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Phonon calculation in a crystal using DFPT
Project 8 - CH-452

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EPFL

February 2, 2022

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Phonons: overview

- Oscillations of atomic structure in a crystal
- Harmonic oscillators: $\propto e^{i(qR + \Omega(q)t)}$
- Dispersion relation: $\Omega(q)$

Phonon types:

- In phase: *acoustic* phonons, $\Omega(q = 0) = 0$.
- Out of phase: *optical* phonons, $\Omega(q = 0) \neq 0$.

DOS (density of states)

$$D(\Omega) = \frac{V}{V_q} \frac{1}{v_g(\Omega)}, \quad v_g(\Omega) = \frac{\partial \Omega}{\partial q}$$

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System description [qet,]

The potential involves all coulomb interactions:

$$V(r, R) = V_{nn}(R) + V_{ne}(r, R) + V_{ee}(r)$$

r electron positions, R nuclei positions.

$$i\hbar\frac{\partial\Phi}{\partial t}(r, R; t) = \left(-\sum_I \frac{\hbar^2}{2M_I}\frac{\partial^2}{\partial^2 R_I} - \sum_i \frac{\hbar^2}{2m}\frac{\partial^2}{\partial^2 r_i} + V(r, R)\right)\Phi(r, R; t)$$

Born-Opperheim approximation (adiabatic)

Electrons are much faster and more lightweight than nuclei:

$$\Phi(r, R; t) \approx \phi(R)\psi(r|R)e^{-\frac{i\hat{E}t}{\hbar}}$$

System description

$$\left(-\sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial^2 r_i} + V(r, R) \right) \psi(r|R) = E(R)\psi(r|R) \quad \text{electrons}$$

$$\left(-\sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial^2 R_I} + E(R) \right) \phi(R) = \hat{E}\phi(R) \qquad \text{nuclei}$$

We treat nuclei as classical particles, so at equilibrium forces are vanishing:

$$F_I^\alpha = -\frac{\partial E(R)}{\partial R_I^\alpha} = 0$$

Phonon dispersion relation

Expand $E(R)$ around equilibrium positions until order two:

$$\sum_{J,\beta}(C_{IJ}^{\alpha\beta}(R) - M_I\omega^2\delta_{IJ}\delta_{\alpha\beta})U_J^{\beta}(R) = 0 \quad C_{IJ}^{\alpha\beta} = \frac{\partial^2 E(R)}{\partial R_I^\alpha \partial R_J^\beta} \quad (1)$$

a set of independent harmonic oscillators for nuclei I and coordinate α.

- $C_{IJ}^{\alpha\beta}(R)$ are called *inter-atomic force constants*
- $U_J^{\beta}(R)$ represent the oscillation amplitudes
- This is a diagonalization problem!

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Phonon dispersion relation

Taking fourier transform on eq. 1, get an equivalent formulation:

$$\sum_{t,s}(\tilde{C}_{st}^{\alpha\beta}(q) - M_s\Omega^2(q)\delta_{st}\delta_{\alpha\beta})U_t^{\beta}(q) = 0$$

Introduce a perturbation $u_s(q)$:

$$R_l[u_s](q) = R_l + \tau_s + u_s(q)e^{iqR_l}$$

$$\tilde{C}_{st}^{\alpha\beta}(q) = \sum_R e^{-iqR}C_{st}^{\alpha\beta} = \frac{1}{N_c}\frac{\partial^2 E}{\partial u_s^*(q)\partial u_t(q)}$$

Evaluate $\tilde{C}_{st}^{\alpha\beta}(q)$ using DFPT!

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DFPT (density functional perturbation theory)

Introduce a perturbation $\delta V_0(\lambda)$ on the system potential $V(r, R)$, then energy and density can be Taylor expanded:

$$E_\lambda = E + \lambda \frac{\partial E}{\partial \lambda} + \frac{1}{2}\lambda^2 \frac{\partial^2 E}{\partial^2 \lambda} + \dots$$

$$\varrho_\lambda = \varrho + \lambda \frac{\partial \varrho}{\partial \lambda} + \frac{1}{2}\lambda^2 \frac{\partial^2 \varrho}{\partial^2 \lambda} + \dots$$

The linear response can be evaluated as function of the perturbed potential.

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DPFT (density functional perturbation theory)

Corollary of Hellmann-Feynman theorem

$$\frac{\partial^2 E}{\partial \lambda \partial \mu} = \int dr \frac{\partial V(r)}{\partial \lambda} \frac{\partial \varrho(r)}{\partial \mu} + \varrho(r) \frac{\partial^2 V(r)}{\partial \lambda \partial \mu}$$

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DPFT (density functional perturbation theory)

Corollary of Hellmann-Feynman theorem

$$\frac{\partial^2 E}{\partial \lambda \partial \mu} = \int dr \frac{\partial V(r)}{\partial \lambda} \frac{\partial \varrho(r)}{\partial \mu} + \varrho(r) \frac{\partial^2 V(r)}{\partial \lambda \partial \mu}$$

In practice:

- set $\lambda = u_s^\alpha(q)$, $\mu = u_t^\beta$, then find $\tilde{C}_{st}^{\alpha\beta}$.
- the unperturbed electrons' system needs to be relaxed first
- $\forall q$ the perturbed electrons' system needs to be relaxed too!

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DPFT: Dielectric properties

Apply an external electric field to the system $\vec{E}$, then the dielectric tensor can be expressed as a linear response too:

$$\varepsilon_\infty^{\alpha\beta} = \delta_{\alpha\beta} + \frac{1}{N_c}\frac{\partial^2 E}{\partial\vec{E}_\alpha \partial\vec{E}_\beta}$$

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Solve electrons' equation in a crystal [cas,]

Periodic boundary conditions in lattice $\implies$ Bloch plane wave basis:

$$\psi_q^j(r) = \sum_{G}^{|G| < G_{max}} c_q^j(G) \cdot e^{i(q+G)r}, \quad E_{cut\psi} = \frac{\hbar^2 G_{max}^2}{2m}$$

Express the *Kohn-Sham* energy functional:

$$E[\varrho, c_q^j(G)] = (K + E_H + E_{XC} + \delta V_0 + V_{en})[\varrho, c_q^j(G)] + V_{nn}(R)$$

Constraint for $\varrho[c_q^j(G)]$ + *orthonormality* of $c_q^j(G)$.

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Solve electrons' equation in a crystal [cas,]

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Express the *Kohn-Sham* energy functional:

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Constraint for $\varrho[c_q^j(G)]$ + *orthonormality* of $c_q^j(G)$.

$E[\varrho, c_q^j(G)]$ sums over all energy levels: set a **cutoff level** $E_{cut\varrho}$.
Preserve high freq. behaviour: **pseudopotentials**. [cas,]

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Algorithm implemented in Quantum Espresso

Setup: compute unperturbed solution (pw.x).

For a given family of reciprocal vectors $\{q\}$:

- Diagonalize perturbed electrons' equation (ph.x)
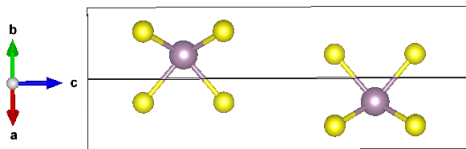- Compute *inter-atomic force constants* in fourier space.

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Algorithm implemented in Quantum Espresso

Setup: compute unperturbed solution (pw.x).

For a given family of reciprocal vectors $\{q\}$:

- Diagonalize perturbed electrons' equation (ph.x)
- Compute *inter-atomic force constants* in fourier space.
- Convert forces into real space (q2r.x).

Algorithm implemented in Quantum Espresso
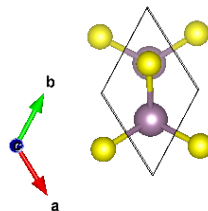
Setup: compute unperturbed solution (`pw.x`).

For a given family of reciprocal vectors $\{q\}$:

- Diagonalize perturbed electrons' equation (`ph.x`)
- Compute *inter-atomic force constants* in fourier space.
- Convert forces into real space (`q2r.x`).
- Diagonalize forces tensor (eq. 1) and get dispersion relation as eigenvalue (`matdyn.x`).

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Crystal structure: overview [Persson, 2016]

(a) Horizontal view.

(b) Vertical view.

Figure 1: Crystal structure visualization of bulk MoS$_2$ restricted to its primitive cell. The primitive cell is *trigonal* shaped. [Momma et al., 2011]

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Crystal structure: parameters [Persson, 2016]

Primitive cell

- $a = b = 3.190$ Å

- $c = 14.879$ Å

- $\alpha = \beta = 90°$

- $\gamma = 120°$

Atoms relative positions

	a	b	c
Mo	0.3333	0.6667	0.25
Mo	0.6667	0.3333	0.75
S	0.3333	0.6667	0.8552
S	0.3333	0.6667	0.6448
S	0.6667	0.3333	0.3552
S	0.6667	0.3333	0.1448

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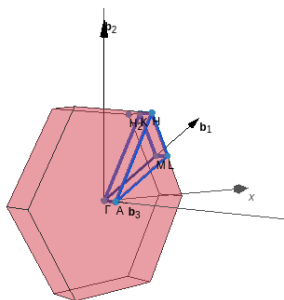## Reciprocal space and phonon calculation path [Hinuma et al., 2017]

Figure 2: Ist brillouin zone of bulk MoS$_2$ (hexagonal). Γ is defined as the center.

High symmetry frequency path
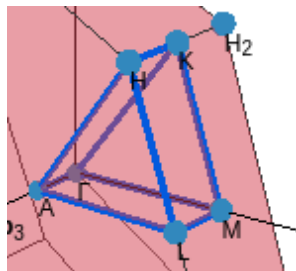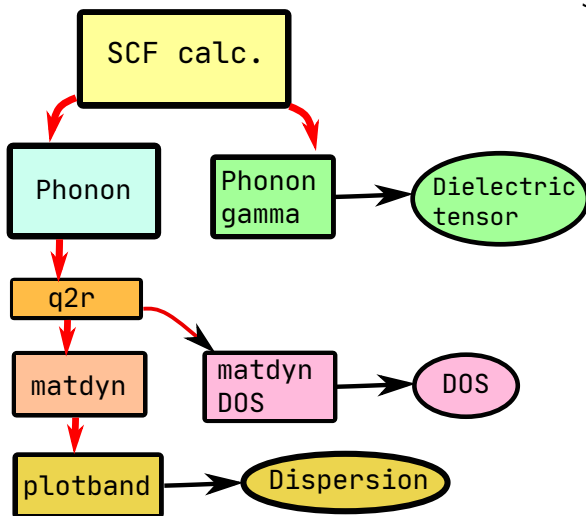
$$\Gamma - M - K - \Gamma - A - L - H - A$$

Figure 3: Path corresponding to the path described above.

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Workflow

Scripts:

- `pw.x`
- `ph.x`
- `q2r.x`
- `matdyn.x`
- `plotband.x`

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Self consistent simulation: system and electron

```
&SYSTEM
  ecutrho =     280
  ecutwfc =     40
  ibrav = 0
  nat = 6
  nosym = .false.
  ntyp = 2
  occupations = 'smearing'
  smearing = 'cold'
  degauss =    1.46d-02
/
```

```
&ELECTRONS
  conv_thr =    1.2-09
  electron_maxstep = 80
  mixing_beta =    0.4
  diago_david_ndim = 4
  scf_must_converge = .true.
/
```

Energy cutoff parameters

- ecutrho: $E_{cut\varrho}$ [Ry].
- ecutwfc: $E_{cut\phi}$ [Ry].

Electron occupation

Allow filling fraction of electrons

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Self consistent simulation: lattice parameters

```
ATOMIC_SPECIES
Mo      95.96      Mo_ONCV_PBEsol-1.0.upf
S       32.065     s_pbesol_v1.4.uspp.F.UPF

ATOMIC_POSITIONS crystal
Mo              0.3333333300        0.6666666700        0.2500000000
Mo              0.6666666700        0.3333333300        0.7500000000
S               0.6666666700        0.3333333300        0.3551740000
S               0.3333333300        0.6666666700        0.8551740000
S               0.6666666700        0.3333333300        0.1448260000
S               0.3333333300        0.6666666700        0.6448260000

K_POINTS {automatic}
    13 13 4 0 0 0

CELL_PARAMETERS angstrom
      3.1903157000        0.0000000000        0.0000000000
     -1.5951578500        2.7628944423        0.0000000000
      0.0000000000        0.0000000000       14.8790040000
```

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Analysis

mos2-bulk.phX.in

```
&inputph
  tr2_ph=1.0d-12,
  niter_ph = 70,
  prefix='mos2-bulk_',
  alpha_mix(1) = 0.4,
  ldisp=.true.,
  fildyn='<output dyn. mat.>',
  nq1=7,nq2=7,nq3=3
/
```

$\Gamma \neq 0$

- ldisp=.false.
- epsil=.true.
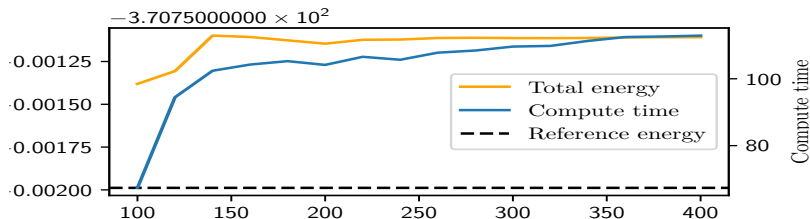- Shift K_POINTS: 1 1 1

matdyn.in

```
&input
   asr='simple',
   amass(1)=95.940000d0,
   amass(2)=32.065000d0,
   flfrc='<q2r input>',
   flfrq='<output>',
   q_in_band_form=.true.,
   q_in_cryst_coord=.true.
/
<k-points integration path>
```
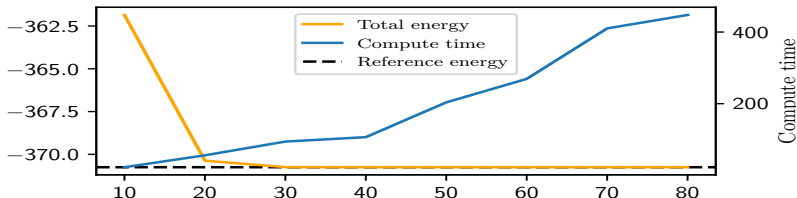
q2r.in

```
&input
  fildyn='<phonon input>',
  zasr='simple',
  flfrc='<output>'
/
```

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`scf` calculations: convergence tests on total energy

(a) Energy cutoff in $U(\rho)$ [Ry].

(b) Energy cutoff in $|\phi_n\rangle$ [Ry].
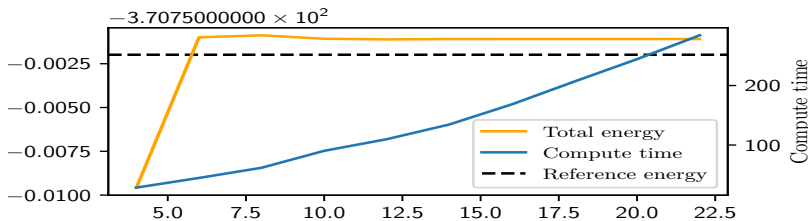
`scf` calculations: convergence tests on total energy

Figure 5: Number of `K_POINTS` discretization along (k_x, k_y).

Advised values by QeTools

- `ecutrho`: 280
- `ecutwfc`: 35
- `K_POINTS`: 12

Reference energy

Increase all values at once:
$E_{ref} = -370.7519 \, \mathrm{Ry}$
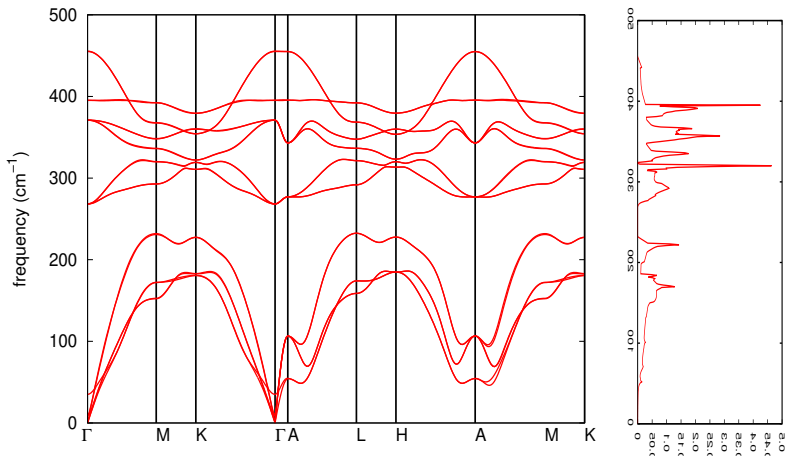
Dispersion relation and DOS

Figure 6: Dispersion relation $\Omega(Q)$ computed along the high symmetry path (frame 17). On the right the density of states (DOS).

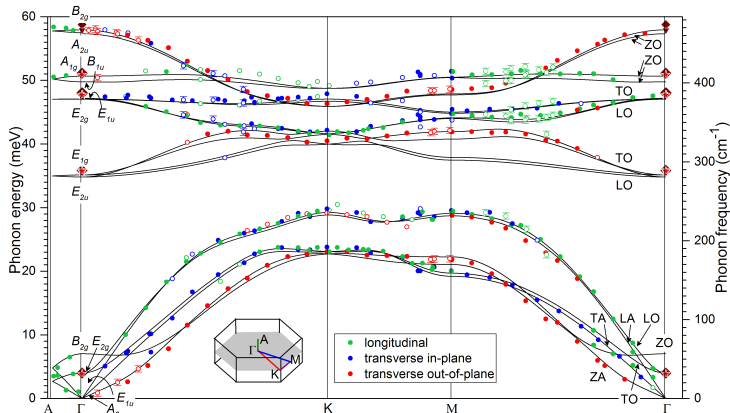# Dispersion relation and DOS: comparison with references

Figure 7: Dispersion relation detected with X-ray Rahman scattering [Tornatzky et al., 2018]. Each color corresponds to a direction.

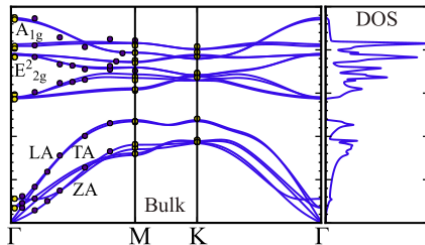## Dispersion relation and `DOS`: comparison with references

Figure 8: Dispersion relation determined by Rahman spectroscopy and a simulated curve [Molina-Sánchez et al., 2015]. Yellow points are experimental data.

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Dielectric tensor

$$\varepsilon = \begin{pmatrix} 12.75 & 0 & 0 \\ 0 & 12.75 & 0 \\ 0 & 0 & 3.29 \end{pmatrix} \quad (2)$$

Error on ε estimation: 0.01
Absolute error with reference
(fig. 9): 0.35

Dielectric Tensor ε_{ij} (total)		
13.00	-0.00	-0.00
-0.00	13.00	0.00
-0.00	0.00	3.27

Figure 9: Reference dielectric tensor
given by *materials project*
[Persson, 2016]

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      Band structure diagram paths based on crystallography.
      Computational Materials Science, 128:140–184.

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      Materials data on mos2 (sg:194) by materials project.
      https://materialsproject.org/docs/calculations.

[Tornatzky et al., 2018]   Tornatzky, H., Gillen, R., Uchiyama, H., and Maultzsch, J. (2018).
      Phonon dispersion of mos2.

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Thank   you!