

# PHONONS IN THE ELK CODE



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*“If you are allowed to measure only one property of a material, make sure it’s the - - - - - ”*

A. Einstein

*“If you are allowed to measure only one property of a material, make sure it’s the heat capacity”*

A. Einstein

## Why phonons?

- ▶ Measured directly with inelastic neutron scattering
- ▶ Thermodynamic quantities at low temperature: heat capacity, entropy, free energy, zero-point
- ▶ Phase transitions from the Gibb's free energy:

$$G(P, T) = E + PV - TS$$

- ▶ Imaginary phonon frequencies indicate lattice instabilities
- ▶ Elastic tensor from  $q \rightarrow 0$  limit of phonon dispersion
- ▶ Thermal expansion coefficient (from mode Grüneisen parameters)
- ▶ Temperature dependence of the band gap
- ▶ Static polarization  $\epsilon(\omega = 0)$
- ▶ Electron-phonon coupling
- ▶ Superconductivity

The ‘equilibrium positions’ of our crystal are the minimum of the Born-oppenheimer potential energy surface:

$$\left( \hat{T}_e + \hat{V}_{e-n}(\underline{\mathbf{R}}) + \hat{V}_{e-e} + E_{n-n}(\underline{\mathbf{R}}) \right) \Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}}) = E(\underline{\mathbf{R}}) \Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}})$$

This is an artificial construct and in some cases may be a poor approximation to the average nuclear positions obtained from the correlated electron-nuclear wavefunction  $\Psi(\underline{\mathbf{r}}, \underline{\mathbf{R}})$

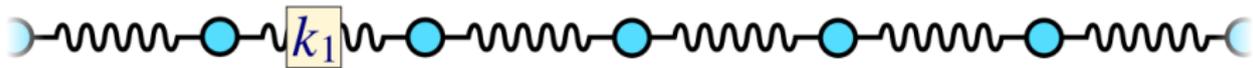
Recent work entitled ‘Exact Factorization of the Time-Dependent Electron-Nuclear Wave Function’ [A. Abedi, N. T. Maitra, and E. K. U. Gross, *Phys. Rev. Lett.* **105**, 123002 (2010)] may make it easier to handle these cases

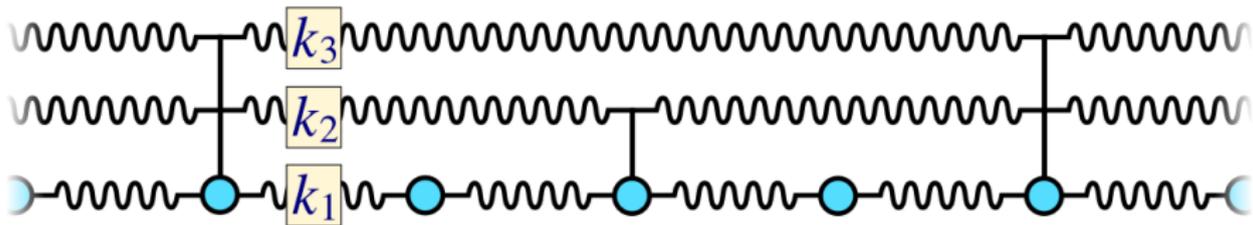
Let's assume that the potential energy surface is harmonic:

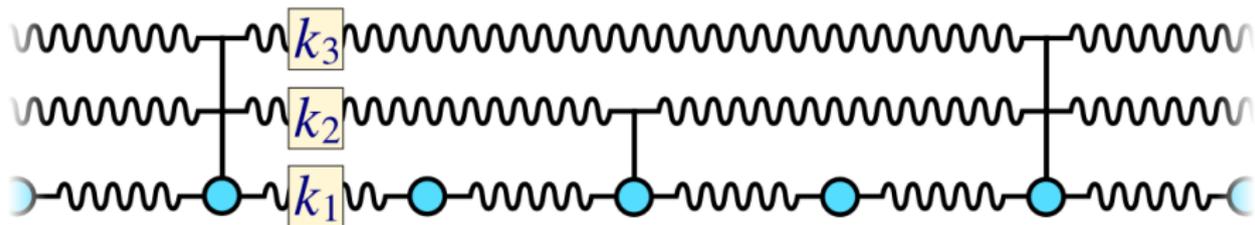
$$E(\underline{\mathbf{R}}) = \underline{\mathbf{U}}^t C \underline{\mathbf{U}} + E(\underline{\mathbf{R}}_0),$$

where  $\underline{\mathbf{U}} \equiv \underline{\mathbf{R}} - \underline{\mathbf{R}}_0$

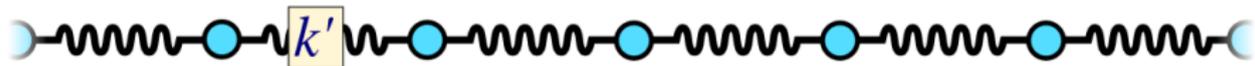








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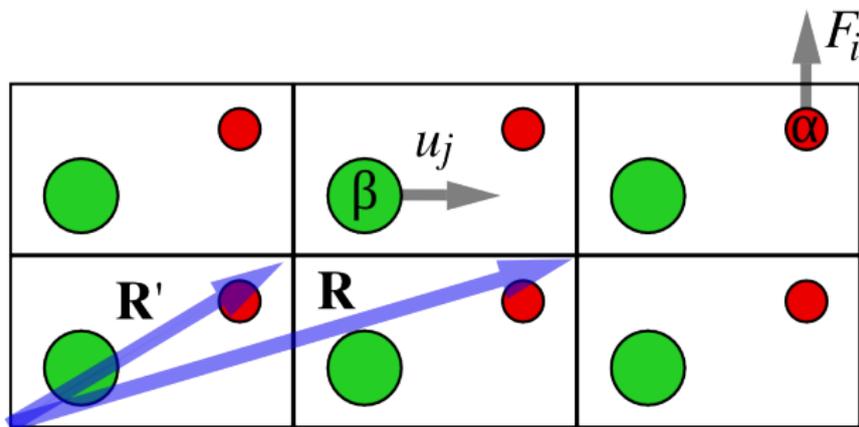


## Elastic matrix

We have to determine the spring constants between atoms:

$$\begin{aligned} C_{\alpha i, \beta j}(\mathbf{R} - \mathbf{R}') &= \frac{\partial^2 E}{\partial u_{\alpha i}(\mathbf{R}) \partial u_{\beta j}(\mathbf{R}')} \\ &= -\frac{\partial F_{\alpha i}(\mathbf{R})}{\partial u_{\beta j}(\mathbf{R}')} \end{aligned}$$

for atoms  $\alpha$ ,  $\beta$ , polarisations  $i$ ,  $j$  and primitive vectors  $\mathbf{R}$ ,  $\mathbf{R}'$



Thus

$$E = E_0 + \frac{1}{2} \sum_{\substack{\alpha i \mathbf{R} \\ \beta j \mathbf{R}'}} C_{\alpha i, \beta j}(\mathbf{R} - \mathbf{R}') u_{\alpha i}(\mathbf{R}) u_{\beta j}(\mathbf{R}') + \dots$$

(no linear term)

Equation of motion:

$$M_\alpha \frac{\partial^2}{\partial t^2} u_{\alpha i}(\mathbf{R}) = - \sum_{\beta j \mathbf{R}'} C_{\alpha i, \beta j}(\mathbf{R} - \mathbf{R}') u_{\beta j}(\mathbf{R}')$$

Use the ansatz

$$u_{\alpha i}(\mathbf{R}) = \frac{1}{\sqrt{2M_\alpha}} \left[ e_{\alpha i}(\mathbf{q}) \exp(i(\mathbf{q} \cdot \mathbf{R} - \omega(\mathbf{q})t)) + \text{c.c.} \right]$$

to get

$$D_{\alpha i, \beta j}(\mathbf{q}) e_{\alpha i}(\mathbf{q}) = \omega^2(\mathbf{q}) e_{\alpha i}(\mathbf{q})$$

where

$$D_{\alpha i, \beta j}(\mathbf{q}) = \frac{1}{\sqrt{M_\alpha M_\beta}} \sum_{\mathbf{R}} \exp(i\mathbf{q} \cdot \mathbf{R}) C_{\alpha i, \beta j}(\mathbf{R})$$

*Ab-initio* approaches for computing the dynamical matrix

- ▶ Supercell Parlinski-Li-Kawazoe method: random displacements and least-squares fitting (Wien2k, VASP)
- ▶ Supercell with molecular dynamics (Fourier transform of trajectories)
- ▶ Supercell method used in Elk
- ▶ Density functional perturbation theory (DFPT)

# Density functional perturbation theory (DFPT)

Start with the Hellmann-Feynman theorem

Let the Hamiltonian depend on some parameter  $\lambda$ , therefore

$$E_\lambda = \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle,$$

where  $\Psi_\lambda$  is the ground-state of  $\hat{H}_\lambda$

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Take the derivative

$$\begin{aligned} \frac{\partial E_\lambda}{\partial \lambda} &= \langle \Psi_\lambda | \partial_\lambda \hat{H}_\lambda | \Psi_\lambda \rangle + \langle \partial_\lambda \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle + \langle \Psi_\lambda | \hat{H}_\lambda | \partial_\lambda \Psi_\lambda \rangle \\ &= \langle \Psi_\lambda | \partial_\lambda \hat{H}_\lambda | \Psi_\lambda \rangle + \partial_{\lambda'} \langle \Psi_{\lambda'} | \hat{H}_\lambda | \Psi_{\lambda'} \rangle \Big|_{\lambda'=\lambda} \end{aligned}$$

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$$\begin{aligned} \frac{\partial E_\lambda}{\partial \lambda} &= \langle \Psi_\lambda | \partial_\lambda \hat{H}_\lambda | \Psi_\lambda \rangle + \langle \partial_\lambda \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle + \langle \Psi_\lambda | \hat{H}_\lambda | \partial_\lambda \Psi_\lambda \rangle \\ &= \langle \Psi_\lambda | \partial_\lambda \hat{H}_\lambda | \Psi_\lambda \rangle + \underbrace{\partial_{\lambda'} \langle \Psi_{\lambda'} | \hat{H}_\lambda | \Psi_{\lambda'} \rangle}_{=0} \Big|_{\lambda'=\lambda} \end{aligned}$$

# Density functional perturbation theory (DFPT)

Only the external potential depends on  $\lambda$

$$\hat{H}_\lambda = \hat{T} + \hat{V}_{\text{ext}}^\lambda + \hat{V}_{e-e}$$

Therefore

$$\begin{aligned}\frac{\partial}{\partial \lambda} \hat{H}_\lambda &= \frac{\partial}{\partial \lambda} \hat{V}_{\text{ext}}^\lambda \\ \Rightarrow \frac{\partial E_\lambda}{\partial \lambda} &= \langle \Psi_\lambda | \partial_\lambda \hat{V}_{\text{ext}}^\lambda | \Psi_\lambda \rangle\end{aligned}$$

Thus finally

$$\frac{\partial E_\lambda}{\partial \lambda} = \int d^3r \rho_\lambda(\mathbf{r}) \frac{\partial}{\partial \lambda} V_{\text{ext}}^\lambda(\mathbf{r})$$

for all  $\lambda$

# Density functional perturbation theory (DFPT)

Taking another derivative:

$$\frac{\partial^2 E_\lambda}{\partial \lambda^2} = \int d^3r \frac{\partial}{\partial \lambda} \rho_\lambda(\mathbf{r}) \frac{\partial}{\partial \lambda} V_{\text{ext}}^\lambda(\mathbf{r}) + \int d^3r \rho_\lambda(\mathbf{r}) \frac{\partial^2}{\partial \lambda^2} V_{\text{ext}}^\lambda(\mathbf{r})$$

Difficult part:

$$\frac{\partial \rho_\lambda(\mathbf{r})}{\partial \lambda}$$

# Density functional perturbation theory (DFPT)

Recall the Kohn-Sham density is equal to the exact density

$$\rho(\mathbf{r}) = \sum_i \phi_i^*(\mathbf{r})\phi_i(\mathbf{r})$$

So we get the linearised Kohn-Sham equations:

$$\begin{aligned}\Delta e_i &= \langle \phi_i | \Delta V_s | \phi_i \rangle \\ (H - \varepsilon_i) | \phi_i \rangle &= -(\Delta H - \Delta \varepsilon_i) | \phi_i \rangle \\ \Delta \rho(\mathbf{r}) &= \sum_i \Delta \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}) + \phi_i^*(\mathbf{r})\Delta \phi_i(\mathbf{r}) \\ \Delta V_s(\mathbf{r}) &= \Delta V_{\text{ext}}(\mathbf{r}) + \Delta V_H(\mathbf{r}) + \int d^3 r' \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})\delta \rho(\mathbf{r}')} \Delta \rho(\mathbf{r})\end{aligned}$$

# Density functional perturbation theory (DFPT)

If the perturbing potential is of the form

$$\Delta V_{\text{ext}}(\mathbf{r}) = -\frac{\partial}{\partial \tau_{\alpha i}} \sum_{\mathbf{R}} \frac{Z_{\alpha}}{|\mathbf{r} + \mathbf{R} - \boldsymbol{\tau}_{\alpha}|} \cos(\mathbf{q} \cdot \mathbf{R})$$

then Bloch state  $|\phi_{i\mathbf{k}}\rangle$  is coupled to states  $|\phi_{i\mathbf{k}+\mathbf{q}}\rangle$  and  $|\phi_{i\mathbf{k}-\mathbf{q}}\rangle$   
the density derivative is

$$\Delta \rho(\mathbf{r}) = \Delta \rho_c(\mathbf{r}) \cos(\mathbf{q} \cdot \mathbf{r}) + \Delta \rho_s(\mathbf{r}) \sin(\mathbf{q} \cdot \mathbf{r})$$

and the same for  $\sin(\mathbf{q} \cdot \mathbf{R})$

# Density functional perturbation theory (DFPT)

We can also use perturbations of the form

$$\Delta V_{\text{ext}}(\mathbf{r}) = -\frac{\partial}{\partial \tau_{\alpha i}} \sum_{\mathbf{R}} \frac{Z_{\alpha}}{|\mathbf{r} + \mathbf{R} - \boldsymbol{\tau}_{\alpha}|} \exp(i\mathbf{q} \cdot \mathbf{R})$$

in which case  $|\phi_{i\mathbf{k}}\rangle$  is coupled to  $|\phi_{i\mathbf{k}+\mathbf{q}}\rangle$  only, and the density derivative is

$$\Delta \rho(\mathbf{r}) = \Delta \tilde{\rho}(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r})$$

and the effective potential derivative is also

$$\Delta V_s(\mathbf{r}) = \Delta \tilde{V}_s(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r})$$

$\Delta \tilde{\rho}$  and  $\Delta V_s$  are lattice periodic

# Density functional perturbation theory (DFPT)

This is very efficient, in the same way that spin-spirals are efficient for incommensurate magnetic structures

The APW basis set depends on the atomic positions – Pulay corrections make implementation of phonons difficult

Previous implementations

- ▶ Henry Krakauer, Rici Yu and Cheng-Zhang Wang
- ▶ Robert Kouba and Claudia Ambrosch-Draxl in Wien2k

Supercell	Linear response
Slow	Fast

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<sup>1</sup>Can be used for thermally stabilizing unstable phases: P. Souvatzis *et al.* 2009 J. Phys.: Condens. Matter **21** 175402

Supercell	Linear response
Slow Easy to implement	Fast Hard to implement

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Supercell	Linear response
Slow Easy to implement Works with all features	Fast Hard to implement Works with fewer features

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Supercell	Linear response
Slow Easy to implement Works with all features Does not require $f_{xc}$	Fast Hard to implement Works with fewer features Requires $f_{xc}$

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Supercell	Linear response
Slow Easy to implement Works with all features Does not require $f_{xc}$ Can include anharmonicity <sup>1</sup>	Fast Hard to implement Works with fewer features Requires $f_{xc}$ Purely harmonic

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## Phonons in Elk

Elk uses an efficient supercell method:

1. Finds the smallest supercell which contains the  $\mathbf{q}$ -vector perturbation
2. then performs calculations with cos-like and sin-like finite displacements
3. computes forces on all atoms and Fourier transforms to generate dynamical matrix rows
4. gathers all the dynamical matrix rows together to produce a phonon dispersion

## Phonons in Elk

This can be run across hundreds of computers sharing a common file system

Each computer checks for the presence of a particular **DYN** file

For example:

**DYN\_Q0104\_0104\_0102\_S02\_A002\_P3.OUT**

(means  $\mathbf{q} = (\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ ,  $\alpha = (1, 2)$ ,  $i = 3$ )

If it does not exist then the computer runs this task

## Phonons in Elk

The phonon dispersion is obtained by Fourier transforming the dynamical matrices to real space:

$$D_{\alpha i, \beta j}(\mathbf{R}) = \sum_{\mathbf{q}} D_{\alpha i, \beta j}(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{R}),$$

evaluating the matrix at an arbitrary  $\mathbf{q}$ -vector:

$$D_{\alpha i, \beta j}(\mathbf{q}') = \sum_{\mathbf{R}} D_{\alpha i, \beta j}(\mathbf{R}) \exp(-i\mathbf{q}' \cdot \mathbf{R}),$$

and diagonalising

The acoustic sum rule is always enforced (acoustic branches go to zero)

LO-TO splitting in polar semiconductors is not yet in Elk

# Phonons in Elk

First-variational Hamiltonian (bordered band diagonal):

	$k_1$	$k_2$	$k_3$	$k_4$	$k_5$	<i>l.o.</i>
$k_1$						
$k_2$						
$k_3$						
$k_4$						
$k_5$						
<i>l.o.</i>						

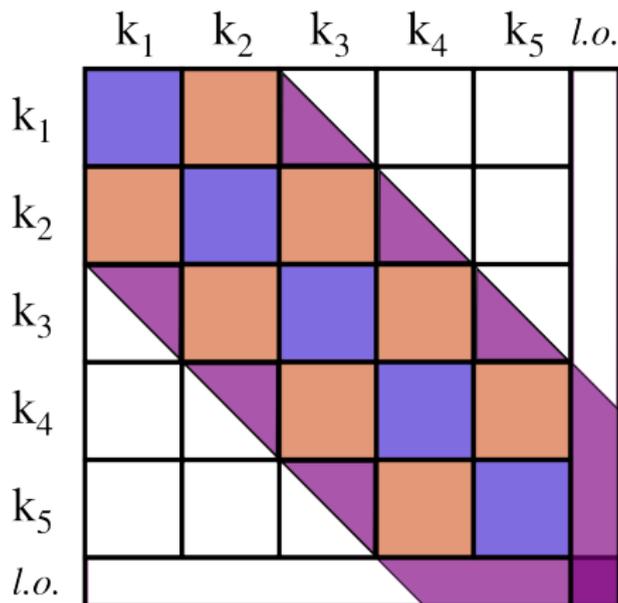
# Phonons in Elk

First-variational Hamiltonian (bordered band diagonal):

	$k_1$	$k_2$	$k_3$	$k_4$	$k_5$	<i>l.o.</i>
$k_1$	Blue	Orange	White	White	White	Purple
$k_2$	Orange	Blue	Orange	White	White	
$k_3$	White	Orange	Blue	Orange	White	
$k_4$	White	White	Orange	Blue	Orange	
$k_5$	White	White	White	Orange	Blue	
<i>l.o.</i>	Purple					

# Phonons in Elk

First-variational Hamiltonian (bordered band diagonal):



Elk also calculates

- ▶ Phonon density of states
- ▶ Heat capacity
- ▶ Entropy
- ▶ Free energy
- ▶ Zero point energy

- ▶ Electron-phonon coupling matrices

$$g_{i\mathbf{k}+\mathbf{q},j\mathbf{k}}^n = \frac{1}{\sqrt{2M\omega_n(\mathbf{q})}} \langle \phi_{i\mathbf{k}+\mathbf{q}} | \mathbf{e}_n(\mathbf{q}) \cdot \Delta \mathbf{V}_s(\mathbf{q}) | \phi_{j\mathbf{k}} \rangle$$

- ▶ Linewidths

$$\gamma_n(\mathbf{q}) = 2\pi\omega_n(\mathbf{q}) |g_{i\mathbf{k}+\mathbf{q},j\mathbf{k}}^n|^2 \delta(\varepsilon_{i\mathbf{k}+\mathbf{q}} - \varepsilon_F) \delta(\varepsilon_{j\mathbf{k}} - \varepsilon_F)$$

(interpolating like the dispersion)

- ▶ The Eliashberg function

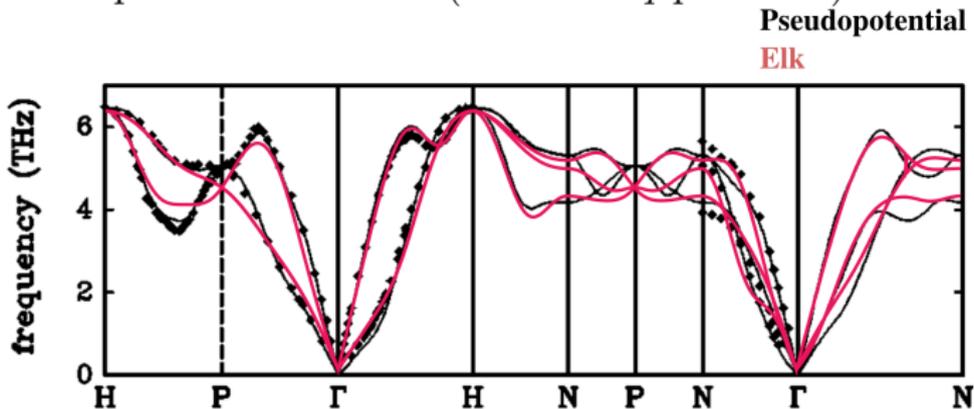
$$\alpha^2 F(\omega) = \frac{1}{2\pi N_F} \sum_{\mathbf{qn}} \frac{\gamma_n(\mathbf{q})}{\omega_n(\mathbf{q})} \delta(\omega - \omega_n(\mathbf{q}))$$

- ▶ Electron-phonon coupling parameter

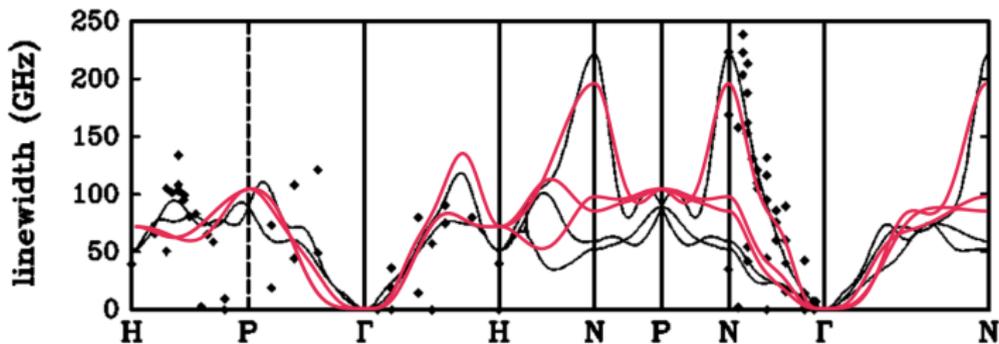
$$\lambda = 2 \int_0^\infty d\omega \frac{\alpha^2 F(\omega)}{\omega}$$

- ▶ McMillan-Allen-Dynes superconducting critical temperature
- ▶ Eliashberg equations and superconducting gap (Antonio Sanna)

Phonon dispersion of bcc Nb ( $4 \times 4 \times 4$   $q$ -point set)



Phonon linewidths of bcc Nb ( $32 \times 32 \times 32$   $k$ -point set)



## Question

Can you think of a situation where at least one of the acoustic phonon branches is quadratic for small  $\mathbf{q}$ , and not linear?

