COMPUTATIONAL ACTIVITY 2

UNIVERSITY of SAN CARLOS
SCIENTIA • VIRTUS • DEVOTIO

Convergence Tests for k-Points and Wave Function Energy Cut-Off with Platinum

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In the DFT calculations, it is beneficial to identify the number of k points where a convergence to the exact result of the integral is observed to reduce computational cost. It is also necessary to determine the kinetic energy cut-off for the solutions to the Schrodinger equation. In this activity, the minimum number of k points and energy cut-off necessary to have a convergence in total energy was investigated using Platinum atoms set-up in an FCC structure with a lattice constant of 3.97 Angstrom. For face-centered cubic structure of Platinum, Quantum Expresso achieves convergence of calculated total free energy at 4 x 4 x 4 k points and wave function energy cut-off of 22.05 Ry.

1. Introduction

In solid state physics, the space of vector **r** is called real space, and the space of vectors **k** is called reciprocal space (or k space). The primitive cell in the reciprocal space is called the Brillouin zone (BZ). Many parts of the mathematical problems posed by DFT require solving the integral over the BZ of a function in k space of the form:

$$\int_{BZ} g(k)\,dk \tag{1}$$

From calculus, this integral can be thought of as the area under the curve defined by g(k). This area can be estimated by summing all the infinitesimally narrow rectangles under the curve. More accurate results can be obtained by increasing the number of discrete points used in the sum.

However, large number of k points require more expensive computational cost. Therefore, it is beneficial to identify the number of k points where a convergence to the exact result of the integral is observed. Most DFT packages offer an option of choosing k points based on the method of Monkhorst and Pack.

Just as the convergence test for k points is an important first step in DFT calculations, it is also necessary to determine the kinetic energy cut-off for the solutions to the Schrodinger equation. An intrinsic property of the supercell approach to DFT is the periodic potential described by Bloch's theorem:

$$\phi_k(r)=\sum_G c_{\boldsymbol{k+G}}\exp[i(\boldsymbol{k+G})\boldsymbol{r}] \tag{2}$$

Substituting this to the Kohn-Sham Schrodinger equation gives:

$$\sum_G\left[\frac{\hbar^2}{2m}|\boldsymbol{k+G}|^2+v_{eff}(\boldsymbol{G})\right]c_{\boldsymbol{k+G}}=\varepsilon\, c_{\boldsymbol{k+G}} \tag{3}$$

This indicates that the solution at even a single point in k space involves a summation over an infinite number of possible values of **G**. Note that the kinetic energy part is:

$$E=\frac{\hbar^2}{2m}|\boldsymbol{k+G}|^2 \tag{4}$$

Computationally, it is practical to truncate the infinite sum to include only solutions with kinetic energies less than some value:

$$E_{cut}=\frac{\hbar^2}{2m}G_{cut}^2 \tag{5}$$

The infinite sum then reduces to

$$\phi_k(r)=\sum_{G<G_{cut}} c_{\boldsymbol{k+G}}\exp[i(\boldsymbol{k+G})\boldsymbol{r}]$$

When DFT calculations are reported, it is important to specify the number of k points and kinetic energy cut-off used so that others can reproduce the results.

In this activity, the minimum number of k points and energy cut-off necessary to have a convergence in total energy was investigated.

The Platinum atoms were set-up in an FCC structure with a lattice constant of 3.97 Angstrom. Quantum Expresso was used to calculate the total energy of the system as a function of k points and kinetic energy cut-off. From the results the minimum number of k points

and kinetic energy cut-off necessary to obtain a convergence of total energy was identified.

2. Results and Discussion

The total free energy of FCC Platinum with at different k points were computed. For this computation the lattice constant of 3.97 Angstrom was used. This lattice constant was determined beforehand to be the lattice constant with the lowest total free energy for FCC Platinum when using this computational model. The energy cut-off was set to 39.1032 Ry for the wave function energy cut-off and 401.3190 Ry for the charge energy cut-off as suggested by the Burai.

Table 1 shows the calculated total free energy of a face-centered cubic structure Platinum with different k points and Figure 1 shows a plot of the values.

Table 1: Total Free Energy of FCC Platinum with Different k Points

K Points	Total Free Energy (Ry)
1.00	-2,987.7599
2.00	-2,989.1897
3.00	-2,989.2292
4.00	-2,989.1813
5.00	-2,989.1833
6.00	-2,989.1857
7.00	-2,989.1910
8.00	-2,989.1888
9.00	-2,989.1887
10.00	-2,989.1892

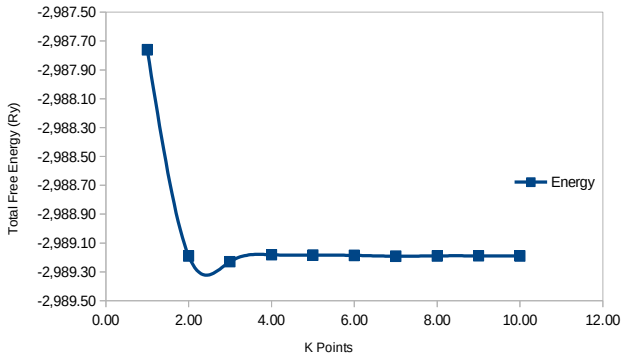

Figure 1 Plot of Total Free Energy of FCC Platinum with Different k Points

For face-centered cubic structure of Platinum, Quantum Expresso achieves convergence of calculated total free energy at 4 x 4 x 4 k points.

Using this observed k point for convergence, the total free energy of FCC Platinum with different wave function energy cut-off were computed. For this computation the lattice constant of 3.97 Angstrom is maintained with the new k point of 4 x 4 x 4. The value of 401.3190 Ry for the charge energy cut-off was also maintained.

Table 2 shows the calculated total free energy of the face-centered cubic structure Platinum with differentwave function energy cut-off and Figure 2 shows a plot of the values.

Table 2: Total Free Energy of FCC Platinum with Different Wave Function Energy Cut-off

Cutoff Energy for WF (Ry)	Total Free Energy (Ry)
7.35	-2,976.5783
14.70	-2,988.4477
22.05	-2,989.1486
29.40	-2,989.1705
36.75	-2,989.1808
44.10	-2,989.1816
51.45	-2,989.1824
58.80	-2,989.1829
66.15	-2,989.1829
73.50	-2,989.183

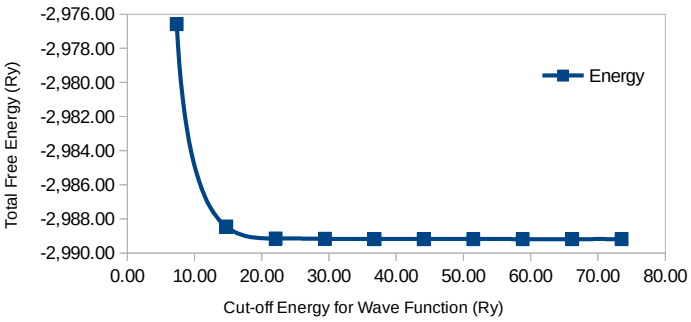

Figure 2 Plot of Total Free Energy of FCC Platinum with Different Wave Function Energy Cut-off

For face-centered cubic structure of Platinum, Quantum Expresso achieves convergence of calculated total free energy at wave function energy cut-off of 22.05 Ry.

3. Conclusion

In this activity, the minimum number of k points and energy cut-off necessary to have a convergence in total energy was investigated.

For face-centered cubic structure of Platinum, Quantum Expresso achieves convergence of calculated total free energy at 4 x 4 x 4 k points and wave function energy cut-off of 22.05 Ry.

Computational Model

DFT calculations were implemented using Quantum Espresso with exchange-correlation term described using the generalized gradient approximation (GGA) based on Perdew-Burke-Ernzerhof (PBE) functional. The interaction between ions and electrons were described using the projector augmented wave (PAW) method. The surface Brillouin zone integrations will be performed using Monkhorst-Pack k-points using Methfessel-Paxton smearing of = 0.01 Ry.

Notes and references

1) Sholl, D., & Steckel, J. A. (2011). Density functional theory: a practical introduction. John Wiley & Sons.