

geometry optimization : E(V) and EOS

In this example we inspect how to optimize the volume and shape of the unit cell in a more explicit way, i.e. not entirely relying on the automatic minimization tool that we discussed in the previous example. The added benefit of this longer procedure is that it gives access to an Equation of State (EOS), from which an important elastic property – the bulk modulus – can be derived.

The example for this procedure will be the [stishovite crystal](#) (a polymorph of SiO₂), with precision settings that are tested to give a reliable stress tensor: `ecutwfc=100`, `ecutrho=400`, 4x4x9 k-points, [this pseudopotential for Si](#) and [this pseudopotential for O](#). You can start from [this experimental cif file](#).

The input file for Quantum Espresso should look like this:

```
&CONTROL
  calculation='scf',
  outdir='.',
  prefix='SiO2-stishovite',
  pseudo_dir='.',
  verbosity='low',
  tprnfor=.true.,
  tstress=.true.,
/

&SYSTEM
 ibrav = 0,
  A = 4.17970,
  nat = 6,
  ntyp = 2,
  ecutwfc=100,
  ecutrho=400,
  input_dft='pbe',
  occupations='smearing',
  smearing='mv',
  degauss=0.005d0,
/

&ELECTRONS
  conv_thr=1d-08,
  mixing_beta=0.7d0,
/

CELL_PARAMETERS {alat}
 1.0000000000000000 0.0000000000000000 0.0000000000000000
 0.0000000000000000 1.0000000000000000 0.0000000000000000
 0.0000000000000000 0.0000000000000000 0.638060147857502

ATOMIC_SPECIES
  O 15.999400d0 O.pbe-kjpaw.UPF
  Si 28.085500d0 Si.pbe-n-kjpaw_psl.0.1.UPF

ATOMIC_POSITIONS {crystal}
  Si 0.0000000000d0 0.0000000000d0 0.0000000000d0
  Si 0.5000000000d0 0.5000000000d0 0.5000000000d0
  O 0.3061370000d0 0.3061370000d0 0.0000000000d0
  O 0.6938630000d0 0.6938630000d0 0.0000000000d0
  O 0.1938630000d0 0.8061370000d0 0.5000000000d0
  O 0.8061370000d0 0.1938630000d0 0.5000000000d0

K_POINTS {automatic}
 4 4 9 0 0 0
```

Run a static calculation for this file (less than 2 minutes). You will notice that the stress tensor is not exactly zero, nor are the forces on the oxygen atoms.

Now prepare 6 other input files, where the lattice parameter a (= the 'A' value under &SYSTEM) is varied in steps of 0.04 Å above and below the initial value. The (3,3) matrix element under CELL_PARAMETERS is the c/a -ratio, and is kept unchanged. This means you have rescaled the unit cell (growing and shrinking), without altering its shape. The coordinates of all internal positions are kept unchanged too.

Run these 6 calculations, and write down each time the total energy. The result will be like this (verify at least one of them):

lattice parameter $a=b$ (Å)	lattice parameter c (Å)	Volume (Å ³)	energy (Ry)	Pressure (xy, kbar)	Pressure (z, kbar)
4.052716	2.585876	42.471743	-260.53643292	455.31	550.28
4.095050	2.612888	43.816658	-260.56192394	320.74	386.35
4.137384	2.639900	45.189670	-260.57940824	202.43	241.62
4.179718	2.666912	46.591068	-260.58959137	98.73	114.13
4.222052	2.693923	48.021144	-260.59312454	8.16	2.24
4.264387	2.720935	49.480189	-260.59061396	-70.69	-95.71
4.306721	2.747947	50.968491	-260.58262898	-139.02	-181.13

If you plot the total energy as a function of unit cell volume (see Fig. 1, 'static' data), then a clear minimum is visible. You can fit a Birch-Murnaghan equation of state through these data, to have a first approximation to the equilibrium volume and bulk modulus. This is the procedure:

Prepare a text file with two columns, the first column being the unit cell volume (a.u.³ or Å³) of each of your 7 calculations, the second column being the corresponding total energy (Ry). Run the 'ev.x', which will ask you some questions. In this case: units (a.u.³ or Å³), 'noncubic' for the type of Bravais lattice, and '1' (= 'birch1') for the equation of state (for fcc, bcc and sc lattices, you have to specify the lattice parameter in your input text file, for all other 'noncubic' lattices, this should be the volume). It will give you in return the equilibrium volume and bulk modulus obtained from fitting a Birch-Murnaghan equation of state through your data points:

```
# equation of state: birch 1st order.  chisq = 0.1361D-10
# V0 = 324.75 a.u.^3,  k0 = 3006 kbar,  dk0 = 4.17  d2k0 = 0.000  emin = -260.59314
# V0 = 48.12 Ang^3,  k0 = 300.6 GPa

#####
# Vol.          E_calc      E_fit      E_diff      Pressure      Enthalpy
# Ang^3         Ry           Ry          Ry           GPa           Ry
#####
42.47          -260.53643    -260.53643    -0.00000     48.75         -259.58665
43.82          -260.56192    -260.56193     0.00000     34.27         -259.87310
45.19          -260.57941    -260.57941    -0.00000     21.55         -260.13263
46.59          -260.58959    -260.58959    -0.00000     10.40         -260.36734
48.02          -260.59312    -260.59312    -0.00000      0.64         -260.57913
49.48          -260.59061    -260.59062     0.00001     -7.89         -260.76979
50.97          -260.58263    -260.58263    -0.00000    -15.33         -260.94097
```

The above procedure – changing the volume only, while keeping the cell shape as well as the positions of the atoms fixed – is a quick yet approximative way to find a good first guess of the

equilibrium volume (and bulk modulus). In order to find a correct and precise DFT-prediction for equilibrium volume and bulk modulus, the unit cell needs to be fully geometry-optimized at every volume in the data set. This means: the volume should be the only degree of freedom in $E(V)$, all other parameters are such that the energy cannot be further reduced for that given volume. Only on such a data set, the equilibrium volume and bulk modulus obtained from an equation of state fit have their correct physical meaning.

Thanks to the stress tensor formalism in Quantum Espresso, it is quite straightforward to obtain such an optimized data set. Inspect the stress tensor obtained in your previous series of calculations (see the table above). The xx and yy stress tensor components are different from the zz stress tensor component, which means that a non-isotropic stress is required to give the unit cell the given volume and shape. For instance, by applying a pressure of 455 kbar along the a - and b -directions, and 550 kbar along the c -direction, the unit cell can be given a volume of 286.6 a.u.³ and a c/a ratio of 0.6381. A correct yet tedious procedure would be to optimize c/a and the atomic positions at this given volume. One would observe that after this optimization, all components diagonal of the stress tensor would become identical: hydrostatic pressure (uniform in all directions). It is easier to go the other way around: apply a hydrostatic pressure, and let Quantum Espresso find the lowest-energy unit cell that is consistent with that pressure. This is a 'vc-relax' type of calculation, with a target pressure that is different from zero. For instance, for the lowest volume in the series, the weighted average of the diagonal elements of the stress tensor is 490 kbar. Set this value as target pressure, and do a vc-relax calculation (expect about 15 minutes). This is the input file:

```
&CONTROL
  calculation='vc-relax',
  outdir='.',
  prefix='SiO2-rutile',
  pseudo_dir='.',
  verbosity='low',
  tprnfor=.true.,
  tstress=.true.,
/

&SYSTEM
 ibrav = 0,
  A = 4.17970,
  nat = 6,
  ntyp = 2,
  ecutwfc=100,
  ecutrho=400,
  input_dft='pbe',
  occupations='smearing',
  smearing='mv',
  degauss=0.005d0,
/

&ELECTRONS
  conv_thr=1d-08,
  mixing_beta=0.7d0,
/

&IONS
```

```

  ion_dynamics='bfgs',
/
&CELL
  cell_dynamics='bfgs',
  press=490.d0,
  press_conv_thr=0.5d0,
/
CELL_PARAMETERS {alat}
  1.0000000000000000  0.0000000000000000  0.0000000000000000
  0.0000000000000000  1.0000000000000000  0.0000000000000000
  0.0000000000000000  0.0000000000000000  0.638060147857502
ATOMIC_SPECIES
  O 15.999400d0 O.pbe-kjpaw.UPF
  Si 28.085500d0 Si.pbe-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS {crystal}
  Si 0.0000000000d0 0.0000000000d0 0.0000000000d0
  Si 0.5000000000d0 0.5000000000d0 0.5000000000d0
  O 0.3061370000d0 0.3061370000d0 0.0000000000d0
  O 0.6938630000d0 0.6938630000d0 0.0000000000d0
  O 0.1938630000d0 0.8061370000d0 0.5000000000d0
  O 0.8061370000d0 0.1938630000d0 0.5000000000d0
K_POINTS {automatic}
  4 4 9 0 0 0

```

This leads to a unit cell that has a volume of 284.76 a.u.³, subject to the specified pressure. You can read the total energy and the lattice parameters for the output file. They are listed in the table underneath (verify at least one case). You can plot these data on the same energy-vs-volume graph as you used for the static series of calculations (fig. 1). The new data points lie systematically below the initial data points. No further optimization of the crystal will lead to an even lower energy at the given volumes.

P _{target} (kbar)	Energy (Ry)	a=b (Å)	c (Å)	Volume (Å ³)			
490	-260.53387783	4.020561	2.610435	42.197465			
342	-260.56055037	4.069161	2.633260	43.601715			
215	-260.57859581	4.118576	2.654240	45.022978			
104	-260.58931187	4.170652	2.673465	46.503158			
6	-260.59319463	4.227807	2.690448	48.090021			
-79	-260.59011059	4.293252	2.704146	49.842854			
-152	-260.57863878	4.376967	2.711916	51.954468			

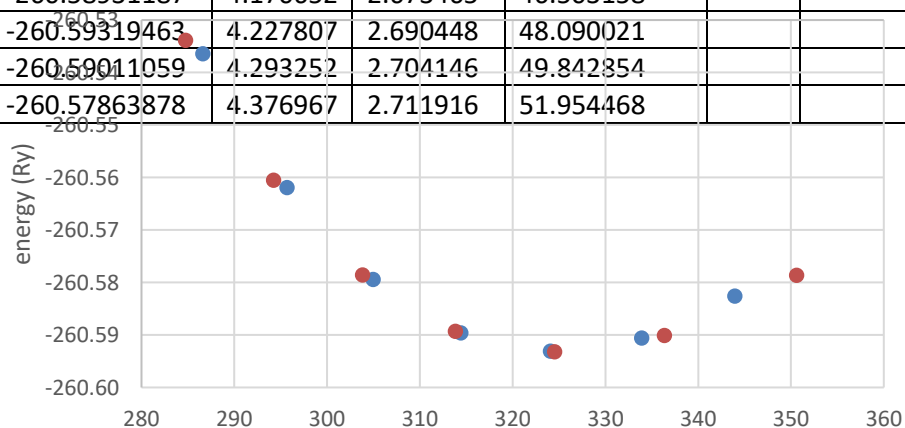


Fig. 1: Energy versus volume for SiO₂ (stishovite). 'static' means: varying the volume while keeping cell shape and atom positions fixed to an initial (experimental) value. 'relaxed' means: full geometry optimization, at this volume.

By fitting a Birch-Murnaghan equation of state through these new data points, you get the correct PBE-prediction for equilibrium volume and bulk modulus of this crystal :

```
# equation of state: birch 1st order.  chisq = 0.2704D-08
# V0 = 325.45 a.u.^3, k0 = 2583 kbar, dk0 = 5.38 d2k0 = 0.000 emin = -260.59319
# V0 = 48.23 Ang^3, k0 = 258.4 GPa

#####
# Vol.          E_calc      E_fit      E_diff     Pressure   Enthalpy
# Ang^3         Ry          Ry          Ry          GPa        Ry
#####
42.20      -260.53388   -260.53385  -0.00003    49.44     -259.57684
43.60      -260.56055   -260.56062   0.00007    34.17     -259.87711
45.02      -260.57860   -260.57860  -0.00000    21.37     -260.13727
46.50      -260.58931   -260.58925  -0.00006    10.37     -260.36815
48.09      -260.59319   -260.59317  -0.00003     0.74     -260.57697
49.84      -260.59011   -260.59019   0.00008    -7.80     -260.76839
51.95      -260.57864   -260.57861  -0.00003   -15.75     -260.95396
```

The equilibrium volume (48.23 Å³) is not too much different from the approximate value found before. The bulk modulus of 258.4 GPa is now a true physically meaningful bulk modulus, which is quite different from the approximate value found before. The column with pressure values is physically meaningful too now, and is the predicted hydrostatic pressure that is required to impose the volume given in the first column.

This procedure to obtain the bulk modulus can be used for any crystal, regardless the number of degrees of freedom they have.