Hands on session:
POLARIZATION via Berry phase with Quantum ESPRESSO

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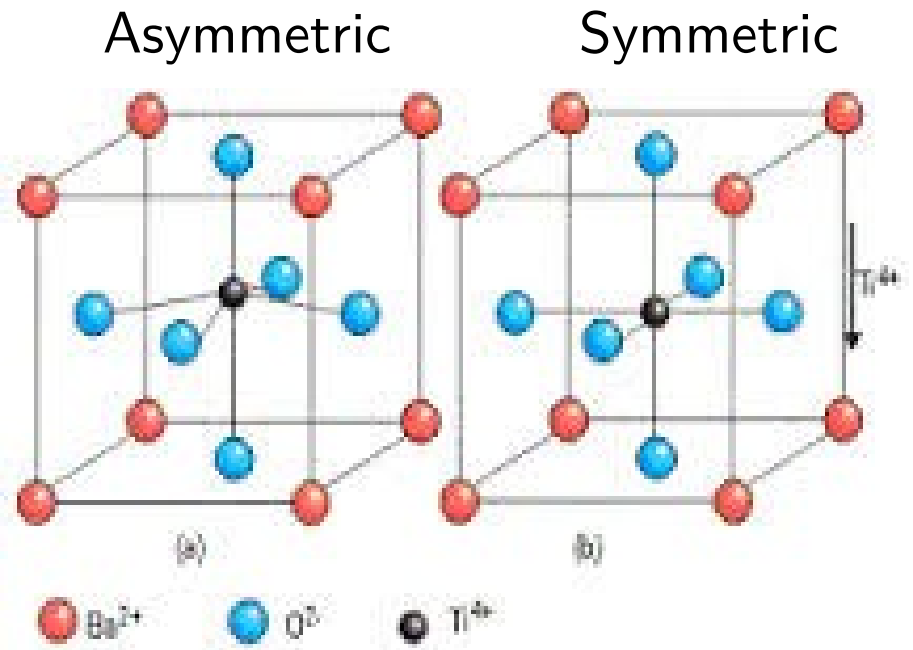
Exercises

Exercise 1: To calculate polarization via Berry phase for symmetric tetragonal $BaTiO_3$

Exercise 2: To optimize the structure of tetragonal $BaTiO_3$ with displaced Ti atom, and calculate the polarization via Berry phase

Exercise 3: To determine the Born effective charges from Polarization for Cubic $BaTiO_3$



Steps that are followed

1) Do a total energy calculation that calculates the charge density (scf) with well converged kmesh and ecutwfc

2) Make sure that the system is insulating at every kpoint.

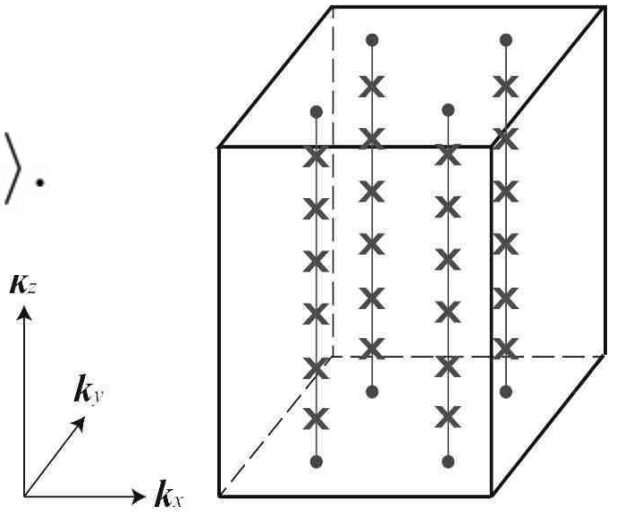
   Berry phase is ill-defined for metals!

3) Run berry phase calculations (nscf) to

   evaluate the Berry phase along k-point strings

$$\phi_{n,j} = \Omega_{\mathrm{BZ}}^{-1} \ \mathrm{Im} \int_{\mathrm{BZ}} d^3k \, \langle u_{n\mathbf{k}} | \mathbf{G}_j \cdot \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle .$$

$$\mathbf{P}_n = \frac{1}{2\pi} \frac{e}{\Omega} \sum_j \phi_{n,j} \, \mathbf{R}_j$$



4) Total polarization = Ionic part + electronic part

5) Spontaneous polarization= P(asymmetric cell) – P(symmetric cell)

Exercise 1: polarization of symmetric tetragonal $BaTiO_3$

- Executable: pw.x

  To run the script: nohup sh job_sy.sh &

Step1: run a scf calculation on the equilibrium structure

Look at sy.scf.in

Exercise 1: polarization of symmetric tetragonal $BaTiO_3$

Step2: run a nscf calculation with sy.bscf.in

/usr/local/apps/espresso-5.1/bin/pw.x < sy.bscf.in > sy.bscf.out

```
&control
   calculation = 'nscf'
   restart_mode='from_scratch',
   prefix='symm',
   pseudo_dir = '../../pseudo',
   outdir='tmp-sy'
   lberry=.true.
   gdir        = 3
   nppstr      = 10
/
K_POINTS {automatic}
10 10 20  0 0 0
```

nscf calculation

For doing Berry phase calculations

direction of the k-point strings in reciprocal space.
Allowed values: 1, 2, 3 where 1= first, 2= second,
3=third reciprocal lattice vector

Number of kpoints in the string along gdir

nppstr = nk3

Exercise 1: polarization of symmetric tetragonal $BaTiO_3$

In sy.bscf.out

K-POINTS STRINGS USED IN CALCULATIONS

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G-vector along string (2 pi/a): 0.00000 0.00000 0.97699

Modulus of the vector (1/bohr): 0.82171

Number of k-points per string: 10 → nppstr

Number of different strings : 6 → Depends on nk1 and nk2

IONIC POLARIZATION

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Ion	Species	Charge	Position			Phase
1	Ba	10.000	0.0000	0.0000	0.0000	0.00000 (mod 2)
2	Ti	12.000	0.5000	0.5000	0.5118	0.00000 (mod 2)
3	O	6.000	0.5000	0.5000	0.0000	0.00000 (mod 2)
4	O	6.000	0.5000	0.0000	0.5118	-1.00000 (mod 2)
5	O	6.000	0.0000	0.5000	0.5118	-1.00000 (mod 2)

IONIC PHASE: 0.00000 (mod 2)

No contribution from ions!

Exercise 1: polarization of symmetric tetragonal $BaTiO_3$

In sy.bscf.out

ELECTRONIC POLARIZATION

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Note: (mod 1) means that the phases (angles ranging from -pi to pi) have been mapped to the interval [-1/2,+1/2) by dividing by 2*pi; (mod 2) refers to the interval [-1,+1)

Spin	String	Weight	First k-point in string			Phase
up	1	0.040000	0.0000	0.0000	0.0000	0.00000 (mod 1)
up	2	0.160000	0.0000	0.2000	0.0000	0.00000 (mod 1)
...						
Up	5	0.320000	0.2000	0.4000	0.0000	0.00000 (mod 1)
Up	6	0.160000	0.4000	0.4000	0.0000	0.00000 (mod 1)
down	1	0.040000	0.0000	0.0000	0.0000	0.00000 (mod 1)
down	2	0.160000	0.0000	0.2000	0.0000	0.00000 (mod 1)
...						
Down	5	0.320000	0.2000	0.4000	0.0000	0.00000 (mod 1)
Down	6	0.160000	0.4000	0.4000	0.0000	0.00000 (mod 1)

nk1 and nk2

The total phase and polarization in symmetric structure = 0

No contribution from electrons!
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Exercise 2: polarization of asymmetric tetragonal $BaTiO_3$

- Executable: pw.x

Step1: Displace Ti atom in +z direction and relax the structure.

Look in relax.in file

```
&control
   calculation = 'relax'
   restart_mode='from_scratch',
   prefix='asymm-relax',
   tstress = .true.
   tprnfor = .true.
   pseudo_dir = '../../pseudo',
   outdir='tmp'
/
ATOMIC_POSITIONS {crystal}
 Ba    0.0000   0.0000   0.0000
 Ti    0.5000   0.5000   0.5200
  O    0.5000   0.5000   0.0000
  O    0.5000   0.0000   0.5000
  O    0.0000   0.5000   0.5000
```

→ Structural relaxation calculation

→ Ti atom is displaced along z

/usr/local/apps/espresso-5.1/bin/pw.x < relax.in > relax.out

Exercise 2: polarization of asymmetric tetragonal $BaTiO_3$

Look at the final relaxed co-ordinates in relax.out file

```
ATOMIC_POSITIONS (crystal)
Ba       0.000000000   0.000000000   0.020604613
Ti       0.500000000   0.500000000   0.530311403
O        0.500000000   0.500000000  -0.015428482
O        0.500000000   0.000000000   0.492256232
O        0.000000000   0.500000000   0.492256232
```

Use the above co-ordinates in asy.scf.in and asy.bscfx.in, asy.bscfy.in and asy.bscfz.in files

Exercise 2: polarization of asymmetric tetragonal $BaTiO_3$

Step2: Repeat Steps 2 and 3 from exercise 1

In asy.bscf.out

IONIC POLARIZATION

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Ion	Species	Charge	Position			Phase
1	Ba	10.000	0.0000	0.0000	0.0211	0.20605 (mod 2)
2	Ti	12.000	0.5000	0.5000	0.5428	0.36374 (mod 2)
3	O	6.000	0.5000	0.5000	-0.0158	-0.09257 (mod 2)
4	O	6.000	0.5000	0.0000	0.5038	0.95354 (mod 2)
5	O	6.000	0.0000	0.5000	0.5038	0.95354 (mod 2)

IONIC PHASE: 0.38429 (mod 2)

Finite contribution from ions!
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Exercise 2: polarization of asymmetric tetragonal $BaTiO_3$

In asy.bscfz.out

ELECTRONIC POLARIZATION

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Note: (mod 1) means that the phases (angles ranging from -pi to pi) have been mapped to the interval [-1/2,+1/2) by dividing by 2*pi; (mod 2) refers to the interval [-1,+1)

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Spin	String	Weight	First k-point in string			Phase
up	1	0.040000	0.0000	0.0000	0.0000	0.06891 (mod 1)
up	2	0.160000	0.0000	0.2000	0.0000	0.03158 (mod 1)
...						
up	5	0.320000	0.2000	0.4000	0.0000	-0.02818 (mod 1)
up	6	0.160000	0.4000	0.4000	0.0000	-0.05090 (mod 1)
down	1	0.040000	0.0000	0.0000	0.0000	0.06891 (mod 1)
down	2	0.160000	0.0000	0.2000	0.0000	0.03158 (mod 1)
...						
down	5	0.320000	0.2000	0.4000	0.0000	-0.02818 (mod 1)
down	6	0.160000	0.4000	0.4000	0.0000	-0.05090 (mod 1)

ELECTRONIC PHASE: -0.01845 (mod 2)

Finite contribution from electrons!

Total polarization is non-zero along z!
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Exercise 2: polarization of asymmetric tetragonal $BaTiO_3$

In asy.bscf.out

SUMMARY OF PHASES

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Ionic Phase: 0.38429 (mod 2)

Electronic Phase: -0.01845 (mod 2)

TOTAL PHASE: 0.36584 (mod 2)

→ Sum of electronic and ionic phases

VALUES OF POLARIZATION

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$P = -ie/(2\pi^3)$*berry phase

The calculation of phases done along the direction of vector 3 of the reciprocal lattice gives the following contribution to the polarization vector (in different units, and being Omega the volume of the unit cell):

P = 2.7973956 (mod 15.2930243) (e/Omega).bohr → Polarization quantum

P = 0.0065551 (mod 0.0358362) e/bohr^2

P = 0.3747686 (mod 2.0488144) C/m^2

} Polarization in different units

The polarization direction is: (0.00000 , 0.00000 , 1.00000)

Exercise 2: polarization of asymmetric tetragonal $BaTiO_3$

Polarization of tetragonal $BaTiO_3$

P(asymmetric phase)- P(symmetric phase)

= 37 $\mu C/cm^2$ - 0 $\mu C/cm^2$

= 37 $\mu C/cm^2$

Why is the polarization not same as in experiments (26 $\mu C/cm^2$)?

Check the convergence of P with nppstr and nk1, nk2

Exercise 3: Born Effective charges for cubic $BaTiO_3$

Step1: Look at scf.in

The Ti atom is displaced by +z direction by 0.01a

Step2: Look at bscf.in

Now run a berry phase calculation along gdir=3

Step3: Calculate the Born Effective charge

$$Z^* = \text{Omega} \frac{dP}{dr}$$