DFT studies on FCC U using Quantum Espresso software.

Introduction.

The main target of the following sections is to know how to build, familiarize and run a DFT simulation using Quantum Espresso software. First, we build our structure, relax it and then do necessary convergence tests to optimize between efficiency and computational costs. We used CIF files from Material Project website to build the structure and then relax it. The cut off energy convergence test optimize the number of plane waves used to describe the system. In addition, K-Points convergence test optimize the sampling of the Brillouin zone.

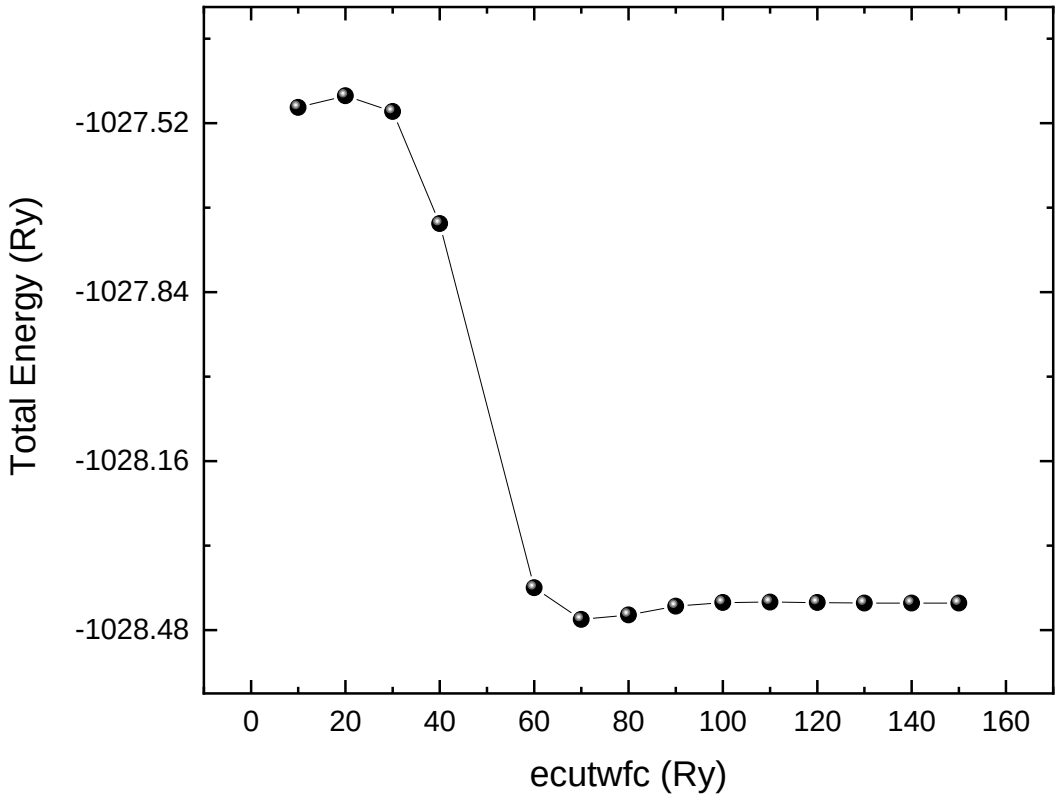
PW.X input for FCC U.

QE input requires a number of data to solve Kohn-Sham equations. One of those data is the atomic positions and the crystal structure. We are dealing with an FCC Uranium. To implement that in the input code there are two methods. One to identify the crystal structure directly through the ibrav card or using the free structure method and add the CELL_POSITIONS card. We will go with the second option, as we will need to manipulate the lattice to calculate the elastic constants and using free structure methods will make it easier for us. One thing to mention is that QE operates using not the conventional unit cell, but the primitive unit cell based on the primitive axis vectors as the most economical way to define a unit cell. In the case of FCC lattices, this allows us to define our periodic crystal containing just a single U atom at the origin [0 0 0]. The following lines represent the part of the input used to build the FCC U structure. In addition to defining the structure, spin polarization was also included, number of atoms and the atoms types. Smearing is included to allow for smooth transition between bands. In addition to that + U, term added and will be discussed later.

```
ibrav                    = 0
! ibrav                    = 0 FCC structure
ATOMIC_POSITIONS (alat)
U             0.0000000000        0.0000000000        0.0000000000
CELL_PARAMETERS alat
0.0     0.5     0.5
0.5     0.0     0.5
0.5     0.5     0.0
```

Cut off energy convergence.

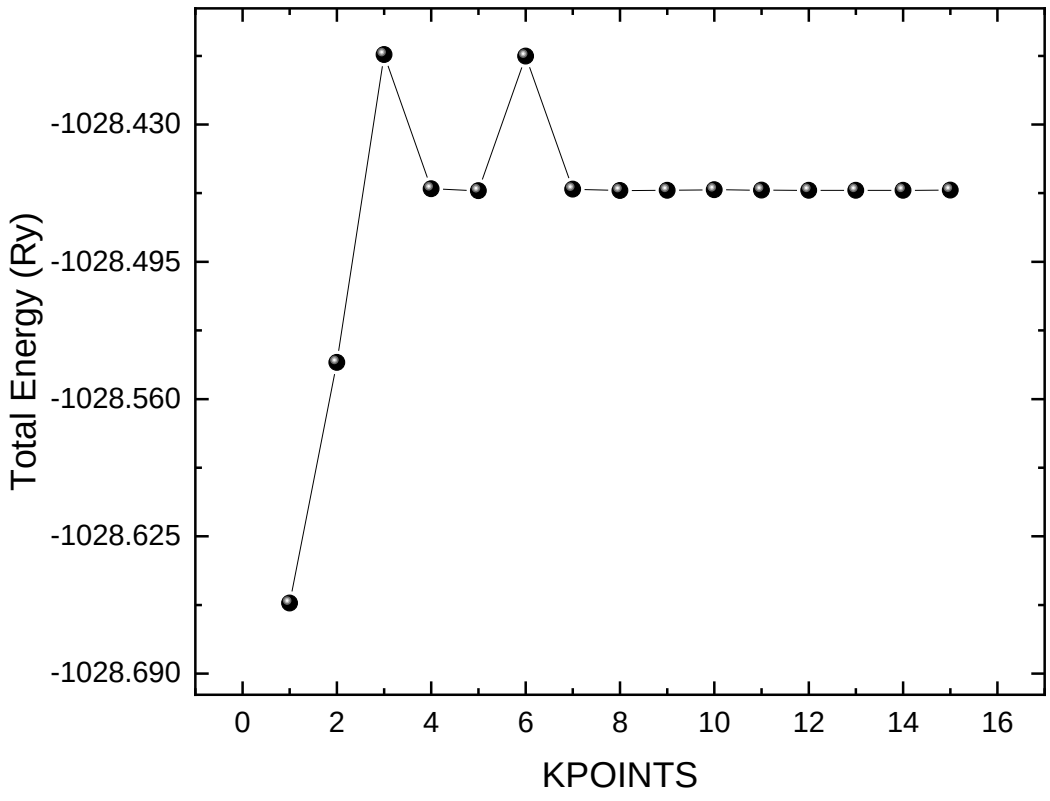
The kinetic energy cut determines how far we can go down for the search of the ground state energy and we vary it from 10 Ry up to 150 Ry and identify the point where no or limited change detected in the total energy. Beyond this point if we increased the cutoff energy it means that we are using more computational resources than we need. The following graph represents the change if the total energy with the cutoff energy. From the curve, we can say that the 70 Ry is a good cutoff energy to use in our calculations. This value will ensure optimized use of computational resources without sacrificing efficacy.



K-points convergence.

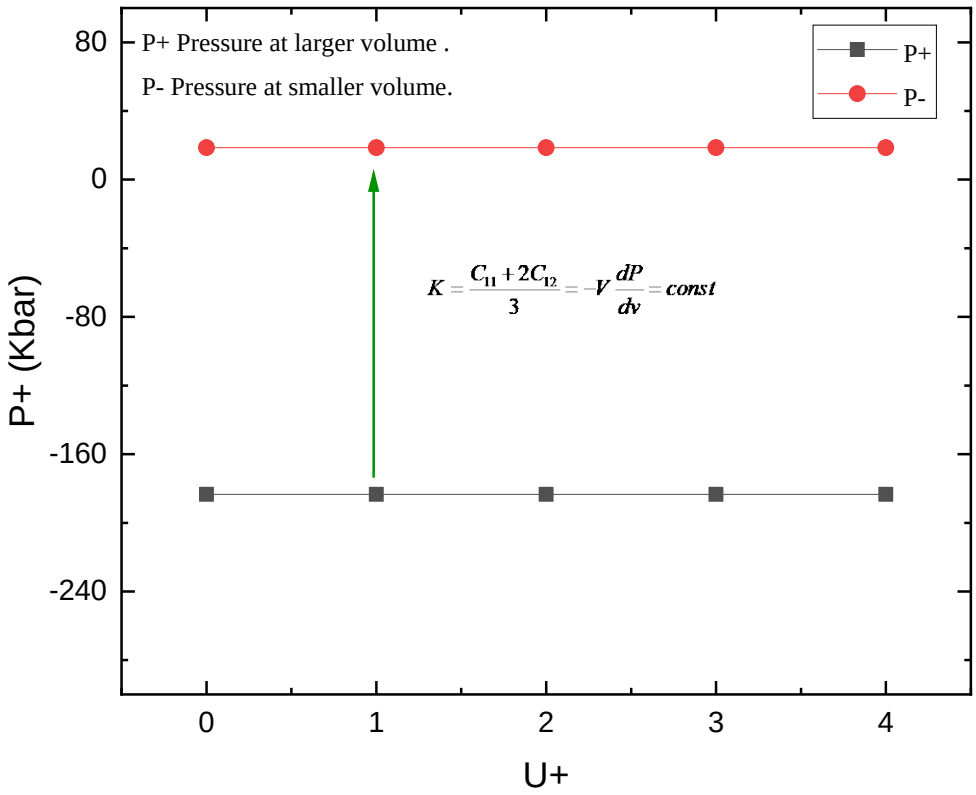
Before going through the test, we should recall that we are dealing with infinite systems using periodic boundary conditions with the help of Bloch theorem to solve Schrodinger. Because of the Bloch theorem, we need to solve Schrodinger-like Kohn Sham equation everywhere in the Brillouin Zone. In reality, we do it for a finite number of K values. The energy of the structure is computed by integrating over the occupied bands of the firs BZ. Thus, summing over a finite number of K-Points is an approximation to perform an integral. So that, we need to make sure that the number of K-Points used is enough to have a converged value for the energy computed by this integral.

Convergence tests for K-points grid is the same as cutoff energy convergence by varying the NK at the same cutoff energy derived from the previous test. The following graph represents the change of the total energy with the change of NK points. It looks very weird and opposite to what we were expecting. Many trials were made to figure out why is behaves like that which ended with nothing. Due to that we are going to use 8 8 8 as our NK points instead of the value from this test which is 1 1 1 because it doesn't make any sense.



Effect of +U on elastic constants.

One of the main problems while doing first principle calculations on Uranium is the fact that f electrons are localized on Uranium atoms and do not spread over the material as usual valence electrons. To overcome this problem, the first correction that has been applied is the LDA+U correction in which a Hubbard U term acting between f electrons is added which allows the opening of an f-f gab. In this section, we are trying to see if the +U term is going to affect the elastic constants or not. To do so, we are going to change the Hubbard term from 0 to 4 ev and see how it's going to affect the bulk modulus which is one of the elastic constants. The bulk modulus defined to be the change in pressure with a small change in volume per atom. We will use a finite difference approximation between different runs with the same Hubbard term to find the bulk modulus for each Hubbard term. Then compare them. In The following graph we can see that the change in the pressure is constant at different +U values and we already implemented the same change in volume value, which means the bulk modulus will not be affected with the change in the +U term.



Appendix.

A. Relaxation input code and batch files.

```
&CONTROL
    calculation = 'relax'
    pseudo_dir  = '.'
    tprnfor     = .TRUE.
    tstress     = .TRUE.
    etot_conv_thr =   1.0000000000d-05
    forc_conv_thr =   1.0000000000d-04
/
&SYSTEM
    ibrav                    = 0
    celldm(1)                = 10.34
    degauss                  =  0.01
    ecutwfc                  =  10
    nat                      = 1
    nspin                    = 2
    ntyp                     = 1
    occupations              = "smearing"
    smearing                 = "gaussian"
    starting_magnetization(1) =  2.00000e-01
    Hubbard_U(1)             =  2.0
/

&ELECTRONS
    conv_thr            =  1.00000e-06
    electron_maxstep    = 200
    mixing_beta         =  4.00000e-01
    startingpot         = "atomic"
    startingwfc         = "atomic+random"
/
&IONS
    ion_dynamics = "bfgs"
/
ATOMIC_SPECIES
U    238.02891  U.pbe-spfn-kjpaw_psl.1.0.0.UPF
ATOMIC_POSITIONS (alat)
U             0.0000000000        0.0000000000        0.0000000000
CELL_PARAMETERS alat
0.0     0.5     0.5
0.5     0.0     0.5
0.5     0.5     0.0
K_POINTS {automatic}
 8  8  8  0 0 0
```

```
#!/bin/bash

'/home/hamdy/QE/qe-6.8/bin/pw.x' <relax.in> relax.out
find ./ -type f -name "*.out" -exec grep 'Final' {} \; > RELAX
```

B. Cutoff energy input and batch files.

```
&CONTROL
    calculation = 'scf'
    pseudo_dir  = '.'
    tprnfor     = .TRUE.
    tstress     = .TRUE.
    etot_conv_thr =   1.0000000000d-05
    forc_conv_thr =   1.0000000000d-04
/
&SYSTEM
    ibrav                    = 0
    celldm(1)                = 10.34
    degauss                  =  0.01
    ecutwfc                  =  10
    nat                      = 1
    nspin                    = 2
    ntyp                     = 1
    occupations              = "smearing"
    smearing                 = "gaussian"
    starting_magnetization(1) =  2.00000e-01
    Hubbard_U(1)             =  2.0
/
&ELECTRONS
    conv_thr            =  1.00000e-06
    electron_maxstep    = 200
    mixing_beta         =  4.00000e-01
    startingpot         = "atomic"
    startingwfc         = "atomic+random"
/
&IONS
    ion_dynamics = "bfgs"
/
ATOMIC_SPECIES
U    238.02891  U.pbe-spfn-kjpaw_psl.1.0.0.UPF
ATOMIC_POSITIONS (alat)
U             0.0000000000        0.0000000000        0.0000000000
CELL_PARAMETERS alat
0.0     0.5     0.5
0.5     0.0     0.5
0.5     0.5     0.0
K_POINTS {automatic}
 8  8  8  0 0 0
```

```
#!/bin/bash

'/home/hamdy/QE/qe-6.8/bin/pw.x' <10.in> 10.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <20.in> 20.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <30.in> 30.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <40.in> 40.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <50.in> 50.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <60.in> 60.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <70.in> 70.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <80.in> 80.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <90.in> 90.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <100.in> 100.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <110.in> 110.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <120.in> 120.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <130.in> 130.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <140.in> 140.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <150.in> 150.out
find ./ -type f -name "*.out" -exec grep '!' {} \; > conv
```

C. K-Points convergence input and batch files.

```
&CONTROL
    calculation = 'scf'
    pseudo_dir  = '.'
    tprnfor     = .TRUE.
    tstress     = .TRUE.
    etot_conv_thr =   1.0000000000d-05
    forc_conv_thr =   1.0000000000d-04
/
&SYSTEM
    ibrav                    = 0
    celldm(1)                = 10.34
    degauss                  =  0.01
    ecutwfc                  =  70
    nat                      = 1
    nspin                    = 2
    ntyp                     = 1
    occupations              = "smearing"
    smearing                 = "gaussian"
    starting_magnetization(1) =  2.00000e-01
    Hubbard_U(1)             =  2.0
/
&ELECTRONS
    conv_thr            =  1.00000e-06
    electron_maxstep    = 200
    mixing_beta         =  4.00000e-01
    startingpot         = "atomic"
    startingwfc         = "atomic+random"
/
&IONS
    ion_dynamics = "bfgs"
/
ATOMIC_SPECIES
U    238.02891  U.pbe-spfn-kjpaw_psl.1.0.0.UPF
ATOMIC_POSITIONS (alat)
U             0.0000000000        0.0000000000        0.0000000000
CELL_PARAMETERS alat
0.0     0.5     0.5
0.5     0.0     0.5
0.5     0.5     0.0
K_POINTS {automatic}
 1  1  1  0 0 0
```

```
#!/bin/bash

'/home/hamdy/QE/qe-6.8/bin/pw.x' <1.in> 1.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <2.in> 2.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <3.in> 3.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <4.in> 4.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <5.in> 5.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <6.in> 6.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <7.in> 7.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <8.in> 8.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <9.in> 9.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <10.in> 10.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <11.in> 11.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <12.in> 12.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <13.in> 13.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <14.in> 14.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <15.in> 15.out
find ./ -type f -name "*.out" -exec grep '!' {} \; > conv
```

D. +U input and batch files.

```
&CONTROL
    calculation = 'scf'
    pseudo_dir  = '.'
    tprnfor     = .TRUE.
    tstress     = .TRUE.
    etot_conv_thr =   1.0000000000d-05
    forc_conv_thr =   1.0000000000d-04
/
&SYSTEM
    ibrav                    = 0
    celldm(1)                = 11.34
    degauss                  =  0.01
    ecutwfc                  =  70
    nat                      = 1
    nspin                    = 2
    ntyp                     = 1
    occupations              = "smearing"
    smearing                 = "gaussian"
    starting_magnetization(1) =  2.00000e-01
    Hubbard_U(1)             =  0.0
/
&ELECTRONS
    conv_thr            =  1.00000e-06
    electron_maxstep    = 200
    mixing_beta         =  4.00000e-01
    startingpot         = "atomic"
    startingwfc         = "atomic+random"
/
&IONS
    ion_dynamics = "bfgs"
/
ATOMIC_SPECIES
U    238.02891  U.pbe-spfn-kjpaw_psl.1.0.0.UPF
ATOMIC_POSITIONS (alat)
U             0.0000000000        0.0000000000        0.0000000000
CELL_PARAMETERS alat
0.0     0.5     0.5
0.5     0.0     0.5
0.5     0.5     0.0
K_POINTS {automatic}
 8  8  8  0 0 0
```

```
&CONTROL
    calculation = 'scf'
    pseudo_dir  = '.'
    tprnfor     = .TRUE.
    tstress     = .TRUE.
    etot_conv_thr =   1.0000000000d-05
    forc_conv_thr =   1.0000000000d-04
/
&SYSTEM
    ibrav                    = 0
    celldm(1)                = 9.34
    degauss                  =  0.01
    ecutwfc                  =  70
    nat                      = 1
    nspin                    = 2
    ntyp                     = 1
    occupations              = "smearing"
    smearing                 = "gaussian"
    starting_magnetization(1) =  2.00000e-01
    Hubbard_U(1)             =  0.0
/
&ELECTRONS
    conv_thr            =  1.00000e-06
    electron_maxstep    = 200
    mixing_beta         =  4.00000e-01
    startingpot         = "atomic"
    startingwfc         = "atomic+random"
/
&IONS
    ion_dynamics = "bfgs"
/
ATOMIC_SPECIES
U    238.02891  U.pbe-spfn-kjpaw_psl.1.0.0.UPF
ATOMIC_POSITIONS (alat)
U             0.0000000000        0.0000000000        0.0000000000
CELL_PARAMETERS alat
0.0     0.5     0.5
0.5     0.0     0.5
0.5     0.5     0.0
K_POINTS {automatic}
8  8  8  0 0 0
```

```
#!/bin/bash

'/home/hamdy/QE/qe-6.8/bin/pw.x' <scf+1.in> scf+1.out
'/home/hamdy/QE/qe-6.8/bin/pw.x' <scf-1.in> scf-1.out
find ./ -type f -name "*.out" -exec grep 'P=' {} \; > elastcons
```