Lattice Dynamics from Linear Response

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Density-Functional Perturbation Theory, Phonons & The (L)APW+LO Method

Density-functional perturbation theory (DFPT)

- KS equations: $\left(\hat{\mathbf{h}}_{\mathrm{KS}} - \epsilon_i\right)\, \psi_i(\boldsymbol{r}) = 0\,; \qquad \hat{\mathbf{h}}_{\mathrm{KS}}(\boldsymbol{r}) = -\frac{\boldsymbol{\nabla}^2}{2} + V_{\mathrm{H}}(\boldsymbol{r}) + V_{\mathrm{xc}}(\boldsymbol{r})$
- perturbation series in orders of generic parameter λ

$$\begin{aligned}
\hat{\mathbf{h}}_{\mathrm{KS}}(\lambda) &= \hat{\mathbf{h}}^0_{\mathrm{KS}} + \lambda\, \delta^1 \hat{\mathbf{h}}_{\mathrm{KS}} + \lambda^2\, \delta^2 \hat{\mathbf{h}}_{\mathrm{KS}} + \dots \\
\psi_i(\boldsymbol{r}; \lambda) &= \psi_i^0(\boldsymbol{r}) + \lambda\, \delta^1 \psi_i(\boldsymbol{r}) + \lambda^2\, \delta^2 \psi_i(\boldsymbol{r}) + \dots \\
\epsilon_i(\lambda) &= \epsilon_i^0 + \lambda\, \delta^1 \epsilon_i + \lambda^2\, \delta^2 \epsilon_i + \dots
\end{aligned}$$

- KS equations in 1st order of λ (linear response) → Sternheimer equation

$$\left(\hat{\mathbf{h}}_{\mathrm{KS}} - \epsilon_i\right)\, \delta^1 \psi_i(\boldsymbol{r}) = -\left(\delta^1 \hat{\mathbf{h}}_{\mathrm{KS}} - \delta^1 \epsilon_i\right)\, \psi_i(\boldsymbol{r})$$

→ SCF cycle: $\dots \to \delta^1 n(\boldsymbol{r}) \to \delta^1 v_{\mathrm{KS}}(\boldsymbol{r}) \to \delta^1 \psi_i(\boldsymbol{r}) \to \delta^1 n(\boldsymbol{r}) \to \dots$

DFPT for phonons

- parameter λ: nuclei positions $\boldsymbol{\tau}_{\kappa \boldsymbol{R}}$
- perturbation δ: collective phonon-like displacement of the nuclei

$$\delta_\kappa^{\boldsymbol{q}} : \boldsymbol{\tau}_{\kappa \boldsymbol{R}} \longrightarrow \boldsymbol{\tau}_{\kappa \boldsymbol{R}} + \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}}\, \delta\boldsymbol{\tau}_\kappa$$

$\boldsymbol{\tau}_{\kappa \boldsymbol{R}} = \boldsymbol{\tau}_\kappa + \boldsymbol{R}$: position of atom κ in unit cell $\boldsymbol{R}$

$\boldsymbol{q}$: phonon wavevector

$\delta\boldsymbol{\tau}_\kappa$: small displacement of atom κ

- $\delta_\kappa^{\boldsymbol{q}}$ is a 3-vector
- $\delta_\kappa^{\boldsymbol{q}}$ carries a wavevector $\boldsymbol{q}$
- no super cells required for finite $\boldsymbol{q}$ (in contrast to *frozen phonon* approach)

DFPT for phonons

- solve Sternheimer equation for $\delta_\kappa^{\boldsymbol{q}}\psi_{n\boldsymbol{k}}(\boldsymbol{r})$, $\delta_\kappa^{\boldsymbol{q}} n(\boldsymbol{r})$, and $\delta_\kappa^{\boldsymbol{q}} v_{\mathrm{KS}}(\boldsymbol{r})$
- from them, compute force response $\delta_\kappa^{\boldsymbol{q}} F_{\kappa'\beta}$

$$\begin{aligned}\delta_{\kappa\alpha}^{\boldsymbol{q}} F_{\kappa'\beta} &= \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}} \frac{\partial F_{\kappa'\beta}}{\partial \tau_{\kappa\boldsymbol{R}\alpha}} \\ &= \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}} \frac{\partial^2 E}{\partial \tau_{\kappa\boldsymbol{R}\alpha}\partial \tau_{\kappa' 0\beta}} = \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}} \Phi_{\kappa\alpha,\kappa'\beta}(\boldsymbol{R},\boldsymbol{0}) \\ &= \sqrt{M_\kappa M_{\kappa'}}\, D_{\kappa\alpha,\kappa'\beta}(\boldsymbol{q})\end{aligned}$$

→ force response to phonon-like perturbation → dynamical matrix

- eigenvalue problem: $\boldsymbol{D}(\boldsymbol{q})\,\boldsymbol{e}_{\nu\boldsymbol{q}} = \omega_{\nu\boldsymbol{q}}^2\,\boldsymbol{e}_{\nu\boldsymbol{q}}$ → phonons

DFPT within the (L)APW+LO method - numerical challenges

- atom-position dependent basis → variation of basis functions

$$\delta_\kappa^{\boldsymbol{q}} \psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum_\mu \delta_\kappa^{\boldsymbol{q}} C_\mu^{n\boldsymbol{k}}\, \phi_{\mu\boldsymbol{k}+\boldsymbol{q}}(\boldsymbol{r}) + \sum_\mu C_\mu^{n\boldsymbol{k}}\, \delta_\kappa^{\boldsymbol{q}} \phi_{\mu\boldsymbol{k}}(\boldsymbol{r})$$

- partitioning of unit cell → additional surface integrals (Leibniz integration rule)

$$\delta_\kappa^{\boldsymbol{q}} \int_\Omega f(\boldsymbol{r}) \mathrm{d}^3 r = \int_\Omega \delta_\kappa^{\boldsymbol{q}} f(\boldsymbol{r}) \mathrm{d}^3 r + \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}} \oint_{\partial\kappa\boldsymbol{R}} \left[f^\kappa(\boldsymbol{r}) - f^{\mathrm{I}}(\boldsymbol{r}) \right] \hat{\boldsymbol{e}} \mathrm{d}S$$

- full-potential all-electron → gradient of core states and diverging ionic potential treated explicitly

Phonons & symmetries

- exploit crystal symmetries $\mathcal{S}$ to reduce $\boldsymbol{k}$ and $\boldsymbol{q}$ points → computational cost
- problem: $\mathcal{S}$ mixes $\boldsymbol{q}$-points, atoms and directions: $\mathcal{S}\delta^{\boldsymbol{q}}_{\kappa\alpha} \longrightarrow \sum_{\beta=1}^{3} S_{\alpha\beta}\, \delta^{\boldsymbol{q}'}_{\kappa'\beta}$
  → $N_{\boldsymbol{q}} \times 3N_{\text{at}}$ calculations simultaneously
- 1. only use symmetries that leave $\boldsymbol{q}$ invariant (small group of $\boldsymbol{q}$)
  → only $3N_{\text{at}}$ calculations but more $\boldsymbol{k}$-points
- 2. use symmetry adapted displacement patterns (irreducible representations (irreps))

$$\delta^{\boldsymbol{q}}_{Id} = \sum_{\kappa,\alpha} p_{\kappa\alpha,Id}(\boldsymbol{q})\, \delta^{\boldsymbol{q}}_{\kappa\alpha}$$

  → symmetries only mix members of irrep → only $D \leq 6$ (dimension of irrep) calculations

Fourier interpolation & polar materials

- calculate dynamical matrices $\boldsymbol{D}(\boldsymbol{q})$ on regular $\boldsymbol{q}$-grid
- Fourier transform to real space grid → IFCs

$$\sum_{\boldsymbol{q}} \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}} \sqrt{M_\kappa M_{\kappa'}}\, D_{\kappa\alpha,\kappa'\beta}(\boldsymbol{q}) = \Phi_{\kappa\alpha,\kappa'\beta}(\boldsymbol{R})$$

- inverse transform to arbitrary wavevector $\boldsymbol{q}'$

$$\sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}'\cdot\boldsymbol{R}}\, \Phi_{\kappa\alpha,\kappa'\beta}(\boldsymbol{R}) = \sqrt{M_\kappa M_{\kappa'}}\, D_{\kappa\alpha,\kappa'\beta}(\boldsymbol{q}')$$

- works if IFCs are short-ranged, *i.e.*, $\boldsymbol{\Phi}(\boldsymbol{R}) \approx 0$ for $|\boldsymbol{R}| > R_{\mathrm{max}}$
  → not in polar materials

Fourier interpolation & polar materials

- displacement induces dipoles $\boldsymbol{p} = \boldsymbol{Z}^*_\kappa \cdot \delta\boldsymbol{\tau}_\kappa$
  → long-ranged electric fields screened by $\boldsymbol{\epsilon}^\infty$
- non-analytic contribution to dynamical matrix (algebraic expression)

$$\boldsymbol{D}(\boldsymbol{q}) = \boldsymbol{D}^{\mathcal{S}}(\boldsymbol{q}) + \boldsymbol{D}^{\mathcal{L}}(\boldsymbol{q}; \boldsymbol{Z}^*, \boldsymbol{\epsilon}^\infty)$$

- interpolation using short-ranged IFCs

$$\boldsymbol{\Phi}^{\mathcal{S}}(\boldsymbol{R}) = \sum_{\boldsymbol{q}} \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}} \sqrt{M_\kappa M_{\kappa'}}\, \boldsymbol{D}^{\mathcal{S}}(\boldsymbol{q}) \longrightarrow \sqrt{M_\kappa M_{\kappa'}}\, \boldsymbol{D}^{\mathcal{S}}(\boldsymbol{q}') = \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}'\cdot\boldsymbol{R}}\, \boldsymbol{\Phi}^{\mathcal{S}}(\boldsymbol{R})$$

$$\boldsymbol{D}(\boldsymbol{q}') = \boldsymbol{D}^{\mathcal{S}}(\boldsymbol{q}') + \boldsymbol{D}^{\mathcal{L}}(\boldsymbol{q}'; \boldsymbol{Z}^*, \boldsymbol{\epsilon}^\infty)$$

Summary

$$D_{\kappa\alpha,\kappa'\beta}(\boldsymbol{q}) \longleftarrow \frac{\partial^2 E}{\partial \tau_{\kappa \boldsymbol{R}\alpha} \partial \tau_{\kappa' 0\beta}} = \frac{\partial F_{\kappa'\beta}}{\partial \tau_{\kappa \boldsymbol{R}\alpha}} \longleftarrow \text{phonon perturbation at } \boldsymbol{q}$$

$$Z^*_{\kappa,\alpha\beta} \longleftarrow \frac{\partial^2 E}{\partial \tau_{\kappa\alpha} \partial \mathcal{E}_\beta} = \frac{\partial P_\beta}{\partial \tau_{\kappa\alpha}} \longleftarrow \text{phonon perturbation at } \boldsymbol{\Gamma}$$

$$\epsilon^\infty_{\alpha\beta} \longleftarrow \frac{\partial^2 E}{\partial \mathcal{E}_\alpha \partial \mathcal{E}_\beta} = \frac{\partial P_\beta}{\partial \mathcal{E}_\alpha} \longleftarrow \text{E-field perturbation}$$

Input File for Phonon Calculations

Use of <libxc>

$$\delta^{\boldsymbol{q}}_{\kappa\alpha} V_{\mathrm{xc}}(\boldsymbol{r}) = \int f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}')\, \delta^{\boldsymbol{q}}_{\kappa\alpha} n(\boldsymbol{r}')\, \mathrm{d}^3 r\ , \qquad f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}') = \frac{\delta^2 E_{\mathrm{xc}}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})\, \delta n(\boldsymbol{r}')}$$

- xc-kernel $f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}')$ taken from *libxc*
  → use `<libxc>` instead of `xctype="..."` in `<groundstate>`
- use of *exciting* internal xc-functionals is possible (but not recommended)

```
<input>
  ...
  <groundstate ...>
    <libxc correlation="XC_GGA_C_PBE" exchange="XC_GGA_X_PBE"/>
  </groundstate>
  ...
</input>
```

The <phonons> element

do

- start Sternheimer scf cycle `"fromscratch"`, resume `"fromfile"` or `"skip"` it
- irreps for which dynamical matrices are available are skipped

```
<input>
  ...
  <phonons
    do="fromscratch"
    method="dfpt"
    ngridq="2 2 2"
    polar="true"
    >
  </phonons>
  ...
</input>
```

The <phonons> element

method

- calculate dynamical matrices using linear response (`"dfpt"`) or super-cell calculations (`"sc"`)

```
<input>
  ...
  <phonons
    do="fromscratch"
    method="dfpt"
    ngridq="2 2 2"
    polar="true"
    >
  </phonons>
  ...
</input>
```

The <phonons> element

ngridq

- specify regular grid of phonon wavevectors $\boldsymbol{q}$

$$\boldsymbol{q} = \frac{n_1}{N_1}\boldsymbol{b}_1 + \frac{n_2}{N_2}\boldsymbol{b}_2 + \frac{n_3}{N_3}\boldsymbol{b}_3$$

  with $n_i = 0, \ldots, N_i - 1$ and `ngridq="N1 N2 N3"`

- for `method="dfpt"` $\boldsymbol{k}$- and $\boldsymbol{q}$-grid must be commensurate

```
<input>
  ...
  <phonons
    do="fromscratch"
    method="dfpt"
    ngridq="2 2 2"
    polar="true"
    >
  </phonons>
  ...
</input>
```

The <phonons> element

polar

- calculate Born-effective charge tensors $\boldsymbol{Z}^*_\kappa$ and dielectric tensor $\boldsymbol{\epsilon}^\infty$ and treat material as polar
- applies to `method="dfpt"` only

```
<input>
  ...
  <phonons
    do="fromscratch"
    method="dfpt"
    ngridq="2 2 2"
    polar="true"
    >
  </phonons>
  ...
</input>
```

Basic output files

- `do="fromscratch"` generates dynamical matrices stored in **DYN_Q****_****_****_S**_A***_P*.OUT**
- each file contains a column $D_{:,\kappa\alpha}(\boldsymbol{q})$
  - *Q****_****_**** → $\boldsymbol{q}$-point coordinates on grid
  - *S** → species index of displaced atom κ
  - *A*** → atom index within species of displaced atom κ
  - *P** → Cartesian direction in which atom is displaced
- if `polar="true"` also Born-effective charges $\boldsymbol{Z}^*$ stored in **ZSTAR.OUT** and dielectric tensor $\boldsymbol{\epsilon}^{\infty}$ stored in **EPSINF.OUT** are generated

Basic output files

ZSTAR.OUT

```
# Born effective charge tensors for all atoms.
# Rows correspond to E-field direction.
# Columns correspond to atom displacement direction.
# Acoustic sum rule has been imposed.
#
# species  1 atom   1 (B  1) :      0.000000     0.000000     0.000000
        2.0242834835         0.0000000000         0.0000000000
        0.0000000000         2.0242834835         0.0000000000
        0.0000000000         0.0000000000         2.0242834835
# species  2 atom   1 (N  1) :      0.250000     0.250000     0.250000
       -2.0242834835         0.0000000000         0.0000000000
        0.0000000000        -2.0242834835         0.0000000000
        0.0000000000         0.0000000000        -2.0242834835
# Acoustic sum rule correction (add to each tensor above to get original value)
        0.0005516235         0.0000000000         0.0000000000
        0.0000000000         0.0005516235         0.0000000000
        0.0000000000         0.0000000000         0.0005516235
```

Basic output files

EPSINF.OUT

```
# High frequency dielectric tensor (clamped nuclei).
#
        4.5252791835        0.0000000000        0.0000000000
        0.0000000000        4.5252791835        0.0000000000
        0.0000000000        0.0000000000        4.5252791835
```

Phonon Properties

Phonon frequencies and eigenvectors: `<qpointset>`

- set `do="skip"` once dynamical matrices have been calculated
- add `<qpointset>` inside `<phonons>` to get phonon frequencies and eigenvectors at any $\boldsymbol{q}$-point → **PHONON.OUT**

```
<phonons do="skip" ...>
  <qpointset>
    <qpoint> 0.0 0.0 0.0 </qpoint>
    <qpoint> 0.5 0.5 0.0 </qpoint>
    <qpoint> 0.5 0.5 0.5 </qpoint>
  </qpointset>
</phonons>
```

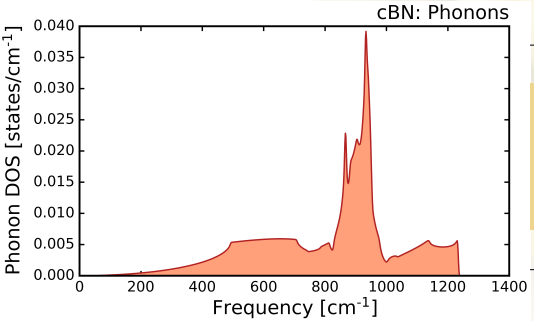
Phonon density of states: <phonondos>

$$D(\omega) = \sum_{\nu} \int_{\mathrm{BZ}} \delta(\omega - \omega_{\nu \boldsymbol{q}}) \, \mathrm{d}^3 q$$

- `ngridqint` → dense integration grid to evaluate BZ integral
- `nwdos` → number of frequency points ω
- `nsmdos` → control smoothing of result

```
<phonons do="skip" ...>
  <phonondos
    ngridqint="70 70 70"
    nwdos="1000"
    nsmdos="2"/>
</phonons>
```

Phonon density of states: <phonondos>



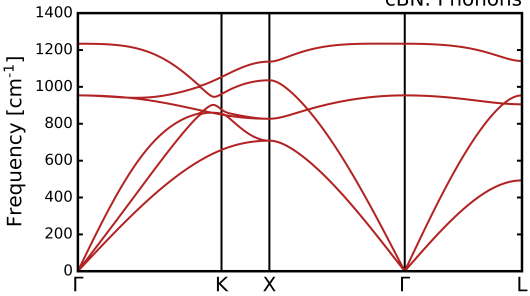

```
<phonons do="skip" ...>
  <phonondos
    ngridqint="70 70 70"
    nwdos="1000"
    nsmdos="2"/>
</phonons>
```

Phonon dispersion: <phonondispplot>

- `steps` → number of steps along path
- `<point>` → list of high-symmetry points along path with respective `coord`inates and `label`

```
<phonons do="skip" ...>
  <phonondispplot>
    <plot1d>
      <path steps="400">
        <point coord="..." label="Gamma"/>
        <point coord="..." label="K"/>
        <point coord="..." label="X"/>
        <point coord="..." label="Gamma"/>
        <point coord="..." label="L"/>
      </path>
    </plot1d>
  </phonondispplot>
</phonons>
```

Phonon dispersion: <phonondispplot>



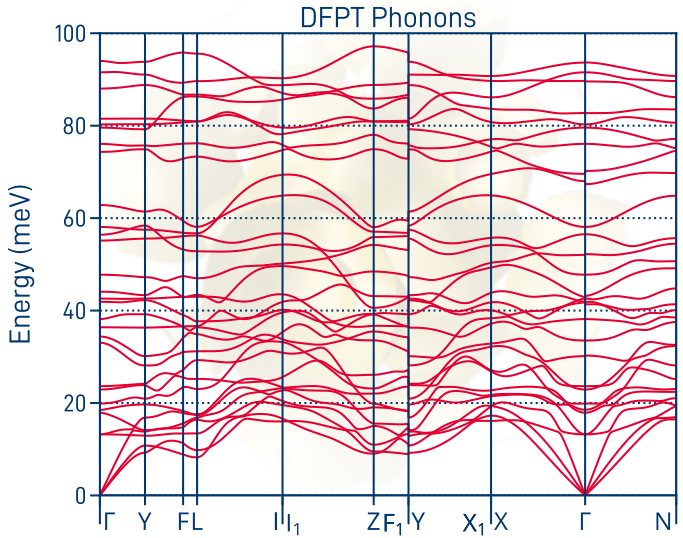

```
<phonons do="skip" ...>
  <phonondispplot>
    <plot1d>
      <path steps="400">
        <point coord="..." label="Gamma"/>
        <point coord="..." label="K"/>
        <point coord="..." label="X"/>
        <point coord="..." label="Gamma"/>
        <point coord="..." label="L"/>
      </path>
    </plot1d>
  </phonondispplot>
</phonons>
```

Thermodynamic properties

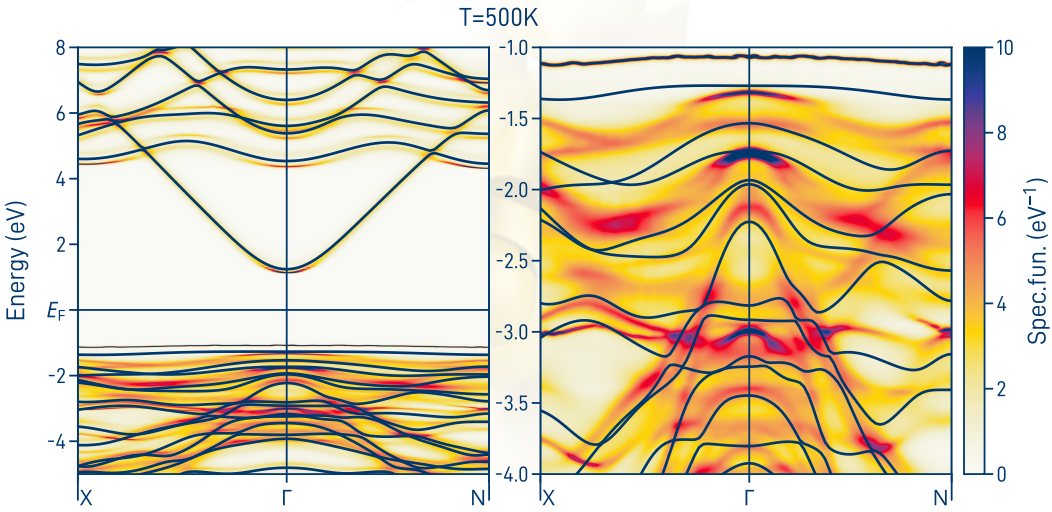
- calculate free energy, entropy and heat capacity as function of temperature derived from phonon DOS

Outlook

More complex materials



Electron–phonon coupling



Questions?