Karlsruhe Institute of Technology

Density Functional Perturbation Theory and Electron-Phonon Coupling

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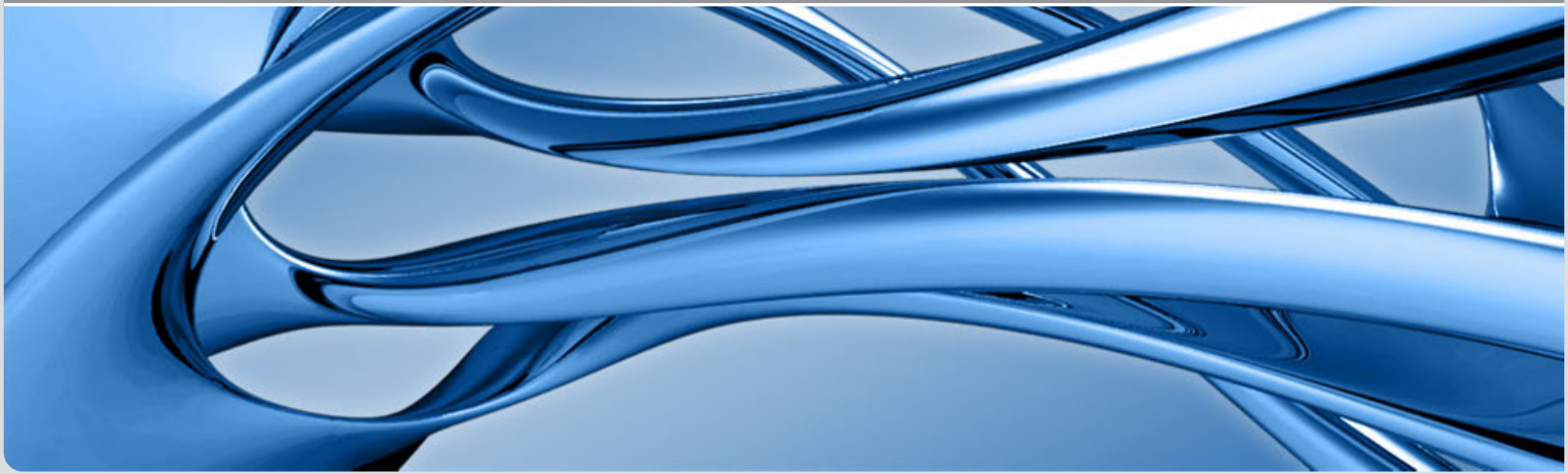

Outline

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Introduction

Electron-ion Hamiltonian

Basic constituents: electrons and ions (nucleus + core electrons)

$$\mathcal{H} = T_e + V_{ee} + T_i + V_{ii} + H_{e-i}$$

- T_e and T_i: kinetic energies of electrons and ions
- V_{ee}: Coulomb interaction among electrons
- V_{ii}: interaction energy among ions
- H_{e-i}: interaction between electrons and ions

- Approximate decoupling of dynamics possible due to very different masses of electron and ions
  - Idea goes back to: M. Born and W. Heisenberg: Ann. d. Phys. **74**, 1 (1926)
  - Correct expansion: M. Born and R. Oppenheimer: Ann. d. Phys, **84**, 457 (1927)
  - Application to solids: G.V. Chester and A. Houghton: Proc. Phys. Soc. **73**, 609 (1959)

Born-Oppenheimer expansion

Task: to solve

$$\mathcal{H}\Psi(\underline{\mathbf{r}},\underline{\mathbf{R}}) = \mathcal{E}\Psi(\underline{\mathbf{r}},\underline{\mathbf{R}})$$

Expansion of ionic coordinates: $\mathbf{R}_i = \mathbf{R}_i^0 + \kappa \mathbf{u}_i$

Small parameter: $\kappa = (m/M)^{1/4} \leq 0.1$ (except H and He)

Lowest order: adiabatic or Born-Oppenheimer approximation

$$\Psi(\underline{\mathbf{r}},\underline{\mathbf{R}}) = \chi(\underline{\mathbf{R}})\psi(\underline{\mathbf{r}};\underline{\mathbf{R}})$$

results in decoupling:

$$\begin{aligned} [T_e + V_{ee} + H_{e-i}(\underline{\mathbf{R}})]\psi_n(\underline{\mathbf{r}};\underline{\mathbf{R}}) &= E_n(\underline{\mathbf{R}})\psi_n(\underline{\mathbf{r}};\underline{\mathbf{R}}) \\ [T_i + V_{ii}(\underline{\mathbf{R}}) + E_n(\underline{\mathbf{R}})]\chi(\underline{\mathbf{R}}) &= \mathcal{E}\chi(\underline{\mathbf{R}}) \end{aligned}$$

Electronic wavefunction depends parametrically on $\underline{\mathbf{R}}$

Beyond adiabatic approximation

Generalized Ansatz

$$\Psi_m(\underline{\mathbf{r}};\underline{\mathbf{R}}) = \sum_n \chi_{mn}(\underline{\mathbf{R}})\psi_n(\underline{\mathbf{r}};\underline{\mathbf{R}})$$

$$\Rightarrow \quad [T_i + V_{ii} + E_n(\underline{\mathbf{R}})]\chi_{mn}(\underline{\mathbf{R}}) + \sum_{n'} \Delta H_{nn'}\chi_{mn'}(\underline{\mathbf{R}}) = \mathcal{E}_m\chi_{mn}(\underline{\mathbf{R}})$$

with

$$\Delta H^{(1)}_{nn'} = -\frac{1}{M}\sum_i \int dr^{3N}\psi^*_n(\underline{\mathbf{r}};\underline{\mathbf{R}})\nabla_{R_i}\psi_{n'}(\underline{\mathbf{r}};\underline{\mathbf{R}})\cdot\nabla_{R_i}$$

$$\Delta H^{(2)}_{nn'} = -\frac{1}{2M}\sum_i \int dr^{3N}\psi^*_n(\underline{\mathbf{r}};\underline{\mathbf{R}})\nabla^2_{R_i}\psi_{n'}(\underline{\mathbf{r}};\underline{\mathbf{R}})$$

Usually $\Delta H^{(1)}$ more important than $\Delta H^{(2)}$

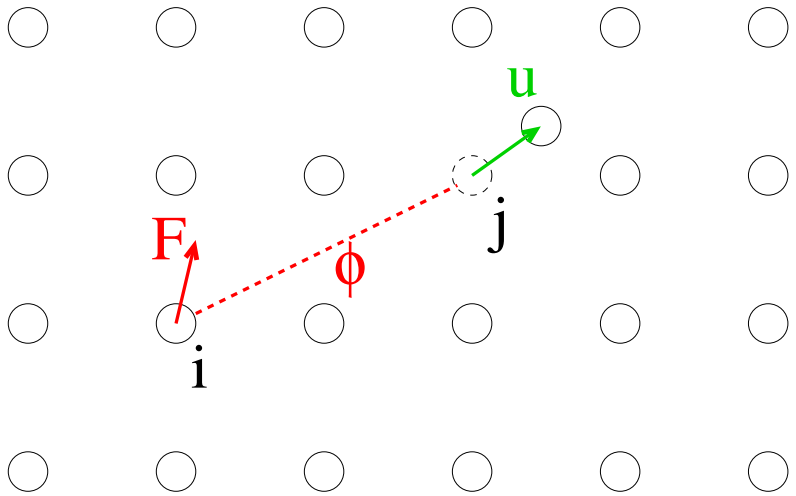
Basic elements of lattice dynamics

Adiabatic approximation: ions move in an effective potential

$$\Omega(\underline{\mathbf{R}}) = E_{el}(\underline{\mathbf{R}}) + V_{ii}(\underline{\mathbf{R}})$$

Expansion around rest positions: $\mathbf{u}_i = \mathbf{R}_i - \mathbf{R}_i^{(0)}$

$$\Omega(\{\mathbf{R}\}) = \Omega^{(0)} + \frac{1}{2}\sum_{ij\alpha\beta} \phi_{\alpha\beta}(i,j)\, u_{\alpha i}\, u_{\beta j} + \ldots$$



Force

$$F_{\alpha i} = -\frac{\delta\Omega}{\delta R_{\alpha i}} = -\sum_{j\beta} \phi_{\alpha\beta}(i,j)\, u_{\beta j}$$

Basic elements of lattice dynamics (2)

Harmonic force constants: $\Phi_{\alpha\beta}(i,j) = \frac{\delta^2\Omega}{\delta R_{\alpha i}\delta R_{\beta j}}$

Dynamical matrix for periodic systems: $i = (l\kappa)$

$$D_{\kappa\alpha\kappa'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_l \Phi_{\alpha\beta}(l\kappa, 0\kappa') e^{-i\mathbf{q}(\mathbf{R}^0_{l\kappa} - \mathbf{R}^0_{0\kappa'})}$$

Normal modes or phonons

$$\sum_{\kappa'\beta} D_{\kappa\alpha\kappa'\beta}(\mathbf{q})\eta_{\kappa'\beta}(\mathbf{q}j) = \omega^2_{\mathbf{q}j}\eta_{\kappa\alpha}(\mathbf{q}j)$$

Second quantization

$$u_{l\kappa\alpha} = e^{i\mathbf{q}\mathbf{R}^0_{l\kappa}} \frac{1}{\sqrt{N_q}} \sum_{\mathbf{q}j} A^{\mathbf{q}j}_{\kappa\alpha}(b_{\mathbf{q}j} + b^\dagger_{-\mathbf{q}j}) \qquad \text{with} \qquad A^{\mathbf{q}j}_{\kappa\alpha} = \frac{\eta_{\kappa\alpha}(\mathbf{q}j)}{\sqrt{2M_\kappa\omega_{\mathbf{q}j}}}$$

First principles approach to lattice dynamics

- given external potential as sum of electron-ion potentials

$$v_{\text{ext}}(\mathbf{r}) = \sum_{l\kappa} v_\kappa(\mathbf{r} - \mathbf{R}_{l\kappa})$$

- task: determine 2nd-order derivatives

$$\Phi_{\alpha\beta}(i,j) = \frac{\delta^2\Omega}{\delta R_{\alpha i}\delta R_{\beta j}}$$

with

$$\Omega(\underline{\mathbf{R}}) = E_{el}(\underline{\mathbf{R}}) + V_{ii}(\underline{\mathbf{R}})$$

TOOL: Density functional perturbation theory

Adiabatic perturbation

$$\frac{\partial^n E_0}{\partial \lambda^n} \longleftrightarrow \text{Physical properties}$$

type of perturbation λ	n	property
atomic displacements $\delta\mathbf{R}_i$	1	atomic force
	2	force constants
	≥ 3	anharmonic force constants
homogeneous strain η	1	stress
	2	elastic constants
	≥ 3	higher order elastic constants
homogeneous electric field $\mathbf{E}$	1	dipole moment
	2	polarizability
$\delta\mathbf{R}_i + \eta$	2+1	Grüneisen parameter
$\delta\mathbf{R}_i + \mathbf{E}$	1+2	Raman scattering cross section

Density functional perturbation theory

Density functional theory

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Interacting electron system

$$\hat{H} = -\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i v_{\text{ext}}(\mathbf{r}_i)$$

$\Uparrow$

Groundstate $\left\{ \begin{array}{l} \text{energy } E_0 \\ \text{density } n_0(\mathbf{r}) \end{array} \right.$

$\Downarrow$

Fictious non-interacting system (Kohn-Sham)

$$\left\{-\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{scr}}[n_0(\mathbf{r})]\right\}\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r}) \qquad n_0(\mathbf{r}) = \sum_i^{occ} |\varphi_i(\mathbf{r})|^2$$

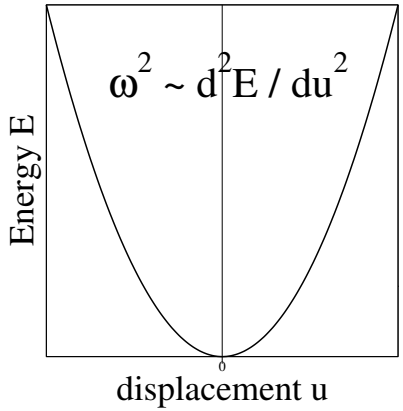
Screening potential: $v_{\text{scr}}[n(\mathbf{r})] = v_H[n(\mathbf{r})] + v_{XC}[n(\mathbf{r})]$

Energy: $E_0 = E_{\text{kin}}^{KS} + \int d^3r n_0(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) + E_H[n_0(\mathbf{r})] + E_{XC}[n_0(\mathbf{r})]$

DFT: application to phonons

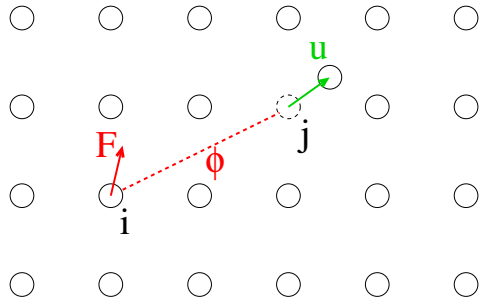
(A) Frozen phonon

- needs only the total energy
- requires information about displacements
- for phonons with q≠0 supercells are needed



(B) Direct method (force constant method)

- no knowledge of eigenvectors needed
- requires only force calculations
- supercells for q≠0 needed
  → expensive for long ranged interactions



(C) Perturbational approach

- perturbative evaluation of $\phi_{\alpha\beta}(i,j) = \frac{\delta^2 E_{tot}}{\delta R_{\alpha i} \delta R_{\beta j}}$
- arbitrary q, no supercell

2nd-order derivatives in DFT

- Adiabatic perturbations via v_{ext}: $\Lambda = \{\lambda_a, a = 1, \ldots, p\}$
- Total energy

$$E^\Lambda = F[n^\Lambda] + \int d^3r n^\Lambda(\mathbf{r}) v^\Lambda_{ext}(\mathbf{r})$$

- Two contributions to 1st-order derivative

$$\frac{\partial E^\Lambda}{\partial \lambda_a} = \int d^3r n^\Lambda(\mathbf{r}) \frac{\partial v^\Lambda_{\text{ext}}(\mathbf{r})}{\partial \lambda_a} + \int d^3r \frac{\delta E^\Lambda}{\delta n(\mathbf{r})} \frac{\partial n^\Lambda(\mathbf{r})}{\partial \lambda_a}$$

- Variational principle $\rightarrow \frac{\delta E^\Lambda}{\delta n(\mathbf{r})} = 0$ for each finite Λ
- 2nd-order derivatives

$$\frac{\partial^2 E^\Lambda}{\partial \lambda_a \partial \lambda_b} = \int d^3r \frac{\partial n^\Lambda(\mathbf{r})}{\partial \lambda_b} \frac{\partial v^\Lambda_{\text{ext}}(\mathbf{r})}{\partial \lambda_a} + \int d^3r n^\Lambda(\mathbf{r}) \frac{\partial^2 v^\Lambda_{\text{ext}}(\mathbf{r})}{\partial \lambda_a \partial \lambda_b}$$

$\rightarrow$ only linear response of $n^\Lambda(\mathbf{r})$ required

Beyond linear response

"2n+1"-theorem of density functional theory (Gonze 1989+1995)

> Knowledge of derivatives $\frac{\partial^j}{\partial \Lambda^j} n_0(\mathbf{r})$ up to order n allows calculation of all derivatives $\frac{\partial^j}{\partial \Lambda^j} E_0$ up to order 2n+1.

Examples:

- Forces (Hellmann-Feynman theorem)

$$\mathbf{F}^{el}(i) = -\frac{\partial}{\partial \mathbf{R}(i)} E_0 = -\int d^3 r\, n_0(\mathbf{r}) \frac{\partial v_{\text{ext}}(\mathbf{r})}{\partial \mathbf{R}(i)}$$

- 3rd-order anharmonic force constants: accessible in linear response

Linear response in Kohn-Sham scheme

Kohn-Sham equations

$$\left\{ -\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right\} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

with effective potential

$$v_{\text{eff}}[n] = v_{\text{ext}} + v_{\text{scr}}[n] = v_{\text{ext}} + v_H[n] + v_{XC}[n]$$

Linear variation

$$\delta v_{\text{eff}}(\mathbf{r}) = \delta v_{\text{ext}}(\mathbf{r}) + \delta v_{\text{scr}}(\mathbf{r}) = \delta v_{\text{ext}}(\mathbf{r}) + \int d^3 r' \, I(\mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}')$$

with kernel

$$I(\mathbf{r}, \mathbf{r}') \equiv \frac{\delta v_{\text{scr}}(\mathbf{r})}{\delta n(\mathbf{r}')} = \frac{\delta v_{\text{H}}(\mathbf{r})}{\delta n(\mathbf{r}')} + \frac{\delta v_{\text{XC}}(\mathbf{r})}{\delta n(\mathbf{r}')} = \frac{2}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{XC}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}$$

Linear response in Kohn-Sham scheme (2)

Density: $n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$ f_i: occupation numbers

Kohn-Sham equations: $\left\{ -\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right\} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$

$$\Rightarrow \quad \delta\psi_i(\mathbf{r}) = \sum_{j(\neq i)} \frac{\langle j|\delta v_{\text{eff}}|i\rangle}{\epsilon_i - \epsilon_j} \psi_j(\mathbf{r})$$

Linear density response

$$\begin{aligned} \delta n(\mathbf{r}) &= \sum_i f_i [\psi_i^*(\mathbf{r})\delta\psi_i(\mathbf{r}) + \delta\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})] \\ &= \sum_{i\neq j} \frac{f_i - f_j}{\epsilon_i - \epsilon_j} \langle j|\delta v_{\text{eff}}|i\rangle \psi_i^*(\mathbf{r})\psi_j(\mathbf{r}) = \int d^3r' \chi_0(\mathbf{r},\mathbf{r}')\delta v_{\text{eff}}(\mathbf{r}') \end{aligned}$$

with charge susceptibility $\chi_0(\mathbf{r},\mathbf{r}') = \sum_{i\neq j} \frac{f_i - f_j}{\epsilon_i - \epsilon_j} \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')$

Linear response in Kohn-Sham scheme (3)

Dielectric screening

$$\left.\begin{aligned} \delta n &= \chi_0 \delta v_{\text{eff}} \\ \delta v_{\text{eff}} &= \delta v_{\text{ext}} + I \delta n \end{aligned}\right\} \quad \Rightarrow \delta v_{\text{eff}} = \delta v_{\text{ext}} + I\chi_0 \delta v_{\text{eff}}$$

or

$$\delta v_{\text{eff}} = [1 - I\chi_0]^{-1} \delta v_{\text{ext}} = \epsilon^{-1} \delta v_{\text{ext}} \quad \text{and} \quad \delta n = \chi_0 \epsilon^{-1} \delta v_{\text{ext}}$$

with the (static) dielectric matrix

$$\epsilon(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') - \int d^3\bar{r} I(\mathbf{r}, \bar{\mathbf{r}}) \chi_0(\bar{\mathbf{r}}, \mathbf{r}')$$

- was historically first route persued (Pick *et al.*1970, Resta 1985)
- tough part: inversion of $\epsilon \rightarrow$ numerically expensive

Linear response: Modern formulation

Simple case: non-metal, gap between conduction and valence states

Starting from

$$\delta n(\mathbf{r}) = \sum_{i \neq j} \frac{f_i - f_j}{\epsilon_i - \epsilon_j} \langle j | \delta v_{\text{eff}} | i \rangle \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r})$$

$$\Rightarrow \quad 2 \sum_{cv} \frac{1}{\epsilon_v - \epsilon_c} \langle c | \delta v_{\text{eff}} | v \rangle \psi_v^*(\mathbf{r}) \psi_c(\mathbf{r})$$

Rewriting

$$\delta n(\mathbf{r}) = 2 \sum_v \psi_v^*(\mathbf{r}) \Delta_v(\mathbf{r})$$

with definition

$$|\Delta_v\rangle = \sum_c \frac{1}{\epsilon_v - \epsilon_c} |c\rangle \langle c | \delta v_{\text{eff}} | v \rangle$$

Linear response: Modern formulation (2)

How to calculate $|\Delta_v\rangle = \sum_c \frac{1}{\epsilon_v - \epsilon_c} |c\rangle\langle c|\delta v_{\text{eff}}|v\rangle$?

Not directly, but use a linear equation!

$$
\begin{aligned}
(H-\epsilon_v)|\Delta_v\rangle &= -\sum_c |c\rangle\langle c|\delta v_{\text{eff}}|v\rangle &&= -P_c \delta v_{\text{eff}}|v\rangle \\
&= (P_v - 1)\delta v_{\text{eff}}|v\rangle
\end{aligned}
$$

- $P_v (P_c)$ projection onto valence (conduction) space
- advantage: final form contains only valence space quantities

"Sternheimer" - equation

atomic physics: Sternheimer, 1954, Phys. Rev. 951, **96** (1954)

solid state: Baroni *et al.*, PRL **59**, 1861 (1987);
Zein, Sov. Phys. Solid State **26**, 1825 (1984)

Linear response: Modern formulation (3)

Self-consistency loop

- Step 1: initial δv_{eff}
- Step 2:

$$(H - \epsilon_\nu)|\Delta_\nu\rangle = (P_\nu - 1)\delta v_{\text{eff}}|\nu\rangle$$

- Step 3:

$$\delta n(\mathbf{r}) = 2\sum_\nu \psi^*_\nu(\mathbf{r})\Delta_\nu(\mathbf{r})$$

- Step 4:

$$\delta v_{\text{eff}} = \delta v_{\text{ext}} + I\delta n$$

- repeat from Step 2 until convergence

$$\Rightarrow \quad \boxed{\delta n \text{ and } \delta v_{\text{eff}}}$$

Application: Phonons in periodic lattices

Periodic displacements

$$\mathbf{R}_{l\kappa} = \mathbf{R}^0_{l\kappa} + \mathbf{u}_{l\kappa} \qquad u_{l\kappa\alpha} = d_{\kappa\alpha} e^{i\mathbf{q}\mathbf{R}^0_{l\kappa}} + d^*_{\kappa\alpha} e^{-i\mathbf{q}\mathbf{R}^0_{l\kappa}}$$

Define operators: $\delta^{\mathbf{q}}_{\kappa\alpha} \equiv \frac{\partial}{\partial d_{\kappa\alpha}}$, $\delta^{-\mathbf{q}}_{\kappa\alpha} \equiv \frac{\partial}{\partial d^*_{\kappa\alpha}} = {\delta^{\mathbf{q}}_{\kappa\alpha}}^*$

Electron-ion potential: $v_{\text{ext}}(\mathbf{r}) = \sum_{l\kappa} v_\kappa(\mathbf{r} - \mathbf{R}_{l\kappa})$

$$\begin{aligned} \Rightarrow \delta^{\mathbf{q}}_{\kappa\alpha} v_{\text{ext}}(\mathbf{r}) &= -\sum_l \nabla^{\mathbf{r}}_\alpha v_\kappa(\mathbf{r} - \mathbf{R}^0_{l\kappa}) e^{i\mathbf{q}\mathbf{R}^0_{l\kappa}} \\ &= -e^{i\mathbf{q}\mathbf{r}} \sum_l e^{i\mathbf{q}(\mathbf{R}^0_{l\kappa} - \mathbf{r})} \nabla^{\mathbf{r}}_\alpha v_\kappa(\mathbf{r} - \mathbf{R}^0_{l\kappa}) \end{aligned}$$

- Operator $\delta^{\mathbf{q}}_{\kappa\alpha}$ carries a momentum $\mathbf{q}$

Application: Phonons in periodic lattices (2)

Electronic contribution to the dynamical matrix

$$D_{\kappa\alpha\kappa'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \delta^{\mathbf{q}}_{\kappa\alpha} \delta^{-\mathbf{q}}_{\kappa'\beta} E \Big|_{\mathbf{u}=0}$$

with

$$\delta^{\mathbf{q}}_{\kappa\alpha} \delta^{-\mathbf{q}}_{\kappa'\beta} E = \sum_{\mathbf{G}} \left[\delta^{\mathbf{q}}_{\kappa\alpha} n(\mathbf{G}+\mathbf{q}) \delta^{-\mathbf{q}}_{\kappa'\beta} v_{\text{ext}}(\mathbf{G}+\mathbf{q}) + \delta^{\mathbf{q}}_{\kappa\alpha} \delta^{-\mathbf{q}}_{\kappa'\beta} v_{\text{ext}}(\mathbf{G}) \right]$$

- no coupling between different **q**
- independent evaluation of dynamical matrix for each **q**

Application: Phonons in periodic lattices (3)

1st-order density

$$\delta^{\mathbf{q}}_{\kappa\alpha} n(\mathbf{q}+\mathbf{G}) = -\frac{4}{V}\sum_{\mathbf{k}v}\langle \mathbf{k}v|e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}}|\Delta^{\mathbf{q}}_{\kappa\alpha}(\mathbf{k}v)\rangle$$

$$|\Delta^{\mathbf{q}}_{\kappa\alpha}(\mathbf{k}v)\rangle = \sum_{c}\frac{|\mathbf{k}+\mathbf{q}c\rangle\langle \mathbf{k}+\mathbf{q}c|\delta^{\mathbf{q}}_{\kappa\alpha} v_{\mathrm{eff}}|\mathbf{k}v\rangle}{\epsilon_c(\mathbf{k}+\mathbf{q})-\epsilon_v(\mathbf{k})}$$

$$(H^{\mathbf{k}+\mathbf{q}}_{KS}-\epsilon_v(\mathbf{k}))|\Delta^{\mathbf{q}}_{\kappa\alpha}(\mathbf{k}v)\rangle = (P^{\mathbf{k}+\mathbf{q}}_{v}-1)\,\delta^{\mathbf{q}}_{\kappa\alpha} v_{\mathrm{eff}}|\mathbf{k}v\rangle$$

- connects unperturbed states $|\mathbf{k}v\rangle$ and $|\mathbf{k}+\mathbf{q}v\rangle$
- involves only valence state quantities $\rightarrow$ from ground state calculation
- calculation of dynamical matrices on a regular $\mathbf{q}$-grid
- smooth dispersions via 3D Fourier interpolation techniques

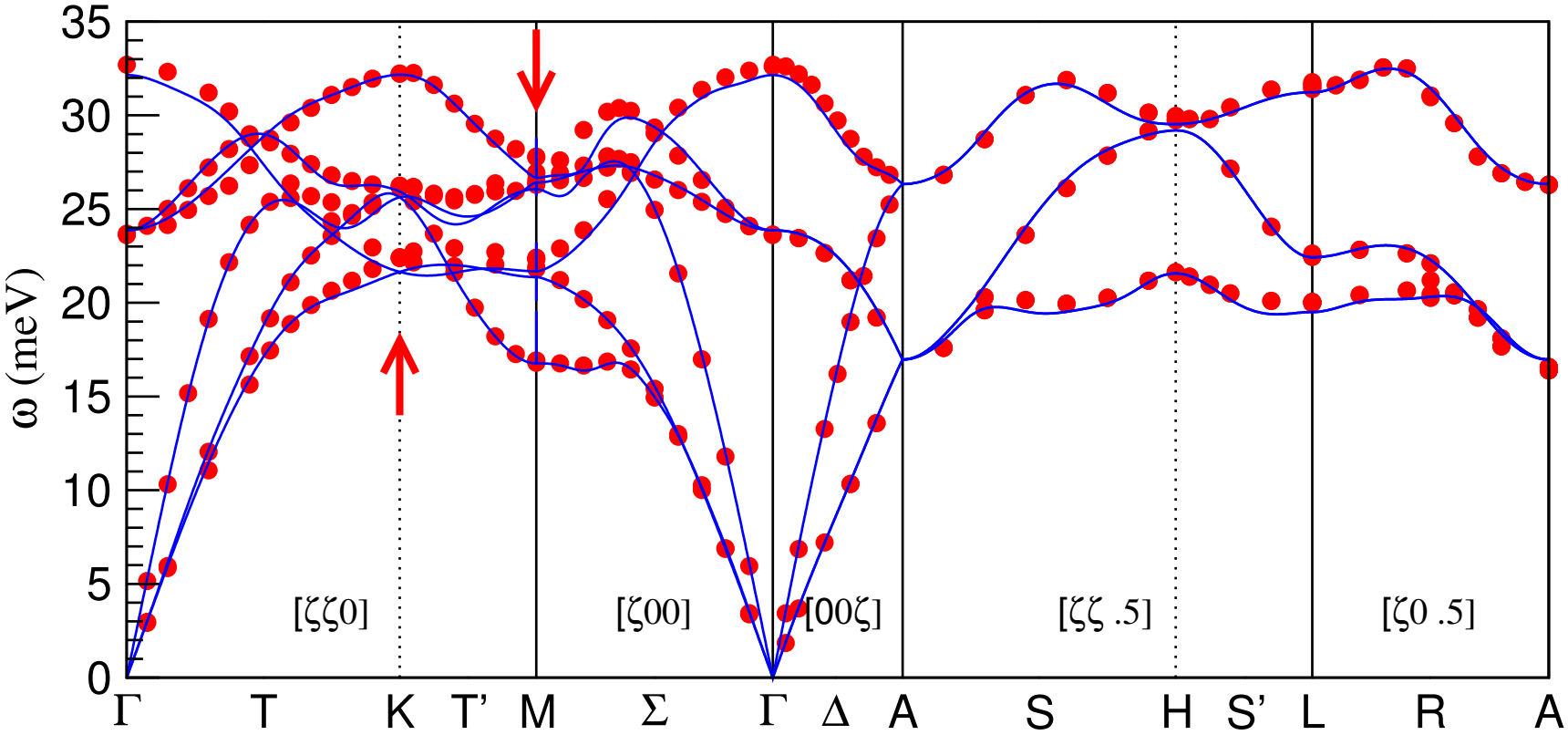
Application: Phonons in periodic lattices (4)

Extensions/generalizations

- Metals: incorporation of fractional occupation numbers (de Gironcoli, PRB **51**, 6773 (1995))
- Spin polarization: dynamical matrix sum of contributions from each spin
- Non-local potentials: dynamical matrix depends explicitly on first-order derivatives of wavefunctions
- Basis-set corrections: additional contributions related to the change of the basis functions under an ionic displacement (like Pulay correction to forces)
- Relativistic corrections: spin-orbit interaction within pseudopontential formulation, requires spinor representation (Dal Corso, J. Phys.: Condens. Matter (2008); Verstraete *et al.*, PRB (2008))

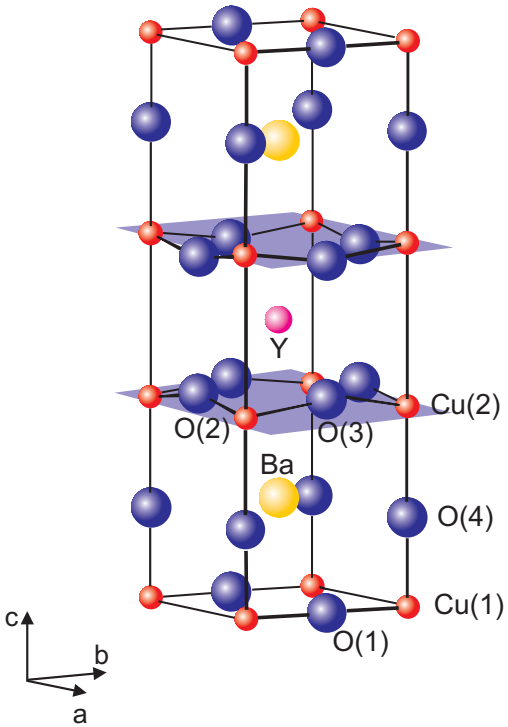
Example(1): Phonon dispersion of Ru (hcp)

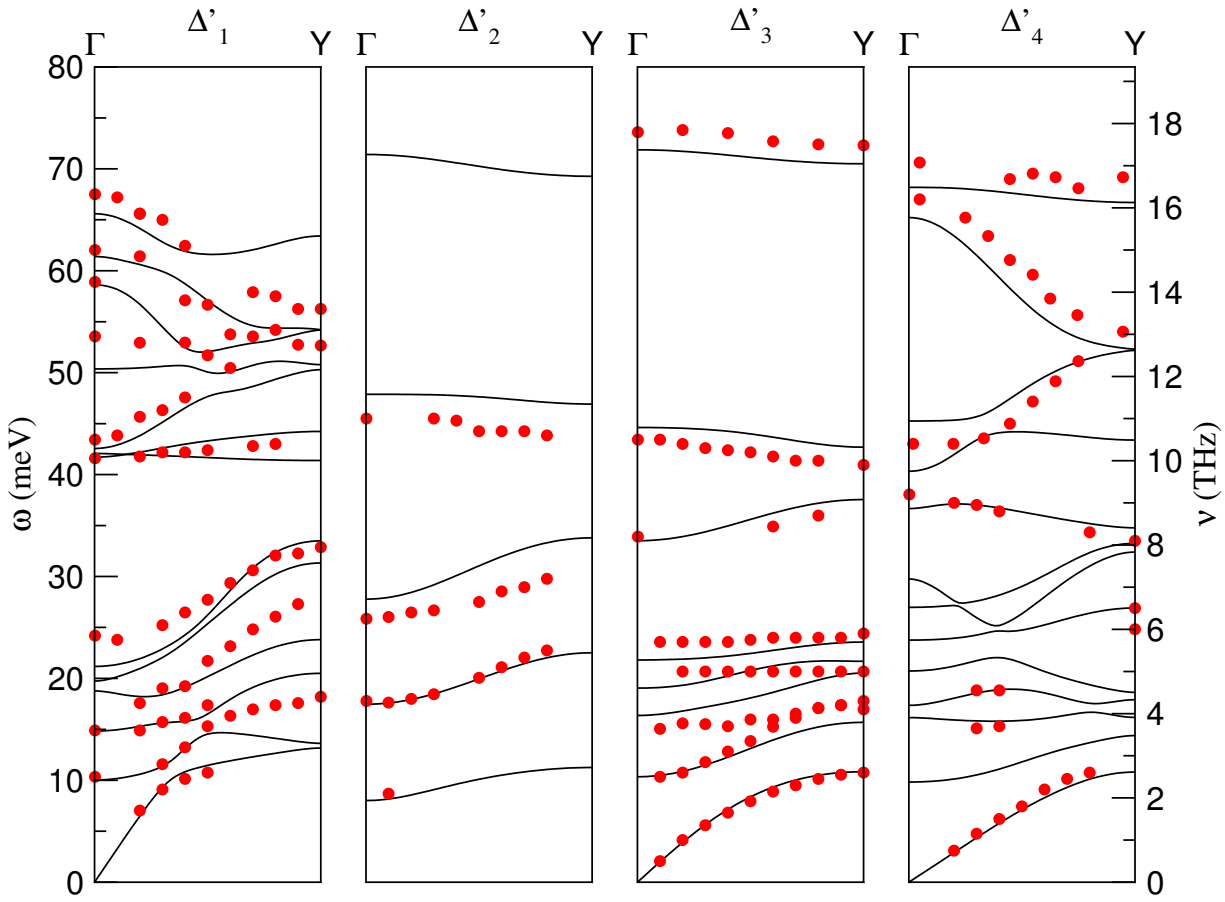
DFPT versus inelastic neutron scattering



(RH *et al.*, PRB **61**, 12059 (2000))

Example(2): Phonon dispersion of $YBa_2Cu_3O_7$





Neutron scattering data: L. Pintschovius and W. Reichardt
DFPT: Bohnen *et al.*, Europhys. Lett. **64**, 104 (2003)

Electron-phonon coupling

Beyond adiabatic approximation

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Until now

- separation of electronic and vibrational dynamics
- solving for the electronic system does not need vibrational information
- electronic subsystem influences vibrations via (static) screening, described by an effective potential for ion dynamics
- no further interaction between electronic and phononic quasiparticles
- phonons have infinite lifetime

One step further

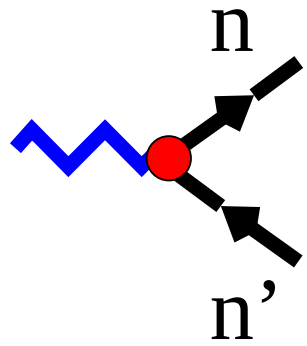
- consider interaction between electron and phonons (to lowest order)
- description of electrons then leaves solid ground for DFT, needs more advanced approaches like time-dependent DFT
- still some properties can be calculated with DFT quantities

Form of coupling

Consider product states $|n\alpha\rangle$ of electronic and phononic wavefunctions

- Adiabatic approximation: $\langle n\alpha|\mathcal{H}|n'\alpha'\rangle \propto \delta_{n,n'}\delta_{\alpha,\alpha'}$
- Non-vanishing off-diagonal elements due to non-adiabatic terms ΔH only. Most important:

$$\langle n\alpha|\Delta H^{(1)}|n'\alpha'\rangle = \int (\chi_\alpha^* \nabla_{\mathbf{R}} \chi_{\alpha'}) \cdot (\psi_n^* \nabla_{\mathbf{R}} \psi_{n'})$$



$$\int \chi_\alpha^* \nabla_{\mathbf{R}} \chi_{\alpha'} \quad \propto \quad \text{phonon creation and annihilation}$$

$$\int \psi_n^* \nabla_{\mathbf{R}} \psi_{n'} \quad \propto \quad \langle n|\nabla_{\mathbf{R}} V|n'\rangle$$

$V(\underline{\mathbf{R}})$: effective potential from electron-ion and electron-electron interaction

Electron-phonon vertex in DFPT

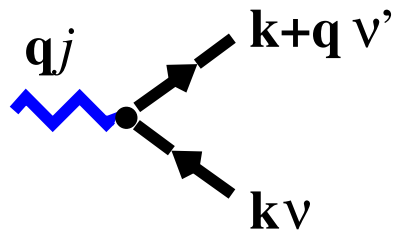
Bare vertex

$$\langle \mathbf{k}+\mathbf{q}\nu' | \delta^{\mathbf{q}}_{\kappa\alpha} v_{\text{ext}} | \mathbf{k}\nu \rangle = -\langle \mathbf{k}+\mathbf{q}\nu' | e^{i\mathbf{q}\mathbf{r}} \sum_l e^{i\mathbf{q}(\mathbf{R}^0_{l\kappa}-\mathbf{r})} \nabla^{\mathbf{r}}_\alpha v_\kappa(\mathbf{r}-\mathbf{R}^0_{l\kappa}) | \mathbf{k}\nu \rangle$$

Normal-mode representation

$$g^{(0)\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu} = \sum_{\kappa\alpha} A^{\mathbf{q}j}_{\kappa\alpha} \langle \mathbf{k}+\mathbf{q}\nu' | \delta^{\mathbf{q}}_{\kappa\alpha} v_{\text{ext}} | \mathbf{k}\nu \rangle$$

$$A^{\mathbf{q}j}_{\kappa\alpha} = \frac{\eta_{\kappa'\beta}(\mathbf{q}j)}{\sqrt{2M_\kappa \omega_{\mathbf{q}j}}}$$

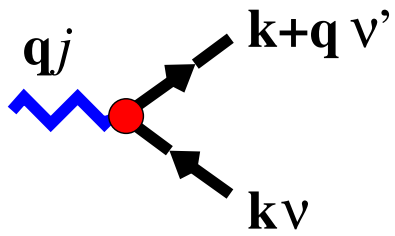


- rigid displacement of electron-ion potential
- ignores screening effects

Electron-phonon vertex in DFPT (2)

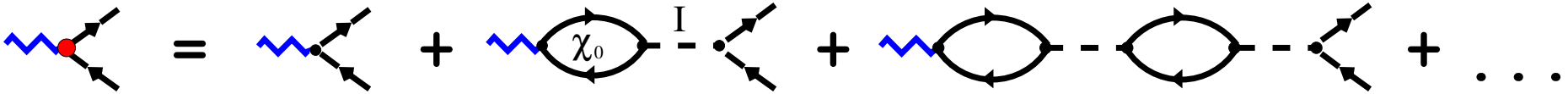
Screened vertex

$$g^{\mathbf{q}\lambda}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu} = \sum_{\kappa\alpha} A^{\mathbf{q}j}_{\kappa\alpha} \langle \mathbf{k}+\mathbf{q}\nu' | \delta^{\mathbf{q}}_{\kappa\alpha} v_{\text{eff}} | \mathbf{k}\nu \rangle$$



easily accessible in DFPT

Relationship to bare vertex: $\delta v_{\text{eff}} = \delta v_{\text{ext}} + I\chi_0 \delta v_{\text{eff}}$



- screening via static Kohn-Sham (non-interacting) susceptibility χ_0
- electron-electron interaction represented by $I = I_H + I_{XC}$
  $\longrightarrow$ includes exchange-correlation

Electron-phonon vertex in DFPT (3)

Technical aspects

$$g^{\mathbf{q}\lambda}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu} = \sum_{\kappa\alpha} A^{\mathbf{q}j}_{\kappa\alpha} \left\langle \mathbf{k}+\mathbf{q}\nu' \middle| \delta^{\mathbf{q}}_{\kappa\alpha} v_{\mathrm{eff}} \middle| \mathbf{k}\nu \right\rangle$$

- most time-consuming part: calculation of $\delta^{\mathbf{q}}_{\kappa\alpha} v_{\mathrm{eff}}$ (DFPT)
- first: corse-grain calculation of $\delta^{\mathbf{q}}_{\kappa\alpha} v_{\mathrm{eff}}$ and/or matrix elements
- then use interpolation techniques to sample matrix elements on dense momentum meshes
- two variants
  - interpolation of $\delta^{\mathbf{q}}_{\kappa\alpha} v_{\mathrm{eff}}$ for arbitrary $\mathbf{q}$, then calculation of matrix elements using exact Kohn-Sham states
  - Wannier-type interpolation technique for matrix elements
    Giustino *et al.*, PRB **76**, 165108 (2007), Calandra *et al.*, PRB **82**, 165111 (2010)

Electron-phonon coupling: Physical effects

Karlsruhe Institute of Technology

EPC influences

- electronic and phononic quasiparticles
- thermodynamics (mass enhancement)
- transport properties
- superconductivity

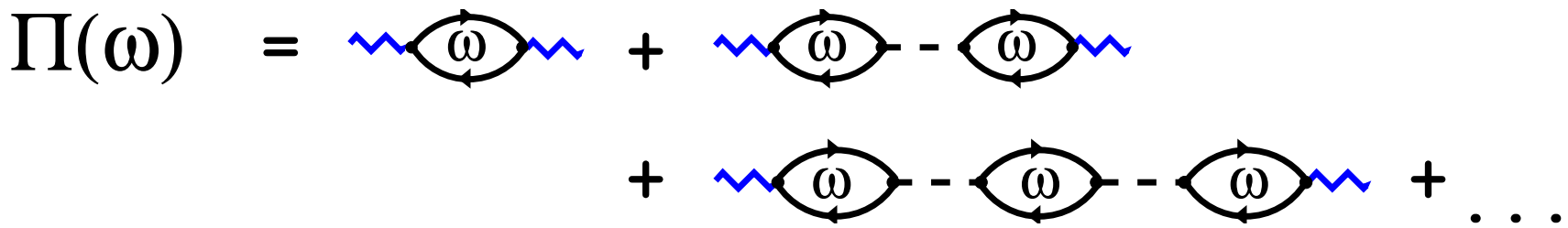
In the following will be focus on:

1. Phonon self-energy and linewidth
2. Phonon-mediated pairing and superconductivity
3. Electron self-energy effects (normal state)

Phonon self-energy: General considerations

Phonon Green's function $$D_{\mathbf{q}j}(\omega) = \frac{2\omega_{\mathbf{q}j}}{\omega^2 - \omega_{\mathbf{q}j}^2 - 2\omega_{\mathbf{q}j}\Pi_{\mathbf{q}j}(\omega)}$$

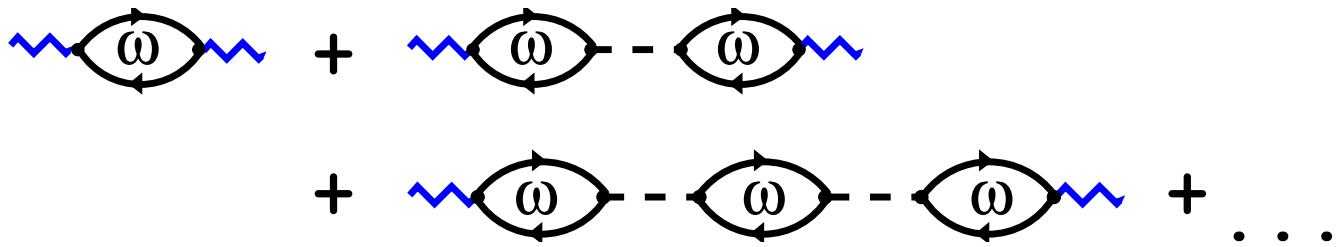
Phonon self-energy $\Pi_{\mathbf{q}j}(\omega)$



- frequency-dependent susceptibility $\chi_{0,\mathbf{q}}(\omega) = \sum_{\mathbf{k}\nu\nu'} \frac{f(\epsilon_{\mathbf{k}\nu}) - f(\epsilon_{\mathbf{k}+\mathbf{q}\nu'})}{\epsilon_{\mathbf{k}\nu} - \epsilon_{\mathbf{k}+\mathbf{q}\nu'} + \omega + i\eta}$
- renormalization determined by $\Pi_{\mathbf{q}j}(\omega)$ with $\omega \approx \omega_{\mathbf{q}j}$; typically much smaller than electronic energies

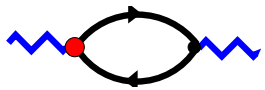
Phonon self-energy: Real part

$\Pi(\omega)$ =



- renormalization of phonon frequency: $\Omega^2_{\mathbf{q}j} = \omega^2_{\mathbf{q}j} - 2\omega_{\mathbf{q}j}\mathrm{Re}\Pi_{\mathbf{q}j}(\Omega_{\mathbf{q}j})$
- $\Omega_{\mathbf{q}j} \ll$ el. energies: static limit appropriate

$\mathrm{Re}\,\Pi(0)$ =



$$\mathrm{Re}\Pi_{\mathbf{q}j}(0) = \frac{1}{N_k}\sum_{\mathbf{k}\nu\nu'} g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}\left(g^{(0)\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu'\mathbf{k}\nu}\right)^* \frac{f(\epsilon_{\mathbf{k}\nu}) - f(\epsilon_{\mathbf{k}+\mathbf{q}\nu'})}{\epsilon_{\mathbf{k}\nu} - \epsilon_{\mathbf{k}+\mathbf{q}\nu'}}$$

- mixture of screened and bare vertices

This term is already contained in DFPT !

Phonon self-energy: Real part (2)

How can this be seen?

$$\mathrm{Re}\Pi_{\mathbf{q}j}(0) = \frac{1}{N_k}\sum_{\mathbf{k}\nu\nu'} g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}\left(g^{(0)\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu'\mathbf{k}\nu}\right)^* \frac{f(\epsilon_{\mathbf{k}\nu}) - f(\epsilon_{\mathbf{k}+\mathbf{q}\nu'})}{\epsilon_{\mathbf{k}\nu} - \epsilon_{\mathbf{k}+\mathbf{q}\nu'}}$$

$$= \frac{1}{N_k}\sum_{\mathbf{k}\nu\nu'}\sum_{\kappa\alpha\kappa'\beta} A^{\mathbf{q}j}_{\kappa\alpha} A^{-\mathbf{q}j}_{\kappa'\beta} \langle \mathbf{k}+\mathbf{q}\nu' | \delta^{\mathbf{q}}_{\kappa\alpha} v_{\mathrm{eff}} | \mathbf{k}\nu\rangle \langle \mathbf{k}\nu | \delta^{-\mathbf{q}}_{\kappa'\beta} v_{\mathrm{ext}} | \mathbf{k}+\mathbf{q}\nu'\rangle$$

$$\times \frac{f(\epsilon_{\mathbf{k}\nu}) - f(\epsilon_{\mathbf{k}+\mathbf{q}\nu'})}{\epsilon_{\mathbf{k}\nu} - \epsilon_{\mathbf{k}+\mathbf{q}\nu'}}$$

Phonon self-energy: Real part (2)

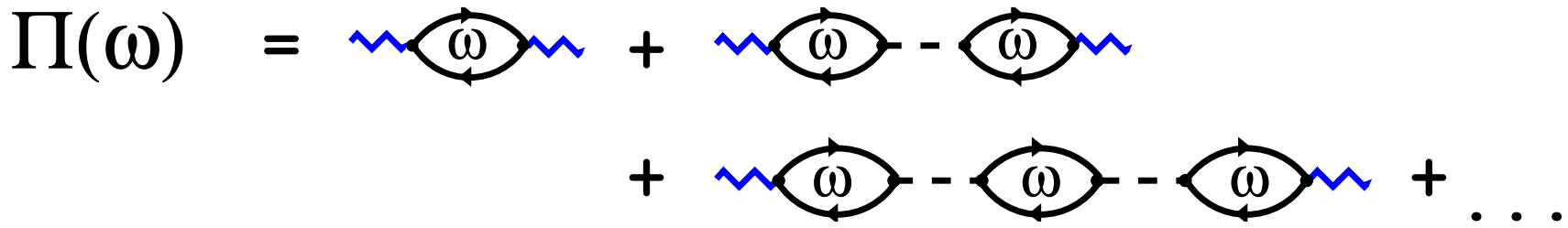
How can this be seen?

$$
\begin{aligned}
\mathrm{Re}\Pi_{\mathbf{q}j}(0) &= \frac{1}{N_k}\sum_{\mathbf{k}\nu\nu'} g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}\left(g^{(0)\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu'\mathbf{k}\nu}\right)^* \frac{f(\epsilon_{\mathbf{k}\nu})-f(\epsilon_{\mathbf{k}+\mathbf{q}\nu'})}{\epsilon_{\mathbf{k}\nu}-\epsilon_{\mathbf{k}+\mathbf{q}\nu'}} \\
&= \frac{1}{N_k}\sum_{\mathbf{k}\nu\nu'}\sum_{\kappa\alpha\kappa'\beta} A^{\mathbf{q}j}_{\kappa\alpha}A^{-\mathbf{q}j}_{\kappa'\beta}\langle\mathbf{k}+\mathbf{q}\nu'|\delta^{\mathbf{q}}_{\kappa\alpha}v_{\mathrm{eff}}|\mathbf{k}\nu\rangle\langle\mathbf{k}\nu|\delta^{-\mathbf{q}}_{\kappa'\beta}v_{\mathrm{ext}}|\mathbf{k}+\mathbf{q}\nu'\rangle \\
&\qquad\times\frac{f(\epsilon_{\mathbf{k}\nu})-f(\epsilon_{\mathbf{k}+\mathbf{q}\nu'})}{\epsilon_{\mathbf{k}\nu}-\epsilon_{\mathbf{k}+\mathbf{q}\nu'}} \\
&= \sum_{\kappa\alpha\kappa'\beta} A^{\mathbf{q}j}_{\kappa\alpha}A^{-\mathbf{q}j}_{\kappa'\beta}\int d^3r\,\delta^{\mathbf{q}}_{\kappa\alpha}n(\mathbf{r})\delta^{-\mathbf{q}}_{\kappa'\beta}v_{\mathrm{ext}}(\mathbf{r})
\end{aligned}
$$

- contribution to dynamical matrix in DFPT
- Static frequency renormalization is taken into account in DFPT

Phonon self-energy: Imaginary part

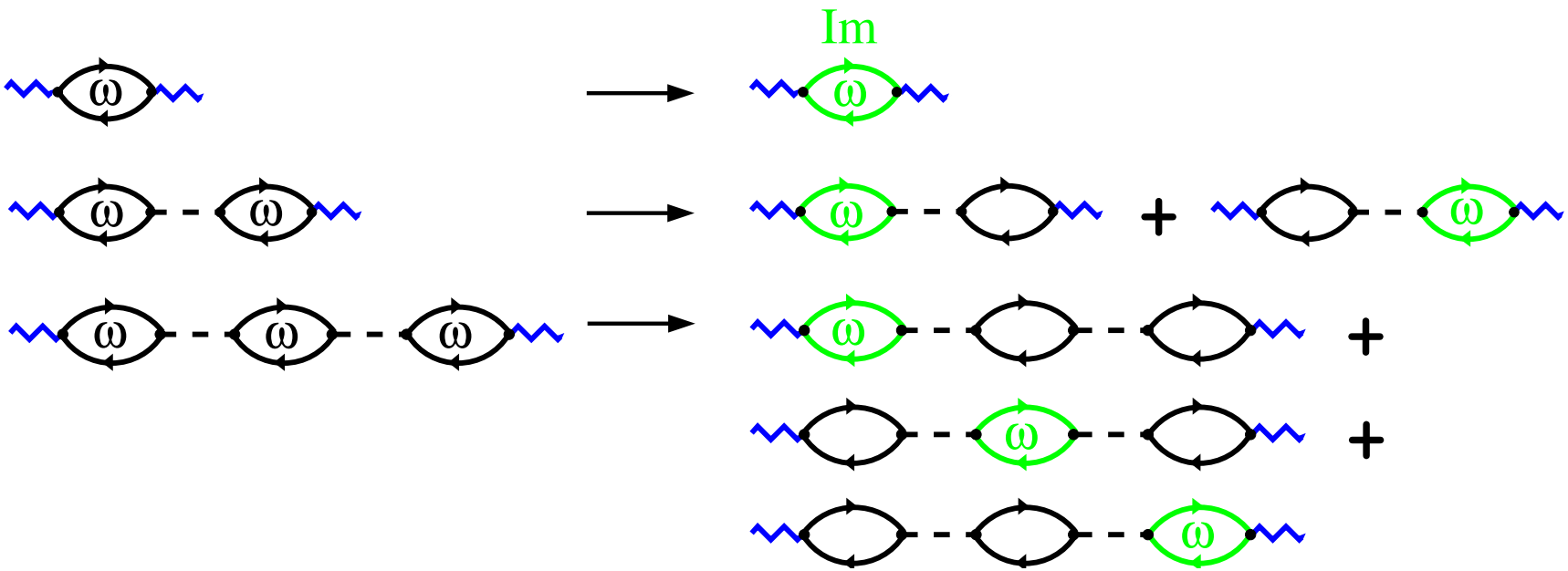
- phonon linewidth: $\gamma_{\mathbf{q}j} \approx -2\mathrm{Im}\Pi_{\mathbf{q}j}(\omega_{\mathbf{q}j})$
- $\mathrm{Im}\Pi_{\mathbf{q}j}(0) = 0 \rightarrow$ finite linewidth true non-adiabatic property



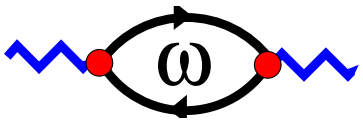
Dominant contribution to $\mathrm{Im}\Pi_{\mathbf{q}j}(\omega)$ for small ω

- $\chi_0(\omega) \approx \chi_0(0) + i\mathrm{Im}\chi_0(\omega)$
- from each diagram retain only terms with a single $\mathrm{Im}\chi_0(\omega)$

Phonon self-energy: Imaginary part (2)

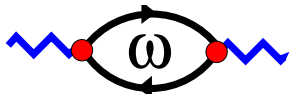


This series can be summed up:

$$\mathrm{Im}\,\Pi(\omega) = \mathrm{Im}$$ 

Both vertices are screened!

Phonon self-energy: Linewidth

$$= -2\ \mathrm{Im}$$ 

$$\gamma_{\mathbf{q}j} = 2\pi \frac{1}{N_k} \sum_{\mathbf{k}\nu\nu'} |g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}|^2 [f(\epsilon_{\mathbf{k}\nu}) - f(\epsilon_{\mathbf{k}+\mathbf{q}\nu'})] \delta[\omega_{\mathbf{q}j} + (\epsilon_{\mathbf{k}\nu} - \epsilon_{\mathbf{k}+\mathbf{q}\nu'})]$$

Simplifications for $\omega_{\mathbf{q}j} \ll$ electronic scale

$$f(\epsilon_{\mathbf{k}\nu}) - f(\epsilon_{\mathbf{k}+\mathbf{q}\nu'}) \approx f'(\epsilon_{\mathbf{k}\nu})(\epsilon_{\mathbf{k}\nu} - \epsilon_{\mathbf{k}+\mathbf{q}\nu'}) \to -f'(\epsilon_{\mathbf{k}\nu})\omega_{\mathbf{q}j}$$

$T \to 0$: $f'(\epsilon_{\mathbf{k}\nu}) \to -\delta(\epsilon_{\mathbf{k}\nu} - \epsilon_F)$ and drop $\omega_{\mathbf{q}j}$ in δ-function

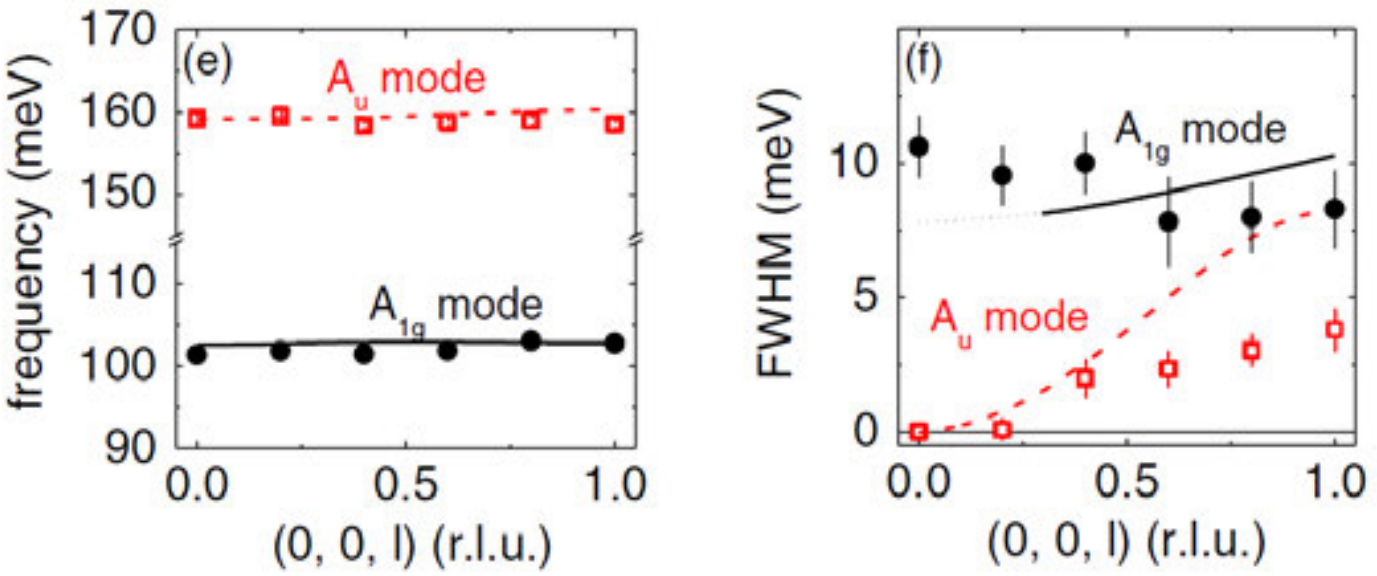
$$\gamma_{\mathbf{q}j} \approx 2\pi\omega_{\mathbf{q}j} \frac{1}{N_k} \sum_{\mathbf{k}\nu\nu'} |g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}|^2 \delta(\epsilon_{\mathbf{k}\nu} - \epsilon_F) \delta(\epsilon_{\mathbf{k}+\mathbf{q}\nu'} - \epsilon_F)$$

Formula often used in context of superconductivity (Allen, PRB **6**, 2577 (1972))

Phonon self-energy: Linewidth (2)

- $\gamma_{\mathbf{q}j}$ measurable quantity (e.g., via inelastic neutron or x-ray scattering)
- $\longrightarrow$ experimental test of *first principles* predictions
- but need to separate from other contributions: anharmonicity, defects

Example: YNi_2B_2C



Weber *et al.*, PRL **109**, 057001 (2012)

Electron-phonon mediated superconductivity

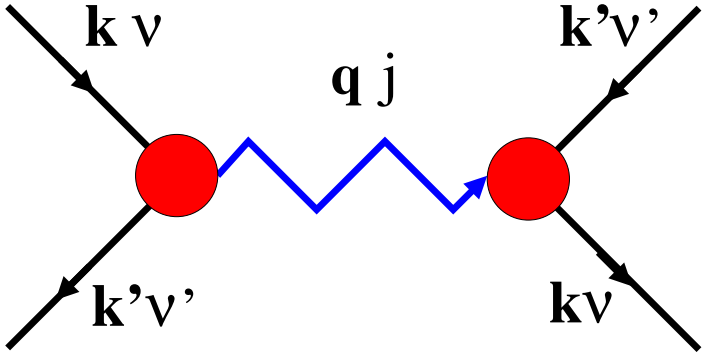
Weak-coupling theory: BCS model
Bardeen, Cooper, Schrieffer (1957)

Strong-coupling theory: Eliashberg (1960)

- Superconducting properties determined by gap equation
- Central quantity: effective electron-electron interaction
- Ingredients: Normal state properties
  - electrons (band structure)
  - lattice vibrations (phonon spectrum)
  - electron-phonon coupling

Superconductivity: Eliashberg function

Phonon-mediated effective electron-electron interaction



Eliashberg function

$$\alpha^2 F_{\mathbf{k}\nu,\mathbf{k}'\nu'}(\omega) = N(\epsilon_F)\frac{1}{N_q}\sum_{\mathbf{q}j}|g^{\mathbf{q}j}_{\mathbf{k}'\nu',\mathbf{k}\nu}|^2\delta(\omega-\omega_{\mathbf{q}j})$$

- lowest order (Migdal theorem)
- effective between states at E_F
- DFPT: access to full momentum dependence

Superconductivity: Isotropic limit

- defect scattering washes out momentum dependence of gap function
- pairing function averaged over Fermi surface is sufficient

$$\begin{aligned}\alpha^2F(\omega) &= \sum_{\mathbf{k}\nu,\mathbf{k}'\nu'} w_{\mathbf{k}\nu} w_{\mathbf{k}'\nu'} \alpha^2F_{\mathbf{k}\nu,\mathbf{k}'\nu'}(\omega) \quad \text{with} \quad w_{\mathbf{k}\nu} = \delta(\epsilon_{\mathbf{k}\nu} - \epsilon_F)/N(\epsilon_F) \\ &= \frac{1}{N(\epsilon_F)} \frac{1}{N_q} \sum_{\mathbf{q}j,\mathbf{k}\nu\nu'} |g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}|^2 \delta(\omega - \omega_{\mathbf{q}j}) \delta(\epsilon_{\mathbf{k}\nu} - \epsilon_F) \delta(\epsilon_{\mathbf{k}+\mathbf{q}\nu'} - \epsilon_F)\end{aligned}$$

Isotropic coupling constant

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

$\lambda < 0.5$ weak coupling , $0.5 < \lambda < 1$ medium, $\lambda > 1$ strong coupling

Superconductivity: Relation to linewidth

Reminder: for $T \to 0$

$$\gamma_{\mathbf{q}j} = 2\pi\omega_{\mathbf{q}j}\frac{1}{N_k}\sum_{\mathbf{k}\nu\nu'}|g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}|^2\delta(\epsilon_{\mathbf{k}\nu}-\epsilon_F)\delta(\epsilon_{\mathbf{k}+\mathbf{q}\nu'}-\epsilon_F)$$

Thus

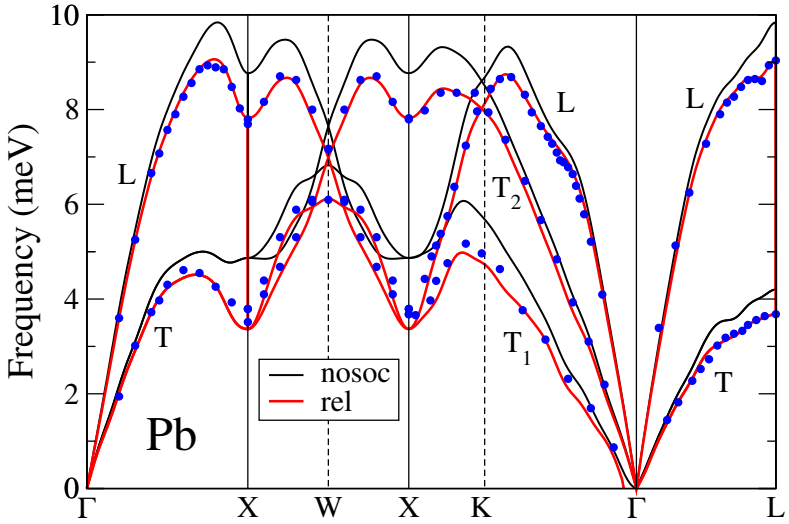
$$\begin{aligned}\alpha^2F(\omega) &= \frac{1}{N(\epsilon_F)}\frac{1}{N_q}\sum_{\mathbf{q}j,\mathbf{k}\nu\nu'}|g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}|^2\delta(\omega-\omega_{\mathbf{q}j})\delta(\epsilon_{\mathbf{k}\nu}-\epsilon_F)\delta(\epsilon_{\mathbf{k}+\mathbf{q}\nu'}-\epsilon_F)\\ &= \frac{1}{2\pi N(\epsilon_F)}\frac{1}{N_q}\sum_{\mathbf{q}j}\frac{\gamma_{\mathbf{q}j}}{\omega_{\mathbf{q}j}}\delta(\omega-\omega_{\mathbf{q}j})\end{aligned}$$

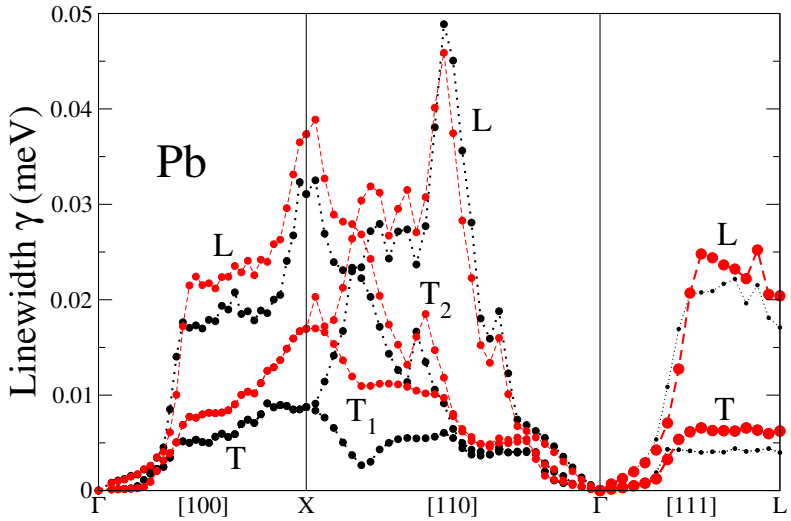
$\frac{\gamma_{\mathbf{q}j}}{\omega_{\mathbf{q}j}}$: dimensionless measure of mode coupling strength

Similar

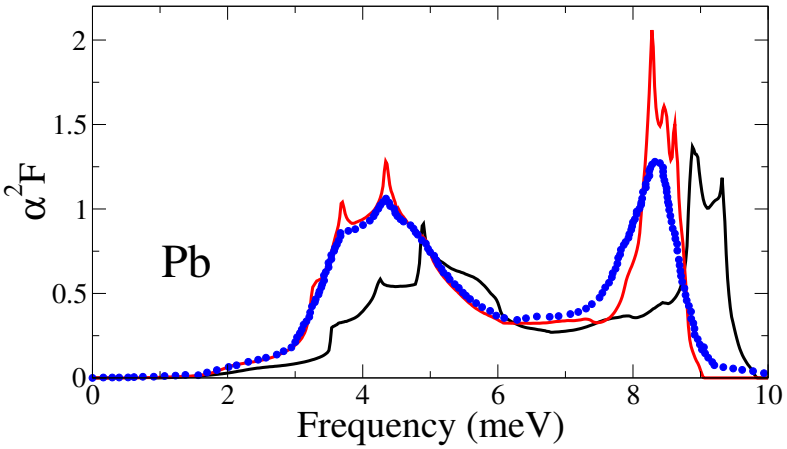
$$\lambda = \frac{1}{\pi N(\epsilon_F)}\frac{1}{N_q}\sum_{\mathbf{q}j}\frac{\gamma_{\mathbf{q}j}}{\omega^2_{\mathbf{q}j}}$$

Superconductivity: Example Pb





INS data from Brockhouse 1962, Stedman 1967



$\lambda_{exp} = 1.55$

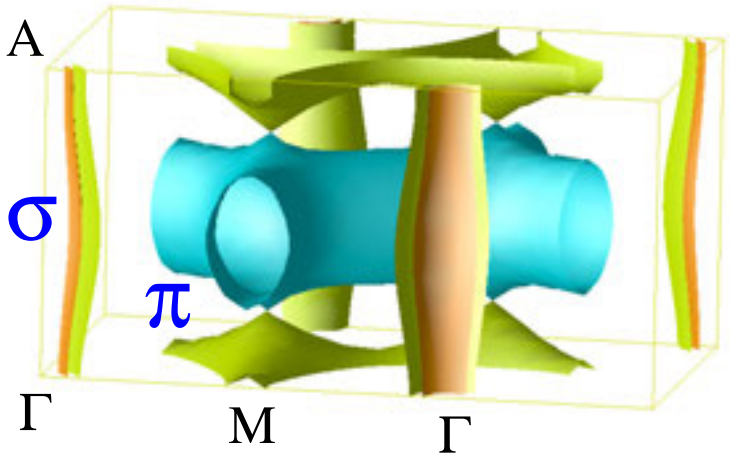
$\lambda_{rel} = 1.56$

$\lambda_{nosoc} = 1.08$

Tunneling spectroscopy: McMillan and Rowell, 1969

theory: RH *et al.*, PRB **81**, 174527 (2010)

Multiband superconductivity



MgB_2: Textbook example

- T_c=39 K
- Fermi surfaces of different character
- weak interband defect scattering

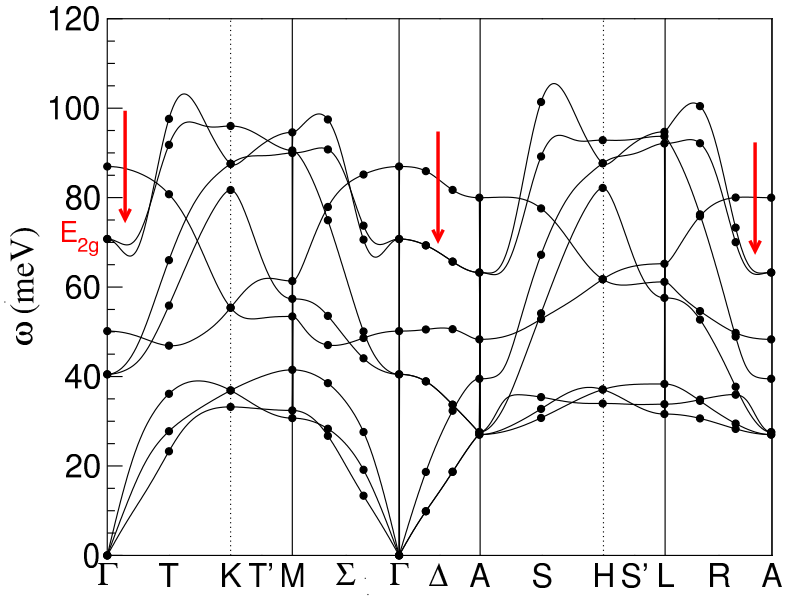
Partial average over individual Fermi surfaces:

$$\alpha^2 F_{\nu\nu'}(\omega) = \frac{1}{N(\epsilon_F)} \frac{1}{N_q} \sum_{\mathbf{q}j,\mathbf{k}} |g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}|^2 \delta(\omega - \omega_{\mathbf{q}j}) \delta(\epsilon_{\mathbf{k}\nu} - \epsilon_F) \delta(\epsilon_{\mathbf{k}+\mathbf{q}\nu'} - \epsilon_F)$$

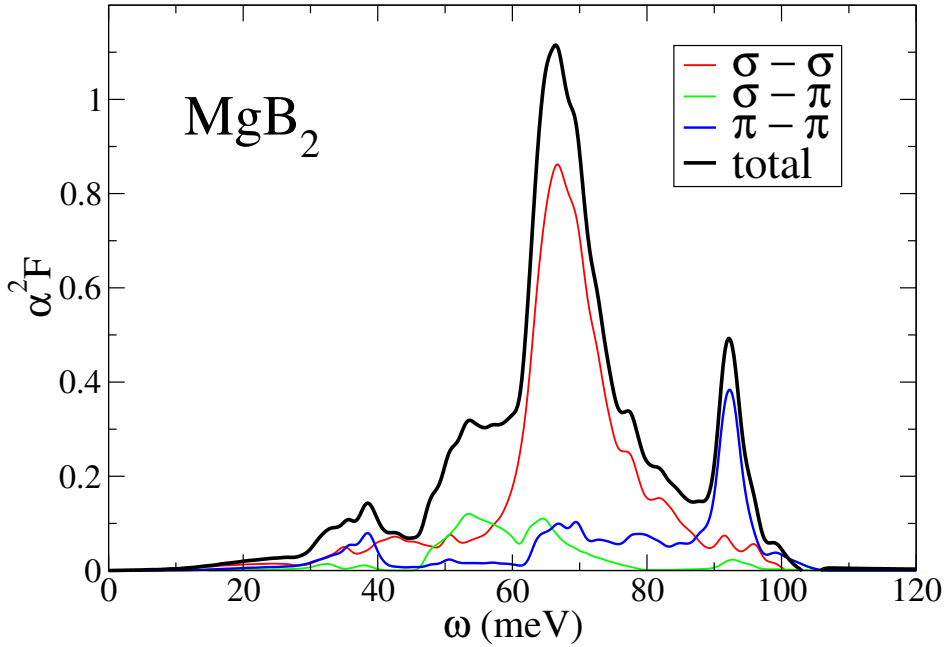
Intra- and interband contributions

Multiband superconductivity (2)

MgB_2: Phonon dispersion



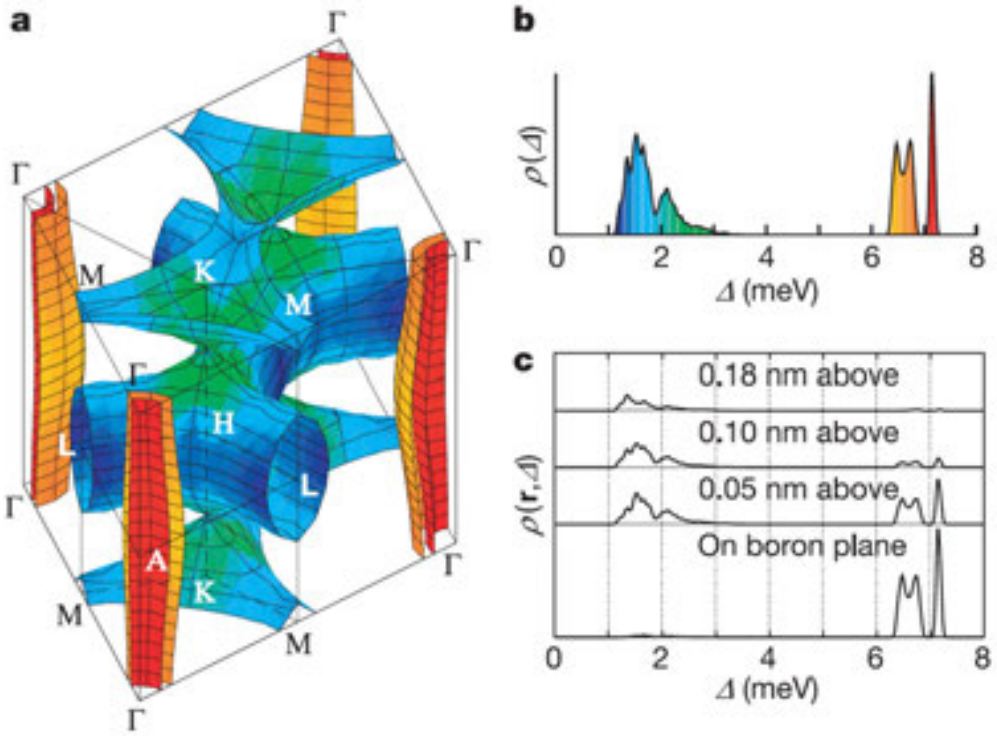
2-band Eliashberg functions



- dominant coupling in σ-σ channel
- huge coupling to specific in-plane B-vibrations (E_{2g}); large softening
- different gaps for σ and π Fermi surfaces; enhances T_c

Superconductivity: Full anisotropy

Solving gap equation using anisotropic Eliashberg function $\alpha^2 F_{\mathbf{k}\nu,\mathbf{k}'\nu'}(\omega)$



- clean limit
- distribution of gaps
- close to 2-gap description
- difficulty: proper momentum dependence of Coulomb pseudopotential μ^*

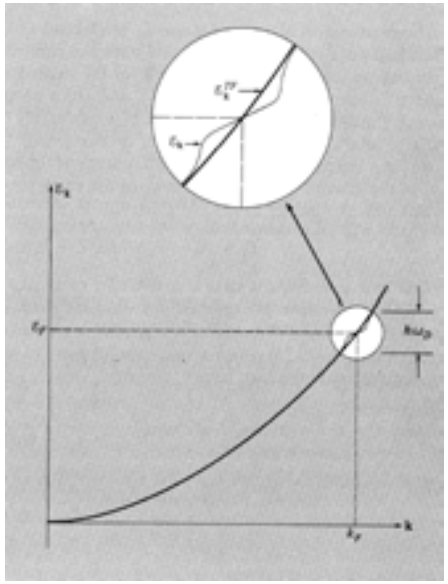
Choi *et al.*, Nature **418**, 758 (2002)

Electron self-energy effects

Renormalization of electronic quasiparticles in the normal state by phonons:

(A) quasiparticle with energies
$|\epsilon - \epsilon_F| < \omega_{\text{phonon}}$

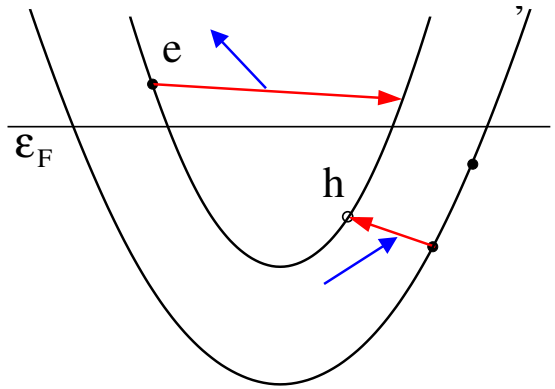
- modified dispersion $\longrightarrow$ kinks
- enhancement of effective mass
- affects thermodynamical and transport properties



from Ashcroft/Mermin

(B) quasiparticles (electrons or holes) away from Fermi energy

- decay via phonons $\longrightarrow$ finite lifetimes
- provides specific information about momentum-/band-dependent EPC

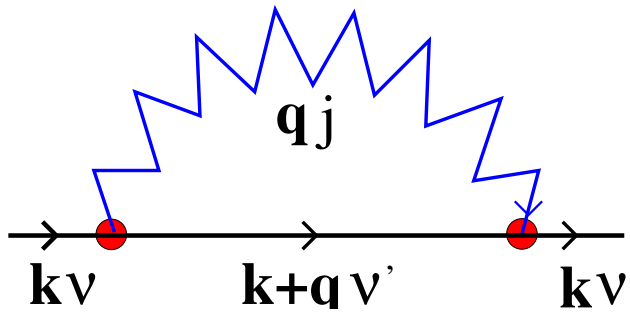


Electron self-energy: Lowest-order

Renormalization

$$G(\mathbf{k}\nu,\epsilon) = \frac{1}{\epsilon - (\epsilon_{\mathbf{k}\nu} - \mu) - \Sigma(\mathbf{k}\nu,\epsilon)} \Rightarrow \left\{ \begin{array}{rcl} \bar{\epsilon}_{\mathbf{k}\nu} & = & \epsilon_{\mathbf{k}\nu} - \mathrm{Re}\Sigma(\mathbf{k}\nu,\bar{\epsilon}_{\mathbf{k}\nu}) \\ \Gamma_{\mathbf{k}\nu} & = & -2\mathrm{Im}\Sigma(\mathbf{k}\nu,\bar{\epsilon}_{\mathbf{k}\nu}) \end{array} \right.$$

Lowest-order to self-energy Σ



$$\Sigma(\mathbf{k}\nu,\epsilon) = \frac{1}{N_q}\sum_{\mathbf{q}j}\sum_{\nu'} |g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}|^2 \left[\frac{b(\omega_{\mathbf{q}j}) + f(\epsilon_{\mathbf{k}+\mathbf{q}\nu'})}{\epsilon + \omega_{\mathbf{q}j} - \epsilon_{\mathbf{k}+\mathbf{q}\nu'} + i\delta} + \frac{b(\omega_{\mathbf{q}j}) + 1 - f(\epsilon_{\mathbf{k}+\mathbf{q}\nu'})}{\epsilon - \omega_{\mathbf{q}j} - \epsilon_{\mathbf{k}+\mathbf{q}\nu'} + i\delta} \right]$$

Two types of processes: phonon creation and annihilation

Quasiparticle lifetimes

Finite lifetime due to absorption or emission of phonons

$$\tau_{\mathbf{k}\nu} \propto (\Gamma_{\mathbf{k}\nu})^{-1} \quad \text{with linewidth} \quad \Gamma_{\mathbf{k}\nu} = -2\mathrm{Im}\Sigma(\mathbf{k}\nu, \bar{\epsilon}_{\mathbf{k}\nu})$$

Lowest-order contribution

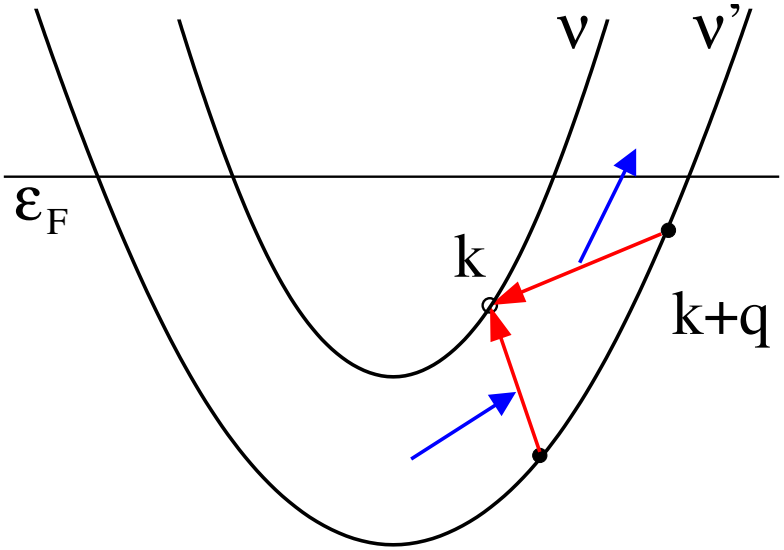
$$\begin{aligned}
\mathrm{Im}\Sigma(\mathbf{k}\nu,\epsilon) &= -\pi \frac{1}{N_q} \sum_{\mathbf{q}j} \sum_{\nu'} |g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}|^2 \Big[(b(\omega_{\mathbf{q}j}) + f(\epsilon_{\mathbf{k}+\mathbf{q}\nu'}))\delta(\epsilon + \omega_{\mathbf{q}j} - \epsilon_{\mathbf{k}+\mathbf{q}\nu'}) \\
&\qquad + (b(\omega_{\mathbf{q}j}) + 1 - f(\epsilon_{\mathbf{k}+\mathbf{q}\nu'}))\delta(\epsilon - \omega_{\mathbf{q}j} - \epsilon_{\mathbf{k}+\mathbf{q}\nu'}) \Big] \\
&= -\pi \int_0^\infty d\omega \Big\{ \alpha^2 F^+_{\mathbf{k}\nu}(\epsilon,\omega)[b(\omega) + f(\omega+\epsilon)] \\
&\qquad + \alpha^2 F^-_{\mathbf{k}\nu}(\epsilon,\omega)[b(\omega) + f(\omega-\epsilon)] \Big\}
\end{aligned}$$

State-dependent spectral functions

$$\alpha^2 F^{\pm}_{\mathbf{k}\nu}(\epsilon,\omega) = \frac{1}{N_q} \sum_{\mathbf{q}j} \delta(\omega - \omega_{\mathbf{q}j}) \sum_{\nu'} |g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}|^2 \delta(\epsilon - \epsilon_{\mathbf{k}+\mathbf{q}\nu'} \pm \omega)$$

Electron self-energy: Spectral functions

$$\alpha^2 F^{\pm}_{\mathbf{k}\nu}(\bar{\epsilon}_{\mathbf{k}\nu}, \omega) = \frac{1}{N_q} \sum_{\mathbf{q}j} \delta(\omega - \omega_{\mathbf{q}j}) \sum_{\nu'} |g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}|^2 \delta(\bar{\epsilon}_{\mathbf{k}\nu} - \epsilon_{\mathbf{k}+\mathbf{q}\nu'} \pm \omega)$$



- $+$: absorption; $-$: emission
- spectral function momentum and band dependent

Quasielastic approximation

$$\alpha^2 F^+_{\mathbf{k}\nu} \approx \alpha^2 F^-_{\mathbf{k}\nu} \equiv \alpha^2 F_{\mathbf{k}\nu}$$

$$\alpha^2 F_{\mathbf{k}\nu}(\epsilon,\omega) = \frac{1}{N_q}\sum_{\mathbf{q}j}\delta(\omega-\omega_{\mathbf{q}j})\sum_{\nu'}|g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}|^2\delta(\epsilon-\epsilon_{\mathbf{k}+\mathbf{q}\nu'})$$

State-dependent coupling parameter

$$\lambda_{\mathbf{k}\nu} = 2\int d\omega \frac{\alpha^2 F_{\mathbf{k}\nu}(\epsilon_{\mathbf{k}\nu},\omega)}{\omega}$$

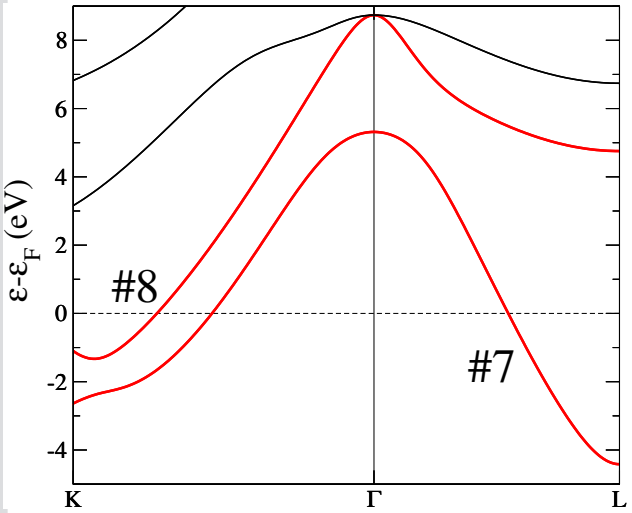
Average at Fermi energy $\rightarrow$ isotropic Eliashberg function

$$\alpha^2 F(\omega) = \sum_{\mathbf{k}\nu} w_{\mathbf{k}\nu}\alpha^2 F_{\mathbf{k}\nu}(\epsilon_F,\omega) \quad \text{with} \quad w_{\mathbf{k}\nu} = \delta(\epsilon_{\mathbf{k}\nu}-\epsilon_F)/N(\epsilon_F)$$

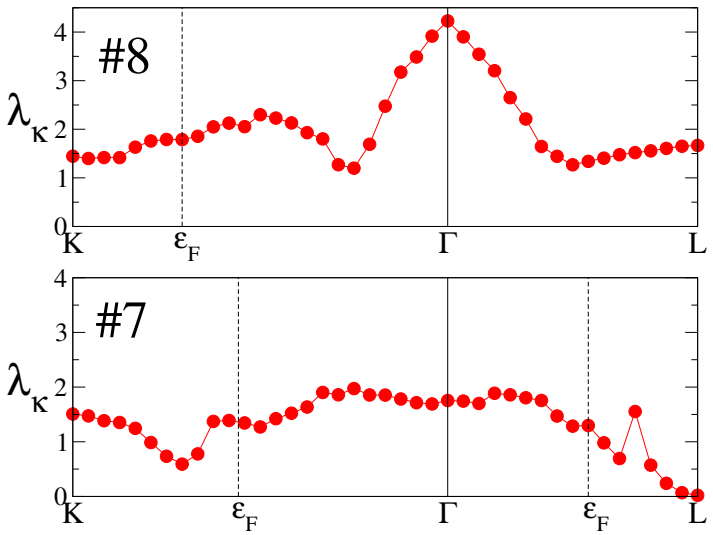
Electron self-energy: $\lambda_{\mathbf{k}\nu}$

Example: Pb bulk

Dispersion



EPC coupling



- large variation of coupling with binding energy and momenta
- band dependent

Electron self-energy: Experimental probe

T-dependence of linewidth

$$\Gamma_{\mathbf{k}\nu}(T) = \pi \int_0^\infty d\omega \left\{ \alpha^2 F_{\mathbf{k}\nu}(\bar{\epsilon}_{\mathbf{k}\nu}, \omega)[2b(\omega) + f(\omega + \bar{\epsilon}_{\mathbf{k}\nu}) + f(\omega - \bar{\epsilon}_{\mathbf{k}\nu})] \right\}$$

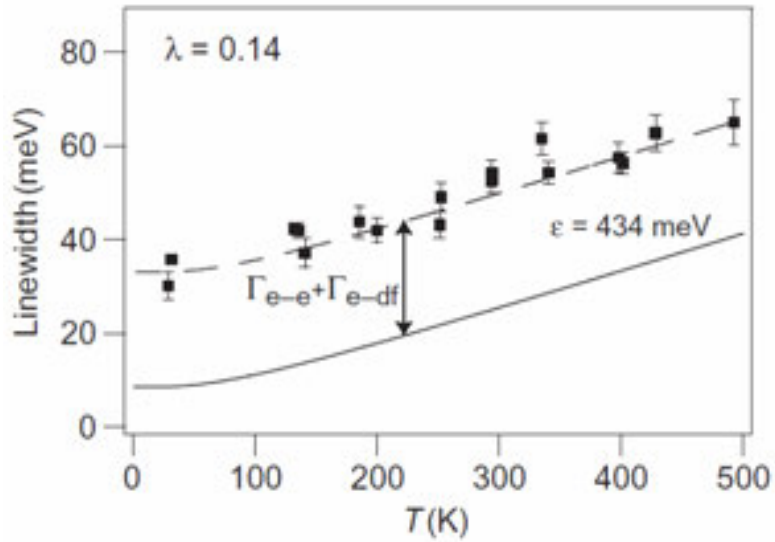
Two limiting cases

- $T \to 0$: $\Gamma_{\mathbf{k}\nu} \to 2\pi \int_0^{\omega_{\max}} d\omega \alpha^2 F_{\mathbf{k}\nu}(\bar{\epsilon}_{\mathbf{k}\nu}, \omega)$
- $T \gg \omega_{\max}$: $\Gamma_{\mathbf{k}\nu} \approx 2\pi\lambda_{\mathbf{k}\nu} k_B T$ $\quad \to \lambda_{\mathbf{k}\nu}$ determines slope of $\Gamma_{\mathbf{k}\nu}(T)$

Surface state at Cu(111)

- large offset from electron-electron and electron-defect scattering
- $\omega_{\max} \approx 30$ meV ≈ 350 K

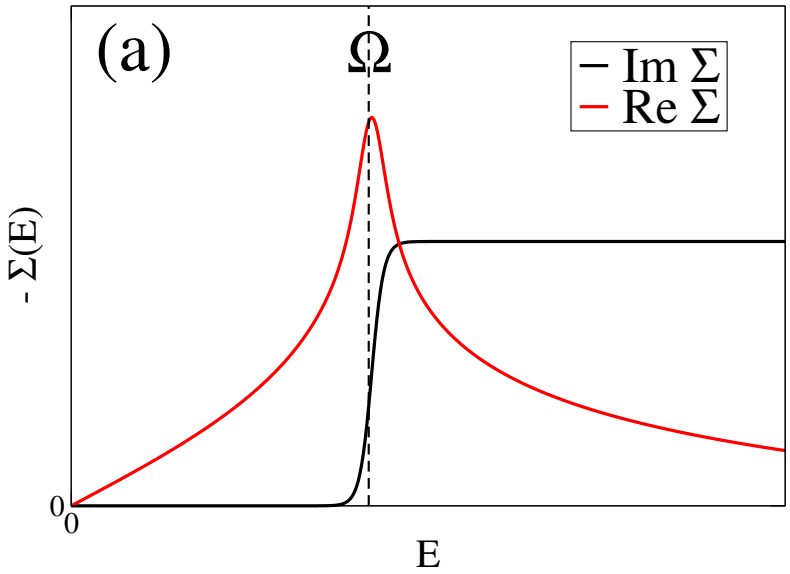
from Hofmann *et al.*, New J.Phys. **11**, 125005 (2009)



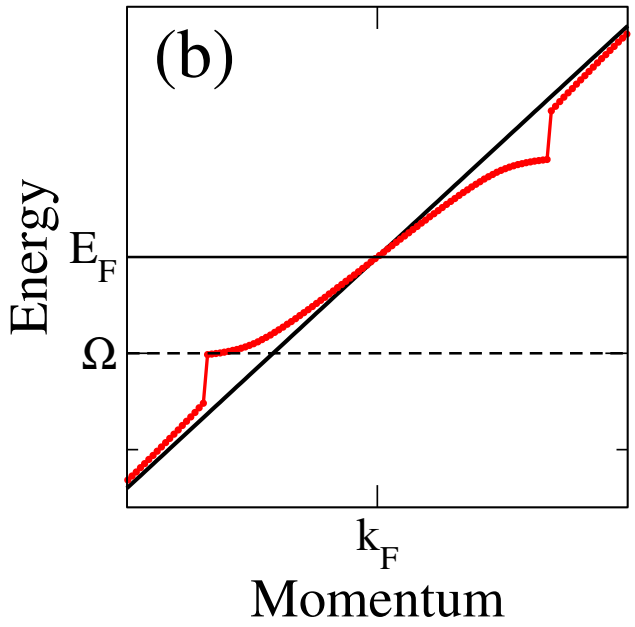
Electron self-energy: Renormalization near E_F

Illustrative example: Einstein model: $\omega_{\mathbf{q}j} \rightarrow \Omega$, $|g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu}|^2 \rightarrow g^2$

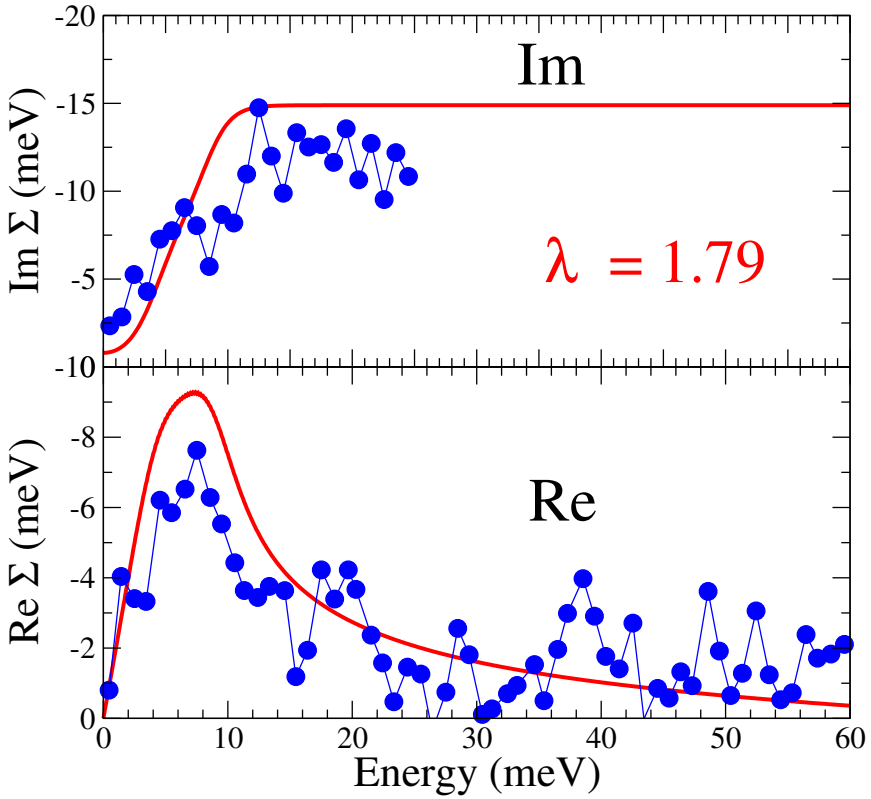
Self-energy

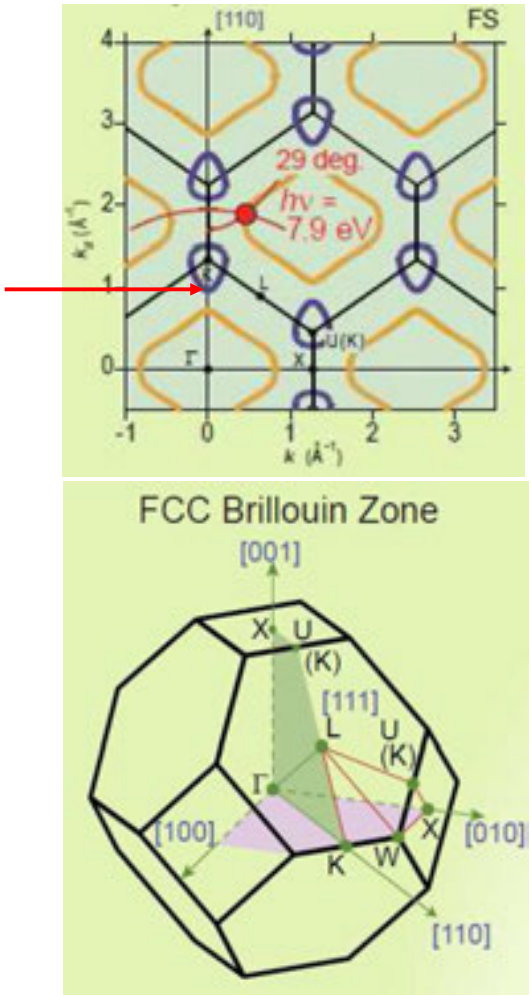


Quasiparticle dispersion



Electron self-energy from ARPES



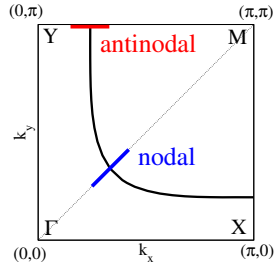


ARPES data after Reinert *et al.*, PRL **91**, 186406 (2003), *ibid* PRL **92**, 089904 (2004) (Erratum)

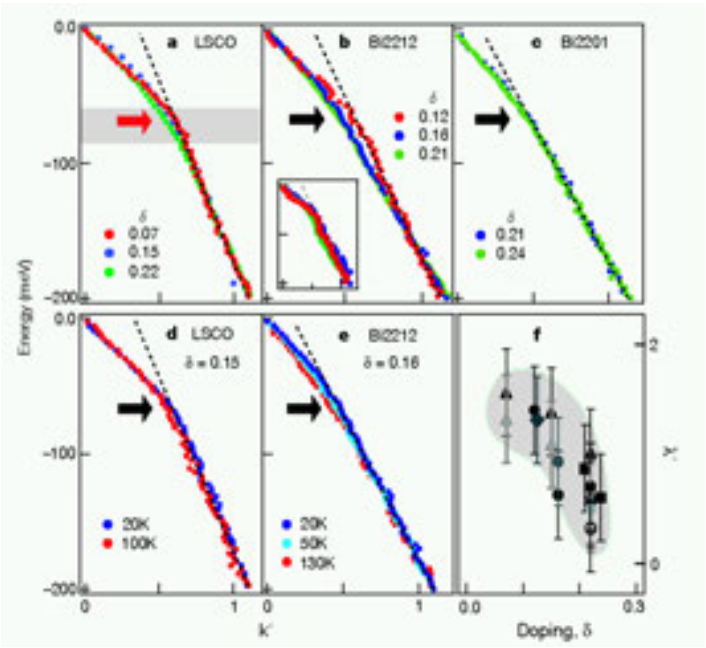
- Pb(110) surface, T=8K
- cut off-symmetry along ΓK line

Electron self-energy: Kinks in Cuprates

Pronounced dispersion kinks observed in many cuprate compounds

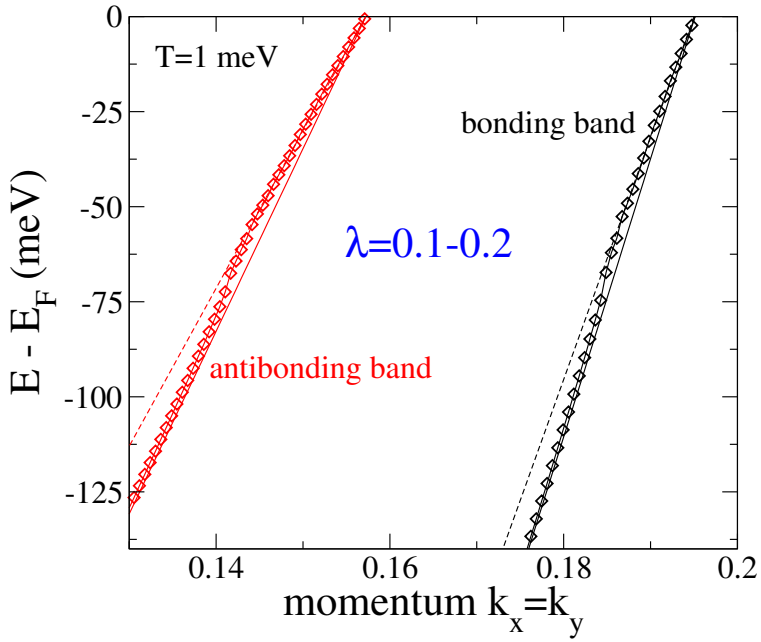


ARPES



Lanzara *et al.*, Nature **412**, 510 (2001)

DFPT



RH *et al.*, PRL **100**, 137001 (2008)

Calculated self-energy 3–5 times too small to explain observed kink

Summary

- introduction to state-of-the-art DFT-based approach to lattice dynamics and electron-phonon coupling
- discussions of foundation and limitations
- DFPT for lattice dynamics is very predictive because it includes static renormalization
- gives insight into the microscopic form of coupling, on the basis of realistic atomic and electronic structures
- estimates for phonon-mediated pairing, provides input for multiband Eliashberg analysis; can provide hints for presence of non-phononic mechanisms
- experimental tests of momentum dependence of EPC are possible via linewidths (phonons or electrons), if coupling is strong enough
- challenge: combination with theories for strongly correlated materials