Lab 2

First-principles calculations of electronic properties of materials: calculation of the elastic constants of bulk CaO

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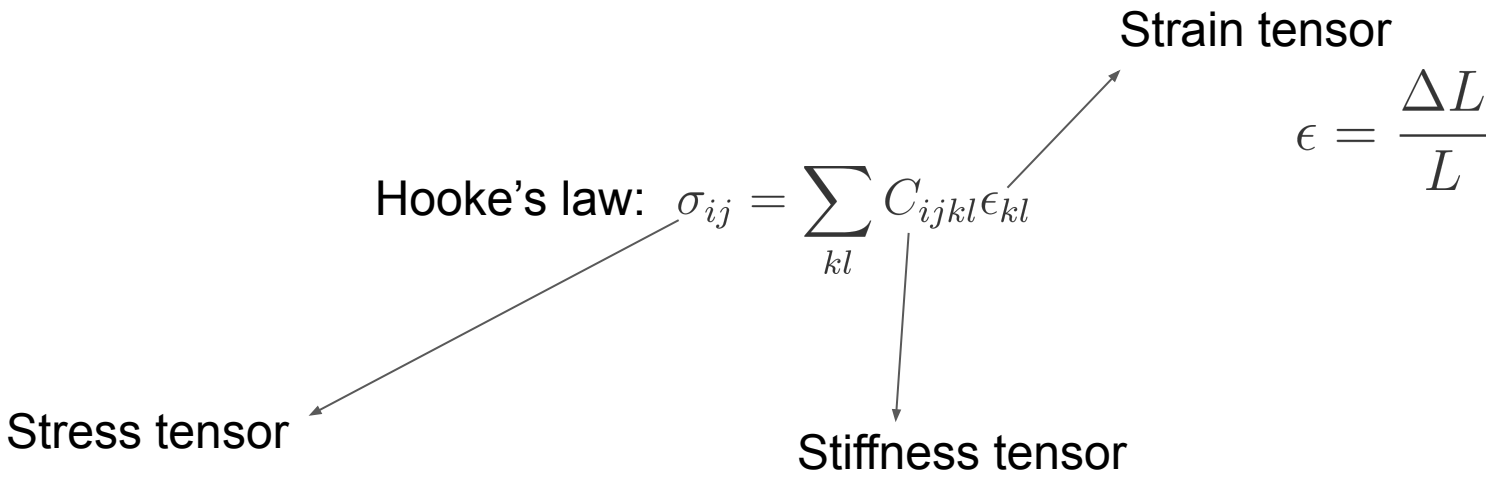
Elastic constants



https://en.wikipedia.org/wiki/Hooke%27s_law

Elastic constants

Hooke's law: $\sigma_{ij} = \sum_{kl} C_{ijkl}\epsilon_{kl}$

→ Only 36 components thanks to symmetries in σ_{ij} and ε_{kl}

Using the Voigt notation for a symmetric tensors, we can rewrite Hooke's Law in matrix-times-vector form (1=xx, 2=yy, 3=zz, 4=yz, 5=zx, 6=xy):

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \hdashline \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{pmatrix} = \left(\begin{array}{ccc:ccc} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ \hdashline C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{array}\right) \begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \hdashline \varepsilon_{yz} \\ \varepsilon_{zx} \\ \varepsilon_{xy} \end{pmatrix}$$

compression (upper-left block) · mixed (upper-right block) · compression (strain) · shear (strain) · stress · mixed · shear · strain

$C_{ij} = C_{ji}$

→ only 21 independent components

https://en.wikipedia.org/wiki/Hooke%27s_law

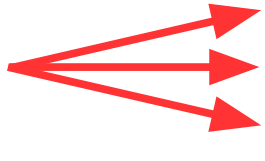
Elastic constants with cubic symmetry

Cubic symmetry: only three independent elastic constants: C_{11}, C_{12} and C_{44}

$$\begin{pmatrix} C_{11} & C_{12} & C_{12} & & & \\ C_{12} & C_{11} & C_{12} & & 0 & \\ C_{12} & C_{12} & C_{11} & & & \\ & & & C_{44} & 0 & 0 \\ & 0 & & 0 & C_{44} & 0 \\ & & & 0 & 0 & C_{44} \end{pmatrix}$$

Transformation due to strain

Lattice vectors of the unit cell



$$\begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix} = \begin{pmatrix} a_{1x} & a_{1y} & a_{1z} \\ a_{2x} & a_{2y} & a_{2z} \\ a_{3x} & a_{3y} & a_{3z} \end{pmatrix}$$

$$\begin{pmatrix} \mathbf{a}'_1 \\ \mathbf{a}'_2 \\ \mathbf{a}'_3 \end{pmatrix} = \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix} \left(\hat{I} + \hat{\varepsilon} \right)$$

strain

where

$$\hat{I} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \hat{\varepsilon} = \begin{pmatrix} e_1 & e_6/2 & e_5/2 \\ e_6/2 & e_2 & e_4/2 \\ e_5/2 & e_4/2 & e_3 \end{pmatrix}$$

strain tensor

Total energy of the distorted lattice

$$E = E_0 - P(V_0)\Delta V + \frac{1}{2}V_0 \sum_{i=1}^{6}\sum_{j=1}^{6} C_{ij}e_i e_j$$

undistorted lattice

pressure of undistorted lattice, volume V_0

change in volume due to strain

Total energy of the distorted lattice

$$E = E_0 - P(V_0)\Delta V + \frac{1}{2}V_0 \sum_{i=1}^{6}\sum_{j=1}^{6} C_{ij}e_i e_j$$

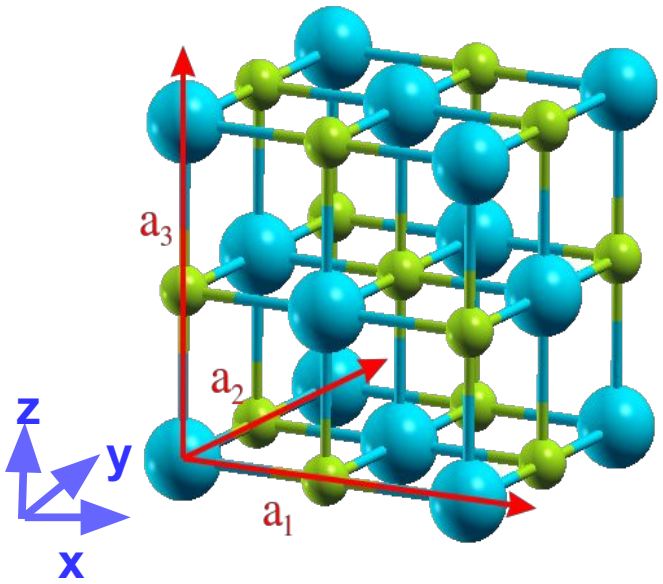
undistorted lattice

pressure of undistorted lattice, volume V_0

change in volume due to strain

This lab: $\Delta V = 0$, we will apply strain with no change in volume allowed.

Strain of the system with a cubic symmetry



Bulk modulus

$$B = \tfrac{1}{3}\,(C_{11} + 2\,C_{12})$$

$$\begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix} = \begin{pmatrix} a_0 & 0 & 0 \\ 0 & a_0 & 0 \\ 0 & 0 & a_0 \end{pmatrix}$$

equilibrium lattice parameter

Determine the positions of 8 inequivalent Ca and O atoms in the conventional unit cell of CaO on the figure above and specify them in your input file.
Remember to change the parameter **nat**.

Determination of the elastic constants C_{11} and C_{12}

tetragonal strain:

$$\hat{\varepsilon} = \begin{pmatrix} x & 0 & 0 \\ 0 & -x & 0 \\ 0 & 0 & \frac{x^2}{1-x^2} \end{pmatrix}$$

no volume change!

find the change in lattice parameters:

$$\begin{pmatrix} \mathbf{a}_1' \\ \mathbf{a}_2' \\ \mathbf{a}_3' \end{pmatrix} = \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix} \left(\hat{I} + \hat{\varepsilon} \right) = \dots$$

Find C_{11} and C_{12} fitting the ΔE function and using the expression for bulk modulus

$$\Delta E(x) = \Delta E(-x) = V_0(C_{11} - C_{12})x^2$$

Relax your structure for every value of **x**, in order to find the minimum of energy!

Determination of the elastic constants C_{11} and C_{12}

tetragonal strain:

$$\hat{\varepsilon} = \begin{pmatrix} x & 0 & 0 \\ 0 & -x & 0 \\ 0 & 0 & \frac{x^2}{1-x^2} \end{pmatrix}$$

no volume change!

find the change in lattice parameters:

$$\begin{pmatrix} \mathbf{a}'_1 \\ \mathbf{a}'_2 \\ \mathbf{a}'_3 \end{pmatrix} = \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix} \left(\hat{I} + \hat{\varepsilon}\right) = \ldots$$

Use the 8-atom orthorhombic unit cell in order to model such a strain

```
   ibrav = 8
celldm(1) = |a'_1|
celldm(2) = |a'_2|/|a'_1|
celldm(3) = |a'_3|/|a'_1|
```

Relax your structure for every value of **x**, in order to find the minimum of energy!

Determination of the elastic constant C_{44}

tetragonal strain:

$$\hat{\varepsilon} = \begin{pmatrix} 0 & \frac{x}{2} & 0 \\ \frac{x}{2} & 0 & 0 \\ 0 & 0 & \frac{x^2}{4-x^2} \end{pmatrix}$$

no volume change!

function to be fitted:

$$\Delta E(x) = \Delta E(-x) = \tfrac{1}{2} V_0 C_{44} x^2$$

Use the 8-atom monoclinic unit cell in order to model such a strain

```
   ibrav = 12
celldm(1) = |a'_1|
celldm(2) = |a'_2|/|a'_1|
celldm(3) = |a'_3|/|a'_1|
celldm(4) = a'_1 · a'_2 / (|a'_1||a'_2|)
```

Relax your structure for every value of **x**, in order to find the minimum of energy!