RESEARCH ARTICLE

Energy Stability Calculations for ultrathin multilayers: a comparison between various models for calculating correlation energy and exchange

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Abstract: The computer codes for Theoretical solid state chemistry (free and paid) are becoming ever more versatile and many computing strategies can be used, such as parallel comparison and vector comparison using many computers in a network, etc. But generally, we use electronic structure calculation models, using Hartree-Fock, to obtain state properties. These include the calculation of thermodynamic properties, with DFT (Density Functional Theory) calculations using a large number of available functions. Therefore, it is very important to understand the implementation and operation of the DFT routine using these codes to determine the available parameters. The growth in spintronics, together with frequent news about advances in quantum computation, has resulted in DMS (Diluted Magnetic Semiconductors) being studied intensively. In this new technology that emerges, the spin of the bearer contains the information that will be used. So, we cannot merely use local charge density as a parameter to calculate interactions between bearers. To solve this, we used LSDA (Local Spin Density Approximation), which uses local spin density, performed based on DFT (Density Functional Theory). As there are too many LSDA parameterizations for exchange correlation potential, we decided to implement some of the most widely used ones and compare the results in order to reach a conclusion regarding which parameterization is most coherent according to our study. LSDA was studied first. This approximation is an efficient and accurate plan to answer the problem of many electrons in a crystal using DFT. Over the years, there has been great progress regarding approximations and perhaps LSDA is not one of the best anymore, but it always shows a safe calculation and its simple application does not depend on big computers. The Generalized Gradient Approximations (GGAs) appeared to correct the approximation problems, which are discussed in Perdew-Burke-Ernzerhof (PBE 96). This approximation was constructed to maintain the correct characteristics of LSDA and add other formal properties. Nowadays, PBE 96 is the most widely-used GGA in theoretical solid state chemistry calculations and this correlation is given by correlation energy of the electron gas. PBE 96 is the functional unit that implements a bond on its functional form through the fixing of one of its parameters. In 2006, WC_GGA (Wu-Cohen) appeared, created by Zhigang Wu and R.E. Cohen. Its parameterization is better for solids when compared with others such as LSDA and PBE 96. The last parameterization is PBESol - GGA (Perdew, et al 2008), which minimizes the dependence on error cancellation between exchange and correlation. One approach to lattice properties is to use a modified function, specially created for solid expansion of the exchange gradient across a wide range of density gradients. With the emergence of a new class of compounds, nanostructured multilayers in F/M/F form appeared where F is a ferromagnetic multilayer and M is a metallic film. In this paper, in addition to describing the parameterizations, we will construct a case study by applying the electronic structure calculations to this new class of compounds, thus creating a scientific paper worthy of publication in the aforementioned book.

Keywords: Stability, Cohesive Energy, Electron Density, Wien 2k.

INTRODUCTION

Computational Theoretical solid state chemistry: The Emergence

With computational theoretical chemistry, it is possible to study graphical simulation models and calculate wave functions for solid structures. The use of first principles methods with various calculation models serves for both solid states and molecules and gases, i.e., there is a huge application for computers within theoretical chemistry. However, there is a difference in chemical and theoretical physicists' perceptions regarding how the inner structure of matter works, and therefore, there are many theories and methods for research to be conducted with, such as first principles calculations, which are methods that involve no experimental information in their execution, using elegant and precise mathematics. The semi-empirical methods are the same as the former, in that they use Hartree-Fock formalism, but consider various approaches and employ some of the parameters observed in experimental processes. The semi-empirical methods succeed the empirical methods, in which two Hamiltonian electron terms are not explicitly included.

The inner state of matter seems to be a never-ending topic, because when one compound is understood, new and better compounds arise with new chemical phenomena, and therefore a response is necessary, which, in our view, can be achieved by investigating the electronic structures of compounds using first principle computational methods. Future chemistry can be uncovered by understanding chemical phenomena which, theoretically, are obtained with the use of computers. It is already known that it is possible, from a computational and mathematical point of view, to isolate systems and study them using data, which is vitally important in building new and better systems with properties to improve the lives of people that use them.

The motivation for writing this paper of the book is to shed light on the following questions, the first of which is: how do the various parameterizations of an electron gas influence the calculation of ground state properties of Bulk Iron? The other question is: how does the crystalline structure influence ground state properties of iron when it passes from a bulk state to a nanostructured multilayer? These two questions will be answered, initially using the BCC structure (Body Centered Cubic) calculation of pure iron (Fe) stability. Correlation and exchange of an electron gas will be used, in the following forms: LSDA (Local Spin Density Approximation); WC-GGA (WU- Cohen 06 – Generalized Gradient Approximation); PERDEW BURKE ERNZERHOF - (GGA- PBE) 08, and PERDEW BURKE ERNZERHOF – (GGA- PBE) 96,in which four parameterizations used to calculate BCC iron properties will be emphasized. Afterwards, the results obtained in the structural properties calculations will be shown, with volume depending on cohesion energy, as well as the results obtained when iron atoms are arranged in multilayers. Some final considerations are made at the end.

Both physicists and chemists have been consolidating our understanding of the intimate properties of solids and molecules for some time. Molecules and solids consist of nuclei and electrons, nuclei being much heavier than electrons and thus having a much more centralized movement than electrons. Therefore, nuclei are fixed in three-dimensional space, in crystalline solids. In a molecule, nuclei also move, but slowly when compared to the speed of electrons. Without violating the uncertainty principle, it could be said that, most of the time, nuclear vibrations have adiabatic effects, mostly causing deformation of electronic states. Thus, if we understand changes in electronic states, it will be possible to understand the operation of various molecule properties and crystalline solids.

In addition, understanding electron distribution in solids allows some of their physical properties to be understood. This implies that the physical problem consists of calculating steady states for interacting electron systems, moving in a periodic electrostatic field originating from fixed nuclei, i.e., obtaining the electronic structure of a compound is based on solving the Schrodinger equation, as well as obtaining wave function regardless of electron time.

By addressing fixed nuclei, the Born-Oppenheimer approximation is used, i.e., electrons and nuclei are treated separately. This enables ground state energy depending on nuclei positions to be calculated, which can be used at a later stage, as potential energy for nuclei movement, for example. Determining the electronic structure of compounds involves considering an infinite number of interacting fermions. In an actual calculation, we are led to calculate some approximation, such as the one-electron approximation. In this case, as a first step, we solve the Schrodinger equation for one electron moving in a mean field of other electrons, adding the nuclei field. This mean field is determined by the distribution of electronic charge and correction for correlation and exchange effects, usually self consistently calculated, as will be seen later.

In recent years, the advent of bigger, faster, and more accurate computers has made it feasible to study the electronic structure of solids with complex crystalline structures containing various different atoms in the primitive cells.

The structure of the potential has a lot to do with the particular type of solution, depending on each site in the structure, the spherically symmetric distribution of the potential around the atom, and the interstitial regions, which unite perfectly with the potential around other sites and are relatively flat. This double nature of the potential gave rise to two types of approaches that can be called firstly the wave representation method, and secondly the partial wave representation methods. In the case for the orthogonal flat wave (OFW) [1,2], it is the increased flat wave methods (IFW) (3,4). Deriving from this, we have three main examples of the partial wave methods, the Korringa-Kohn-Rostoker method (KKR) [4,5], which was one of the first to use muffin tin spheres, which increase understanding considerably regarding the electronic structure of real compounds, the cellular method [6], and the linear combination of atomic orbitals (LCAO) [7,8].

The theoretical foundations that provide a satisfactory basis for the use of the approximation of one electron are in the density functional theory (DFT) from Hohenberg-Kohn-Sham [09,10]. This theory explains that any ground state property of a system of many electrons is a single function of electron density and ground state energy (which is therefore a function of density) is minimal with the correct density. In the approximation of local density to functional density, similarly to the XCI Slater method [11], an effective potential of an electron that is a function of local electron density is obtained, which in turn depends on the effective Schroedinger equation for one electron, which inevitably leads to self consistent calculations.

Other methods have also emerged with DVM [12] ("Discrete Variational Method"), SPR-LMT0 [12,13] ("Spin Polarized Relativistic Linear Muffin-Tin Orbital") and FLMTO [14] ("Full Linear

Muffin-Tin Orbital"). Currently, first principle methods to study defects in a crystalline lattice are employed [12,13]. The generalized gradient approximation is also used, which works with a non-local density function developed by J. Perdew and others [13].

First principle calculation of band structure is a very important tool for studying thin and multilayer films. These systems are investigated by techniques such as Mössbauer and X-ray diffraction or magnetization measurements [15,16].

The modern calculation of first principles applied to magnetic multilayers feature, as a starting point, studies conducted by Gyorffy and others [17,18]. These calculations were motivated by observations made by Slater [19] of Ni/Cu alloys using ferromagnetic resonance. However, it should be considered that at that time, it was difficult for experimental physics to build very thin layers (from 5 to 15 angstroms), and comparison between calculations were very difficult.

More recent studies use first principles methods such as those carried out by Kraft and others [20], using FLAPW ("Full Linear Augmented Plane Waves"). This paper is consistent with experimental work carried out by Celinski and others [20]. Regarding magnetic multilayers, in recent years there have been very promising advances in both theoretical and experimental studies, which can be verified in the complete references on the subject [21].

Currently, there has been an evolution in the group of properties calculated such as energy bands and density of states, electron densities and spin densities, structure factor of x-ray forces, equilibrium geometry, structure optimization, phonons molecular dynamics, spin-orbit coupling of emission and absorption of x-ray, and energy loss of spectra of optical properties of Fermi surfaces.

These new properties are available in various codes and the main ones are:

- VASP: (*Vienna Ab-initio Simulation Package – Projector Augmented-Wave*): VASP is a code of plane waves, *all-electron*, within the PAW method (*Projector-Augmented Wave*) to describe electron-nuclei interactions, in which numerical techniques for the diagonalization of the Hamiltonian DFT is used. Such resources allow total energies to be calculated and structural optimizations can be applied to systems of hundreds (even thousands) of atoms. G. Kresse and D. Joubert implemented PAW in VASP, which also uses *ultra-soft* pseudo-potentials. The results detailed in the [22] reference show that the methods are equivalent in most cases.

- SIESTA: (*Spanish Initiative for Electronic Simulations with Thousands of Atoms*): auto consistent computational method based on DFT, which uses standard pseudo-potential and numerical linear combinations of atomic orbital bases, including multiple orbital *zetas* and polarization. The exchange-correlation is treated with LDA and GGA. Numerical subterfuges are used to make a certain number of mathematical operations, with memory increasing linearly with system size.

-LAPW: the linearized augmented plane wave method (LAPW) is among the most accurate methods for performing electronic structure calculations in crystals. It is based on density functional theory for the treatment of exchange and correlation and uses, for example, the approximation of local spin density (LSDA). Several forms of LSDA potentials exist in the literature, but recent improvements using generalized gradient approximation (GGA) are also available. For valence, it was observed that relativistic effects can be included in either scale relativistic treatments (Koelling and Harmon 77) or in the second variation method including spin-orbit coupling (Macdonald 80, Novak 97). Central states are treated fully and relativistically (Desclaux 69).

The models proposed by these calculation packages involve some features that depend on the researcher's aim. In this paper, we are interested in calculating the electronic structure of iron ultrathin layers and understanding parameterization of the electronic structure of ultrathin multilayers. We also observed the behavior of electrons when iron bulk atoms are placed in a new crystalline structure. Therefore, the LAPW (linearized augmented plane wave method) was more appropriate due to the given parameterization and its adaptability to the crystalline structure of multilayers, thereby facilitating the study on solid state chemistry.

Our study aims to investigate very thin surfaces, which have been investigated for a while now, though interest in studying of thin films has intensified recently due to their application in new technological systems. As well as research on thin films, multilayers have emerged, which are compounds consisting of a periodic structure of alternating layers of different materials, which provide very interesting scientific research. Ultra thin films are layers with thicknesses of less than 10 angstroms, forming a single monolayer or multilayers with thicknesses of tens of angstroms. There are still many issues to be resolved with regards to these materials, thus requiring theoretical studies, ranging from quantum to band structure calculations. On the other hand, the development of new experimental techniques has advanced greatly in recent years, enabling faster construction of this new class of materials with lower costs. The most popular techniques are vacuum deposition and sputtering. Currently, thin films play a number of roles, such as in devices and integrated circuits that are present in the connections of device active regions, performing communication between devices and collaborating in external access to circuits. Among the main applications is corrosion control. Metal corrosion is the transformation of a material or metal alloy via its chemical or electrochemical interaction resulting from a particular exposure, which is a process that results in the formation of corrosion products and energy release. If this surface is protected from environmental action, this process can be avoided, and thus an application for thin film arises. However this must have good energetic stability in order not to do react with the environment. This energy stability will be theoretically studied via cohesion energy in this paper.

COMPUTATIONAL METHOD

In recent times, scientific concepts and views of scientific models have improved. In the case of theoretical chemistry, there was a great advance with the emergence of theoretical methods for solving some particular problems, including numerically solving the Schroedinger equation using a computer, which is different from the analytical solutions that can be carried out using well known analytical methods. Although a strict pathway to representing and to understanding the system under study is observed, it should be possible to find new features via alternative pathways. This alternative pathway is a numerical method and is almost unknown to chemistry students, due to its high applicability in highly complex problems, but without it, there would be no access to important theoretical features, such as orbital model, fluid properties, etc.

A field of great interest in Condensed Matter Physics is the system investigation of interacting bodies. Quantum mechanics is proposed to describe these systems through the Schroedinger or Dirac equation, depending on the treatment of relativistic effects. However, it is not possible to find analytical solutions in any case that involves a number of bodies larger than two. In order to describe many-body systems, two approaches using computational methods have been proposed. The first is called the *ab-initio* approach. This approach is not characterized by the absence of approximation, but by the fact that adjustable physical parameters are not used. The second one, called the semi-empirical approach, depends on some information from experimental results. In this approach some physical parameters cannot be determined, for example, the mean interaction between the *spins* of two sites, which must be adjusted by experimental results or *ab-initio* calculations. This study is restricted to the first approach, i.e. it uses Density Functional Theory (DFT) more specifically. DFT is a theory that transforms the problem of many bodies into the problem of a single body which moves in an effective potential and uses electron density as a key variable. With DFT it is possible to study materials with broad applications [22,16]. Currently, computational methods based on DFT are able to address very complex systems and physical effects, such as, crystals with defects, optical transitions, and electronic correlations, among others.

LAPW (Linear Augmented Plane Waves) is the method used, which is a modification of APW (Augmented Plane Wave Method from Slater), inserted into the Wien2k computer code [23]. The basic idea, which led to the construction of LAPW, is based on the fact that in regions distant from nuclei, crystalline potential is approximately plane. Thus, the solution to the Schroedinger equation [09,10] can be expressed as a linear combination of a reasonable number of plane waves. On the other hand, in the regions near nuclei, the potential suffers great fluctuations, because the solution requires a combination of a very large number of plane waves. Therefore, the electronic wave functions are best represented by the product of two factors: one is the radial function, equivalent to the solution to the radial Schroedinger equation using the spherical part of crystalline potential, and the other which describes the dependence of the angles via spherical harmonics. As a result, the crystalline area is divided into two distinct regions, these being the region within sites and the interstitial region, in which the different basis sets are used.

In order to perform electronic structure calculations, the crystalline structure of a solid should be defined which can be considered as atoms (or molecules) that are arranged according to a well defined three-dimensional lattice that is replicated infinite times, thereby achieving a long-range order of interactions. Most metals and most solid amorphous or non-crystalline ceramics in general, have no regularity in the distribution of atoms and can be considered extremely viscous liquids, which occurs in glass, pitch, and various polymers. To evaluate the degree of replication of a crystal structure, it is necessary to define which structural unit is being replicated, i.e. to define atom positions on the crystalline axes representing the material as a whole, which is called the unit cell. A complete description of the structure as a whole is the main feature of the unit cell, including stoichiometry, with the fewest possible number of atoms.

In order to model our calculations, the unit cell of an iron atom as a BCC *(Body Centered Cubic)* was used. Figure 1 represents this crystalline structure as a unit cell.

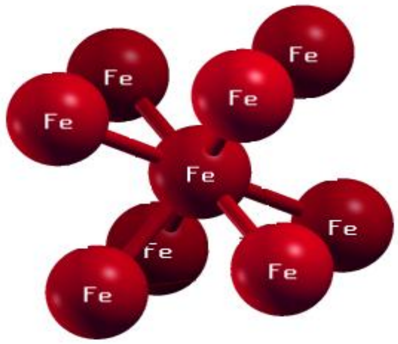
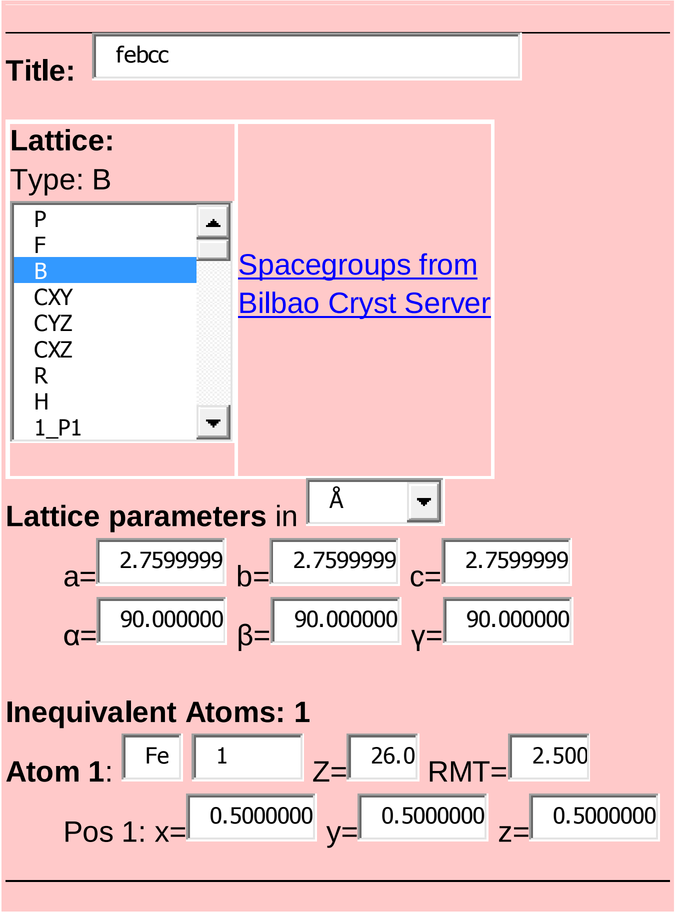


Figure 1: Crystalline cell of Fe-BCC.



Title: febcc

Lattice:
Type: B

Lattice parameters in Å

a= 2.7599999 b= 2.7599999 c= 2.7599999
α= 90.000000 β= 90.000000 γ= 90.000000

Inequivalent Atoms: 1

Atom 1: Fe 1 Z= 26.0 RMT= 2.500
Pos 1: x= 0.5000000 y= 0.5000000 z= 0.5000000

Figure 2: Crystalline structure used in BCC-Fe calculation.

In figure 3, a representation of a TETRAGONAL structure is observed: $a = b \neq c$ angles: $\alpha = \beta = \gamma = 90°$. Figure 2 shows the structure of multilayers calculated in various parameterizations. In this structure, red spheres represent the iron I site; grey ones represent the iron II site, and in turn, red ones represent the iron III site.

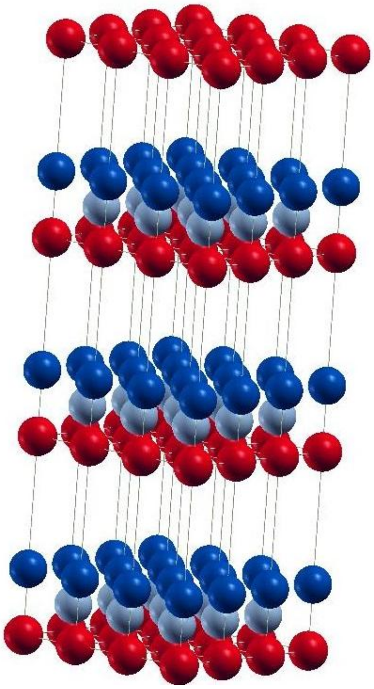
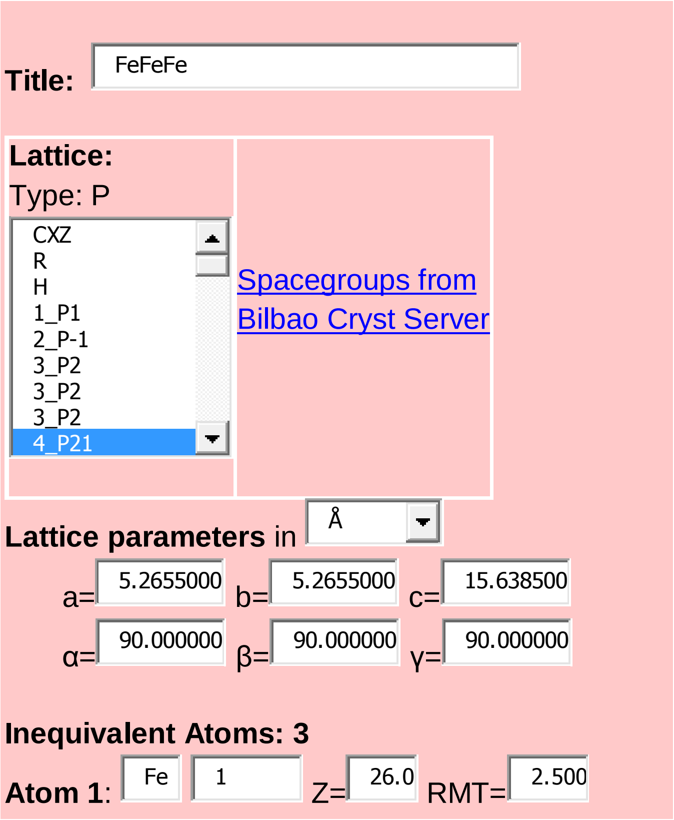


Figure 3: Iron multilayer structure.

This figure merely illustrates for a better visualization of the proposed calculations, which are the true crystalline positions as shown in Figure 4. The structure is calculated with the atomic positions in Figure 4.



Title: FeFeFe

Lattice:

Type: P

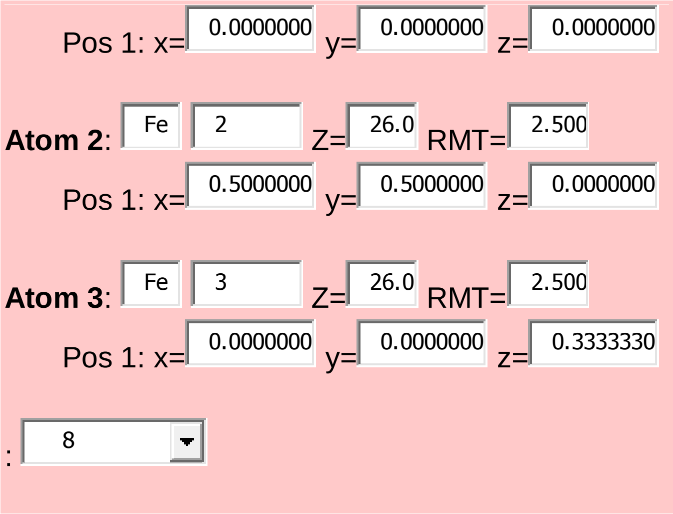
Lattice parameters in Å

a= 5.2655000 b= 5.2655000 c= 15.638500

α= 90.000000 β= 90.000000 γ= 90.000000

Inequivalent Atoms: 3

Atom 1: Fe 1 Z= 26.0 RMT= 2.500



Pos 1: x= 0.0000000 y= 0.0000000 z= 0.0000000

Atom 2: Fe 2 Z= 26.0 RMT= 2.500
Pos 1: x= 0.5000000 y= 0.5000000 z= 0.0000000

Atom 3: Fe 3 Z= 26.0 RMT= 2.500
Pos 1: x= 0.0000000 y= 0.0000000 z= 0.3333330

: 8

Figure 4: Crystalline structure used in the calculation of multilayers.

Used Parameterizations

In Figure 4 in which there are the atomic positions, we can see that the Fe3 would be on the surface, very far from the Fe1 and thus simulating the vacuum forming in the multilayer. Computational theoretical solid state chemistry is fundamentally concerned with understanding and exploiting electrons properties, which have been known since the development of quantum mechanics. Thus, it recognizes that, at least in principle, almost all material properties can be addressed by understanding the electronic structure. Unfortunately, the electrons and nuclei that compose materials comprise a strong interaction between electron - electron, and this makes a direct solution to the Schroedinger equation an extremely impractical proposal.

The codes for calculating electronic structure cited above (free and paid) have become increasingly versatile in their calculating possibilities. Currently, codes initially focused on Hartree-Fock electronic structure calculations involve much more than this. Calculations of thermodynamic properties are included, and calculations using DFT with a large number of functions available. Therefore, it is important to know how DFT routines in these codes are implemented and operate and also what the functions available are called. The generalized gradient approximation (GGAS) emerged to correct approximation problems with gradients, but the vast majority of the time approximation of correlation and exchange is still used, which this paper will address.

We begin our discussion with the older local spin approximation (Local Density Approximation - LSDA), which is an efficient and accurate method for solving the problem of many electrons (with nuclei in fixed positions) within density functional theory (DFT). Thus, the total energy of a system is described below, where spin densities $\rho(r)$ are in terms of total energy:

$$\begin{aligned} Etot(\rho\uparrow,\rho\downarrow) = {} & Ts(\rho\uparrow,\rho\downarrow) + Eee(\rho\uparrow,\rho\downarrow) + ENe(\rho\uparrow,\rho\downarrow) \\ & + Exc(\rho\uparrow,\rho\downarrow) + ENN \end{aligned} \qquad \textbf{(1)}$$

where ENN is the Coulomb repulsion energy of fixed nucleus one, Ts is the kinetic energy (particles do not interact), Eee is the electron-electron repulsion, ENe is the attraction of nuclear electrons, and Exc is the correlation and exchange-correlation between the electrons.

The density functional theorem and LSDA is based on Hohenberg-Kohn [09,10]. They state that the total energy, E, of a non-polarized-spin system interacts with electrons from an external potential and it is precisely determined in function of the ground state electron density, ρ,

$$E = E[\rho] \tag{2}$$

The extension to spin-polarized systems is simple. Energy and other properties of the ground state become spin functional density, which in the general case, is given as a spin-orbit component. In the collinear case, the sufficient spin-up and spin-down densities are given by equation,

$$E = E[\rho \uparrow, \rho \downarrow] \tag{3}$$

Local spin density approximation (LSDA), [24] in solid - state chemistry calculations, remained limited up until the late 1970s, when various calculations that demonstrated feasibility and accuracy of the approach in determining solid and molecule properties appeared. There are several studies on why LSDA is or is not suitable for calculating the properties of this or that material. Over time, there have been great advances in approximations, and because of that, perhaps LSDA is no longer one of the best methods. But everything depends on the calculations and results to be obtained. In this regard, further comparative studies are necessary.

The development of first - principles calculation models comes with gradients of electron density, i.e., the generalized gradient approximation (Generalized Gradient Approximation - GGA) [25] corrected thinking that uniform-density electron gas (UEG) is suitable for all parametrizations, when in truth it is only suitable for Local Spin Density Approximation (LSDA). For more information, consult reference [26], which takes into account the electron density of an atom, as well as the gradient of electronic density around neighboring atoms, and thereby acquires a semi-local character. With this approximation, it is possible to obtain various parameterizations for the gradient of electron density depending on the gradient treatment, therefore leading to different functions. In this paper, three parameterizations will be used, proposed by Perdew, Burke and Ernzerhof (PBE-96) [25], by Wu and Cohen (WC) [27] and by PBE-sol [28], in which each one has its own features and applications.

The equation that expresses the general form for the energy exchange and correlation function in the approximation of generalized gradient is:

$$E_{XC}^{GGA}[\rho] = \int \rho(\vec{r}) f\big(\rho(\vec{r}), \nabla\rho(\vec{r})\big) d^3\vec{r} \tag{4}$$

Where $\overset{\rho(\vec{r}),\nabla\rho(\vec{r})}{f}$ depends on charge density and a parameterization for the charge gradient, which can be modeled according to various criteria depending on the parameterization chosen (PBE, WC, PBE-Sol).

In the most general form of the GGA gradient, the method is extended as follows, according to Equation 5:

$$\text{V(r)=}\quad \begin{array}{l} \sum_{LM} V_{LM}(r) Y_{LM}(\hat{r}) \ \ inside\ sphere \\ \displaystyle\sum_{K} V_K e^{iK.r}\ outside\ sphere \end{array} \tag{5}$$

The charge density is comparable, therefore there are no approximations, and it is possible to use a procedure called the 'Full-Potential' method. This procedure corresponds to it being spherical within spheres, leading considerations at medium volume in the interstitial region.

We first reported the parameterization from Zhigang Wu and R. E. Cohen, who developed a more accurate parameterization compared to the existing one at the time (LSDA, PBE96). Based on this, radial correlation and exchange functions have a diffused tail, within the interstitial space between one atom and another, with the cross section in the tail of radial functions given by the factor H $\left[1+\left(\frac{u}{u_x}\right)^2\right] exp\left[-\left(\frac{u}{u_x}\right)^2\right]$.

Where u is the distance between the atom center and the interstitial space and atom, and u_x, is the fixed radial cut. Improving the lattice constant at equilibrium calculations for some solids, it is observed that LSDA parameterization underestimates the tail of the correlation and exchange functions. On the other hand, PBE96 parameterization overestimates such values. WC also predicts more precise modulus volumes for solids than when calculated by LSDA and PBE96.

A pragmatic approach to lattice properties is to use a modified function (pseudo potential), especially for solids that exchange gradient expansion through a wide range of density gradients. This produces better lattice constants than PBE and excellent energy because they are dominated by modern density gradients.

We choose $\beta = 0.046$ and $\mu = \mu GE$ (within PBE form) for PBEsol, for better results adjustment. PBEsol should improve the calculation of surface energy more than LSDA. For closer examination, the β and μ parameters are well defined in reference [29]. We made the choices suggested in page 3 of this reference.

Thus, we may have violated the linear response requirement in favor of good surface energies. PBEsol is fairly close to LSDA, because it leaves greater electron density near to the nucleus. The dominant contribution to surface energy is from the inner zone close to the surface, leaving few electrons on the outside.

Therefore, it is noted that the main difference is in the expansion of the function tails within spheres. Thus, there are various ways of understanding the correlation and exchange term. We do not want to end the discussion, but the aim is to collaborate, in the near future, in developing new correlation and exchange terms in order to discover the chemical and physical properties of matter in crystalline states and molecular forms, thus possibly extending to other materials such as colloids and polymers.

In the next section, the calculation methodology will be applied in two systems: iron in its bulk structure will serve as a control system, because some properties, such as lattice parameter and magnetic moment, exist in experimental data; and the ultrathin multilayer system, in order to expand our knowledge of new systems.

RESULTS AND DISCUSSION

Application of Electronic Structure Calculation Model in Two Systems

Structural Properties

The structural properties of compounds are also the consequence of their electronic structure, i.e., if we correctly identify the wave function and describe the correlation and exchange interaction , important structural properties can be obtained, such as volume, lattice parameter and the hardness of the compound, represented by Bulk modulus (B). We can also measure the enthalpy of formation and its cohesion energy, which are phenomena caused by the distribution of electrons in compounds. Furthermore, it is possible to relate system energy with deformation by performing the Bulk modulus calculation, which is the change in volume when subjected to variations in total energy.

State equations (EOS) have been proposed by some researchers over time. In the 90s, important ideas were proposed by Murnaghan's EOS [29]. Currently, the band structure calculations have developed and there has been a significant improvement in total energy calculations due to the volume of the unit cell.

Thus, unit cell volume is obtained at V_0 equilibrium and isothermal properties, as Bulk modulus $B = -V_0 \frac{dP}{dV}$; where $\frac{dP}{dV}$ is derived first in relation to pressure or $B = -V_0 \frac{dE^2}{d^2V}$ where $\frac{dE^2}{d^2V}$ is derived second in relation to energy. B_0' is first derived from Bulk modulus in relation to pressure and $B_0' = -V_0 \frac{dB_0}{dP}$; Therefore, it can be written that $B_0' = -V_0 \frac{dE^3}{d^3V}$ i.e., is third derived from energy due to volume.

In band structure calculations, it is easier to calculate the formation energy curve due to volume than the pressure curve due to volume. However, to obtain EOS, it is necessary to calculate pressure due to volume. For a fixed number of particles at zero temperature, pressure is given by: $P(V) = \frac{B_0}{B_0'}\left[\left(\frac{V_0}{V}\right)^{B_0'} - 1\right]$ as zero temperature that pressure is given by $P(V) = -\frac{dE(V)}{dV}$ where $\frac{dE(V)}{dV}$ is first derived from energy due to volume as described $\int dE = \int PdV$; thus by integrating P(V) two forms are obtained, one with B_0 and B'_0 , which are independent from volume, and thus, $E_{B_0,B_0'cte}(V) = \frac{B_0}{B_0'} V \left[\left(\frac{V_0}{V}\right)^{B_0'} \frac{1}{B_0'-1} + 1\right] + C_{B_0,B_0'cte}$[21] is found. The $C_{B_0,B_0'cte}$ constant can be changed to $C_b = -\frac{B_0V_0}{B_0-1}$ constant, which may now be written as follows: $E_{B_0,B_0'cte}(V) = \frac{B_0}{B_0'(B_0'-1)} V \left[B_0'\left(1 - \frac{V_0}{V}\right) + \left(\frac{V_0}{V}\right)^{B_0'} - 1\right] + C_b$. However, to discuss the stability of compounds, it is not only necessary to calculate the total energy of the system, but also the formation energy, which is defined by:

$$E_F = E_{tot} - \sum E_x^i \qquad \textbf{(6)}$$

In which E_F= Energy of formation, E_{tot} = Total energy, and E_x^i= sum of crystalline energy of each atom.

Formation energy shows us how much energy we must provide to form the compound, i.e., to turn it from its crystalline structure into a new structure. This can be described as the difference between the energy of bulk states and the total energy of the system. In Table 1, it is noted that all parameterizations indicate low formation energy, i.e., compounds form easily, with the exception of the calculations using GGA-PBE, showing a formation energy in the same order of greatness as cohesion energy. In addition, the signal of formation energy oscillates, proving very easy to form multilayers from an energy point of view. Negative energy indicates that we must provide energy to the system. Positive energy indicates that the system loses energy into the environment when it is forming [29].

In Table 1, we also find the calculations performed with different parameterizations of electronic correlation, with two spin directions for Fe Bulk. Thus, we have the energy of cohesion and also find the lattice parameter and Bulk modulus. It can be noted that the closest parameterization to the experimental data is GGA PBE 96, because the Bulk iron experimental value is 2.81 Angstroms [30], and other parameterizations offer lower results than the experimental data. We concluded that the parameterization does not yet describe the interaction between close neighbor electrons and therefore the total energy of the system has been calculated with little accuracy, providing a wrong parameter. Therefore, we use the total energy of the system to calculate the cohesive energy, in order to find the balanced lattice parameter. This calculation will be described later.

LSDA parameterization, which uses only local effects, is the worst of all, and thus we can state that it does not work for calculating the total energy of a system, because it ignores the terms distant from the nucleus. However, it is noted that LSDA parameterization is the largest Bulk modulus, and GGA PBE 96 is the lowest found, although all agree at first because the difference is small. On the other hand, cohesion energy is also higher in the case of LSDA.

In Table 2 the calculations performed with different parameterizations of electronic correlation are shown, with two spin directions, for ultrafine multilayers of Fe/Fe/Fe (atomic layers of iron) as well as the lattice parameter, the enthalpy of formation, and Bulk modulus, and formation energy. All parameterizations have a significant increase in the lattice parameter of pure iron, which experimentally is 2.81 Angstroms, when arranged in multilayers. We all also agree that when the number of electrons grows in a system, there is an increase in the lattice parameter, due to the higher number of electrons in the system. The expansion of the iron crystalline lattice is due to distant electrons from the nucleus, thus LSDA had the lowest result since it has no radial functions of correlation and exchange with a distant tail from core the nucleus, as in the other parameterizations. Bulk modulus sharply falls when iron is arranged in ultrathin layers, therefore the arrangement of electrons in a system and the arrangement of atoms in a crystalline lattice are of great importance in the Bulk modulus, since the structure of atoms is the same as the Bulk, thus showing that atomic position is extremely important for properties such as Bulk modulus and lattice parameter. The parameter that best calculated Bulk modulus was GGA EBP, since the experimental Bulk modulus is 170GPa [31].

Table 1: Parametrons using various parameterizations**.**

	LSDA	**GGA PBE**	**GGA WC**	**GGA PBSol**
Febcc				
a eq	2.2139	2.8351	2.7599	2.7728
B	252.7543	192.8987	239.6572	208.6584
Ec	-0.4685	-0.3424	-0.3812	-0.3806

a eq= lattice parameter in equilibrium (Angstroms)/ B= Bulk Modulus (GPa)/ Ec= Cohesive Energy (Ry)

Table 2: Parametrons using various parameterizations**.**

	LSDA	**GGA PBE**	**GGA WC**	**GGA PBSol**
			FeFeFe	
a eq	5,0970	5,2655	5,1663	5,1882
B	83,0846	71,2130	82,5410	79,9268
Ec	-1,3777	- 1,1250	-1,2832	-1,2912
Ef	0,2473	-1,1300	0,6577	0,2215

a eq= lattice parameter in equilibrium (Angstroms)/ B= Bulk Modulus (GPa)/ Ec= Cohesive Energy (Ry)/ Ef= Formation Energy (Ry).

For a discussion of stability, it is necessary to calculate the energy of cohesion, which is defined as the energy required to separate constituent atoms from a solid [29]. Cohesive energy ranges with the distance between the atoms in a solid (unit cell volume) and reaches a minimum. Cohesive energy corresponds to this minimum and is called balance cohesion energy, i.e. the point where the internal pressure of a solid is zero, and thus the volume balance can be found, and consequently, the lattice parameter. Therefore, energy of cohesion can be calculated using the following equation:

$$E_C = E_{tot} - \sum_{n}^{x} E_{ix}^{\acute{a}tomo} \tag{7}$$

where E_{tot} is the total energy of the compound, $E_{ix}^{\acute{a}tomo}$ is the energy of each atom in the compound in its free state. Here cohesion energy per unit cell will be used, in contrast to articles [29], which used per atom. Table 1 shows the calculation of Bulk iron cohesion energy and no experimental data was found in the literature. We note that cohesion energy is associated to Bulk modulus, because the higher the Bulk modulus, the greater the energy of cohesion, in the case of Bulk iron. Due to it being negative, cohesion energy implies that we must provide energy for the separation of compound atoms.

In the case of multilayers with a negative value, all parameterizations agree that we must provide energy for multilayer unbalance. We also see that when we do not take into account the effects of the generalized gradient, we find higher cohesion energy, both in the multilayer and bulk iron. The sum of energy of free atoms is different from the compound, thus the energy due to the crystalline structure is greater than when compared to other parameterizations.

Density of Electrons

In quantum mechanics, and in particular, theoretical solid state chemistry, electron density is a measure of the probability of an electron occupying an infinitesimal element of surrounding space at any point. It is a scalar quantity, usually indicated as ρ (R) or N (R). On the other hand, the density determines the modulus wave function as a phase factor, providing the formal basis of density functional theory.

In Hartree-Fock, wave function theories are generally represented as a singular Slater determinant, constructed from N orbitals, φ_k, with corresponding occupations n_k. In these situations, density simplifies to:

$$\rho(r) = \sum_{k=1}^{n} n_k \left|\varphi_{k,}(r)\right|^2 \tag{8}$$

With the application of this theory, figures can be assembled:

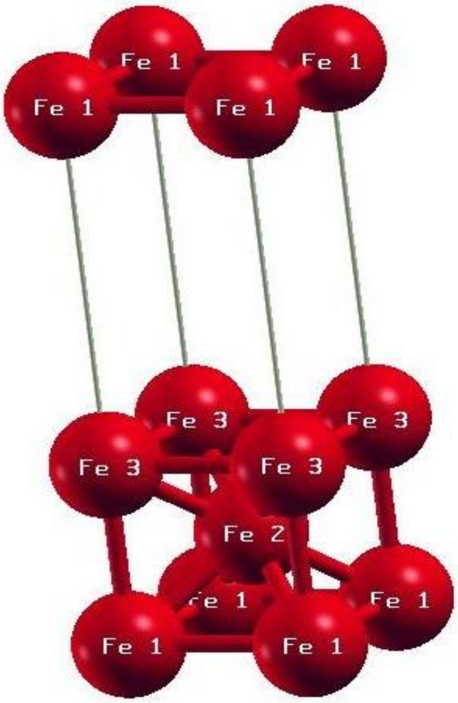


Figure 5: Unit cell of multilayers.

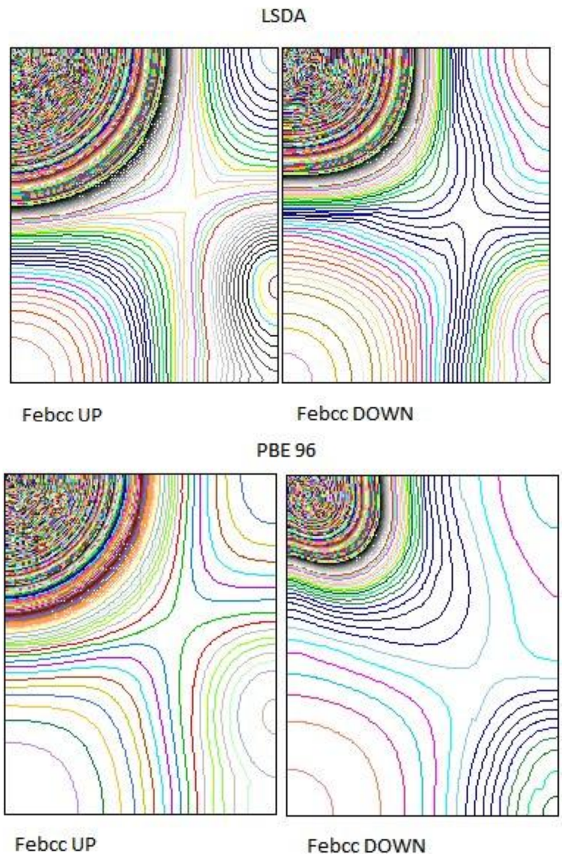


Figure 6: Electron Density for Fe BCC using LSDA and PBE 96 parameterization, in the (1,0,0).

As shown in figures 5 and 6, that represents the probability of finding electrons, which is shown by curves, in parameterizations used case in paper for Fe BCC in the direction (1,0,0),. The figures were constructed with the limits -1 to 1 eV and a step of 0.0001 eV.

LSDA parameterization has a high probability density in the region close to the iron atom, because black lines in *up* electron density also show a uniform distribution of lines, which means that they are spherically and symmetrically distributed from core the nucleus, thus showing that iron suffers almost no influence from neighbor atoms, as would be expected from a BCC structure. The *down* electron density shows the same features as the *up* states, however with a small distortion in symmetry, with it no longer being spherically symmetrical. This similarity between the *up* and *down* states is due to LSDA parameterization not taking into account the effects of function tails and referring to only local interaction. But the difference between probabilities generates properties such as magnetization of BCC iron atoms. In Figure 6 we also find the electron density calculated using the PBE96 parameterization and we note that this parameterization already has non -local effects. These non - local effects are evident, especially in *down* states of the bcc iron structure, because there are more curves closer to the interstitial region, indicating the probability of finding electrons in other energies. It is also noted that the difference between *up* and *down* states is higher than in LSDA.

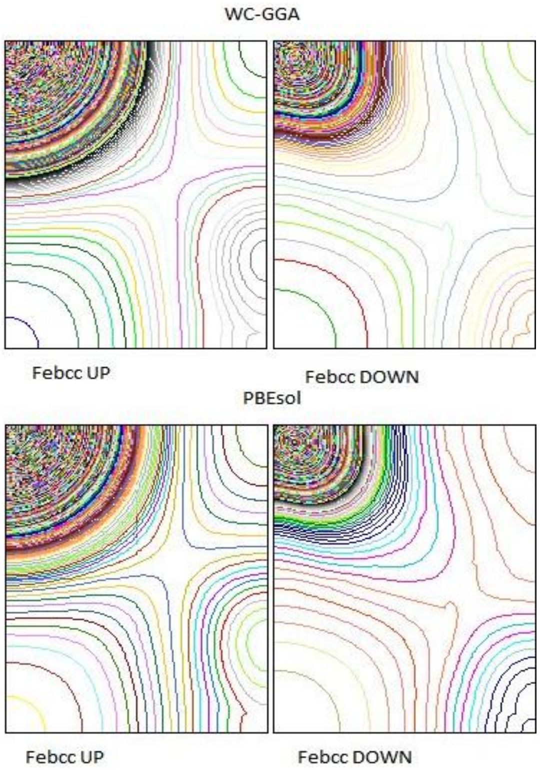


Figure 7: electron density for Fe BCC using WC_GGA and PBEsol parameterization.

In Figure 7, electron density uses WC-GGA parameterization and also PBEsol parameterization. Here we see that the truncation of tails of functions causes a slight change in *up* electron density, in all parameterizations. The differences are in *down* states due to similarities between the parameterizations that use GGA, with some slight changes, such as in PBE 96 showing a difference in the probability of finding different electrons from the two other parameterizations, in *up* states, because PBE 96 does not truncate the correlation and exchange function, and the other two parameterizations do truncate, thus highlighting the differences. In the next section, we will be applying the iron ultrafine multilayer theory and will assemble the electron densities for the four parameterizations. We will also see the effects of a crystalline structure and new interactions between iron atoms in relation to a bulk state.

Probability density of electrons distributed in an iron ultrathin multilayer

In Figure 8, electron density is in the plane (1,0,0), i.e., the probability of finding electrons near the nucleus, because the LSDA parameter is used for correlation calculation and electron exchange , which does not use GGA approximation, and thus there are no nonlocal effects. In this crystal structure, in multilayer form, three different sites were found in its unit cell, unlike bulk iron, which has only one. The probabilities of *up* electrons, which are equal in bulk iron, are spherically distributed around nuclei, as expected in LSDA. There are electrons with probability to be found in two different sites, thus showing few covalent interactions, but mostly predominating ionic interactions, i.e., electrons are located near to the nucleus. As in the case of bulk iron, *down* electrons are mismatched with the *up* state, thus showing that the compound remains ferromagnetic. As LSDA presents only calculations located in nuclei, there is a strong electron density near these. In the *d* region, we find some lines of probability indicating that there are some states located in this position, which are reflections of the other layers, which the figures focus on. We can say that the stability of various layers is due to these electrons, thereby increasing the cohesion energy of multilayers. This is easy to see if we observe Tables 1 and 2, since the cohesive energy grows when arranged in ultrathin multilayers. In Figure 3 we also find the first calculations that take into account non - local effects. Proposing studies on nonlocal effects, we note that the *up* and *down* states have a greater difference than in LSDA calculations, but the electron distribution in *down* states remains spherically symmetrical. There are also electrons that are likely to be in two sites characterizing covalent bonds.

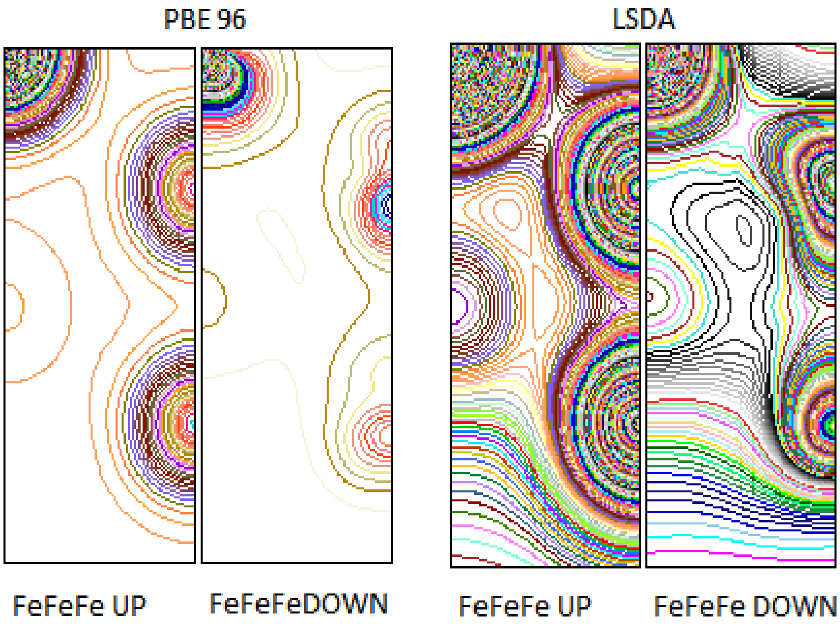


Figure 8: Electron density for ultrafine multilayer using PBE96 and LSDA parameterization.

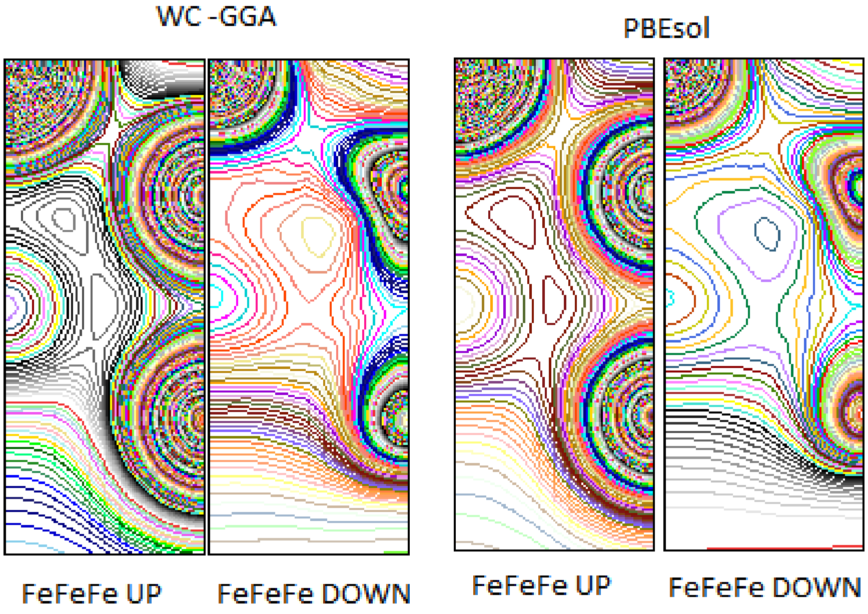


Figure 9: Electron density for ultrafine multilayer using WC-GGA and PBEsol parameterization.

In Figure 9, we present the electron density for ultrathin multilayers in WC-GGA and PBEsol parameterizations, which are parameterizations that take into account non-local effects, but in contrast to PBE 96, truncate wave functions with tails of different functions. In the calculations where wave functions are truncated, we can see that they are closer to LSDA, and so we can imagine that it is possible that those functions that were truncated provide better precision than LSDA and the simple expansion of PBE96. If we observe recent calculations of compounds such as γ-Fe4X (X = B, C, N, and O), the electron density is spherically and symmetrically distributed, showing a new result here from multi thin multilayers [31].

We can see, therefore, in all calculations, that there is a great difference between *up* and *down* states, showing the ferromagnetic character of ultra thin multilayers. This difference is more pronounced here than in the case of bulk iron, and thus we can say that from a magnetic point of view that there is increased magnetization of ultra thin multilayers.

Table 3: Magnetic properties of the FeFeFe compound

	LSDA	**GGA PBE**	**GGA WC**	**GGA PBSol**
		FeFeFe		
MMI	0.26896	0.1597	0.32139	0.205050
Fe1	2.69231	2.9272	3.07872	2.846500
Fe2	1.88812	2.1866	2.80776	2.054930
Fe3	2.69224	2.9266	3.07857	2.846850

We can define the magnetic moment as the occupation of the spin up electrons minus spin down electrons, below Fermi energy. The magnetic moment of Iron in its bcc bulk state is in the order of 2.12 μ_B [30]. It can be noted in Table 3, in which we find the magnetic moment of the multilayers and the interstitial region, that all of the parametrizations agree that Fe3 increases the magnetic moment more than the other sites, in relation to bcc iron. The Fe2 site obtained the lowest magnetic moment, in relation to bcc iron. The Fe1 site also increased considerably in relation to bcc iron. Here we see that the geometric situation and position of the crystalline cell influence magnetization a lot.

In order for us to understand the magnetization of multilayers we advise the introduction of Density of States (DOS). More was included on total density of states. The Density of States calculation provides precious information regarding electrons in a solid, in terms of density of states $\rho(\omega)$, the function of which tells us how many available states exist in an energy range ω to $\omega + d\omega$. When the $\in_n(\vec{k})$ auto values are known, the density of states is obtained by the following equation:

$$\rho(\omega) = \sum_{n} \sum_{\vec{k}} \delta\,(\omega - \in_n(\vec{k}) \qquad \textbf{(9)}$$

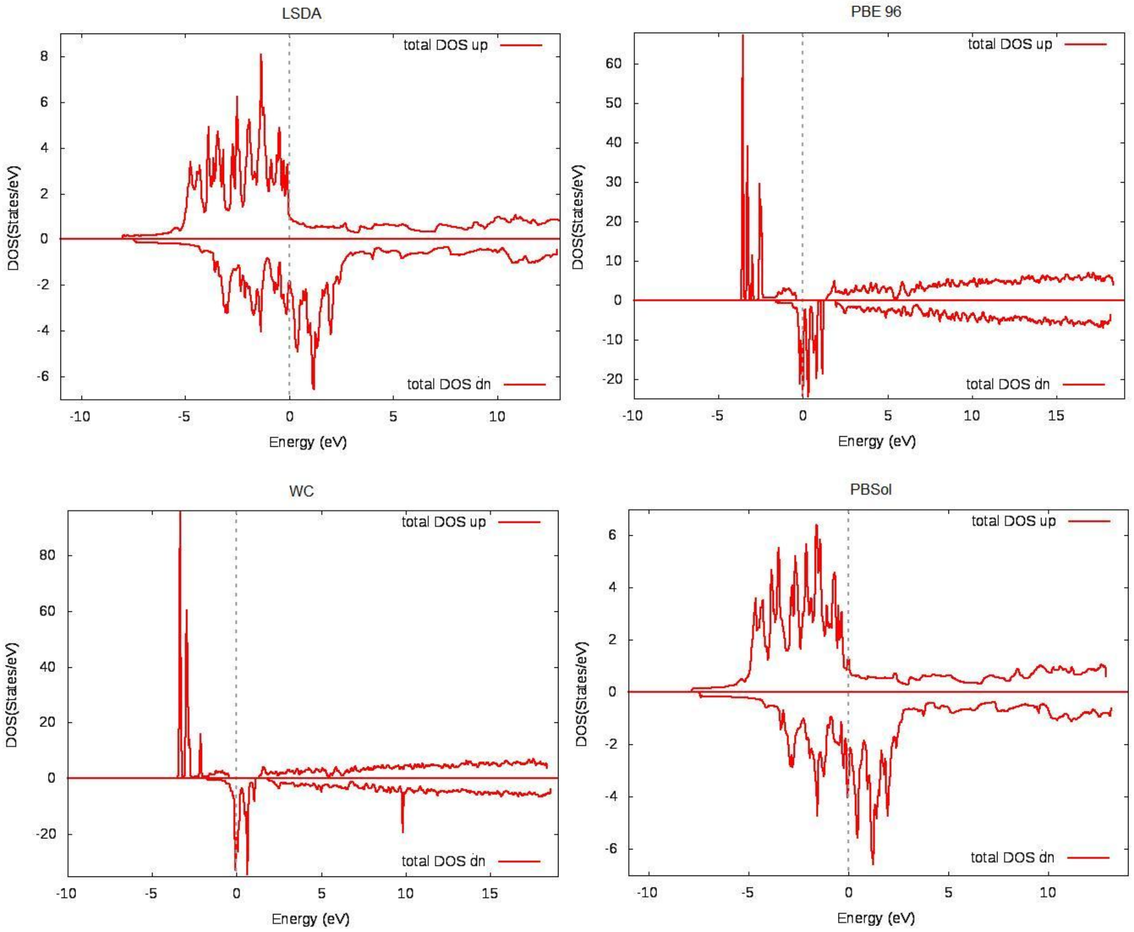


Figure 10: Total Density of States for the Iron ultrafine multilayers

In figure 10 we present the total Density of States for the ultrafine multilayers of iron, calculated with four the parametrizations used in this paper. We approximate Fermi energy to zero for a better overview. We note that in all of the figures the magnetic character is well accentuated, since the up and down electron curves exhibit considerable differences, characterizing a ferromagnetic structure. We also note similarity in the arrangement of Density of States between the LSDA and PBSOL parametrizations, in which DOS is quite spread out and features no pure states. The PB96 and WC parametrizations present pure states, showing well pronounced peaks in the energy region between -5eV and 0 eV, differing from PBE96, which presents 4 pronounced peaks. The states above the Fermi energy are very similar between the four parametrizations. If we compare with more recent papers, we perceive that the multilayer format provides this increase in magnetization [33]; that is, the geometry of the system strongly influences its magnetization.

CONCLUSIONS

To close our paper on computational theoretical solid state chemistry, we will briefly discuss the knowledge we acquired by carrying out this study. We noted that computers can be used to help in understanding complex systems with multiple atoms distributed and several different compounds in different crystalline structures. In economic terms, we predict various compound properties even before the construction of these compounds in experimental or industrial laboratories, thus increasing the economic viability of projects. The study of computational theoretical chemistry ranges from graphical simulation models to wave function calculations for solid and non-crystalline structures. The use of first principles calculation methods with various calculations models serves for both solid states and molecules and gases, i.e. computers can be widely applied within theoretical chemistry.

In relation to applying the theory proposed, we can conclude that:

The parameterization with the best result from an experimental point of view is GGA PBE 96, since the experimental value of iron is 2.81 angstroms. It is concluded that the parametrizations do not yet describe the interaction between close neighbor electrons, and therefore the total energy of a system was calculated with little precision, providing an inaccurate parameter.

All of the parametrizations increase significantly in the pure iron structure, which is experimentally 2.81 angstroms when arranged in multilayers. The parametrizations indicate that when the number of electrons in the system grows, there is an increase in the structure parameter, since the parameter is greater than the lattice due to the greater number of electrons in the system. The expansion in the iron crystalline structure is due to the electrons distant from the nucleus, thus LSDA has the lowest result, given that there are no radial correlation and exchange functions with a tail far from the nucleus, as in the other parametrizations.

The module volume calculation shows that it falls markedly when iron is arranged in ultrafine layers, therefore the arrangement of electrons in the system and the arrangement of atoms in the crystalline structure is of vital importance. The parameterization that best calculates module volume was GGA EBP, since the experimental module volume is 170 GPa.

LSDA parameterization has a high probability density in the region close to the iron atom, since the black lines above the electron density also show a uniform distribution of lines, which means that they are spherically and symmetrically distributed around the nucleus.

We found the electron density calculated using the other parameterization. We noted that this parameterization has non-local effects. These non-local effects are evident, especially in iron structure down states, because there are no more curves closer to the interstitial region, indicating a probability of finding electrons in other energies. It is also noted that the difference between up and down states is greater that in LSDA, both in the ultrafine multilayers and in the Bulk iron.

We can note that for the magnetic moment of the multilayers and the interstitial region, all of the parametrizations agree that Fe3 increases the magnetic moment in relation to the bcc iron more than the other sites. The Fe2 site was the one in which the lowest magnetic moment was found in relation to the bcc iron. The Fe1 site also increased considerably in relation to the bcc iron.

In relation to total Density of State we showed that the state is ferromagnetic, since the density of up states has more states than the down states below the Fermi energy, for all parametrizations. All of the parametrizations also present free down states above the Fermi energy.

Finally, this type of discussion should lead to new studies, in which other system properties will be discussed, taking many calculations into account. The main message behind this study is it shows that we are far from having a standard model for electronic structure calculations, and that the microscopic world can be understood using other theories and/or quantum computing.

REFERENCES

[01] Felicov, L. M, Energy Bands in Metals an Alloys, Metallurgical society conferences, 1968, 45, 73.

[02] Herman, F.; Kortum, R. L.; Kuglin, C. D. and Van dyke, J. P. In: Methods in Computational Physics; Alder. B., Fernbach. S. and Roternberg. M., Ed.; Academic Press: New York, 1968; Vol. 8, pp. 193.

[03] Staler, J. C., Wave Functions in a Periodic Potential, Phys. Rev ., 1937, 51, 846.

[04] Mattheiss, L. F., Wood, J. H., Switendick, A. C. In: Methods in Computational Physics; Alder. B., Fernbach. S. and Roternberg. M., Ed.; Academic Press: New York, 1968, 8, 63. OK (Não possuia alguns dados)

[05] Korringa, J., On the calculation of the energy of a Bloch wave in a metal, Physica, 1947, 13, 392. OK

[06] Segall, B., Ham, F. S. In: Methods in Computational Physics; Alder. B., Fernbach. S. and Roternberg. M., Ed; Academic Press: New York, 1968, 8, 251.

[07] Altmann, S. L., Bradley, C. J. The band structure of hexagonal close-packed metals: I. The cellular method, Proc. Phys. Soc., 1965, 86, 915.

[08] Deegan, R. A., Twose, W. D. Modifications to the Orthogonalized-Plane-Wave Method for Use in Transition Metals: Electronic Band Structure of Niobium, Phys. Rev., 1967, 164, 993.

[09] Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas, Phys. Rev., 1964, 136, B864.

[10] Kohn, W.; Sham, L. J. Self- Consistent Equations Including Exchange and correlations effects, Phys. Rev. B, 1964, 140, A1133.

[11] Slater, J. C. Role of local geometry in the spin and orbital structure of transition metal compounds Phys Rev. B, 1951, 81, 385.

[12] Elzain, M. E.; Yousif, A. Computational studies of the hyperfine field in α-Fe, Hiperfine interaction., 1994, 94, 511.

[13] Perdew, J.P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation, Plys. Rev. B, 1992, 46, 6671.

[14] Guo, G.Y.; Ebert, H. First-principles studies of the magnetic hyperfine field in Fe multilayers, Hiperfine interaction, 1996, 11, 98.

[15] Garcia, P.F.; Meinhaldt, A. D.; Suna, A. Sputtering pressure effects and temperature dependent magnetism of Co/Pd multilayers, Appl. Plys. Lett., 1985, 47, 178.

[16] Draaisma, H. G.; Jonge, W. J. M. J. The influence of structural disorder on magnetic domain formation in perpendicular anisotropy thin films, Magn. Magn. Mat., 1987, 66, 351.

[17] Gyorffy, B.L. Electronic Structure of Disordered Alloys, Surfaces and Interfaces, Plys. Rev B., 1972, 5, 2382.

[18] Phariseau. P.; Gyorffy, B. L.; Stocks, G. M. In: Eletrons in Disordered Metals and Metallic Surfaces; Phariseau. P., Gyorffy, B. L. and Scheire. L., Eds.; Plenum Press: New York, 1979; Vol 42, pp. 01-47.

[19] Butler, F. A.; Bloom, F. K.; Brown, E. Modification of the Orthogonalized-Plane-Wave Method Applied to Copper, Phys. Rev., 1969, 180, 744.

[20] Kraft, T.; Marcus, P. M.; Scheffler, M. Eletronic Theoryfor Nolimoke, Plys Rev. B, 1994, 49, 511.

[21] Fu, C. L.; Painter, G. S. Point defects and the binding energies of boron near defect sites in Ni_3Al: A first-principles investigation, Acta Mater, 1997, 45, 481.

[22] Andersen , K. O.; Jepsen, O. Properties of the Ultrathin Multilayer Ground State of Fe/Pd, Plysica B., 1977,91, 317.

[23] WIEN2K. Electronic Structure Calculation of Solids. http://www.wien2k.at [Accessed June 2016].

[24] Perdew J.P.; Burke S.; Ernzerhof M. Generalized Gradient Approximation Made Simple, Phys. Rev. Let., 1996, 77, 3865.

[25] Perdew J.P.; Wang, Y. Accurate and simple analytic representation of the electron-gas correlation energy, Phys. Rev. B, 1992, 45, 13244.

[26] Peverati, R.; Truhlar, D. G. M11-L: A Local Density Functional That Provides Improved Accuracy for Electronic Structure Calculations in Chemistry and Physics. The Journal of Physical Chemistry Letters, 2012, 3, 117-124.

[27] Wu, Z.; Cohen, R. More accurate generalized gradient approximation for solids, 2006, Phys. Rev. B, 73, 235116.

[28] Perdew J.P. et al. Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces, Phys. Rev. Let., 2008, 100, 136406.

[29] Murnaghan F.D., The Compressibility of Media under Extreme Pressures , Proc. Natl.

Acad. Sci. USA, 1944, 30, 244.

[30] Structutal Properties of the Iron. http://personales.unican.es/junqueraj/JavierJunquera_files/Metodos/Structuralproperties/Lattice-constant-si/Exercise-structure-si.pdf [Accessed July 2016].

[31] Dos Santos, A.V. Consequences on the electronic structure and hyperfine of iridium-iron alloys when transformed into substituted iron iridium nitrides. Journal of Materials Research, 2014, 29, 959.

[32] Dos Santos, A.V.; Samudio Pérez, C.A.; Muenchen, D.; Anibele, T. P. First principles calculations of the magnetic and hyperfine properties of Fe/N/Fe and Fe/O/Fe multilayers in the ground state of cohesive energy. Solid State Communications, 2015, 201, 120-124.

[33] Dos Santos, A.V.; Samudio Pérez, C.A. Ab initio investigation of the substitution effects of 2p elements on the electronic structure of γ-Fe4X (X = B, C, N, and O) in the ground state. Journal of Materials Research, 2016, 31, 202–212.