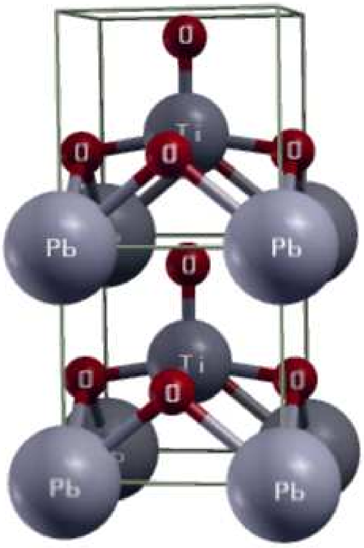
# Tutorial 3: Piezoelectric constant of $PbTiO_3$ (approx. 20 mins)

For the calculation of piezoelectric constant two reference structures of $PbTiO_3$ have been chosen. One is a ferroelectric equilibrium tetragonal structure (lambda1 sown below) and another structure (lambda2) is the perturbed structure where -0.1% of strain has been applied in the Z direction. In both structure the relaxation of internal degrees of freedom was performed in advance.



## 1 Case lambda1 (unperturbed ferroelectric state)

1.0 Copy the tutorial files to your local directory

```
$ cp -r ~/group/tutorials-BerryPI/tutorial3 ~/tutorials-BerryPI/tutorial3
```

1.1 Change the current directory to `~/tutorials-BerryPI/tutorial3/lambda1`

1.2 Perform WIEN2k initialization

```
$ init_lapw -b -vxc 13 -ecut -6 -numk 230 -rkmax 6
```

Here "-vxc 13" stands for PBE-GGA as exchange correlation function."-ecut -6" means the separation energy of -6 Ry has been chosen to separate core electron from valance electron. “-numk 230" means that 230 k points has been chosen in Brillouin zone which generates 6*6*6 size k-mesh in the symmetric Brillouin zone. "-rkmax 6" indicates that the product between the smallest muffin tin radius and the K_max was chosen as 6.

1.3 Execute WIEN2k SCF calculation

```
$ run_lapw
```

Important: Do not use iterative diagonalization (-it switch) during standard SCF cycle. This can lead to incorrect polarization values.

1.4 Run BerryPI

```
$ berrypi -p$(pwd) -k6:6:6
```

Here "-p$(pwd)" means that BerryPI program is running for the case (PbTiO3) located in the current directory. "-k6:6:6" means the calculation is being done using 6*6*6 k-mesh in the full Brillouin zone (non symmetric) with a total of 216 k points.

Note: k-mesh in BerryPI should not necessarily be identical to that used in the SCF cycle

1.5 Once the calculation is completed, write down the results

```
      ---POLARIZATION IN C/m^2 FOR [0 to 2] PHASE/2PI RANGE---

TOTAL POLARIZATION: [ _____________ , _____________ , ______________]

     ---POLARIZATION IN C/m^2 FOR [-1 to +1] PHASE/2PI RANGE---

TOTAL POLARIZATION: [ _____________ , _____________ , ______________]
```

Here three total polarization values corresponds to X,Y and Z components of polarization, respectively.

Please, keep in mind that the absolute value of polarization is not a measurable quantity; only the difference matters.

## 2 Case lambda2 (strained ferroelectric structure)

A compressive strain of -0.1% has been applied in the Z direction to the initial ferroelectric structure. Here, "`lambda2.struct`" contains the structural information about the strained state. The relaxation of atomic position due to the applied strain has been performed in advance to speed up the computation.

2.1 Copy all files from `lambda1` to `lambda2` directory

```
$ cp * ../lambda2
```

2.2 Change the current directory to `lambda2`

```
$ cd ../lambda2
```

2.3 Remove the `lambda1.struct` file.

```
$ rm lambda1.struct
```

2.4 Rename all `lambda1.*` files to `lambda2.*` files

```
$ rename_files lambda1 lambda2
```

2.5 Restore original k-mesh taking into account the symmetry

```
$ x kgen
```

with 230 k-points (shifted mesh)

2.6 Initialize the electron density according to the new structure

```
$ x dstart
```

2.7 Run standard SCF cycle.

```
$ run_lapw
```

2.8 Run BerryPI

```
$ berrypi -p$(pwd) -k6:6:6
```

2.9 Once the calculation is completed, write down the results

```
      ---POLARIZATION IN C/m^2 FOR [0 to 2] PHASE/2PI RANGE---

TOTAL POLARIZATION: [ _____________ , _____________ , ______________]

     ---POLARIZATION IN C/m^2 FOR [-1 to +1] PHASE/2PI RANGE---

TOTAL POLARIZATION: [ _____________ , _____________ , ______________]
```

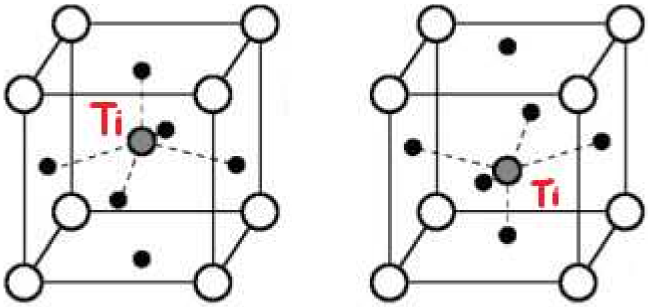
### 3 Piezoelectric coefficient

Calculation of the piezoelectric coefficient is performed by computing the change is polarization with respect to the applied strain. Piezoelectric coefficient can be defined as,

$$e_{ZZ}=\frac{d\,P_Z}{d\,\epsilon_Z}\;=$$

In this case, the change in polarization $d\,P_Z$ corresponds to the difference between the Z component of polarization in `lambda2` and `lamdba1` cases.

Compare the magnitude of $e_{ZZ}$ with experimental values of 3.35-6.50 C/m^2 [1-3] and a DFT value of 3.23 C/m^2 [4]. How will the sign of $d\,P_Z$ change if we flip the Ti atom as shown below? Will this affect the sign of $e_{ZZ}$ ?



[1] Z. Li, M. Grimsditch, X. Xu, and S.-K. Chan, Ferroelectrics 141, 313 (1993).
[2] A. G. Kalinichev, J. D. Bass, B. N. Sun, and D. A. Payne, J. Mater. Res. 12, 2623 (1997).
[3] S. Ikegami, T. Ueda, and T. Nagata, J. Acoust. Soc. Am. 50, 1060 (1971)
[4] G. Sághi-Szabó, R.E. Cohen, H. Krakauer Phys. Rev. Lett., 80 (1998), p. 4321