



Computational methods in Materials Science studies

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Abstract

Recent years have seen a great improvement in the field of density functional Theory (DFT) calculation of electronic structure and properties of crystalline materials. There are many reasons that explain the current successful application of DFT to materials science related problems: The super speed of computers, software improvements and theory advancement. Based on these three pillars, we the computing scientists were able to understand the ground state properties of cubic scandium trifluoride (ScF₃) and if need arises, we willalso be able to explore the immense realm of the virtual materials. Indeed, high-throughput techniques for the search of novel crystal structures and the determination of band structure traits have become very popular in the field of computational materials science. Despite these, many challenges are still being faced. Common to all computational materials scientists is the unquenchable thirst for higher speed and better accuracy in DFT calculations. This paper aims to present recent advances in the theory and computational methods in DFT calculation of materials as well as to highlight computational results on structural properties of cubic ScF₃ in comparison to experimental and other theoretical studies. We employed DFT as implemented in the Quantum ESPRESSO computer code. The obtained lattice parameters of between 3.96Å to 4.06Å was in agreement with the experimental lattice parameter of 4.03Å.

Keywords: DFT, materials science, computational methods.

1. Materials science

This is a prime field in research that entails the study of materials propertiesand how these properties are determined by a material's composition and structure. Materials science grew out of an amalgam of various fields like solid-state physics, metallurgy and chemistry just but a few(Ohring, 2001). The reason for this fusion of fields is due to the fact that the rich variety of materials properties cannot be understood within the context of any single discipline. With a basic understanding of the origins of properties, materials can be selected and tuned for enormous variety of applications, ranging from structural steels to computer microchips(Gandhi& Thompson, 1992). Materials science is fertile in engineering activities such as electronics and energy conversion among others.The many materials we study and to which materials science is applied, are usually divided into four categories: metals, polymers, semiconductors, and ceramics (Callister & Rethwisch, 2012).The advancement in quantum mechanics has given us a clear view of the behavior of matter and also the ability to guide



investigation with theory. Two factors are to be applauded in relation to computational materials science. The first factor is the exponential growth of computer-processing power. Secondly, the combined effort of Walter Kohn and John Pople, who developed simplified but accurate solutions to the equations of quantum mechanics(Kohnet al, 1996). The above factors have made it possible to design new materials from scratch using supercomputers and density functional theory.

The approach above is called high-throughput computational materials design, and the idea is simple: use supercomputers to virtually study hundreds or thousands of chemical compounds at a time, quickly and searching for the best building blocks for a new material, be it a battery electrode, a metal alloy or a new type of semiconductor. Recently we have seen many serious predictions such that we are nearing the end of Moore's law(Joy, 2000). Computational methods involve simulating materials at all sizes; from nanowires to bulk materials, using methods such as density functional theory and molecular dynamics, among others. In this paper, we will give a focus on density functional theory.

1.1 Density functional theory (DFT)

The application of density functional theory calculations is rapidly becoming a standard tool for diverse materials modelling problems in materials science (Sholl & Steckel, 2001). This is because DFT is a phenomenally successful approach to finding solutions to the fundamental equation that describes the quantum behaviour of atoms and molecules. The entire application of DFT is built on two fundamental mathematical theorems illustrated by Kohn and Hohenberg and the derivation of a set of equations by Kohn and Sham in the mid-1960s(Casida &Huix-Rotllant, 2012). The first theorem proved by Hohenberg and Kohn is: *The ground-state energy from Schrödinger's equation is a unique functional of the electron density*(Hohenberg, & Kohn, 1964). This theorem implies that there is a mapping between the ground-state wave function and the ground-state electron density. In this first theorem, we learn that the ground state electron density uniquely determines all properties in a system including the energy and the wave function of the ground state. Although Hohenberg-Kohn theorem rigorously proves that a functional of the electron density exists and that it can be used to solve the Schrödinger equation, the theoremsay nothing about what the functional actually is (Sholl, & Steckel, 2001).

The second Hohenberg-Kohn theorem defines an important property of the functional: *The electron density that minimises the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation* (Kohn, 1999). Let it be known that from the second theorem, if the 'true' functional were known, then we could vary the electron density until the energy from the functional is minimised. This variation principle is used in practice with approximate forms of the functional. A more precise way to write down the energy functional as described by the Hohenberg-Kohn second theorem is

$$E[\{\psi_i\}] = E_{\text{known}}[\{\psi_i\}] + E_{\text{XC}}[\{\psi_i\}], \quad (1.1)$$

Here, the functional has been split into two, the $E_{\text{known}}[\{\psi_i\}]$, and everything else, E_{XC} . The "known" term include the following

$$E_{\text{known}}[\{\psi_i\}] = \frac{\hbar^2}{2m} \sum_i \int \psi_i^* \nabla^2 \psi_i d^3 r + \int V(r) n(r) d^3 r + \frac{e^2}{2} \int \int \frac{n(r)n(r')}{|r-r'|} d^3 r d^3 r' + E_{\text{ion}}, \quad (1.2)$$

The terms on the RHS of *equation 1.2* are electron kinetic energies, the Coulomb interactions between the electron and the nuclei, the Coulomb interactions between the pairs of electrons and



the Coulomb interactions between pairs of the nuclei. The term $E_{xc}[\{\psi_i\}]$ in equation 1.1 is the exchange-correlation functional and it is defined to include all the quantum mechanical effects that are not included in the “known” terms (Wesolowski & Warshel, 1993). Assuming that we can express the as-yet undefined exchange correlation energy functional in a useful manner, it is still difficult to find the minimum energy solution of the total energy functional. This difficulty was solved by Kohn and Sham (Kohn & Sham, 1965), who showed that the task of finding the right electron density can be expressed in a way that involves solving a set of equations in which each equation only involves a single electron. The Kohn-Sham equations have the form

$$\left[\frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{xc}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r), \quad (1.3)$$

Equation 1.3 is superficially similar to the time independent nonrelativistic Schrödinger equation (Nelson, 1966) only that it misses the summations that appear in the full Schrödinger equation. This is because the solution to Kohn-Sham equation is a single electron wave function that depend only on three spatial variables $\psi_i(r)$. On the LHS of equation 1.3 are the three potentials, V , V_H and V_{xc} . V defines the interaction between an electron and the collection of atomic nuclei, V_H is called the Hartree potential (Slater, 1951) and is defined by

$$V_H(r) = e^2 \int \frac{n(r')}{|r-r'|} d^3r', \quad (1.4)_{Th}$$

is potential describes the Coulomb repulsion between the electron being considered in one of the Kohn-Sham equations and the total electron density defined by all electrons in the problem. V_{xc} defines the exchange correlation contributions to the single electron equations.

$$V_{xc}(r) = \frac{\delta E_{xc}(r)}{\delta n(r)}, \quad (1.5)$$

V_{xc} can formally be defined as a “functional derivative” of the exchange-correlation energy. From this discussion, the process is circular. To solve the Kohn-Sham equations, we need to know the single electron wave function and to know these wave functions, we must solve the Kohn-Sham equations. To break this circle, the problem is treated iteratively using the following algorithm.

Define an initial, trial electron density, $n(r)$.

Solve the Kohn-Sham equations defined using the trial electron density to find the single particle wave functions, $\psi_i(r)$.

Calculate the electron density defined by the Kohn-Sham single particle wave functions from step 2, $n_{KS} = 2 \sum_i \psi_i^*(r) \psi_i(r)$.

Compare the calculated electron density, $n_{KS}(r)$, with the electron density used in solving the Kohn-Sham equations, $n(r)$. If this two densities are the same, then this is the ground state electron density and it can be used to compute the total energy. If the two densities are different, then the trial electron density must be updated in some way.

1.2 Challenges encountered in DFT calculations

It is important to note that DFT calculations are not exact solutions of the Schrödinger equation. This inexactness arises since the exact functional that Hohenberg-Kohn theorem applies is not



known(Koentopp *et al*, 2008). Any time we perform a DFT calculation, there is always an intrinsic uncertainty that exists within the energies calculated with DFT and the true ground-state energies of the Schrödinger equation. We can't estimate the uncertainty apart from making a careful comparison with the experimental measurements. There are many physical situations where the accuracy of a DFT calculations is good enough to make powerful predictions about the properties of complex materials but in some cases it is not expected to be accurate. We will briefly explain such cases. One such case is that DFT has a limited accuracy in the calculation of electronic excited states. This can be deduced from the Hohenberg-Kohn theorems which only apply to the ground state energy. Another inaccuracy arising from DFT calculations is the underestimation of calculated band gaps in semiconducting and insulating materials. Standard DFT calculations with existing functionals have limited accuracy for band gaps with errors larger than 1 eV being noted when comparing with experimental data. Another situation where DFT calculations will give inaccurate results is associated with the weak van der Waals attractions between atoms and molecules. Van der Waals interactions are a direct result of long range electron correlation and describing these interactions with DFT is challenging. Last but not least is the computational challenge that arise when solving the mathematical problem posed by DFT. Calculations involving a thousand or more atoms are computationally expensive and are reserved for very few individuals that are able to develop or access the state of the art computer codes and equally using the world's largest computers.

1.3 The computation process in materials science using DFT

Several packages have been developed in which DFT has been implemented. Right from the open source packages to the commercial packages. One is able to make a choice depending on a number of factors. One such package that is used in this work is the Quantum ESPRESSO code (Giannozzi *et al*, 2009), it falls among the many open source packages and it is written using python programming language (Van , 2007), a high-level programming language. The operation of quantum ESPRESSO package is mainly subdivided into three parts. The input (coding), processing (assembling and interpreting) and the output (build and run). In the case of DFT, input scripts are written using the shell programming language (Sobell & Helmke, 2005) or python programming language. The input script contains information regarding the system under study, i.e the cell parameters and the way the atoms are arranged, the Bravais lattice and any other relevant information on the system. During processing, the assemblers do convert the shell or python codes into machine language, a language that the computer processors understand. The speed of the processing depends on the architecture of the hardware of the computer used. After processing, interpretation and compilation of the programming code is done. In this particular case, python and shell languages are not compiled but are interpreted to check for any errors. If all is fine, the program is then 'build' and run to give the expected results readable by human as useful information.

1.4 Computation of Structural properties in cubic ScF₃

Scandium Trifluoride (ScF₃) is a trivalent metal fluoride that belongs to the family of perovskite-type compounds that have the general formula ABX₃, but in this case, A-Cation site is vacant. The crystal structure of ScF₃ can be cited as ReO₃-type. Cubic Scandium Trifluoride (ScF₃) is a material that contracts when exposed to heat. Not many materials are known to behave this way. Such materials have many interesting technological applications yet some of its properties are



yet to be fully explored using computational methods. We engaged state-of-the-art *ab initio* methods based on density functional theory (DFT) to study structural and Mechanical properties of ScF₃. The calculated values of the lattice parameter, atomic volumes, bulk modulus and elastic constants agree with the existing experimental and theoretical data. We did our calculation using different exchange-correlation functionals and plane augmented wave pseudo potentials. This information will be used to show the predictive nature of DFT as a standard tool in materials science.

2. Computational methodology

All the calculations of full energies, optimized geometries were carried out using the quantum ESPRESSO computer code and were performed in the framework of Density Functional Theory (DFT). We did our calculations with five (5) exchange –correlations (XC); the Perdew-Burke-Ernzerhof (PBE) (Perdew *et al*, 1996), the Perdew-Wang-91 functional (PW91) (Perdew *et al*, 1992), the Wu-Cohen functional (WC) (Wu & Cohen, 2006), the enhanced Perdew-Burke-Ernzerhof functional for solids (PBEsol) (Perdew *et al*, 2008) and the Perdew-Zunger functional (PZ) (Perdew & Zunger, 1981). We picked these exchange-correlations since they are computationally efficient and no adjustable parameter was required. The core–valence electron interaction was described by Projector Augmented Wave (PAW) pseudo-potentials from the 0.3.1 version of the library of Dal Corso (Dal Corso, 2014). The crystal structure of ScF₃ was relaxed at 0K and 0GPa. After convergence tests, a cut-off energy of 60 Ry for the plane wave basis was chosen. The Monkhorst-Pack scheme and the Brillouin zone integration was performed at 8x8x8 k-point meshes (Monkhorst & Pack, 2005). Post-processing of data in this paper was done using the Thermo-pw software. We obtained our results by fitting the energy-volume data to the Murnaghan equation of state (Murnaghan, 1944). The energy- volume data were obtained as follows; the volume of the simple cubic structure of ScF₃ was deformed by a single parameter ϵ such that the lattice spacing was defined as $a = a_0(1 + \epsilon)$ where a_0 was the theoretical equilibrium parameter that was extracted from Materials project database (Jain *et al*, 2013). We then fitted to the Murnaghan equation of state a series of total energy values for 21 sets of volumes with ϵ ranging from -0.05 to +0.05 in steps of +0.005.

3. Computational results in comparison to experimental and other studies.

Table 1: Indicating the calculated values of the lattice parameter, Bulk modulus, the first pressure derivative the Volume per atom, minimum energy and the Bond lengths of ScF₃ using different exchange correlations (XC)

Exchange Correlation	Reference	a_0 (Å)	Dev Of a_0	B ₀ (GPa)	B'_0	Volume per atom (Å ³)	E ₀ (Ry)	Bond length Sc-F (Å)
PBE	This work	4.06	0.74%	92.8	4.31	16.67	-335.73	2.03
PBESOL	This work	4.01	0.05%	99.7	4.48	16.15	-332.10	2.01
PW91	This work	4.05	0.49%	93.9	4.31	16.50	-336.62	2.03
PZ	This work	3.96	1.74%	110.2	4.67	15.62	-328.87	1.98
WC	This work	4.01	0.05%	99.4	4.48	16.17	-334.18	2.01



EXPERIMENT	a	4.03	-	88.8		16.36		2.01
PBE	b	4.03	0.00%	-		16.36		2.02
HF-DFT PBEO	b	4.05	0.49%	-		16.61		2.03
LCAO method	b	4.03	0.00%	-		16.36		2.01

^aCody *et al*, 2014

^b(Zhgun *et al*, 2012)

From table 1 above, the lattice parameter in the 5 XCs agreed well with the experimental data and past DFT calculations apart from PBE and PZ which gave a high and low lattice constant. The bond lengths were similar in each simulation and agreed with the experiment. It is generally well known that PBE and PZ predict ground state properties that are higher and lower respectively compared to the other exchange correlation functionals (Wu *et al*, 2004). The lattice constant obtained in PBESOL and WC agrees perfectly to the experiment one thus making DFT a standard tool in material prediction.

Conclusion

The aim of this work was to illustrate the inclusion of computational methods in materials science. Since many studies have gone a long way to illustrate the effectiveness of DFT as a standard tool in materials modelling, we employed the theory in predicting the ground state properties of cubic ScF₃. The calculated values of the lattice parameters, bulk modulus and the bond lengths were in agreement with values obtained from other related studies. From our calculation, DFT as a tool was able to complement the experimental approaches as well as predicting other properties like the volume per atom and total energy of cubic ScF₃. Since the tool worked on our system, it could equally work on a different one since the theory remains unchanged. We state clearly that the future of science lies in simulation due the prowess exhibited by DFT in this study and that of other related scholars.

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