

*Workshop on the SCAN density functional: Fundamentals, practices, and extensions*

*Temple university, Philadelphia*

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**Hands-on tutorial 3**

# **Phonon calculations with SCAN**

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# Overview

- **Purposes**
  - = Calculate basic phonon properties by VASP + Phonopy
  - = Understand new features of SCAN for phonon properties
- **Approaches**
  - = SCAN for force calculation
  - = Finite difference method: “Frozen” phonons in supercells (DFPT is not implemented for SCAN in current VASP)
- **Codes**
  - = VASP
  - = Phonopy
- **Materials**
  - = Si
  - = BaTiO<sub>3</sub>
- **Main references**
  - = <https://atztogo.github.io/phonopy/> (Phonopy)
  - = Nature Chemistry 8, 831 (2016) (SCAN features)

# The 3D Harmonic Crystal

Force constant matrix: 
$$\Phi_{\alpha\beta}(il, jl') = \frac{\partial^2 E}{\partial r_\alpha(l) \partial r_\beta(l')} = - \frac{\partial F_\alpha(il)}{\partial r_\beta(jl')}$$

From finite differences: 
$$\Phi_{\alpha\beta}(il, jl') \approx - \frac{F_\alpha(il)}{\Delta r_\beta(jl')}$$

Sum over atom  $j$  in adjacent unit cells  $l' \rightarrow$  supercell expansion to improve accuracy

Dynamical matrix: 
$$D_{\alpha\beta}(i, j, \mathbf{q}) = \frac{1}{\sqrt{m_i m_j}} \sum_{l'} \Phi_{\alpha\beta}(i0, jl') \exp[i\mathbf{q} \cdot (\mathbf{r}(jl') - \mathbf{r}(i0))]$$

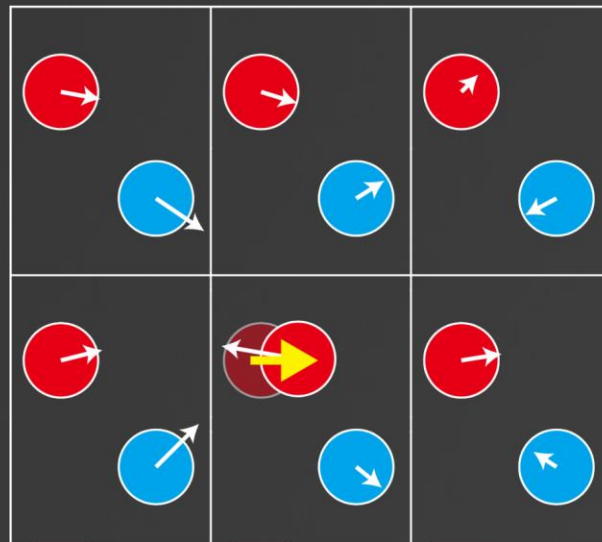
After diagonalisation: 
$$e(\mathbf{q}) \cdot \Omega(\mathbf{q}) = D(\mathbf{q}) \cdot e(\mathbf{q})$$

- The force constant matrix  $\Phi_{\alpha\beta}(il, jl')$  can be obtained either from finite-displacement calculations, or using DFPT
- The number of displacements which need to be evaluated to construct the dynamical matrix can be reduced by symmetry

# Finite difference method

Displace one atom, and measure forces on all atoms

$$\Phi_{ij}(\mathbf{M}\boldsymbol{\mu}, \mathbf{N}\boldsymbol{\nu}) \simeq -\frac{F_i[\mathbf{M}\boldsymbol{\mu}; \Delta r_j(\mathbf{N}\boldsymbol{\nu})]}{\Delta r_j(\mathbf{N}\boldsymbol{\nu})}$$



↗ Force on an atom ( $F_i$ )

→ Atomic displacement ( $\Delta r_j$ )

# Thermal properties

Thermal properties are calculated from frequencies.

Quantum mechanics is necessary to derive them.

Helmholtz free energy

$$F = \frac{1}{2} \sum_{\mathbf{q},s} \hbar\omega(\mathbf{q},s) + k_B T \sum_{\mathbf{q},s} \ln[1 - \exp(-\hbar\omega(\mathbf{q},s)/k_B T)]$$

Entropy

$$S = -k_B \sum_{\mathbf{q},s} \ln[1 - \exp(-\hbar\omega(\mathbf{q},s)/k_B T)] - \frac{1}{T} \sum_{\mathbf{q},s} \frac{\hbar\omega(\mathbf{q},s)}{\exp(\hbar\omega(\mathbf{q},s)/k_B T) - 1}$$

Heat capacity at constant volume

$$C_V = \sum_{\mathbf{q},s} k_B \left[ \frac{\hbar\omega(\mathbf{q},s)}{k_B T} \right]^2 \frac{\exp(\hbar\omega(\mathbf{q},s)/k_B T)}{[\exp(\hbar\omega(\mathbf{q},s)/k_B T) - 1]^2}$$

# Phonopy code

## Welcome to phonopy

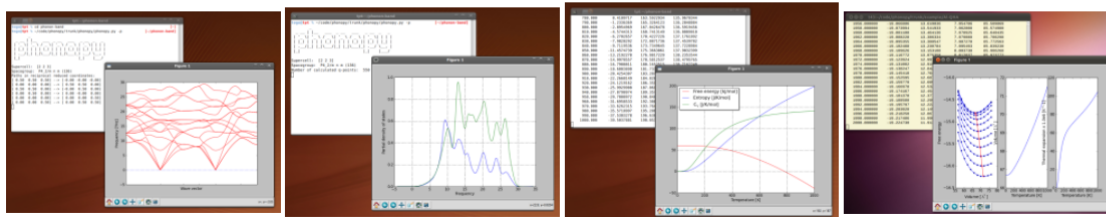
**Phonopy** is an open source package for phonon calculations at harmonic and quasi-harmonic levels.

**Phono3py** is another open source package for phonon-phonon interaction and lattice thermal conductivity calculations. See the document at <http://atztogo.github.io/phono3py/>

**Phonon database:** A collection of first principles phonon calculations is available as open data at <http://phonondb.mtl.kyoto-u.ac.jp/>, where the raw data of phonopy & VASP results are downloaded.

## Selected features

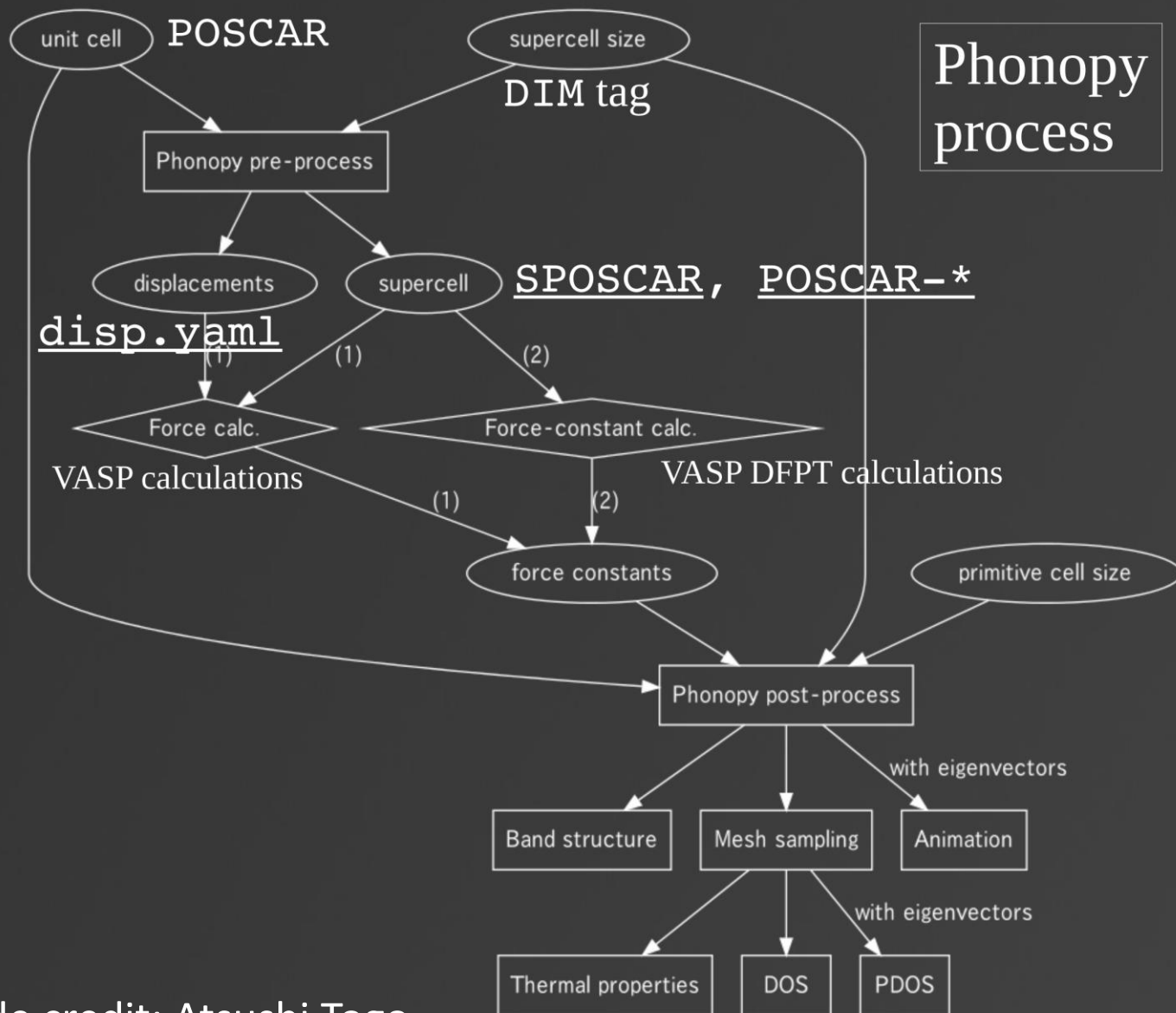
- [Phonon band structure, phonon DOS and partial-DOS](#)
- [Phonon thermal properties](#): Free energy, heat capacity ( $C_v$ ), and entropy
- [Phonon group velocity](#)
- [Thermal ellipsoids / Mean square displacements](#)
- [Irreducible representations of normal modes](#)
- [Quasi-harmonic approximation](#): Thermal expansion, heat capacity at constant pressure ( $C_p$ ),
- [Mode Grüneisen parameters](#)
- [Non-analytical-term correction](#): LO-TO splitting ([Born effective charges and dielectric constant are required.](#))
- [Interfaces to calculators](#): VASP, VASP DFPT, Abinit, Pwscf, Siesta, Elk, FHI-aims, Wien2k, CRYSTAL
- [Python APIs](#)



Atsushi Togo  
(Kyoto University, Japan)



# Work flow of Phonopy



Slide credit: Atsushi Togo

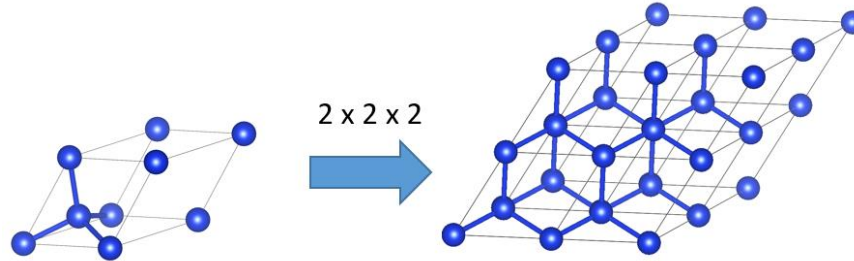
# Why SCAN?

- SCAN can accurately predict geometry and energy based on a static lattice model. SCAN will become more and more important for studying material properties.
- Lattice dynamics can be calculated on top of a static lattice model. The predicted phonon properties sensitively depend on calculated forces. Since SCAN is able to accurately predict geometry and energy, we also expect good predictions of phonon properties.
- Calculating force accurately is usually a challenging task especially when systems have competing bonding interactions. Theoretically, it is essential to recognize different bondings such as by SCAN.
- Calculation effort of SCAN is acceptable. This is important for the phonon property calculations with the frozen phonon approach, which introduces phonon modes into large supercells.



# Work flow: an example of Silicon

1. Structural relaxation (of primitive cell) using VASP
2. Pre-process by Phonopy: Generate supercells and introduce atomic displacements



Each supercell contains a phonon mode – one atomic displacement.  
The number of generated supercells depends on crystal symmetry.

3. Calculate atomic forces of supercells using VASP as a calculator  
Do not relax the supercell structures!
4. Post-process by Phonopy to get final results
  - Collect force sets; Generate force constants
  - A part of dynamical matrix is built from the force constants
  - Phonon frequencies and eigenvectors are calculated from the dynamical matrices with the specified q-points.

# Accurate force calculation by SCAN

## INCAR

```
System      = Silicon

#SCAN functional
GGA         = PE
METAGGA     = SCAN
LASPH       = .True.
ADDGRID     = .True.
#SCAN functional

PREC        = Accurate
LREAL       = .False.
IALGO       = 38
EDIFF       = 1E-08
ENCUT       = 500
NELM        = 200
NEDOS       = 3000
ISMEAR      = 0
SIGMA       = 0.01
LWAVE       = .False.
LCHARG      = .False.

#Ionic relaxation
IBRION      = 1
ISIF        = 3
NSW         = 100
EDIFFG      = -0.001
```

Accurate force is essential to avoid *false soft modes*, but its calculation is usually very difficult!

**ADDGRID=.TRUE.**

VASP uses an additional support grid for the evaluation of the augmentation charges. The additional grid helps to reduce the noise in the forces significantly.

**LREAL=.FALSE.**

Projection operators are evaluated in real-space or in reciprocal space.

**LASPH = .TRUE.**

non-spherical contributions from the gradient corrections inside the PAW spheres will be included as well. This is essential for accurate total energies when meta-GGAs are used, since these functionals often result in aspherical charge densities.

# Accurate force calculation by SCAN

## Note on POTCAR

meta-GGA calculations require [POTCAR](#) files that include information on the kinetic energy density of the core-electrons. To check whether a particular [POTCAR](#) contains this information, type:

```
grep kinetic POTCAR
```

This should yield at least the following lines (for each element on the file):

```
kinetic energy-density  
mkinetic energy-density pseudized
```

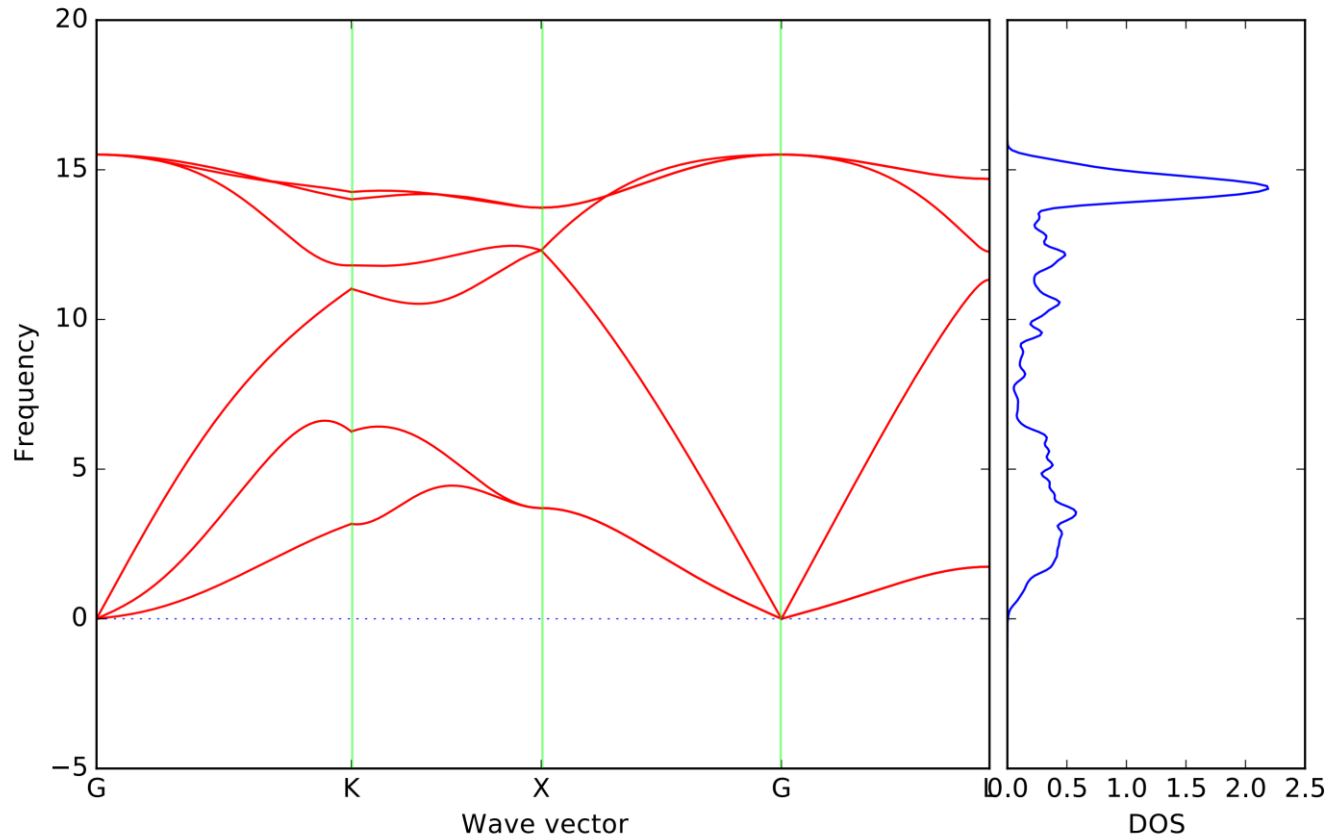
and for PAW datasets with partial core corrections:

```
kinetic energy density (partial)
```

## Note on convergence issues

If convergence problems are encountered, it is recommended to preconverge the calculations using the PBE functional, to read the PBE WAVCAR file. Furthermore, ALGO = A (conjugate gradient algorithm for orbitals) is often more stable than charge density mixing, in particular, if the system contains vacuum regions.

# Results: Phonon 'band structure' and density of states



More details can be found here:

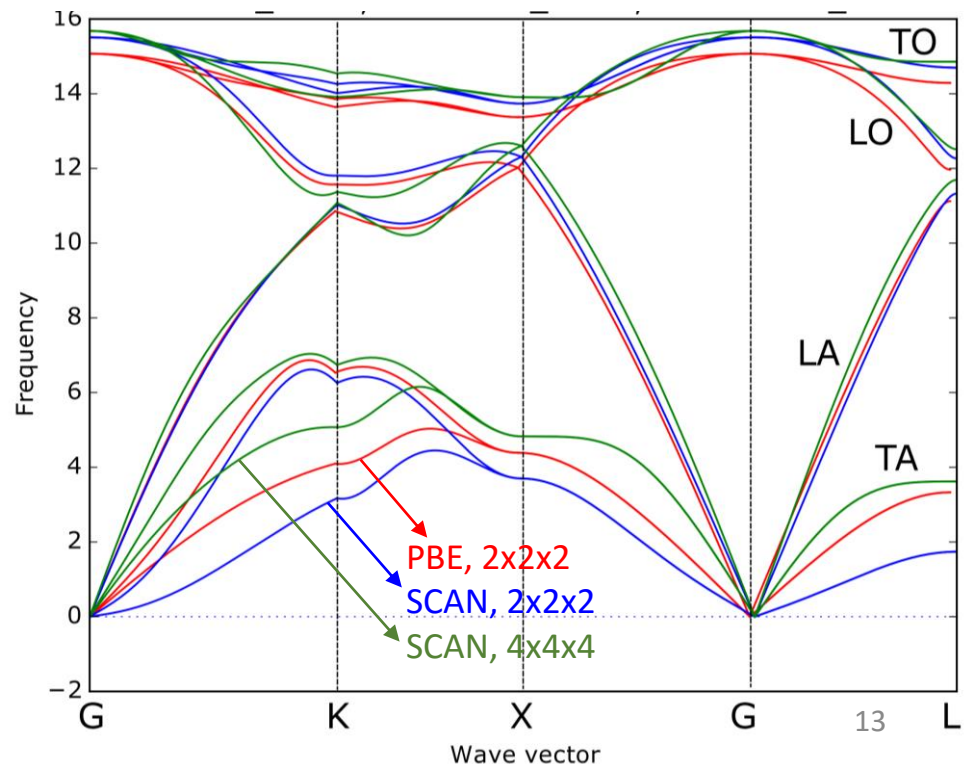
<https://atztego.github.io/phonopy/examples.html>

# Convergence issue of SCAN

- Supercell size is usually a key factor for a well-converged calculation of phonon properties.
- It is relatively easy to converge supercell size for LDA/PBE. The convergence seems to be more difficult for SCAN.
  - ✓ For the SCAN calculation with 2x2x2 supercells, TA-modes along G-L path are too soft compared with experimental results.
  - ✓ The results are significantly improved with 4x4x4 supercells.

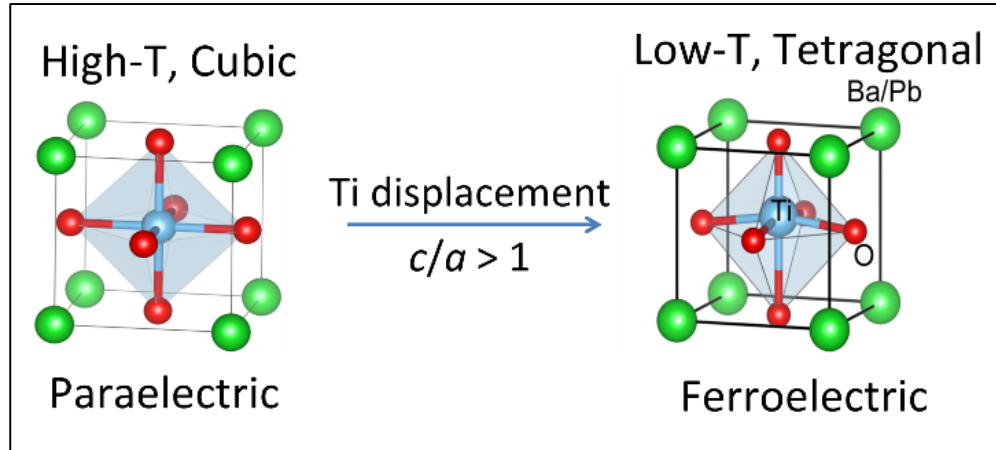
- Reason of the convergence issue: **SCAN can better capture intermediate- and long-range interactions**

Phonon dispersion relation of Si with different supercell sizes and exchange-correlation functionals



# Phonon properties of ferroelectrics

-- A case study of prototypical  $\text{BaTiO}_3$



- Phonon properties is widely used in studying ferroelectric instabilities.
- Two structural distortions during phase transition
  - Ti ion displaces from  $\text{TiO}_6$  center towards one O ion along z direction
  - Lattice constants is distorted by the Ti displacement
- Ti displacement indicates an dynamical structural instability, which is shown as **soft phonon modes** (i.e., phonon modes with negative vibrational frequencies) from the calculated phonon band structure.

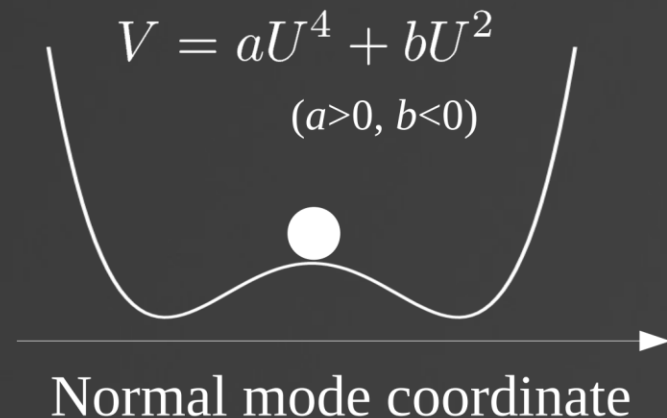
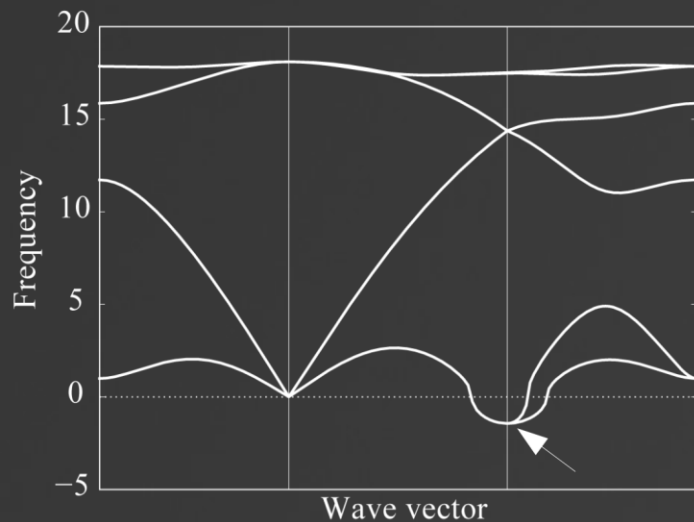
# Imaginary mode

$$\omega^2 < 0$$

Imaginary frequency appears when crystal structure is dynamically unstable through the imaginary mode.

Sometimes it relates to phase transition, or may be used to check if virtual crystal structure is stable or not.

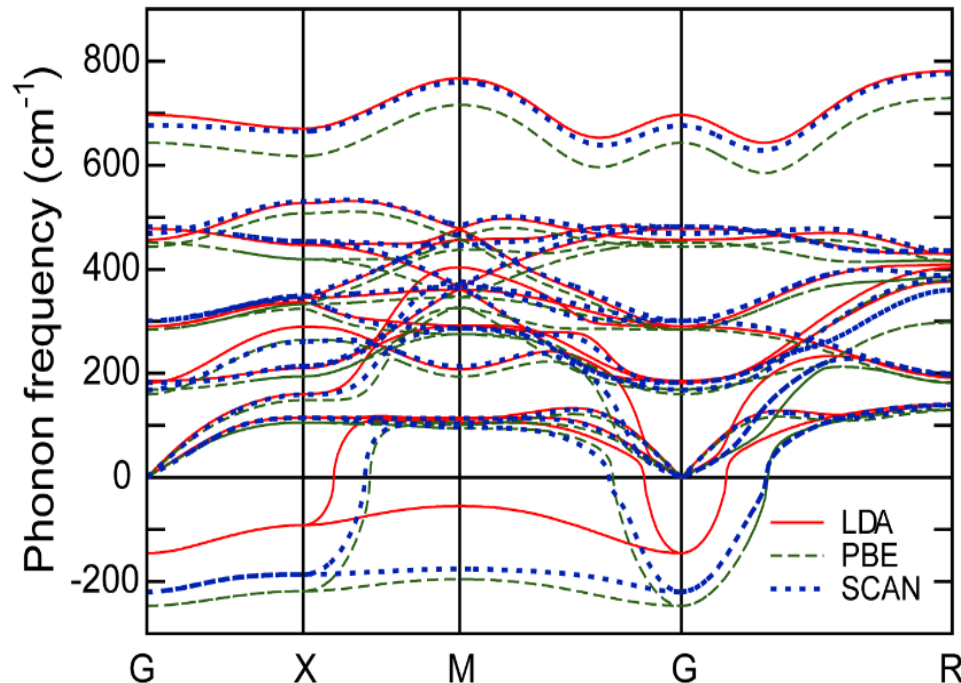
\*In phonopy output, imaginary frequencies are shown as negative values.



# Results: Phonon 'band structure' and density of states

Phonon frequencies of BaTiO<sub>3</sub> at the Brillouin zone center. The three  $\Gamma_{15}$  modes are triply degenerate, and the  $\Gamma_{25}$  mode is triply degenerate.

Modes	LDA	PBE	B1-WC <sup>a</sup> /HSE <sup>d</sup>	SCAN	Experiment
BaTiO <sub>3</sub>					
$\Gamma_{15}(\text{TO1})$	-145	-247	-145(-213) <sup>a</sup>	-220	--
$\Gamma_{15}(\text{TO2})$	186	169	195( 195) <sup>a</sup>	183	182 <sup>b</sup>
$\Gamma_{25}$	290	285	299( 298) <sup>a</sup>	290	306 <sup>b,c</sup>
$\Gamma_{15}(\text{TO3})$	479	452	482( 476) <sup>a</sup>	476	482 <sup>b</sup>



Phonon dispersion relation of BaTiO<sub>3</sub> calculated by three exchange-correlation functionals: LDA, PBE, and SCAN



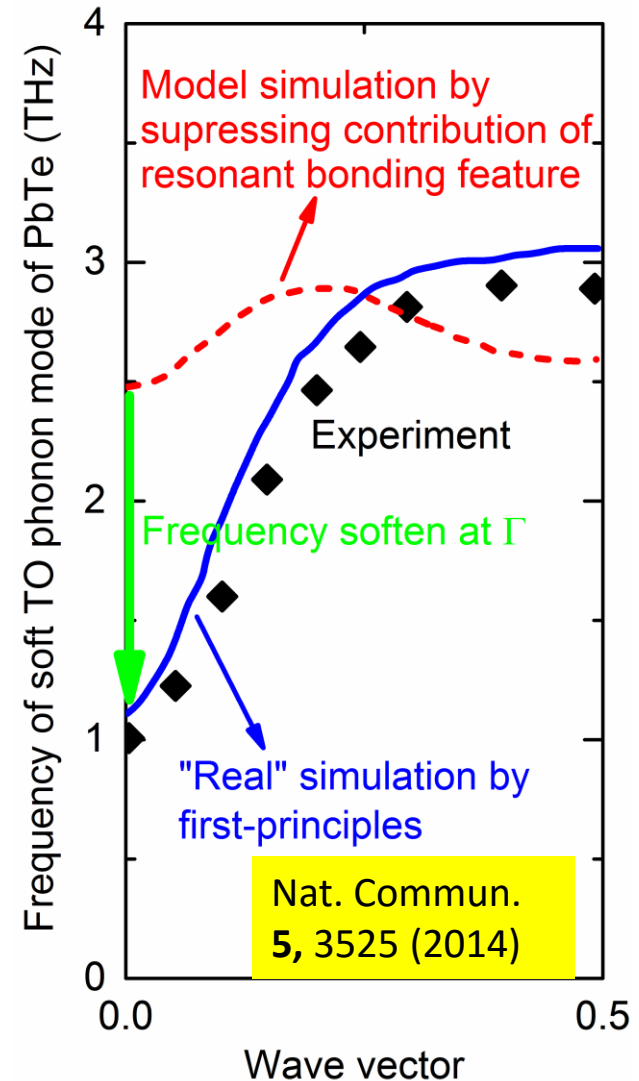
# Why LDA is better than PBE for phonon properties?

## LDA

- Bonding strength overestimation  
→ phonon over-stiffen
- Polarizability overestimation  
→ enhances resonant bonding feature  
→ phonon over-soften

## PBE

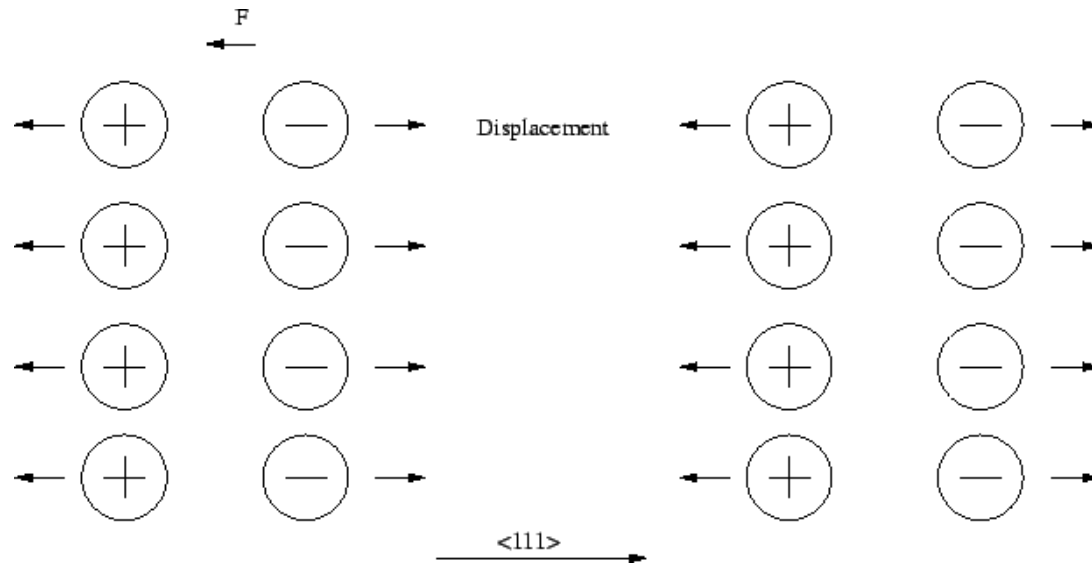
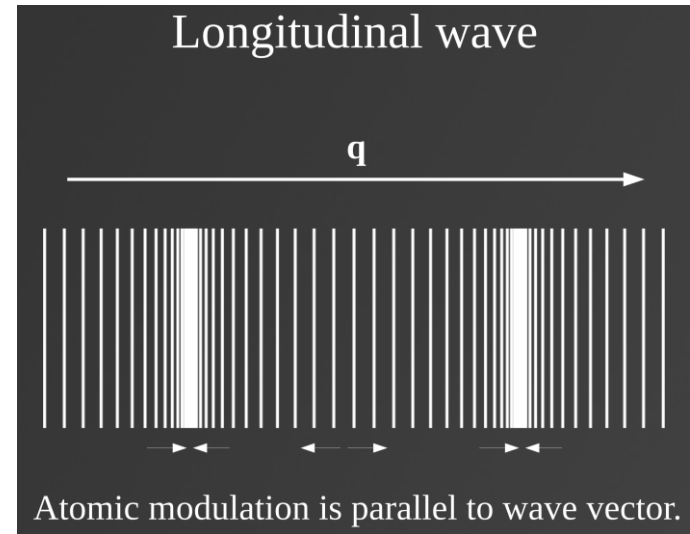
- Bonding strength underestimation  
→ phonon over-soften
- Polarizability overestimation  
→ enhances resonant bonding feature  
→ phonon over-soften



# Note on LO/TO splitting (1)

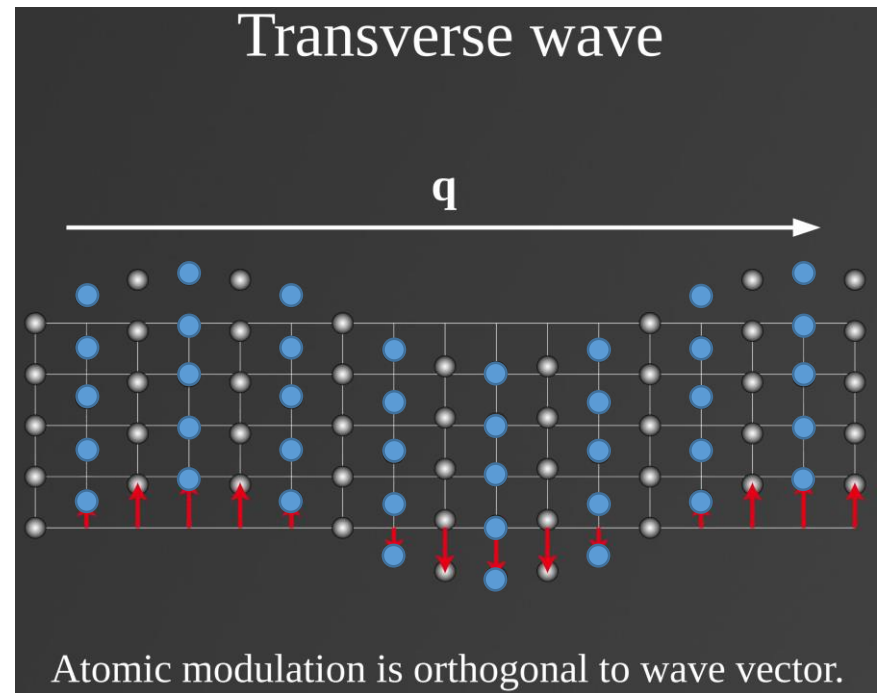
Consider a long wave LO phonon propagating along the  $[111]$  direction in a zinc-blende polar crystal. The positive and negative ions lie on separate planes perpendicular to the direction of propagation.

Under excitation of a LO mode, the planes move apart. The LO mode is accompanied by an extra restoring force due to the Coulomb interaction. This additional force then leads to the **frequency change**.



## Note on LO/TO splitting (2)

Under excitation of a TO mode, those planes slide past each other. Therefore, there is no additional force induced by the TO mode.



LO/TO splitting can be modelled by a non-analytical correction to the phonon frequencies using the Born effective charge and macroscopic dielectric tensors.

## Note on LO/TO splitting (3)

# Non-analytical term correction

Dynamical matrix at  $\mathbf{q} \rightarrow 0$  are corrected by non-analytical term correction. R. M. Pick *et al.*, PRB 1, 910, (1970)

$$D_{ij}^N(\mu\nu, \mathbf{q} \rightarrow \mathbf{0}) = D_{ij}(\mu\nu, \mathbf{q} \rightarrow \mathbf{0}) + \frac{4\pi}{\sqrt{M_\mu M_\nu} \Omega_0} \frac{[\sum_k q_k Z_{\mu,ki}^*][\sum_{k'} q_{k'} Z_{\nu,k'j}^*]}{\sum_{ij} q_i \epsilon_{ij}^\infty q_j}$$

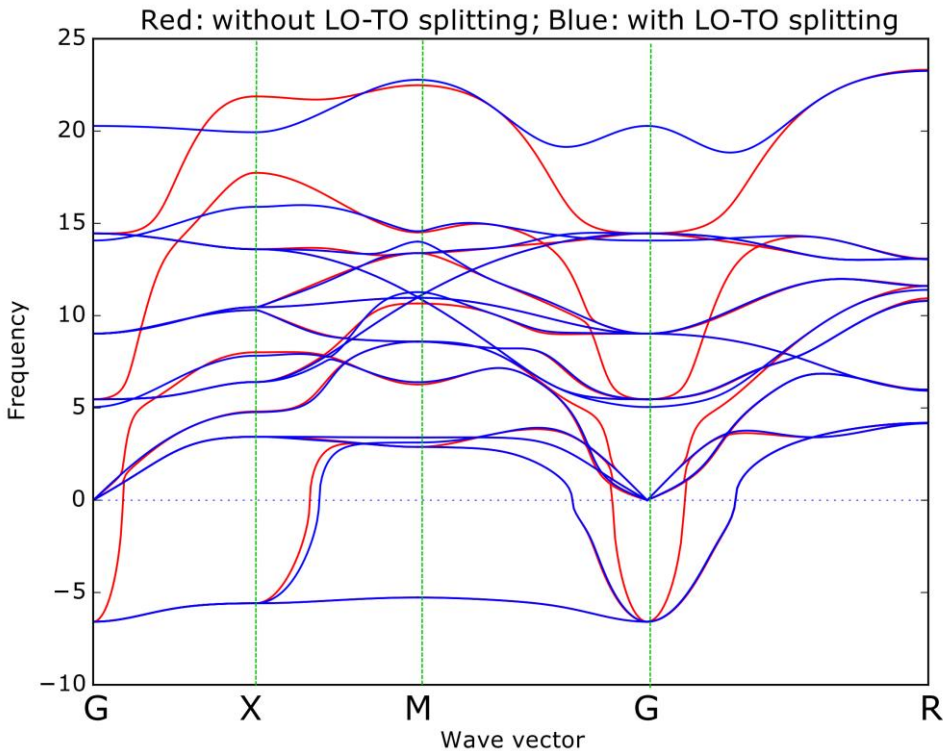
\*Z: Born effective charge tensor,  $\epsilon$ : dielectric tensor

At general  $\mathbf{q}$ -points, force constants are corrected by interpolation scheme of Wang *et al.* (J. Phys.: Condens. Matter. 22, 202201 (2010))

```
% phonopy --nac
```

Born effective charge and dielectric tensors are necessary to use this option and those are summarized in BORN file.

# Note on LO/TO splitting (4)



A comparison of phonon dispersion relation with and without considering the LO-TO splitting

To considering the splitting between longitudinal and transverse optical modes, we need to calculate Born effective charge (BEC). For LDA and PBE calculations, BEC can be easily calculated by density functional perturbation theory (DFPT):

```
LEPSILON = .TRUE.
```

For SCAN, we need to use finite electric field approach (<https://cms.mpi.univie.ac.at/wiki/index.php/LCALCEPS>):

```
LALCEPS = .TRUE.  
EFIELD_PEAD = 0.002 0.002 0.002
```

# SCAN functional and DFPT approach in VASP

```

EEEEEE RRRRRR RRRRRR 000000 RRRRRR   ###   ###   ###
E      R      R      R      R      0      0      R      R      ###   ###   ###
E      R      R      R      R      0      0      R      R      ###   ###   ###
EEEE   RRRRRR RRRRRR 0      0      RRRRRR   #     #     #
E      R      R      R      R      0      0      R      R      ###   ###   ###
E      R      R      R      R      0      0      R      R      ###   ###   ###
EEEEEE R      R      R      R      000000 R      R      ###   ###   ###

```

You have switched on METAGGA and linear response routines.  
This combination is currently not supported.  
If you have selected LOPTICS=.TRUE., VASP will continue but some  
matrix elements [H,r] are neglected (you might try to use  
LPEAD=.TRUE. which works irrespective of H).  
In all other cases VASP will stop now. S000 sorry...

----> I REFUSE TO CONTINUE WITH THIS SICK JOB ..., BYE!!! <----

**Note:** For standard DFT functionals,  $\epsilon_\infty$ ,  $Z^*$ , and  $e^{(0)}$  may be more easily calculated from density functional perturbation theory (see [LEPSILON=.TRUE.](#)). For functionals that depend **not only on the density but also explicitly on the orbitals**, like hybrid functionals and meta-GGAs, density functional perturbation theory is presently **not implemented** and [LEPSILON=.TRUE.](#) is not applicable. <https://cms.mpi.univie.ac.at/wiki/index.php/LCALCEPS>

For SCAN functional, kinetic energy density:  $\tau = (1/2) \sum_i^{\text{occ}} |\nabla \phi_i|^2$