Anharmonic lattice dynamics of clathrates explained by vibrational dynamical mean-field theory

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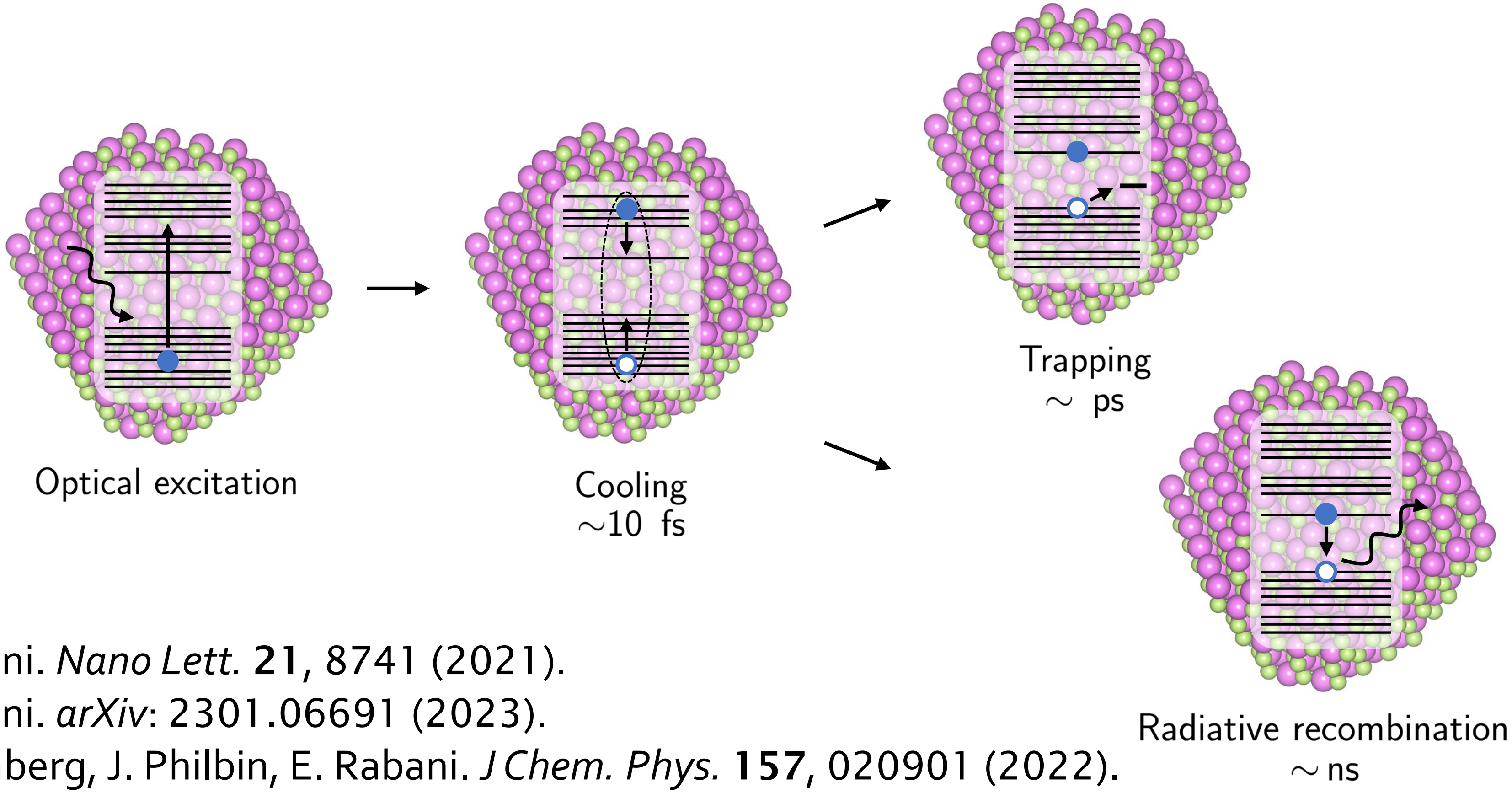
PhD: How are optoelectronic properties of QDs affected by atomic vibrations?

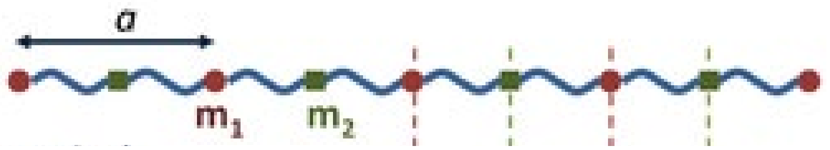
- Understanding exciton-phonon coupling and its impact on processes such as exciton cooling, photoluminescence, and trapping

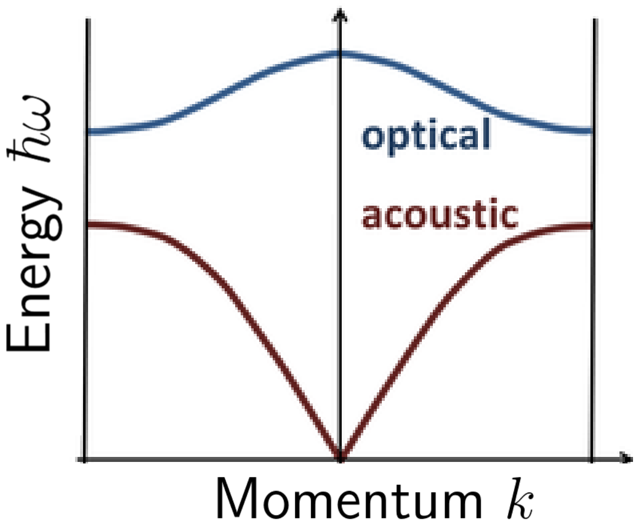


D. Jasrasaria, E. Rabani. *Nano Lett.* **21**, 8741 (2021).
D. Jasrasaria, E. Rabani. *arXiv*: 2301.06691 (2023).
D. Jasrasaria, D. Weinberg, J. Philbin, E. Rabani. *J Chem. Phys.* **157**, 020901 (2022).

Postdoc: How can we rationally control vibrational properties of materials?

- Simplest picture: collection of non-interacting phonons
  - Phonons are quantized, collective oscillations of the lattice
  - Carry sound and heat, and can interact with light

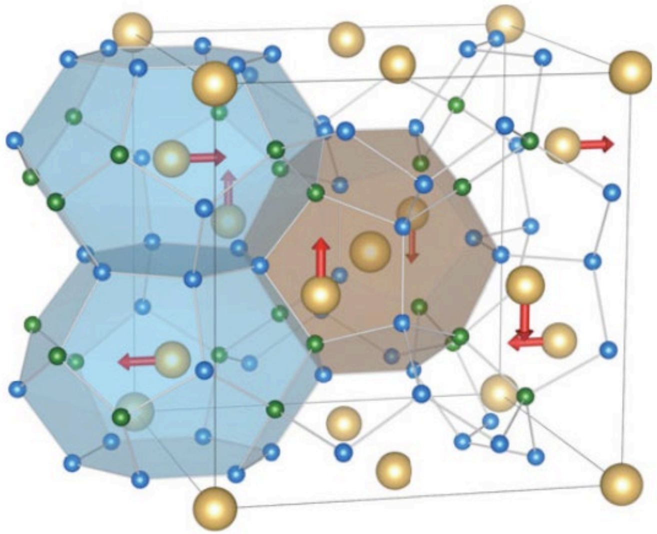


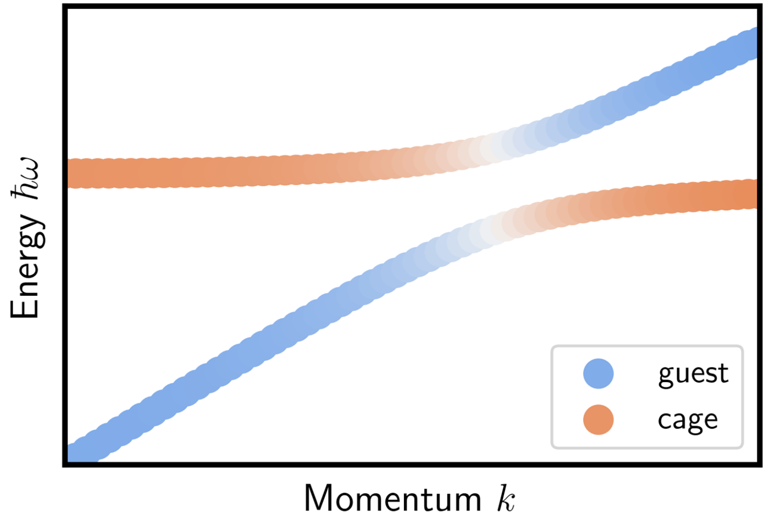


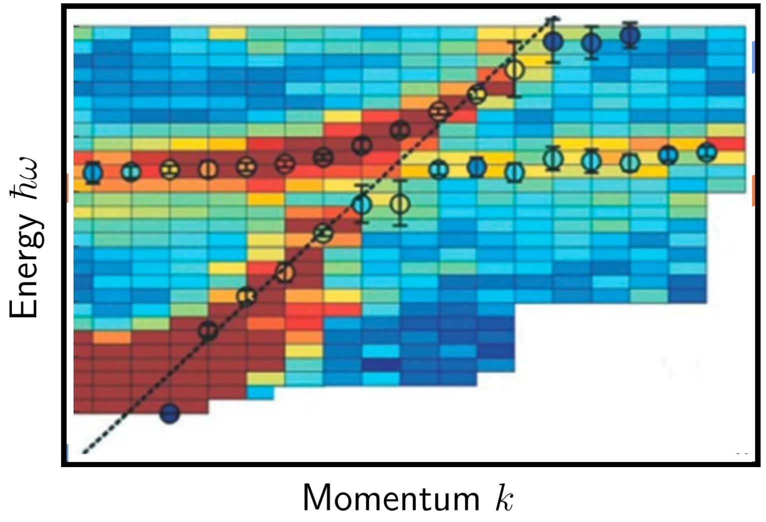
- Some materials have significant "anharmonicity" (phonon-phonon interactions)

Thermoelectrics convert heat to electricity

- Good thermoelectrics have low thermal conductivities
  - Anharmonic vibrational structure (i.e., phonon-phonon interactions)
- Clathrates: cage-like structures with loosely bound, embedded guest
- Hybridization of cage acoustic mode and guest optical mode



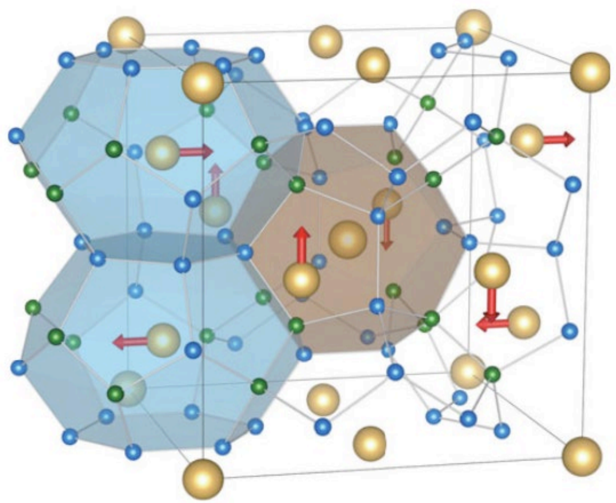


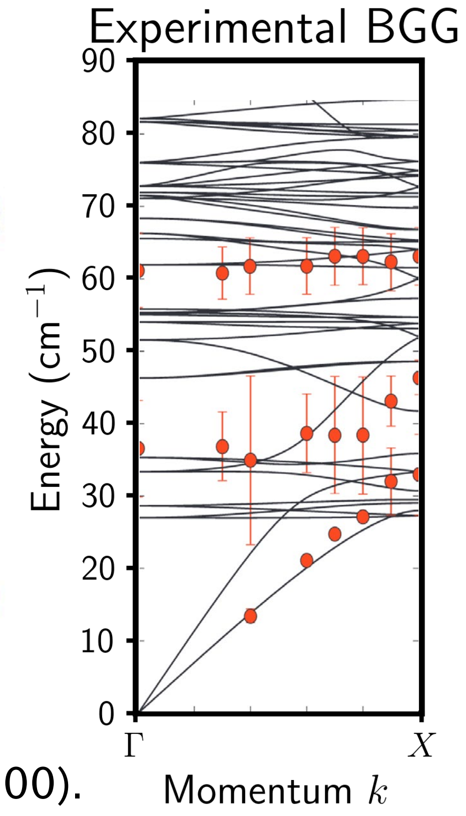


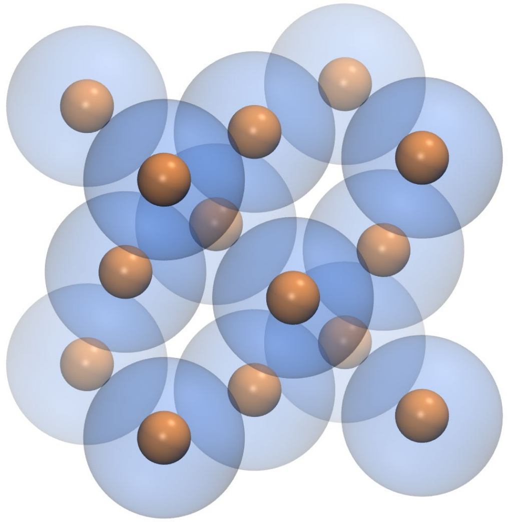
T. Tadano, S. Tsuneyuki. *Phys. Rev. Lett.* **120**, 105901 (2018).
M. Christensen et al. *Nature Mater.* **7**, 811 (2008).

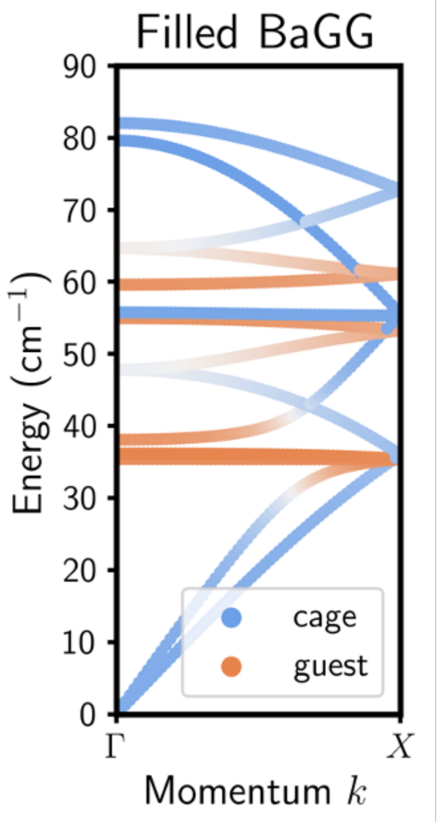
Developing a coarse-grained clathrate model: $Ba_8Ga_{16}Ge_{30}$ and $Sr_8Ga_{16}Ge_{30}$

- Lattice of large “cage” atoms with Lennard-Jones interactions
- Small “guest” atom with quartic interaction with its own cage









J. Dong et al. *J. Appl. Phys.* **87**, 7726 (2000).
T. Tadano et al. *Phys. Rev. Lett.* **114**, 095501 (2015).

Accounting for anharmonicity

- Anharmonic single-particle phonon Green's function:

$$i\hbar D_{\lambda\lambda'}(\boldsymbol{k},\omega) = \int_0^\infty dt e^{i\omega t} \langle [u_\lambda(\boldsymbol{k},t), u_{\lambda'}(-\boldsymbol{k},0)] \rangle$$

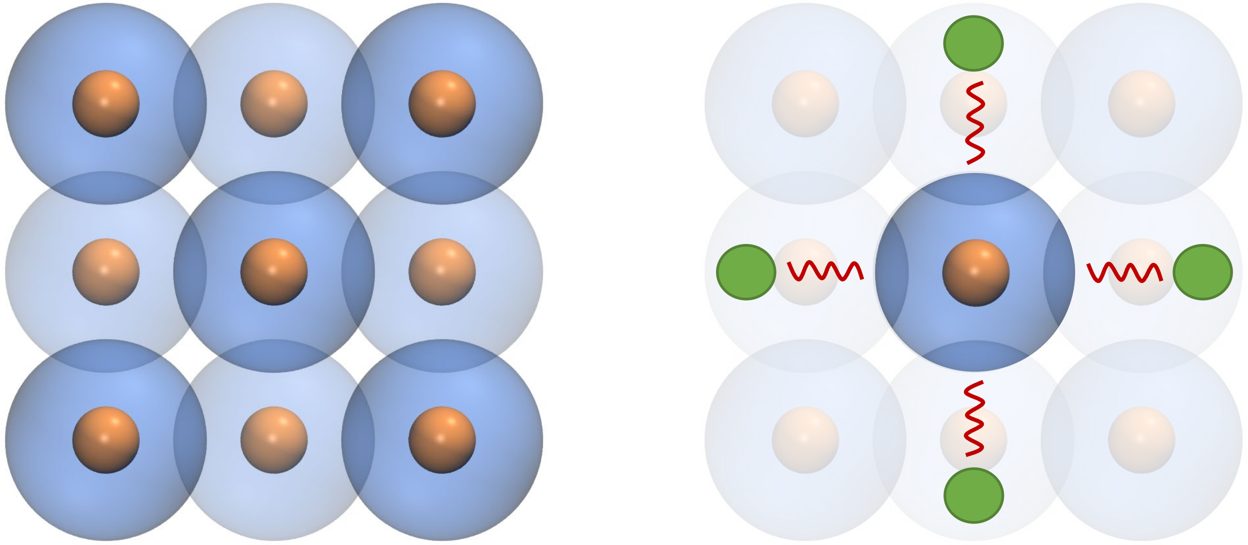
  - Could calculate using MD… challenging!

- Write anharmonic GF in terms of noninteracting GF and self-energy

$$\boldsymbol{D}^{-1}(\boldsymbol{k},\omega) = \boldsymbol{D}_0^{-1}(\boldsymbol{k},\omega) - \boldsymbol{\pi}(\boldsymbol{k},\omega)$$

VDMFT: Map lattice dynamics onto impurity problem

- Nonperturbatively solve for self-energy of a finite **system coupled to** a **harmonic bath**
  - Key approximation of local self-energy: $\boldsymbol{\pi}(\boldsymbol{k}, \omega) \approx \boldsymbol{\pi}(\omega)$



$$H_\mathrm{s} = \sum_\alpha \frac{\boldsymbol{p}_\alpha^2}{2m_\alpha} + V_\mathrm{loc}(\{\boldsymbol{R}_\alpha\})$$

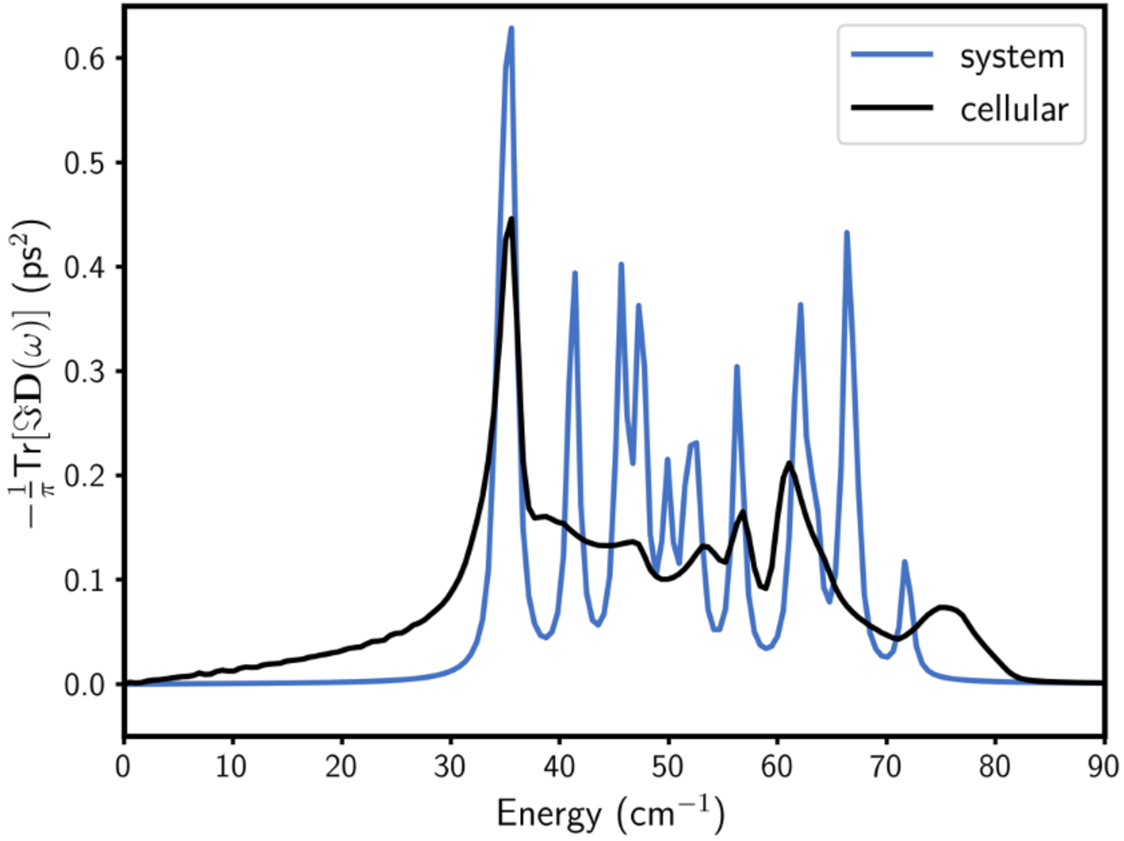
$$H_\mathrm{b} = \frac{1}{2}\sum_m \left(p_m^2 + \omega_m^2 x_m^2\right)$$

$$H_\mathrm{sb} = \sum_{\alpha i m} c_{\alpha i, m} u_{\alpha i} x_m$$

P. Shih, T. C. Berkelbach. *Phys. Rev. B* **106**, 144307 (2022).

1) Defining the impurity problem

- Difference between the **lattice GF** and **system GF** defines **system-bath coupling**: $\boldsymbol{\Delta}(\omega) = \boldsymbol{D}_{\text{sys}}^{-1}(\omega) - \boldsymbol{D}_{C}^{-1}(\omega)$



2) Calculating impurity GF

- Impurity GF (anharmonic system + harmonic bath):

$$i\hbar D_{\mathrm{imp}}(\omega) = \int_0^\infty dt e^{i\omega t} \langle [u(t), u(0)] \rangle$$

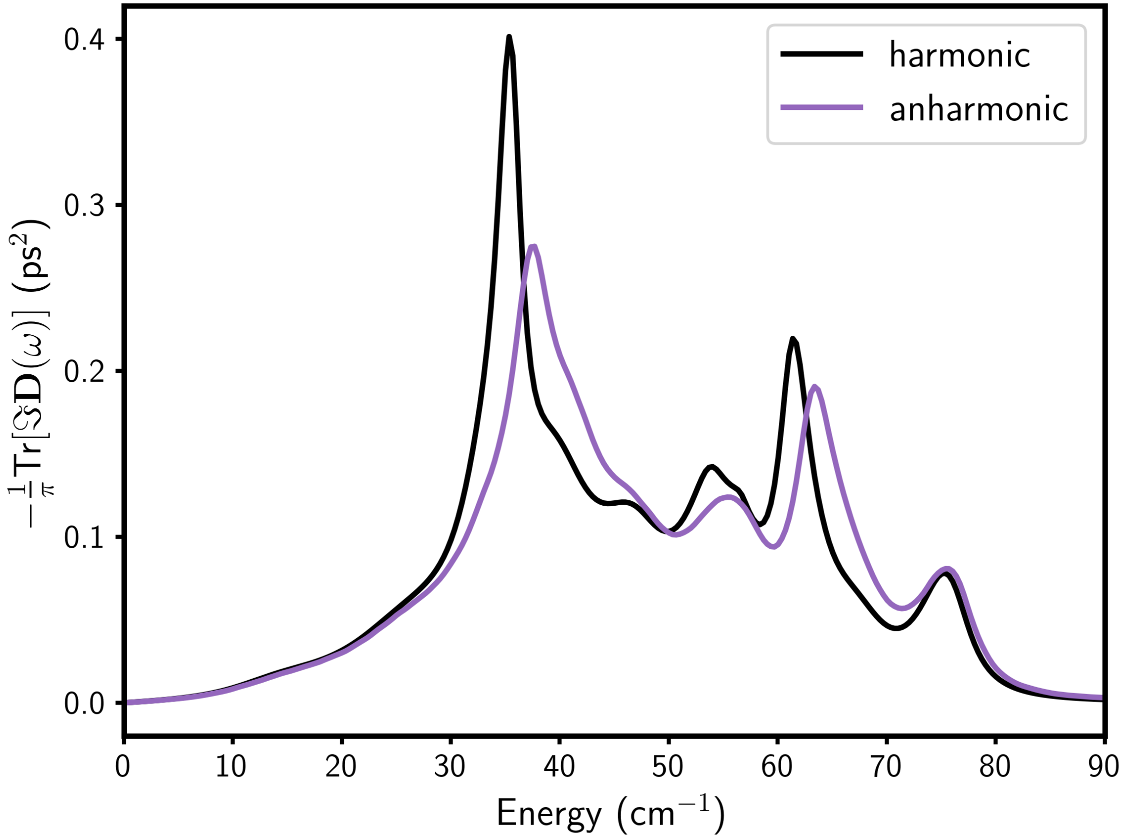
- Use generalized Langevin equation to solve system dynamics
  - Non-Markovian (frequency-dependent) **friction** makes it **dynamical** MFT

$$\ddot{u}(t) = -\frac{dV}{du} - \int_0^t ds \gamma(t-s)\dot{u}(s) + \xi(t)$$

M. Ceriotti, G. Bussi, M. Parrinello. *J. Chem. Theory Comput.* **6**, 1170 (2010).

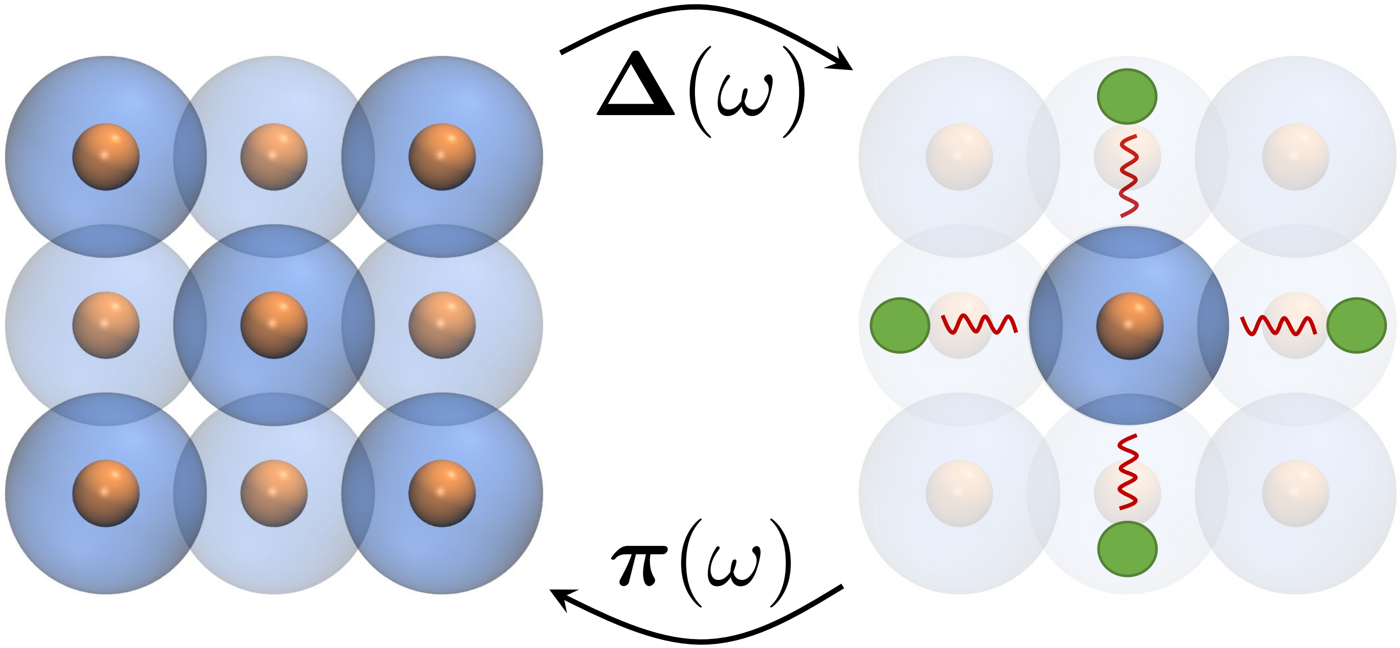
3) Getting (local) self-energy

- Difference between impurity **anharmonic GF** and **harmonic GF** is the **self-energy**: $\boldsymbol{\pi}(\omega) = \boldsymbol{D}_{\mathrm{imp},0}^{-1}(\omega) - \boldsymbol{D}_{\mathrm{imp}}^{-1}(\omega)$



4) Iterate (if needed…)

- Use self-energy to define lattice GF that includes anharmonicity
  - New cellular GF, new system GF, new **hybridization**
  - New impurity GF and GF0, new self energy
- Eventually, convergence when $\boldsymbol{D}_C(\omega) = \boldsymbol{D}_{\text{imp}}(\omega)$

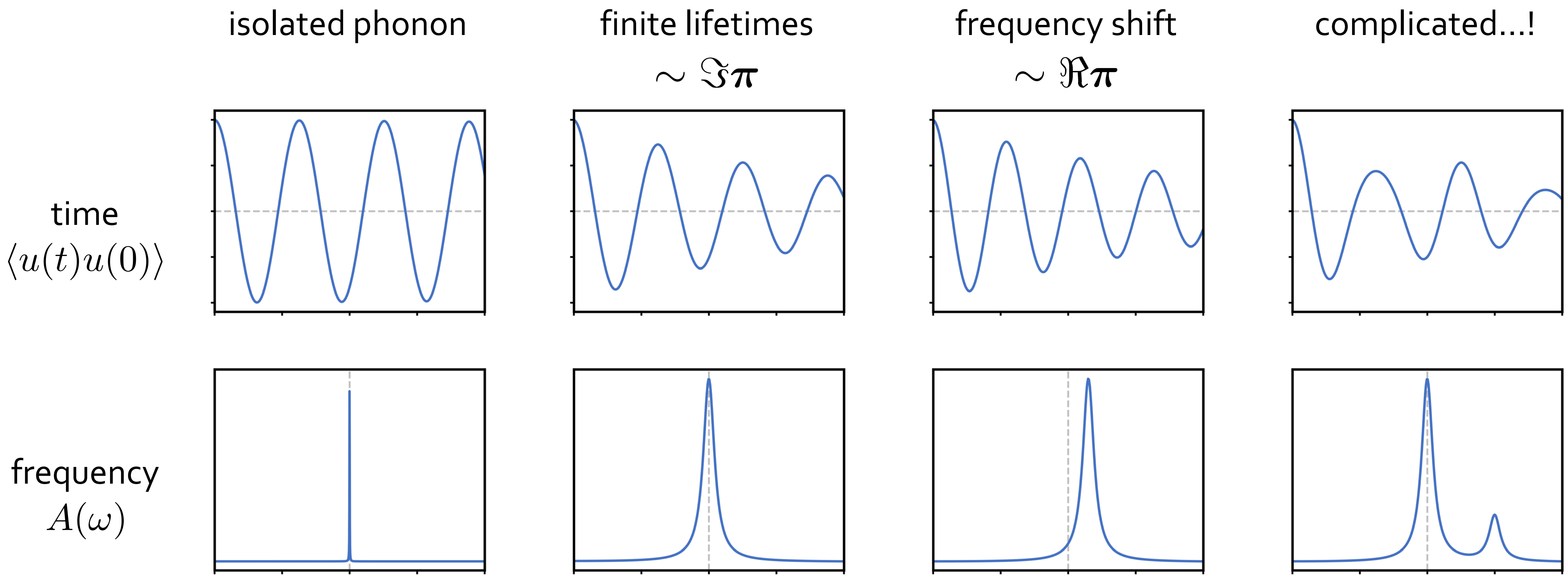


Anharmonic spectral function

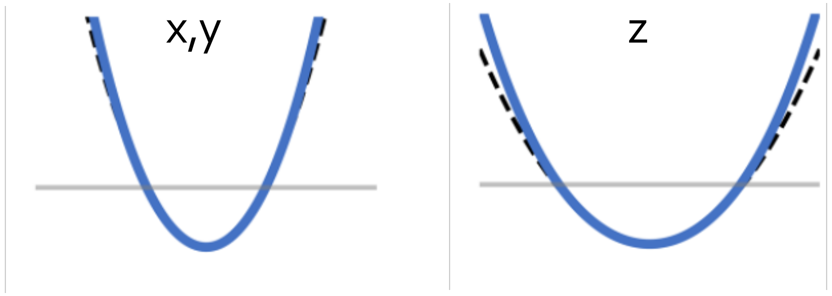
$$D^{-1}(\boldsymbol{k},\omega) = D_0^{-1}(\boldsymbol{k},\omega) - \boldsymbol{\pi}(\boldsymbol{k},\omega)$$

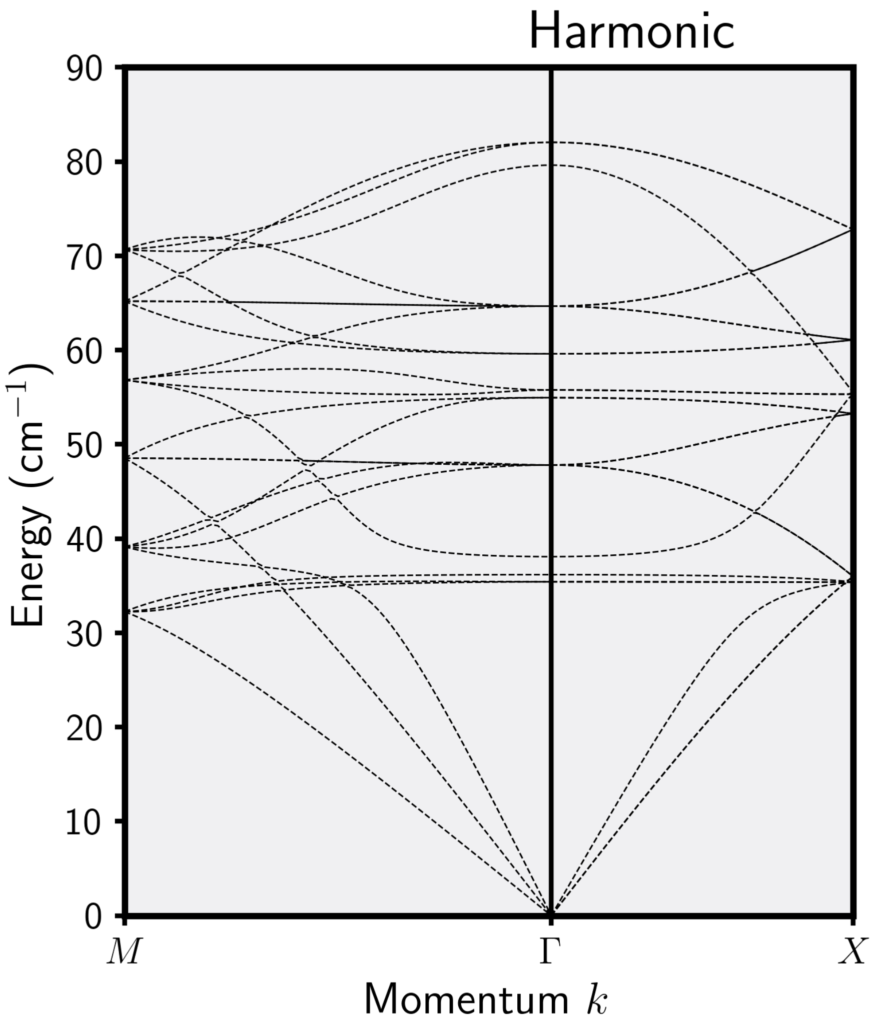
Anharmonic spectral function

$$A(\boldsymbol{k}, \omega) = -\frac{1}{\pi} \mathrm{Tr}[\Im \boldsymbol{D}(\boldsymbol{k}, \omega)]$$



VDMFT: BaGG at 300K





D. Jasrasaria, T. C. Berkelbach. *In preparation*.

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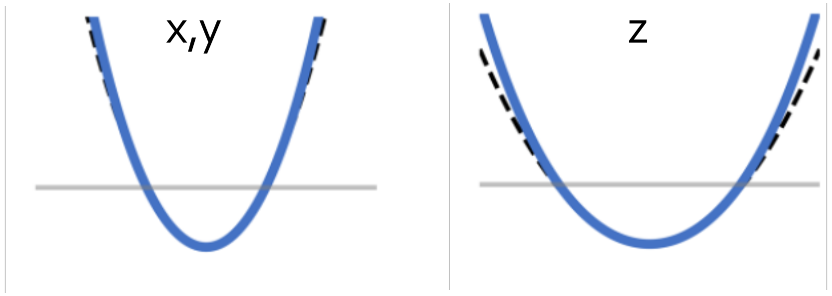

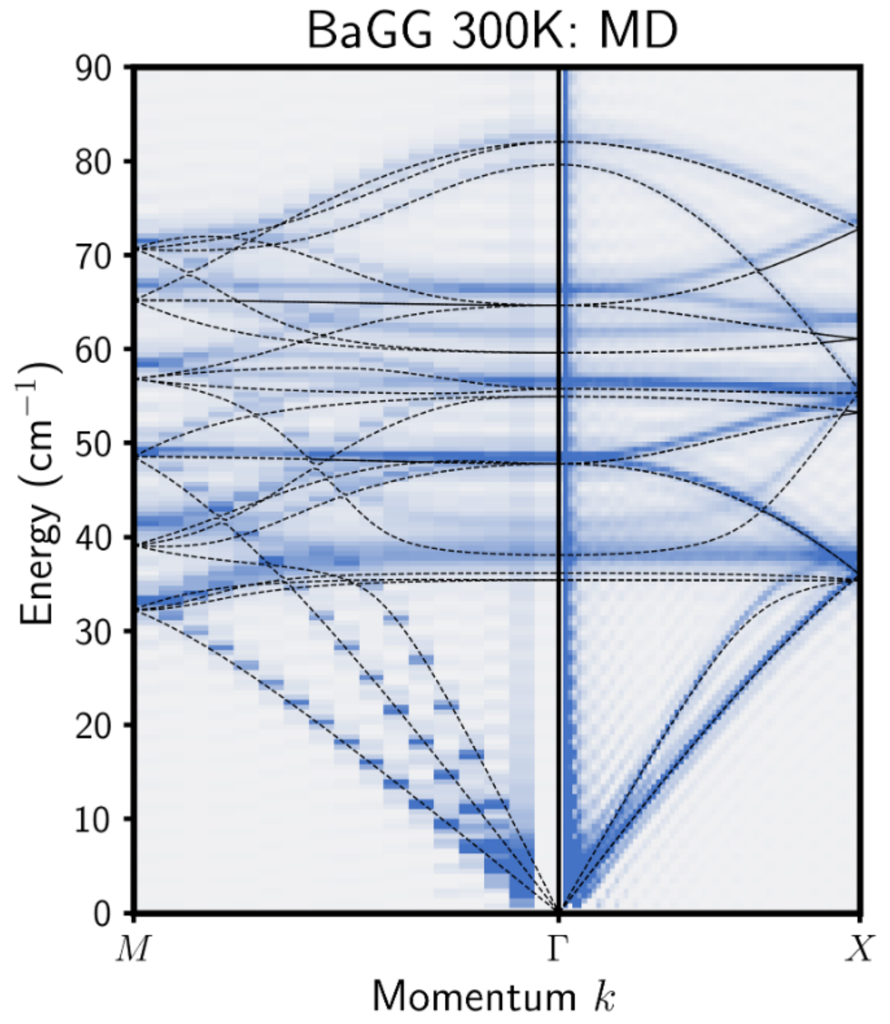

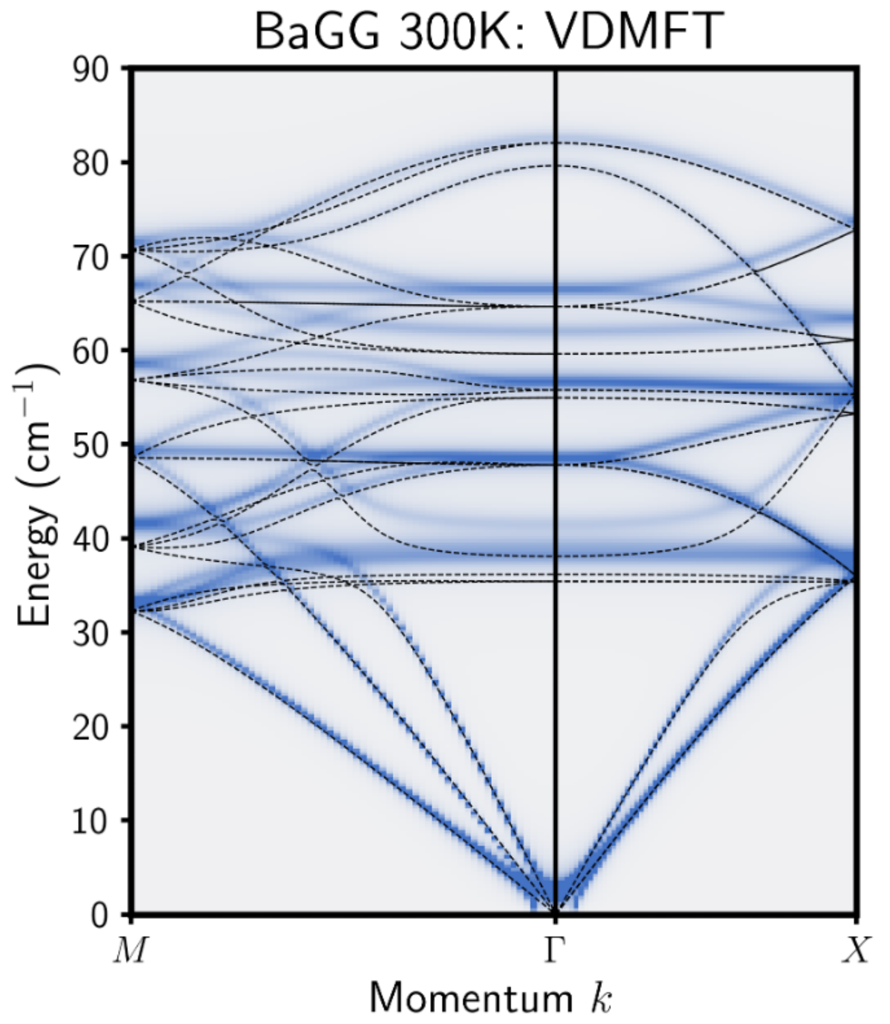

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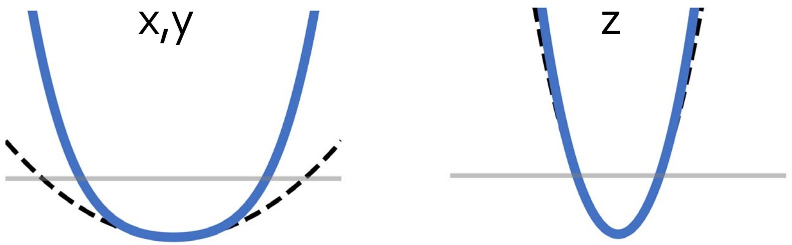
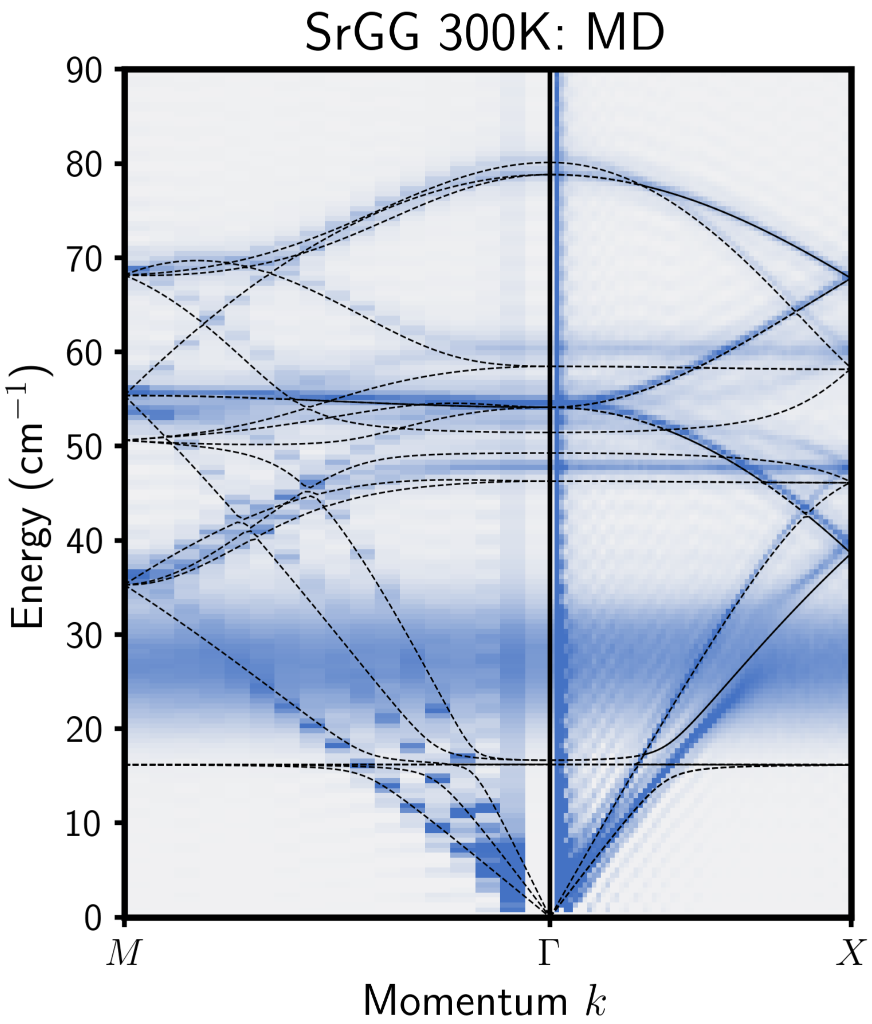
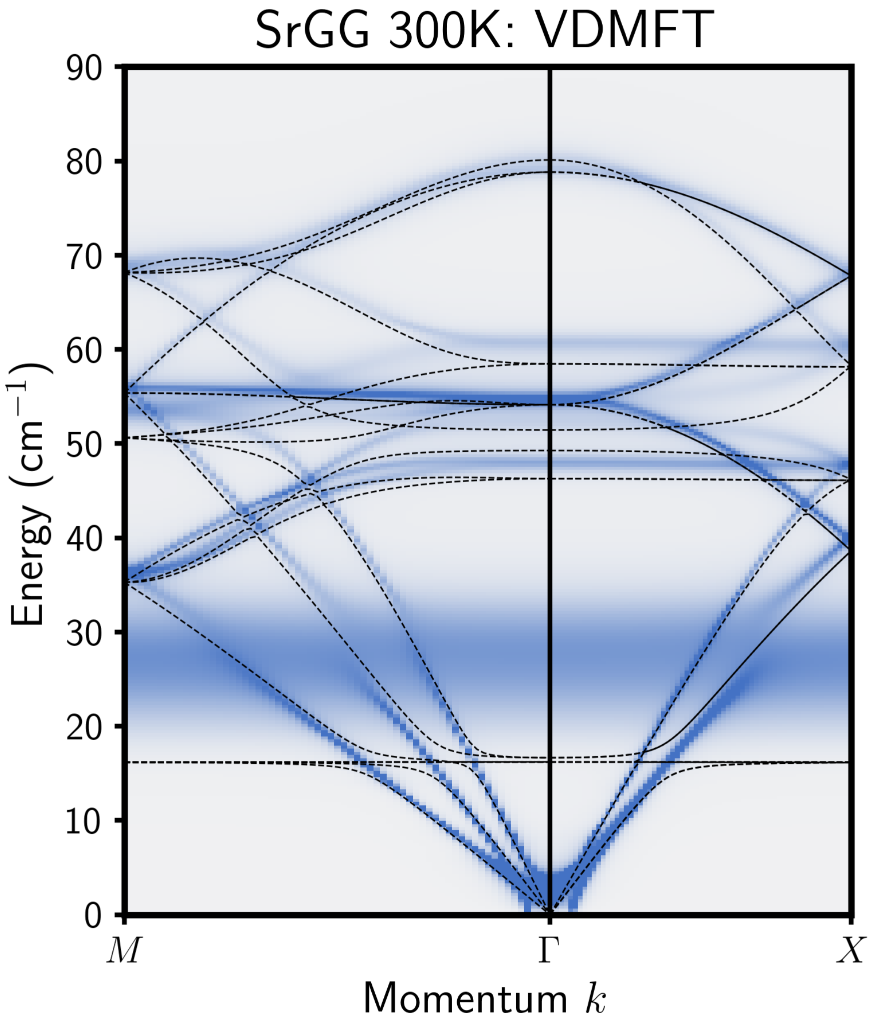
Turning up anharmonicity: SrGG at 300K







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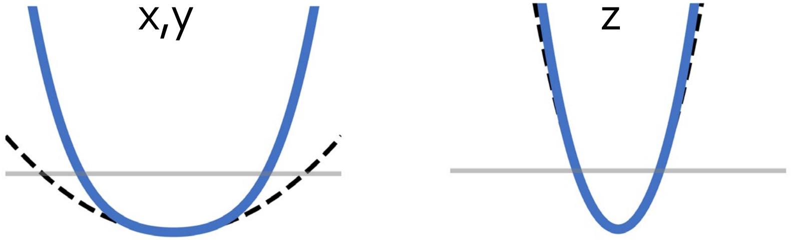

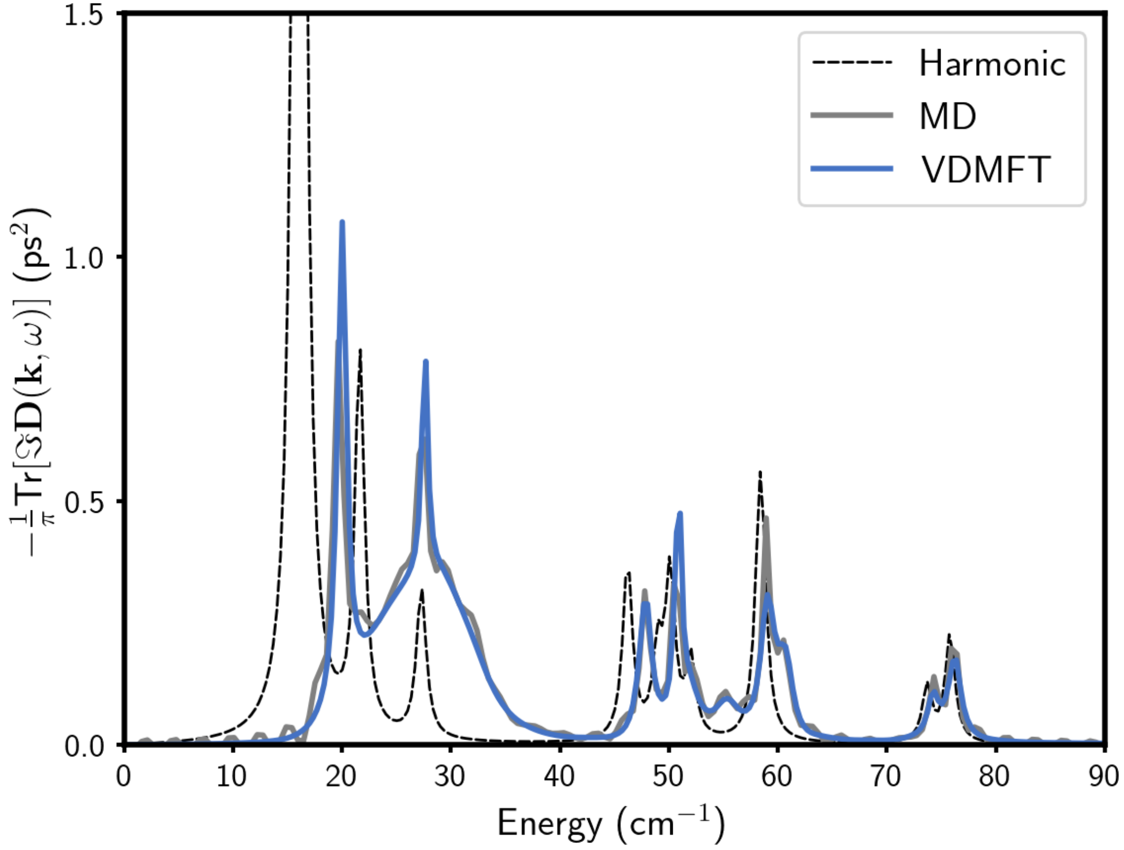

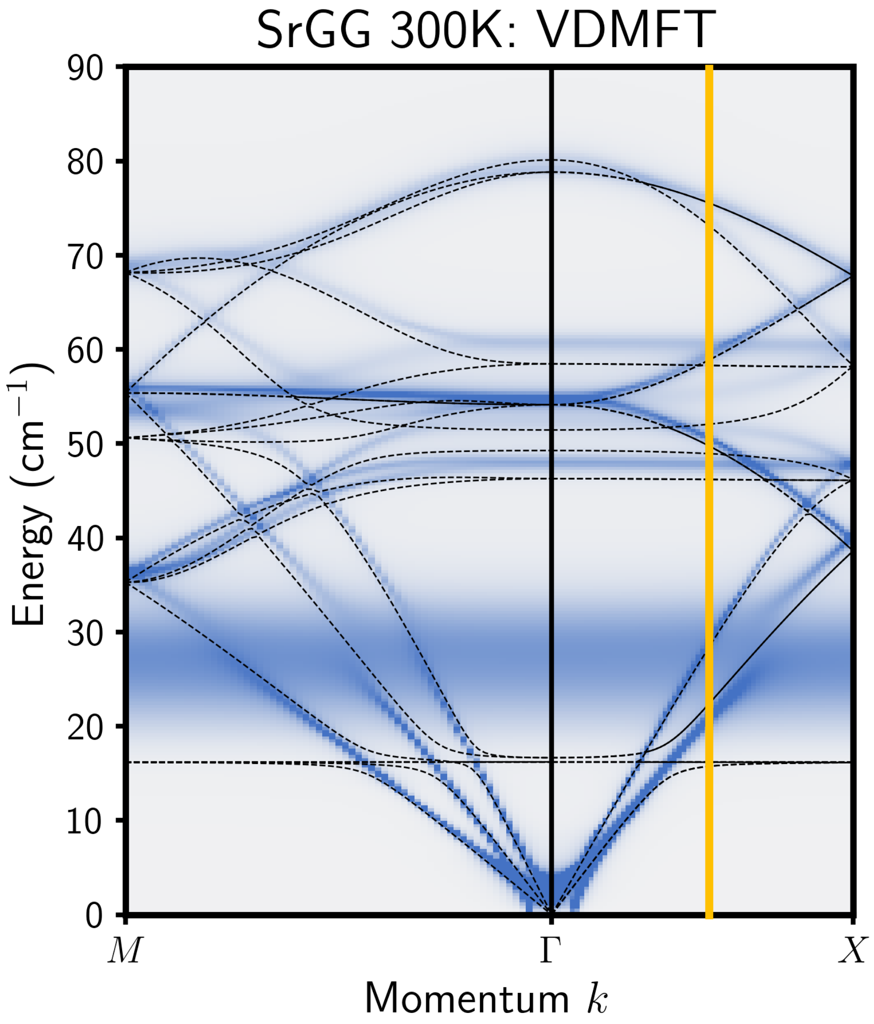

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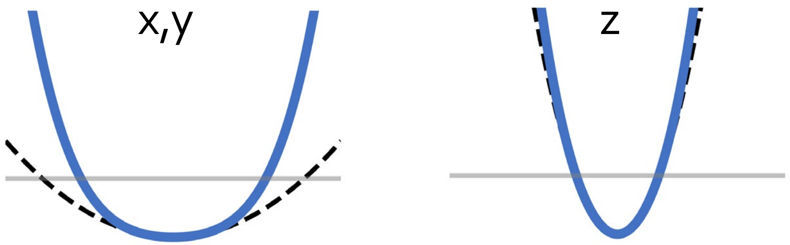
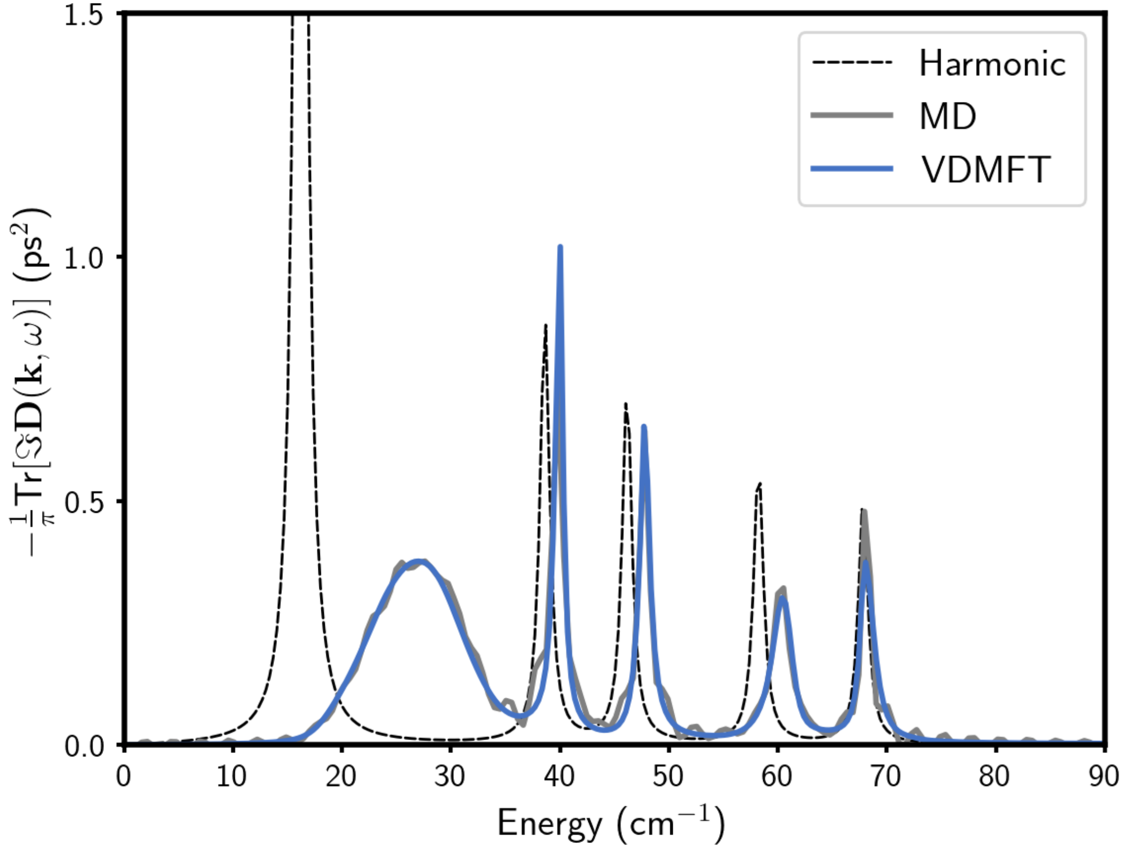
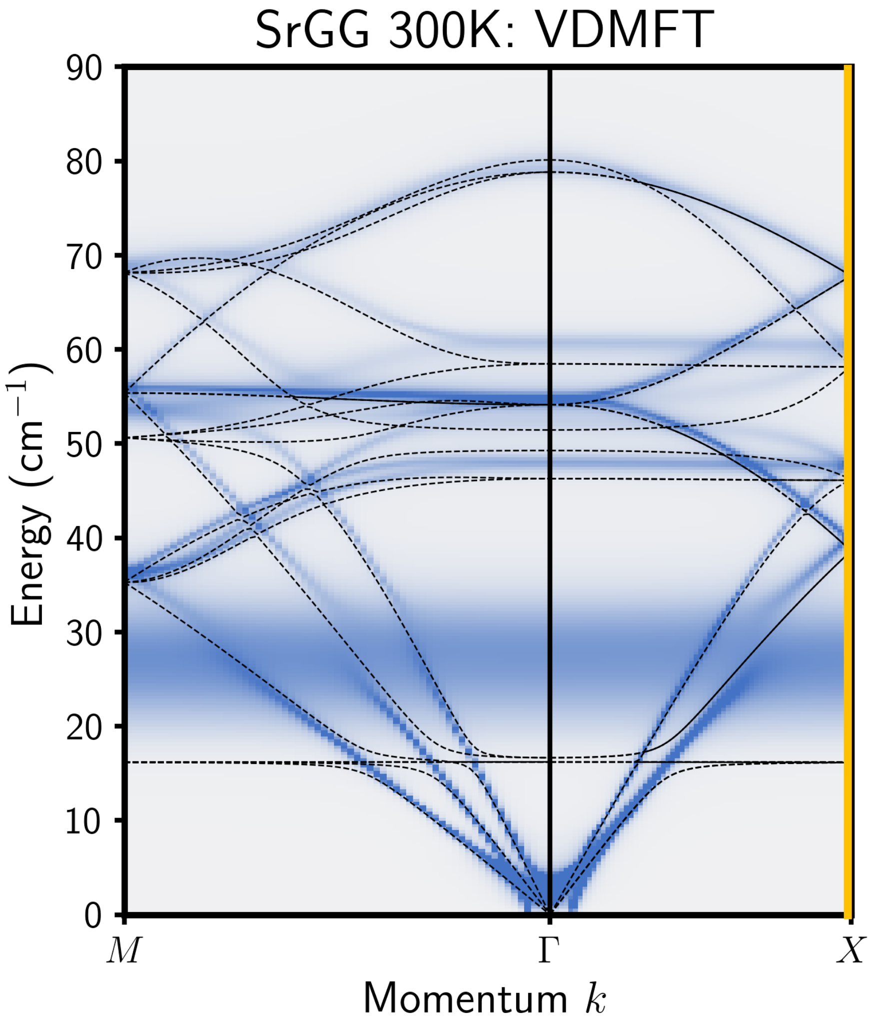
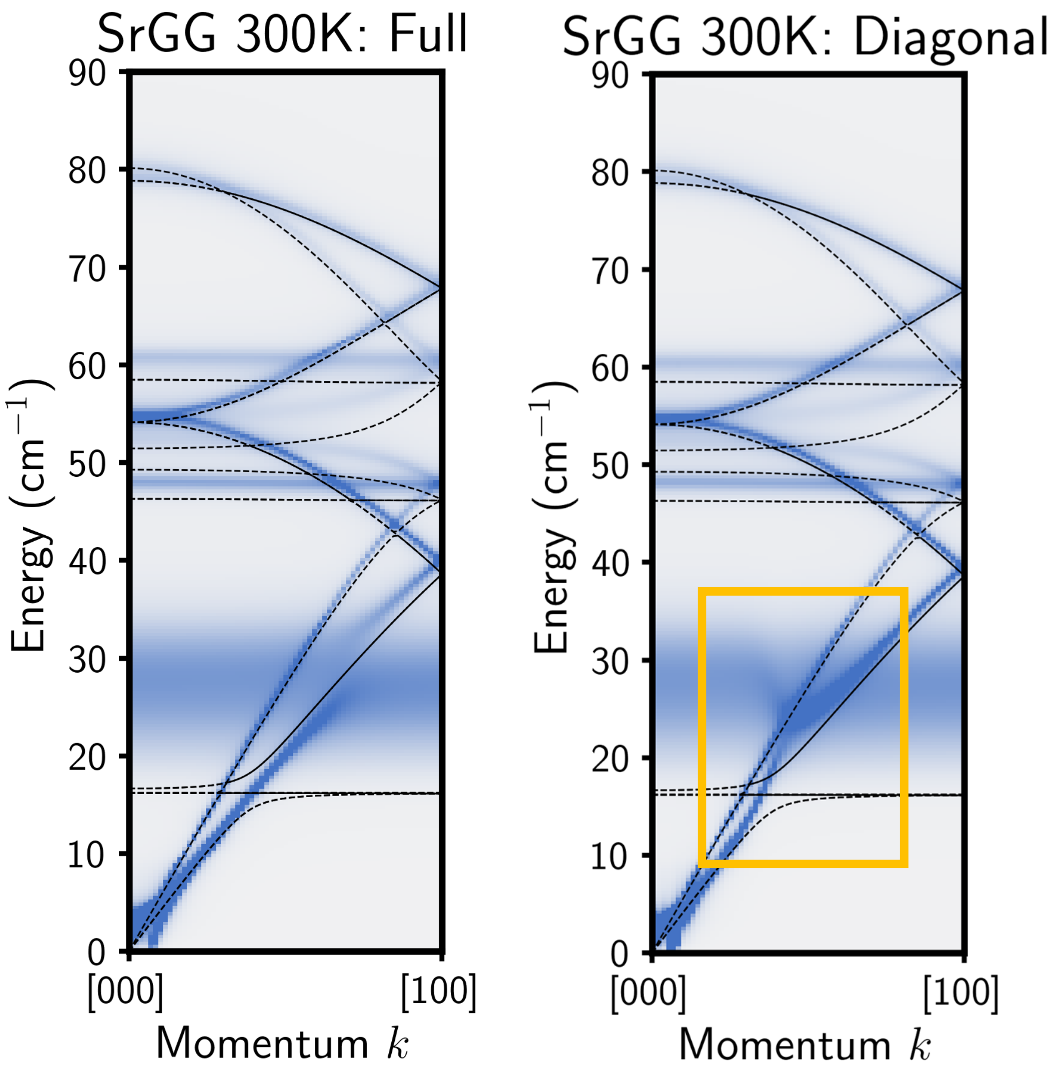






How important is the *full* self-energy?

- Diagonal approximation
  - Neglects non-diagonal elements of self-energy: $\boldsymbol{D}^{-1} \rightarrow \boldsymbol{D}$
- Significant **anharmonic** hybridization between cage-acoustic and guest-rattling modes
- Phonon picture is not valid!

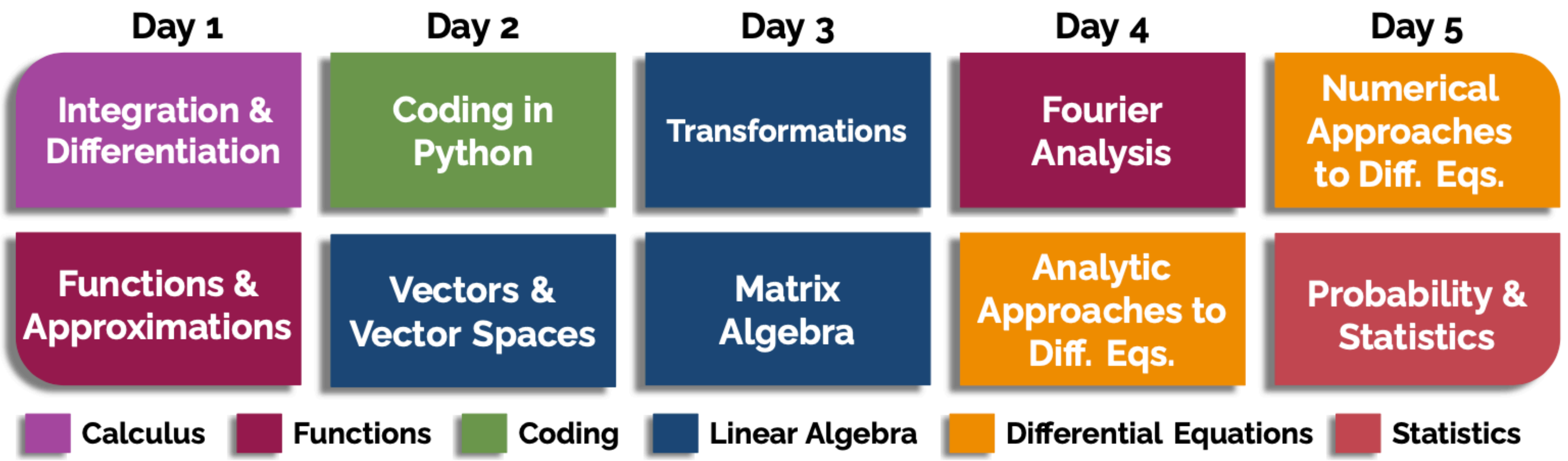


Summary and looking forward

- VDMFT calculates anharmonic phonon GF
    - Includes local anharmonicity exactly
    - Successfully calculates phonon spectral function for model clathrates with various degrees of anharmonicity
    - Cheaper than MD and can account for nuclear quantum effects
- Can use phonon GF to compute thermal conductivity
    - Phonon hybridization is key to clathrates' low thermal conductivity

College of Chemistry Math Bootcamp

- Student-initiated, designed, and taught for incoming physical chemistry students centered around group problem solving



- Content freely available at **chemmathbootcamp.com**

R. Clune*, A. Das*, **D. Jasrasaria***, E. Rossomme, O. Cohen, A. Baranger. *chemRxiv:2022-dl84f* (2022).

Acknowledgements

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PTL PHOTONICS AT THERMODYNAMIC LIMITS

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