How to compute the Born effective charge tensor

$$Z^{\star}_{\kappa,\alpha\beta} = \Omega_0 \left. \frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}=0}$$

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Definition of the Born effective charges, also known as dynamical charges

For periodic solids, the Born effective charge of atom κ is a tensor defined as the coefficient of proportionality at the linear order and under the condition of zero macroscopic electric field, between the macroscopic polarization per unit cell created in direction β and a cooperative displacements of atoms κ in direction α

$$Z^{\star}_{\kappa,\alpha\beta} = \Omega_0 \left. \frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}=0}$$

Units: electron charges

Read pages 106 and following of Philippe Ghosez's PhD thesis
http://www.phythema.ulg.ac.be/webroot/misc/books/PhD-Ph.Ghosez.pdf

In SIESTA computed from finite differences of the bulk spontaneous polarization

```
SystemName          Bulk SrTiO3
#                   Centrosymmetric paraelectric configuration
#                   LDA-CA
#                   1200 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     3.8715 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

XC.functional          LDA
XC.authors             CA
MeshCutoff             1200 Ry
MD.TypeOfRun            FC
MD.FCDispl              0.01 bohr
BornCharge              .true.
WriteForces             .true.
WriteCoorStep           .true.
%block PolarizationGrids
  20   4   4  yes
   4  20   4  yes
   4   4  20  yes
%endblock PolarizationGrids
Eigenvectors     .true.
%block BandLines
1   0.0   0.0   0.0   \Gamma            # Compute eigenvectors only at \Gamma
%endblock BandLines
```

$$Z^{\star}_{\kappa,\alpha\beta} = \Omega_0 \left. \frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}=0}$$

$SrTiO_3$ in the centrosymmetric bulk cubic structure

To compute the phonons, the atomic masses are introduced in this block

We are going to displace all the atoms in the unit cell 0.01 Bohrs along the x, y, and z direction

For each atomic configuration, we compute the macroscopic polarization with this Polarization Grid in reciprocal space

Born effective charges dumped into a file: SystemLabel.BC

$$Z^{\star}_{\kappa,\alpha\beta} = \Omega_0 \left. \frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}=0}$$

```
 x          y          z
x    2.5227042  0.0000000  0.0000000  |
y    0.0000000  2.5227042  0.0000000  | Born effective charges for Ba
z    0.0000000  0.0000000  2.5227043  |
-----------------------------------------------
x    7.5522144  0.0000000  0.0000000  |
y    0.0000000  7.5522144  0.0000000  | Born effective charges for Ti
z    0.0000000  0.0000000  7.5522132  |
-----------------------------------------------
x   -2.0647380  0.0000000  0.0000000  |
y    0.0000000 -2.0647380  0.0000000  | Born effective charges for O1
z    0.0000000  0.0000000 -5.9514365  |
-----------------------------------------------
x   -2.0647380  0.0000000  0.0000000  |
y    0.0000000 -5.9514365  0.0000000  | Born effective charges for O2
z    0.0000000  0.0000000 -2.0647380  |
-----------------------------------------------
x   -5.9514365  0.0000000  0.0000000  |
y    0.0000000 -2.0647380  0.0000000  | Born effective charges for O3
z    0.0000000  0.0000000 -2.0647380  |
-----------------------------------------------
```

Acoustic sum rule

It is important that the acoustic sum rule is preserved by the Born effective charges
(if we displace the whole solid rigidly, no polarization should be generated)

$$\sum_{\kappa} Z^{\star}_{\kappa,\alpha\beta} = 0$$

In our simulation, taking $\alpha = \beta = x$, and rounding to the third significant digit

2.523 + 7.552 -2.065 -2.065 -5.951 = -0.006

To fulfill the acoustic sum rule, we divide the sum by the number of atoms

-0.006/ 5 = -0.0012

Substracting this same amount to all the atoms

2.524 + 7.553 - 2.064 - 2.064 - 5.949 = 0

Comparison with previous results

Table 4. Born effective charges of various ABO_3 compounds in their cubic structure. The Born effective charges of the A and B atoms are compared to the *nominal* ionic charges Z_A and Z_B. (Adapted from [148])

ABO_3	Z^*_A	Z^*_B	$Z^*_{O\parallel}$	$Z^*_{O\perp}$	Z^*_A/Z_A	Z^*_B/Z_B	Method	Reference
nominal	3	3	−2	−2				
$BiAlO_3$	6.22	2.84	−2.34	−3.38	2.07	0.95	DFT (LDA)	[123]
$BiGaO_3$	6.29	3.11	−2.58	−3.40	2.10	1.04	DFT (LDA)	[123]
nominal	2	4	−2	−2				
$CaTiO_3$	2.58	7.08	−5.65	−2.00	1.29	1.77	DFT (LDA)	[142]
$SrTiO_3$	2.56	7.26	−5.73	−2.15	1.28	1.82	DFT (LDA)	[148]
	2.54	7.12	−5.66	−2.00	1.27	1.78	DFT (LDA)	[142]
	2.55	7.56	−5.92	−2.12	1.28	1.89	DFT (LDA)	[126]
	2.4	7.0	−5.8	−1.8	1.2	1.8	experiment	[149]
$BaTiO_3$	2.77	7.25	−5.71	−2.15	1.39	1.81	DFT (LDA)	[148]
	2.75	7.16	−5.69	−2.11	1.38	1.79	DFT (LDA)	[142]
	2.61	5.88	−4.43	−2.03	1.31	1.47	Pseudo-SIC	[47]
	2.9	6.7	−4.8	−2.4	1.45	1.68	experiment	[149]
$BaZrO_3$	2.73	6.03	−4.74	−2.01	1.37	1.51	DFT (LDA)	[142]
$PbTiO_3$	3.90	7.06	−5.83	−2.56	1.95	1.77	DFT (LDA)	[142]
$PbZrO_3$	3.92	5.85	−4.81	−2.48	1.96	1.46	DFT (LDA)	[142]
nominal	1	5	−2	−2				
$NaNbO_3$	1.13	9.11	−7.01	−1.61	1.13	1.82	DFT (LDA)	[142]
$KNbO_3$	0.82	9.13	−6.58	−1.68	0.82	1.83	DFT (LDA)	[150]
	1.14	9.23	−7.01	−1.68	1.14	1.85	DFT (LDA)	[142]
	1.14	9.37	−6.86	−1.65	1.14	1.87	DFT (LDA)	[151]
	1.07	8.12	−5.38	−1.80	1.07	1.62	HF	[48, 49]
nominal	-	6	−2	−2				
WO_3	-	12.51	−9.13	−1.69	-	2.09	DFT (LDA)	[152]

Adapted from
Ph. Ghosez *et al.* ,
Phys. Rev. B 58, 6224 (1998)

First-principles studies of ferroelectric oxides
K. M. Rabe and Ph. Ghosez, included in
Physics of Ferroelectrics. A Modern Perspective.
Topics in Applied Physics
K. Rabe, Ch. Ahn, and J. –M. Triscone (Editors)
Springer-Verlag, Heidelberg (2007)

Phonon frequencies and eigenvectors at the Γ-point

- Go to the directory
$cd <your_siesta_path>/Util/Vibra/Src

- To compile the vibra suite with the same arch.make as in siesta, type
$make

- Go back to the directory where you are running the exercise and type
$ <your_siesta_path>/Util/Vibra/Src/vibra < SrTiO3.fdf

- You get the file SrTiO3.bands with the eigenvalues and SrTiO3.vectors with the eigenvectors

```
Computing Eigenvalues and Eigenvectors
  eigenvalue #           1  omega= -5.325837240466150E-006
  eigenvalue #           2  omega=  2.752977718151550E-006
  eigenvalue #           3  omega=  9.783693863922063E-006
  eigenvalue #           4  omega=   16.0767628308708
  eigenvalue #           5  omega=   16.0767632923528
  eigenvalue #           6  omega=   16.0779498787851
  eigenvalue #           7  omega=   179.758878489337
  eigenvalue #           8  omega=   179.758878606216
  eigenvalue #           9  omega=   179.758906052441
  eigenvalue #          10  omega=   228.416376629259
  eigenvalue #          11  omega=   228.416376742234
  eigenvalue #          12  omega=   228.416376842902
  eigenvalue #          13  omega=   563.619220152611
  eigenvalue #          14  omega=   563.619220160393
  eigenvalue #          15  omega=   563.619220208914
```

Three frequencies are zero,
They correspond to translational modes