Center for Molecular Modeling

Computational Materials Physics

Department of Materials Science and Engineering

geometry optimization 1 : unit cell volume

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http://molmod.ugent.be
http://www.ugent.be/ea/dmse/en
my talks on Youtube: http://goo.gl/P2b1Hs

Long ago, you learned how to make predictions for ideal gases :

$$PV = nRT$$

[R=8.3145 J/(mol K)]

Two easy questions:

1. Find the volume of 1 mole ideal gas at ambient conditions ($P=10^5$ Pa, T=293 K)
2. How much needs the pressure to be increased to reduce this volume by 1% ?

Now we ask the same questions for a solid, say fcc Al :

1. What is the volume taken by 1 mole of Al atoms in a fcc crystal, at 0 K and without external pressure ?
2. How much needs the pressure to be increased to reduce this volume by 1% ?

In 30 minutes from now, you'll be able to calculate the answer. Almost as quickly as for the ideal gas.

What we did so far

DFT

- total energy (and E_{coh})
- chemical bond info

(DOS, band structure, density plots)

Useful to answer questions as:

- Can this material exist ?
- How strong are the bonds?
- What is the type of binding?

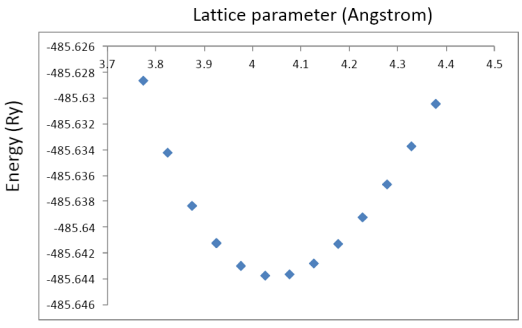
Yet, there is more – much more…

Go back to fcc Al

Calculate the total energy for each of these lattice parameters:

3.700 Å
3.750 Å
3.800 Å
3.850 Å
3.900 Å
3.950 Å
4.000 Å
4.050 Å
4.100 Å
4.150 Å
4.200 Å
4.250 Å
4.300 Å
4.350 Å

energy versus volume (or lattice parameter)



What do you conclude from this ?

energy versus volume (or lattice parameter)

$a_0^{PBE} \approx 4.05$ Å

1 mole Al-atoms in fcc crystal:
111.0412 au^3/(prim unit cell) (=1 atom)
6.7 cm^3

What do you conclude from this ?

energy versus volume

Fitting the E(V)-data allows to squeeze even more information out of it:

Polynomial fit : numerically not very stable

Better: Equation of State (EoS)

➔ A few-parameter expression that has an intrinsic shape that naturally mimics the behaviour of solids. The parameters often have a physical meaning.

Derivation of **Murnaghan equation** (valid up to 5% volume change):

http://en.wikipedia.org/wiki/Murnaghan_equation_of_state

Form suitable for fitting of experiments: $\left[B_1 = \frac{\partial B_0}{\partial P}\right]$

$$V(P) = V_0\left[1 + P\left(\frac{B_1}{B_0}\right)\right]^{-\frac{1}{B_1}} \quad \text{or} \quad P(V) = \frac{B_0}{B_1}\left(\left(\frac{V_0}{V}\right)^{B_1} - 1\right)$$

Form suitable for fitting of DFT calculations:

$$E(V) = E_0 + \frac{B_0 V}{B_1}\left(\frac{\left(\frac{V_0}{V}\right)^{B_1}}{B_1 - 1} + 1\right) - \frac{B_0 V_0}{B_1 - 1}$$

V_0 = volume at equilibrium
B_0 = bulk modulus at equilibrium
B_1 = pressure derivative of bulk modulus at equil.
E_0 = energy at equilibrium

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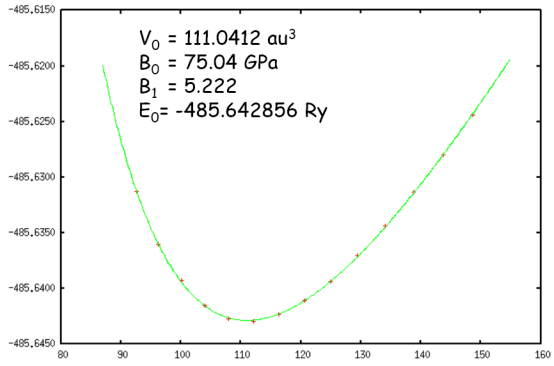
Murnaghan EOS for fcc Al



V (au³)	E (Ry)	P (GPa)
108.568325	-485.642709	1.7935
108.738435	-485.642729	1.6619
108.908545	-485.642747	1.5316
109.078655	-485.642764	1.4025
109.248765	-485.642780	1.2746
109.418875	-485.642794	1.1480
109.588985	-485.642806	1.0227
109.759096	-485.642817	0.8985
109.929206	-485.642827	0.7755
110.099316	-485.642835	0.6537
110.269426	-485.642842	0.5331
110.439536	-485.642848	0.4136
110.609646	-485.642852	0.2952
110.779756	-485.642855	0.1780
110.949866	-485.642856	0.0619
111.119976	-485.642856	-0.0531
111.290086	-485.642855	-0.1670
111.460196	-485.642852	-0.2798
111.630306	-485.642848	-0.3916
111.800417	-485.642843	-0.5023
111.970527	-485.642837	-0.6120
112.140637	-485.642829	-0.7206
112.310747	-485.642820	-0.8283
112.480857	-485.642810	-0.9349
112.650967	-485.642798	-1.0405

$$P(V) = \frac{B_0}{B_1}\left(\left(\frac{V_0}{V}\right)^{B_1} - 1\right)$$

1% volume reduction
P=0.77 GPa ≈ 10^9 Pa ❷

equilibrium volume
(V_0=111.04 au³)

a Murnaghan fit is not a parabola

small B_0
large B_0

full= Murnaghan
dashed = parabola fit
through minimum