First Principle 2017-Fall Homework 3 Solution

Kai-Hsin Wu (吳愷訢)*
Department of Physics and Center of Theoretical Sciences, National Taiwan University, Taipei 10607, Taiwan

1. The following shows the result of Al and Na:

- Al

(1) a_0 using volume optimization:

$$a_0 = 4.05000$$

(2) Variation with different a_0:

$a_0(\mathring{A})$	$E(eV)$
3.90	-14.541085
3.95	-14.665726
4.00	-14.735369
4.05	-14.757538
4.10	-14.738699
4.15	-14.684395
4.20	-14.599834

(3) the following figure shows the energy (E) v.s. V :

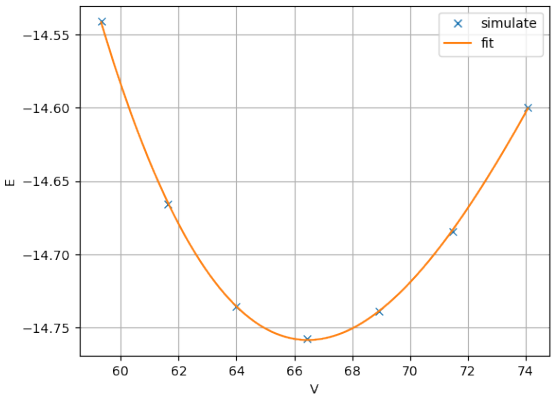

FIG. 1. Al-fcc E-V

* r05222003@ntu.edu.tw

By using third order polyfit, and with the following formula, we can get the bulk-modulus B and the minimum a_0:

$$B = V\frac{\partial^2}{\partial V^2}E$$
$$V = a_0^3$$

$$a_0 = 4.050723 \ \ \mathring{A}$$
$$B = 74.608739 \ \ GPa$$

(4) Consider the free electron HF energy density and seek for the minimum of r_s :

$$e^{HF} = \frac{A}{r_s^2} - \frac{\beta}{r_s}$$
$$A = 2.21$$
$$B = 0.916$$

Where the unit of energy is Ry and r_s is in unit of bohr radius ($bohr$). The minimum is at :

$$r_s^* = \frac{2A}{\beta}(bohr) = 2.553467 \ \ \mathring{A}$$

using following relation by which we consider 4 free electrons per unit-cell, we can estimate the lattice constant a_0 :

$$\frac{4\pi}{3}r_s^3 = n^{-1}$$
$$\frac{N_{free}}{a_0^3} = n$$

$$a_0 = \left(\frac{16\pi}{3}\right)^{1/3} r_s$$
$$\approx 6.1737 \ \ \mathring{A}$$

For Bulk modulus, we have following relation. by which we express Ω in terms of r_s:

$$\frac{N}{\Omega} = n = \frac{3}{4\pi r_s^3}$$
$$B = \Omega\frac{\partial^2 E}{\partial \Omega^2}$$
$$= \frac{1}{12\pi r_s}\left[\frac{-2}{r_s}e^{HF'} + e^{HF''}\right]$$
$$= \frac{1}{6\pi r_s^4}\left[\frac{5A}{r_s} - 2\beta\right]$$

we have the bulk modulus at r_s^*

$$B = \frac{\beta^4}{6\pi(2A)^4}\frac{\beta}{2}(Ry/bohr^3)$$
$$\approx 18.468GPa$$

- Na

(1) a_0 using volume optimization:

$$a_0 = 4.04669$$

(2) Variation with different a_0:

$a_0(\mathring{A})$	$E(eV)$
3.9241059	-1.437731
3.9645606	-1.443730
4.0050153	-1.447706
4.0454700	-1.449866
4.0859247	-1.449972
4.1263794	-1.448133
4.1668341	-1.445039
4.2072888	-1.440498

(3) the following figure shows the energy (E) v.s. V :

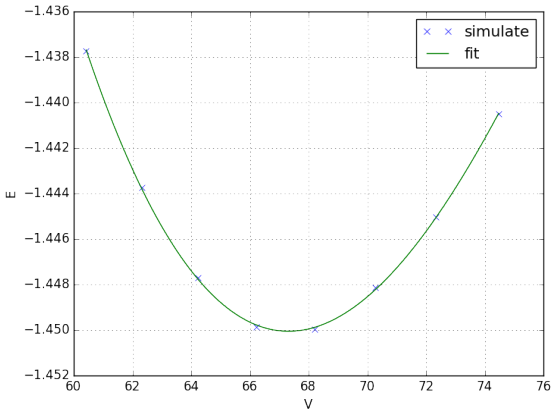

FIG. 2. Na-fcc E-V

By using third order polyfit, and with the following formula, we can get the bulk-modulus B and the minimum a_0:

$$B = V\frac{\partial^2}{\partial V^2}E$$
$$V = a_0^3$$

$$a_0 = 4.06802437 \ \ \mathring{A}$$
$$B = 4.83347453 \ \ GPa$$

(4) Consider the free electron HF energy density and seek for the minimum of r_s :

$$e^{HF} = \frac{A}{r_s^2} - \frac{\beta}{r_s}$$
$$A = 2.21$$
$$B = 0.916$$

Where the unit of energy is Ry and r_s is in unit of bohr radius ($bohr$). The minimum is at :

$$r_s^* = \frac{2A}{\beta}(bohr) = 2.553467 \ \ \mathring{A}$$

using following relation by which we consider 2 free electrons per unit-cell, we can estimate the lattice constant a_0 :

$$\frac{4\pi}{3} r_s^3 = n^{-1}$$
$$\frac{N_{free}}{a_0^3} = n$$

$$a_0 = \left(\frac{8\pi}{3}\right)^{1/3} r_s$$
$$\approx 5.186047 \ \ \mathring{A}$$

For Bulk modulus, we have following relation. by which we express Ω in terms of r_s:

$$\frac{N}{\Omega} = n = \frac{3}{4\pi r_s^3}$$
$$B = \Omega \frac{\partial^2 E}{\partial \Omega^2}$$
$$= \frac{1}{12\pi r_s}\left[\frac{-2}{r_s} e^{HF'} + e^{HF''}\right]$$
$$= \frac{1}{6\pi r_s^4}\left[\frac{5A}{r_s} - 2\beta\right]$$

we have the bulk modulus at r_s^*

$$B = \frac{\beta^4}{6\pi(2A)^4}\frac{\beta}{2}(Ry/bohr^3)$$
$$\approx 18.468 GPa$$

2. For bcc Fe , doing LDA and GGA method with FM and NM :

- LDA

(1) a_0 using volumn optimization :

$$a_0^{FM} = 2.744294 \ \mathring{A}$$
$$a_0^{NM} = 2.694591 \ \mathring{A}$$

(2) minimization energy with variated a_0 and are showed in figure below:

FM		NM	
$a_0(\mathring{A})$	$E(eV)$	$a_0(\mathring{A})$	$E(eV)$
2.60	-8.967318	2.55	-8.672935
2.65	-9.121350	2.60	-8.863644
2.70	-9.206677	2.65	-8.964152
2.75	-9.228247	2.70	-8.988743
2.80	-9.202380	2.75	-8.952579
2.85	-9.135795	2.80	-8.867398
2.90	-9.048763	2.85	-8.742378
2.95	-8.935725	2.90	-8.585827

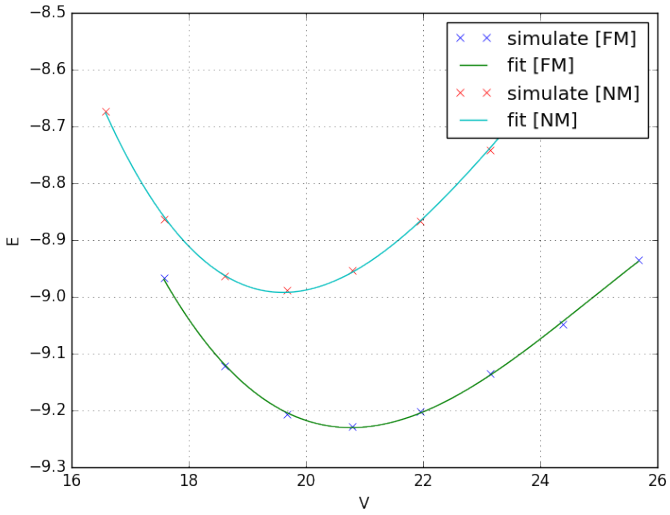

FIG. 3. Fe-bcc LDA E-V

The minimized a_0 and B of bcc Fe with FM and NM are :

$$a_0^{FM} = 2.746787\mathring{A} \qquad B^{FM} = 134.99746GPa$$
$$a_0^{NM} = 2.694740\mathring{A} \qquad B^{NM} = 175.45431GPa$$

We see that the FM case has minimal energy, which shows the ground state is Ferromagnetic.

- GGA

  (1) a_0 using volumn optimization :

$$a_0^{FM} = 2.82214 \ \mathring{A}$$
$$a_0^{NM} = 2.75412 \ \mathring{A}$$

  (2) minimization energy with variated a_0 and are showed in figure below:

FM		NM	
$a_0(\mathring{A})$	$E(eV)$	$a_0(\mathring{A})$	$E(eV)$
2.70	-8.009989	2.70	-7.724527
2.75	-8.108553	2.75	-7.757336
2.80	-8.151154	2.80	-7.737622
2.85	-8.158445	2.85	-7.674045
2.90	-8.135495	2.90	-7.575350
2.95	-8.077445	2.95	-7.448175
3.00	-8.000995	3.00	-7.298845

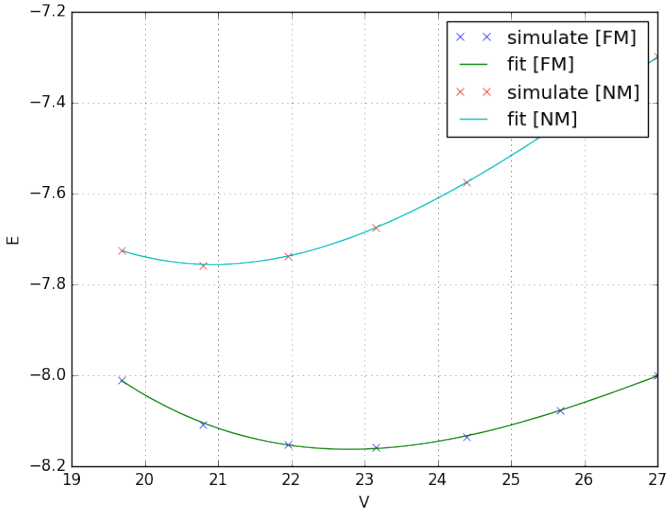

FIG. 4. Fe-bcc GGA E-V

The minimized a_0 and B of bcc Fe with FM and NM are :

$$a_0^{FM} = 2.834269\mathring{A} \qquad B^{FM} = 93.907626GPa$$
$$a_0^{NM} = 2.755061\mathring{A} \qquad B^{NM} = 124.57160GPa$$

We see that the FM case has minimal energy, which consist with the GGA results that the ground state is Ferromagnetic.

3. • Si

   (1) a_0 using volumn optimization :

   $$a_0^{Si} = 5.46078 \ \ \mathring{A}$$

   • Ge

   (1) a_0 using volumn optimization :

   $$a_0^{Ge} = 5.76822 \ \ \mathring{A}$$

   • GaAs

   (1) a_0 using volumn optimization :

   $$a_0^{GaAs} = \ \ \mathring{A}$$