A report on FCC U structure studied utilizing DFT.

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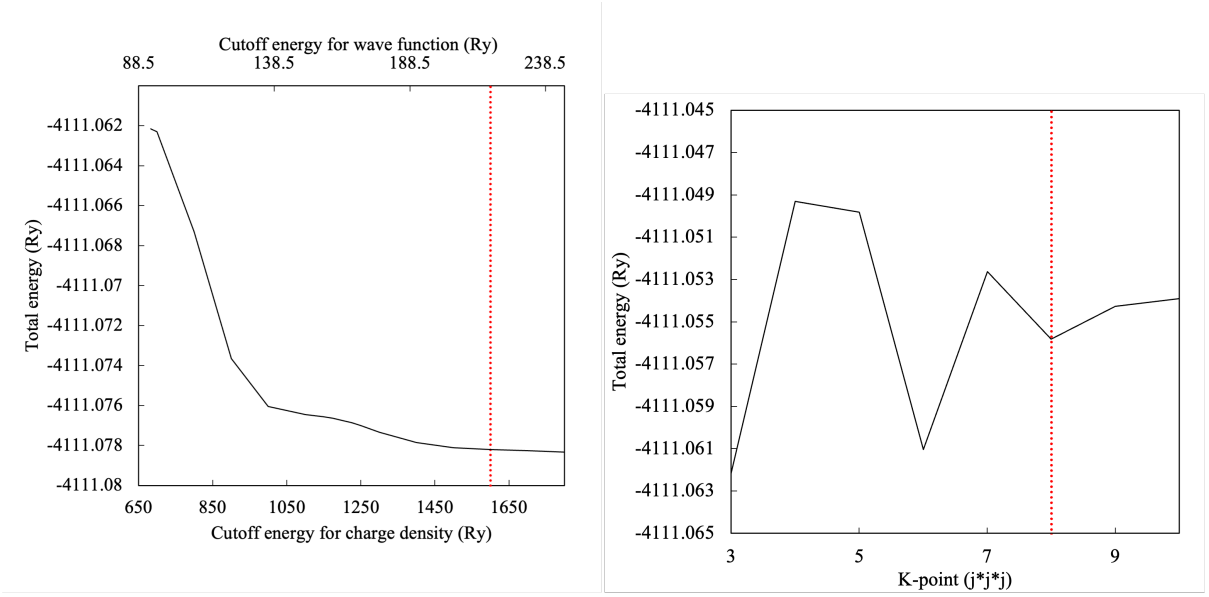
1 Problem statement

Considering a theoretical FCC U crystal calculate its lattice parameters using density functional theory (DFT). Show the convergence criteria. Finally, by changing Hubbard U term from 0 to 4 eV, discuss its effects on elastic constants (or bulk modulus).

2 Solution

2.1 Methodology

Systems are investigated using the Quantum Espresso (QE) which is a suite of Open-Source computer codes for electronic structure calculations and materials modeling at the nano-scale. Face centered cubic (FCC) crystal system of Uranium is studied here considering only four atoms within the supercell. Simulations are running for different lattice parameter until the equilibrium cohesive energy at 0K temperature and zero pressure is attained in self-consistent mode of QE. The estimated energy error is maintained below the convergence threshold of 1meV per atom. By fitting Equation of State (EOS) structural properties (lattice parameters and bulk modulus) of FCC U is estimated. Calculations are performed using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) density functional (DFT) implementation for the description of exchange-correlation with an additional Hubbard U term. The main aim of the Hubbard U is to correct for the effects of self-interaction of f electrons. Hubbard U values 0, 1 ,3 eV. Hubbard U value 0 eV means, no Hubbard U is considered. An U PAW pseudo-potential is utilized with 6d1.5 7s2.0 7p0. 5f2.5 valence electronic configuration a core represented by Rn. This pseudopotential has generated by Dr. Andrea Dal Corso using "atomic" code. Convergence test for both energy cutoff and k-point mesh is performed. Because of U being metal, calculations were repeated considering Methfessel and Paxton's (M-P) smearing method of the first order is used with a width of 0.2 eV as per Beeler *et al.* (2010)



(a) (b)

Figure 1: (Convergence test for (a) cutoff energy and (b) k-point. Red dotted line means converged or selected values for further calculations.

[1] to determine the partial occupancy for each wave function. Furthermore, spin polarization is included in the calculation assuming magnetic U.

2.2 Results

Convergence result of cutoff energies is shown in figure 1 (a). Two cutoff energies are considered in the current calculation one is energy cutoff for charge density (ecutrho) and another one is energy cutoff for wave function (ecutwcf). Ecutrho is changed between 700 Ry and 1800 Ry maintaining the ratio of ecutwcf and ecutrho 0.1361369 constant as per the pseudo-potential file. To keep the computations less expensive, k-point mesh is kept 3 X 3 X 3 and Hubbard U term equals to 1.0eV. As the kinetic energy cutoff ecutwfc (Ry) determines the size of the Plane-Wave (PW) basis set used to expand wavefunctions (i.e. Kohn-Sham orbitals), higher value needs a larger computational power. In this regard, we need to test the convergence of the cutoff energies. For the current project, the converged values of ecutwcf and ecutrho are approximately 218 Ry (2964 eV) and 1600 Ry respectively. Though the cutoff energy seems very high compared to other PAW based pseudo-potentials (258 eV), Crocombette *et al.* (2001) also observed a very high cutoff energy (2448 eV) [1]. There is another unfavorable side of larger cutoff energy. Because of larger basis set, uncertainty in lattice parameter is higher, which may lead to poor convergence.

The second step of the current problem solution is to test the convergence of k-point mesh. As, our given system is cubic, reciprocal lattice is also cubic. More points in k-point mesh

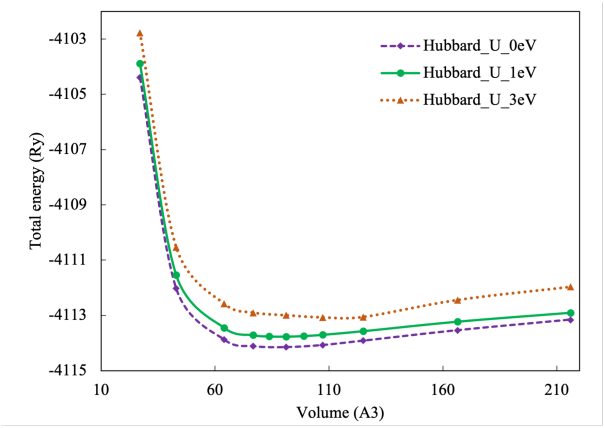


Figure 2: Total energy in Ry unit vs. total volume in A^3 unit plot for different Hubbard U values.

indicates more point to perform calculations, which prompts to better accuracy. Again, it requires more computational power. For a system with small numbers of atoms generally requires larger value of k-point. In the current case, we are only considering four atoms, so we need a larger k-point grid. Convergence test result for k-point is shown in figure 1(b) and selected k-point mesh is 8 X 8 X 8. All of the calculations shown in figure 1(b) are conducted at the minimum cutoff energies as per the pseudo-potential. During the convergence tests, lattice constants are kept fixed at the value of 3.4 Å.

Varying the lattice parameter applying the proper cutoff energy and k-point to the sampling, total energy of the system determined in the self-consistent mode of QE. Results from the DFT calculation (shown in figure) are fitted with Murnaghan [2] equation of state (EOS) function. In this, EOS, bulk modulus is considered proportional to pressure. From the fitting parameters, equilibrium cohesive energy or total energy at zero pressure, equilibrium bulk modulus, and equilibrium volume at zero pressure is calculated. This calculation is carried out for three conditions to observe the effect of Hubbard U term.

Increasing the Hubberd U value shifts the E vs. V (see figure 2) upward. Another criterion observed is that for higher Hubbard U value, convergence of the calculations is higher.Similar problem arises at larger lattice parameters (greater than or equal to 5Å). Equilibrium lattice constant of the FCC U varies between 4.375 Åto 4.625 Åfor the condition of changing Hubbard U term. Typically Uranium attains a BCC phase at higher temperature and orthorhombic structure at lower temperature [3]. Zero pressure equilibrium volume per atom values are 19.98 $Å^3$ and 20.15 $Å^3$ for low and high temperature phases respectively. From the current calculation, zero pressure equilibrium volume per atom value is approximately 22.5 $Å^3$. Because of higher symmetry, typically FCC phases are observed at higher temperature phase of materials, for example iron [4]. If this is also valid for uranium, then when uranium is cooled from very

high temperature (FCC) to high temperature phase (BCC), it will experience an contraction of about 10%. In contrast to this, for iron, expansion occurs.

3 Conclusion

The problem related to lattice constant calculation of FCC U based on variable assumption is perform via density functional theory utilizing Quantum espresso. For better accuracy, for each of the Hubbard U values separate convergence tests should be performed. Though lattice parameters do not vary significantly with Hubbard U term, bulk modulus might be. Additional calculations are required to calculate the bulk modulus at different Hubbard U. Moreover, by changing the pseudo-potential function, converged cutoff energy should be recalculated.

References

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