Molecules and Light

A Journey into the World of Theoretical Spectroscopy

IULIA EMILIA BRUMBOIU
Abstract

Two of the main technological challenges of the century are the production of clean energy, on the one hand, and the development of new materials for electronic and spintronic applications that could increase the speed and the storage capacity of regular electronic devices, on the other hand. Organic materials, including fullerenes, organic polymers and organic molecules with metal centres are promising candidates for low-cost, flexible and clean technologies that can address these challenges. A thorough description of the electronic properties of such materials is, therefore, crucial. The interaction of electromagnetic radiation with the molecule can provide the needed insight into the electronic and vibrational levels and on possible chemical interactions. In order to explain and interpret experimentally measured spectra, a good theoretical description of the particular spectroscopy is necessary. Within density functional theory (DFT), the current thesis discusses the theoretical tools used to describe the spectroscopic properties of molecules with emphasis on two classes of organic materials for photovoltaics, molecular electronics and spintronics. Specifically, the stability of the fullerene derivative PC$_{60}$BM is investigated in connection with its use as an electron acceptor in organic solar cells and the valence band electronic structure of several transition metal phthalocyanines is studied for their possible application in electronics and spintronics. The spectroscopies discussed in the current work are: the photoelectron spectroscopy of the valence band, X-ray photoelectron spectroscopy of the core levels, near-edge X-ray absorption fine structure, Infrared and Raman vibrational spectroscopies

Keywords: Theoretical spectroscopy, XPS, NEXAFS, PCBM, Metal phthalocyanine, Organic solar cells

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ISSN 1651-6214
urn:isbn:se:uu:diva-300123 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-300123)
List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I *Near-edge X-ray Absorption Fine Structure Study of the C$_{60}$-Derivative PCBM*

*Iulia Emilia Brumboiu*, Ana Sofia Anselmo, Barbara Brena, Andrzej Dzwilewski, Krister Svensson and Ellen Moons


II *Elucidating the 3d Electronic Configuration in Manganese Phthalocyanine*

*Iulia Emilia Brumboiu*, Roberta Totani, Monica de Simone, Marcello Coreno, Cesare Grazioli, Luca Lozzi, Heike C. Herper, Biplab Sanyal, Olle Eriksson, Carla Puglia and Barbara Brena


III *The Influence of Oxygen Adsorption on the NEXAFS and Core-Level XPS Spectra of the C$_{60}$ Derivative PCBM*

*Iulia Emilia Brumboiu*, Leif Ericsson, Rickard Hansson, Ellen Moons, Olle Eriksson, and Barbara Brena


IV *Atomic Contributions to the Valence Band Photoelectron Spectra of Metal-Free, Iron and Manganese Phthalocyanines*

Ieva Bidermane, *Iulia Emilia Brumboiu*, Roberta Totani, Cesare Grazioli, Nina Shariati-Nilsson, Heike C. Herper, Olle Eriksson, Biplab Sanyal, Barbara Ressel, Monica de Simone, Luca Lozzi, Barbara Brena and Carla Puglia


V *Influence of Electron Correlation on the Electronic Structure and Magnetism of Transition-Metal Phthalocyanines*

*Iulia Emilia Brumboiu*, Soumyajyoti Haldar, Johann Lüder, Olle Eriksson, Heike C. Herper, Barbara Brena and Biplab Sanyal

*Journal of Chemical Theory and Computation*, 12, 1772-1785 (2016)
VI  *Ligand Effects on the Linear Response Hubbard U: The case of Transition Metal Phthalocyanines*  
*Iulia Emilia Brumboiu*, Soumyajyoti Haldar, Johann Lüder, Olle Eriksson, Heike C. Herper, Barbara Brena and Biplab Sanyal  
in *manuscript*

VII  *The Valence Band Electronic Structure of Cobalt Phthalocyanine from Optimally Tuned Range-Separated Hybrid Functionals*  
*Iulia Emilia Brumboiu* and Barbara Brena  
in *manuscript*

VIII  *Photon and Binding Energy Dependent Valence Band Photoelectron Spectroscopy of Organic Molecules*  
*Iulia Emilia Brumboiu* and Barbara Brena  
in *manuscript*

IX  *C1s NEXAFS Investigations of PC$_{60}$BM Exposed to Oxygen: a Novel Approach for the Comparison of Computed and Experimental Spectra*  
*Iulia Emilia Brumboiu*, Leif Ericsson, Vanja Blazinic, Rickard Hansson, Ellen Moons and Barbara Brena  
in *manuscript*

X  *Spectroscopy of Photo-Oxidized PC$_{60}$BM*  
in *manuscript*

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Comments on my own contribution

For all the articles where I am the first author, I had the main responsibility for analysing the data, preparing the figures and writing the manuscript. Articles I, II, III, IV, IX and X are the fruits of theory-experiment collaborations. For these studies I had the main responsibility of performing the theoretical calculations. Articles V and VI are in collaboration with colleagues from the Materials Theory division and I have performed part of the theoretical calculations, analysed the data and prepared the manuscripts. Articles VII and VIII are theoretical works done in collaboration with my main supervisor, Dr. Barbara Brena. I had the main responsibility for designing the studies, performing the calculations and writing the manuscripts.

Additional publications, not included in the thesis:

- **Manipulation of Spin State of Iron Porphyrin by Chemisorption on Magnetic Substrates**
  Sumanta Bhandary, Barbara Brena, Pooja M. Panchmatia, **Iulia Emilia Brumboiu**, Matthias Bernien, Claudia Weis, Bernhard Krumme, Corrina Etz, Wolfgang Kuch, Heiko Wende, Olle Eriksson, and Biplab Sanyal

- **Investigating the Electronic Structure of Cobalt Phthalocyanine - addressing the ground state configuration and the atomic character of the HOMO**
  Teng Zhang, **Iulia Emilia Brumboiu**, Johann Lüder, Cesare Grazioli, Valeria Lanzilotto, M. Stupar, Monica de Simone, Marcello Coreno, Barbara Ressel, M. Pedio, Barbara Brena and Carla Puglia
  *in manuscript*
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Part I:
Introduction
1. Organic Materials and Spectroscopy

The development of science and technology during the last century has brought about solutions to many of humanity’s problems. Transportation and communication infrastructures make it possible to reach almost any part of the world and, on average, the life expectancy, quality of life and access to information have increased globally [1–3]. These recent developments have also lead to the emergence of new challenges such as overpopulation, lack of access to energy, pollution [4] or problems of information storage and management.

Population growth and the development of society, on the one hand, require ever increasing amounts of energy, while, on the other hand, industrial pollution and large emissions of greenhouse gases are not compatible with a sustainable future [4]. The development and implementation of clean energy sources, such as solar, are, therefore, crucial. Earth’s outer atmosphere receives an average energy of 340 J per m² every second as electromagnetic radiation from the Sun [5]. Approximately 48% arrives at the surface of the planet, while the rest is reflected [5]. By considering the illuminated area as half the surface of the Earth, the total power carried by this radiation corresponds to roughly 416000 TW, 20 000 times larger than the total power consumption of the entire human population, corresponding to 17.5 TW¹ [6, 7]. Most of the energy sources used on Earth today, except geothermal, nuclear and tidal, originate ultimately from the Sun [8], but a direct conversion of solar energy to electrical, as performed by photovoltaic devices (PVs), could satisfy humanity’s energy needs for generations to come having less environmental impact compared to current energy sources [9].

Another interesting aspect of today’s society is the immense increase in information production. According to the World Bank, in the year 2013 alone there have been approximately 2.2 million articles published in scientific and technical journals, corresponding to an average of 6000 per day [10]. In order for all this information to become knowledge, it must be stored, sorted and analysed such that the access to the valuable part (for technology, society or the individual) is facilitated. Computers are already omnipresent and make information storage and processing easy, but there is a strong need for further miniaturization and improvement of electronic devices.

For tackling the two challenges mentioned above, organic molecules either as single-molecule devices or organic molecular materials² [12] have been

¹The value of 17.5 TW is calculated by dividing the total energy consumed by all human activities in one year (in TJ) with the time interval, i.e. one year (in s).
²Organic molecular materials are composed of a large number of molecules, but the properties of the system as a whole originate at the molecular level [11].
proposed for possible technological applications such as organic photovoltaics (OPVs), molecular electronics or spintronics [13–16]. The advantages of organics over other types of materials include device flexibility, low cost, low environmental impact, high production efficiency and low energy payback times [15–18]. In addition, the electronic and magnetic properties of organic molecules can be combined to build from bottom-up ever more complex devices [15]. The bottom-up approach consists in assembling a device from fundamental building blocks by making use of the self-organization properties of organic molecules. The process entails better precision and overcomes the size limitations of top-down approaches such as conventional lithography [19].

Both in the case of single molecule devices and in the case of molecular materials, the properties of the single molecule are essential and a thorough understanding of the molecular electronic structure is a crucial step in explaining how properties emerge and can be controlled [20]. The interaction of electromagnetic radiation with the molecular system, or, conversely, the emission of radiation by the system, can provide the needed information if a good theoretical description of the spectroscopic process exists. The current thesis aims to describe, analyse and use different theoretical spectroscopy tools in order to investigate the properties of several molecules of interest in the fields of photovoltaics, electronics and spintronics. The spectroscopies analysed here are the photoelectron spectroscopy of the valence band (VB-PES), X-ray photoelectron spectroscopy (XPS) of the core levels, near-edge X-ray absorption fine structure (NEXAFS), Infrared (IR) and Raman vibrational spectroscopies. Part I is an introduction to spectroscopy, to organic solar cells and to the fields of molecular electronics and spintronics. Part II contains the details of density functional theory (DFT), which is the framework used throughout this thesis. Part III entails the analysis of each spectroscopy and the description of the theoretical tools used to calculate a particular spectrum with examples from different organic molecules, while Part IV contains final remarks and a future outlook.

1.1 Principles of Spectroscopy

Electromagnetic waves are oscillations of an electric and a magnetic field propagating perpendicular to each other with the speed of light [21]. The properties of a particular type of radiation and, subsequently, its interaction with matter depend on the wavelength. An electromagnetic wave is quantized and can be viewed as a stream of elementary energy packets called photons. Each photon carries an energy \( E \) proportional to the frequency \( \nu \) of the radiation, or inversely proportional to its wavelength \( \lambda \):

\[
E = h \nu = \frac{h \cdot c}{\lambda}
\] (1.1)
where $h$ is the Planck constant and $c$ represents the speed of light\textsuperscript{3}.

According to its energy or wavelength, electromagnetic radiation can be classified from $\gamma$ to radiowaves, as depicted in Figure 1.1 [22, 23]. When interacting with matter, light can only be absorbed or emitted in discrete quanta. In the particular case of molecules, the emission or absorption of a photon directly corresponds to a transition between two molecular energy levels. If the final state is lower in energy than the initial state, a photon carrying the energy difference is emitted\textsuperscript{4}. If the final state is, instead, higher in energy than the initial one, an incoming photon of energy matching the difference between these states is absorbed and leads to the excitation of the molecule. The conservation of energy can be written as [24]:

$$\Delta E = E_f - E_i = h\nu$$

where $\Delta E$ is the difference in energy between the final state $E_f$ and the initial state $E_i$, $h$ is the Planck constant and $\nu$ is the frequency of the absorbed or emitted photon.

In this way, measuring the characteristics (wavelength, energy or frequency) of absorbed or emitted radiation, or, conversely, of emitted electrons due to light absorption, can give information on the molecular energy levels. Spectroscopy employs precisely these interactions between radiation and matter and the resulting spectrum can be mapped to particular transitions in the studied system. The spectroscopies described in this thesis make use of electromagnetic radiation included in the region of the spectrum spreading from the low energy part of the X-rays (soft X-Rays), through the Ultraviolet (UV) and visible regions and down to the Infrared (IR). Photons of each of these types carry different energies (see equation 1.1 and Figure 1.1), and, consequently, accompany different kinds of transitions corresponding to energy differences which spread across several orders of magnitude.

### 1.2 Energy Levels in Molecules

In order to connect each spectroscopy to the information which it can provide, the energy levels of organic molecules must be analysed first. If no approximations were made, this problem would remain very complicated [25, 26], but, by assuming that the different possible motions of the molecular components (nuclei and electrons) are separable (Born-Oppenheimer approximation) it is possible to write the total energy of the system as a sum of the following components [22]:

$$E_{total} = E_e + E_{rot} + E_{vib}$$

\textsuperscript{3}The energy can also be written as $\hbar\omega$, where $\hbar$ is the reduced Planck constant, equal to $h/2\pi$, and $\omega$ is the wavenumber. This is, in fact, the expression used later on in the thesis.

\textsuperscript{4}The energy difference between the final and initial state can also be employed differently, as, for example, in the emission of an Auger electron.
Figure 1.1. The types of electromagnetic radiation with their wavelengths and energies on a logarithmic scale [23].

where $E_{\text{total}}$ is the total energy of the molecule, $E_e$ is the energy corresponding to the electrons and $E_{\text{rot}}$ and $E_{\text{vib}}$ are the rotational and, respectively, vibrational energies of the nuclei. The translational energy of the nuclei and the energies associated to the electron spin and nuclear states were left out for clarity. The energy corresponding to electronic transitions is much larger than the energy difference between vibrational levels which is, in turn, larger than the energy associated with transitions between rotational levels. This is illustrated in Figure 1.2 which shows a schematic representation of two electronic states of the H$_2$ molecule. The first potential energy curve (at lower energy) corresponds to the ground state (GS) configuration, where the two individual atoms would have their electron in the 1$s$ state if the molecule dissociated, i.e. H(1$s$)+H(1$s$) [27]. The curve has a minimum at the equilibrium position $R_{e\text{GS}}$ and the system remains bound for as long as the energy added does not exceed the dissociation energy. The second potential energy curve is an electronic excited state of the H$_2$ molecule corresponding to a H(1$s$)+H(2$p$) situation [27]. The excited state has a different equilibrium H-H distance, $R_{e\text{XS}}$, and a different dissociation energy. The difference in energy between the ground and excited states (10.2 eV) corresponds to an electronic 1$s$-2$p$ transition - the same order of magnitude as UV radiation (see Figure 1.1). In molecules containing other elements (like C, N, O or transition metals) the electronic core levels are pushed further down in energy. In the case of carbon, the energy required to promote a 1$s$ electron to the first unoccupied electronic level is of approximately 280 eV (depending on the system) and, in this case, soft X-ray photons can be employed to drive the transition [28].

Figure 1.2 shows also that each electronic many-body state has a vibrational and rotational fine structure. Assuming harmonic oscillations, the vibrational eigenvalues ($\varepsilon_v$) can be written as [25]:

$$\varepsilon_v = (\nu + \frac{1}{2})\hbar\omega$$  (1.4)
$E (\text{eV})$

Dissociation Energy

$H(1s) + H(1s)$

$H(1s) + H(2p)$

$ZPE$

$0$

$1$

$v=3$

$\text{vibrational energy levels}$

$\text{rotational energy levels}$

$10.2 \text{ eV (electronic trans.)}$

$R_{\text{H-H}} (\text{Å})$

$H(1s) + H(1s)$

$1s$

$2p$

$\text{ES}$

$\text{Dissociation Energy}$

$\text{GS}$

$0$

$1$

$v=3$

$1s$

$2p$

$\text{GS}$

$\text{ES}$

$0$

$1$

$v=3$

$\text{GS}$

$\text{ES}$

$\text{ReGS}$

$\text{ReXS}$

$\text{E (eV)}$

$\text{Dissociation Energy}$

$\text{H(1s) + H(2p)}$

$\text{10.2 eV (electronic trans.)}$

$\text{vibrational energy levels}$

$\text{rotational energy levels}$

$\text{Figure 1.2. Schematic representation of two molecular energy states of the H}_2\text{ molecule [25, 27].}$

where $v=0, 1, 2 \ldots$ is an integer, $\hbar$ is the reduced Planck constant and $\omega$ is the wavenumber corresponding to the vibrational frequency.

From the equation it follows that at $v=0$ the energy is equal to $1/2\hbar\omega$. This is the zero point energy denoted ZPE in the figure. Vibrational transitions are at least an order of magnitude lower in energy than electronic transitions. For example, stretching vibrations involving a H-X bond (where X is a heavier element) take place above 3000 cm$^{-1}$ (0.4 eV on the energy scale). Other types of vibrations and vibrations involving heavier elements entail energies lower than 0.4 eV. Transitions between vibrational levels are excited by IR photons$^5$.

Although out of the scope of this thesis, it is interesting to note that rotations are two orders of magnitude lower in energy and transitions between rotational levels are performed on gas molecules using low energy Infrared radiation (far IR) or microwaves [22, 27].

$^5$Or by visible light of a well-defined wavelength, as in Raman spectroscopy. The processes will be discussed in more detail in Part III.
2. Organic Photovoltaics

The sun is a reliable source of energy and the direct conversion of solar energy into electric energy to be used or stored (for example, chemically in batteries) is a viable solution to the current issues regarding energy and pollution in human society [29]. Solar cells make use of the photovoltaic effect, i.e. the production of a voltage as a result of the absorption of photons by a semiconductor [30], in order to transform solar energy (carried by electromagnetic radiation) into useful electrical energy [9]. There are many different types of solar cells which have been constantly developing with records reaching nowadays 46% efficiency in multijunction devices using GaInAs and GaInP [31], as can be seen in Figure 2.1. The most common type of solar cells are based on silicon and include bulk, crystalline or heterojunction devices [32].

Si has an optical band gap ($E_g$) of 1.11 eV, corresponding to 1117 nm in wavelength. Photons having an energy at least equal to $E_g$ are absorbed by the material, leading to the excitation of electrons from the valence band. After the light absorption process, the excited electrons are not free and, in the absence of a mechanism designed for charge separation, they would recombine with the valence holes. In Si solar cells, as well as in other semiconductor based PVs, charge separation is facilitated by a p-n junction obtained by doping one side of the cell with an n-dopant (intrinsically negative), while the other side is p-doped (intrinsically positive). This results in a built-in voltage in the depletion region, at the interface between the two sides of the cell, which overcomes the binding energy of the electron-hole pair and allows for the flow of electrical current through the device.

There is a limit to the maximum efficiency that can be reached by a single p-n junction photovoltaic device. Figure 2.2 represents the solar spectrum at the top of Earth’s atmosphere and, respectively, at sea level, after components of the atmosphere (ozone, oxygen, water and carbon dioxide) have absorbed specific wavelengths [9, 34, 35]. As can be seen from the figure, the solar irradiance at the top of the atmosphere is well described by the emission spectrum of a black body at a temperature of approximately 5777 K [35]. Assuming black body radiation from the sun and that all the photons with energy higher than the band gap are absorbed and produce the same effect as photons of energy strictly equal to $E_g$ [36, 37], a detailed balance of the incident and generated power density leads to an ultimate efficiency ($u_g$) of single p-n junction devices. The efficiency $u_g$ is shown as a function of the band gap in the inset.
Figure 2.1. Record cell efficiencies for several types of photovoltaics selected from reference [33]. This plot is courtesy of National Renewable Energy Laboratory, Golden, CO.

of Figure 2.2 and it has been calculated using the following equation [36]:

\[
u_g = x_g \frac{\int_{x_g}^{\infty} \frac{x^3}{e^x-1} \, dx}{\int_{0}^{\infty} \frac{x^2}{e^x-1} \, dx}
\]  \hspace{1cm} (2.1)

where the change of variable \( x = \frac{hv}{kT_s} \) has been performed, and \( x_g = \frac{E_g}{kT_s} \). The constants \( h \) and \( k \) are the Planck and, respectively, the Boltzmann constant, \( T_s \) is the temperature of the surface of sun (5777 K) and \( \nu \) is the frequency of the incoming photon.

As can be seen in the inset of Figure 2.2, the ultimate efficiency has a maximum of approximately 45% which is reached around a band gap of 1.1 eV, corresponding exactly to the optical band gap of Si. If the actual irradiance spectrum at sea level is considered and several recombination pathways\(^1\) are included, the limiting efficiency for crystalline silicon single-junction devices is determined slightly below 30% [37]. The high efficiencies listed in Figure 2.1 are obtained by combining concentrator optics\(^2\) with multijunction devices that make use of semiconductors with different band gaps such as to match the solar spectrum as close as possible and optimize light absorption [38].

Besides having an optimal band gap, the largest advantage of Si is the fact that it is the second most abundant element on Earth (after oxygen) [39]. On the other hand, it can rarely be found in its pure form, occurring usually in the form of silicates or silicon dioxide (SiO\(_2\)) [39]. These require high tempera-

\(^1\)Radiative and nonradiative (Auger or free carrier absorption [37]).
\(^2\)Optics used to increase the energy density by concentrating the incoming photons on a small area [38].
Figure 2.2. The emission spectrum of a black body with a temperature of 5777 K shown in comparison to the solar spectrum measured at the top of the atmosphere (in gray) and at sea level (in orange) [34, 35, 40]. The inset represents the variation of the ultimate efficiency as a function of band gap calculated using equation 2.1 [36].

There are other possible technologies for photovoltaics including gallium arsenide (GaAs) cells, thin film cells based on cadmium, indium, gallium and selenide (CIGS) or cadmium telluride (CdTe). In addition, novel devices are emerging such as dye-sensitized solar cells, quantum dot cells, perovskites and organic photovoltaics (OPVs) [33].

Among the emerging photovoltaic technologies, organics have recently become a viable alternative to silicon which is currently taking up to 90% of the photovoltaics market [32]. A great advantage of OPVs is that they can be manufactured by roll-to-roll printing which ensures a fast, large-scale and low-cost production [41, 42] with low environmental impact [17, 43, 44]. In addition, organic materials require low processing temperatures and allow for the fabrication of low-weight, flexible devices [43]. The record power conversion efficiencies (PCE) have reached more than 10% [33], but even 5% efficient devices have short energy payback times (EPBT)\(^3\) and, consequently, high energy return factors (ERF)\(^4\) [18, 44].

An OPV device consists of an active layer embedded between two electrodes [45, 46] (inset of Figure 2.3 a). The active layer is a mixture, usually

---

\(^3\)EPBT is defined as the time required for the solar cell to produce the energy invested for its fabrication [18].

\(^4\)ERF is the inverse of EPBT and it expresses how many times the device pays back the energy invested in it, during its lifetime [17].
bulk heterojunction (BHJ), of a light absorbing organic polymer, acting as an electron donor, and a fullerene derivative, the electron acceptor. The BHJ consists of well-separated and percolated domains of donor and acceptor materials, as shown in Figure 2.3 a. There are many possible polymers that can be employed as electron donors and one example is the poly(3-hexylthiophene) (P3HT) conjugated polymer (depicted in Figure 2.3 b). The class of electron acceptors is, instead, mostly limited to fullerenes and fullerene derivatives, among which the most widely used is the [6,6]-phenyl-C_{61}-butyric acid methyl ester (PC_{60}BM, represented in Figure 2.3 b) [29,45,47–49]. The polymer and fullerene are dissolved together in the same solvent and deposited by regular printing techniques (for example, roll-to-roll) between two electrodes: a transparent one, indium-tin oxide (ITO)\(^5\), and a regular one as, for example, silver (Ag)\(^6\). A layer of poly(3,4-ethylenedioxythiophene) poly-(styrenesulfonate) (PEDOT:PSS), which is a good hole conductor, is applied in between the ITO and the active layer, while a metal oxide, as, for instance, ZnO, is applied at the other electrode interface in order to facilitate electron transfer from the acceptor material to the cathode [29].

One of the most important parameters of a solar cell is its power conversion efficiency (\(\eta_e\)) [54, 55]:

\[
\eta_e = \frac{P_M}{P_{in}}
\]  

\(^{5}\)The indium component of ITO is a scarce resource and, recently, ITO-free devices have been built [50–52].

\(^{6}\)Metal current-collecting grids can be produced by printing techniques as well [51].
defined as the ratio between the maximum power produced by the device \( P_M = I_{MP} \cdot V_{MP} \)\(^7\) and the power corresponding to the incoming light \( P_{in} \).

Besides \( \eta_e \), there are three other important parameters of a solar cell, the open circuit voltage \( (V_{oc}) \), the short-circuit current \( (I_{sc}) \) and the fill factor \( (FF) \), which can be all determined from the current-voltage \( (IV) \) curve of a device. An example is depicted in Figure 2.3 a. The \( IV \) curve is constructed by connecting the solar cell to a variable resistance \( (R_{var}) \) and measuring the current \( (I) \) and voltage \( (V) \) for different \( R_{var} \) values. This can be done when the OPV is illuminated or under dark conditions, resulting in the two different curves represented in Figure 2.3 a. From the orange curve (device under illumination), \( I_{sc} \) and \( V_{oc} \) are found at the intersection of the curve with the two axes. The fill factor is defined as \([54, 55]\)

\[
FF = \frac{I_{MP} \cdot V_{MP}}{I_{sc} \cdot V_{sc}}
\]

where \( I_{MP} \) and \( V_{MP} \) are the current and, respectively, voltage, corresponding to the maximum power, \( P(I, V) = I \cdot V \). The fill factor can be basically calculated from the \( IV \) curve as the ratio between the areas of the two rectangles marked in Figure 2.3 a. One of the main directions of OPV research is to fabricate devices with higher efficiencies, higher \( V_{oc} \), \( I_{sc} \) and \( FF \).

The two fundamental processes for solar energy conversion, light absorption and charge separation, take place in the active layer of the cell. The most important electronic levels involved are the frontier orbitals of the organic donor and acceptor molecules. More specifically, these are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the materials\(^8\). When an incoming photon with energy higher or equal to the HOMO-LUMO gap encounters the conjugated polymer it is absorbed and, as a result, promotes an electron from the occupied electronic levels to unoccupied ones. This is the light absorption step in the energy conversion process, marked with (I) in Figure 2.3 b. The excited electron and the valence hole\(^9\) form a bound exciton with binding energy of typically 0.4-0.5 eV [45]. The role of the fullerene is to dissociate the exciton and create a free electron in the PC\(_{60}BM\) domain and a free hole in the polymer domain. The LUMO\(_a\) of PC\(_{60}BM\) is lower in energy than the LUMO\(_d\) and the energy difference between them is high enough as to overcome the exciton binding energy. This leads to charge separation, the second step of the light harvesting process, marked with (II) in Figure 2.3 b. In addition to its electron affinity, PC\(_{60}BM\) and other fullerene derivatives exhibit good electron transport properties [47]. Once the exciton is dissociated, the free charge can be then quickly trans-

\(^7\)\(I_{MP}\) and \(V_{MP}\) are simply the voltage and current at which maximum power is achieved.

\(^8\)The frontier orbitals of the conjugated polymer (donor) are denoted HOMO\(_d\) and LUMO\(_d\), while the corresponding orbitals of the fullerene (acceptor) are denote HOMO\(_a\) and LUMO\(_a\).

\(^9\)The positive charge localized in the valence electronic levels, created by the nucleus as a consequence of the absence of the electron, now excited.
ported through the PC_{60}BM domain to the cathode, with sweep-out times\(^{10}\) of less than 1 \(\mu\)s [47].

There are many loss mechanisms that can occur and reduce the overall efficiency of the OPV and any of its other three parameters \((V_{oc}, I_{sc}, \text{ and } FF)\). Firstly, there is a probability that the excited electron directly recombines with the valence hole, proportional to the excited state life-time and the distance from the donor-acceptor interface. If the polymer and PC_{60}BM domains are too large, excitons created too far from the interface remain bound and recombine [56]. Oppositely, too small domains hinder the transport of the free charges to the electrodes, resulting in charge accumulation [56]. In addition, back-donation and the recombination of the electron already on the acceptor with the donor valence hole is also possible. The presence of charge traps at the donor-acceptor interface greatly facilitates this process [47, 57]. Such traps can occur due to defects or chemical modifications of the fullerene and polymer which arise during the fabrication and functioning of the device. In fact, OPVs and their separate organic constituents have been shown to undergo degradation processes during operation [46, 54, 58–66].

In the specific case of PC_{60}BM, spectroscopic and mobility studies [60, 67, 68] show that the material sustains deterioration under exposure to air, water or oxygen, especially if illuminated at the same time. There are several proposed photodegradation mechanisms including chemical reactions with molecular oxygen, diffusion of impurities (such as water or oxygen) through the PC_{60}BM film or photodimerization [57, 60, 64], but the exact mechanism remains under debate. Photo-oxidation and the diffusion of O\(_2\) through the PC_{60}BM film creates trap states and recombination centres [57], reducing charge mobility and, consequently the \(I_{sc}\) of the OPV device. Elucidating the mechanism of photodegradation is, therefore, of high importance for the stability and functioning of organic solar cells. The combination of different spectroscopies could shed light on the deterioration processes, especially when combined with a theoretical description of the spectroscopic signals. This will be the topic of Part III where the DFT-calculated spectroscopies (NEXAFS, XPS, IR and Raman) of possible PC_{60}BM degradation products will be thoroughly discussed.

\(^{10}\)The sweep-out time is the time interval necessary for the photogenerated free charge carriers to leave the active layer and be collected in the external electric circuit [47].
3. Phthalocyanines and Molecular Spintronics

Molecular electronics and spintronics are newly emerging fields of research having as a main purpose the improvement of information storage and processing [20], as alternatives or supplements to existing complementary metal-oxide-semiconductor (CMOS) technologies [69]. They entail the use of organic molecules in general and organic molecules with unpaired spin in particular as the main active components of electronic and spin-based devices [70, 71] such as transistors, molecular switches, sensors [69, 70], spin storage and memory devices and, ultimately, quantum computers [72]. Molecular electronics and spintronics make use of the charge and, respectively, spin degrees of freedom of an individual molecule as a platform for logical operations [73]. A large variety of classes of organic molecules and organic molecular materials have potential applications in the two fields including conducting polymers, deoxyribonucleic acid (DNA), fullerenes and carbon nanotubes. In particular, porphyrins and phthalocyanines, highly symmetric organic molecules with a metallic center, constitute promising candidates for different molecular electronics and, especially, spintronics technologies [74–76].

The molecular structure of a transition metal phthalocyanine (TMPc) is represented in Figure 3.1. It consists of a symmetric ligand containing four isoindole rings1 connected together by an aza-nitrogen (N_{aza}) bridge and incorporating at the center a transition metal (TM). Transition metals which can be incorporated include (but are not limited to) the 3rd row metals such as manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni) or copper (Cu), having increasingly more electrons to occupy the metal 3d levels2. In the ground state of the single TM atom, the five d levels are degenerate. Once the atom is placed in the highly symmetric field of the organic ligand, which has D_{4h} symmetry in the case of the five transition metals mentioned above, the levels split as shown in the inset to Figure 3.1. The inset shows a schematic and simplified representation of the splitting of the d levels as predicted within group and ligand field theory [77–79]. The d_{x^2−y^2}, directed towards the isoindole nitrogen (N_{iso}) atoms, is predicted the highest in energy and last to be occupied [78,80]. In the D_{4h} point group it has b_{1g} symmetry. Three other d levels have lower eigenvalues and become occupied first. They are the d_\pi of a_{1g} symmetry, the d_\pi of e_g symmetry and the d_{xy} of b_{2g} symmetry. In the majority

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1The isoindole ring consists of a pyrrole (marked in yellow in Figure 3.1) and a phenyl component (marked in orange in the same figure).
2From 5 d electrons to 9, in the case of the enumerated transition metals.
Figure 3.1. Molecular structure of a transition metal phthalocyanine. The transition metal atom is in yellow, C atoms are gray, N blue and H white. The x- and y- axes are in the molecular plane, while the z-axis is perpendicular (and not shown). The pyrrole (marked in yellow) and the phenyl (marked in orange) molecular moieties form the isoindole ring. The orange arrow represents the total unpaired spin of the molecule. The inset shows the splitting of the $d$ levels when the metal is placed at the center of a $D_{4h}$ symmetric ligand.

of TMPcs, the $d_{xz}$ and $d_{yz}$ remain degenerate$^3$ and are denoted together as $d_{\pi}$.

The exact ordering and eigenvalues of the $d$ states largely depend on the particular transition metal atom and its interaction with the ligand. In general, in TMPcs, the $d$ level positions are such that some of the $d$ electrons remain unpaired and result in a non-zero molecular spin. For example, in the ground state MnPc has a spin of $3/2$, FePc has a total spin of 1, while CoPc and CuPc have a spin of $1/2$.$^4$ Due exactly to this unpaired spin, TMPcs are ideal for designing different molecular spintronics devices [73] which typically involve the adsorption of the molecules on metal surfaces or in between metal electrodes. In the following, two interesting examples will be discussed.

The first example is a MnPc-based memory device, depicted in Figure 3.2 and based on the experiments by Liu and co-workers described in reference [75]. It involves a MnPc molecule deposited on a gold surface, Au(111). In the ground state, the MnPc on Au(111) has a total spin of 3/2 and, at low enough temperatures (4.2 K, in the case of the measurements described in the reference), exhibits a Kondo resonance$^5$. This resonance appears as a peak centred at 0 bias voltage in the differential conductance curve measured by scanning

---

$^3$MnPc is one exception: due to a Jahn-Teller distortion the degeneracy of the $d_{xz}$ and $d_{yz}$ orbitals is lifted.

$^4$NiPc is, instead, a closed shell molecule, with all $d$ electrons paired and zero total spin.

$^5$The Kondo resonance occurs due to the interaction of the localized spin of the MnPc molecule with the many electrons of the non-magnetic metal surface.
Figure 3.2. Schematic representation of a spintronic memory device based on MnPc. The logic state 0 is achieved when the molecule has low spin, while 1 is represented by the high spin molecule. Writing is performed by adsorbing or desorbing a H atom to the central metal using an STM tip. Reading is performed using the Kondo signature of the high spin state. Based on reference [75].

The total spin of the MnPc can be manipulated by hydrogen adsorption to the central metal. MnPc-H on Au(111) has a total spin state of 1 and does not exhibit the Kondo resonance. If a voltage pulse is then applied using the STM tip, the H atom desorbs and the spin ground state is recovered. It is easy to imagine how this mechanisms could be used to design a storage device based on single molecule bits. One of the spin-states, the ground state, for instance, could be assigned to a logical 1, while the other state to a logical 0. Writing information to the molecular bit could then be performed using hydrogen adsorption or voltage pulses, while reading would involve the detection of the Kondo resonance peak [75]. In this way, information could be stored or processed by employing the spin degree of freedom of single MnPc molecules. One advantage of such a device is that it would further reduces the size of one bit from approximately 20 nm (the state-of-the art magnetic bits of today) [82] to several Å (i.e. by one order of magnitude). The main challenge, instead, is the fact that the Kondo resonance is detected only at very low temperatures and it is lost above a certain threshold called the Kondo temperature [83]. Another important challenge is the fact that the control over the spin state depends on the adsorption of H, in other words a chemical reaction. For molecular electronic devices, fast access times are critical and, unfortunately, incompatible with a chemical approach.

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STM involves measuring the tunnelling current between a conductive (atomic-sized) tip and a conductive surface, in this particular case Au(111). The current (I) is measured for different bias voltages (i.e. the voltage difference between the tip and the surface, V) and the differential conductance is obtained simply by taking the derivative of the IV curve [81].
to spin-switching [73]. The use of electromagnetic radiation or electric fields to reversibly control spin properties is, instead, very much compatible with the required fast access times [73] and possible device architectures involving phthalocyanines are already under investigation [84].

The second example involves precisely the electronic control, though not of the spin, but of the current passing through a molecular junction. A molecular junction is obtained by the deposition of an organic molecule in between two metal electrodes. Typically, the spin or charge current through the junction can only be controlled by magnetic fields or ferromagnetic electrodes [85–87]. However, Saygun and co-workers have recently proven theoretically that the electric control of the charge current is possible [85]. By using a spin dimer instead of a single molecule, it is possible to tune the exchange interaction between the molecular spins and the tunnelling current, making possible the integration of such junctions in regular electronic devices. The architecture of a coupled spin dimer built using two TMPcs is schematically represented in Figure 3.3 and consists of two TMPcs deposited together in between two metal leads. The control over the current and exchange interaction is exerted by the voltage bias ($V_{bias}$).

The dependence of the effective exchange parameter ($J_{12}$) and of the tunnelling current ($I$) on $V_{bias}$ are represented as insets to Figure 3.3. The graphs show that there are two regimes of device functioning: a region centred at 0 mV, where the spins are ferromagnetically coupled (i.e. the spins align parallel to each other) and two regions where the spins are antiferromagnetically coupled (i.e. anti-parallel spins). The current depends linearly on the bias voltage.

---

7CoPc could be a good candidate for such a device.

8The voltage bias represents the voltage difference between the two electrodes. It is defined by the difference between the chemical potential corresponding to each lead: $V_{bias} = \mu_1 - \mu_2$ [12, 85].
in the ferromagnetic regime and it can be greatly enhanced or reduced by con-
trolling the effective exchange interaction between the two molecular spins [85]. In addition, the study shows that the energy level alignment between the molecular HOMO levels and the conduction bands of the two electrodes has a relatively strong influence on the current-voltage profile. These results are immensely significant as they open the door for merging molecular spintronics with regular electronic devices.

In both of the applications described above, alongside the valence ligand orbitals, the \( d \) levels of the central metal play crucial roles. A good theoretical description of these levels and their interaction with the ligand states is essential. The difficulties of describing localized and strongly correlated \( d \) electrons and the possible approaches to do so within DFT have been studied in the present thesis and will be discussed in Part II, specifically referring to the case of TMPcs. Finally, Part III will touch upon the valence band electronic structure of several phthalocyanines by analysing two possibilities of calculating their corresponding photoelectron VB spectra.
Part II: Theory
4. Density Functional Theory

4.1 The Many-Body Problem

As mentioned in the introduction, the interaction of electromagnetic radiation with organic molecules promotes transitions between molecular energy levels, shedding light on the chemical bonding or the electronic and magnetic properties of the system. For interpreting measured spectroscopical signals, a good theoretical description of the light absorption and electronic transition\(^1\) process is essential. The theoretical representation of a spectroscopic process entails, in principle, two important steps. First, the molecular energy levels must be determined and, second, the intensities of relevant photon-mediated transitions between these energy levels must be calculated. The following chapters will treat the first step mentioned above, while Part III will focus on the second step for each specific spectroscopy. Both steps are treated within the framework of density functional theory (DFT).

Let’s consider an organic molecule with \(N\) nuclei and \(n\) electrons. The entire information about the molecular system and its time evolution is contained in the many-body wavefunction, \(\Psi\), which satisfies the time-dependent Schrödinger equation\(^2\):

\[
\hat{H}\Psi (\{R_I\}, \{r_i\}, t) = i\hbar \frac{\partial}{\partial t} \Psi (\{R_I\}, \{r_i\}, t) \tag{4.1}
\]

where \(\hat{H}\) is the Hamiltonian operator containing all interactions within the system, \(\{R_I\}\) are the space coordinates of the nuclei (a set of 3 for each nucleus), \(\{r_i\}\) the coordinates of the electrons (including the spin, a set of 4 for each electron) and \(t\) is the time variable.

In the majority of cases, including the systems investigated here, the time-dependence of the wavefunction can be reduced to a trivial phase factor \((e^{-iEt/\hbar})\) and the Schrödinger equation takes the time-independent form:

\[
\hat{H}\Psi (\{R_I\}, \{r_i\}) = E \Psi (\{R_I\}, \{r_i\}) \tag{4.2}
\]

where the Hamiltonian is written as\(^2\):

\[
\hat{H} = -\sum_{i=1}^{n} \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{I=1}^{N} \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{i \neq j}^{n,n} \frac{1}{4\pi\varepsilon_0} \frac{\epsilon^2}{|r_i - r_j|} + \frac{1}{2} \sum_{I \neq J}^{N,N} \frac{1}{4\pi\varepsilon_0} \frac{Z_I Z_J \epsilon^2}{|R_I - R_J|} - \sum_{I,i}^{N,n} \frac{1}{4\pi\varepsilon_0} \frac{Z_I \epsilon^2}{|R_I - r_i|} \tag{4.3}
\]

\(^1\)Or vibrational transition.
The first two terms in the Hamiltonian are the kinetic energy operators corresponding to the electrons and, respectively, to the nuclei. The third and fourth terms represent the electron and nuclear Coulomb repulsion, respectively \((Z)\) represents the atomic number), while the last term is the electron-nucleus Coulomb attraction. The reduced Planck constant is denoted \(\hbar\) \((\hbar = h/2\pi)\), \(\varepsilon_0\) is the vacuum permittivity, \(e\) represents the elementary charge (i.e. the magnitude of the charge carried by a single electron), \(m_e\) denotes the electron mass and \(M_I\) is the mass of nucleus \(I\).

In order to determine the molecular properties of interest, it is required to solve the Schrödinger equation and find the many-body wavefunction along with its energy eigenvalue(s). This task is far from straightforward and analytical solutions to the Schrödinger equation can be found only for very simple systems such as the hydrogen atom. Further approximations need to be made in order to simplify the problem. As a first step, it is reasonable to assume that the lighter electrons adiabatically adjust to the motion of the heavier nuclei\(^2\), allowing for the decoupling of the electronic and nuclear motions \([91]\):

\[
\Psi(\{R_I\}, \{r_i\}) = \psi(\{R_I\}) \cdot \psi(\{r_i\})
\]

This constitutes the Born-Oppenheimer approximation (BOA)\(^3\) and it reduces the initial problem to a purely electronic problem, where the nuclear coordinates enter only as parameters. The corresponding Hamiltonian and eigenvalue equation become:

\[
\hat{H}_e = -\sum_{i=1}^{n} \frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j}^{n,n} \frac{1}{4\pi \varepsilon_0} \cdot \frac{e^2}{|r_i - r_j|} - \sum_{I,i}^{N,N} \frac{1}{4\pi \varepsilon_0} \frac{Z_I e^2}{|R_I - r_i|}
\]

\[
\hat{H}_e \psi(\{r_i\}) = E_e \psi(\{r_i\})
\]

where \(E_e\) is the total energy of the electrons for a fixed nuclear configuration.

Within the BOA, the kinetic energy of the nuclei is neglected, while the nuclear repulsion contributes as constant to the total energy \([90, 92]\):

\[
E_{NN} = \frac{1}{2} \sum_{I \neq J}^{N,N} \frac{Z_I Z_J e^2}{4\pi \varepsilon_0 |R_I - R_J|}
\]

Before addressing the electronic problem in detail, which will be the topic of the following chapter, let’s assume that \(E_e\) and \(\psi(\{r_i\})\) are known. It is then possible to analyse the nuclear motion in the average potential created by the electrons, in which case, the Hamiltonian and eigenvalue problem for the

\(^2\)This assumption is generally valid, but it fails in some special cases, such as, for instance, phonon-mediated phenomena in metals \([89, 90]\).

\(^3\)For a detailed derivation of the Born-Oppenheimer approximation and a discussion on its validity see appendix A of reference \([90]\).
nuclei can be written as [92]:

\[ \hat{H}_n = -\sum_{l=1}^{N} \frac{\hbar^2}{2 M_l} \nabla^2_I + \langle \hat{H}_e \rangle (\{R_I\}) + \frac{1}{2} \sum_{I \neq J} \frac{1}{4 \pi \varepsilon_0} \frac{Z_I Z_J e^2}{|R_I - R_J|} + 1 \sum_{I=1}^{N} \frac{\hbar^2}{2 M_l} \nabla^2_I + \varepsilon (\{R_I\}) \] (4.8)

where \( \langle \hat{H}_e \rangle (\{R_I\}) \) represents the average Hamiltonian operator corresponding to the electrons, depending parametrically on the nuclear coordinates. The two terms in \( \hat{H}_n \) which depend on the coordinates of the nuclei can be grouped together in \( \varepsilon (\{R_I\}) \) which represents the potential energy surface of the molecular system\(^4\). Performing a geometry optimization entails attempting to locate the energy minimum on this surface, usually by considering the gradient of the function \( \varepsilon (\{R_I\}) \) and moving along the surface in a descent direction [93].

Coming back to the electronic Hamiltonian and the corresponding eigenvalue problem (equations 4.5 and 4.6), the task of finding the many-body wavefunction which describes the \( n \)-electron system remains far from trivial, even after having performed the Born-Oppenheimer approximation. The main difficulty is caused by the fact that electron motion is correlated. This is due to the electron-electron interaction term in the Hamiltonian, the last term in the following equation:

\[ \hat{H}_e = \sum_{i=1}^{n} \left( -\frac{\hbar^2}{2 m_e} \nabla^2_i - \sum_{l=1}^{N} \frac{1}{4 \pi \varepsilon_0} \frac{Z_l e^2}{|R_l - r_i|} \right) + \frac{1}{2} \sum_{i \neq j} \frac{1}{4 \pi \varepsilon_0} \frac{e^2}{|r_i - r_j|} \] (4.9)

For convenience, the kinetic one-electron operator is denoted \( \hat{t}_i \), the electron-nucleus interaction is written more generally as an interaction of the electron with an external potential (\( \hat{v}_{ext} \)) and the electron repulsion is denoted \( \hat{v}_{ee} \).

What correlation\(^5\) actually means is that the motion of electron \( i \) and, consequently, its interaction with the fixed nuclei, are affected by the \textit{instantaneous} repulsion from the remaining \( n-1 \) electrons of the molecular system [93]. Correspondingly, electron \( i \) plays its part in influencing the motion of the other electrons. This makes the \( n \)-electron problem extremely difficult to solve without additional approximations. One alternative is to completely neglect electron correlation and replace the many-body problem with \( n \) single-particle

\(^4\) An example for the H\(_2\) molecule is represented in Figure 1.2 from Part I.

\(^5\) Not to be confused with the correlation functional.
problems. In this approach, each electron is described by a one-electron wavefunctions (molecular orbital) and interacts only with an average potential created by the other electrons. The many-body wavefunction is written in terms of an initial guess for the orbitals and the ground state is found by iteratively improving this guess until self-consistency is achieved. By taking the many-body wavefunction to be a Slater determinant of single-electron functions, the antisymmetry property of fermions is fulfilled. This is the basic idea behind the Hartree-Fock (HF) method. Although it makes the problem manageable for molecules containing a small number of electrons, the HF method has two main shortcomings: it completely neglects electron correlation and it scales exponentially with $n$, making the study of large systems difficult.

Another alternative, which aims to provide a way around these two shortcomings, is to map the many-body problem onto an effective single-particle problem including correlation and, at the same time, replace the complicated $4n$-variable wavefunction with a simpler $3$-variable object, the electron density, $\rho$:

$$\rho(r) = n \int_{r_2} \cdots \int_{r_n} \psi^*(r, r_2, \ldots, r_n) \psi(r, r_2, \ldots, r_n) \, dr_2 \cdots dr_n \quad (4.10)$$

In order to be able to use $\rho$ at the place of $\psi$ in the electronic problem it is necessary to show that (1) the electron density provides the same information as the wavefunction and (2) there is a way to determine the ground state and related observables using $\rho$. The Hohenberg-Kohn theorems prove these principles and constitute the theoretical basis for density functional theory (DFT).

### 4.2 The Hohenberg-Kohn Theorems

The first Hohenberg-Kohn theorem (HK-I) states that there is a one-to-one correspondence between the electron density and the external potential $\hat{V}_{\text{ext}}$ and, consequently, the Hamiltonian, wavefunction and all other properties of the system are determined by the density:

**HK-I:** [... the potential $\hat{v}_{\text{ext}}(r)$ is determined uniquely, except for a constant, by the ground state particle density $\rho_0(r)$. Since the Hamiltonian is thus fully determined, except for a constant shift of the energy, it follows that the many-body wavefunctions for all states (ground and excited) are determined. Therefore all properties of the system are completely determined given only the ground state density $\rho_0(r)$](quoted from reference [88], p. 122).

---

6 The exchange interaction is included exactly.

7 Self-consistency is achieved when the energy difference between two consecutive iterations is lower than an a priori set threshold.

8 Where $V_{\text{ext}} = \sum_{i=1}^n \hat{v}_{\text{ext}}(r_i)$. In addition, $T = \sum_{i=1}^n \hat{t}_i$ and $V_{\text{ee}} = 1/2 \sum_{i \neq j}^n \hat{v}_{\text{ee}}(r_i, r_j)$. 

34
The second theorem (HK-II) represents the variational principle stated in terms of the electron density and it provides a strategy for finding the ground state:

**HK-II**: A universal functional for the energy $E[\rho]$ in terms of the density $\rho(r)$ can be defined, valid for any potential $\hat{v}_{\text{ext}}(r)$. For any particular $\hat{v}_{\text{ext}}(r)$, the exact ground state energy of the system is the global minimum value of this functional, and the density $\rho(r)$ that minimizes the functional is the ground state density $\rho_0(r)$ (quoted from reference [88], p. 122).

HK-I can be proven by using the *reductio ad absurdum* argument [88, 90]. Assume that the same ground state electron density $\rho_0(r)$ gives rise to two different ground states, with wavefunctions $\psi^{(1)}$ and $\psi^{(2)}$, coupled to two different Hamiltonians, $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$. The Hamiltonians differ only in the external potential:

\[
\hat{H}^{(1)} = \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}}^{(1)}
\]

\[
\hat{H}^{(2)} = \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}}^{(2)}
\]

and the wavefunctions follow the eigenvalue equations:

\[
\hat{H}^{(1)} \psi^{(1)} = E^{(1)} \psi^{(1)}
\]

\[
\hat{H}^{(2)} \psi^{(2)} = E^{(2)} \psi^{(2)}
\]

Here, $E^{(1)}$ and $E^{(2)}$ represent the ground state energies.

Using the eigenvalue equation 4.13 and the variational principle applied to ground state (1):

\[
\left\langle \psi^{(1)} \left| \hat{H}^{(1)} \right| \psi^{(1)} \right\rangle = E^{(1)} < \left\langle \psi^{(2)} \left| \hat{H}^{(1)} \right| \psi^{(2)} \right\rangle
\]

where the strict inequality holds for non-degenerate ground states\(^9\). The last term in inequality 4.15 can be expressed as:

\[
\left\langle \psi^{(2)} \left| \hat{H}^{(1)} \right| \psi^{(2)} \right\rangle = \left\langle \psi^{(2)} \left| \hat{H}^{(1)} - \hat{H}^{(2)} + \hat{H}^{(2)} \right| \psi^{(2)} \right\rangle = \left\langle \psi^{(2)} \left| \hat{H}^{(2)} \right| \psi^{(2)} \right\rangle + \left\langle \psi^{(2)} \left| \hat{H}^{(1)} - \hat{H}^{(2)} \right| \psi^{(2)} \right\rangle = E^{(2)} + \int r \left[ \hat{v}_{\text{ext}}^{(1)}(r) - \hat{v}_{\text{ext}}^{(2)}(r) \right] \rho_0(r) \, dr
\]

By combining equation 4.16 with inequality 4.15, it follows that:

\[
E^{(1)} < E^{(2)} + \int r \left[ \hat{v}_{\text{ext}}^{(1)}(r) - \hat{v}_{\text{ext}}^{(2)}(r) \right] \rho_0(r) \, dr
\]

\(^9\)HK-I has been proven for degenerate ground states as well. For the general argument, including degenerate ground states, see reference [91], p. 18.
Using the same procedure, a similar inequality is obtained for $E^{(2)}$:

$$E^{(2)} < E^{(1)} + \int [\hat{v}_{\text{ext}}^{(2)}(\mathbf{r}) - \hat{v}_{\text{ext}}^{(1)}(\mathbf{r})] \rho_0(\mathbf{r}) d\mathbf{r} \quad (4.18)$$

By summing the two inequalities (4.17 and 4.18), the integrals cancel out and the result is the contradiction $E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)}$. This shows that the initial assumption according to which the same density corresponded to two different ground states, with two different external potentials, was false. Thus, the ground state density uniquely (to within a constant) determines the external potential ($\hat{V}_{\text{ext}}$), the Hamiltonian and other properties of the system, having an equivalent information content as the wavefunction:

$$\psi(\{\mathbf{r}_i\}) \Leftrightarrow \rho(\mathbf{r}) \quad (4.19)$$

When it comes to HK-II, it immediately follows from HK-I combined with the variational principle. Assume a system described by Hamiltonian $\hat{H}$, with a ground state density $\rho_0(\mathbf{r})$ which uniquely corresponds to the ground state wavefunction $\psi_0$. Since the wavefunction and the electron density are equivalent from the information content point of view, the total energy can be written as a functional of the density, $E_0 = E_0[\rho_0(\mathbf{r})] = \langle \psi_0 | \hat{H} | \psi_0 \rangle$. A different density $\rho(\mathbf{r})$ necessarily (due to HK-I) corresponds to a different wavefunction $\psi$. Using the variational principle:

$$E_0[\rho_0(\mathbf{r})] \leq \langle \psi | \hat{H} | \psi \rangle = E[\rho] \quad (4.20)$$

where equality is achieved only when $\psi = \psi_0$, i.e. when $\rho = \rho_0$. The ground state density is therefore the density which minimizes the total energy.

### 4.3 The Kohn-Sham Approach

The two Hohenberg-Kohn theorems show that the electron density provides the same information as the wavefunction and they make available a way to computationally arrive to the ground state: by making use of the variational principle for the energy functional [91]. Explicitly, the energy functional for the $n$-electron system, excluding the constant nuclear repulsion, is [88, 90]:

$$E[\rho] = T[\rho] + E_{ee}[\rho] + E_{\text{ext}}[\rho] = F_{\text{HK}}[\rho] + E_{\text{ext}}[\rho] \quad (4.21)$$

where $T[\rho]$ is the kinetic energy of the electrons as a functional of the density, $E_{ee}[\rho]$ is the energy corresponding to the electron-electron interaction, while $E_{\text{ext}}[\rho] = \int \hat{v}_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$ is the interaction energy with the external potential created by the nuclei. The first two terms can be grouped together in the $F_{\text{HK}}[\rho]$ functional which is universal in the sense that it does not depend on
the external potential and it is the same for all electron systems [88, 93].

In order to find the ground state, a variational search could in principle be performed, if the form of the $F_{HK} [\rho]$ functional would be known. However, electron correlation, as discussed in Section 4.1, poses an important problem for finding the exact expression for the universal functional. In particular, the kinetic term ($T[\rho(r)]$) and the non-classical part ($E_{ncl}[\rho(r)]$) of the electron-electron interaction cannot be expressed explicitly in terms of the density, while the classical electrostatic electron repulsion energy (or Hartree energy) can be written as:

\[
E_{cl}[\rho(r)] = \frac{1}{2} \int_{r_1} \int_{r_2} \frac{\rho(r_1) \rho(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2 \quad (4.22)
\]

\[
F_{HK} [\rho(r)] = E_{cl}[\rho(r)] + E_{ncl}[\rho(r)] + T[\rho(r)] \quad (4.23)
\]

In order to be able to express the unknown terms in the energy functional, Kohn and Sham [96] proposed to replace the interacting electron system with an auxiliary system of non-interacting particles having the same density. Each independent particle is described by a single-electron Kohn-Sham (KS) orbital ($\chi_i$) and the difference between the interacting and non-interacting systems (i.e. everything unknown) is concealed in the exchange and correlation functional (denoted $E_{xc}$):

\[
E_{cl}[\rho(r)] + E_{ncl}[\rho(r)] + T[\rho(r)] = E_{cl}[\rho(r)] + T_s[\rho(r)] + E_{xc}[\rho(r)] \quad (4.24)
\]

Using the KS orbitals, the kinetic energy of the non-interacting system is expressed as:

\[
T_s[\rho(r)] = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \langle \chi_i(r) | \nabla^2 | \chi_i(r) \rangle \quad (4.25)
\]

while the electron density becomes a functional of the KS orbitals:

\[
\rho(r) = \sum_{i=1}^{n} | \chi_i(r) |^2 \quad (4.26)
\]

At this point, the only component of the energy functional which has not been explicitly expressed in terms of the electron density is the exchange and correlation. Approximations to calculate it will be the topic of the following section, but let’s assume for the moment that $E_{xc}[\rho(r)]$ is known. In this case, the energy functional can be written as\(^{10}\):

\[
E_{KS}[\rho(r)] = T_s[\rho(r)] + E_{cl}[\rho(r)] + E_{ext}[\rho(r)] + E_{xc}[\rho(r)] \quad (4.27)
\]

According to HK-II, the ground state density is the one which minimizes the energy. Since the energy can be written in terms of the KS orbitals, it is possible to derive variational equations in terms of $\chi_i$ by using the method of Lagrange multipliers with orthonormalization constraints for the orbitals\(^{11}\).

\(^{10}\) The notation $E_{KS}$ is introduced here only in order to keep track of the independent particle approximation performed by the use of the auxiliary non-interacting system.

\(^{11}\) The orthogonality and normalization condition is written as: $\langle \chi_i | \chi_j \rangle = \delta_{ij}$. 

37
We define the Lagrange functional, \( L \):
\[
L = E_{KS}[\rho(r)] - \sum_{i,j}^{n,n} \varepsilon_{ij} \left( \langle \chi_i | \chi_j \rangle - \delta_{ij} \right) \tag{4.28}
\]
where \( \varepsilon_{ij} \) are the Lagrange multipliers and \( \delta_{ij} \) is the Kronecker delta, resulting from the orthogonality and normalization of the KS orbitals.

The Lagrange function must be stationary with respect to orbital variation, i.e. \( \delta L = 0 \). In order to determine \( \delta L \), it is necessary to know the functional derivative of \( E_{KS} \) with respect to \( \chi_i \)\(^{12} \):
\[
\frac{\delta E_{KS}[\rho(r)]}{\delta \chi_i^*(r)} = \frac{\delta}{\delta \chi_i^*(r)} \left( T_s[\chi_i(r)] + E_{cl}[\rho(r)] + E_{ext}[\rho(r)] + E_{xc}[\rho(r)] \right) = \\
= \frac{\delta T_s[\chi_i(r)]}{\delta \chi_i^*(r)} + \left( \frac{\delta E_{cl}[\rho(r)]}{\delta \rho(r)} + \frac{\delta E_{ext}[\rho(r)]}{\delta \rho(r)} + \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)} \right) \delta \rho(r) = \\
= -\frac{\hbar^2 V_i^2}{2m_e} \chi_i(r) + \left( \frac{\delta E_{cl}[\rho(r)]}{\delta \rho(r)} + \frac{\delta E_{ext}[\rho(r)]}{\delta \rho(r)} + \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)} \right) \chi_i(r) = \\
= -\frac{\hbar^2 V_i^2}{2m_e} \chi_i(r) + \hat{\nabla}_{cl}(r) + \hat{\nabla}_{ext}(r) + \hat{\nabla}_{xc}(r) \chi_i(r) \tag{4.29}
\]
The total variation of the energy will be the sum over all \( \chi_i \) and \( \chi_i^* \):
\[
\delta E_{KS} = \sum_{i=1}^{n} \langle \delta \chi_i \left| \left[ -\frac{\hbar^2 V_i^2}{2m_e} + \hat{\nabla}_{cl}(r) + \hat{\nabla}_{ext}(r) + \hat{\nabla}_{xc}(r) \right] + \chi_i \right| \delta \chi_i \rangle + \\
+ \sum_{i=1}^{n} \langle \chi_i \left| \left[ -\frac{\hbar^2 V_i^2}{2m_e} + \hat{\nabla}_{cl}(r) + \hat{\nabla}_{ext}(r) + \hat{\nabla}_{xc}(r) \right] \delta \chi_i \rangle \tag{4.30}
\]
We denote the sum of operators in equation 4.30 as \( \hat{h}_{KS} \) and take the variation of the Lagrange function:
\[
\delta L = \sum_{i=1}^{n} \left( \langle \delta \chi_i | \hat{h}_{KS} | \chi_i \rangle + \langle \chi_i | \hat{h}_{KS} | \delta \chi_i \rangle \right) - \sum_{i,j}^{n,n} \varepsilon_{ij} \left( \langle \delta \chi_i | \chi_j \rangle + \langle \chi_j | \delta \chi_i \rangle \right) \tag{4.31}
\]
The KS equations are obtained by setting \( \delta L \) to zero and taking into consideration that \( \langle \chi_i | \delta \chi_j \rangle = \langle \delta \chi_i | \chi_j \rangle^* \) \cite{92}. In addition, the Lagrange multipliers are elements of a Hermitian matrix which can be diagonalized through a unitary transformation \( (\varepsilon_{i\neq j} = 0, \varepsilon_{ii} = \varepsilon_i) \) \cite{96, 97}:
\[
\hat{h}_{KS} \chi_i = \varepsilon_i \chi_i \tag{4.32}
\]
\(^{12}\)For performing the functional derivative, the complex conjugate \( \chi_i^* \) has been chosen for convenience, such that the differentiation of the kinetic term and of the electron density result in \( \chi_i \). The outcome is simply the complex conjugate if the differentiation is performed with respect to \( \chi_i \).
Figure 4.1. Schematic representation of the steps taken to arrive at the Kohn-Sham equations. (a) The full problem is replaced with the problem of \( n \) interacting electrons moving in the external potential created by the nuclei. (b) The problem of interacting electrons formulated in terms of the many-body wavefunction \( \psi \) is reformulated in terms of the electron density \( \rho \). (c) The interacting electron system is replaced by an auxiliary non-interacting system plus exchange and correlation.

If the exchange and correlation functional is known, a self-consistent field (SCF) procedure can be employed to solve the set of \( n \) eigenvalue equations and determine the orbitals which minimize the total energy.

Before discussing in more detail \( E_{xc}[\rho(\mathbf{r})] \) and the KS orbitals, let’s recapitulate all the steps taken to reach this point. Figure 4.1 illustrates these steps for the case of the benzene molecule. By separating the electronic and nuclear motions (Born-Oppenheimer approximation), the full problem is replaced by the simpler (but still unsolvable) one of \( n \) interacting charges moving in the external potential created by the fixed nuclei (Figure 4.1 a). The external potential represented in the figure is in atomic units (Hartree energy divided by elementary charge) and has been calculated for the molecular structure of benzene on a 6 \( \times \) 6 Å\(^2\) grid of 200 \( \times \) 200 points by using the equation:

\[
v_{\text{ext}}(\mathbf{r}) = \sum_{I=1}^{N} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}|}
\]

where \( N = 12 \) represents the number of nuclei in benzene, \( \mathbf{R}_I \) are the in-plane coordinates (x and y) of nucleus \( I \) with \( Z_I \) atomic number and \( \mathbf{r} \) represents the
position on the grid. The motion of the \( n \) electrons is, at this point, described by the many-body wavefunction, a mathematical object which varies with \( 4n \) variables (3 spatial and 1 spin coordinate for each electron). The Hohenberg-Kohn theorems allow the replacement of the wavefunction with the electron density \( \rho \) for describing the interacting electron system (Figure 4.1 b). The ground state density is a function of only the 3 spatial coordinates and it determines the external potential, the wavefunction and all other properties of the system.

Even when using the density, the interacting electron problem remains unsolvable. By replacing the real system with an auxiliary non-interacting one and including the unknowns in the exchange and correlation functional (Figure 4.1 c) the problem becomes manageable and can be computationally solved through a SCF approach. In order to be able to apply the SCF procedure, the KS orbitals must be defined and approximations are needed for the \( E_{xc} \) functional.

### 4.4 Functionals and Basis Sets

The exchange and correlation functional represents the difference between the fully interacting system and the non-interacting system introduced by Kohn and Sham [96]. It cannot be explicitly calculated except in very simple systems, such as the uniform electron gas (UEG). UEG is an infinite system of uniformly distributed (interacting) electrons of charge density \( \rho_0 \) neutralized by a uniform positive background of density \( \rho_+ \). The electron gas is homogeneous and therefore \( \rho_0 \) is a constant. Since the system is infinite, it only makes sense to discuss the exchange and correlation energy density, i.e. the energy per particle \( (\varepsilon_{xc}) \) [91]. It is useful to separate \( \varepsilon_{xc} \) into an exchange part \( (\varepsilon_x) \) and a correlation part \( (\varepsilon_c) \). The exchange energy density can be analytically computed, while the correlation, determined analytically for low and high density regimes, can be determined for the whole range by Monte-Carlo calculations combined with different interpolations schemes [88, 90, 91]. The expression for the exchange energy density of a UEG is [88]:

\[
\varepsilon_x = -\frac{3e^2}{4} \left( \frac{6}{\pi \rho_0} \right)^{1/3}
\]

(4.34)

The exchange and correlation \( (xc) \) energy densities in the uniform electron gas constitute the basis for approximating the functional \( E_{xc}[\rho(\mathbf{r})] \) in the case of real, generally inhomogeneous, systems.

---

13The external potential has been calculated using atomic units: \( e = 1 \) and \( 1/(4\pi\varepsilon_0) = 1 \).
14The electron density depicted in Figure 4.1 b and c in units of fundamental charge per unit volume \( (\tau) \) is for illustrative purposes only. It has been calculated using equation 4.26 and assuming Gaussian type orbitals for the s states of H and the \( p_x \) and \( p_y \) states of C.
4.4.1 Local Density Approximation

The simplest approach is to locally approximate the $xc$-energy of an inhomogeneous electron system of density $\rho(r)$ with the value calculated by using the UEG model with $\rho_0 = \rho(r)$ (denoted $\varepsilon_{xc}^{UEG}$) at each point $r$. This constitutes the local density approximation (LDA). Within LDA, the $xc$-functional is written as [91]:

$$E_{xc}^{LDA}[\rho(r)] = \int \varepsilon_{xc}^{UEG}(\rho) \cdot \rho(r) \, dr = \int \left[ \varepsilon_{xc}^{UEG}(\rho) + \varepsilon_{c}^{UEG}(\rho) \right] \cdot \rho(r) \, dr \quad (4.35)$$

where $\varepsilon_{xc}^{UEG}$ is replaced with the expression in equation 4.34 and $\varepsilon_{c}^{UEG}$ is replaced with the expression determined by interpolating between the low and high density regimes. The different interpolation schemes give rise to the different flavours of LDA [90], as, for example, the Vosko-Wilk-Nusair (VWN) [98], Perdew-Wang-92 (PW92) [99] or Perdew-Zunger (PZ81) [100] functionals.

LDA works best for systems which are similar to the UEG model, such as the valence electrons in simple metals [101]. However, it is less effective in highly inhomogeneous systems such as atoms or molecules, where the electron density has strong variations. In spite of this fact, LDA performs better than expected due to a cancellation of errors between the exchange and correlation parts [97].

4.4.2 Generalized Gradient Approximation

The next step, aiming to provide better performance for inhomogeneous systems, is to include the gradient of the local density ($\nabla \rho$) in the expression for exchange and correlation. This is the basic idea behind the generalized gradient approximation (GGA), where the $xc$-functional is determined as [88]:

$$E_{xc}^{GGA}[\rho(r)] = \int \varepsilon_{xc}(\rho, \nabla \rho) \cdot \rho(r) \, dr = \int \varepsilon_{xc}^{UEG}(\rho) \cdot F_{xc}(\rho, \nabla \rho) \cdot \rho(r) \, dr \quad (4.36)$$

where $\varepsilon_{xc}^{UEG}$ is the exchange energy density of a uniform electron gas of density equal to $\rho(r)$ and $F_{xc}$ is a dimensionless function of the density and its gradient. $F_{xc}$ can be further separated into an exchange ($F_x$) and a correlation part ($F_c$). There exist many possible forms for $F_x$, such as the one proposed by Perdew, Burke and Ernzerhof (PBE) [102, 103] or by Becke (B88) [104], while examples of $F_c$ include the correlation functional by Lee, Yang and Parr (LYP) [105, 106].
4.4.3 Basis Sets

Having found approximations for the \(xc\)-functional, it is now possible to solve the Kohn-Sham equations and find the single-particle wavefunctions \(\chi_i\) and their eigenvalues. The practical way of performing such calculations is to start with an initial guess for the \(\chi_i\) orbitals and construct the electron density using equation 4.26. Having the density, the potentials \(\hat{v}_{\text{ext}}(\mathbf{r})\), \(\hat{v}_{\text{cl}}(\mathbf{r})\) and \(\hat{v}_{\text{xc}}(\mathbf{r})\) are constructed and used in \(n\) eigenvalue problems as the one in equation 4.32. The set of \(n\) integro-differential equations\(^{15}\) is solved, resulting in a set of eigenvalues and eigenvectors. The eigenvectors constitute the new KS orbitals and are used to re-calculate the density, which, in turn, determines the new potentials and eigenvalue equations. The procedure is repeated until self-consistency is achieved.

The important question to ask at this point is: what mathematical form should be used for expressing the \(\chi_i\) functions? Since each \(\chi_i\) is a single-particle wavefunction describing a (KS-)electron in a molecule, in other words a molecular orbital (MO), it is very useful to treat each individual \(\chi_i\) as a linear combination of atomic orbitals (LCAO) \([101, 107]\). An atomic orbital (AO), which will be denoted as \(\Phi_\mu\), is expressed, in turn, as a linear combination of basis functions \((g_s)\):

\[
\chi_i = \sum_{\mu=1}^{N} c_{\mu i} \Phi_\mu = \sum_{\mu=1}^{N} \left( c_{\mu i} \sum_{s=1}^{NBF} d_{\mu s} g_s \right)
\]

Here, \(N\) represents the number of atomic orbitals and depends on the chemical species present in the molecule, while \(NBF\) is the number of basis functions. Finally, \(c_{\mu i}\) represents the contribution of atomic orbital \(\mu\) to molecular orbital \(\chi_i\). The unknowns of the KS problem are now the coefficients \(c_{\mu i}\).

By replacing the \(\chi_i\) in the KS equations with their expansion, the integro-differential problem becomes a compact matrix equation written in terms of the Kohn-Sham and overlap matrices \([101]\):

\[
\hat{h}_{\text{KS}} \chi_i(\mathbf{r}) = \varepsilon_i \chi_i(\mathbf{r}) \iff
\hat{h}_{\text{KS}} \left( \sum_{\mu=1}^{N} c_{\mu i} \Phi_\mu(\mathbf{r}) \right) = \varepsilon_i \sum_{\mu=1}^{N} c_{\mu i} \Phi_\mu(\mathbf{r})
\]

By multiplying equation 4.38 with \(\Phi_\nu\) and performing the integral over the entire volume:

\[
\sum_{\mu=1}^{N} c_{\mu i} \int_\mathbf{r} \Phi_\nu(\mathbf{r}) \hat{h}_{\text{KS}} \Phi_\mu(\mathbf{r}) \, d\mathbf{r} = \varepsilon_i \sum_{\mu=1}^{N} c_{\mu i} \int_\mathbf{r} \Phi_\nu(\mathbf{r}) \Phi_\mu(\mathbf{r}) \, d\mathbf{r}
\]

\(^{15}\)The kinetic term is a differential operator, while the potentials are integral operators.
The integrals in equation 4.39 can be viewed as matrix elements of the KS ($H_{\text{KS}}$) and overlap ($S$) matrices, where the matrix elements are defined as:

$$H_{\nu\mu}^{\text{KS}} = \int_r \Phi_{\nu}(r) \hat{h}_{\text{KS}} \Phi_{\mu}(r) \, dr$$  \hspace{1cm} (4.40)

$$S_{\nu\mu} = \int_r \Phi_{\nu}(r) \Phi_{\mu}(r) \, dr$$  \hspace{1cm} (4.41)

Introducing also a matrix for the coefficients $\epsilon_{\mu i}$ ($C$) and a diagonal matrix for the eigenvalues $\epsilon_i = \epsilon_{ii}$ ($\epsilon$), the KS equations are rewritten in the matrix form:

$$H_{\text{KS}} C = SC \epsilon$$  \hspace{1cm} (4.42)

which can be solved by numerical diagonalization procedures.

The integrals involved in the calculation of the KS and overlap matrix elements are determined by using the basis set expansion of the atomic orbitals. There are many possible types of mathematical functions that can be used as a basis set, including Gaussian type orbitals (GTOs) and plane-waves (PWs) which are the two types used for the calculations presented here. GTOs are widely used for molecular systems, while PWs are advantageous in bulk systems, where the unit cell is infinitely repeated using periodic boundary conditions.

A Gaussian type orbital is defined with respect to a nucleus of coordinates $(x_I, y_I, z_I)$:

$$g_{l_x, l_y, l_z} = \frac{N_l}{\pi^l} \frac{(x-\xi)^{l_x}(y-\eta)^{l_y}(z-z)^{l_z}}{e^{-\alpha[(x-\xi)^2+(y-\eta)^2+(z-z)^2]}}$$  \hspace{1cm} (4.43)

where $N_l$ is a normalization factor, $\alpha$ represents the orbital exponent, while $l = l_x + l_y + l_z$ defines the type of GTO: s, if $l = 0$, p if $l = 1$, d if $l = 2$ and so on.

Since the multiplication of two Gaussian functions is simply another Gaussian and integration can be easily performed analytically, GTOs are computationally very effective for finite systems [101]. In practice, an atomic orbital is not merely a GTO, but a linear combination of GTOs, called a contracted Gaussian function (CGF)\(^{16}\) (as anticipated by equation 4.37).

### 4.5 Problems of DFT

Throughout this chapter, we have seen how to map the many-body problem onto a system of $n$ effective single-particle equations where the relevant interactions are described in terms of the electron density. The corresponding matrix equation (4.42) can be iteratively solved and the procedure is computationally effective even for systems with a large number of atoms. However, the

\(^{16}\)The CGF has the advantage of better fitting the more physically meaningful Slater type orbitals, with correct cusp behaviour at $r \to 0$ and correct exponential decay at $r \to \infty$ [101].
approximations made along the way for the exchange and correlation functionals introduce errors which can become important for specific systems. Since both LDA and GGA are essentially based on the uniform electron gas model, they are not expected to work well for systems in which the density has significant spatial variations, such as atoms and molecules, especially if containing highly localized electrons (for example, d or f). The molecular structures optimized by LDA or GGA are similar, but LDA strongly delocalizes charges and overestimates binding energies. Charge delocalization is also an issue of GGA, but the binding energies are generally improved [91]. Intriguingly, LDA and GGA provide reasonable results in many cases where they are expected to fail. This is rather due to a cancellation of local errors, than to an intrinsic merit of the functionals [91]. In addition to these, it is important to discuss other three issues related to approximate $xc$-functionals based on the UEG model: the problem of self-interaction, the behaviour of the $xc$-potential at the asymptotic limit and the lack of discontinuity of the $\hat{v}_{xc}$ functional derivative.

The KS equations (4.32) are formally identical to the HF equations. The difference lies in the fact that, in HF, correlation is neglected completely, while the exchange interaction ($\hat{K}$) is fully included. For an electron in molecular orbital $\chi_i$, the HF equation reads [92]:

$$\left[-\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{I=1}^{N} \frac{1}{4\pi\varepsilon_0} \frac{Z_I e^2}{|R_I - r_i|} + \sum_{j=1}^{n} \left( \hat{f}_j(r_i) - \hat{K}_j(r_i) \right) \right] \chi_i(r_i) = \epsilon_i \chi_i(r_i)$$

(4.44)

where the $\hat{f}$ operator describes the classical electron repulsion and $\hat{K}$ is the exchange operator.

The equation allows for the Coulomb interaction of the electron with itself, but this spurious self-interaction is cancelled by the exchange term, since the diagonal matrix elements of the exchange operator are equal to the corresponding matrix elements of the Coulomb operator ($J_{ii} = K_{ii}$) [108]:

$$J_{ij} = \langle \chi_i(r_1) \chi_j(r_2) \rangle \frac{1}{|r_1 - r_2|} \chi_i(r_1) \chi_j(r_2)$$

(4.45)

$$K_{ij} = \langle \chi_i(r_1) \chi_j(r_2) \rangle \frac{1}{|r_1 - r_2|} \chi_j(r_1) \chi_i(r_2)$$

(4.46)

In the case of DFT, it is illustrative to take the example of a one-electron atom, such as hydrogen. The total energy of the electron should only be composed of the kinetic term and the electron-nuclear attraction. However, there is a non-zero interaction of the electron with itself, expressed in terms of the density according to equation 4.22. The exact $xc$-functional would completely cancel the erroneous self-interaction, but this is not the case with approximate functionals obtained from LDA or GGA [97, 109]. This problem is especially important in finite systems [91] and for systems with localized and strongly
correlated electrons [88].

In addition to the self-interaction error, approximations to the exchange and correlation based on the UEG model do not have the correct behaviour at long range (for \( r \to \infty \)). Since the classical potential \( \hat{v}_{el}(\mathbf{r}) \) behaves as \( 1/r \) in the asymptotic limit and because the \( xc \)-potentials should cancel the self-interaction error, \( \hat{v}_{xc}(\mathbf{r}) \) must have the same \( 1/r \) behaviour at \( r \to \infty \) [101]. However, in LDA, where \( \hat{v}_x \) is proportional to \( \rho^{1/3}(\mathbf{r}) \), the potential follows the decay of the electron density. For finite systems, like atoms or molecules, this decay is exponential:

\[
\lim_{r \to \infty} \rho(\mathbf{r}) \propto e^{-\alpha r} \Rightarrow \lim_{r \to \infty} \hat{v}^{\text{LDA}}_x(\mathbf{r}) \propto e^{-\alpha r/3}
\]  

(4.47)

where \( \alpha \) is a system-dependent constant. Although equation 4.47 refers to LDA, the error is present in GGA as well [110].

The direct proportionality of the exchange potential to the density leads to the erroneous behaviour of \( \hat{v}_{xc} \) in the asymptotic limit [91]. Besides this, in most approximations to exchange and correlation the functional derivative of the potential is a continuous function of the number of electrons and does not exhibit the so-called derivative discontinuity. The derivative discontinuity is related to the extension of DFT to non-integer particle numbers. By starting from expression 4.21, it is possible to construct a variational equation with respect to \( \rho \), where the constrain is that the density should integrate to the total number of particles [91, 97]:

\[
\frac{\delta E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} - \mu_L = 0
\]  

(4.48)

Here, the Lagrange multiplier \( \mu_L \) represents the chemical potential \( \mu \) when the particle number is an integer [91]. Equation 4.48 is, however, valid even for densities which integrate to non-integer particle numbers:

\[
\int_r \rho(\mathbf{r}) \, d\mathbf{r} = n + \eta, \quad \text{with} \quad n \in \mathbb{N} \quad \text{and} \quad 0 \leq \eta < 1
\]  

(4.49)

In this case, the energy minimum is obtained for densities which are linear combinations of the ground state density for the \( n \)-particle system and the density for the \( (n+1) \)-particle system and the total energy is a superposition [91]:

\[
E(n + \eta) = (1 - \eta) \cdot E(n) + \eta \cdot E(n + 1)
\]  

(4.50)

---

17The exchange part of the \( xc \)-potential is generally larger than the correlation [91] which, in addition, is short ranged [101]. To illustrate the asymptotic problem, we, therefore, only analyse the behaviour of \( \hat{v}_x \).

18In the case of the exchange functional by Becke [104], the potential decays as \( 1/r^2 \). The insufficient binding characteristic to exponentially decaying \( xc \)-potentials is present in this functional as well [110].

19For this reason, in finite systems, the Rydberg states are incorrectly described by LDA [91].
In other words, the total energy linearly depends on the particle number if we are restricted to two neighbouring integers, \( n \) and \( n + 1 \). The slope is given by \( \mu = \partial E(n) / \partial n \). Since it can be shown that [91]:

\[
\begin{align*}
\mu(n + \eta) &= E(n) - E(n - 1) = -IE \\
\mu(n - \eta) &= E(n + 1) - E(n) = -EA
\end{align*}
\]  

(4.51) (4.52)

it follows that \( \mu(n) \) is discontinuous at integer particle numbers and, consequently, the functional derivative of the total energy must be discontinuous as well. In equations 4.51 and 4.52, \( n \) is the number of electrons for which charge neutrality is ensured, \( IE \) represents the ionization energy of the highest occupied molecular orbital (HOMO) and \( EA \) is the electron affinity of the lowest unoccupied molecular orbital (LUMO).

Let’s consider now the energy functional in the KS picture (equation 4.27), which, in view of the conclusion from the previous paragraph has a discontinuous functional derivative with respect to integer particle numbers. The functional derivative of the classical electron repulsion does not have discontinuities. It must be therefore the kinetic and \( xc \)-terms which contribute, instead. Within LDA and GGA, the derivative of \( E_{xc}[\rho(r)] \) varies continuously with the particle number and the discontinuity of \( \mu(n) \) results only from the non-interacting kinetic term [97]. Since \( \mu(n) \) is directly related to \( IE \) and \( EA \) (equations 4.51 and 4.52), it follows that the band (HOMO-LUMO) gap obtained using approximate \( xc \)-functionals which lack derivative discontinuity originates only in the kinetic term of the auxiliary non-interacting electron system and is, therefore, erroneous. The missing \( xc \)-contribution is one of the reasons why gaps are underestimated by UEG-based DFT functionals [97].

Both the self-interaction error and the lack of derivative discontinuity can be traced back to the behaviour of the approximate \( xc \)-potential which is the "heel of Achilles" for KS-DFT. This is, of course, expected, since all the unknowns that differentiate between a simple non-interacting electron system and the fully interacting one are hidden in the \( E_{xc} \) term. Different alternatives for improving the performance of \( xc \)-functionals by partly mitigating (some of) these deficiencies have been proposed and include orbital-dependent self-interaction corrections [100], DFT+U [111–113] or hybrid functionals [114, 115]. The following chapter will discuss the electronic structure of TMPcs in connection with two of the possibilities for improving GGA results: the DFT+U approach and the optimal tuning of range-separated hybrid (OT-RSH) functionals.
5. DFT for Organic Molecules with Metallic Centres

We have already met the transition metal phthalocyanines in Chapter 3. They are very interesting for applications in molecular electronics and spintronics, where a TMPc is deposited on a metal surface or in between metal electrodes. In such applications, the electronic structure of the individual molecule plays an important role. What is meant by electronic structure in the context of KS-DFT is the set of eigenvalues, both of occupied and unoccupied states, determined by solving the KS equations. These eigenvalues, i.e. the energies of the one-electron KS orbitals, do not have a precise physical meaning \[116\] in the sense that they do not represent, with the exception of the HOMO eigenvalue, electron removal or addition energies \[88\]. However, according to the Janack theorem \[117\], they have a well defined mathematical meaning \[88\], implying that the derivative of the total energy with respect to the occupation of state \(\chi_i\) is exactly the KS eigenvalue:

\[
\varepsilon_i = \frac{\partial E[\rho(r)]}{\partial \theta_i}
\]  

(5.1)

where \(\theta_i\) represents the occupation of state \(\chi_i\). In addition, the analysis of simple systems, such as the uniform electron gas or free atoms, shows that the KS eigenvalues determined by exact DFT\[1\] correspond rather well to the energies calculated with more accurate methods\[2\]. This is in particular true for occupied orbitals and for unoccupied states not far from the gap \[116\]. For model systems, where exact solutions are possible, the comparison between LDA, exact DFT and the analytical solution shows that the poor performance of LDA eigenvalues is due to the approximation of \(\hat{v}_{xc}\) rather than to intrinsic problems of KS-DFT \[116\]. This result validates, at least to some extent, the common practice of using DFT-calculated eigenvalues as excitation energies and comparing the ground state electronic structure to phototelectron spectroscopy measurements. It also opens up the possibility to improve theory-experiment agreement by developing better approximations to the \(xc\)-potential

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1The term exact refers to the exchange and correlation functional within the Kohn-Sham formalism. For model systems, such as the uniform electron gas, exchange and correlation can be determined with very high accuracy. In addition, for small molecules, very accurate \(xc\)-potentials can be reconstructed from the charge density calculated by configuration interaction (CI) \[110,118\].

2By many-body perturbation theory or analytically, depending on the system.
and trying to address the issues of self-interaction, incorrect asymptotic behaviour or lack of derivative discontinuity already discussed.

In the light of the final section from the previous chapter ("Problems of DFT"), TMPcs pose a double challenge for approximate xc-functionals: they are, on the one hand, large but finite systems, not entirely suitable to be described using LDA or GGA functionals and, on the other hand, they contain transition metals. TMs are in particular problematic due to the 3d electrons which tend to be highly localized and correlated, in other words, completely outside the area of validity of UEG-based approximations.

Let’s, for the moment, give GGA the benefit of the doubt and analyse the computed electronic structures of two phthalocyanines in comparison to experimental photoelectron spectroscopy (PES) data. PES is measured by using incident electromagnetic radiation (UV or soft X-Rays) of energy high enough to ionize valence electrons. By recording the kinetic energies of the emitted photoelectrons it is possible to determine, from energy conservation, the binding energies of these electrons in the molecule. The PES spectrum represents therefore an image of the valence band electronic structure of the system. PES will be discussed in detail in Part III of this thesis, but one important note is that different atomic orbitals in different elements have unique photoionization cross-sections [119, 120]. This means that by using different photon energies for the incident radiation it is possible to disentangle, for example, metallic states from ligand ones3, giving a very important experimental insight into the electronic structure of organic molecules with metal centres.

Figure 5.1 shows the calculated ground state electronic structure of metal-free phthalocyanine (H2Pc) and MnPc calculated using the Perdew-Burke-Ernzerhof functional for exchange and correlation [102,103]4. From the figure it becomes clear that the eigenvalue determined using PBE does not match the experimentally measured ionization energy of the HOMO. This happens for metal-free as well as for manganese phthalocyanine, as the binding energy (BE) of the HOMO is underestimated by approximately 1.7 eV in both. After performing a rigid shift, the experimentally measured features can be more or less assigned to calculated bands, but the calculated spectrum appears contracted. This is, in fact, a general feature of GGA-calculated spectra and it has been observed in other phthalocyanines [127–130], other organic molecules [131, 132] and by using other GGA functionals besides PBE [132]. In addition, there is one important thing to note about the MnPc in Figure 5.1 b. By comparing the VB-PES measurement at low photon energy (21.2 eV) with the measurement performed at high photon energy (1486.7 eV), it is possible to

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3The states with metal contribution are more likely to be excited by higher energy photons (40 eV and above), while the probability to excite ligand 2p states is higher at low photon energies (for example, 21.2 eV) [121–123].

4The calculations have been performed with Gaussian 09 D.01 [124], using the 6-31G(d,p) basis set [125] for the H, C and N atoms and the cc-pVTZ basis set [126] for Mn.
find the peaks to which the metal $d$ states contribute. The experimental data\(^5\) reveals that the HOMO peak, alongside the peaks in the region between 7-12 eV binding energy, have contributions from 3$d$ metal orbitals. The calculations, on the other hand, predict metal $d$ levels in a much narrower energy window (7-9 eV BE). In order to be able to rely on DFT results for organic molecules with metal centres it is, therefore, important to go beyond GGA and try to improve the description of both the ligand states and metal $d$ levels. We will first focus on the $d$ levels alone by discussing the DFT+U method, while the question about the ligand states will be addressed in the context of optimally tuned range-separated hybrid (OT-RSH) functionals.

### 5.1 Strongly Correlated Electrons by DFT+U

As we have seen, localized and strongly correlated electrons ($d$-orbitals, in the case of TMPcs) pose a challenge for DFT at the LDA or GGA level of theory. The erroneous description of such electrons is inherent to UEG-based approximations and, in particular, the self-interaction error can lead to a strong charge delocalization \([111]\). A system where the underestimation of electron

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\(^5\)The two spectra were normalized at 12.5 eV BE.
localization is especially obvious is a Mott insulator, for which LDA and GGA yield a metallic ground state, instead of the correct insulating one [111]. On the other hand, a simple Hubbard model manages to represent the physics of a Mott system exceptionally well [109, 111]:

\[
\hat{H}_{\text{Hub}} = t \sum_{i,j,\sigma} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}
\] (5.2)

This single-orbital Hubbard Hamiltonian, \( \hat{H}_{\text{Hub}} \) describes a set of localized electrons moving on a lattice of sites denoted by the letters \( i \) and \( j \). The electrons with spin \( \sigma \) are treated within the tight binding formalism and can hop between sites with the hopping rate \( t \). \( U \) is the on-site Coulomb repulsion. The Hamiltonian is written using second quantization notation where \( \hat{c}^\dagger, \hat{c} \) and \( \hat{n} \) are the electron creation, annihilation and number operators, respectively.

The success of the Hubbard model in capturing the physics of Mott insulators, as well as other challenging systems such as rare-earth compounds [109], has lead to the idea of integrating the Hubbard Hamiltonian in the DFT formalism to selectively correct the description of the correlated electrons, while the other states are treated using regular LDA or GGA [112, 113, 134]. Within the new approach, denoted as DFT+U, the energy can be written as a functional of both the density and the on-site occupation number \( \{ \theta_{\sigma mm'} \}_m \) [111]:

\[
E_{\text{DFT}+U} [\rho(r), \{ \theta_{\sigma mm'} \}] = E_{\text{KS}} [\rho(r)] + E_{\text{Hub}} [\{ \theta_{\sigma mm'} \}] - E_{\text{dc}} [\{ \theta_{\sigma mm'} \}] (5.3)
\]

where \( E_{\text{KS}} \) is the DFT energy functional, \( E_{\text{Hub}} \) is the Hubbard energy correction defined for the localized states and \( E_{\text{dc}} \) is a double-counting term removing the contribution of the \( d \) electrons already included in \( E_{\text{KS}} \). The occupation numbers, \( \theta_{\sigma mm'} \), are obtained by projecting the KS orbitals onto a localized basis set \( \Phi_m \):

\[
\theta_{\sigma mm'} = \sum_{i=1}^{n} \langle \chi_i | \Phi_m \rangle \langle \Phi_{m'} | \chi_i \rangle
\] (5.4)

The Hubbard energy correction can then be obtained, in the spirit of the HF approach, as [112]:

\[
E_{\text{Hub}} [\{ \theta_{\sigma mm'} \}] = \frac{1}{2} \sum_m \left[ \langle \Phi_m | \hat{\nu}_{ee} | \Phi_m \rangle \theta_{\sigma mm'}^\sigma \theta_{m'm'}^{-\sigma} + \right.
\]

\[
\left. + \left( \langle \Phi_m | \hat{\nu}_{ee} | \Phi_{m'} \rangle - \langle \Phi_{m'} | \hat{\nu}_{ee} | \Phi_m \rangle \right) \theta_{\sigma mm'}^\sigma \theta_{m'm'}^{-\sigma} \right]
\]

(5.5)

where \( \hat{\nu}_{ee} \) is the electron-electron operator from equation 4.9 and the sum is performed on all the possible combinations of localized states \( \Phi_m \).

\( \sigma \) designates the magnetic quantum number and \( \sigma \) the spin (\( \alpha \) or \( \beta \)). For simplicity, we are considering here only 3\( d \) orbitals and only one metal site. The individual atomic \( d \) orbitals differ only in the magnetic quantum number and spin and, therefore, the two numbers are used to designate a particular state.
The matrix elements from equation 5.5 can be obtained from the Slater integrals [111, 112]. In practice, however, these integrals are not calculated, but represented in terms of the effective Coulomb ($U$) and Hund exchange ($J$) interactions which enter the computational problem as parameters [111]:

$$\frac{1}{(2l+1)^2} \sum_{\Phi_m, \Phi_{m'}} \langle \Phi_m \Phi_{m'} | \hat{v}_{ee} | \Phi_m \Phi_{m'} \rangle = U$$ (5.6)

$$\frac{1}{2l(2l+1)} \sum_{m \neq m', m'} \langle \Phi_m \Phi_{m'} | \hat{v}_{ee} | \Phi_{m'} \Phi_m \rangle = J$$ (5.7)

where $l$ is the orbital quantum number.

Since estimating the correlation (of the $d$ electrons) already included in the DFT functional is not an entirely simple task, there are several ways of defining the double counting term, $E_{dc}$. The most widely used approaches include the approximation derived in the fully localized limit or the one derived around mean field. Within the fully localized limit, $E_{dc}$ is expressed as [135]:

$$E_{dc} = \frac{U}{2} \theta(\theta - 1) - \frac{J}{2} \sum_{\sigma} \theta^\sigma (\theta^\sigma - 1)$$ (5.8)

where $\theta^\sigma = \sum_m \theta^\sigma_{mm}$ represents the trace of the occupation matrix for the localized states with spin $\sigma$, while $\theta$ is simply the total trace for both spins. This represents the rotationally-invariant and fully orbital dependent formulation of DFT+U, as proposed by Lichtenstein and co-workers [112]. There exists a simpler approach, proposed by Dudarev et al. [113, 134], where the orbital-dependent electronic interactions are replaced by a spherical average, allowing the use of an effective $U$ value which combines the Hund exchange parameter with the Hubbard Coulomb parameter [111, 113]:

$$U_{\text{eff}} = U - J$$ (5.9)

resulting in the following expression for the energy functional [111, 135]:

$$E_{\text{DFT+U}}[\rho(\mathbf{r}), \{\theta^\sigma_{mm}\}] = E_{\text{KS}}[\rho(\mathbf{r})] + \frac{U_{\text{eff}}}{2} \sum_{\sigma} \theta^\sigma (\theta^\sigma - 1)$$ (5.10)

Similarly to the Lichtenstein approach, $U_{\text{eff}}$ enters as a parameter in the practical implementation of the Dudarev method. Since $U_{\text{eff}}$ is a parameter, one important question to ask is which value should be used. What is the effect of $U_{\text{eff}}$ on the electronic and magnetic properties of a particular class of materials? How does it influence the electronic structure and how do the DFT+U calculations compare to experimental VB-PES measurements? By construction, we can already guess that $U_{\text{eff}}$ will have little influence on the ligand states, but which is its influence on the metal $d$ levels? In order to answer some of these questions, Figure 5.2 a shows the calculated HOMO-LUMO
gaps determined using PBE+U for five TMPcs: MnPc, FePc, CoPc, NiPc and CuPc. $U_{\text{eff}}$ takes values between 0 and 5 eV. The methods used for this calculation and all the results are described in detail in Paper V [136].

From Figure 5.2 it becomes evident that the HOMO-LUMO gap of each different TMPc is differently affected by the change in $U_{\text{eff}}$. In the case of MnPc, the gap starts off (at $U_{\text{eff}} = 0$ eV) as very small (we have already seen this in Figure 5.1) and it becomes only slightly larger with the increase in $U_{\text{eff}}$. Similarly, the gap of NiPc appears largely unaffected by the Hubbard parameter, while the gap of CuPc undergoes a moderate increase. It is only FePc and CoPc which sustain more important changes. In both cases, the gap is largely underestimated at the start ($U = 0$), undergoing an increase with $U_{\text{eff}}$ to flatten out at around $U_{\text{eff}} = 3$ eV. In order to understand these changes of the gaps, it is very useful to analyse the calculated electronic structure and see how the levels shift as $U_{\text{eff}}$ is increased. Figure 5.2 b-g is an example, where the individual $d$ states of CoPc are represented in comparison to the total calculated density of states (DOS) for each different value of $U_{\text{eff}}$. In CoPc, the seven $d$ electrons are distributed such that the $d_{x^2-y^2}$ level remains

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7One important note is that these calculations have been performed for the single molecule in the Vienna *ab initio* simulation package (VASP) [137–140] using a plane-wave basis set in combination to projector augmented-wave (PAW) potentials [141, 142].
The positions of the $d$ orbitals of CoPc separated in in-plane ($d_{xy}$ and $d_{x^2-y^2}$) and out-of-plane ($d_{z^2}$ and $d_{\pi}$), calculated using $U_{\text{eff}}$ (a) 4 eV and (b) 6 eV represented in comparison to VB-PES measurements performed on CoPc thin films at 27 eV and 125 eV photon energies from reference [143]. The calculated 3$d$ bands have been shifted such that the HOMO (not shown) is centred at 0. The measured spectra have been shifted such that the first peak matches the calculated HOMO. The orange dotted lines mark the positions of the experimental $d$ bands. The calculated results are adapted from Paper V [136].

completely empty, while the $d_{z^2}$ is singly occupied. As $U_{\text{eff}}$ is increased, both the occupied and unoccupied $d$ levels move away from the gap, but the orbitals are differently affected: some shift more, others less, some grow in intensity, while some become fainter. In CoPc, the empty spin down $d_{z^2}$ state shifts the most, while the two $d_{x^2-y^2}$ are the least affected. The ligand states remain, as we could already guess, largely unaffected by $U_{\text{eff}}$. The behaviours of the different electronic states explain the changes observed in the HOMO-LUMO gaps. For CoPc, the HOMO orbital originates exclusively in the ligand according to all DFT+U calculations from Figure 5.2 b-g. On the other hand, the LUMO has $d_{z^2}$ character at low values of $U_{\text{eff}}$. As the Hubbard parameter is increased, the $d_{z^2}$ shifts away from the gap, surpassing (when $U_{\text{eff}} = 3$ eV) the ligand orbital located 1.5 eV above the HOMO. This ligand orbital becomes the new LUMO and, since it is largely unaffected by the Hubbard $U$, the gap stops changing, as we have seen in Figure 5.2 a. A similar analysis can explain the trends observed in the other TMPcs.

We have just caught a glimpse of how $U_{\text{eff}}$ can influence some of the electronic properties of a TMPc. The main idea of the DFT+U approach is to improve the description of a sub-set of orbitals which pose difficulties for the regular LDA and GGA, without modifying the way the other states are treated. Even though the method does not mitigate all problems, it is especially use-
ful for maintaining a reasonable accuracy to cost ratio for large systems, such as TMPcs deposited on different surfaces. The question to ask at this point is which of the $U_{\text{eff}}$ values from Figure 5.2 should be used in calculations. This is quite a tricky question, especially when it comes to molecules on surfaces, but we can start by analysing how each single-molecule $U_{\text{eff}}$ compares to VB-PES experiments where the position of the $d$ levels can be uncovered. The comparison for CoPc using $U_{\text{eff}} = 4 \, \text{eV}$ and $U_{\text{eff}} = 6 \, \text{eV}$ is depicted in Figure 5.3. Values of $U_{\text{eff}}$ lower than 4 eV result in Co $d$ states which are too close to the gap and do not reproduce the positions of the experimental $d$ bands. Higher values shift the occupied $d$ levels towards much too high binding energies, also failing to reproduce the experimental results.

An alternative is to calculate the system-dependent $U$ value in some way. The Hubbard $U$ can be defined as the second derivative of the energy with respect to on-site occupation numbers [144]:

$$U = \frac{\partial^2 E_{\text{KS}}[\rho(\mathbf{r})]}{\partial (\theta_d)^2} \bigg|_{\theta_d = \theta_d^{\text{KS}}} \quad (5.11)$$

where $\theta_d$ denotes the occupation of a particular $d$ state.

In this sense, $U$ represents the curvature of the energy with respect to the number of electrons [145]. Thinking back to the section Problems of DFT, we know that the true energy functional should have discontinuities at integer particle numbers and should linearly depend on $\theta$ otherwise. This is not the case for $E_{\text{KS}}[\rho(\mathbf{r})]$ derived within LDA or GGA. In this light, $U$ is related to the spurious curvature of the LDA or GGA energy functional at non-integer occupation numbers. The form of equation 5.11 already suggests a simple way to calculate $U$: determine the dependence of $E_{\text{KS}}$ on $\theta_d$ by varying the occupation and calculating the corresponding energy; from $E_{\text{KS}}[\theta_d]$ calculate the functional derivative around the occupation predicted by regular DFT ($\theta_d^{\text{KS}}$) [145]. In practice, however, there are two problems to overcome. The first one is related to the fact that the perturbation applied to the correlated electrons modifies the kinetic energy term by affecting also the electrons from unperturbed sites. The kinetic response to the perturbation should be subtracted to avoid double-counting errors [145]:

$$U = \frac{d^2 E_{\text{KS}}[\theta_d]}{d (\theta_d)^2} - \frac{d^2 E^{0}_{\text{KS}}[\theta_d]}{d (\theta_d)^2} \quad (5.12)$$

where the second term represents the independent electron contribution which has to be subtracted [145].

The second problem is related to the implementation of equation 5.12 in practice. Since it is more practical to modify the KS potential instead than to constrain the actual occupation, $\theta_d$, Cococci and De Gironcoli [134] proposed a method for computing the Hubbard $U$ term from the linear response of the occupation numbers to small perturbations of the potential at the Hubbard
where \( \hat{\nu}_{KS}(\mathbf{r}) = \hat{\nu}_{cl}(\mathbf{r}) + \hat{\nu}_{ext}(\mathbf{r}) + \hat{\nu}_{xc}(\mathbf{r}) \) is the Kohn-Sham potential from equation 4.29, \( \alpha \) is the amplitude of the potential shift and \( \hat{P}_d^I \) is the projector operator corresponding to the localized \( d \) states \( \Phi_m \):

\[
\hat{P}_d^I = \sum_m |\Phi_m(\mathbf{r})\rangle \langle \Phi_m(\mathbf{r})|
\]

The ground state energy is obtained by minimizing the perturbed energy functional with respect to the density. By changing the variable of the minimization procedure and writing the energy as a functional of the occupation numbers the following expression can be derived [145]:

\[
E[\theta_d^I] = \min_{\alpha_I} \{E[\alpha_I] - \sum_I \alpha_I \theta_d^I\}
\]

where \( I \) designates the atomic site.

Using equation 5.15, the second derivative of the energy with respect to the occupation numbers can be expressed in terms of \( \alpha \). By defining the response function \( \chi_{IJ} \):

\[
\chi_{IJ} = \frac{d \theta_d^I}{d \alpha_J}
\]

as the change in occupation at site \( I \) (\( \theta_d^I \)), due to a perturbation of the potential at site \( J \) (\( \alpha_J \)), \( U \) can be calculated from the bare (\( \chi_0 \)) and self consistent response (\( \chi \)) [111, 134, 145]:

\[
U = -\frac{d \alpha_J}{d \theta_d^I} + \frac{d \alpha_J}{d \theta_d^{0I}} = (- \chi^{-1} + \chi_0^{-1})_{II}
\]

where \( U \) is diagonal element \( II \), while \( \chi \) and \( \chi_0 \) are the response matrices constructed using the matrix elements from equation 5.16. The bare response function represents the correction to avoid double-counting. It is calculated by considering the changes in occupation with \( \alpha \) applied to a well converged LDA or GGA potential at the first iteration of the SCF procedure, when the response does not involve electron-electron interactions and corresponds to an independent electron picture [145]. \( \chi \) is, instead, the self consistent response obtained from the variation of the occupation as a function of \( \alpha \) at the last SCF iteration.

The calculated \( U \) values determined from the linear response approach (ULR) described above are listed in Table 5.1 for the five TMPcs discussed in this chapter. The details of the calculations are presented in Paper V [136] and Paper VI. The linear response parameters are shown in comparison to the \( U_{eff} \) values which compared the best with experiment. These values have been determined in the same way as we have done for CoPc.
Table 5.1. Linear response values for the Coulomb parameter, $U_{LR}$, in comparison to values determined by matching the experimental 3d region observed by VB-PES, $U_{\text{eff}}^{\text{PES}}$. Adapted from Paper V [136].

<table>
<thead>
<tr>
<th>TMPc</th>
<th>$U_{LR}$ (eV)</th>
<th>$U_{\text{eff}}^{\text{PES}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnPc</td>
<td>6.2</td>
<td>4</td>
</tr>
<tr>
<td>FePc</td>
<td>4.4</td>
<td>4-5</td>
</tr>
<tr>
<td>CoPc</td>
<td>6.1</td>
<td>4-6</td>
</tr>
<tr>
<td>NiPc</td>
<td>8.2</td>
<td>5-7</td>
</tr>
<tr>
<td>CuPc</td>
<td>3.7</td>
<td>4-5</td>
</tr>
</tbody>
</table>

With the exception of MnPc, where a different type of pseudopotential has been used for the linear response calculation, the $U_{LR}$ values match well with the the values determined by comparison to VB-PES. More importantly, the trends observed when going from Fe to Cu are roughly similar when comparing $U_{LR}$ with the average of the $U_{\text{eff}}^{\text{PES}}$ intervals. It is, in addition, possible to study the influence of both the pseudopotential and the ligand atoms on the calculated linear response $U$. Equations 5.16 and 5.17 allow perturbing and checking the response of sites different than that of the localized $d$ electrons. By including sites from the ligand shells in the linear response calculation, the influence of particular types of atoms can be determined. Such calculations show that, in the case of TMPcs, the N atoms directly bound to the metal center play the most important role in the linear response $U$ (Paper VI), modifying $U_{LR}$ by some hundreds of meV. In addition, even if $U_{LR}$ should only depend on the approximation for the energy functional, the linear response value can differ by up to 1 eV, depending on which type of pseudopotential is used in the calculation [146].

We have seen that for the single molecules it is possible to determine an interval of reliable $U$ values which can be used in calculations involving single TMPc molecules. However, DFT+U improves the description of only the correlated electrons, leaving the ligand states largely unaffected. For single molecules and using localized basis sets such as the GTOs described in the previous chapter, there are other methods to improve the description of all molecular states, not only the $d$ levels. One such method involves including a portion of HF exact exchange to GGA to obtain what is called a hybrid functional. The value of the DFT+U method becomes especially obvious in cases where the use of a hybrid functional is either too expensive [147, 148] or inappropriate, as is the case of molecules adsorbed on metal surfaces [149]. But can the $U$ values determined for single TMPc molecules listed in Table 5.1 be of any use for such a situation? We argue that they indeed can be, at least in the case of physisorbed molecules. The argument is two-fold. First, the

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8Hybrid functionals are implemented also in codes with periodic boundary conditions, but the calculations become computationally very expensive.

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molecular structure hardly changes upon physisorption and, second, our linear response calculations show that, from the ligand, it is the chemically bound atoms which play the major part in influencing the $U_{LR}$ value. This suggests that, from the $U$ point of view, a physisorbed situation would be similar to a single molecule one. The linear response calculations in combination to the $U$ intervals determined for single molecules in comparison to VB-PES data can give clues about the trends for $U$ in this particular class of materials. Combining this knowledge with linear response calculations for the molecule on the surface (or the molecule in the presence of some of the surface atoms) could then help infer which $U_{eff}$ values are reliable for the surface adsorption situation.

We have seen throughout this section how the description of the metal $d$ levels can be improved by using the DFT+U method, we have discussed the influence of $U$ on the electronic structure and we have examined two possibilities for determining a reliable $U$ value (or interval). As already mentioned, for organic molecules with metal centres, DFT+U is especially valuable in cases involving the adsorption of the molecule on a surface. However, the inclusion of the Hubbard correction selectively to the strongly correlated states means that the ligand will continue to be affected by the problems of the approximate $xc$-potential. The following section describes one possibility of improving the description of both the metal and the ligand states.

5.2 Optimally Tuned Range-Separated Hybrid Functionals

In the previous section, the Hubbard model was incorporated within the DFT formalism to selectively ameliorate the description of the localized and strongly correlated states. The improvement provided by DFT+U can be linked to the fact that the $U$ term reduces the self-interaction error and rectifies to some extent the lack of derivative discontinuity of the LDA and GGA potentials. Performing the $U$ correction for some states but not others makes perfect sense, since different MOs carry different self-interaction errors (SIE), depending on how localized they are [110, 132]. However, because the ligand states are not corrected for SIE, the contraction of the DOS with respect to the VB-PES peaks observed with PBE (Figure 5.1) remains a problem. One idea to remedy this issue is to create orbital-dependent functionals where a different correction is performed for each and every single-electron state separately [110]. Such orbital-dependent approaches include the meta-generalized-gradient approximation (MGGA), self-interaction correction (SIC) [100, 150] and hybrid functionals [114, 151, 152]. Among these, the hybrids are, by far, the most widely used owing to the combination of relatively low computational cost and reasonable accuracy [110]. The idea behind a hybrid functional is to combine
GGA\textsuperscript{9} with a portion of HF exact exchange written in terms of the KS-orbitals (equation 4.46) \[88, 101, 110\]:

\[ E_{xc}^{hyb}[\rho(r), \{\chi_i\}] = \alpha E_{x}^{HF}[\{\chi_i\}] + (1 - \alpha)E_{x}^{DFT}[\rho(r)] + E_{c}^{DFT}[\rho(r)] \] (5.18)

where \( E_{xc}^{hyb} \) is the hybrid exchange and correlation energy functional, \( E_{x}^{HF} \) is the exact exchange, \( E_{x}^{DFT} \) is the GGA exchange functional, \( E_{c}^{DFT} \) is the GGA correlation, while \( \alpha \) is a parameter between 0 and 1 which determines the portion of exact exchange included in the hybrid.

The parameter \( \alpha \) can be determined either by fitting the calculated results to a large set of thermochemistry data, as in the case of the B3LYP functional\textsuperscript{10} [114, 151], or from theoretical considerations, such as in the case of the PBE-based hybrid (PBEh) functional proposed by Perdew, Burke and Ernzerhof [152]. In PBEh, \( \alpha = 0.25 \), while in functionals based on empirical fitting, \( \alpha \) takes values around 0.2 (if the fitting is carried out for atomic and molecular data) \[110\].

How do hybrid functionals perform when it comes to the electronic structure of TMPcs? To recapitulate the case of PBE (Figure 5.1), for MnPc and H\textsubscript{2}Pc, the binding energy of the HOMO level was underestimated by approximately 1.7 eV, while total densities of states calculated for these two molecules appeared contracted in comparison to corresponding VB-PES spectra.

Figure 5.4 shows the same comparison between experiment and theory in the case of the B3LYP functional\textsuperscript{11}. The binding energy of the HOMO level is still largely underestimated (by approximately 1.4-1.5 eV), but after performing a rigid shift to match the first experimental peak, the calculated DOS reproduce well the VB-PES bands for both H\textsubscript{2}Pc and MnPc. The addition of a portion of exact exchange thus fulfils its purpose of ameliorating the self-interaction error for both metal and ligand states. But what about the position of the calculated HOMO level? According to the ionization potential (IP) theorem [153], the KS-calculated eigenvalue of the highest occupied molecular orbital must be exactly equal to the energy required to ionize this level (if the exact form of the \( xc \)-potential is used), and, therefore, \( \varepsilon_{HOMO} \) should in principle reproduce with reasonable accuracy the experimentally measured HOMO ionization energy. Figure 5.4 clearly shows that this is not the case. Other studies confirm the same result for calculations performed on other organic molecules using B3LYP or other hybrid functionals [132, 154]. For the majority of materials science questions, the fact that a rigid shift is needed in order to obtain the correct ionization energy for the HOMO is not a major problem. However, when it comes to transport properties, optical excitations or exciton

\textsuperscript{9}There are also LDA-based hybrid functional, but they are not widely used \[110\], so we will limit the discussion to GGA-based hybrids.
\textsuperscript{10}In reality, the B3LYP functional is written in terms of three parameters which are adjusted to fit thermochemistry data. See reference \[110\] p. 33 for details.
\textsuperscript{11}Except for the functional, the details of the calculation are the same as in the PBE case. See p. 48.
Figure 5.4. Valence band electronic structure of (a) H$_2$Pc and (b) MnPc calculated using the B3LYP functional [114], represented in comparison to VB-PES measurements performed on film samples. The H$_2$Pc measured data is from Paper IV [133], while the two spectra of MnPc are from Paper II [80]. The experimental spectra have been shifted such that the HOMO (HOMO-1, for MnPc) peak matches the HOMO (HOMO-1) ionization energy of the gas phase molecule (6.4 eV). A Gaussian broadening of 0.6 eV constant full width at half maximum (FWH) has been added to the calculated discrete eigenvalue spectrum in order to facilitate the comparison to experiment. The contribution of the Mn 3$d$ levels is in orange.

binding energies, the accurate positioning of the HOMO and LUMO orbitals is very relevant [155] and, thus, it’s important to find out what causes this problem and how to mitigate it. The origin of the error can, in fact, be traced back to the behaviour of the $xc$-potential. Since exact exchange is only partly included in hybrids, in order not to disturb the balance between exchange and correlation in the approximate functional [155], the $xc$-potential continues to decay too fast in the long range limit of $r \rightarrow \infty$ [110], while still lacking derivative discontinuity [156]. In order to remedy this, one idea, as proposed by Leininger et al. [157], is to separate the exchange into short- and long range, where the long range part can be fully treated using HF exchange, while the short range, where correlation is more important, is treated using GGA [155]. The division between short- and long range is performed by partitioning the Coulomb repulsion operator [158]:

$$\frac{1}{r_{12}} = \frac{1}{r_{12}} - [\alpha + \beta \cdot \text{erf}(\gamma \cdot r_{12})] + \frac{\alpha + \beta \cdot \text{erf}(\gamma \cdot r_{12})}{r_{12}}$$

(5.19)

where $r_{12} = |r_1 - r_2|$ represents the interelectron distance, erf is the error function, $\gamma$ is the range separation and $\alpha$ and $\beta$ are two other parameters taking values between 0 and 1 (discussed in more detail later on). The first term in equation 5.19 defines the short range (SR) interaction treated using the ap-
proximate DFT exchange, while the second term defines the long range (LR) interaction treated within HF formalism [158–160]:

$$E_{x,SR}^{DFT} = -\frac{1}{4} \int_{\tilde{r}} \int_{r_{12}} [\rho_{1}(\tilde{r}, r_{12})]^{2} \frac{1 - [\alpha + \beta \cdot \text{erf}(\gamma \cdot r_{12})]}{r_{12}} d\tilde{r} dr_{12} \quad (5.20)$$

$$E_{x,LR}^{HF} = -\frac{1}{2} \sum_{i,j} \langle \chi_{i}(r_{1}) | \chi_{j}(r_{2}) \rangle \left| \frac{\alpha + \beta \cdot \text{erf}(\gamma \cdot r_{12})}{r_{12}} \right| \chi_{i}(r_{2}) \chi_{j}(r_{1}) \rangle \quad (5.21)$$

$\chi_{i}$ are the Kohn-Sham orbitals, $\rho_{1}(\tilde{r}, r_{12})$ represents the first order density matrix and $\tilde{r} = 1/2(r_{1} - r_{2})$.

In the original range-separated hybrid (RSH) proposed by Leininger et al. [157], $\alpha = 0$, $\beta = 1$, while $\gamma$ controls the mixing between the two types of exchange (HF and DFT). The idea is that exchange and correlation play roles of different importance at different ranges, while the correct asymptotic behaviour is recovered at $r_{12} \to \infty$ since the HF exchange takes over in this limit. The generalized form in equation 5.19 allows the mixing of a portion of exact exchange $\alpha$ over the entire range [158, 159]. In this case, the condition $\alpha + \beta = 1$ must be fulfilled in order to recover the correct asymptotic behaviour [158].

Figure 5.5 shows how $\alpha$ and $\gamma$ control the mixing between HF and DFT exchange at different interelectron distances, $r_{12}$, for different functionals. In the case of regular hybrids, such as PBEh (shown in Figure 5.5 a), a fixed proportion of $E_{x}^{HF}$ is combined with $E_{x}^{DFT}$ over the full range. This is equivalent with setting $\gamma$ to 0, since $\text{erf}(0 \cdot r_{12}) = 0$. For range-separated hybrid functionals, represented in Figure 5.5 b and c, $\gamma$ determines the sharpness with which the proportion of exchange from DFT goes to zero. The larger the $\gamma$, the more short ranged the DFT component is. The $\alpha$ parameter, marked by horizontal dotted lines in Figure 5.5 c, controls instead the amount of exact exchange included over the full range [159]. The larger $\alpha$ is, the higher the percentage of HF exchange included at short range ($r_{12} \to 0$) and onwards.

The only important question is: what values should be chosen for $\alpha$ and $\gamma$? One possibility is to fit the functional to a set of reference data. This is the strategy employed in most range-separated hybrids [156, 159, 161–167]. Another alternative is to optimally tune the parameters for a particular system such that the IP theorem is obeyed\(^{12}\) [158]. This is the basic idea behind OT-RSH functionals and the main motivation for performing such a system-dependent tuning is that different systems require significantly different $\gamma$ values for obtaining accurate results [158]. This could be also traced back to the fact that the self-interaction error and the lack of derivative discontinuity affect systems differently (we have already seen that different systems require different $U$ values as well).

\(^{12}\)More generally, $\gamma$ can be tuned such that a physically motivated condition is fulfilled [168]. In the case of molecules, it has been shown that imposing the IP theorem provides electronic structures of similar accuracy as GW calculations [169–171].
Figure 5.5. Schematic representation of the mixing between HF and DFT exchange in (a) PBEh, (b) RSH functionals as proposed in reference [157] and (c) generalized RSH functionals as proposed in reference [158]. In (b) and (c) γ is in units of bohr$^{-1}$, while the HF contribution is determined as $\alpha + \beta \cdot \text{erf}(\gamma \cdot r_{12})$.

5.2.1 The Electronic Structure of CoPc from OT-RSH

In the previous paragraphs, we have laid out the foundations for range-separated hybrid functionals and we have seen that the parameters controlling the mixing between exact and DFT exchange can be optimally tuned such that the IP theorem is fulfilled. In the case of a neutral molecule, the IP theorem can be written as:

$$\varepsilon_{HOMO} = -IE$$  \hspace{1cm} (5.22)

where $IE$ stands for ionization energy and $\varepsilon_{HOMO}$ is the KS eigenvalue of the highest occupied molecular orbital. The ionization energy can be calculated quite accurately within GGA by using total energies, instead of energy eigenvalues. Within the $\Delta$Kohn-Sham formalism, $IE$ is calculated as follows:

$$IE_{\Delta KS} = E_{KS}(n-1) - E_{KS}(n)$$  \hspace{1cm} (5.23)

where $E_{KS}(n-1)$ is the KS total energy of the cation and $E_{KS}(n)$ is the total energy of the neutral molecule.

By requiring that the HOMO eigenvalue be equal to the $\Delta$KS ionization energy, the parameters in the OT-RSH functional can be determined entirely from first principle.

Let’s now see how an OT-RSH performs in the case of CoPc. We will attempt to answer two questions here: first, how does $\gamma$ influence the calculated electronic structure of CoPc? and second, how does the calculated electronic structure obtained using the optimal $\gamma$ compare to experimental data? Throughout, we will assume $\alpha = 0^{13}$. A more detailed discussion, including other values for $\alpha$, is presented in Paper VII.

Figure 5.6 shows the calculated HOMO-LUMO gaps of CoPc determined

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13The ingredients of the calculation are similar as for the PBE case described at p. 48. The calculations were performed in G09 [124] and the DFT component of the RSH exchange was described by PBE [102, 103].
Figure 5.6. (a) HOMO-LUMO gaps calculated for $\alpha = 0$, using different values for the range separation parameter ($\gamma$). (b)-(f) Calculated electronic structure of CoPc using the five $\gamma$ values from (a) (in bohr$^{-1}$). The individual $d$ contributions are shown alongside the N 2$p$ (dark gray), C 2$p$ (gray) and total (light gray) densities of states. The HOMO is denoted by H and the LUMO by L. The results are adapted from Paper VII.

for different values of the range separation parameter. The values were chosen in the range 0.1-0.3 bohr$^{-1}$, matching reported values in the literature for similar systems [158, 171]. From pure PBE calculations, the HOMO-LUMO gap obtained for CoPc is approximately 0.2 eV (see Figure 5.2, $U_{\text{eff}} = 0$), a large underestimation with respect to the optical gap of CoPc films, measured at 2.88 eV [172]. From Figure 5.6 a, the HOMO-LUMO gap is already predicted to be 2.9 eV by the RSH using $\gamma = 0.1$ bohr$^{-1}$. As $\gamma$ is increased, the gap steadily increases undergoing a change of slope at $\gamma = 0.2$ bohr$^{-1}$. The changes observed in the behaviour of the gap can be explained by checking the calculated electronic structure. The calculated total DOS at different $\gamma$ values is shown alongside the N 2$p$ and C 2$p$ partial DOS in Figure 5.6 b-f. The individual Co 3$d$ levels are also included in the figure. At low $\gamma$ (0.1 and 0.15) the LUMO of CoPc is the $d_{z^2}$ orbital (this was also the case for low values of $U_{\text{eff}}$, see Figure 5.2). This orbital is more affected by the way exchange is included in the calculations and shifts more than the ligand states when $\gamma$ is increased (i.e. the DFT exchange contribution becomes more short ranged). Similarly, the other $d$ levels shift more compared to the ligand states when the range parameter is increased. At $\gamma$ values larger than 0.2 bohr$^{-1}$, the $d_{z^2}$ is no longer the LUMO, as it surpasses another molecular orbital originating in ligand 2$p$ states. The new LUMO is less affected by $\gamma$ and, therefore, the change
in HOMO-LUMO gap slows down, leading to the change of slope observed in Figure 5.6 a.

The densities of states presented in Figure 5.6 b-f show that the molecular orbitals can shift towards quite high binding energy for large values of $\gamma$ (at $\gamma = 0.3$ bohr$^{-1}$ the HOMO-1 peak is at 8.2 eV BE). How do these calculated electronic structures compare to measured data and which is the optimal range separation ($\gamma_{opt}$)? In order to find $\gamma_{opt}$, we attempt to enforce the IP theorem. The calculated $\Delta$KS ionization energy, determined as the total energy difference between the CoPc cation and CoPc in the ground state, is 6.12 eV. Figure 5.7 a displays the difference between the eigenvalue of the HOMO level and the calculated IE. The figure shows that the HOMO, originating exclusively in C 2$p$ states of the ligand, moves towards higher binding energies as the range separation parameter is increased. At a value of $\gamma = 0.149$ bohr$^{-1}$, the curve $|\varepsilon_{\text{HOMO}}| - IE$ intersects 0 and the IP theorem is fulfilled. This is the optimal value we are looking for.

Figure 5.7 b shows the calculated total DOS using $\gamma_{opt} = 0.149$ bohr$^{-1}$ in comparison to VB-PES measurements from reference [173] and inverse PES (IPES) data from reference [174]. In IPES, the unoccupied electronic levels are probed by a beam of electrons with well defined kinetic energy. When entering the sample, the electrons decay to empty states at lower energy. If the decay is radiative, the emitted radiation gives information on the binding
energy of the former unoccupied electronic states and the measured spectrum reflects the empty electronic levels of the system [175]. The IPES spectrum presented in Figure 5.7 has been shifted by 4.95 eV towards higher binding energies, such that the corresponding HOMO level from its PES counterpart matches the spectra from reference [173].

The comparison between experiment and theory is very good. In fact, without any shift required, the calculated eigenvalue of the HOMO level (6.12 eV, by construction) is only 0.18 eV away from the experimental measured value (6.30 eV). This is because the ΔKS IE is already quite good in reproducing experimental ionization energies. In addition, all experimental VB-PES bands are well reproduced by the theoretical total spectrum. The agreement in peak position between theory and experiment is very good for peaks B and C, while D appears slightly shifted in the calculation. Moreover, the position of the calculated 3d levels matches well with their position in the experiment, revealed by the use of the high photon energy radiation. Finally, when it comes to the IPES, the two experimental peaks, denoted 1 and 2 in Figure 5.7, are also well reproduced in the calculation.

The RSH functional using PBE exchange and with γ optimized such that the IP theorem is fulfilled provides, for CoPc, an electronic structure which reproduces very well the measured VB-PES and IPES spectra. We have restricted here the discussion to α = 0.0, which, in the case of CoPc, turns out to provide a good agreement with experiment. In the case of CuPc, a value of α = 0.17 is instead required [158]. In general, if both α and γ are optimized for the IP theorem, the results obtained for gas-phase molecules are comparable to those provided by the GW method [158].

Throughout the previous chapters, we have seen how the many-body electronic problem can be addressed within DFT and how the calculated results perform with respect to experiment. In the examples shown here, the comparison was performed between calculated electronic structure and VB-PES measurements, although the electronic structure constituted only the first step in the description of the spectroscopic process. The second step of theoretically describing a spectroscopy entails the calculation of the relevant photon-mediated transitions. The following part will discuss specific spectroscopies and the possible theoretical approaches to describe each of them.
Part III:
Theoretical Spectroscopy
6. Overview of Electronic and Vibrational Spectroscopy

After having discussed the methods for determining the electronic structure of molecules, it is now time to address the spectroscopic process itself. The spectroscopies included in this thesis belong to two different categories: electronic and, respectively, vibrational. Electronic spectroscopies, as the name suggests, cover transitions in absorption or emission between electronic levels [24]. Vibrational spectroscopies, on the other hand, are related to transitions between vibrational levels (see Part I, Figure 1.2.). We will focus on three types of electronic and two types of vibrational transitions, schematically depicted in Figure 6.1.

To begin with, the photoelectron spectroscopy of the valence band (VB-PES), which we have already met in Part II, consists in the photoionization of valence electrons by electromagnetic radiation of well defined photon energy. The process is illustrated in Figure 6.1 b. An incident photon of energy $\hbar \omega$, large enough to ionize valence electrons (typically UV or soft X-rays), is absorbed, resulting in the emission of an electron with energy $E_{\text{kin}}$. By recording the different kinetic energies of emitted electrons it is possible to infer their binding energy in the material:

$$IE_i = |\varepsilon_i| = E_{\text{kin}} - \hbar \omega - \Omega \quad (6.1)$$

where $|\varepsilon_i|$ ($IE_i$) is the binding (ionization) energy of the $i^{\text{th}}$ valence molecular orbital and $\Omega$ is the work function $^1$.

The core level X-ray photoelectron spectroscopy (XPS) works in a similar way as VB-PES, but the energy of the electromagnetic radiation (soft X-rays) is tuned in such a way as to ionize core levels, instead of valence states. Carbon 1s orbitals typically have ionization energies of approximately 286 eV, while oxygen 1s levels ionize at approximately 532 eV$^2$. Due to such large differences in binding energies of core levels from different elements, XPS can provide great insight into the chemical composition of materials [177].

A complementary spectroscopy to XPS is X-ray absorption (XAS). In our case, the discussion will be limited to the near-edge absorption fine structure

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$^1$The work function represents the minimum energy required to remove an electron from the surface of a film. In the case of isolated atoms or molecules, the work function is 0.

$^2$The values are averages and have been calculated using data from reference [176]. Depending on the chemical bonds formed by the atom and the species bonded to it, the IE differs by several eV from the average value [176].
Figure 6.1. Single-particle picture of the spectroscopies included in this thesis. (a) Ground state electronic structure, (b) valence-band PES, (c) 1s XPS and (d) 1s NEXAFS. The vibrational spectroscopies are represented on a different energy scale: (e) vibrational IR and (f) Raman spectroscopy (Stokes scattering).

(NEXAFS) region of the XAS spectrum. The transitions that give rise to the NEXAFS spectrum are depicted in Figure 6.1 d. A photon of energy $\hbar \omega$ is absorbed, promoting the transition of a core electron to unoccupied levels of the molecule. By recording which photons (in terms of energy) are absorbed, it is possible to infer the unoccupied electronic structure of the molecular system. However, it is more usual to perform NEXAFS measurements in fluorescence or electron yield [178]. These techniques involve the excitation of the system using soft X-rays and the detection of photons (fluorescence) or electrons (electron yield) emitted as a consequence of the de-excitation process. From the energies of these photons or electrons it is then possible to determine the NEXAFS spectrum. Since the chemical environment of the core-excited atom affects the binding energy of the 1s electron, NEXAFS (and XPS) provides important information about the chemical bonding in molecules.

Finally, the vibrational spectroscopies are depicted in Figure 6.1 e and f. The Infrared (IR) absorption process involves the absorption of a low energy photon which promotes the transition of the molecular system to a higher vibrational energy level. Raman spectroscopy is complementary to IR and it involves the absorption of visible highly collimated light with well defined photon energy. Light absorption promotes the entire molecular system to an excited (electronic) energy level. With a small probability, the de-excitation process leaves the molecule in a different vibrational level of the ground state.
By recording emitted photons of slightly different energy than those used for excitation it is possible to determine the ground state vibrational levels. Because the energy differences involved are very small (of the order of 0.05-0.4 eV), it is important to use incident electromagnetic radiation with very specific wavelength, such as the one produced by lasers. Due to a different mechanism, related to the dependence of the vibrational frequencies on the atomic weight of the nuclei involved, IR and Raman can provide complementary information (to XPS and NEXAFS) regarding the chemical bonding in molecular systems.

Electronic spectroscopies are the main focus of Chapters 7 and 8, while IR and Raman are discussed in more detail in Chapter 9. Before addressing each spectroscopy by itself, let’s analyse first the theoretical principles and approximations involved in the description of electronic transitions.

6.1 Principles of Electronic Spectroscopy

The interaction of molecules with electromagnetic radiation can be addressed within time-dependent perturbation theory. Since we restrict the discussion to electronic transitions, the Hamiltonian describing the interaction of the electrons with light can be written as [179]:

$$\hat{H}_{\text{int}} = \hat{H}_e + \hat{V}(t)$$  \hspace{1cm} (6.2)

where $\hat{H}_e$ is the unperturbed electron Hamiltonian and $\hat{V}(t)$ is the potential by the incoming electromagnetic radiation. Explicitly:

$$\hat{V}(t) = \frac{e}{m_e c} A(r, t) \cdot \hat{p}$$  \hspace{1cm} (6.3)

$A$ is the vector potential of the electromagnetic radiation and $\hat{p}$ is the momentum operator. By assuming the incident radiation to be a plane wave of polarization $\varepsilon$ and wave-vector $k$:

$$A(r, t) = A_0 \varepsilon \left[ e^{i(kr - \omega t)} + e^{-i(kr - \omega t)} \right]$$  \hspace{1cm} (6.4)

and by calculating the first order transition probability [179], we derive the Fermi golden rule for a photon-absorption process:

$$\Gamma_{i \rightarrow f} = \frac{4\pi^2 e^2}{m_e^2 \tau} \frac{1}{\omega} \left| \langle \psi_f | e^{i\mathbf{k} \cdot \mathbf{r}} \hat{p} | \psi_i \rangle \right|^2 \delta_{E_f - E_i - \hbar \omega}$$  \hspace{1cm} (6.5)

here $\tau$ represents the volume, while $\psi_f$ and $\psi_i$ are the many-body wavefunctions of the final and, respectively, initial state, with the corresponding total energies $E_f$ and $E_i$. The Kronecker $\delta$ ensures the energy conservation.

By further assuming that the wavelength of the radiation is large compared
to atomic size (assumption valid for visible, UV and soft X-rays), $e^{ikr}$ can be expanded in series [179]:

$$e^{ikr} = 1 + ikr + ...$$ (6.6)

The dipole approximation consists in keeping just the first term of the expansion, resulting in the following expression for the dipole transition probability:

$$\Gamma_{i\rightarrow f} = \frac{4\pi^2e^2}{m^2} \frac{1}{\tau \omega} |\langle \psi_f | \mathbf{p} | \psi_i \rangle|^2 \delta_{E_f - E_i - \hbar \omega}$$ (6.7)

If the initial and final states are eigenfunctions of the unperturbed Hamiltonian ($\hat{H}_0$), 6.7 can be re-written in terms of the position operator, $\mathbf{r}$:

$$\Gamma_{i\rightarrow f} = \frac{4\pi^2e^2}{\tau} \frac{\omega^2_{ji}}{\omega} |\mathbf{e} \langle \psi_f | \mathbf{r} | \psi_i \rangle|^2 \delta_{E_f - E_i - \hbar \omega}$$ (6.8)

where $\omega_{ji} = (E_f - E_i)/\hbar$.

Equation 6.8 involves the many-body wavefunctions for the final (after absorption) and initial (prior absorption) states. However, in Part II, we have seen that these wavefunctions are not readily available since the many-body problem is impossible to solve without making approximations. Within the framework of DFT, we would like to be able to describe the transition in terms of the single-electron orbitals. By assuming that the spectroscopic transition is a one-electron process [180, 181] and by considering that the many-body wavefunction can be constructed as an antisymmetric linear combination of single-electron orbitals (as a Slater determinant, for example) [91], we can re-write equation 6.10 in terms of the two single-electron states involved in the transition:

$$\Gamma_{i\rightarrow f} = \frac{4\pi^2e^2}{\tau} \frac{\omega^2_{ji}}{\omega} |\mathbf{e} \langle \chi_f | \mathbf{r} | \chi_i \rangle|^2 |\langle \psi_f | \psi_i \rangle|^2 \delta_{E_f - E_i - \hbar \omega}$$ (6.9)

where $\langle \psi_f | \psi_i \rangle$ represents the codeterminant of the orbital overlap after the single-electron wavefunctions $\chi_f$ and $\chi_i$ have been removed. If the remaining orbitals remain unaffected by the transition, the overlap can be approximated to one. The transition probability can then be written only in terms of the two single-electron wavefunctions involved:

$$\Gamma_{i\rightarrow f} = \frac{4\pi^2e^2}{\tau} \frac{\omega^2_{ji}}{\omega} |\mathbf{e} \langle \chi_f | \mathbf{r} | \chi_i \rangle|^2 \delta_{E_f - E_i - \hbar \omega}$$ (6.10)
7. Photoelectron Spectroscopy of the Valence Band

In Chapter 5 we used photoelectron spectroscopy measurements of the valence band in order to determine how well a particular approximation for the xc-functional worked in the case of phthalocyanines. We also analysed spectra recorded at different photon energies in order to find out the position of the metal d levels. This was possible because different atomic orbitals have different photoionization cross-sections [119, 120]. However, the comparison theory-experiment was always performed using directly the calculated electronic structure of the Pc, without any consideration for the transition probability from equation 6.10. Until now, we have considered that all ionizations from valence states take place with the same probability, such that we can assume the same intensity for each molecular orbital in the theoretical spectrum. This is, actually, not the case in the experiment. It is now time to address the question of how to account for the fact that different orbitals are ionized with different probability.

7.1 Photon Energy Dependent PES

To illustrate just how different the cross-sections ($\sigma_\mu$) are for different types of atomic orbitals, Figure 7.1 shows the comparison between the calculated $\sigma_\mu$ for the 2p states in carbon and nitrogen and for the 3d states in manganese, iron, cobalt and nickel. The values are from reference [121] and have been calculated for free atoms, assuming dipole transitions between the atomic levels and continuum states\(^1\). Figure 7.1 shows that there are important differences between the two types of atomic orbitals. The 2p states of C or N are more likely to be ionized by low photon energy radiation and the probability asymptotically decreases to 0 as the photon energy is increased. The metal d levels, on the other hand, are less likely to be excited by low energy photons. The 3d cross-sections reach a maximum at approximately 50 eV, with the larger metals reaching a peak at larger energies.

Given these differences in transition probability between different atomic shells, how do we incorporate the knowledge of atomic photoionization cross-sections into a photon energy dependent valence band spectrum of a molecule?

\(^1\)In reference [121] the initial state wavefunctions are determined using the Hartree-Fock equations, while the final state is determined as proposed by Cooper and Manson [182, 183].
Figure 7.1. Calculated atomic photoionization cross-sections for the C and N 2p states shown in comparison to the 3d cross-sections of Mn, Fe, Co and Ni.

This can be done simply by using the LCAO representation of the KS molecular orbitals from equation 4.37 (Part II, Section 4.4.3) and assuming that the total cross-section of each MO can be obtained from the cross-sections of its constituent AOs. In the Gelius model, the molecular photoionization cross-section ($\sigma_i$) is written as [120]:

$$\sigma_i = \sum_{\mu=1}^{N} c_{\mu i}^2 \sigma_{\mu}$$  \hspace{1cm} (7.1)

where $c_{\mu i}$ is the contribution of the atomic orbital $\mu$ to the $i^{th}$ molecular orbital and the sum is over all atomic orbitals $\mu$.

One idea of how to include the atomic cross-sections in the calculation of the valence band spectrum of a molecule is to partition the single-electron molecular orbitals into atomic contributions and multiply the atomic component with its corresponding $\sigma_{\mu}$. In order to do so, we must allocate a fraction of electron to each AO, but the way to do so is not completely unambiguous. There are several possibilities for performing one such population analysis, including Mulliken [184], Löwdin [185] and $c^2$ [186]. All approaches are sensitive to the basis set used for the calculation, but the Mulliken population analysis can result in negative contributions, or contributions larger than 1$^2$. In the following we will use the $c^2$ method, where the contribution of atomic orbital $\Phi_{vi}$ to the molecular state $\chi_i$ is expressed as:

$$\frac{c_{vi}^2}{\sum_{\mu=1}^{N} c_{\mu i}^2}$$  \hspace{1cm} (7.2)

$^2$Or 2, for closed-shell systems.
Figure 7.2. Valence band electronic structure of (a) H$_2$Pc and (b) MnPc calculated using the B3LYP functional [114], and multiplied by the photoionization cross-sections. The photon energy is 130 eV for H$_2$Pc; 21.2 eV and 1486.7 eV for MnPc. The experimental data is the same as in Figure 5.4. For the spectra multiplied by the cross-section a broadening with Gaussian functions of variable FWHM has been performed as described in the text. The constant 0.4 eV FWHM spectrum of H$_2$Pc is shown for comparison (in gray). The spectra of MnPc have been normalized at the C 2$p$ peak at 13.6 eV binding energy, marked by an arrow in the figure. Based on results from Papers II [80] and IV [133].

After calculating the electronic structure within DFT and determining the values for the coefficients $\{c_{\mu i}\}$, it’s then possible to compute the atomic contributions using the $c^2$ method. Each atomic contribution is multiplied with its corresponding atomic photoionization cross-section from references [121, 122] and the total spectrum is determined by summing up the individual components [80, 129, 130].

Figure 7.2 shows how the theoretical spectra obtained with the new approach compare to VB-PES experiments in the case of H$_2$Pc and MnPc. The electronic structure is the one determined by B3LYP as described in Chapter 5 (see Figure 5.4). The B3LYP spectra shown in the figure are shifted by 1.4 eV (1.5 eV, MnPc) towards higher binding energy in order to match the experimental first peak.

In the case of H$_2$Pc, the atomic contributions from C, N and H levels have been multiplied with the corresponding photoionization cross-sections at 130 eV photon energy. All components have been summed and a Gaussian broadening with Gaussian functions of variable FWHM has been added as was performed for the results in Paper II [80]. The FWHM was kept constant (0.3 eV) at low binding energies and then linearly increased to 2.0 eV in the interval 6.5 eV to 10 eV BE. A constant FWHM spectrum (0.4 eV) is shown for comparison. The same variable broadening was performed for MnPc at both photon
energies (21.2 and 1486.7 eV photon energy). In addition, the two spectra are normalized with respect to a C 2p peak at 13.6 eV BE.

The comparison experiment-theory for H2Pc in Figure 7.2 a is remarkably good. The inclusion of the atomic photoionization cross-section results in a theoretical spectrum which reproduces very well the relative intensities of the measured bands. This is also the case for MnPc (Figure 7.2 b). When comparing the spectra determined at low (21.2 eV) and high (1486.7 eV) photon energies, the changes in peak position and intensity are well captured by the calculated spectra. The case of MnPc is, in fact, very interesting and illustrates the importance of including the effect of photoionization cross-sections in the theoretical spectrum. As discussed in Paper II [80] and references therein, the ground state electronic structure of MnPc has been under debate, with several possible configurations of the d levels inferred from experiment or calculated by DFT. In the case of MnPc films, the comparison between experimental data measured at two different photon energies with theoretical spectra of three possible electronic configurations, where the atomic photoionization cross-sections had been taken into account, could pinpoint to one of the three as the most likely. See Paper II [80] for details.

As we have seen, the combination of a reasonably accurate functional with the description of transition probabilities by atomic photoionization cross-section can lead to very good agreement between theory and experiment and open up the possibility for accurate assignment of the experimental bands. However, it is very important to remember the approximations made along the way, in particular the assumption that the transition probability of an electron in an isolated atom can be directly used as a contribution in the transition probability of an electron from a molecular orbital. We have also assumed that the transition probability only depends on the photon energy. This is, in fact, not completely valid as ionization probabilities have been also shown to depend on the binding energy of the molecular orbital which is excited [187, 188].

7.2 Photon and Binding Energy Dependent PES

The previous section ended with a note on the potential limitations of using the probability to ionize atomic shells in order to describe the ionization of molecular orbitals. In this section, we will analyse one possible alternative to include the binding energy (BE) dependence of the cross-sections into the calculated PES spectrum. The idea, described in reference [187], is to directly compute equation 6.10 using the calculated KS orbitals and the wavefunctions of the ionized electron in the continuum. The first approximation, valid in the limit of high electron kinetic energies, is to describe the ejected photoelectron as a plane-wave normalized inside a box of volume Ω [187, 189]:

\[ \chi_f(r) = \frac{1}{\sqrt{\Omega}} e^{i(k_e \cdot r)} \]  

(7.3)
where $k_e$ is the wave-vector of the photoelectron and $r$ is the position.

Using equation 7.3 and expanding $\chi_i$ as a linear combination of atomic orbitals (Part I, Chapter 4.4.3), the dipole transition probability can be written as:

$$
\Gamma_{i \rightarrow f} = \frac{4\pi^2 e^2 \omega^2_{ji}}{\tau \Omega} \left| \langle e^{i(k_e \cdot r)} | r \left| \sum_{\mu=1}^{N'} c_{\mu i} \Phi_{\mu}(r) \right. \rangle \delta_{\epsilon_k - \epsilon_i - \hbar \omega} \right|^2
$$

(7.4)

where $\epsilon_k$ is the kinetic energy of the photoelectron and $\epsilon_i$ is the KS eigenvalue of orbital $\chi_i$. As in equation 4.37, $\Phi_{\mu}$ is an AO and the summation is over all the $N'$ atomic orbitals in the molecule. The coefficients $\{c_{\mu i}\}$ are self-consistently determined along with the eigenvalues $\epsilon_i$, while $\Phi_{\mu}(r)$ is further expanded in terms of the basis functions (equations 4.37 and 4.43). With this and by taking the constant terms out the bracket, the transition probability becomes:

$$
\Gamma_{i \rightarrow f} = N_\Gamma \cdot \frac{\omega^2_{ji}}{\omega} \left| \sum_{\mu=1}^{N'} c_{\mu i} \sum_{s=1}^{NBF} d_{\mu s} \left( \langle e^{i(k_e \cdot r)} | r \left| g_{s}(r) \right. \rangle \right) \right|^2 \delta_{\epsilon_k - \epsilon_i - \hbar \omega}
$$

(7.5)

where all the constants have been grouped in $N_\Gamma$.

Equation 7.5 allows us to calculate the dipole transition probability from a molecular orbital to a free electron by simply determining the dipole-mediate overlap between a plane-wave and the basis functions (we will use the Gaussian type orbitals). There are, however, two vectors in equation 7.5 which still need to be defined, before any practical calculations are possible. The first is the polarization vector $\boldsymbol{e}$. Assuming non-polarized electromagnetic radiation, we must integrate $\boldsymbol{e}$ over all possible directions. The integration leads to a constant factor of $2/3$ [187] which can be incorporated into the $N_\Gamma$ constant. The second vector which needs to be defined is the wave-vector of the ejected photoelectron $k_e$. Its magnitude can be calculated from the kinetic energy which is, in turn, determined from energy conservation:

$$
\epsilon_k = \hbar \omega + \epsilon_i
$$

(7.6)

$$
 k_e = \frac{\sqrt{2m_e \epsilon_k}}{\hbar}
$$

(7.7)

note that $\epsilon_i$ has negative value.

In addition, we integrate over all possible $k_e$ directions. This translates into performing an integration on a sphere of radius $k_e$, which, in our approach, is carried out using the Lebedev quadrature [190]. With this, all ingredients necessary for performing the calculation of the VB-PES are available and the final equation is:

$$
\Gamma_{i \rightarrow f} = N_\Gamma \cdot \frac{\omega^2_{ji}}{\omega} \left| \sum_{\mu=1}^{N'} \sum_{s=1}^{NBF} c_{\mu i} \sum_{s=1}^{NBF} d_{\mu s} \left( \langle e^{i(k_e \cdot r)} | r \left| g_{s}(r) \right. \rangle \right) \right|^2 \delta_{\epsilon_k - \epsilon_i - \hbar \omega}
$$

(7.8)
Figure 7.3. Valence band electronic structure of (a) H_2Pc and (b) NiPc calculated using the B3LYP functional [114]. Photon- and binding energy dependent PES spectra, denoted $\sigma(BE)$, were calculated at 130 eV photon energy (H_2Pc), 21.2 and 125 eV (NiPc). The experimental data is from Paper IV [133] (H_2Pc) and from reference [143] (NiPc). The measured NiPc spectra have been shifted to align their first peak to the calculated HOMO. A broadening with Gaussian functions of variable FWHM has been performed as described in the previous section (7.1). The calculated spectra of NiPc have been normalized at 11.0 eV binding energy, marked by an arrow in the figure. Based on results from Paper VIII.

where the sum over $\phi$ and $\theta$ marks the summation over all possible photoelectron directions.

Figure 7.3 shows the calculated results for two phthalocyanines, H_2Pc and NiPc. The DFT-calculated eigenvalues and $\{c_{\mu i}\}$ coefficients were used in equation 7.8, alongside Gaussian orbital exponents and coefficients from the basis set. A total transition probability was computed for each KS orbital. The discrete spectrum obtained by joining together each individual contribution was broadened using Gaussian functions of variable FWHM as described previously (Section 7.1).

Figure 7.3a shows a comparison between the previous calculated VB spectrum of H_2Pc (using constant $\sigma_\mu$) and the new photon and binding energy dependent spectrum denoted $\sigma(BE)$. In the low binding energy region of the spectrum (6.4-15 eV BE), the new method slightly improves the comparison with experiment, in the sense that the intensities of peaks C and D relative to peak B are better matched. However, the new method leads to a great overestimation of the intensity at high binding energies (above 15 eV BE) marked with an asterisk (*) in the figure. This failure could be due to the fact that the atomic orbital coefficients further away from the HOMO-LUMO gap do not add up to 1 as they should. When performing a population analysis, this problem is usually remedied by using the $c^2$ method, for example. The $c^2$ par-
titioning was used in the previous section (7.1), but not here.

In the case of NiPc, shown in Figure 7.3 b alongside two measurements performed at different photon energies, the experimental trends are reproduced, with the exception of the region between 8 and 9 eV BE, where the calculated spectra lack the intensity observed in the measurements. This, however, could be more a problem of the functional than a problem of the $\sigma(BE)$ method, since the calculated electronic structure of NiPc lacks eigenvalues in this region.

The approach presented here for calculating photon and binding energy dependent PES spectra performs similarly to the constant $\sigma$ approach of the previous section. It has the advantage that it gives access to the polarization vector of the electromagnetic radiation and to the direction of the ejected photoelectron, making possible the simulation of angle-resolved PES spectra. Further improvements could be achieved by considering a different partitioning of the KS orbitals and including a more accurate description of the photoelectrons [189,191].
8. Core Level Spectroscopies

Core level spectroscopies involve transitions of electrons to or from core states accompanied by either absorption of X-rays or emission. The focus here will be on absorption processes resulting in two types of outcomes: the photoionization of $1s$ core levels (as in XPS) or transitions from $1s$ levels to unoccupied molecular orbitals (as in NEXAFS). The following two sections will analyse in more detail the ways to calculate each of these spectroscopies. In order to illustrate the information content that they provide, alongside the strengths and limitations of the calculation techniques, we will apply them to investigate PC$_{60}$BM and its stability in organic photovoltaics. We have already met PC$_{60}$BM in Chapter 2. Briefly, it is one of the most widely used electron acceptors in OPVs and, similarly to other components of organic solar cells, it undergoes degradation when exposed to air, oxygen or water, especially under illumination [46, 60, 67, 68]. Possible degradation final products include PC$_{60}$BM dimers [64], molecules with oxygen [60], hydroxide or other groups adsorbed on the fullerene cage or PC$_{60}$BM films where oxygen or water have diffused into [46]. Since XPS and NEXAFS are sensitive to the chemical bonding and environment of a particular atomic species [180, 192], they can be used to pinpoint which of the possible products are more likely. We will limit the discussion to oxygen and we will attempt in the following to determine the changes to the O $1s$ XPS and NEXAFS and C $1s$ NEXAFS produced by the adsorption of oxygen in different configurations.

The subsequent sections are organized as follows: first the technique for calculating the particular spectroscopy is discussed and second, the influence of oxygen adsorption on the calculated spectrum of PC$_{60}$BM is examined.

8.1 X-Ray Photoelectron Spectroscopy

XPS has been already briefly introduced in Chapter 7. In essence, the photoinduced process is the same as was the case for the VB-PES: the absorption of a photon with enough energy results in the ionization of an electronic level. The difference between XPS and PES lays in the fact that the ionized electron originates from different molecular states. In the first, it is from a core level ($1s$, in our case), while in the second it is from the valence. In contrast to valence orbitals, which are delocalized and contain contributions from AOs of different atoms, core levels retain their atomic character and remain localized around the nucleus. In addition, different elements have very different binding
energies (and therefore IEs) for the core levels. For example, the measured binding energy of the C 1s state in various compounds has a value around 286 eV, while in the case of O, the 1s level has a binding energy of around 532 eV. Besides offering information on the atomic species present in a sample, XPS performed at a specific absorption edge (i.e., using photon energies tuned for a particular element and core level) gives insight into the chemical environment of the photoionized atom. Because the ionization involves, in this case, only one atomic species, there is no need to include the effects of the atomic photoionization cross-section as was performed for VB-PES. The main problem of calculating XPS spectra lays, therefore, only in finding accurate binding energies for the core levels in molecules. Since these levels are localized they are affected to a larger extent than valence levels by the shortcomings of the approximate xc-potential discussed in Chapter 4 (Problems of DFT). It is therefore not enough to simply construct the XPS spectrum using the eigenvalues of the core levels as obtained in a ground state (GS) calculation (initial state method [193, 194]).

One possibility to improve upon initial state binding energies is the transition state method proposed by Slater [195, 196]. This approach is based on the Janack theorem from equation 5.1, expressing the eigenvalue of a KS orbital, $\chi_i$, as the derivative of the total energy with respect to the occupation number $\theta_i$. By writing the Janack theorem for the total energy of the neutral system ($E_n$) and for the energy of the core-ionized one ($E_{n-1}$, having 1 electron removed from the 1s level), the IE of $\chi_{1s}$ can be calculated as [117]:

$$IE^{TS}_{1s} = E_{n-1} - E_n = \int_0^1 \varepsilon_{1s}(\theta) \, d\theta \quad (8.1)$$

where $\varepsilon_{1s}(\theta)$ represents the eigenvalue of the 1s orbital as a function of the fractional occupation $\theta$.

The first approximation to calculate the integral in equation 8.1 is to evaluate it at midpoint, i.e. at an occupation of $\theta = 0.5$. This is the main idea in the Slater transition state method: in order to determine the ionization energy of a particular state, simply perform the calculation using a fractional occupation of 0.5 for that state [117, 195, 196]. The eigenvalue $\varepsilon_{1s}(0.5)$ is the IE searched for.

Another approach is to directly calculate the total energy difference between the ground state and the system with an ionized core. This requires performing two SCF calculations, one to determine the ground state and one to determine the total energy of the system where the occupation of the 1s state has been set to 0. In this approach, called $\Delta$Kohn-Sham, the ionization energy is simply the energy difference between the ground state and the core ionized state:

$$IE^{\Delta KS}_{1s} = E^{KS}_{n} - E^{KS}_{n-1} \quad (8.2)$$

Since approximate xc-functionals are quite accurate in total energy differences, even the use of GGA provides good agreement in comparison to ex-
Table 8.1. Calculated $O^1s$ ionization energies for the $PC_{60}BM$ molecule. The first column contains experimental values from Paper III [199], while columns two, three and four contain the ground state (GS) eigenvalues, the transition state method (TS), and, respectively, the $\Delta KS$ ionization energies.

<table>
<thead>
<tr>
<th>Origin</th>
<th>Experiment (eV)</th>
<th>GS (eV)</th>
<th>TS (eV)</th>
<th>$\Delta KS$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-O-C</td>
<td>533.41</td>
<td>512.27</td>
<td>540.52</td>
<td>538.61</td>
</tr>
<tr>
<td>O=C</td>
<td>532.05</td>
<td>510.65</td>
<td>538.81</td>
<td>536.70</td>
</tr>
</tbody>
</table>

Figure 8.1. Molecular structure of (a) pristine $PC_{60}BM$ and several possible degradation final products containing (b)-(c) one single bonded oxygen atom, (d) two double bonded oxygen atoms or (e)-(g) two single bonded oxygen atoms on the $C_{60}$ cage. The broken C-C $\sigma$ bonds are marked with dotted lines. The figure is adapted from Paper III [199].

Experimental values. The values obtained by the three methods for the ionization energies of the $O^1s$ levels of $PC_{60}BM$ are listed in Table 8.1 in comparison to experimental values. All three calculations, initial state, transition state and $\Delta KS$, have been performed using the GGA exchange functional by Becke [104] and the correlation functional by Perdew [197], using the quantum chemistry software StoBe [198]. The details of the $\Delta KS$ calculation can be found in Paper III [199]. The ground state and transition state calculations are performed similarly, the only difference being the occupation of the $O^1s$ level (1.0 in GS and 0.5 in TS).

$PC_{60}BM$, represented in Figure 8.1 a, contains in its pristine form two oxygen atoms. One is single bonded to its C neighbours, represented in blue in the figure, and the other is double bonded, represented in purple. The two atoms have different ionization energies as shown in Table 8.1. The higher binding energy value corresponds to the single bonded oxygen, while the lower one to the double bonded oxygen. The eigenvalues determined by the ground state calculation are large underestimations of the measurements, as the calculated binding energies are approximately 20 eV lower than the experimental ones.
Figure 8.2. (a) Calculated O 1s XPS spectra of a PC_{60}BM molecule shown in comparison to the experimentally measured spectrum of a pristine PC_{60}BM film. (b) and (c) Calculated XPS spectra of PC_{60}BM with one oxygen atom adsorbed on the cage. The signal from the additional oxygen is marked in orange (for a 6-6 adsorption site) or in yellow (for a 5-6 adsorption site). (d)-(f) Spectra calculated for PC_{60}BM with two additional oxygen atoms adsorbed on the cage. The inset in (f) shows the bonding configuration before and after oxygen adsorption. The single bonds are in light gray, while the double bonds are marked in red.

The TS and ΔKS greatly improve the calculated ionization energies for the two oxygen atoms. While the TS calculated values are approximately 7 eV larger in binding energy, the ΔKS values overestimate the experiment by approximately 5 eV. Since the calculation is performed on a single molecule, this difference of 5 eV is due to the work function of the measured PC_{60}BM film, not accounted for in the calculation. The ΔKS method comes closest to the experimentally measured values and it has been used to perform the calculations reported in Paper III [199], some of which are shown in Figure 8.2.

The figure shows the calculated O 1s spectra of PC_{60}BM with one or two oxygen atoms adsorbed on the cage. The adsorption configurations are depicted in Figure 8.1, where the O atom can bind either at the intersection of two hexagonal faces of the fullerene cage (denote 6-6) or at the intersection of a hexagon and a pentagon (denoted 5-6). The 6-6 bonds between cage C atoms are shorter (1.4 Å) than the 5-6 bonds (1.45 Å) and can be therefore regarded as double bonds (marked in dark gray in Figure 8.1). The 5-6 bonds are marked in light gray and have single bond character [200, 201].

The XPS signals in Figure 8.1 have been calculated as described in Paper III [199]. Briefly, the ionization energies of all the O atoms in the particular configuration have been determined using the ΔKS method. A Gaussian broadening has been added on top of the discrete spectrum using Gaussian
functions of 1.0 eV FWHM and the spectra have been shifted by 5.2 eV towards lower binding energies in order to match the pristine PC60BM experimental first peak. After the shift, the theory-experiment comparison for the pristine molecule (Figure 8.2 a) is quite good, suggesting that the model used in the computation is appropriate.

From Figure 8.2 b and c, we see that the peak corresponding to the adsorbed oxygen is located in between the two pristine peaks. In the case of a 6-6 adsorption configuration, the additional oxygen contributes to the low binding energy region (peak 2), while a 5-6 configuration contributes to the high binding energy (peak 1). This is also the case for most configurations with two oxygens adsorbed, suggesting the possibility of fingerprinting the position in which oxygen adsorbs on the cage by O 1s XPS. The situation is, however, more complicated. One complication appears in configuration (5,6)-(5,6) PC60BM-O (Figure 8.1 e). Here, two oxygen atoms adsorb on 5-6 sites of the same hexagon, but their calculated signals, in Figure 8.2 f, contribute to peak 2 instead of peak 1, as did the rest of the 5-6 configurations. This unexpected result can be explained by analysing the bonding configuration of the C atoms at the adsorption site. The hexagon in question before and after oxygen adsorption is depicted as an inset to Figure 8.2 f. The double bonds (1.4 Å) are marked with red, while the single bonds (1.45 Å) are light gray. These assignments have been made based on the C-C bond lengths. When a single oxygen atom is adsorbed on a 5-6 site, the σ bond between the two C atoms at the adsorption site breaks (see Figure 8.1 c). A single 6-6 adsorption, on the other hand, breaks only the π component of the C-C double bond. However, when two oxygens adsorb at 5-6 sites of the same hexagon, the σ bonds which are expected to break do not. Instead, two π bonds break and the remaining one swaps to a neighbouring site, as depicted in the inset to Figure 8.2 f. The final chemical environment after adsorption is more similar to the 6-6 situation than to the 5-6 one. By considering all configurations (including the additional ones reported in Paper III [199]), the conclusion is that O 1s XPS can be used to gain interesting insights into the oxygen adsorption on the fullerene cage of PC60BM. Even if XPS alone cannot pinpoint to a particular type of adsorption (5-6 versus 6-6), it can determine if the C-C bond at the oxygen adsorption site has been broken or not.

As the results above show, an accurate enough theoretical description of the XPS spectroscopic process can help identify some of the chemical modifications taking place at molecular level. If combined with other spectroscopies (such as NEXAFS, discussed in the following), core-level XPS is a valuable tool for the characterization of chemical bonding in molecules.

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1Two cases are shown in Figure 8.2 d and e, but several other configurations are reported in the Supporting Information of Paper III [199].
8.2 Near-Edge X-Ray Absorption Fine Structure

A spectroscopy which can give complementary information to core-level XPS is the near-edge X-ray absorption fine structure (NEXAFS). If a sample is exposed to X-rays in a continuous spectrum, particular wavelengths are absorbed and result in absorption peaks which can be recorded. These peaks correspond to excitations from different atomic shells, as represented schematically in Figure 8.3 a and b. Depending on the excited atomic level, the absorption peaks are classified as K-edges (excitations from the 1s orbital), L-edges (excitations from 2s or 2p orbitals) and so on. By zooming in into a particular absorption edge (the K-edge, in our example), small oscillatory features become visible (Figure 8.3 c). The features in the near-edge region (up to 30-40 eV from the edge) are related to transitions to the unoccupied states of the system, while the features above the 30-40 eV threshold are related to interference effects with the wavefunction of the electron backscattered from neighbouring atoms [202]. In the following, we will address only the NEXAFS region of the spectrum and will be interested to calculate the 1s signal for organic molecules (like PC60BM) starting from the DFT electronic structure.

Since the NEXAFS peaks are directly related to transitions from the 1s state to unoccupied molecular orbitals, the first possible approach would be to calculate the transition probabilities using equation 6.10 and the KS-wavefunctions determined in a ground state calculation. However, this method results in a poor description of the NEXAFS energies and intensities [203–205]. The reason for this is the fact that the remaining electrons readjust to the newly created core hole and one of the approximations used to obtain equation 6.10 (the sudden approximation\(^2\)) is not valid for NEXAFS. One possible solution to overcome this problem and introduce in the calculation the effects of the core hole is to simply replace the core-excited atom with its heavier neighbour from the periodic table. The eigenvalues and eigenfunctions determined from a ground state calculation using the Z+1 atom can be then used to compute the transition probabilities of equation 6.10 and construct the NEXAFS spectrum [204, 206, 207]. Spectra computed in this way reproduce well experimental data in the case of many organic molecules [206], but the Z+1 approximation gives poor results in the case of metals, where the core hole is more delocalized.

A more rigorous way to include the relaxation effects due to the core hole is to use the transition state method of Slater [195, 196]. The calculation is performed by setting the occupation of the core level of interest to 0.5 and allowing the electronic structure to converge in the presence of this half core hole. The KS-orbitals and their corresponding eigenvalues are then used to

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\(^2\) The sudden approximation refers to the fact that the transition due to photo-absorption happens much faster compared to the relaxation times of the electrons not directly involved [28]. This allowed for the separation of the many-body wavefunction into an active one-electron part and a passive codeterminant in equation 6.9.
compute the transition probabilities. The Slater transition state method works well in general, but fails in the case of highly aromatic carbon-based systems, where the unoccupied levels are delocalized over the entire molecule. This is the situation for fullerenes, for example, where a full core hole on the C 1s level is required to completely account for relaxation effects [203].

In order to illustrate the performance of the full core hole approach, we analyse in the following the calculated C 1s NEXAFS spectrum of PC_{60}BM. The computational methods used are described at length in Paper I [199] and IX. Briefly, the relaxed molecular structure\(^3\) is used to determine the dipole transition matrix elements in StoBe [198]. This is done by performing a SCF calculation where the 1s orbital of a particular carbon atom in the molecule has an occupation of 0.0. The obtained unoccupied KS-orbitals, which are described in terms of linear combinations of GTOs (see Chapter 4, section 4.4.3) are the directly used in equation 6.10 alongside the 1s function. For non-polarized radiation, the polarization vector \(\varepsilon\) averages to a contribution of 2/3 as discussed previously[187, 209]. After separating \(\mathbf{r}\) in its x, y and z components, the total transition probability becomes:

\[
\Gamma_{i\rightarrow f} = N \Gamma^* \left( \left| \langle \chi_f | x | 1s \rangle \right|^2 + \left| \langle \chi_f | y | 1s \rangle \right|^2 + \left| \langle \chi_f | z | 1s \rangle \right|^2 \right) \delta_{E_f - E_{1s} - \hbar \omega} \tag{8.3}
\]

where all constants from the pre-factor in equation 6.10 have been included in \(N\).

Equation 8.3 is applied to determine the NEXAFS spectrum of each individual C atom by computing the transition probabilities from the 1s orbital to

---

\(^3\)Optimized in G09 [124] using the B3LYP functional [104] and the 6-31G(d,p) basis set [125].
Figure 8.4. (a) Calculated C 1s NEXAFS spectrum of PC$_{60}$BM shown in comparison to the measured spectrum of a pristine film. (b) Comparison between the measured NEXAFS of a pristine film and a photodegraded PC$_{60}$BM film exposed to oxygen under illumination for 19h. In addition, calculated results for two possible photodegradation final products, (6,6)-(6,6) PC$_{60}$BM-O and PC$_{58}$BM, are shown. (c) Difference between the experimental NEXAFS spectra of the pristine and photodegraded films, compared to the difference between pristine and (6,6)-(6,6) PC$_{60}$BM-O calculated results. (d) The same comparison in the case of PC$_{58}$BM. Based on results from Paper I [210] and IX.

all the unoccupied levels in the molecule. A variable Gaussian broadening is added to the each discrete spectrum (see Paper I [210] for more details) and the spectra are summed up together in order to obtain the NEXAFS of the molecule.

Figure 8.4 displays the calculated C 1s NEXAFS spectrum of PC$_{60}$BM in comparison to the measured total electron yield spectrum. The inset to the figure illustrates the electron yield technique. The basic idea is to detect the electrons emitted as a consequence of X-ray irradiation. After the photoexcitation of core 1s electrons to unoccupied levels, the core hole can be filled through Auger decay. By measuring the energies of the secondary ejected electrons (created by the scattering of primary Auger electrons in the sample), it is possible to reconstruct the NEXAFS spectrum [181]. Since only electrons
from the first few nanometres of the sample have energies high enough to escape and be detected, the TEY technique reveals information about the surface of the sample (the first 10 nm, approximately).

The comparison experiment-theory in Figure 8.4 is very good. The experimental peaks (denoted 1-4, and S) can be assigned to specific transitions by comparing the total calculated spectrum to spectra obtained by summing only the contributions from selected atoms in the molecule. In this way (see Paper I [210] for details), peaks 1, 2 and 3 are assigned to transitions from 1s orbitals of cage and phenyl atoms to unoccupied molecular orbitals. The shoulder to peak 1, denoted S in Figure 8.4 a, originates from cage C atoms as well. Peak 4 contains, in addition, contributions from sp³ hybridized carbons (the atoms at the attachment point and the remaining C atoms from the side-chain).

When pristine PC₆₀BM films are exposed to air under illumination, the C 1s NEXAFS spectrum undergoes significant changes even after only 30 minutes of exposure [68]. The changes entail the strong decrease of peaks 1, 2 and 3 and the increase of peak 4. In light of the assignments performed before and since a similar photodegradation is observed in the case of C₆₀, the deterioration mechanism must involve chemical modifications of the fullerene cage such that the sp² hybridized atoms become sp³ hybridized. However, the degradation process in air is likely very complex, so we will have a look instead at the degradation process during oxygen exposure. The measured C 1s NEXAFS spectrum of PC₆₀BM films exposed to oxygen under illumination (with light from a solar simulator) for 19 hours is shown in Figure 8.4 b in comparison to the pristine spectrum and calculated spectra of two possible degradation final products. One is the configuration from Figure 8.1 g, while the second, denoted PC₅₈BM, is, as the name suggests, a PC₆₀BM molecule where two C atoms have been removed from the cage. Figure 8.4 b shows only minor changes between the pristine sample and the 19h exposed one. A careful examination of the two spectra reveals that there are some differences such as a small decrease in peaks 1, 2 and 3, a slightly more noticeable increase in shoulder S and no obvious change in peak 4. The two modified PC₆₀BM structures selected here show similar trends as observed in the experiment when they are compared to the calculated pristine spectrum. In the calculated spectra, the changes from pristine to modified are, however, very large. We should have in mind that the calculations are performed on a single molecule and, therefore, the computed spectrum would only explain the measurement if all the molecules in the film underwent the (same) modification. It may very well be that only a fraction of the PC₆₀BMs experience the chemical change. In this case, the spectrum to be compared to the experiment should be a linear combination between the calculated pristine and modified configuration:

\[
S_{\text{exp}} = (1 - x) \cdot P + x \cdot M
\]

(8.4)

where \(S_{\text{exp}}\) represents the experimental photodegraded spectrum, \(P\) is the calculated NEXAFS of the pristine molecule, \(M\) is the calculated NEXAFS of
the modified configuration and $x$ represents the fraction of molecules which undergo degradation in the experiment.

Assuming further that the experimental pristine spectrum is fully described by the calculated one (i.e. all molecules in the film are in the pristine form)$^4$:

$$S_{\text{pristine}} = P$$

and taking the difference $S_{\text{pristine}} - S_{\text{exp}}$, we arrive at the following expression:

$$S_{\text{pristine}} - S_{\text{exp}} = x \cdot (P - M) \quad (8.5)$$

Equations 8.5 suggest that by analysing the difference spectra it is possible to find the more likely photodegradation final products and estimate how many of the molecules undergo the modification$^5$.

Figures 8.4 c and d show two examples of difference spectra. The spectrum in blue is the experimental one, obtained by subtracting the 19h exposed from the pristine. The spectra in black are obtained as the difference between the pristine calculated NEXAFS and the calculated spectrum of (6,6)-(6,6) PC$_{60}$BM-O and PC$_{58}$BM. The comparison between the intensities of the measured and theoretical difference spectra suggests that approximately 20% of the molecules at the surface of the PC$_{60}$BM film undergo chemical changes during exposure to oxygen under illumination. Both modifications are possible, since they compare similarly well to the measurement. Even if a particular configuration cannot be determined by this method alone, as discussed in Paper IX, the technique offers the possibility to discard some of the (many) possible photodegradation final products as unlikely. A combination of several different spectroscopies could, however, shed more light into the process.

We have seen throughout this section how a simple model for calculating the 1$s$ NEXAFS spectrum of organic molecules performs in comparison to experiment and what kind of information can be extracted from it. The approximations made should be, however, always kept in mind. The spectrum measured for a film was modelled by a single molecule calculation. This turned out to be an appropriate model, taking into consideration the good agreement between the calculated and measured spectra of the pristine PC$_{60}$BM. This might not be the case in other systems. Secondly, the relaxation effects due to the core-hole have been take into account only statically and relativistic effects have been completely excluded. This is not a problem for 1$s$ transitions, where the inclusion of the mass velocity and Darwin term result in a simple rigid shift [211], but these effects, especially spin-orbit coupling, become very important in the case of metal L-edges [177]. Other methods, based on many-body perturbation theory, are more appropriate in such situations. In addition,

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$^4$The assumption is supported by the very good comparison between experiment and theory in Figure 8.4 a.

$^5$Note the underlying assumption that only one modification takes place during exposure. This assumption is likely valid for the oxygen exposure case, but probably not valid for air exposure under illumination where strong changes to the NEXAFS spectrum are observed.
vibrational modes might influence the shape of the 1s NEXAFS [28], especially in gas and liquid-phase samples and methods to include vibrations into the calculated spectrum have been proposed [212–214]. Finally, different approaches have been formulated to calculate the X-ray absorption spectra, like, for example, the Mahan, Nozieres and de Dominicis (MND) theory, based on a Green Function method to treat dynamical screening effects. The method has been implemented in combination with plane-wave DFT [215–217].
9. Vibrational Spectroscopies

So far, we have only discussed the electronic part of the many-body problem first defined in equations 4.1 and 4.2 (Chapter 4, Section 4.1). The study of molecular vibrations brings us back to the full Hamiltonian and to the Born-Oppenheimer approximation, where the electronic and nuclear motions were separated. We will now take the other path opened by the BOA and focus on the nuclear problem alone. Assuming that the electronic part is solved, the nuclear Hamiltonian is described by equation 4.8, which we rewrite here:

\[
\hat{H}_n = -\sum_{I=1}^{N} \frac{\hbar^2}{2M_I} \nabla_I^2 + \mathcal{E}(\{R\}) \tag{9.1}
\]

where \(\mathcal{E}(\{R\})\) is the potential energy operator, containing an average contribution from the interaction with the electrons. If plotted against the nuclear coordinates \(\{R\}\), \(\mathcal{E}\) represents the potential energy surface which we have already encountered in Part I (Figure 1.2).

There are three possible types of nuclear motion: translations, rotations and vibrations. Considering the motion in the coordinate system of the center of mass (CM)\(^1\), there are 3 possible translations, 3 rotations and 3\(N\)-6 vibrations\(^2\). Leaving translations out of the discussion and by further considering that the vibrational and rotational motions as separable (approximation valid for small displacements with respect to the equilibrium geometry [90]), it is possible to write an eigenvalue equation independently for the vibrational and rotational components, respectively [218]. In a semi-classical approach and by considering only harmonic motion, the problem of molecular vibrations can be re-written in the form of a secular equation [218, 219]:

\[
\det |V_q - \lambda T_q| = 0 \tag{9.2}
\]

where \(V_q\) is the potential energy matrix, \(T_q\) is the kinetic energy matrix and \(\lambda\) will correspond to a vibrational frequency. Specifically, the matrix elements in the two energy matrices are defined as [218]:

\[
v_{ij} = \frac{1}{2} k_{ij} q_i q_j \tag{9.3}
\]

\[
t_i = \frac{1}{2} M_I \frac{\partial q_i}{\partial t} \tag{9.4}
\]

\(^1\)There are 3 coordinates for each nucleus, resulting in a total of \(3N\) degrees of freedom.

\(^2\)In the case of linear molecules, there are only 2 true rotations and, therefore, the number of vibrations is \(3N-5\)
where \( q_i \) is a nuclear degree of freedom (for example, the \( x \) coordinate of one of the nuclei), \( k_{ij} \) is the force constant determined as the second derivative of the potential with respect to \( q_i \) and \( q_j \) and \( M_i \) is the mass of the nucleus to which the \( q_i \) coordinate belongs.

In practice, the equation is re-written by multiplying it with the inverse of the kinetic energy matrix and by switching to internal coordinates [218, 220], the equation becomes:

\[
T_q^{-1}U_q\mathbf{L} = \mathbf{L} \Lambda
\]  

(9.5)

where \( \mathbf{L} \) are normal mode vectors and \( \Lambda \) is the eigenvalue matrix\. Using equation 9.5, the vibrational eigenvectors and eigenvalues can be determined by numerical diagonalization procedures.

Finding the vibrational frequencies solves, however, only half of our problem. The second step is to determine the Infrared (IR) and Raman transition probabilities. These are directly related to two properties of the molecule: the dipole moment (\( \mu \)) and the polarizability (\( \alpha \)). The dipole moment is a vector describing the charge distribution in the molecular system, while the polarizability is a tensor, representing the shape and volume of the electronic cloud [218]:

\[
\mu = \mu_x \hat{x} + \mu_y \hat{y} + \mu_z \hat{z}
\]

(9.6)

\[
\alpha = \begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{pmatrix}
\]

(9.7)

where \( \hat{x}, \hat{y} \) and \( \hat{z} \) are the unit vectors of the coordinate axes.

The dipole moment is responsible for IR transitions, while the polarizability is responsible for Raman transitions [218]

\[
\Gamma_{IR} = \left| \langle v_f | \mu | v_i \rangle \right|^2
\]

(9.8)

\[
\Gamma_{Ram.} = \left| \langle v_f | \alpha | v_i \rangle \right|^2
\]

(9.9)

where \( v_i \) and \( v_f \) are the vibrational initial and final states and \( \mu \) and \( \alpha \) are components of the dipole vector and, respectively, the polarizability tensor.

Around the equilibrium geometry and for small atomic displacement, each component of the polarizability tensor or the dipole vector can be expanded in a Taylor series:

\[
\mu = \mu_0 + \left( \frac{\partial \mu}{\partial q} \right)_0 q + \frac{1}{2} \left( \frac{\partial^2 \mu}{\partial q^2} \right)_0 q^2 + ...
\]

(9.10)

\[
\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial q} \right)_0 q + \frac{1}{2} \left( \frac{\partial^2 \alpha}{\partial q^2} \right)_0 q^2 + ...
\]

(9.11)

\(^3\)The off-diagonal elements of \( \Lambda \) are zero and the diagonal elements are \( \lambda \), the vibrational frequencies.
The first term, \( \mu_0 \) results in a zero matrix element. Similarly, \( \alpha_0 \) gives rise to the Rayleigh scattering\(^4\). The third terms in both equations are very small and can be neglected [218]. It is the first partial derivatives (\( \partial \mu / \partial q \) and, respectively \( \partial \alpha / \partial q \)) which give rise to non-zero matrix elements and therefore to the IR and Raman intensities. The complete way to determine these intensities is described in detail in reference [218].

Since the vibrational frequencies are directly related to the atomic species which compose the molecule and are sensitive to chemical changes, determining the IR and Raman spectra for the photodegradation final products can help support the conclusions that might be drawn from the core-level spectroscopies. An example of the changes which the spectra can undergo is shown in Figure 9.1. The spectra shown in the figure were determined using the

\(^4\)Rayleigh scattering is the elastic scattering of light by the molecule. The incident and scattered radiation have exactly the same wavelength.
B3LYP functional [114] and the 6-31G(d,p) basis set [125] and were calculated for pristine PC$_{60}$BM and the modified structure displayed in Figure 8.1 d. The modified structure, denoted PC$_{60}$BM=O$_2$, contains two double bonded O atoms on the fullerene cage, where a C-C bond breaks at the adsorption site. Since the harmonic approximation becomes worse for higher frequencies, the spectra have been scaled by a factor of 0.9614 [221] for frequencies above 1000 cm$^{-1}$. In addition, a Gaussian broadening of 10 cm$^{-1}$ FWHM has been added to the discrete spectra, which were also normalized to the set maximum.

The calculated IR and Raman spectra of the pristine and modified PC$_{60}$BM present differences that can be used to fingerprint the PC$_{60}$BM=O$_2$ structure. Since the intensities have been normalized to each individual set maximum, comparing peak intensities does not tell too much. However, when new peaks appear in the spectrum they can be used to identify the modified configuration from the pristine.

In the case of the IR spectra, in Figure 9.1 a, the most interesting peaks are those centred around 1720-1750 cm$^{-1}$. The pristine PC$_{60}$BM has only one peak in this region, at 1755 cm$^{-1}$ assigned to a stretching vibration of the C=O from the side-chain. In the PC$_{60}$BM=O$_2$ structure, a peak appears at 1751 cm$^{-1}$ with a small shoulder at 1728 cm$^{-1}$. Interestingly, none of these two corresponds to the pristine normal mode. Instead they are due to stretching vibrations (in-phase, 1751 cm$^{-1}$, and out-of-phase, 1728 cm$^{-1}$) of the adsorbed oxygen atoms.

In the case of the Raman spectra, PC$_{60}$BM=O$_2$ develops new peaks in many parts of the frequency window shown. Most notable are the peaks at 1751 cm$^{-1}$ and 1728 cm$^{-1}$, which appear in an empty region of the pristine PC$_{60}$BM spectrum. These two are very good candidates for fingerprinting the modified structure. In addition, a peak at 1412 cm$^{-1}$ becomes dominant in the PC$_{60}$BM=O$_2$ spectrum. It is related to stretching vibration of the C-C bonds at the oxygen adsorption site and could be also used for fingerprinting.

We have seen that the vibrational spectroscopies can give some insights into the chemical modifications of PC$_{60}$BM. The theoretical modelling of vibrational spectra can help identify one modification or the other by predicting which peaks would be present in the experiment. However, it is not always easy to assign measured peaks to calculated ones. This is the case for large non-symmetric molecules where the spectra can be very rich. In addition, the error introduced by the harmonic approximation at high frequencies can further complicate the assignment process. Vibrational IR and Raman results can support and complement other spectroscopies in order to provide insightful information regarding chemical modifications of organic molecules.
Part IV:
Final Remarks
Throughout this thesis we analysed some of the possible theoretical tools to describe spectroscopic processes in the case of organic molecules. The methods were all based on density functional theory, introduced in Part II, Chapter 4. The problem of theoretically describing a spectroscopic process was divided into two sub-problems: (I) the description of the electronic structure and (II) the description of the particular electronic or vibrational process giving rise to the spectroscopic signal. For (I), we analysed the performance of different exchange and correlation functionals and discussed possible alternatives to improve upon the results. In particular, the DFT+U method was used to better describe the strongly correlated electrons of the central metal in transition metal phthalocyanines. DFT+U was employed for single molecules, but its main utility for organics is in modelling molecules adsorbed on surfaces or deposited between metal electrodes. These are typical situations in molecular electronics and spintronics applications and the inclusion of the substrate in the calculation is the natural step to take from here.

In addition to the DFT+U method, the performance of hybrid functionals, which include a fixed percentage of exact exchange added to the GGA functional, was analysed in comparison to valence band photoelectron spectroscopy measurements. Within a rigid energy shift, the electronic structure provided by the hybrids describes very well the measured data. Optimally tuned range separated hybrid functionals, where the interaction between electrons is optimally partitioned into a short-range and a long-range contribution, were also analysed. These functionals overcome the necessity to apply a rigid shift in the binding energy scale by improving the description of the asymptotic behaviour of the \( xc \)-potential. The calculated eigenvalues of the the HOMO and the orbitals in the frontier region were in very good agreement with the experimentally measured peak positions.

The second step, (II), was analysed in detail for several spectroscopies in Part III. The spectroscopies included were the VB-PES, core level XPS and core level NEXAFS, Infrared and Raman. In the case of the VB-PES, the calculated spectrum was obtained either by multiplying each atomic component by the corresponding atomic photoionization cross-section or by calculating the dipole transition probability from a molecular orbital to a photoelectron described as a plane-wave. Both methods gave comparable results for the TMPcs, but the second one opens the possibility of calculating angle-resolved PES spectra. The inclusion of the light polarization direction and angular distribution for the emitted photoelectrons is a very interesting future project,
where the symmetry of molecular orbitals could be analysed in connection to calculated peak intensities and measured angle-resolved data.

The core level soft X-ray spectroscopies were analysed in connection to the stability of PC$_{60}$BM, an electron acceptor molecule in polymer solar cells. The XPS ionization energies were determined as energy differences between the calculated ground state and the core-ionized system ($\Delta$Kohn-Sham). The NEXAFS spectrum was modelled by calculating the dipole transition probabilities in the presence of a core hole. Both types of calculations were performed using GGA and the resulting spectra were in good agreement with the experiments. On the basis of these outcomes, further calculations were performed to predict how the XPS and NEXAFS spectra would look like for PC$_{60}$BM if oxygen atoms would be adsorbed on its fullerene cage. These results can help identify the bonding configuration of oxygen on the fullerene cage after an oxidation process. In the case of NEXAFS, an interesting future project is to calculate the transition probabilities using the electronic structure determined by hybrid or OT-RSH functionals. It would be very interesting to see how the $xc$-functional influences the calculated spectra.

Finally, the vibrational IR and Raman spectroscopies were shortly discussed in Chapter 9. The changes in the calculated spectra for one possible final product of PC$_{60}$BM photodegradation were identified in comparison to the pristine calculated spectra.

It is our hope that a combination of different spectroscopies could shed more light on the degradation of fullerenes and that our calculated results can help pinpoint to a specific photodegradation pathway. The addition of valence band calculations can explain the trends observed in NEXAFS, while an interesting continuation of this project is to include other fullerene derivatives, different polymers and the polymer:fullerene couple.
Två av de viktigaste materialtekniska utmaningarna under det kommande århundradet är att utveckla nya material för produktionen av ren energi och för elektroniska och spintroniska komponenter. Vissa organiska material, såsom fulleren, organiska polymerer och organiska molekyler med metallcentra är lovande kandidater för dessa två områden. Fördelen med organiska material är att de kostar lite, är flexibla och vanligtvis är miljövänliga.

En grundlig förståelse av de elektroniska egenskaperna hos dessa organiska molekyler är därför mycket viktigt. Experimentellt studeras ett materialets elektronstruktur genom att analysera hur materialet växelverkar med elektromagnetsk strålning, såsom synligt ljus, röntgenstrålar eller infrarött ljus. Ljusabsorptionen leder till övergångar mellan molekylära energinivåer, vilket avspeglas i materialets absorptionsspektrum. Eftersom dessa energinivåer är kvantifierade (dvs. de har endast särskilda diskreta värden), kan endast specifika våglängder av strålnings absorberas. Detta medför att interaktionen mellan den elektromagnetsiska strålningen och molekylen ger detaljerad information om de elektroniska energinsnivåerna, vibrationstillstånden och om möjliga kemiska interaktioner.

I syfte att förklara och tolka experimentellt uppmätta spektra krävs en bra teoretisk beskrivning av den specifika spektroskopin. Denna avhandling analyserar några av de teoretiska modellerna för att beskriva elektronisk- och vibrationsspektroskop, särskilt fotoelektronspektroskop av valensbandet, röntgenfotolektronspektroskop, en typ av röntgenabsorptionsspektroskop som kallas NEXAFS, infraröd- och Raman-spektroskop. De teoretiska modellerna används för att beräkna spektra av ftalocyanin med övergångsmetallscentrum och ett fullerenderivat som kallas PC<sub>60</sub>BM.


Den andra molekylen som studeras är fullerenederivatet PC<sub>60</sub>BM som används som elektronacceptor i organiska solceller. En organisk solcell är sammansatt av två aktiva material: en organisk polymer som absorberar synligt
ljus och en fulleren som leder bort de exciterade elektronerna. Figuren nedan visar hur denna process fungerar.

Polymerens elektroniska nivåer markeras som HOMOd (den sista ockuperade orbitalen) och LUMOd (den första tomma orbitalen), medan fullerenens elektroniska nivåer markeras som HOMOa och LUMOa. Ljusabsorptionen leder till att elektronen från HOMOd exciteras till LUMOd. LUMOa har lägre energi än LUMOd och därför hoppar elektronen vidare från polymeren till fullerenen. I fullerenområdet förflyttar den fria elektronen sig till zinkoxid-skiktet och ger upphov till en elektronisk ström.

12. Acknowledgements

Nothing of this would have been possible if Barbara, Biplab and Olle would not have given me the chance to come to Uppsala. I am really really grateful to you for giving me this chance and for helping me along the way! Barbara, thank you very very very very very much for all the help, support and encouragements! You managed to perfectly combine guiding me with letting me pursue my own ideas.

To Ellen, I am very grateful to you for having included me in the PCBM project. It has been extremely interesting and it allowed me to learn a lot. I am immensely grateful to you and Leif for the incredible work you have done in the last weeks in order to help me with the thesis.

To Carla, alongside Roberta, Ieva and Teng, it has been great to work with each of you in the different TMPcs projects. I hope our paths will meet again.

To my academic brother, Johann, thank you for everything: for ideas, discussions and medicine! Som it has been a pleasure to have you as a collaborator! I am very grateful to you, Heike, first of all for the delicious cakes! but also for all the help with the different manuscripts and for fruitful discussions.

Of course, Uppsala would not have been as nice and funny without the special people in the group. I refer, of course, to the Brain trainer, who has been training my brain from the moment I arrived. Jonathan, you know what I mean, don’t you? Besides this terrible joke, I am very grateful for all your help with my questions about the thesis, for your encouragements and for the inspiration! Without you, this thesis would have looked very different! Sara, it was great to go swimming together! A big thank you to my grandson! May you be very very happy and ride your motorcycle in beautiful places. Master Raghu, thank you for your words of wisdom and for asking me daily about my ethics course homework. Master Shifu, I wish you all the best and hope our paths will meet more often. Vancho, I think of you every day at lunch time and I thank you. A thank you to Diana for passing by and asking me if I want coffee. A very warm thank you to Inka for the juggling brakes, that, unfortunately, became rare when we started to work hard. Tack, Patrik, för all din hjälp och för din falkblick! To Beatriz for the chocolate :). To Sumanta for the skateboard signs! To the scattering events who sent me to Uppsala!

Un mulțumesc din suflet domnului profesor Vasile Chiș care mi-a deschis acest drum. Mulțumesc mama și tata!

Ciok, ti ringrazio per tutto il tuo aiuto! Si tu non c’eri, io non avrei avuto sopravissuto a tutto questo...
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