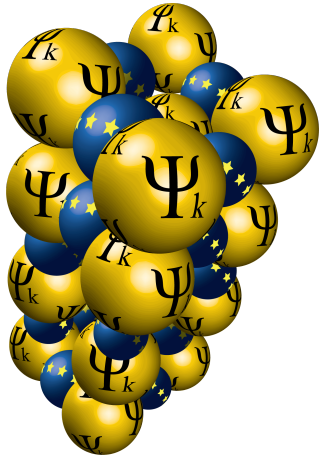
ICTP/Psi-k/CECAM School on Electron-Phonon Physics from First Principles

Trieste, 19-23 March 2018



Centre Européen de Calcul Atomique et Moléculaire

Lecture Thu.1

Electron-phonon effects in ARPES and IXS

Feliciano Giustino

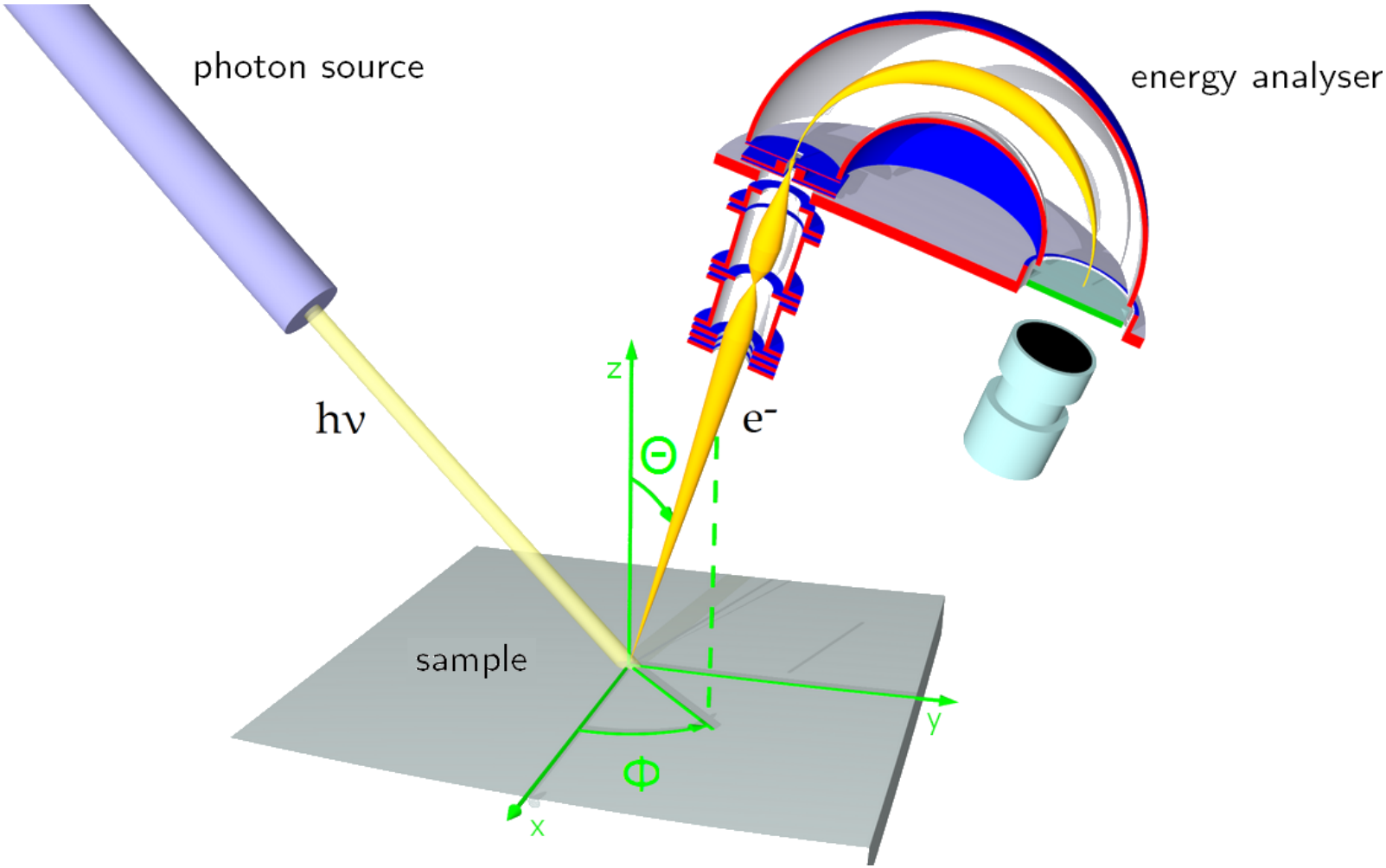
Department of Materials, University of Oxford

Department of Materials Science and Engineering, Cornell University

Lecture Summary

- Satellites in photoelectron spectroscopy
- Phonon Green's function and self-energy
- Connection with density-functional perturbation theory
- Non-adiabatic phonons
- Phonon lifetimes
- Electron-phonon matrix element and Fröhlich interaction

Angle-resolved photoelectron spectroscopy (ARPES)



commons.wikimedia.org/wiki/File:ARPESgeneral.png

ARPES kinks and satellites

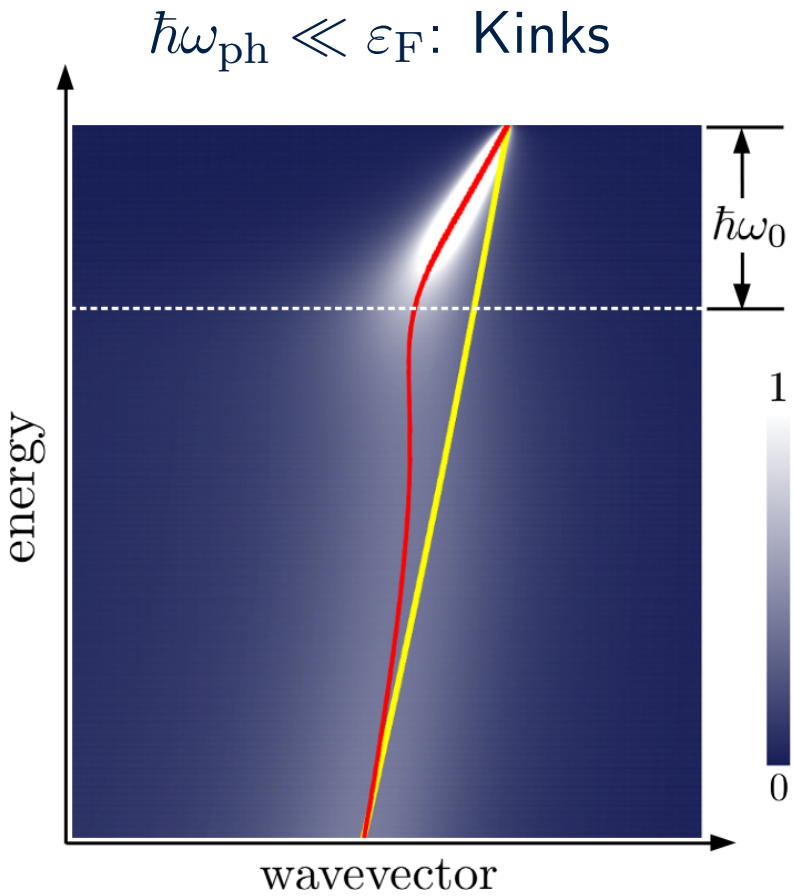


Figure from Giustino, Rev. Mod. Phys. 89, 015003 (2017)

ARPES kinks and satellites

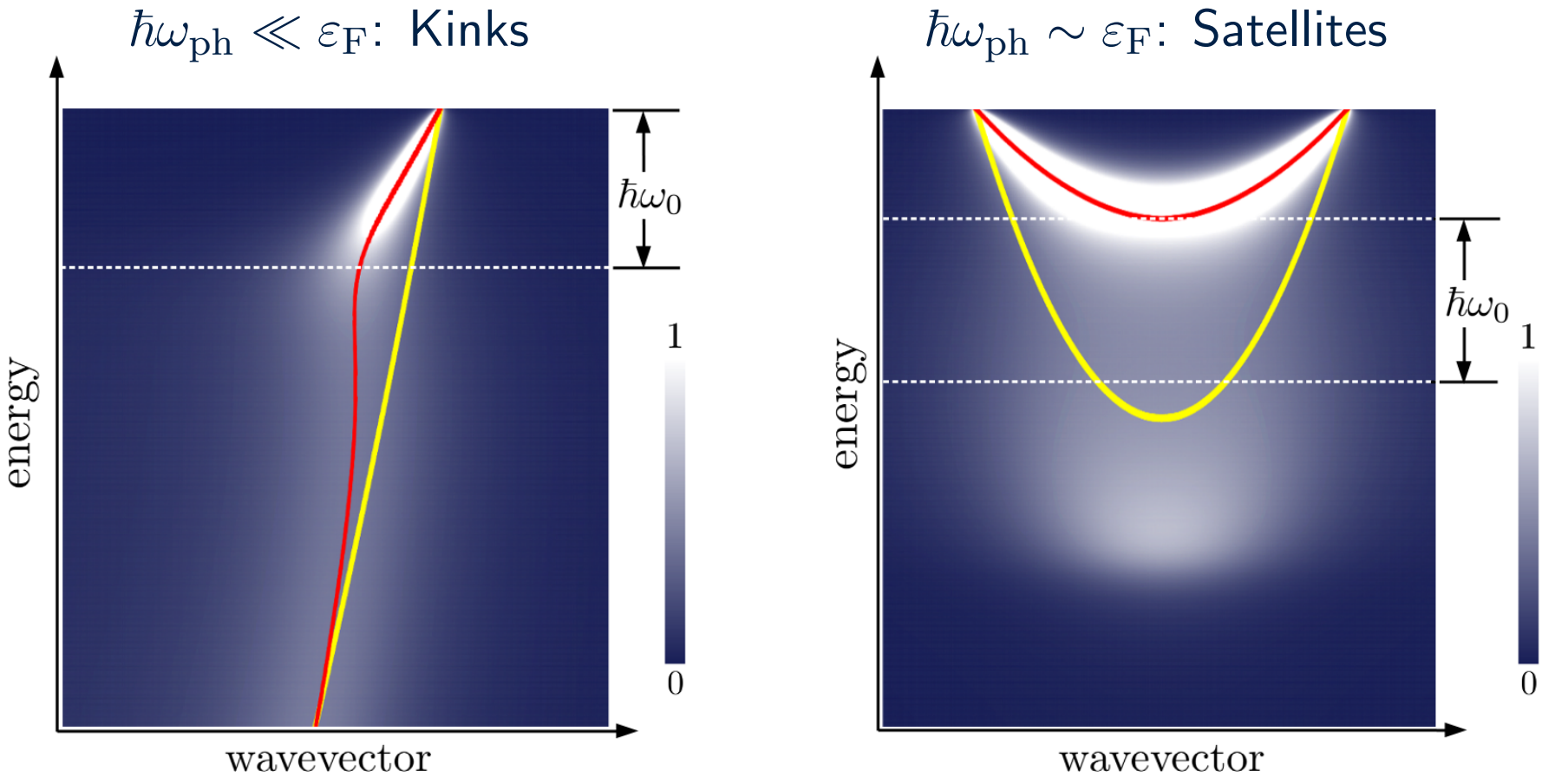
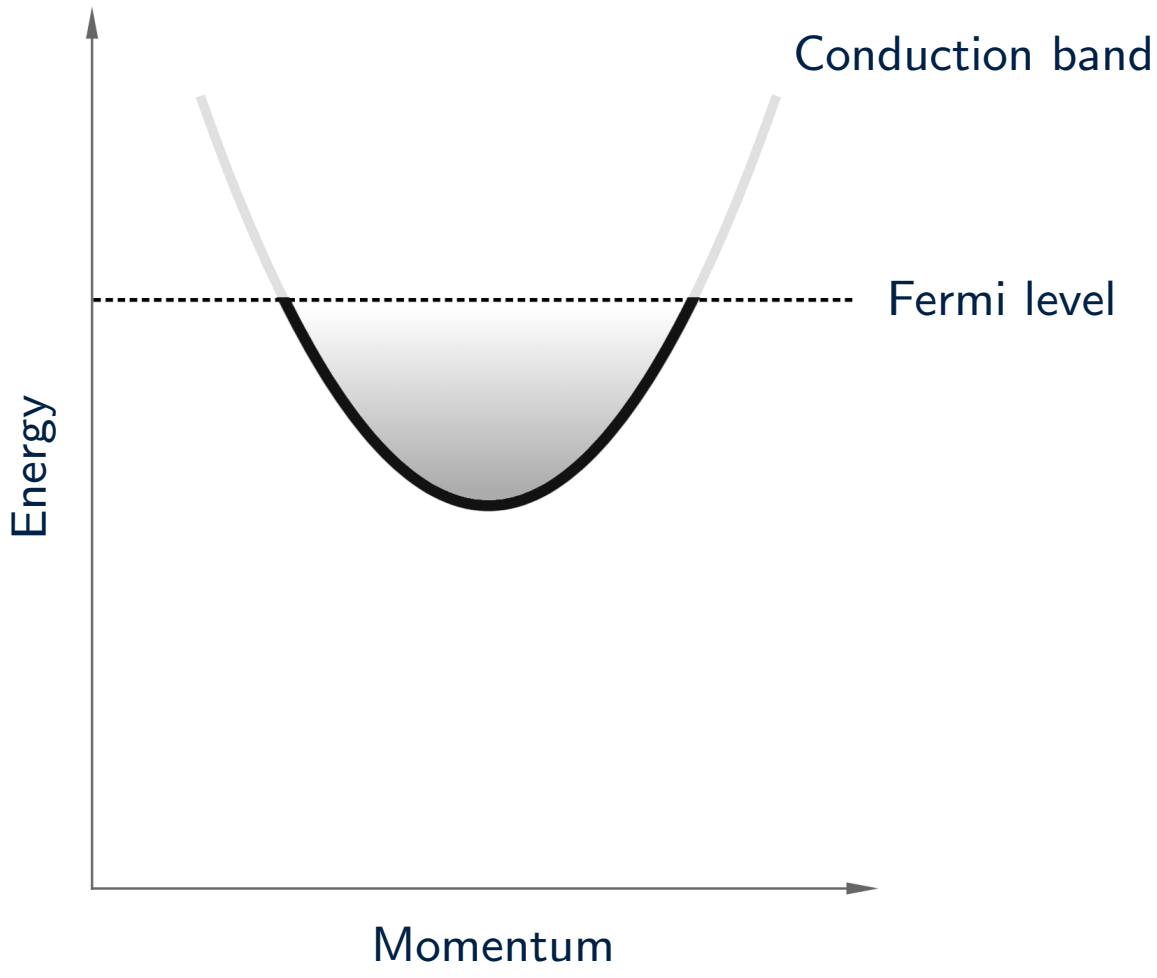
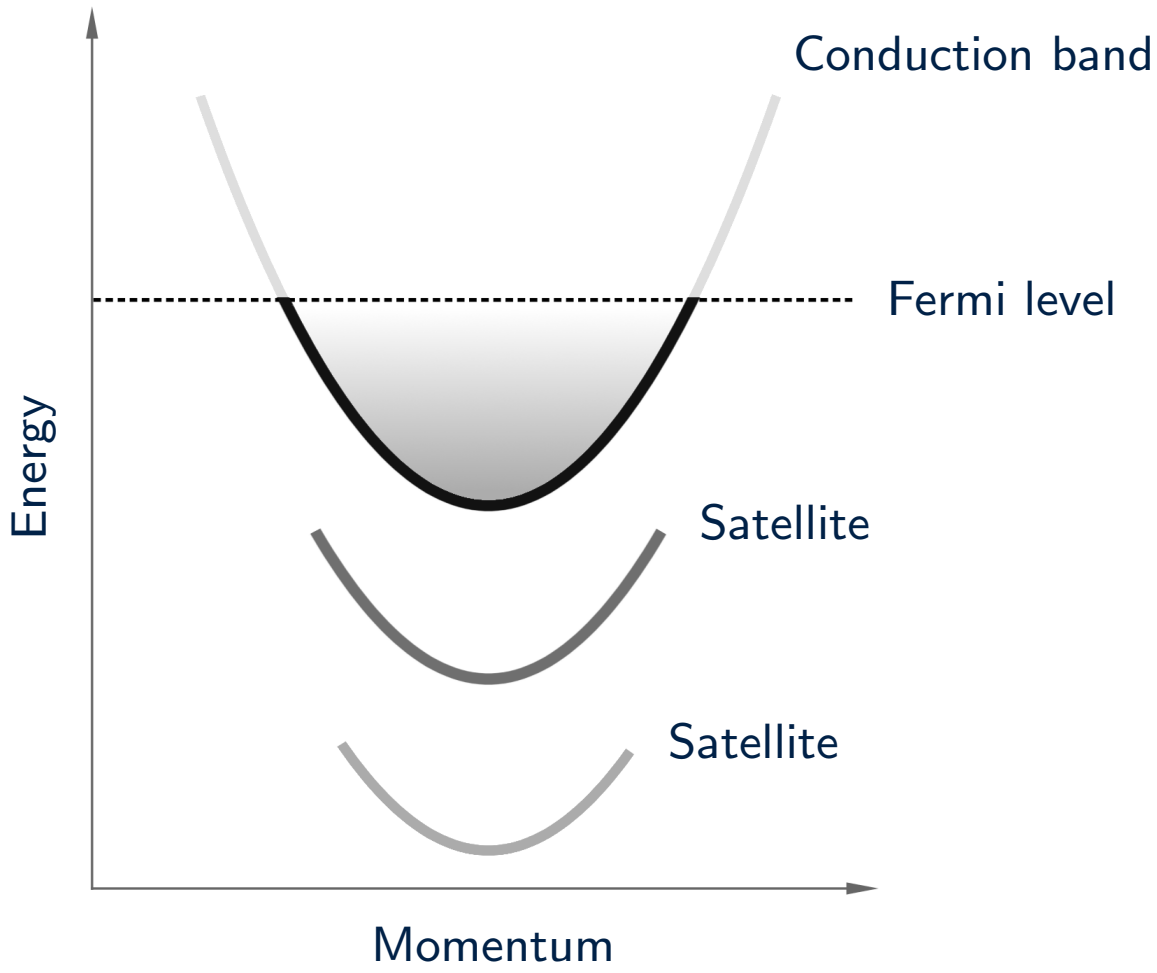


Figure from Giustino, Rev. Mod. Phys. 89, 015003 (2017)

ARPES on doped transition-metal oxides



ARPES on doped transition-metal oxides



ARPES on doped transition-metal oxides

- Example: $SrTiO_3(001)$ surface

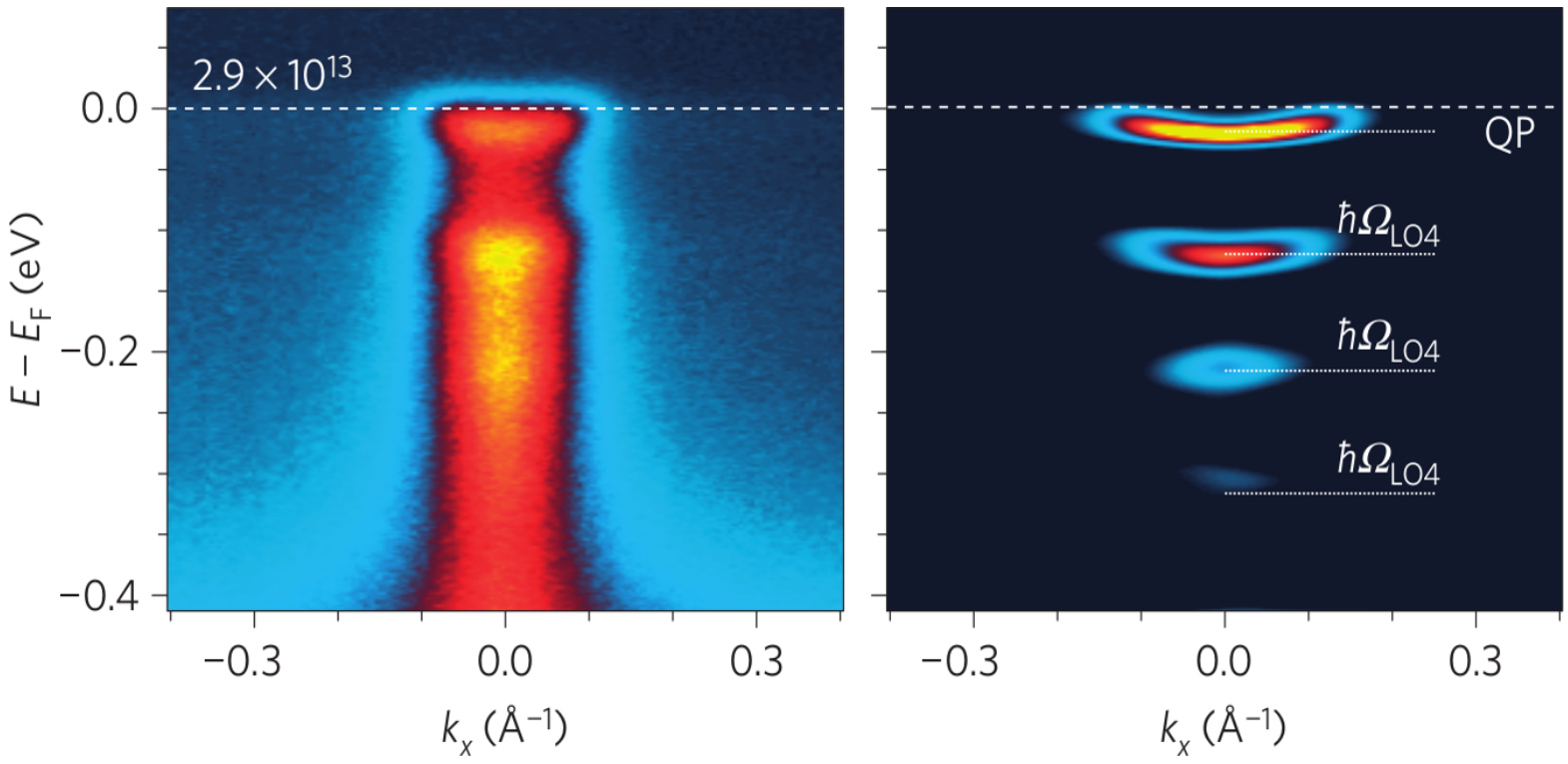
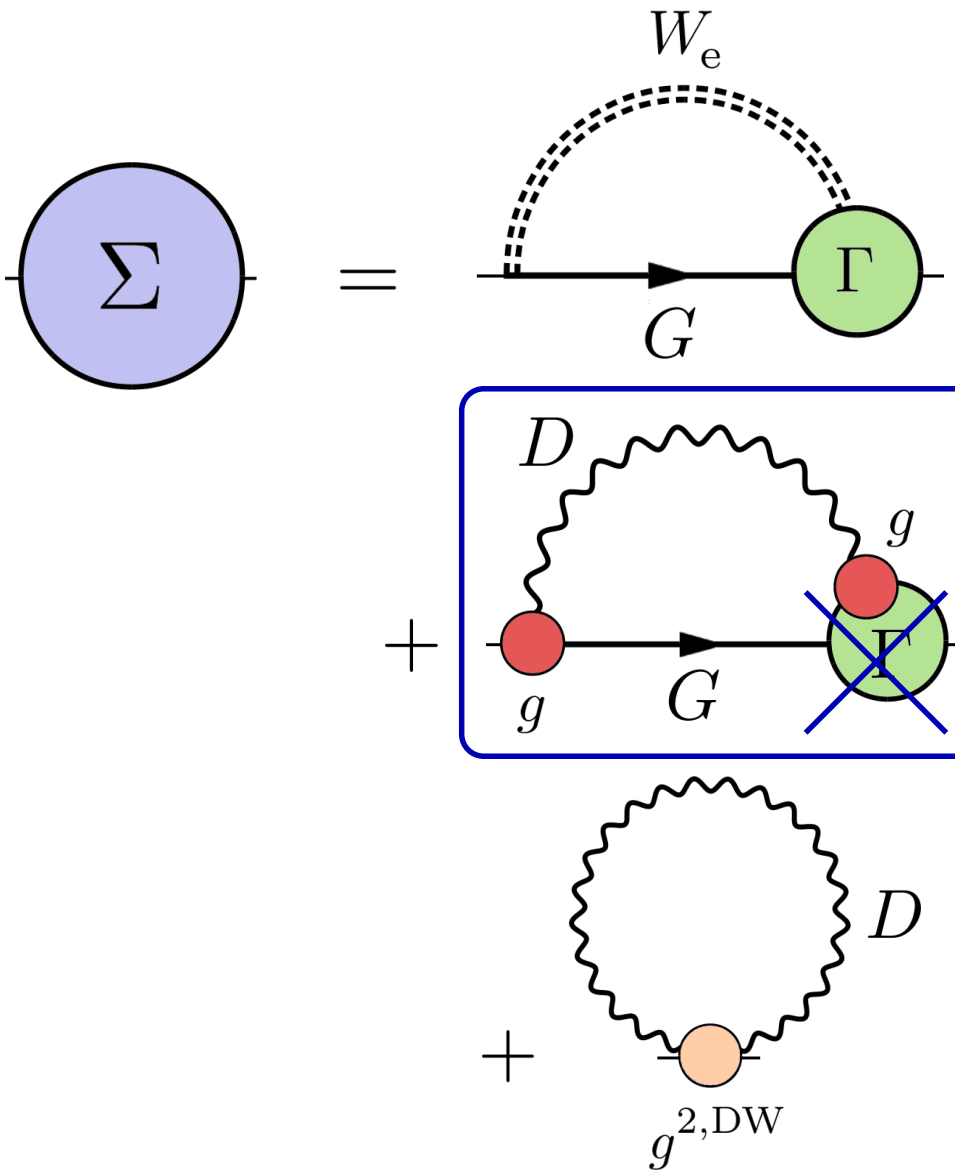


Figure from Wang et al, Nature Mater. 15, 835 (2016)

Diagrammatic representation of the self-energy



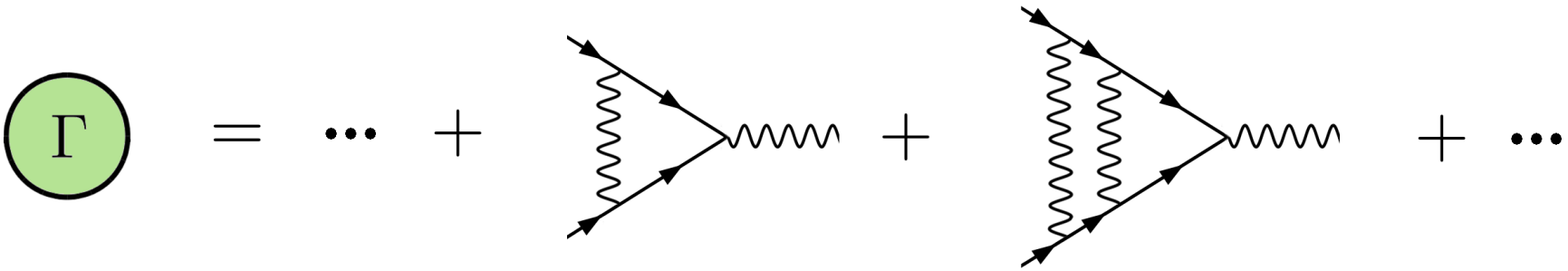
Standard GW self-energy

(we will ignore this from now on)

Fan-Migdal self-energy

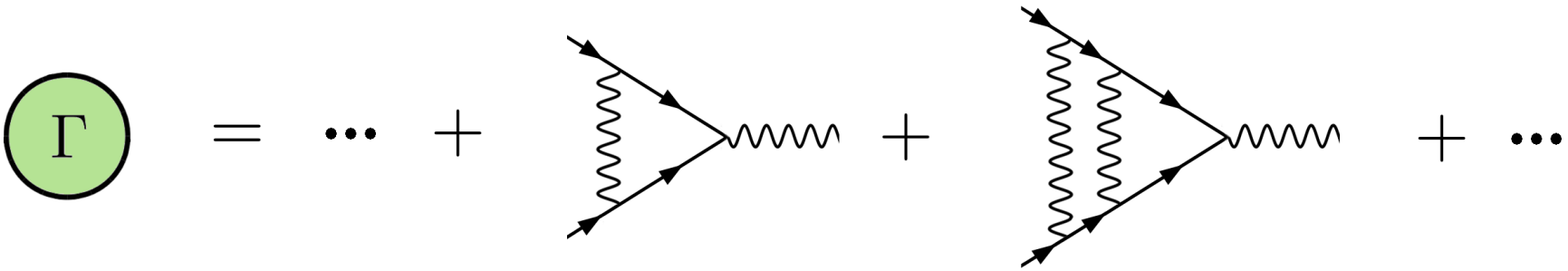
Debye-Waller self-energy

Cumulant expansion method



Aryasetiawan et al, Phys. Rev. Lett. 77, 2268 (1996);
Gumhalter et al, Phys. Rev. B 94, 035103 (2016);
Zhou et al, J. Chem. Phys. 143, 184109 (2015);
Nery et al, arXiv:1710.07594 (2017); &

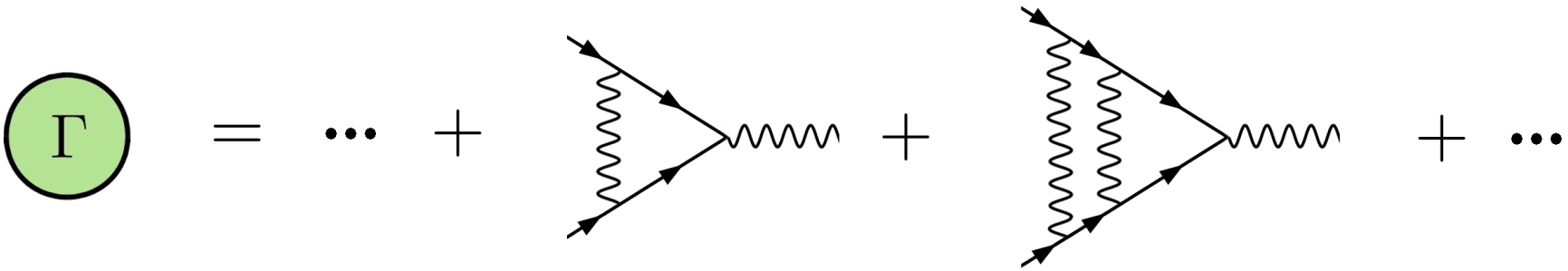
Cumulant expansion method



$$\Sigma^{\mathrm{FM}}_{n\mathbf{k}}(\omega)$$

Aryasetiawan et al, Phys. Rev. Lett. 77, 2268 (1996);
Gumhalter et al, Phys. Rev. B 94, 035103 (2016);
Zhou et al, J. Chem. Phys. 143, 184109 (2015);
Nery et al, arXiv:1710.07594 (2017); &

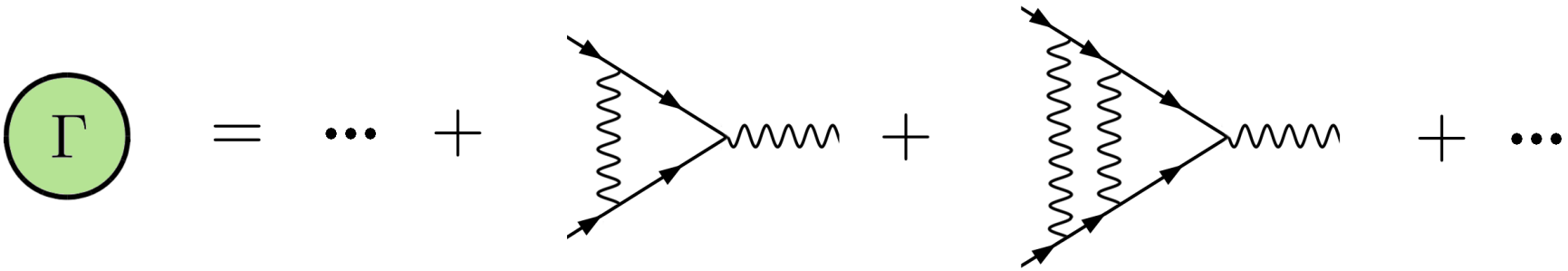
Cumulant expansion method

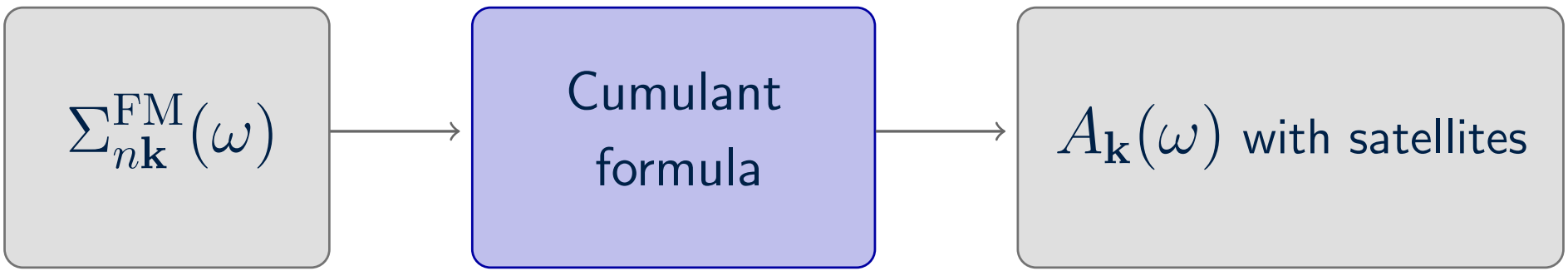


$\Sigma^{\mathrm{FM}}_{n\mathbf{k}}(\omega)$ → Cumulant formula

Aryasetiawan et al, Phys. Rev. Lett. 77, 2268 (1996);
Gumhalter et al, Phys. Rev. B 94, 035103 (2016);
Zhou et al, J. Chem. Phys. 143, 184109 (2015);
Nery et al, arXiv:1710.07594 (2017); &

Cumulant expansion method



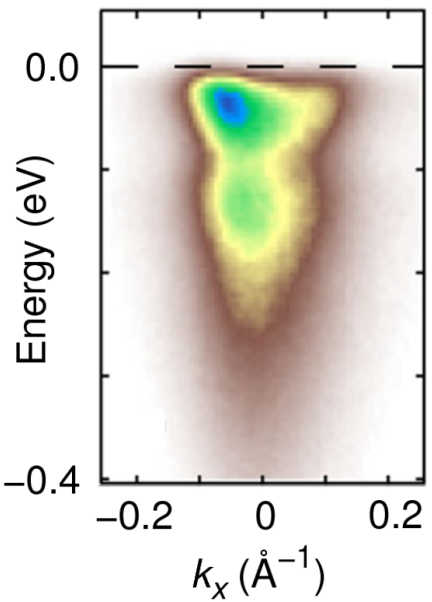


Aryasetiawan et al, Phys. Rev. Lett. 77, 2268 (1996);
Gumhalter et al, Phys. Rev. B 94, 035103 (2016);
Zhou et al, J. Chem. Phys. 143, 184109 (2015);
Nery et al, arXiv:1710.07594 (2017); &

Cumulant expansion method

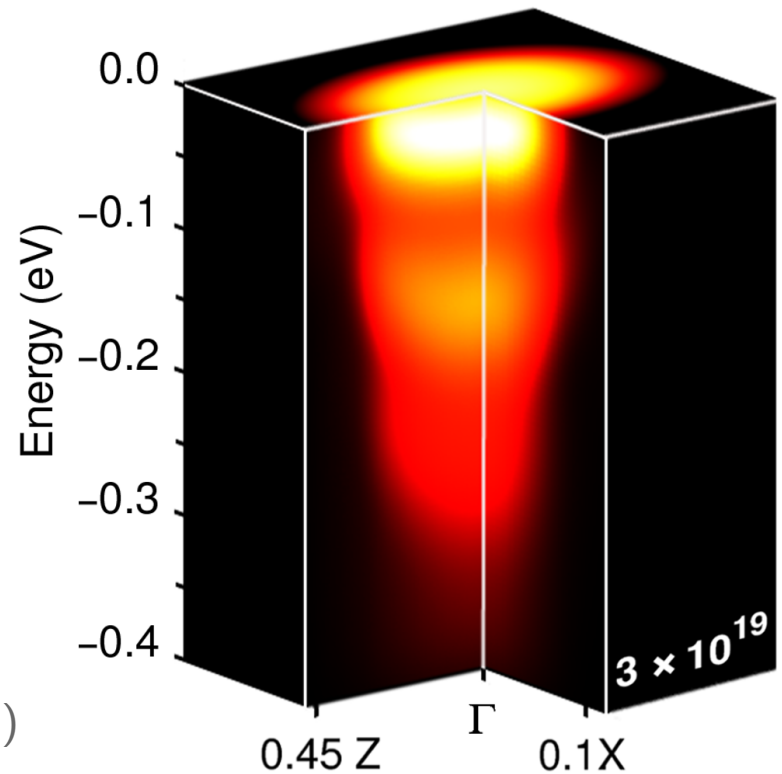
- Example: n-doped TiO_2 anatase

ARPES experiment



Moser et al,
PRL 110, 196403 (2013)

Calculation



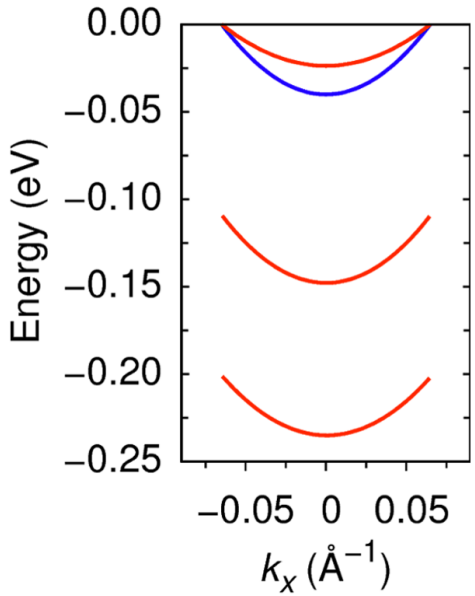
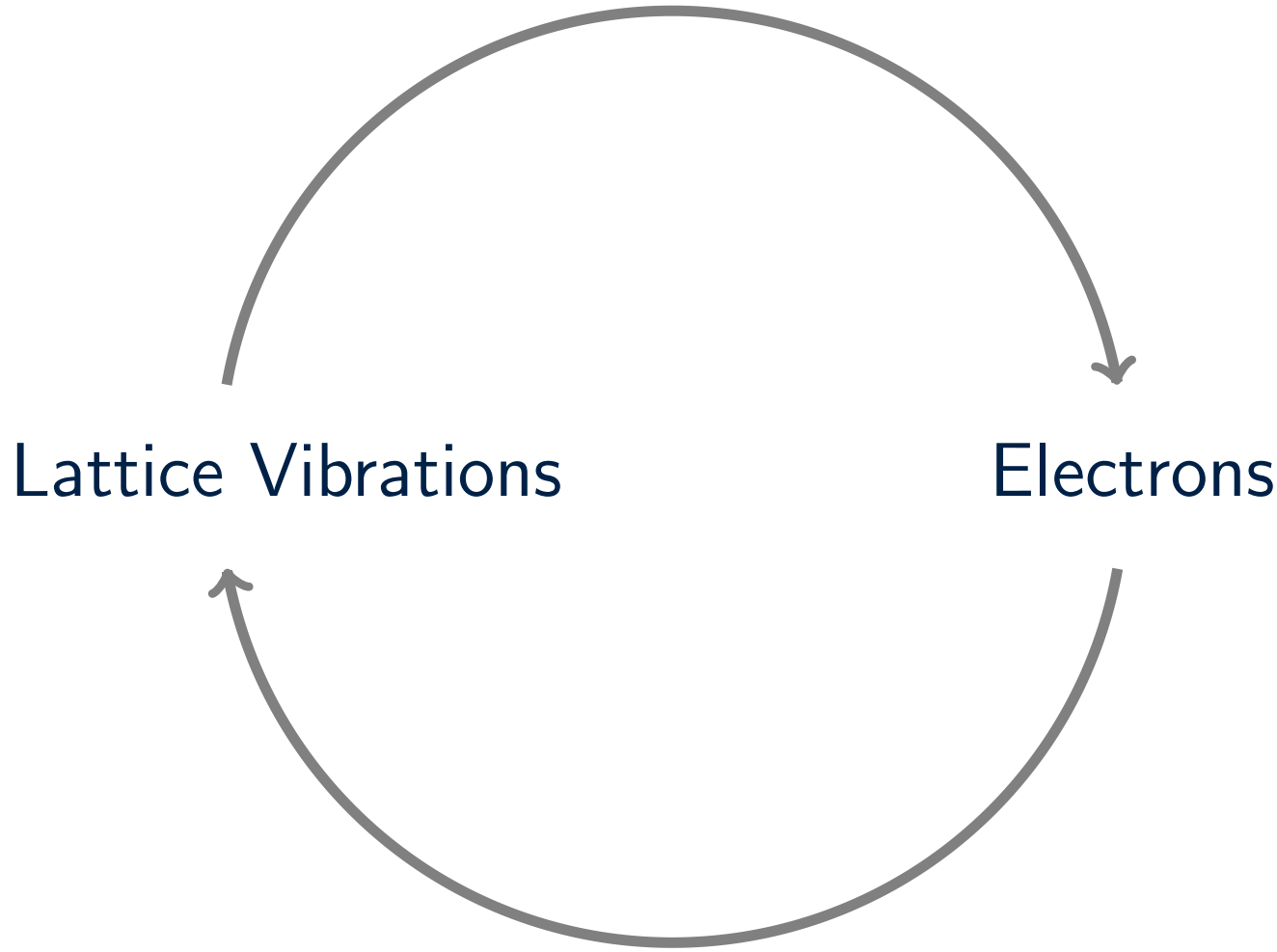
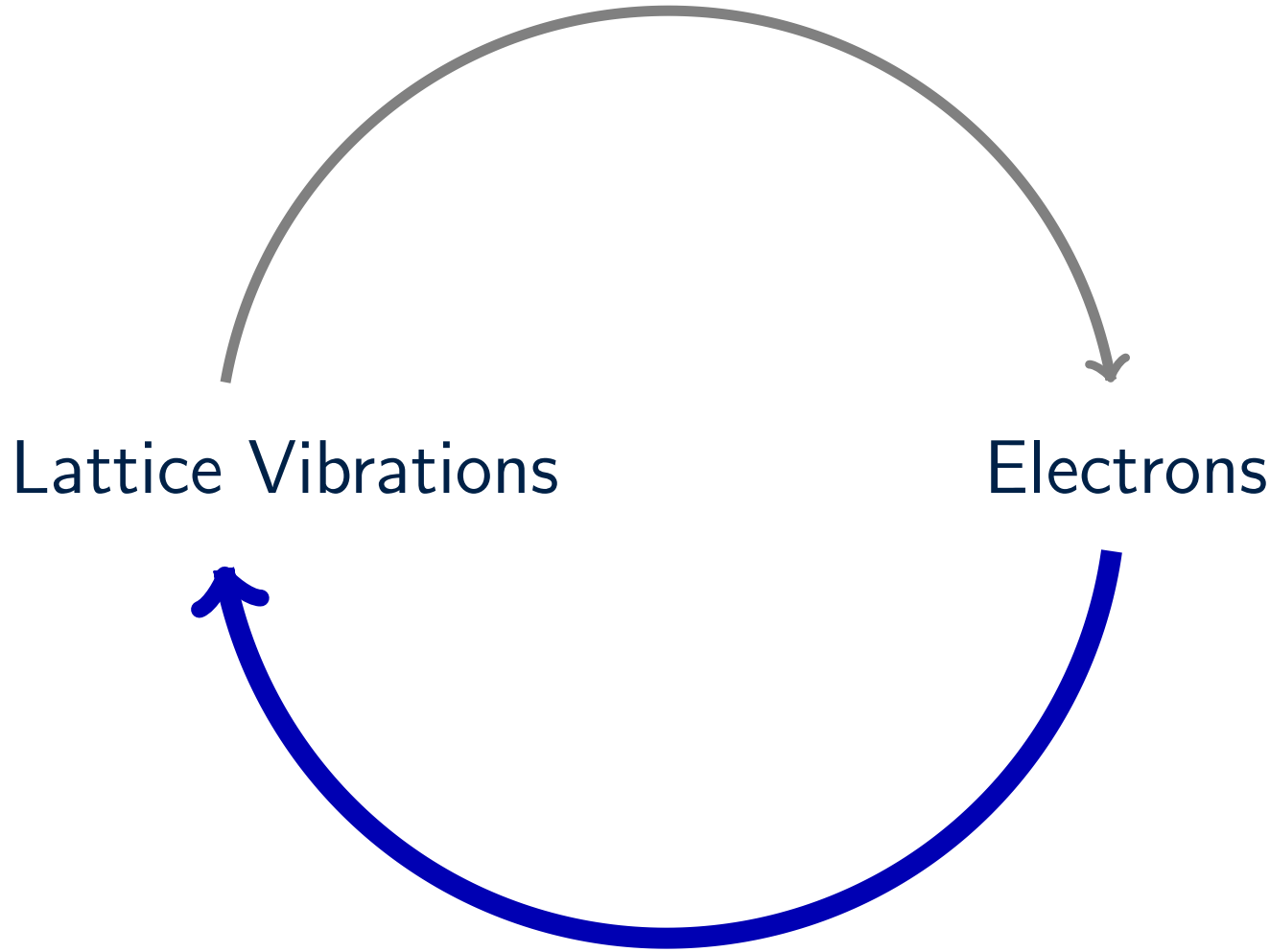


Figure from Verdi et al, Nat. Commun. 8, 15769 (2017)


Lattice Vibrations
Electrons


Lattice Vibrations
Electrons

Time-evolution of atomic displacements

Central quantity to study phonons in a many-body framework:
the displacement-displacement correlation function (Lecture Wed.1)

$$\mathbf{D}_{\kappa\kappa'}(tt') = -\frac{i}{\hbar}\langle \hat{T}\, \Delta\hat{\boldsymbol{\tau}}_{\kappa}(t)\, \Delta\hat{\boldsymbol{\tau}}^{\mathsf{T}}_{\kappa'}(t')\rangle$$

3×3 matrices in the Cartesian coordinates

Time-evolution of atomic displacements

Central quantity to study phonons in a many-body framework:
the displacement-displacement correlation function (Lecture Wed.1)

$$\mathbf{D}_{\kappa\kappa'}(tt') = -\frac{i}{\hbar}\langle \hat{T}\, \Delta\hat{\boldsymbol{\tau}}_{\kappa}(t)\, \Delta\hat{\boldsymbol{\tau}}^{\mathsf{T}}_{\kappa'}(t')\rangle$$

3×3 matrices in the Cartesian coordinates

Heisenberg time evolution of atomic displacements

$$i\hbar\frac{d}{dt}\Delta\hat{\boldsymbol{\tau}}_{\kappa}(t) = [\Delta\hat{\boldsymbol{\tau}}_{\kappa}(t), \hat{H}]$$

Time-evolution of atomic displacements

Central quantity to study phonons in a many-body framework:
the displacement-displacement correlation function (Lecture Wed.1)

$$\mathbf{D}_{\kappa\kappa'}(tt') = -\frac{i}{\hbar}\langle \hat{T}\, \Delta\hat{\boldsymbol{\tau}}_{\kappa}(t)\, \Delta\hat{\boldsymbol{\tau}}^{\mathsf{T}}_{\kappa'}(t')\rangle$$

3×3 matrices in the Cartesian coordinates

Heisenberg time evolution of atomic displacements

$$i\hbar\frac{d}{dt}\Delta\hat{\boldsymbol{\tau}}_{\kappa}(t) = [\Delta\hat{\boldsymbol{\tau}}_{\kappa}(t), \hat{H}]$$

Make it look like Newton's equation by taking the 2nd derivative

$$M_{\kappa}\frac{d^2}{dt^2}\Delta\hat{\boldsymbol{\tau}}_{\kappa} = -\frac{M_{\kappa}}{\hbar^2}[[\Delta\hat{\boldsymbol{\tau}}_{\kappa}, \hat{H}], \hat{H}]$$

Time-evolution of atomic displacements

Central quantity to study phonons in a many-body framework:
the displacement-displacement correlation function (Lecture Wed.1)

$$\mathbf{D}_{\kappa\kappa'}(tt') = -\frac{i}{\hbar}\langle \hat{T}\, \Delta\hat{\boldsymbol{\tau}}_{\kappa}(t)\, \Delta\hat{\boldsymbol{\tau}}^{\mathsf{T}}_{\kappa'}(t')\rangle$$

3×3 matrices in the Cartesian coordinates

Heisenberg time evolution of atomic displacements

$$i\hbar\frac{d}{dt}\Delta\hat{\boldsymbol{\tau}}_{\kappa}(t) = [\Delta\hat{\boldsymbol{\tau}}_{\kappa}(t), \hat{H}]$$

Make it look like Newton's equation by taking the 2nd derivative

$$M_{\kappa}\frac{d^2}{dt^2}\Delta\hat{\boldsymbol{\tau}}_{\kappa} = \underbrace{-\frac{M_{\kappa}}{\hbar^2}[[\Delta\hat{\boldsymbol{\tau}}_{\kappa}, \hat{H}], \hat{H}]}_{\text{dimensions of force}}$$

Many-body phonon self-energy

$$M_\kappa \frac{\partial^2}{\partial t^2} \mathbf{D}_{\kappa\kappa'}(tt') =$$

Many-body phonon self-energy

Using Schwinger's functional derivative technique

$$M_\kappa \frac{\partial^2}{\partial t^2} \mathbf{D}_{\kappa\kappa'}(tt') = -\mathbf{I}_{3\times 3}\,\delta_{\kappa\kappa'}\delta(tt') - \sum\nolimits_{\kappa''}\int dt''\; \mathbf{\Pi}_{\kappa\kappa''}(tt'')\,\mathbf{D}_{\kappa''\kappa'}(t''t')$$

Many-body phonon self-energy

Using Schwinger's functional derivative technique

$$M_\kappa \frac{\partial^2}{\partial t^2} \mathbf{D}_{\kappa\kappa'}(tt') = -\mathbf{I}_{3\times 3}\,\delta_{\kappa\kappa'}\delta(tt') - \sum\nolimits_{\kappa''}\int dt''\; \mathbf{\Pi}_{\kappa\kappa''}(tt'')\,\mathbf{D}_{\kappa''\kappa'}(t''t')$$

Many-body phonon self-energy

Using Schwinger's functional derivative technique

$$M_\kappa \frac{\partial^2}{\partial t^2} \mathbf{D}_{\kappa\kappa'}(tt') = -\mathbf{I}_{3\times 3}\,\delta_{\kappa\kappa'}\delta(tt') - \sum\nolimits_{\kappa''} \int dt''\, \underbrace{\mathbf{\Pi}_{\kappa\kappa''}(tt'')}_{\text{phonon self-energy}}\, \mathbf{D}_{\kappa''\kappa'}(t''t')$$

Many-body phonon self-energy

Using Schwinger's functional derivative technique

$$M_\kappa \frac{\partial^2}{\partial t^2} \mathbf{D}_{\kappa\kappa'}(tt') = -\mathbf{I}_{3\times 3}\,\delta_{\kappa\kappa'}\delta(tt') - \sum\nolimits_{\kappa''}\int dt''\, \underbrace{\mathbf{\Pi}_{\kappa\kappa''}(tt'')}_{\text{phonon self-energy}}\, \mathbf{D}_{\kappa''\kappa'}(t''t')$$

$$\mathbf{\Pi}_{\kappa\kappa'}(\omega) = \frac{\partial^2}{\partial \boldsymbol{\tau}_\kappa \partial \boldsymbol{\tau}_{\kappa'}^{\mathsf{T}}} \int d\mathbf{r}\; \epsilon_{\mathrm{e}}^{-1}(\boldsymbol{\tau}_\kappa, \mathbf{r}, \omega)\, \frac{e^2 Z_\kappa Z_{\kappa'}}{4\pi\epsilon_0 |\mathbf{r} - \boldsymbol{\tau}_{\kappa'}|}$$

Many-body phonon self-energy

Using Schwinger's functional derivative technique

$$M_\kappa \frac{\partial^2}{\partial t^2} \mathbf{D}_{\kappa\kappa'}(tt') = -\mathbf{I}_{3\times 3}\,\delta_{\kappa\kappa'}\delta(tt') - \sum\nolimits_{\kappa''}\int dt''\, \underbrace{\mathbf{\Pi}_{\kappa\kappa''}(tt'')}_{\text{phonon self-energy}}\, \mathbf{D}_{\kappa''\kappa'}(t''t')$$

$$\mathbf{\Pi}_{\kappa\kappa'}(\omega) = \frac{\partial^2}{\partial \boldsymbol{\tau}_\kappa \partial \boldsymbol{\tau}_{\kappa'}^{\mathsf{T}}} \int d\mathbf{r}\; \epsilon_{\mathrm{e}}^{-1}(\boldsymbol{\tau}_\kappa, \mathbf{r}, \omega)\, \frac{e^2 Z_\kappa Z_{\kappa'}}{4\pi\epsilon_0 |\mathbf{r} - \boldsymbol{\tau}_{\kappa'}|} - \text{(self force)}$$

Many-body phonon self-energy

Using Schwinger's functional derivative technique

$$M_\kappa \frac{\partial^2}{\partial t^2} \mathbf{D}_{\kappa\kappa'}(tt') = -\mathbf{I}_{3\times 3}\,\delta_{\kappa\kappa'}\delta(tt') - \sum_{\kappa''}\int dt''\, \underbrace{\mathbf{\Pi}_{\kappa\kappa''}(tt'')}_{\text{phonon self-energy}}\, \mathbf{D}_{\kappa''\kappa'}(t''t')$$

$$\mathbf{\Pi}_{\kappa\kappa'}(\omega) = \frac{\partial^2}{\partial \boldsymbol{\tau}_\kappa \partial \boldsymbol{\tau}_{\kappa'}^{\mathsf{T}}} \int d\mathbf{r}\; \epsilon_{\mathrm{e}}^{-1}(\boldsymbol{\tau}_\kappa, \mathbf{r}, \omega)\, \frac{e^2 Z_\kappa Z_{\kappa'}}{4\pi\epsilon_0 |\mathbf{r} - \boldsymbol{\tau}_{\kappa'}|} - \text{(self force)}$$

$\mathbf{\Pi}$ contains the spring constants for a Coulomb interaction between nuclei, screened by the electronic dielectric matrix

Many-body phonon self-energy

Using Schwinger's functional derivative technique

$$M_\kappa \frac{\partial^2}{\partial t^2} \mathbf{D}_{\kappa\kappa'}(tt') = -\mathbf{I}_{3\times 3}\,\delta_{\kappa\kappa'}\delta(tt') - \sum\nolimits_{\kappa''}\int dt''\, \underbrace{\mathbf{\Pi}_{\kappa\kappa''}(tt'')}_{\text{phonon self-energy}}\, \mathbf{D}_{\kappa''\kappa'}(t''t')$$

$$\mathbf{\Pi}_{\kappa\kappa'}(\omega) = \frac{\partial^2}{\partial \boldsymbol{\tau}_\kappa \partial \boldsymbol{\tau}_{\kappa'}^{\mathsf{T}}} \int d\mathbf{r}\; \epsilon_{\mathrm{e}}^{-1}(\boldsymbol{\tau}_\kappa, \mathbf{r}, \omega)\, \frac{e^2 Z_\kappa Z_{\kappa'}}{4\pi\epsilon_0 |\mathbf{r} - \boldsymbol{\tau}_{\kappa'}|} - \text{(self force)}$$

$\mathbf{\Pi}$ contains the spring constants for a Coulomb interaction between nuclei, screened by the electronic dielectric matrix

example: $E_{\mathrm{tot}} = \frac{1}{2} C(\tau - \tau_0)^2 \longrightarrow \frac{\partial^2 E_{\mathrm{tot}}}{\partial \tau^2} = C$

Many-body vibrational eigenfrequencies

$$\mathbf{D} = \begin{pmatrix} \mathbf{D}_{11} & \mathbf{D}_{12} & \dots & \mathbf{D}_{1N} \\ \mathbf{D}_{21} & \mathbf{D}_{22} & \dots & \mathbf{D}_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{D}_{N1} & \mathbf{D}_{N2} & \dots & \mathbf{D}_{NN} \end{pmatrix}_{3N \times 3N}$$

Many-body vibrational eigenfrequencies

$$\mathbf{D} = \begin{pmatrix} \mathbf{D}_{11} & \mathbf{D}_{12} & \dots & \mathbf{D}_{1N} \\ \mathbf{D}_{21} & \mathbf{D}_{22} & \dots & \mathbf{D}_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{D}_{N1} & \mathbf{D}_{N2} & \dots & \mathbf{D}_{NN} \end{pmatrix}_{3N\times 3N} \qquad \mathbf{\Pi} = \begin{pmatrix} \mathbf{\Pi}_{11} & \mathbf{\Pi}_{12} & \dots & \mathbf{\Pi}_{1N} \\ \mathbf{\Pi}_{21} & \mathbf{\Pi}_{22} & \dots & \mathbf{\Pi}_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{\Pi}_{N1} & \mathbf{\Pi}_{N2} & \dots & \mathbf{\Pi}_{NN} \end{pmatrix}_{3N\times 3N}$$

Many-body vibrational eigenfrequencies

$$\mathbf{D} = \begin{pmatrix} \mathbf{D}_{11} & \mathbf{D}_{12} & \dots & \mathbf{D}_{1N} \\ \mathbf{D}_{21} & \mathbf{D}_{22} & \dots & \mathbf{D}_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{D}_{N1} & \mathbf{D}_{N2} & \dots & \mathbf{D}_{NN} \end{pmatrix}_{3N\times 3N} \qquad \mathbf{\Pi} = \begin{pmatrix} \mathbf{\Pi}_{11} & \mathbf{\Pi}_{12} & \dots & \mathbf{\Pi}_{1N} \\ \mathbf{\Pi}_{21} & \mathbf{\Pi}_{22} & \dots & \mathbf{\Pi}_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{\Pi}_{N1} & \mathbf{\Pi}_{N2} & \dots & \mathbf{\Pi}_{NN} \end{pmatrix}_{3N\times 3N}$$

$$\mathbf{M} = \begin{pmatrix} M_1 & 0 & \dots & 0 \\ 0 & M_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & M_N \end{pmatrix}_{3N\times 3N}$$

Many-body vibrational eigenfrequencies

$$\mathbf{D} = \begin{pmatrix} \mathbf{D}_{11} & \mathbf{D}_{12} & \dots & \mathbf{D}_{1N} \\ \mathbf{D}_{21} & \mathbf{D}_{22} & \dots & \mathbf{D}_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{D}_{N1} & \mathbf{D}_{N2} & \dots & \mathbf{D}_{NN} \end{pmatrix}_{3N\times 3N} \qquad \mathbf{\Pi} = \begin{pmatrix} \mathbf{\Pi}_{11} & \mathbf{\Pi}_{12} & \dots & \mathbf{\Pi}_{1N} \\ \mathbf{\Pi}_{21} & \mathbf{\Pi}_{22} & \dots & \mathbf{\Pi}_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{\Pi}_{N1} & \mathbf{\Pi}_{N2} & \dots & \mathbf{\Pi}_{NN} \end{pmatrix}_{3N\times 3N}$$

$$\mathbf{M} = \begin{pmatrix} M_1 & 0 & \dots & 0 \\ 0 & M_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & M_N \end{pmatrix}_{3N\times 3N}$$

Equation of motion for the displacement-displacement correlation function in matrix form

$$\mathbf{M}\,\omega^2\,\mathbf{D}(\omega) = \mathbf{I}_{3N\times 3N} + \mathbf{\Pi}(\omega)\,\mathbf{D}(\omega)$$

Many-body vibrational eigenfrequencies

Formal solution: phonon Green's function in Cartesian coordinates

$$\mathbf{D}(\omega) = \left[\mathbf{M}\,\omega^2 - \mathbf{\Pi}(\omega) \right]^{-1}$$

Many-body vibrational eigenfrequencies

Formal solution: phonon Green's function in Cartesian coordinates

$$\mathbf{D}(\omega) = \left[\mathbf{M}\,\omega^2 - \mathbf{\Pi}(\omega) \right]^{-1}$$

The resonant frequencies are the solutions of the nonlinear equations

$$\Omega(\omega) = \omega$$

where $\Omega^2(\omega)$ an eigenvalue of the many-body dynamical matrix

$$\mathbf{M}^{-1/2}\,\mathbf{\Pi}(\omega)\,\mathbf{M}^{-1/2} \longrightarrow \frac{\Pi_{\kappa\alpha,\kappa'\alpha'}(\omega)}{\sqrt{M_\kappa M_{\kappa'}}}$$

Connection with density-functional perturbation theory

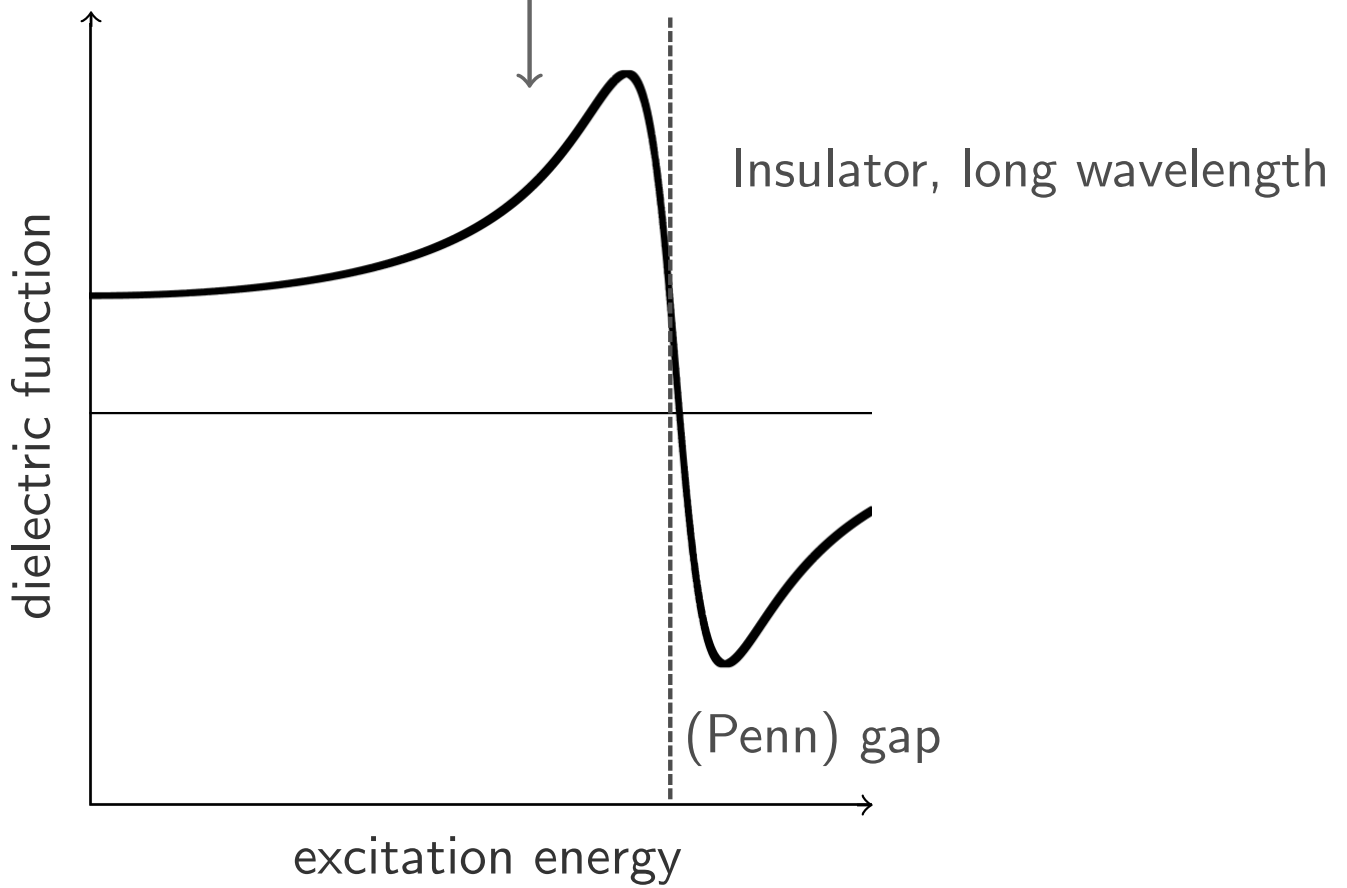
$$\Pi_{\kappa\alpha,\kappa'\alpha'}(\omega) = \frac{\partial^2}{\partial\tau_{\kappa\alpha}\partial\tau_{\kappa'\alpha'}} \int d\mathbf{r}\ \epsilon_{\rm e}^{-1}(\boldsymbol{\tau}_\kappa, \mathbf{r}, \omega)\ \frac{e^2 Z_\kappa Z_{\kappa'}}{4\pi\epsilon_0 |\mathbf{r} - \boldsymbol{\tau}_{\kappa'}|} - \text{(self force)}$$

Connection with density-functional perturbation theory

$$\Pi_{\kappa\alpha,\kappa'\alpha'}(\omega) = \frac{\partial^2}{\partial\tau_{\kappa\alpha}\partial\tau_{\kappa'\alpha'}} \int d\mathbf{r}\, \epsilon_{\mathrm{e}}^{-1}(\boldsymbol{\tau}_\kappa, \mathbf{r}, \omega) \frac{e^2 Z_\kappa Z_{\kappa'}}{4\pi\epsilon_0 |\mathbf{r} - \boldsymbol{\tau}_{\kappa'}|} - (\text{self force})$$

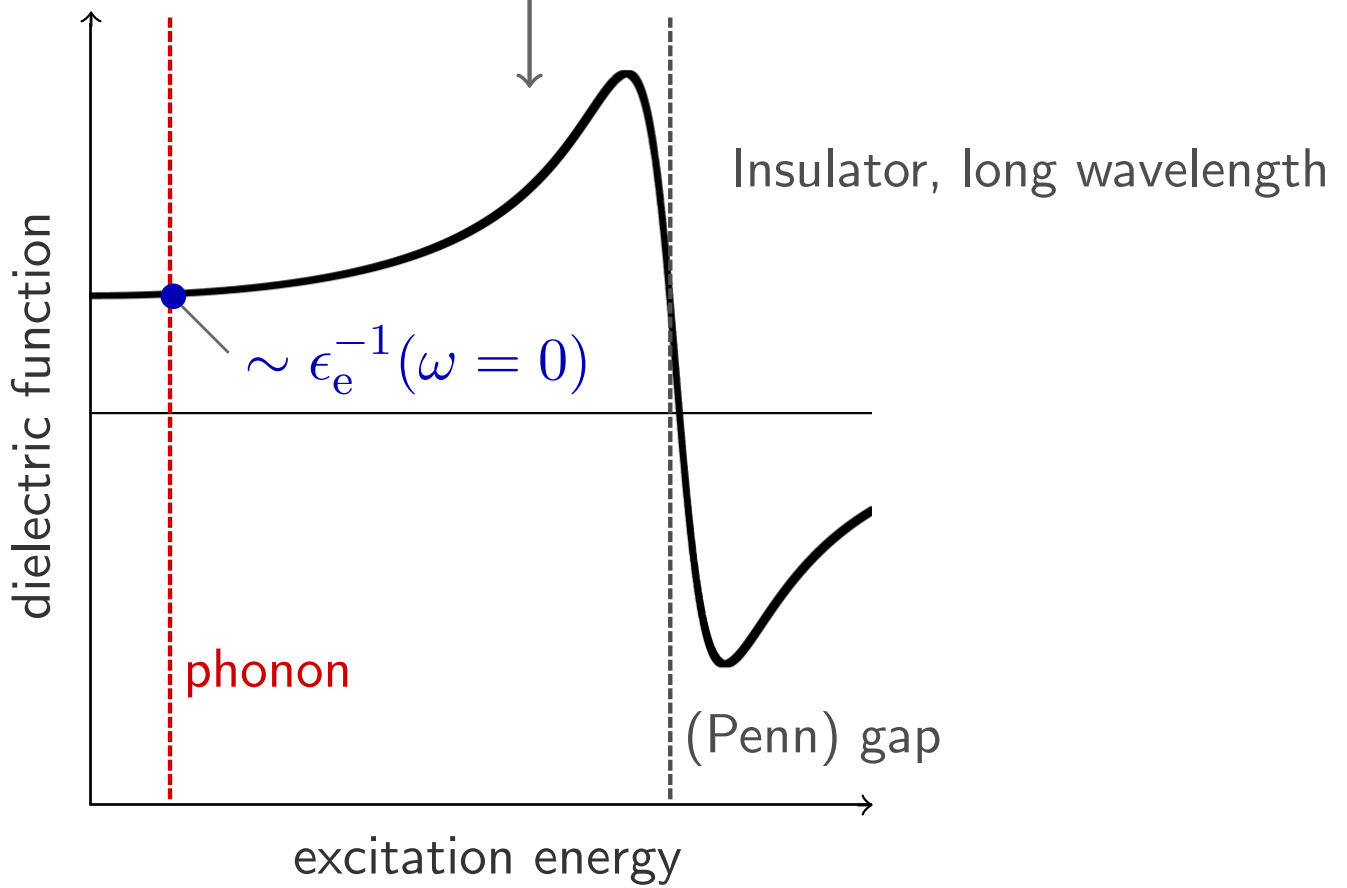
Connection with density-functional perturbation theory

$$\Pi_{\kappa\alpha,\kappa'\alpha'}(\omega) = \frac{\partial^2}{\partial\tau_{\kappa\alpha}\partial\tau_{\kappa'\alpha'}} \int d\mathbf{r}\, \epsilon_{\mathrm{e}}^{-1}(\boldsymbol{\tau}_\kappa, \mathbf{r}, \omega) \frac{e^2 Z_\kappa Z_{\kappa'}}{4\pi\epsilon_0 |\mathbf{r} - \boldsymbol{\tau}_{\kappa'}|} - \text{(self force)}$$



Connection with density-functional perturbation theory

$$\Pi_{\kappa\alpha,\kappa'\alpha'}(\omega) = \frac{\partial^2}{\partial\tau_{\kappa\alpha}\partial\tau_{\kappa'\alpha'}} \int d\mathbf{r}\, \epsilon_{\rm e}^{-1}(\boldsymbol{\tau}_\kappa, \mathbf{r}, \omega) \frac{e^2 Z_\kappa Z_{\kappa'}}{4\pi\epsilon_0 |\mathbf{r} - \boldsymbol{\tau}_{\kappa'}|} - \text{(self force)}$$



Connection with density-functional perturbation theory

We call adiabatic self-energy the $\mathbf{\Pi}$ evaluated using the static screening

$$\mathbf{\Pi}^{\mathrm{A}} = \mathbf{\Pi}\left(\omega = 0\right)$$

Connection with density-functional perturbation theory

We call adiabatic self-energy the $\mathbf{\Pi}$ evaluated using the static screening

$$\mathbf{\Pi}^{\mathrm{A}} = \mathbf{\Pi}\left(\omega = 0\right)$$

After some algebra this becomes

$$\mathbf{\Pi}^{\mathrm{A}}_{\kappa\alpha,\kappa'\alpha'} = \frac{\partial^2 U_{\mathrm{nn}}}{\partial\tau_{\kappa\alpha}\,\partial\tau_{\kappa'\alpha'}} + \int d\mathbf{r}\,\frac{\partial^2 V^{\mathrm{en}}(\mathbf{r})}{\partial\tau_{\kappa\alpha}\,\partial\tau_{\kappa'\alpha'}}\langle\hat{n}_{\mathrm{e}}(\mathbf{r})\rangle + \int d\mathbf{r}\,\frac{\partial V^{\mathrm{en}}(\mathbf{r})}{\partial\tau_{\kappa\alpha}}\frac{\partial\langle\hat{n}_{\mathrm{e}}(\mathbf{r})\rangle}{\partial\tau_{\kappa'\alpha'}}$$

Connection with density-functional perturbation theory

We call adiabatic self-energy the $\mathbf{\Pi}$ evaluated using the static screening

$$\mathbf{\Pi}^{\mathrm{A}} = \mathbf{\Pi}\left(\omega = 0\right)$$

After some algebra this becomes

$$\mathbf{\Pi}^{\mathrm{A}}_{\kappa\alpha,\kappa'\alpha'} = \frac{\partial^2 U_{\mathrm{nn}}}{\partial\tau_{\kappa\alpha}\,\partial\tau_{\kappa'\alpha'}} + \int d\mathbf{r}\,\frac{\partial^2 V^{\mathrm{en}}(\mathbf{r})}{\partial\tau_{\kappa\alpha}\,\partial\tau_{\kappa'\alpha'}}\langle\hat{n}_{\mathrm{e}}(\mathbf{r})\rangle + \int d\mathbf{r}\,\frac{\partial V^{\mathrm{en}}(\mathbf{r})}{\partial\tau_{\kappa\alpha}}\frac{\partial\langle\hat{n}_{\mathrm{e}}(\mathbf{r})\rangle}{\partial\tau_{\kappa'\alpha'}}$$

$$n^{\mathrm{DFT}}(\mathbf{r})$$

DFT electron density

Connection with density-functional perturbation theory

We call adiabatic self-energy the $\mathbf{\Pi}$ evaluated using the static screening

$$\mathbf{\Pi}^{\mathrm{A}} = \mathbf{\Pi}\left(\omega = 0\right)$$

After some algebra this becomes

$$\Pi^{\mathrm{A}}_{\kappa\alpha,\kappa'\alpha'} = \frac{\partial^2 U_{\mathrm{nn}}}{\partial\tau_{\kappa\alpha}\,\partial\tau_{\kappa'\alpha'}} + \int d\mathbf{r}\,\frac{\partial^2 V^{\mathrm{en}}(\mathbf{r})}{\partial\tau_{\kappa\alpha}\,\partial\tau_{\kappa'\alpha'}}\langle\hat{n}_{\mathrm{e}}(\mathbf{r})\rangle + \int d\mathbf{r}\,\frac{\partial V^{\mathrm{en}}(\mathbf{r})}{\partial\tau_{\kappa\alpha}}\frac{\partial\langle\hat{n}_{\mathrm{e}}(\mathbf{r})\rangle}{\partial\tau_{\kappa'\alpha'}}$$

$$\Pi^{\mathrm{A}}_{\kappa\alpha,\kappa'\alpha'} = \frac{\partial^2 E^{\mathrm{DFT}}_{\mathrm{tot}}}{\partial\tau_{\kappa\alpha}\,\partial\tau_{\kappa'\alpha'}}$$

$n^{\mathrm{DFT}}(\mathbf{r})$
DFT electron density

DFPT matrix of force constants
(Lecture Mon.2)

Phonons beyond DFPT: Non-adiabatic effects

Relation between **adiabatic** and **non-adiabatic** Green's functions

$$\mathbf{D}^{-1}(\omega) \;=\; \mathbf{M}\,\omega^2 - \mathbf{\Pi}(\omega)$$

Phonons beyond DFPT: Non-adiabatic effects

Relation between **adiabatic** and **non-adiabatic** Green's functions

$$\begin{aligned} \mathbf{D}^{-1}(\omega) &= \mathbf{M}\,\omega^2 - \mathbf{\Pi}(\omega) \\ [\mathbf{D}^{\mathrm{A}}(\omega)]^{-1} &= \mathbf{M}\,\omega^2 - \mathbf{\Pi}^{\mathrm{A}} \end{aligned}$$

Phonons beyond DFPT: Non-adiabatic effects

Relation between **adiabatic** and **non-adiabatic** Green's functions

$$\begin{aligned} \mathbf{D}^{-1}(\omega) &= \mathbf{M}\,\omega^2 - \mathbf{\Pi}(\omega) \\ [\mathbf{D}^{\mathrm{A}}(\omega)]^{-1} &= \mathbf{M}\,\omega^2 - \mathbf{\Pi}^{\mathrm{A}} \\ \hline - \mathbf{D}^{-1}(\omega) + [\mathbf{D}^{\mathrm{A}}(\omega)]^{-1} &= \mathbf{\Pi}(\omega) - \mathbf{\Pi}^{\mathrm{A}} \end{aligned}$$

Phonons beyond DFPT: Non-adiabatic effects

Relation between **adiabatic** and **non-adiabatic** Green's functions

$$\begin{aligned} \mathbf{D}^{-1}(\omega) &= \mathbf{M}\,\omega^2 - \mathbf{\Pi}(\omega) \\ [\mathbf{D}^{\mathrm{A}}(\omega)]^{-1} &= \mathbf{M}\,\omega^2 - \mathbf{\Pi}^{\mathrm{A}} \\ \hline - \mathbf{D}^{-1}(\omega) + [\mathbf{D}^{\mathrm{A}}(\omega)]^{-1} &= \underbrace{\mathbf{\Pi}(\omega) - \mathbf{\Pi}^{\mathrm{A}}}_{\text{non-adiabatic self-energy } \Pi^{\mathrm{NA}}} \end{aligned}$$

Phonons beyond DFPT: Non-adiabatic effects

Relation between **adiabatic** and **non-adiabatic** Green's functions

$$\begin{aligned} \mathbf{D}^{-1}(\omega) &= \mathbf{M}\,\omega^2 - \mathbf{\Pi}(\omega) \\ [\mathbf{D}^{\mathrm{A}}(\omega)]^{-1} &= \mathbf{M}\,\omega^2 - \mathbf{\Pi}^{\mathrm{A}} \\ \hline - \mathbf{D}^{-1}(\omega) + [\mathbf{D}^{\mathrm{A}}(\omega)]^{-1} &= \underbrace{\mathbf{\Pi}(\omega) - \mathbf{\Pi}^{\mathrm{A}}}_{\text{non-adiabatic self-energy } \Pi^{\mathrm{NA}}} \end{aligned}$$

Dyson's equation for the phonon Green's function

$$\mathbf{D} = \mathbf{D}^{\mathrm{A}} + \mathbf{D}^{\mathrm{A}}\,\mathbf{\Pi}^{\mathrm{NA}}\,\mathbf{D}$$

Phonons beyond DFPT: Non-adiabatic effects

Adiabatic phonon Green's function (DFPT)

(diagonal part in eigenmode representation)

$$D^{\mathrm{A}}_{\mathbf{q}\nu}(\omega) = \frac{2\omega_{\mathbf{q}\nu}}{\omega^2 - (\omega_{\mathbf{q}\nu} - i0^+)^2} = \frac{1}{\omega - \omega_{\mathbf{q}\nu} + i0^+} - \frac{1}{\omega + \omega_{\mathbf{q}\nu} - i0^+}$$

Phonons beyond DFPT: Non-adiabatic effects

Adiabatic phonon Green's function (DFPT)

(diagonal part in eigenmode representation)

$$D^{\mathrm{A}}_{\mathbf{q}\nu}(\omega) = \frac{2\omega_{\mathbf{q}\nu}}{\omega^2 - (\omega_{\mathbf{q}\nu} - i0^+)^2} = \frac{1}{\omega - \omega_{\mathbf{q}\nu} + i0^+} - \frac{1}{\omega + \omega_{\mathbf{q}\nu} - i0^+}$$

Combine this with Dyson's equation to find the complete Green's function

$$D_{\mathbf{q}\nu}(\omega) = \frac{2\omega_{\mathbf{q}\nu}}{\omega^2 - \omega^2_{\mathbf{q}\nu} - 2\omega_{\mathbf{q}\nu}\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega)}$$

Phonons beyond DFPT: Non-adiabatic effects

Quasiparticle approximation

$$\frac{2\,\omega_{\mathbf{q}\nu}}{\omega^2 - \omega^2_{\mathbf{q}\nu} - 2\omega_{\mathbf{q}\nu}\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega)} \longrightarrow \frac{2\,\tilde{\Omega}_{\mathbf{q}\nu}}{\omega^2 - \tilde{\Omega}^2_{\mathbf{q}\nu}} \quad \text{with} \quad \tilde{\Omega}_{\mathbf{q}\nu} = \Omega_{\mathbf{q}\nu} - i\gamma_{\mathbf{q}\nu}$$

Phonons beyond DFPT: Non-adiabatic effects

Quasiparticle approximation

$$\frac{2\,\omega_{\mathbf{q}\nu}}{\omega^2 - \omega^2_{\mathbf{q}\nu} - 2\omega_{\mathbf{q}\nu}\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega)} \longrightarrow \frac{2\,\tilde{\Omega}_{\mathbf{q}\nu}}{\omega^2 - \tilde{\Omega}^2_{\mathbf{q}\nu}} \quad \text{with} \quad \tilde{\Omega}_{\mathbf{q}\nu} = \Omega_{\mathbf{q}\nu} - i\gamma_{\mathbf{q}\nu}$$

$$\Omega_{\mathbf{q}\nu} \simeq \omega_{\mathbf{q}\nu} + \mathrm{Re}\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu}) \qquad \text{frequency shift}$$

$$\gamma_{\mathbf{q}\nu} \simeq \left|\mathrm{Im}\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu})\right| \qquad \text{phonon broadening}$$

(expressions valid when $|\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu})| \ll \omega_{\mathbf{q}\nu}$)

Phonons beyond DFPT: Non-adiabatic effects

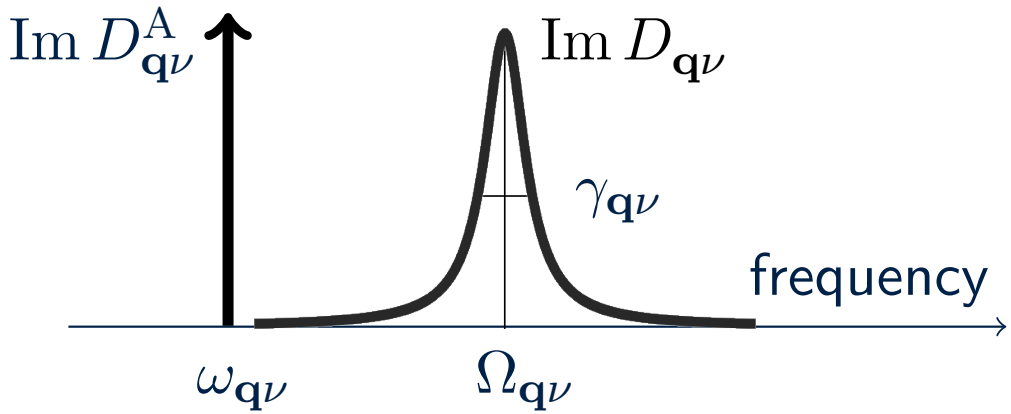
Quasiparticle approximation

$$\frac{2\,\omega_{\mathbf{q}\nu}}{\omega^2 - \omega^2_{\mathbf{q}\nu} - 2\omega_{\mathbf{q}\nu}\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega)} \longrightarrow \frac{2\,\tilde{\Omega}_{\mathbf{q}\nu}}{\omega^2 - \tilde{\Omega}^2_{\mathbf{q}\nu}} \quad \text{with} \quad \tilde{\Omega}_{\mathbf{q}\nu} = \Omega_{\mathbf{q}\nu} - i\gamma_{\mathbf{q}\nu}$$

$$\Omega_{\mathbf{q}\nu} \simeq \omega_{\mathbf{q}\nu} + \mathrm{Re}\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu}) \qquad \text{frequency shift}$$

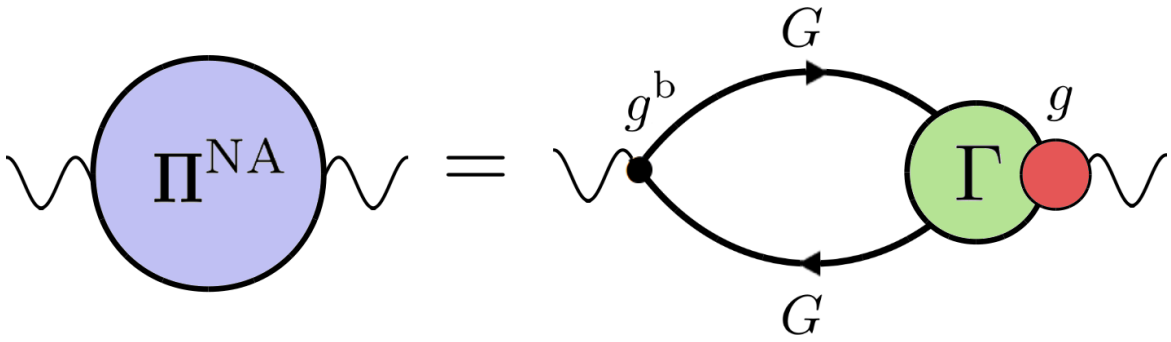
$$\gamma_{\mathbf{q}\nu} \simeq \left|\mathrm{Im}\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu})\right| \qquad \text{phonon broadening}$$

(expressions valid when $|\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu})| \ll \omega_{\mathbf{q}\nu}$)



Diagrammatic representation of the phonon self-energy

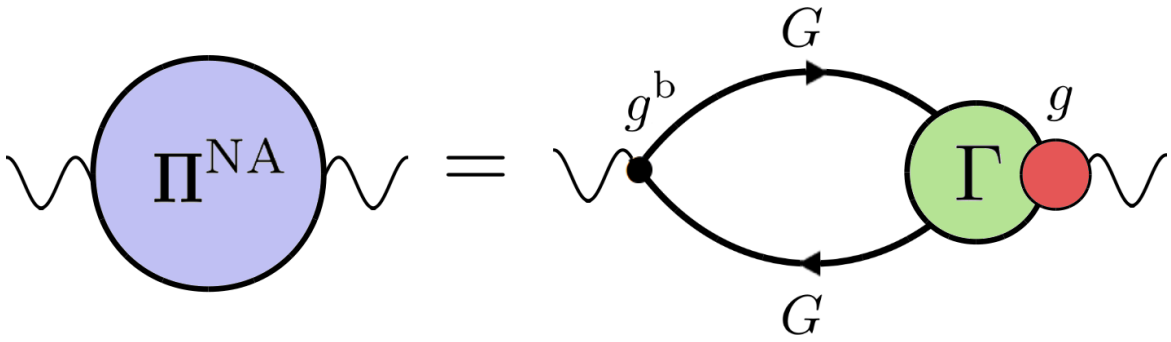
Non-adiabatic self-energy



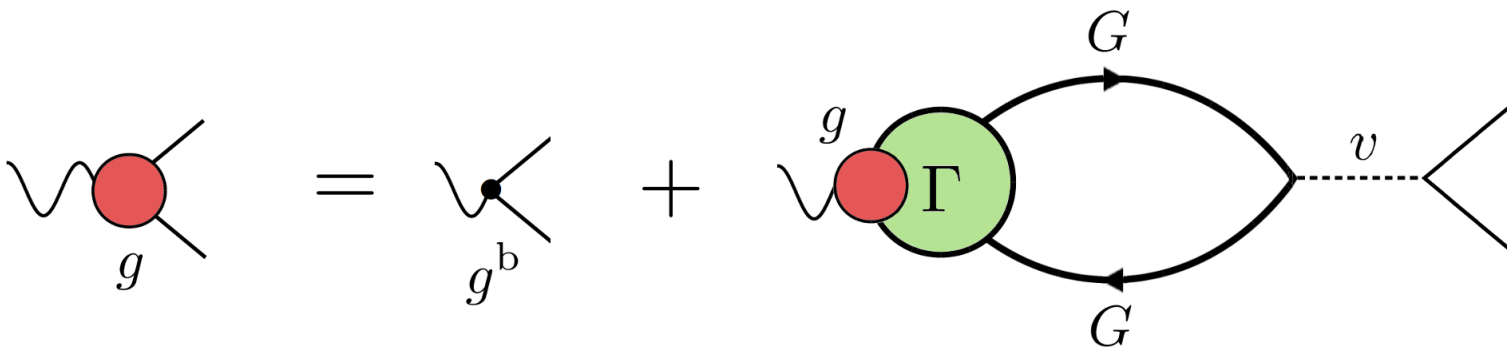
Figures from Giustino, Rev. Mod. Phys. 89, 015003 (2017)

Diagrammatic representation of the phonon self-energy

Non-adiabatic self-energy



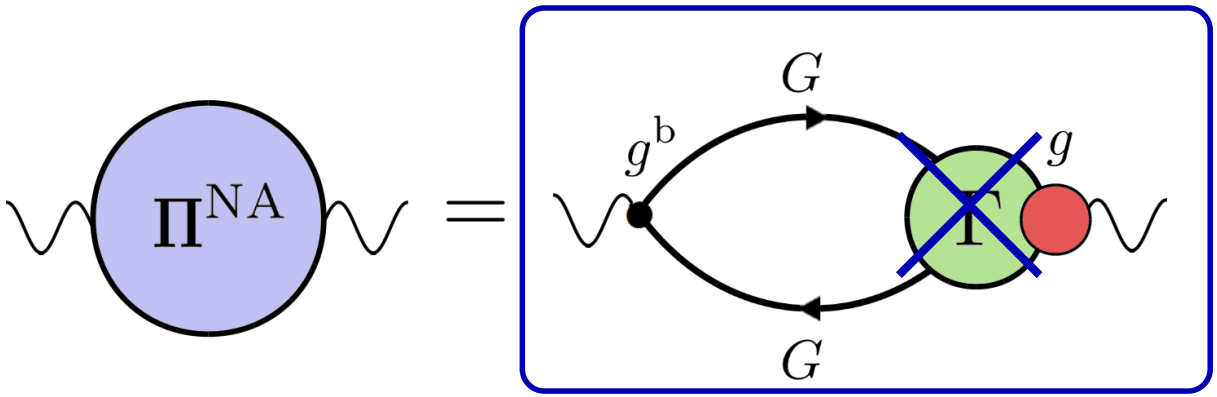
Dyson equation for the screened matrix element



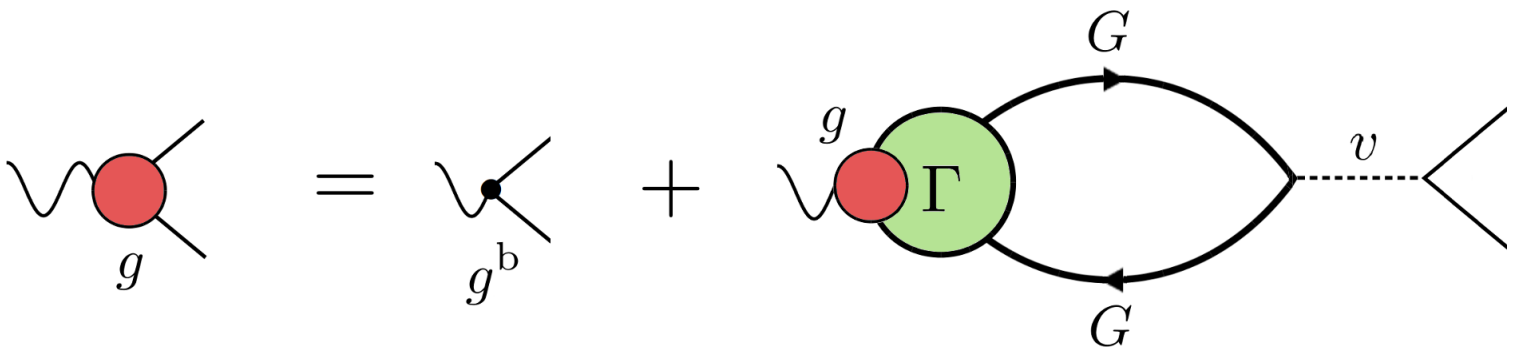
Figures from Giustino, Rev. Mod. Phys. 89, 015003 (2017)

Diagrammatic representation of the phonon self-energy

Non-adiabatic self-energy



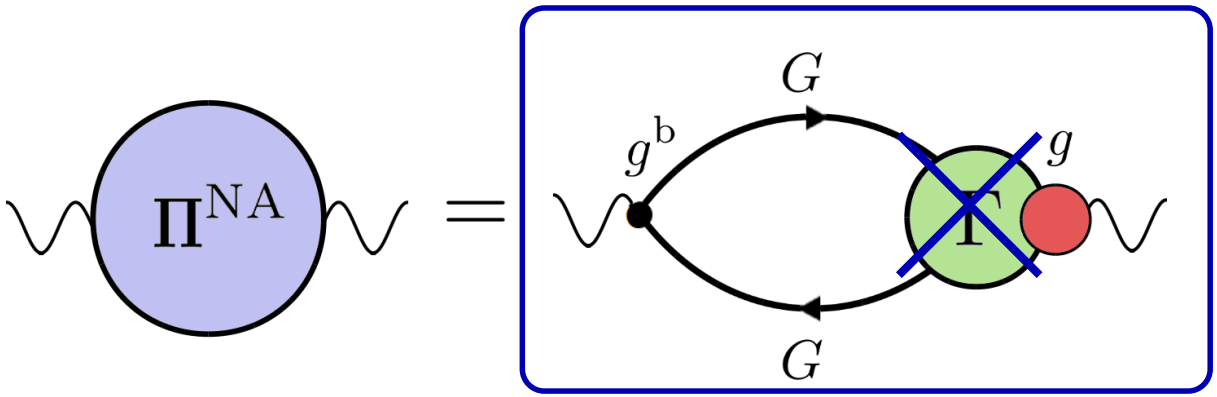
Dyson equation for the screened matrix element



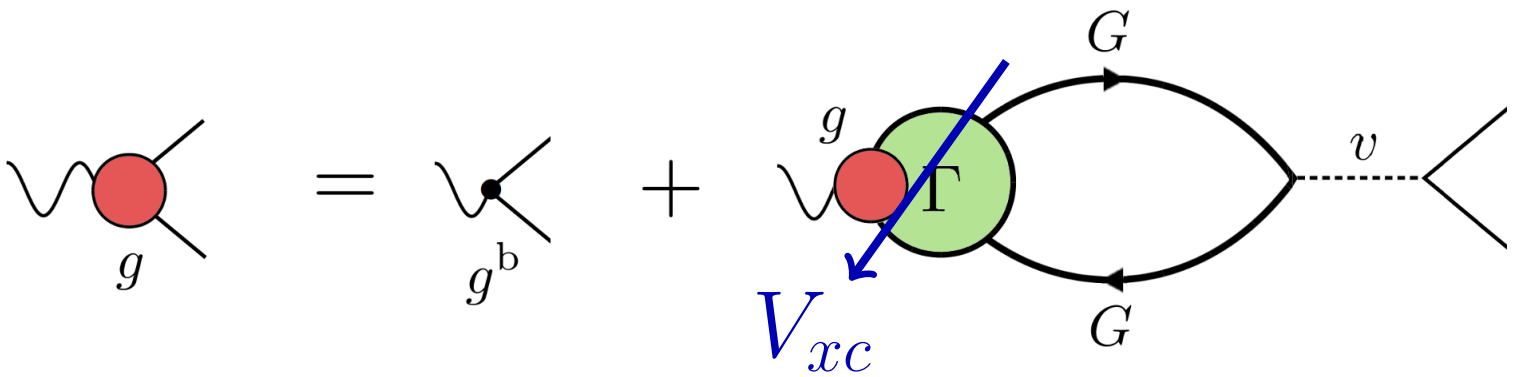
Figures from Giustino, Rev. Mod. Phys. 89, 015003 (2017)

Diagrammatic representation of the phonon self-energy

Non-adiabatic self-energy



Dyson equation for the screened matrix element



Figures from Giustino, Rev. Mod. Phys. 89, 015003 (2017)

Phonon self-energy in practice

$$\hbar\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega) = 2\sum_{mn}\int\frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q}) g^{*}_{mn\nu}(\mathbf{k},\mathbf{q})$$
$$\times\left[\frac{f_{m\mathbf{k}+\mathbf{q}}-f_{n\mathbf{k}}}{\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}-\hbar(\omega+i\eta)} - \frac{f_{m\mathbf{k}+\mathbf{q}}-f_{n\mathbf{k}}}{\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}}\right]$$

Phonon self-energy in practice

Bare
matrix element

$$\hbar\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega) = 2\sum_{mn}\int\frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q}) g^{*}_{mn\nu}(\mathbf{k},\mathbf{q})$$
$$\times\left[\frac{f_{m\mathbf{k}+\mathbf{q}}-f_{n\mathbf{k}}}{\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}-\hbar(\omega+i\eta)} - \frac{f_{m\mathbf{k}+\mathbf{q}}-f_{n\mathbf{k}}}{\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}}\right]$$

Phonon self-energy in practice

Bare matrix element

Screened matrix element

$$\hbar\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega) = 2\sum_{mn}\int\frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q})\, g^{*}_{mn\nu}(\mathbf{k},\mathbf{q})$$

$$\times\left[\frac{f_{m\mathbf{k}+\mathbf{q}}-f_{n\mathbf{k}}}{\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}-\hbar(\omega+i\eta)} - \frac{f_{m\mathbf{k}+\mathbf{q}}-f_{n\mathbf{k}}}{\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}}\right]$$

Phonon self-energy in practice

Bare matrix element

Screened matrix element

$$\hbar\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega) = 2\sum_{mn}\int\frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q})\, g^{*}_{mn\nu}(\mathbf{k},\mathbf{q})$$

$$\times\left[\frac{f_{m\mathbf{k}+\mathbf{q}}-f_{n\mathbf{k}}}{\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}-\hbar(\omega+i\eta)} - \frac{f_{m\mathbf{k}+\mathbf{q}}-f_{n\mathbf{k}}}{\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}}\right]$$

Dynamical structure on the scale of electronic excitations

Phonon self-energy in practice

Bare matrix element

Screened matrix element

$$\hbar\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega) = 2\sum_{mn}\int\frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q})\, g^{*}_{mn\nu}(\mathbf{k},\mathbf{q})$$

$$\times\left[\frac{f_{m\mathbf{k}+\mathbf{q}}-f_{n\mathbf{k}}}{\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}-\hbar(\omega+i\eta)} - \frac{f_{m\mathbf{k}+\mathbf{q}}-f_{n\mathbf{k}}}{\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}}\right]$$

Dynamical structure on the scale of electronic excitations

Most calculations so far used the approximation or replacing $g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q})$ by $g_{mn\nu}(\mathbf{k},\mathbf{q})$

Phonon self-energy in practice

Non-adiabatic phonon frequency shift

$$\mathrm{Re}\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu}) = \frac{2}{\hbar}\sum_{mn}\int\frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q}) g^{*}_{mn\nu}(\mathbf{k},\mathbf{q})$$
$$\times(f_{m\mathbf{k}+\mathbf{q}} - f_{n\mathbf{k}})\left[\frac{1}{\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}} - \hbar\omega_{\mathbf{q}\nu}} - \frac{1}{\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}}}\right]$$

Phonon self-energy in practice

Non-adiabatic phonon frequency shift

$$\mathrm{Re}\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu}) = \frac{2}{\hbar}\sum_{mn}\int\frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q}) g^{*}_{mn\nu}(\mathbf{k},\mathbf{q})$$

$$\times(f_{m\mathbf{k}+\mathbf{q}} - f_{n\mathbf{k}})\left[\frac{1}{\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}} - \hbar\omega_{\mathbf{q}\nu}} - \frac{1}{\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}}}\right]$$

$\neq 0$ only if $|n\mathbf{k}\rangle$ is occupied and $|m\mathbf{k}+\mathbf{q}\rangle$ is empty (or viceversa)

Phonon self-energy in practice

Non-adiabatic phonon frequency shift

$$\mathrm{Re}\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu}) = \frac{2}{\hbar}\sum_{mn}\int\frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q}) g^{*}_{mn\nu}(\mathbf{k},\mathbf{q})$$

$$\times(f_{m\mathbf{k}+\mathbf{q}} - f_{n\mathbf{k}})\left[\frac{1}{\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}} - \hbar\omega_{\mathbf{q}\nu}} - \frac{1}{\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}}}\right]$$

$\neq 0$ only if $|n\mathbf{k}\rangle$ is occupied and $|m\mathbf{k}+\mathbf{q}\rangle$ is empty (or viceversa)

larger than band gap

Phonon self-energy in practice

Non-adiabatic phonon frequency shift

$$\mathrm{Re}\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu}) = \frac{2}{\hbar}\sum_{mn}\int\frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q}) g^{*}_{mn\nu}(\mathbf{k},\mathbf{q})$$

$$\times(f_{m\mathbf{k}+\mathbf{q}} - f_{n\mathbf{k}})\left[\frac{1}{\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}} - \hbar\omega_{\mathbf{q}\nu}} - \frac{1}{\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}}}\right]$$

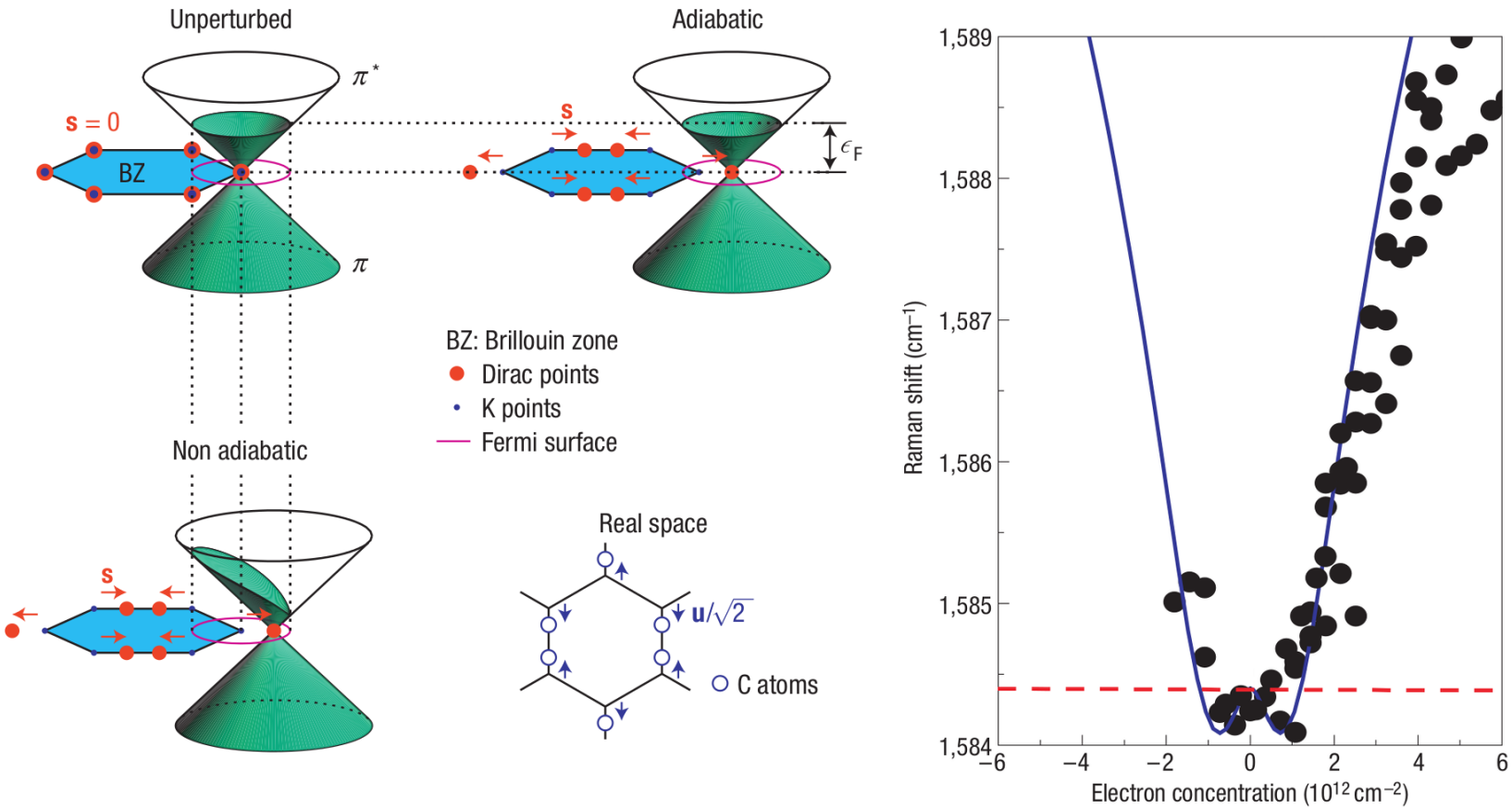
$\neq 0$ only if $|n\mathbf{k}\rangle$ is occupied and $|m\mathbf{k}+\mathbf{q}\rangle$ is empty (or viceversa)

larger than band gap

- Small effect in systems with large gap
- Can be significant in small or zero-gap systems (metals, graphene, degenerate semiconductors)

Examples of non-adiabatic phonons

- Non-adiabatic Kohn-anomaly in graphene

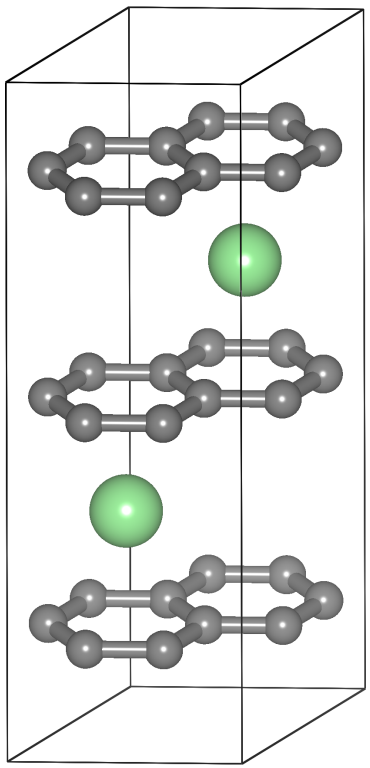


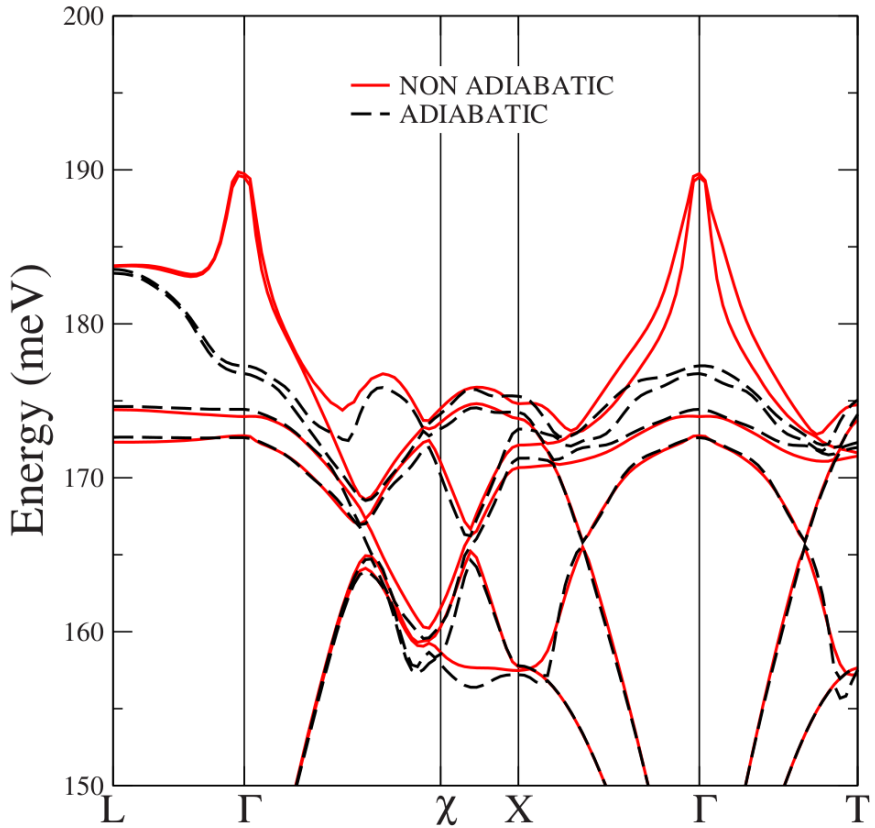
Figures from Pisana et al, Nat. Mater. 6, 198 (2007)

[Approximation: replaced $g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q})$ by $g_{mn\nu}(\mathbf{k},\mathbf{q})$]

Examples of non-adiabatic phonons

- Non-adiabatic phonons in CaC_6



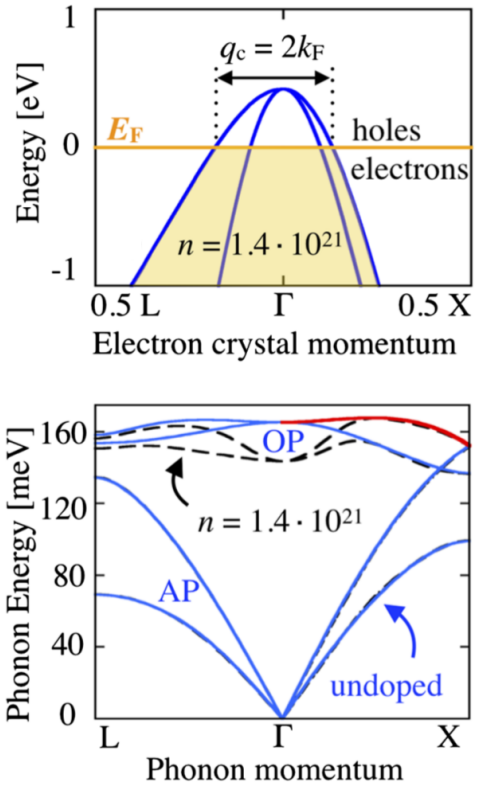


Right figure from Calandra et al, Phys. Rev. B 82, 165111 (2010)

[Approximation: replaced $g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q})$ by $g_{mn\nu}(\mathbf{k},\mathbf{q})$]

Examples of non-adiabatic phonons

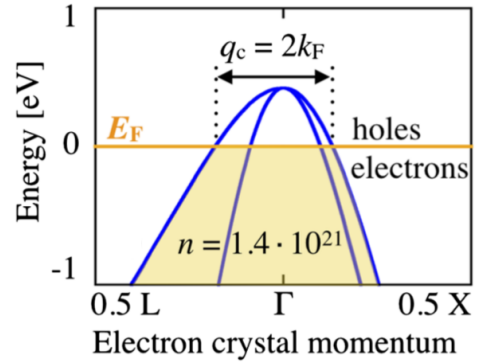
- Spectral function of boron-doped diamond

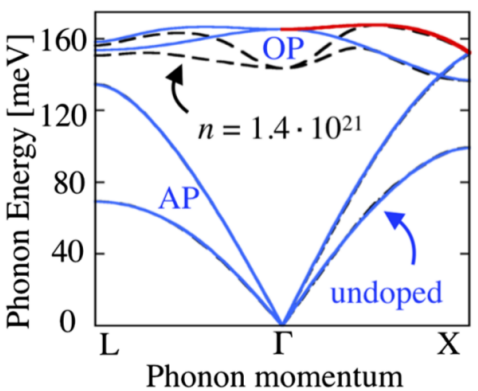


Figures from Caruso et al, Phys. Rev. Lett. 119, 017001 (2017)

Examples of non-adiabatic phonons

- Spectral function of boron-doped diamond





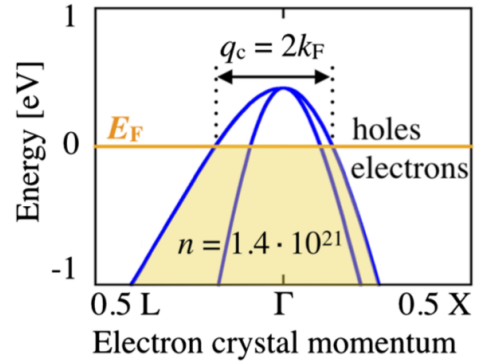
$$A_{\mathbf{q}}(\omega) = \frac{1}{\pi} \sum_{\nu} \mathrm{Im} \frac{2\omega_{\mathbf{q}\nu}}{\omega^2 - \omega^2_{\mathbf{q}\nu} - 2\omega_{\mathbf{q}\nu}\, \Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega)}$$

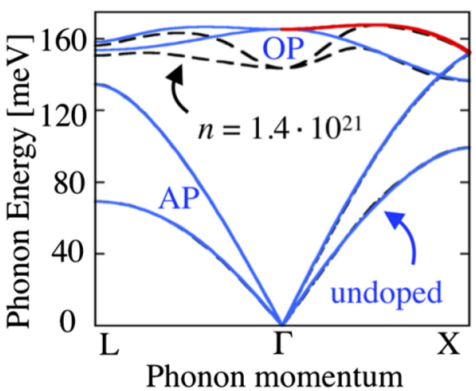
Figures from Caruso et al, Phys. Rev. Lett. 119, 017001 (2017)

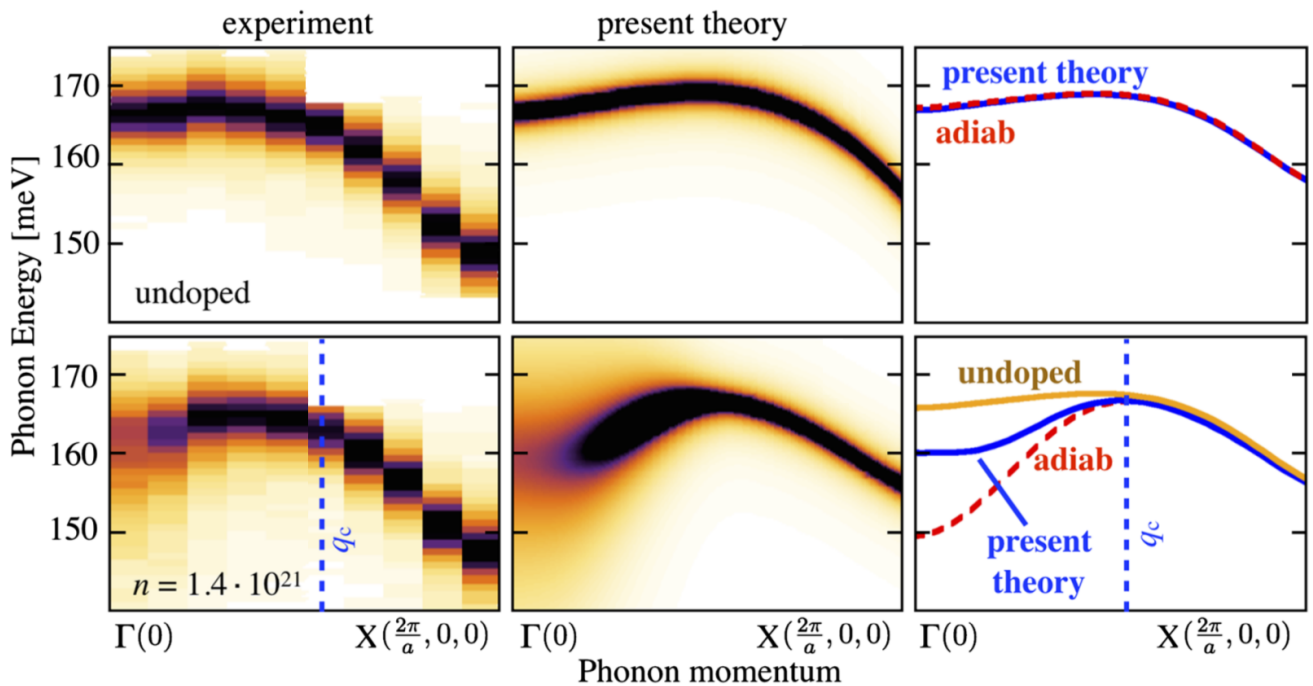
Examples of non-adiabatic phonons

- Spectral function of boron-doped diamond

$$A_{\mathbf{q}}(\omega) = \frac{1}{\pi} \sum_{\nu} \mathrm{Im} \frac{2\omega_{\mathbf{q}\nu}}{\omega^2 - \omega^2_{\mathbf{q}\nu} - 2\omega_{\mathbf{q}\nu}\, \Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega)}$$







Figures from Caruso et al, Phys. Rev. Lett. 119, 017001 (2017)

Phonon lifetimes from electron-phonon interactions

$$\frac{1}{\tau_{\mathbf{q}\nu}} = 2\gamma_{\mathbf{q}\nu} = 2\left|\mathrm{Im}\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu})\right|$$

Phonon lifetimes from electron-phonon interactions

$$\frac{1}{\tau_{\mathbf{q}\nu}} = 2\gamma_{\mathbf{q}\nu} = 2\left|\mathrm{Im}\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu})\right|$$

$$\frac{1}{\tau_{\mathbf{q}\nu}} = \frac{2\pi}{\hbar} 2 \sum_{mn} \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q}) g^{*}_{mn\nu}(\mathbf{k},\mathbf{q}) \times (f_{m\mathbf{k}+\mathbf{q}} - f_{n\mathbf{k}})\, \delta(\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}} - \hbar\omega_{\mathbf{q}\nu})$$

Phonon lifetimes from electron-phonon interactions

$$\frac{1}{\tau_{\mathbf{q}\nu}} = 2\gamma_{\mathbf{q}\nu} = 2\left|\mathrm{Im}\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu})\right|$$

$$\frac{1}{\tau_{\mathbf{q}\nu}} = \frac{2\pi}{\hbar} 2 \sum_{mn} \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q}) g^{*}_{mn\nu}(\mathbf{k},\mathbf{q})$$

$$\times \left(f_{m\mathbf{k}+\mathbf{q}} - f_{n\mathbf{k}}\right) \delta(\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}} - \hbar\omega_{\mathbf{q}\nu})$$

$|m\mathbf{k}+\mathbf{q}\rangle$ above $|n\mathbf{k}\rangle$

Phonon lifetimes from electron-phonon interactions

$$\frac{1}{\tau_{\mathbf{q}\nu}} = 2\gamma_{\mathbf{q}\nu} = 2\left|\mathrm{Im}\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu})\right|$$

$$\frac{1}{\tau_{\mathbf{q}\nu}} = \frac{2\pi}{\hbar} 2 \sum_{mn} \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q}) g^{*}_{mn\nu}(\mathbf{k},\mathbf{q}) \times (f_{m\mathbf{k}+\mathbf{q}} - f_{n\mathbf{k}})\, \delta(\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}} - \hbar\omega_{\mathbf{q}\nu})$$

$|m\mathbf{k}+\mathbf{q}\rangle$ empty

$|\mathbf{k}\rangle$ occupied

$|m\mathbf{k}+\mathbf{q}\rangle$ above $|n\mathbf{k}\rangle$

Phonon lifetimes from electron-phonon interactions

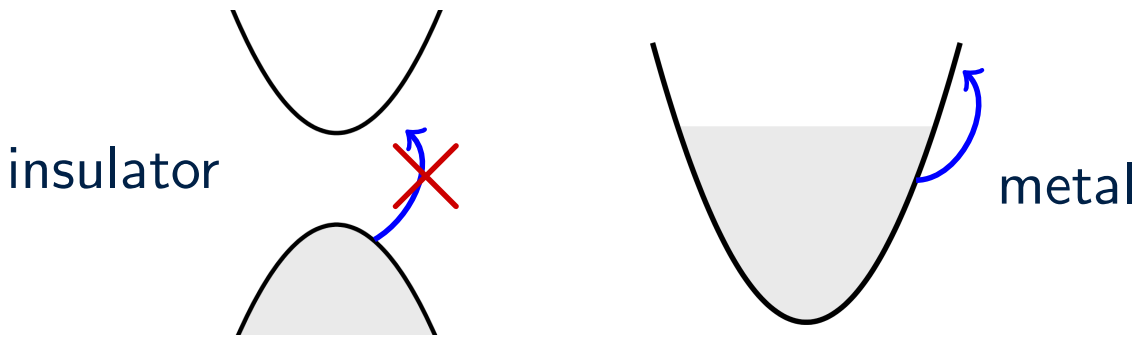
$$\frac{1}{\tau_{\mathbf{q}\nu}} = 2\gamma_{\mathbf{q}\nu} = 2\left|\mathrm{Im}\,\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega_{\mathbf{q}\nu})\right|$$

$$\frac{1}{\tau_{\mathbf{q}\nu}} = \frac{2\pi}{\hbar} 2 \sum_{mn} \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q}) g^{*}_{mn\nu}(\mathbf{k},\mathbf{q})$$

$$\times \left(f_{m\mathbf{k}+\mathbf{q}} - f_{n\mathbf{k}}\right) \delta(\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}} - \hbar\omega_{\mathbf{q}\nu})$$

$|m\mathbf{k}+\mathbf{q}\rangle$ empty $|n\mathbf{k}\rangle$ occupied

$|m\mathbf{k}+\mathbf{q}\rangle$ above $|n\mathbf{k}\rangle$



Phonon lifetimes from electron-phonon interactions

Approximation often employed in the literature

- Approximate $g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q})$ using $g_{mn\nu}(\mathbf{k},\mathbf{q})$
- Taylor-expand Fermi-Dirac functions using $f_{m\mathbf{k}+\mathbf{q}} = f(\varepsilon_{n\mathbf{k}} + \omega_{\mathbf{q}\nu})$
- Take limit of zero temperature: $\partial f/\partial\varepsilon \simeq -\delta(\varepsilon - \varepsilon_{\mathrm{F}})$
- Neglect phonon energy

Phonon lifetimes from electron-phonon interactions

Approximation often employed in the literature

- Approximate $g^{\mathrm{b}}_{mn\nu}(\mathbf{k},\mathbf{q})$ using $g_{mn\nu}(\mathbf{k},\mathbf{q})$
- Taylor-expand Fermi-Dirac functions using $f_{m\mathbf{k}+\mathbf{q}} = f(\varepsilon_{n\mathbf{k}} + \omega_{\mathbf{q}\nu})$
- Take limit of zero temperature: $\partial f/\partial\varepsilon \simeq -\delta(\varepsilon - \varepsilon_{\mathrm{F}})$
- Neglect phonon energy

$$\gamma_{\mathbf{q}\nu} = 2\pi\,\omega_{\mathbf{q}\nu} \sum_{mn} \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} \left|g_{mn\nu}(\mathbf{k},\mathbf{q})\right|^2 \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{\mathrm{F}})\,\delta(\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathrm{F}})$$

'Double-delta' approximation to the phonon linewidth in **metals**

(Note this is the half-width at half-maximum)

Example of phonon linewidths

- Phonon linewidths of MgB_2, IXS vs. DFT

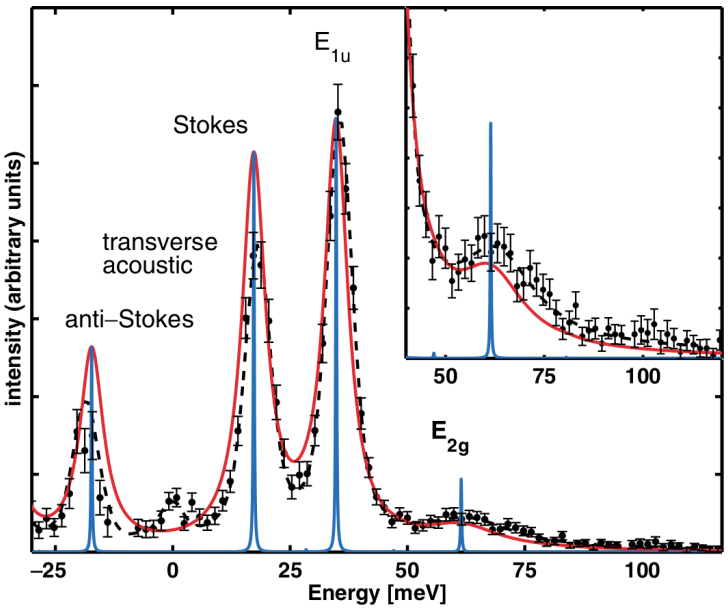
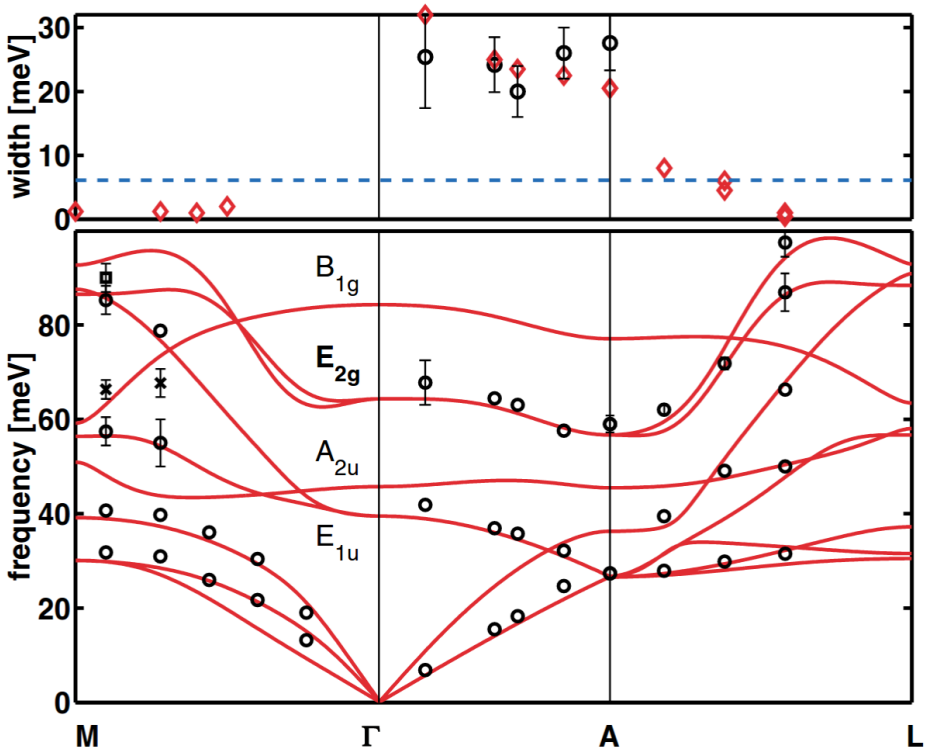


FIG. 1 (color online). Energy loss scan in almost transverse geometry measured at $\mathbf{Q} = (1\ 2\ 0.3)$ corresponding to 0.6 Γ-A. The data, normalized to the incident flux, are shown with the least-squares fit (dashed line) and the *ab initio* spectrum with and without broadening due to experiment and electron phonon coupling (solid lines).



Figures from Shukla et al, Phys. Rev. Lett. 90, 095506 (2003)

The electron-phonon matrix element

Matrix element from many-body theory

$$g_{mn\nu}(\mathbf{k},\mathbf{q}) = \langle u_{m\mathbf{k}+\mathbf{q}}| \int d\mathbf{r}' \; \epsilon_{\mathrm{e}}^{-1}(\mathbf{r},\mathbf{r}',\omega)\, \Delta_{\mathbf{q}\nu} v^{\mathrm{en}}(\mathbf{r}') \; |u_{n\mathbf{k}}\rangle$$

The electron-phonon matrix element

Matrix element from many-body theory

$$g_{mn\nu}(\mathbf{k},\mathbf{q}) = \langle u_{m\mathbf{k}+\mathbf{q}}| \int d\mathbf{r}' \, \epsilon_{\mathrm{e}}^{-1}(\mathbf{r},\mathbf{r}',\omega) \Delta_{\mathbf{q}\nu} v^{\mathrm{en}}(\mathbf{r}') \, |u_{n\mathbf{k}}\rangle$$

Exact dielectric matrix

(includes all el-el and el-ph interactions)

The electron-phonon matrix element

Matrix element from many-body theory

$$g_{mn\nu}(\mathbf{k},\mathbf{q}) = \langle u_{m\mathbf{k}+\mathbf{q}}| \int d\mathbf{r}' \, \epsilon_{\mathrm{e}}^{-1}(\mathbf{r},\mathbf{r}',\omega) \Delta_{\mathbf{q}\nu} v^{\mathrm{en}}(\mathbf{r}') \, |u_{n\mathbf{k}}\rangle$$

Exact dielectric matrix

(includes all el-el and el-ph interactions)

In DFT we approximate $\epsilon_{\mathrm{e}}^{-1}(\mathbf{r},\mathbf{r}',\omega)$ as $\epsilon_{\mathrm{DFT}}^{-1}(\mathbf{r},\mathbf{r}')$

& pseudopotential approximation

The electron-phonon matrix element

Matrix element from many-body theory

$$g_{mn\nu}(\mathbf{k},\mathbf{q}) = \langle u_{m\mathbf{k}+\mathbf{q}} | \int d\mathbf{r}' \, \epsilon_{\mathrm{e}}^{-1}(\mathbf{r},\mathbf{r}',\omega) \Delta_{\mathbf{q}\nu} v^{\mathrm{en}}(\mathbf{r}') \, | u_{n\mathbf{k}} \rangle$$

Exact dielectric matrix

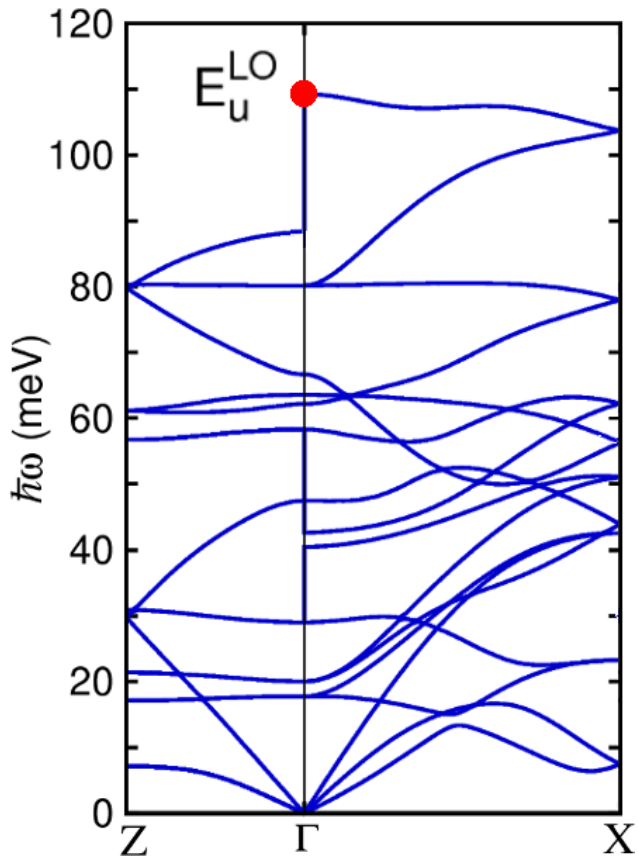
(includes all el-el and el-ph interactions)

In DFT we approximate $\epsilon_{\mathrm{e}}^{-1}(\mathbf{r},\mathbf{r}',\omega)$ as $\epsilon_{\mathrm{DFT}}^{-1}(\mathbf{r},\mathbf{r}')$
& pseudopotential approximation

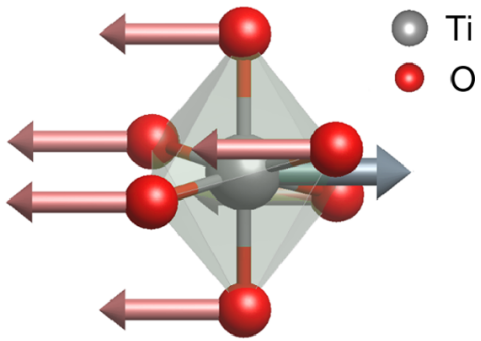
- Sensitivity to XC functional
- Suppression of non-adiabatic effects in the matrix elements

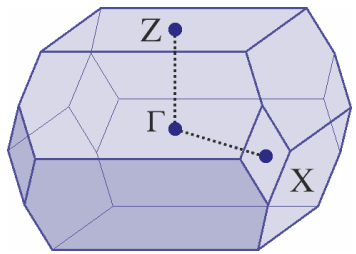
The electron-phonon matrix element

- Wannier interpolation in the presence of Fröhlich interactions



TiO_2 anatase





Figures from Verdi et al, Phys. Rev. Lett. 115, 176401 (2015)

The electron-phonon matrix element

- Wannier interpolation in the presence of Fröhlich interactions

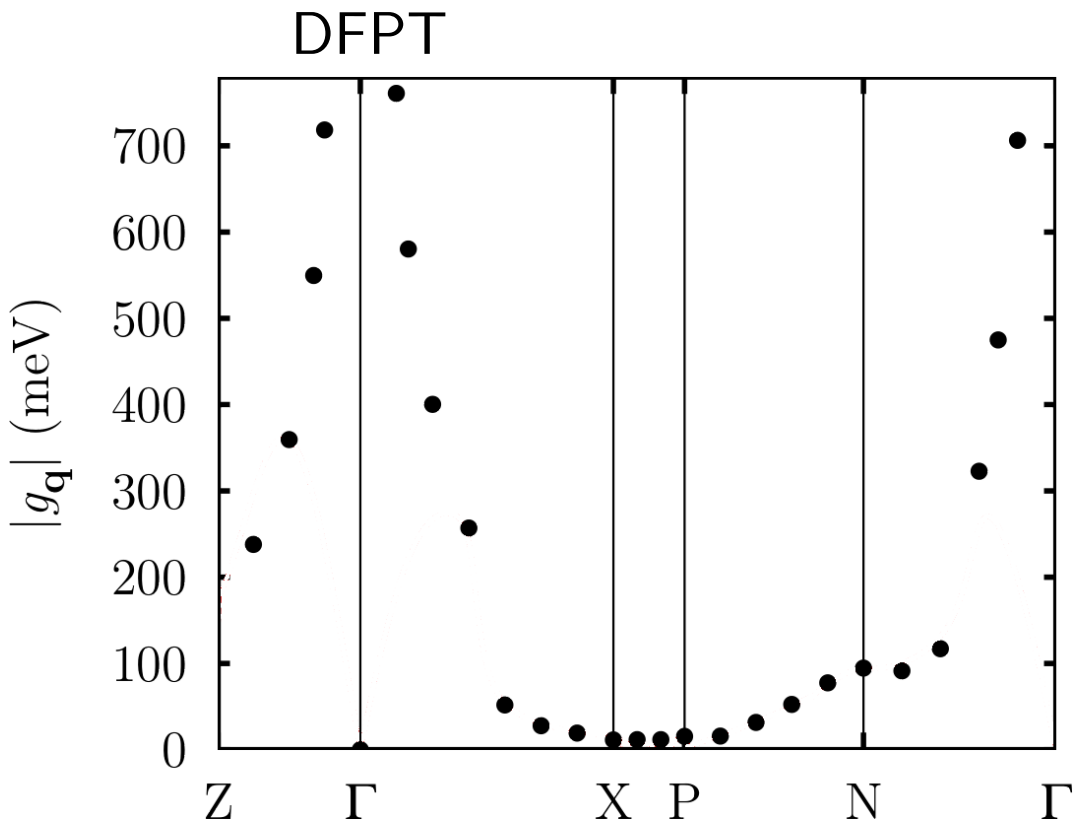


Figure from Verdi et al, Phys. Rev. Lett. 115, 176401 (2015)

The electron-phonon matrix element

- Wannier interpolation in the presence of Fröhlich interactions

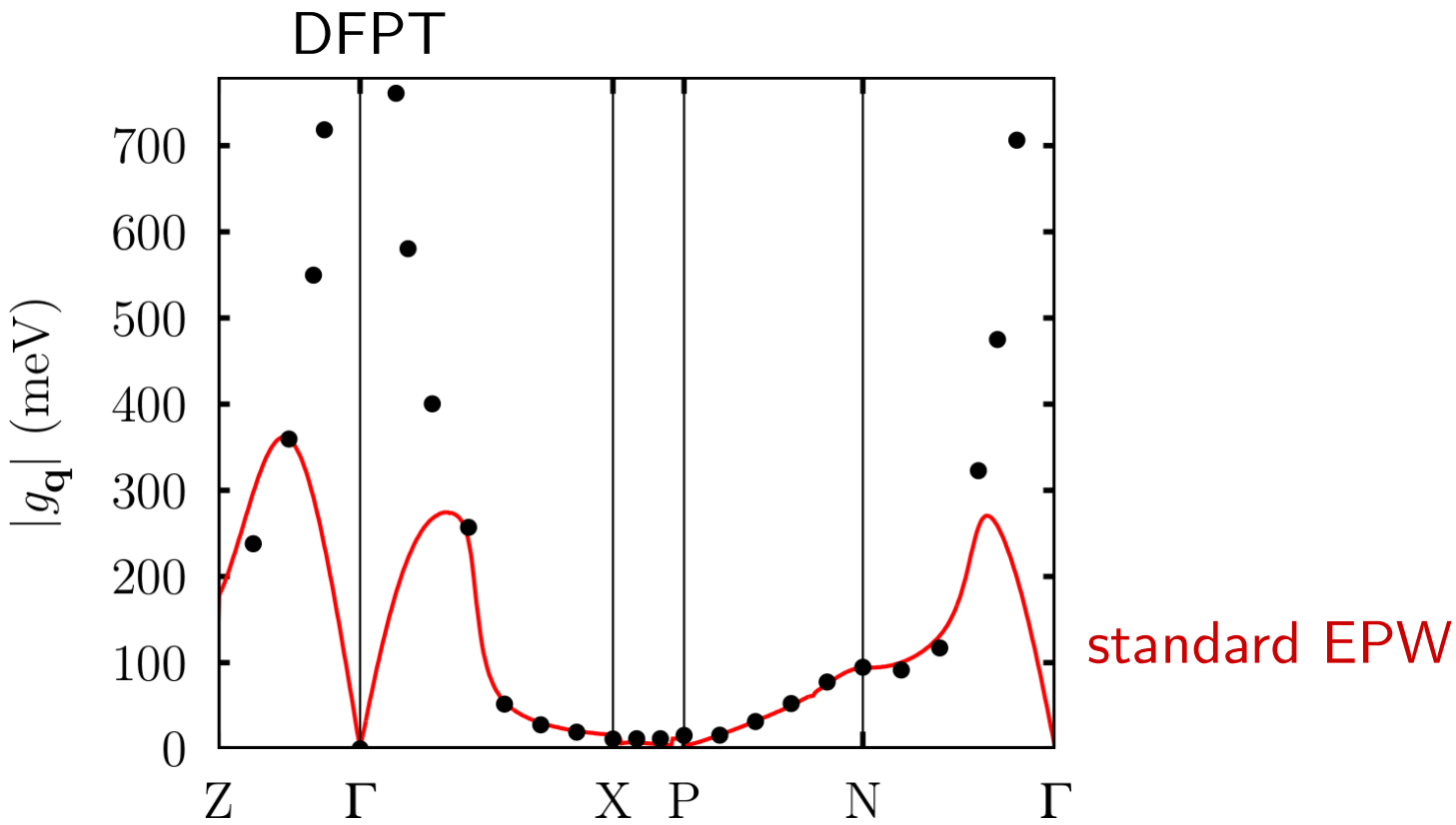


Figure from Verdi et al, Phys. Rev. Lett. 115, 176401 (2015)

The electron-phonon matrix element

- Wannier interpolation in the presence of Fröhlich interactions

$$g(\mathbf{k},\mathbf{q}) = g^{\mathcal{S}}(\mathbf{k},\mathbf{q}) + g^{\mathcal{L}}(\mathbf{k},\mathbf{q})$$

The electron-phonon matrix element

- Wannier interpolation in the presence of Fröhlich interactions

$$g(\mathbf{k},\mathbf{q}) = g^{\mathcal{S}}(\mathbf{k},\mathbf{q}) + g^{\mathcal{L}}(\mathbf{k},\mathbf{q})$$

$$g^{\mathcal{L}}(\mathbf{k},\mathbf{q}) = i\frac{4\pi}{\Omega}\frac{e^2}{4\pi\varepsilon_0}\sum_{\kappa}\left(\frac{\hbar}{2N_p M_\kappa\,\omega_{\mathbf{q}}}\right)^{\frac{1}{2}} \times$$

$$\sum_{\mathbf{G}\neq-\mathbf{q}} \frac{(\mathbf{q}+\mathbf{G})\cdot\mathbf{Z}^*_\kappa\cdot\mathbf{e}_\kappa(\mathbf{q})}{(\mathbf{q}+\mathbf{G})\cdot\boldsymbol{\epsilon}^\infty\cdot(\mathbf{q}+\mathbf{G})}\langle\psi_{\mathbf{k}+\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G})\cdot(\mathbf{r}-\boldsymbol{\tau}_\kappa)}|\psi_{\mathbf{k}}\rangle_{\mathrm{sc}}$$

The electron-phonon matrix element

- Wannier interpolation in the presence of Fröhlich interactions

$$g(\mathbf{k},\mathbf{q}) = g^{\mathcal{S}}(\mathbf{k},\mathbf{q}) + g^{\mathcal{L}}(\mathbf{k},\mathbf{q})$$

$$g^{\mathcal{L}}(\mathbf{k},\mathbf{q}) = i\frac{4\pi}{\Omega}\frac{e^2}{4\pi\varepsilon_0}\sum_{\kappa}\left(\frac{\hbar}{2N_p M_\kappa\,\omega_{\mathbf{q}}}\right)^{\frac{1}{2}} \times$$
$$\sum_{\mathbf{G}\neq-\mathbf{q}} \frac{(\mathbf{q}+\mathbf{G})\cdot\mathbf{Z}^*_\kappa\cdot\mathbf{e}_\kappa(\mathbf{q})}{(\mathbf{q}+\mathbf{G})\cdot\boldsymbol{\epsilon}^\infty\cdot(\mathbf{q}+\mathbf{G})}\langle\psi_{\mathbf{k}+\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G})\cdot(\mathbf{r}-\boldsymbol{\tau}_\kappa)}|\psi_{\mathbf{k}}\rangle_{\mathrm{sc}}$$

The electron-phonon matrix element

- Wannier interpolation in the presence of Fröhlich interactions

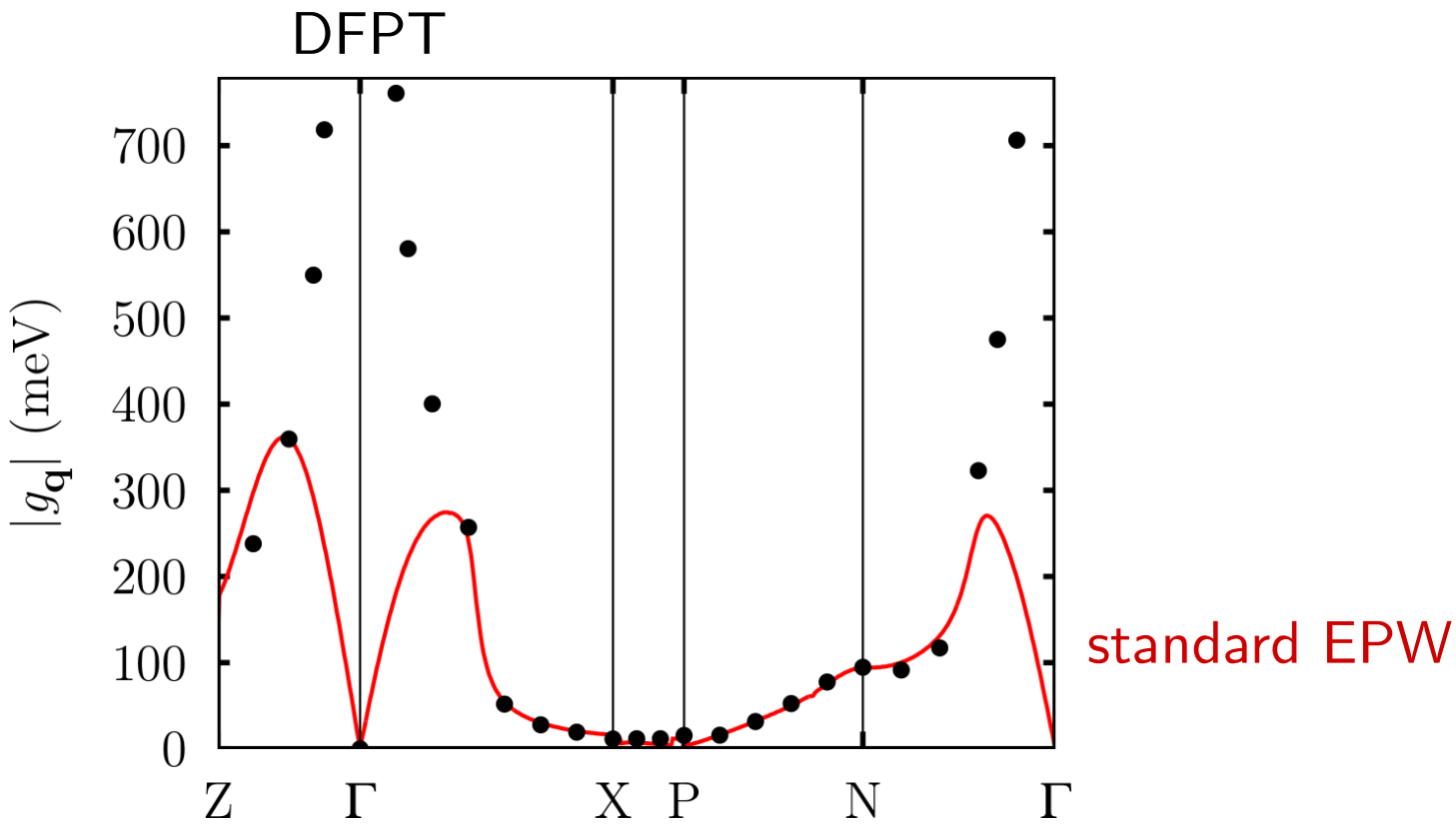


Figure from Verdi et al, Phys. Rev. Lett. 115, 176401 (2015)

The electron-phonon matrix element

- Wannier interpolation in the presence of Fröhlich interactions

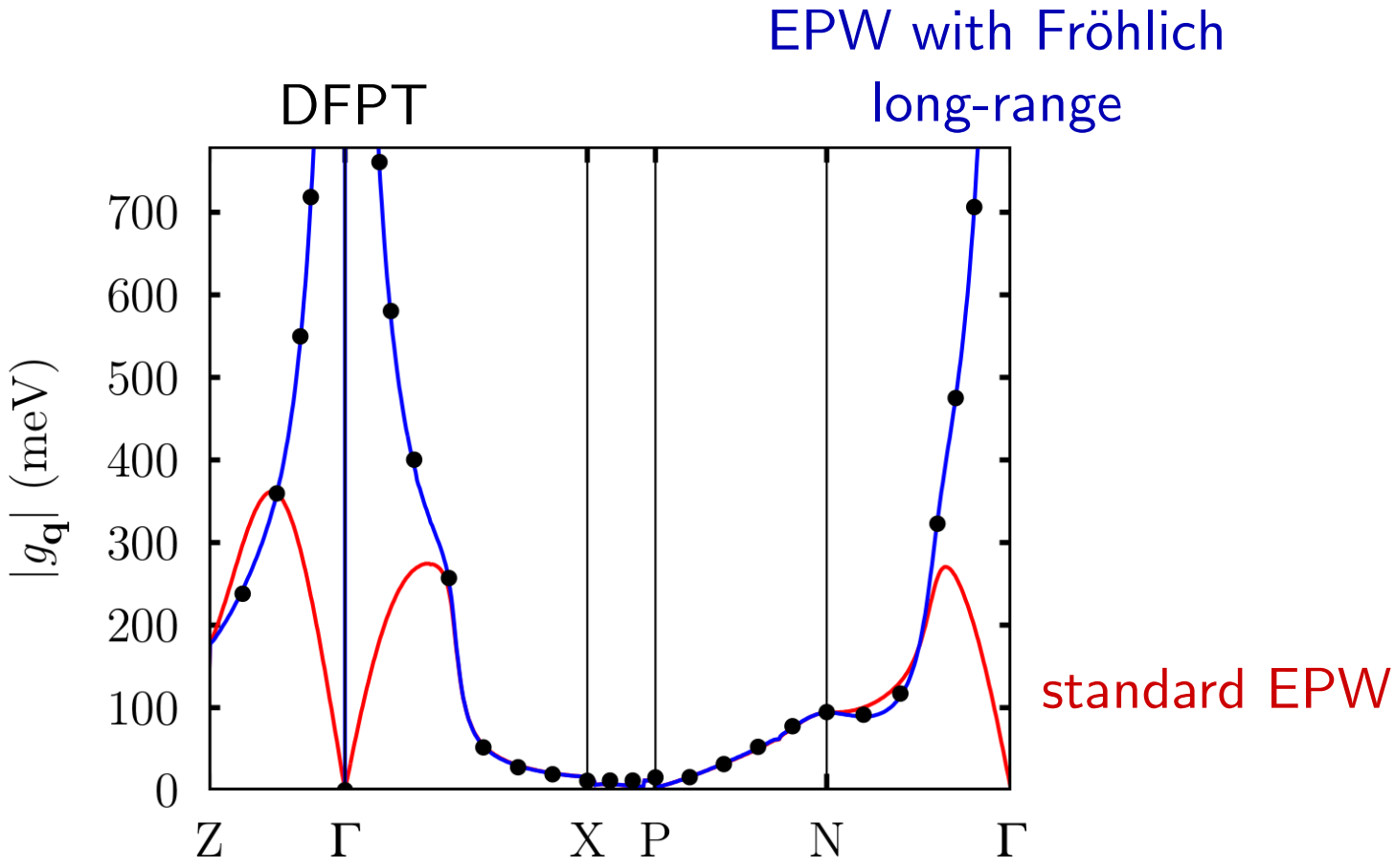


Figure from Verdi et al, Phys. Rev. Lett. 115, 176401 (2015)

Take-home messages

- Quantum field theory offers a rigorous and unambiguous framework to study phonons beyond DFT
- We can calculate non-adiabatic corrections to the phonon dispersion relations
- We can calculate phonon linewidths and lifetimes associated with electron-phonon interactions

References

- F. Giustino, Rev. Mod. Phys. 89, 015003 (2017) [link]
- G. Baym, Ann. Phys. 14, 1 (1961) [Link]
- E. G. Maksimov, Sov. Phys. JETP 42, 1138 (1976) [Link]
- L. Hedin and S. Lundqvist, *Effects of electron-electron and electron-phonon interactions on the one-electron states of solids*, Ed. Seitz, Turnbull, and Ehrenreich, Solid State Physics, Vol. 23 (Academic, 1969)
- M. Calandra, G. Profeta, and F. Mauri, Phys. Rev. B 82, 165111 (2010)
- T. Kato, T. Kobayashi, and M. Namiki, Prog. Theor. Phys. 15, 3 (1960) [Link]
- C. Verdi and F. Giustino, Phys. Rev. Lett. 115 (17), 176401 (2015) [Link]
- J. Sjakste, N. Vast, M. Calandra, and F. Mauri, Phys. Rev. B 92, 054307 (2015) [Link]