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# Day 4 Hands on: Forces and phonons

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Today's theme:

- 1) Relaxations: adsorption of oxygen on graphene and automatic lattice constant optimization
  - 2) Phonons: compute phonon in  $\Gamma$  and along the BZ, for Si and AIAs
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# **Exercise 1:**

**Learning Goals: optimize atomic position and lattice constants**

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# Exercise 1

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Topics of the exercise:

1. How to perform relaxation of atomic structure (graphane and oxygen adsorption)
  2. Understanding forces.
  3. Optimizing the lattice constant of Silicon and comparing with total energy approaches
  4. Understanding stresses.
-

# Exercise 1.1: graphane and O adsorption

## Input file scf calculation

```
&CONTROL
calculation = 'scf',
prefix = 'Graphane',
outdir = '/tmp',
pseudo_dir = '../pseudo',
/

&SYSTEM
....
....
/

&ELECTRONS
conv_thr = 1.0d-8
/

ATOMIC_SPECIES
C 12.0107 C.pbe-rrkjus.UPF
H 1.00007 H.pbe-rrkjus.UPF

ATOMIC_POSITIONS alat
...

K_POINTS automatic
991 000
```

## Input file for relaxation

```
&CONTROL
calculation = 'relax',
prefix = 'Graphane',
outdir = '/tmp',
pseudo_dir = '../pseudo',
/
```

This relaxes **only** the **atomic positions**

```
&SYSTEM
....
....
/
```

```
&ELECTRONS
conv_thr = 1.0d-8
/
```

```
&IONS
/
```

lons is jargon for atoms, this cell must appear!

```
ATOMIC_SPECIES
C 12.0107 C.pbe-rrkjus.UPF
H 1.00007 H.pbe-rrkjus.UPF
```

```
ATOMIC_POSITIONS alat
...
```

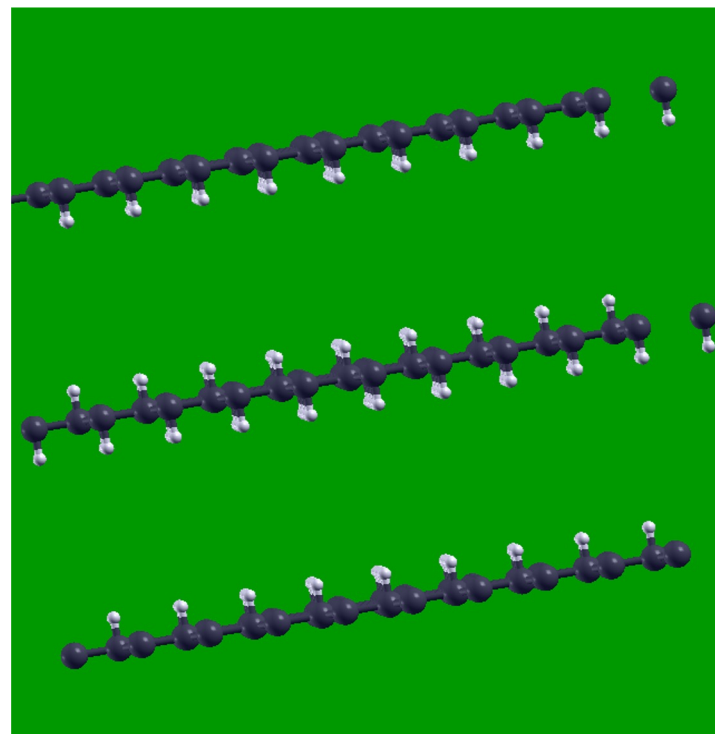
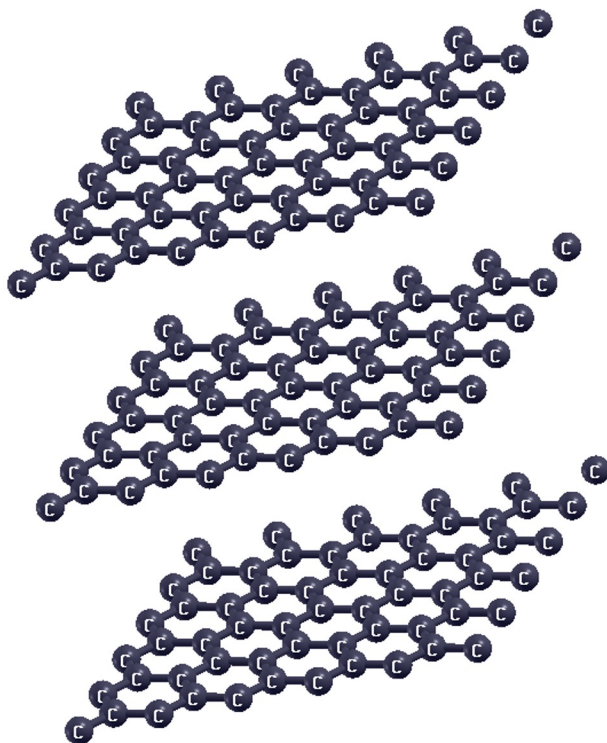
```
K_POINTS automatic
991 000
```

# Exercise 1.1: graphane

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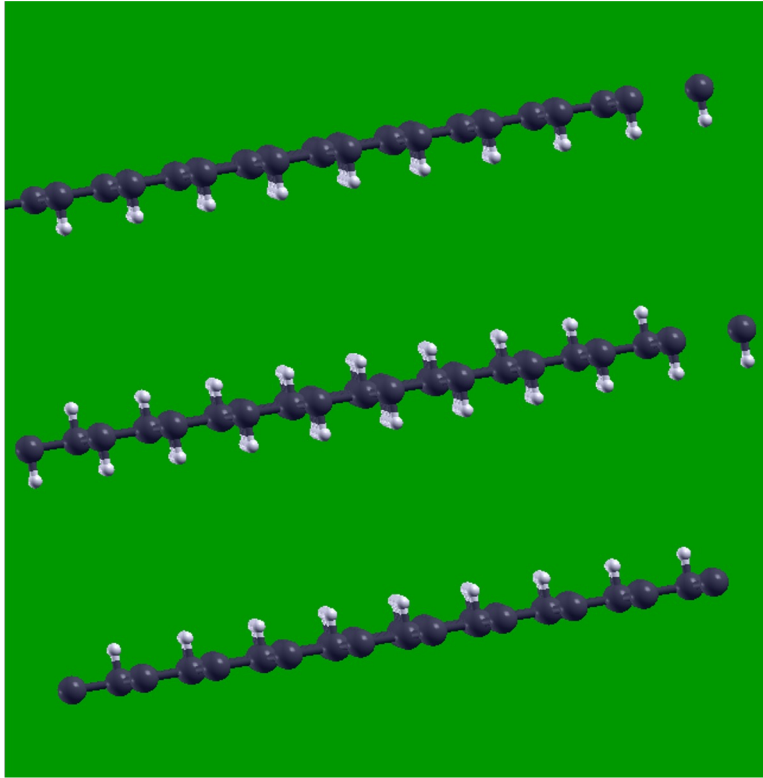
Graphane is hydrogenated graphene:

- H saturates double-bonds and destroys the  $\pi$ -delocalized cloud
- remove tendency to be planar (why?)

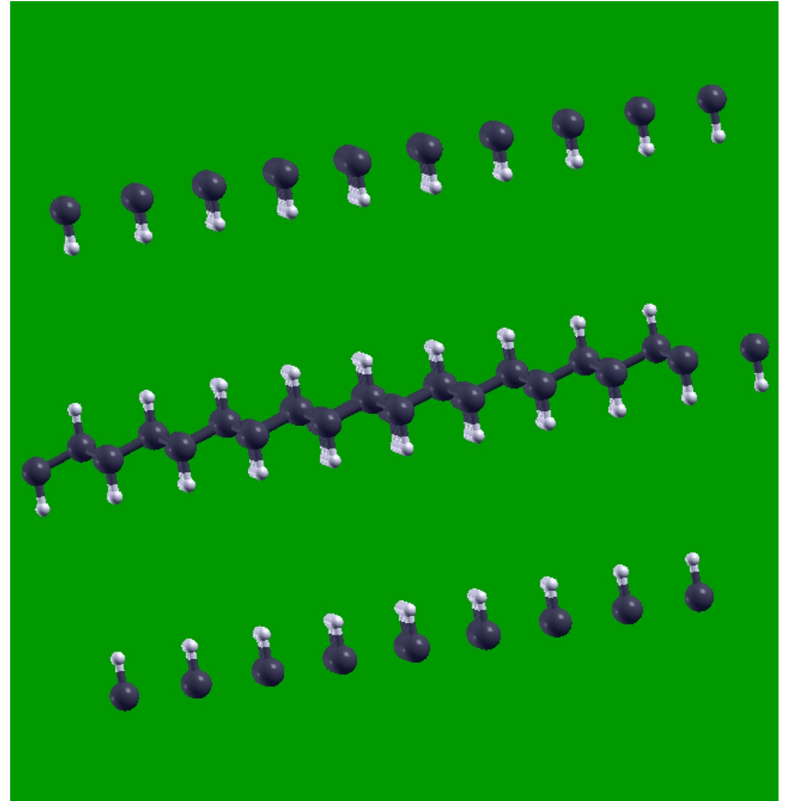


# Exercise 1.1: graphane buckling

---



Relax  
→



# Exercise 1.1: finding forces

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## Output relaxation file

Iteration #1

Forces acting on atoms (cartesian axes, Ry/au):

atom	1	type	2	force =	-0.00000000	-0.00000000	0.29668613
atom	2	type	1	force =	0.00000000	0.00000000	0.24378433
atom	3	type	1	force =	0.00000000	0.00000000	-0.24378433
atom	4	type	2	force =	0.00000000	0.00000000	-0.29668613

Total force = 0.543053    Total SCF correction = 0.000031

**What is the condition on forces for the material to be in equilibrium?**

Iteration #6

Forces acting on atoms (cartesian axes, Ry/au):

atom	1	type	2	force =	0.00000000	0.00000000	0.00017761
atom	2	type	1	force =	0.00000000	0.00000000	-0.00064644
atom	3	type	1	force =	0.00000000	0.00000000	0.00064644
atom	4	type	2	force =	0.00000000	-0.00000000	-0.00017761

Total force = 0.000948    Total SCF correction = 0.000003

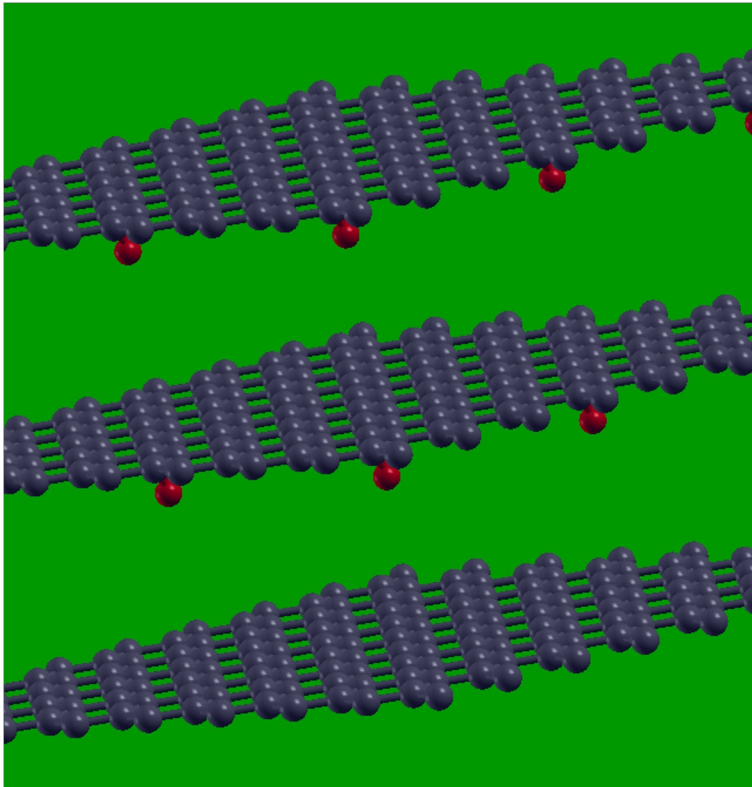
Energy error = 2.7E-05 Ry

Gradient error = 6.5E-04 Ry/Bohr

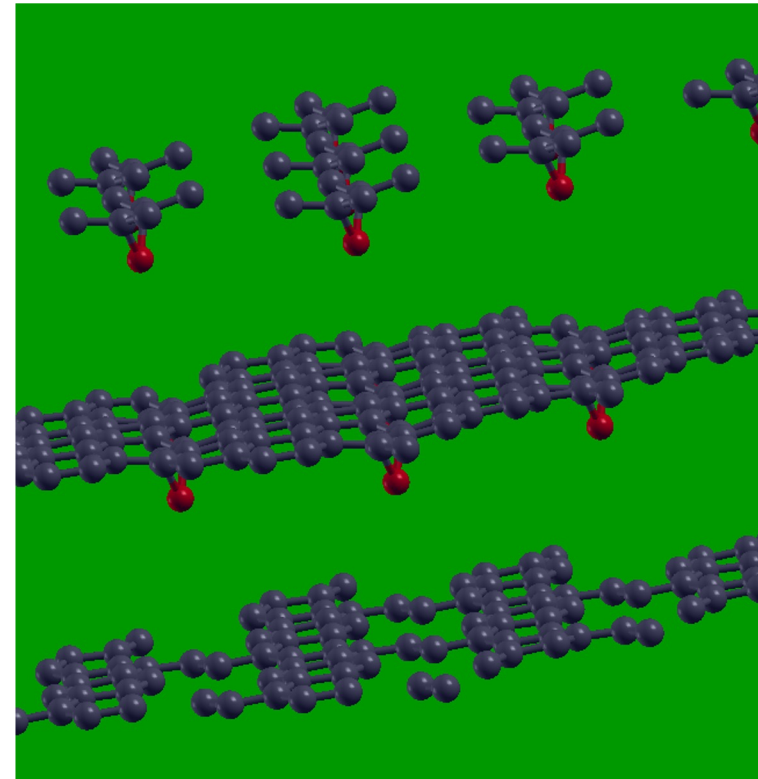
# Exercise 1.1: O adsorption on graphene

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Oxygen is strongly electronegative → electron acceptor



Relax  
→





# Exercise 1.1: optimizing silicon

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## Input file for cell relaxation

```
&CONTROL
  calculation='vc-relax',
  prefix='silicon',
  pseudo_dir='../pseudo/',
  outdir='../tmp'
/
&SYSTEM
  ibrav = 2,
  celldm(1) = 10.6,
  nat = 2,
  ntyp = 1,
  nbnd=10,
  ecutwfc = 36,
/
&ELECTRONS
/
&IONS
/
&CELL
/
ATOMIC_SPECIES
  Si 28.086 Si.pz-vbc.UPF
ATOMIC_POSITIONS
  Si 0.00 0.00 0.00
  Si 0.25 0.25 0.25
K_POINTS automatic
  6 6 6 1 1 1
```

← This relaxes **both cell and atomic positions**

← We need also a CELL section

# Exercise 1.1: finding stresses

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## Output relaxation file

Iteration #1

Forces acting on atoms (cartesian axes, Ry/au):

```
atom  1 type  1  force =   0.00000000   0.00000000   0.00000000
atom  2 type  1  force =   0.00000000   0.00000000   0.00000000
```

Total force = 0.000000 Total SCF correction = 0.000000

Computing stress (Cartesian axis) and pressure

total stress (Ry/bohr**3)			(kbar)	P=	
-0.00057789	-0.00000000	0.00000000	-85.01	-0.00	0.00
-0.00000000	-0.00057789	0.00000000	-0.00	-85.01	0.00
0.00000000	0.00000000	-0.00057789	0.00	0.00	-85.01

Iteration #6

Forces acting on atoms (cartesian axes, Ry/au):

```
atom  1 type  1  force =  -0.00000000  -0.00000000  -0.00000000
atom  2 type  1  force =   0.00000000   0.00000000  -0.00000000
```

Total force = 0.000000 Total SCF correction = 0.000000

Computing stress (Cartesian axis) and pressure

total stress (Ry/bohr**3)			(kbar)	P=	
0.00000194	0.00000000	-0.00000000	0.29	0.00	-0.00
0.00000000	0.00000194	-0.00000000	0.00	0.29	-0.00
-0.00000000	-0.00000000	0.00000194	-0.00	-0.00	0.29

**End of exercise 1**

**Questions?**

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# Topics of the following session: Phonons

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- Exercise 2: Phonons at Gamma in non-polar materials
- Exercise 3: Phonons dispersion in non-polar materials
- Exercise 4: Phonon at Gamma in polar materials

Optional:

- Exercise 5: Phonon dispersion in polar materials
-

# Introduction: Phonons

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Normal mode frequencies, , and eigenvectors, are determined by the secular equation:


$$\sum_{s',\beta} \tilde{D}_{s\alpha,s'\beta}(\mathbf{q}) \tilde{\mathbf{u}}_{s'\beta}(\mathbf{q}) = \omega_{\mathbf{q}}^2 \tilde{\mathbf{u}}_{s\alpha}(\mathbf{q})$$

where

$$\tilde{D}_{s\alpha,s'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\mathbf{R}, \mathbf{R}'} \boxed{\frac{\partial^2 E_{\text{tot}}}{\partial u_{s\alpha}(\mathbf{R}) \partial u_{s'\beta}(\mathbf{R}')}} e^{i\mathbf{q}(\mathbf{R}-\mathbf{R}')}$$

is the **dynamical matrix**.

Interatomic Force  
Constant (IFC)



This Matrix can be calculated from linear response and diagonalized to get phonon modes at  $\mathbf{q}$ .

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# **Exercise 2:**

## **Phonons at Gamma in non-polar materials**

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# Exercise 2: Phonons at $\Gamma$ in non-polar materials

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Go to the directory with the input files:

```
cd ~/ASESMA2025/Day4/example2.phonon.Gamma.Si/
```

In this directory you will find:

- *README.md* – File describing how to do the exercise
  - *Si.scf.in* – Input file for the SCF ground-state calculation
  - *Si.ph.in* – Input file for the phonon calculation at  $\Gamma$
  - *Si.dynmat.in* – Input file to impose the acoustic sum rule
  - **reference** – Directory with the reference results
-

# Exercise 2: Phonons at $\Gamma$ in non-polar materials

```
&CONTROL
calculation = 'scf',
prefix = 'si',
pseudo_dir = '../pseudo/',
outdir = '../tmp'
/
&SYSTEM
ibrav = 2,
celldm(1) = 10.2,
nat = 2,
ntyp = 1,
ecutwfc = 60,
ecutrho = 720
/
&ELECTRONS
mixing_beta=0.7,
conv_thr=1d-10,
/
ATOMIC_SPECIES
Si 28.086 Si.pz-vbc.UPF
ATOMIC_POSITIONS
Si      0.00  0.00  0.00
Si      0.25  0.25  0.25
K_POINTS automatic
4 4 4  1 1 1
```

**Step 1:** Perform a Self-Consistent Field ground-state calculation for silicon at the equilibrium structure using the pw.x program.

```
mpirun -np 4 pw.x -in Si.scf.in > Si.scf.out
```

↑  
Input

↑  
Output

Smaller than for  
simple total  
energy!



# Exercise 2: Phonons at $\Gamma$ in non-polar materials

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Input file for phonon at Gamma

**Step 2:** Perform a phonon calculation at  $\Gamma$  using the ph.x program.

```
mpirun -np 4 ph.x -in Si.ph.in > Si.ph.out
```

```
&inputph
```

```
prefix = 'si',
```

```
tr2_ph = 1.0d-14,
```

```
amass(1) = 28.0855,
```

```
epsil = .true.
```

```
outdir = './tmp'
```

```
fildyn = 'Si.dyn',
```

```
/
```

```
0.0 0.0 0.0
```



The same prefix as in the SCF calculation



Threshold for self-consistency



Atomic mass



To calculate the dielectric tensor and effective charges



Directory for temporary files



File containing the dynamical matrix



Coordinates of the q point ( $\Gamma$ ) in units of  $2\pi/a$  in the Cartesian reference system

# Exercise 2: Phonons at $\Gamma$ in non-polar materials

Dynamical matrix file: **Si.dyn**

Dielectric Tensor:

13.581468280806	-0.000000000000	-0.000000000000
0.000000000000	13.581468280806	0.000000000000
-0.000000000000	0.000000000000	13.581468280806

Effective Charges E-U:  $Z_{\{\alpha\}\{s,\beta\}}$

atom #	1		
	-0.069382139635	-0.000000000000	-0.000000000000
	-0.000000000000	-0.069382139635	-0.000000000000
	-0.000000000000	-0.000000000000	-0.069382139635
atom #	2		
	-0.069382139635	0.000000000000	0.000000000000
	0.000000000000	-0.069382139635	-0.000000000000
	0.000000000000	-0.000000000000	-0.069382139635

Dielectric constant and Born effective charges (BECs)

$$Z_{s,\alpha\beta}^* = \frac{V}{e} \frac{\partial P_\alpha}{\partial u_{s,\beta}(\mathbf{q} = 0)} = \frac{1}{e} \frac{\partial F_{s\beta}}{\partial \mathcal{E}_\alpha(\mathbf{q} = 0)}$$

# Exercise 2: Phonons at $\Gamma$ in non-polar materials

Dynamical matrix file: **Si.dyn**

Diagonalizing the dynamical matrix

$q = ( \quad 0.000000000 \quad 0.000000000 \quad 0.000000000 )$

```
*****
freq ( 1) = 0.369224 [THz] = 12.315990 [cm-1]
( -0.502437 0.000000 0.469222 0.000000 0.165492 0.000000 )
( -0.502437 0.000000 0.469222 0.000000 0.165492 0.000000 )
freq ( 2) = 0.369224 [THz] = 12.315990 [cm-1]
( -0.186720 0.000000 0.040185 0.000000 -0.680824 0.000000 )
( -0.186720 0.000000 0.040185 0.000000 -0.680824 0.000000 )
freq ( 3) = 0.369224 [THz] = 12.315990 [cm-1]
( 0.461186 0.000000 0.527462 0.000000 -0.095350 0.000000 )
( 0.461186 0.000000 0.527462 0.000000 -0.095350 0.000000 )
freq ( 4) = 15.306901 [THz] = 510.583264 [cm-1]
( 0.700260 -0.000000 -0.059885 0.000000 -0.077779 0.000000 )
( -0.700260 0.000000 0.059885 -0.000000 0.077779 0.000000 )
freq ( 5) = 15.306901 [THz] = 510.583264 [cm-1]
( 0.067676 0.000000 0.700365 0.000000 0.070066 0.000000 )
( -0.067676 0.000000 -0.700365 0.000000 -0.070066 0.000000 )
freq ( 6) = 15.306901 [THz] = 510.583264 [cm-1]
( -0.071103 0.000000 0.076832 0.000000 -0.699315 0.000000 )
( 0.071103 0.000000 -0.076832 0.000000 0.699315 0.000000 )
*****
```

Acoustic modes (in-phase)



Optical modes (out-of-phase)



# Exercise 2: Phonons at $\Gamma$ in non-polar materials

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## Acoustic sum rule at $\Gamma$

Problems with the frequency of the acoustic phonon mode at  $\Gamma$  and with effective charges.

Because of the numerical inaccuracies the interatomic force constants (IFC) and effective charges ( $Z^*$ ) do not strictly satisfy the acoustic sum rule (ASR).

ASR comes directly from the continuous translational invariance of the crystal: if we translate the whole solid by a uniform displacement, the forces acting on the atoms must be zero

$\Rightarrow$  for each cartesian direction  $\alpha, \beta$  and  $s, s'$ -th atom:

$$\sum_{Rj} C_{s\alpha, s'\beta}(\mathbf{R}) = 0, \quad \sum_j Z_{s\alpha\beta}^* = 0$$

As a consequence, the frequencies of the acoustic modes at Gamma must be zero.

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# Exercise 2: Phonons at $\Gamma$ in non-polar materials

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## Acoustic sum rule at $\Gamma$

Reason for numerical inaccuracy:

- Insufficiently accurate SCF thresholds (in pw.x and/or ph.x)
  - XC energy is computed in real space. More problematic for GGA than in LDA, for US pseudopotentials it could require large *ecutrho*.
  - K-points sampling not accurate enough (especially, BECs and dielectric constant required denser k-point sampling).
-

# Exercise 2: Phonons at $\Gamma$ in non-polar materials

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## Acoustic sum rule at $\Gamma$

The acoustic sum rule (ASR) can however be imposed after the phonon calculations. To do this we use the `dynmat.x` program that imposes the ASR on the elements of the dynamical matrix and diagonalize it.

**Step 3:** Run a `dynmat.x` calculation to impose the ASR


```
mpirun -np 4 dynmat.x -in Si.dynmat.in > Si.dynmat.out
```

The input file is `Si.dynmat.in` :

```
&input  
fildyn = 'Si.dyn',  
asr = 'simple',  
/
```



File containing the dynamical matrix



A way to impose the acoustic sum rule (simple, crystal, one-dim, zero-dim, all)

# Exercise 2: Phonons at $\Gamma$ in non-polar materials

The program dynmat.x produces the file **dynmat.out** which contains the new acoustic frequencies, which are exactly equal to zero

```
q =      0.0000      0.0000      0.0000
*****
freq ( 1) =      0.000000 [THz] =      0.000000 [cm-1]
( 0.000000 0.000000 0.707107 0.000000 0.000000 0.000000 )
( 0.000000 0.000000 0.707107 0.000000 0.000000 0.000000 )
freq ( 2) =      0.000000 [THz] =      0.000000 [cm-1]
( -0.707107 0.000000 0.000000 0.000000 0.000000 0.000000 )
( -0.707107 0.000000 0.000000 0.000000 0.000000 0.000000 )
freq ( 3) =      0.000000 [THz] =      0.000000 [cm-1]
( 0.000000 0.000000 0.000000 0.000000 0.707107 0.000000 )
( 0.000000 0.000000 0.000000 0.000000 0.707107 0.000000 )
freq ( 4) =     15.302447 [THz] =     510.434704 [cm-1]
( 0.000000 0.000000 0.707107 0.000000 0.000000 0.000000 )
( 0.000000 0.000000 -0.707107 0.000000 0.000000 0.000000 )
freq ( 5) =     15.302447 [THz] =     510.434704 [cm-1]
( 0.000000 0.000000 0.000000 0.000000 -0.707107 0.000000 )
( 0.000000 0.000000 0.000000 0.000000 0.707107 0.000000 )
freq ( 6) =     15.302447 [THz] =     510.434704 [cm-1]
( -0.707107 0.000000 0.000000 0.000000 0.000000 0.000000 )
( 0.707107 0.000000 0.000000 0.000000 0.000000 0.000000 )
*****
```

---

# **Exercise 3:**

## **Phonons dispersion in non-polar materials**

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# Exercise 3: Phonons dispersion in non-polar materials

---

Go to the directory with the input files:

```
cd ~/ASESMA2025/Day4/example3.phonon.dispersion.Si/
```

In this directory you will find:

- *README.md* – File describing how to do the exercise
  - *Si.scf.in* – Input file for the SCF ground-state calculation
  - *Si.ph.in* – Input file for the phonon calculation at  $\Gamma$
  - *Si.q2r.in* – Input file for calculation of Interatomic Force Constants
  - *Si.matdyn.in* – Input file for Fourier Interpolation for various q points
  - *Si.plotband.in* – Input file for plotting a phonon dispersion
  - **reference** – Directory with the reference results
-

# Exercise 3: Phonons dispersion in non-polar materials

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**Step 1:** Perform a Self-Consistent Field ground-state calculation for silicon at the equilibrium structure using the pw.x program.

```
mpirun -np 4 pw.x -in Si.scf.in > Si.scf.out
```


**Step 2:** Perform a phonon calculation on a uniform grid of q points the ph.x program.

```
mpirun -np 4 ph.x -in Si.ph.in > Si.ph.out
```

Flags for the calculation on a grid  
Uniform grid of q points:

$$q_{ijk} = \frac{i-1}{nq1} \mathbf{G}_2 + \frac{j-1}{nq2} \mathbf{G}_1 + \frac{k-1}{nq3} \mathbf{G}_1$$

```
&inputph  
prefix = 'si',  
tr2_ph = 1.0d-14,  
amass(1) = 28.0855,  
ldisp = .true.,  
nq1 = 4,  
nq2 = 4,  
nq3 = 4,  
outdir = './tmp'  
fildyn = 'Si.dyn',  
/
```



# Exercise 3: Phonons dispersion in non-polar materials

---

4x4x4 = 64 q-points => Use of symmetry => 8 non-equivalent q points

The file Si.dyn0 contains a list of the non-equivalent q points (8, in this case).

```
4    4    4
8
0.0000000000000000E+00  0.0000000000000000E+00  0.0000000000000000E+00
-0.2500000000000000E+00  0.2500000000000000E+00 -0.2500000000000000E+00
0.5000000000000000E+00 -0.5000000000000000E+00 0.5000000000000000E+00
0.0000000000000000E+00 0.5000000000000000E+00 0.0000000000000000E+00
0.7500000000000000E+00 -0.2500000000000000E+00 0.7500000000000000E+00
0.5000000000000000E+00 0.0000000000000000E+00 0.5000000000000000E+00
0.0000000000000000E+00 -0.1000000000000000E+01 0.0000000000000000E+00
-0.5000000000000000E+00 -0.1000000000000000E+01 0.0000000000000000E+00
```

The phonon code ph.x generates a file for every non-equivalent q point (Si.dyn1, Si.dyn2, ..., Si.dyn8), which contain information about dynamical matrices, phonon frequencies and atomic displacements

---

# Exercise 3: Phonons dispersion in non-polar materials

**Step 3:** Calculation of the Interatomic Force Constants (IFC) using the q2r.x program

IFCs in reciprocal space (Fourier transform of IFCs):

$$\tilde{C}_{s\alpha,s'\beta}(\mathbf{q}) = \frac{\partial^2 E_{\text{tot}}}{\partial \tilde{\mathbf{u}}_{s\alpha}(\mathbf{q}) \partial \tilde{\mathbf{u}}_{\beta}(\mathbf{q})}$$

where  $\alpha, \beta$  are the cartesian direction and  $s, s'$  the atomic index

$$C_{s\alpha,s'\beta}(\mathbf{R}) = \sum_{\mathbf{q}_n} \tilde{C}_{s\alpha,s'\beta}(\mathbf{q}) e^{i\mathbf{q}_n(\mathbf{R}-\mathbf{R}')}$$

$$\tilde{C}_{s\alpha,s'\beta}(\mathbf{q}) \longrightarrow C_{s\alpha,s'\beta}(\mathbf{R})$$

Fourier transforms of IFCs on a grid of  $\mathbf{q}$  points  
 $nq_1 \times nq_2 \times nq_3$  in reciprocal space

IFCs in a supercell  $nq_1 \times nq_2 \times nq_3$   
in real space

# Exercise 3: Phonons dispersion in non-polar materials

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**Step 3:** Calculation of the Interatomic Force Constants (IFC) using the q2r.x program

```
mpirun -np 4 q2r.x -in Si.q2r.in > Si.q2r.out
```

&input

fildyn = 'Si.dyn',

zasr = 'simple',

flfrc = 'Si444.fc',

/

← File containing the dynamical matrix

← A way to impose the acoustic sum rule (simple, crystal, one-dim, zero-dim, all)

← Output file of the interatomic force constants

Note: The denser the grid of q points, the larger the vectors R for which the IFCs are calculated.

---

# Exercise 3: Phonons dispersion in non-polar materials

**Step 4:** Calculate phonons at generic  $\mathbf{q}'$  points using IFC using the matdyn.x code

$$\tilde{C}_{s\alpha,s'\beta}(\mathbf{q}) = \sum_{\mathbf{R}} C_{s\alpha,s'\beta}(\mathbf{R}) e^{-i\mathbf{q}' \cdot \mathbf{R}}$$

$C_{s\alpha,s'\beta}(\mathbf{R})$



$\tilde{C}_{s\alpha,s'\beta}(\mathbf{q}')$

Fourier interpolation

IFC's on a grid in real space

Fourier transforms of IFC's at generic  $\mathbf{q}'$  points in reciprocal space

```
&input
```

```
asr = 'simple',
```

```
amass(1) = 28.0855,
```

```
flfrc = 'Si444.fc',
```

```
flfrq = 'Si.freq'
```

```
/
```

```
396
```

```
0.000000 0.000000 0.000000 0.000000
```

```
0.012658 0.000000 0.000000 0.012658...
```

```
mpirun -np 4 matdyn.x -in Si.matdyn.in > Si.matdyn.out
```

← File containing the the interatomic force constants from q2r.x

← Output file with the interpolated frequencies

← Number of  $\mathbf{q}$  points

Coordinates of the  $\mathbf{q}$  points

# Exercise 3: Phonons dispersion in non-polar materials

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**Step 5:** Plot the phonon dispersion using the plotband.x program and gnuplot.

```
plotband.x < Si.plotband.in > Si.plotband.out
```

Si.freq	←	Input file with the frequencies at various q' points
0 600	←	Range of frequencies for a visualization
freq.plot	←	Output file with frequencies which will be used for plot
freq.ps	←	Plot of the dispersion (we will produce another one)
0.0	←	Fermi level (needed only for band structure plot)
100.0 0.0	←	Freq. step and reference freq. on the plot freq.ps

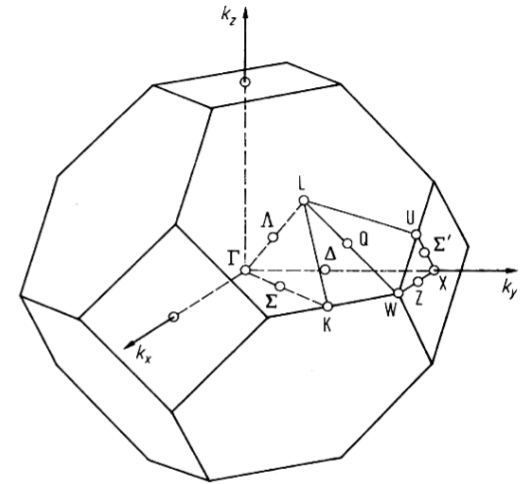
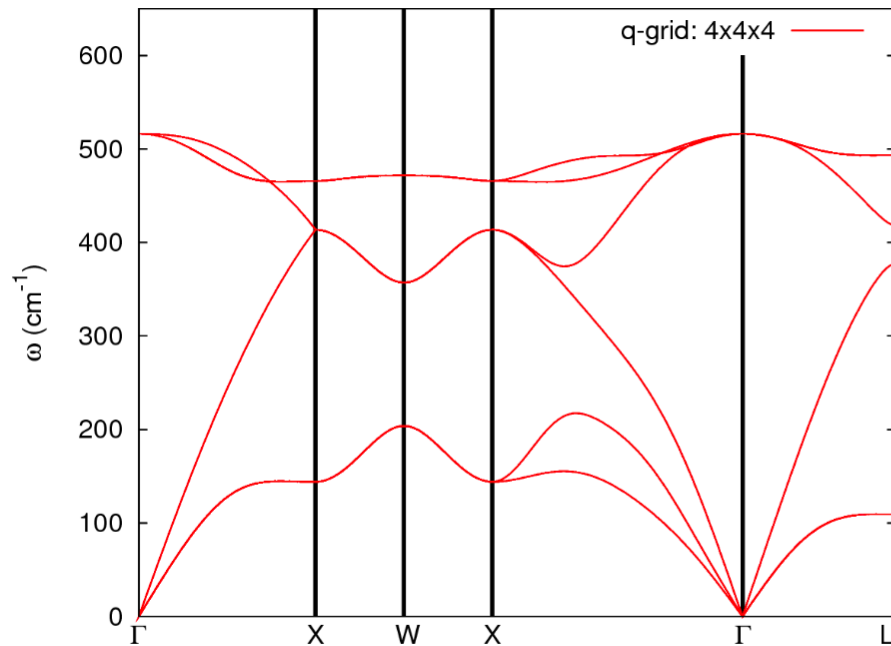
Use gnuplot and the file **plot\_dispersion.gp** in order to plot the phonon dispersion of silicon (look at the file experimental\_data.dat for the experimental reference).

You will get a postscript file phonon\_dispersion.eps which you can visualize.

---

# Exercise 3: Phonons dispersion in non-polar materials

Phonon dispersion of silicon along some high-symmetry directions in the Brillouin zone (file phonon\_dispersion.eps).





# Exercise 3: Phonons dispersion in non-polar materials

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How to determine whether the quality of the Fourier interpolation is satisfactory?  
Compare with the direct calculation (no interpolation)!

**Homework-1:** Perform a direct phonon calculation (no interpolation) at several  $\mathbf{q}'$  points and make a comparison with the phonon frequencies obtained from the interpolation. (Use exercise2 as an example).

Some  $\mathbf{q}'$  points along the Gamma-X high symmetry line are listed in the file `reference/q_points_direct_calc.txt`

**Homework-2:** Perform a phonon dispersion calculation for several  $\mathbf{q}$ -points grids (eg.  $2 \times 2 \times 2$ ,  $4 \times 4 \times 4$ , and  $6 \times 6 \times 6$ ) and compare the dispersions. Do they converge?

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## Exercise 3: Phonons dispersion in non-polar materials

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The phonon modes are not always easy to visualize, especially if we are not at  $\Gamma$ . An online phonon visualizer is very helpful in this regard.

<https://interactivephonon.materialscloud.io>

Let's click on the link and look at your phonons.

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# **Exercise 4:**

## **Phonons at Gamma in polar materials**

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# Phonons in polar materials

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**Polar materials in the  $q = 0$  limit:** a macroscopic electric field appears as a consequence of the long-range character of the Coulomb interaction (incompatible with Periodic Boundary Conditions). A non-analytic term must be added to Interatomic Force Constants at  $\mathbf{q} = 0$ :

$$\tilde{C}_{s\alpha,s'\beta}(\mathbf{q}) = \tilde{C}_{s\alpha,s'\beta}^{analytic} + \frac{4\pi (\mathbf{q} \cdot \mathbf{Z}_s^*)_{\alpha} (\mathbf{q} \cdot \mathbf{Z}_s^*)_{\beta}}{V \mathbf{q} \cdot \boldsymbol{\varepsilon}_{\infty} \cdot \mathbf{q}}$$

Effective charges  $Z_s^*$  are related to polarization  $P$  induced by a lattice

$$Z_{s,\alpha\beta}^* = V \frac{\partial P_{\alpha}}{\partial u_s^{\beta}}$$

Dielectric tensor  $\varepsilon_{\infty}^{\alpha\beta}$  is related to polarization  $P$  induced by an electric field  $E$ :

$$\varepsilon_{\infty}^{\alpha\beta} = \delta_{\alpha\beta} + 4\pi \left. \frac{\partial P_{\alpha}}{\partial E_{\beta}} \right|_{u_s(\mathbf{q}=0)=0}$$

All of the above can be calculated from (mixed) second order derivatives of the total energy.

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## Exercise 4: Phonons at Gamma in polar materials

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Go to the directory with the input files:

```
cd ~/ASESMA2025/Day4/example4.phonon.Gamma.AIAs/
```

In this directory you will find:

- *README.md* – File describing how to do the exercise
  - *AIAs.scf.in* – Input file for the SCF ground-state calculation
  - *AIAs.ph.in* – Input file for the phonon calculation at  $\Gamma$
  - *AIAs.dynmat.in* – Input file for Fourier Interpolation for various q points
  - ***reference*** – Directory with the reference results
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# Exercise 4: Phonons at Gamma in polar materials

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**Step 1:** Perform a Self-Consistent Field ground-state calculation for AlAs at the equilibrium structure using the pw.x program.

```
mpirun -np 4 pw.x -in AlAs.scf.in > AlAs.scf.out
```

**Step 2:** Perform a phonon calculation in Gamma using ph.x.

```
mpirun -np 4 ph.x -in AlAs.ph.in > AlAs.ph.out
```

```
Phonons at Gamma
&inputph
prefix = 'AlAs',
tr2_ph = 1.0d-14,
amass(1) = 26.98,
amass(2) = 74.92,
epsil = .true.
outdir = './tmp'
fildyn = 'AlAs.dyn',
/
0.0 0.0 0.0
```

# Exercise 4: Phonons at Gamma in polar materials

In the file **ph.AIs.out** you will find information about the dielectric tensor and effective charges (BECs)

```
Effective charges (d Force / dE) in cartesian axis with asr applied:
  atom      1      Al Mean Z*:      4.43445
E*x (      4.43445      0.00000      -0.00000 )
E*y (      0.00000      4.43445      -0.00000 )
E*z (     -0.00000     -0.00000      4.43445 )
  atom      2      As Mean Z*:     -4.43445
E*x (     -4.43445     -0.00000      0.00000 )
E*y (     -0.00000     -4.43445      0.00000 )
E*z (      0.00000      0.00000     -4.43445 )
```

$$Z_{s,\alpha\beta}^* = \frac{V}{e} \frac{\partial P_\alpha}{\partial u_{s,\beta}(\mathbf{q} = 0)} = \frac{1}{e} \frac{\partial F_{s\beta}}{\partial \varepsilon_\alpha(\mathbf{q} = 0)}$$

Diagonalizing the dynamical matrix

```
q = (      0.000000000      0.000000000      0.000000000 )
```

```
*****
freq (   1) =     -0.062455 [THz] =     -2.083289 [cm-1]
freq (   2) =     -0.062455 [THz] =     -2.083289 [cm-1]
freq (   3) =     -0.062455 [THz] =     -2.083289 [cm-1]
freq (   4) =     11.807415 [THz] =    393.852972 [cm-1]
freq (   5) =     11.807415 [THz] =    393.852972 [cm-1]
freq (   6) =     11.807415 [THz] =    393.852972 [cm-1]
*****
```


← No LO-TO splitting

# Exercise 4: Phonons at Gamma in polar materials

**Step 3:** Impose Acoustic Sum Rule and add the non analytic LO-TO splitting using the dynmat.x program

```
mpirun -np 4 dynmat.x -in AlAs.dynmat.in > AlAs.dynmat.out
```

```
&input
  fildyn = 'AlAs.dyn',
  asr='simple',
  amass(1)=26.98,
  amass(2)=74.92
  q(1) = 1.0,
  q(2) = 0.0,
  q(3) = 0.0
/
```



Direction in the Brillouin zone along which we want to compute the LO-TO splitting

IR activities are in  $(D/A)^2/\text{amu}$  units

#	mode	[cm <sup>-1</sup> ]	[THz]	IR
1		-0.00	-0.0000	0.0000
2		0.00	0.0000	0.0000
3		0.00	0.0000	0.0000
4		393.86	11.8075	22.8709
5		393.86	11.8075	22.8709
6		430.19	12.8969	22.8709

LO-TO splitting



# Exercise 4: Phonons at Gamma in polar materials

**Step 3:** Impose Acoustic Sum Rule and add the non analytic LO-TO splitting using the dynmat.x program

```
mpirun -np 4 dynmat.x -in AlAs.dynmat.in > AlAs.dynmat.out
```

```
&input
  fildyn = 'AlAs.dyn',
  asr='simple',
  amass(1)=26.98,
  amass(2)=74.92
  q(1) = 1.0,
  q(2) = 0.0,
  q(3) = 0.0
/
```

IR activities are in (D/A)^2/amu units

#	mode	[cm-1]	[THz]	IR
1		-0.00	-0.0000	0.0000
2		0.00	0.0000	0.0000
3		0.00	0.0000	0.0000
4		393.86	11.8075	22.8709
5		393.86	11.8075	22.8709
6		430.19	12.8969	22.8709

IR intensities

$$I_{IR}(\nu) = \sum_{\alpha} \left| \sum_{s\beta} Z_s^{*\alpha\beta} u_s^{\beta}(\nu) \right|^2$$

can be calculated directly from effective charges and phonon displacement patterns

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# **Exercise 5 (Optional): Phonons dispersion in polar materials**

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# Exercise 5: Phonons dispersion in polar materials

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Go to the directory with the input files:

```
cd ~/ASESMA2025/Day4/example5.phonon.dispersion.AIAs/
```

In this directory you will find:

- *README.md* – File describing how to do the exercise
  - *AIAs.scf.in* – Input file for the SCF ground-state calculation
  - *AIAs.ph.in* – Input file for the phonon calculation at  $\Gamma$
  - *AIAs.q2r.in* – Input file for calculation of Interatomic Force Constants
  - *AIAs.matdyn.in* – Input file for Fourier Interpolation for various q points
  - *AIAs.plotband.in* – Input file for plotting a phonon dispersion
  - **reference** – Directory with the reference results
-

# Exercise 5: Phonons dispersion in polar materials

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**Step 1:** Perform a Self-Consistent Field ground-state calculation at the equilibrium structure using the pw.x program.

```
mpirun -np 4 pw.x -in AlAs.scf.in > Si.scf.out
```

**Step 2:** Perform a phonon calculation on a uniform grid of q points the ph.x program.

```
mpirun -np 4 ph.x -in AlAs.ph.in > AlAs.ph.out
```

**Step 3:** Calculation of the Interatomic Force Constants (IFC) using the q2r.x program

```
mpirun -np 4 q2r.x -in AlAs.q2r.in > AlAs.q2r.out
```

**Step 4:** Calculate phonons at generic  $\mathbf{q}'$  points using IFC using the matdyn.x code

```
mpirun -np 4 matdyn.x -in AlAs.matdyn.in > AlAs.matdyn.out
```

**Step 5:** Plot the phonon dispersion using the plotband.x program and gnuplot.

```
plotband.x < AlAs.plotband.in > AlAs.plotband.out
```

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(Note: some parts of the input files are left empty for you to fill !

**Thank you!**

**Questions?**

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