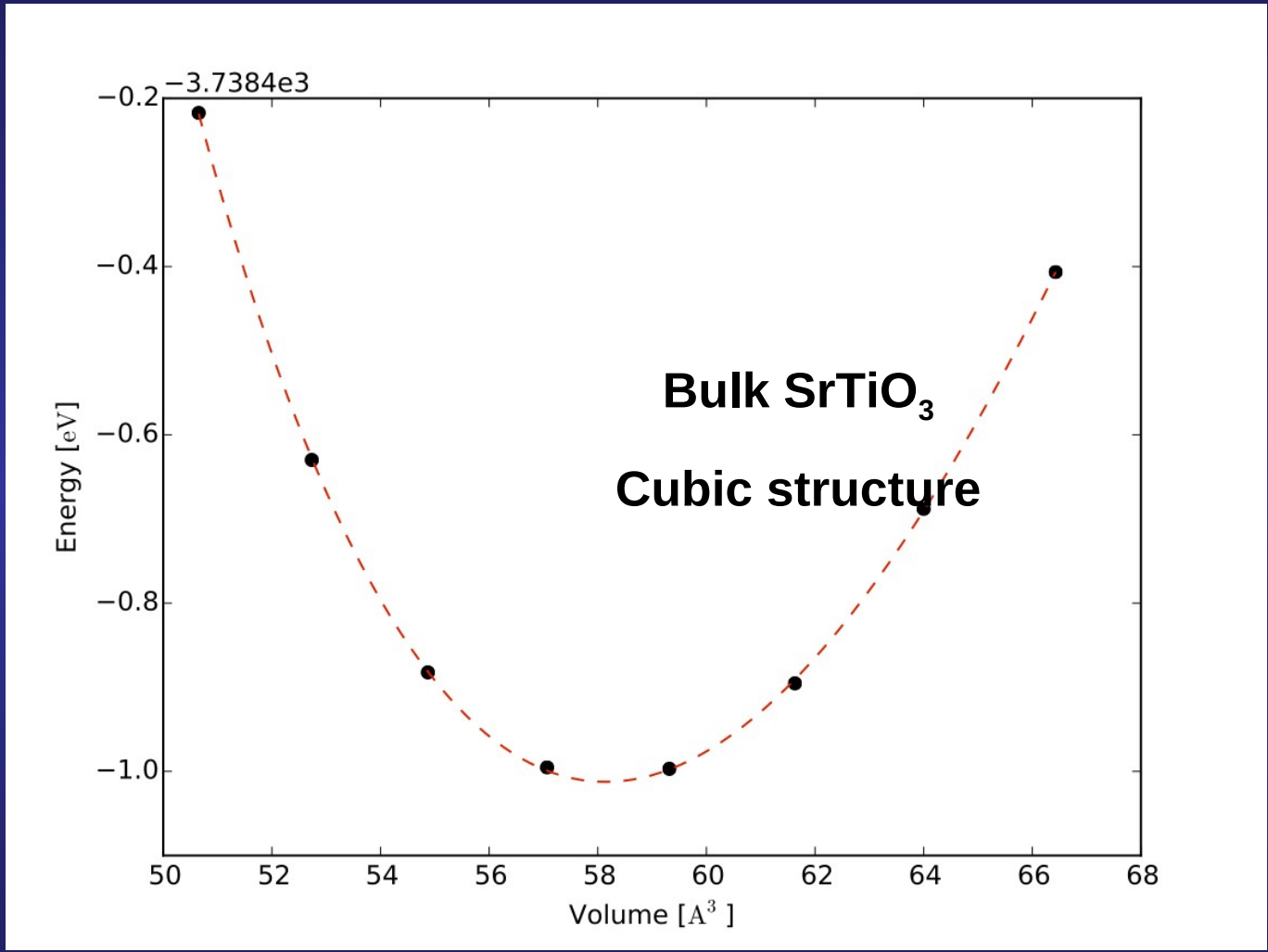
Computing lattice constant, bulk modulus and equilibrium energies of bulk cubic $SrTiO_3$



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Information required to run a first-principles simulation

Number and species of the atoms in the unit cell,

N

Lattice vectors and lattice constants

Ω

Position of all the atoms

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

$T = 0$

$S = 0$

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 Ω

First test: determine theoretical predictions for Ω_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 $B = -\Omega \frac{dP}{d\Omega} = \Omega \frac{d^2 E}{d\Omega^2}$

Why Ω_0 and B:

- **Can be measured with great accuracy.**
- **Can be extrapolated at $T = 0$**

Ω_0 and B can be measured with great accuracy and extrapolated at $T = 0$

Table 3 Crystal structures of the elements

The data given are at room temperature for the most common form, or at the stated temperature in deg K. (Inorganic Crystal Structure Database (ICSD) online.

H[1] 4K hcp 3.75 6.12																	He[4] 2K hcp 3.57 5.83
Li 78K bcc 3.491	Be hcp 2.27 3.59											B rhomb.	C diamond 3.567	N 20K cubic 5.66 (N_2)	O complex (O_2)	F	Ne 4K fcc 4.46
Na 5K bcc 4.225	Mg hcp 3.21 5.21	← Crystal structure →										Al fcc 4.05	Si diamond 5.430	P complex	S complex	Cl complex (Cl_2)	Ar 4K fcc 5.31
		← *a* lattice parameter, in Å →															
		← *c* lattice parameter, in Å →															
K 5K bcc 5.225	Ca fcc 5.58	Sc hcp 3.31 5.27	Ti hcp 2.95 4.68	V bcc 3.03	Cr bcc 2.88	Mn cubic complex	Fe bcc 2.87	Co hcp 2.51 4.07	Ni fcc 3.52	Cu fcc 3.61	Zn hcp 2.66 4.95	Ga complex	Ge diamond 5.658	As rhomb.	Se hex. chains	Br complex (Br_2)	Kr 4K fcc 5.64
Rb 5K bcc 5.585	Sr fcc 6.08	Y hcp 3.65 5.73	Zr hcp 3.23 5.15	Nb bcc 3.30	Mo bcc 3.15	Tc hcp 2.74 4.40	Ru hcp 2.71 4.28	Rh fcc 3.80	Pd fcc 3.89	Ag fcc 4.09	Cd hcp 2.98 5.62	In tetr. 3.25 4.95	Sn (α) diamond 6.49	Sb rhomb.	Te hex. chains	I complex (I_2)	Xe 4K fcc 6.13
Cs 5K bcc 6.045	Ba bcc 5.02	La hex. 3.77 *ABAC*	Hf hcp 3.19 5.05	Ta bcc 3.30	W bcc 3.16	Re hcp 2.76 4.46	Os hcp 2.74 4.32	Ir fcc 3.84	Pt fcc 3.92	Au fcc 4.08	Hg rhomb.	Tl hcp 3.46 5.52	Pb fcc 4.95	Bi rhomb.	Po sc 3.34	At —	Rn —
Fr —	Ra —	Ac fcc 5.31															

Ce fcc 5.16	Pr hex. 3.67 *ABAC*	Nd hex. 3.66	Pm —	Sm complex	Eu bcc 4.58	Gd hcp 3.63 5.78	Tb hcp 3.60 5.70	Dy hcp 3.59 5.65	Ho hcp 3.58 5.62	Er hcp 3.56 5.59	Tm hcp 3.54 5.56	Yb fcc 5.48	Lu hcp 3.50 5.55
Th fcc 5.08	Pa tetr. 3.92 3.24	U complex	Np complex	Pu complex	Am hex. 3.64 *ABAC*	Cm —	Bk —	Cf —	Es —	Fm —	Md —	No —	Lr —

Ch. Kittel, Introduction to Solid State Physics, Eighth Edition, J. Wiley & sons (2005)

Ω_0 and B can be measured with great accuracy and extrapolated at $T = 0$

Table 3 Isothermal bulk modulii and compressibilities at room temperature

After K. Gschneidner, Jr., Solid State Physics 16, 275–426 (1964); several data are from F. Birch, in *Handbook of physical constants*, Geological Society of America Memoir 97, 107–173 (1966). Original references should be consulted when values are needed for research purposes. Values in parentheses are estimates. Letters in parentheses refer to the crystal form. Letters in brackets refer to the temperature:

[a] = 77 K; [b] = 273 K; [c] = 1 K; [d] = 4 K; [e] = 81 K.

Bulk modulus in units 10^{12} dyn/cm² or 10^{11} N/m²
Compressibility in units 10^{-12} cm²/dyn or 10^{-11} m²/N

H [d] 0.002 500																	He [d] 0.00 1168
Li 0.116 8.62	Be 1.003 0.997											B 1.78 0.562	C [d] 4.43 0.226	N [e] 0.012 80	O	F	Ne [d] 0.010 100
Na 0.068 14.7	Mg 0.354 2.82											Al 0.722 1.385	Si 0.988 1.012	P [b] 0.304 3.29	S [r] 0.178 5.62	Cl	Ar [a] 0.013 79
K 0.032 31.	Ca 0.152 6.58	Sc 0.435 2.30	Ti 1.051 0.951	V 1.619 0.618	Cr 1.901 0.526	Mn 0.596 1.68	Fe 1.683 0.594	Co 1.914 0.522	Ni 1.86 0.538	Cu 1.37 0.73	Zn 0.598 1.67	Ga [b] 0.569 1.76	Ge 0.772 1.29	As 0.394 2.54	Se 0.091 11.0	Br	Kr [a] 0.018 56
Rb 0.031 32.	Sr 0.116 8.62	Y 0.366 2.73	Zr 0.833 1.20	Nb 1.702 0.587	Mo 2.725 0.366	Tc (2.97) (0.34)	Ru 3.208 0.311	Rh 2.704 0.369	Pd 1.808 0.553	Ag 1.007 0.993	Cd 0.467 2.14	In 0.411 2.43	Sn [g] 1.11 0.901	Sb 0.383 2.61	Te 0.230 4.35	I	Xe
Cs 0.020 50.	Ba 0.103 9.97	La 0.243 4.12	Hf 1.09 0.92	Ta 2.00 0.50	W 3.232 0.309	Re 3.72 0.269	Os (4.18) (0.24)	Ir 3.55 0.282	Pt 2.783 0.359	Au 1.732 0.577	Hg [c] 0.382 2.60	Tl 0.359 2.79	Pb 0.430 2.33	Bi 0.315 3.17	Po (0.26) (3.8)	At	Rn
Fr (0.020) (50.)	Ra (0.132 (7.6)	Ac (0.25) (4.)															

Ce [γ] 0.239 4.18	Pr 0.306 3.27	Nd 0.327 3.06	Pm (0.35) (2.85)	Sm 0.294 3.40	Eu 0.147 6.80	Gd 0.383 2.61	Tb 0.399 2.51	Dy 0.384 2.60	Ho 0.397 2.52	Er 0.411 2.43	Tm 0.397 2.52	Yb 0.133 7.52	Lu 0.411 2.43
Th 0.543 1.84	Pa (0.76) (1.3)	U 0.987 1.01	Np (0.68) (1.5)	Pu 0.54 1.9	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Ch. Kittel, Introduction to Solid State Physics, Eighth Edition, J. Wiley & sons (2005)

Bulk $SrTiO_3$: a perovskite oxide that at high temperatures crystallizes in the simple cubic structure

Go to the directory where the exercise on the structure of Si is stored

Inspect the input file, $SrTiO_3$.fdf

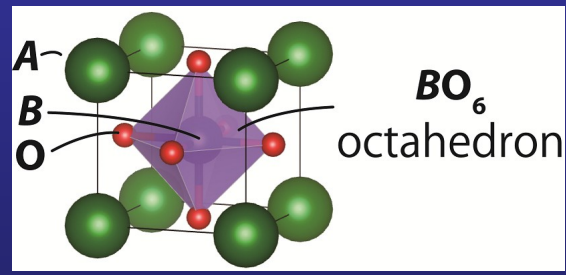
```
SystemName          Bulk SrTiO3
#                   Centrosymmetric paraelectric configuration
#                   LDA-CA
#                   400 Ry
#                   6 x 6 x 6; 0.5 0.5 0.5 MP mesh

SystemLabel         SrTiO3
NumberOfAtoms       5
NumberOfSpecies     3

%block ChemicalSpeciesLabel
 1  38  Sr
 2  22  Ti
 3  8   O
%endblock ChemicalSpeciesLabel

LatticeConstant     3.70 Ang
%block LatticeVectors
    1.000   0.000   0.000
    0.000   1.000   0.000
    0.000   0.000   1.000
%endblock LatticeVectors

AtomicCoordinatesFormat    Fractional
%block AtomicCoordinatesAndAtomicSpecies
    0.00000000    0.00000000    0.00000000   1  87.62       Sr
    0.50000000    0.50000000    0.50000000   2  47.867      Ti
    0.50000000    0.50000000    0.00000000   3  15.9994     O
    0.50000000    0.00000000    0.50000000   3  15.9994     O
    0.00000000    0.50000000    0.50000000   3  15.9994     O
%endblock AtomicCoordinatesAndAtomicSpecies

%block kgrid_Monkhorst_Pack
   6   0   0    0.5
   0   6   0    0.5
   0   0   6    0.5
%endblock kgrid_Monkhorst_Pack
```

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

The theoretical lattice constant of $SrTiO_3$ for this first example

Cubic $SrTiO_3$ structure:

Simple cubic lattice



+ a basis of five 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 Ω

Run the code,

siesta < $SrTiO_3$.fdf > $SrTiO_3$.3.70.out

The name of the output file is free, but since we are running bulk $SrTiO_3$ with this lattice constant, this seems very sensible…

For this particular example, run from 3.70 Å up to 4.05 Å in steps of 0.05 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 =" $SrTiO_3$.*.out > $SrTiO_3$.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 Ω

Edit the $SrTiO_3$.evslc.dat file and leave only two columns:

```
cubic
3.70    -3738.617262
3.75    -3739.029827
3.80    -3739.282341
3.85    -3739.395325
3.90    -3739.396974
3.95    -3739.295355
4.00    -3739.088046
4.05    -3738.806515
```

Add a first line with the kind of lattice (cubic, bcc, fcc, diamond…)

Lattice constant (in Å)

Energy of the unit cell (in eV)

Procedure to compute the equilibrium volume and bulk modulus

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

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

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

E_0 total energy at the minimum

To do this, we have prepared an script in python

python fit_results.py $SrTiO_3$.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

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

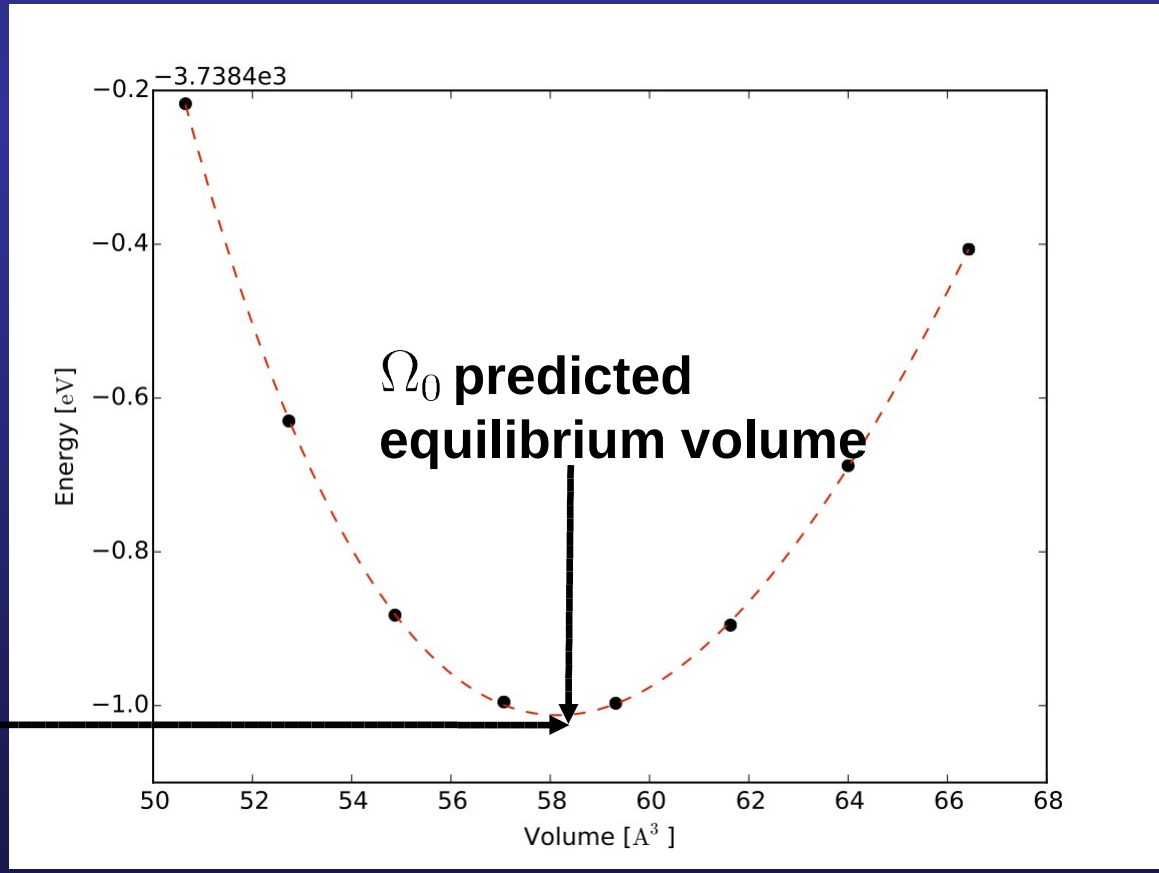
F. D. Murnaghan,

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**

E_0 **total energy at the minimum**



Comparison of predicted equilibrium properties with experimental values are routine tests for calculations

Table 2. Experimental and theoretical lattice constants (in Å) of the cubic perovskite structure of various ABO_3 compounds

Compound	Experiment	Theory	Method	Reference
I–V compounds				
$KNbO_3$	4.016	3.956 (±0.003)	DFT (LDA)	[32, 35, 36, 38]
		4.028 (±0.010)	DFT (GGA)	[35, 38]
		4.011	DFT (WDA)	[38]
$NaNbO_3$	3.937	3.914	DFT (LDA)	[32, 36]
$KTaO_3$	3.983	3.938 (±0.018)	DFT (LDA)	[35, 38, 115]
		4.033 (±0.002)	DFT (GGA)	[35, 38]
		3.972	DFT (WDA)	[38]
II–IV compounds				
$CaTiO_3$	3.836	3.809 (±0.003)	DFT (LDA)	[32, 36]
$SrTiO_3$	3.905	3.862 (±0.012)	DFT (LDA)	[32, 35, 36, 38, 40, 41]
		3.941 (±0.007)	DFT (GGA)	[35, 38, 40]
		3.917	DFT (WDA)	[38]
		3.94	B3LYP	[40]
		3.92	HF	[40]
$BaTiO_3$	4.000	3.947 (±0.013)	DFT (LDA)	[28, 32, 35–38, 40, 41]
		4.028 (±0.005)	DFT (GGA)	[35, 38, 40, 41]
		4.009	DFT (WDA)	[38]
		4.04	B3LYP	[40]
		4.01	HF	[40]
$CdTiO_3$	3.800	3.805	DFT (LDA)	[116]
$PbTiO_3$	3.969	3.888 (±0.005)	DFT (LDA)	[29, 32, 36, 38, 97]
		3.965 (±0.005)	DFT (GGA)	[38, 40]
		3.933	DFT (GGA')	[42]
		3.941	DFT (WDA)	[38]
		3.96	B3LYP	[40]
		3.94	HF	[40]
$PbZrO_3$	4.133	4.115 (±0.008)	DFT (LDA)	[32, 36, 89, 117]
$BaZrO_3$	4.193	4.152 (±0.004)	DFT (LDA)	[32, 36, 118]
		4.207	DFT (GGA)	[119]
$SrZrO_3$	4.101	4.17	DFT (GGA)	[119]
$SrHfO_3$	4.069	4.069	DFT (LDA)	[120]
$PbVO_3$			DFT (LDA)	[121, 122]
III–III compounds				
$BiGaO_3$	–	3.83	DFT (LDA)	[123]
$BiAlO_3$	–	3.75	DFT (LDA)	[123]
$BiScO_3$	–	3.99	DFT (LDA)	[124]
$YScO_3$	–	3.92	DFT (LDA)	[124]

```
$ python fit_results.py SrTiO3.evslc.dat
 V0      =  58.1422 A^3
 E0      =  -3739.4125 eV
 B(V0)   =  1.2868 eV/A^3
 B'(V0) =  4.2267
Theoretical lattice constant: 3.8740 A
```

Ph. Ghosez and K. M. Rabe,
First-Principles Studies of Ferroelectric Oxides
In
Physics of Ferroelectrics
A Modern Perspective
Springer (Berlin 2007)