Variation of Numerical Noise in DFT Calculations with Unit Cell Parameters

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(Dated: December 11, 2022)

Density functional theory works on the quantum mechanical axiom that everything there is to know about a material (a multi electron system), can be determined by a many body wave function, which in turn is related to density of multi electron system. Since its introduction in 1964-65, Density Functional Theory has contributed immensely to science, specifically to the field of material science. The accuracy and precision of DFT calculations are established by measuring the numerical noise in the output. This study is an attempt at validating the application of density functional theory for crystalline material by finding the variation in Numerical Noise in DFT calculations with unit cell parameters.

Keywords: Density Functional Theory; wave function; quantum mechanics; crystal structure.

I. INTRODUCTION

Computational physics, when combined with theory, explains the why behind material physics, and it helps us in predicting the previously unobserved chemical phenomenon. Density Functional Theory is a computational quantum mechanical modelling method which is used in physics, chemistry and material science to understand the properties of material using fundamental laws of quantum mechanics [1]. For multi electron systems, conventional quantum mechanics isn't feasible to use, e.g., even for a single small water molecule, approx 900 interactions have to calculated. There are several approximation methods used in computational models which can be broadly classified by Fig. 1

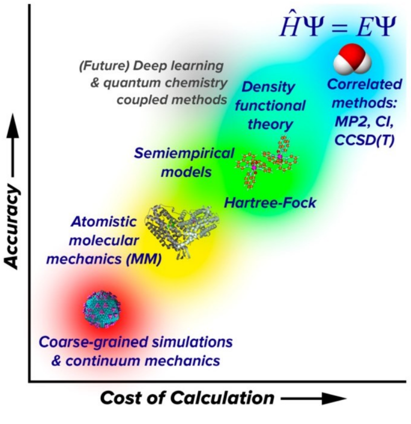

FIG. 1. Accuracy vs cost for various computational methods [2]

Our field of interest on this paper is density functional theory, which was postulated in 1964 by Hohenberb and Kohn, for which Kohn also received the noble prize in 1998. The basic axiom for DFT is that "All ground state properties can be cast as a functional of the charge density that must be minimised in energy." Since all computational methods, including DFT, use some approximation; its a common practice to keep track of numerical noise in DFT results while attempting DFT calculations. Numerical noise can be defined as lack of precision while attempting the same calculation with different set of parameters. In this study, we have attempted finding impact of the choice of the unit cell on numerical noise in DFT calculations.

II. METHODS

The density functional theory calculations for this study were carried out using Quantum Mobile package (version 21.05.1). Perdew-Burke-Ernzehof (PBE) exchange correlation function approximation was used as implemented in Quantum Expresso code (QE) code. The CIF file (Crystallographic Information File) for Aluminium FCC unit cell was obtained from materialsproject.org [3, 4]

CIF2CELL package (version 2.0.0a3) [5] was used for generating input file for Quantum Espresso. VESTA and XCRYSDEN package was used for visualising unit cells and varying the unit cell parameters. The pseudopotential used for the study were obtained from standard solid-state pseudopotentials (SSSP) library at materialscloud.org/sssp [6].

For basic convergence testing, k-point mesh (computational mesh in reciprocal space), and Ecutwfc and Ecutrho, to determine the wave function and density basis set size cut off, respectively, was optimised by variation against total energy value. Geometry optimisation towards the ground state was performed by "relax" and "vc-relax" calculations for coordinates and cell shape respectively. Birch-Murrnaghan fit was used for determining the equilibrium volume by E(V) scan and EOS fit.

The cell parameters were varied by varying choice of primitive unit cell and numerical noise on these was calculated by observing the change in total energy parame-

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ter for all.

III. RESULTS AND DISCUSSION

A. Basic Convergence Testing

For optimisation of k-point mesh, variation was done from 1x1x1 mesh to 47x47x47 in step size two, against the hydrostatic pressure (kbar). The optimum mesh size was found to 29x29x29, which is somewhat dense and offered a run-time of 14.04 seconds, and -5.83 kbar hydrostatic pressure.

Ecutwfc and Ecutrho, the wave function and density basis set size cut off were also optimised against hydrostatic pressure (kbar). Ecutwfc was varied from 9 to 69 in steps of ten, the optimum value being 29 (run time 13.22, hydrostatic pressure -5.82 kbar). Similarly, Ecutrho varied from 45 to 345 in steps of fifty, the optimum value being 145. The trend for these is shown in figure 2. Multiplication factor between these two was varied from 2 to 6 in step of one, and five was found to be the optimum value.

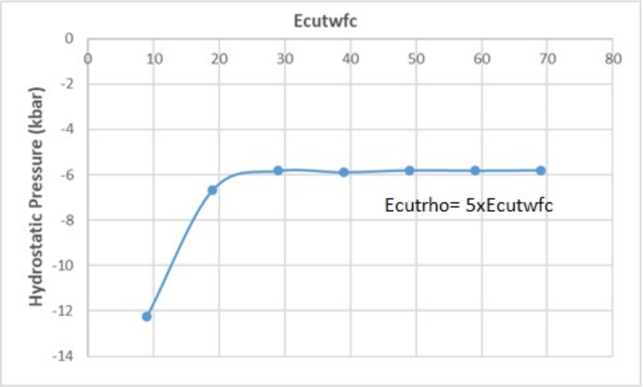


FIG. 2. Convergence test: hydrostatic pressure vs. energy cut off

B. Geometry Optimisation

Geometry optimisation results are summarised in the table 1 below-

Geometry optimisation using energy and pressure variation for scf, relax and vc-relax calculations

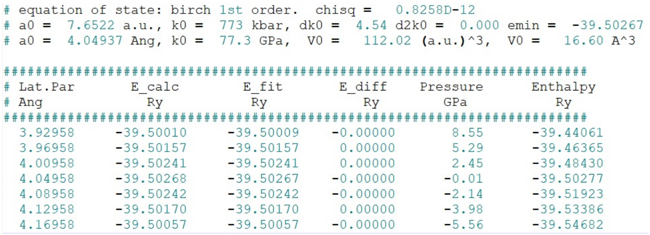
Calculation	Total energy (Ry)	Hydrostatic press.(kbar)
scf	-39.500489	−2.09
relax	-39.5004899	−2.09
vc-relax	-39.502675	−0.12

Final volume obtained by vc-relax calculation was 111.20770 cubic a.u. (16.47928 cubic Ang).

C. Birch-Murrnaghan equation of state: E(V) and EOS fit

E(V) scan and EOS fit was performed to determine Birch-Murrnaghan fit in order to obtain the equilibrium volume.

For this study, first E(V) scan was done by varying cell lattice parameter was varied in steps of 0.02 Ang., three step below and above the initial value. Energy and pressure variation with the same was recorded. Next step was to fix the target pressure so that volume is the only degree of freedom. From the resulting volume from each calculation, and E(V) was performed using ev.x command. The Birch-Murnaghan equation of state obtained is shown in figure 3 below. Next step was to fix the target pressure so that volume is the only degree of freedom. From the resulting volume from each calculation, and E(V) was performed using ev.x command. The Birch-Murnaghan equation of state obtained is shown in figure 4 below.



```
# equation of state: birch 1st order.  chisq =   0.8258D-12
# a0 =  7.6522 a.u., k0 =  773 kbar, dk0 =  4.54 d2k0 =  0.000 emin =  -39.50267
# a0 =  4.04937 Ang, k0 =  77.3 GPa,  V0 =   112.02 (a.u.)^3,  V0 =   16.60 A^3

##########################################################################
# Lat.Par       E_calc        E_fit       E_diff    Pressure      Enthalpy
# Ang             Ry           Ry            Ry        GPa           Ry
##########################################################################
  3.92958     -39.50010     -39.50009    -0.00000       8.55     -39.44061
  3.96958     -39.50157     -39.50157     0.00000       5.29     -39.46365
  4.00958     -39.50241     -39.50241     0.00000       2.45     -39.48430
  4.04958     -39.50268     -39.50267    -0.00000      -0.01     -39.50277
  4.08958     -39.50242     -39.50242    -0.00000      -2.14     -39.51923
  4.12958     -39.50170     -39.50170     0.00000      -3.98     -39.53386
  4.16958     -39.50057     -39.50057    -0.00000      -5.56     -39.54682
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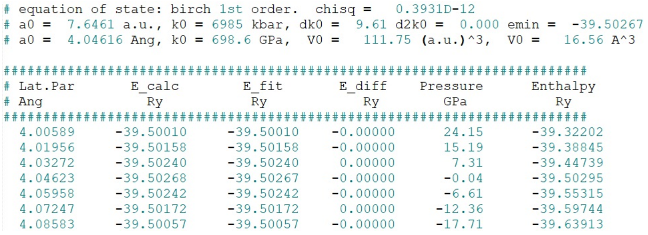
FIG. 3. E(v) scan for Birch-Murnaghan equation of state



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# equation of state: birch 1st order.  chisq =   0.3931D-12
# a0 =  7.6461 a.u., k0 = 6985 kbar, dk0 =  9.61 d2k0 =  0.000 emin =  -39.50267
# a0 =  4.04616 Ang, k0 = 698.6 GPa,  V0 =   111.75 (a.u.)^3,  V0 =   16.56 A^3

##########################################################################
# Lat.Par       E_calc        E_fit       E_diff    Pressure      Enthalpy
# Ang             Ry           Ry            Ry        GPa           Ry
##########################################################################
  4.00589     -39.50010     -39.50010    -0.00000      24.15     -39.32202
  4.01956     -39.50158     -39.50158    -0.00000      15.19     -39.38845
  4.03272     -39.50240     -39.50240     0.00000       7.31     -39.44739
  4.04623     -39.50268     -39.50267    -0.00000      -0.04     -39.50295
  4.05958     -39.50242     -39.50242    -0.00000      -6.61     -39.55315
  4.07247     -39.50172     -39.50172     0.00000     -12.36     -39.59744
  4.08583     -39.50057     -39.50057    -0.00000     -17.71     -39.63913
```

FIG. 4. EOS fit for Birch-Murnaghan equation of state

DFT calculation on the input file generated from this data showed total energy of -39.50267533 Ry, zero hydrostatic pressure and zero stress on the axes (new lattice constant being 4.03934 Ang.).

D. Primitive unit cell variation

Eight different variation for primitive cell were done, having the same volume as obtained from Birch-Murghan equation of state (EOS fit). Figure 5 shows all eight cells visualised using Gaussview 06.

After the DFT calculations on each of these cells, results were summarised in figure 6. Initial unit cell with three fold symmetry was found to have the lowest energy,

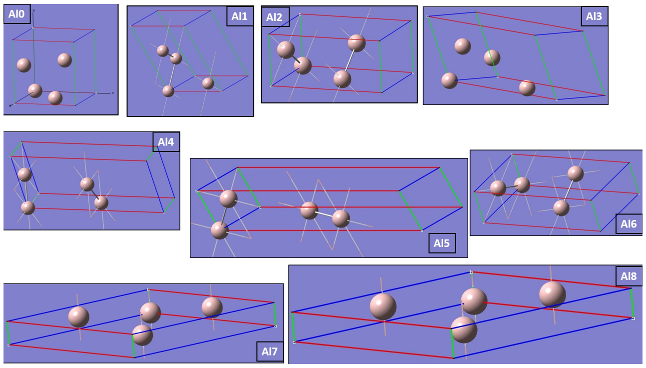
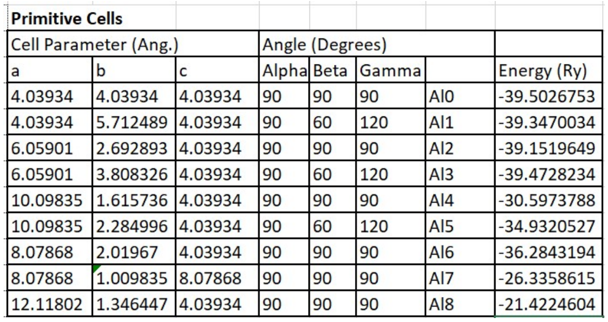


FIG. 5. Primitive cell variation, visualisaiton with Gaussview 06

moving from there as the choice for parameters got more unsymmetrical, value of total energy increased. [floatfix]



Primitive Cells

Cell Parameter (Ang.)			Angle (Degrees)				
a	b	c	Alpha	Beta	Gamma		Energy (Ry)
4.03934	4.03934	4.03934	90	90	90	Al0	-39.5026753
4.03934	5.712489	4.03934	90	60	120	Al1	-39.3470034
6.05901	2.692893	4.03934	90	90	90	Al2	-39.1519649
6.05901	3.808326	4.03934	90	60	120	Al3	-39.4728234
10.09835	1.615736	4.03934	90	90	90	Al4	-30.5973788
10.09835	2.284996	4.03934	90	60	120	Al5	-34.9320527
8.07868	2.01967	4.03934	90	90	90	Al6	-36.2843194
8.07868	1.009835	8.07868	90	90	90	Al7	-26.3358615
12.11802	1.346447	4.03934	90	90	90	Al8	-21.4224604

FIG. 6. Primitive cell parameters and corresponding total energy calculated using DFT

IV. CONCLUSION

The basic convergence testing resulted in a unit cell which was 0.757% smaller in volume than the initial volume generated from the cif file from Materials Project. From the equilibrium volume, eight primitive unit cells were generated which did not give the total energy value equal to the initial unit cell. This might be because of the fact that the initial cell had three fold symmetry. This can be concluded by this study that alternate unit cells having similar volume will not return similar value of total energy.

V. ACKNOWLEDGMENTS

We would like to express our gratitude for Prof. Stefaan Cottenier for providing an excellent platform for learning the basic theory underlying DFT calculations, the necessary skills and knowledge to work with Quantum ESPRESSO, with interactive weekly webinars, and for always being responsive to the doubts and queries in this work.

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