Computing lattice constant, bulk modulus and equilibrium energies of solids.

Bulk Si

Diamond structure

- Volume ($V_0$) = 39.61 Å³
- Energy ($E_0$) = -215.4759 eV
- Bulk modulus ($B(V_0)$) = 119 GPa
- Pressure derivative of the bulk modulus ($B'(V_0)$) = 11.23 eV
Information required to run a first-principles simulation

Number and species of the atoms in the unit cell,

Lattice vectors and lattice constants

Position of all the atoms

After the Born Oppenheimer approx., are assumed to be fixed, no thermal vibrations ($T = 0$)

$N$  \quad \Omega

$T = 0$

$S = 0$

The most convenient thermodynamic potential in first-principles theoretical analysis is the total energy $E(N, \Omega, S)$ at $T = 0$

It is straightforward to carry out electronic structure calculations at fixed $\Omega$
First test: determine theoretical predictions for $\Omega_0$ and $B$ for the known zero-pressure crystal structure

Definition of some fundamental quantities

**Energy**

$$E(N, \Omega, S)$$

**Pressure**

$$P = -\frac{dE}{d\Omega}$$

**Bulk modulus**

$$B = -\Omega \frac{dP}{d\Omega} = \Omega \frac{d^2E}{d\Omega^2}$$

**Why $\Omega_0$ and $B$:**

- Can be measured with great accuracy.
- Can be extrapolated at $T = 0$
$\Omega_0$ and $B$ can be measured with great accuracy and extrapolated at $T = 0$.

\( \Omega_0 \) and \( B \) can be measured with great accuracy and extrapolated at \( T = 0 \)

<table>
<thead>
<tr>
<th>Element</th>
<th>( \Omega_0 )</th>
<th>( B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.116</td>
<td>8.62</td>
</tr>
<tr>
<td>Na</td>
<td>0.068</td>
<td>14.7</td>
</tr>
</tbody>
</table>

Bulk Si: a covalent solid that crystallizes in the diamond structure

Go to the directory where the exercise on the structure of Si is stored.
Inspect the input file, Si.fdf

More information at the Siesta web page http://www.icmab.es/siesta and follow the link Documentations, Manual

The theoretical lattice constant of Si for this first example

Diamond structure:
FCC lattice

+ a basis of two atoms

Sampling in k in the first Brillouin zone to achieve self-consistency
Procedure to compute the equilibrium volume and bulk modulus

Step 1: Given a structure, compute the energy $E$ for several values of the volume $\Omega$

Run the code,

```
siesta < Si.fdf > Si.5.43.out
```

The name of the output file is free, but since we are running bulk Si with the experimental lattice constant, this seems very sensible...

For this particular example, run from 5.35 Å up to 5.49 Å in steps of 0.02 Å.
Save each output file in a different file

Save in a file the data needed to plot the energy versus volume curve

```
grep "Total =" Si.*.out > Si.evslc.dat
```
Procedure to compute the equilibrium volume and bulk modulus

Step 1: Given a structure, compute the energy $E$ for several values of the volume $\Omega$

Edit the Si.evslic.dat file and leave only two columns:

Lattice constant (in Å)  Energy of the unit cell (in eV)

diamond
5.35  -215.456759
5.37  -215.467051
5.39  -215.474158
5.41  -215.476121
5.43  -215.474288
5.45  -215.469333
5.47  -215.461829
5.49  -215.451340

Add a first line with the kind of lattice (cubic, bcc, fcc, diamond...
Procedure to compute the equilibrium volume and bulk modulus

Step 1: Given a structure, compute the energy $E$ for several values of the volume $\Omega$

Example: Si in the diamond structure

Number of atoms in the unit cell fixed
Symmetry of the unit cell fixed
Temperature is fixed ($T=0 \Rightarrow S=0$)
Procedure to compute the equilibrium volume and bulk modulus

Step 2: Fit to an analytic form, e.g., the Murnaghan equation of state

\[
E(\Omega) = E_0 + \frac{B_0 \Omega}{B'_0} \left[ \frac{(\frac{\Omega_0}{\Omega})^{B'_0}}{B'_0 - 1} + 1 \right] - \frac{\Omega_0 B_0}{B'_0 - 1}
\]

F. D. Murnaghan,
Proc. Nat. Acad. Sci. USA, 30, 244 (1944)

\(B_0\) bulk modulus at the equilibrium volume

\(B'_0\) pressure derivative of the bulk modulus at the equilibrium volume

To do this, we have prepared an script in python

```
python fit_results.py Si.evslc.dat
```
Procedure to compute the equilibrium volume and bulk modulus

Step 2: Fit to an analytic form, e. g. , the Murnaghan equation of state

$$E(\Omega) = E_0 + \frac{B_0 \Omega}{B_0'} \left[ \left( \frac{\Omega_0}{\Omega} \right)^{B_0'} - 1 \right] + 1 - \frac{\Omega_0 B_0}{B_0' - 1}$$

$B_0$ bulk modulus at the equilibrium volume

$B_0'$ pressure derivative of the bulk modulus at the equilibrium volume

$E_0$ total energy at the minimum

F. D. Murnaghan,
Proc. Nat. Acad. Sci. USA, 30, 244 (1944)
Comparison of predicted equilibrium properties with experimental values are routine tests for calculations.

<table>
<thead>
<tr>
<th>Element</th>
<th>Exp</th>
<th>LAPW</th>
<th>Other PW</th>
<th>PW</th>
<th>DZP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>$a$</td>
<td>4.08$^a$</td>
<td>4.05$^b$</td>
<td>4.07$^c$</td>
<td>4.05</td>
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<tr>
<td></td>
<td>B</td>
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<td>198$^b$</td>
<td>190$^c$</td>
<td>191</td>
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<tr>
<td></td>
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<td>-</td>
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<tr>
<td>MgO</td>
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<td>4.26$^e$</td>
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<td>4.10</td>
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<tr>
<td></td>
<td>B</td>
<td>152$^d$</td>
<td>147$^e$</td>
<td>-</td>
<td>168</td>
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<tr>
<td></td>
<td>$E_c$</td>
<td>10.30$^d$</td>
<td>10.40$^e$</td>
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<td>11.90</td>
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<tr>
<td>C</td>
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<td>3.54$^f$</td>
<td>3.54$^g$</td>
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<tr>
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<td>$E_c$</td>
<td>7.37$^a$</td>
<td>10.13$^f$</td>
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<tr>
<td>Si</td>
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<td>5.41$^h$</td>
<td>5.38$^g$</td>
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<td>B</td>
<td>99$^a$</td>
<td>96$^h$</td>
<td>94$^g$</td>
<td>96</td>
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<tr>
<td></td>
<td>$E_c$</td>
<td>4.63$^a$</td>
<td>5.28$^h$</td>
<td>5.34$^g$</td>
<td>5.37</td>
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<td>Na</td>
<td>$a$</td>
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<td>4.05$^i$</td>
<td>3.98$^g$</td>
<td>3.95</td>
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<td>1.44$^i$</td>
<td>1.28$^g$</td>
<td>1.22</td>
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<tr>
<td>Cu</td>
<td>$a$</td>
<td>3.60$^a$</td>
<td>3.52$^b$</td>
<td>3.56$^g$</td>
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<tr>
<td></td>
<td>B</td>
<td>138$^a$</td>
<td>192$^b$</td>
<td>172$^g$</td>
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<tr>
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<td>4.88</td>
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</tr>
<tr>
<td></td>
<td>B</td>
<td>43$^a$</td>
<td>-</td>
<td>54</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$E_c$</td>
<td>2.04$^a$</td>
<td>-</td>
<td>3.77</td>
<td>-</td>
</tr>
</tbody>
</table>

### Accuracy of the xc functionals in the structural and electronic properties

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>-1%, -3%</td>
<td>+1%</td>
</tr>
<tr>
<td>$B$</td>
<td>+10, +40%</td>
<td>-20%, +10%</td>
</tr>
<tr>
<td>$E_c$</td>
<td>+15%</td>
<td>-5%</td>
</tr>
<tr>
<td>$E_{\text{gap}}$</td>
<td>-50%</td>
<td>-50%</td>
</tr>
</tbody>
</table>

**LDA:** crude approximation but sometimes is accurate enough (structural properties, ...).

**GGA:** usually tends to overcompensate LDA results, not always better than LDA.