A), and resonant (RIXS) (B) radiative emission processes. The core electron is ionized in XES, and excited to an unoccupied level in RIXS. In the XES process the final state is a valence ionized atom or molecule, while in RIXS it is an optically excited state.

### 2.4 Decay of the core excited state

The core excitation or ionization produced by photon absorption results in a nonstable state, bound to decay. The decay can be non-radiative or radiative. The dominating decay channel is generally the non-radiative one, that occurs through the Auger electron emission, which is a radiationless transition involving two electrons. A possible radiative decay channel is x-ray emission, where a valence electron decays into the core hole, emitting radiation. Although the radiative decay has considerably lower probability with respect to the Auger decay, powerful spectroscopies have been developed in order to exploit this effect, in spite of the experimental challenges like the often poor count rate. Detailed and unique information about the valence electronic structure and the chemical environment of atoms and molecules is obtained using these techniques.

The emission experiments are performed in two regimes: the non resonant or normal regime, known as x-ray emission spectroscopy (XES), where the incoming photon energy is well above the resonant threshold, and the resonant regime, also known as the resonant inelastic x-ray scattering (RIXS), where the photon energy is set to a selected resonance. Often, in a RIXS experiment, the exciting radiation is tuned at several values in the energy region close to the resonance. The schemes of the emission process off resonance and at resonance are presented in figure 2.4.

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12 This is valid for the excitation of the K shell of light atoms, and for the excitation of the L shell for atoms with $Z<90$ [5].
The two processes can be described according to the following relations:

\[ \text{Non - resonant : } A + h\omega \rightarrow A^+_c \rightarrow A^+_v + h\omega' \quad (2.23) \]
\[ \text{Resonant : } A + h\omega \rightarrow A^+_c \rightarrow A^*_v + h\omega' \quad (2.24) \]

In these expressions A represents the ground state of the system, \( A^+_c \) and \( A^+_v \) are the core and the valence ionized states, \( A^*_c \) and \( A^*_v \) are the core and the valence excited states respectively, and \( \omega \) and \( \omega' \) are the frequencies of the incoming and out-coming photons. The resonant process is clearly of inelastic nature, and can be viewed as the inelastic scattering of a photon by a molecule. The theoretical treatment for the non-resonant and resonant emission are different. In the XES description it is often accepted to separate the ionization and the emission events, as the ionization does not pose further conditions to the electron decay. The electron deexcitation in non-resonant emission is described within the dipole approximation framework, in analogy with the electronic transitions in the NEXAFS:

\[ \Gamma_{i\rightarrow f} = \frac{2\pi}{\hbar} |\epsilon < \Phi_f | \Phi_i >|^2 \delta(E_i - E_f - \hbar \omega) \quad (2.25) \]

As mentioned above, the process consists of a transition between two atomic/molecular levels, and the same selection rules as for an electron excitation hold in this case. A different approach has to be adopted for the resonant emission and it will be described below for the case of randomly oriented molecules. The RIXS process is more properly viewed as a quasi-simultaneous two-photon absorption-emission process, whose cross section is expressed by the Kramers-Heisenberg scattering amplitude\[6,7\]

\[ F_{\nu n}(\omega, \omega') = \sum_k \alpha \omega_{\nu k} \omega_{n k}(\nu) \frac{(d_{\nu k} \cdot e_1)(e_2 \cdot d_{kn}(\nu))}{\omega - \omega_{\nu k} + i\Gamma_{\nu k}} + \frac{(e_2 \cdot d_{\nu k})(d_{kn}(\nu) \cdot e_1)}{\omega' + \omega_{\nu k}} \quad (2.26) \]

Here, the indices \( k \) represent a core level, \( n \) a valence occupied level, and \( \nu \) an unoccupied level. \( d_{\nu k} \) is the probability for the absorption \((k \rightarrow \nu)\) and \( d_{kn}(\nu) \) the probability for the emission \((n \rightarrow k)\) transitions. The remaining terms \( \omega \) and \( \omega' \) and \( e_1 \) and \( e_2 \) are the frequencies and the polarization vectors of the incoming and emitted photons. \( \Gamma_{\nu k} \) is the lifetime of the intermediate state. The first term of this expression is also denoted as the resonant anomalous scattering term, and is responsible
for a resonance in case $\omega$ equals $\omega_{nk}$. The second term, the non resonant scattering term, is important only far from resonance and can therefore be neglected at resonance. The differential cross section of RIXS for scattering in a solid angle is:

$$\frac{d^2\sigma}{d\omega'd\Omega} = \sum_{\nu} \sum_n \frac{\omega'}{\omega} |F_{\nu n}(\omega)|^2 \Delta(\omega - \omega' - \omega_{\nu n}, \Gamma_{\nu n})$$  \hspace{1cm} (2.27)

where $\Gamma_{\nu n}$ is the life time broadening of the final state, that is an optically excited state. A convolution of the RIXS differential cross section with the distribution function $\Phi$ of the incoming photon beam (usually a gaussian function), gives a representation of the experimental situation:

$$\frac{d\sigma(\omega', \omega_0)}{d\Omega} = \int d\omega \frac{d^2\sigma}{d\omega'd\Omega} \Phi(\omega - \omega_0)$$  \hspace{1cm} (2.28)

According to the energy conservation law, the frequency of the emitted photons ($\omega'$) exhibits a Raman shift (or Stokes shift) relative to the frequency of the incoming photon ($\omega$), of the amount:

$$\omega' = \omega + \omega_{\nu n}$$  \hspace{1cm} (2.29)

where $\omega_{\nu n}$ is the frequency of the transition $n \rightarrow \nu$. This gives rise to a peak whose energy position varies with $\omega$. 

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**Figure 2.5:** Illustration of the symmetry selection rules for the RIXS process, and of the difference with the XES.
2.4 Decay of the core excited state

With respect to normal emission, RIXS is characterized by stricter selection rules. In fact, its cross section has a strong dependence on the polarization of the absorbed and emitted photons, and on the symmetries of the electronic levels involved [8]. The general symmetry selection rules for RIXS have been expressed by means of group theory [8]. The difference in selection rules between XES and RIXS is shown in Figure 2.5. In the scheme, an electron is initially resonantly excited into an ungerade level (u). Due to the dipole selection rules, only gerade levels (g) can be excited into the u levels. And only a u level can decay into the g core hole. If there is a nearly-degenerate core level of u symmetry, it is possible to select the transition from this u level into the g unoccupied by tuning the exciting energy, and consequently the g symmetric valence level will decay into the u core hole. The initial and final state in this scheme have the same symmetry. In the case of non-resonant emission, instead, both transitions are allowed. For resonant excitation, in each case only one emission peak is selected, either u or g, while in XES one observes both peaks. Clearly, the RIXS selection rules are more complex in case of other types of symmetries, but this qualitatively explains that, due to symmetry reasons, many of the features of the XES are suppressed in RIXS. An example of this difference in XES and RIXS is discussed in PAPER VI.
Theoretical methods

Quantum mechanics based methods have been applied throughout this work to calculate total energies and geometries of molecules, and to study their electronic structures as well as their soft x-ray spectra. The application of quantum mechanics to molecular problems in different physical and chemical states leads to a detailed knowledge of the electron distribution. The methods, generally known as quantum chemical methods, are based on the solution of the Schrödinger equation. This task can be performed either \textit{ab initio}, i.e. without any reference to the experimental data, or \textit{empirically} by using parameters obtained by fitting atomic data, or through a combination of the two approaches. However, the solution of the Schrödinger equation for multi electron, multi nuclear systems is a very complex task. Therefore, methods based on different types of approximations have been developed. In this chapter the theories employed in this work will be briefly described and particular attention will be dedicated to the aspects that are closely related to the papers presented.

3.1 The Born-Oppenheimer approximation

The non-relativistic Hamiltonian operator for a molecule may be written as a sum of electronic, nuclear and mixed terms as follows:

\[
H_{\text{tot}} = \hat{T}_N + \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} + \hat{V}_{NN}
\]

In this expression $T$ indicates the kinetic energy, $V$ the potential energy, and $N$ and $e$ are the indices for the nuclei and for the electrons respectively. This expression is based on some approximations, since several
3 Theoretical methods

types of intereactions and contributions to the total Hamiltonian have been neglected: relativity, the spin-orbit and the spin-spin couplings, for instance, are not included. However, these approximations are valid - and are commonly used - for a vast number of applications. The total energy of the molecule (E) is derived from the eigenvalue equation:

\[ H_{\text{tot}} \Psi(r, R) = E \Psi(r, R) \] (3.2)

The wave function \( \Psi \) is a function of the electronic (r) and of the nuclear (R) coordinates. The expression can be considerably simplified by observing that the nuclei are much heavier than the electrons, and therefore the electron movement is much faster than that of the nuclei. The nuclear positions can be assumed as fixed during the electronic motion. In this perspective, the nuclear kinetic energy term \( T_N \) can be neglected in the calculations, and the nuclear repulsion \( V_{NN} \) can be treated as a constant. In this approximation, one is left with a Hamiltonian for the electrons, which only depends on the electronic coordinates. The nuclear coordinates, from variables, become parameters for the electronic equation: in other words, the electronic wave functions depend parametrically on the nuclear configuration. The Schrödinger equation for the electronic motion becomes:

\[ (\hat{H}_e + \hat{V}_{NN}) \Psi_e = U \Psi_e \] (3.3)

where \( U \) is the total electronic energy including the nuclear repulsion. As the wave function is not altered by including a constant term in the Hamiltonian, the pure electronic energy is obtained as:

\[ \hat{H}_e \Psi_e = E_e \Psi_e \] (3.4)

The separation of the electronic and nuclear coordinates, is known as the Born-Oppenheimer (BO) approximation and is one of the cardinal points in the quantum mechanics treatment of molecular systems. Although the BO approximation is valid in a large number of cases, it is bound to fail whenever the nuclear motion becomes important. For instance when the vibronic coupling, or the coupling between the electronic and the vibrational motion of the nuclei, cannot be neglected, or when significant distortions in the molecules come into play. In the BO approximation, the nuclei move on a potential energy surface (PES), whose points are
3.2 The Slater determinant

solutions of the electronic Schrödinger equation 3.4. The BO approximation breaks down when solutions of the Schrödinger equation are close together. In this case the BO based PES does not foresee the possibility of crossing between two close lying PES. One aspect of this problem is discussed in PAPERS X and XI, in relation with the nuclear distortion and vibrations correlated to core electron excitation.

3.2 The Slater determinant

To solve the Schrödinger equation, it is necessary to work out a convenient representation for the electronic wave function. A basic requirement is that the wave function of an N-fermions system has to obey the Pauli exclusion principle\(^1\), which states that two fermions cannot occupy the same individual quantum state.\(^2\) The wave function for such a system must be antisymmetric with respect to permutations of couples of the identical particles. Considering N individually occupied electronic states, \(\Phi_i\), mutually orthonormal, the total antisymmetrical state may be expressed by a Slater determinant constructed as:

\[
\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\phi_1(1) & \phi_2(1) & \ldots & \phi_N(1) \\
\phi_1(2) & \phi_2(2) & \ldots & \phi_N(2) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_1(N) & \phi_2(N) & \ldots & \phi_N(N)
\end{vmatrix}
\]  

(3.5)

The elements of the determinant (3.5) are the spin orbitals, i.e. one electron functions obtained as the product of a spatial orbital multiplied by a spin function.

3.3 Solving the Schrödinger equation: Hartree-Fock

The application of the Schrödinger equation 3.4 to a Slater determinant, and the minimization of the spin-orbitals with respect to the energy via a variational method, leads to the Hartree Fock (HF) equations. The

\(^1\)The exclusion principle was formulated by Pauli in 1925, to explain the structure of complex atoms.

\(^2\)All the elementary particles with spin 1/2 occurring in nature, such as electrons, protons and neutrons, are fermions, while those with integer spin are bosons. The exclusion principle holds only for fermions.
3 Theoretical methods

ground state energy and wave functions are obtained by the minimization of the energy functional. Detailed derivations are found in quantum mechanics or quantum chemistry text books as for example [9–11]. The HF equations are eigenvalue equations of the form:

$$F_i \phi_i = \varepsilon_i \phi_i$$

(3.6)

where $F(i)$ is the Fock operator. The HF equations define an independent particle model, in which each electron moves independently from the others, in an average potential field generated by the remaining nuclei and electrons. This is the keypoint of the HF method, as the complexity of the multielectron problem is simply treated by an average electronic potential. The form of the Fock operator is the following:

$$F_i = h_i + \sum_j^N (J_{ij} - K_{ij})$$

(3.7)

where the one electron operator $h_i$ describes the motion of the $i^{th}$ electron in the potential field of the nuclei, and contains both the kinetic energy term and the Coulombian electron-nuclear attraction. $J$ and $K$ are electron operators describing the two-electron repulsion ($J$) and the electron exchange interaction ($K$). The solution of the Hartree Fock equation is found through an iterative procedure called the self consistent field (SCF) method, which is a particular case of the variational method. It is necessary to make an initial guess of the spin-orbitals in order to calculate the initial electronic potential, and then use the eigenvalue equation to calculate the new spin-orbitals, until the self consistency criteria are met. The outcome of the process is an orthonormal set of Hartree-Fock spin orbitals, $\phi_i$, intended as a set of molecular orbitals (MO), (the so-called canonical MO). The latter are chosen as a convenient set of orbitals to carry out the variational calculation. The energy of the MO is explicitly calculated as:

$$\varepsilon_i = \langle \phi_i | F_i | \phi_i \rangle = h_i - \frac{1}{2} \sum_{ij}^N (J_{ij} - K_{ij})$$

(3.8)

and the total energy, $E$, of the system is given by:

$$E = \sum_i^N \varepsilon_i - \frac{1}{2} \sum_{ij}^N (J_{ij} - K_{ij}) + V_{nn}$$

(3.9)
3.4 Koopmans’ theorem

The total energy does not correspond to the sum of the orbital energies. It is interesting to note that the HF method is applicable not only to electrons in an atom or molecule, but also in solids as well as to any systems of identical particles in a potential[9]. The HF method has a number of limitations, which have motivated the development of new approaches. The lack of electron correlation in HF is one of those, which has been overcome by several methods like, for instance, the Configuration interaction (CI), the multi-configuration self-consistent field (MCSCF) and, later, the Density Functional Theory (DFT) methods. The electron correlation has been defined by Löwdin [12] as the difference between the exact non-relativistic energy of the system and the HF energy obtained in the limit when the basis set reaches completeness.

3.4 Koopmans’ theorem

In order to solve the Hartree Fock equations it is necessary to choose a basis set to describe in a proper way the spin orbitals of the Slater determinant. The main prerequisite these functions have to satisfy, is that their behaviour is analogous to that of the electrons in the specific problem. For instance, in treating molecular systems, a gaussian basis set approach is generally favoured, while in the study of periodic systems like solids, a periodic approach with plane waves is often adopted. The spin orbit functions \( \phi_i \), solutions of the HF equations, correspond to an orbital energy \( \varepsilon \), and the total number of electrons of the system studied determines how many of these levels are occupied. The remaining orbitals are the so-called virtual orbitals, and are unoccupied. The Koopmans’ theorem provides a way to calculate the ionization potential (IP) of an occupied electronic orbital. It states that the IP of an electronic energy level equals the orbital energy taken with the positive sign. The orbital energy is, in fact, always expressed by a negative value for any bonded state. In HF, the energy of a N electron system in the ground state, and its energy after removal of one electron from the orbital k, for instance,
3 Theoretical methods

are given by the two following expressions:

\[ E_N = \sum_{i}^{N} \epsilon_i - \frac{1}{2} \sum_{ij}^{N} (J_{ij} - K_{ij}) + V_{nm} \]  \hspace{1cm} (3.10)

\[ E_{N-1}^k = \sum_{i}^{N-1} \epsilon_i - \frac{1}{2} \sum_{ij}^{N-1} (J_{ij} - K_{ij}) + V_{nn} \]  \hspace{1cm} (3.11)

and their difference is:

\[ E_N - E_{N-1}^k = h_k + \sum_{i=1}^{N} (J_{ki} - K_{ki}) = \epsilon_k \]  \hspace{1cm} (3.12)

This energy corresponds to the orbital energy of the k\textsuperscript{th} level. This is an approximate way to calculate the IP. In fact it assumes that the orbitals remain frozen after the electron ionization, i.e. no electron relaxation of the remaining electrons take place.

3.5 Density functional theory

The density functional theory (DFT) method has become more and more popular during the last decades, and perhaps it is, nowadays, the most frequently used approach in molecular and solid state physics and chemistry. It allows to compute relatively large systems at a reasonable computational cost, and it treats many problems at a sufficiently high accuracy. In DFT, the 3N variable problem of a system with N electrons is transformed into a 3 variable problem. DFT assumes, on a mathematical basis, that all the ground state properties of a system of N electrons are determined by the electron density, which is a function of 3 space variables. The density is given, in general, by the integral of the square of the wave function of the N-electron system, according to the expression:

\[ \rho(\mathbf{r}) = N \int \ldots \int |\Psi|^2 ds_1 dx_2 \ldots dx_N \]  \hspace{1cm} (3.13)

where \( \Psi \) is the wave function of the N-electron system, and depends on the spatial and spin coordinates. The integral of \( \rho \) over the whole space is equal to the total number of electrons:

\[ \int \rho(\mathbf{r})d\mathbf{r} = N \]  \hspace{1cm} (3.14)
3.5 Density functional theory

In practice, \( \rho(r) \) is expressed by the one-electron basis functions. The formulation of DFT is based on the two theorems of Hohenberg and Kohn[13]. The first one states that, given a system of N electrons, the external potential is uniquely determined by the electron density (a part from eventual additive constants); this is the exact potential of the system and accounts for all the possible electronic interactions including the correlation energy neglected in the HF approach. The second theorem establishes a variational principle for the calculation of the energy as a functional of the density. The energy, in fact, is expressed in DFT as a functional of the density. This theorem implies an important computational consequence that makes the theory practically usable: given a good energy functional, it is possible to minimize it in order to get the best energy via a variational approach.

The energy functional is composed by several terms, but only a part of those are exactly known. The functional assumes the following form:

\[
E[\rho] = T[\rho] + V_{Ne}[\rho] + V_{ee}[\rho]
\] (3.15)

Here, \( T \) is the kinetic energy functional and \( V_{Ne} \) and \( V_{ee} \) account for the interaction of the electrons with the nuclei and with the other electrons. The expression for the functionals can be conveniently re-elaborated as follows:

\[
E[\rho] = F_{HK}[\rho] + V_{Ne}[\rho]
\] (3.16)
\[
F_{HK}[\rho] = T[\rho] + V_{ee}[\rho]
\] (3.17)
\[
V_{ee}[\rho] = J[\rho] + \text{non classical term}
\] (3.18)

This expression highlights the functional \( F_{HK} \), that contains the exchange-correlation electronic interaction through the kinetic energy, and the \( V_{ee} \) terms. The \( V_{ee} \) is the sum of the the classical repulsion \( J[\rho] \) and of the non classical term, which gives the major part of the exchange-correlation energy.

Mathematically, it would be conceptually possible to reach an exact resolution of the electronic energy functional problem. However, the main difficulty in DFT is that the exact exchange correlation functional is not known. Due to the good results obtained by the DFT technique in a large number of applications in the last decades, a lot of effort is still being put into the development and testing of new functionals. A condition for the validity of the HK formulation is the N-representability: the HK theorems
3 Theoretical methods

hold if the density is indeed obtainable from some antisymmetric wave function.\(^3\) This requirement on the density is mathematically expressed by 3.14 together with the conditions:

\[
\rho(r) \geq 0 \quad (3.19)
\]

\[
\int |\nabla \rho(r)|^2 dr > \infty \quad (3.20)
\]

The decisive step into the computational application of the DFT was made by Kohn and Sham in 1965, with the introduction of the orbital formulation for the calculation of the kinetic energy term. Their treatment of the problem leads to the Kohn Sham equations, that correspond to a system of non interacting electrons moving in a potential \(V_{\text{eff}}\):

\[
\left[-\frac{1}{2}\nabla + v_{\text{eff}}\right] \psi_i = \epsilon_i \psi_i \quad (3.21)
\]

where the \(\phi_i\) are the KS orbitals. The effective potential \(v_{\text{eff}}\) is given by:

\[
v_{\text{eff}} = v(r) + \int \frac{\rho(r')}{|r-r'|} dr' + v_{\text{xc}}(r) \quad (3.22)
\]

where \(v(r)\) is the external potential due to the electron nuclei interactions, \(\int \frac{\rho(r')}{|r-r'|} dr'\) is the electrostatic potential due to the electronic distribution, and \(v_{\text{xc}}(r)\) is the exchange-correlation potential. The equations have to be solved in an iterative way, in analogy with the HF method. Moreover, the KS equations have a form that is very similar to the HF equations, but in DFT the exact exchange term \(J\) is replaced by the exchange correlation potential.

The orbital formulation, according to a chosen basis set, of the KS equations looks like:

\[
\hat{H}_{\text{KS}} \psi_i = \epsilon_i \psi_i \quad (3.23)
\]

and the density is given by:

\[
\rho(r) = \sum_{i}^{\text{occ}} \sum_{s}^{\text{spin}} |\Psi(r, s)|^2 \quad (3.24)
\]

\(^3\)A more strict condition, the \(v\)-representability, requires that the energy density is indeed a density associated with the antisymmetric ground state wave function of a potential \(v(r)\). However the N-representability can usually be considered a sufficient condition [13–15]
3.5 Density functional theory

A fundamental and intriguing question follows the KS formulation: what is the meaning of the KS orbitals? They were introduced essentially as a mathematical tool to calculate the kinetic energy for a system of N non interacting electrons. In this sense, they do not necessary have a physical significance. However, comparisons with experimental data show that their energies, very often, well match the measured electronic energy levels. They are constructed from a non-interacting reference system, which has the same electron density as the real interacting system.

3.5.1 Exchange and correlation functionals

The development of efficient exchange-correlation functionals is the key for the success of density functional theory. In this section the functionals that have been used in this thesis are briefly introduced. Traditionally, the functionals are separated into an exchange and a correlation part. The \textit{ab initio} functionals are built without any parametrization deriving from experimental data. One approach is to develop a functional that only depends on the electron density. This is the case of the exchange functional known as \textit{local density approximation} (LDA), which treats the density locally as for a homogeneous electron gas. The LDA has evolved into the \textit{local spin density approximation} (LSDA), where the densities of the electrons of different spin are considered independently, which is relevant for open shell systems. The correlation energy functional for a uniform electron gas has been developed by Vosko, Wilk and Nusair (VWN) [16]. This functional is often used in combination with the Slater exchange [17–19]. The \textit{Generalized Gradient Approximation} (GGA) goes beyond the LDA approach, by extending the functional dependency to the gradient of the density. Very popular GGA exchange functionals, used in several papers of this thesis, are the Perdew and Wang (PW86) [20] and Becke (B88) [21]. They are built by introducing corrections to the LSDA exchange functionals by adding terms depending on the gradient of the electronic density. Perdew has also introduced a gradient corrected correlation functional, the P86 [22]. New correlation functionals, not based on corrections of the LSDA, were developed by Lee, Yang and Parr (LYP) [23, 24]. Another group is formed by the hybrid functionals, in which the exchange energy is given exactly, according to the HF treatment. In the papers presented, the Becke’s three parameter hybrid functional, known as B3LYP, has been widely used; it includes a fraction of the exact HF exchange.[25]
3.6 Time dependent density functional theory

Time dependent DFT (TD-DFT) [26,27] is the extension of DFT to the case of a time dependent applied field: in other words the DFT external potential \( v(r) \) is, in this case, also a function of time, \( v(r,t) \). An example is the excitation of a N-electron system by a photon beam, which can be represented as a periodic electro-magnetic potential with a frequency \( \omega \). The response of the system to this perturbation is determined by TDDFT. The problem requires the solution of the time-dependent Schrödinger equation, which expresses the time evolution of the system:

\[
i \frac{\partial}{\partial t} \Psi(r,t) = \hat{H}(t) \Psi(r,t)
\]  

(3.25)

where \( \Psi(r,t) \) is a many-body wave function of N electrons. The mathematical foundation of TDDFT is given by the work of Runge and Gross [26]. The key concept, in analogy with the stationary DFT, is the one to one mapping between the time dependent electron density \( \rho(r,t) \) and the time dependent potential \( v(r,t) \), formalized by the Runge-Gross theorem. The latter is the analogous of the Hohenberg-Kohn theorem. The time dependent density \( \rho(r,t) \) uniquely determines the external potential \( v(r,t) \).\(^4\) The potential uniquely determines the time dependent wave function, which is, therefore, a function of the time dependent density. The expectation value for any time dependent operator is a unique functional of the density. Even though an evident correspondence exists between the mathematical treatment of DFT and TD-DFT, in the latter new concepts needed to be introduced, bringing a higher level of complexity. For instance, the TD-DFT functionals depend also on the initial wave function. However, this dependency can still be simplified in a large number of cases, since, when the initial state \( \Psi_0 \) is a non-degenerate ground state, it is a unique functional of the density, due to the HK theorems [27]. The time dependent Kohn-Sham scheme constitutes the practical framework for this theory. The many particle wave function for non-interacting fermions is a time-dependent Slater determinant \( \Phi(t) \), that is a functional of the time dependent density, \( \Phi[\rho](t) \). The time dependent Kohn-Sham equations are derived by assuming the existence (and unicity) of a single particle potential \( v_{\text{eff}}(r,t) \) such that the density of the Kohn-Sham electrons is identical to that of the non-interacting particles:

\(^4\)Apart from a possible additive function, purely time dependent.
3.6 Time dependent density functional theory

\[ \rho(r, t) = \sum_{n=1}^{N} |\Psi_n(r, t)|^2 \]  \hspace{1cm} (3.26)

Then, the non interacting system is described by the following Kohn-Sham equation:

\[ i \frac{\partial}{\partial t} \Psi_n(r, t) = \left( -\frac{\nabla^2}{2} + v_{eff}(r, t) \right) \Psi_n(r, t) \]  \hspace{1cm} (3.27)

where the non interacting effective potential is given by:

\[ v_{eff}(r, t) = v(r, t) + \int d\rho \frac{\rho(r', t)}{|r - r'|} + v_{xc}[\rho] \]  \hspace{1cm} (3.28)

In this equation the various terms are the analogous of the ground state DFT treatment of equation 3.22. Furthermore, also in this case, the exchange correlation potential is not known, and needs to be approximated.

Among the many applications of the TDDFT, the calculation of the electronic excitation energies is the most relevant for this work [28-33]. In a system of N electrons, the response to a time dependent perturbation, like an electric field of frequency \( \omega \), is provided by the dynamic polarizability \( \alpha(\omega) \):

\[ \alpha(\omega) = \sum_i \frac{f_i}{\omega_i^2 - \omega^2} \]  \hspace{1cm} (3.29)

where the poles of the function, \( \omega_i \), correspond to the excitation energies, and the residues \( f_i \) determine the oscillator strengths. [28] The dynamic polarizability and other time-dependent properties can be calculated with the application of Response Theory to TDDFT. A modern formulation using the quasi-energy approach and that goes beyond the so-called local adiabatic approximation, was derived in Ref. [34].
Calculation of spectroscopies

The application of quantum chemical methods that is most relevant for this thesis, is the study of the atomic and molecular inner shell processes, achieved through the description and simulation of the soft x-ray spectroscopies introduced in the previous chapters. A variety of quantum chemical programs have been developed during the last thirty/forty years, and are nowadays available - either for free or on the market. These programs are capable of calculating a wide range of physical and chemical properties, from ground state total energies to chemical reaction transition states. Many of these codes have been implemented with the aim of theoretically generating the spectra resulting from XPS, NEXAFS, XES, RIXS, and to interpret the mechanisms at the basis of these spectroscopies. The procedures that are used need to describe inner shell events like core excitation, electron decay, and so on. The real process at the electronic level is produced by a complex interplay among all the elements of the system, and, in general, it is necessary to adopt some approximations in the theoretical descriptions. The methods that have been used throughout the papers presented in this thesis are based on DFT (in PAPER VI also on HF theory, due to the complexity of the polymeric molecule), which, in general, has proved to be very precise in comparison with the experimental results. There is, however, a high interest in studying the limitations of some usual approximations, and to improve the techniques to reach a deeper understanding of the inner shell processes. The methods that have been used in the papers presented in
4 Calculation of spectroscopies

this thesis will be briefly described in the following sections, where the
calculation of the electronic transitions into the continuum (XPS) and be-
tween two bonded states (as in NEXAFS XES and RIXS) is introduced.
The computation of the vibrational profiles connected to the electron ex-
citations will be presented in the final part.

4.1 Electron transitions

Different computational methods need to be adopted for the calculation of
the IP’s and of the absorption and emission spectra. The values of the IP’s
are associated to the main lines of the core and valence band photoelectron
spectra. From the oscillator strengths describing the transitions among
two atomic or molecular levels, the absorption and emission spectra are
simulated.

4.1.1 Ionization potentials: ΔKS approach

The IP of core and valence levels were not calculated on the basis of the
Koopmans’ theorem, instead, the total energy of the system was opti-
mized in the neutral ground state, and then re-optimized after the core
ionization, in the N-1 electron system[35]. This constitutes the ΔKS
procedure, that we have used within the Kohn-Sham (KS) orbital based
DFT approach. This procedure largely improves the results with respect
to the frozen orbital approximation. The IP for the $k^{th}$ level is, in this
case, given by the difference between the energy optimized core ionized
and ground states, as in the following scheme:

$$IP_k = E_{\text{opt}}|_{n_k=0} - E_{\text{opt}}|_{n_k=1}$$  (4.1)

The same type of procedure, in HF theory, is referred to as ΔSCF.

4.1.2 Absorption spectra

The generation of absorption and emission spectra implies greater dif-
culties, and the methods developed to this scope are more complex.
Evidently, the determination of all the transition energies by following
the ΔKS approach, by calculating all possible terms like the following
(showing a $1s \rightarrow \pi^*$ transition):

$$IP_k = E_{\text{opt}}|_{n_{1s}=0,n_{\pi^*}=1} - E_{\text{opt}}|_{n_{1s}=1,n_{\pi^*}=0}$$  (4.2)
4.1 Electron transitions

would be too expensive from a computational point of view, and also too complex, to be performed for all the possible excitations.

The Static Exchange approximation

In a different approach, convenient computational methods have been implemented on the basis of the Static Exchange (STEX) approximation. The STEX method was first introduced by Hunt and Goddard in 1969 [36] and was successively implemented in the HF-SCF framework [37–39]. The STEX treats the core excitation as an independent particle event. The contribution to the molecular potential of the excited electron is neglected, and is calculated, instead, only by the core ionized molecule, that is a (N-1) electron system with a core hole. The calculation of the absorption spectrum follows successive steps. The initial state is the system’s ground state. To determine the final state, first a fully relaxed optimization of the core hole state is performed, with the valence orbitals frozen, followed by a valence orbital calculation with the core hole frozen. Finally, by diagonalizing the STEX Hamiltonian, the excited orbital is generated, so that the excited state orbitals are orthonormal with respect to the relaxed core hole orbitals. The excitation energies are obtained by summing the core IP to the eigenvalues of the STEX Hamiltonian. The oscillator strengths are calculated from the dipole matrix between the ground and the final STEX states.

The Transition Potential method

Another method to generate absorption spectra was implemented at the DFT level, based on the transition potential (TP) concept [35]. The TP concept was originally introduced by Slater [40], and further improved into different computational frameworks. The TP approach, in analogy with the STEX method, allows to overcome the problem of calculating all the ionization and excitation energies by the ΔKS method. The main advantage of DFT in this context refers to in the introduction of the correlation, as mentioned in the previous chapter.

The orbital binding energy in the TP scheme is computed as the derivative of the total energy with respect to the orbital occupation number. To take into account the relaxation, the energy should be approximated by calculating the derivative in the point corresponding to the occupation 0.5. The procedure can be carried out by choosing different
fractional occupation. The occupation 0.0 represents the full core hole, and the quality of the spectra generated by the consideration of the full core hole and by the 0.5 occupation has been tested in several systems, like in Ref. [41]. In this work, we have observed, for instance, that the 0.5 fractional occupation and the full core hole approaches give similar results in the case of the phthalocyanines. The conclusions are different in the case of the fullerene molecules, where the importance of considering the full core hole effect to obtain results comparable with the experiments has been demonstrated in Ref. [41].

In the TP method, the initial and final states are computed in a single KS calculation, and a double basis set technique is employed. In the first part of the calculation, the molecular wave function is generated by a good basis set, which later is augmented by a larger basis set (19s 19p 19d) on the core excited center. The oscillator strengths are derived from the dipole matrix of the set of orthogonal vectors obtained. The transition energies are computed by summing the IP to the set of KS eigenvalues. To simulate the continuum part of the NEXAFS spectrum, corresponding to energies above the IP, the Stieltjes imaging technique is used[42–44]. The TP method has been used throughout the papers presented in this thesis.

### 4.1.3 Emission spectra

In the calculation of the absorption and emission spectra, we make use of the final state rule, that was formulated by von Barth and Grossman in 1979[45], for the calculation of the XES spectra of metals, and later on generalized to finite molecular systems by Privalev, Gel’mukhanov, and Ågren [46,47]. The final state rule says that accurate absorption and emission spectra of simple metals can be calculated from the final state potentials of the x-ray processes: these are the neutral ground state for the emission, and an excited state with a core hole for the absorption[45,48]. Von Barth and Grossman analyzed the role played by the core hole potential in the description of the emission process, in order to understand why the theoretical descriptions of the XES that neglect the core hole potential give a superior match with the experiment. They justified the final state rule by assuming a multi-electron effect: they showed that the effect of the emission process is to switch off the strong perturbation induced by the core hole (and, inversely, the absorption process switches it on)[48]. The final state rule is now generally adopted also for
4.2 The Franck-Condon principle

The Franck-Condon principle is crucial for the calculation of the emission spectra of molecules \([46,47]\). The procedure involves only ground state electronic levels: the final state for the XES process is actually a valence hole state, but in these calculations the valence relaxation is neglected. The computational approach is based on the frozen orbital approximation (the same followed by the Koopmans’ theorem). The single electron dipole matrix for the XES is the following:

$$I \propto |\langle \phi_{\text{core-hole}}^{\text{GS}}| r |\phi_{v}^{\text{GS}} \rangle |^2$$

(4.3)

where $\phi_{\text{core-hole}}^{\text{GS}}$ is the core hole level in the ground state and $\phi_{v}^{\text{GS}}$ is a valence level in the ground state. The more complex RIXS spectra are also calculated on the basis of the ground state electronic levels. The electron transitions are estimated by equation (2.26), where, differently from the XES case, two transitions have to be taken into consideration. The calculations of the emission spectroscopies are implemented both at the HF and at the DFT level.

4.2 The Franck-Condon principle

The photo-electron and absorption spectral features are often characterized by a fine structure where a significant contribution comes from the vibrational frequencies that get excited. The impact of the vibrational frequencies on these peaks is described by the Franck-Condon (FC) factors, which determine the energy position, and weigh the intensity, of each vibrational line. A molecule is characterized by some vibrational frequencies, $\omega$, linked to its degrees of freedom, and each frequency determines a vibrational normal mode. The vibrational levels for a frequency $\omega$ can be calculated, in first approximation, according to a simple harmonic oscillator model: the one-dimensional potential energy surface in the direction of the selected vibrational mode, is approximated by a parabolic curve. The lowest possible vibrational energy for a molecule, $E_0$, is called the zero point energy, and it is always different from zero. The value of $E_0$ is given by $\frac{1}{2}h\omega$, and the energies of the successive vibrational levels are obtained from the series:

$$E_\nu = (\nu + \frac{1}{2}) h\omega$$

(4.4)

where $\nu$ is the vibrational quantum number. The existence of the zero point energy derives from the quantum mechanical treatment, since, in
the classical framework, the system is in principle allowed to possess zero vibrational energy. A more realistic potential, for a molecule, would be an anharmonic oscillator. One example is the Morse function, which has an analytical expression of the type:

$$E = D_{eq} [1 - e\{a(r_{eq} - r)\}]^2$$  \hspace{1cm} (4.5)

where the variable $r$ is a vibrational mode, $D_{eq}$ is the dissociation energy\(^1\), and $r_{eq}$ is the point where the energy has the minimum. The energy levels of the anharmonic oscillator are not equally spaced, and become closer and closer to each other with the increasing of the vibrational quantum number. The vibrational energies are obtained according to the following expression:

$$E^{\text{anh}}_{\nu} = \omega_e \{1 - \chi_e (\nu + \frac{1}{2}) (\nu + \frac{1}{2})^2 \}$$  \hspace{1cm} (4.6)

where the oscillation frequency decreases with increasing $\nu$, and $\chi_e$ is the anharmonicity constant. There is no quantum mechanical restriction on the change in the vibrational quantum number $\nu$ during an electronic excitation, and, in general, many vibrational lines are excited in the same time, each with different probability. If $\nu$ and $\nu'$ designate, respectively, the ground state and the core excited state vibrational levels, then each vibrational peak can be labeled by the couple of numbers: ($\nu', \nu$). The FC principle states that during the very short time in which an electronic transition occurs, the vibrating nuclei do not change appreciably their positions. This means that the calculation of the FC factors can take place within the BO approximation. Possible intensity distributions associated with an electron transition, are shown in the sketch of Figure 4.1. The changes in the shape of the resulting peak depends on the potential energy surfaces of the initial and final states. In the diagrams in part A, B and C of Figure 4.1, the excited PES is shifted in three different ways with respect to the ground state PES. This scheme exemplifies how the most intense contribution comes every time from the vertical transition, which corresponds, in the three cases shown here, to a different vibrational mode. The resulting spectral shapes are sketched on the side of each couple of potentials.

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\(^1\) $D_{eq}$ includes the zero point energy.
4.2 The Franck-Condon principle

![Diagram of Franck-Condon Principle]

Figure 4.1: Illustration of the Franck-Condon principle. The PES for the ground and core excited state are plotted as a function of a molecular coordinate \( R \), that could be, for instance, an interatomic distance. In A, B and C the minima of the excited state PES are differently positioned with respect to the ground state PES, producing different spectral shapes (rotated diagrams).

4.2.1 The linear coupling model

A practical scheme for the calculation of the FC factors is provided by the linear coupling model (LCM)\(^{[49,50]}\), based on the assumption that an harmonic oscillator approximation describes both the ground state and the excited state PES. According to this model, the Hamiltonians describing the initial and the final states differ only in terms that are linear in the normal coordinates, meaning that the potential surfaces of the two states are the same, but centered at different equilibrium positions. The vibrational energies are given by:

\[
E(n_1, n_2, ..., n_M) = - \sum_{i=1}^{q} n_i \hbar \omega_i
\]  \hspace{1cm} (4.7)
where \( n_i \) is the vibrational quantum number of the \( i^{th} \) mode, and \( \omega_i \) is its vibrational frequency. The multidimensional FC factor in the LCM model assumes the following expression, that is a product of Poisson distributions:

\[
FC(0; n_1, ..., n_M) = \exp\left( - \sum_{i=1}^{M} a_i \right) \prod_{i=1}^{M} \frac{a_i^{n_i}}{n_i!} \quad (4.8)
\]

In this equation, \( a_i \) is a parameter that accounts for the difference in equilibrium position between the initial and the final state, and is given by the expression:

\[
a_i = \frac{G_i^2}{2\hbar \omega_i^3} \quad (4.9)
\]

where \( G_i \) is the energy gradient of the normal mode at the ground state equilibrium geometry, \( G_i = \left( \delta E / \delta q_i \right)_{(q_i=0)} \). When the geometrical structure of an excited state is considerably different than that of the ground state, the parameter \( a_i \) is modified according to:

\[
a_i = \frac{\delta q_i^2 \mu_i \omega_i^{exc}}{2\hbar \omega_i^{gs}} \quad (4.10)
\]

where \( \delta q_i \) is the change in the normal coordinate for the \( i^{th} \) vibrational mode, \( \omega_i^{exc} \) and \( \omega_i^{gs} \) are the vibrational frequencies for the normal mode \( i \) in the final and initial states respectively, and \( \mu_i \) is the reduced mass for the normal coordinate. Also in this case, it is possible to calculate the FC factors and the energies of the vibrational modes according to the linear approximation.[50,51] The LC model, and the necessity to explore complex PES in the electronic excitation process, going beyond the harmonic approximation, are discussed in PAPERS X and XI.
Phthalocyanines and shake-up calculations

The phthalocyanines (Pc’s), as well as the related molecules like naphthalocyanines and tetraazaporphyrins, are a very popular subject of investigation due to their great deal of useful applications. An example is the phthalocyanine blue pigment industrially produced, that is commonly adopted for printing inks and paints; but Pc’s are often used also in more sophisticated devices as xerographic machines, electrochromic displays and organic conductors, among many others[52].

The Pc’s are stable, conjugated aromatic macrocycles, with very interesting optical and electric properties[53,54]. In Figure 5.1 the atomic geometry of a metal free and a metal Pc are shown. Pc’s have a porphyrin like structure, bonded to four extra benzene rings. The central part of the molecule is either occupied by two hydrogen atoms (metal free or H₂Pc), or by a metal atom (metal Pc), as indicated in Figure 5.1. The molecular structure is either planar (like in the H₂Pc, NiPc, FePc) or distorted in a umbrella-like shape (as in PbPc[55]), where the metal atom sticks out from the molecular plane and all the other atoms are rearranged. They are van der Waals interacting molecules, that can be used as building blocks for materials whose properties, like conductivity, color, reactivity, can be tuned by changing the central metal.

The Pc’s are characterized by some typical features like their absorption spectrum\(^1\), that originates the known blue-green colour, and by their

\(^1\)the absorption spectrum is related to the valence band structure. It is characterized by a sharp and intense Q band, due to the HOMO-LUMO transition, and a broader
chemical stability, usually attributed to the aromatic structure. The employment of Pc’s in advanced technology, and the possibility to design new Pc-based materials for specific applications, requires an accurate knowledge of their fundamental properties. The electrical conductivity in Pc’s is intrinsically connected with their electronic structure and with the morphology of the Pc materials. Generally, Pc’s in the solid state, i.e. in crystalline arrangement, behave as insulators, with very low conductivities, often around $10^5 \text{S} \cdot \text{cm}^{-1}$, at room temperature.\[52\]

The Pc’s crystallize in chains that can cohere to form ordered films or larger crystal structures, according to some typical stackings called $\alpha$, $\beta$, $\chi$ etc. \[56\]. Each of the many different observed stackings is characterized by a defined angle between the normal to the molecular plane and the stacking direction. The reciprocal distance of the molecules in these structures, does not allow a sufficient overlap between the frontier $\pi$ molecular orbitals of adjacent Pc’s, and therefore no conduction band is formed, reducing greatly the charge carrier mobility in these films. Conduction in

and less intense B band. The Q band covers wavelength widths between 660 to 720 nm, and the larger B band between 300 and 450 nm.
these structures occurs, as in other organic conductors, via electron hopping upon application of an electric field, that is the only mechanism that allows charge carriers mobility [52]. This kind of electrical conductivity is temperature dependent. One way to increase the conductivity of such molecules is to build polymeric stacked Pc’s, where the Pc’s are bridged by some ligands. These systems can either favour the carriers hopping or modify the electronic structure and relative band gaps. Enhancement of the conductivity is also reached by means of oxidation-reduction agents, that increase the charge carrier density and even their mobility, after the possible structural rearrangement of the molecule. The various molecular stackings can be modified by changes in the inclination of the molecules. This can favour the overlap of the frontier $\pi$ orbitals leading to a significant improvement in the conductivity. These effects have been considered, for instance, for the development of sensor detecting gases[52].

Semiconductivity has been observed in Pc’s, and exploited in semiconductor devices like Organic Field Effect Transistors.[57] Other applications of Pc’s that are related to their linear and non linear optical absorption, are the design of optical filters for the protection of light sensitive optical sensors.[58] The photoconduction\(^2\) is exploited in the production of charge generating materials for the Xerographic reproduction. Moreover, Pc’s find applications in the field of biomimetics [59, 60], due to their similarity to the active sites of haemoglobin and chlorophyll.

The Pc’s are characterized by a very low room-temperature vapour pressure of $10^{-14}$ Torr, that facilitates the preparation and study of thin films in ultra high vacuum (UHV) conditions. This has made possible to study the Pc’s by a variety of soft x-ray spectroscopies, like XPS and NEXAFS, in order to determine their electronic and morphological structure.

The studies of Pc’s included in this thesis are focused in two main directions: the determination of the shake-up spectrum and the analysis of the electronic structure and molecular orientation in Pc films. For the calculation of the Pc shake-up states (PAPERS I, II and IV), a new approach has been introduced, particularly convenient for shake-up transitions of large molecules as Pc’s. The electronic structure and the molecular orientation of Pc films have been studied in (PAPERS III

\(^2\)a photoconductor is a semiconducting material that is non-conductive when isolated from radiation, but conductive when exposed to radiation like visible light or x-radiation.
5 Phthalocyanines and shake-up calculations

![Diagram of the two-steps model](image)

**Figure 5.2:** Schematic diagram of the two-steps model used to calculate the shake-up transitions. Step A is simulated by the successive steps B and C: **A:** the core electron ionization and the associated shake-up transition; **B:** the Z+1 approximation represents the core ionization; **C:** valence electron transition in the Z+1 approximation.

and IV), by the analysis the nitrogen 1s NEXAFS spectra in comparison with the experimental results.

### 5.1 C1s shake-up of phthalocyanines

The carbon 1s photoelectron spectrum of Pc has been the subject of contrasting interpretations for about thirty years [61-64], and no calculations had been reported for this system that could shed light upon this question. In PAPERS I, II and IV a new method for the shake-up calculation has been introduced, and applied to the study of the C1s shake-up states of the H₂Pc and NiPc. The computational approach is based on the TDDFT for the determination of the excitation energies. The excited atom is approximated by the *equivalent core* (EC) approximation, known also as the Z+1 approximation. The Z+1 approximation is based on the consideration that the potential sensed by the valence electrons of a core excited atom, can be represented by adding a positive charge in the nucleus. In practice, the core excited atom can be substituted by the following atom in the periodic table, but, to keep the number of electrons unchanged, a positive charge must be added.

The method we have introduced, simulates the shake-up process according to a two-steps model, as illustrated in Figure 5.2. The shake-up
5.1 C1s shake-up of phthalocyanines

Table 5.1: The experimental and theoretical energy and intensity of the main C1s shake-up features of the benzene.

<table>
<thead>
<tr>
<th>Benzene Main Shake-up Peaks</th>
<th>Experiment†</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>En. (eV)</td>
<td>Int. (%)</td>
</tr>
<tr>
<td></td>
<td>5.8 ±0.1</td>
<td>2.21</td>
</tr>
<tr>
<td></td>
<td>7.15 ±0.05</td>
<td>5.52</td>
</tr>
<tr>
<td></td>
<td>8.4 ±0.1</td>
<td>4.47</td>
</tr>
<tr>
<td></td>
<td>9.8 ±0.2</td>
<td>2.01</td>
</tr>
<tr>
<td></td>
<td>10.9 ±0.1</td>
<td>3.42</td>
</tr>
<tr>
<td>Theory</td>
<td>En. (eV)</td>
<td>Int. (%)</td>
</tr>
<tr>
<td></td>
<td>5.95</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>7.12</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>9.15</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>10.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Assignment</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2b1(π) → 3b1(π*)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1a2(π) → 2a2(π*)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1b1(π) → 3b1(π*)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2b1(π) → 4b1(π*)</td>
<td></td>
</tr>
</tbody>
</table>

† experimental data taken from ref. [65]

formation, part A of Figure 5.2, is decomposed in two steps: first the core hole is described by the Z+1 approximation (part B); the excitation energies are then calculated by TDDFT for this configuration (C). Usually, the TDDFT is employed to compute the optical excitation of valence electrons: in the present application, the energy of the shake-up is related to the optical excitation energies of a core-ionized molecule (represented by Z+1 approximation). The use of TDDFT is particularly convenient for the calculation of the shake-up transitions, because the electron correlation is automatically included, and, furthermore, many excitations of the valence electrons are simultaneously calculated. The involvement of σ and π type orbitals is always fully considered, as are both singlet and triplet type states. The intensities of the shake-up transitions are calculated on the basis of the sudden approximation as the squared overlap between the initial and final states. This is reduced to the squared overlap between the excited orbital in the final state with the occupied orbital in the ground state. The quality of the method has been verified for the benzene molecule (C₆H₆) in (PAPER I). Benzene is an excellent test case, because its C1s shake-up spectrum has been thoroughly studied both theoretically and experimentally[65–70]. The results we have obtained are summarized in Table 5.1 for the main shake-up states of singlet character, in comparison with recent experimental data [65].

In Table 5.1 the positions are expressed as the energy difference with respect to the main peak, and the intensity as the percent (%) of the main peak intensity (assumed to amount to 100%). The results obtained, both in terms of the energy position and intensity, and the transitions
5 Phthalocyanines and shake-up calculations

Figure 5.3: **A**: the experimental C1s XPS of metal free phthalocyanine; the three main peaks are labeled 1 to 3. **B**: A table with the energy position of the three main peaks in the experimental spectra of three different Pc’s (H2Pc, NiPc, and PbPc).

assignments, are in very good agreement with previous works.

As a first application to a larger system, this method has been employed to determine shake-up states related to the C1s XPS of H2Pc. In the C1s XPS experimental spectra of many Pc’s, three main peaks are distinguishable: the experimental spectrum of H2Pc from **PAPER I** of Figure 5.3 is a typical example\(^3\). The main peak at 284.9 eV, labeled 1, is assigned to the XPS main line of the 24 benzene carbons; the second peak at 286.2 eV, labeled 2, to the main line of the 8 pyrrole carbons, and the third, lower intensity feature at about 288.3 eV, labeled 3, to a shake-up transition associated to the photoionization of the pyrrole carbons. The character of the carbon atoms in the Pc’s is illustrated in Figure 5.1. The energy positions of these three typical features are practically unchanged also in the same spectra of many metal Pc’s, as can be seen in the table at the right hand side in Figure 5.3, where the energy of peaks 1, 2 and 3 in two metal Pc’s (NiPc and PbPc), are compared with those of H2Pc. The two main lines lie between 284.76 and 284.9 eV, and 286.06 and 286.2 eV, and the third peak between 287.97 and 288.12 eV, is located at about 1.8-1.9 eV from the pyrrole main line.

The intensity ratio of the peaks guided by this assignment and carried out by the three-peak fitting of the experiment (shown in Figure

\(^3\)The mentioned Pc spectra are collected for bulk Pc’s, generally in thick films specimens.

46
5.1 C1s shake-up of phthalocyanines

![Graph showing 3 and 4 peak fittings for H_2Pc C1s XPS](image)

**Figure 5.4:** 3- and 4-peak fittings for the H_2Pc C1s XPS. In the 3-peak fitting only the shake-up related to the pyrrole C is considered, leading to an overestimation of the total pyrrole C intensity (dark gray area) with respect to the benzene C intensity (light gray area). The effect is considerably corrected by a 4-peak fitting, where also the benzene C shake-up is included.

5.4), however, does not agree with the 1:3 value that is expected by the relative pyrrole:benzene carbon ratio. For H_2Pc, the pyrrole peaks result responsible for a value as high as 33% of the total signal: their intensity is clearly overestimated. A solution to this problem was already advanced in [61], by supposing the existence of a fourth peak, corresponding to a shake-up structure related to the benzene carbons. The energy position of this shake-up could be similar to that of the pyrrole related shake-up, which means it could lie at about 2 eV from the benzene main peak. The benzene shake-up peak would in this case fall very close to the higher intensity pyrrole main line, and it would be very difficult to distinguish from the other peaks. The proposed four peak structure is illustrated in Figure 5.4.

In **PAPER I** and **II**, we report the calculated energies and intensities of the main shake-up features of H_2Pc. The calculations have been performed for each of the eight non-equivalent carbons of the molecule, shown in Figure 5.1. The main result is that shake-up peaks, of significant intensity, are associated to both the pyrrole and the benzene carbon. We could thus confirm the validity of the hypothesis that there are shake-up states associated with the benzene carbons. The computations thus confirmed also that peak 3 of Figure 5.3, indeed coincides with shake-
5 Phthalocyanines and shake-up calculations

Table 5.2: Theoretical shake-up energies and intensities of C1s in $H_2Pc$. Only the states with intensity higher than 1% are reported.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>En. (eV)</th>
<th>Int. (%)</th>
<th>Carbon</th>
<th>En. (eV)</th>
<th>Int. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_1$</td>
<td>1.96</td>
<td>12.1</td>
<td>C$_4$</td>
<td>1.74</td>
<td>7.2</td>
</tr>
<tr>
<td>C$_2$</td>
<td>1.91</td>
<td>4.1</td>
<td>C$_5$</td>
<td>2.06</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>2.80</td>
<td>3.7</td>
<td></td>
<td>1.48</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>2.94</td>
<td>2.3</td>
<td></td>
<td>2.06</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>3.14</td>
<td>1.2</td>
<td></td>
<td>3.1</td>
<td>1.9</td>
</tr>
<tr>
<td>C$_3$</td>
<td>1.76</td>
<td>6.8</td>
<td>C$_6$</td>
<td>1.96</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>2.07</td>
<td>7.4</td>
<td>C$_7$</td>
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<tr>
<td></td>
<td>3.16</td>
<td>1.3</td>
<td></td>
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</tbody>
</table>

up transitions associated to the pyrrole carbon. As suggested by the experimentalists, the benzene shake-up peak is hidden below the higher intensity main line pyrrole carbons. The shake-up transitions related to the benzene and pyrrole carbons are located at almost the same distance from the respective main lines. Table 5.2 helps to compare the behaviour of the shake-up transitions associated to the various carbons.

One or more shake-up states were calculated for all carbon atoms at about 1.7 to 2 eV from the main line. In all these cases, the main transition involved is the excitation from HOMO to LUMO. The position of the shake-up lines shifted by the respective calculated ionization potentials (IP) are reported in Figure 5.5. The theoretical spectrum has been convoluted by a Gaussian curve of 0.8 full width at half maximum (FWHM) to reproduce the experimental spectrum.

In Figure 5.5 the theoretical shake-up spectra calculated for three different Pcs are compared: $H_2Pc$ (PAPER I), NiPc, (PAPER IV), and PbPc (unpublished results). In all cases the theoretical shake-up lines were convoluted with a Gaussian curves of 0.8 eV FWHM. Despite the $H_2Pc$ peaks are slightly broader, reflecting the lower symmetry of the molecule (see Figure 5.1), considerable similarities can be pointed out from these results. The general shake-up structure for benzene and pyrrole carbons is the same in all three Pcs. The benzene carbon shake-up falls very close to the pyrrole main line in all cases. The benzene shake-up is formed by

\[ ^4 \text{The energy scale is aligned to the experimental data.} \]
5.2 Orientation of phthalocyanine films

bunches of shake-up lines distributed at around 2 eV from the benzene main peak. The pyrrole shake-up is mainly generated by a single peak of considerable intensity (about 20%). Further transitions are located at about 3 to 4 eV from the benzene main peak, in the region of the pyrrole shake-up.

The TDDFT calculations of the shake-up states have shown to be very accurate for large molecules like Pc’s. This approach provides detailed information of the photoelectron spectra of large systems, allowing to understand not only the properties of core orbitals, but also the properties of the valence band and of the unoccupied orbitals.

5.2 Orientation of phthalocyanine films

When deposited on several types of substrates, the Pc’s tend to form ordered films, which can be prepared under UHV conditions and studied by soft x-ray spectroscopies. It is possible to exploit the polarization dependence of the NEXAFS spectroscopy to determine the orientation of the molecules in the films with respect to the surface plane. These studies provide, in the same time, also a description of the molecular unoccupied electronic states. We have applied this technique to H$_2$Pc (PAPER III) and FePc films (PAPER IV).

A thick FePc film was evaporated in situ $^5$ on a clean silicon surface

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$^5$inside the UHV experimental station.
5 Phthalocyanines and shake-up calculations

![FePc/Si(100) - N1s NEXAFS](image)

**Figure 5.6**: A: spatial resolved calculated N1s NEXAFS spectra of FePc. The x, y, and z axes are defined with respect to the molecular orientation, shown in the right upper part. B: The theory vs experiment comparison, simulating the case in which the FePc molecular plane (yz) is orthogonal to the substrate. The experimental geometries are indicated by the vectors E (light polarization) and n (normal to the substrate). C: the NEXAFS spectra atom resolved for the two non-equivalent nitrogens.

In Figure 5.6 are illustrated the theoretical and experimental results. The theoretical N K-edge NEXAFS spectra are shown in Figure 5.6 (part A), where the intensities obtained along the different x, y, and z direction (indicated in the Figure) are resolved. The intensity along the x direction (orthogonal to the molecular ring) reflects the N1s excitation into the unoccupied π type orbitals, while the intensities along the y and z directions show the excitations into the unoccupied σ type orbitals. By focusing the analysis on the spectral structures before the IP (at 403.6 eV for N1 and 403.3 eV for N2), it results that the calculation along x is the richest of high intensity features (four peaks at 398.2 eV, 399.8 eV, 401.7 eV and 403.2 eV), while along y and z only two smaller peaks appear (at 398.7 eV and 399.7 eV). The continuum structures, described by the Stieltjes imaging approach, have very weak intensity in the normal direction (x), and, inversely, very strong intensity in the in-plane direction (yz). The measurements were performed on the N1s edge at three different geometries, as sketched in Figure 5.6: the sample was positioned so that
5.2 Orientation of phthalocyanine films

The light polarization vector \( \mathbf{E} \) was oriented parallel, normal and at 45° with respect to the surface (the vector \( \mathbf{n} \) indicates the direction normal to the surface). The comparison between the experimental and theoretical results (Figure 5.6), shows that, when \( \mathbf{E} \) is parallel to the surface (orthogonal to \( \mathbf{n} \)), the excitation is prevailing directed to the \( \pi \) orbitals, and when \( \mathbf{E} \) is normal to the surface (parallel to \( \mathbf{n} \)), the excitation is mostly directed to the \( \sigma \) orbitals. This suggests that the molecular plane lies at an angle close to the normal to the surface, with the molecules in the film standing on the substrate. In Figure 5.6 (part B), the case in which the molecular rings are standing exactly at 90° with respect to the substrate surface is simulated by composing the theoretical spectra of part A. The sum of the y and z components would in this case correspond to the spectra taken with \( \mathbf{E} \) normal to the surface, and the same spectrum plus an equal percentage of the x component would represent the case of \( \mathbf{E} \) parallel to the surface. The discrepancies between these simulations and the experimental data demonstrate that the orientation of the FePc with respect to the surface is affected by a tilting absorption angle. The theoretical NEXAFS spectra were computed separately for each of the two non-equivalent N (described in the table of Figure 5.1). The resulting spectra, where the x, y and z components are summed together, are shown in Figure 5.6 part C. The \( N_1 \) nitrogen atoms are directly bonded to the iron atom, while the \( N_2 \) is bonded to two carbon atoms. The small shift in energy between the \( N_1 \) and \( N_2 \) NEXAFS spectra is likely to be related to the different IP’s (a chemical shift of 0.3 eV is predicted by the calculations between \( N_1 1s \) and \( N_2 1s \)). The electronic structure of the two atomic sites is different: it is evident from the different intensities of the threshold peaks at around 398 and from the peaks at about 400 eV, and these difference are probably due to the bonding of the \( N_1 \) to the Fe central atom.
6

Soft x-ray spectroscopy of large molecules

The soft x-ray spectroscopies are extremely valid tools in the determination of the morphological and electronic structure of large molecules. In this chapter the sensitivity of the emission spectroscopies like XES and RIXS to the conformation of a polymer will be discussed (PAPER VI). The soft x-ray spectra of recently synthesized fullerenes have been calculated and analyzed (PAPER VII and VIII).

6.1 The conformation of poly(ethylene oxide)

The poly(ethylene oxide) (PEO) compound finds a particularly important application as solid polymer electrolyte (SPE) [71]. SPE are used in rechargeable lithium ion batteries [72], that are nowadays the best portable energy sources available. The insertion of solid electrolytes can improve the practical usage of these devices. PEO based electrolytes exploit its capability of dissolving alkali salts, with which it forms various complexes. The ion transport mechanism in SPE is still poorly understood. In order to shed light on the relation between the conductivity and the molecular structure of the complexes and of the PEO, many studies are devoted to the analysis of the structure of pure PEO and of PEO in complexes. In PAPER VI we have analysed the applicability of the XES and RIXS techniques for the determination of the geometrical arrangement of PEO polymers. Four possible structures have been selected,
which had been previously proposed either for the pure PEO, or for PEO in various complexes.

The PEO chain is composed of repeating sequences of \((\text{CH}_2\text{CH}_2\text{O})\) monomers. Depending on the dihedral angles among the successive OCCO, CCOC and COCC segments, the atoms in the monomers are arranged in different ways. The possible conformations of the segments are divided into two groups: *trans* (T), when the dihedral angle is zero, and all the carbon and oxygen atoms are coplanar, and *gauche* (G) otherwise. Figure 6.1 presents the structural models we have studied. The *helix* is the conformation of the pure PEO crystal, and was determined by Takahashi and Tadokoro in 1973 by x-ray diffraction analysis [73]. In the helix, the units are characterized by a repeating T\(_2\)G sequence, and form a helicoidal structure slightly distorted from a perfect D\(_7\) point group. We have then considered a simple zig-zag chain, formed by an all-T sequence, the *planar zig-zag* model. A planar zig-zag structure has been proposed for pure PEO in some particular conditions, like for example, in a stretched sample fixed on a sample holder under tension (in this case the release of the tension resulted in the conversion to the helix structure [74]). Moreover, PEO has been observed to adopt a planar zig-zag structure upon blending [75] and in freeze-dried PEO, prepared in diluted benzene solution, in which case it is a stable conformation also at room temperature [76]. The two configurations named *zig-zag I* and *zig-zag II* have been proposed for

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**Figure 6.1:** The PEO conformations analysed are shown in side- and top-view. The lateral arrows indicate the repeating unit of each model.
6.1 The conformation of poly(ethylene oxide)

PEO Valence Band PES

![PEO Valence Band PES](image)

**Figure 6.2:** The valence band PES calculated for the four PEO models, and compared with the experimental peaks measured in Ref. [80].

PEO complexes like PEO CdPS$_3$[77] (zig-zag I), PEO HgCl$_2$[74, 78] and PEO NaSCn[79] (zig-zag II). Their structures are still helicoidal like the pure PEO crystal, but more compressed. Zig-zag I is formed by a T$_5$G conformation and zig-zag II by a TG$_2$TG$^-$ conformation$^1$.

6.1.1 The calculated electronic structure

The theoretical spectra obtained for the valence band of the models are shown in Figure 6.2, based on B3LYP/DFT calculations. The chains were approximated by 12 monomer units$^2$, terminated by the methyl group (CH$_3$). The vertical lines represent the experimental peaks measured for a PEO film and are labeled according to the nomenclature of the original paper[80]. The analysis of the several features of the valence band reveals their orbital origin. The peaks D correspond to the oxygen lone pair;

$^1$The gauche monomers are often labeled G$^+$ (or G) or G$^-$ depending on the direction of the resulting rotation.

$^2$The size of the chains has been chosen after studying the variation of the DOS of chains of various length. At 12 monomers the evolution of the spectral features can be considered complete.
6 Soft x-ray spectroscopy of large molecules

the second peak, D₁, is composed additionally by a small part of carbon 2p. In the region C, the 2p orbitals form interatomic bonds (carbon-carbon, carbon-hydrogen and carbon-oxygen), while the regions B and A are largely populated of 2s orbitals. Even though the valence band of all the models has an overall similar structure, with peaks located in the same positions as the experimental ones, there are some unique features that differentiate each of them and allow to identify each conformation. For instance, in the zig-zag II structure, some peaks are doubled (A₁, B₃, D₁), and the peaks D₁ and D₂ have similar low intensity unlike the other models. The planar zig-zag is characterized by a region between about 7 and 9 eV, with very low intensity.

The XES and RIXS spectra, calculated for the C and O K-edge, are shown in Figure 6.3. The comparison of the spectra of the four models leads to the following general observations. The RIXS spectra are in general characterized by a lower number of features, due to the stricter selection rules with respect to the XES. This is particularly evident for the zig-zag model, that possesses the highest degree of symmetry of the four. The RIXS symmetry selectivity is a powerful tool to distinguish among similar structures: for instance, a small peak at 527.1 eV in the oxygen zig-zag I spectrum allows to identify this model with respect to the, otherwise, very similar helix spectrum. The oxygen spectra are strongly affected by the structural differences in the higher energy region, where the lone pair orbitals lie. It can moreover be evidenced from the cal-

Figure 6.3: The calculated carbon and oxygen K edges XES and RIXS of the four PEO models.
calculations, how the carbon spectra, especially in the RIXS regime, are sensitive to the local structure and symmetry changes. The theoretical calculations of the valence band PES, the XES and the RIXS show that it is possible to distinguish among the four polymeric conformations by analysing spectroscopical results. The spectroscopies can therefore be used as fingerprints to determine the structure of the PEO.

### 6.2 Fullerenes

The fullerene family is becoming larger and larger every year, since from time to time, new molecules are synthesized. Much attention is directed toward the production of substitute doped fullerenes (or etherofullerenes)\(^3\) or of full-carbon cages of different sizes. The goal of these efforts is the production of fullerene materials with electronic properties exploitable in technological applications. The substitution of other atoms in the fullerene cage, for example, changes the properties of the molecule, often increasing the reactivity with respect to the C\(_{60}\), that is only van der Waals interacting. Elements that are often used as substitutes are boron and nitrogen\([81,82]\). The big challenge is to produce these molecules in macroscopic amounts. The production of fullerenes of the C\(_{60-x}N_x\) type, has been successful with C\(_{50}N\) \([82]\), that is a very reactive molecule, only

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\(^3\)Fullerenes in which carbon atoms are replaced by atoms of other elements.
6 Soft x-ray spectroscopy of large molecules

stable in the form of dimers. In very recent years, two new molecules have been grown: a new azafullerene, the C$_{48}$N$_{12}$\cite{83}, and an all-carbon cage of 50 atoms, stabilized by ten chlorine atoms, the C$_{50}$Cl$_{10}$\cite{84}. The C$_{50}$Cl$_{10}$ is one of the few fullerenes with less than 50 carbons to have been successfully synthesized in the laboratory. We have characterized the electronic structures of these molecules by theoretically simulating their soft x-ray spectra.

6.2.1 Two isomers of C$_{48}$N$_{12}$

Two low energy structures have been proposed for C$_{48}$N$_{12}$, that we have analysed in PAPER VII. The two isomers are represented in Figure 6.4, DAZAF1\cite{85} and DAZAF2\cite{86}. The twelve nitrogens are distributed one per each pentagonal face$^4$ in both structures. DAZAF2, unlike DAZAF1, is characterized by two antipodal triphenilene type structures: the triphenilene is formed by four full-carbon hexagons, and three pentagons. This results in a different distribution of the nitrogens among the hexagons in the two isomers. And, consequently, it generates different chemical environments for the carbon and nitrogen atoms. This is detectable in their photoelectron spectra, and emerges by the calculation of their IP’s. In DAZAF1 there are 2 full-carbon hexagons, 12 hexagons with one nitrogen and 6 hexagons with two nitrogens; in DAZAF2 there are eight full-carbon hexagons, and the remaining twelve hexagons all contain two nitrogens. We found eight non-equivalent carbons and two non-equivalent nitrogens in each isomer. In Figure 6.5 are shown the theoretical XPS spectra of the carbon and nitrogen 1s level. The multiple peaks visible in the spectra, derive from the core level shift due to the different types of chemical bondings of each atom. In DAZAF1 there are two types of carbon, that are bonded either to three other carbons, or to two carbons and one nitrogen; in DAZAF2, moreover, there is a third type of carbons, bonded to one carbon and two nitrogens. The three possibilities are sketched in Figure 6.5, along with their respective IP’s. The theoretical XPS spectra are built by convoluting the calculated IP’s by a Gaussian function of 0.3 eV FWHM. From the analysis of the IP’s obtained, it is possible to draw the conclusion that the electron binding energy of the carbon 1s orbital increases when the atom is bonded to one nitrogen, and it increases more

$^4$Any fullerene cage is characterized by exactly 12 pentagonal faces, plus a variable number of hexagonal faces.
6.2 Fullerenes

![Graph showing C1s and N1s XPS spectra of isomers DAZAF1 and DAZAF2.](image)

**Figure 6.5:** The calculated C1s and N1s XPS spectra of the isomers DAZAF1 and DAZAF2.

If the atom is bonded to two nitrogens. The C1s chemical shifts, moreover, provide a mean to distinguish between the two types of isomers in an XPS experiment. The electronic structures of DAZAF1 and DAZAF2, which emerge from the NEXAFS and XES calculations, present a large number of peaks. By comparing these spectra with the theoretical NEXAFS spectrum of C\(_{60}\), (Figure 6.6) which is characterized by the high I\(_h\) symmetry, it is evident that in C\(_{48}\)N\(_{12}\) there is a lift of the degeneracy of the unoccupied states with respect to the Buckminster fullerene. The NEXAFS theoretical spectra of DAZAF1 and DAZAF2 were obtained by summing the contributions of all the eight non-equivalent carbons. The lift of degeneracy of the orbitals with respect to the C\(_{60}\) is observed also for the occupied orbitals. The Mullikan population analysis has shown that the valence band orbitals are characterized by a strong mixing of the nitrogen and carbon components. A considerable difference between the two isomers is that the HOMO-1 orbital in DAZAF1 is of pure carbon character, while in DAZAF 2 it has both carbon and nitrogen characters.
Figure 6.6: The theoretical NEXAFS spectra of DAZAF1 and DAZAF2. The spectra of each of the eight inequivalent atoms in both isomers are shown. The total spectra are compared with the NEXAFS spectrum of $C_{60}$.

6.2.2 The electronic structure of $C_{50}Cl_{10}$

The molecular structure of $C_{50}Cl_{10}$ has been determined out of a total of 271 possible isomers in experimental[84] and theoretical works [87]. The molecule has a highly symmetric structure belonging to the $D_{5h}$ group, with four non-equivalent carbon atoms. The structure is illustrated in Figure 6.7. The Cl atoms lay along the equator of the molecule. The ge-

Figure 6.7: The $D_{5h}$ symmetric structure proposed for $C_{50}Cl_{10}$. The four non-equivalent carbon atoms that characterize this isomer are labeled $C_1$ to $C_4$. 

60
metrical configuration of the D$_{5h}$ isomer meets also the stability rule for the fullerenes: it has been observed that the lower the number of adjacent pentagons in the cage, the more stable the structure. C$_{50}$ is actually the smallest possible fullerene in which no more than two pentagonal faces need to be placed next to each other. We have simulated the valence band photoelectron spectra of C$_{50}$Cl$_{10}$ as a function of the exciting photon energies, indicated in Figure 6.8. The energies considered vary from 21.2 eV and 40.8 eV (corresponding the He I and He II excitation sources, often used in the laboratories), 132.3 eV, 300 eV, 600 eV, up to 1253.6 eV, the Mg K$\alpha$ line, and 1486.6 eV, the Al K$\alpha$ line, the last two often used in the laboratory X-ray sources. The total spectra were obtained according to the Gelius model [88], by multiplying the intensity of each orbital by the photoionization cross sections calculated by Yeh and Lindau [89] for different photon energies. In Figure 6.8 the partial density of states (DOS) of C and Cl are plotted separately. It is shown by the results that at all excitation energies except at 40.8 eV, the spectrum is dominated by an intense Cl peak at -8.8 eV, and the C related structures are hardly visible. It is only at the excitation energy of the He II source,

Figure 6.8: Valence band XPS of C$_{50}$Cl$_{10}$. A: the partial density of states for chlorine and carbon are shown separately; B: the valence band spectra calculated at different excitation energies. Each spectrum is formed by the sum of the C and Cl orbital contributions, each multiplied by the photoabsorption cross section.
that a spectrum characterized by the carbon features appears. In fact, only at 40.8 eV, the cross section of the C orbitals are high enough so that the carbon peaks are predominant in the photoelectron spectrum.
Vibrational profiles of absorption resonances

The core excitation is a process that strongly influences the electronic structure of a molecule, and generally induces atomic displacements. Many molecules are only affected in the stretching vibrational modes, like the symmetric methane and ethane [50]. But, in some cases, the core excited final state may exhibit considerable morphological modifications, that can even lead to the dissociation of the molecule (the photofragmentation). For example, small triatomic linear molecules like CO$_2$[90–93] and N$_2$O [90, 92, 94–97] have shown to assume a bent geometry after the excitation of the carbon and nitrogen 1s, respectively, into the LUMO $\pi^*$ state. The same happens to the larger acetonitrile (CH$_3$CN)[98, 99], where the bending affects the CCN segment. Detailed information about the geometrical distortions caused by the core excitations can be revealed by the study of the vibrational profile of the related resonances. The experimental high resolution absorption spectra are, in many cases, able to resolve the vibrational fine structure[49, 50, 100, 101]. The challenge for the theory is to interpret the origin of the vibrational progression, and to explain the dynamics of the core excitation. We have studied the vibrational profiles of acetonitrile (PAPER X) and dinitrogen oxyde (PAPER XI). Both molecules are subject to the Renner-Teller (RT) effect[96]. In the ground state they have a twofold degenerate $\pi^*$ orbital. The RT effect breaks the degeneracy upon the N1s→$\pi^*$ transition, by bending the linear molecule, or the linear segment of the molecule. The degenerate $\pi^*$ splits into the RT states a’ and a”. The excitation into a’ leads to a bent final state of
low energy, and the excitation into \( a'' \) maintains the linear geometry, and has higher energy. The degenerate \( \pi^* \) orbitals of acetonitrile involved are shown in Figure 7.1 in the neutral ground state and in the excited state. The vibrational fine structures of the \( \pi^* \) absorption resonance of the CH\(_3\)CN and N\(_2\)O are only visible through the broadening and the asymmetry of the peaks. This effect is connected to the morphological modifications induced by the RT effect. In \textit{PAPER X} and \textit{XI} we have calculated the vibrational profile associated to the \( \pi^* \) resonance in both molecules.

### 7.1 The Renner-Teller effect on the N\(_2\)O 1\( s \rightarrow 3\pi^* \) excitation

In N\(_2\)O, two different non-equivalent nitrogens can be excited: the terminal nitrogen (\( N_t \)) and the central nitrogen (\( N_c \)). The difference between the final geometries depending on the selective excitation of \( N_t \) or of \( N_c \) is still under debate. Essentially the experimental results propose two opposite pictures. LeBrun \textit{et al.} [95] and Machida \textit{et al.} [94] find a larger bending after excitation of \( N_t \), while Adachi \textit{et al.} [96], who performed also
7.1 The Renner-Teller effect on the $\text{N}_2\text{O}$ $1s \rightarrow 3\pi^*$ excitation

Table 7.1: The optimized geometrical structures of the neutral ground state and the $\text{N}1s^13\pi$ excited states of $\text{N}_2\text{O}$. The DFT/B3LYP and the HF results are compared for the selective excitation of $\text{N}_t$ and $\text{N}_c$. The values obtained for the interatomic distances $\text{NN}$ and $\text{NO}$, and the angle $\theta(\text{N}_t\text{N}_c\text{O})$ (°) are listed.

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<th>$\text{N}_c$ excitation</th>
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</tr>
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<td>$\theta(\text{NNO})$ (°)</td>
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<td>119.82 179.96</td>
</tr>
</tbody>
</table>

$ab$ $initio$ SCF calculations, propose a larger bending after the excitation of $\text{N}_c$.

We have analysed this problem by performing geometry optimizations of the final excited states for each nitrogen, and by comparing the structures resulting from HF-SCF, DFT/BLYP and DFT/B3LYP calculations. The calculations of the core excitations were performed in the triplet restricted open shell configuration. Successively the energy of the singlet excited states are determined. In Table 7.1 are listed the geometrical parameters that characterize the structures obtained by HF and DFT/B3LYP$^1$.

In the bent excited configuration, the optimized angles resulting by the excitation of the terminal nitrogen, ($\text{N}_t$), are very similar for the HF and the DFT/B3LYP calculations, amounting to 137.12° (HF) and 134.37° (DFT). Also the interatomic distances obtained are similar. The linear excited geometries obtained with the two methods with respect to the excitation of the terminal nitrogen, are also comparable.

In the excitation of the central nitrogen, ($\text{N}_c$), the difference is remarkable, with a bending angle of 119.82° for HF, and of 133.09° for DFT/B3LYP (the latter is similar to the $\text{N}_t$ excitation value). In this case,

$^1$The DFT/BLYP results are comparable with those obtained from DFT/B3LYP.
case, the HF method gives a very large NO distance, amounting to 1.77Å, indicating dissociation of this bond. The NO bond is only elongated to 1.32Å in the DFT/B3LYP description. The HF calculations, unlike the DFT/B3LYP calculations, predict the NO bonding dissociation also for the linear excited state. The DFT/B3LYP calculations described were performed in the triplet restricted open shell configuration. A singlet calculation predicts instead a smaller bending angle of the central nitrogen (125°). The singlet correction applied to the DFT description gives results for the different bending angles in line with the finding of Ref. [96].

7.2 Vibrational analysis of the 1s→π* excitation in acetonitrile

The asymmetric and broad line shape of the N K edge π* resonance of acetonitrile hides a rich vibrational structure. This is originated by the double geometries induced by the RT splitting. The calculation of the vibrational profile presupposes the determination of the potential energy surface for the excited states and the use of linear coupling model. The PES is a multidimensional curve, that lies in a 3N-3 dimensional space, where N is the number of atoms. In this problem, however, one vibrational
7.2 Vibrational analysis of the 1s→π* excitation in acetonitrile

Figure 7.3: The potential energy curve along the CCN bending angle in acetonitrile. The angle is equal to zero when the CCN segment is linear. The core excited wave functions with vibrational quantum number 0 (near the bent excited state), 15, 16, and 17 (close to the potential barrier) are plotted.

mode should be treated differently and it corresponds to the bending angle CCN. The acetonitrile PES is therefore studied along this coordinate[49]. The PESs deriving by the excitation into the a’ and a” RT states are sketched in Figure 7.2. The lower curve corresponds to the excitation into a’, resulting in the bent excited state, and the upper curve to the excitation into a”, that gives the linear final state. The zero on the CCN bending coordinate corresponds in this case to the linear configuration of the CCN segment.

Four regions are indicated in Figure 7.2. The bent final state lies in the region A, the linear final state lies in the region B. The region C represents the transition state between the two symmetrical bent configurations. In the diagram, the diabatic (dashed line) and the adiabatic (solid line) PES are shown. The two diabatic curves intersect in the region D. In the linear coupling model (LCM), only the diabatic potentials, described by an harmonic curve, should be considered. However, in this case the bending motion occurs along an adiabatic curve characterized by a transition state (TS). The vibrational profile was calculated in each zone shown in Figure 7.3. In region B the LCM was applied. The calculation of the vibrational frequencies for the adiabatic potential, shown in Figure 7.3 was performed analytically as for a double well potential[102], and the FC fac-
Vibrational profiles of absorption resonances

Figure 7.4: Comparison of the calculated vibrational envelop for the N1s→π* resonance in acetonitrile with the experimental spectrum. The total spectrum is obtained by adding together the diabatic and adiabatic contributions.

The total vibrational envelop is obtained as a sum of the vibrational profiles described[93]. To determine the weight of each component, the vibronic coupling between the TS state and the minimum of the upper curve, needs to be estimated, in order to represent the region of the excitation. To this scope the Landau Zener probability is used, which evaluates the ratio between the diabatic and the adiabatic components. In acetonitrile, we obtain that the Landau Zener probability to follow the diabatic curve amounts to 60%, with an energy distance between the points B and C of 0.22 eV. The theoretical vibrational profile for the NEXAFS N\textit{t} 1s→π* excitation is shown in Figure 7.4, where the final result is compared to the experimental curve.
References


69
REFERENCES

REFERENCES

REFERENCES


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