

# Maximally localized Wannier orbital

Bridge the plane wave basis and the  
atomic orbital basis

## Plane wave basis set

$$\varphi(\mathbf{r}) = \sum_{\mathbf{G}} C(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}$$

- Large number of basis
- Complete but inefficient
- Needs pseudopotential

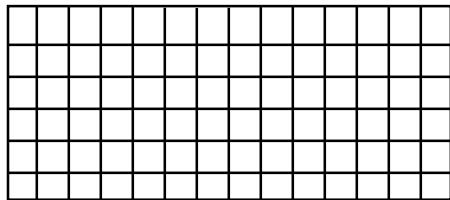
## Atomic orbital basis set

$$\varphi(\mathbf{r}) = \sum_{\tau, \alpha} C_{\tau} \phi_{\alpha}(\mathbf{r} - \mathbf{R}_{\tau})$$

1s, 2s, 2p, ...

- Prepare atomic orbitals
- Not complete but efficient
- Core can be described

## Real space mesh



- Large number of basis
- Complete but inefficient
- Needs pseudopotential
- $\nabla^2$  cannot be done analytically

## Augmented plane wave basis set

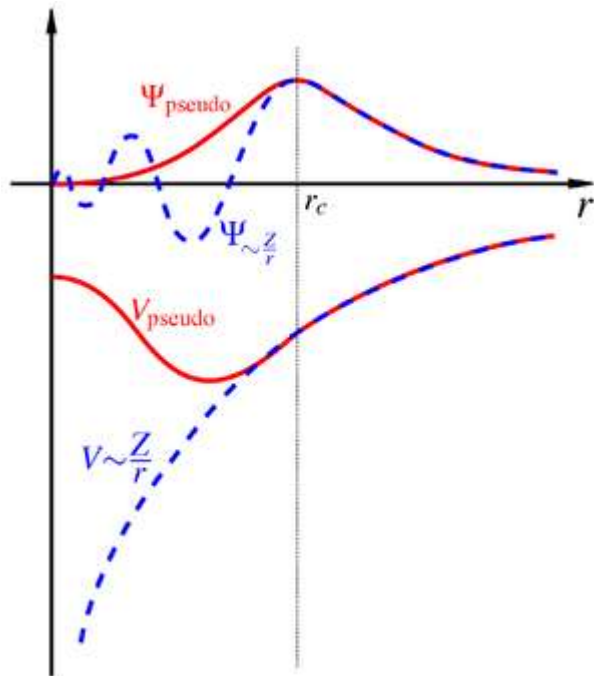
$$\varphi(\mathbf{r}) = \sum_{\alpha, nlm} R_{nl}(\mathbf{r} - \mathbf{R}_{\alpha}) Y_{lm}(\mathbf{r} - \mathbf{R}_{\alpha})$$

inside the core region

- Solve radial Schrödinger eq. to get  $R$
- Match  $R$  to plane wave at the sphere
- Core can be accurately described

# Pseudopotential

$$-\frac{1}{2} \frac{d^2}{dr^2} R_l(r) + \frac{1}{2} \frac{l(l+1)}{r^2} R_l(r) + V(r) R_l(r) = E_l R_l(r)$$



Original potential is too deep  
Wave function oscillates near the core

Assume smooth wave function  
Get the effective potential ( $l$ -dependent)

$$-\frac{1}{2} \frac{d^2}{dr^2} R_l^{\text{ps}}(r) + \frac{1}{2} \frac{l(l+1)}{r^2} R_l^{\text{ps}}(r) + V_l^{\text{ps}}(r) R_l^{\text{ps}}(r) = E_l R_l^{\text{ps}}(r)$$

Pseudopotential has been constructed

## Type of pseudopotential

- Norm conserving pseudopotential
- Ultrasoft pseudopotential
- Projector augmented wave

Pseudopotential represented using projection operator (PAW)

$$-\frac{1}{2} \frac{d^2}{dr^2} R_l^{\text{ps}}(r) + \frac{1}{2} \frac{l(l+1)}{r^2} R_l^{\text{ps}}(r) + V_l^{\text{ps}}(r) R_l^{\text{ps}}(r) = E_l R_l^{\text{ps}}(r)$$

$$V_l^{\text{ps}}(r) = \langle r | \sum_{\alpha} \left\{ V_l^{\text{ps}} |R_{l\alpha}^{\text{ps}}\rangle + \left( V_l |R_{l\alpha}\rangle - V_l^{\text{ps}} |R_{l\alpha}^{\text{ps}}\rangle \right) \frac{\langle R_{l\alpha}^{\text{ps}} | V_l^{\text{ps}}}{\langle R_{l\alpha}^{\text{ps}} | V_l^{\text{ps}} | R_{l\alpha}^{\text{ps}} \rangle} \right\}$$

When operated to  $R_{l\alpha}^{\text{ps}}$ , original behavior  $\langle r | V_l | R_{l\alpha} \rangle$  inside the core, while the pseudized one  $\langle r | V_l^{\text{ps}} | R_{l\alpha}^{\text{ps}} \rangle$  outside.

## Formulation

Change the basis  
afterwards!

Maximally localized  
Wannier orbital

# Basic idea

- Wannier orbital (original one)

Bloch function is given by  $\psi_{nk}(\mathbf{r}) = u_{nk}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}$  and  $u_{nk}(\mathbf{r}) = u_{nk}(\mathbf{r} + \mathbf{R})$ .

Wannier orbital is defined as  $w_{\mathbf{R}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}} \psi_{nk}(\mathbf{r})$

- For any lattice vector  $\mathbf{R}'$ ,  $w_{\mathbf{R}}(\mathbf{r} + \mathbf{R}') = w_{\mathbf{R}}(\mathbf{r})$ , so that  $w_{\mathbf{R}}(\mathbf{r}) = w(\mathbf{r} - \mathbf{R})$
- Bloch function can be written as a superposition of the Wannier
- Orthogonal to each other  $\langle w_{\mathbf{R}} | w_{\mathbf{R}'} \rangle = \delta_{\mathbf{R}, \mathbf{R}'}$

Wannier is generally localized in space,  
but not so much

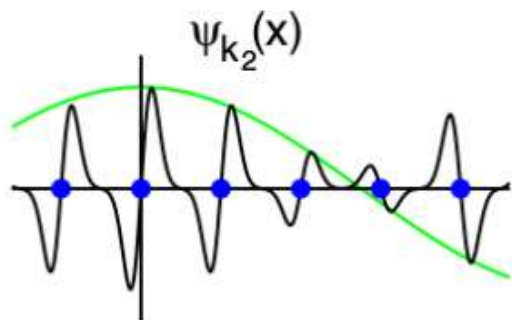
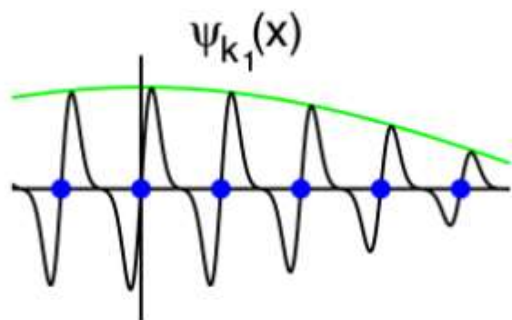
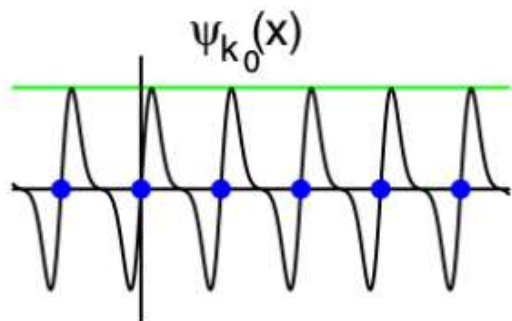


PdN

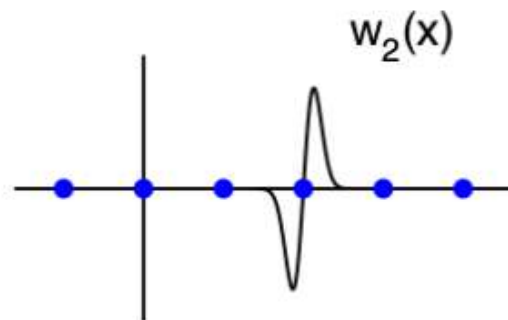
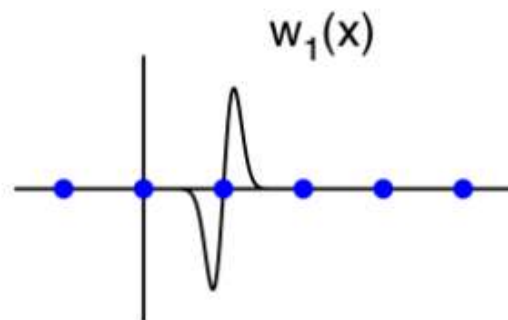
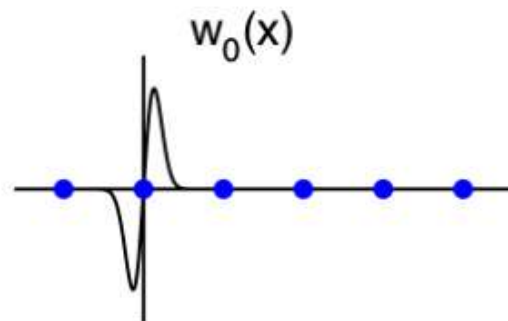


# Illustration of the Wannier

## Bloch functions



## Wannier functions



# Maximally localized Wannier fn.

- Superpose Bloch functions not only w.r.t. BZ, but also w.r.t. band.

$$|R_n\rangle = \frac{\Omega}{(2\pi)^3} \int_{BZ} \sum_m U_{mn}^k |\psi_{mk}\rangle e^{-ikR} dk \quad \equiv w_n(\mathbf{r} - \mathbf{R})$$

- Coefficients  $U_{mn}^k$  are determined to minimize the spatial extension

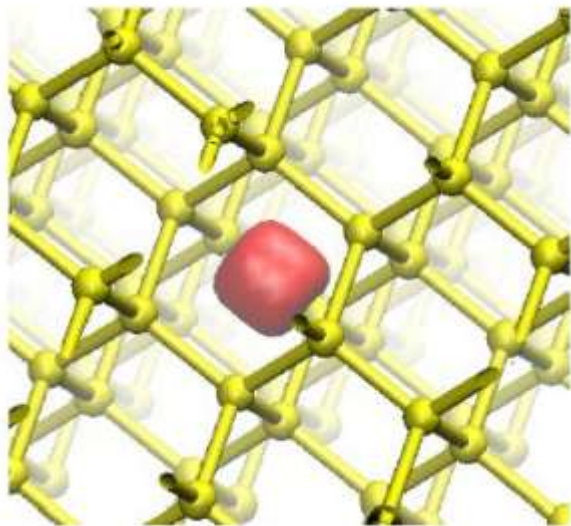
$$L = \sum_n (\langle 0_n | r^2 | 0_n \rangle - \langle 0_n | r | 0_n \rangle^2)$$

Spread from the  
Wannier center

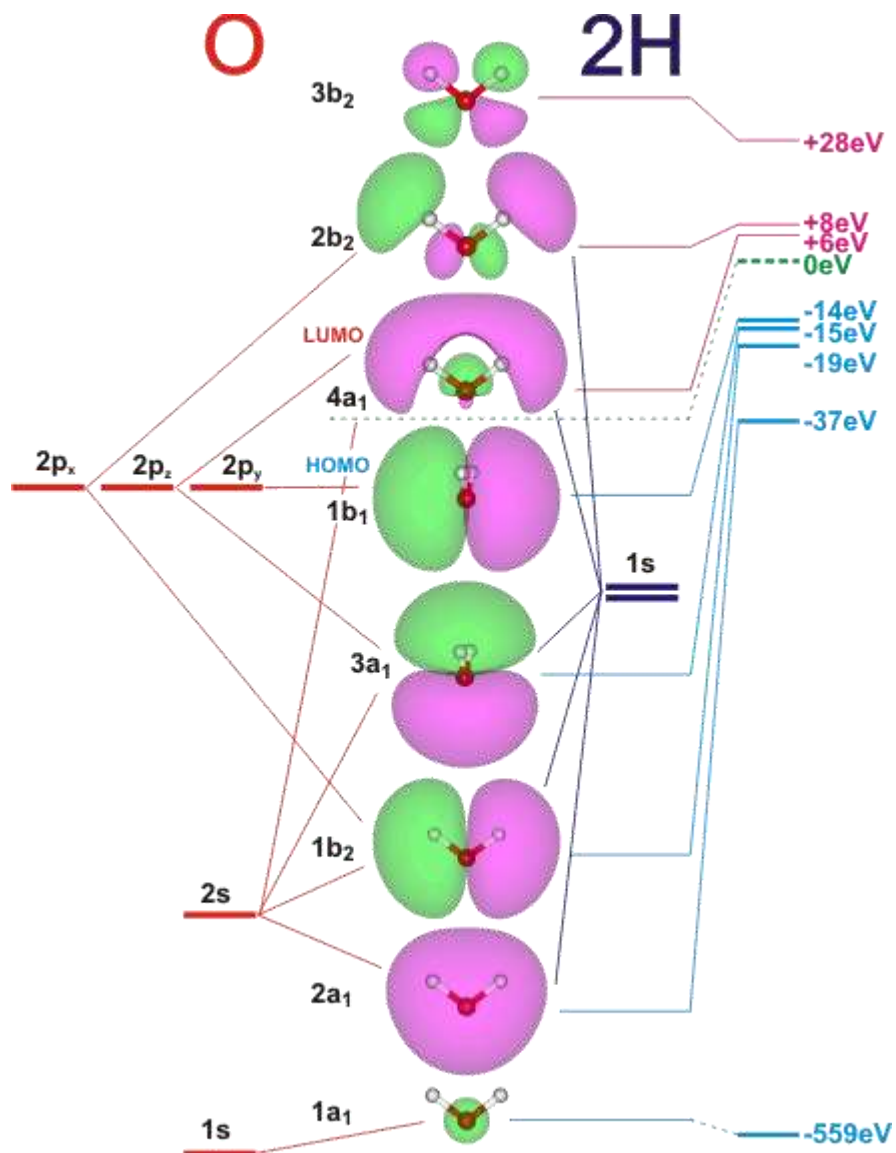
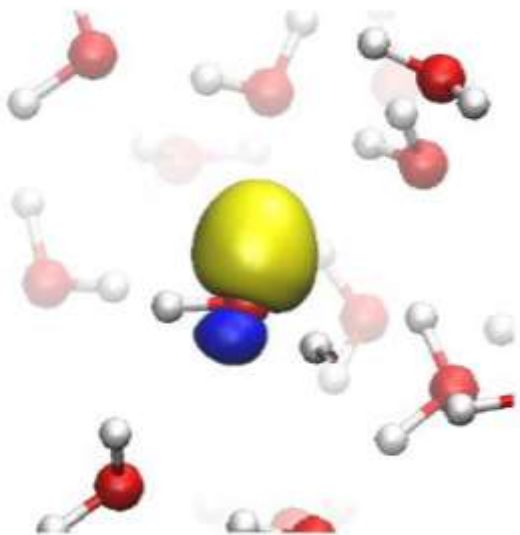
- MLWF thus constructed mimics atomic orbitals



# sp<sup>3</sup> bond in silicon



# water



# Property

- Matrix element for position operators

$$\langle \mathbf{R}_n | \mathbf{r} | \mathbf{0}_m \rangle = i \frac{\Omega}{(2\pi)^3} \int_{BZ} \langle u_{nk} | \nabla_{\mathbf{k}} | u_{mk} \rangle e^{i\mathbf{k}\mathbf{R}} d\mathbf{k}$$

$$\langle \mathbf{R}_n | \mathbf{r}^2 | \mathbf{0}_m \rangle = i \frac{\Omega}{(2\pi)^3} \int_{BZ} \langle u_{nk} | \nabla_{\mathbf{k}}^2 | u_{mk} \rangle e^{i\mathbf{k}\mathbf{R}} d\mathbf{k}$$

# Numerical technique

- Matrix element for position operators

$$\langle \mathbf{R}_n | \mathbf{r} | \mathbf{0}_m \rangle = i \frac{\Omega}{(2\pi)^3} \int_{BZ} \langle u_{nk} | \nabla_k | u_{mk} \rangle e^{i\mathbf{k}\mathbf{R}} d\mathbf{k}$$

$$\nabla_k u_{mk} = \sum_b w_b \mathbf{b} [u_{mk+b} - u_{mk}]$$

$\mathbf{b}$ : nearest neighbor mesh point in discretized BZ

$$\langle \mathbf{0}_n | \mathbf{r} | \mathbf{0}_n \rangle = -\frac{1}{N} \sum_{\mathbf{k}, \mathbf{b}} w_b \mathbf{b} \operatorname{Im}(\ln \langle u_{nk} | u_{nk+b} \rangle)$$

$M_{nm}^{(\mathbf{k}, \mathbf{b})} \equiv \langle u_{nk} | u_{mk+b} \rangle$ , plays the central role in calculating the localized Wannier orbitals.

# Numerical technique (*continued*)

- Likewise

$$\langle \mathbf{0}_n | \mathbf{r}^2 | \mathbf{0}_n \rangle = -\frac{1}{N} \sum_{k,b} w_b \{1 - |\langle u_{nk} | u_{nk+b} \rangle|^2 + |\text{Im}(\ln \langle u_{nk} | u_{nk+b} \rangle)|^2\}$$

# Wannier90

- Make a tight-binding Hamiltonian from the quantum espresso output
- One can interpolate bands for detailed analysis
- One can calculate the polarization within a bulk crystal
- It makes easy to calculate electronic conductance
- One can calculate Berry's phase

# How to install

1. copy config/make.inc.gfortran to make.inc.
  2. make
- If you already have ifort or other compiler, use it because it will be faster.
  - Required compilers and libraries have been installed in MateriApps!
  - Depending on the environment, you may be required to install older version than 3.0.0.

# How to use (example01)

Files prepared:

- gaas.mmn The overlap matrices  $M(k,b)$
- gaas.amn Projection  $A(k)$  of the Bloch states onto a set of trial localized orbitals

# How to use (example01)

```
! Gallium Arsenide: Tutorial Example 1
```

```
num_wann = 4
```

```
num_iter = 20
```

```
! SYSTEM
```

```
begin unit_cell_cart
```

```
bohr
```

```
-5.367 0.000 5.367
```

```
0.000 5.367 5.367
```

```
-5.367 5.367 0.000
```

```
end unit_cell_cart
```

```
begin atoms_frac
```

```
Ga 0.00 0.00 0.00
```

```
As 0.25 0.25 0.25
```

```
end atoms_frac
```

```
begin projections
```

```
As:sp3
```

```
end projections
```

```
! KPOINTS
```

```
mp_grid : 2 2 2
```

```
begin kpoints
```

```
0.0 0.0 0.0
```

```
0.0 0.0 0.5
```

```
0.0 0.5 0.0
```

```
0.0 0.5 0.5
```

```
0.5 0.0 0.0
```

```
0.5 0.0 0.5
```

```
0.5 0.5 0.0
```

```
0.5 0.5 0.5
```

```
end kpoints
```

We set this flag to read the bloch states from a formatted file. This is to ensure the example works on all platforms. The default (.false.) state should be used on production runs

```
wfn_formatted=.true.
```

If you want to plot MLWF, Wannier\_plot=.true.



# How to use (example01)

- wannier90.x
- See gaas.wout for output

-----  
Final State

WF centre and spread	1	( -0.866253, 1.973841, 1.973841 )	1.11672024
WF centre and spread	2	( -0.866253, 0.866253, 0.866253 )	1.11672024
WF centre and spread	3	( -1.973841, 1.973841, 0.866253 )	1.11672024
WF centre and spread	4	( -1.973841, 0.866253, 1.973841 )	1.11672024
Sum of centres and spreads		( -5.680188, 5.680188, 5.680188 )	4.46688098

Spreads (Ang <sup>2</sup> )	Omega I	=	3.956862958
=====	Omega D	=	0.008030049
	Omega OD	=	0.501987969
Final Spread (Ang <sup>2</sup> )	Omega Total	=	4.466880976

# How to plot (example01)

## Xcrysden

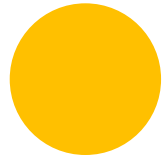
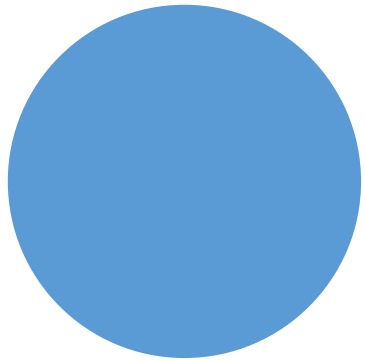
1. Open a xsf file
2. Operate Tools/data grid + (ok)
3. Change the isovalue + (submit)

## Vesta

1. Just open a xsf file

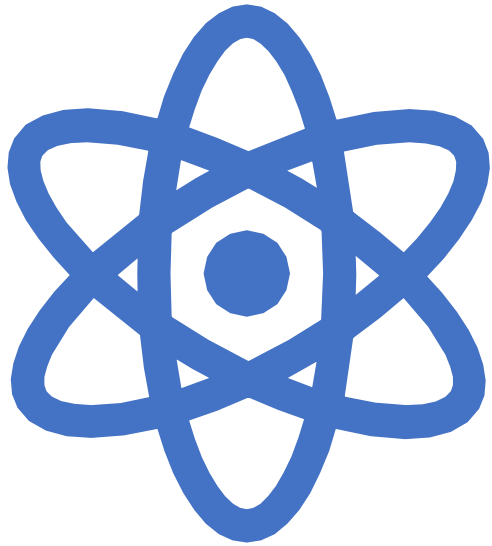
# Interconnect with QE

- QE to get the electron density  
pw.x < copper.scf > scf.out
- QE to get Bloch orbitals on a mesh  
pw.x < copper.nscf > nscf.out
- Wannier90 to make the overlap mmn file  
wannier90.x -pp copper
- Make the projection amn file  
pw2wannier90.x < copper.pw2wan > pw2wan.out
- Wannier90 to get MLWF  
wannier90.x copper



What one can do  
with MLWF

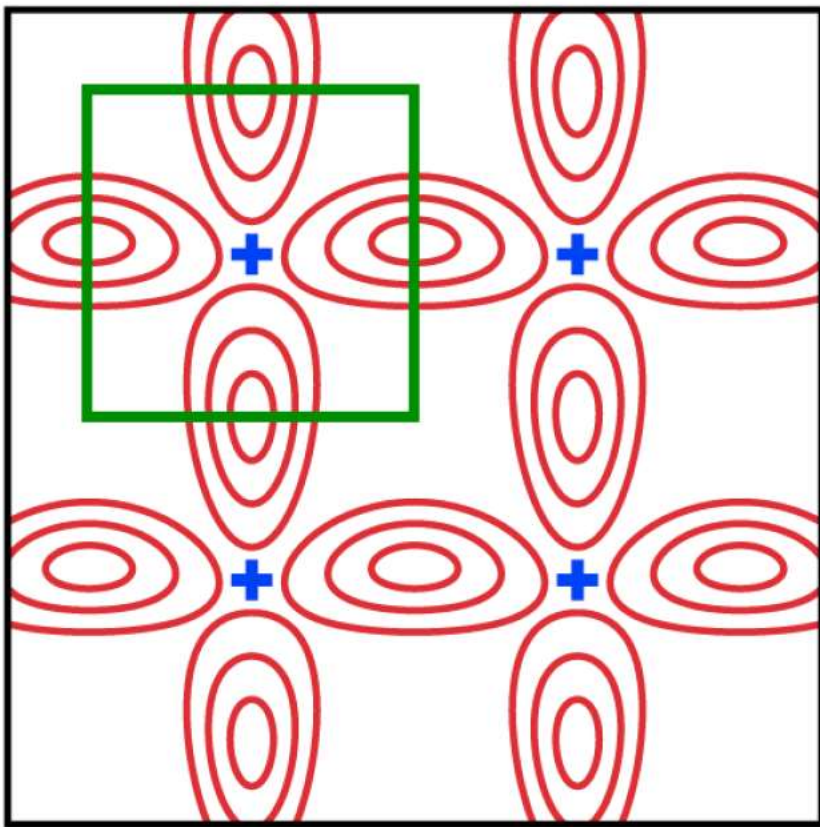
polarization of a  
crystal



# Modern theory of polarization

Invented in 1990s

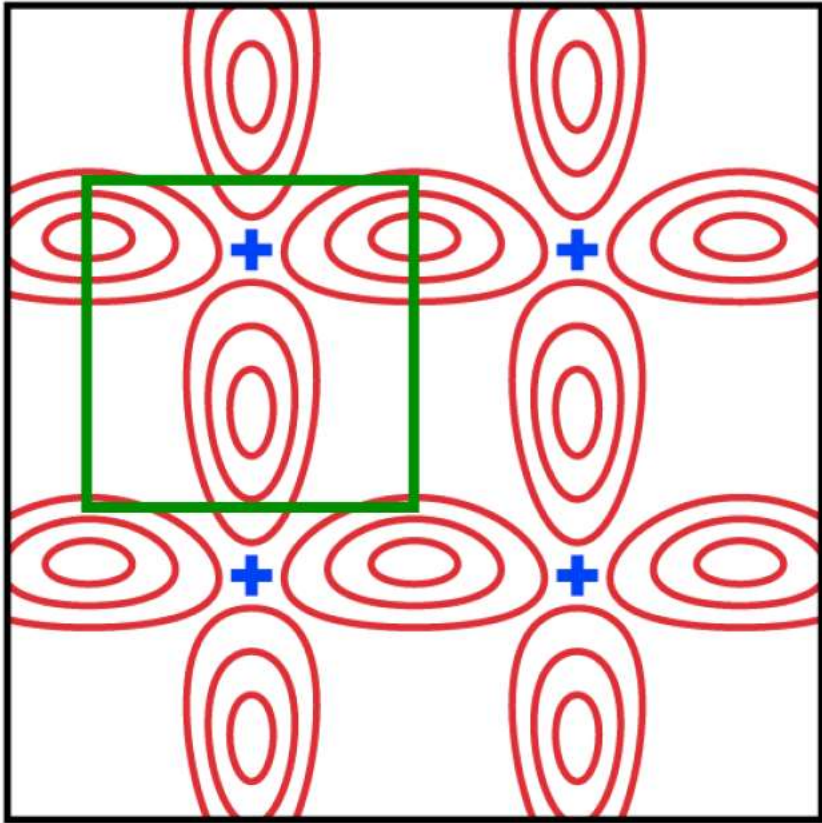
$$\mathbf{P} = \frac{1}{\Omega} \int_{\text{cell}} d\mathbf{r} r \rho(\mathbf{r})$$



$$\mathbf{d}_{\text{cell}} = \int_{\text{cell}} \mathbf{r} \rho(\mathbf{r}) d^3r$$

$$\mathbf{d}_{\text{cell}} \approx \mathbf{0}$$

$$\mathbf{P} = \frac{1}{\Omega} \int_{\text{cell}} d\mathbf{r} r \rho(\mathbf{r})$$

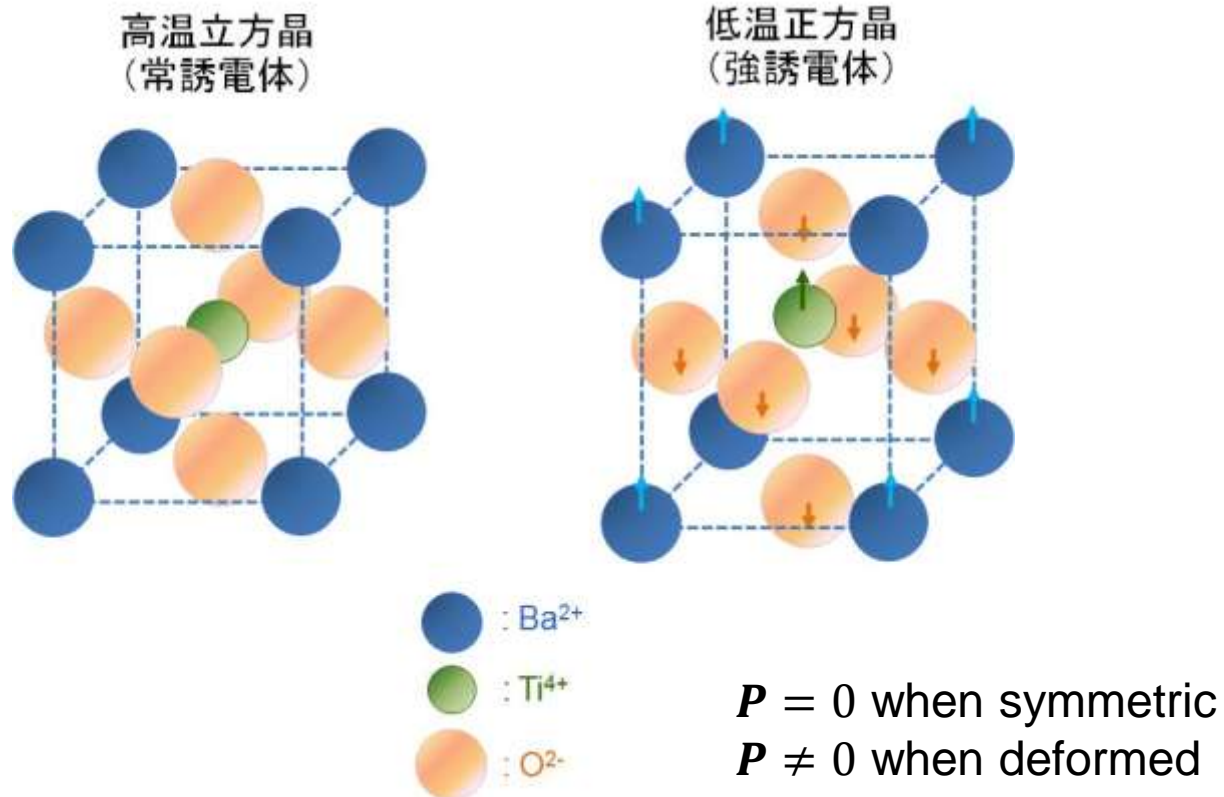


$$\mathbf{d}_{\text{cell}} = \int_{\text{cell}} \mathbf{r} \rho(\mathbf{r}) d^3r$$

$$\mathbf{d}_{\text{cell}} = \uparrow$$

## ill-defined “crystalline polarization”

- Consider a ferroelectric crystal such as  $\text{BaTiO}_3$
- The crystal is not polarized when not deformed but is polarized when deformed along a soft mode.





## “crystalline polarization” from current

- Integrate the current associated with deformation

$$\mathbf{P} = \int dt \frac{1}{\Omega} \int_{cell} d\mathbf{r} \mathbf{j}(\mathbf{r}, t)$$

Let us slowly change the deformation parameter  $\lambda(t)$  ( $0 \leq \lambda \leq 1$ )

- Rate of change in the Bloch state is, from perturbation theory,

$$|\delta\psi_{nk}\rangle = -i\hbar\delta\lambda \sum_{m \neq n} \frac{\langle\psi_{mk}|\partial_\lambda|\psi_{nl}\rangle}{E_{nk} - E_{mk}} |\psi_{mk}\rangle$$

- Current density is thereby the expectation value of  $\mathbf{p}$

$$\mathbf{j}_n = \frac{d\mathbf{P}_n}{dt} = \frac{i\hbar e\dot{\lambda}}{(2\pi)^3} \sum_{m \neq n} \int d^3k \frac{\langle\psi_{nk}|\mathbf{p}|\psi_{ml}\rangle \langle\psi_{mk}|\partial_\lambda|\psi_{nl}\rangle}{E_{nk} - E_{mk}} + c.c.$$

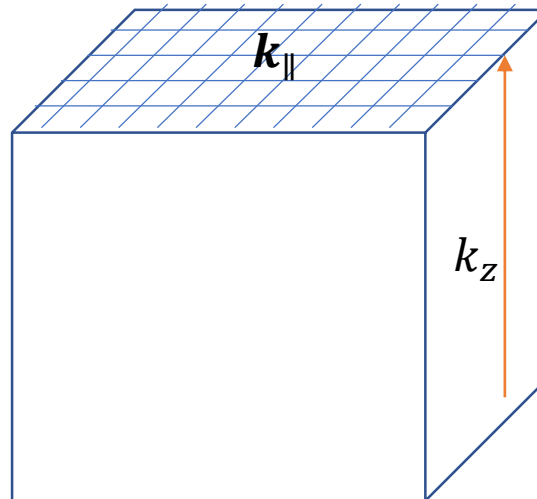
- This can be simplified using the Green’s theorem as

$$\mathbf{j}_n = \frac{ie\dot{\lambda}}{(2\pi)^3} \oint \langle\nabla_k u_{nk}|\partial_\lambda u_{nk}\rangle \cdot d\mathbf{k} + c.c. \quad \text{See e.g. RMP by Resta}$$

- When integrated over  $t$  and summed over  $n$

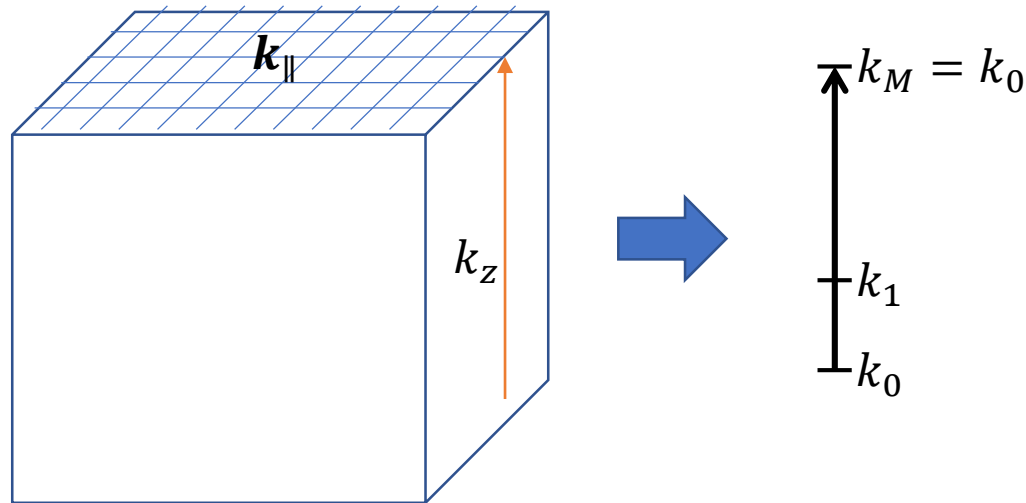
$$P(\lambda) = \frac{e}{(2\pi)^3} \text{Im} \sum_n \int \langle u_{nk} | \nabla_{\mathbf{k}} | u_{nk} \rangle \cdot d\mathbf{k}$$

$$\Delta P = P(1) - P(0) = P(1)$$



- 1D case

$$P_n = \frac{e}{2\pi} \phi_n = \frac{e}{2\pi} \text{Im} \int_{-\pi/L}^{\pi/L} dk \langle u_{nk} | \partial_k | u_{nk} \rangle$$



$$P_n = -e \text{Re} \left[ \int_{-\frac{\pi}{L}}^{\frac{\pi}{L}} \frac{dk}{2\pi} \langle u_{nk} | -i \partial_k | u_{nk} \rangle \right] = -e \text{Re} \left[ \int_{-\pi/L}^{\pi/L} \frac{dk}{2\pi} \langle u_{nk} | r | u_{nk} \rangle \right]$$

$\propto$  Wannier center  $R$

Polarization is described as charge x Wannier center

Since contribution from the nuclei is

$$P_{\text{ion}} = \frac{e}{\Omega} \sum_{\tau} Z_{\tau} R_{\tau},$$

the polarization is, in total,

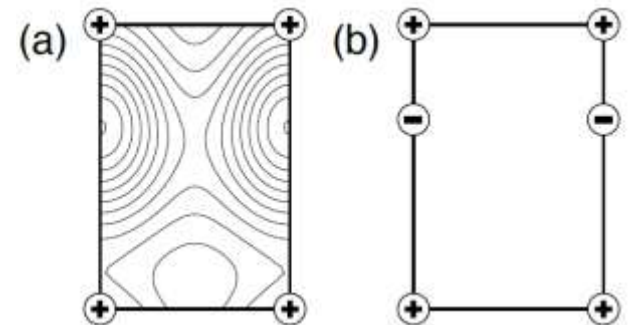
$$P = \frac{e}{(2\pi)^3} \text{Im} \sum_n \int dk \langle u_{nk} | \nabla_k | u_{nk} \rangle + \frac{e}{\Omega} \sum_{\tau} Z_{\tau} R_{\tau}$$

Using the notation that

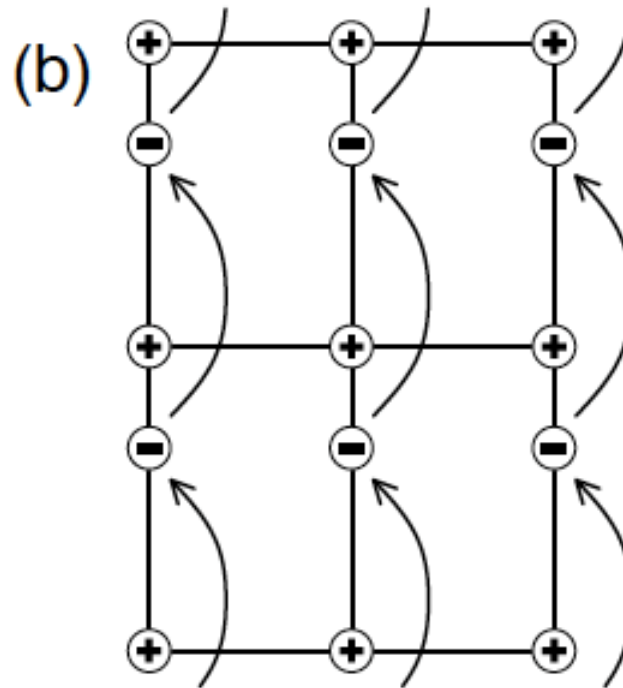
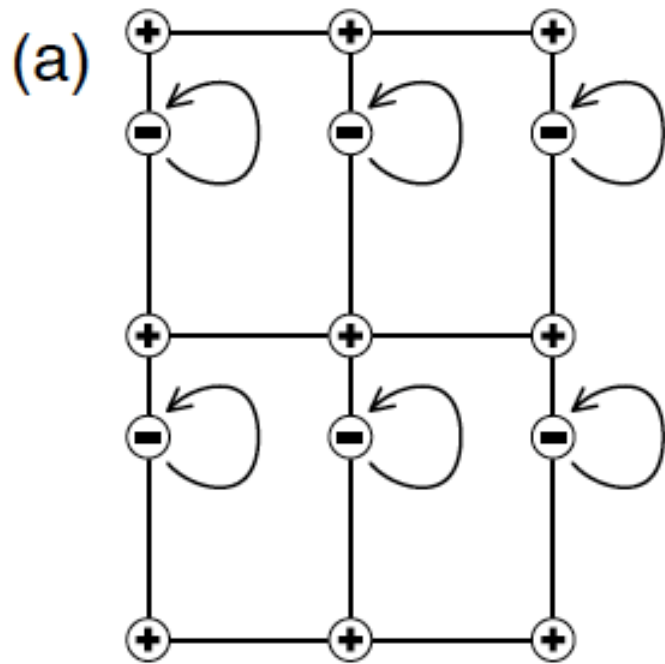
$$w_n(r - R) = \Omega \int_{BZ} \frac{d^3k}{(2\pi)^3} e^{ik(r-R)} u_{nk}(r)$$

$$P_n = -\frac{e}{\Omega} r_{nR} = -\frac{e}{\Omega} \langle w_{nR} | r | w_{nR} \rangle$$

$$P = \frac{e}{\Omega} \sum_{\tau} \left( Z_{\tau} R_{\tau} - \sum_n r_{nR_{\tau}} \right)$$

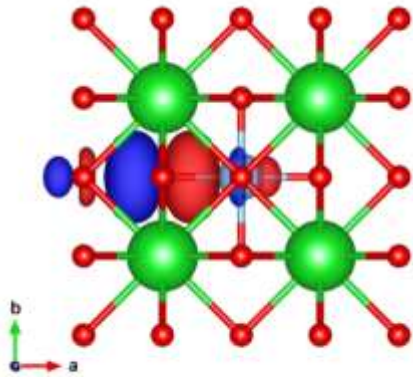
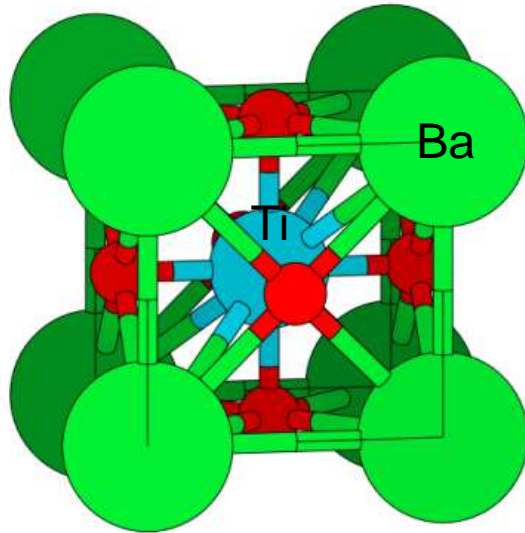


One can determine the polarization up to the modulo of  $e/\Omega$

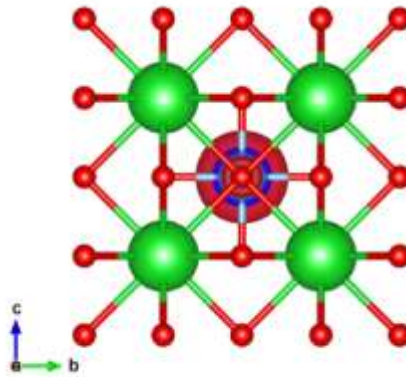


# BaTiO<sub>3</sub>

## Example9



(a) top



(b) side

**&control****calculation = 'scf'****restart\_mode='from\_scratch',****prefix='batio3',****pseudo\_dir = '../..//pseudo/',****outdir='./'****/****&system****ibrav= 1, celldm(1) =7.44266, nat= 5, ntyp= 3,****ecutwfc =40.0,****/****&electrons****conv\_thr = 1.0d-10****/****ATOMIC\_SPECIES****O 8 O.pbe-van\_ak.UPF****Ti 22 Ti.pbe-sp-van\_ak.UPF****Ba 56 Ba-vdb-usp-pbe.UPF****ATOMIC\_POSITIONS {crystal}****Ba 0.0 0.0 0.0****Ti 0.5 0.5 0.5****O 0.0 0.5 0.5****O 0.5 0.5 0.0****O 0.5 0.0 0.5****K\_POINTS {automatic}****8 8 8 0 0 0**

**&control**

**calculation = 'nscf'**  
**restart\_mode='from\_scratch',**  
**prefix='batio3',**  
**pseudo\_dir = './../pseudo/',**  
**outdir='./'**

/

**&system**

**ibrav= 1, celldm(1) =7.44266, nat= 5, ntyp= 3,**  
**ecutwfc =40.0,**

/

**&electrons**

**conv\_thr = 1.0d-10**

/

**ATOMIC\_SPECIES**

**O 8 O.pbe-van\_ak.UPF**

**Ti 22 Ti.pbe-sp-van\_ak.UPF**

**Ba 56 Ba-vdb-usp-pbe.UPF**

**ATOMIC\_POSITIONS {crystal}**

**Ba 0.0 0.0 0.0**

**Ti 0.5 0.5 0.5**

**O 0.0 0.5 0.5**

**O 0.5 0.5 0.0**

**O 0.5 0.0 0.5**

**K\_POINTS crystal**

**64**

**0.00000000 0.00000000 0.00000000 1.562500e-02**

**0.00000000 0.00000000 0.25000000 1.562500e-02**

**(skipping 61 lines)**

**0.75000000 0.75000000 0.75000000 1.562500e-02**



**&inputpp**

**outdir = './'**

**prefix = 'batio3'**

**seedname = 'BaTiO3'**

**spin\_component = 'none'**

**write\_mmn = .true.**

**write\_amn = .true.**

**write\_unk = .true.**

**/**

```
num_wann    = 9
num_iter    = 50
```

```
!here we exclude all bands except the O2p bands
exclude_bands : 1,2,3,4,5,6,7,8,9,10,11
```

```
guiding_centres = T
```

```
begin atoms_frac
Ba 0.0 0.0 0.0
Ti 0.5 0.5 0.5
O 0.0 0.5 0.5
O 0.5 0.5 0.0
O 0.5 0.0 0.5
end atoms_frac
```

```
begin kpoint_path
```

```
L 0.50000 0.50000 0.50000 G 0.00000 0.00000 0.00000
G 0.00000 0.00000 0.00000 X 0.50000 0.00000 0.50000
X 0.50000 -0.50000 0.00000 K 0.37500 -0.37500 0.00000
K 0.37500 -0.37500 0.00000 G 0.00000 0.00000 0.00000
end kpoint_path
bands_plot = T
```

```
!!To plot the WF
!wannier_plot = T
!wannier_plot_supercell = 2
!wannier_plot_list = 2
!restart = plot
```

```
begin projections
```

```
O:p
```

```
end projections
```

```
begin unit_cell_cart
```

```
bohr
```

```
7.44266 0.0 0.0
```

```
0.0 7.44266 0.0
```

```
0.0 0.0 7.44266
```

```
end unit_cell_cart
```

```
mp_grid : 4 4 4
```

```
begin kpoints
```

```
0.00000000 0.00000000 0.00000000
```

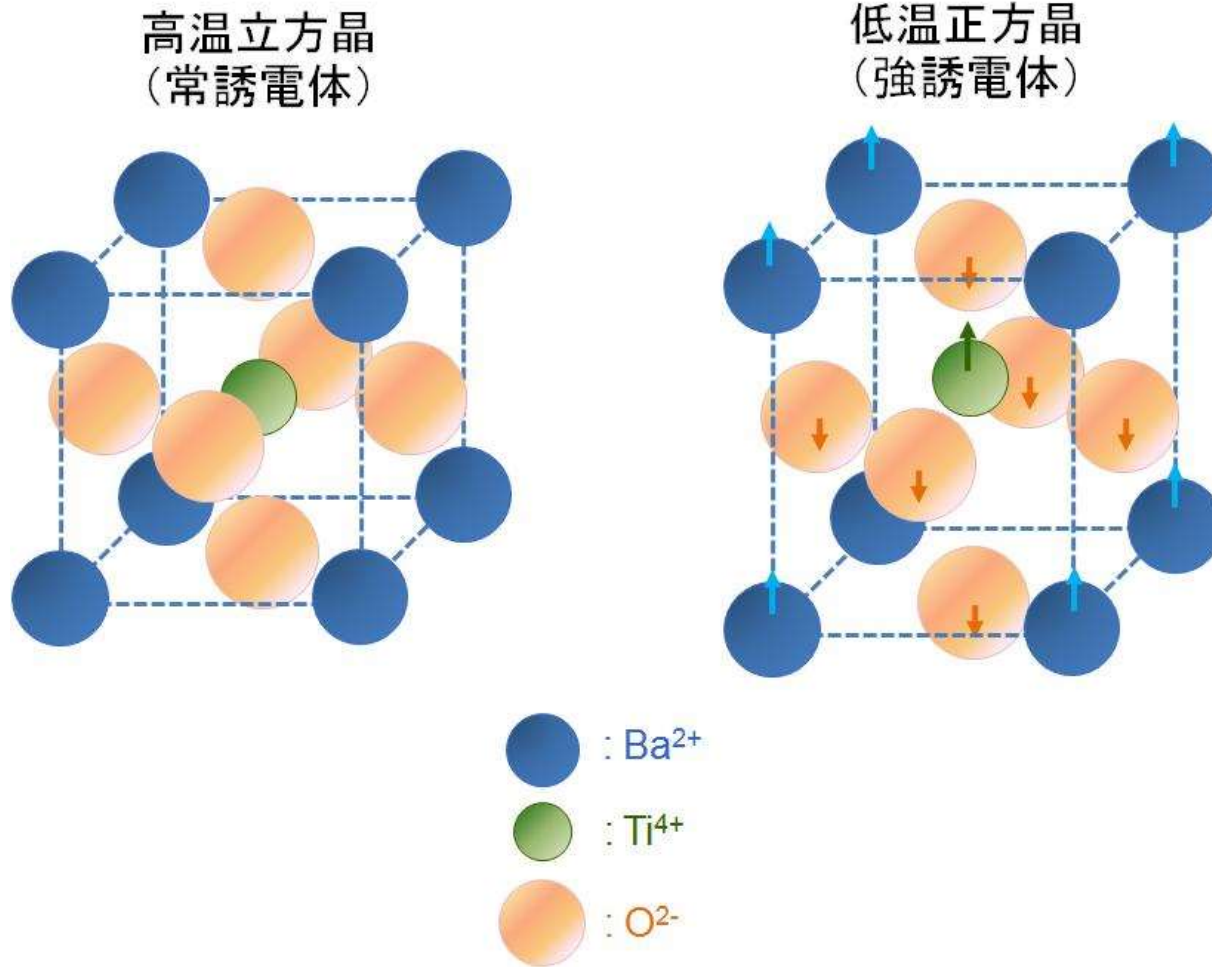
```
0.00000000 0.00000000 0.25000000
```

```
(skipping 61lines)
```

```
0.75000000 0.75000000 0.75000000
```

```
end kpoints
```

Do the geometry optimization



See the displacement of the Wannier center to obtain the polarization