Karlsruhe Institute of Technology

Linear Response and Electron-Phonon Coupling

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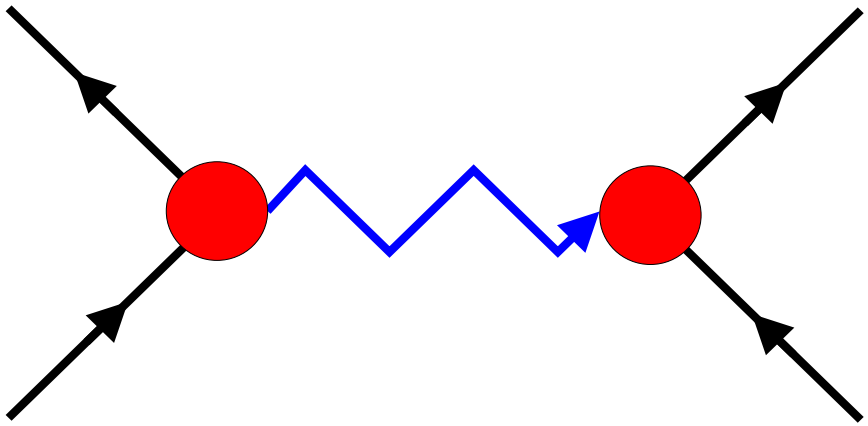


Outline

1. Linear response in density functional theory
   - Adiabatic perturbations
   - Basics of density functional theory
   - Linear-response formulation
2. Electron-phonon coupling
   - General considerations
   - Density functional perturbation theory
3. Applications
   - Fröhlich Hamiltonian and many-body perturbation
   - Renormalization of electronic properties
   - Phonon renormalization
   - Transport
   - Phonon-mediated pairing
4. Extensions: LDA+U and beyond

Linear response in density functional theory

Adiabatic perturbation

$$Q_n = \left. \frac{d^n E}{d\lambda^n} \right|_{\lambda \to 0}$$

type of perturbation λ	order n	physical property Q
displacements of atoms	1	atomic force
$\delta\mathbf{R}$	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
$\delta\mathbf{R} + \eta$	2+1	Grüneisen parameter
$\delta\mathbf{R} + \mathbf{E}$	1+2	Raman scattering cross section

Basics of density functional theory

Interacting electron system

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

DFT framework: Hohenberg-Kohn (1964)

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

Minimization $\rightarrow$ ground-state energy+density: $E_0 = E[n_0]$, $n_0(\mathbf{r})$

Practical approach: Kohn-Sham (1965)

Fictious non-interacting reference system

$$F[n] = T_s[n] + E_H[n] + E_{XC}[n]$$

Basics of density functional theory (2)

Single-partice (Kohn-Sham) equations

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

Effective potential

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

with

$$v_H(\mathbf{r})[n] = \frac{\delta E_H}{\delta n(\mathbf{r})} \qquad v_{XC}(\mathbf{r})[n] = \frac{\delta E_{XC}}{\delta n(\mathbf{r})}$$

Density

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

$E_{XC}[n]$: exchange-correlation; approximated (LDA, GGA, ...)

Energy derivatives

- Adiabatic perturbations: $v_{\text{ext}}^{\Lambda}, \quad \Lambda = \{\lambda_a, a = 1, \ldots, p\}$
- Energy functional

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

- Variational principle

$$\frac{\delta E^{\Lambda}[n]}{\delta n(\mathbf{r})} = 0 \rightarrow n_0^{\Lambda}(\mathbf{r})$$

- Ground-state energy

$$E_0^{\Lambda} = F[n_0^{\Lambda}] + \int d^3 r n_0^{\Lambda}(\mathbf{r}) v_{ext}^{\Lambda}(\mathbf{r})$$

- Two contributions to 1st-order derivative

$$\frac{\partial E_0^{\Lambda}}{\partial \lambda_a} = \int d^3 r n_0^{\Lambda}(\mathbf{r}) \frac{\partial v_{\text{ext}}^{\Lambda}(\mathbf{r})}{\partial \lambda_a} + \cancel{\int d^3 r \frac{\delta E^{\Lambda}[n]}{\delta n(\mathbf{r})} \frac{\partial n_0^{\Lambda}(\mathbf{r})}{\partial \lambda_a}}$$

Energy derivatives

- 1st derivative

$$\frac{\partial E_0^\Lambda}{\partial \lambda_a} = \int d^3 r n_0^\Lambda(\mathbf{r}) \frac{\partial v_{\text{ext}}^\Lambda(\mathbf{r})}{\partial \lambda_a}$$

- 2nd derivatives

$$\frac{\partial^2 E_0^\Lambda}{\partial \lambda_a \partial \lambda_b} = \int d^3 r \frac{\partial n_0^\Lambda(\mathbf{r})}{\partial \lambda_b} \frac{\partial v_{\text{ext}}^\Lambda(\mathbf{r})}{\partial \lambda_a} + \int d^3 r n_0^\Lambda(\mathbf{r}) \frac{\partial^2 v_{\text{ext}}^\Lambda(\mathbf{r})}{\partial \lambda_a \partial \lambda_b}$$

- Evaluate for $\Lambda \to 0$

$\to$ only linear response of $n_0^\Lambda(\mathbf{r})$ required

Energy derivatives (2)

”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)

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

- 2nd and 3rd order accessible in linear response

Linear response within Kohn-Sham scheme

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 within Kohn-Sham scheme (2)

Variation of effective potential $v_{\text{eff}}[n] = v_{\text{ext}} + v_H[n] + v_{XC}[n]$

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

with kernel

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

Dielectric screening

$$\delta n = \chi_0 \delta v_{\text{eff}}\,, \quad \delta v_{\text{eff}} = \delta v_{\text{ext}} + I\delta n \quad \Rightarrow \delta v_{\text{eff}} = \delta v_{\text{ext}} + I\chi_0 \delta v_{\text{eff}}$$

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

$\epsilon(\mathbf{r},\mathbf{r}')$: (static) dielectric matrix

- historically first route persued (Pick *et al.*1970, Resta 1985)

Modern formulation: Density functional perturbation theory

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

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

DFPT (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)

Iterative solution: $\rightarrow \delta n$ and δv_{eff}

Electron-phonon coupling

General considerations

Born-Oppenheimer expansion

$$\mathbf{R}_i = \mathbf{R}_i^0 + \kappa \mathbf{u}_i \qquad \kappa = (m/M)^{1/4} \leq 0.1 \qquad \text{(except H and He)}$$

Lowest order: adiabatic or Born-Oppenheimer approximation

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

$\rightarrow$ decoupling

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

- Electronic wavefunction depends parametrically on $\underline{\mathbf{R}}$
- Ions move in an effective potential (electrons in ground state)

$$\Omega(\underline{\mathbf{R}}) = V_{ii}(\underline{\mathbf{R}}) + E_0(\underline{\mathbf{R}})$$

General considerations

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

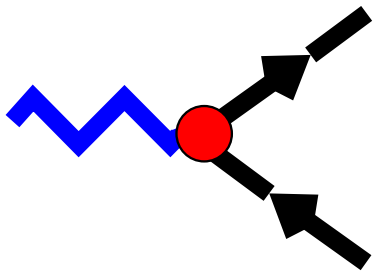
$$\Omega(\{\mathbf{R}\}) = \Omega^{(0)} - \sum_{i\alpha} F_{i\alpha} u_{i\alpha} + \frac{1}{2} \sum_{ij\alpha\beta} \phi_{\alpha\beta}(i,j)\, u_{i\alpha} u_{j\beta} + \ldots$$

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

Electron-phonon vertex

1st order beyond the adiabatic approximation: $\langle n | \delta_{\mathbf{R}} V | n' \rangle$

$$\delta_{\mathbf{R}} V \propto \mathbf{u} \cdot \nabla V^0|_{\mathbf{R}_0}$$



$\mathbf{u} \propto b + b^\dagger \rightarrow$ phonon creation/annihilation

Density functional perturbation theory (DFPT)

Phonons in periodic lattices

$i \to (ls)$: unit cell / ion in unit cell $\qquad \mathbf{R}_i^0 \to \mathbf{R}_{ls}^0 = \mathbf{R}_l^0 + \mathbf{R}_s^0$

Dynamical matrix

$$D_{s\alpha s'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum \Phi_{\alpha\beta}(ls, 0s') e^{-i\mathbf{q}(\mathbf{R}_{ls}^0 - \mathbf{R}_{0s'}^0)}$$

Normal modes

$$\sum_{s'\beta} D_{s\alpha s'\beta}(\mathbf{q}) \eta_{s'\beta}(\mathbf{q}j) = \omega_{\mathbf{q}j}^2 \eta_{s\alpha}(\mathbf{q}j)$$

Periodic displacements

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

Define operators: $\quad \delta_{s\alpha}^{\mathbf{q}} \equiv \frac{\partial}{\partial d_{s\alpha}}, \delta_{s\alpha}^{-\mathbf{q}} \equiv \frac{\partial}{\partial d_{s\alpha}^*} = \delta_{s\alpha}^{\mathbf{q}\,*}$

DFPT: Phonons in periodic lattices (2)

Electronic contribution to the dynamical matrix

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

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

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

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

DFPT: Phonons in periodic lattices (3)

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

1st-order density

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

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

- no coupling between different $\mathbf{q}$
- involves only valence state quantities $\rightarrow$ from ground state calculation $\mathbf{q}$-grid

Electron-phonon vertex in DFPT

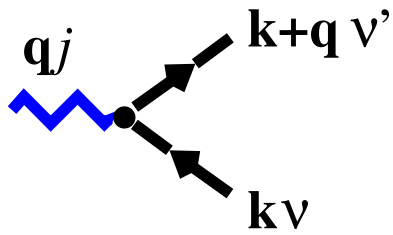
Bare vertex

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

Normal-mode representation

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

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

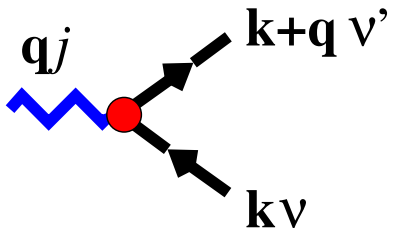


- rigid displacement of electron-ion potential
- ignores screening effects

Electron-phonon vertex in DFPT (2)

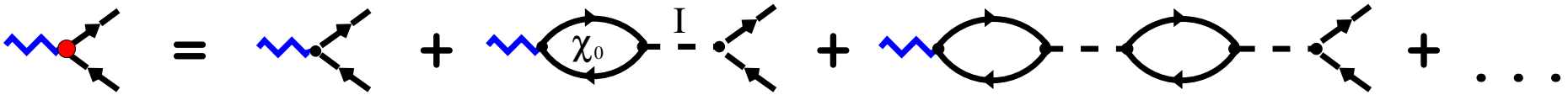
Screened vertex

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



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 $I = I_H + I_{XC}$
  $\rightarrow$ includes exchange-correlation

Applications

Fröhlich Hamiltonian

Minimal Hamiltonian (Fröhlich 1952)

$$
\begin{aligned}
H &= H_e + H_{ph} + H_{e-ph} \\
H_e &= \sum_{\mathbf{k}\nu\sigma} \epsilon_{\mathbf{k}\nu} c^\dagger_{\mathbf{k}\nu\sigma} c_{\mathbf{k}\nu\sigma} \\
H_{ph} &= \sum_{\mathbf{q}j} \omega_{\mathbf{q}j} \left(b^\dagger_{\mathbf{q}j} b_{\mathbf{q}j} + \frac{1}{2} \right) \\
H_{e-ph} &= \sum_{\mathbf{k}\nu\nu'\sigma} \sum_{\mathbf{q}j} g^{\mathbf{q}j}_{\mathbf{k}+\mathbf{q}\nu',\mathbf{k}\nu} c^\dagger_{\mathbf{k}+\mathbf{q}\nu'\sigma} c_{\mathbf{k}\nu\sigma} \left(b_{\mathbf{q}j} + b^\dagger_{-\mathbf{q}j} \right)
\end{aligned}
$$

- H_e: band electrons (noninteracting)
- H_{ph}: harmonic phonons
- H_{e-ph}: lowest-order electron-phonon interaction

Compact notation: $k = (\mathbf{k}\nu)$, $k' = (\mathbf{k}'\nu')$, $q = (\mathbf{q}j)$ no spin

$$
\rightarrow \qquad g^q_{k',k} = g^{\mathbf{q}j}_{\mathbf{k}'\nu',\mathbf{k}\nu} \delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}}
$$

Fröhlich Hamiltonian

Minimal Hamiltonian (Fröhlich 1952)

$$
\begin{aligned}
H &= H_e + H_{ph} + H_{e-ph} \\
H_e &= \sum_k \epsilon_k c_k^\dagger c_k \\
H_{ph} &= \sum_q \omega_q \left(b_q^\dagger b_q + \frac{1}{2} \right) \\
H_{e-ph} &= \sum_{k,k'} \sum_q g^q_{k',k} c_{k'}^\dagger c_k \left(b_q + b_{-q}^\dagger \right)
\end{aligned}
$$

- H_e: band electrons (noninteracting)
- H_{ph}: harmonic phonons
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Compact notation: $k = (\mathbf{k}\nu)$, $k' = (\mathbf{k}'\nu')$, $q = (\mathbf{q}j)$ no spin

$$
\rightarrow \qquad g^q_{k',k} = g^{\mathbf{q}j}_{\mathbf{k}'\nu',\mathbf{k}\nu} \delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}}
$$

Many-body perturbation

Dyson equations and self-energies

Electrons $\quad G(k, i\omega_n)^{-1} = G_0(k, i\omega_n)^{-1} - \Sigma(k, i\omega_n)$

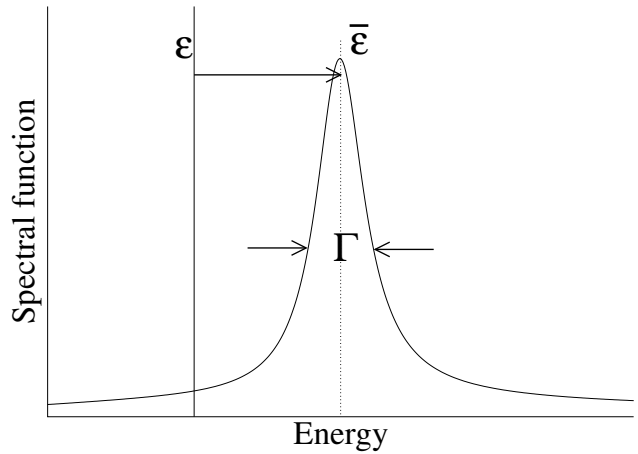
Phonons $\quad D(q, i\nu_m)^{-1} = D_0(q, i\nu_m)^{-1} - \Pi(q, i\nu_m)$

Quasiparticle picture

Retarded GF: $G(k, \epsilon) = G(k, i\omega_n \to \epsilon + i\delta) = [\epsilon - \epsilon_k - \Sigma(k, \epsilon)]^{-1}$

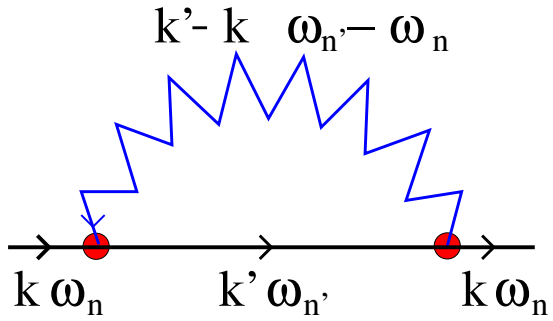
Small Σ

- QP-energy shift: $\bar{\epsilon}_k = \epsilon_k + \mathrm{Re}\Sigma(k, \bar{\epsilon}_k)$
- Linewidth ($\propto 1/\tau$): $\Gamma_k = -2\mathrm{Im}\Sigma(k, \bar{\epsilon}_k)$



Renormalization of electronic properties

Electron self-energy



After analytic continuation: $i\omega_n \rightarrow \epsilon + i\delta$

$$\Sigma_{ep}(k,\omega) = \frac{1}{N_q}\sum_{k',q} |g^q_{k',k}|^2 \left[\frac{b(\omega_q) + f(\epsilon_{k'})}{\omega + \omega_q - \epsilon_{k'} + i\delta} + \frac{b(\omega_q) + 1 - f(\epsilon_{k'})}{\omega - \omega_q - \epsilon_{k'} + i\delta}\right]$$

Electron self-energy

$$\mathrm{Im}\Sigma_{ep}(k,\epsilon) = -\pi \frac{1}{N_q} \sum_{k',q} |g^q_{k',k}|^2 \left[\delta(\epsilon - \epsilon_{k'} + \omega_q)(b(\omega_q) + f(\epsilon_{k'})) \right.$$
$$\left. + \delta(\epsilon - \epsilon_{k'} - \omega_q)(b(\omega_q) + 1 - f(\epsilon_{k'}))\right]$$

Collect all q-dependent parts

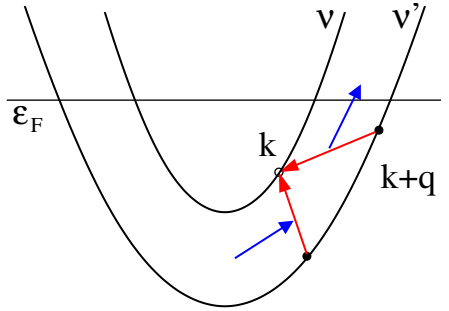
$$\mathrm{Im}\Sigma_{ep}(k,\epsilon) = -\pi \sum_{k'} \frac{1}{N_q} \sum_{q} |g^q_{k',k}|^2 \int d\omega \delta(\omega - \omega_q)$$
$$\left[\delta(\epsilon - \epsilon_{k'} + \omega)(b(\omega) + f(\epsilon_{k'})) \right.$$
$$\left. + \delta(\epsilon - \epsilon_{k'} - \omega)(b(\omega) + 1 - f(\epsilon_{k'}))\right]$$

Introduce

$$\alpha^2 F^{\pm}_k(\epsilon,\omega) = \frac{1}{N_q} \sum_q \delta(\omega - \omega_q) \sum_{k'} |g^q_{k',k}|^2 \delta(\epsilon - \epsilon_{k'} \pm \omega)$$

Electron self-energy

Scattering processes



$$\mathrm{Im}\Sigma_{ep}(k,\epsilon) = -\pi \int_0^\infty d\omega \Big\{ \alpha^2 F_k^+(\epsilon,\omega)[b(\omega)+f(\omega+\epsilon)] + \alpha^2 F_k^-(\epsilon,\omega)[b(\omega)+f(\omega-\epsilon)] \Big\}$$

"+": phonon emission "–": absorption

Quasielastic approximation

$$\alpha^2 F_k^+ \approx \alpha^2 F_k^- \approx \alpha^2 F_k(\epsilon,\omega) = \frac{1}{N_q} \sum_q \delta(\omega-\omega_q) \sum_{k'} |g^q_{k',k}|^2 \delta(\epsilon-\epsilon_{k'})$$

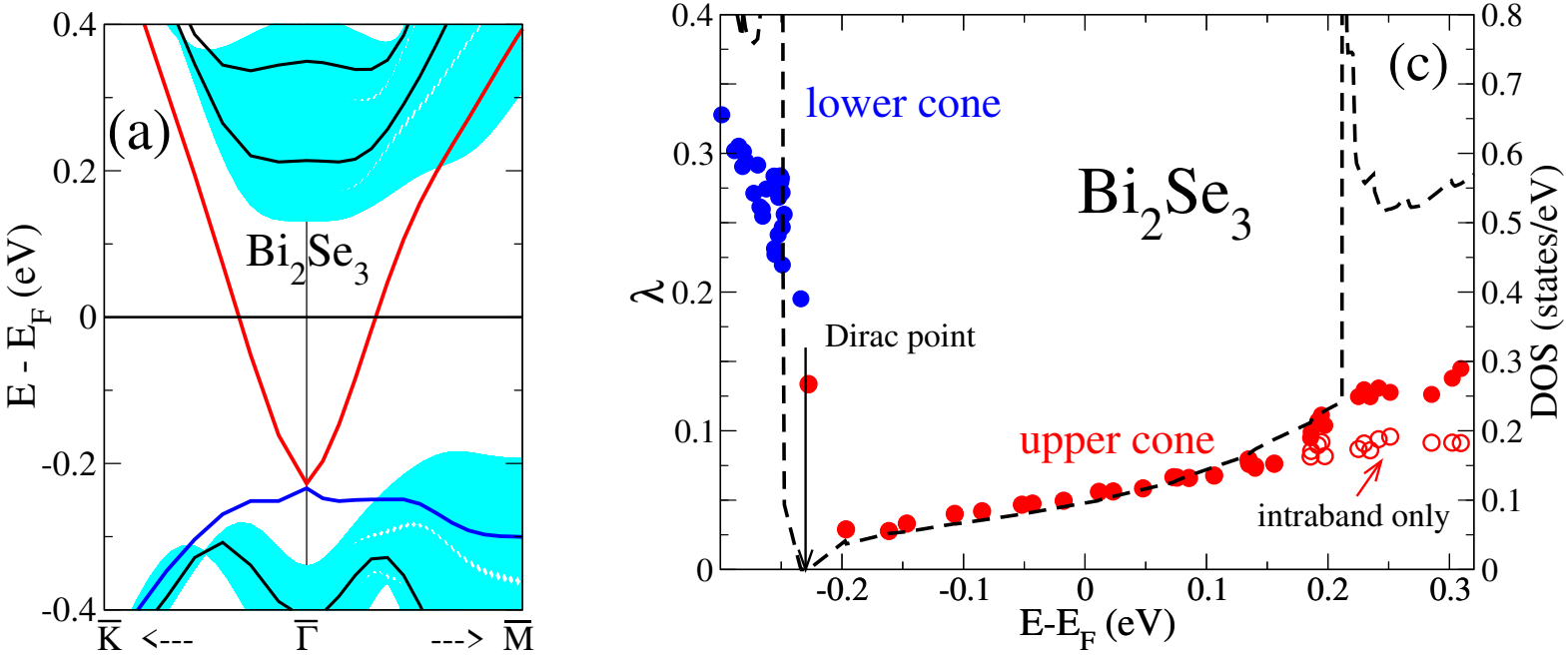
Coupling constant

$$\lambda_k = 2 \int d\omega \frac{\alpha^2 F_k(\bar{\epsilon}_k,\omega)}{\omega}$$

depends on electronic state!

Electron self-energy: Example

Topological insulator Bi_2Se_3: surface Dirac cone



RH, Sklyadneva, Chulkov, Sci. Rep. **7**, 1095 (2017)

- Coupling in upper cone increases linearly with binding energy
- Small λ guarantees well defined quasiparticles at room temperature

Electron self-energy: Experimental probes

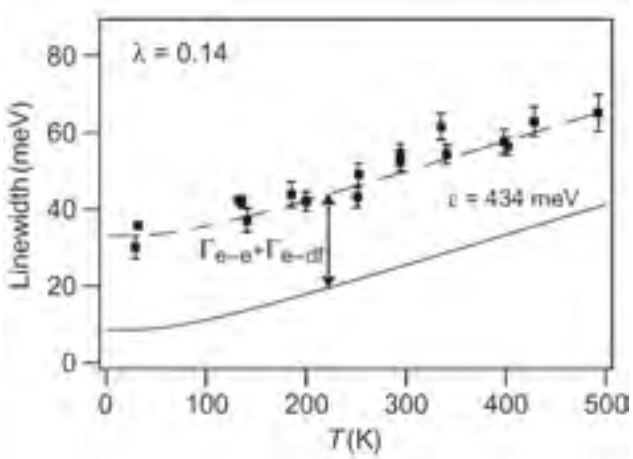
(1) Slope of of $\mathrm{Re}\Sigma_{ep}$ at E_F

$$\lambda_k = -\left.\frac{\partial \mathrm{Re}\Sigma_{ep}(k,\epsilon)}{\partial \epsilon}\right|_{\epsilon=0,T=0}$$

$$\bar{\epsilon}_k = \epsilon_k + \mathrm{Re}\Sigma(k,\bar{\epsilon}_k) \quad \Rightarrow \quad \begin{aligned} \bar{v}_F &= v_F/(1+\lambda_{k_F}) \\ m_k^* &= m_k(1+\lambda_k) \end{aligned}$$

(2) T-dependence of linewidth

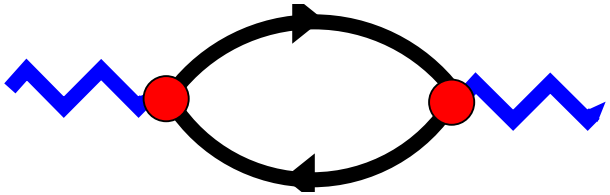
$$\begin{aligned} \Gamma_k(T) &= \pi \int_0^\infty d\omega \left\{ \alpha^2 F_k(\bar{\epsilon}_k,\omega)[2b(\omega) + f(\omega+\bar{\epsilon}_k) + f(\omega-\bar{\epsilon}_k)] \right\} \\ &\approx 2\pi\lambda_k T \qquad \text{for } T \gg \omega_{\mathrm{ph}} \end{aligned}$$



Cu(111) surface state

ARPES data after McDougall *et al.*, PRB **51**, 13891 (1995)

Phonon renormalization



Phonon self-energy: leading order

$$\Pi_q(\omega) = \frac{1}{N_k} \sum_{k',k} |g^q_{k',k}|^2 \frac{f(\epsilon_k) - f(\epsilon_{k'})}{\omega + \epsilon_k - \epsilon_{k'} + i\delta}$$

Real part $\rightarrow$ frequency renormalization: static part included in DFPT

Linewidth

$$\gamma_q = -2\mathrm{Im}\Pi_q(\omega_q) = 2\pi \frac{1}{N_k} \sum_{k',k} |g^q_{k',k}|^2 [f(\epsilon_k) - f(\epsilon_{k'})] \delta[\omega_q + (\epsilon_k - \epsilon_{k'})]$$

Phonon renormalization (2)

$$\gamma_q = 2\pi \frac{1}{N_k} \sum_{k',k} |g^q_{k',k}|^2 [f(\epsilon_k) - f(\epsilon_{k'})] \delta[\omega_q + (\epsilon_k - \epsilon_{k'})]$$

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

$$f(\epsilon_k) - f(\epsilon_{k'}) \approx f'(\epsilon_k)(\epsilon_k - \epsilon_{k'}) \rightarrow -f'(\epsilon_k)\omega_q$$

$T \rightarrow 0$: $f'(\epsilon_k) \rightarrow -\delta(\epsilon_k)$ and drop ω_q in δ-function

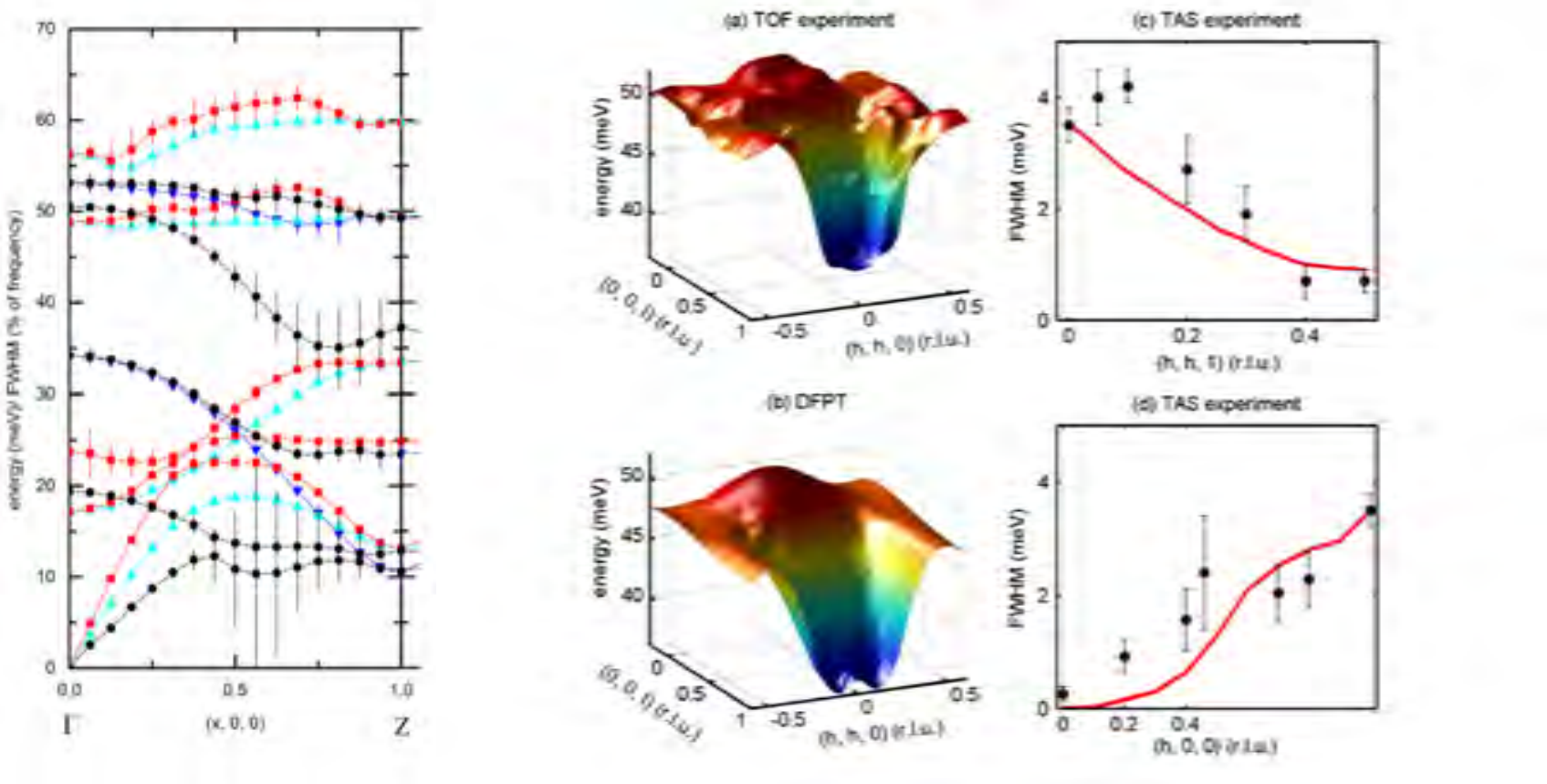
$$\gamma_q = 2\pi\omega_q \frac{1}{N_k} \sum_{k',k} |g^q_{k',k}|^2 \delta(\epsilon_k)\delta(\epsilon_{k'})$$

Allen, PRB **6**, 2577 (1972)

- γ_q measurable quantity (e.g., via inelastic neutron or x-ray scattering)
- $\rightarrow$ experimental test of theoretical predictions
- but need to separate from other contributions: anharmonicity, defects

Phonon renormalization (3): Example

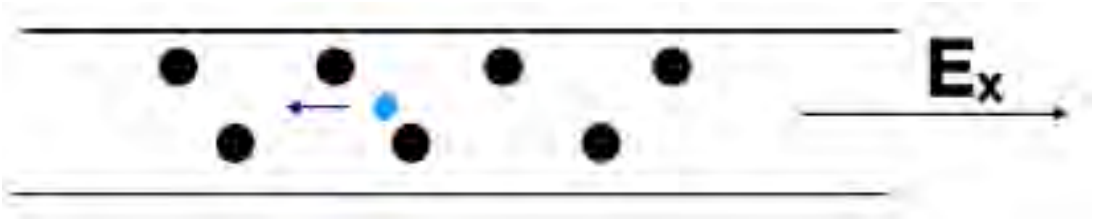
YNi_2B_2C



Weber *et al.*, PRL **109**, 057001 (2012), PRB **89**, 104503 (2014)

Transport

Example: electric current



Semi-classical picture: steady state characterized by new distribution F_k

$$j_x = -\frac{2e}{V}\frac{1}{N_k}\sum_k F_k(v_k)_x$$

Electrical conductivity:

$$\sigma_{xx} = j_x / E_x$$

Transport (2)

Boltzmann transport equations

$$-eE_x \frac{\partial F_k}{\partial k_x} = \left(\frac{\partial F_k}{\partial t}\right)_{\text{coll}}$$

Ludwig Eduard Boltzmann

LHS: change in occupation due to electric field
RHS: rate of change in occupation due to collisions

$$\left(\frac{\partial F_k}{\partial t}\right)_{\text{coll}} = \sum_{k'} \left(P_{k'k} F_{k'}[1 - F_k] - P_{kk'} F_k[1 - F_{k'}]\right)$$

$P_{kk'}$: probability of scattering from state (k) to (k')

Electron-phonon scattering: annihilation and creation processes

$$P_{kk'} = \frac{2\pi}{N_q} \sum_q |g^q_{k'k}|^2 \left[b(\omega_q)\delta(\epsilon_{k'} - \epsilon_k - \omega_q) + (b(\omega_q) + 1)\delta(\epsilon_{k'} - \epsilon_k + \omega_q)\right]$$

Transport: Electron-phonon scattering

Small field: Linear expansion

$$F_k = f_k + f_k^1 \, , f_k^1 \propto E_x$$

Linearized Boltzmann equation:

$$LHS : -eE_x \frac{\partial F_k}{\partial k_x} \rightarrow -eE_x \frac{\partial f_k}{\partial k_x} = -eE_x \frac{\partial f_k}{\partial \epsilon_k} \frac{\partial \epsilon_k}{\partial k_x} = -eE_x \frac{\partial f_k}{\partial \epsilon_k} (v_k)_x$$

$$\begin{aligned} RHS : \quad & \sum_{k'} \quad \left(P_{k'k} (f_{k'}^1 [1 - f_k] - f_{k'} f_k^1) - P_{kk'} (f_k^1 [1 - f_{k'}] - f_k f_{k'}^1) \right) \\ = \quad & \sum_{k'} \quad P_{kk'} \left(-f_k^1 \frac{1 - f_{k'}}{1 - f_k} + f_{k'}^1 \frac{f_k}{f_{k'}} \right) \end{aligned}$$

using detailed balance: $P_{k'k} f_{k'} [1 - f_k] = P_{kk'} f_k [1 - f_{k'}]$

Transport: Relaxation time approximation

Approximation: $f^1_{k'} = 0$

$$RHS \to \sum_{k'} P_{kk'} \left(-f^1_k \frac{1 - f_{k'}}{1 - f_k} \right) = -f^1_k / \tau_k$$

Solution

$$f^1_k = eE_x \frac{\partial f_k}{\partial \epsilon_k} (v_k)_x \tau_k$$

Conductivity

$$\begin{aligned} \sigma_{xx} &= -\frac{2e}{VE_x} \frac{1}{N_k} \sum_k F_k (v_k)_x = -\frac{2e}{VE_x} \frac{1}{N_k} \sum_k f^1_k (v_k)_x \\ &= \frac{2e^2}{V} \frac{1}{N_k} \sum_k \left(-\frac{\partial f_k}{\partial \epsilon_k} \right) (v_k)_x (v_k)_x \tau_k \end{aligned}$$

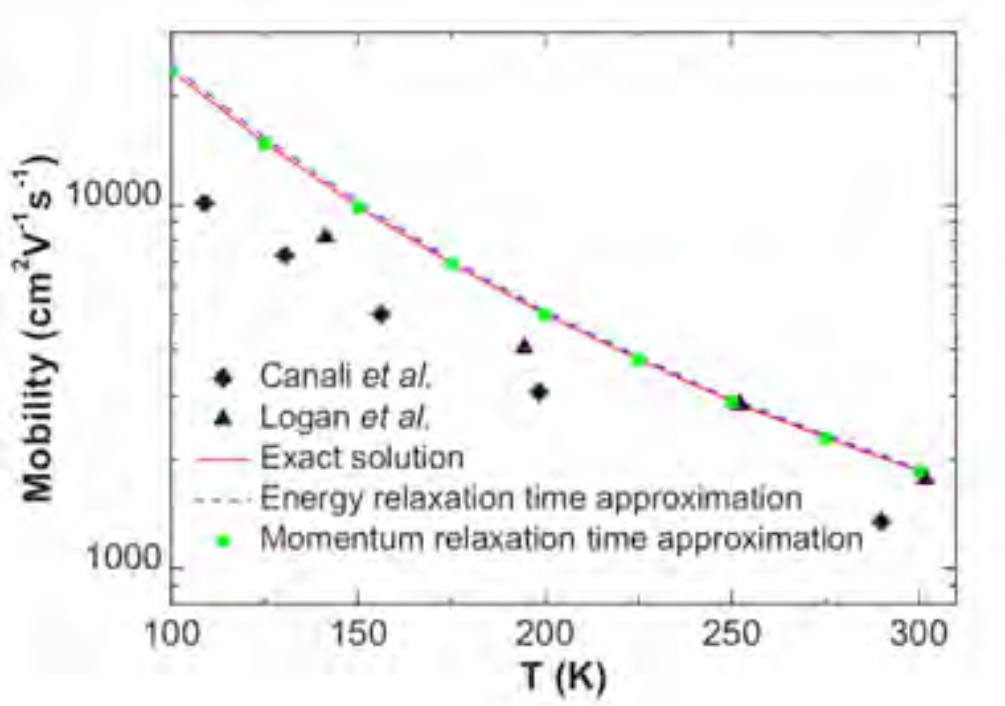
Transport: EPC relaxation time

$$
\begin{aligned}
1/\tau_k &= \sum_{k'} P_{kk'} \left(\frac{1-f_{k'}}{1-f_k} \right) \\
&= \sum_{k'} \sum_{q} \frac{2\pi}{N_q} |g^q_{k'k}|^2 \Big[b(\omega_q)\delta(\epsilon_{k'} - \epsilon_k - \omega_q) \\
&\quad + (b(\omega_q)+1)\delta(\epsilon_{k'} - \epsilon_k + \omega_q) \Big] \left(\frac{1-f_{k'}}{1-f_k} \right) \\
&= \Gamma_k \quad \text{Linewidth of el. quasiparticle}
\end{aligned}
$$

- Evaluation of k-dependence is cumbersome
- Applications to transport in semiconductors

Transport: EPC relaxation time

Example: Mobility of Si



$$\mu = \frac{\sigma}{ne}$$

Wu Li, PRB **92**, 075405 (2015)

Transport: Metals

Effective relaxation time: Variational approach (Ziman 1960)

$$\frac{1}{\tau} = 2\pi \int d\omega \frac{x}{\sinh^2 x} \alpha^2_{\rm tr} F(\omega) \qquad x = \frac{\omega}{2T}$$

Transport spectral function

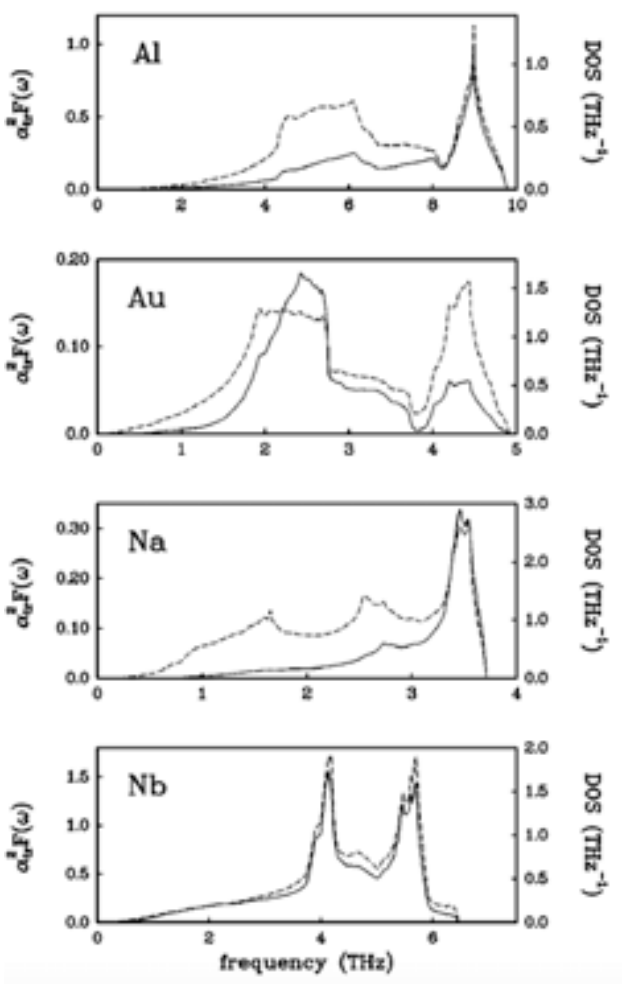
$$\alpha^2_{\rm tr} F(\omega) = \frac{1}{N_q} \sum_q \delta(\omega - \omega_q) \frac{1}{N(0)} \frac{1}{N_k} \sum_{kk'} |g^q_{k'k}|^2 \eta_{k'k} \delta(\epsilon_k) \delta(\epsilon_{k'})$$

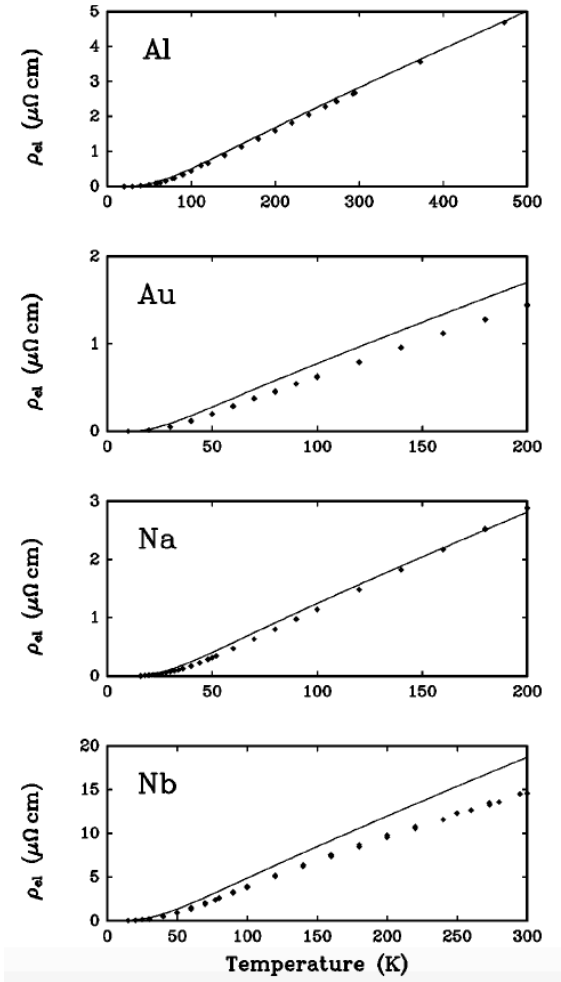
Efficiency factor: $\eta_{k'k} = 1 - \frac{\mathbf{v}_k \mathbf{v}_{k'}}{|\mathbf{v}_k|^2}$

Conductivity

$$\sigma_{xx} = \tau \frac{2e^2}{V} \frac{1}{N_k} \sum_k \Big(- \frac{\partial f_k}{\partial \epsilon_k} \Big) (v_k)_x (v_k)_x = \tau \frac{2e^2 N(0)}{V} < v_x^2 >$$

Transport: Metals (2)





Bauer *et al.*, PRB **57**, 11276 (1998)

Phonon-mediated pairing

Microscopic theories of superconductivity

- Weak coupling: BCS model by Bardeen, Cooper, Schrieffer (1957)
- Strong coupling: Eliashberg (1960)

Eliashberg gap equations (isotropic)

$$
\begin{aligned}
i\omega_n(1 - Z(i\omega_n)) &= -\pi T \sum_{n'} \Lambda(\omega_n - \omega_{n'}) \frac{\omega_{n'}}{\sqrt{\omega_{n'}^2 + \Delta(i\omega_{n'})^2}} \\
\Delta(i\omega_n) Z(i\omega_n) &= \pi T \sum_{n'} \Lambda(\omega_n - \omega_{n'}) \frac{\Delta(i\omega_{n'})}{\sqrt{\omega_{n'}^2 + \Delta(i\omega_{n'})^2}}
\end{aligned}
$$

$\Delta(i\omega_n)$: Gap function

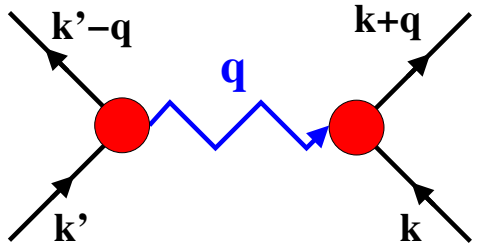
$Z(i\omega_n)$: Quasiparticle renormalization factor

$\Lambda(\nu_m)$: Pairing interaction

Electron-phonon pairing interaction

Kernel

$$\Lambda(\nu_m) = \int d\omega \frac{2\omega\alpha^2 F(\omega)}{(\nu_m)^2 + \omega^2}$$



Eliashberg function

$$\alpha^2 F(\omega) = \frac{1}{N_q} \sum_q \delta(\omega - \omega_q) \frac{1}{N(0)} \frac{1}{N_k} \sum_{kk'} |g^q_{k'k}|^2 \delta(\epsilon_k)\delta(\epsilon_{k'})$$

- effective between states at E_F

Coupling constant: Maximum of $\Lambda(\nu_m)$ at $\nu_m = 0$

$$\lambda = \Lambda(0) = 2 \int d\omega \frac{\alpha^2 F(\omega)}{\omega}$$

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

Relation to phonon linewidth

Reminder: for $T \to 0$

$$\gamma_q = 2\pi\omega_q \frac{1}{N_k} \sum_{k',k} |g^q_{k',k}|^2 \delta(\epsilon_k)\delta(\epsilon_{k'})$$

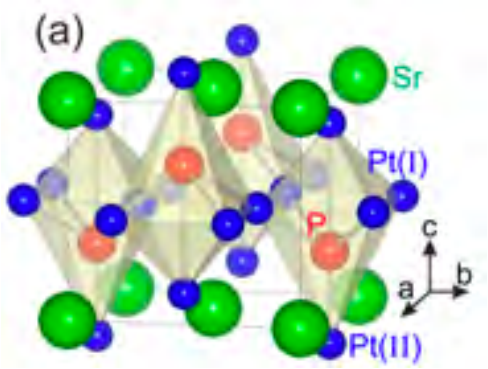
$$\begin{aligned} \Rightarrow \alpha^2F(\omega) &= \frac{1}{N_q}\sum_q \delta(\omega-\omega_q)\frac{1}{N(0)}\frac{1}{N_k}\sum_{kk'}|g^q_{k'k}|^2\delta(\epsilon_k)\delta(\epsilon_{k'}) \\ &= \frac{1}{2\pi N(0)}\frac{1}{N_q}\sum_q \frac{\gamma_q}{\omega_q}\delta(\omega-\omega_q) \end{aligned}$$

$\frac{\gamma_q}{\omega_q}$: dimensionless measure of mode coupling strength

Similar

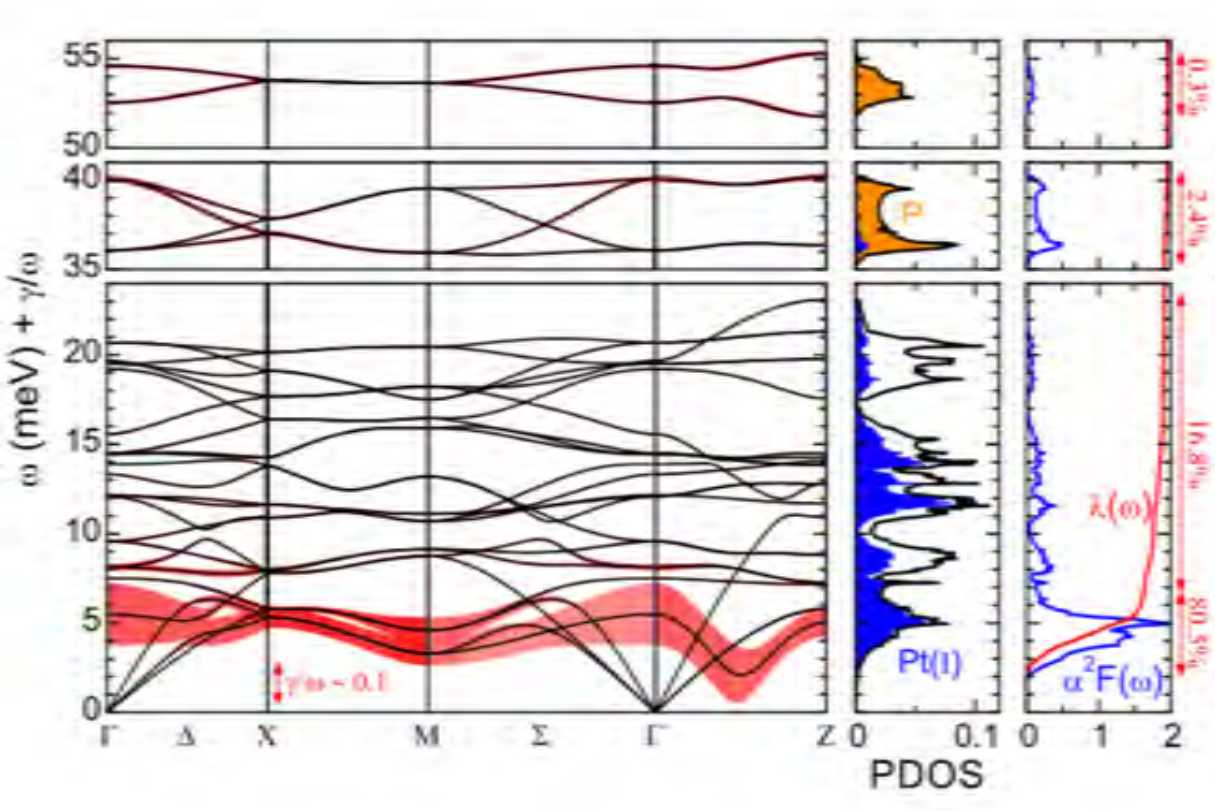
$$\lambda = \frac{1}{\pi N(0)}\frac{1}{N_q}\sum_q \frac{\gamma_q}{\omega_q^2}$$

Superconductivity: Example $SrPt_3P$



$T_C = 8.4$ K

Zocco *et al.*, PRB **92**, 220504 (2015)



- Predicts soft-mode (Pt(1)) with strong coupling, confirmed by IXS measurements
- Contributes 80% to total $\lambda \approx 2$

Extensions: LDA+U and beyond

LDA+U

- Correction to DFT functional to improve descripton of local correlations
- Introduced by Anisimov *et al.* (1991), various extensions exist
- Correlated subspace via atomic-like orbitals: $\Phi_a(\mathbf{r})$ with $a = (lm\sigma)$

Functional

$$E = E_{\text{local}} + E_U$$

E_{local}: DFT functional in local approximation (LDA or GGA)

$$E_U = \frac{1}{2} \sum_{abcd} \langle ab|v_c|cd\rangle (\rho_{ac}\rho_{bd} - \rho_{ad}\rho_{bc}) - E_{\text{dc}}[\{\rho_{ab}\}]$$

Orbital density matrix

$$\rho_{ab} = \sum_{i}^{\text{occ}} \langle i|b\rangle \langle a|i\rangle$$

$\langle ab|v_c|cd\rangle$: Coulomb potential, few pararmeters (like U or J)

E_{dc}: double counting correction

LDA+U: Effective potential

$$v_{\text{eff}} = v_{\text{ext}} + v_{\text{scr}}[n(\mathbf{r})] + \hat{v}_U[\{\rho_{ab}\}]$$

$$\begin{aligned} \hat{v}_U &= \sum_{ab} v_{ab} |a\rangle\langle b| = \sum_{ab} v_{ab} \hat{Q}_{ab} \\ v_{ab} &= \frac{\delta E_U}{\delta \rho_{ba}} = \sum_{cd} \left(\langle ac|v_c|bd\rangle - \langle ad|v_c|cb\rangle \right) \rho_{cd} - \left(v_{\text{dc}}\right)_{ab} \end{aligned}$$

Complications for linear response:

- Non-local potential $\hat{v}_U$
- v_{eff} functional of both $n(\mathbf{r})$ and ρ_{ab}
- Correlated subspace attached to atom postions

LDA+U: Linear response

Linear response of orbital density matrix

$$\rho_{ab} = \sum_{i}^{\mathrm{occ}} \langle i | \hat{Q}_{ba} | i \rangle$$

$$\begin{aligned}
\delta\rho_{ab} &= \delta\rho_{ab}^{(el)} + \delta\rho_{ab}^{(b)} \\
\delta\rho_{ab}^{(el)} &= \sum_{i}^{\mathrm{occ}} \left(\{\delta\langle i|\}\hat{Q}_{ba}|i\rangle + \langle i|\hat{Q}_{ba}\{\delta|i\rangle\} \right) \\
\delta\rho_{ab}^{(b)} &= \sum_{i}^{\mathrm{occ}} \langle i|\delta\hat{Q}_{ba}|i\rangle
\end{aligned}$$

LDA+U: Energy derivatives

1st order

$$\frac{\partial E}{\partial \lambda} \rightarrow \sum_{ab} \frac{\delta E_U}{\delta \rho_{ab}} \left(\frac{\partial \rho_{ab}^{(b)}}{\partial \lambda} \right)$$

- Only "bare" part contributes (Hellman-Feynman theorem)

2nd order

$$\frac{\partial^2 E}{\partial \lambda_1 \partial \lambda_2} \rightarrow \sum_{abcd} \frac{\delta^2 E_U}{\delta \rho_{ab} \delta \rho_{cd}} \left(\frac{\partial \rho_{ab}^{(b)}}{\partial \lambda_1} \right) \left(\frac{\partial \rho_{cd}}{\partial \lambda_2} \right) + \sum_{ab} \frac{\delta E_U}{\delta \rho_{ab}} \frac{\partial}{\partial \lambda_2} \left(\frac{\partial \rho_{ab}^{(b)}}{\partial \lambda_1} \right)$$

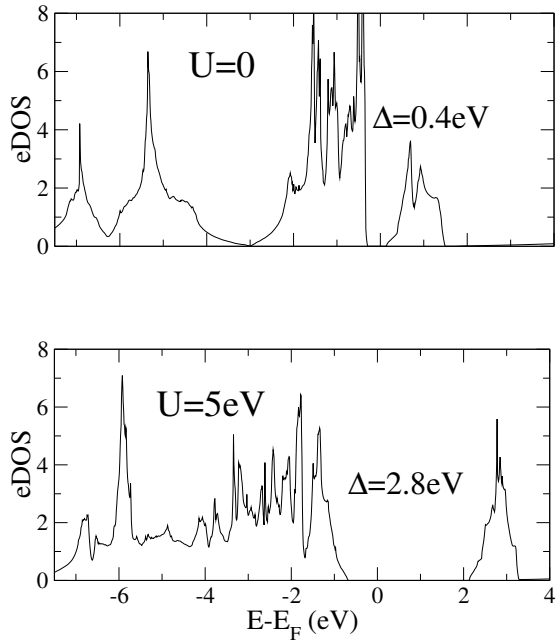
- Requires full linear response $\delta \rho_{ab}$ and $\delta n(\mathbf{r}')$

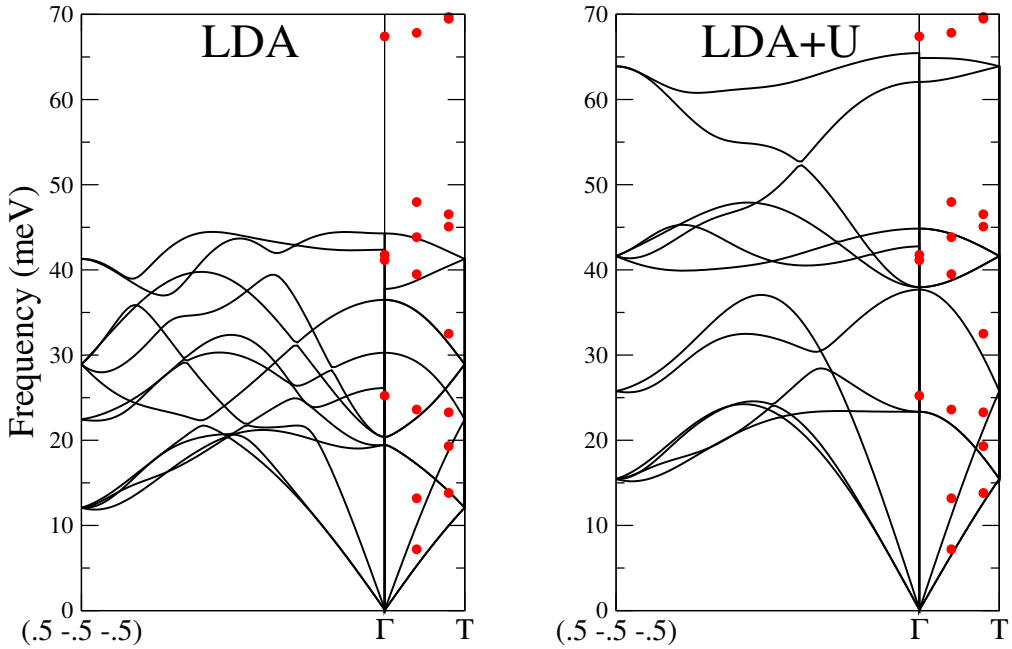
$$\delta v_{\text{eff}}(\mathbf{r}) = \delta v_{\text{ext}}(\mathbf{r}) + \int d^3 r' I(\mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}') + \sum_{abcd} I_{ab,cd} \delta \rho_{cd} \hat{Q}_{ab} + \sum_{ab} v_{ab} \delta \hat{Q}_{ab}$$

Interaction kernel: $I_{ab,cd} = \frac{\partial v_{ab}}{\partial \rho_{cd}} = \frac{\partial^2 E_U}{\partial \rho_{ab} \partial \rho_{cd}}$

LDA+U: Example NiO

- NiO: rocksalt structure, AFM along [111], large optical gap (3.1 eV)
- Charge-transfer insulator, correlated Ni-3d





Exp. data after Reichardt *et al.*, J.Phys.C **8**, 3955 (1975)

- LDA: small gap, soft spectrum → too much screening
- LDA+U: larger gap, reduced screening, harder spectrum

Beyond DFT+U

Linear response and electron-phonon coupling: extensions

1. Hybrid functionals
2. GW approach
3. DFT + Dynamical Mean-Field Theory (DMFT)

Beyond DFT+U

1. Hybrid functionals
   - Exact exchange, non-local

$$E_X^{\text{exact}}[n] = \frac{1}{2}\sum_{ij}\int d^3r_1\, d^3r_2\, \frac{\psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_1)\psi_i(\mathbf{r}_2)}{\mathbf{r}_1 - \mathbf{r}_2}$$

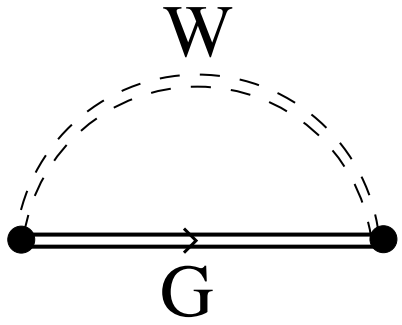
   - $E_{XC} \rightarrow E_X^{\text{exact}} + E_C^{\text{local}}$
   - Improves descriptions of wave functions and energies (band gaps)
   - Evaluation of non-local exchange $\rightarrow$ numerically expensive
   - Phonons and EPC: no full linear response implementation
   - Applications: frozen phonon and supercell approach

Beyond DFT+U

1. Hybrid functionals
2. GW approach

Quasi-particle equation

$$v_{XC} \rightarrow \hat{\Sigma} \approx GW$$



- $\hat{\Sigma}$ expressed by Green's function G and electron-electron interaction W
- Advantage: improves descriptions of quasi particles
- Numerically expensive (W non-local)

- Phonons and EPC: frozen phonon and supercell approach
- Recently: a more elaborate linear-response formulation (Li *et al.*, PRL **122**, 186402 (2019))

$$\delta v_{\text{eff}}^{GW} = \delta v_{\text{eff}}^{DFT} - \delta v_{XC} + \delta\hat{\Sigma}$$

Beyond DFT+U

1. Hybrid functionals
2. GW approach
3. DFT + Dynamical Mean-Field Theory (DMFT)
   - Frequency-dependent self energy: $\Sigma(\omega)$
   - Many-body impurity problem embedded in periodic lattice
   - Unified framework: Kotliar *et al.*, Rev. Mod.Phys. **78**, 865 (2006)
   - Linear-response formulation: Savrasov, Kotliar, PRL **90**, 056401 (2003)

$$\delta v_{\text{eff}}(\mathbf{r}), \delta\Sigma(\omega): \text{functionals of } \delta n(\mathbf{r}), \delta G(\omega)$$

Summary

- Introduction to linear-response techniques and electron-phonon coupling from a DFT perspective
- DFPT approach: provides insight into the microscopic form of coupling, on the basis of realistic atomic and electronic structures
- Full energy and momentum dependence of coupling matrix elements
- Applications: quasiparticle renormalization (electrons and phonons); transport; phonon-mediated pairing
- Challenge: extend method to approaches with more accurate treatment of strongly correlated systems