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Practical Calculations of Phonons with Abinit

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DFPT vs TDEP

- Phonons in a nutshell: compute derivatives of the total energy. Can be analytical or numerical.

- Analytical: solve the Sternheimer equation (aka the « derivative » of the Schrödinger equation).

  Density Functional Perturbation Theory, DFPT (Baroni *et al.*, Rev. Mod. Phys. **73**, 515 (2001))

- Numerical: perform finite differences.

  Finite displacements.

- DFPT:
  - Pros:
    - Analytical most accurate.
    - Calculations on primitive unit cells fastest.
    - Phonons calculated analytically on any **q** point not size dependent.
    - No size dependency defects, alloys, etc.
  - Cons:
    - The maths are ugly hinders implementation (electron correlations, spin-orbit coupling, etc.)
    - No temperature effects extrapolation to finite T with (quasi)harmonic approximation.
    - Not very useful for phases that are dynamically unstable at 0K.

DFPT vs TDEP

- Finite displacements:
  - Pros:
    - Conceptually simple: possible with any *ab initio* code.
    - Finite temperature effects (molecular dynamics)
  - Cons:
    - Numerical less accurate than DFPT.
    - Primitive cell point only. Other **q** points require (very) large supercells.
    - Supercell is be mapped back onto the primitive cell perfect crystals or substitutional defects.
    - *Ab Initio* Molecular Dynamics (AIMD) can take months computationally demanding.

DFPT in Practice...

- Three main steps:
  - Ground State calculation:
    - Relevant keywords: `tolwfr`, `nline`, `nnsclo`, `prtwf`.
    - GS calculation must be VERY accurate (`tolwfr 1e-20`)
  - DFPT calculation at different q points:
    - Relevant keywords: `rfphon`, `rfatpol`, `rfdir`, `qptopt`, `ngqpt`.
  - Post-Processing
    - `mrgddb`: merging of DDB files that contain the dynamical matrices at each qpoint.
    - `anaddb`: Extrapolation to other qpoints for the nice looking final spectrum (but anaddb can actually do plenty of cool stuff)
- Pro tip 1: in DFPT calculation, use a different dataset (`ndtset`) for each qpoint.
- Pro tip 2: The DFPT is the main calculation → use dataset indexes only for the GS calculation.

Phonons in Al: the DFPT Datasets

```
# ================================
# DATASET 2-9: DFPT CALCULATIONS
# ================================

# These are the keywords that apply to all other dataset.


# Some useful stuff to avoid crashing when reading GS wavefunctions...
ecutsm 0.5
dilatmx 1.15

# SCF cycle
nstep 300
ecut 20
pawecutdg 20
tolvrs 1e-07
nband 4

# DFPT keywords
rfphon 1        # The perturbation is phonon-type
rfatpol 1 1     # Index of atoms that will be displaced
rfdir 1 1 1     # Directions of perturbations

iscf 7          # As mentioned above, DFPT calcs use a different
                # SCF algorithm than GS calcs

qptopt 1        # q-point grid generation
ngqpt 4 4 4     # q-point grid
nshiftq 1       # Number of shifts of the q-point grid
shiftq 0 0 0    # Shift of the q-point grid

nqpt 1          # Each DFPT dataset will cover 1 q-point
iqpt: 0         # Starting q-point (0 because the 1st dataset is the GS calc)
iqpt+ 1         # q-point increment (1 because each dataset will compute 1 q-point)
```

Phonons in Al: the GS Dataset

```
# ###################################
# DATASET 1: GROUND STATE CALCULATION
# ###################################

# These are the keywords that apply to the 1st DATASET only.

tolwfr1 1e-20   # GS wavefunctions must be VERY well converged!

nline1 10       # These two keywords will greatly help convergence
nnsclo1 5       # of the wavefunctions

iscf1 17        # The GS calculation uses a different scf algorithm
                # (which is the default algorithm), unlike DFPT calcs

getwfk1 0       # Unlike all other dataset, no need to read the GS
                # wavefunctions

rfphon1 0       # The 1st dataset is a GS calculation,
                # not a DFPT calculation like all the others

nqpt1 0         # No q-point calculation in the GS dataset

kptopt1 1       # Unlike DFPT calcs, the GS dataset can take advantage
                # of all symmetries for the k-point grid generation

prtwf1 1        # We're printing the GS wavefunctions
```

Phonons in Al: Other Variables

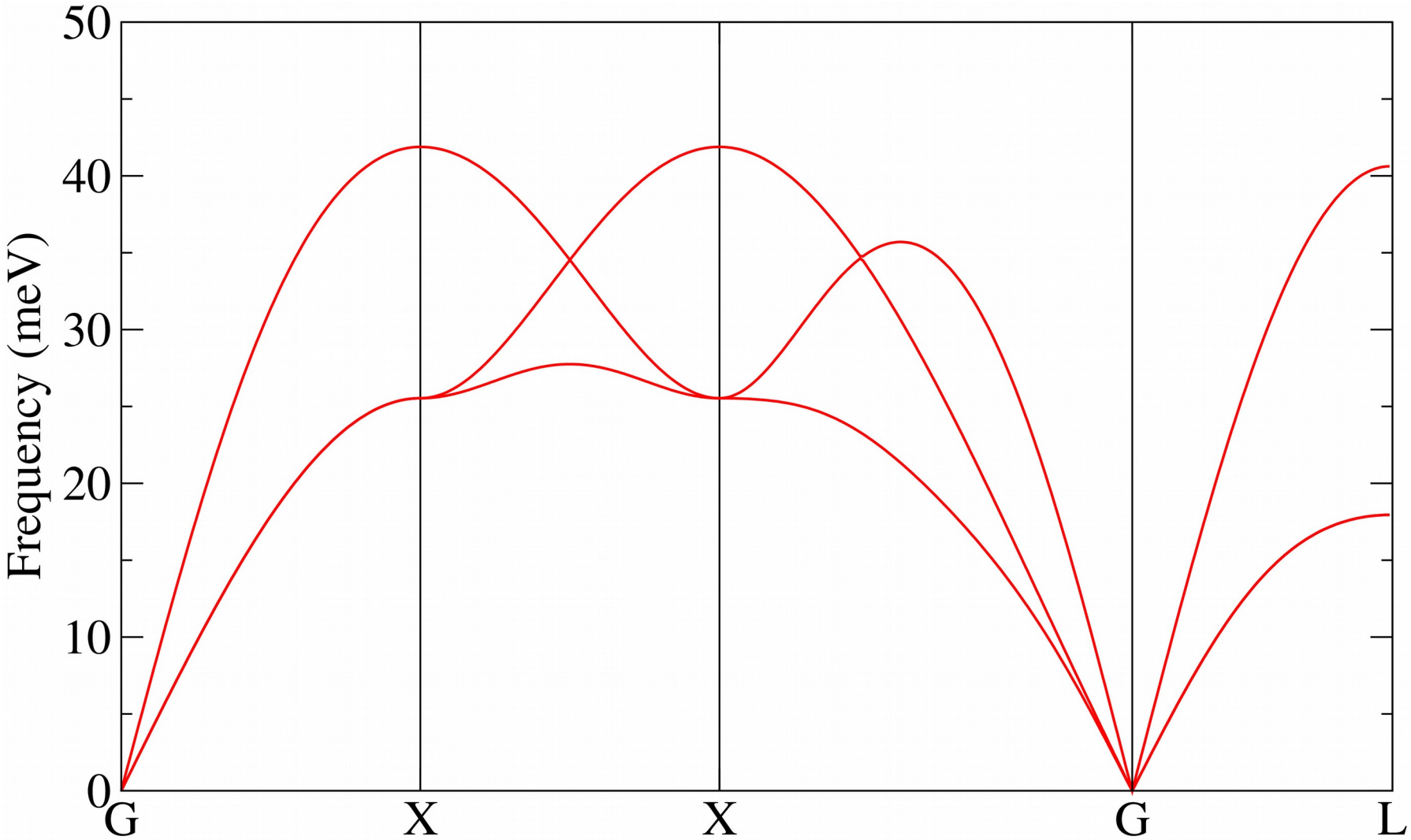
```
# Structural Parameters
natom 1
ntypat 1
typat 1
znucl 13

acell 3*7.52512692850695e+00 Bohr

rprim
 0.0 0.5 0.5
 0.5 0.0 0.5
 0.5 0.5 0.0

xred 3*0

occopt 3
tsmear 1e-03

# K-Point Grid
kptopt2 2       # The 2nd dataset is the Gamma q-point, it can use
                # some symmetries for the k-point grid generation

kptopt 3        # All other DFPT dataset cannot use symmetries
ngkpt 16 16 16
nshiftk 1
shiftk 0 0 0

# Output files
prtwf 0         # Do not print wavefunctions for DFPT calcs
prtden 0        # Do not print density at all
```

MRGDDB / ANADDB

```
mrgddb.out
Nothing
9
output_DS1_DDB
output_DS2_DDB
output_DS3_DDB
output_DS4_DDB
output_DS5_DDB
output_DS6_DDB
output_DS7_DDB
output_DS8_DDB
output_DS9_DDB
```

```
# ANADDB file

ifcflag 1                # Compute the interatomic force constants
                         # This is used to plot the phonon density of states

brav 2                   # The bravais lattice. See abinit website for info
ngqpt 4 4 4              # q-point grid. Must be the same as in the DFPT calc
nqshft 1                 # Number of q-point shifts
q1shft 0 0 0             # q-point shifts

prtdos 1                 # We print the phonon DOS
ng2qpt 32 32 32          # q-point grid for the phonon DOS. It must
                         # be much finer than the first grid. But don't worry
                         # the calculation is extremely fast. You can indulge.

enunit 1                 # Print frequencies in real experimental units,
                         # not some lousy units like Ha

nph1l 425                # Number of q-point for the phonon spectrum

qph1l                    # All q-point coordinates for the phonon spectrum! LOL
                         # I personally use Excel to generate them.
0.0000  0.0000  0.0000  1.0000 # Gamma
0.0050  0.0000  0.0050  1.0000
0.0100  0.0000  0.0100  1.0000
0.0150  0.0000  0.0150  1.0000
0.0200  0.0000  0.0200  1.0000
```

Result : Phonon Spectrum of Al



Phonons in qAgate: condensing modes

- DFPT can be used to calculate phonons in structures with defects. Exemple: diffusion coefficients.
- qAgate can help visualize stuff → cf. Marcus' talk.