Memory Effects on Iron Oxide Filled Carbon Nanotubes

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Licentiate Thesis

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ISBN 978-91-7501-885-0

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Tryck: Universitetsservice US-AB
Abstract

In this Licentiate Thesis, the properties and effects of iron and iron oxide filled carbon nanotube (Fe-CNT) memories are investigated using experimental characterization and quantum physical theoretical models. Memory devices based on the simple assembly of Fe-CNTs between two metallic contacts are presented as a possible application involving the resistive switching phenomena of this material.

It is known that the electrical conductivity of these nanotubes changes significantly when the materials are exposed to different atmospheric conditions. In this work, the electrical properties of Fe-CNTs and potential applications as a composite material with a semiconducting polymer matrix are investigated. The current voltage characteristics are directly related to the iron oxide that fills the nanotubes, and the effects are strongly dependent on the applied voltage history. Devices made of Fe-CNTs can thereby be designed for gas sensors and electric memory technologies.

The electrical characterization of the Fe-CNT devices shows that the devices work with an operation ratio (ON/OFF) of 5 µA. The applied operating voltage sequence is −10 V (to write), +8 V (to read ON), +10 V (to erase) and +8 V (to read OFF) monitoring the electrical current. This operation voltage (reading ON/OFF) must be sufficiently higher than the voltage at which the current peak appears; in most cases the peak position is close to 5 V. The memory effect is based on the switching behavior of the material, and this new feature for technological applications such as resistance random access memory (ReRAM).

In order to better understand the memory effect in the Fe-CNTs, thesis also presents a study of the surface charge configuration during the operation of the memory devices. Here, Raman scattering analysis is combined with electrical measurements. To identify the material electronic state over a wide range of applied voltage, the Raman spectra are recorded during the device operation and the main Raman active modes of the carbon nanotubes are studied. The applied voltage on the carbon nanotube G-band indicates the presence of Kohn anomalies, which are strongly related to the material’s electronic state. As
expected, the same behavior was shown by the other carbon nanotube main modes. The ratio between the D- and G-band intensities (I_D/I_G) is proposed to be an indicative of the operation’s reproducibility regarding a carbon nanotube memory cell. Moreover, the thermal/electrical characterization indicates the existence of two main hopping charge transports, one between the carbon nanotube walls and the other between the filling and the carbon nanotube. The combination of the hopping processes with the possible iron oxide oxygen migration is suggested as the mechanism for a bipolar resistive switching in this material.

Based on these studies, it is found that the iron oxide which fills the carbon nanotube, is a major contribution to the memory effect in the material. Therefore, a theoretical study of hematite (i.e., α-Fe_2O_3) is performed. Here, the antiferromagnetic (AFM) and ferromagnetic (FM) configurations of α-Fe_2O_3 are analyzed by means of an atomistic first-principles method within the density functional theory. The interaction potential is described by the local spin density approximation (LSDA) with an on-site Coulomb correction of the Fe d-orbitals according to the LSDA+U method. Several calculations on hematite compounds with high and low concentrations of native defects such as oxygen vacancies, oxygen interstitials, and hydrogen interstitials are studied. The crystalline structure, the atomic-resolved density-of-states (DOS), as well as the magnetic properties of these structures are determined.

The theoretical results are compared to earlier published LSDA studies and show that the Coulomb correction within the LSDA+U method improves both the calculated energy gaps and the local magnetic moment. Compared to the regular LSDA calculations, the LSDA+U method yields a slightly smaller unit-cell volume and a 25% increase of the local magnetic for the most stable AFM phase. This is important to consider when investigating the native defects in the compound. The effect is explained by better localization of the energetically lower Fe d-states in the LSDA+U calculations. Interestingly, due to the localization of the d-states the intrinsic α-Fe_2O_3 is demonstrated to become an AFM insulator when the LSDA+U method is considered.

Using the LSDA+U approach, native defects are analyzed. The oxygen vacancies are observed to have a local effect on the DOS due to the electron doping. The oxygen and hydrogen interstitials influence the band-gap energies of the AFM structures. Significant changes are observed in the ground-state energy and also in the magnetization around the defects; this is correlated to Hund’s rules. The presence of the native defects (i.e., vacancies, interstitial oxygen and interstitial hydrogen) in the α-Fe_2O_3 structures changes the Fe–O and Fe–Fe bonds close to the defects, implying a reduction of the energy gap as well as the local magnetization. The interstitial oxygen strongly stabilizes the AFM phase, also decreases the band-gap energy without forming any defect states in the band-gap region.
For those who spent their time and efforts to understand nature.
Preface

The following papers are included in this Licentiate thesis:


The author has contributed to the following research, which is not discussed in this Licentiate thesis:


## Contents

**Abstract** ................................................................................................................................. iii
**Preface** ......................................................................................................................................... vii

**Chapter 1** ................................................................................................................................... 11

- Introduction ................................................................................................................................. 11
- Memory devices ............................................................................................................................ 13
- Semiconductor memory devices ............................................................................................... 13
- Resistive memories ...................................................................................................................... 17

**Chapter 2** ................................................................................................................................... 21

- Carbon nanotubes ....................................................................................................................... 21
  - Process and synthesis of carbon nanotubes ........................................................................... 23
  - The multi-walled filled carbon nanotube .............................................................................. 24
  - The iron and iron oxide carbon nanotubes ........................................................................... 24

**Chapter 3** ................................................................................................................................... 27

- Iron oxides ................................................................................................................................... 27
- Hematite ...................................................................................................................................... 28

**Chapter 4** ................................................................................................................................... 31

- Theoretical approach .................................................................................................................. 31
- The many-particles problem ....................................................................................................... 32
- Density functional theory ........................................................................................................... 35
- The Kohn-Sham approach .......................................................................................................... 36
- The local spin density approximation ....................................................................................... 38
- Correction to the local spin density approximation ................................................................. 39
- Summary ...................................................................................................................................... 40

**Acknowledgments** ...................................................................................................................... 41

**Summary of papers and author’s contribution** ........................................................................ 42

**Paper 1** ...................................................................................................................................... 49

- Iron- and iron oxide-filled multi-walled carbon nanotubes: electrical properties and memory devices .................................................................................................................. 49

**Paper 2** ...................................................................................................................................... 63
Resistive switching in iron oxide-filled carbon nanotubes........................................63

Paper 3 ........................................................................................................................................85

Effects of native defects on the structural and magnetic properties of hematite
$\alpha$-Fe$_2$O$_3$..................................................................................................................................85
Chapter 1
Introduction

The development of societies is usually linked to the ability of their members to produce and manipulate materials to meet their needs. For instance, ancient civilizations were designated by their level of development in relation to a specific material, such as the Stone Age and the Bronze Age.

Nowadays, we are experiencing quite a similar trend in our society; however, this is not related to a single material, but rather to the ability to work with very small materials. Recently, it was shown that certain materials present new and improved properties when their sizes are controlled on a scale of a few atoms, typically close to $10^{-9}$ m (called a nanometer). This gives rise to a new science and technology field denominated nanoscience and nanotechnology, which involves nanostructures and nanoparticles.

Many technological improvements triggered by nanoscience have been developed over the last decade, such as in antibacterial clothes [1], internal drug deliveries [2], high-strength composites [3], energy storage [4], various sensor applications [5, 6], field emission displays [7, 8], radiation sources [9], nanometer-sized semiconductor devices [10, 11, 12], probes [13, 14] and many more. The great success of nanotechnology is that new materials and/or novel material structures either allow the development of new properties or improve their old properties, simply by reducing the feature size. In most cases, this is due to a reduction in particle size which increases the total active area and, consequently, enhances the chemical reactivity of the material [15]. When the volume of the particle is reduced, the proportion of atoms on the surface changes...
drastically. For example, in a cube that has an edge of length \(a\), if the atom has an average diameter \(d\), then \(a/d\) atoms can be placed on an edge; following this idea the number of atoms in the cube can be estimated by \((a/d)^3\). On each face there will be \((a/d)^2\) atoms; as the cube has six faces, the cube must have \(6(a/d)^2\) atoms on its surface. Thus, the fraction of atoms on the surface can be roughly estimated by \(6(d/a)\). In a solid cube with 1 cm\(^3\) of volume, the percentage of surface atoms is of \(6 \times 10^{-6}\%\), when \(10^{-10}\) m is assumed as the atom diameter. However, the ratio of the surface atoms of the solid reaches \(6\%\) when the volume of the cube is reduced to \(10\) nm\(^3\). The increase of the atoms proportion on the surface is responsible for the material’s surface energy modification. This energy is related to the difference between the bulk and the material’s surface, as the atoms on the surface are in a low state of order due to the missing surrounding atoms. In order to illustrate this fact, one can imagine an atom surrounded by other 12 atoms in a faced-centered cubic unit cell (FCC), where the bond energy is shared equally with all atoms. Here, it is important to consider a simple model with a solid composed of spherical molecules in a close-packed arrangement. If three of these atoms are removed (in this case, it is a simple way to illustrate the creation of a surface), then new energy will be divided between nine atoms, which creates an excess of energy in this new configuration. This is a simple model that does not consider many other possible configurations. However, it is possible to demonstrate that the surface’s energy is higher when the surface total area increases. This extra energy is unnoticeable in systems of ordinary size, as the number of atoms on the surface is an insignificant fraction of the total number of atoms. In order to explain this difference, the total energy can be written as a simple contribution of the volume atoms and the surface atoms:

\[
E = E_v V \left(1 + \frac{E_s A}{E_v V}\right). \tag{1.1}
\]

Here, \(V\) and \(A\) are the volume and area, \(E_v\) and \(E_s\) are the energy per unit volume and the energy per unit area. In order to increase the second term of the equation by 1%, one can estimate the minimum particle size needed. Assuming that \((E_s/E_v) \approx 10^{-10}\) [16] the \(A/V\)-ratio reaches a value higher than \(10^8\). Considering the cubic particle mentioned above and the ratio given by \(A/V = 6/a\), the particle size can be calculated with an edge of \(6 \times 10^{-8}\) m. It is possible to conclude, even using this simple model, that a particle size of 60 nm is needed in order to achieve a 1% increase in total energy. Based on to many studies that consider quantum mechanical effects, it is well known that some material properties are modified substantially even when the particle size is higher than the number present above.
The surface energy is a key factor for many material properties such as electrical and thermal transport, reactivity and chemical stability, among others. Thus, this reduction in the particle size to the nanoscale increases significantly the material’s surface. Therefore, it is possible to conclude that many material properties may be enhanced by a reduction in particle size to the nanoscale.

Nanoscience has made a great contribution to many improvements in electronic devices. In this licentiate we discuss experimentally and theoretically the contribution of a nanomaterial, more specifically carbon nanotubes filled with metal iron oxide (see: Chapter 2). An overview of these devices is provided in the following text.

Memory devices

Every day we interact with all different kinds of electronic devices such as electronic chips, memories, memory cards, computer processors, sensors, light emission diodes (LEDs), lasers, photodetectors, and solar cells, among others. Electronic memories are the most common devices applied to many industrial and commercial activities.

An electronic device that is able to retain information for a certain period of time is called a memory. Memories in electronic devices can be magnetic or semiconductor. The difference between them is the physical property used to store information. In magnetic memories, the material’s magnetic moment is utilized in order to store information, while in electronic memories, also known as solid state memories, information is recorded by electronic charges. Some of these memories are called non-volatile devices [16], and they can store information indefinitely until it is deleted or some new information is recorded. Since the present Licentiate thesis focuses on semiconductors memories, that type of devices will be discussed further.

Semiconductor memory devices

One of the advantages of semiconductor memories is the possibility to construct many memory cells in a small area using high speed recording /reading. Storage time depends on the structural configurations of the device. Memories which present a millisecond storage time are called volatile, and, in most cases, in these devices the memory bit needs to be refreshed repeatedly. Moreover, there are non-volatile semiconductor memories that can store information for many years, even when the power supply is shut down.
The field effect transistor (FET) is a basic element in semiconductor memory. The FET is an electronic device constructed with a three terminal (electrodes) geometry. The device uses the semiconductor properties of the material, usually silicon or germanium, to control the flux of charge between the electrodes. There are several FET architectures, with small variations in the structure that increases their functionality.

Currently, metal-oxide semiconductor (MOS) technology completely dominates the fabrication of memories because of its capacity of integration, high density, low cost, and low power consumption. The silicon MOS transistor consists of a source and a drain terminal separated by a channel and a gate terminal on top, separated by an insulating silicon dioxide (SiO$_2$), which induces the semiconductor by the applied voltage to allow the charges to flow between the source and the drain.

![Schematic view of a metal oxide semiconductor (MOS) transistor](image)

**Fig. 1.1:** A schematic view of a metal oxide semiconductor (MOS) transistor $n$-type. The back regions are the electrical metal contact, the hatched area is the $n$-type doped region whereas the inversion layer is the region where the substrate $p$-type will change for an $n$-type in the presence of the applied field.

The characteristics of the semiconductors ($p$-type or $n$-type)\(^1\) define the direction of the electric current. Fig. 1.1 shows a schematic view on an $n$-type MOS transistor. For the $p$-type transistor device, the direction of the current is reversed.

Generally, a memory cell consists of a capacitor and one transistor in series. Fig. 1.2 shows a single memory cell, discharged (a) with non-recorded information and charged (b) with recorded information. It is formed by a metal-oxide-semiconductor field-effect transistor (MOSFET) in series with a capacitor.

The source and gate electrical contacts are used as connections between address electrodes. The region $n+$ (predominance of electrons) of the drain makes the

---

\(^1\) According to the model of conduction in semiconductors, the material $p$-type carries the majority of the holes and the $n$-type carries the majority of the electrons.
connection in series with the capacitor \( p \)-type (predominance of holes) and the metal film; they are separated by a dielectric layer. The terminal of the capacitor is grounded in most memory types.

The storage of information is represented by a ‘1’ bit. This record of information is accomplished by applying a voltage on the gate to create a depletion layer allowing the flow of charges between the source and the ground. By applying the current between these two terminals, the charges will access the capacitor and charge it. Information has been written by charging the capacitor.

The voltage on the gate must be large enough to create an inversion layer between the source and the drain. After the application of the pulse, the inversion layer of the transistor disappears, but the charge remains in the capacitor. The time limit, in the order of a few milliseconds (ms), depends on the thermal generation of carriers.

![Fig. 1.2: Memory cell formed by a MOSFET in series with a capacitor. (a) Before applying voltage the information is not recorded. (b) After applying a voltage pulse the information is recorded while the capacitor is charged.](image)

Memory cells are connected to memory logic integrated circuits using metal meshes to address stored information. Fig. 1.3 represents an electronic microchip of RAM (random access memory) which allows higher speed of recording and reading than the serial magnetic.

The mesh has a matrix format, where rows and columns are the connections between word line (WL) and bits line (BL), respectively. Source terminals are connected to the BL and the capacitors are connected to the ground. This arrangement allows random access to any address, or cell, by applying two pulses of voltage.

Structural changes in the cell base, as shown in Fig. 1.2, can give rise to a number of other types of memories [17], volatile or non-volatile, with different functions and applications. Fig. 1.4 shows the classification of memories.
Volatile memories may be of SRAM type (static random access memory) or of DRAM (dynamic random access memory) type. The memory shown in Fig. 1.3 is dynamic and the structure always needs feedback via electrical pulse. On the other hand, the static memory can store information for years, if it is fed with a minimum applied field.

The group of non-volatile memories is larger and can be subdivided into two groups, named ROM (read only memory), used only for reading, and RAM (random access memory, used for both recording and reading. Each of these types of memories has different functionality. For some circuits it is important to have information stored without the possibility of being erased. One example is the EEPROM (electrically erasable programmable read only memory) that can be both ROM and RAM, which is used only for reading; still, the information can be recorded electrically.

There are also other types of memory: PROM (programmable read only memory) and EPROM (electrically programmable read only memory). These memories can be recorded electrically, but can only be completely erased using external electric current, UV radiation or X-ray. In summary, these memories can be constructed for different needs and with different applications. Nanotechnology can contribute to the improvement of all kinds of memories; some works have pointed out that carbon nanotubes [11, 18, 19], molecules [20, 21] and nanoparticles [22] can increase the efficiency and the density of memory cells, thus reducing the device sizes or increasing the capacity to store information.

Fig. 1.3: A schematic model for a matrix of an integrated circuit formed by cells of RAM memory. It describes transistors in series to capacitors, in which the source of the transistor is connected to bit lines (BL), while the gate of the transistor is connected to word lines (WL).
Resistive memories

Resistive memories (memristive) are a new class of non-conventional memories in which the operation is based on the non-linear conductivity presented by metal oxides or organic compounds. Basically memristive devices have an electrical resistance that can retain a state of internal resistance based on the history of the applied voltage and current. One advantage of these devices is the possibility to assemble it in a simple capacitor-like (Fig. 1.5a and 1.5b) structure which leads to an increase in memory cell density (Fig. 1.5c) by using a matrix as assembly. Another interesting feature is the high values of ON/OFF ratios, which achieve more than 10-fold of difference together with the fast time response (approximately 1 nanosecond) [24].

Many different materials have been studied as memristive device, and most of them use a simple metal-insulator-metal structure. Among the most frequently studied materials are the metal oxides (e.g. SiO [25], NiO [26], Fe$_2$O$_3$ [27], TiO$_2$ [28] and SrTiO$_3$ [29]). In regard to the current versus voltage (I-V) behavior of memristive memories, they can be classified as unipolar and bipolar. The unipolar resistive switching is commonly described by a non-dependence of the polarization, being related only to the intensity of the applied voltage. On the contrary, the bipolar behavior shows a dependence of the applied voltage direction in order to generate a lower resistance state (LRS); without this opposite voltage, the device will remain in a high resistance state (HRS).

The driving mechanisms for these changes in material conductivity have been commonly described by a filamentary conduct path (filamentary-type) or oxygen ion migration (ion-type). This filamentary-type includes the generation
of small conducting paths (Fig. 1.5a) through a soft dielectric breakdown which leads to LRS. During the operation process, these filaments are interrupted near to the metal electrode by a thermal redox or anodization process [30]. The bipolar behavior originates from the oxygen migration motivated by a high applied voltage (Fig. 1.5b). The voltage application forces the ions (oxygen or vacancies) to move from one direction to another resulting in a non-linear conductivity which, can lead the material to a LRS.

![Memristive cells: (a) filamentary-type where the white lines crossing the electrodes are the filament path generated by an external applied voltage; (b) ion-type where the small bolls on the top represent the oxygen vacancy ions; (c) representation of many memory cells assembly as a matrix where the memory cell can be accessed using the Bit line and the Word line.](image)

Although each material and device assembly needs an in-depth study in order to understand the mechanism behind its electrical behavior, the general explanation for the electrical switching in these devices is straightforward. During the studies of Chua L. O. on the mathematical relations between two terminal devices in early 1970 [30], he noticed that there were four different circuit elements: inductor, resistor, capacitor and memristor, which had been unknown until then. The memristor should present a memristance ($M$) which tailors the charge flux ($d\varphi$) dependence of charge ($q$) with the relation $d\varphi = Mdq$. For linear elements $M$ is a constant and is equal to resistance. However, when $M$ is dependent on $q$, the above relation can present a non-linear behavior, which leads to interesting potential applications such as memory devices.

Nanoscale devices should show interesting features regarding the memristance due to its large non-linear ionic transport. In fact, the reduced particles size increases the electric field effect on the ionic charges. Regarding this fact,
Strukov et al. [31] demonstrated that the conductivity state changes ($w$) should be dependent of the dopant mobility ($\mu$), the semiconductor thickness ($D$) and the low resistance ($R_{ON}$) by the equation:

$$w(t) = \mu \frac{R_{ON}}{D} q(t).$$  \hspace{1cm} (1.2)

These two terminal switching behaviors are often found in many materials and device assemblies, like organic films [32] and metal oxides [33] among others. These non-linear charge flux behavior detected in many two-terminal devices are now understood as memristive devices are dependent on the ionic charge movement. These properties allow new applications for these materials in integrated circuits as non-volatile or semi-non-volatile memories, which can harness the voltage applied intensity to modulate the charge transport.
Chapter 2
Carbon nanotubes

Like diamond, graphite, fullerene and other structures shown in Fig. 2.1, carbon nanotubes (CNTs) can also be considered an allotropic form of pure carbon, as its composition contains only carbon-carbon bonds.

Several carbon nanotube applications have been suggested [34-37], especially due to its combined hardness, strength and electrical conduction properties [36, 38]. For example, the use of carbon nanotubes has been recommended in gas sensors [5], LEDs [7, 39], displays [8], photodetectors [40, 41], field-effect transistors [11], nanofibers for building muscles and synthetic ultra-resistant composites [42] and many other applications that use the properties of carbon nanotubes individually or together with other materials.

Carbon nanotubes can be divided into two classes: those that are formed by a single layer of graphene, called single-walled nanotubes (SWNTs) and those that are formed by several layers of graphene, called multiple wall nanotubes (MWNTs). In Fig. 2.2, the main types of nanotubes are presented.

Single-walled carbon nanotubes are divided into three categories, depending on the angle that the graphene sheet was rolled: armchair, zigzag or chiral. The winding angle determines whether nanotubes are metallic conductors or semiconductors. These three categories have different properties: all armchair have metallic properties and the other two structures can be metallic or semiconducting, depending on the diameter of the nanotube.

The difference in the properties of this carbon allotropic form lies on how their atoms are arranged. In a carbon-carbon structure, the atoms have a covalent bond with different $sp^3$, $sp^2$, $sp$ hybridizations. For instance, the $sp^3$, which has a full filled orbital $p$, is responsible for the hardness of the diamond. The other carbon structures as graphene, fullerenes and carbon nanotubes have in most
cases the $sp^2$ hybridization with a delocalized electron, creating the possibility of electrical conduction.

The MWNTs with a structure free of defects have electronic properties similar to the SWNT. The reason for this is that the electronic conductance occurs preferentially in the longitudinal direction of the nanotube, and there is only a small interaction between the walls. This property allows the nanotube to support a high level of the electric current.

MWNTs thermal conductivity measurements have shown an excellent heat transport rate (> 3000 W/mK), higher even than the natural diamond and the graphite (both 2000 W/mK) [43].

Superconducting properties were also observed for SWNT with tube diameters of $d = 1.4$ nm at temperatures of $T \approx 0.55$ K. A smaller tube diameter ($d = 0.5$ nm) allows superconductivity at a higher temperature ($T \approx 5$ K) [44].
Industry and scientists have invested great effort on the large scale production of SWNTs or MWNTs, thereby reducing the final cost to make viable its industrial application. The methods of manufacturing carbon nanotubes are voltaic arc-discharge, high power laser ablation and chemical vapour deposition. The diameter of these nanotubes ranges from 0.4 nm to 3 nm for SWNTs and from 1.4 nm to 100 nm for MWNTs. However, all these growth techniques generate nanotubes with a high concentration of impurities, as well as amorphous carbon material. These impurities, or amorphous carbon structures, can be removed with an acid treatment. However, this treatment involves additional damage to the nanotubes, which introduce other impurities or defects in the material.

A challenge for nanotube manufacturers is to achieve a synthesis in which all nanotubes have the same electrical properties. This is a major problem for the manufacturing of devices, because every synthesis batch will contain both metallic and semiconducting nanotubes, which differ in their electrical properties.

**Fig. 2.2:** Schematic representation of the structures of carbon nanotubes (a) armchair, (b) zigzag and (c) to chiral SWNTs. (d) Image of a SWNT made of a tunnelling microscope shows the angle of twist of the chiral nanotube of 1.3 nm in diameter. (e) Image of a MWNT made in a transmission electron microscope in high resolution mode (HRTEM). (f) Computer simulation of the structure of a MWNT. The figure is comes from ref. 36.
Chapter 2 Carbon Nanotubes

The multi-walled filled carbon nanotube

One of the most promising structural advances for CNTs is to fill their cavities with different functional materials such as metals and oxides. This results in novel synergistic CNT properties. In this case, the CNT develops a shield which increases the environment protection and lifetime. Another improvement occurs in the crystalline and in the wire form of the inner material. An example is the possibility to manipulate the filled-carbon nanotube whenever the inner material presents magnetic properties, another is to use the gas affinity of the inner material protected by the carbon nanotube. A common and successful method to produce filled nanotubes with chemical vapor deposition (CVD), where the pyrolysis of metallocenes like Fe, Co or Ni occurring in two stages. Each kind of CNT needs specific processes with different parameters and structural modifications to the CVD furnace.

The iron and iron oxide carbon nanotubes

Carbon nanotubes with multiple layers (MWNTs) filled with iron oxide used in this work were manufactured by the CVD technique at the Group of Materials Chemistry laboratory, located at the Federal University of Paraná [45]. The manufacturing process of a carbon nanotubes involves the pyrolysis of an organometallic precursor (ferrocene) heated in a furnace at 300 ºC, where sublimation occurs. Through a flow of argon, the ferrocene is transported to a second oven at 900 ºC, where the pyrolysis occurs, and thereby forming carbon nanotubes with multiple layers and filled with iron oxide.

The nanotubes prepared by this method have good performance contrary to other techniques due to the fact that the catalyst ferrocene is both a source of carbon for the formation of the nanotube and the metal precursor to its own formation. Of all the mass produced, approximately 4% is amorphous carbon, 36% corresponding to an iron species and the remainder (60%) corresponds to nanotubes filled with iron oxide or iron [45].

Fig. 2.3 shows images of the transmission electron microscopy (TEM) carried out on nanotubes produced by this technique. In (c) and (d), images are shown in a high resolution mode, where it is possible to measure the distance between each feature wall of the MWNT. Image analysis showed the presence of a large quantity of MWNTs, of which 87% were completely filled with iron oxide. The length of these nanotubes varies from a few nanometers up to 10 µm, and the diameter ranges from 8 nm to 140 nm (and 50% had diameters between 23 and 48 nm).
Fig. 2.3: Transition electron microscopy (a,b) and high resolution transition electron microscopy (c,d) of the Fe-CNT. The image (d) is the increase of the region target in the (c). Images from ref. 45.
Chapter 2 Carbon Nanotubes
Chapter 3
Iron oxides

Iron oxides are common compounds found in many places like the soil and rocks dispersed in water, as well in living organisms. They are composed of iron (Fe) and oxygen (O) and/or hydroxyl (OH). Usually iron oxides have a crystalline structure such as a hexagonal close packing (hcp) or a cubic close packing (ccp). The structure of these iron oxides is commonly determined by X-ray diffraction or high resolution electron microscopy. The structures are also confirmed by first-principles calculations. There are many applications involving iron oxides in various technological fields like electrochemistry, biology, chemical sensors, and magnetic and electronic devices [46, 47].

In iron oxide structures, iron 3d-orbitals have a large influence on the electronic and magnetic features of the material. An orbital is a region in space occupied by one single electron or a pair of electrons with different spin. There are five different available d-orbitals, each one with a different orientation in space. According to Pauli’s exclusion principle, the orbital is occupied one by one, first with one spin direction and then with the next spin direction. If the number of electrons is not exactly two times the number of orbitals, one or more orbitals will have a single electron (called an unpaired electron) and this defines many important characteristics of the material. The Fe$^{3+}$ ion has five unpaired d-electrons and Fe$^{2+}$ has two paired and four unpaired electrons.

---

A crystalline structure is a periodic repetition as a unit cell with a parallelepiped form. The needed required are the dimensions of the unit cell a, b, and c as well as the angles between this sides α, β, and γ.

Hexagonal structure (hcp) where a = b ≠ c and α = β = 90°, and γ =120°.

Cubic structure where a = b = c and α = β = γ = 90°. There are three possibilities of packing: simple cubic (sc), face-centred cubic (fcc) and body-centred cubic (bcc).

Spin (intrinsic angular moment) is the part of total angular momentum of a particle, atom, nucleus, etc, that is distinct from the orbital angular momentum.
Chapter 3 Iron oxides

There are sixteen iron oxides (Tab. 3.1). The basic structure units are Fe (O, OH)$_6$ or Fe (O)$_4$, and the various oxides differ in their atomic arrangement. In some cases, anions (Cl$^-$, SO$_4^{2-}$, and CO$_3^{2-}$) participate in the structure, including new properties.

**Tab. 3.1 Iron oxides [50]**

<table>
<thead>
<tr>
<th>Oxide-hydroxides and hydroxides</th>
<th>Oxides</th>
</tr>
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<tbody>
<tr>
<td>Goethite $\alpha$–FeOOH</td>
<td>Hematite $\alpha$–Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Lepidocrocite $\gamma$–FeOOH</td>
<td>Magnetite Fe$_3$O$<em>4$ (Fe$^{\text{II}}$ Fe$</em>{\text{III}}^3$ O$_4$)</td>
</tr>
<tr>
<td>Akaganéte $\beta$–FeOOH</td>
<td>Maghemite $\gamma$–Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Schwertmannite Fe$<em>{16}$O$</em>{16}$ (OH)$_y$ (SO$_4$)$_z$·nH$_2$O</td>
<td>$\beta$–Fe$_2$O$_3$</td>
</tr>
<tr>
<td>$\Delta$–FeOOH</td>
<td>$\varepsilon$–Fe$_2$O$_3$</td>
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<tr>
<td>Feroxyhyte $\delta$–FeOOH</td>
<td>Wüstite FeO</td>
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<td>High pressure FeOOH</td>
<td></td>
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<tr>
<td>Ferrihydrite Fe$_5$HO$_8$·4H$_2$O</td>
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<tr>
<td>Bernalite Fe(OH)</td>
<td></td>
</tr>
<tr>
<td>Fe(OH)$_2$</td>
<td></td>
</tr>
<tr>
<td>Green Rusts $\text{Fe}<em>{\text{II}}^{	ext{III}}$Fe$</em>{y}$ (OH)$_{3x+2y-2}$ (A$^-$)$_x$; A$^-$$=\text{Cl}^-; \frac{1}{2}\text{SO}_4^{2-}$</td>
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</table>

The range of iron oxides is very wide and the material properties are very different for each structure. This Licentiate we will focuses on the hematite $\alpha$–Fe$_2$O$_3$ and magnetite Fe$_3$O$_4$, as it will be shown that they are of particular interest for electromagnetic applications.

**Hematite**

The iron oxide phase hematite (Greek: hema = blood) is a very common mineral found in many places in the world. Its smaller structure is composed of two irons and three oxygen atoms, and is represented by $\alpha$–Fe$_2$O$_3$. Many applications have been proposed for this mineral as catalysts in chemical reactions [48] magnetic and electronic devices [49], sensor devices [50] as well as a promising
material for nanotechnology applications [51, 52]. Its complex structure has motivated many studies over the years to understand their properties which, until now, are not entirely explained [53, 54].

The hematite unit cell structure is hexagonal with the following parameters: \( a = 0.5034 \text{ nm}, \ c \approx 134 \text{ Å} \) and \( \gamma = 120^\circ \) [55]. It is also possible to write in the rhombohedral coordinated with \( a = 0.5427 \text{ nm} \) and \( \alpha = 55.3^\circ \). Fig. 4.1 shows the atomic arrangement for the \( \alpha-\text{Fe}_2\text{O}_3 \) unit cell in (a) hexagonal and (b) rhombohedral symmetry.

This oxide presents antiferromagnetic behavior below 956 K (\( T_c \)) and it is only weakly ferromagnetic at room temperature. In addition, its growth is highly dependent on the external conditions. Scanning tunneling microscopy and low energy diffraction studies showed that structures such as \( \text{FeO (111)} \) can co-exist with \( \alpha-\text{Fe}_2\text{O}_3(0001) \) [56]. The agreement between theoretical studies and experimental results has proved that the insulating characteristic of this material is strongly dependent on the unit cell volume due to the strong interaction between Fe 3\( d \) and O 2\( p \) orbitals [57].

![Unit cell representation ball-and-stick model](image)

**Fig. 3.1:** Unit cell representation ball-and-stick model, the colours light and dark grey represent the iron and the oxygen atom respectively; (a) rhombohedral; (b) hexagonal close pack (hcp) to \( \text{Fe}_2\text{O}_3 \).
Chapter 3 Iron oxides
Chapter 4

Theoretical approach

In a first-principles (parameter-free) calculation, a solid material is a system of many interacting particles, involving about $10^{22}$ nuclei and $10^{23}$ electrons per cube-centimeter. It is an enormous challenge to solve this many-particle problem. Density functional theory (DFT) is a conceptual approach to describe the many-particle system by its total density alone, instead of describing all single particles. The DFT tries to describe the total energy as functional of the charge density, however, to date an explicit expression of this relation does not exist. Therefore, the DFT needs to be complemented by a method to describe interactions between particles. The DFT together with the Born-Oppenheimer approximation and the Kohn-Sham equation is a method to map the many-particle problem into many single-electron equations with an effective potential. The great novelty of this approach is the possibility to reconstruct most material in a rather simple way through the fundamental arrangement of its particles and, thereby, be able to understand the properties of materials.

A solid material calculation is successful when the prediction made by the theoretical study is in agreement with the experimental results. DFT in combination with the Kohn-Sham equation is in principle exact if the effective potential is described exactly. However, finding the exact potential is not only a simple task since the number of particles involved is too large, but also because the explicit expression of the effective potential should be able to describe various types of materials. Therefore, it has been impossible to reach an analytical solution for the mathematical equation of the potential. In order to make it possible to know the exact properties of different materials, and to date
there, is no exact description of this potential. Instead one has to rely on some approximation to the many-electron interaction. The most commonly used approximation is the local spin density approximation (LSDA). The LSDA relies on the interactions in a homogeneous electron gas, and these interactions are also expected to be important in a solid. In the LSDA, the effective potential describes rather well various properties of numerous types of material, and the LSDA has been very successful method over the last 40 years. Many theoretical methods have been used to improve the LSDA to better describe the materials’ behavior. One of the relatively easy-to-understand idea to improve the LSDA is to replace some part of the interactions in a homogeneous electron gas with interaction of local atoms. This method involves self-interaction-like correction of the Coulomb potential. This on-site orbital dependent correction potential $U$ is spatially more localized and more anisotropic, which is important for better describing atomic-like $d$-states. Although the LSDA+U method is a relatively simple method, it has the main advantage of not increasing the computation time or disk space requirements. The method has been very successful to describe a metallic system involving, for instance transition metal semiconductors.

The many-particles problem

The objective of the quantum mechanics theory is to describe the many-particles interaction system of a wave function $\Psi_{\text{total}}(r_1, \ldots, r_n, R_1, \ldots R_t)$ for the whole system of materials, involving complex internal interaction potential as well as an external potential. The total wave function includes the wave functions of all electrons and the wave functions of all nuclei. The most important quantity to calculate is the ground-state total energy ($E_{\text{total}}$) of the system. Once the ground-state properties are known, it is possible to estimate other properties and reconstruct realistic system with respect to experimental measurements.

The fundamental equation related to the wave function and the total energy is the Schrödinger’s many-particle equation. The eigenvalue equation of the Schrödinger equation is written as:

$$H_{\text{total}} \Psi_{\text{total}} = E_{\text{total}} \Psi_{\text{total}}.$$

(4.1)

The Hamiltonian operator ($H_{\text{total}}$) describes the interactions between the particles as well as the influence of external potential. Solving this equation will generate the eigenfunctions and total energy eigenvalues of the system. In theoretical modeling of materials, which is considered Coulomb-like interactions in the electron-nucleus system with $n$ electrons and $N$ nuclei, the Hamiltonian is written as:
Chapter 4 Theroretical approach

\[ H_{\text{total}} = -\sum_{i}^{\infty} \frac{\hbar^2}{2m_0} \nabla_i^2 + \frac{1}{2} \sum_{i\neq j}^{\infty} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{N} \frac{Z_a e^2}{|\mathbf{r}_i - \mathbf{R}_a|} \]

(4.2)

Here, the electron’s mass and position are represented by \( m_0 \) and \( \mathbf{r}_i \) respectively, and the nucleus is represented by \( M_a \) and \( \mathbf{R}_a \), respectively. The first term of the Eq. (4.2) represents the electronic kinetic energy of the electrons and the second term is the repulsive electron-electron correlation interactions. The third term is the attractive electron-nucleus interaction and the two remaining terms are the kinetic energy of the nuclei and the repulsive nucleus-nucleus interaction relation.

Although it appears straightforward to solve the equation, as the Hamiltonian is known, the number of interacting particles in a solid material makes the problem very complex and an analytical solution without approximations unattainable in this case. Therefore, if we were able to calculate the wave function of one particle per pico-second, the total calculation process for a small unit of one material will still last for more than a billion years due to the number of particles. Moreover, the Hamiltonian works on the single-particle wave functions, while we do not know how the full wave function \( \Psi_{\text{total}}(\mathbf{r}_1, \ldots, \mathbf{r}_n, \mathbf{R}_1, \ldots, \mathbf{R}_t) \) depends on the single-particle wave functions. Therefore, it is necessary to make suitable approximations to solve this many-particle problem.

The first approach is to employ the Born-Oppenheimer approximation (BOA). In this approach the nuclei are assumed to have fixed positions. This assumption is based on the fact that the electrons have a much higher smaller mass (\( m_e \approx 9 \times 10^{-31} \) kg) than the nuclei mass (\( M_a \approx 2 \times 10^{-27} \) kg for one proton). If a nucleus is moved suddenly, one can assume that all electrons respond instantaneously on this nucleus motion. Thus, the nuclei can be treated as an external potential acting on the electrons. As a consequence of this approximation the total wave function of the Eq. (4.1) can be split in an electronic part and a nuclei part, that is:

\[ \Psi_{\text{total}} = \Psi_e \times \Psi_n. \]

(4.3)

Thereby, it is possible to simplify the Hamiltonian equation using only the terms related to the electron \( H_e \) and an operator \( H_n \) for the nuclei potential. The electronic Hamiltonian is now expressed as

\[ H_e = -\sum_{i}^{\infty} \frac{\hbar^2}{2m_0} \nabla_i^2 + \frac{1}{2} \sum_{i\neq j}^{\infty} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{N} \frac{Z_a e^2}{|\mathbf{r}_i - \mathbf{R}_a|}, \]

(4.4)

\[ H_e \Psi_e = E_e \Psi_e, \]
which is the electronic part of the Schrödinger equation. Moreover, within the regular BOA, the $H_{\text{nuclear}}$ for the nuclei potential can be shown to be in the form of

$$
H_n = -\sum_{\alpha}^{N} \frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2 + \frac{1}{2} \sum_{\alpha \neq \beta}^{N,N} \frac{Z_{\alpha}Z_{\beta}e^2}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} + E_e,
$$

(4.5)

$$
H_n \Psi_n = E_{\text{total}} \Psi_n,
$$

which couples the electronic part to the full total energy.

Within the BOA, the many-particle problem (involving both electrons and nuclei) has been divided into two coupled equations, one for the electrons $\Psi_e(r_1, \ldots, r_n)$ and one for the nuclei $\Psi_n(R_1, \ldots, R_N)$. The electronic Schrödinger equation can be solved independently of the nuclear part. Thereby, one only has to know the positions of the nuclei and not the nuclear wave function in order to calculate the electronic wave function and the electronic energy. This simplifies the calculations considerably.

However, even with the BOA the electronic Hamiltonian problem is still impossible to solve. There stills a too large number of electrons-electrons interactions in the second term of the Eq. (4.4), and the Hamiltonian works on the single-electron wave functions, while we do not know how the full wave function $\Psi_e(r_1, \ldots, r_n)$ depends on the single-particle wave functions.

The former problem, that is the large number of electrons, is a numerical problem that will briefly be discuss later. The latter problem, that is how full wave function may depend on the single-particle wave functions, is a conceptual problem. There are two main approaches to solve this. In one approach which tries to describe or guess $\Psi_e$ in terms of the single-electron wave functions $\psi_j(r)$. This is the Hartree and Hartree-Fock based approach. The main difference between the Hartree and the Hartree-Fock is that in the Hartree-Fock the determinant of one-electron wave functions is antisymmetric according to the Pauli’s exclusion principle. Thereby, the so called exchange interaction is included. Still the electron-electron correlation is not properly described with the original Hartree-Fock wave function.

In the second approach one tries to find an expression for the electronic Hamiltonian that can operate directly on $\Psi_e$. That is, to find an explicit relation between $\Psi_e$ and $E_e$ without the knowledge of single-electron wave functions $\psi_j(r)$. The density functional theory is such an approach. This approach is the foundation for the first-principles method used in this thesis.
Chapter 4 Theoretical approach

Density functional theory

The first idea behind the density functional theory (DFT) comes from 1927, when Thomas and Fermi \cite{58, 59} suggested the use of the charge density to calculate the electronic structure of the atoms. This idea is a generalization of the Thomas-Fermi’s idea for an interaction many-body system under an external potential $V_{\text{ext}}(\mathbf{r})$. However, this idea was not theoretically consolidated. In the middle of 1960 \cite{60}, Hohenberg and Kohn derived the basic theory of DFT, and the theory is based on two main theorems.

Accordingly to the first theorem of Hohenberg-Kohn (HK), any property of a system that has a measurable quantity is a unique functional of the density $\rho(\mathbf{r})$. That is, the density of the system determines all ground state properties of the system. Importantly, the total ground-state energy $E_0 = E[\rho_0]$ where $\rho_0(\mathbf{r}) = |\Psi_0(\mathbf{r}_1, \ldots, \mathbf{r}_n)|^2$ is the ground-state density of the electronic wave function. As a consequence, the theorem states that only one potential corresponds to the ground-state density $\rho_0(\mathbf{r})$.

The second theorem states that a universal function of the energy, for any external potential $V_{\text{ext}}(\mathbf{r})$, has its local minimum in the ground state density $\rho_0(\mathbf{r})$. This means that one can find the ground-state energy by minimizing the total energy with respect to the density; $E[\rho_0] < E[\rho]$. In fact, these are the fundamental explanations about these theorems, and an extensive demonstration of these ideas can be found in the literature, for instance in the Refs. 61 and 62.

These two HK theorems make it possible to find all ground-state properties based only on the density of the electrons. In Eq. (4.6), for example, the electronic Hamiltonian part of the electronic density is written as:

$$<\Psi_e | H_e | \Psi_e > = E[\rho(\mathbf{r})].$$

(4.6)

The innovation behind these ideas is the change of parameter. Now, we have universal functional for any system that is described in terms of the density. The electronic wave function that contains the parameters of all electrons positions (3×$n$ parameter for a system with $n$ electrons) is not needed, but only need 3 parameters of the density $\rho(\mathbf{r})$. This is a significant simplification. However, these ideas do not represent a practical solution to the problem, but rather indicate a possibility.

The first theorem states that there exists a functional $E[\rho]$ that is unique. That is, there exists an expression $E[\rho]$ that depends only on the density $\rho(\mathbf{r})$ and the external potential $V_{\text{ext}}(\mathbf{r})$. The functional can be divided into $E[\rho] = T[\rho] + U[\rho]$ which contain the kinetic and potential parts, respectively. However, the problem is not know what this expression explicitly. The expression is expected to be complex because it should be able to describe any type of many-electron system (solids, liquids, molecules, etc).
The task is therefore to find a way to calculate the total energy $E[\rho] = T[\rho] + U[\rho]$. In 1965, using the fundamental idea behind the DFT, Kohn and Sham (KS) proposed a method to solve this issue. The method is based on an ansatz to replace the original many-body problem through auxiliary independent electron wave functions [63].

**The Kohn-Sham approach**

The Kohn-Sham approach assumes that there is a system of independent auxiliary electronic-like wave functions that has the same ground-state density as the true interacting system [61]. That is, if this constructed system has the same ground-state density as the true system, then the energy shall be equal to the true total ground-state energy according to the DFT.

The approach starts with the true energy functional $E[\rho] = T[\rho] + U[\rho]$ that contains the kinetic and potential parts, respectively. As we cannot calculate $T[\rho]$ and $U[\rho]$ because we have not the expression for those functionals. Instead, we calculate something similar to those functionals and subsequently try to model the remaining part separately. That is, for independent (but interacting) electrons we know how to calculate the kinetic $T_s$ and potential $U_s$ energies. We therefore rewrites the true energy functional as $E[\rho] = T_s[\rho] + U_s[\rho] \{ T[\rho] - T_s[\rho] \} + \{ U[\rho] - U_s[\rho] \}$, and then define the exchange-correlation function as $E_{xc}[\rho] = \{ T[\rho] - T_s[\rho] \} + \{ U[\rho] - U_s[\rho] \}$. Then, we have $E[\rho] = T_s[\rho] + U_s[\rho] + E_{xc}[\rho]$, and the unknown part is now $E_{xc}[\rho]$. The advantage of this method is to use an equivalent independent-electron system to describe main parts of the kinetic and potential energies, and the remaining complex many-electron terms are included in the exchange-correlation $E_{xc}[\rho]$ functional of the density $\rho(\mathbf{r})$. Thus, we can assume that the KS approach works not with independent particles but rather with interacting density.

So, we have

$$E[\rho] = T_s[\rho] + U_s[\rho] + E_{xc}[\rho], \quad (4.7)$$

and we shall use independent single-electron auxiliary electronic-like wave functions $\psi_j(\mathbf{r})$. The full wave function of independent wave function is described by the Hartree approach $\Psi_e(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \psi_1(\mathbf{r}_1) \cdot \psi_2(\mathbf{r}_2) \cdots \psi_j(\mathbf{r}_j) \cdots \psi_n(\mathbf{r}_n)$ with the density $\rho(\mathbf{r}) = \sum |\psi(\mathbf{r})|^2$. Moreover, the kinetic and potential energies of a system with independent single-electrons are:
Chapter 4 Theoretical approach

\[ T_j[\rho] = \sum_j \int \psi^*_j(r) \left( -\frac{\hbar^2}{2m} \nabla^2 + V_{ext}(r) \right) \psi_j(r) dr \] (4.8)

\[ U_s[\rho] = \frac{1}{2} \int \int \frac{e^2}{|r-r'|} \rho(r') \rho(r) dr dr' + \int V_{xc}(r) \rho(r) dr . \]

Here, the external potential is the potential from the nuclei. Moreover, the first term in the potential energy is the Hartree energy and self-interaction is not included in that term.

Eqs. (4.7) and (4.8) describe the total energy. These expressions are exact if \( E_{xc}[\rho] \) is exact. To derive the single-electron equations we vary the total energy with respect to the wave functions \( \psi_j(r) \). That is, we change the single-particle wave functions to minimize the total energy. Then, we will find the ground state density and then the exact ground-state energy. When we vary the single-particle wave functions we have to ensure that the wave functions are still normalized so that each electron has a possibility equal to 1 to be found in the system.

\[ \frac{\delta}{\delta \psi_j} \left\{ E[n] - \sum_i \varepsilon_i \left[ \int \psi^*_i \psi_j \, dr - \delta_{ij} \right] \right\} = 0. \] (4.9)

From the mathematics of the functional derivatives, the result is

\[ \left\{ -\frac{\hbar^2}{2m_c} \nabla^2 + \int \frac{e^2 n(r')}{|r-r'|} dr' + V_{xc}(r) \right\} \psi_j(r) = \varepsilon_j \psi_j(r) , \] (4.9)

where \( V_{xc} = \partial E_{xc}/\partial \rho \) is the exchange-correlation potential. Eq. (4.9) is the so-called single-electron KS equation. Combining Eq. (4.9) with Eq. (4.7) one can show that the total energy can be written as a function of the density \( \rho(r) \) and can be described by making visible all the well-known terms of the independent-particles system:

\[ E[\rho] = \sum_j \varepsilon_j - \frac{1}{2} \int \int \frac{e^2}{|r-r'|} \rho(r') \rho(r) dr dr' - \int V_{xc}(r) \rho(r) dr + E_{xc}[\rho]. \] (4.10)

To clarify the terms of this equation, the first term is the single-electron energies for the independent-electrons of the KS approximation. The external potential is not directly present in the equation because it is included in the single-electron energies. The second term represents the Hartree electron interaction energy. These first two terms are both included in the total energy in the regular Hartree approximation. The two remaining terms are corrections to the Hartree approximation, and they make the expression in principle exact. Here, \( V_{xc} = \partial E_{xc}/\partial \rho \) and \( E_{xc} \) are the exchange-correlation potential and energy, respectively. These terms represent the many-electron exchange and correlation effects.

Eqs. (4.9) and (4.10) still have the problem that one has to solve the KS equation for \( 10^{23} \) electrons for a system with the volume of one cube-centimeter (see...
earlier discussion). The solution to this problem is to use the Bloch function \( \psi_j(r) \rightarrow \psi_{n,k}(r) = \exp(ik \cdot r) \cdot u_{b,k}(r) \) where \( k \) describe discrete \( k \)-states in the reciprocal space, and \( b \) indicates band index in the first Brillouin zone. The wave function and it energy for \( \{ b; k' \} \) and \( \{ b; k \} \) are similar if \( k' \approx k \). Therefore one has to calculate only a few \( k \)-states (typically 10–100 instead of \( 10^{23} \)) and then interpolate to describe the remaining states.

The calculation of \( E_{xc} \) is still a difficult task, and many research efforts have been employed to obtain a good approximation for this term. The most commonly used approximation is the local spin density approximation.

The local spin density approximation

The fundamental idea of the KS approach is to split the true energy functional into an independent-electron kinetic energy, the long-range Hartree terms and the remaining exchange-correlation functional. The exchange-correlation energy is unknown, so it has to be approximated. The simplest way to approximate the exchange-correlation is to assume electronic density \( \rho \) for the homogeneous electron gas. Once this approach is assumed, the exchange-correlation energy needs to be described accurately for the homogeneous electron gas. The homogeneous has been parameterized by quantum Monte Carlo simulation \([64]\).

Normally, one expresses this energy in energy per particle \( E_{xc}[\rho] = \int \rho(r) \varepsilon_{xc}[\rho] \, dr \).

The exchange and correlation can then be represented as:

\[
\varepsilon_{xc}(\rho) = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \cdot \rho^{1/3} + \left\{ \begin{array}{ll}
A \ln r_s + B + Cr_s \ln r_s + Dr_s & r_s \leq 1 \\
\gamma \ln(1 + \beta_1 r_s + \beta_2 r_s^2) & r_s > 1
\end{array} \right.
\]  

(4.11)

where \( r_s = (3/4\pi \rho)^{1/3} \) and the constant density is \( \rho = n/\Omega \) for \( n \) electron in the volume of \( \Omega \). In the local density approximation (LDA), one assumes that this expression can also be used for non-homogenous densities by simply replacing \( \rho \) with \( \rho(r) \). This is of course an approximation to the true exchange-correlation of non-homogenous electron gas, but the analytical solution exchange and correlation for relation energy can be known with great accuracy for each atom, which is considered a homogeneous electron gas, using the quantum Monte Carlo simulation or other mathematical method.

A more general solution for this exchange-correlation functional is to allow the spin-up density to be different to the spin-down density. This type of spin-polarized calculation is important when investigating the magnetic properties of materials. Also here, the density one may assume that the expression to be the same as in a homogeneous electron gas. The generalization is called the local spin density approximation (LSDA):
Chapter 4 Theoretical approach

\[ E_{xc}^{\text{LSDA}} \left[ \rho \uparrow, \rho \downarrow \right] = \int \rho(r) e_{xc}^{\uparrow, \downarrow} \rho \uparrow(r), \rho \downarrow(r) dr. \]  \hspace{1cm} (4.12)

The LSDA presents relatively good results for materials that have densities that are comparable to the homogeneous density, that is, materials like metals. However, after many years using the LSDA, many other materials have been described quite accurately compared with experimental data [65]. For non-polarized systems, one can set \( \rho^\uparrow(r) = \rho^\downarrow(r) = \rho(r)/2 \) which then describes the regular LDA.

The LSDA (and LDA) is the first level of approximation. Although, this method has been a very successful method over the last 40 years, many theoretical methods have been used to improve LSDA. One of the most known examples is the generalized gradient approximation (GGA), where the exchange-correlation term is accurate by a gradient term of the density \( e_{xc}(\rho^\uparrow, \rho^\downarrow, |\nabla \rho^\uparrow|, |\nabla \rho^\downarrow|, \ldots) \). One might think GGA will generate much better results, however, in most of the cases, the changes in the final result are insignificant [66]. Instead, several methods have been proposed for the exchange-correlation functionals that involve and describe more atomic-like and localized densities. There are hundreds potentials (different GGA, Hartree-Fock-mixed/hybridized, screened, etc) that have been proposed over the last 20-30 years. It is beyond of the scope of this thesis to discuss all these different approaches, and here we describe the LSDA+U approach that has been employed in the present work.

**Correction to the local spin density approximation**

During the last years, many theoretical methods have been tested to try to improve the LSDA in order to better describe the exchange-correlation potentials. At this point, the theory becomes more restricted and any case should be tested and compared with the experimental results. One relatively straightforward method is the LSDA+U [67]. The objective of this method is to shift the localized orbital relative to the other orbital; this should correct the errors found in the LSDA calculations. This method was applied to obtain better results for strongly correlated materials that have many electrons in the \( d \)- and/or \( f \)-like orbitals, states such as transition metals, oxide materials, rare earth compounds, high-temperature superconductors, among others [68].

The LSDA+U method involves self-interaction-like correction Coulomb potential. This on-site orbital dependent correction potential \( U \) is spatially more localized and more anisotropic, which is important for better describing atomic-like \( d \)-states. Although the LSDA+U method is a relatively simple method, it has the main advantage of not increasing the computation time or disk space requirements. The LSDA+U is a relatively easy-to-understand idea to improve
the LSDA and to replace some part of the interactions in a homogeneous 
electron gas with localized atomic-like interactions [69].

The total energy within the LSDA+U is described as

$$E[\rho] = E_{\text{LSDA}}[\rho] + E_{\text{HF}}[\rho] + E_{\text{dc}}[\rho].$$  \hspace{1cm} (4.13)

The first term on the right hand side is the regular DFT/LSDA. The second term 
is the additional correction potential $U$. This is an on-site (screened) Hartree-
Fock-like intra-atomic interaction that can be applied to the atomic-like orbitals 
on each atom. The third term is the so called ‘double counting energy’ which is 
subtracted from the LSDA energy in order to balance what is added by the 
correction potential.

**Summary**

The goal of the methods and approximation (BOA, DFT, KS equation, LSDA, 
and LSDA+U) is to describe the ground state properties of the system with 
sufficient accuracy. In these calculations the symmetry of the solid crystal 
studied is a consequence of the minimum state of energy and regulated by the 
internal and external potential generated by the interacting electrons. The 
methods and approximations are however still under the subject of extensive 
improvements to provide more accurate results. Nowadays, the DFT together 
with the KS approach is the most commonly employed first-principles method 
for studying materials and large molecules.

In the present work, the LSDAU+U exchange-correlation potential was used in 
the KS equation, described within the DFT. The single-electron wave functions 
were described by the projector’s augmented wave (PAW) method [70]. This is 
a mathematical approach that defines a smooth part for wave functions that are 
very pronounced, as the wave functions for the valence band. All calculations 
were performed by the Vienna ab initio simulation package (VASP) [71], which 
uses all the approximations and methods mentioned above. The VASP package 
has been extensively tested and used by numerous researchers, and VASP has 
been accepted as a rather reliable package by the scientific community. Details 
of the calculations are described in paper 3 of the Supplements.
Acknowledgments

I would like to express my gratitude to Prof. Clas Persson and his team for all the support, friendship and patience during this period. Especially, Gustavo for the thesis support on the final stretch. I also acknowledge financial support from the European EM-ECW Program EUBRANEX, the Swedish Energy Agency, the Swedish Research Council, the Brazilian agencies CNPq, CAPES-REUNI and the access provided to supercomputer resources at NSC and HPC2N through SNIC/SNAC.
Summary of papers and author’s contribution

This Licentiate Thesis is a compilation of three scientific papers. The author of this thesis has contributed in all three papers to a major extent.


It is known that the electrical conductivity of these nanotubes changes significantly when the materials are exposed to different atmospheric conditions. In this work, the electrical properties of iron- and iron oxide-filled CNTs and possible applications as a composite material with a semiconducting polymer matrix were investigated. It was found that the current voltage characteristics were directly related to the iron oxide that fills the nanotubes, and the effects were strongly dependent on the applied voltage history. Devices made of CNTs can thereby be designed to be used as gas sensors and in memory technologies where the writing, reading and erasing can be done electrically.

The author C. E. Cava has planned and arranged the device preparation, the electrical experimental setup, and made the electrical measurements. The Fe-CNT samples were prepared by M.C. Schnitzler. The author discussed and analyzed the results together with the co-authors, and he wrote the paper with complementary contribution from the other authors.

Iron oxide-filled carbon nanotubes (Fe-MWCNTs) which are produced from ferrocene pyrolysis, present a non-linear electrical behavior. The Raman scattering analysis was combined with electrical measurements, and the main Raman active modes of the carbon nanotubes were studied. The results revealed a charge bipolarization on this material. We could demonstrate that there was a presence of Kohn anomalies, and a strong modification of the electronic state. Moreover, the ratio between the D band and G band intensities (I_D/I_G) were analyzed to better understand the material electronic structure and the memory device operation. The I_D/I_G analysis demonstrated that the process has good reversibility and this indicated the maximum voltage needed for recording information. The electronic transport was shown to be governed by the hopping between the nanotube shells and also the hopping between the filling and the nanotube. The combination of these processes with iron oxide oxygen migration was specific to this type of Fe-MWCNTs. The effect was suggested to be a bipolar resistive switching between two different electronic states. The switching behavior aggregated to a carbon nanotube provides this material class with new features and opens the possibility of its application in resistance random access memory.

In this paper, the author C. E. Cava planned and arranged the device preparation, the electrical and Raman experimental set up, and made the measurements. He also synthesized the Fe-CNT samples. The author discussed and analyzed the results together with the co-authors, and he wrote the paper with complementary contribution from the other authors.


A theoretical study of the α-Fe₂O₃ was performed by means of an atomistic first-principles method within the density functional theory (DFT). The interaction potential was described by the local spin density approximation (LSDA). To correct the LSDA exchange-correlation interaction, the LSDA+U^{SIC} method with a rotationally invariant self-interaction-like correction Coulomb potential was selected.

The antiferromagnetic (AFM) and ferromagnetic (FM) configurations of α-Fe₂O₃ were analyzed. α-Fe₂O₃ with high and low concentrations of native defects such as oxygen vacancies, oxygen interstitials, and hydrogen interstitials were studied. The present theoretical results were compared to earlier published LSDA studies, and showed that the Coulomb correction within the LSDA+U^{SIC}
method improved both the calculated energy gaps and the local magnetic moment. The reason for this was explained by a better localization of the energetically lower Fe $d$-states in the LSDA+$U^{SIC}$ calculations. When the LSDA+$U^{SIC}$ method was considered, it was found that due to the localization of the $d$-states the intrinsic $\alpha$-Fe$_2$O$_3$ became an AFM insulator. Moreover, oxygen vacancies were observed to have a local effect on the DOS due to the electron doping. The oxygen and hydrogen interstitials influenced the band-gap energies of the AFM structures. Significant changes were observed in the ground-state energy and also in the magnetization around the defects.

In this paper, the author C. E. Cava planned and arranged the calculations as well as the results analyses with the collaboration of the co-authors. He wrote the paper with complementary contribution from the other authors.
References

References


References


