Tutorial 1: Spontaneous polarization in \( \text{BaTiO}_3 \) (approx. 20 mins)

For the calculation of spontaneous polarization of \( \text{BaTiO}_3 \) two structures has been chosen. One is tetragonal non-centrosymmetric (\( \lambda_1 \)), where the atoms were displaced from the equilibrium centrosymmetric positions in \( Z \) direction, and another structure is a centrosymmetric structure (\( \lambda_0 \)).

1 Case \( \lambda_1 \) (non-centrosymmetric)

We begin with the non-centrosymmetric structure, since it has the lowest symmetry.

1.0 Copy the tutorial files to your local directory

$ cp -r ~/group/tutorials-BerryPI/tutorial1 ~/tutorials-BerryPI/tutorial1

1.1 Change the current directory to \( ~/\text{tutorials-BerryPI/tutorial1/lambda1} \)

1.2 Perform WIEN2k initialization

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

Here "-vxc 13" stands for PBE-GGA as the exchange correlation functional."-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 \( 6\xi 6\xi 6 \) size k-mesh in the symmetric Brillouin zone. "-rkmax 6" indicates that the product between the smallest muffin tin radius and the \( K_{\text{max}} \) was chosen as 6 for tutorial purposes.

1.3 Execute WIEN2k SCF calculation in order to obtain the self-consistent electron density.

$ run_lapw

Important: Do not use iterative diagonalization (-it switch) during the SCF cycle. This can lead to
1.4 Run BerryPI

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

Here “-p$(pwd)” means that BerryPI program is running for the case (BaTiO3) located in the current directory. “-k6:6:6” means the calculation is being done using $6\xi6\xi6$ k-mesh in the full Brillouin zone 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 take a note of the polarization values

---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.

Note: The total polarization has been reported twice for different pi wrapping approaches.

2 Case lambda0

The atoms are brought in centrosymmetric arrangement in order to compare its polarization with the non-centrosymmetric structure.

2.1 Copy all files from lambda1 to lambda0 directory

$ cp * ../lambda0

2.2 Change the current directory to lambda0

$ cd ../lambda0

2.3 Remove the lambda1.struct file.

$ rm lambda1.struct
2.4 Rename all \texttt{lambda1.*} files to \texttt{lambda0.*} files with
\begin{verbatim}
$ rename_files lambda1 lambda0
\end{verbatim}
2.5 Restore original k-mesh taking into account the symmetry
\begin{verbatim}
$ x kgen
\end{verbatim}
with 230 k-points (shifted)
2.6 Initialize the electron density according to the new structure
\begin{verbatim}
$ x dstart
\end{verbatim}
2.7 Run standard SCF cycle.
\begin{verbatim}
$ run_lapw
\end{verbatim}
2.8 Run BerryPI
\begin{verbatim}
$ berrypi -p$(pwd) -k6:6:6
\end{verbatim}
2.9 Once the calculation is completed the results will be printed like this
\begin{verbatim}
---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: [ __________ , __________ , __________ ]
\end{verbatim}

\section*{3 Spontaneous polarization}

Calculation of Spontaneous Polarization using the Z components of polarizations obtained in lambda1 and lambda0. The spontaneous polarization is defined as the difference in the polarization between the centrosymmetric (lambda1) and non-centrosymmetric (lambda0) structures.
\begin{equation}
P_s = P_z(\text{lambda1}) - P_z(\text{lambda0}) =
\end{equation}
\begin{verbatim}
________________ - _____________ = ______________  C/m^2
\end{verbatim}
Check whether the different $\pi$ -wrappings affect the result? Here only Z components of polarization is considered because the atoms in non-centrosymmetric structure are displaced only in Z direction relative to the centrosymmetric structure.

The obtained spontaneous polarization value can be compared to the experimental spontaneous polarization of 0.26 C/m$^2$ [1] and other DFT values of 0.22- 0.29 C/m$^2$ [2-3].