American University of Beirut

European Center for Nuclear Research (CERN)

Report

Summer Student Programme 2014

DFT Calculations Using WIEN2k to Determine Oxygen Defect Structure of Rare Earth Doped Ceria

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June 16-August 29 2014

"Go confidently in the direction of your dreams. Live the life you have imagined". This is what the great American poet and philosopher Henry Thoreau once said. However, this task faces a lot of struggling, some ups and downs, and a great deal of disappointments. Nevertheless, if one is insistent enough, getting there will be inevitable. During my last year as a Physics undergraduate at the American University of Beirut, I had a fright that my scientific journey will not be according to my "dreams", and that I won't be able to accomplish real breakthroughs in Physics because of limitations provided by my nationality, my financial status and my academic level. However, when I got accepted for the Summer Student Program at the world's best research center, CERN, the path came back to its track. My project at CERN was a bit far from what I really want to study in Physics, yet it's always important to learn new things, which will definitely be helpful one day. The project was mainly focused on calculating Oxygen defects in rare earth doped Ceria using the computer program **WIEN2K**, which is based on the Density Functional Theory (DFT), used in Solid State Physics and Physical Chemistry. In this report, the theoretical picture behind DFT will be discussed briefly and in a much unsophisticated way, so that uninvolved people may be able to get a grasp of what's happening in solids, more precisely metals. In addition, a small explanation for the functioning of the program **WIEN2K** will be given. Moreover, some of the results and their interpretation will be described, and what implications do they have on the project. Finally, a conclusion is given, which will include how life at CERN during 8 weeks was fascinating and enriching.

First of all, the quest for understanding atomic behavior inside solids has been long studied and investigated, especially after the revolution of Quantum Mechanics. The latter gave us one very important equation, the Schrödinger equation, which describes the motion of particles subject to a certain force. In solids, there is a huge collection of charged particles, both positive (nuclei, more precisely protons) and negative (electrons), interacting via the Coulomb interaction, which is due to the fact that these particles are charged. However, the enormous number of particles in the system makes solving the Schrödinger equation by hand extremely difficult, yet never impossible. Therefore, Physicists, being lazy, had to come up with some approximations, to reduce the complexity of the problem. The first level of approximation came from Bohr and Oppenheimer, who said that the motion of the protons inside the solid can be neglected, since they're much heavier than electrons, and therefore they're practically immobile. This reduced the number of variables inside the solid by half, which makes this approximation a true blessing. The second level

of approximation came with the introduction of DFT by P. Hohenberg and W. Kohn. The basic principle behind DFT is that, given some external potential (or force times distance) the ground state density of a system(which is the lowest possible level of density a system can have), can directly be found, and from this density, the energy of the system, which is what we want eventually, is derived. Now, in order to get these results, one has to solve this "fixed up" Schrödinger equation. In order to do that, we need to define basis vectors for our Hilbert Space. I know that you reached a chock now once you've read these names, but bear with me. Like in our everyday life, to specify the position of something, we need to know where it is in terms back or forth (the x-axis), left or right (the y-axis) and up or down (the z-axis). Each of these axes requires a basis vector, a mathematical creature of unit length that shows the direction of the axis, and only this direction. Our everyday life experience with geometrical entities defines something called "Euclidian Space". However, to define the motion of small particles, from which we are composed, we need something called "Hilbert Space" which, like any other geometrical space, needs basis vector. In this space we need not just three, but an infinite number of basis vectors in order to define the motion of each particle correctly. The third and final approximation came with identifying these basis vectors. A good number of attempts have been made, and most of them resulted in almost correct answers, but now the task becomes related to the efficiency of calculations, since we are dealing with computers, which cost money, electricity and so on. This leads us to our next subject, the program **WIEN2K**.

Second of all, the power of the program **WIEN2K** came with its use of basis vectors in such a way that gives us a very good approximation of the system, in a very good efficient way. The program was developed by Peter Blaha, Karlheinz Shwarz, Georg Madsen, dieter Kvasnicka and Joachim Luitz at the Institute of Theoretical and Physical Chemistry in the Vienna University of Technology. The basis vectors used in this program are called "Linearized Augmented Plane Waves + local orbitals" (LAPW+lo). The principle idea behind these basis vectors (or functions) is to define a spherical region around each atom, called the *muffin tin radius* with radius R_α, and to divide each basis vector into two parts. The first part, which is inside the sphere, is defined by an oscillating function, while the second part, which is outside the sphere, depends on the radial part of the solution to the Schrödinger equation, and on its first order derivative with respect to energy. Once these basis functions are implanted into the Schrödinger equation, the latter can be solved and the energy of the system can be obtained. One more thing needs to be mentioned about these basis

functions. In an atom, electrons which are closer to the nucleus (called core electrons) are usually less affected by the surrounding atoms, while those who are farther from the nucleus (called valance electrons) are not. Thus, each one of these electrons should be treated differently. But how to differentiate between the two types of electrons from each other? One has to define some sort of energy separation between these two, which will be expressed in the basis functions, thus treating each part differently.

Now, concerning the program from a computational point of view, **WIEN2K** is written in Fortran 90 and requires a UNIX operating system, for the different programs inside it are linked together via C-shell scripts. It has also been implanted on different computer systems, such as Pentium systems running under Linux, IBM RS6000 etc. Moreover, the program can be accessed via a graphical user interface, through a web browser, and it's called **w2web**, which facilitates commands and computations for those who are not very familiar with C-shell script, such as myself. Through the **w2web**, one has to first insert the lattice parameters, which are represented by the distances from the origin in the unit cell to the position of the next atom, thus there are 3 distance parameters (usually called a, b and c), and then we need to define the angle between each of the axes, thus we get three angular parameters (usually called α, β, and γ). Afterwards, one has to specify the type of atoms that are being considered, along with they're R_{α}. Then, by pushing through a succession of buttons, one can begin to generate the different calculations of the cell, two of which are very important to mention. The first is the energy separation between core electrons and valance electrons, which is usually taken to be 6 Ry (this is a different unit for energy, called Rayleigh), however sometimes one has to change it depending on the chosen R_{α}. The second is the size of the computational calculations, which are represented by the "k-mesh", which should be optimized as much as possible depending on the chosen sample. Then after finishing with the "button pushing" stage, one can run the code and, after a few days of waiting for the calculations to finish, one gets the results, which are the subject of our next section.

Third of all, our project concentrated on studying the effect of introducing oxygen vacancies (to be explained shortly afterwards) into rare earth doped ceria. Thus, we introduced the parameters necessary to simulate Cerium oxide (ceria), and then we change one of the cerium atoms into a rare earth metal atom, and finally we remove one of the oxygen atoms of our sample, thus creating an oxygen vacancy inside the structure. This vacancy will start moving from one atomic site into the

other until an equilibrium level is reached, depending on the initial location of this vacancy with respect to the doped material. There are four different types of vacancy cites that can be created, which have been described by S. Grieshammer, B. O.H. Grope, J. Koettgen and M. Martin in their paper "A Combined DFT+U and Monte Carlo Study on Rare Earth Doped Ceria". In the project, we prepared simulations for doped ceria with every possible rare earth metal, which are the following: Lanthanum, Praseodymium, Neodymium, Promethium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, and Ytterbium. And for each doped sample, the four types of vacancies were prepared separately. Unfortunately, due to lack of time, we weren't able to simulate all of these samples, but they are considered for future projects. We got results for Cadmium doped ceria and Europium doped Ceria with the first type of Vacancy for both. Moreover, these results can be compared to data taken from experiments, which are done by Prof. Jens. These results are very interesting, and give us a better knowledge of which material is best to be used in solar panels, one of the best alternative energy resources that will be responsible for sustaining the human kind. All these results were done during the most amazing experience I had in my life, the subject of the final section.

Finally, I would like to describe how being a summer student at CERN was and what type of knowledge I gained and the different activities I did in this experience. The first few days at CERN were a bit intricate, for I always had a difficulty in coping with different environments and cultures, especially if this culture is greatly different from mine. Being a Summer Student at CERN was an adventure since the day I was trying to get the VISA. Unfortunately, the Swiss Embassy at my resident country Qatar was not very cooperative in giving me the VISA. This resulted in a delay of 3 weeks to come to the program, although there have been direct involvement of my supervisor and the Non-Member states summer student coordinators. After arriving to CERN and settling all the formalities, my supervisor and I worked on setting up the computers necessary for the calculations of our code, which was my first ever experience with machines and how to build them. Later on, the main work was practicing the w2web, along with learning a bit how to write C-shell scripts. During this time I must be grateful to my supervisor for being patient, for my brain has difficulty in digesting information related to computer coding. In addition, reading a number of scientific journals related to the project was done regularly, along with listening to lectures about the program presented by Professor Blaha himself. So this project gave me a great deal of wonderful information about the field of Solid State Physics and Physical Chemistry, in addition to basic information about

computer properties, hardware and software. On the other hand, the first 4 weeks of the program were accompanied by series of lectures concerned with Particle Physics, detector physics, data analysis and cosmology. The lectures were presented by a few of the world's best Physicists, which gave me a great opportunity to meet them, and ask them questions. Moreover, the Theoretical Physics department was in my priorities since I came here to CERN, for eventually my dream is to work in theoretical Physics, and this gave me the best chance to meet a few of our time's great theoreticians, and discuss with them different ideas and concepts in High Energy Physics, General Relativity and such. The most noticeable among them was Professor John Ellis, who was very friendly and enthusiastic for meeting me. I had a very fruitful discussion as well with Prof. Wolfgang Lershe and Dr. Ahmad Zein Assi, who are both string theorists. The seminars at the department were no strangers to me, and it ended fascinatingly with a lecture by Professor Juan Maldacena.

Besides the academic side of the amazing journey, I had the opportunity to meet fellow students from different cultures, different fields of study and different classes. And this rich environment of differences opens up opportunity for fruitful discussions. Moreover, the city of Geneva provided a great place for site-seeing, in addition to visiting other places like the Jura Mountain, Annecy in France, and many other places where great time with good friends has been passed. This remarkable time of my life will remain engraved in my memory and the memory of my friends and family, the time when I was a Summer Student at CERN.

References:

1- S. Cottenier, *Density Functional Theory and the family of (L)APW-methods: a step-by-step introduction*, 2002-2013 (2nd edition), ISBN 978-90-807215-1-7 (freely available at http://www.wien2k.at/reg user/textbooks).

2- Peter Blaha, Karlheinz Schwarz, Georg Madsen, Dieter Kvasnicka, Joachim Luitz, User's Guide, WIEN2k 13.1 (Release 06/26/2013**)**