First Principle 2017-Fall Homework 3 Solution

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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 :

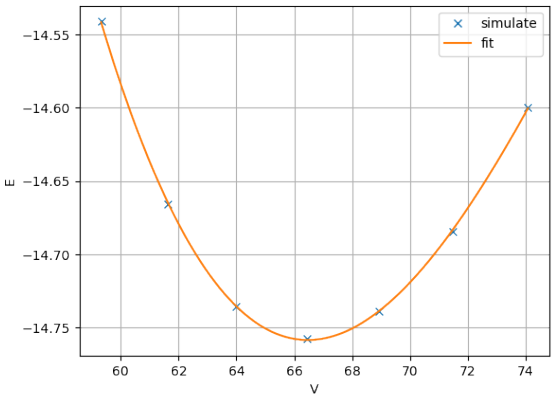

FIG. 1. Al-fcc E-V

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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 :

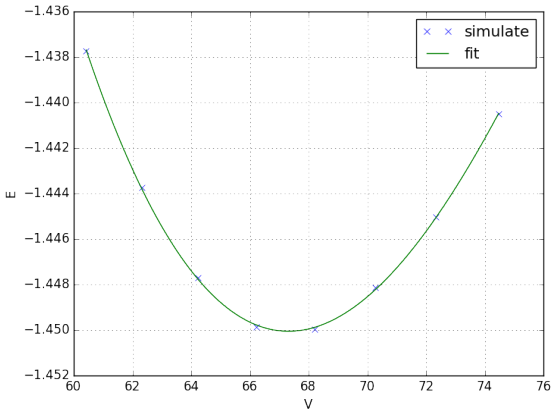

FIG. 2. Na-fcc E-V

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

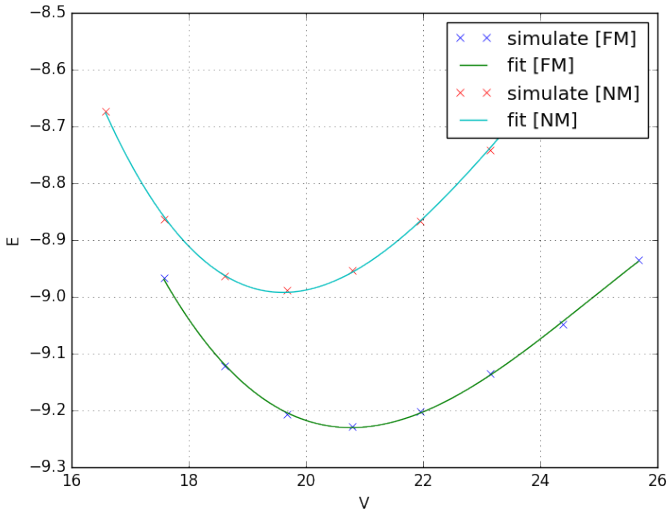

FIG. 3. Fe-bcc LDA E-V

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

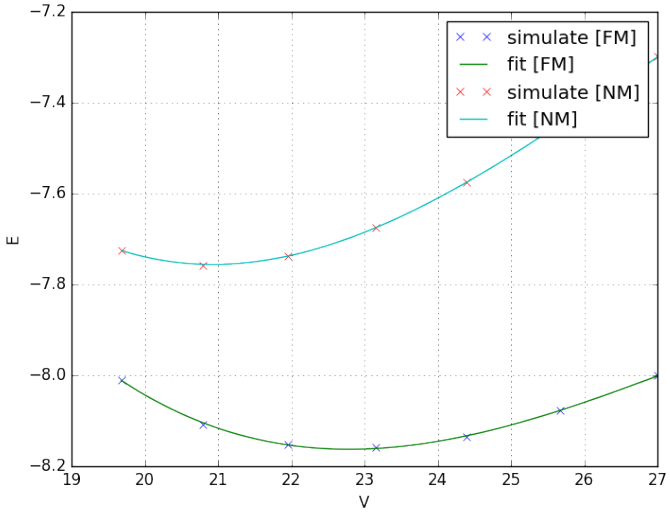

FIG. 4. Fe-bcc GGA E-V

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. GGA band gaps of typical semiconductors, the following experiment value comes from [1]

- Si

(1) a_0 using volumn optimization :

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

(2) The band structure and density of state are shown below :

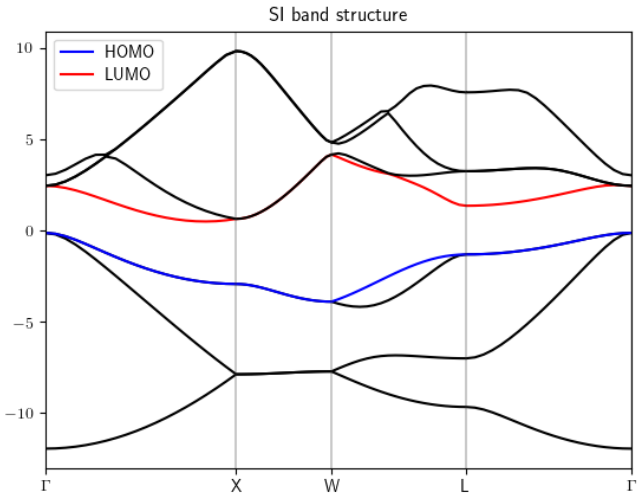

FIG. 5. Si band-structure

The band gap E_g^{Si} is :

$$E_g^{Si} = 0.6245 \ \ eV$$

Experiment values :

$$E_g^{exp} = 1.17eV$$
$$a_0^{exp} = 5.431\mathring{A}$$

- Ge

  (1) a_0 using volumn optimization :

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

  (2) The band structure and density of state are shown below :

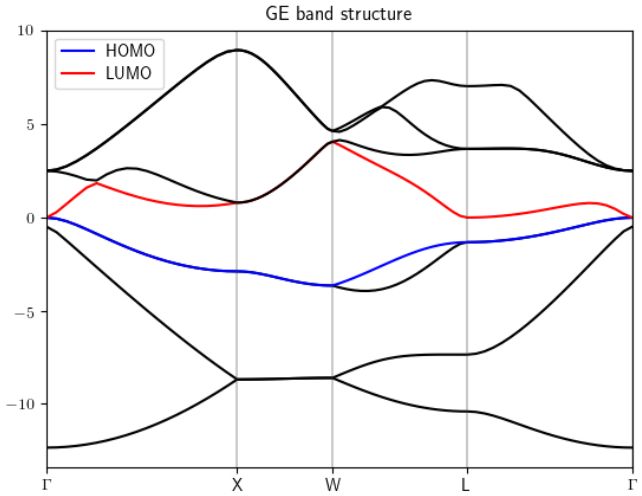

FIG. 6. Ge band-structure

The band gap E_g^{Ge} is :

$$E_g^{Ge} = 0.0 \ \ eV$$

Experiment values :

$$E_g^{exp} = 0.74eV$$
$$a_0^{exp} = 5.658\mathring{A}$$

- GaAs

  (1) a_0 using volumn optimization :

$$a_0^{GaAs} = 5.751291 \ \ \mathring{A}$$

  (2) The band structure and density of state are shown below :

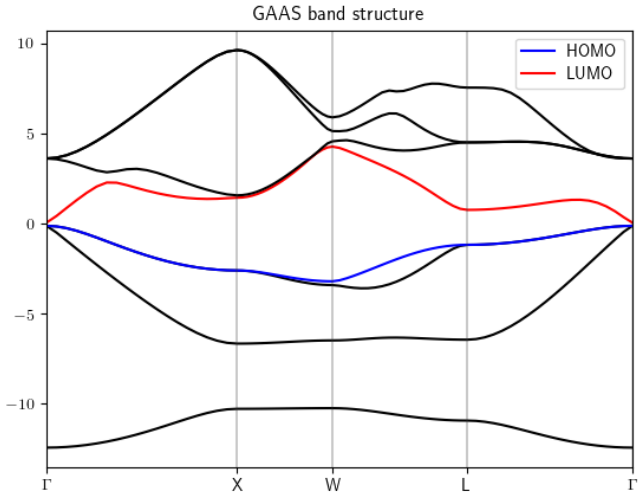

FIG. 7. GaAs band-structure

The band gap E_g^{GaAs} is :

$$E_g^{GaAs} = 0.1755 \ \ eV$$

Experiment values :

$$E_g^{exp} = 1.52eV$$
$$a_0^{exp} = 5.65325\mathring{A}$$

4. GGA, GGA+U of NiO in AF-II

the structure of NiO in AF-II :

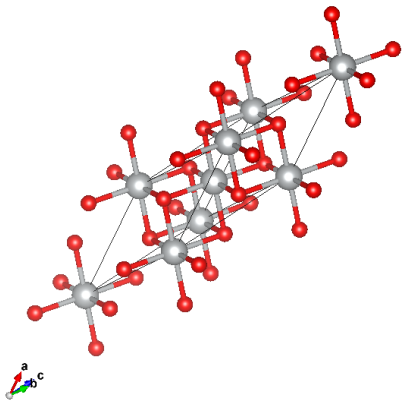

FIG. 8. NiO-AFII lattice structure

- GGA

(1) the band structure and total DOS

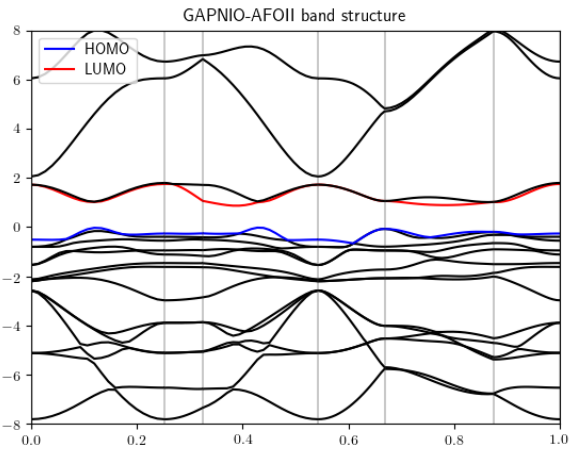

FIG. 9. NiO-AFII band-structure

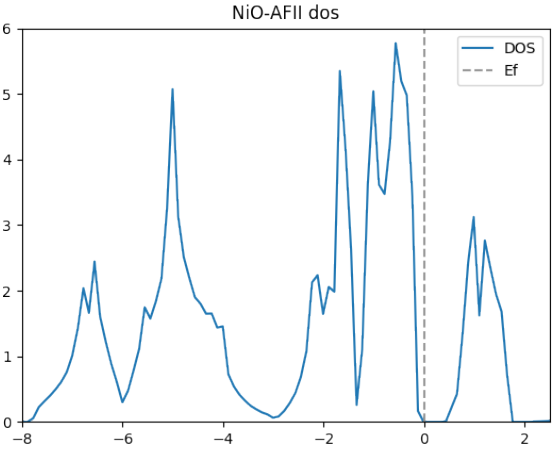

FIG. 10. NiO-AFII density of state

(2) density of state of Ni

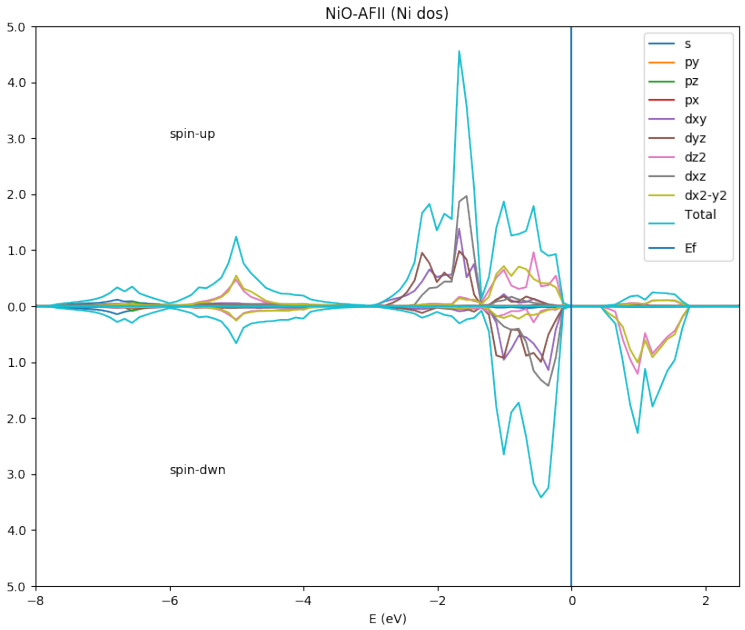

FIG. 11. Ni in NiO density of state

Energy gap E_g ,total magnetic moment m and Ni moment m_{Ni}:

$$E_g = 0.8936eV$$
$$m = 0.0000\mu_B$$
$$m_{Ni} = 1.011\mu_B$$

- GGA+U

(1) the band structure and total DOS

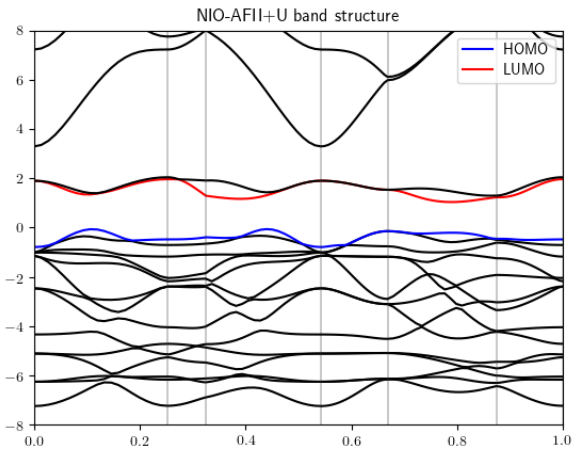

FIG. 12. NiO-AFII band-structure GGA+U

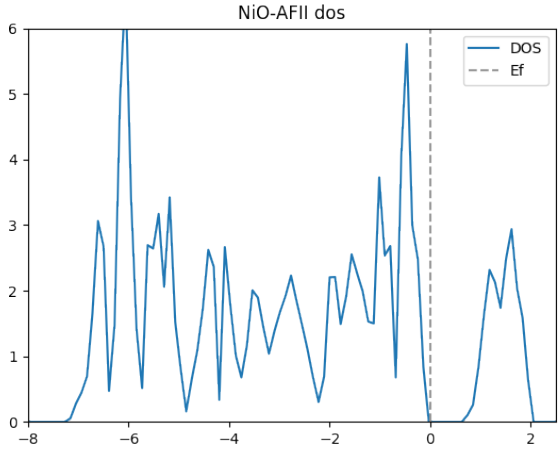

FIG. 13. NiO-AFII density of state GGA+U

(2) density of state of Ni

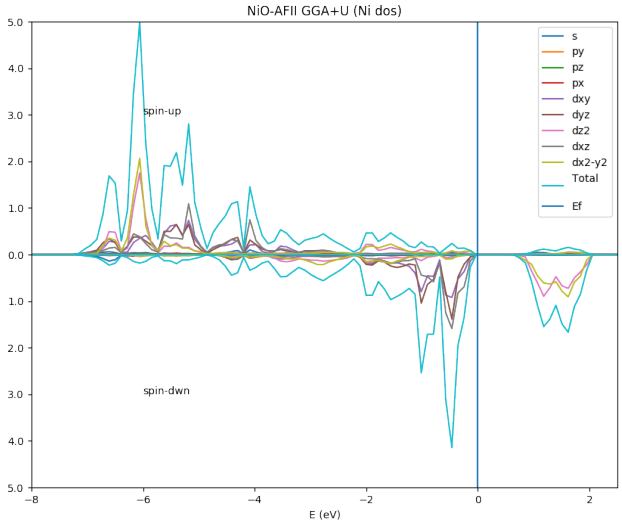

FIG. 14. Ni in NiO density of state GGA+U

Energy gap E_g ,total magnetic moment m and Ni moment m_{Ni}:

$$\begin{aligned} E_g &= 1.0973eV \\ m &= 0.0000\mu_B \\ m_{Ni} &= 1.106\mu_B \end{aligned}$$

By apply U_eff on Ni, we decouple the Ni and O energy part, as a result, the AF magnetic property contributed form Ni can be calculate more accurate.

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[1] K. C., *Introduction to Solid State Physics, 6th Ed. (1986), p. 185.* (Wiley).