Lecture 4:

Spectral functions and spectroscopic properties with SSCHA

Raffaello Bianco

Free Energy Hessian: a static theory

$$D^{(\mathrm{F})} = \frac{1}{\sqrt{MM}} \left. \frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}} \right|_{\mathcal{R}_{\mathrm{eq}}}$$

Generalized dynamical matrix

The corresponding spectrum describes vibrational excitations with infinite lifetime

We need a dynamic theory

SCHA quasiparticles

SCHA is a "Hartree-Fock"-like theory for phonons

Hartree-Fock	SCHA
Variational method **Electronic Free Energy**	**Variational** method **Ionic Free Energy**
Effective **non-interacting fermions**	Effective **non-interacting bosons**
Take into account **electron-electron interaction**	Take into account **phonon-phonon interaction**

SCHA effective harmonic Hamiltonian

$$H^{\mathrm{SCHA}} = K + \frac{1}{2}(R - \mathcal{R}^{\mathrm{MIN}}) \cdot \Phi^{\mathrm{MIN}} \cdot (R - \mathcal{R}^{\mathrm{MIN}})$$

this Hamiltonian defines SCHA quasipartcles

SCHA quasiparticles

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Harmonic phonons

Harmonic propagator

Replaced by

SCHA quasiparticles dressed harmonic phonons

SCHA propagator

SCHA quasiparticles

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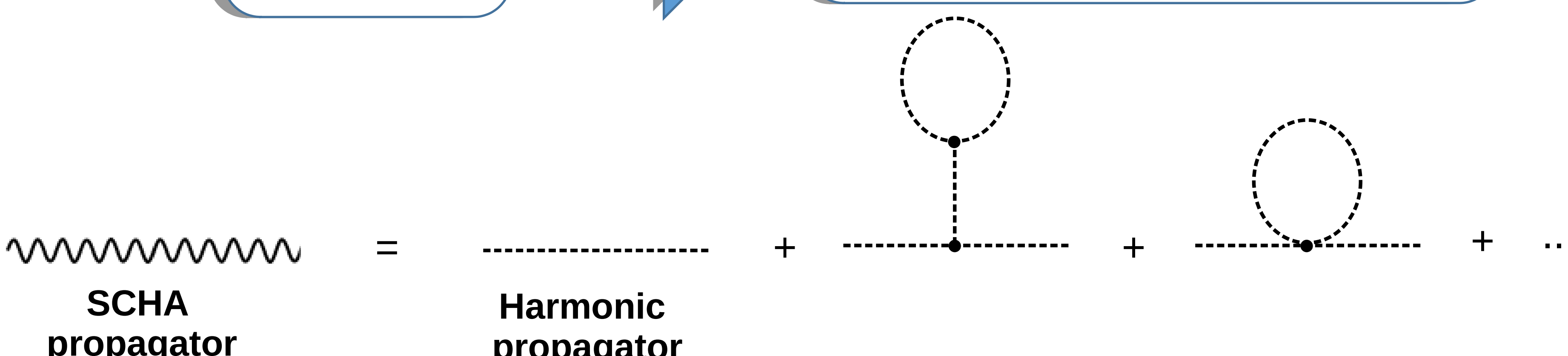
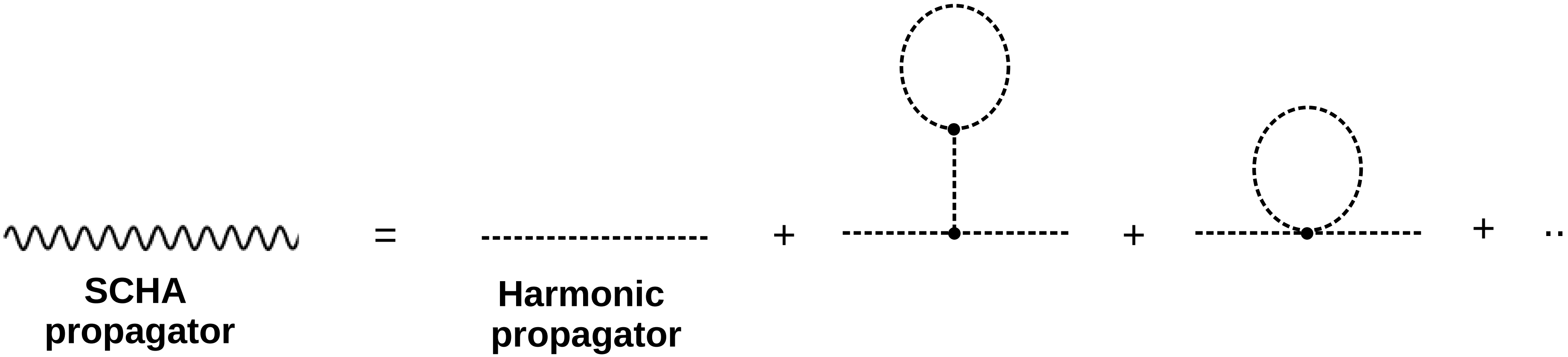
Harmonic phonons → Replaced by → **SCHA quasiparticles = dressed harmonic phonons**



SCHA quasiparticles

SCHA phonons include anharmonicty at some level...



...but they are non-interacting quasiparticles

SCHA quasiparticles

$$H = H^{\mathrm{SCHA}} + \Delta V$$

**We need to include
the effect of this interaction at some level….**

$$\begin{aligned}\Delta V &= V - V^{\mathrm{SCHA}} \\ &= V - \frac{1}{2}(R - \mathcal{R}_{\mathrm{eq}}) \cdot \Phi \cdot (R - \mathcal{R}_{\mathrm{eq}})\end{aligned}$$

Time-dependent SCHA (TD-SCHA) is the theory developed to describe the dynamics of interacting SCHA quasiparticles...

**L. Monacelli and F. Mauri Phys. Rev. B 103, 104305 (2021)
A. Siciliano et al.,Phys. Rev. B 107, 174307 (2023)**

SCHA Green function

$$G(\tau) = -\langle T_\tau u(\tau) u(0) \rangle_{\rho_\Phi}$$

Green function
(displacement-displacement correlation function)

$$G(\tau) \xrightarrow{\text{Matzubara transf.}} G(i\omega_n) \xrightarrow{\text{Analytic prolong.}} G(z)$$

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Nonint. SCHA phonon propagator

$$G^{(0)}(z) = \frac{\mathbb{1}}{z^2 - D}$$

SCHA dyn. matrix

$$D = \frac{\Phi}{\sqrt{MM}}$$

SCHA Green function

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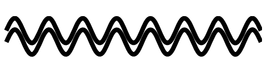
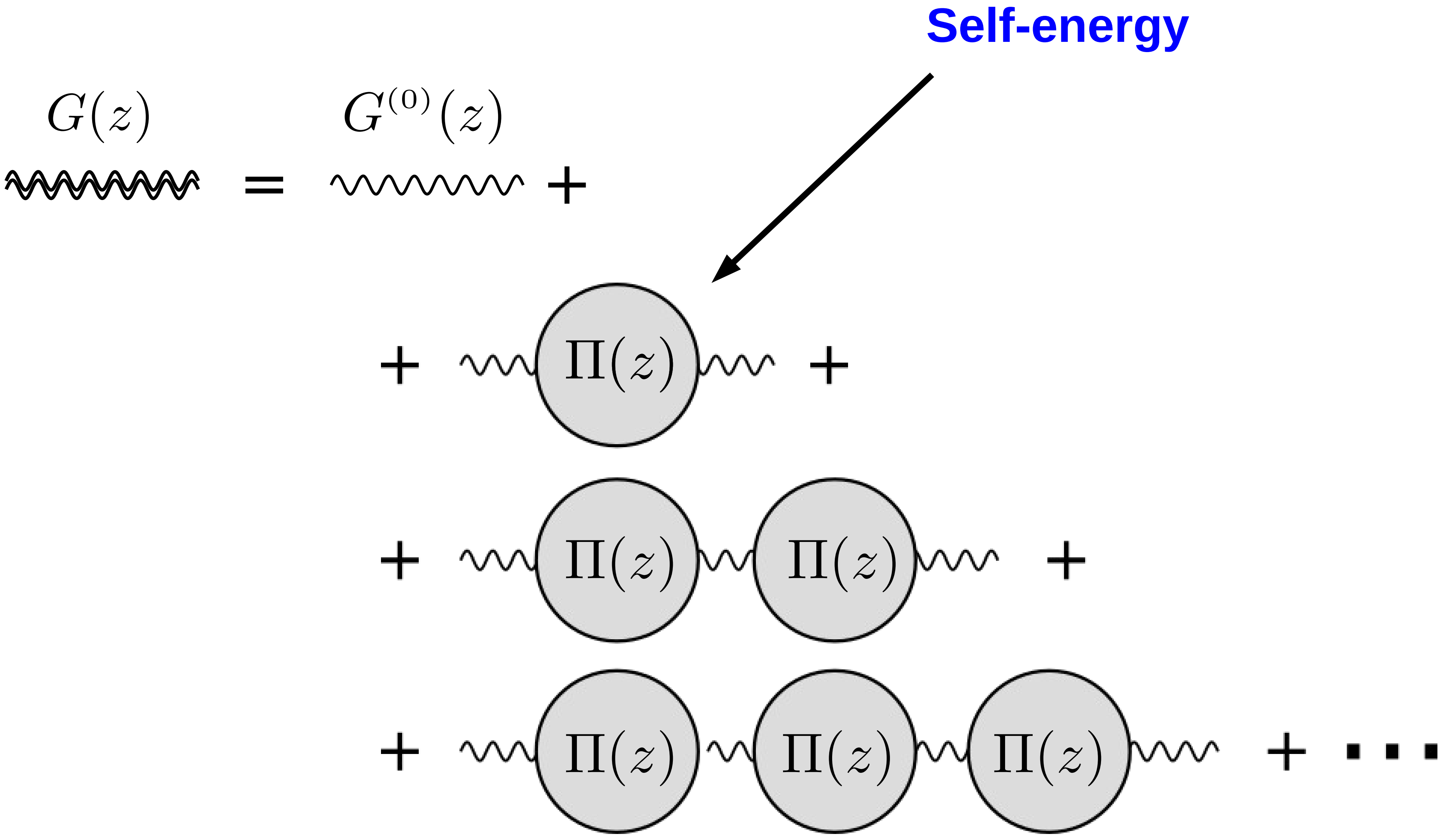
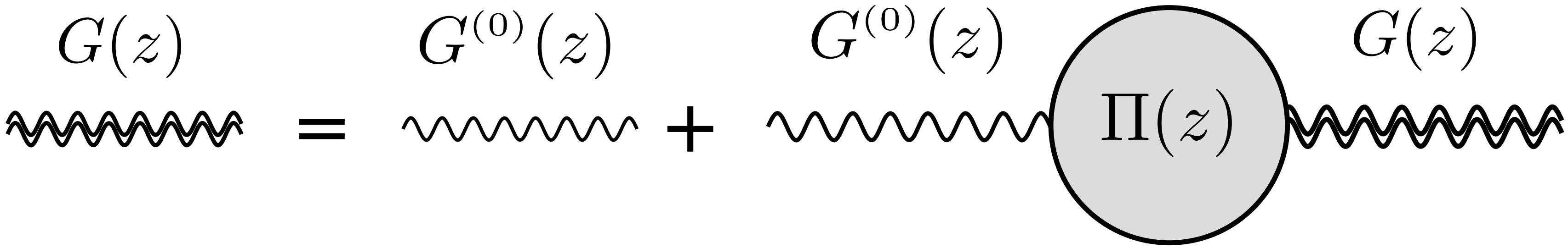


$$G(z)$$

SCHA Green function



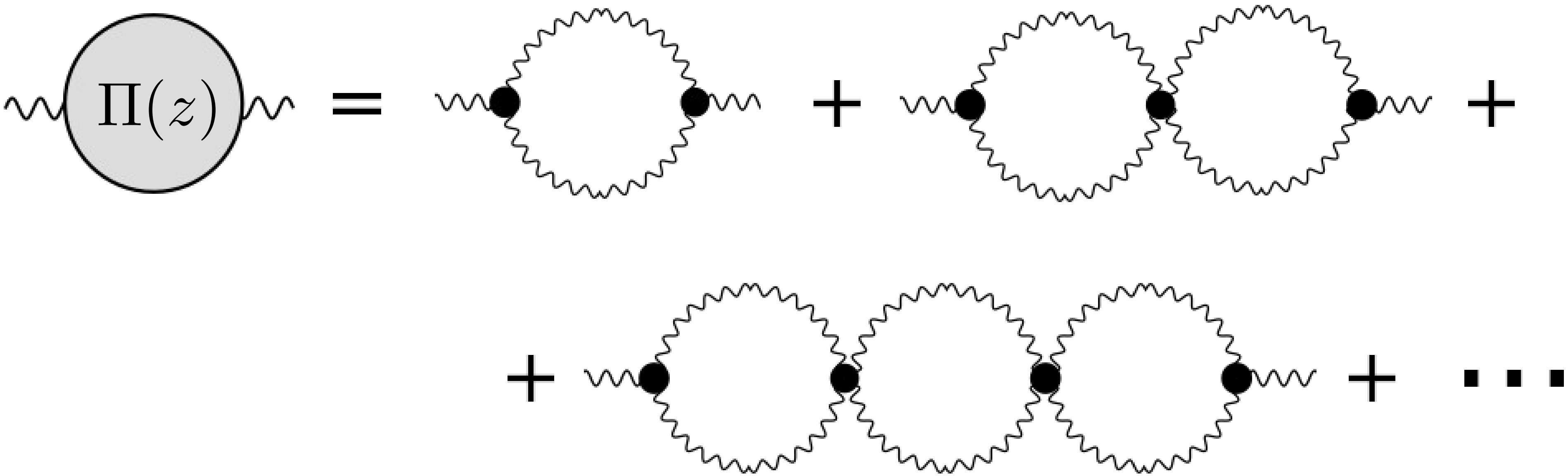
SCHA Green function



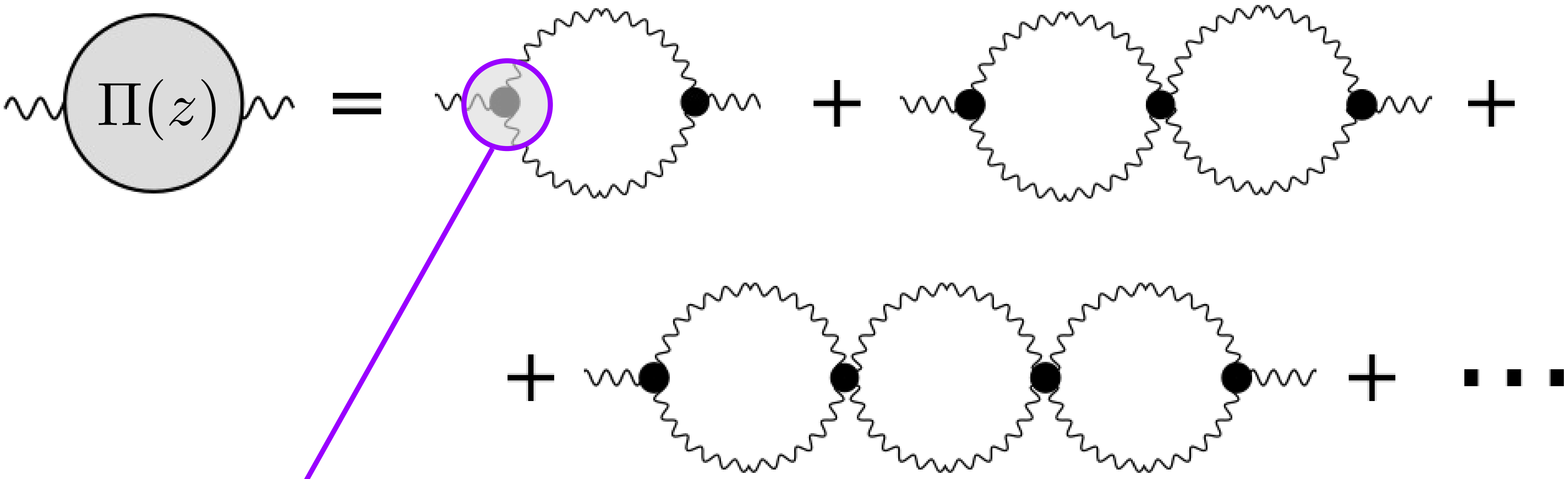
Dyson equation

$$G(z) = G^{(0)}(z) + G^{(0)}(z)\,\Pi(z)\,G(z)$$

SCHA self-energy



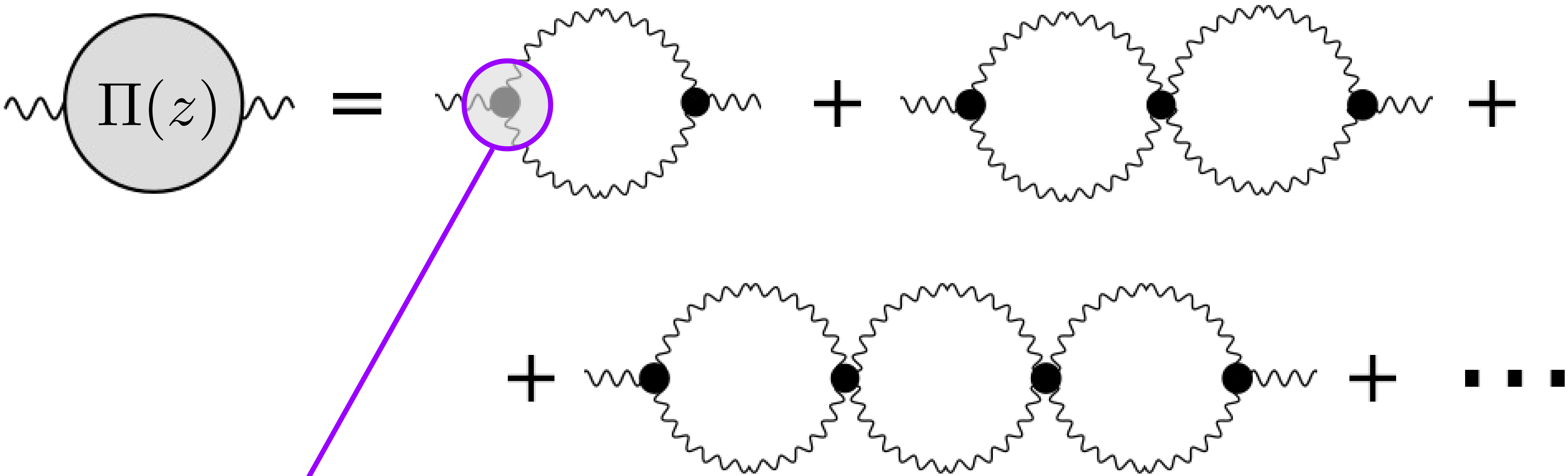
SCHA self-energy



$$\overset{(3)}{D} = \frac{\overset{(3)}{\Phi}}{\sqrt{MMM}}$$

$$\overset{(3)}{\Phi} = \left\langle \frac{\partial^3 V}{\partial R \partial R \partial R} \right\rangle_{\rho_\Phi}$$

SCHA self-energy



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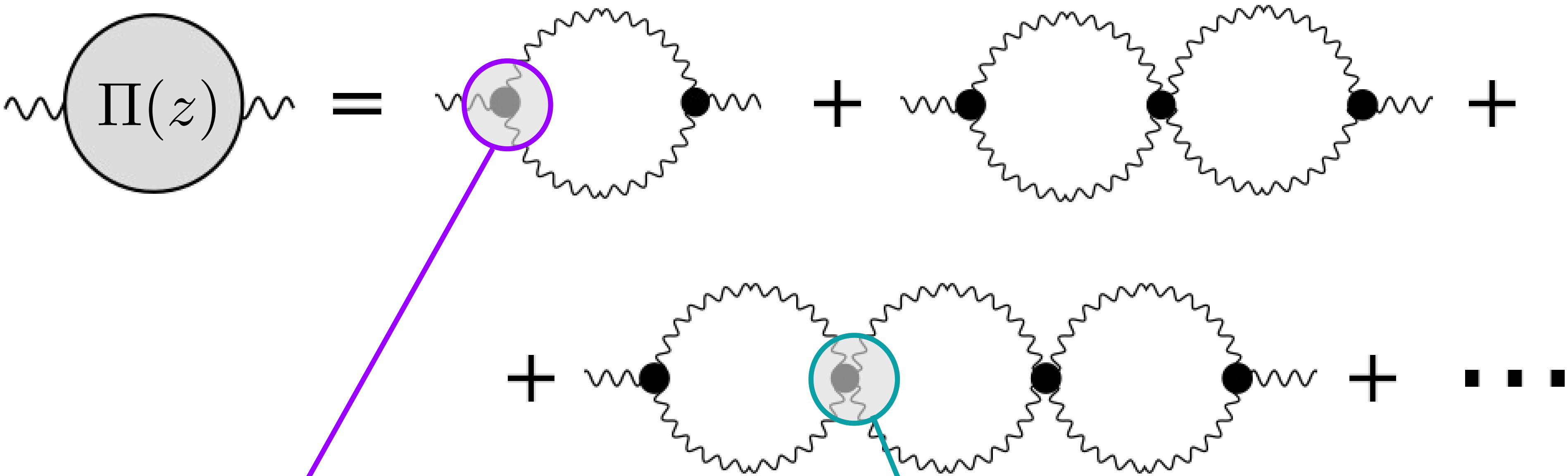
SCHA self-energy

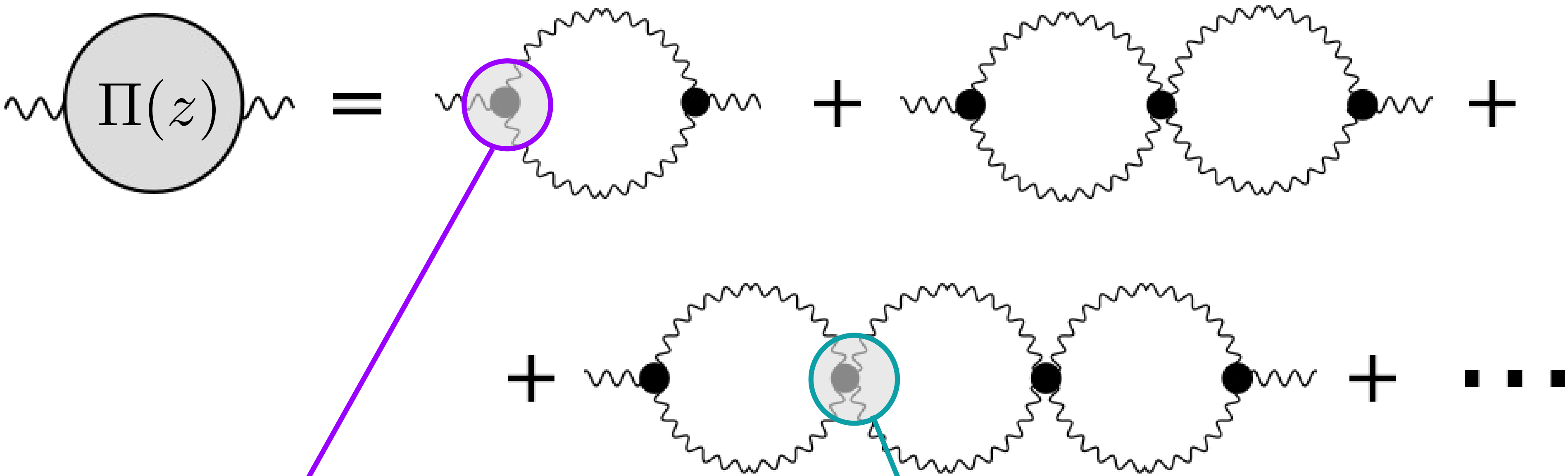


$$\overset{(3)}{D} = \frac{\overset{(3)}{\Phi}}{\sqrt{MMM}}$$

$$\overset{(4)}{D} = \frac{\overset{(4)}{\Phi}}{\sqrt{MMMM}}$$

$$\overset{(4)}{\Phi} = \left\langle \frac{\partial^4 V}{\partial R \partial R \partial R \partial R} \right\rangle_{\rho_\Phi}$$

SCHA self-energy



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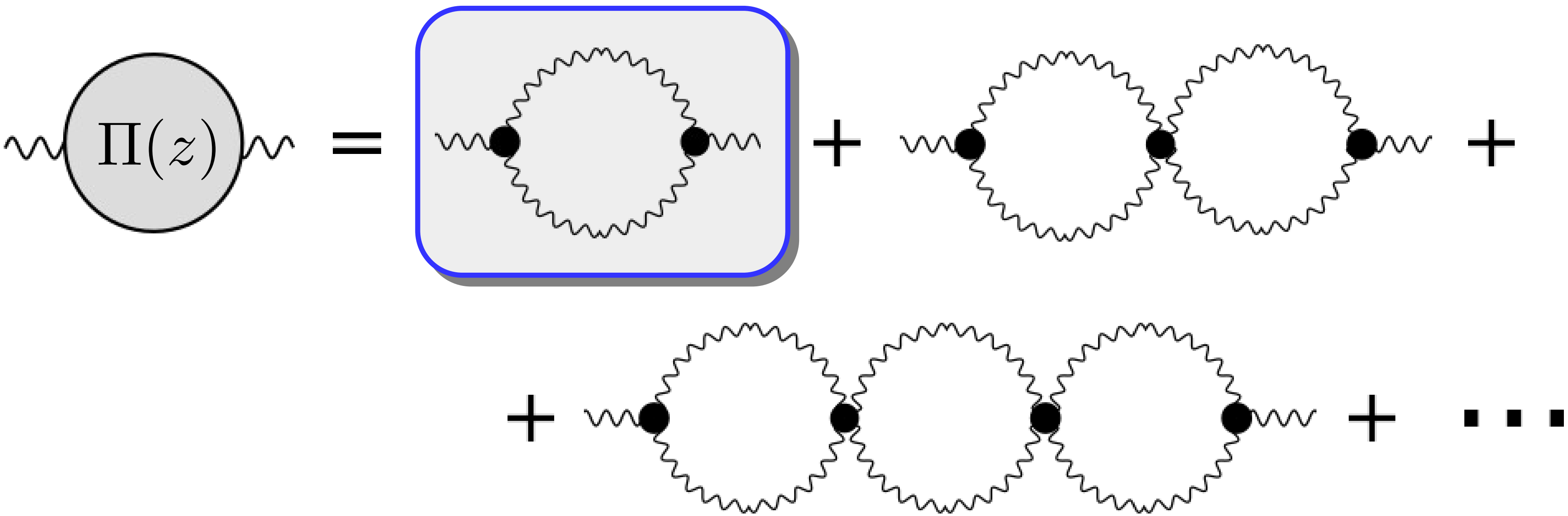
SCHA self-energy



$$\Pi(z) = \overset{(3)}{D} : \Lambda(z) : \overset{(3)}{D}$$

SCHA self-energy

$$[\Lambda(z)]^{abcd} = \sum_{\mu\nu} \mathcal{F}(\omega_\mu, \omega_\nu, z)\, e_\mu^a e_\nu^b e_\mu^c e_\nu^d$$

$$\mathcal{F}(\omega_\mu, \omega_\nu, z) = \frac{\hbar}{4\omega_\nu\omega_\mu}\left[\frac{(\omega_\mu - \omega_\nu)(n_\mu - n_\nu)}{(\omega_\mu - \omega_\nu)^2 - z^2} - \frac{(\omega_\mu + \omega_\nu)(1 + n_\mu + n_\nu)}{(\omega_\mu + \omega_\nu)^2 - z^2}\right]$$

ω_μ **Freq.**

e_μ^a **Eigenmod.**

of $D = \frac{\Phi}{\sqrt{MM}}$

$$n_\mu = \frac{1}{e^{\beta\omega_\mu} - 1}$$

$$\Pi(z) = \overset{(3)}{D} : \Lambda(z) : \overset{(3)}{D}$$

SCHA self-energy

$$[\Lambda(z)]^{abcd} = \sum_{\mu\nu} \mathcal{F}(\omega_\mu, \omega_\nu, z)\, e_\mu^a e_\nu^b e_\mu^c e_\nu^d$$

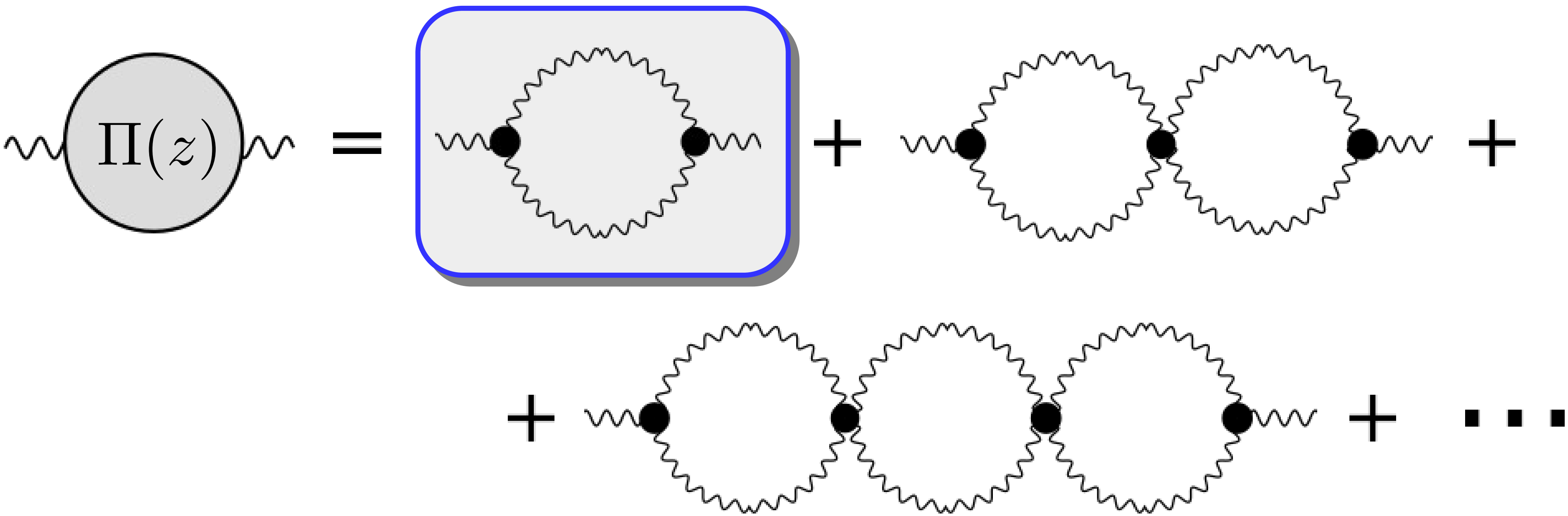
$$\Lambda[0] = \Lambda$$

used in the Hessian formula for

$$D^{(\mathrm{F})} = \frac{1}{\sqrt{MM}} \frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}}\bigg|_{\mathcal{R}_{\mathrm{eq}}}$$

$$\Pi(z) = \overset{(3)}{D} : \Lambda(z) : \overset{(3)}{D}$$

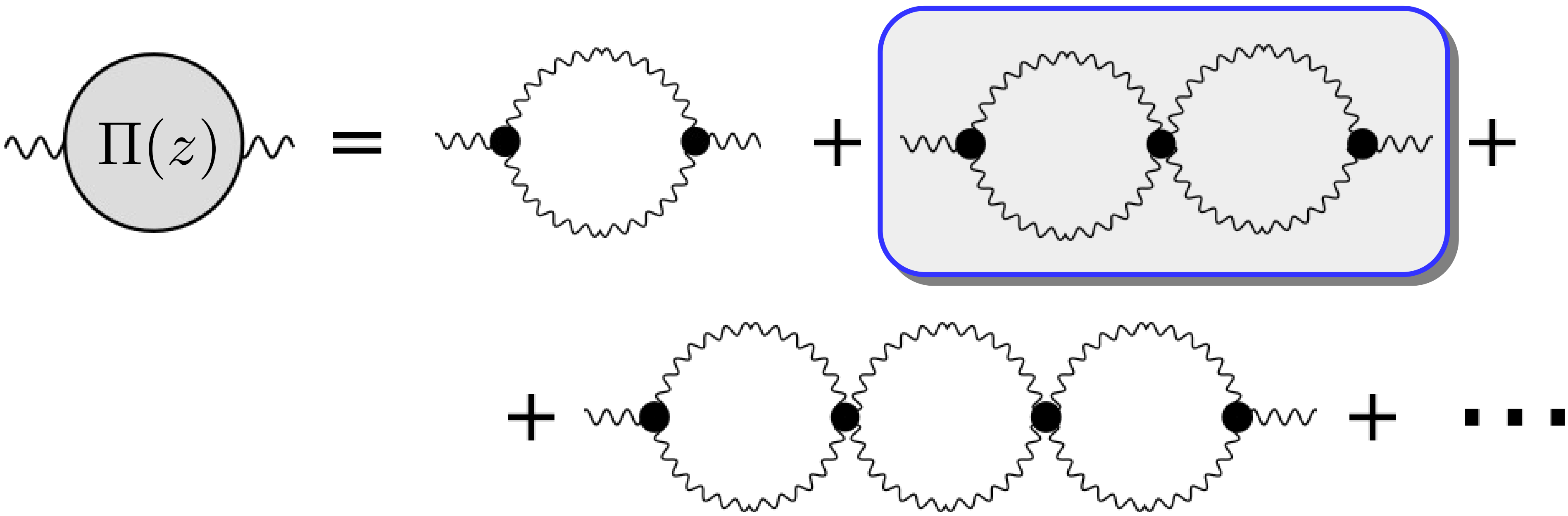
SCHA self-energy



$$\Pi(z) = \overset{(3)}{D} : \Lambda(z) : \overset{(3)}{D}$$

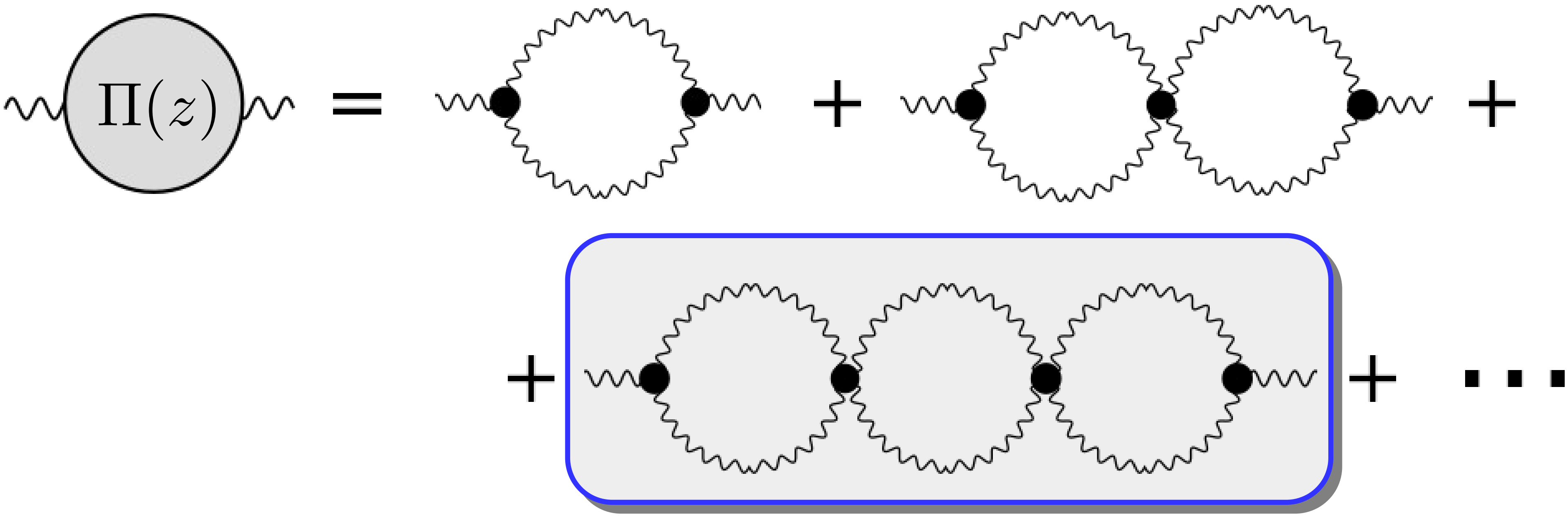
Self-energy in the bubble approx.
(usually good enough)

SCHA self-energy



$$\Pi(z) = \overset{(3)}{D} : \Lambda(z) : \overset{(3)}{D} + \overset{(3)}{D} : \Lambda(z) : \overset{(4)}{D} : \Lambda(z) : \overset{(3)}{D}$$

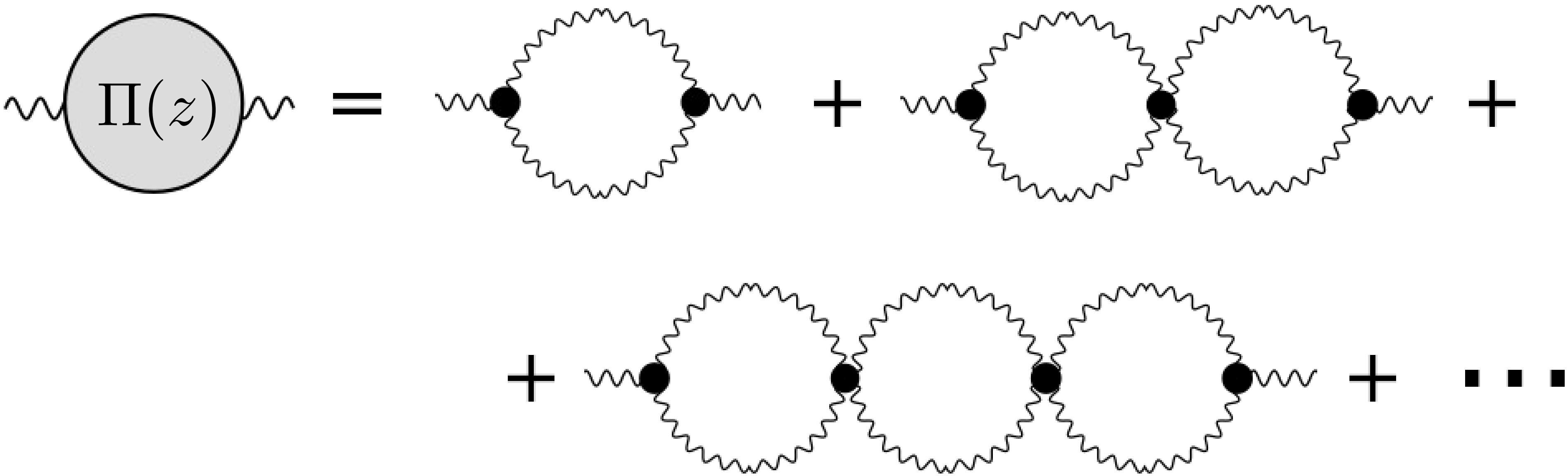
SCHA self-energy



$$\Pi(z) = \overset{(3)}{D} : \Lambda(z) : \overset{(3)}{D} + \overset{(3)}{D} : \Lambda(z) : \overset{(4)}{D} : \Lambda(z) : \overset{(3)}{D}$$

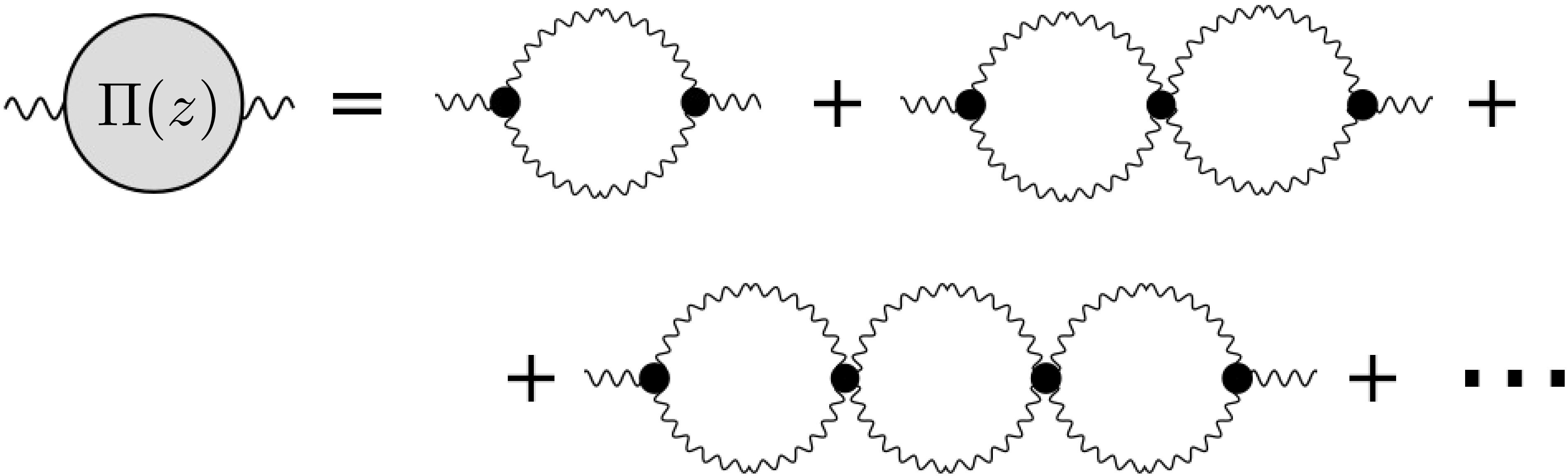
$$+ \overset{(3)}{D} : \Lambda(z) : \overset{(4)}{D} : \Lambda(z) : \overset{(4)}{D} : \Lambda(z) : \overset{(3)}{D} + \cdots$$

SCHA self-energy



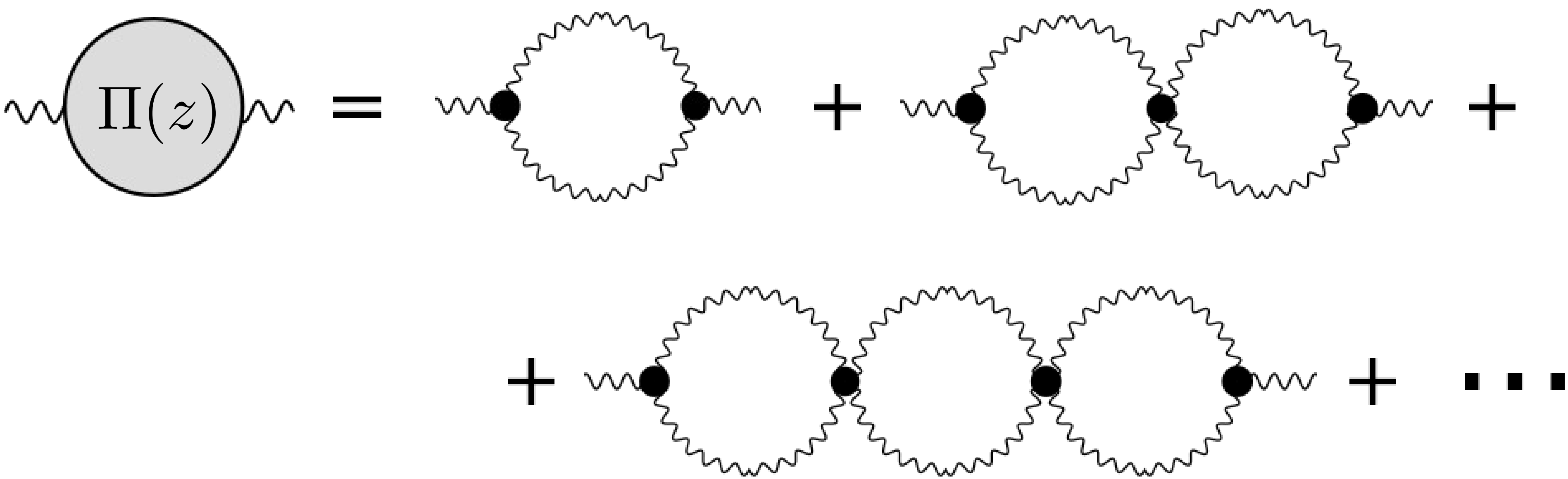
$$\Pi(z) = \overset{(3)}{D} : \Lambda[z] : \frac{1}{\mathbb{1} - \overset{(4)}{D} : \Lambda[z]} : \overset{(3)}{D}$$

SCHA self-energy



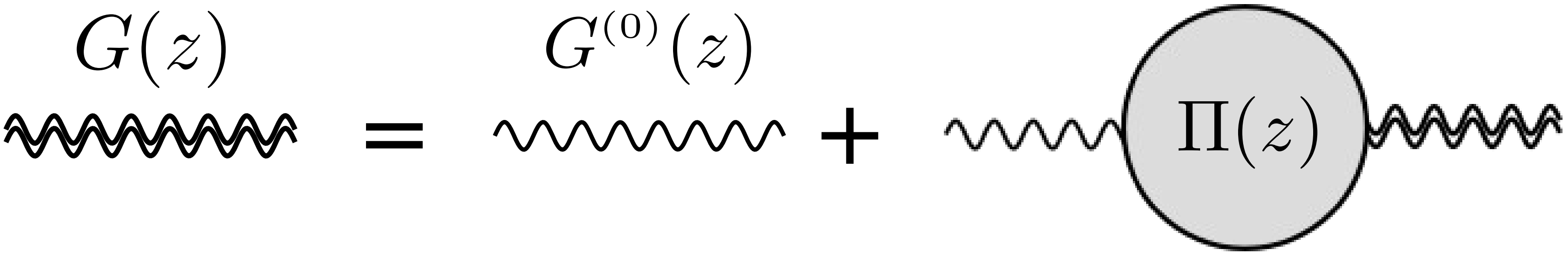
$$D^{(\mathrm{F})} = D + \overset{(3)}{D} : \Lambda[0] : \frac{1}{\mathbb{1} - \overset{(4)}{D} : \Lambda[0]} : \overset{(3)}{D}$$

SCHA self-energy



$$D^{(\mathrm{F})} = D + \Pi(0)$$

SCHA Green function



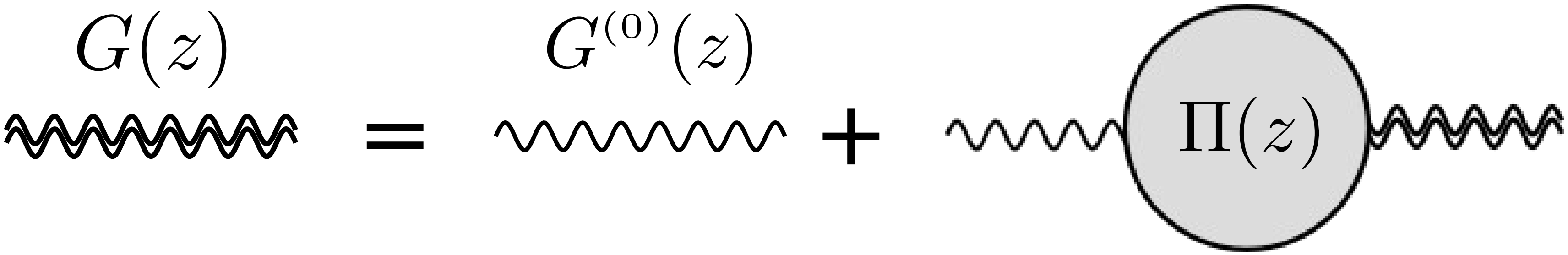
$$G(z) = G^{(0)}(z) + G^{(0)}(z)\,\Pi(z)\,G(z)$$

with:

$$G^{(0)}(z) = \frac{\mathbb{1}}{z^2 - D}$$

$$G(z) = \frac{\mathbb{1}}{z^2 - (D + \Pi(z))}$$

SCHA Green function



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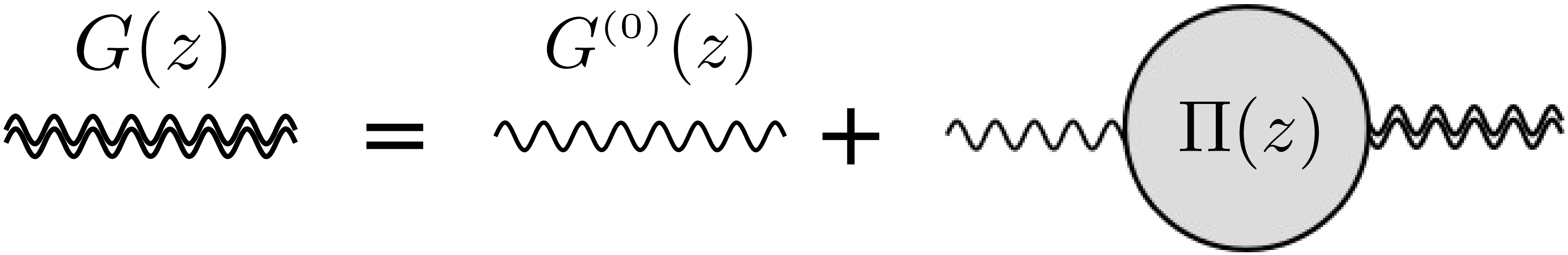
Static limit

SCHA Green function



$$G(z) = G^{(0)}(z) + G^{(0)}(z)\,\Pi(z)\,G(z)$$

with:

$$G^{(0)}(z) = \frac{\mathbb{1}}{z^2 - D}$$

$$G(z) = \frac{\mathbb{1}}{z^2 - (D + \Pi(z))}$$

$$G(0) = \frac{\mathbb{1}}{z^2 - (D + \Pi(0))} = \frac{\mathbb{1}}{z^2 - D^{(\mathrm{F})}}$$

Static limit

$$G(0) = \frac{\mathbb{1}}{z^2 - D^{(\mathrm{F})}}$$

The static limit (*z*=0) is correctly recovered

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- **In a static condition, the situation is described by real-symmetric dynamical marix, given by the free energy Hessian**

Static limit

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The static limit (*z*=0) is correctly recovered

- **In a static condition, the situation is described by real-symmetric dynamical marix, given by the free energy Hessian**
- **In the static limit, the quasiparticle energies are given by the frequencies of the free energy Hessian**

Static limit

$$G(0) = \frac{\mathbb{1}}{z^2 - D^{(\mathrm{F})}}$$

The static limit (z=0)
is correctly recovered

- In a static condition, the situation is described by
real-symmetric dynamical marix, given by the free energy Hessian

- In the static limit, the quasiparticle energies
are given by the frequencies of the free energy Hessian

Green function
has pole at zero enegy:
phonon softening

⟺

Free energy Hessian
has null eigenvalue:
Lattice instability

Spectral function

$$\boldsymbol{\sigma}(\boldsymbol{\Omega}) = -\mathbf{Im}\mathbf{Tr}\boldsymbol{G}\underbrace{(\boldsymbol{\Omega} + \boldsymbol{i}\mathbf{0}^{+})}_{}$$

$z \rightarrow \boldsymbol{\Omega} \in \mathbb{R}$ **from above**

- **Quasiparticle energy spectrum**

- **Measured through inelastic scattering experiments (neutron, x-ray,...)**

Spectral function

$$\boldsymbol{\sigma(\Omega) = -\mathrm{Im}\mathrm{Tr}G(\Omega + i0^+)}$$

Non-interacting SCHA quasiparticles spectrum

$$G^{(0)}(z) = \frac{\mathbb{1}}{z^2 - D}$$

$$\sigma(\Omega) = \sum_\mu \sigma_\mu(\Omega)$$

with:

$$\sigma_\mu(\Omega) = \delta(\Omega - \omega_\mu)$$

ω_μ **freq. of** D

Each mode contributes to the energy spectrum with a Dirac-delta peak (zero width → infinite lifetime), centered around its frequency

Spectral function

$$\boldsymbol{\sigma}(\boldsymbol{\Omega}) = -\mathbf{Im}\mathbf{Tr}\boldsymbol{G}(\boldsymbol{\Omega} + \boldsymbol{i}\mathbf{0}^{+})$$

Spectrum in the static limit

$$G^{(\mathrm{stat})}(z) = \frac{\mathbb{1}}{z^2 - D - \Pi(0)}$$

$$= \frac{\mathbb{1}}{z^2 - D^{(\mathrm{F})}}$$

$$\sigma(\Omega) = \sum_{\mu} \sigma_{\mu}(\Omega)$$

with:

$$\sigma_{\mu}(\Omega) = \delta(\Omega - \Omega_{\mu})$$

Ω_{μ} **freq. of** $D^{(\mathrm{F})}$

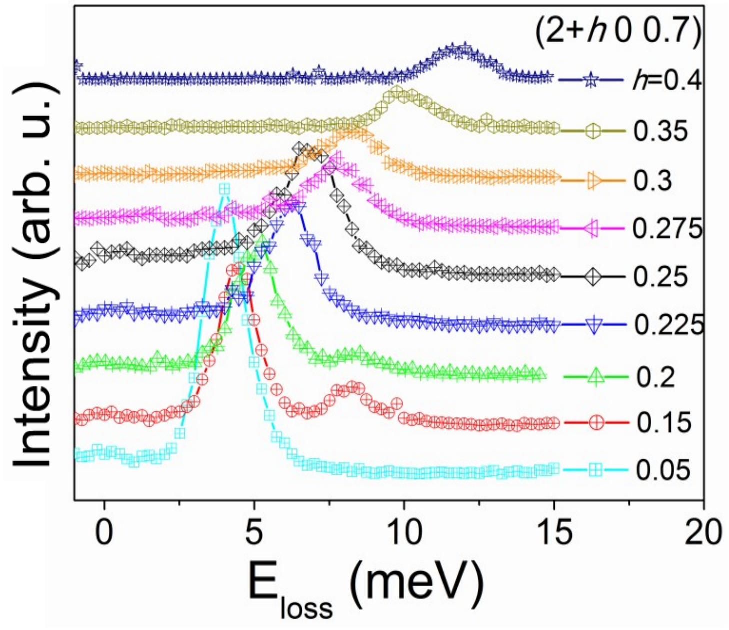
Dirac-delta peaks centered around free energy Hessian frequencies

Spectral function

In general, the spectral function is very different from a series of Dirac-delta peaks

$$\sigma(\Omega) = -\frac{2\Omega}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\left[\frac{\mathbb{1}}{(\Omega + i0^+)^2 - D - \Pi(\Omega + i0^+)}\right]$$

Inelastic x-ray scattering experiment



Diego et al., Nat Commun. 12, 598 (2021)

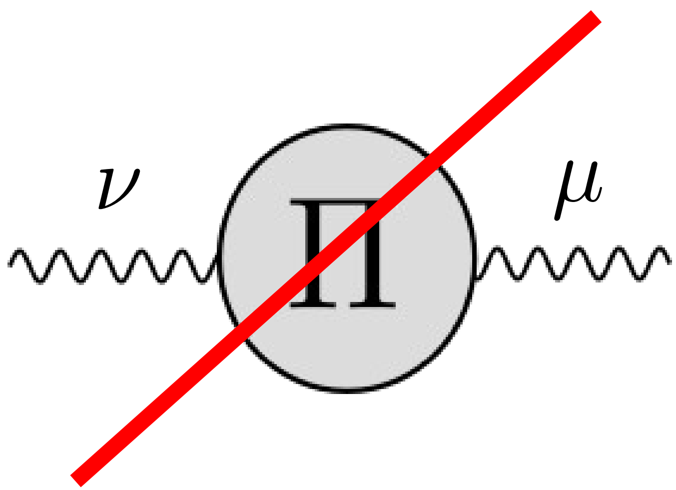
Spectral function

No mode-mixing approx.

(usually good, however see D. Dangić et al., *arXiv:2303.07962*)

The interaction do not mix different SCHA modes $\Leftrightarrow$ **The self-energy in the SCHA mode basis Is diagonal**

$$\Pi_{\mu\nu}(z) = \delta_{\mu\nu}\Pi_{\mu\mu}(z)$$



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$$\sigma(\Omega) = \sum_{\mu} \sigma_{\mu}(\Omega)$$

$$\sigma_{\mu}(\Omega) = \frac{1}{\pi} \frac{-\mathrm{Im}\mathcal{Z}_{\mu}(\Omega)}{[\Omega - \mathrm{Re}\mathcal{Z}_{\mu}(\Omega)]^2 + [\mathrm{Im}\mathcal{Z}_{\mu}(\Omega)]^2}$$

with: $\mathcal{Z}_{\mu}(\Omega) = \sqrt{\omega_{\mu}^2 + \Pi_{\mu\mu}(\Omega + i0^+)}$

Spectral function

No mode-mixing approx.
(usually good, however see D. Dangić et al., *arXiv:2303.07962*)

The interaction do not mix different SCHA modes ⟷ The self-energy in the SCHA mode basis Is diagonal

$$\Pi_{\mu\nu}(z) = \delta_{\mu\nu}\Pi_{\mu\mu}(z)$$

Lorentzian-like shape,
but with center and width depending on Ω

$$\sigma_\mu(\Omega) = \frac{1}{\pi}\frac{-\mathrm{Im}\mathcal{Z}_\mu(\Omega)}{[\Omega - \mathrm{Re}\mathcal{Z}_\mu(\Omega)]^2 + [\mathrm{Im}\mathcal{Z}_\mu(\Omega)]^2}$$

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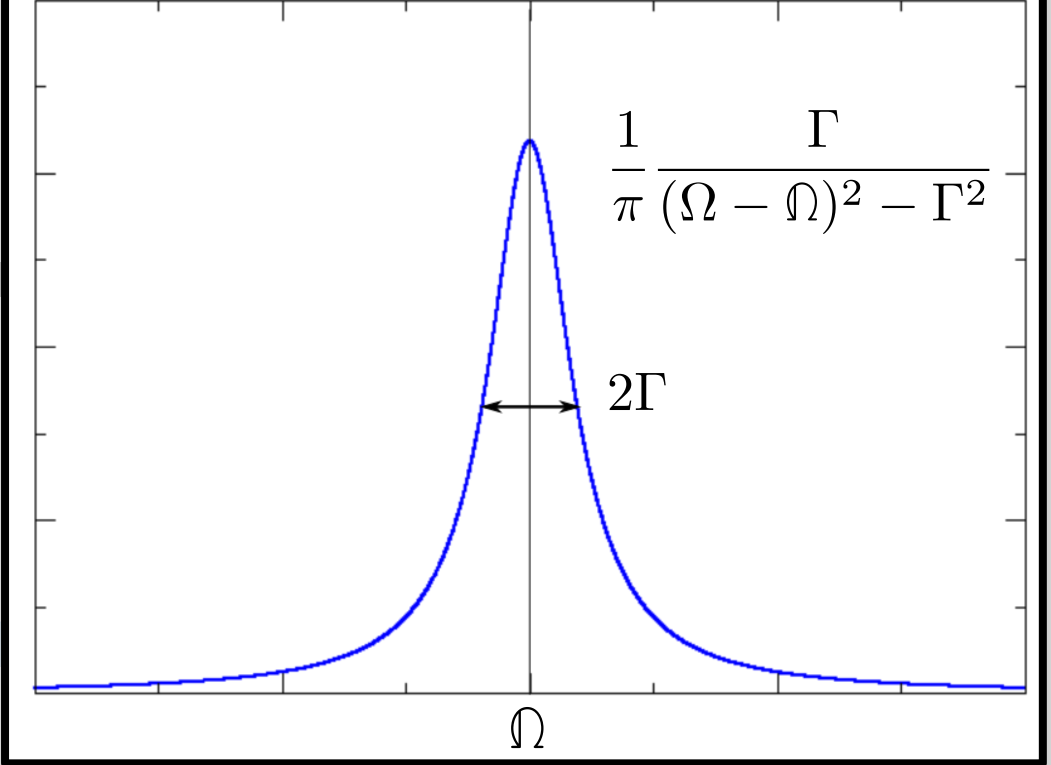
Spectral function

Lorentzian
centered in Ω
and with
full width at half maximum(FWHM) 2Γ



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with: $\mathcal{Z}_\mu(\Omega) = \sqrt{\omega_\mu^2 + \Pi_{\mu\mu}(\Omega + i0^+)}$

In some cases the spectral function can be approximated pretty well with a Lorentzian (i.e. quasiparticle picture is correct):

$$\sigma_\mu(\Omega) = \frac{1}{\pi}\frac{\Gamma_\mu}{[\Omega - \Omega_\mu)]^2 + \Gamma_\mu^2}$$

$$\Omega_\mu = \mathrm{Re}\mathcal{Z}_\mu(\Omega_\mu)$$

A self-consistent condition

$$\Gamma_\mu = -\mathrm{Im}\mathcal{Z}_\mu(\Omega_\mu)$$

$$\mathcal{Z}_\mu(\Omega) = \sqrt{\omega_\mu^2 + \Pi_{\mu\mu}(\Omega + i0^+)}$$

In some cases the spectral function can be approximated pretty well with a Lorentzian (i.e. quasiparticle picture is correct):

$$\sigma_\mu(\Omega) = \frac{1}{\pi} \frac{\Gamma_\mu}{[\Omega - \mho_\mu)]^2 + \Gamma_\mu^2}$$

one-shot approximation

$$\boxed{\begin{aligned} \mho_\mu &= \mathrm{Re}\mathcal{Z}_\mu(\mho_\mu) \\ \Gamma_\mu &= -\mathrm{Im}\mathcal{Z}_\mu(\mho_\mu) \end{aligned}} \quad \simeq \quad \boxed{\begin{aligned} \mho_\mu &= \mathrm{Re}\mathcal{Z}_\mu(\omega_\mu) \\ \Gamma_\mu &= -\mathrm{Im}\mathcal{Z}_\mu(\omega_\mu) \end{aligned}}$$

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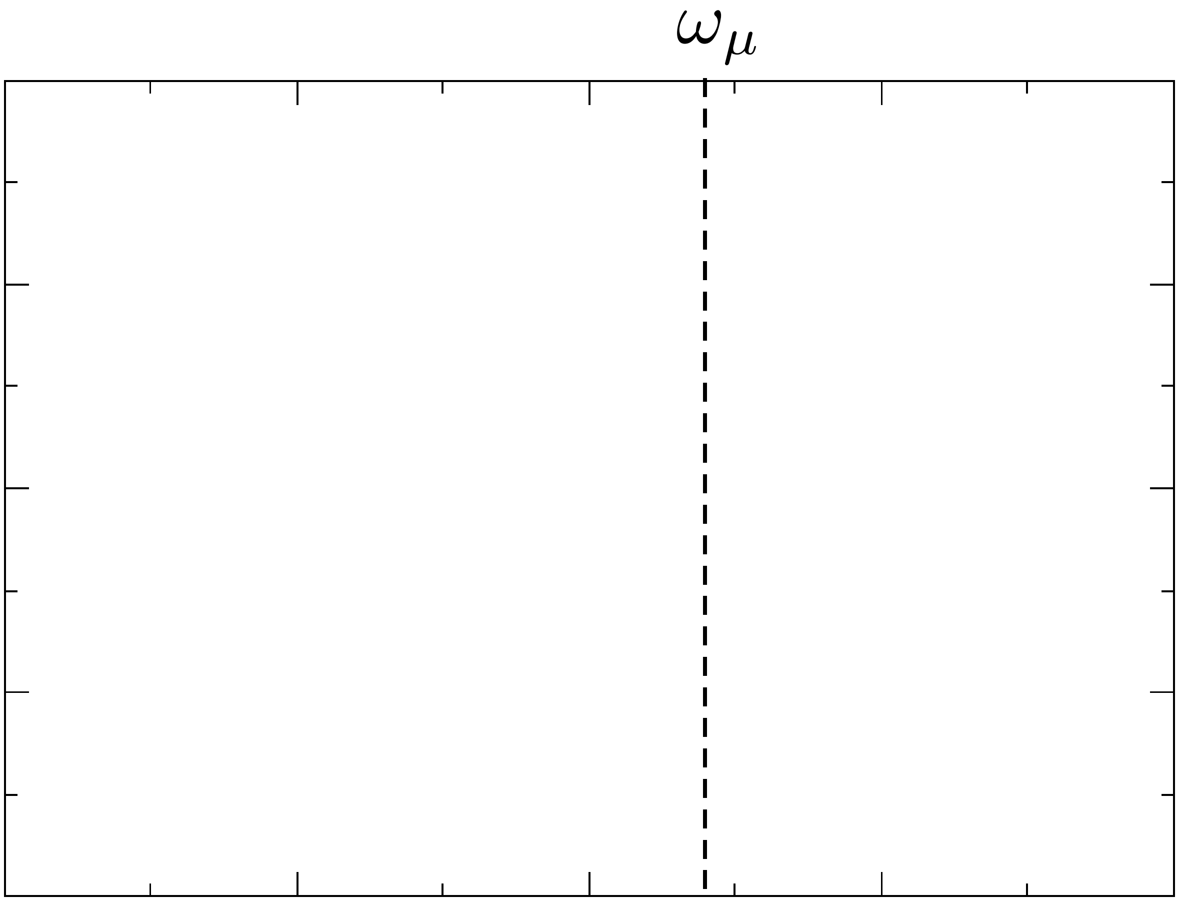
$$\mathcal{Z}_\mu(\Omega) = \sqrt{\omega_\mu^2 + \Pi_{\mu\mu}(\Omega + i0^+)}$$

---

if $\Pi_{\mu\mu} \ll \omega_\mu^2 \longrightarrow \begin{cases} \Omega_\mu = \dfrac{1}{2\omega_\mu}\mathrm{Re}\Pi_{\mu\mu}(\omega_\mu) \\ \Gamma_\mu = -\dfrac{1}{2\omega_\mu}\mathrm{Im}\Pi_{\mu\mu}(\omega_\mu + i0^+) \end{cases}$

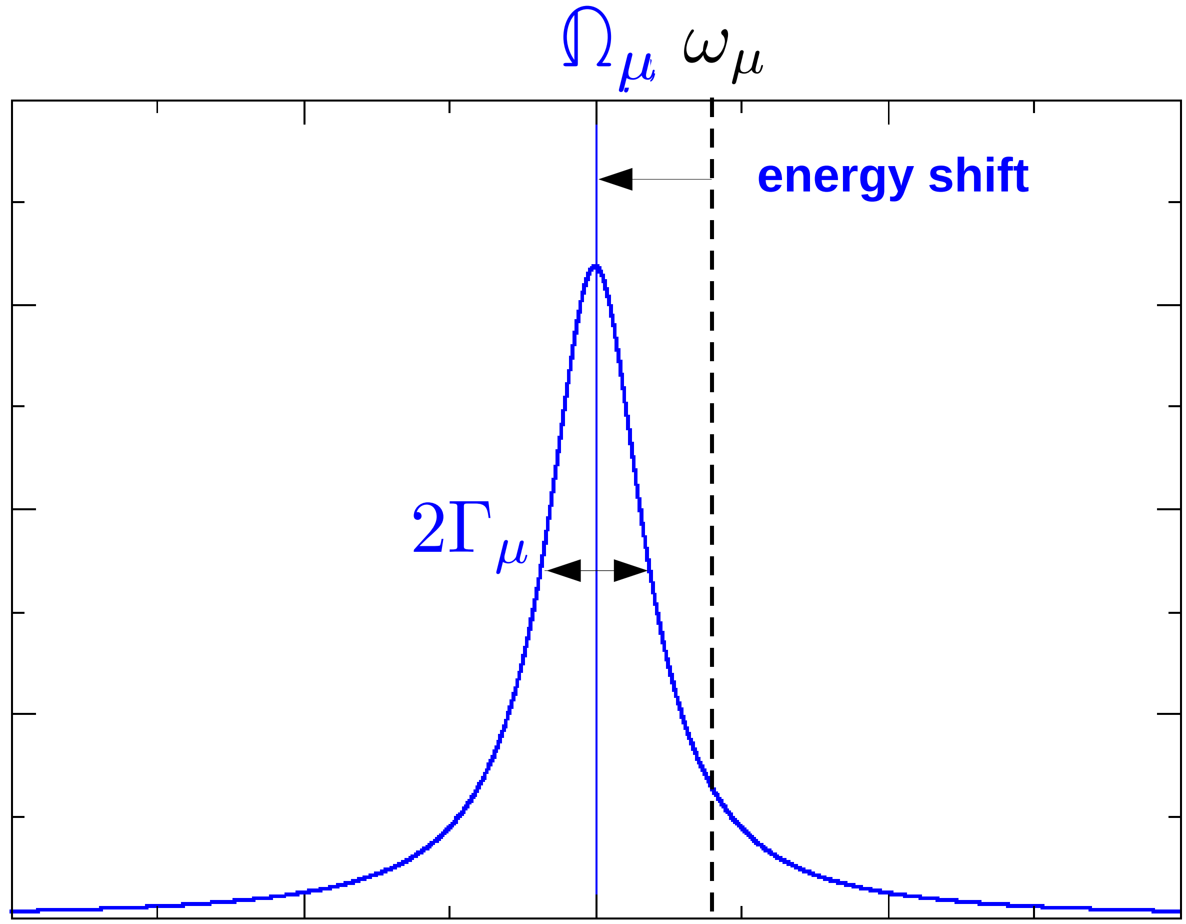
In summary



μ-mode SCHA phonon quasiparticle:

Infinite lifetime (i.e. zero width), because noninteracting

In summary



No mixing-mode approx.

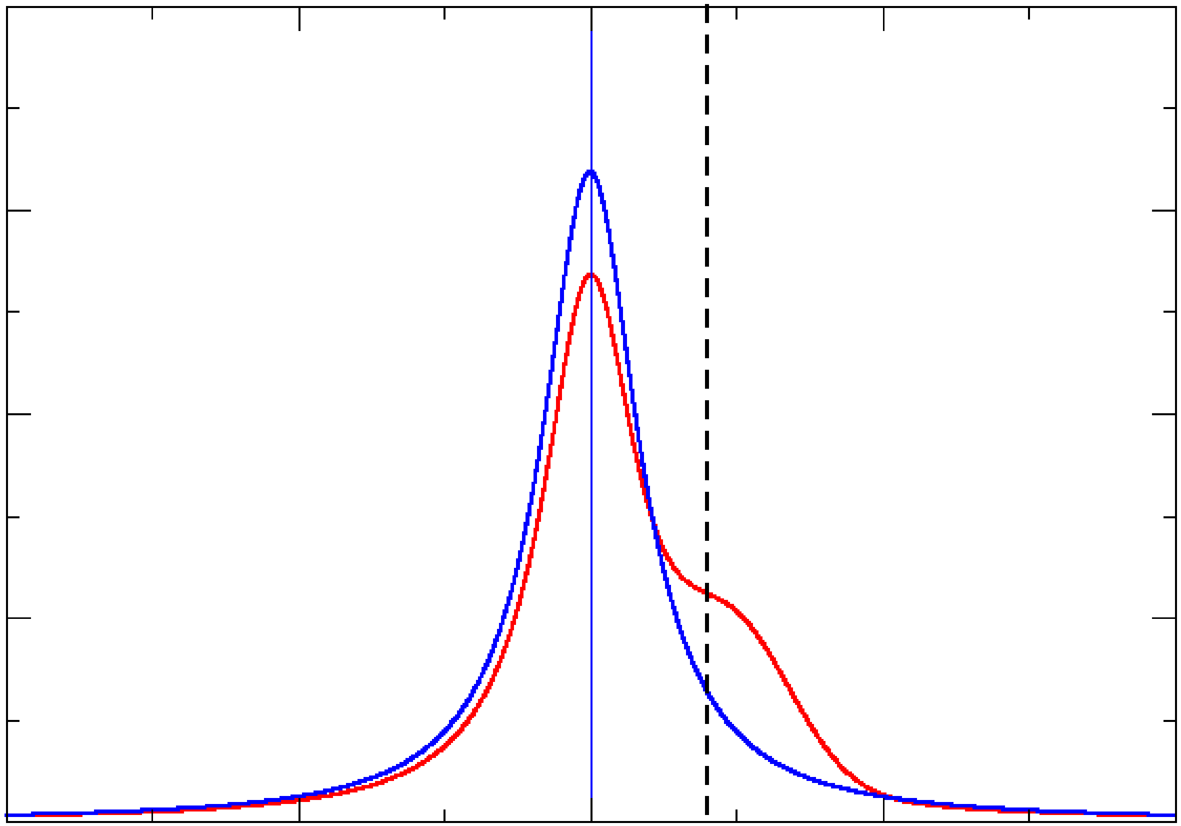
Lorentzian picture:

Collective excitation seen as a quasiparticle with definite energy Ω_μ **and finite lifetime** $\tau_\mu = 1/2\Gamma_\mu$

$$\left(\Delta E \, \Delta t = \frac{\hbar}{2} \right)$$

In summary

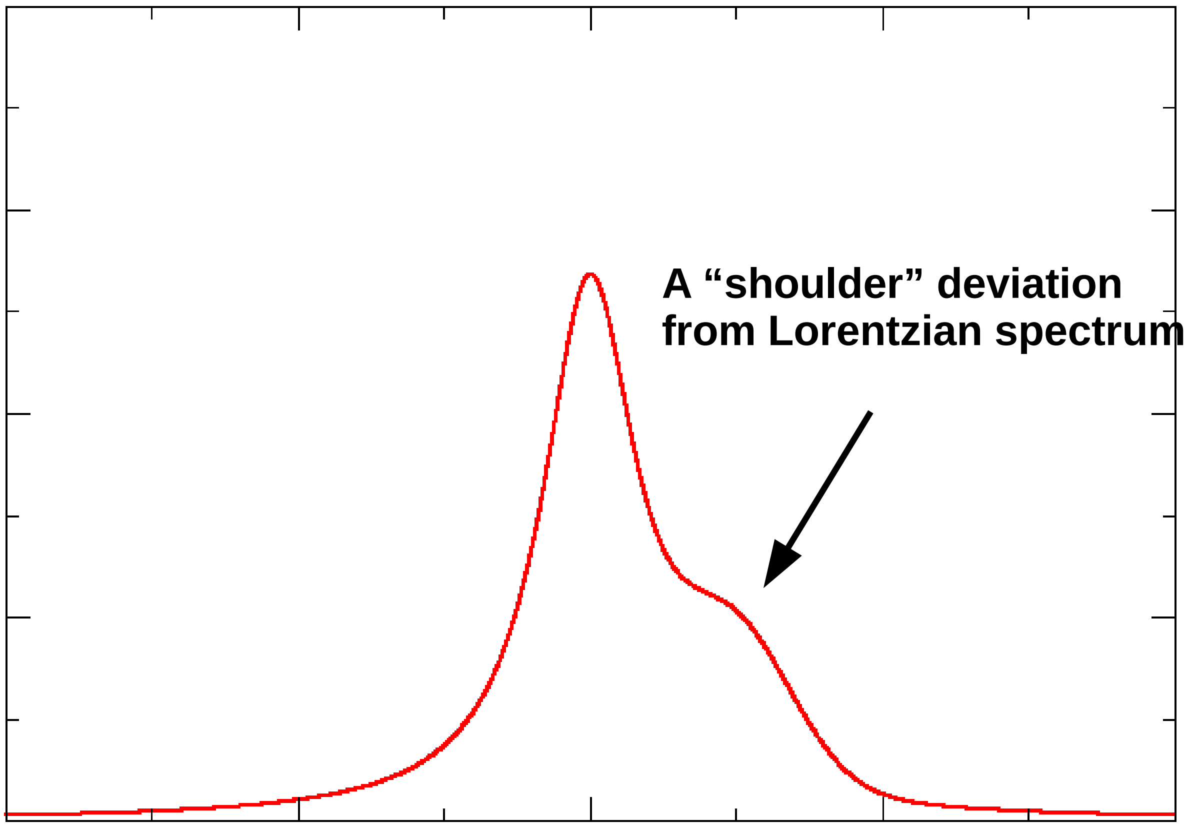
No mixing-mode approx.



If the full μ-mode spectral function is like this...

In summary

No mixing-mode approx.



...Lorentzian picture is not appropriate:

Collective excitation cannot be seen as a quasiparticle with definite energy and lifetime

In summary

Collective excitations of the vibrational field

Energy spectrum that can be probed with inelastic scattering experiments

a

quasiparticle with definite energy and lifetime

In summary

Collective excitations of the vibrational field

Energy spectrum that can be probed with inelastic scattering experiments

Interaction between SCHA quasiparticles does not mix different SCHA modes (i.e. it does not “destroy” the mode concept)

Meaningful to interpret the energy spectrum as the superposition of the energy spectrum of each mode.

a

quasiparticle with definite energy and lifetime

In summary

Collective excitations of the vibrational field

Energy spectrum that can be probed with inelastic scattering experiments

Interaction between SCHA quasiparticles does not mix different SCHA modes (i.e. it does not "destroy" the mode concept)

Meaningful to interpret the energy spectrum as the superposition of the energy spectrum of each mode.

Self-energy of a SCHA-phonon mode is "small"

The spectrum of that mode can still be described as a quasiparticle (phonon) with definite enegy (different from the corresponding SCHA quasiparticle energy) and finite lifetime

a

quasiparticle with definite energy and lifetime

In summary

A real-space supercell notation has been used so far taking into account the crystal-lattice symmetry, we can write pseudomomentum dependent quantities:

$$D(\boldsymbol{q}), \qquad \omega_\mu(\boldsymbol{q})$$

$$D^{(\mathrm{F})}(\boldsymbol{q}), \quad \Omega_\mu(\boldsymbol{q})$$

$$\sigma(\boldsymbol{q},\Omega), \quad \Omega_\mu(\boldsymbol{q}), \; \Gamma_\mu(\boldsymbol{q})$$

a

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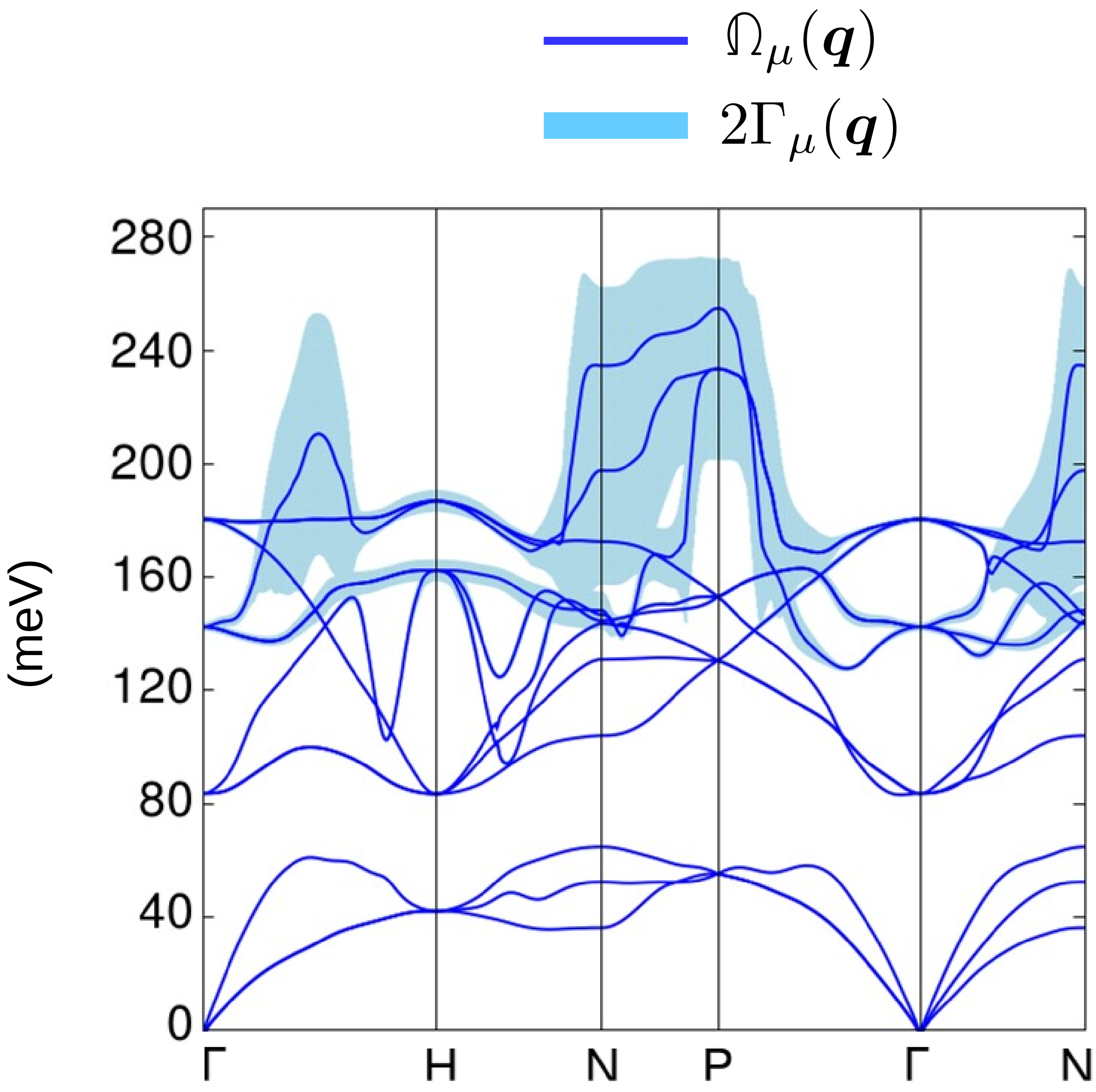
$\Omega_\mu(\boldsymbol{q})$ **Can be plotted to have a first idea of the phonon spectrum at low frequency, but foremost to detect structural instabilities...**

$\Omega_\mu(\boldsymbol{q}) \pm \Gamma_\mu(\boldsymbol{q})$ **gives the correct phonon dispersion**

a

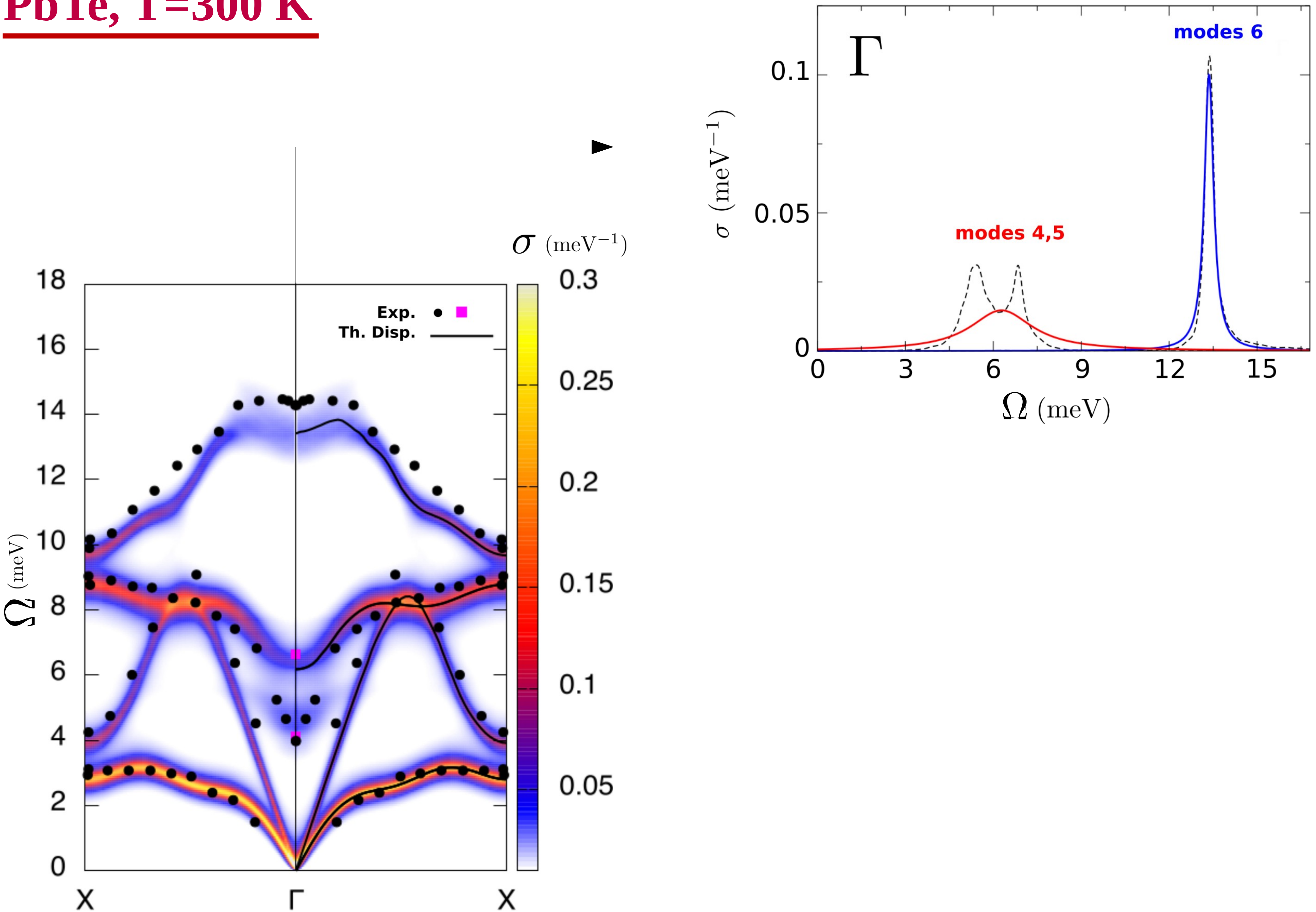
quasiparticle with definite energy and lifetime

H_3S, P=150GPa



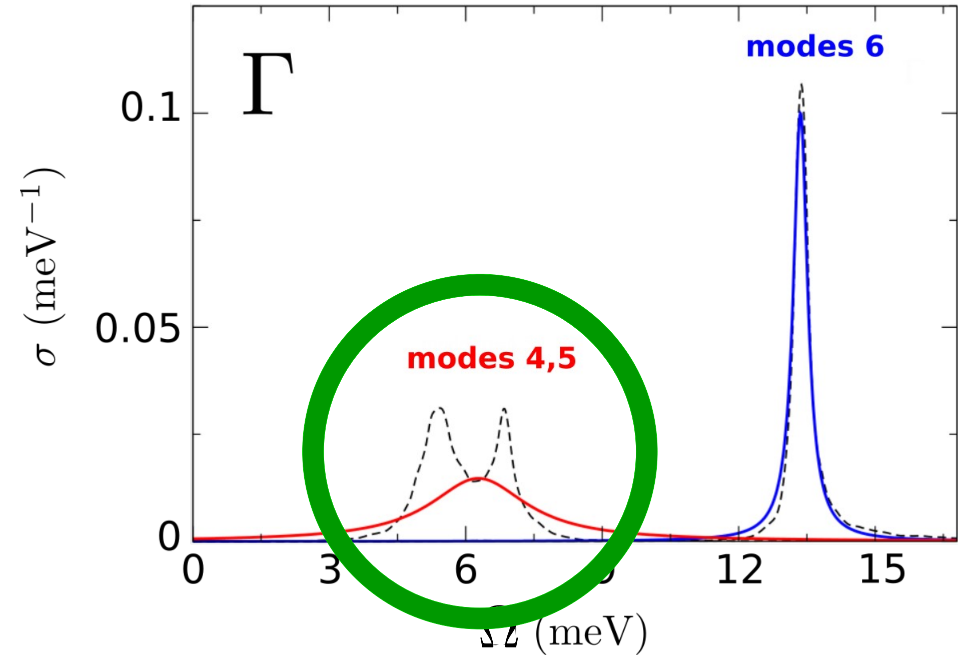
Bianco *et al.*, Physical Review B 97, 2018

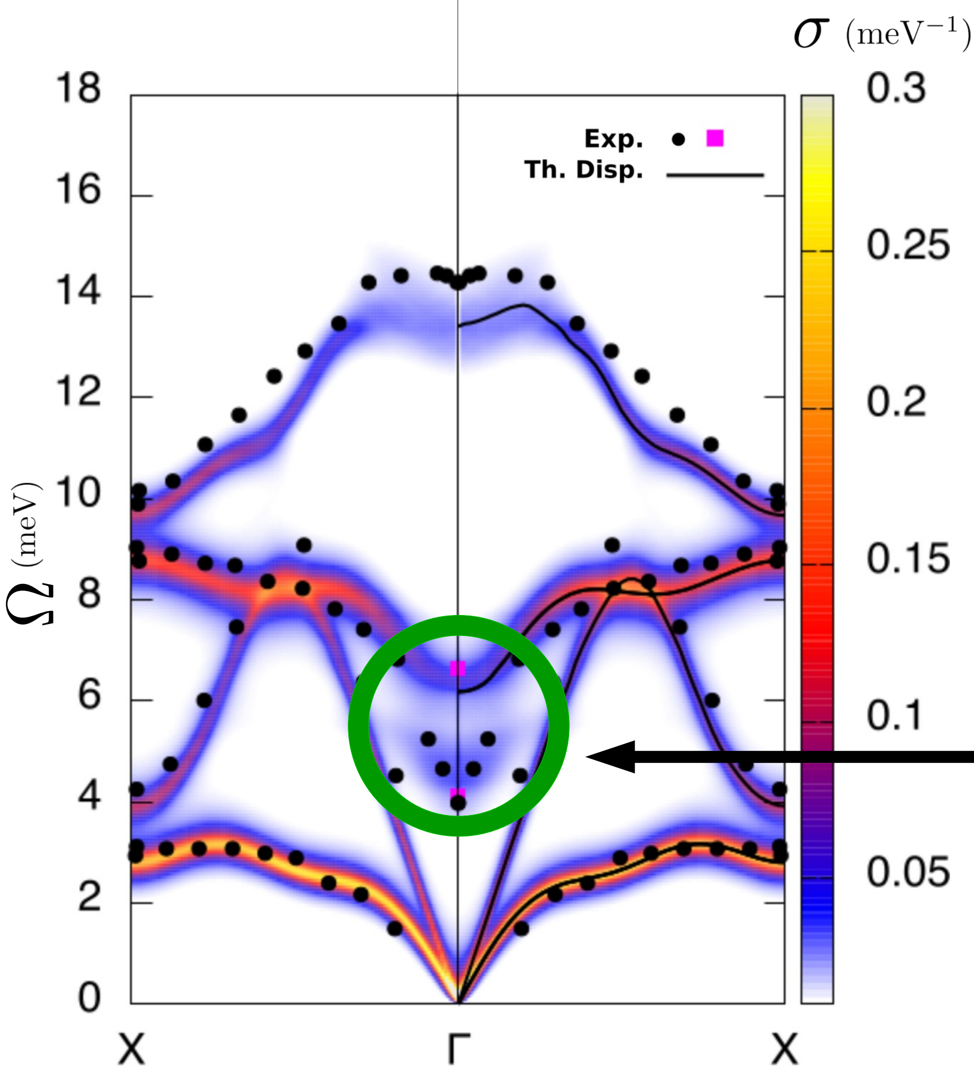
PbTe, T=300 K



Ribeiro *et al.*, PRB, 97, 014306 (2018)

PbTe, T=300 K





NON-LORENTZIAN CHARACTER

SATELLITE

Ribeiro *et al.*, PRB, 97, 014306 (2018)