Predicting the Elastic Constant of the Theoretical FCC Uranium Using QE

ABSTRACT

Metallic uranium is one the candidate fuel for the advanced reactors. As it has different crystal structures, a fully understanding for the characteristic of each phase is necessary in order to predict the behavior inside the reactor. One of these phases is the U-FCC which has limited evidence on its existence. Hence, the main method to inspect its characteristics is by using simulation and computational methods. In this work, Density Functional Theory (DFT) has been used to perform simple calculations on the U-FCC. A convergency studies are performed to obtain the optimum values for the k points and cutoff energy. Then predicting the elastic modulus by constructing the stress-strain curve is done. The effect of the Hubbard potential on the elastic constant is investigated.

CONTENTS

1. INTRODUCTION

The metallic uranium is one of the main nuclear fuels candidates for advanced reactors, especially fast reactor. A fully understanding of the behavior of this alloy is necessary to be able to predict its behavior under different conditions and during operation. Uranium can exist in many phases depending on the chemical composition and the environment conditions. These phases include α-U (orthorhombic), β-U(tetragonal), γ-U (BCC), body- centered tetragonal, and FCC. The evidence on the existence of the FCC-U is still not clear and research is still going on to prove the existence of the FCC-U. [1] However, a complete understanding of this structure is necessary to how uranium behaves. Hence, the main method to investigate FCC-U behavior is using simulation and computational methods.

A few works have been done on FCC-U using computational methods, especially DFT. A main work has been done by J. P. Crocombette, et. al. [2]. Authors studied the point defect in the uranium dioxide using the plane wave pseudopotential method. This pseudopotential has been generated with the Troullier-Martins method.[2] Then they focused on the studying the lattice parameters and their changes under pressure. Another work is done C.D. Taylor [3], where he investigated FFC-U using First-principles calculations based on the projector augmented-wave (PAW) technique. In this work, Taylor calculated the lattice constants, the elastic moduli and other properties for FCC. B. Beeler and others [4] also studied the different phases of U including FCC using Projector Augmented Wave method and the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE–GGA) of the exchange correlation.

In this work a simple study is performed to investigate the elastic properties of the U-FCC. A convergence study is performed before doing any calculations to ensure that we use the optimum values of the k points and cutoff energy. Then, the elastic constant is calculated for different values of Hubbard potential to investigate its effect on the elastic modulus.

2. METHODS

1.1. Density Functional Theory

The most sophisticated theory that describes the behavior of a material is the quantum theory. In order to calculate the materials properties using this theory, we need to solve the Schrödinger Wave Equation. This equation has two forms, one is time-dependent and the other is the time-independent form. The main goal for solving any of these two equations is to obtain the wave function of the material which can be used to

calculate many other properties. Unfortunately, solving these two equations is not easy, especially the time-dependent from and the complex systems which have more than one particle.[5]

The Density Functional Theory has been introduced as a substitute for the QM theory to make the calculation of the materials and the complex systems' properties easier. So, it's considered as the most popular quantum mechanical modeling method for solid state physics. As we mentioned, this is because its good accuracy compared to the computational cost. In stead of representing the system properties in terms of the wave function, as in QM, the properties, such as the total energy, are expressed as in terms of the electron density. It's obvious that in order to be able to make the calculations easier, we need to make some assumptions that may be valid in most cases and systems. The main assumption adopted in the DFT is the Born-Oppenheimer (BO) approximation. This assumption states that, as the ions are much heavier than the electrons, they may be considered as static particles. Hence, we can neglect ion-ion interactions and the ionic kinetic energy.

Two main theorems represent the basics of the DFT as a valid solution are the first and second Hohenberg and Kohn theorems. The first Hohenberg and Kohn theorem states that 'the ground state of any interacting many-particles system with a given fixed inter-particle interaction is a unique functional of the electron density $n\left(\vec{r}\right)$. So, the ground state wave function can be written as a unique functional of the ground state electron density as follow:

$$\Psi_o = \Psi\left[n_o\right]$$
[1]

and ground state energy as:

$$E\left[\Psi\left[n_o\right]\right] = \left\langle \Psi\left[n_o\right]\middle| \hat{T} + \hat{V} + \hat{U}\middle| \Psi\left[n_o\right]\right\rangle$$
[2]

The second Hohenberg and Kohn theorem states that for a constant number of electrons N, the electron density $n\left(\vec{r}\right)$ which minimizes $E[n]$ has to be the ground state electron density of the N-electron system. According to this theorem, if we started from and arbitrary electron density $n_o\left(\vec{r}\right)$ and minimized it until we reach the minimum E_{min}, the equivalent n will be the exact ground-state electron density.

With these theorems, we know that we can express the total energy -or other properties- in terms of the electron density and we can obtain a unique solution for the energy of the ground state. Even though, we still miss an important part to ensure the validity of the DFT. The two theorems above are applicable even for a Hamiltonian without electron-electron interactions. According to Kohn and Sham proposed conclusion it is possible to represent the ground state density $n\left(\vec{r}\right)$ of the interacting N-electron system (with Hamiltonian (1)) as the ground state density of a non-interacting system of N electrons in a fictitious external potential, called self-consistent potential (υ_{scf}), constructed in such a way that the correct ground state density is reproduced.[6] Accordingly, if the electrons of the system are non-interacting, the Schrödinger equation could be decoupled in N independent equations called Kohn & Sham equations. By solving these equations, we can obtain what is called Kohn & Sham orbitals which can be used to calculate the ground state charge density according to the following equation:

$$\left\{-\frac{\hbar^2\nabla^2}{2m}+\upsilon_{scf}\left(\vec{r}\right)\right\}\psi_i\left(\vec{r}\right)=\varepsilon_i\psi_i\left(\vec{r}\right) \qquad [3]$$

The self-consistent algorithm is used to reach an acceptable value of the $n\left(\vec{r}\right)$ as follows:

1) Starting with an initial density $n_o\left(\vec{r}\right)$;

2) Construct $\upsilon_{scf}\left(\vec{r}\right)$;

3) Solve the last equation given the value of the $\upsilon_{scf}\left(\vec{r}\right)$;

4) Calculate the $n_1\left(\vec{r}\right)$;

5) Repeat the steps from 2-4;

6) Stop if the $n_i\left(\vec{r}\right)$ doesn't change too much from trial to another, according to a specific criterion.

DFT can be used to calculate many properties, such as, the total energy of the system, the band structure and the density of states (DOS); forces and stress acting on each atom, elastic properties, and many other properties. On the other hand, it can't be used to calculate other properties such as time-dependent properties like diffusion properties and decay characteristics. This is because DFT is valid to calculate the ground state energy only.

1.2. Quantum Espresso:

According to the official website of the Quantum Espresso (QE), it can be defined as an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale.[8] It is based on density-functional theory, plane waves, and pseudopotentials. A main part of the DFT calculations on solids is to use Bloch theorem, which has serious advantages. For example, the Hamiltonian could be considered as a diagonal in $\left(\vec{k}\right)$ and the DFT calculations can be restricted to a single unit cell. So, the last equation according to Bloch theorem could rewritten as:

$$\left\{-\frac{\hbar^2}{2m}\left(\frac{1}{i}\Delta+\vec{k}\right)^2+\upsilon_{scf}\left(\vec{r}\right)\right\}u_{\vec{k}}\left(\vec{r}\right)=\varepsilon_{\vec{k}}u_{\vec{k}}\left(\vec{r}\right) \quad [4]$$

where $u_{\vec{k}}\left(\vec{r}\right)$ are lattice-periodic functions. For to the previous equation, it can be solved for different values of $\left(\vec{k}\right)$ and for each $\left(\vec{k}\right)$, we will have a set of $\varepsilon_i\left(\vec{k}\right)$ which is called the dispersion relationship.

We need additional methods to be able to solve equation [4] numerically. A suitable solution is to expand the wave function $u_{\vec{k}}\left(\vec{r}\right)$ as a sum of basis set functions and each function is weighed with a coefficient. To obtain the right solution, we need to obtain the right coefficients of these functions. This job is much easier to do than solving the equation itself as it's basically solving a set of linear equations which can be done using the machine. In order to obtain the exact solution, we need to consider an infinity sum of basis set functions, which is impractical. Instead, we can truncate the expansion and consider enough basis functions to describe the required properties. In QE, this is done in terms of the plane waves.

i.   Energy Cutoff

In QE, the cutoff energy represents the number of the plane waves included in the calculation. As we increase the cutoff energy, the number of the plane waves increase which increase the accuracy of the calculation but make the running time longer. The optimal value of the cutoff energy which gives us enough accuracy and saves time and computational power depends on many factors, including the element, cell size, and the chemical environment. To obtain this value, we need to perform a convergence study on our system. To do so, we need to run calculations with different values of cutoff energy (Ecutwfc in the input file). Then we determine the total energy for each cutoff energy value. We keep changing the cutoff value

and track the total energy until it converges. To obtain the convergence point we need to set a criterion. Usually, 1-2 meV/atom value is used. So, if the difference in the total energy between two different cutoff energy values is less than 1-2 meV/atom we consider the total energy converged.

  ii. K Points and Brillouin Zone Sampling

We mentioned that equation [4] can be solved for a given $\left(\vec{k} \right)$. However, many properties depend on the dispersion relationship for all possible values of $\left(\vec{k} \right)$ in the first Brillouin Zone (BZ). Theoretically, we have infinite number of $\left(\vec{k} \right)$. Of course, this is impossible to have practically, instead, the code samples this zone with a discrete grid. Determining the optimum number of $\left(\vec{k} \right)$ needs some experience. However, for ground state calculation, no many $\left(\vec{k} \right)$ are required but for studying the DOS, we may need a lot of k points. To reduce the number of k points and help speeding up the convergence, the code does smearing on the occupations. This smearing speeds up the calculations by allowing, for example, sum over a Gaussian. The larger the smearing, the lass k points required. However, increasing the smearing to very big values may result in unreasonable results. So, we need to be careful with using the smearing.

  iii. Pseudopotential

Pseudopotential is a very important concept in the DFT as its usage could reduce the number of plane waves required for the simulation. This is done by modifying the ionic potential without affecting the chemical properties of the atom. There are many pseudopotentials generated by different methods. Using pseudopotentials may be tricky and the user should be aware of the application and the suitable use of the pseudopotentials. QE uses pseudopotentials is the .UPF format and there many databases of pseudopotentials on the internet. Some of pseudopotentials may need high computational power but they generate enough accurate results.

3. RESULTS

3.1. K points convergence

In order to ensure that we use the optimum value of the k points, a series of calculations have been performed at a fixed value of cutoff energy and different values of k points. The following k points have been considered:

1. 2 x 2 x 2
2. 3 x 3 x 3
3. 4 x 4 x 4
4. 6 x 6 x 6
5. 8 x 8 x 8
6. 10 x 10 x 10

The cutoff energy has been fixed at value = 39 eV. In figure 1, the total energy is plotted against the number of k points to show the convergence and pick up the optimum value of k points. As we can see in figure 1, the total energy converged very well at k points = 4. However, we can notice that the total energy for k points = 3x3x3 is a little low. To ensure that we are picking the optimum point according to a certain criterion, the difference in total energy between the k point = 10x10x10 and the other points have been calculated. K points 6x6x6 has a difference = 2.5 meV/atom which is accepted according to the criterion mentioned earlier. Hence, 6x6x6 has been considered as the optimum k points value and will be used in the rest of the calculations.
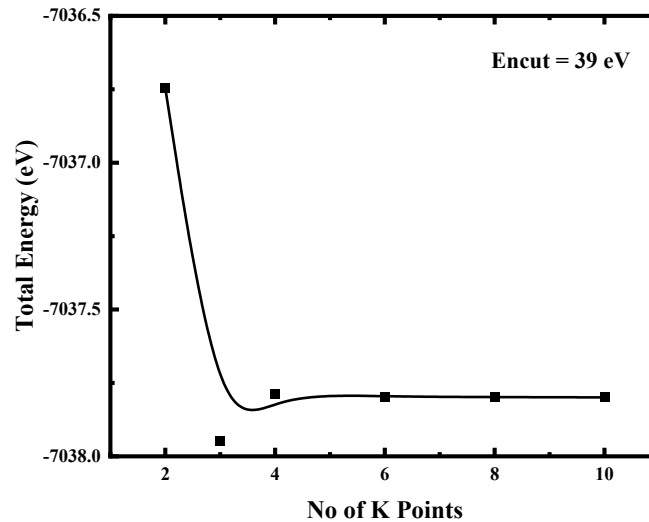

Figure 1: The convergence of number of k points

3.2. Convergence of cutoff energy

For cut energy, different values range from 80 to 160 eV have been considered. The k points value has been kept fixed at the optimum value obtained previously, i.e. 6x6x6. Figure 2 shows the convergence of the cutoff energy and energy of 120 eV seems to be an optimum value. Hence, it will be used in the rest of the calculations.
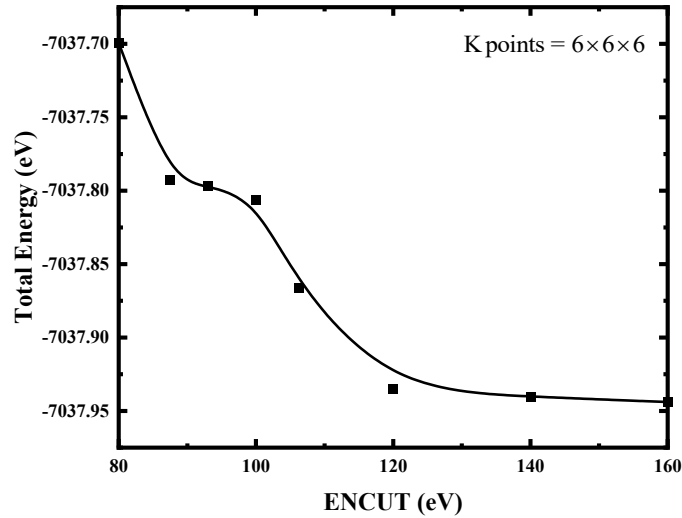

Figure 2: The convergence of the cutoff energy

3.3. Calculating the elastic constant:

In this work, we used the method of the stress-strain curve to calculate the elastic modulus. In this method we calculate the stress applied on the lattice after applying some strain. So, we need to obtain the relaxed lattice parameter first. We do so by performing a calculation for the system with type "vc-relax" where the lattice is allowed to relax to different atomic positions and lattice parameters. After obtaining the relaxed lattice parameters and atomic positions, we perform "sfc" calculations and changing the lattice parameters in 1 direction (x-direction) with a value equivalent to the strain. By plotting the stress applied on the cell versus the strain, we can construct the stress-strain curve and then calculate the elastic constant. Figure 3 shows the results of the stress and the strain values for different

Hubbard potential. It's really hard to obtain a type of the dependence of the elastic modulus on the Hubbard potential as the stress-strain curves obtained are not ideal. Most probably, this requires more
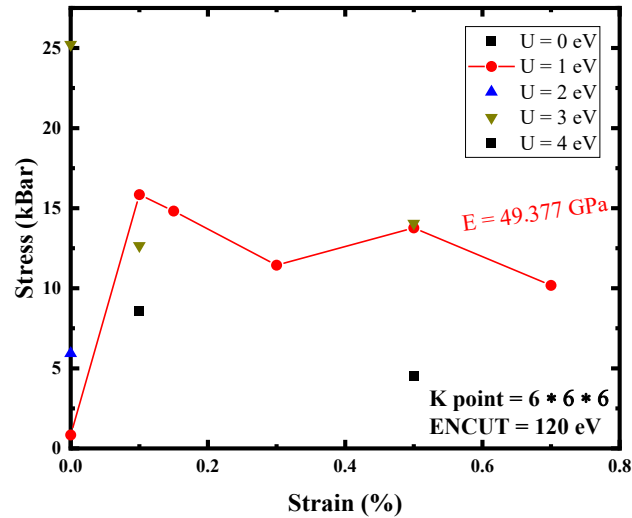
runs and calculations to decrease the scattering in the data. As we can see, we were able to construct a well defined stress-strain curve for U = 1 eV. The calculated elastic constant from this curve is ~ 49.377 GPa. This values is comparable to the value reported by B. Beeler [4]. Beeler obtained a Elastic constant C_{11} about 46 GPa using PBE approximation.

4. SUMMARY AND CONCLUSIONS

The DFT has been used to study the characteristics of the U-FCC. Quantum Espresso code has been utilized to perform the calculations. Convergence study for the k points revealed that the optimum value is 6x6x6 points. For the cutoff energy of the wave function, a value of 120 eV provides a good accuracy and has been considered as optimum. The elastic constant is investigated by constructing the stress-strain curve in the elastic region. Even though the constructed stress-strain curves were not ideal, a value of E obtained was comparable to those reported in the literature. In order to increase the accuracy of the calculations, we need to increase the number of runs perform calculations for more strain values.

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