O 61.7: CALCULATION OF PHONON SPECTRA WITH THE FLAPW METHOD USING DENSITY FUNCTIONAL PERTURBATION THEORY

03/29/2023 I ALEXANDER NEUKIRCHEN

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MAX DRIVING THE EXASCALE TRANSITION

RWTH AACHEN UNIVERSITY

JÜLICH Forschungszentrum

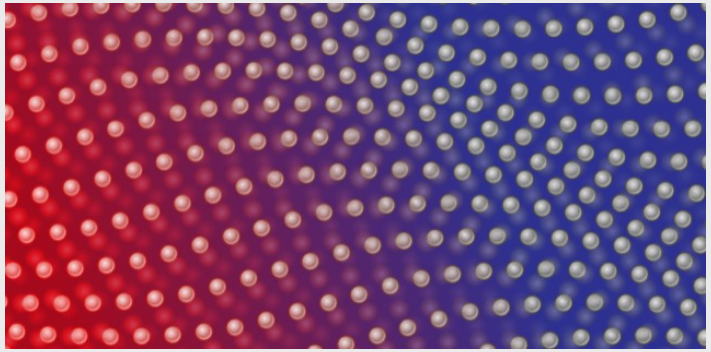
Wandel gestalten

Mitglied der Helmholtz-Gemeinschaft

PHONONS

at the heart of

Heat & Sound

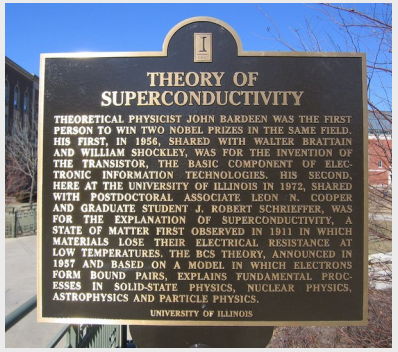


December 2, 2019, APS *Physics* 12, 135, APS / **Alan Stonebraker**

- Specific heat, thermal conductivity and expansion, ...
- Speed of sound, phononic crystals, ...

Electric transport

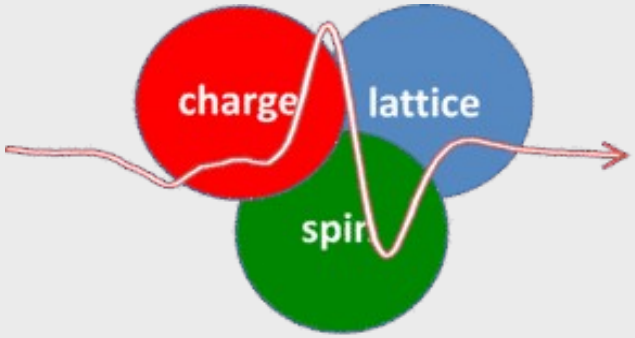
Georg Simon Ohm (wikipedia.org)



University of Illinois (wikipedia.org)

- Classical Ohmic resistance
- Superconductivity

Spin-lattice phenomena



https://www2.physik.uni-bielefeld.de/4560.html

- Spin-relaxation, spin-flip lifetime
- Orbitronics
- Quasiparticles (magnons,...)

ENERGY LANDSCAPE

Central quantities in dealing with phonons

$$E_{\text{tot}} = \int_{\Omega} \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r})\{-V_{\text{eff}}(\boldsymbol{r}) + \frac{1}{2}V_{\text{H}}(\boldsymbol{r}) + V_{\text{ext}}(\boldsymbol{r}) + \varepsilon_{\text{xc}}[\rho(\boldsymbol{r})]\} + \sum_{i\boldsymbol{k}} \tilde{f}_{i\boldsymbol{k}}\varepsilon_{i\boldsymbol{k}} + TS + E_{\text{ion-ion}}$$

Perturbation

$$\begin{aligned} E_{\text{tot}}(\boldsymbol{w}) &= E_{\text{tot}}|_{\boldsymbol{w}=0} + \left[\frac{\partial}{\partial \boldsymbol{w}^T} E_{\text{tot}}|_{\boldsymbol{w}=0}\right] \cdot \boldsymbol{w} + \boldsymbol{w}^T \cdot \left[\frac{1}{2}\frac{\partial^2}{\partial \boldsymbol{w}\partial \boldsymbol{w}^T} E_{\text{tot}}|_{\boldsymbol{w}=0}\right] \cdot \boldsymbol{w} + \ldots \\ &\equiv E_{\text{tot}}^{(0)} + \boldsymbol{E}_{\text{tot}}^{(1)T} \cdot \boldsymbol{w} + \boldsymbol{w}^T \cdot \underline{\boldsymbol{E}}_{\text{tot}}^{(2)} \cdot \boldsymbol{w} + \ldots \end{aligned}$$

Harmonic part:

$$E_{\text{tot}}^{(2)\beta j \alpha i} = \frac{1}{2}\frac{\partial^2 E_{\text{tot}}}{\partial w_{\beta j}\partial w_{\alpha i}}\Big|_{w=0}$$

FINITE DISPLACEMENT

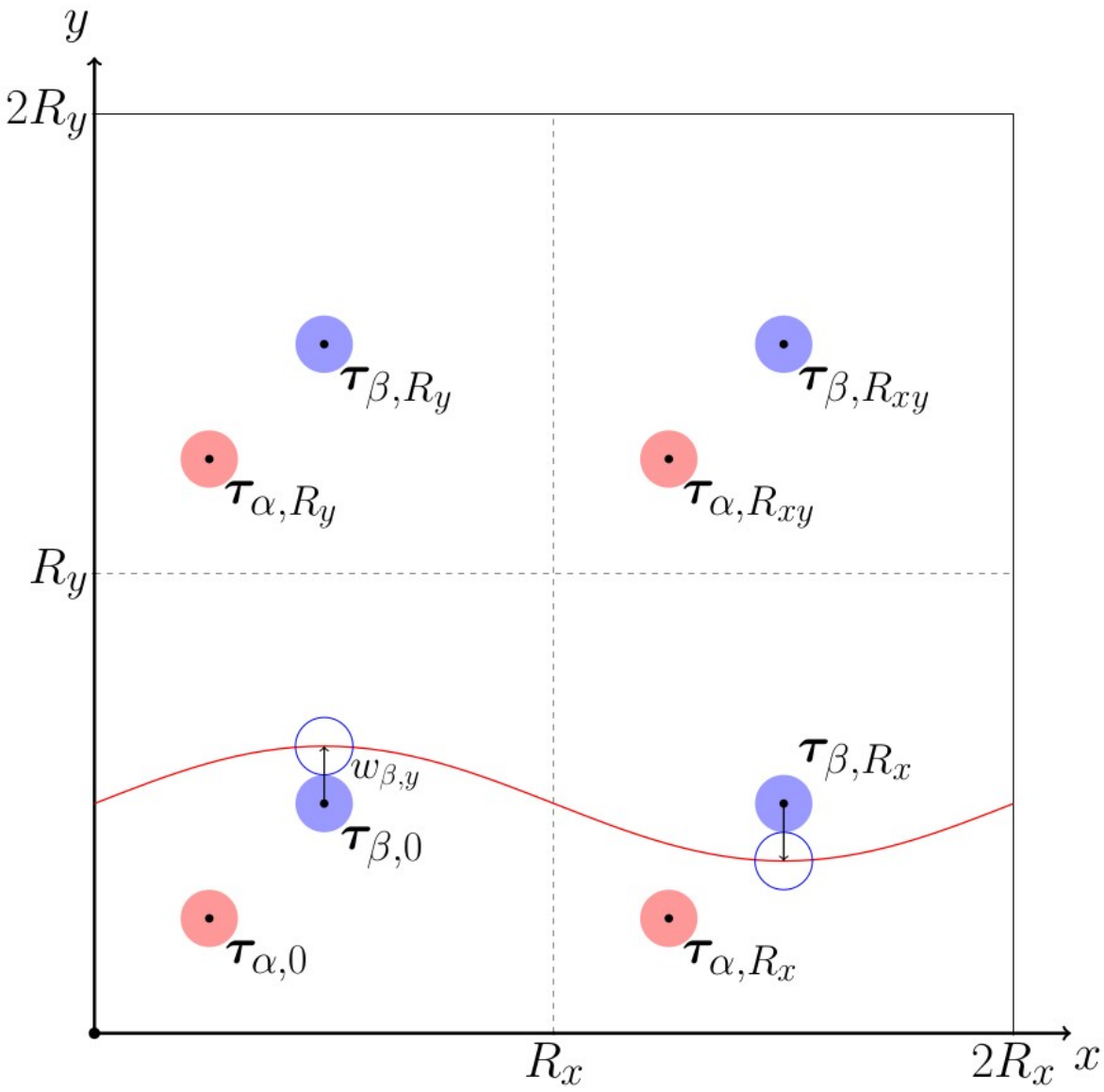
Standard Ab-Initio Method Using Frozen Phonons

First order perturbation ~ Atomic forces:

$$F_{\alpha i} = -\frac{\partial E_{\text{tot}}}{\partial \tau_{\alpha i}}$$

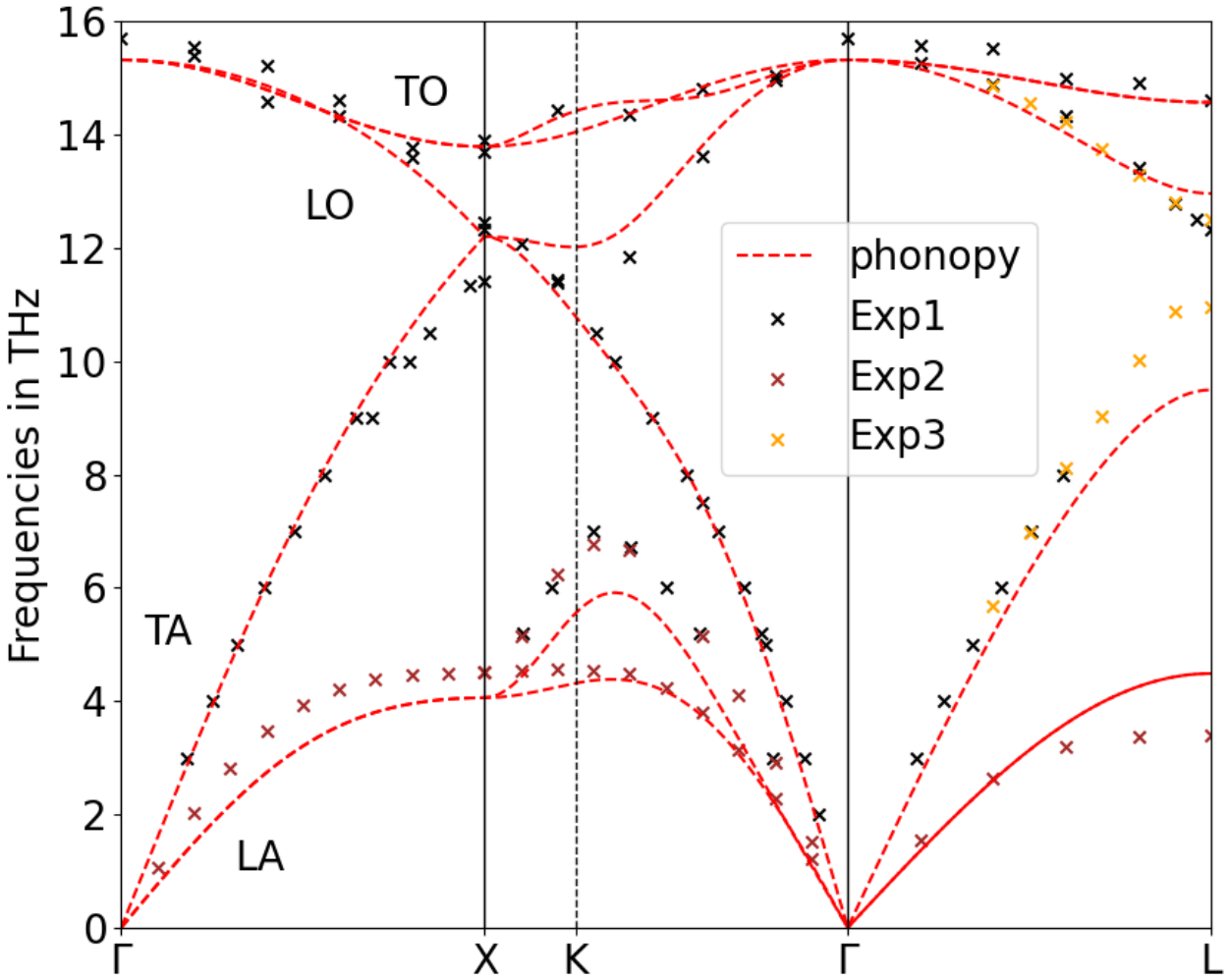
Manually displace atoms and calculate difference quotient:

$$\frac{\partial^2 E_{\text{tot}}}{\partial w_{\beta j} \partial w_{\alpha i}}\Big|_{\boldsymbol{w}=0} \approx -\frac{F_{\alpha i}[\tau_{\beta j} + w_{\beta j}] - F_{\alpha i}[\tau_{\beta j}]}{w_{\beta j}}$$



WORKED EXAMPLE

Silicon with FLEUR+phonopy



https://phonopy.github.io/phonopy/

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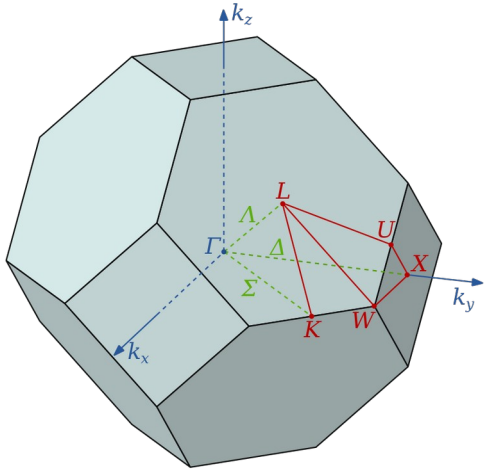
Phonopy constructs displaced supercell(s) from perfect unit cell



FLEUR calculates the forces

Phonopy interpolates a full dispersion

Exp1: Phys. Rev. B 50, 13347
Exp2: Phys. Rev. B 6, 3777
Exp3: Z. Phys.B - CondensedMatter 78, 405-410 (1990)

DENSITY FUNCTIONAL PERTURBATION THEORY

Analytical scheme up to 2nd order

Perturbation of atom αR

$$w_{\alpha R} = Q_\alpha e^{iq\cdot R} + Q_\alpha^* e^{-iq\cdot R}$$

Yields dynamical matrix

$$E_{\mathrm{tot}}(q) = \ldots + Q^\dagger \cdot \underline{D}(q) \cdot Q + \ldots$$

Sternheimer equation

Implicit dependence → explicit self-consistency

$$(H - \varepsilon_{\nu k})|\Psi^{(1)}_{\nu kq}\rangle = -(V^{(1)}(q) - \varepsilon^{(1)}_{\nu k}(q))|\Psi_{\nu k}\rangle$$

OUR METHOD: FLAPW

All-Electron Full-Potential Linearized Augmented Plane-Wave

Core and valence electrons | 1/r singularity

LAPW basis

$$\varphi_{\boldsymbol{kG}}(\boldsymbol{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} \exp(\mathrm{i}(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{r}) & , \boldsymbol{r} \in \mathrm{IR} \\ \sum_{lm\lambda} a_{lm\lambda}^{\boldsymbol{kG}\gamma} u_{l\lambda}^{\gamma}(r_\gamma) Y_l^m(\Omega_\gamma) & , \boldsymbol{r} \in \mathrm{MT}^\gamma \end{cases}$$

Magnetism | 3d- and 4f-electrons | Advanced geometries

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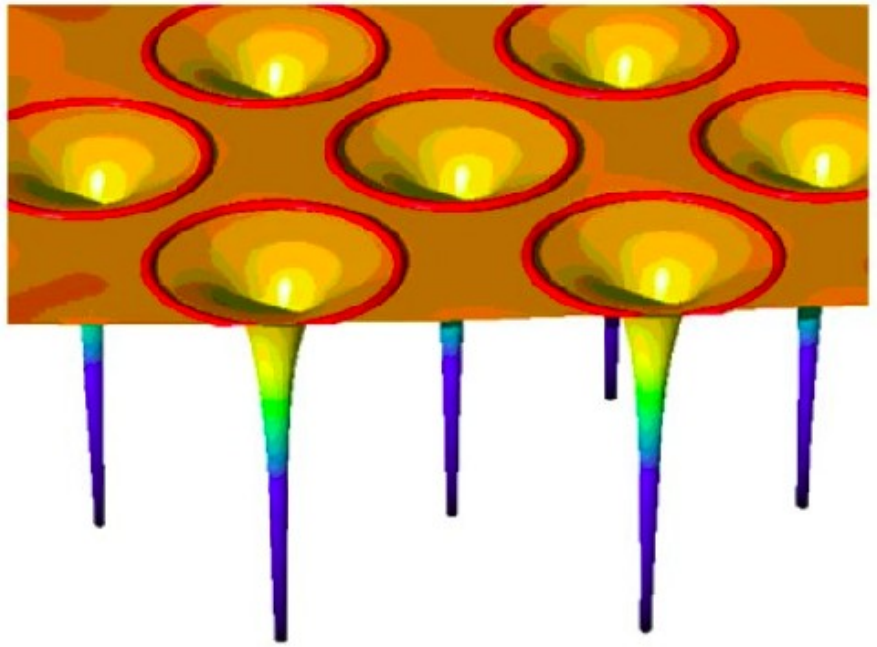


Also in: **Exciting**: R. Kouba et al. Phys. Rev. B 64, 184306 (2001), **Elk**: K. Dewhurst and S. Sharma
Flair: J. H. Lee et al., PhD thesis and Phys. Rev. B 73, 172405 (2006)

Wave function

$$\Psi_{\nu\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} z_{\nu\boldsymbol{kG}} \varphi_{\boldsymbol{kG}}(\boldsymbol{r})$$

First-order wave-function variation

$$\Psi_{\nu\boldsymbol{kq}}^{(1)\beta j+}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} z_{\nu\boldsymbol{kGq}}^{(1)\beta j+} \varphi_{\boldsymbol{kGq}}(\boldsymbol{r}) + z_{\nu\boldsymbol{kG}} \varphi_{\boldsymbol{kG}}^{(1)\beta j}(\boldsymbol{r})$$

Contains: First-order basis variation (displaced atom β)

$$\varphi_{\boldsymbol{kG}}^{(1)\beta j}(\boldsymbol{r}) = \Theta(\boldsymbol{r} \in \mathrm{MT}^\beta)(\mathrm{i}(\boldsymbol{k}+\boldsymbol{G}) - \nabla_j)\varphi_{\boldsymbol{kG}}^{\beta}(\boldsymbol{r})$$

STERNHEIMER EQUATION

Phonons from DFPT within the All-Electron FLAPW Method

$$\left(H(\boldsymbol{kq},\boldsymbol{kq}) - \varepsilon_{\nu\boldsymbol{k}} S(\boldsymbol{kq},\boldsymbol{kq})\right) \cdot \boldsymbol{z}^{(1)\beta\, j+}_{\nu\boldsymbol{kq}}$$
$$= -\left(V^{(1)\beta\, j+}(\boldsymbol{kq},\boldsymbol{k}) - \delta_{\boldsymbol{q}0}\varepsilon^{(1)\beta\, j}_{\nu\boldsymbol{k}} S(\boldsymbol{k},\boldsymbol{k})\right) \cdot \boldsymbol{z}_{\nu\boldsymbol{k}}$$

Also in plane wave basis

FLAPW-specific correction terms

$$+ \sum_{\boldsymbol{G}'\boldsymbol{G}} \hat{\boldsymbol{e}}_{\boldsymbol{G}'} \left(\langle \varphi^{(1)\beta\, j}_{\boldsymbol{kG}'\boldsymbol{q}} | H - \varepsilon_{\nu\boldsymbol{k}} | \varphi^{\beta}_{\boldsymbol{kG}} \rangle_{\mathrm{MT}^\beta} + \langle \varphi^{\beta}_{\boldsymbol{kGq}} | H - \varepsilon_{\nu\boldsymbol{k}} | \varphi^{(1)\beta\, j}_{\boldsymbol{kG}} \rangle_{\mathrm{MT}^\beta} \right) \hat{\boldsymbol{e}}^{T}_{\boldsymbol{G}} \cdot \boldsymbol{z}_{\nu\boldsymbol{k}}$$

$$+ \sum_{\boldsymbol{G}'\boldsymbol{G}} \hat{\boldsymbol{e}}_{\boldsymbol{G}'} \left(\int_{\mathrm{MT}^\beta} \mathrm{d}\boldsymbol{r}\, \nabla_j \varphi^{\beta *}_{\boldsymbol{kG}'\boldsymbol{q}} (H - \varepsilon_{\nu\boldsymbol{k}}) \varphi^{\beta}_{\boldsymbol{kG}} + \int_{\Omega} \mathrm{d}\boldsymbol{r}\, \Theta^{(1)\beta\, j+} \varphi^{IR*}_{\boldsymbol{kG}'\boldsymbol{q}} (H - \varepsilon_{\nu\boldsymbol{k}}) \varphi^{IR}_{\boldsymbol{kG}} \right) \hat{\boldsymbol{e}}^{T}_{\boldsymbol{G}} \cdot \boldsymbol{z}_{\nu\boldsymbol{k}}$$

Resulting dynamical matrix:

$$D^{\beta\, j+,\alpha i-}(\boldsymbol{q}) = \frac{1}{2}\left\{ \int_{\Omega} \mathrm{d}\boldsymbol{r}\, \rho^{(1)\beta+j} V^{(1)\alpha-}_{\mathrm{ext}} + \ldots + \sum_{\boldsymbol{k}} D^{\beta\, j+,\alpha i-}_{\boldsymbol{k}}(\boldsymbol{q}) + D^{\beta\, j+,\alpha i-}_{\text{ion-ion}}(\boldsymbol{q}) \right\}$$

COMPUTATIONAL METHODS

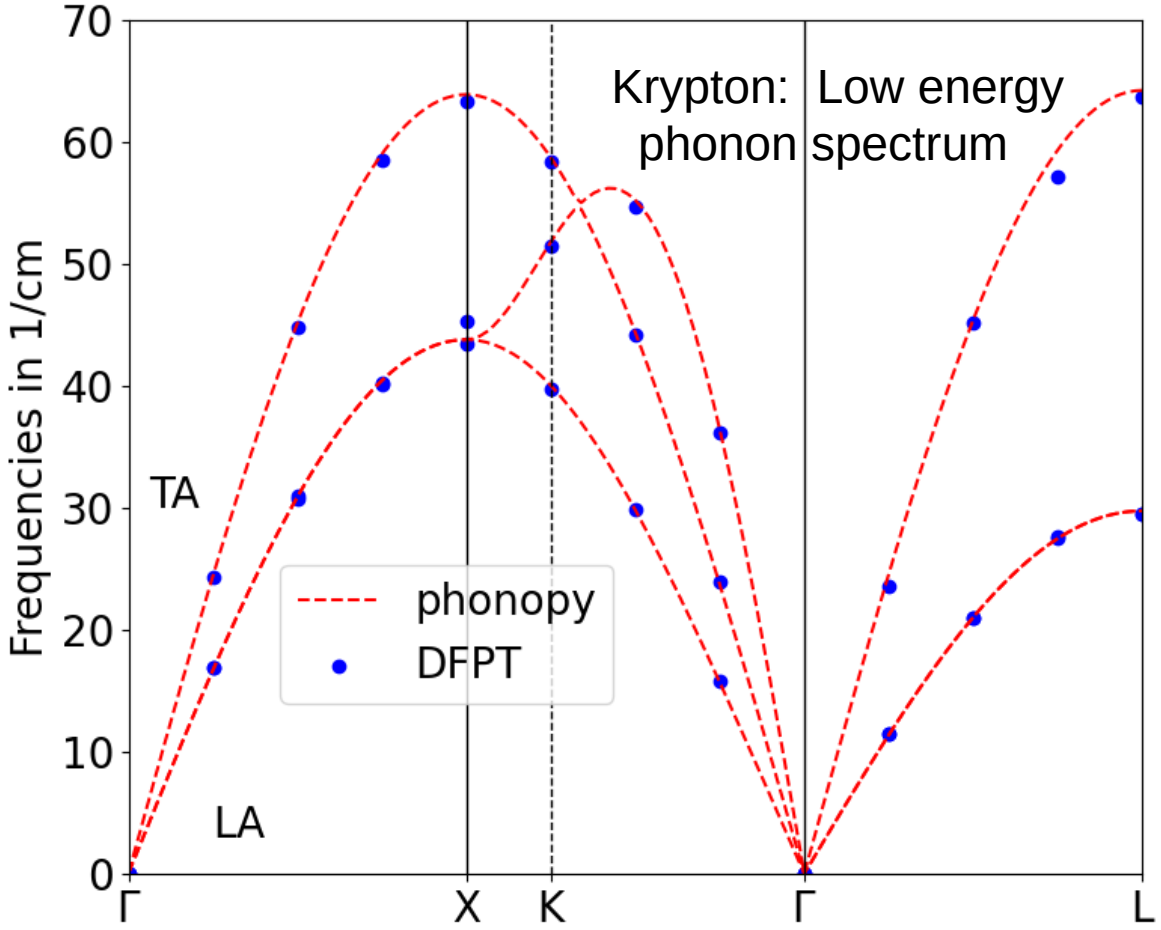
Phonons from DFPT within the All-Electron FLAPW Method

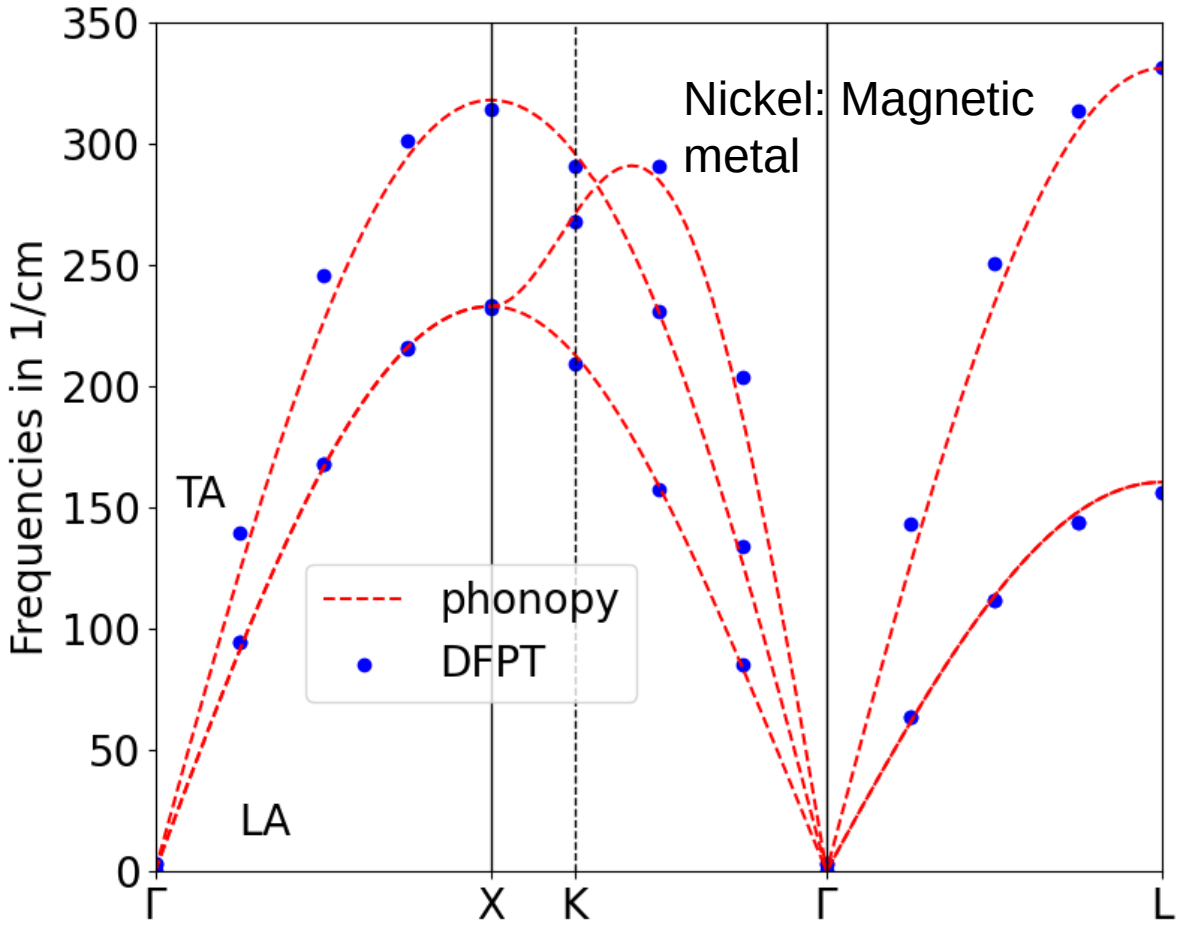
Coulomb singularity	Weinert (J. Math. Phys. 22, 2433 (1981))
Basis set variation	Pulay (Molec. Phys. 17, 2 (1969))
Application to variations	Klüppelberg (FZJ Key technologies 119 (2015))
Different orders of magnitude in energy	Reformulations for required precision Cancellation of volatile gradient terms (incomplete basis vs surfaces)

Initial FLEUR implementation by Christian-Roman Gerhorst as juPhon package (thesis 2022, to be published)

RESULTS

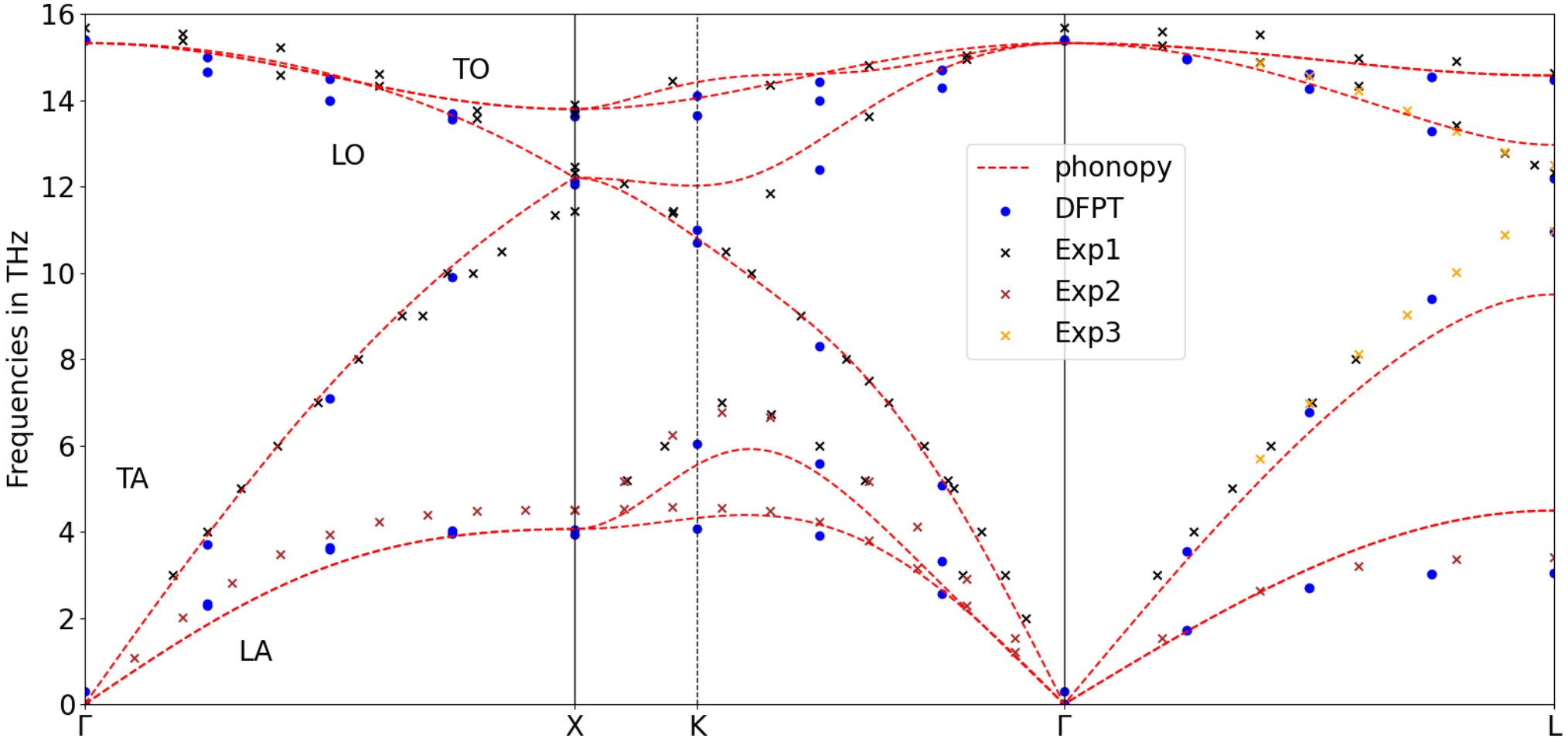
Comparison of DFPT (FLEUR) with Finite Displacement (FLEUR+phonopy)





SILICON REVISITED

Improving upon problematic regions



HIGHLIGHTS

Take-home messages

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Successful ab-initio DFPT implementation within the all-electron FLAPW framework:
DFPT results based on the the all-electron FLAPW DFT code FLEUR (albeit still WIP)

All electron code:
Full potential, 3d- and 4f-electrons, complex geometries

Comparetively small magnitude of total energy variation mastered:
Pulay and surface terms, analytical cancellations

Wide range of possible further developments:
Complex magnetism, quasiparticle interactions

See you in Jülich:

Hands-on Tutorial

8th May-12th May 2023

www.flapw.de/handson