Raman and Infrared spectra of strongly anharmonic materials

MoRe-TEM

European Research Council
Established by the European Commission

Sapienza Università di Roma

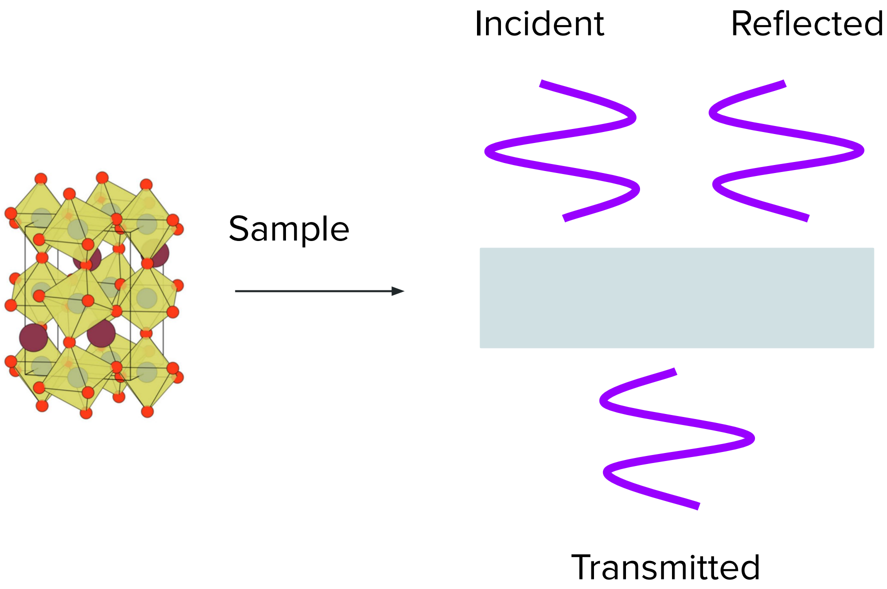
SSCHA
Stochastic Self-Consistent Harmonic Approximation

Speaker: Antonio Siciliano
La Sapienza University of Rome

Outline

- General principles of infrared absorption and Raman scattering
- Applications
- Missing terms in the light-matter interactions and anharmonic effects
- The approach of Time-Dependent SCHA

Infrared response



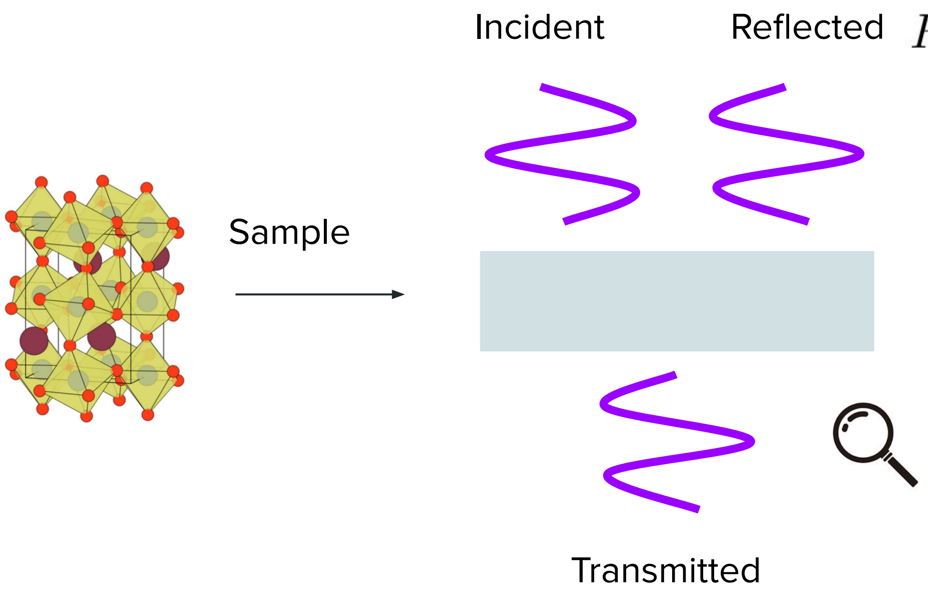
IR light 700 nm/1 mm 1.5 eV/1.5 meV

- Long wave-length normal modes
- Chemical composition
- Crystal symmetry
- Phase diagrams
- Non destructive: linear response, (no heat, no macroscopic/irreversible changes)

Infrared response

Ratio of energy flux

$$R(\omega) = \frac{I_{\mathrm{R}}(\omega)}{I_{\mathrm{I}}(\omega)} = \left|\frac{\sqrt{\epsilon(\omega)} - 1}{\sqrt{\epsilon(\omega)} + 1}\right|^2$$



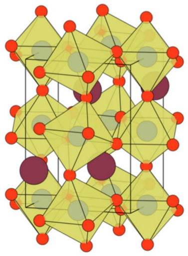
What is measured $T(\omega) = \frac{I_{\mathrm{T}}(\omega)}{I_{\mathrm{I}}(\omega)} = (1 - R(\omega))^2 e^{-\alpha(\omega)}$

Excitations

Absorption $$\alpha(\omega) = \frac{L\omega}{c} \mathrm{Im}[\sqrt{\epsilon(\omega)}]$$

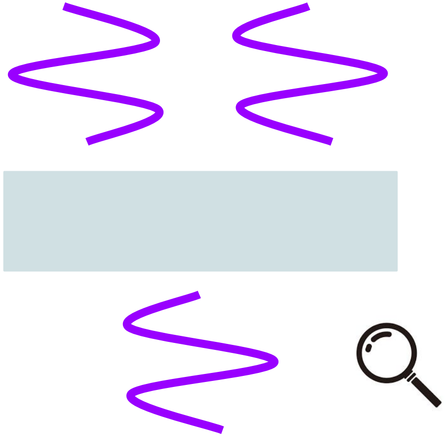
Dielectric constant...

Infrared response



Sample →

Incident   Reflected



Transmitted

$$T(\omega) = \frac{I_{\mathrm{T}}(\omega)}{I_{\mathrm{I}}(\omega)} = (1 - R(\omega))^2 e^{-\alpha(\omega)}$$

Key quantity

$$\boldsymbol{\epsilon}(\omega) = \mathbf{1} + 4\pi\boldsymbol{\chi}(\omega)$$

$$\boldsymbol{P}(\omega) = \boldsymbol{\chi}(\omega) \cdot \boldsymbol{E}(\omega)$$

Low energy (meV)
Vibrations,
optical phonons

$$\boldsymbol{\epsilon}(\omega) = \boldsymbol{\epsilon}_{\mathrm{el}}(\omega) + \boldsymbol{\epsilon}_{\mathrm{ph}}(\omega)$$

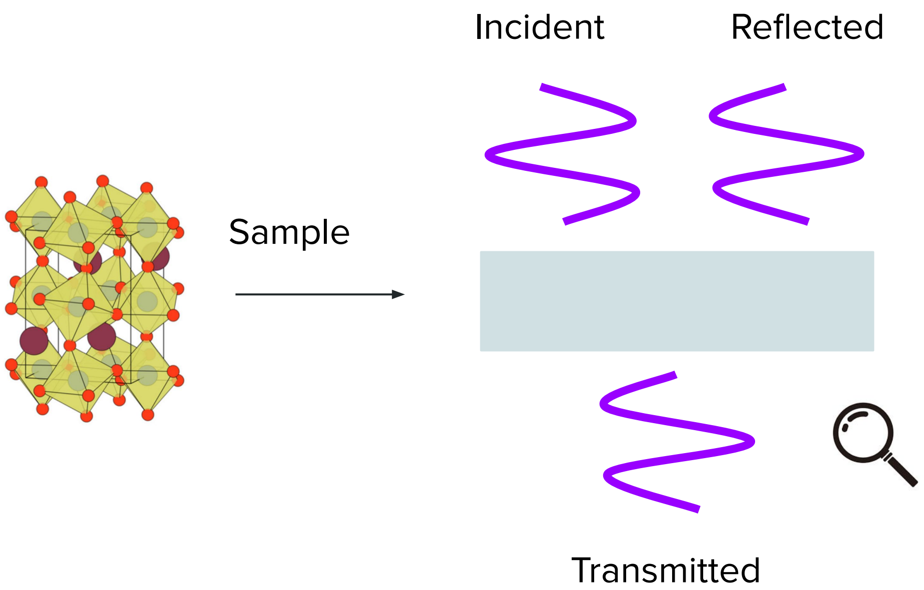
High energy (eV):
excitons,
band-band transitions

Plot for insulator...

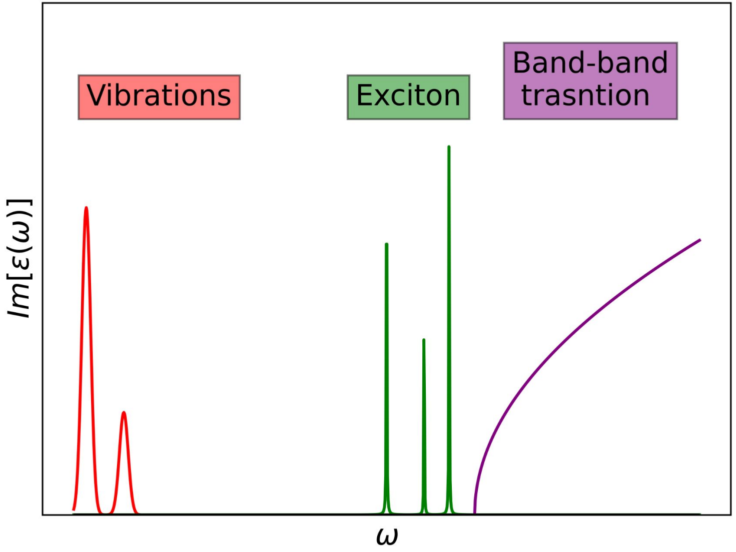
Infrared response

Dielectric constant

$$\epsilon(\omega) = \epsilon_{\rm el}(\omega) + \epsilon_{\rm ph}(\omega)$$

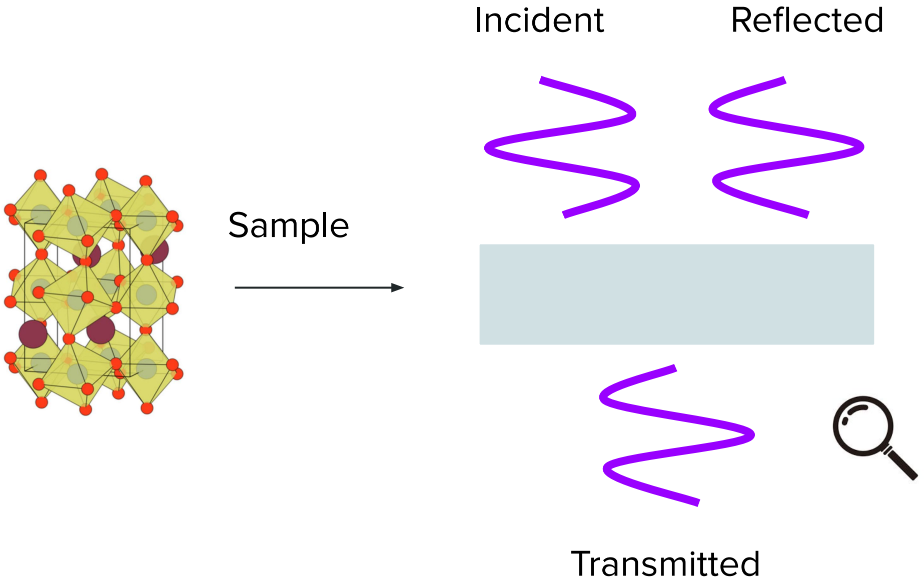


$$T(\omega) = \frac{I_{\rm T}(\omega)}{I_{\rm I}(\omega)} = (1 - R(\omega))^2 e^{-\alpha(\omega)}$$



- Normal modes (fingerprint of structure)
- Chemical bonds
- Chemical environment
- Model?

Infrared response



$$T(\omega) = \frac{I_{\mathrm{T}}(\omega)}{I_{\mathrm{I}}(\omega)} = (1 - R(\omega))^2 e^{-\alpha(\omega)}$$

Dielectric constant

$$\boldsymbol{\epsilon}(\omega) = \boldsymbol{\epsilon}_{\mathrm{el}}(\omega) + \boxed{\boldsymbol{\epsilon}_{\mathrm{ph}}(\omega)}$$

Phononic contribution

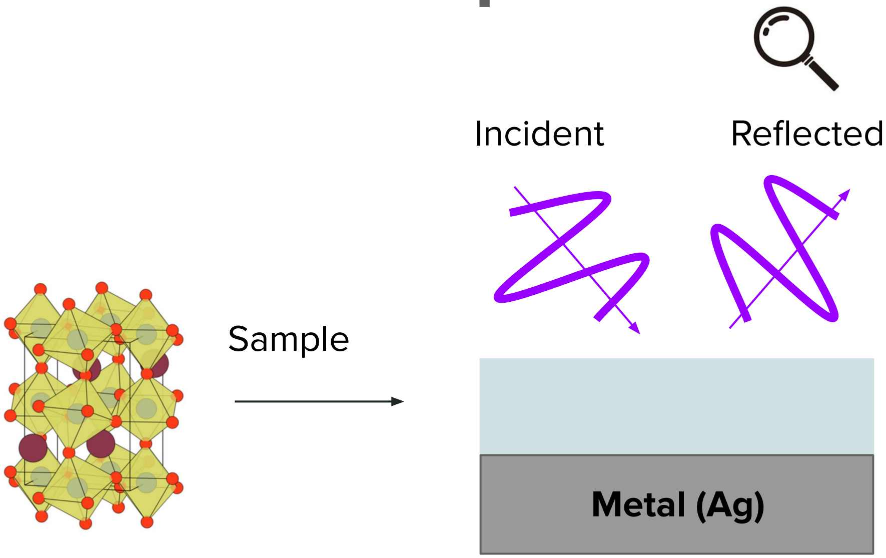
$$\epsilon_{\mathrm{ph},\alpha\beta}(\omega) = \frac{4\pi}{V} \sum_{\mu}^{\mathrm{opt}} \frac{p_{\alpha}^{\mu} p_{\beta}^{\mu}}{\omega_{\mu}^2 - (\omega + i\gamma_{\mu})^2}$$

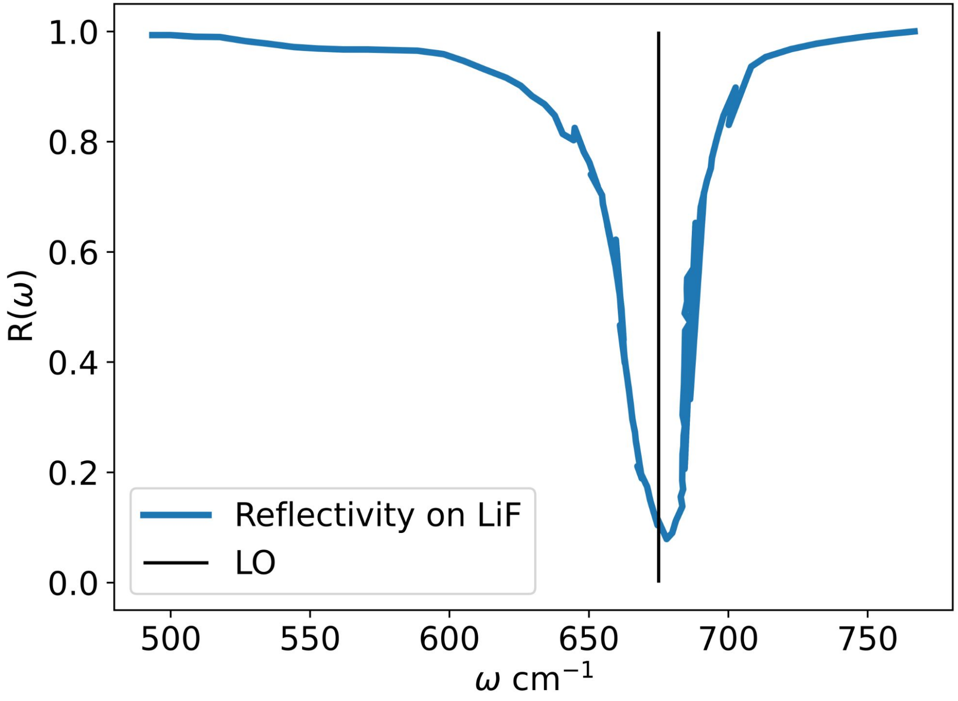
$$p_{\alpha}^{\mu} = \sum_{b}^{\mathrm{uc}} \sum_{\beta}^{xyz} e Z_{\alpha,b\beta} \frac{e_{\mu}^{b\beta}}{\sqrt{m_b}}$$

Light-phonon coupling

What can we see? Only TO phonons. Non-normal incidence also LO phonons (LiF)...

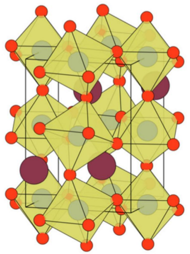
Infrared response

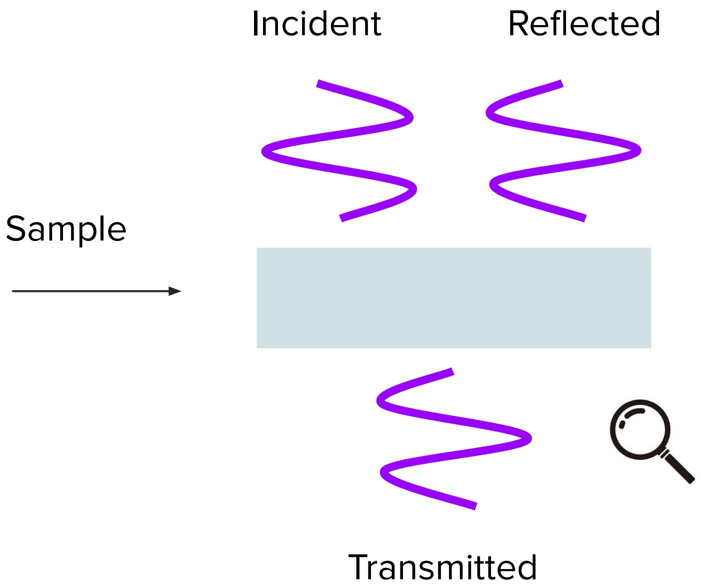




Diagrams?

Infrared response

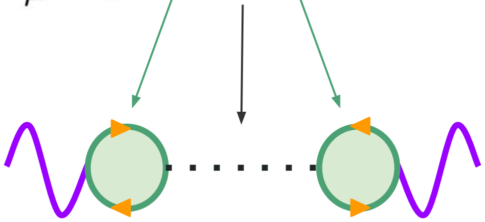




$$T(\omega) = \frac{I_{\mathrm{T}}(\omega)}{I_{\mathrm{I}}(\omega)} = (1 - R(\omega))^2 e^{-\alpha(\omega)}$$

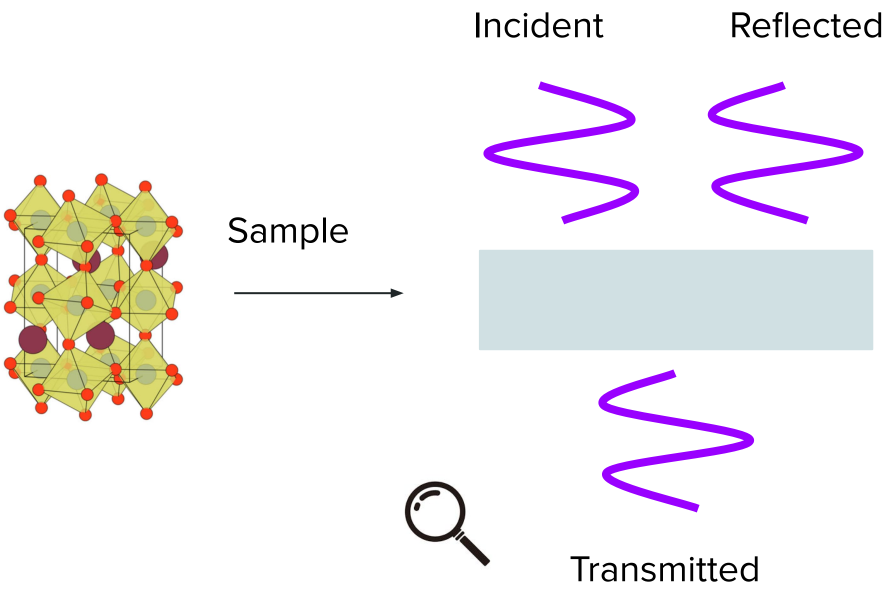
Phononic contribution

$$\epsilon_{\mathrm{ph},\alpha\beta}(\omega) = \frac{4\pi}{V} \sum_{\mu}^{\mathrm{opt}} \frac{p_{\alpha}^{\mu} p_{\beta}^{\mu}}{\omega_{\mu}^2 - (\omega + i\gamma_{\mu})^2}$$



- Diagrams: E.M. interaction mediated by electrons e-ph coupling
- Ingredients?

Infrared response



Phonons

$$\frac{d^2 E_{\mathrm{el}}}{d\boldsymbol{R}_a d\boldsymbol{R}_b}$$

Effective charges

$$Z_{\alpha,b} = \frac{d^2 E_{\mathrm{el}}}{dE_\alpha d\boldsymbol{R}_b}$$

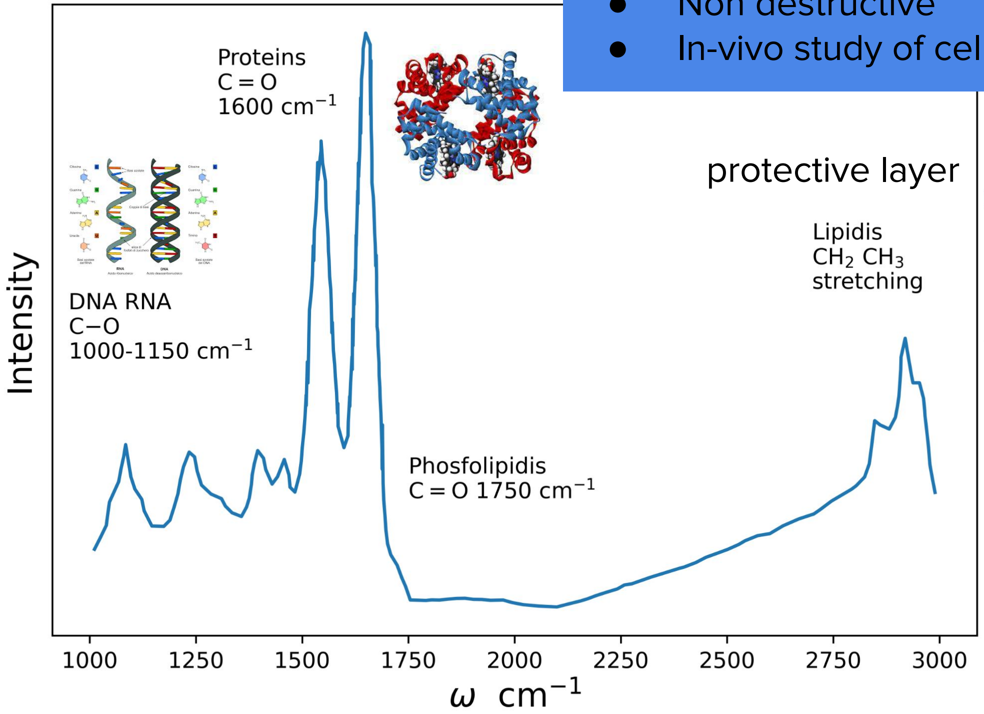
Lifetimes

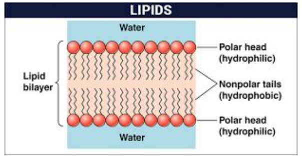
$$\frac{d^3 E_{\mathrm{el}}}{d\boldsymbol{R}_a d\boldsymbol{R}_b d\boldsymbol{R}_c}$$

Example?

Infrared spectroscopy

- Molecular info
- Chemical group fingerprint
- Non destructive
- In-vivo study of cells/tissue + drugs





200 cm^{-1} = 300 K = 25 meV = 50 µm = 7 THz

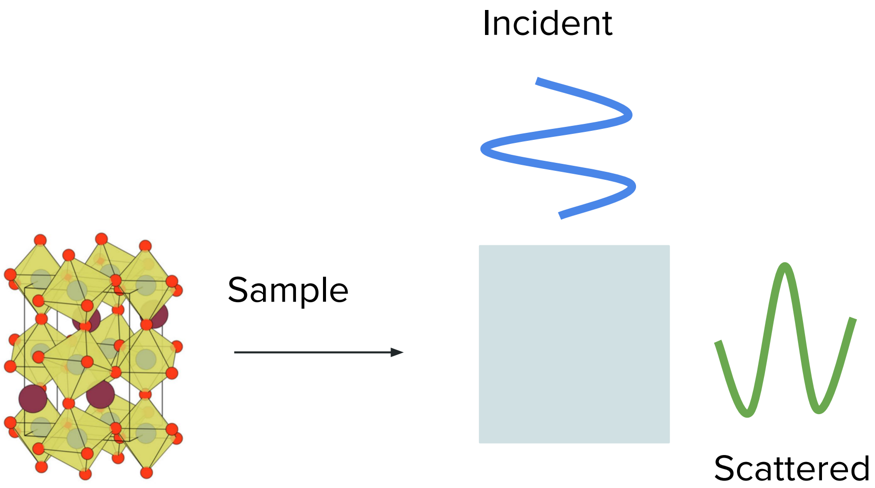
Another complementary approach...

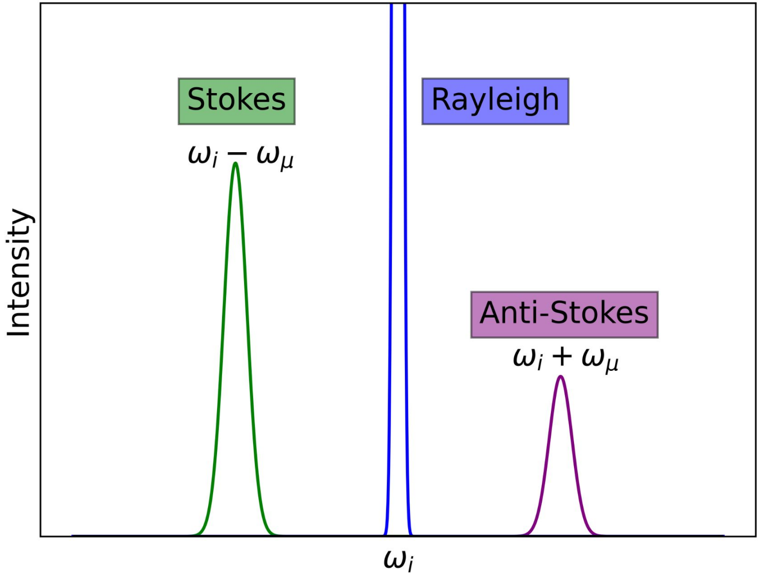
Refs: S. Lupi Sapienza Terahertz group

Raman response

Scattering VIS light (400/700 nm 1.5/3 eV ~10^4 cm^{-1})

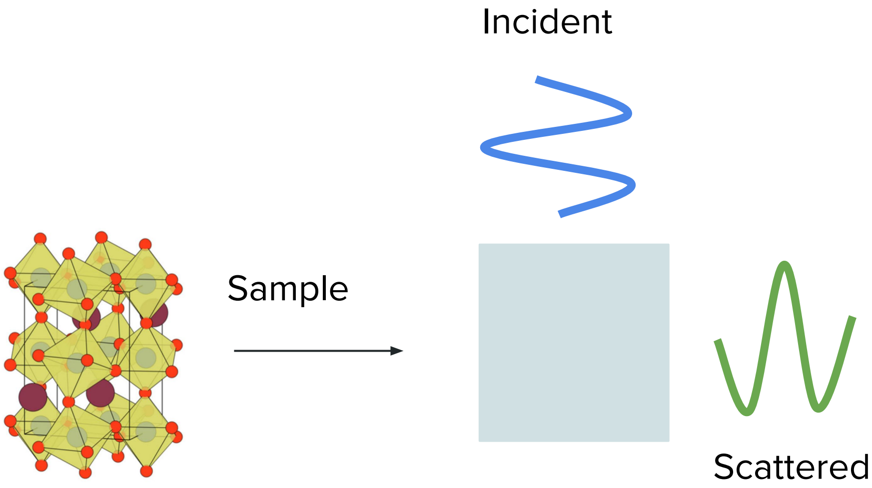
- Semiconductors
- Non-resonant (spontaneous)
- No electronic excitations

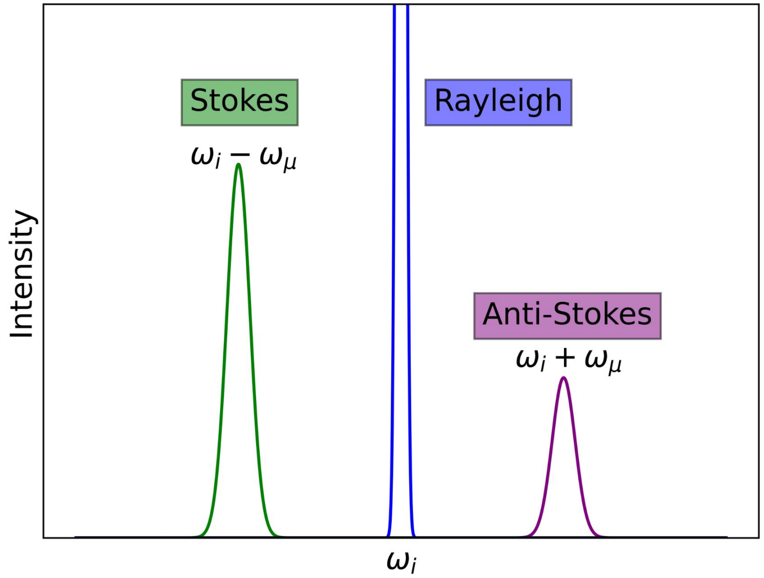




Exp configuration $\underline{k}_i$ ($\underline{pol}_i$, $\underline{pol}_{out}$) $\underline{k}_{out}$

Raman response



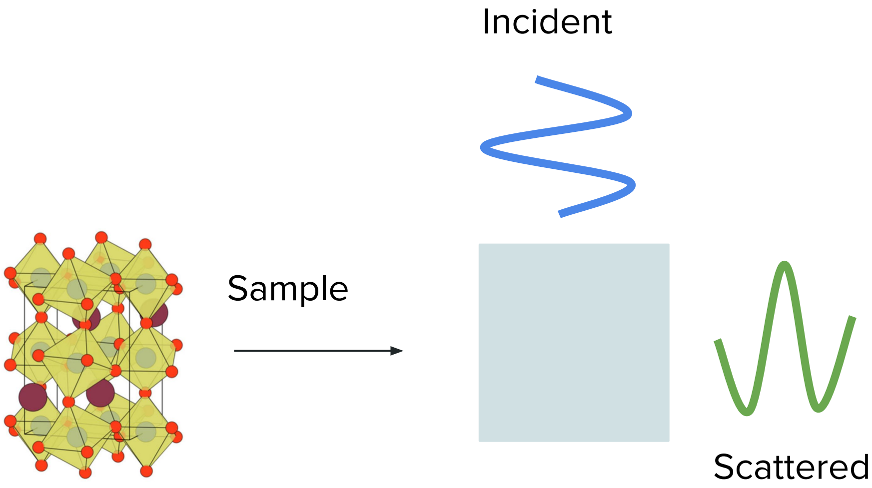


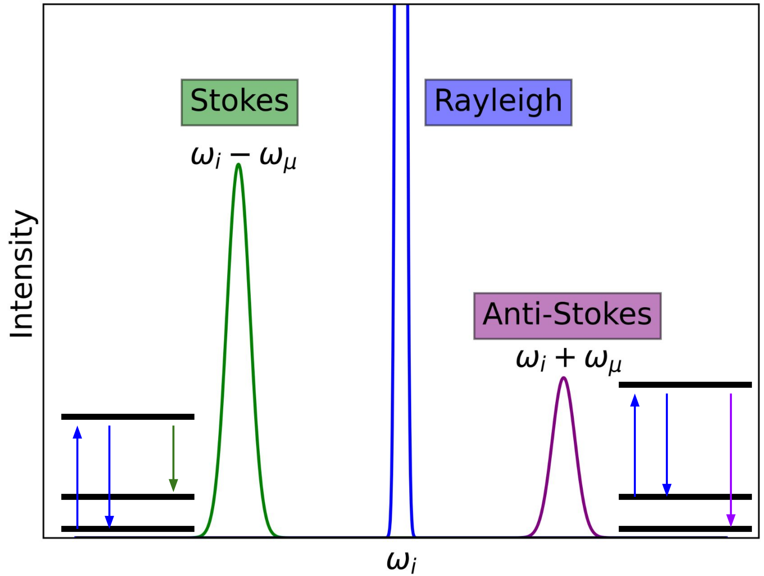
Quantum-thermal fluctuations

Zone-center optical phonons

$$
\begin{aligned}
\boldsymbol{P}(t) &= \boldsymbol{\chi}(\boldsymbol{R}(t), \omega_{\mathrm{i}}) \cdot \boldsymbol{E}(\omega_{\mathrm{i}}) \cos(\omega_{\mathrm{i}} t) \\
&= \left[\boldsymbol{\chi}(\boldsymbol{\mathcal{R}}_{\mathrm{BO}}, \omega_i) + \sum_a^{3\mathrm{uc}} \frac{\partial \boldsymbol{\chi}(\boldsymbol{\mathcal{R}}_{\mathrm{BO}}, \omega_{\mathrm{i}})}{\partial R_a} \frac{e_\mu^a}{\sqrt{m_a}} \cos(\omega_\mu t) \right] \cdot \boldsymbol{E}(\omega_{\mathrm{i}}) \cos(\omega_{\mathrm{i}} t) \\
&= \boldsymbol{P}^{\mathrm{el}} \cos(\omega_{\mathrm{i}} t) + \boldsymbol{P}_\mu^{\mathrm{ph}} \left\{ \cos[(\omega_{\mathrm{i}} + \omega_\mu) t] + \cos[(\omega_{\mathrm{i}} - \omega_\mu) t] \right\}
\end{aligned}
$$

Raman response





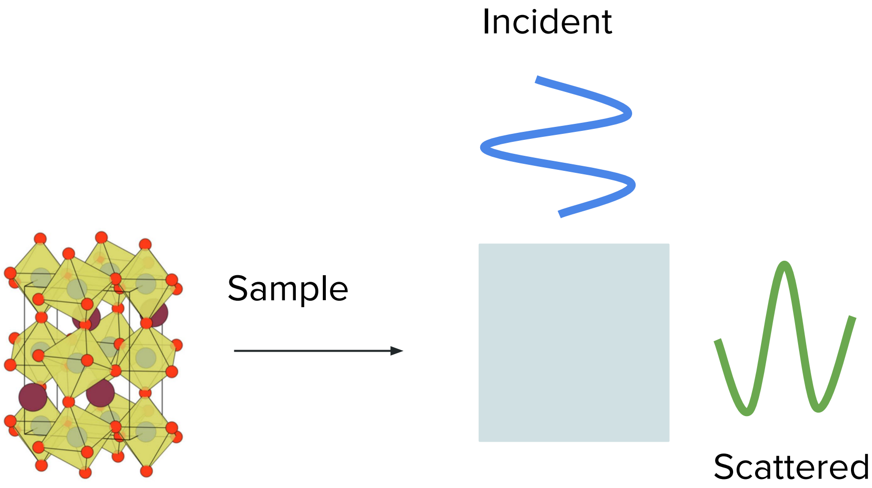
Positions of the peaks...

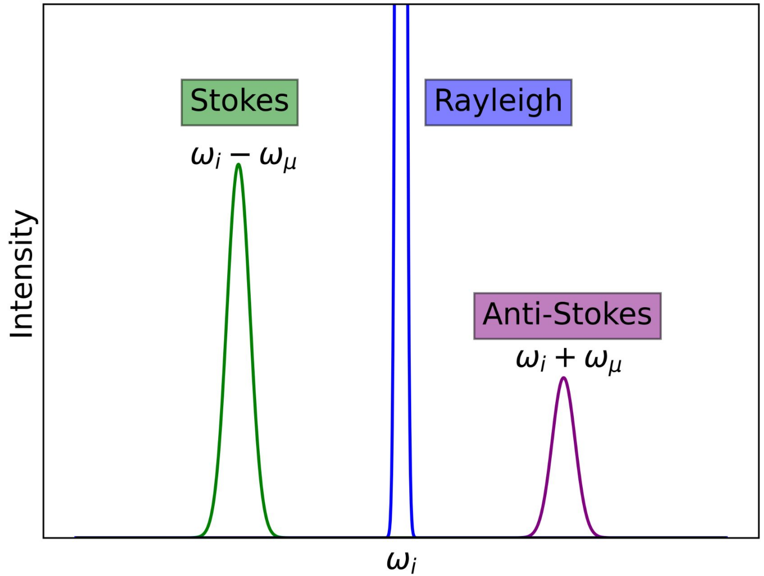
$$\boldsymbol{P}(t) = \boldsymbol{P}^{\text{el}} \cos(\omega_{\text{i}} t) + \boldsymbol{P}_{\mu}^{\text{ph}} \left\{ \cos[(\omega_{\text{i}} + \omega_\mu)t] + \cos[(\omega_{\text{i}} - \omega_\mu)t] \right\}$$

Anti-Stokes   Stokes

What about the **different intensity**? Statistical mechanics...

Raman response





Radiating dipole + infinite lifetime

$$I = \left| \sum_{a}^{\mathrm{uc}} \sum_{\alpha}^{xyz} \boldsymbol{E}^{\mathrm{i}} \cdot \frac{\partial \boldsymbol{\chi}(\boldsymbol{\mathcal{R}}_{\mathrm{BO}})}{\partial R_{a\alpha}} \cdot \boldsymbol{E}^{\mathrm{f}} \frac{e_{\mu}^{a\alpha}}{\sqrt{m_a}} \right|^2$$

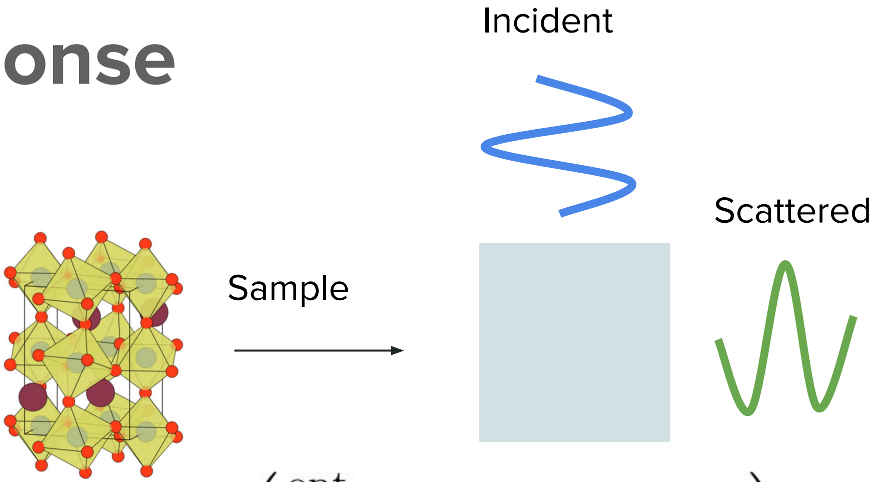
Raman tensor

$$\Xi_{\alpha\beta,a} = \frac{\partial \chi_{\alpha\beta}(\boldsymbol{\mathcal{R}}_{\mathrm{BO}})}{\partial R_a}$$

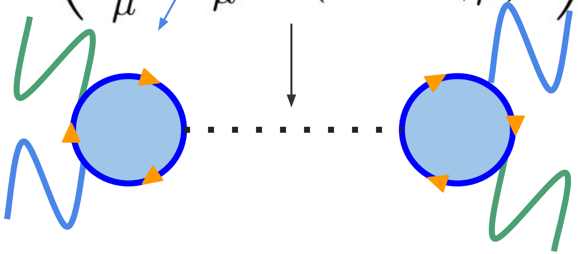
- Adiabatic
- Only e$^-$ response (VIS)
- Insulator
- Zero phonon freq
- Indep of light freq

Diagrams?

Raman response



$$I(\omega)_{\text{Raman}} \propto -\operatorname{Im}\left(\sum_{\mu}^{\text{opt}} \frac{\Xi_{\alpha\beta,\mu}\Xi_{\alpha\beta,\mu}}{\omega_\mu^2 - (\omega + i\gamma_\mu)^2}\right)$$



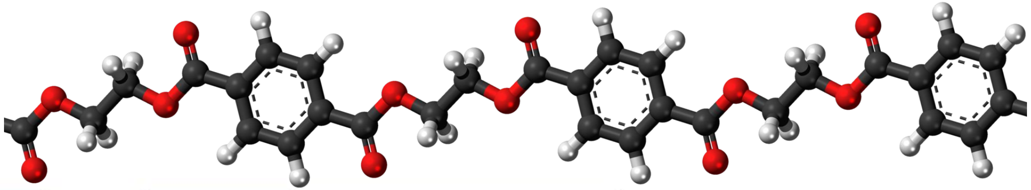
Example?

$$\frac{d^2 E_{\text{el}}}{d\boldsymbol{R}_a d\boldsymbol{R}_b}$$

$$\Xi_{\alpha\beta,a} = \frac{dE_{\text{el}}}{dE_\alpha dE_\beta d\boldsymbol{R}_a}$$

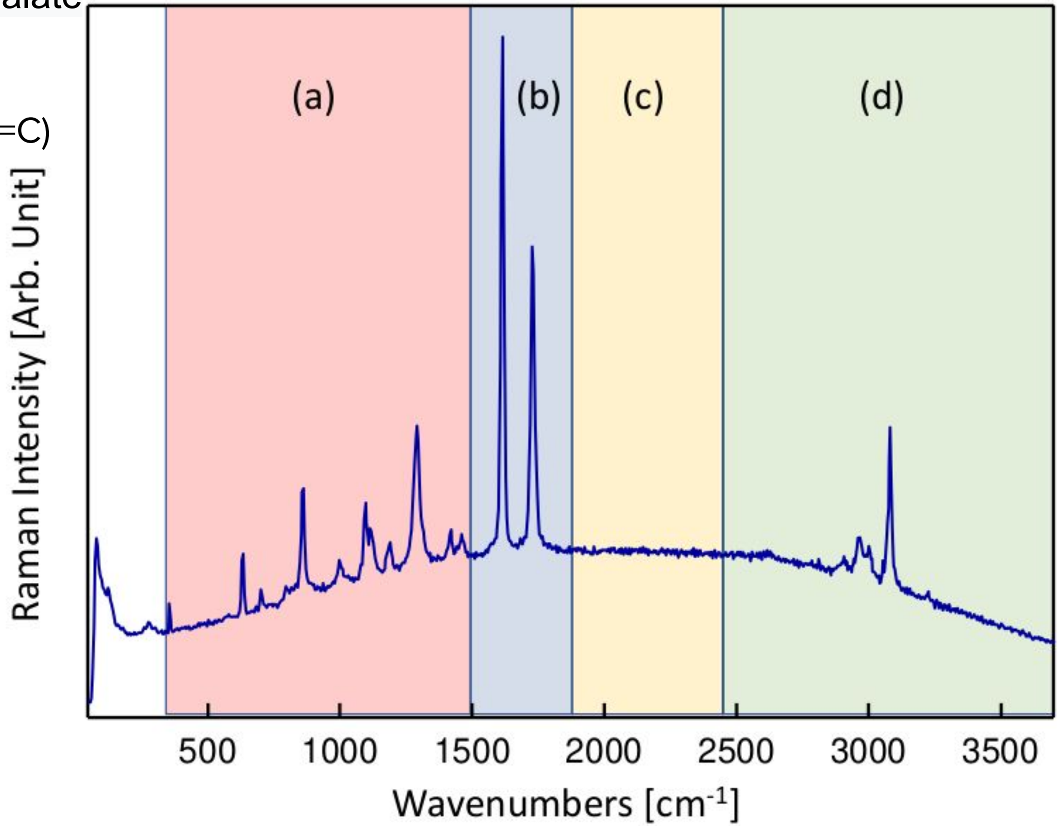
$$\frac{d^3 E_{\text{el}}}{d\boldsymbol{R}_a d\boldsymbol{R}_b d\boldsymbol{R}_c}$$

Raman spectroscopy



Polyethylene terephthalate (PET)

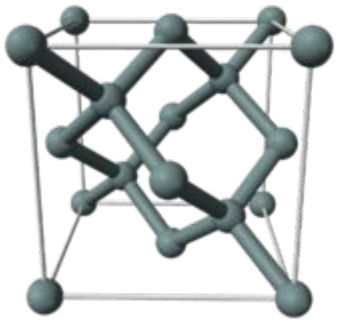
1. Aromatic ring
2. Double bonds (C=O C=C)
3. Triple bonds
4. Hydrogen stretching



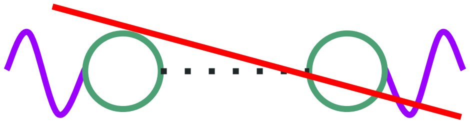
Single peaks!
Strange spectra?

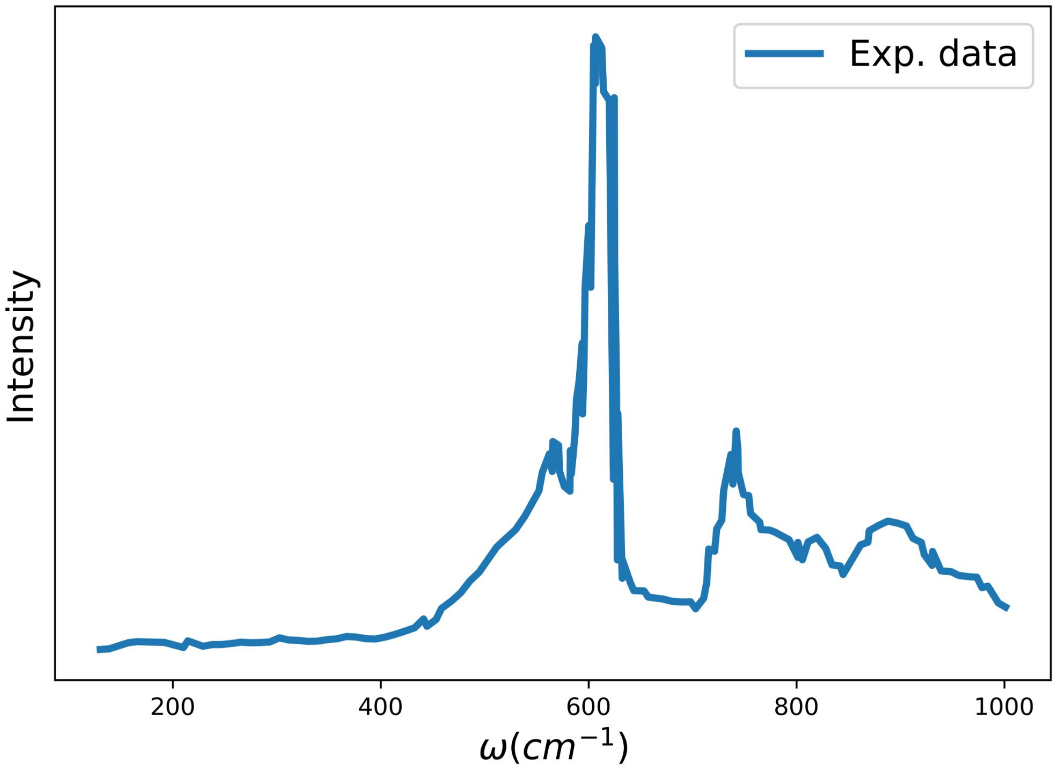
Refs: C. Emmanuello, Phd thesis

IR with inversion symmetry?



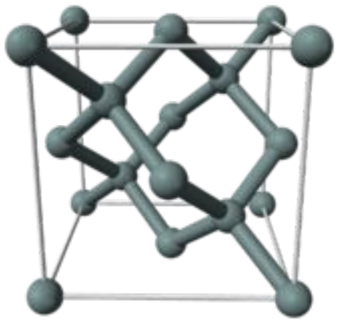
- **Silicon** inversion symmetry -> **NO IR**
- Signal is quite broad
- IR light -> no electrons

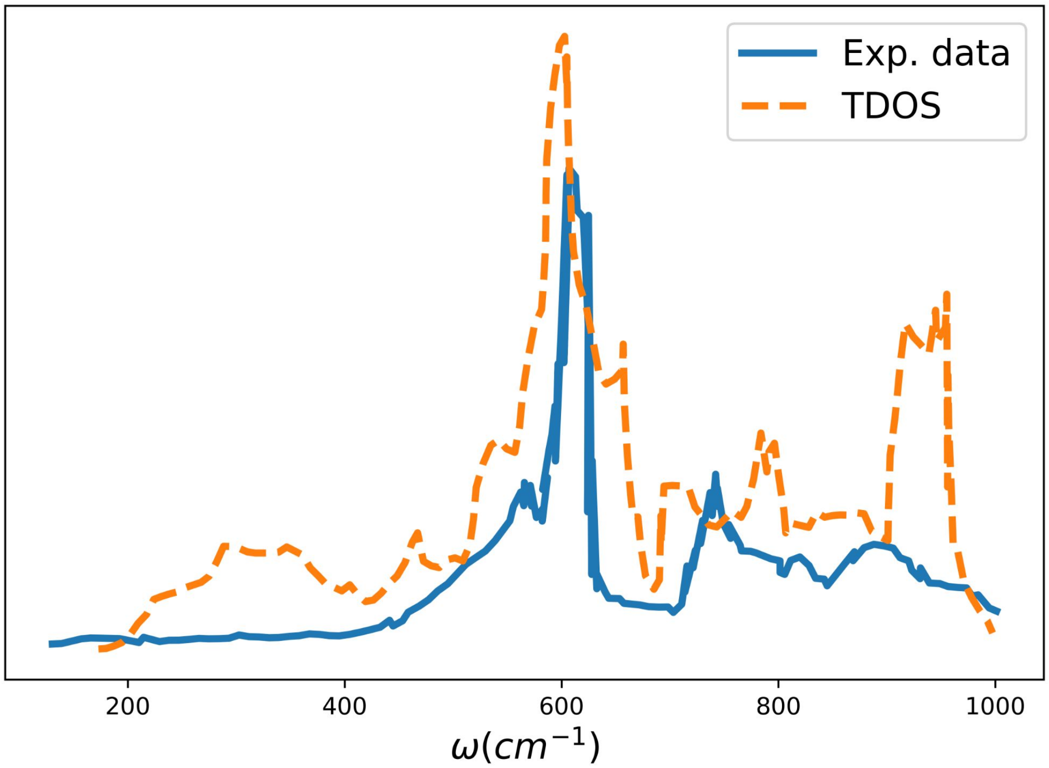




Refs: G. Deinzer and D. Strauch Phys. Rev. B 69, 045205, 2004

What is missing in IR?





- **Silicon** inversion symmetry -> **NO IR**
- Signal is quite broad
- IR light -> no electrons
- Two-phonon DOS?

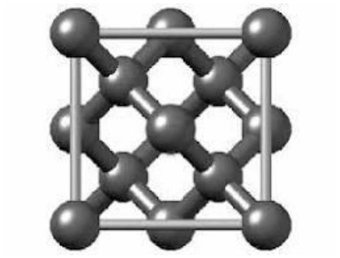
$$\mathrm{TDOS}(\omega) = \sum_{\mu\nu} \delta(\omega_\mu + \omega_\nu - \omega)\delta(\boldsymbol{q}_\mu - \boldsymbol{q}_\nu)$$

Signal = two-phonon DOS 'modulated'

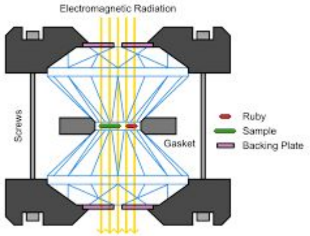
Refs: G. Deinzer and D. Strauch Phys. Rev. B 69, 045205, 2004

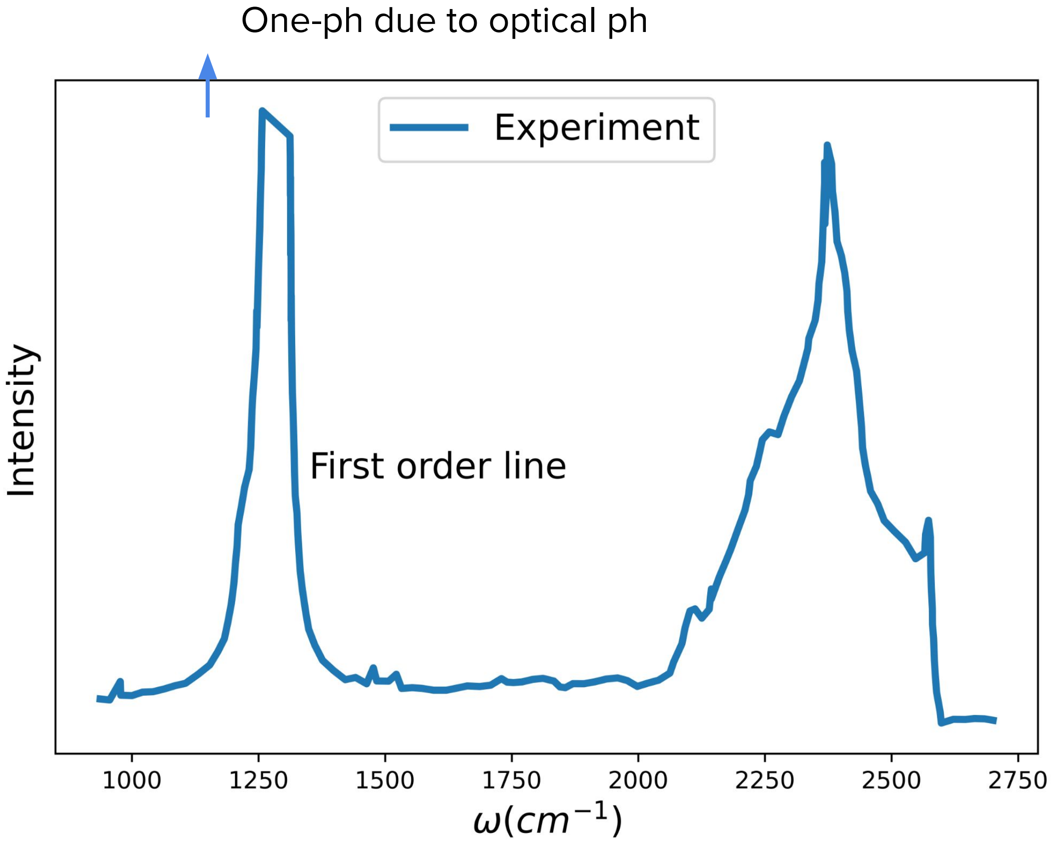
Similar effect in Raman

Diamond



Background important in diamond anvil cell experiments



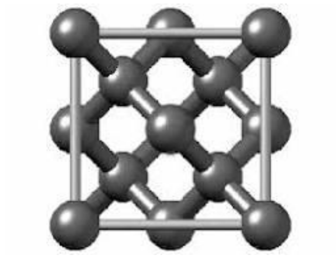


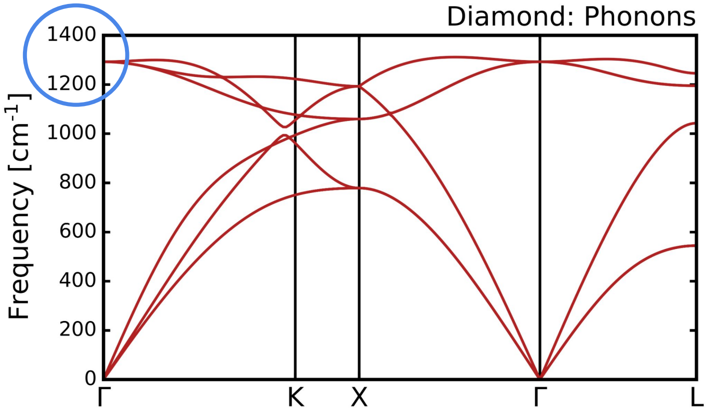
Refs: W. Windl et al.. Phys. Rev. B 49, 8764, 1994

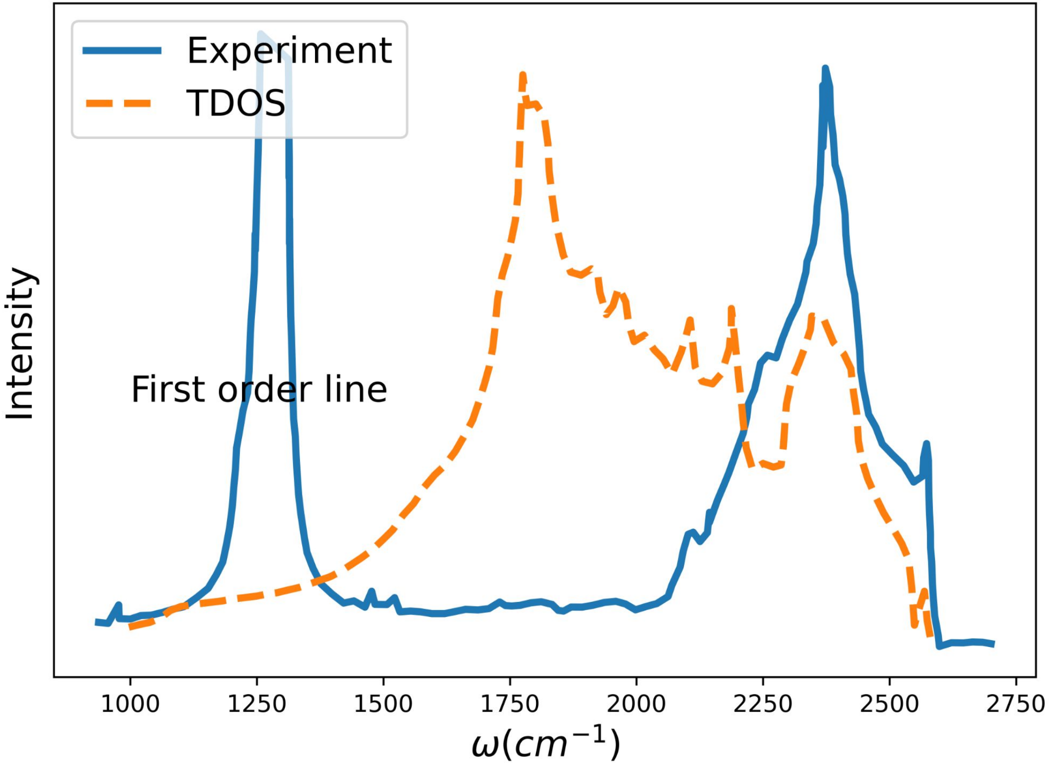
Similar effect in Raman

Signal = two-phonon DOS ‘modulated’?
Theoretical perspective?

Diamond



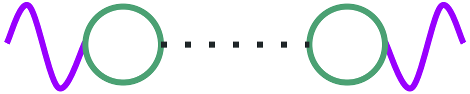




Refs: W. Windl et al.. Phys. Rev. B 49, 8764, 1994

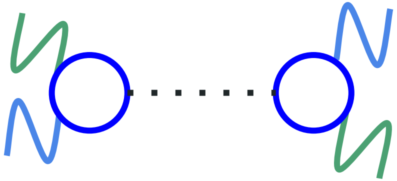
The theoretical perspective

$$I(\omega)_{\mathrm{IR}} \propto -\mathrm{Im}\left(\sum_{\mu}^{\mathrm{opt}} Z_{\alpha,\mu}\mathcal{G}^{(0)}_{\mu\mu}(\omega)Z_{\beta,\mu}\right)$$



$$Z_{\alpha,\mu} = \frac{dE_{\mathrm{el}}}{dE_\alpha \underline{dR_\mu}}$$

$$I(\omega)_{\mathrm{Raman}} \propto -\mathrm{Im}\left(\sum_{\mu}^{\mathrm{opt}} \Xi_{\alpha\beta,\mu}\mathcal{G}^{(0)}_{\mu\mu}(\omega)\Xi_{\alpha\beta,\mu}\right)$$



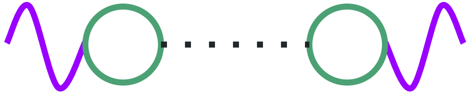
$$\Xi_{\alpha\beta,\mu} = \frac{dE_{\mathrm{el}}}{dE_\alpha dE_\beta \underline{dR_\mu}}$$

- Different couplings
- **Derivative in the phonon = e/ph coupling**
- Same phonon propagator →
- Different selection rules (TO vs LO/TO)

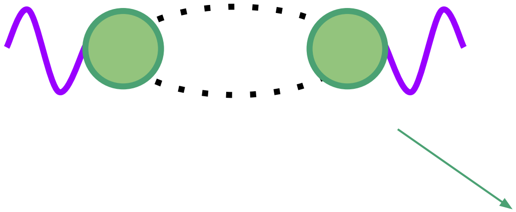
$$\mathcal{G}^{(0)}_{\mu\nu}(\omega) = \frac{\delta_{\mu\nu}}{\omega^2 - \omega_\mu^2}$$

The theoretical perspective

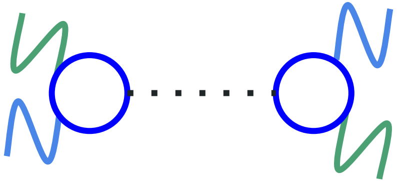
$$I(\omega)_{\mathrm{IR}} \propto -\,\mathrm{Im}\left(\sum_{\mu}^{\mathrm{opt}} Z_{\alpha,\mu}\mathcal{G}^{(0)}_{\mu\mu}(\omega)Z_{\beta,\mu}\right)$$



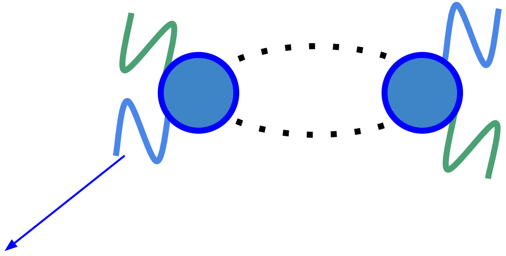
$$I(\omega)_{\mathrm{IR}} \propto -\,\mathrm{Im}\left(\sum_{\mu\nu} \frac{\partial Z_{\alpha,\mu}}{\partial R_\nu}\chi^{(0)}_{\mu\nu}(\omega)\frac{\partial Z_{\beta,\mu}}{\partial R_\nu}\right)$$



$$I(\omega)_{\mathrm{Raman}} \propto -\,\mathrm{Im}\left(\sum_{\mu}^{\mathrm{opt}} \Xi_{\alpha\beta,\mu}\mathcal{G}^{(0)}_{\mu\mu}(\omega)\Xi_{\alpha\beta,\mu}\right)$$



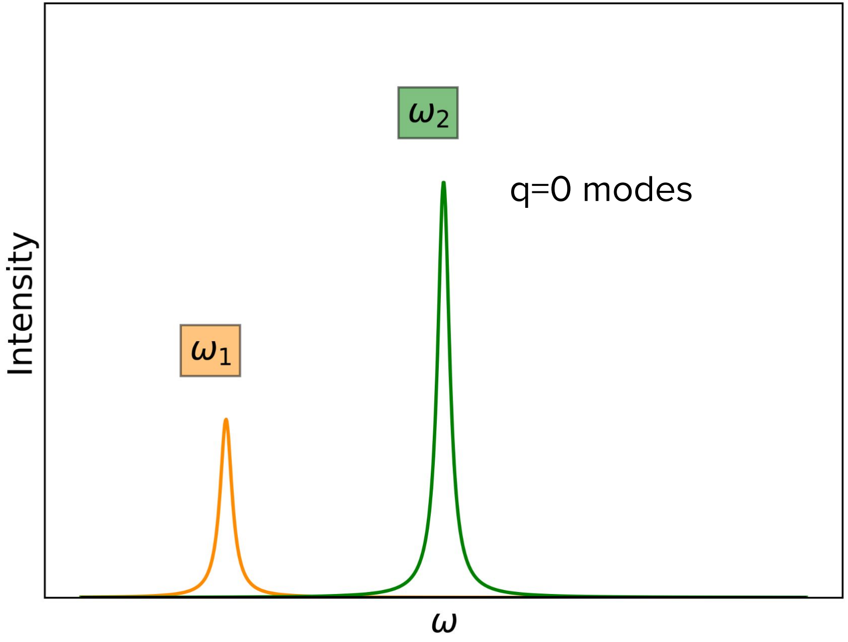
$$I(\omega)_{\mathrm{Raman}} \propto -\,\mathrm{Im}\left(\sum_{\mu\nu} \frac{\partial \Xi_{\alpha\beta,\mu}}{\partial R_\nu}\chi^{(0)}_{\mu\nu}(\omega)\frac{\partial \Xi_{\alpha\beta,\mu}}{\partial R_\nu}\right)$$



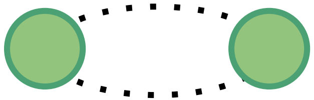
Add a derivative (**break selection rules**): **higher order photon-phonon coupling**

What are two-phonon effects?

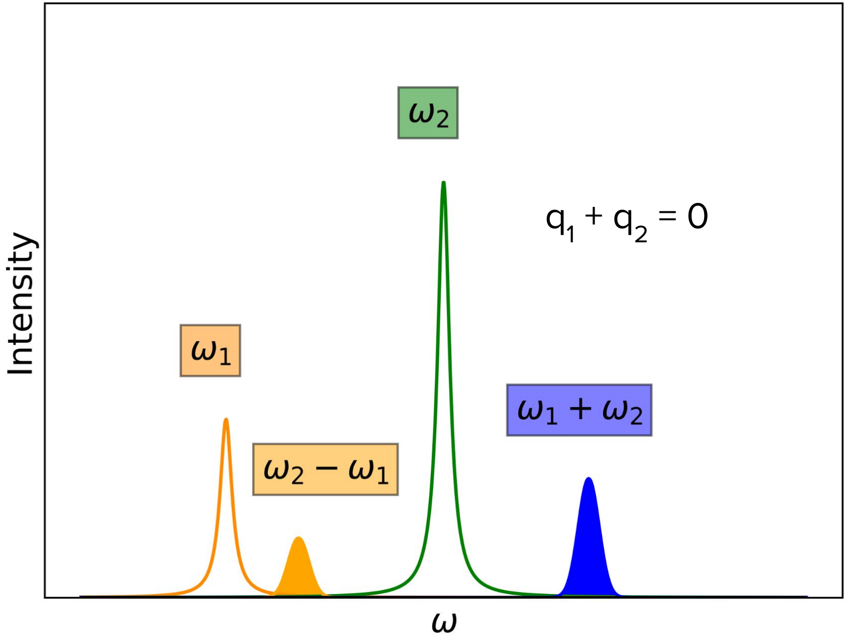
Simple model: two IR/Raman active vibrations



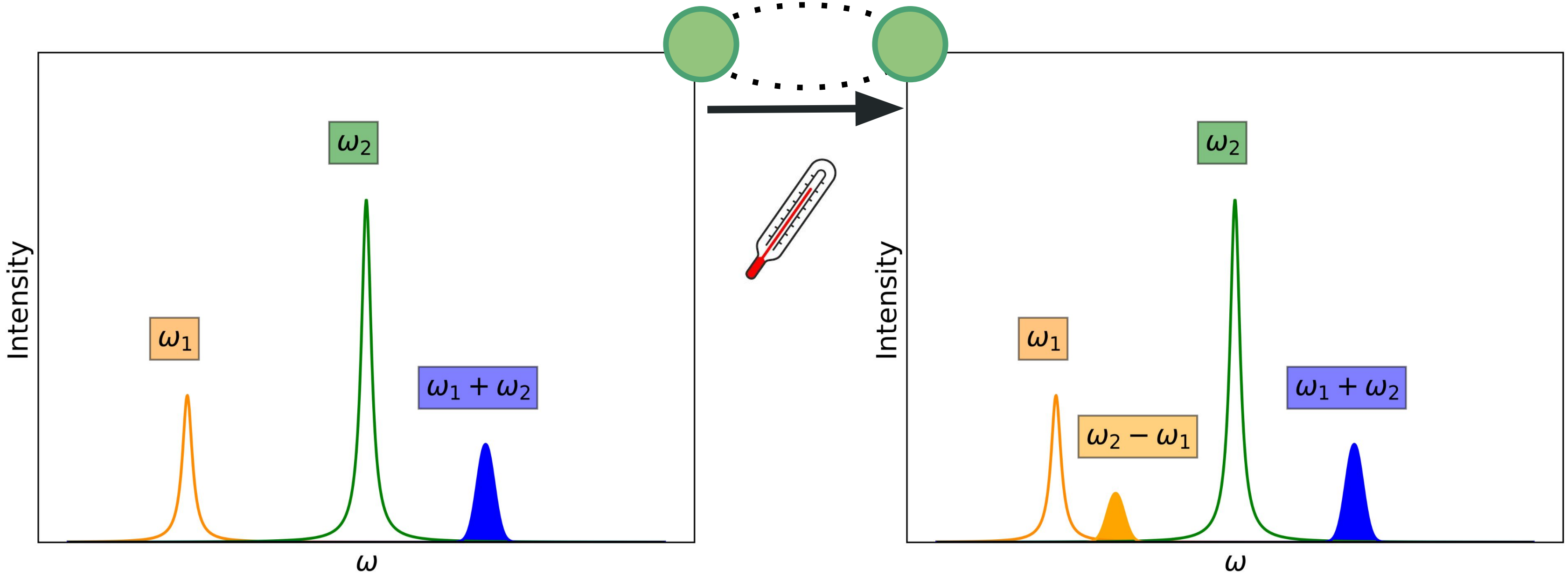
What are two-phonon effects?

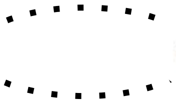


- No selection rules,
- Only energy-momentum conservation!
- Creation/annihilation processes
- Temperature dependence?



What are two-phonon effects?

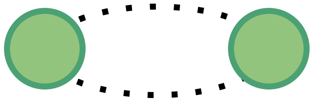




$$\boldsymbol{\chi}^{(0)}(\omega) = \frac{\hbar}{4\omega_\mu\omega_\nu}\left[\frac{(n_\mu - n_\nu)(\omega_\mu - \omega_\nu)}{[(\omega_\mu - \omega_\nu)^2 - \omega^2]} - \frac{(1 + n_\mu + n_\nu)(\omega_\mu + \omega_\nu)}{[(\omega_\mu + \omega_\nu)^2 - \omega^2]}\right]$$

Resonant ***Anti-Resonant***

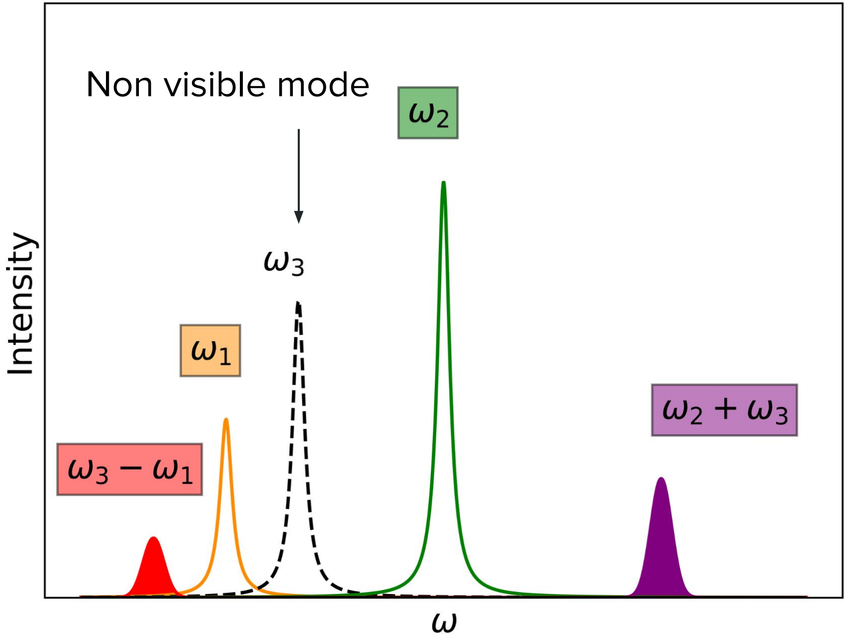
What are two-phonon effects?



No selection rules!

See the invisible

- Zone-center inactive by symmetry
- Also combination of off zone-center (see example)



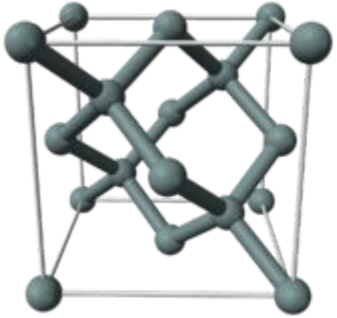
Back to applications!

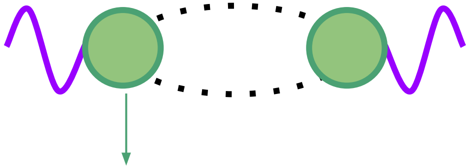
STO: quantum paraelectric cubic phase, TO phonon in 2-ph Raman?

Refs: U. Balachandran et al., Communications of the American Ceramic Society, 1982; T. Sekine et al. Solid State Comunications, 1976

Two-phonon IR

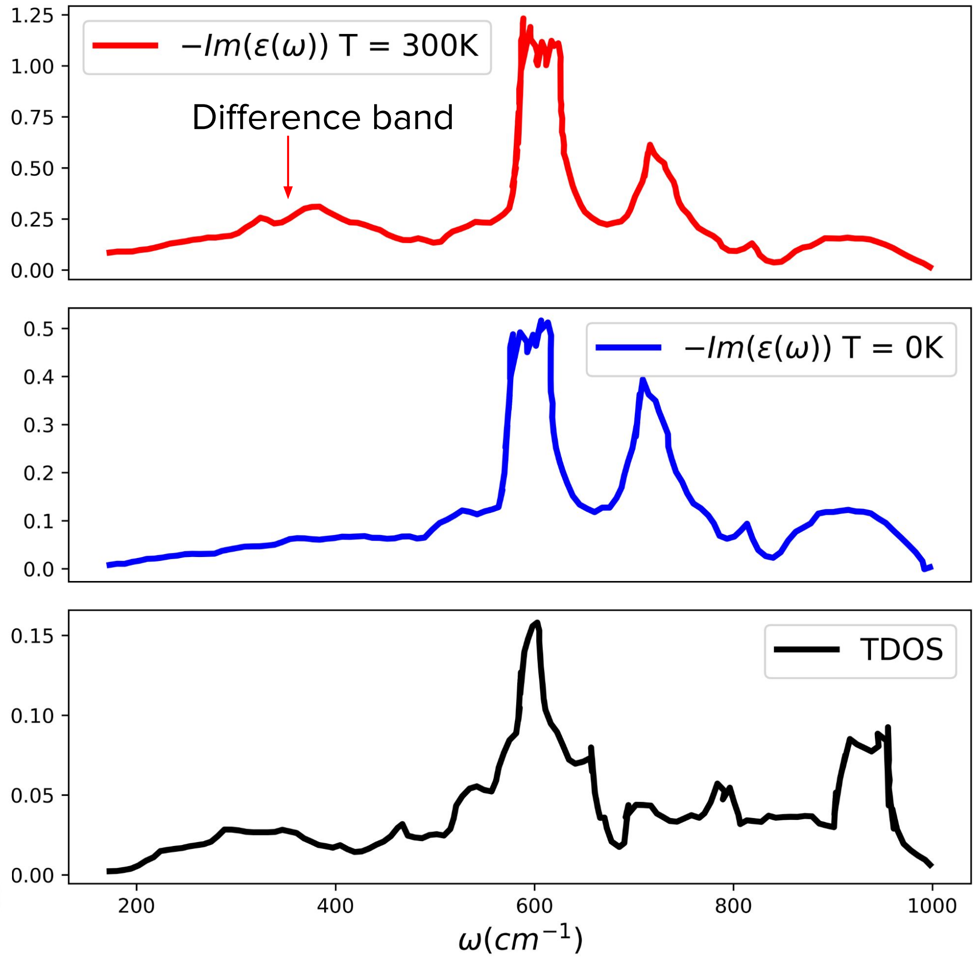
Silicon





Vertex modulation!

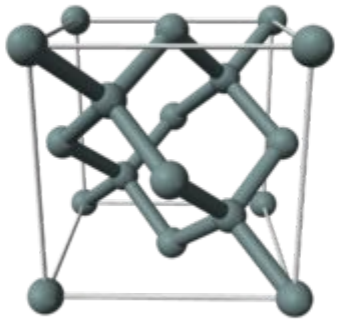
$$I(\omega)_{\mathrm{IR}} \propto -\mathrm{Im}\left(\sum_{\mu}^{\mathrm{opt}} \frac{\partial Z_{\alpha,\mu}}{\partial R_\nu} \chi^{(0)}_{\mu\nu}(\omega) \frac{\partial Z_{\beta,\mu}}{\partial R_\nu}\right)$$

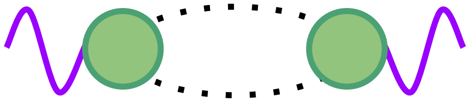


Refs: G. Deinzer and D. Strauch Phys. Rev. B 69, 045205, 2004

Two-phonon IR

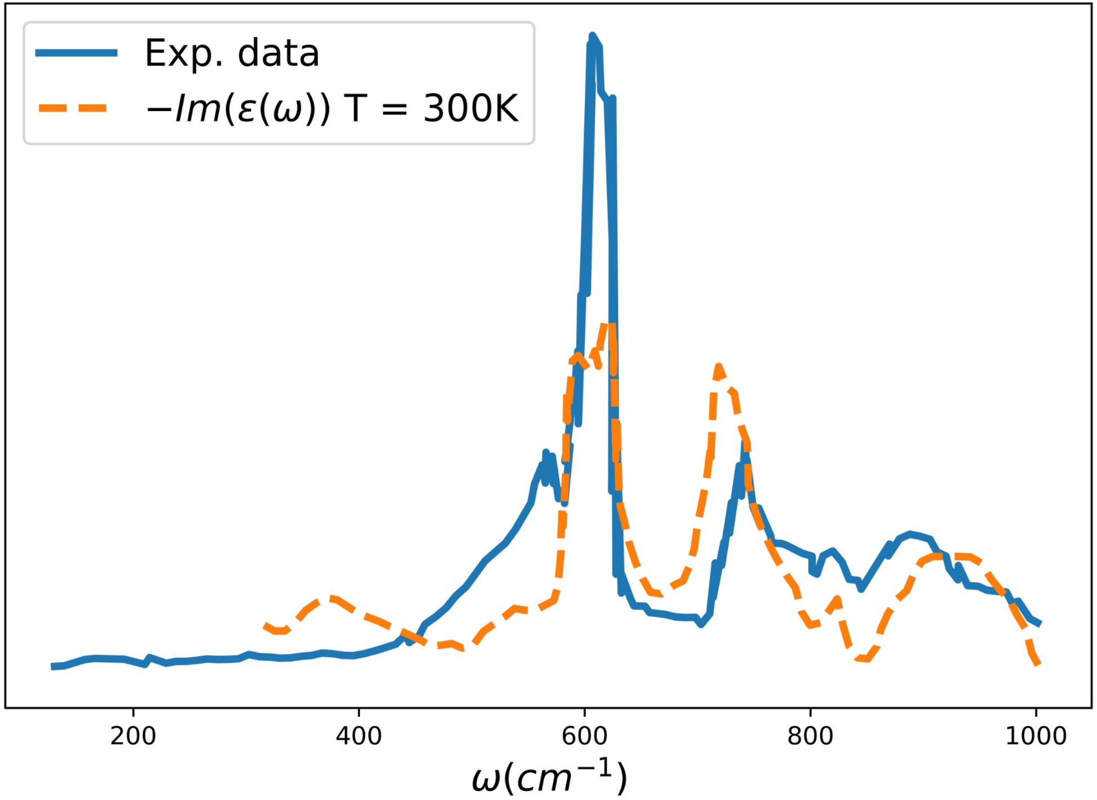
Silicon





Ingredients:

- Harmonic phonons
- Combination of L/TO L/TA at zone boundaries
- Vertex

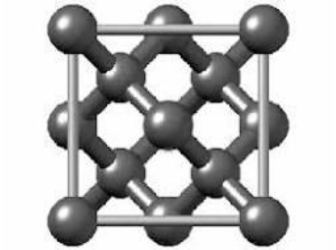


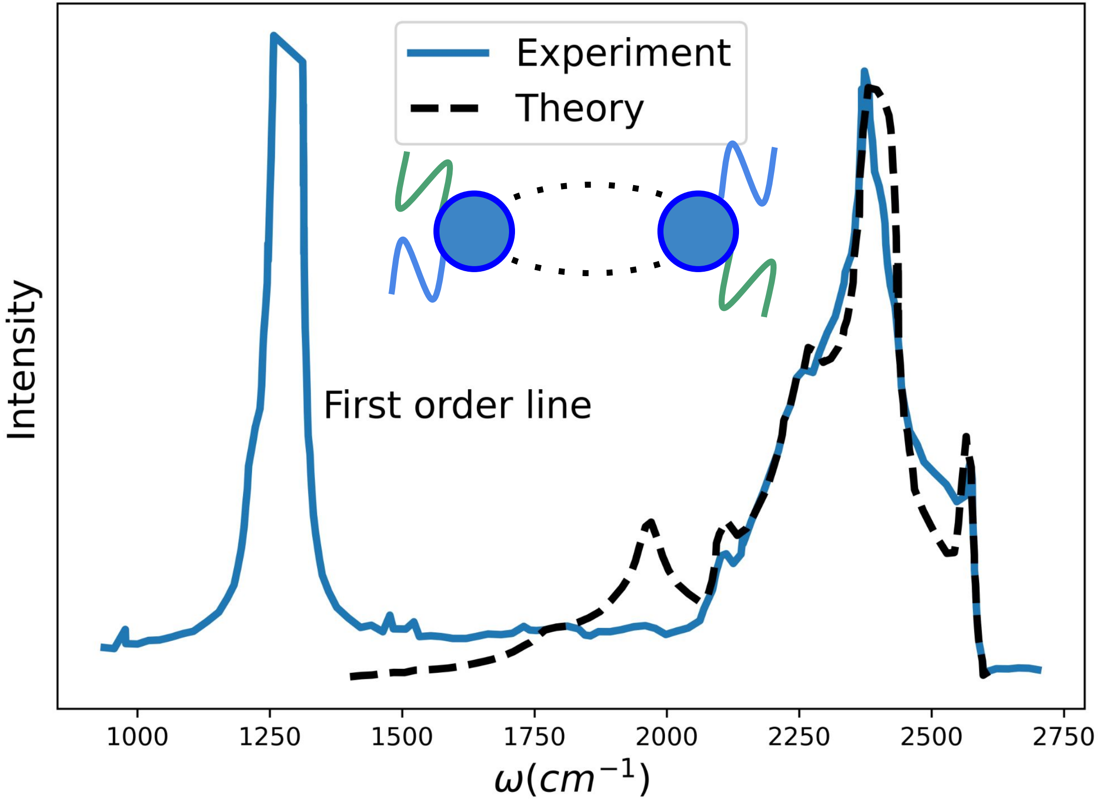
Refs: G. Deinzer and D. Strauch Phys. Rev. B 69, 045205, 2004

Two-phonon Raman

$$I(\omega)_{\text{Raman}} \propto -\text{Im}\left(\sum_{\mu}^{\text{opt}} \frac{\partial \Xi_{\alpha\beta,\mu}}{\partial R_\nu} \chi^{(0)}_{\mu\nu}(\omega) \frac{\partial \Xi_{\alpha\beta,\mu}}{\partial R_\nu}\right)$$

Diamond



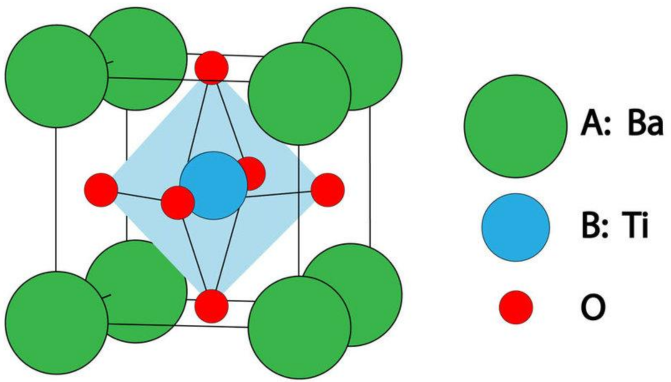


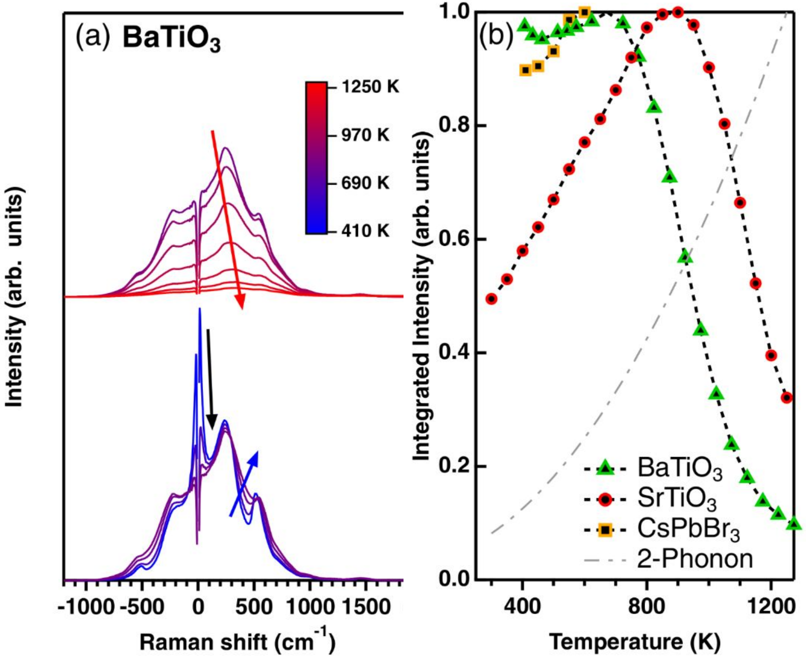
- **Expensive DFPT calculations**
- **Low symmetry?**
- **Is always harmonic theory enough?**
- **Anharmonic**

\+ **2ph example?**

Refs: W. Windl et al.. Phys. Rev. B 49, 8764, 1994

Two-phonon + anharmonic effects





Anharmonic DW with tunneling

= dynamical disorder + average cubic symmetry (no Raman)

Refs: M. Menahem et al. Phys. Rev. Materials 7, 044602, 2023; R. Masuki, et al., Phys. Rev. B 106, 224104, 2022

Infrared and Raman as response function

$$I_{\mathrm{IR}}(\omega) \propto -\,\mathrm{Im}\left(\sum_{\nu\mu}^{\mathrm{opt}} Z_{\alpha,\mu}\mathcal{G}^{(0)}_{\mu\nu}(\omega)Z_{\beta,\nu}\right)$$

$$\propto -\,\mathrm{Im}\left(\int dt e^{i\omega t}\sum_{\mu\nu}^{\mathrm{opt}} Z_{\alpha,\mu}\left\langle u_{\mu}(t)u_{\nu}(0)\right\rangle Z_{\beta,\nu}\right)$$

$$\propto -\,\mathrm{Im}\left(\int dt e^{i\omega t}\left\langle p_{\alpha}(t)p_{\beta}(0)\right\rangle\right)$$

dipole correlation function

↓

same for Raman

Infrared and Raman as response function

- **Useful formulation for MD**
- **Physical picture?**

$$I_{\mathrm{IR}}(\omega) \propto -\operatorname{Im}\left(\sum_{\nu\mu}^{\mathrm{opt}} Z_{\alpha,\mu}\mathcal{G}^{(0)}_{\mu\nu}(\omega)Z_{\beta,\nu}\right)$$

$$\propto -\operatorname{Im}\left(\int dte^{i\omega t}\sum_{\mu\nu}^{\mathrm{opt}} Z_{\alpha,\mu}\left\langle u_{\mu}(t)u_{\nu}(0)\right\rangle Z_{\beta,\nu}\right)$$

$$\propto -\operatorname{Im}\left(\int dte^{i\omega t}\left\langle p_{\alpha}(t)p_{\beta}(0)\right\rangle\right)$$

dipole correlation function

$$I_{\mathrm{Raman}}(\omega) \propto -\operatorname{Im}\left(\int dte^{i\omega t}\left\langle \chi_{\alpha\beta}(t)\chi_{\alpha\beta}(0)\right\rangle\right)$$

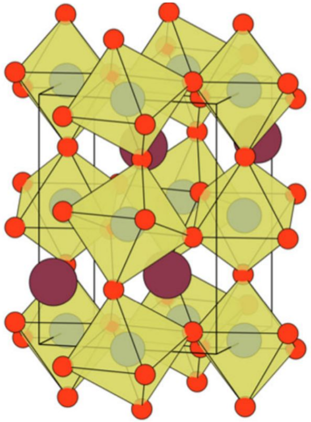
polarizability correlation function

What is a response function?

$$\int dt e^{i\omega t} \langle p_\alpha(t) p_\beta(0) \rangle \qquad \int dt e^{i\omega t} \langle \chi_{\alpha\beta}(t) \chi_{\eta\lambda}(0) \rangle$$

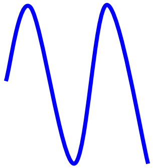
Probe field, e.g. how the material reacts

$$\langle \mathcal{A}(\boldsymbol{R}) \rangle_{(0)} + \langle \mathcal{A}(\boldsymbol{R}) \rangle_{(1)}$$

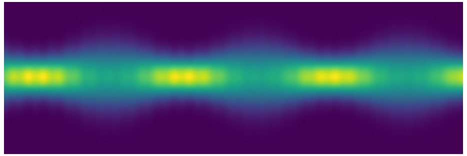


Pump field (small), e.g. X-ray, neutrons, Infrared, Raman etc.

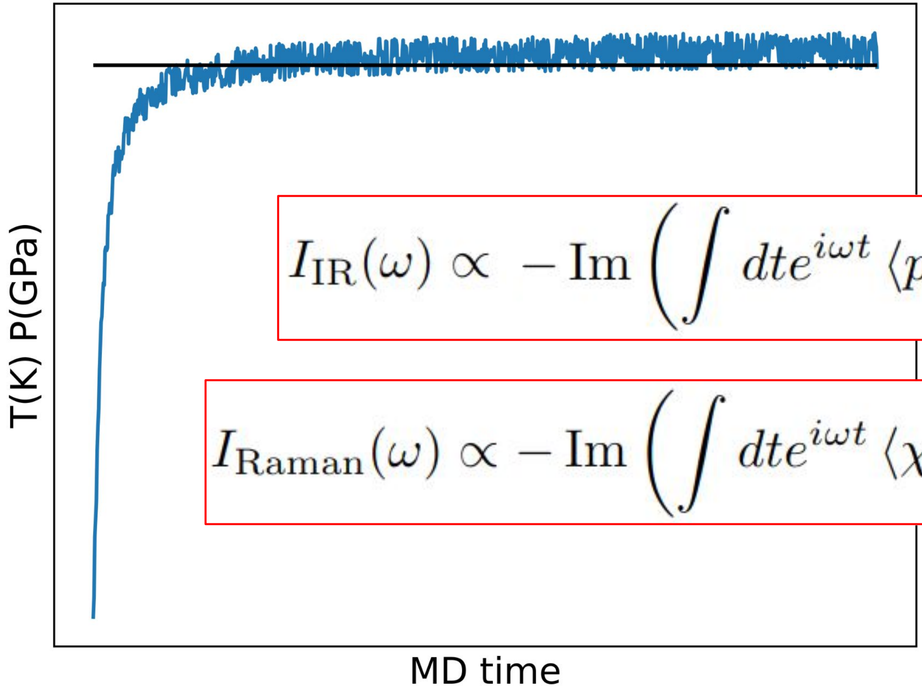
$$\mathcal{B}(\boldsymbol{R}) \mathcal{V}(t)$$



Trigger the interactions in the material



Infrared and Raman as response function



Molecular dynamics (classical) average on the atomic equilibrium ensemble

$$I_{\mathrm{IR}}(\omega) \propto -\mathrm{Im}\left(\int dt e^{i\omega t} \langle p_\alpha(t) p_\beta(0)\rangle\right)$$

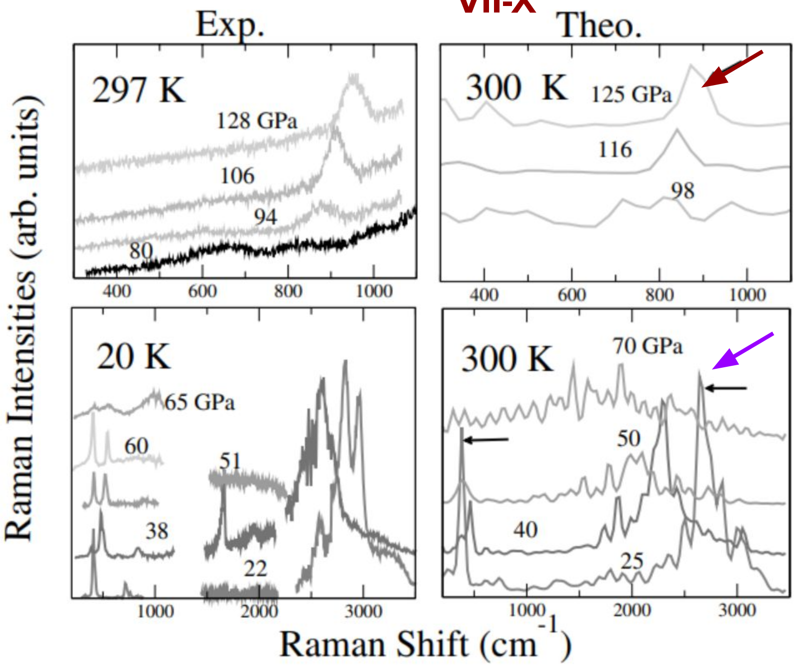
$$I_{\mathrm{Raman}}(\omega) \propto -\mathrm{Im}\left(\int dt e^{i\omega t} \langle \chi_{\alpha\beta}(t) \chi_{\eta\lambda}(0)\rangle\right)$$

A practical MD example before the SCHA theory...

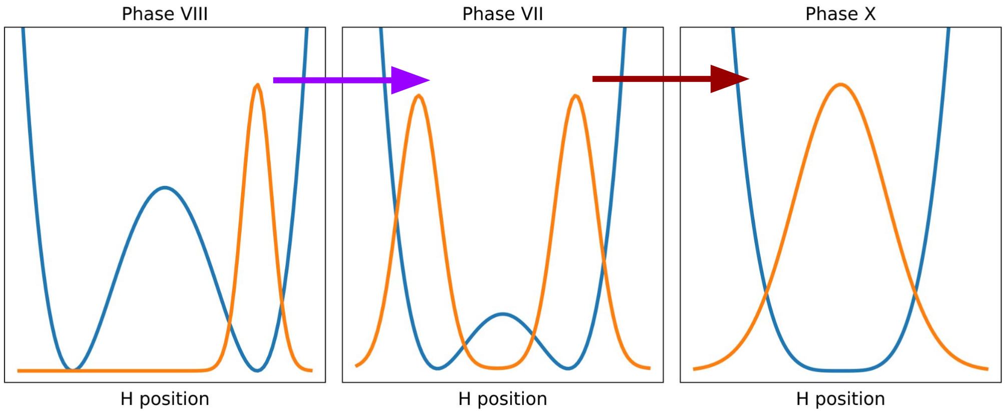
Molecular Dynamics Raman

$$I_{\text{Raman}}(\omega) \propto -\text{Im}\left(\int dt e^{i\omega t} \langle \chi_{\alpha\beta}(t)\chi_{\eta\lambda}(0)\rangle\right)$$

VII-X



VIII-VII



O-H stretching disappears O-O stretching appears

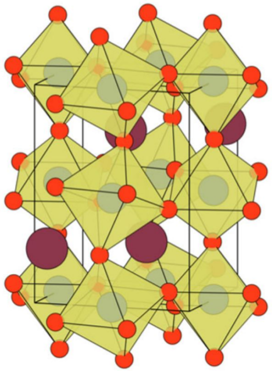
Classic + full anharmonic. **Quantum???**

Refs: A. Putrino and M. Parrinello, Phys. Rev. Lett. 88, 176401, 2002

Time-dependent phenomena

- We consider N particles at equilibrium in the Born-Oppenheimer approximation

$$H^{(\mathrm{BO})} = \sum_{a=1}^{3N} \frac{P_a^2}{2m_a} + V^{(\mathrm{BO})}(\boldsymbol{R})$$

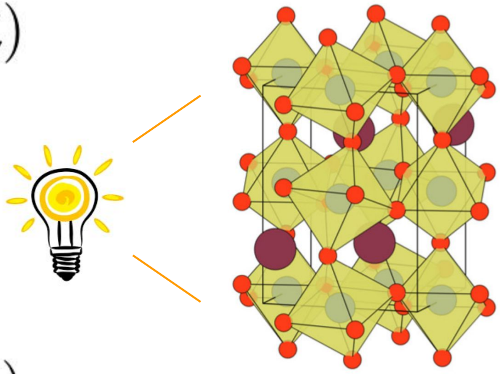


Time-dependent phenomena

- We consider N particles at equilibrium in the Born-Oppenheimer approximation:

$$H^{(\mathrm{BO})} = \sum_{a=1}^{3N} \frac{P_a^2}{2m_a} + V^{(\mathrm{BO})}(\boldsymbol{R})$$

- An external potential is turned on:



$$H(t) = \sum_{a=1}^{3N} \frac{P_a^2}{2m_a} + V^{(\mathrm{tot})}(\boldsymbol{R}, t)$$

Mediated by electrons!

$$V^{(\mathrm{tot})}(\boldsymbol{R}, t) = V^{(\mathrm{BO})}(\boldsymbol{R}) + V^{(\mathrm{ext})}(\boldsymbol{R}, t)$$

Classical and quantum evolution

- The classical Liouville evolution

$$\frac{\partial}{\partial t}\rho_{\mathrm{cl}}(\boldsymbol{R},\boldsymbol{P},t) + i\mathcal{L}^{\mathrm{cl}}\rho_{\mathrm{cl}}(\boldsymbol{R},\boldsymbol{P},t) = 0 \qquad i\mathcal{L}^{\mathrm{cl}}\circ = -H(t)\overleftrightarrow{\Lambda}\circ$$

Poisson brackets

$$\overleftrightarrow{\Lambda} = \sum_{a=1}^{3N}\left(\frac{\overleftarrow{\partial}}{\partial R_a}\frac{\overrightarrow{\partial}}{\partial P_a} - \frac{\overleftarrow{\partial}}{\partial P_a}\frac{\overrightarrow{\partial}}{\partial R_a}\right)$$

Classical and quantum evolution

- The classical Liouville evolution

$$\frac{\partial}{\partial t}\rho_{\mathrm{cl}}(\boldsymbol{R},\boldsymbol{P},t) + i\mathcal{L}^{\mathrm{cl}}\rho_{\mathrm{cl}}(\boldsymbol{R},\boldsymbol{P},t) = 0 \qquad i\mathcal{L}^{\mathrm{cl}}\circ = -H(t)\overleftrightarrow{\Lambda}\circ$$

- The Wigner-Liouville quantum approach

$$\rho_{\mathrm{w}}(\boldsymbol{R},\boldsymbol{P},t) = \int \frac{d\boldsymbol{R}' e^{-\frac{i}{\hbar}\boldsymbol{P}\cdot\boldsymbol{R}'}}{(2\pi\hbar)^{3N}} \left\langle \boldsymbol{R} + \frac{\boldsymbol{R}'}{2} \middle| \hat{\rho}(t) \middle| \boldsymbol{R} - \frac{\boldsymbol{R}'}{2} \right\rangle$$

Quasi distribution

$$O_{\mathrm{w}}(\boldsymbol{R},\boldsymbol{P}) = \int d\boldsymbol{R}' e^{-\frac{i}{\hbar}\boldsymbol{P}\cdot\boldsymbol{R}'} \left\langle \boldsymbol{R} + \frac{\boldsymbol{R}'}{2} \middle| \hat{O} \middle| \boldsymbol{R} - \frac{\boldsymbol{R}'}{2} \right\rangle$$

Replace density matrix and operators with functions

Classical and quantum evolution

- The classical Liouville evolution

$$\frac{\partial}{\partial t}\rho_{\text{cl}}(\boldsymbol{R},\boldsymbol{P},t) + i\mathcal{L}^{\text{cl}}\rho_{\text{cl}}(\boldsymbol{R},\boldsymbol{P},t) = 0 \qquad i\mathcal{L}^{\text{cl}}\circ = -H(t)\overleftrightarrow{\Lambda}\circ$$

- The Wigner-Liouville quantum approach

$$\rho_{\text{w}}(\boldsymbol{R},\boldsymbol{P},t) = \int \frac{d\boldsymbol{R}' e^{-\frac{i}{\hbar}\boldsymbol{P}\cdot\boldsymbol{R}'}}{(2\pi\hbar)^{3N}} \left\langle \boldsymbol{R} + \frac{\boldsymbol{R}'}{2} \right| \hat{\rho}(t) \left| \boldsymbol{R} - \frac{\boldsymbol{R}'}{2} \right\rangle$$

$$O_{\text{w}}(\boldsymbol{R},\boldsymbol{P}) = \int d\boldsymbol{R}' e^{-\frac{i}{\hbar}\boldsymbol{P}\cdot\boldsymbol{R}'} \left\langle \boldsymbol{R} + \frac{\boldsymbol{R}'}{2} \right| \hat{O} \left| \boldsymbol{R} - \frac{\boldsymbol{R}'}{2} \right\rangle$$

$$\boxed{\langle O_{\text{w}} \rangle_{\rho_{\text{w}}} = \int d\boldsymbol{R} \int d\boldsymbol{P} O_{\text{w}}(\boldsymbol{R},\boldsymbol{P})\rho_{\text{w}}(\boldsymbol{R},\boldsymbol{P},t)}$$

Classical and quantum evolution

- The classical Liouville evolution

$$\frac{\partial}{\partial t}\rho_{\mathrm{cl}}(\boldsymbol{R},\boldsymbol{P},t) + i\mathcal{L}^{\mathrm{cl}}\rho_{\mathrm{cl}}(\boldsymbol{R},\boldsymbol{P},t) = 0 \qquad i\mathcal{L}^{\mathrm{cl}}\circ = -H(t)\overset{\leftrightarrow}{\Lambda}\circ$$

- The Wigner-Liouville evolution

$$\frac{\partial}{\partial t}\rho_{\mathrm{w}}(\boldsymbol{R},\boldsymbol{P},t) + i\mathcal{L}\rho_{\mathrm{w}}(\boldsymbol{R},\boldsymbol{P},t) = 0 \qquad i\mathcal{L} = i\mathcal{L}^{\mathrm{cl}} + i\mathcal{L}^{\mathrm{q}}$$

Quantum effects as
high power
of Poisson brackets

$$\boxed{i\mathcal{L}^{\mathrm{q}}\circ = -\sum_{n=1}^{+\infty}\frac{(-\hbar^2)^n}{2^{2n}(2n+1)!}H(t)\left(\overset{\leftrightarrow}{\Lambda}\right)^{2n+1}\circ}$$

- **Quantum chemistry**: quantum initial condition with P.I. + classical evolution
- SCHA = Gaussian = Harmonic...

Classical and quantum evolution

- The classical Liouville evolution

$$\frac{\partial}{\partial t}\rho_{\rm cl}(\boldsymbol{R},\boldsymbol{P},t) + i\mathcal{L}^{\rm cl}\rho_{\rm cl}(\boldsymbol{R},\boldsymbol{P},t) = 0 \qquad i\mathcal{L}^{\rm cl}\circ = -H(t)\overleftrightarrow{\Lambda}\circ$$

- The Wigner-Liouville quantum evolution:

$$\frac{\partial}{\partial t}\rho_{\rm w}(\boldsymbol{R},\boldsymbol{P},t) + i\mathcal{L}\rho_{\rm w}(\boldsymbol{R},\boldsymbol{P},t) = 0 \qquad i\mathcal{L} = i\mathcal{L}^{\rm cl} + i\mathcal{L}^{\rm q}$$

$$i\mathcal{L}^{\rm q}\circ = -\sum_{n=1}^{+\infty}\frac{(-\hbar^2)^n}{2^{2n}(2n+1)!}H(t)\left(\overleftrightarrow{\Lambda}\right)^{2n+1}\circ$$

- When do they coincide?

$$H(t) = \sum_{a=1}^{3N}\frac{P_a^2}{2m_a} + \frac{1}{2}\sum_{ab=1}^{3N}(R-R_0(t))_a K_0(t)_{ab}(R-R_0(t))_b$$

Classical=Quantum

TD-SCHA...

Time-Dependent SCHA

- Gaussian approximation in the Wigner-Liouville formalism

$$\tilde{\rho}(t) = \mathcal{N}(t)\exp\Big[-\frac{1}{2}(\boldsymbol{R}-\boldsymbol{\mathcal{R}}(t))\cdot\boldsymbol{\alpha}(t)\cdot(\boldsymbol{R}-\boldsymbol{\mathcal{R}}(t))$$
$$-\frac{1}{2}(\boldsymbol{P}-\boldsymbol{\mathcal{P}}(t))\cdot\boldsymbol{\beta}(t)\cdot(\boldsymbol{P}-\boldsymbol{\mathcal{P}}(t))$$
$$+(\boldsymbol{R}-\boldsymbol{\mathcal{R}}(t))\cdot\boldsymbol{\gamma}(t)\cdot(\boldsymbol{P}-\boldsymbol{\mathcal{P}}(t))\Big]$$

Ansatz for the Wigner distribution!
Red = free parameters

position-momentum coupling ensures quantum effects

Refs: L.Monacelli, F. Mauri, PRB 103, 104305 2021; A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

Time-Dependent SCHA

- Gaussian approximation in the Wigner-Liouville formalism

$$\widetilde{\rho}(t) = \mathcal{N}(t)\exp\Big[-\frac{1}{2}(\boldsymbol{R}-\boldsymbol{\mathcal{R}}(t))\cdot\boldsymbol{\alpha}(t)\cdot(\boldsymbol{R}-\boldsymbol{\mathcal{R}}(t)) \\ -\frac{1}{2}(\boldsymbol{P}-\boldsymbol{\mathcal{P}}(t))\cdot\boldsymbol{\beta}(t)\cdot(\boldsymbol{P}-\boldsymbol{\mathcal{P}}(t)) \\ +(\boldsymbol{R}-\boldsymbol{\mathcal{R}}(t))\cdot\boldsymbol{\gamma}(t)\cdot(\boldsymbol{P}-\boldsymbol{\mathcal{P}}(t))\Big]$$

- **Self-consistent evolution**

$$\frac{\partial}{\partial t}\widetilde{\rho}(t) + i\mathcal{L}^{\mathrm{sc}}\widetilde{\rho}(t) = 0 \qquad i\mathcal{L}^{\mathrm{sc}}\circ = -\mathcal{H}(\widetilde{\rho})\overset{\leftrightarrow}{\Lambda}\circ$$

$$\mathcal{H}(\widetilde{\rho}) = \sum_{a=1}^{3N}\frac{P_a^2}{2m_a} + \delta\boldsymbol{R}(t)\cdot\left\langle\frac{\partial V^{(\mathrm{tot})}(\boldsymbol{R},t)}{\partial\boldsymbol{R}}\right\rangle_{\widetilde{\rho}(t)} + \frac{1}{2}\delta\boldsymbol{R}(t)\cdot\left\langle\frac{\partial^2 V^{(\mathrm{tot})}(\boldsymbol{R},t)}{\partial\boldsymbol{R}\partial\boldsymbol{R}}\right\rangle_{\widetilde{\rho}(t)}\cdot\delta\boldsymbol{R}(t)$$

Time-Dependent SCHA

- Equations for equal-time correlators (free parameters)

- Newton (Ehrenfest) equations of motion

$$\frac{d}{dt}\left\langle \widetilde{\boldsymbol{R}}\right\rangle_{\widetilde{\rho}(t)} = \left\langle \widetilde{\boldsymbol{P}}\right\rangle_{\widetilde{\rho}(t)}$$

$$\frac{d}{dt}\left\langle \widetilde{\boldsymbol{P}}\right\rangle_{\widetilde{\rho}(t)} = -\left\langle \frac{\partial V^{(\mathrm{tot})}}{\partial \widetilde{\boldsymbol{R}}}\right\rangle_{\widetilde{\rho}(t)}$$

$$\frac{d}{dt}\left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{R}}\right\rangle_{\widetilde{\rho}(t)} = \left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{P}}\right\rangle_{\widetilde{\rho}(t)} + \left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{R}}\right\rangle_{\widetilde{\rho}(t)}$$

$$\frac{d}{dt}\left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{P}}\right\rangle_{\widetilde{\rho}(t)} = -\left\langle \frac{\partial^2 V^{(\mathrm{tot})}}{\partial \widetilde{\boldsymbol{R}}\partial \widetilde{\boldsymbol{R}}}\right\rangle_{\widetilde{\rho}(t)} \cdot \left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{P}}\right\rangle_{\widetilde{\rho}(t)} - \left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{R}}\right\rangle_{\widetilde{\rho}(t)} \cdot \left\langle \frac{\partial^2 V^{(\mathrm{tot})}}{\partial \widetilde{\boldsymbol{R}}\partial \widetilde{\boldsymbol{R}}}\right\rangle_{\widetilde{\rho}(t)}$$

$$\frac{d}{dt}\left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{P}}\right\rangle_{\widetilde{\rho}(t)} = \left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{P}}\right\rangle_{\widetilde{\rho}(t)} - \left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{R}}\right\rangle_{\widetilde{\rho}(t)} \cdot \left\langle \frac{\partial^2 V^{(\mathrm{tot})}}{\partial \widetilde{\boldsymbol{R}}\partial \widetilde{\boldsymbol{R}}}\right\rangle_{\widetilde{\rho}(t)}$$

Time-Dependent SCHA

- Equations for equal-time correlators (free parameters)

$$\frac{d}{dt}\left\langle \widetilde{\boldsymbol{R}} \right\rangle_{\widetilde{\rho}(t)} = \left\langle \widetilde{\boldsymbol{P}} \right\rangle_{\widetilde{\rho}(t)}$$

$$\frac{d}{dt}\left\langle \widetilde{\boldsymbol{P}} \right\rangle_{\widetilde{\rho}(t)} = -\left\langle \frac{\partial V^{(\mathrm{tot})}}{\partial \widetilde{\boldsymbol{R}}} \right\rangle_{\widetilde{\rho}(t)}$$

$$\frac{d}{dt}\left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{R}} \right\rangle_{\widetilde{\rho}(t)} = \left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{\widetilde{\rho}(t)} + \left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{R}} \right\rangle_{\widetilde{\rho}(t)}$$

$$\frac{d}{dt}\left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{\widetilde{\rho}(t)} = -\left\langle \frac{\partial^2 V^{(\mathrm{tot})}}{\partial \widetilde{\boldsymbol{R}}\partial \widetilde{\boldsymbol{R}}} \right\rangle_{\widetilde{\rho}(t)} \cdot \left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{\widetilde{\rho}(t)} - \left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{R}} \right\rangle_{\widetilde{\rho}(t)} \cdot \left\langle \frac{\partial^2 V^{(\mathrm{tot})}}{\partial \widetilde{\boldsymbol{R}}\partial \widetilde{\boldsymbol{R}}} \right\rangle_{\widetilde{\rho}(t)}$$

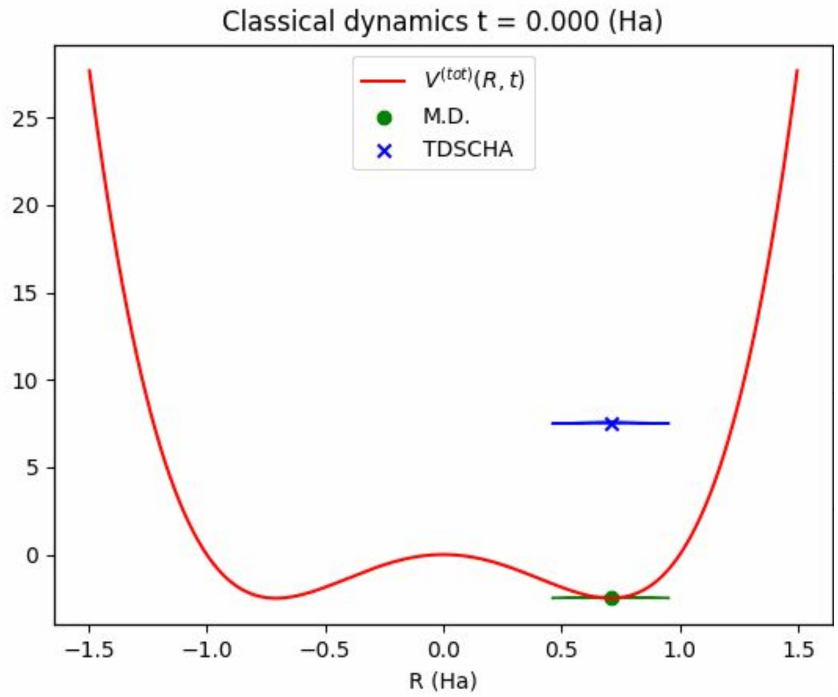
$$\frac{d}{dt}\left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{\widetilde{\rho}(t)} = \left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{\widetilde{\rho}(t)} - \left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{R}} \right\rangle_{\widetilde{\rho}(t)} \cdot \left\langle \frac{\partial^2 V^{(\mathrm{tot})}}{\partial \widetilde{\boldsymbol{R}}\partial \widetilde{\boldsymbol{R}}} \right\rangle_{\widetilde{\rho}(t)}$$

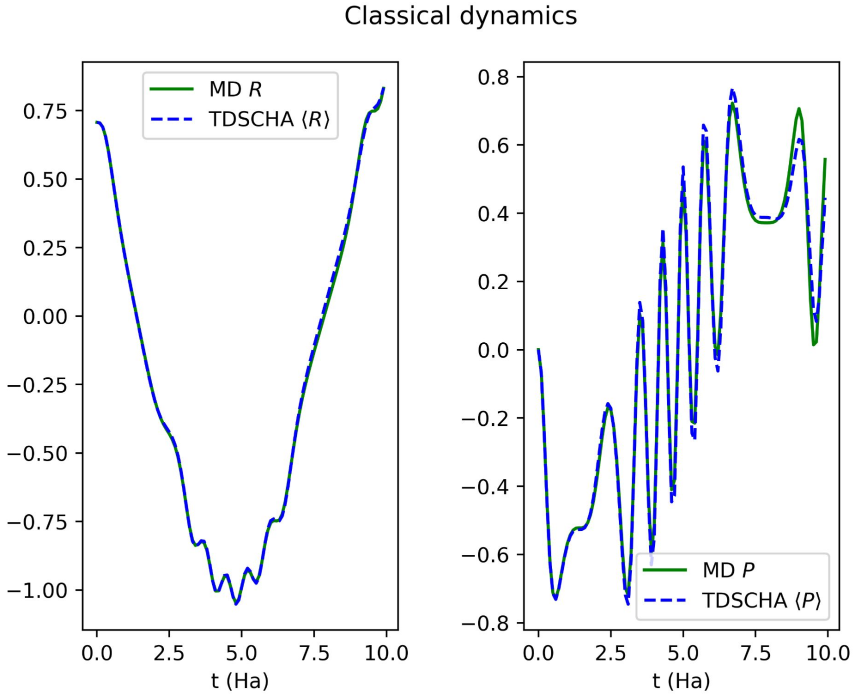
- Newton (Ehrenfest) equations of motion
- **Equal time correlators = free parameters**
- Momentum (diffusion, transport)

- Quantum/classical evolution

Time-Dependent SCHA

- Classical evolution = MD!





Time-Dependent SCHA

- Equations for equal-time correlators (free parameters)

$$\frac{d}{dt}\left\langle \widetilde{\boldsymbol{R}} \right\rangle_{\widetilde{\rho}(t)} = \left\langle \widetilde{\boldsymbol{P}} \right\rangle_{\widetilde{\rho}(t)}$$

$$\frac{d}{dt}\left\langle \widetilde{\boldsymbol{P}} \right\rangle_{\widetilde{\rho}(t)} = -\left\langle \frac{\partial V^{(\mathrm{tot})}}{\partial \widetilde{\boldsymbol{R}}} \right\rangle_{\widetilde{\rho}(t)}$$

$$\frac{d}{dt}\left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{R}} \right\rangle_{\widetilde{\rho}(t)} = \left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{\widetilde{\rho}(t)} + \left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{R}} \right\rangle_{\widetilde{\rho}(t)}$$

$$\frac{d}{dt}\left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{\widetilde{\rho}(t)} = -\left\langle \frac{\partial^2 V^{(\mathrm{tot})}}{\partial \widetilde{\boldsymbol{R}}\partial \widetilde{\boldsymbol{R}}} \right\rangle_{\widetilde{\rho}(t)} \cdot \left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{\widetilde{\rho}(t)} - \left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{R}} \right\rangle_{\widetilde{\rho}(t)} \cdot \left\langle \frac{\partial^2 V^{(\mathrm{tot})}}{\partial \widetilde{\boldsymbol{R}}\partial \widetilde{\boldsymbol{R}}} \right\rangle_{\widetilde{\rho}(t)}$$

$$\frac{d}{dt}\left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{\widetilde{\rho}(t)} = \left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{\widetilde{\rho}(t)} - \left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{R}} \right\rangle_{\widetilde{\rho}(t)} \cdot \left\langle \frac{\partial^2 V^{(\mathrm{tot})}}{\partial \widetilde{\boldsymbol{R}}\partial \widetilde{\boldsymbol{R}}} \right\rangle_{\widetilde{\rho}(t)}$$

- Newton (Ehrenfest) equations of motion
- Equal time correlators
- Momentum (diffusion, transport)

Semiclassical? NO
Non perturbative
anharmonic!

- Quantum/classical evolution
- TDSCHA is exact for quantum TD harmonic oscillator

Time-Dependent SCHA: stationary solution

- Stationary solution of TD-SCHA = SCHA!

$$\tilde{\rho}^{(0)}(\boldsymbol{R},\boldsymbol{P}) = \mathcal{N}^{(0)} \exp\left[-\frac{1}{2}\tilde{\boldsymbol{P}}\cdot\left\langle\tilde{\boldsymbol{P}}\tilde{\boldsymbol{P}}\right\rangle_{(0)}^{-1}\cdot\tilde{\boldsymbol{P}} - \frac{1}{2}\delta\tilde{\boldsymbol{R}}\cdot\left\langle\delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{R}}\right\rangle_{(0)}^{-1}\cdot\delta\tilde{\boldsymbol{R}}\right]$$

Non diagonal correlations = quantum

$$\left\langle\frac{\partial V^{\mathrm{BO}}}{\partial\tilde{\boldsymbol{R}}}\right\rangle_{(0)} = \boldsymbol{0} \quad \left\langle\tilde{\boldsymbol{P}}\right\rangle_{(0)} = \boldsymbol{0} \qquad \left\langle\delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{P}}\right\rangle_{(0)} = \boldsymbol{0}$$

$$\left\langle\delta\tilde{\boldsymbol{P}}\delta\tilde{\boldsymbol{P}}\right\rangle_{(0)} = \left\langle\delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{R}}\right\rangle_{(0)}\cdot\left\langle\frac{\partial^2 V^{(\mathrm{BO})}}{\partial\tilde{\boldsymbol{R}}\partial\tilde{\boldsymbol{R}}}\right\rangle_{(0)}$$

Equilibrium condition + no R-P correlations + sc equipartion theorem
propagators?

Time-Dependent SCHA: stationary solution

- Stationary solution of TD-SCHA = SCHA!

$$\widetilde{\rho}^{(0)}(\boldsymbol{R},\boldsymbol{P}) = \mathcal{N}^{(0)} \exp\left[-\frac{1}{2}\widetilde{\boldsymbol{P}}\cdot\left\langle\widetilde{\boldsymbol{P}}\widetilde{\boldsymbol{P}}\right\rangle_{(0)}^{-1}\cdot\widetilde{\boldsymbol{P}} - \frac{1}{2}\delta\widetilde{\boldsymbol{R}}\cdot\left\langle\delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{R}}\right\rangle_{(0)}^{-1}\cdot\delta\widetilde{\boldsymbol{R}}\right]$$

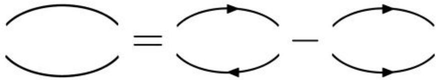
SCHA Phonons = $\left\langle \frac{\partial^2 V^{(\mathrm{BO})}}{\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}} \right\rangle_{(0)}$

SCHA single and double propagators: starting point of linear response

<u>N.B.: auxiliary quantities as KS orbitals in DFT</u>

$$\boldsymbol{\mathcal{G}}^{(0)}(\omega) = \text{———} = \frac{\delta_{\mu\nu}}{\omega^2-\omega_\mu^2}$$

$\boldsymbol{\chi}^{(0)}(\omega) =$



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

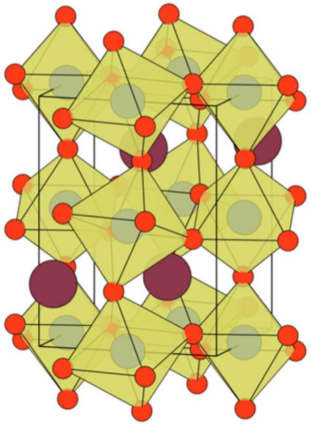
Time-Dependent SCHA: linear response

- Infrared and Raman simulation: we know the response formula!

$$\int dt e^{i\omega t} \langle p_\alpha(t) p_\beta(0) \rangle \qquad \int dt e^{i\omega t} \langle \chi_{\alpha\beta}(t) \chi_{\eta\lambda}(0) \rangle$$

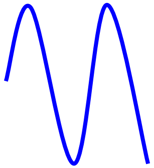
Probe field, e.g. how the material reacts

$$\langle \mathcal{A}(\boldsymbol{R}) \rangle_{(0)} + \langle \mathcal{A}(\boldsymbol{R}) \rangle_{(1)}$$



Perturb the SCHA equilibrium solution

$$\widetilde{\rho}(t) = \widetilde{\rho}^{(0)} + \widetilde{\rho}^{(1)}(t)$$



$$\mathcal{B}(\boldsymbol{R})\mathcal{V}(t)$$

Mediated by electrons

Refs: L.Monacelli, F. Mauri, PRB 103, 104305 2021; A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

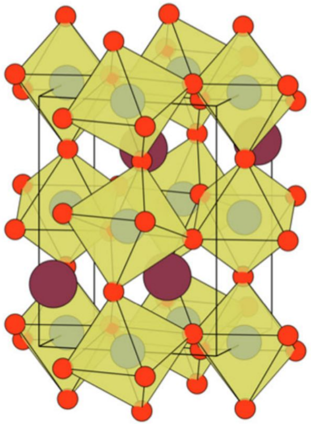
Time-Dependent SCHA: linear response

- Infrared and Raman simulation: we know the response formula!

$$\int dt e^{i\omega t} \langle p_\alpha(t) p_\beta(0) \rangle \qquad \int dt e^{i\omega t} \langle \chi_{\alpha\beta}(t) \chi_{\eta\lambda}(0) \rangle$$

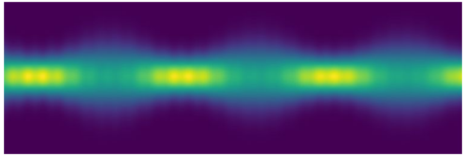
Probe field, e.g. how the material reacts

$$\langle \mathcal{A}(\boldsymbol{R}) \rangle_{(0)} + \langle \mathcal{A}(\boldsymbol{R}) \rangle_{(1)}$$



Perturb the SCHA equilibrium solution
= perturb the correlators (free parameters)

$$\boldsymbol{\mathcal{L}}(\omega) \cdot \begin{bmatrix} \widetilde{\boldsymbol{\mathcal{R}}}^{(1)} \\ \left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{R}} \right\rangle_{(1)} \\ \left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{(1)} \end{bmatrix} = \boldsymbol{p}\mathcal{V}(\omega)$$



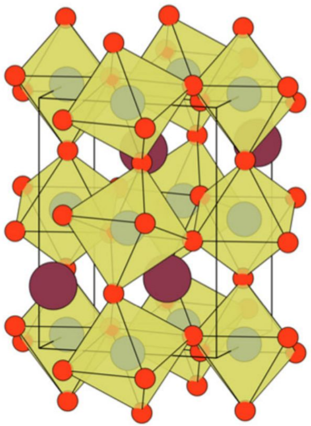
Time-Dependent SCHA: linear response

- Infrared and Raman simulation: we know the response formula!

$$\int dt e^{i\omega t} \langle p_\alpha(t) p_\beta(0) \rangle \qquad \int dt e^{i\omega t} \langle \chi_{\alpha\beta}(t) \chi_{\eta\lambda}(0) \rangle$$

Probe field, e.g. how the material reacts

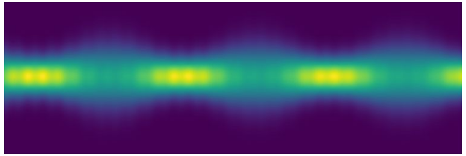
$$\langle \mathcal{A} \rangle_{(1)}(\omega) = \boldsymbol{r}^\dagger \cdot \begin{bmatrix} \widetilde{\boldsymbol{\mathcal{R}}}^{(1)} \\ \left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{R}} \right\rangle_{(1)} \\ \left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{(1)} \end{bmatrix}$$



Perturb the SCHA equilibrium solution

$$\boldsymbol{\mathcal{L}}(\omega) \cdot \begin{bmatrix} \widetilde{\boldsymbol{\mathcal{R}}}^{(1)} \\ \left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{R}} \right\rangle_{(1)} \\ \left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{(1)} \end{bmatrix} = \boldsymbol{p}\mathcal{V}(\omega)$$

Gaussian

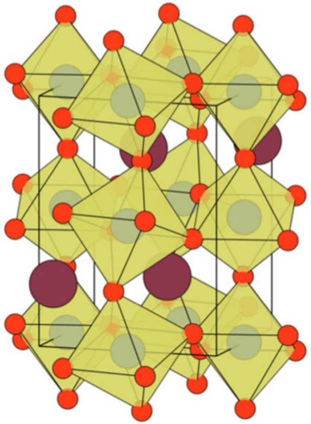


Time-Dependent SCHA: linear response

- How to build the response?

Probe field, e.g. how the material reacts

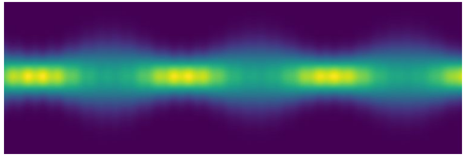
$$\langle \mathcal{A} \rangle_{(1)}(\omega) = \boldsymbol{r}^\dagger \cdot \begin{bmatrix} \widetilde{\boldsymbol{\mathcal{R}}}^{(1)} \\ \left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{R}} \right\rangle_{(1)} \\ \left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{(1)} \end{bmatrix}$$



Perturb the SCHA equilibrium solution

$$\boldsymbol{\mathcal{L}}(\omega) \cdot \begin{bmatrix} \widetilde{\boldsymbol{\mathcal{R}}}^{(1)} \\ \left\langle \delta\widetilde{\boldsymbol{R}}\delta\widetilde{\boldsymbol{R}} \right\rangle_{(1)} \\ \left\langle \delta\widetilde{\boldsymbol{P}}\delta\widetilde{\boldsymbol{P}} \right\rangle_{(1)} \end{bmatrix} = \boldsymbol{p}\mathcal{V}(\omega)$$

Gaussian

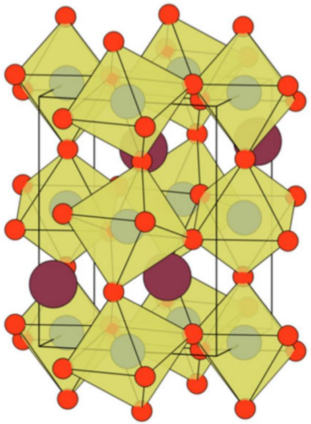


$$\chi(\omega)_{\mathcal{A},\mathcal{B}} = \boldsymbol{r}^\dagger \cdot \boldsymbol{\mathcal{L}}(\omega)^{-1} \cdot \boldsymbol{p}$$

Expression?

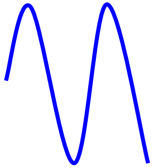
Probe field, e.g. how the material reacts

$$\langle \mathcal{A}(\boldsymbol{R}) \rangle_{(0)} + \langle \mathcal{A}(\boldsymbol{R}) \rangle_{(1)}$$



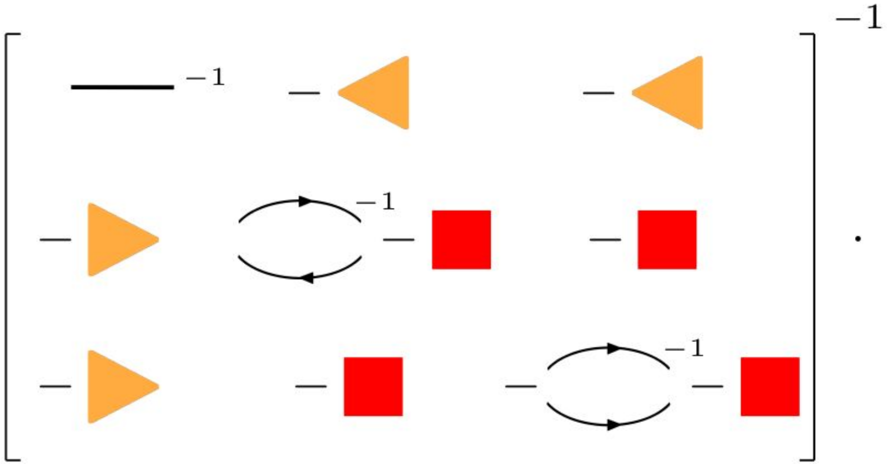
Pump field (small), e.g. X-ray, neutrons, Infrared, Raman etc.

$$\mathcal{B}(\boldsymbol{R})\mathcal{V}(t)$$



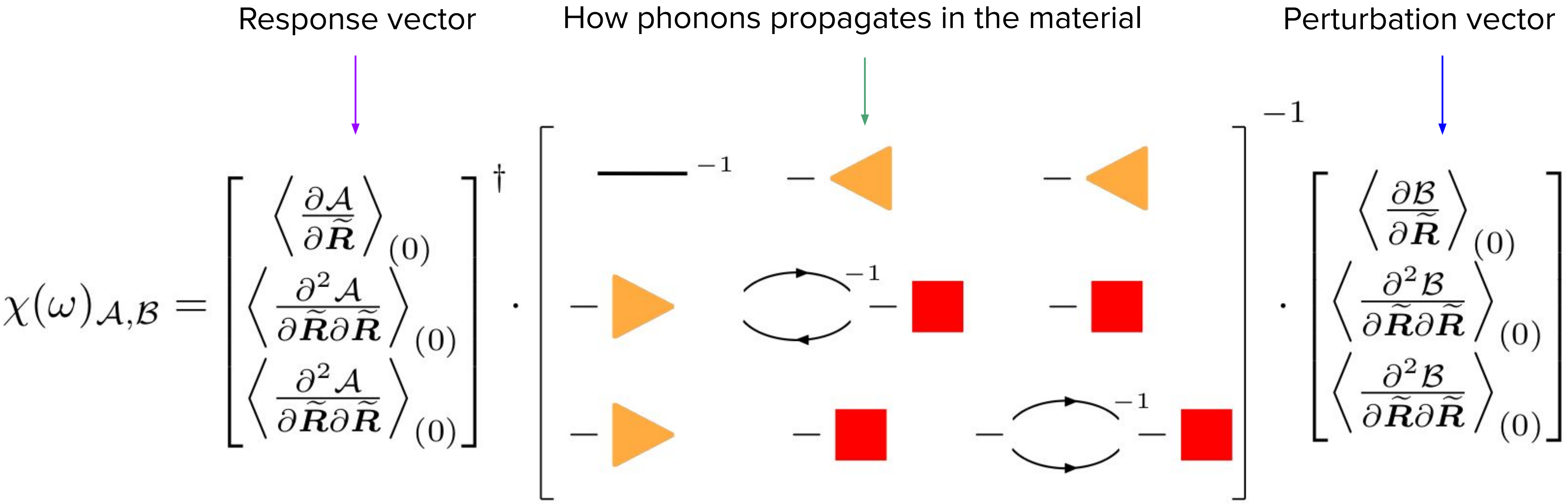
What is this in TDSCHA? A simple (?) matrix vector product

$$\chi(\omega)_{\mathcal{A},\mathcal{B}} = \begin{bmatrix} \left\langle \frac{\partial \mathcal{A}}{\partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 \mathcal{A}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 \mathcal{A}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \end{bmatrix}^{\dagger} \cdot$$



$$\cdot \begin{bmatrix} \left\langle \frac{\partial \mathcal{B}}{\partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 \mathcal{B}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 \mathcal{B}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \end{bmatrix}$$

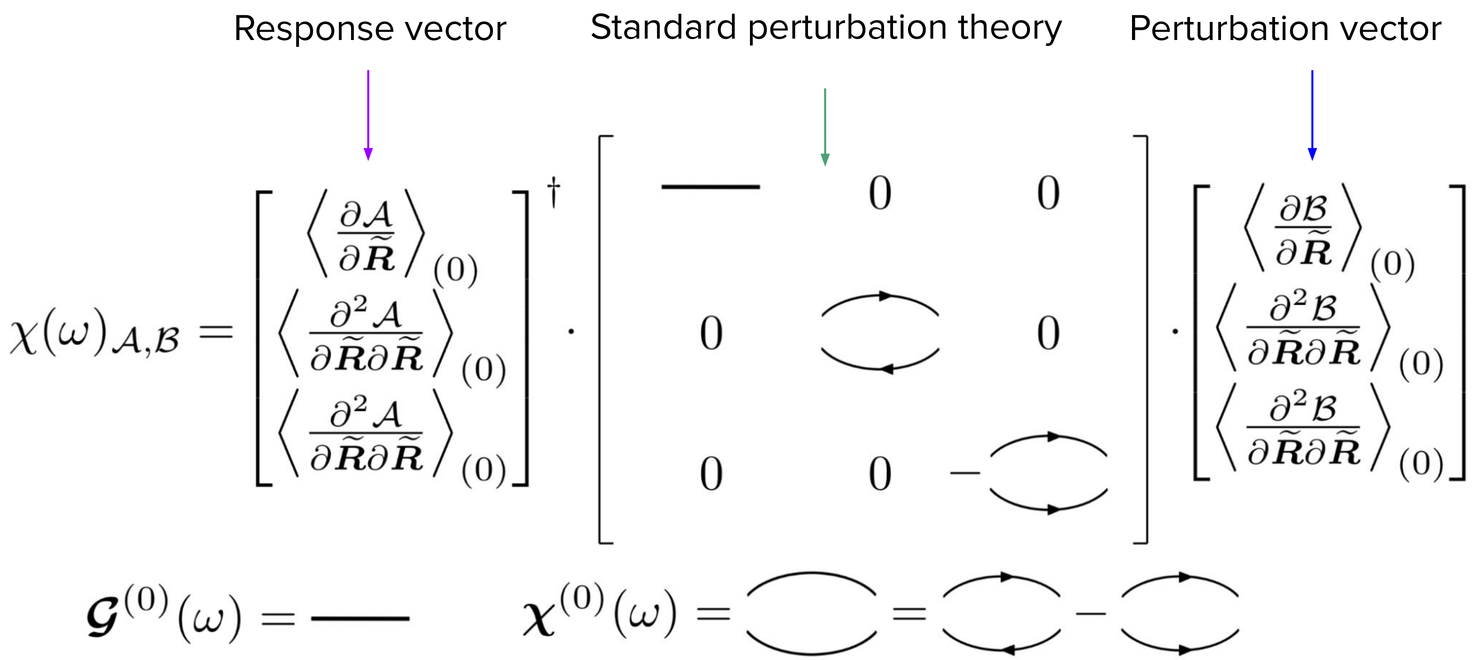
Interacting linear response in TD-SCHA



Scattering ver $\overset{(3)}{\boldsymbol{D}} = \blacktriangleleft = \left\langle \frac{\partial V^{(\mathrm{BO})}}{\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}} \right\rangle_{(0)}$ $\overset{(4)}{\boldsymbol{D}} = \blacksquare = \left\langle \frac{\partial V^{(\mathrm{BO})}}{\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}} \right\rangle_{(0)}$

Refs: A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023, R. Bianco et al., Phys. Rev. B 96, 014111, 2017

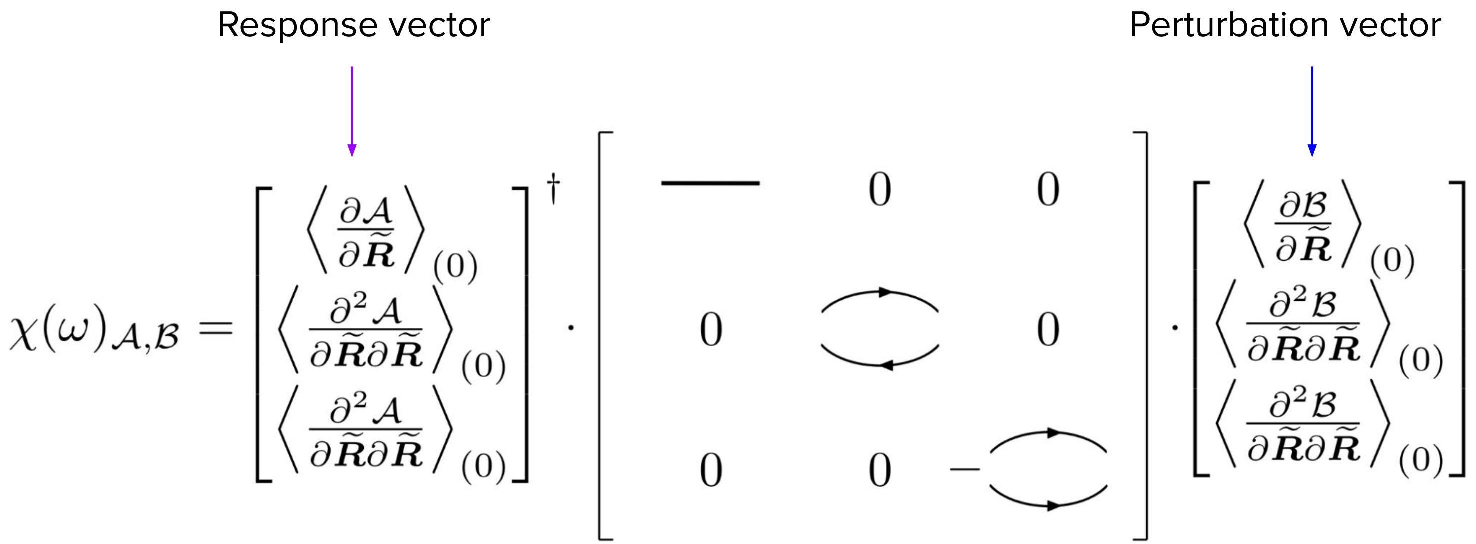
Non-interacting response in TD-SCHA



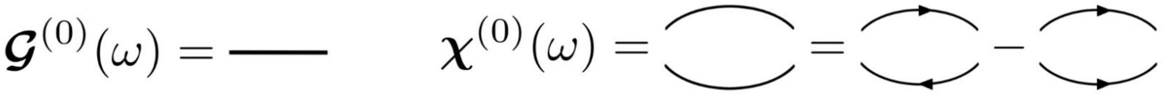
These are not harmonic phonons!!!
How to get them?

Refs: A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023, R. Bianco et al., Phys. Rev. B 96, 014111, 2017

SCHA propagators: how to get them?

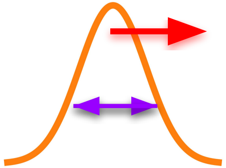


Many body propagators



How to get the propagators?

$$\mathcal{A} = \mathcal{B} = \widetilde{R}_\mu$$



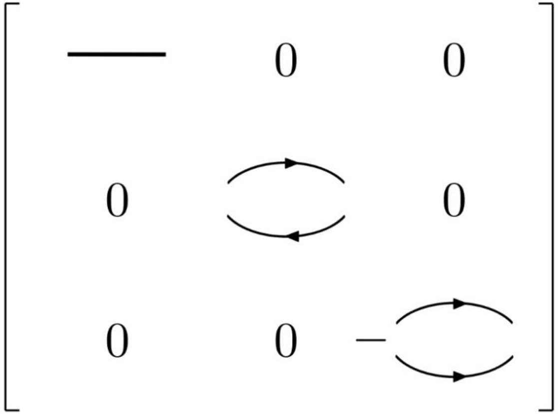
$$\mathcal{A} = \mathcal{B} = \widetilde{R}_\mu \widetilde{R}_\nu$$

SCHA response function?

Refs: A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

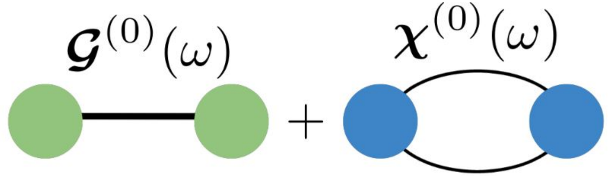
Non-interacting response in TD-SCHA

$$\chi(\omega)_{\mathcal{A},\mathcal{B}} = \begin{bmatrix} \left\langle \frac{\partial \mathcal{A}}{\partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 \mathcal{A}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 \mathcal{A}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \end{bmatrix}^\dagger \cdot$$



$$\cdot \begin{bmatrix} \left\langle \frac{\partial \mathcal{B}}{\partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 \mathcal{B}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 \mathcal{B}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \end{bmatrix}$$

$$\chi(\omega)_{\mathcal{A},\mathcal{A}} =$$



$$= \left\langle \frac{\partial \mathcal{A}}{\partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)}$$

$$= \left\langle \frac{\partial^2 \mathcal{A}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)}$$

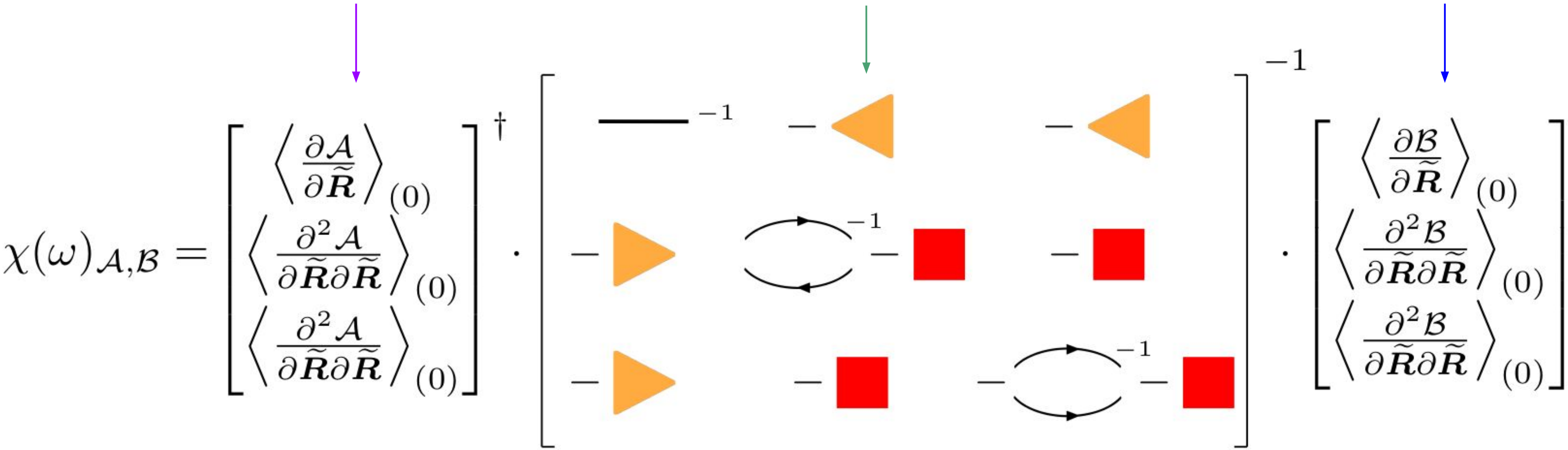
Interaction?

Natural: two-phonon!

Refs: A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

Interacting linear response in TD-SCHA

Response vector — How phonons propagates in the material — Perturbation vector



$\overset{(3)}{\boldsymbol{D}} =$  $= \left\langle \frac{\partial V^{(\mathrm{BO})}}{\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}} \right\rangle_{(0)}$ $\overset{(4)}{\boldsymbol{D}} =$  $= \left\langle \frac{\partial V^{(\mathrm{BO})}}{\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}} \right\rangle_{(0)}$

What are the interacting propagators?

Refs: A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

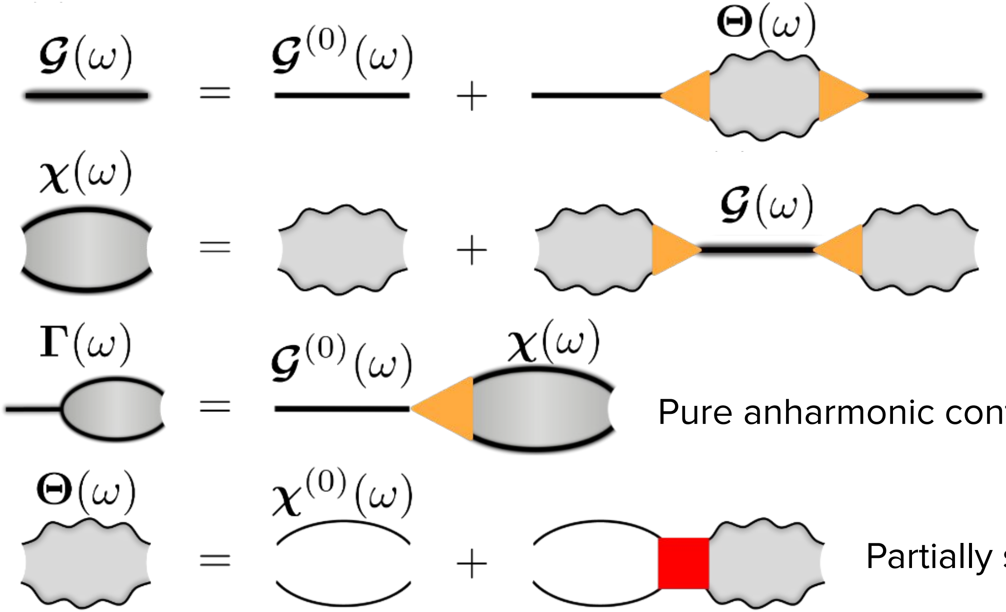
TD-SCHA propagators

The perturbations

$\mathcal{A} = \mathcal{B} = \tilde{\boldsymbol{R}}$

$\mathcal{A} = \mathcal{B} = \tilde{\boldsymbol{R}}\tilde{\boldsymbol{R}}$

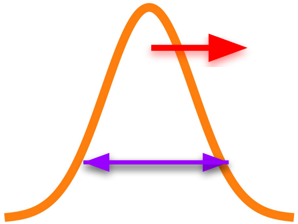
$\mathcal{A} = \tilde{\boldsymbol{R}} \quad \mathcal{B} = \tilde{\boldsymbol{R}}\tilde{\boldsymbol{R}}$



Physical phonons + lifetimes

Pure anharmonic contribution

Partially screened 2-phonon

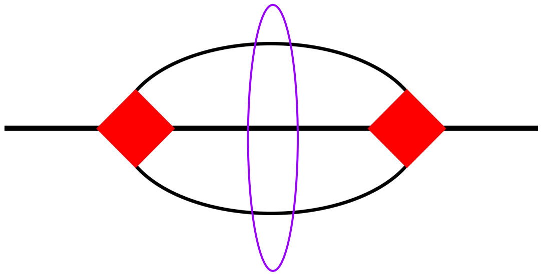


Can we ask more?

$$\overset{(3)}{\boldsymbol{D}} = \blacktriangleleft = \left\langle \frac{\partial V^{(BO)}}{\partial\tilde{\boldsymbol{R}}\partial\tilde{\boldsymbol{R}}\partial\tilde{\boldsymbol{R}}} \right\rangle_{(0)} \quad \overset{(4)}{\boldsymbol{D}} = \blacksquare = \left\langle \frac{\partial V^{(BO)}}{\partial\tilde{\boldsymbol{R}}\partial\tilde{\boldsymbol{R}}\partial\tilde{\boldsymbol{R}}\partial\tilde{\boldsymbol{R}}} \right\rangle_{(0)}$$

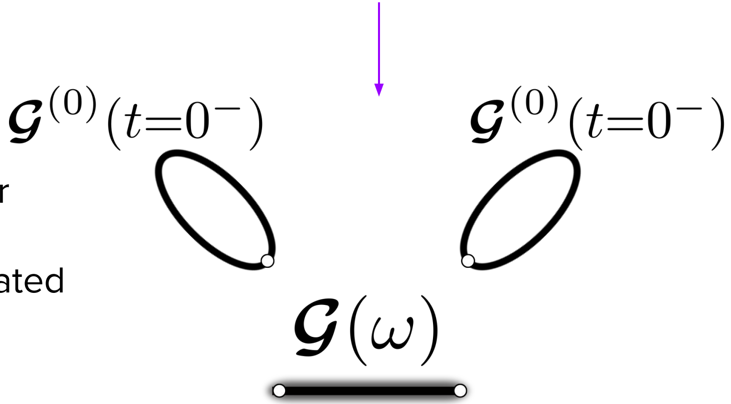
Refs: A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

3-phonon propagation?

Saturn diagram = 

$$\mathcal{A} = \mathcal{B} = \widetilde{R}\widetilde{R}\widetilde{R}$$

3-phonon excitation (Gaussian+Wick theorem?)

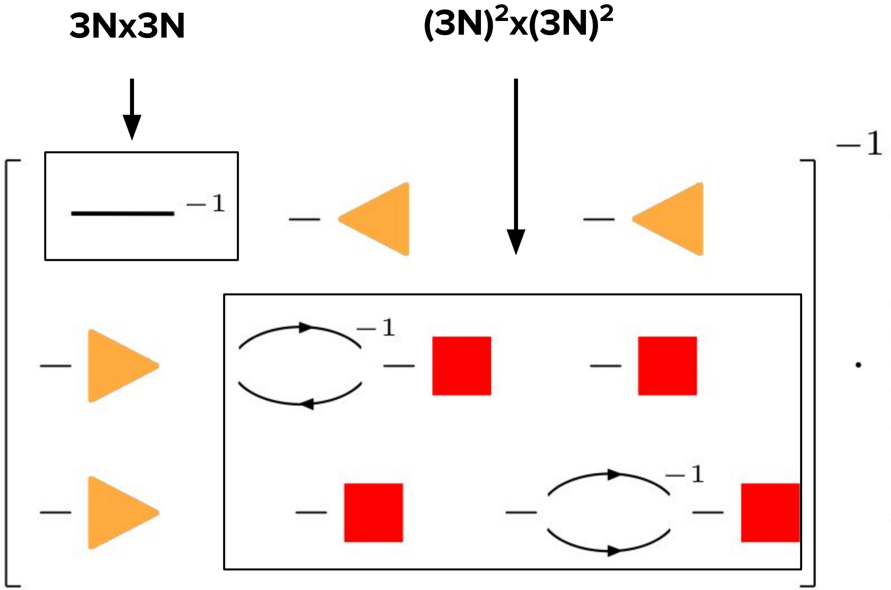


- TDSCHA 3-phonon propagator disconnected = irrelevant
- Hierarchy of diagrams is truncated
- **Practical calculations of response function?**

Refs: A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

Interacting linear response in TD-SCHA

$$\chi(\omega)_{\mathcal{A},\mathcal{B}} = \begin{bmatrix} \left\langle \frac{\partial \mathcal{A}}{\partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 \mathcal{A}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 \mathcal{A}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \end{bmatrix}^{\dagger} \cdot$$



$$\cdot \begin{bmatrix} \left\langle \frac{\partial \mathcal{B}}{\partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 \mathcal{B}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 \mathcal{B}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \end{bmatrix}$$

- Storage of the matrix is hard
- Full inversion scales as N^6
- One shot **(Lanczos=no inversion)** calculation for all frequencies
- No MD trajectories!

Refs: L.Monacelli, F. Mauri, PRB 103, 104305 2021 A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

Lanczos algorithm

Key quantity: response function

$$\chi(\omega)_{\mathcal{A},\mathcal{B}} = \boldsymbol{r} \cdot (\boldsymbol{\mathcal{L}} + \omega^2)^{-1} \cdot \boldsymbol{p}$$

Full inversion scales as $(N^2)^3$

$$\boldsymbol{S}^{-1} \cdot \boldsymbol{\mathcal{L}} \cdot \boldsymbol{S} = \boldsymbol{\mathcal{T}}$$

Tridiagonal form

$$\boldsymbol{\mathcal{T}} = \begin{bmatrix} a_1 & b_1 & \dots & \dots & 0 \\ c_1 & a_2 & \ddots & & \vdots \\ & \ddots & \ddots & \ddots & \\ \vdots & & \ddots & \ddots & b_{N-1} \\ 0 & & & c_{N-1} & a_N \end{bmatrix}$$

Refs: L.Monacelli, F. Mauri, PRB 103, 104305 2021, D.Rocca et al., J. Chem. Phys. 128, 154105 (2008)

Lanczos algorithm

Key quantity: response function

$$\chi(\omega)_{\mathcal{A},\mathcal{B}} = \boldsymbol{r}\cdot(\boldsymbol{\mathcal{L}}+\omega^2)^{-1}\cdot\boldsymbol{p}$$

Full inversion scales as $(N^2)^3$

$$\boldsymbol{S}^{-1}\cdot\boldsymbol{\mathcal{L}}\cdot\boldsymbol{S}=\boldsymbol{\mathcal{T}}$$

Tridiagonal form

$$\boldsymbol{\mathcal{T}} = \begin{bmatrix} a_1 & b_1 & \dots & \dots & 0 \\ c_1 & a_2 & \ddots & & \vdots \\ & \ddots & \ddots & \ddots & \\ \vdots & & \ddots & \ddots & b_{N-1} \\ 0 & & & c_{N-1} & a_N \end{bmatrix}$$

Lanczos algorithm

$$\boldsymbol{p}_1 = \frac{\boldsymbol{p}}{\sqrt{\boldsymbol{p}\cdot\boldsymbol{p}}} \qquad \boldsymbol{r}_1 = \boldsymbol{r}\frac{\sqrt{\boldsymbol{p}\cdot\boldsymbol{p}}}{\boldsymbol{r}\cdot\boldsymbol{p}} \longrightarrow \boldsymbol{p_1}\cdot\boldsymbol{r_1}=1$$

$$a_k = \boldsymbol{r}_k\cdot\mathcal{L}\cdot\boldsymbol{p}_k$$

$$b_k\boldsymbol{p}_{k+1} = (\mathcal{L}-a_k)\cdot\boldsymbol{p}_k - c_{k-1}\boldsymbol{p}_{k-1}$$

$$c_k\boldsymbol{r}_{k+1} = (\mathcal{L}-a_k)\cdot\boldsymbol{r}_k - b_{k-1}\boldsymbol{r}_{k-1}$$

$$\boldsymbol{p}_k\cdot\boldsymbol{r}_l = \delta_{kl} \qquad \boldsymbol{S} = \begin{bmatrix}\boldsymbol{p}_1 & \boldsymbol{p}_2 & \dots & \boldsymbol{p}_N\end{bmatrix} \qquad \boldsymbol{S}^{-1} = \begin{bmatrix}\boldsymbol{r}_1 \\ \boldsymbol{r}_2 \\ \dots \\ \boldsymbol{r}_N\end{bmatrix}$$

Only matrix application scales as N^2

Hands-on…

Refs: L.Monacelli, F. Mauri, PRB 103, 104305 2021, D.Rocca et al., J. Chem. Phys. 128, 154105 (2008)

Lanczos algorithm

$$\boldsymbol{p}_k \cdot \boldsymbol{r}_l = \delta_{kl} \qquad \boldsymbol{S} = \begin{bmatrix} \boldsymbol{p}_1 & \boldsymbol{p}_2 & \dots & \boldsymbol{p}_N \end{bmatrix} \qquad \boldsymbol{S}^{-1} = \begin{bmatrix} \boldsymbol{r}_1 \\ \boldsymbol{r}_2 \\ \dots \\ \boldsymbol{r}_N \end{bmatrix}$$

Response in the Lanczos basis ⟶

$$\begin{aligned}
\chi(\omega)_{\mathcal{A},\mathcal{B}} &= (\boldsymbol{r}\cdot\boldsymbol{p})\,\boldsymbol{r}_1 \cdot \boldsymbol{S} \cdot \left[\boldsymbol{S}^{-1} \cdot (\boldsymbol{\mathcal{L}} + \omega^2)^{-1} \cdot \boldsymbol{S}\right] \cdot \boldsymbol{S}^{-1} \cdot \boldsymbol{p}_1 \\
&= (\boldsymbol{r}\cdot\boldsymbol{p})\,\boldsymbol{r}_1 \cdot \boldsymbol{S} \cdot \left[\boldsymbol{S}^{-1} \cdot (\boldsymbol{\mathcal{L}} + \omega^2) \cdot \boldsymbol{S}\right]^{-1} \cdot \boldsymbol{S}^{-1} \cdot \boldsymbol{p}_1 \\
&= (\boldsymbol{r}\cdot\boldsymbol{p})\,\boldsymbol{r}_1 \cdot \boldsymbol{S} \cdot \left[\boldsymbol{\mathcal{T}} + \omega^2\right]^{-1} \cdot \boldsymbol{S}^{-1} \cdot \boldsymbol{p}_1 \\
&= (\boldsymbol{r}\cdot\boldsymbol{p})\,[(\boldsymbol{\mathcal{T}} + \omega^2)^{-1}]_{11}
\end{aligned}$$

Refs: L.Monacelli, F. Mauri, PRB 103, 104305 2021, D.Rocca et al., J. Chem. Phys. 128, 154105 (2008)

Lanczos algorithm

Response in the Lanczos basis →

$$\begin{aligned}\chi(\omega)_{\mathcal{A},\mathcal{B}} &= (\boldsymbol{r}\cdot\boldsymbol{p})\,\boldsymbol{r}_1\cdot\boldsymbol{S}\cdot\left[\boldsymbol{S}^{-1}\cdot(\boldsymbol{\mathcal{L}}+\omega^2)^{-1}\cdot\boldsymbol{S}\right]\cdot\boldsymbol{S}^{-1}\cdot\boldsymbol{p}_1\\ &= (\boldsymbol{r}\cdot\boldsymbol{p})\,\boldsymbol{r}_1\cdot\boldsymbol{S}\cdot\left[\boldsymbol{S}^{-1}\cdot(\boldsymbol{\mathcal{L}}+\omega^2)\cdot\boldsymbol{S}\right]^{-1}\cdot\boldsymbol{S}^{-1}\cdot\boldsymbol{p}_1\\ &= (\boldsymbol{r}\cdot\boldsymbol{p})\,\boldsymbol{r}_1\cdot\boldsymbol{S}\cdot\left[\boldsymbol{\mathcal{T}}+\omega^2\right]^{-1}\cdot\boldsymbol{S}^{-1}\cdot\boldsymbol{p}_1\\ &= (\boldsymbol{r}\cdot\boldsymbol{p})\left[(\boldsymbol{\mathcal{T}}+\omega^2)^{-1}\right]_{11}\end{aligned}$$

Recursive 2x2 inversion

$$\begin{bmatrix} A & B \\ C & D\end{bmatrix}^{-1}_{11} = \left(A - B\cdot D^{-1}\cdot C\right)^{-1}$$

$$\boldsymbol{\mathcal{T}}+\omega^2 = \begin{bmatrix} a_1+\omega^2 & b_1 & \cdots & \cdots & 0 \\ c_1 & a_2+\omega^2 & \ddots & & \vdots \\ & \ddots & \ddots & \ddots & \\ \vdots & & \ddots & \ddots & b_{N-1} \\ 0 & & & c_{N-1} & a_N+\omega^2 \end{bmatrix}$$

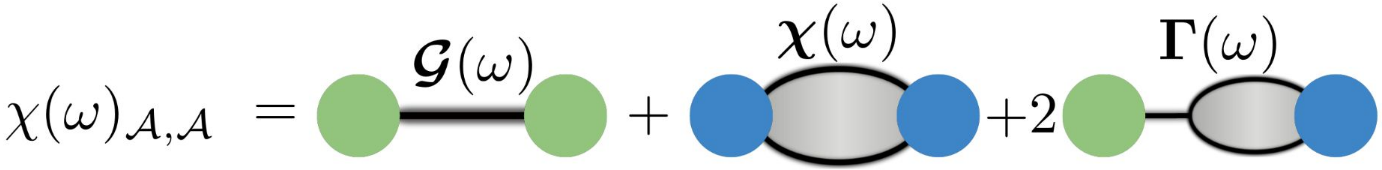
(A: $a_1+\omega^2$; B: $b_1 \cdots \cdots 0$; C: $c_1 \cdots 0$; D: the remaining block)

- **No MD**
- **Unbiased (ab-initio)**
- **Low-symm**
- **What is the response function?**

$$\chi(\omega)_{\mathcal{A},\mathcal{B}} = (\boldsymbol{r}\cdot\boldsymbol{p})\left(\omega^2+a_1-\frac{b_1c_1}{\omega^2+a_2-\frac{b_2c_2}{\omega^2+\dots}}\right)^{-1}$$

Refs: L.Monacelli, F. Mauri, PRB 103, 104305 2021, D.Rocca et al., J. Chem. Phys. 128, 154105 (2008)

TD-SCHA response function



 $= \left\langle \frac{\partial \mathcal{A}}{\partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)}$

 $= \left\langle \frac{\partial^2 \mathcal{A}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)}$

One-phonon coupling

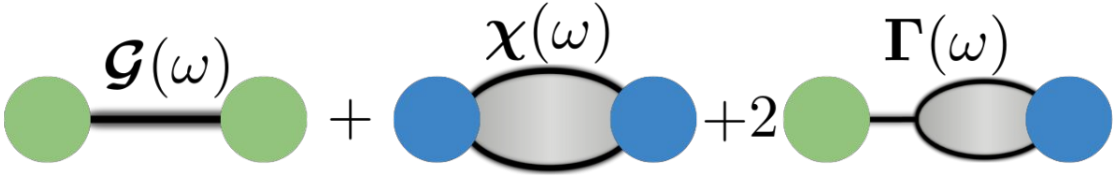
Two-phonon coupling

What we see in exp are TDSCHA phonons not the SCHA ones

Refs: L.Monacelli, F. Mauri, PRB 103, 104305 2021; A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

TD-SCHA infrared

Dipole-dipole response function!

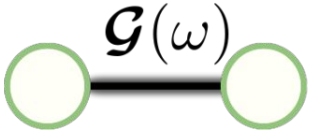
$\chi(\omega)_{p_\alpha,p_\alpha} =$ 

 $= \langle Z \rangle_{(0)}$

 $= \left\langle \frac{\partial Z}{\partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} = \langle \delta\boldsymbol{R}\delta\boldsymbol{R} \rangle_{(0)}^{-1} \cdot \langle \delta\boldsymbol{R} Z \rangle_{(0)}$

Quantum-thermal fluctuations

No higher order electronic response!

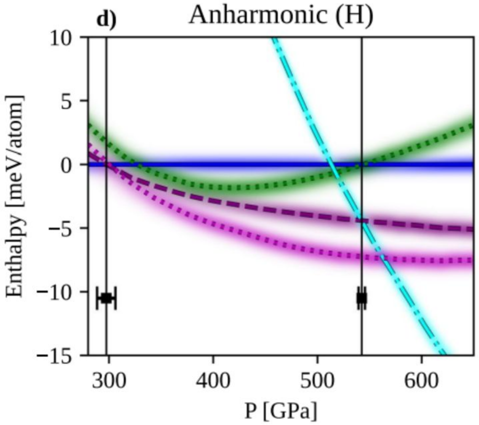
$\chi(\omega)_{p_\alpha,p_\alpha} =$ 

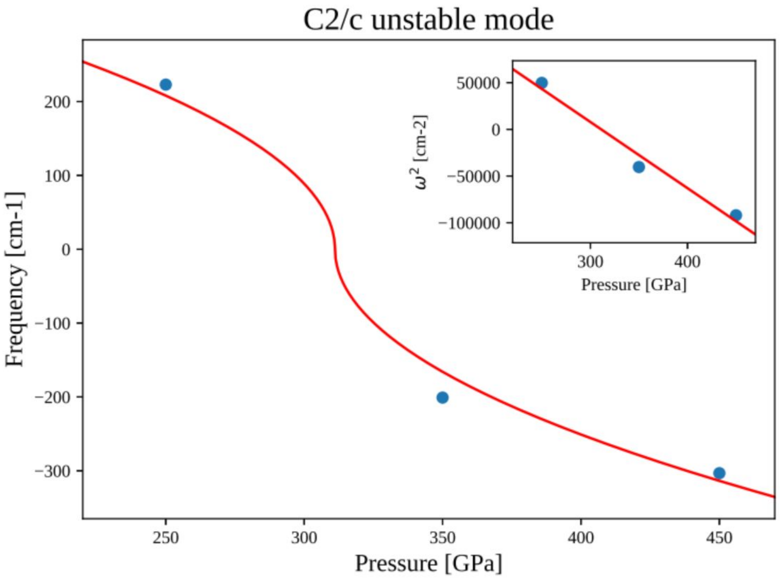
 $= Z\left(\mathcal{R}_0\right)$

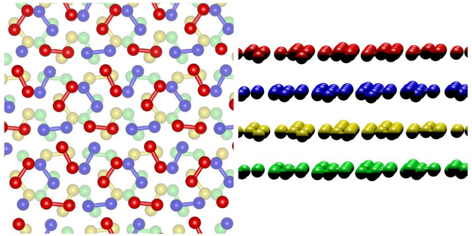
Refs: A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

High-pressure molecular hydrogen C2c

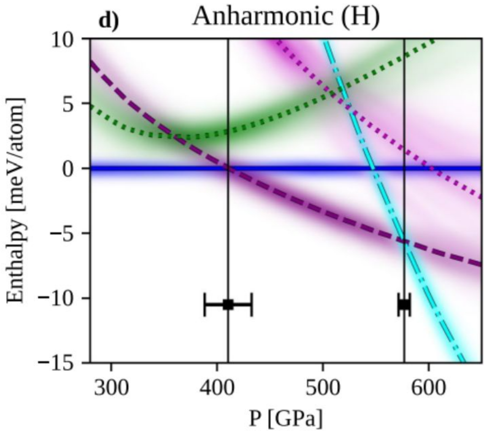
DFT







DMC

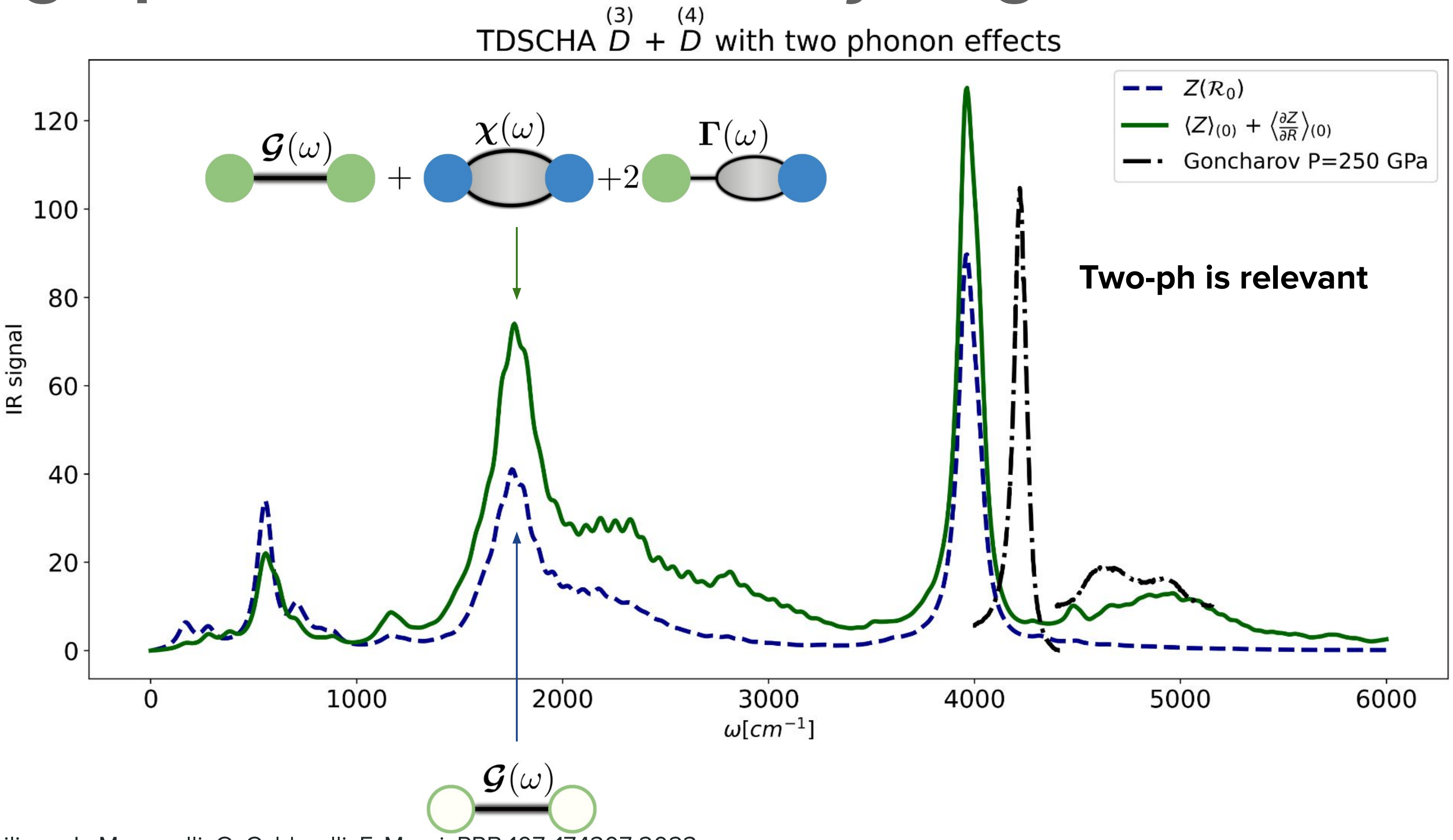


$$\overset{(3)}{\boldsymbol{D}} = ◀ = \left\langle \frac{\partial V^{(\mathrm{BO})}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \quad \overset{(4)}{\boldsymbol{D}} = ■ = \left\langle \frac{\partial V^{(\mathrm{BO})}}{\partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}} \partial \widetilde{\boldsymbol{R}}} \right\rangle_{(0)}$$

Non-perturbative (hands-on)!

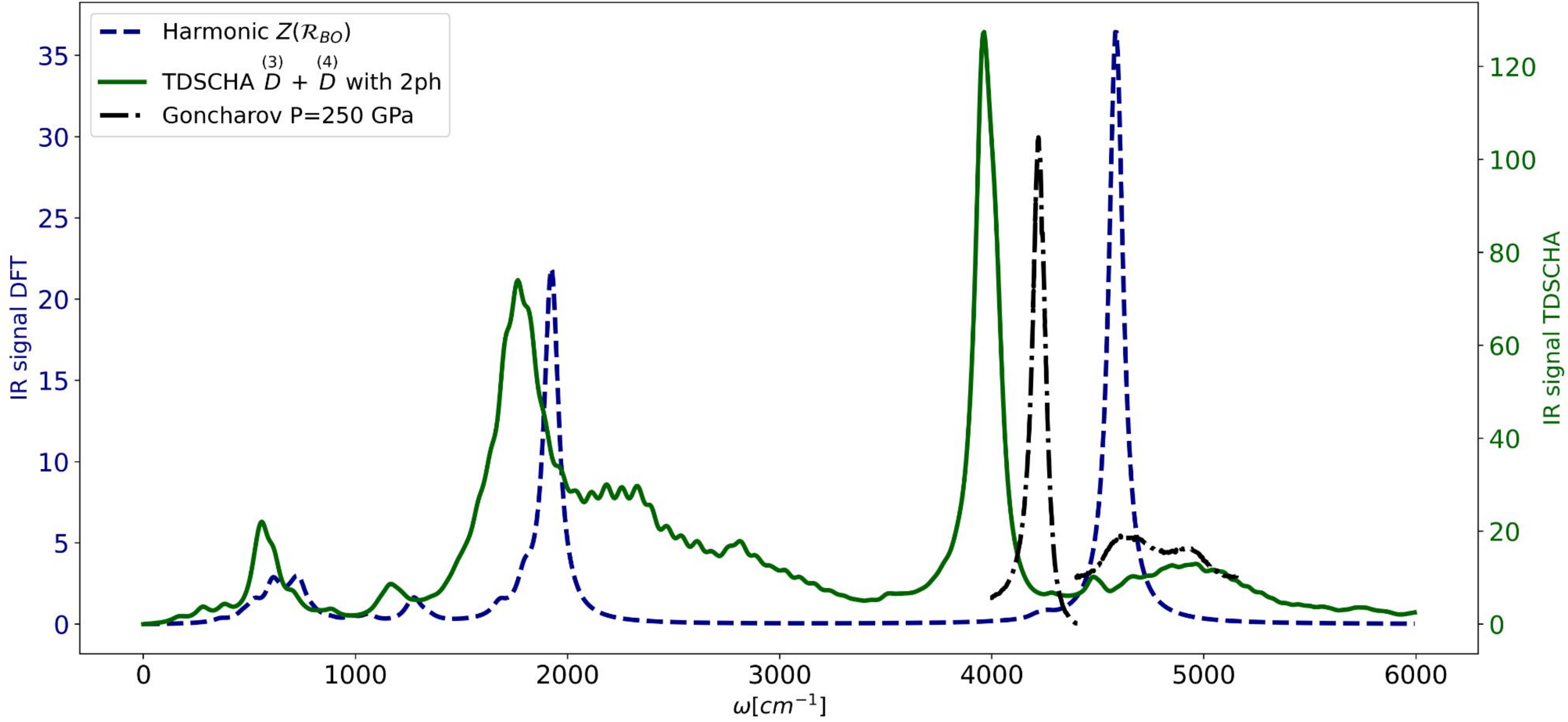
Refs: L. Monacelli et al., Nature Physics 19, 845-850 (2023)

High-pressure molecular hydrogen C2c



Refs: A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

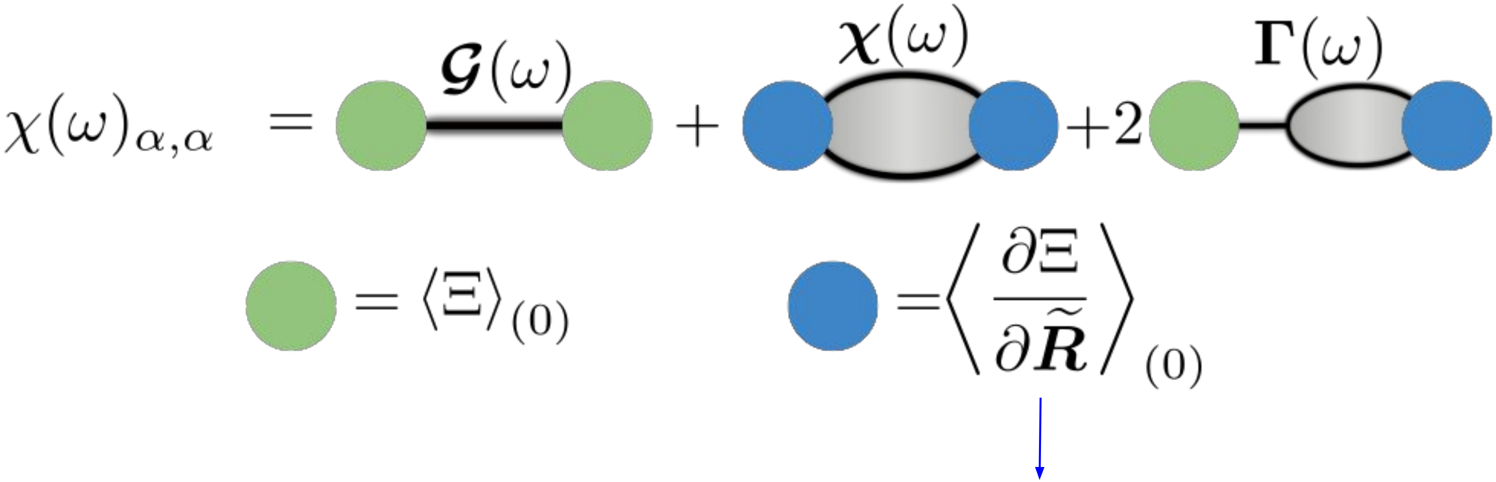
High-pressure molecular hydrogen C2c



Refs: A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

TD-SCHA Raman

polarizability-polarizability response function!

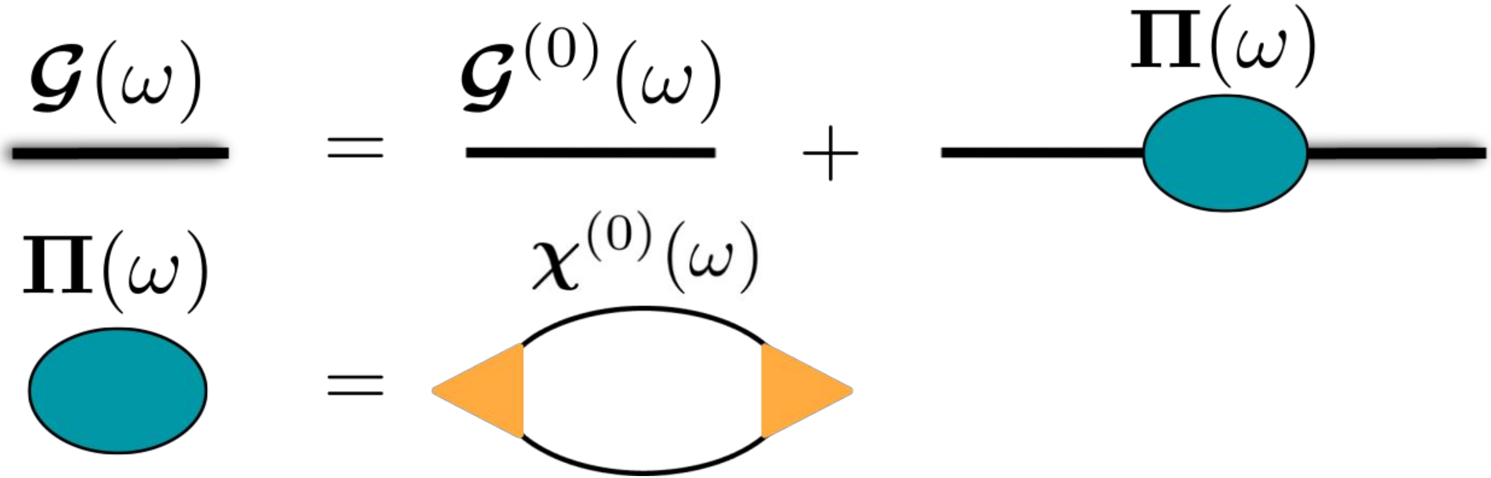


No higher order electronic response!

Refs: L.Monacelli, F. Mauri, PRB 103, 104305 2021; A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

TD-SCHA Ice XI

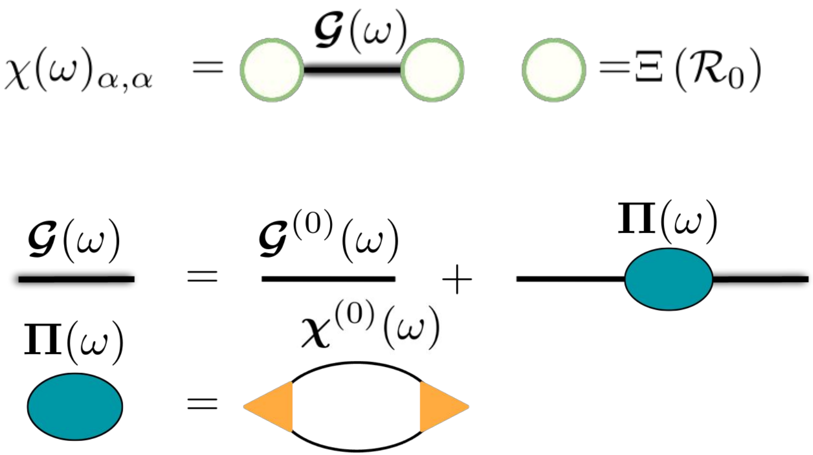
Proton ordered phase of phase below 72 K

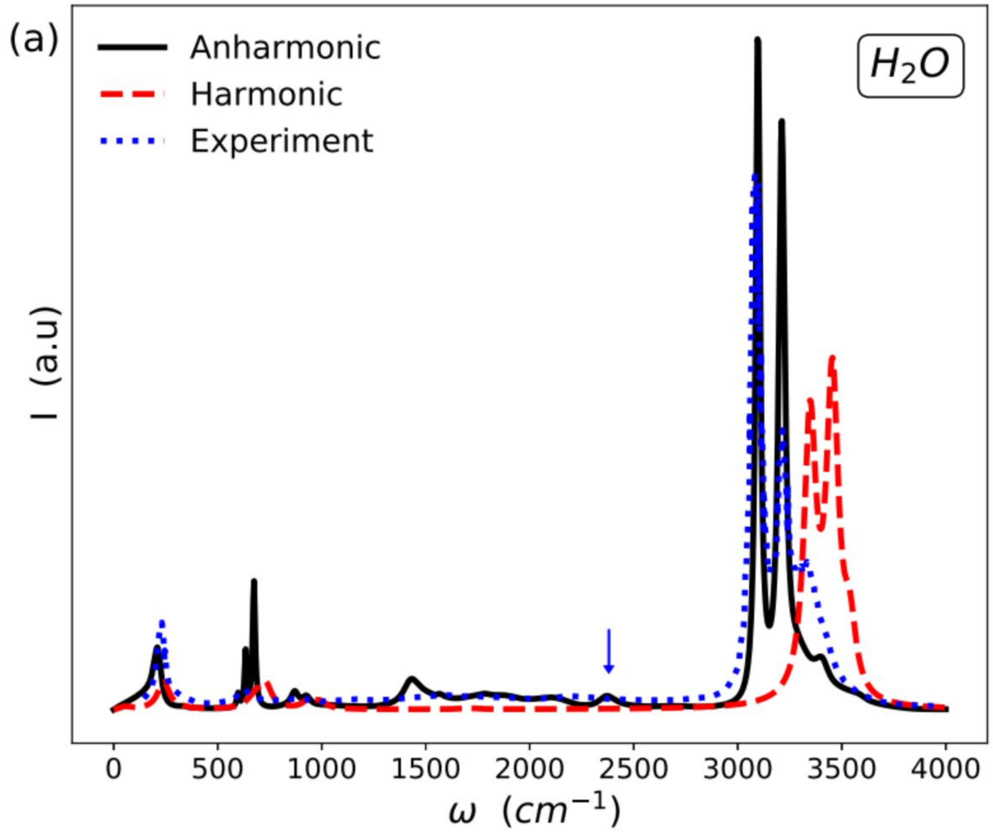


Bubble approximation = no 4-phonon vertex

Refs: M. Cherubini et. al., J. Chem. Phys. 155, 184502 (2021)

TD-SCHA Raman in Ice XI

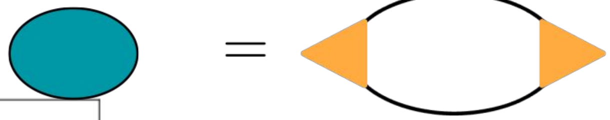




Refs: M. Cherubini et. al., J. Chem. Phys. 155, 184502 (2021)

TD-SCHA Ice XI

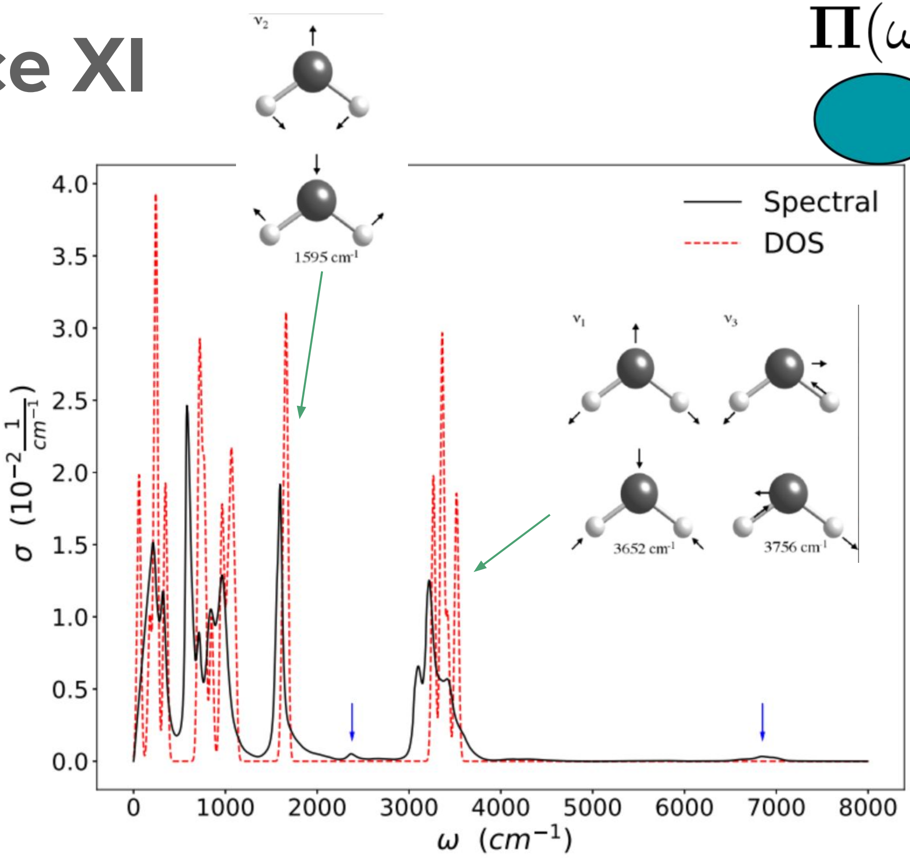
$$\mathbf{\Pi}(\omega) = \chi^{(0)}(\omega)$$



Overtones vs two ph?

Spectral function

- Translational modes
- Librations
- Narrow bending
- Stretching



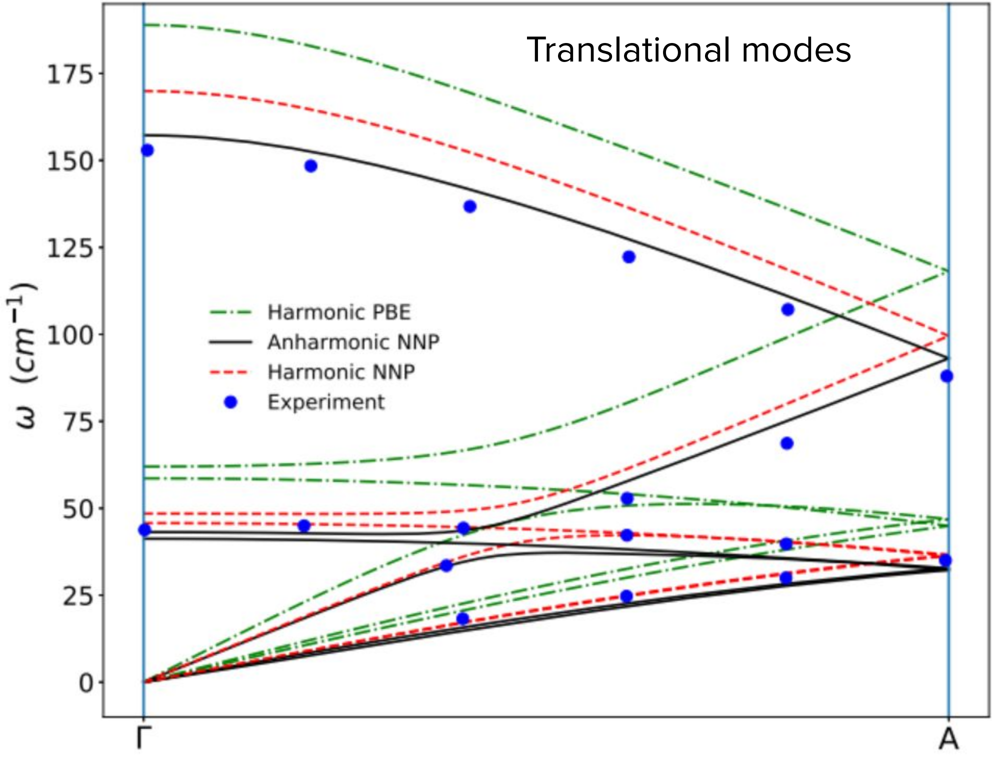
Overtones: librations + bending, stretching + stretching

Refs: M. Cherubini et. al., J. Chem. Phys. 155, 184502 (2021)

TD-SCHA Ice XI

Inter-molecular soft H bonds + intra-molecular hard covalent OH

Description of acoustic phonons is key in thermal transport



Refs: M. Cherubini et. al., J. Chem. Phys. 155, 184502 (2021)

Conclusions

- Harmonic vs SCHA vs TDSCHA = physical
- Scattering vertex
- Higher-order phonon response/perturbation without DFPT
- Flexible response function (Neutron, X-ray) for position-dependent perturbations

Thank you for the attention!

MoRe-TEM

European Research Council

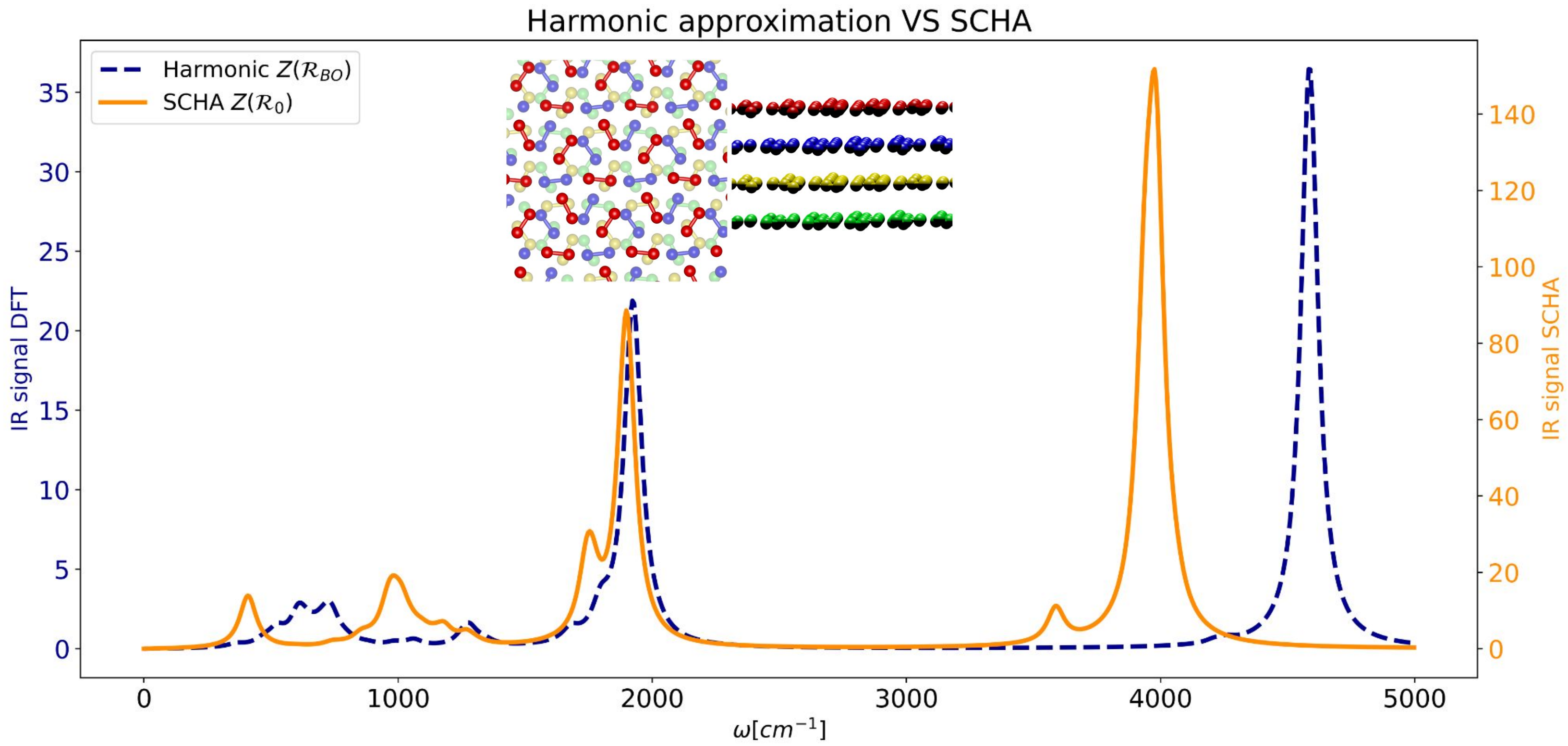
Established by the European Commission

SAPIENZA UNIVERSITÀ DI ROMA

SSCHA

Stochastic Self-Consistent Harmonic Approximation

High-pressure molecular hydrogen C2c



Refs: A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

Time-Dependent SCHA

- Equations for equal-time correlators (free parameters)

$$\frac{d}{dt}\left\langle\tilde{\boldsymbol{R}}\right\rangle_{\tilde{\rho}(t)} = \left\langle\tilde{\boldsymbol{P}}\right\rangle_{\tilde{\rho}(t)}$$

$$\frac{d}{dt}\left\langle\tilde{\boldsymbol{P}}\right\rangle_{\tilde{\rho}(t)} = -\left\langle\frac{\partial V^{(\text{tot})}}{\partial\tilde{\boldsymbol{R}}}\right\rangle_{\tilde{\rho}(t)}$$

$$\frac{d}{dt}\left\langle\delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{R}}\right\rangle_{\tilde{\rho}(t)} = \left\langle\delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{P}}\right\rangle_{\tilde{\rho}(t)} + \left\langle\delta\tilde{\boldsymbol{P}}\delta\tilde{\boldsymbol{R}}\right\rangle_{\tilde{\rho}(t)}$$

$$\frac{d}{dt}\left\langle\delta\tilde{\boldsymbol{P}}\delta\tilde{\boldsymbol{P}}\right\rangle_{\tilde{\rho}(t)} = -\left\langle\frac{\partial^2 V^{(\text{tot})}}{\partial\tilde{\boldsymbol{R}}\partial\tilde{\boldsymbol{R}}}\right\rangle_{\tilde{\rho}(t)}\cdot\left\langle\delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{P}}\right\rangle_{\tilde{\rho}(t)} - \left\langle\delta\tilde{\boldsymbol{P}}\delta\tilde{\boldsymbol{R}}\right\rangle_{\tilde{\rho}(t)}\cdot\left\langle\frac{\partial^2 V^{(\text{tot})}}{\partial\tilde{\boldsymbol{R}}\partial\tilde{\boldsymbol{R}}}\right\rangle_{\tilde{\rho}(t)}$$

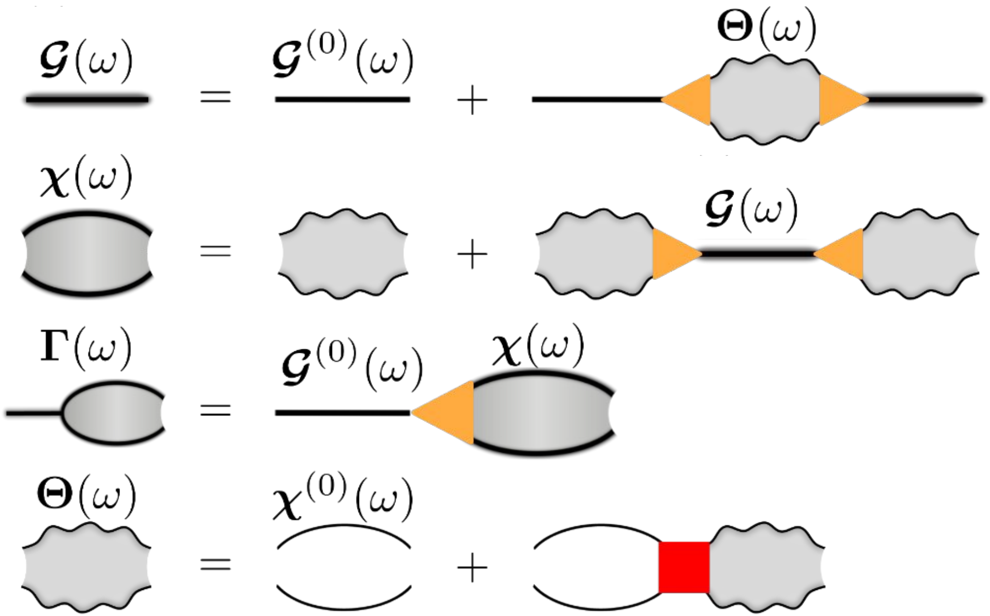
$$\frac{d}{dt}\left\langle\delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{P}}\right\rangle_{\tilde{\rho}(t)} = \left\langle\delta\tilde{\boldsymbol{P}}\delta\tilde{\boldsymbol{P}}\right\rangle_{\tilde{\rho}(t)} - \left\langle\delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{R}}\right\rangle_{\tilde{\rho}(t)}\cdot\left\langle\frac{\partial^2 V^{(\text{tot})}}{\partial\tilde{\boldsymbol{R}}\partial\tilde{\boldsymbol{R}}}\right\rangle_{\tilde{\rho}(t)}$$

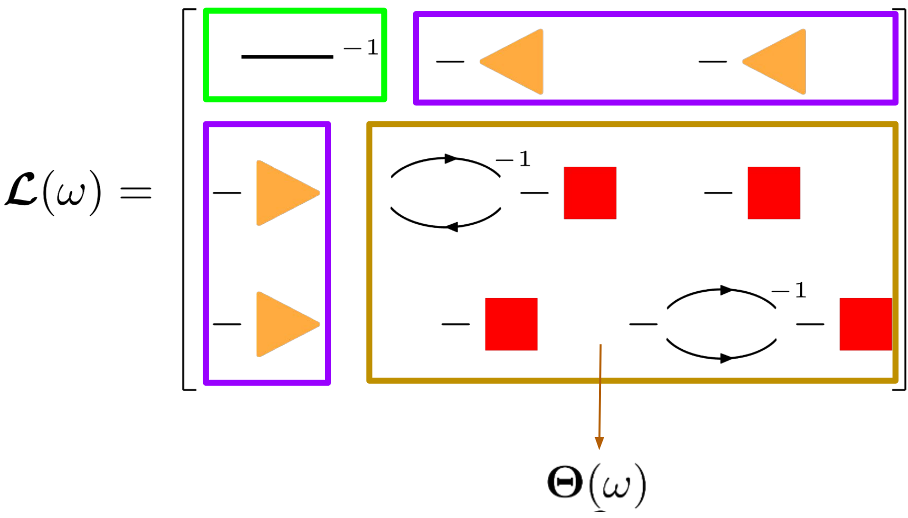
- Newton (Ehrenfest) equations of motion
- Equal time correlators
- Momentum (diffusion-transport)

$$\left\langle\frac{\partial^2 V^{(\text{tot})}}{\partial\tilde{\boldsymbol{R}}\partial\tilde{\boldsymbol{R}}}\right\rangle_{\tilde{\rho}(t)} = \left\langle\delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{R}}\right\rangle_{\tilde{\rho}(t)}^{-1}\cdot\left\langle\delta\tilde{\boldsymbol{R}}\frac{\partial V^{(\text{tot})}}{\partial\tilde{\boldsymbol{R}}}\right\rangle_{\tilde{\rho}(t)}$$

Only forces needed for full evolution

TD-SCHA propagators





Each propagator correspond to an element of the inverse tensor propagator

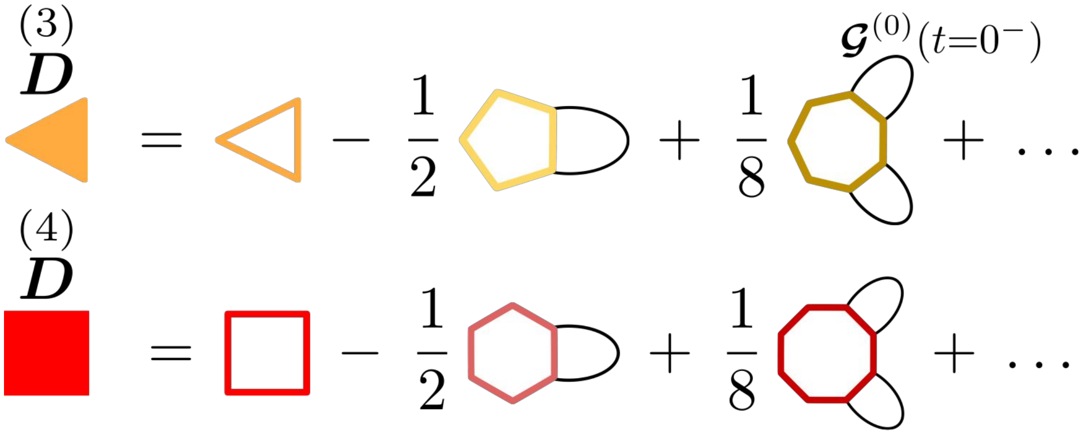
Can we ask more?

Refs: L.Monacelli, F. Mauri, PRB 103, 104305 2021; A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

Is this perturbation theory?

$$\overset{(3)}{\boldsymbol{D}} = \blacktriangleleft = \left\langle \frac{\partial V^{(\mathrm{BO})}}{\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}} \right\rangle_{(0)} \quad \overset{(4)}{\boldsymbol{D}} = \blacksquare = \left\langle \frac{\partial V^{(\mathrm{BO})}}{\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}\partial\widetilde{\boldsymbol{R}}} \right\rangle_{(0)}$$

SCHA averages



$$\overset{(3)}{\boldsymbol{D}}{}^{(0)} = \triangleleft \qquad \overset{(4)}{\boldsymbol{D}}{}^{(0)} = \square$$

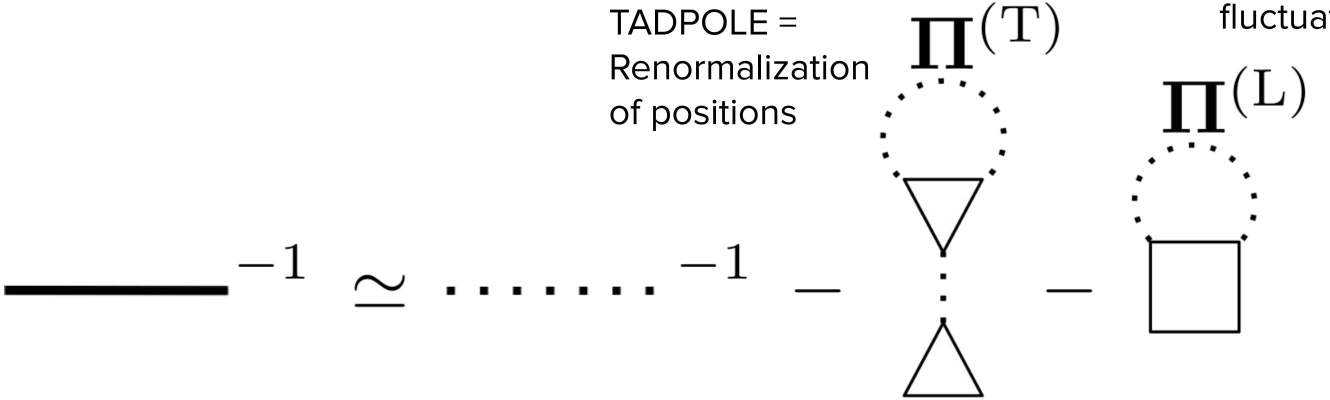
DFT anharmonic tensor computed **at SCHA positions**

Refs: A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023

SCHA phonons vs Harmonic phonons

LOOP =
Quantum-thermal
fluctuations

TADPOLE =
Renormalization
of positions



SCHA

Harmonic

DFT anharmonic
tensor computed at
BO positions

Refs: A. Siciliano, L. Monacelli, G. Caldarelli, F. Mauri, PRB 107, 174307 2023