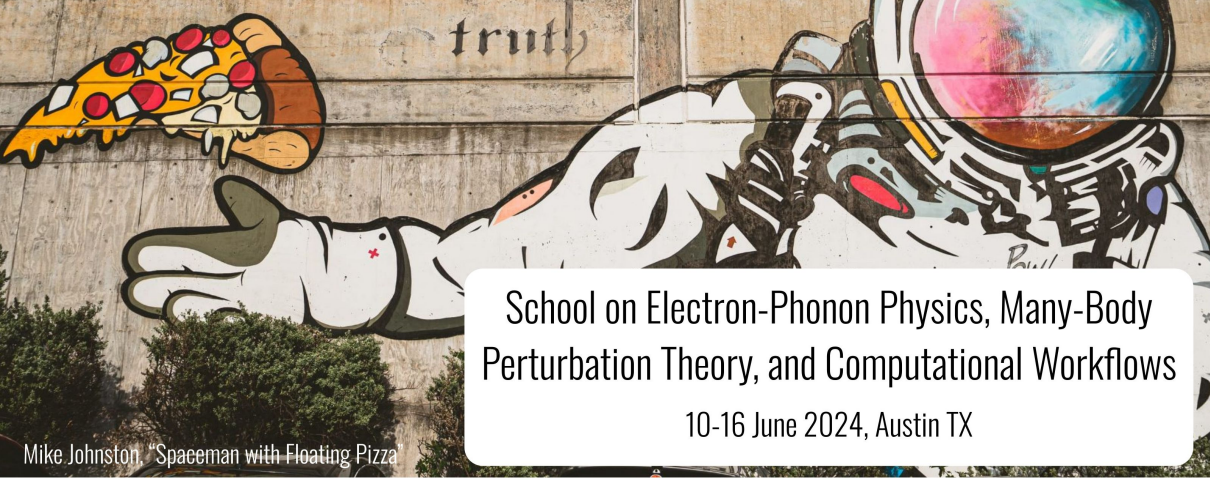

Mike Johnston, "Spaceman with Floating Pizza"

School on Electron-Phonon Physics, Many-Body Perturbation Theory, and Computational Workflows

10-16 June 2024, Austin TX

U.S. DEPARTMENT OF ENERGY

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Lecture Fri.1

The Special Displacement Method

Marios Zacharias

INSA Rennes, CNRS, Institut FOTON - UMR 6082, F-35000 Rennes, France

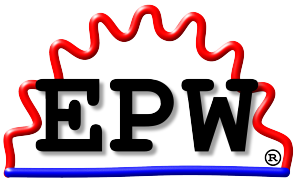
Univ. Rennes

Lecture Summary

- Nonperturbative approaches to electron-phonon and anharmonicity
- Phonons and normal coordinates transformation
- From the stochastic framework to deterministic
- Theory of the special displacement method (SDM)
- Self-consistent anharmonic special displacements (A-SDM)
- Applications

Codes for perturbative and nonperturbative calculations

Calculation of electron-phonon properties using, e.g.:



$g_{mn,\nu}(\mathbf{k},\mathbf{q})$ from DFPT in the unit-cell

Displaced nuclei in large supercells; $g_{mn,\nu}(\mathbf{k},\mathbf{q})$ is not explicitly used

Codes for perturbative and nonperturbative calculations

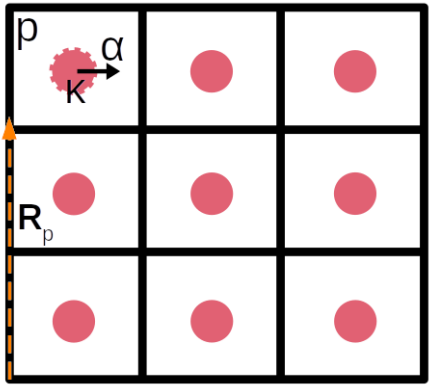
Calculation of anharmonic phonons using, e.g.:

Self-consistent phonon theory by displacing nuclei in supercells; $C^n_{p_1,\cdots,p_n}$ is or is not explicitly used

Phonons from first-principles (recap)

We rely first on the harmonic approximation and expand the PES

$$U^{\{\tau\}} = U_0 + \frac{1}{2} \sum_{\substack{p\kappa\alpha \\ p'\kappa'\alpha'}} \frac{\partial^2 U}{\partial \tau_{p\kappa\alpha} \partial \tau_{p'\kappa'\alpha'}} \Delta\tau_{p\kappa\alpha} \Delta\tau_{p'\kappa'\alpha'}.$$



Phonons from first-principles (recap) (Mon.3.Giannozzi)

1. Harmonic approximation for the PES

$$U^{\{\tau\}} = U_0 + \sum_{\substack{p\kappa\alpha \\ p'\kappa'\alpha'}} \frac{\partial^2 U}{\partial \tau_{p\kappa\alpha} \partial \tau_{p'\kappa'\alpha'}} \frac{\Delta\tau_{p\kappa\alpha}\Delta\tau_{p'\kappa'\alpha'}}{2}$$

2. Evaluate the IFCs from finite differences or DFPT:

$$C_{p\kappa\alpha,p'\kappa'\alpha'} = \frac{\partial^2 U}{\partial \tau_{p\kappa\alpha} \partial \tau_{p'\kappa'\alpha'}} = \frac{\partial F_{p\kappa\alpha}}{\partial \tau_{p'\kappa'\alpha'}}$$

3. Evaluate the dynamical matrix as:

$$D_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}) = \sum_{p'} \frac{C_{0\kappa\alpha,p'\kappa'\alpha'}}{\sqrt{M_\kappa M_{\kappa'}}} e^{i\mathbf{q}\cdot(\mathbf{R}_{p'}+\boldsymbol{\tau}_{\kappa'}-\boldsymbol{\tau}_\kappa)}$$

4. Diagonalize the dynamical matrix:

$$\sum_{\kappa'\alpha'} D_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}) e_{\kappa'\alpha',\nu}(\mathbf{q}) = \omega^2_{\mathbf{q}\nu} e_{\kappa\alpha,\nu}(\mathbf{q})$$

$\{\omega_{\mathbf{q}\nu}, e_{\kappa\alpha,\nu}(\mathbf{q})\}$ define the phonons.

5. For polar materials include the dipole-dipole interaction term:

$$D^{\mathrm{dd}}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}\to 0) = \frac{4\pi e^2}{\sqrt{M_\kappa M_{\kappa'}}\Omega} \frac{\sum_\beta q_\beta Z^*_{\kappa,\beta\alpha} \sum_{\beta'} q_{\beta'} Z^*_{\kappa',\beta'\alpha'}}{\sum_{\beta\beta'} q_\beta \epsilon^\infty_{\beta\beta'} q_{\beta'}}$$

Nuclei displacements

Born-Oppenheimer Molecular dynamics
$\Delta\tau_{p\kappa\alpha}(t)$ from equation of motion:

$$M_\kappa \ddot{\tau}_{p\kappa\alpha}(t) = -\frac{\partial U}{\partial \tau_{p\kappa\alpha}} = F_{p\kappa\alpha}$$

Nuclei displacements

Born-Oppenheimer Nonperturbative methods

$\Delta\tau_{p\kappa\alpha}$ from:

$$\Delta\tau_{p\kappa\alpha} = \left(\frac{M_0}{M_\kappa}\right)^{1/2} \sum_\nu e_{p\kappa\alpha,\nu}\, x_\nu$$

Nuclei displacements

Born-Oppenheimer Nonperturbative methods

$\Delta\tau_{p\kappa\alpha}$ from:

$$\Delta\tau_{p\kappa\alpha} = \left(\frac{M_0}{M_\kappa}\right)^{1/2} \sum_\nu e_{p\kappa\alpha,\nu}\, x_\nu$$

apply a smooth Berry connection

Nuclei displacements

Born-Oppenheimer Nonperturbative methods

$\Delta\tau_{p\kappa\alpha}$ from:

$$\Delta\tau_{p\kappa\alpha} = \left(\frac{M_0}{M_\kappa}\right)^{1/2} \sum_\nu S_\nu e_{p\kappa\alpha,\nu}\, x_\nu$$

± 1; need to be determined

Nuclei displacements

Born-Oppenheimer Nonperturbative methods

$\Delta\tau_{p\kappa\alpha}$ from:

$$\Delta\tau_{p\kappa\alpha} = \left(\frac{M_0}{M_\kappa}\right)^{1/2} \sum_\nu S_\nu e_{p\kappa\alpha,\nu}\, x_\nu$$

amount of displacement; need to be determined

Taylor expansion with respect to $\Delta\tau_{\kappa\alpha}$ and x_ν

$$U = U_0 + \sum_{\kappa\alpha} \frac{\partial U}{\partial \tau_{\kappa\alpha}} \Delta\tau_{\kappa\alpha} + \frac{1}{2} \sum_{\substack{\kappa\alpha \\ \kappa'\alpha'}} \frac{\partial^2 U}{\partial \tau_{\kappa\alpha} \partial \tau_{\kappa'\alpha'}} \Delta\tau_{\kappa\alpha} \Delta\tau_{\kappa'\alpha'} + \frac{1}{3!} \sum_{\substack{\kappa\alpha \\ \kappa'\alpha' \\ \kappa''\alpha''}} \frac{\partial^3 U}{\partial \tau_{\kappa\alpha} \partial \tau_{\kappa'\alpha'} \partial \tau_{\kappa''\alpha''}} \Delta\tau_{\kappa\alpha} \Delta\tau_{\kappa'\alpha'} \Delta\tau_{\kappa''\alpha''}$$

Homework to use:

$$\Delta\tau_{\kappa\alpha} = \left(\frac{M_0}{M_\kappa}\right)^{1/2} \sum_\nu e_{\kappa\alpha,\nu}\, x_\nu$$

$$\sum_{\kappa\alpha} e_{\kappa\alpha,\nu} e_{\kappa\alpha,\nu'} = \delta_{\nu\nu'}$$

$$\frac{\partial}{\partial \tau_{\kappa\alpha}} = \left(\frac{M_\kappa}{M_0}\right)^{1/2} \sum_\nu e^\nu_{\kappa\alpha} \frac{\partial}{\partial x_\nu}$$

Taylor expansion with respect to $\Delta\tau_{\kappa\alpha}$ and x_ν

$$U = U_0 + \sum_{\kappa\alpha} \frac{\partial U}{\partial \tau_{\kappa\alpha}} \Delta\tau_{\kappa\alpha} + \frac{1}{2} \sum_{\substack{\kappa\alpha \\ \kappa'\alpha'}} \frac{\partial^2 U}{\partial \tau_{\kappa\alpha} \partial \tau_{\kappa'\alpha'}} \Delta\tau_{\kappa\alpha} \Delta\tau_{\kappa'\alpha'} + \frac{1}{3!} \sum_{\substack{\kappa\alpha \\ \kappa'\alpha' \\ \kappa''\alpha''}} \frac{\partial^3 U}{\partial \tau_{\kappa\alpha} \partial \tau_{\kappa'\alpha'} \partial \tau_{\kappa''\alpha''}} \Delta\tau_{\kappa\alpha} \Delta\tau_{\kappa'\alpha'} \Delta\tau_{\kappa''\alpha''}$$

Homework to use:

$$\Delta\tau_{\kappa\alpha} = \left(\frac{M_0}{M_\kappa}\right)^{1/2} \sum_\nu e_{\kappa\alpha,\nu}\, x_\nu$$

$$\sum_{\kappa\alpha} e_{\kappa\alpha,\nu} e_{\kappa\alpha,\nu'} = \delta_{\nu\nu'}$$

$$\frac{\partial}{\partial \tau_{\kappa\alpha}} = \left(\frac{M_\kappa}{M_0}\right)^{1/2} \sum_\nu e^\nu_{\kappa\alpha} \frac{\partial}{\partial x_\nu}$$

$$U = U_0 + \sum_\nu \frac{\partial U}{\partial x_\nu} x_\nu + \frac{1}{2} \sum_{\nu\nu'} \frac{\partial^2 U}{\partial x_\nu \partial x_{\nu'}} x_\nu x_{\nu'} + \frac{1}{3!} \sum_{\nu,\nu',\nu''} \frac{\partial^3 U}{\partial x_\nu \partial x_{\nu'} \partial x_{\nu''}} x_\nu x_{\nu'} x_{\nu''}$$

Taylor expansion with respect to $\Delta\tau_{\kappa\alpha}$ and x_ν

$$U = U_0 + \sum_{\kappa\alpha} \frac{\partial U}{\partial \tau_{\kappa\alpha}} \Delta\tau_{\kappa\alpha} + \frac{1}{2} \sum_{\substack{\kappa\alpha \\ \kappa'\alpha'}} \frac{\partial^2 U}{\partial \tau_{\kappa\alpha} \partial \tau_{\kappa'\alpha'}} \Delta\tau_{\kappa\alpha} \Delta\tau_{\kappa'\alpha'} + \frac{1}{3!} \sum_{\substack{\kappa\alpha \\ \kappa'\alpha' \\ \kappa''\alpha''}} \frac{\partial^3 U}{\partial \tau_{\kappa\alpha} \partial \tau_{\kappa'\alpha'} \partial \tau_{\kappa''\alpha''}} \Delta\tau_{\kappa\alpha} \Delta\tau_{\kappa'\alpha'} \Delta\tau_{\kappa''\alpha''}$$

Homework to use:

$$\Delta\tau_{\kappa\alpha} = \left(\frac{M_0}{M_\kappa}\right)^{1/2} \sum_\nu e_{\kappa\alpha,\nu}\, x_\nu$$

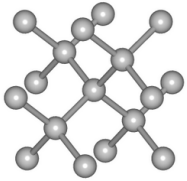
$$\sum_{\kappa\alpha} e_{\kappa\alpha,\nu} e_{\kappa\alpha,\nu'} = \delta_{\nu\nu'}$$

$$\frac{\partial}{\partial \tau_{\kappa\alpha}} = \left(\frac{M_\kappa}{M_0}\right)^{1/2} \sum_\nu e^\nu_{\kappa\alpha} \frac{\partial}{\partial x_\nu}$$

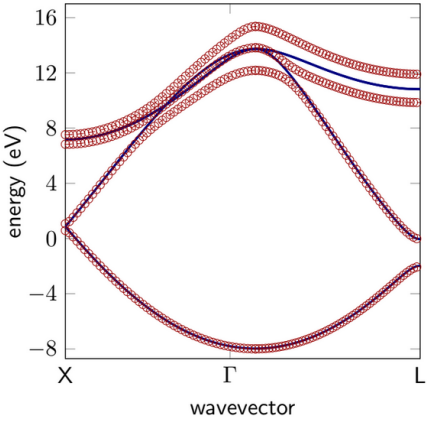
$$U = U_0 + \sum_\nu \frac{\partial U}{\partial x_\nu} x_\nu + \frac{1}{2} \sum_{\nu\nu'} \frac{\partial^2 U}{\partial x_\nu \partial x_{\nu'}} x_\nu x_{\nu'} + \frac{1}{3!} \sum_{\nu,\nu',\nu''} \frac{\partial^3 U}{\partial x_\nu \partial x_{\nu'} \partial x_{\nu''}} x_\nu x_{\nu'} x_{\nu''}$$

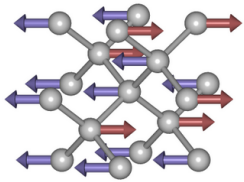
U can be replaced essentially with any observable $\mathcal{O}$, for example,
$\varepsilon_{\mathrm{g}}, \epsilon_2(\omega), \sigma(\omega), \cdots$

Effects on electronic structure: Slide from Giustino Mon.1



diamond





Γ-point optical mode
0.015 Å C-displacement

see tutorial `exerciseC`

$$\Delta\tau_{\kappa\alpha} = \left(\frac{M_0}{M_\kappa}\right)^{1/2} e_{\kappa\alpha,\nu}\, x_\nu, \quad \varepsilon_v^x = \varepsilon_v^0 + \frac{\partial\varepsilon_v}{\partial x_\nu} x_\nu + \frac{1}{2}\frac{\partial^2\varepsilon_v}{\partial x_\nu^2} x_\nu^2 + \frac{1}{3!}\frac{\partial^3\varepsilon_v}{\partial x_\nu^3} x_\nu^3 + \cdots$$

Nonperturbative Approaches - Literature I

Common goal is to evaluate a physical property $\mathcal{O}$ at temperature T:

$$\langle \mathcal{O} \rangle_T = \frac{1}{Z} \mathrm{Tr}\Big[\exp(-\beta_T H)\mathcal{O}\Big] \Rightarrow \Gamma_{\alpha\to\beta}(\omega, T) = \frac{1}{Z} \sum_n \exp(-E_{\alpha n}/k_\mathrm{B}T)\, \Gamma_{\alpha n\to\beta}(\omega)$$

Sum over nuclear states

Partition function

Boltzmann factor

Path Integral Molecular Dynamics (PIMD):

- F. Della Sala, R. Rousseau, A. Görling, D. Marx, Phys. Rev. Lett. 92, 183401 (2004)
- R. Ramírez, P. C. Herrero, E. R. Hernández, Phys. Rev. B 73, 245202 (2006)
- M. Rossi, P. Gasparotto, M. Ceriotti Phys. Rev. Lett. 117, 115702 (2016)
- A. Kundu, M. Govoni, H. Yang, M. Ceriotti, F. Gygi, G. Galli, Phys. Rev. Materials 5, L070801 (2021)
- A. M. Alvertis, J. B. Haber, E. A. Engel, S. Sharifzadeh, J. B. Neaton, Phys. Rev. Lett. 130, 086401 (2023)

ab initio Molecular Dynamics (aiMD):

- A. Franceschetti Phys. Rev. B 76, 161301(R) (2007)
- R. Ramírez, P. C. Herrero, R. E. Hernández, M. Cardona, Phys. Rev. B 77, 045210 (2008)
- O. Hellman, I. A. Abrikosov, and S. I. Simak, Phys. Rev. B 84, 180301(R) (2011)
- M. Zacharias, M. Scheffler, C. Carbogno, Phys. Rev. B 102, 045126 (2020)

Nonperturbative Approaches - Literature II

PI for nuclei with Quantum Monte Carlo (QMC) for electrons:

- C. Pierleoni, D. M. Ceperley, M. Holzmann, Phys. Rev. Lett. 93, 146402 (2004)
- V. Gorelov, D. M. Ceperley, M. Holzmann, C. Pierleoni, J. Chem. Phys. 153, 234117 (2020)

Importanse Sampling Monte Carlo (ISMC):

- C. E. Patrick, F. Giustino, Nat. Commun. 4, 2006 (2013)
- B. Monserrat, R. J. Needs, and C. J. Pickard, J. Chem. Phys. 141, 134113 (2014)
- I. Errea, M. Calandra, and F. Mauri, Phys. Rev. B 89, 064302 (2014)
- M. Zacharias, C. E. Patrick, F. Giustino, Phys. Rev. Lett. 115, 177401 (2015)
- A. van Roekeghem, J. Carrete, N. Mingo, Comp. Phys. Communic. (2021)
- L. Monacelli, *et al* J. Phys.: Condens. Matter 33, 363001 (2021).

Special Displacement Method (SDM):

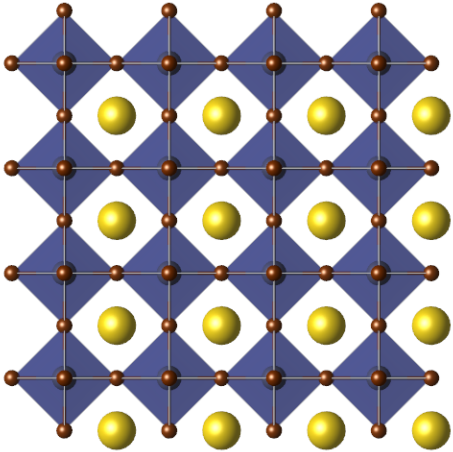
- M. Zacharias, F. Giustino, Phys. Rev. B 94, 075125 (2016)
- F. Karsai, M. Engel, E. Flage-Larsen, G. Kresse, New J. Phys. 20 123008 (2018)
- M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020)
- M. Zacharias, G. Volonakis, F. Giustino, J. Even Phys. Rev. B 108, 035155 (2023)

Other supercell approaches: Finite Differences (FD), Thermal Lines (TL):

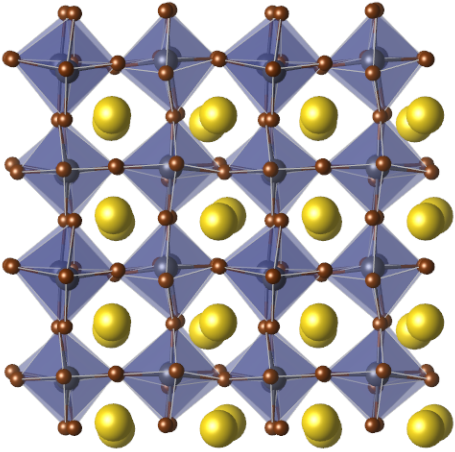
- R. B. Capaz, C. D. Spataru, P. Tangney, M. L. Cohen, S. G. Louie, Phys. Rev. Lett. 94, 036801 (2005)
- G. Antonius, S. Poncé, P. Boulanger, M. Côté, X. Gonze, Phys. Rev. Lett. 112, 215501 (2014)
- B. Monserrat, J. Phys.: Condens. Matter 30, 083001 (2018)

The special displacement method (SDM) in a snapshot ...

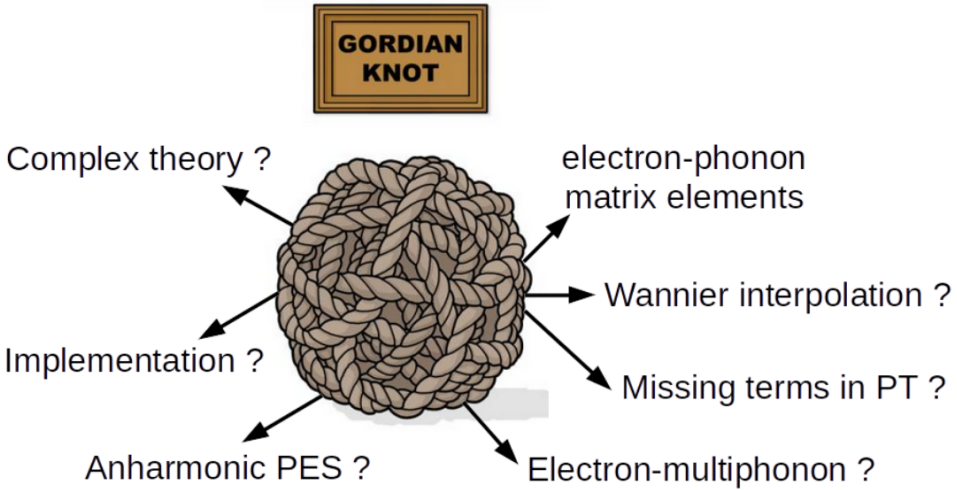
High-symmetry configuration
(static-equilibrium)



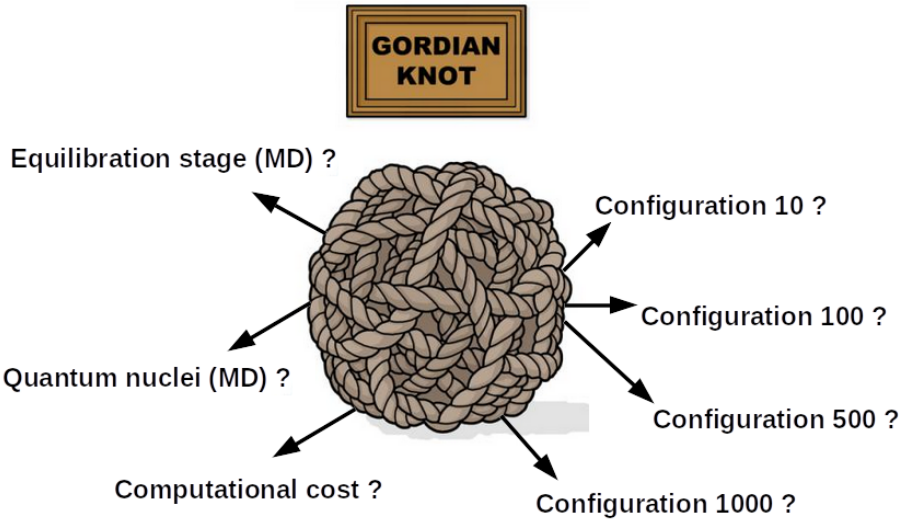
ZG configuration
(thermal equilibrium)



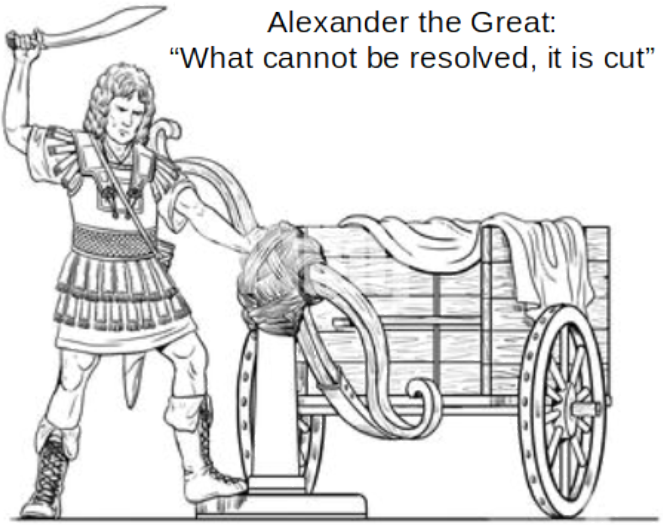
Why useful ? (Compared to perturbative approaches)



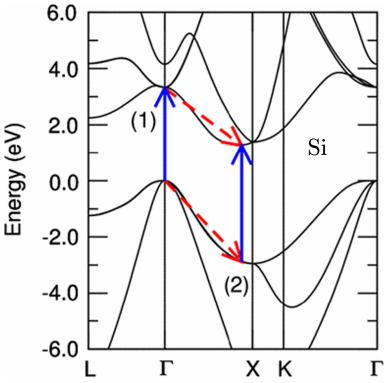
Why useful ? (compared to MD or MC)



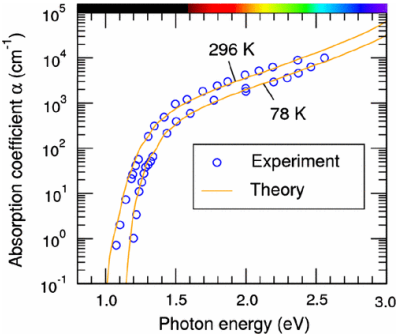
Why useful ?



Phonon-assisted optical spectra (Wed.3.Kioupakis and Sat.6.Tiwari)



J. Noffsinger, E. Kioupakis, C. G. Van de Walle, S. G. Louie, M. L. Cohen, Phys. Rev. Lett. 108, 167402 (2012)



Phonon-assisted transition rate in the Hall-Bardeen-Blat (HBB) theory:

$$\Gamma_{v\to c}(\omega) \propto \sum_{\nu} \left| \sum_{n\neq c} \frac{p_{vn} g_{nc,\nu}}{\varepsilon_n - \varepsilon_v - \hbar\omega} + \sum_{n\neq v} \frac{g_{vn,\nu} p_{nc}}{\varepsilon_n - \varepsilon_v \pm \hbar\omega_\nu} \right|^2 \delta(\varepsilon_c - \varepsilon_v \pm \hbar\omega_\nu - \hbar\omega)$$

Temperature-dependent band structures (see also Sat.4.Lihm)

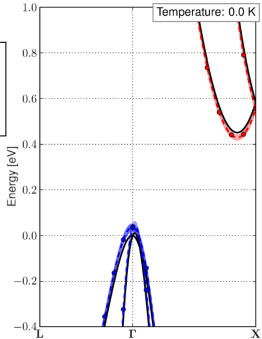
Temperature-dependence of the energy levels in the Allen-Heine theory:

$$\Delta\varepsilon_c(T) = \sum_\nu \left[\sum_{n\neq c} \frac{|g_{cn\nu}|^2}{\varepsilon_c - \varepsilon_n} + h_{c\nu\nu} \right] (2n_{\nu,T} + 1)$$

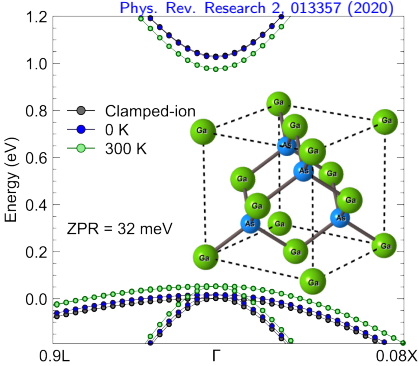
Perturbative first-principles applications:

- A. Marini, PRL 101, 106405 (2008)
- F. Giustino *et al.*, PRL 105, 265501 (2010)
- E. Cannuccia *et al.*, PRL 107, 255501 (2011)
- X. Gonze *et al.*, Ann. Phys. 523, 168 (2011)
- G. Antonius, *et al*, PRL 112, 215501 (2014)
- S. Poncé *et al*, PRB 90, 214304 (2014)
- A. Molina-Sánchez, *et al*, PRB 93, 155435 (2016)
- J. P. Nery, *et al*, PRB 97, 115145 (2018)
- A. Miglio, *et al*, npj CM 6, 167 (2020)
- J.-M. Lihm and C.-H. Park, PRX 12, 039901 (2022)
- M. Engel, *et al*, PRB 106, 094316 (2022)

S. Poncé *et al*, J. Chem. Phys. 143, 102813 (2015)



M. Zacharias, F. Giustino,
Phys. Rev. Research 2, 013357 (2020)



Williams-Lax Theory

1. Herzberg-Teller rate as the starting point:

$$\Gamma_{\alpha n\to\beta}(\omega) = \sum_m \frac{2\pi}{\hbar} |\langle \chi_{\alpha n}| P^x_{\alpha\beta} |\chi_{\beta m}\rangle|^2 \delta(E_{\beta m} - E_{\alpha n} - \hbar\omega)$$

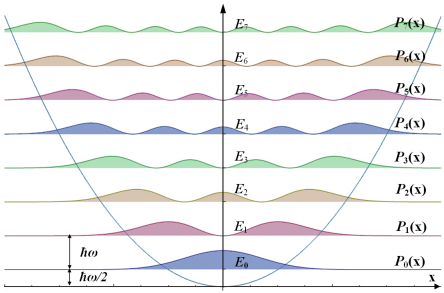
Williams-Lax Theory

1. Herzberg-Teller rate as the starting point:

$$\Gamma_{\alpha n\to\beta}(\omega)=\sum_m \frac{2\pi}{\hbar}|\left\langle\chi_{\alpha n}\right| P^x_{\alpha\beta}\left|\chi_{\beta m}\right\rangle|^2\delta(E_{\beta m}-E_{\alpha n}-\hbar\omega)$$

2. Semiclassical approximation: replace $E_{\beta m}$ with the adiabatic potential energy surface E^x_β:

$$\Gamma^{(\mathrm{SC})}_{\alpha n\to\beta}(\omega)=\frac{2\pi}{\hbar}\left\langle\chi_{\alpha n}\right| |P^x_{\alpha\beta}|^2\delta(E^x_\beta-E^x_\alpha-\hbar\omega)\left|\chi_{\alpha n}\right\rangle$$



Williams-Lax Theory

1. Herzberg-Teller rate as the starting point:

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2. Semiclassical approximation: replace $E_{\beta m}$ with the adiabatic potential energy surface E^x_β:

$$\Gamma^{(\mathrm{SC})}_{\alpha n\to\beta}(\omega)=\frac{2\pi}{\hbar}\left\langle\chi_{\alpha n}\right| |P^x_{\alpha\beta}|^2\delta(E^x_\beta-E^x_\alpha-\hbar\omega)\left|\chi_{\alpha n}\right\rangle$$

3. Thermal average, Harmonic approximation, and Mehler's formula:

$$\Gamma^{(\mathrm{SC})}_{0\to\beta}(\omega;T)=\prod_\nu\int dx_\nu \frac{\exp(-x_\nu^2/2\sigma^2_{\nu,T})}{\sqrt{2\pi}\sigma^2_{\nu,T}}|P^x_{0\beta}|^2\delta(E^x_\beta-E^x_0-\hbar\omega)$$

wtih $\sigma^2_{\nu,T}=(2n_{\nu,T}+1)\,l^2_\nu$.

- F. E. Williams, Phys. Rev. 82, 281 (1951)
- M. Lax, J. Chem. Phys. 20, 1752 (1952)
- C. E. Patrick, F. Giustino, Nat. Commun. 4, 2006 (2013)
- C. E. Patrick, F. Giustino, J. Phys. Condens. Matter 26, 365503 (2014)
- M. Zacharias, DPhil Thesis , University of Oxford (2017)

Williams-Lax Theory

4. We make contact with DFT and write for the potential energy surface:

$$\lim_{N_e \to \infty} E^x_\beta - E^x_0 = \varepsilon^x_c - \varepsilon^x_v$$

- M. Zacharias, C. E. Patrick, F. Giustino, Phys. Rev. Lett. 115, 177401 (2015)
- M. Zacharias, F. Giustino, Phys. Rev. B 94, 075125 (2016)

Williams-Lax Theory

4. We make contact with DFT and write for the potential energy surface:

$$\lim_{N_e \to \infty} E^x_\beta - E^x_0 = \varepsilon^x_c - \varepsilon^x_v$$

5. Imaginary part of the dielectric function at finite T:

$$\epsilon_2^{\mathrm{SC}}(\omega; T) = \prod_\nu \int dx_\nu \frac{\exp(-x_\nu^2/2\sigma^2_{\nu,T})}{\sqrt{2\pi\sigma^2_{\nu,T}}} \epsilon_2^x(\omega)$$

and in the indipendent-particle picture:

$$\epsilon_2^x(\omega) \propto \frac{1}{\omega^2} \sum_{cv} |p^x_{cv}|^2 \delta(\varepsilon^x_c - \varepsilon^x_v - \hbar\omega)$$

- M. Zacharias, C. E. Patrick, F. Giustino, Phys. Rev. Lett. 115, 177401 (2015)
- M. Zacharias, F. Giustino, Phys. Rev. B 94, 075125 (2016)

Williams-Lax Theory

4. We make contact with DFT and write for the potential energy surface:

$$\lim_{N_e \to \infty} E^x_\beta - E^x_0 = \varepsilon^x_c - \varepsilon^x_v$$

5. Imaginary part of the dielectric function at finite T:

$$\epsilon_2^{\mathrm{SC}}(\omega; T) = \prod_\nu \int dx_\nu \frac{\exp(-x_\nu^2/2\sigma^2_{\nu,T})}{\sqrt{2\pi\sigma^2_{\nu,T}}} \epsilon_2^x(\omega)$$

and in the indipendent-particle picture:

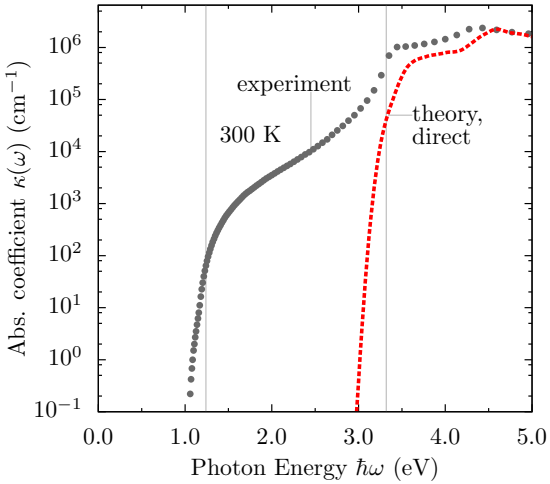
$$\epsilon_2^x(\omega) \propto \frac{1}{\omega^2} \sum_{cv} |p^x_{cv}|^2 \delta(\varepsilon^x_c - \varepsilon^x_v - \hbar\omega)$$

Interpretation: Monte Carlo integral, a weighted average of the spectra for different nuclei configurations.

- M. Zacharias, C. E. Patrick, F. Giustino, Phys. Rev. Lett. 115, 177401 (2015)
- M. Zacharias, F. Giustino, Phys. Rev. B 94, 075125 (2016)

Silicon optical absorption in the Williams-Lax theory

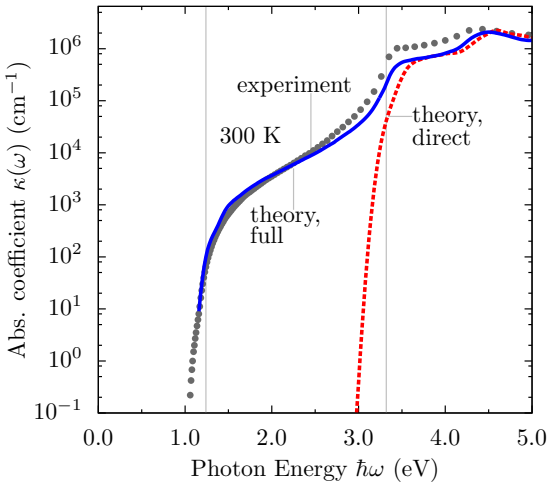
DFT-LDA calculations with nuclei at equilibrium



M. Zacharias, C. E. Patrick, F. Giustino, Phys. Rev. Lett. 115, 177401 (2015)

Silicon optical absorption in the Williams-Lax theory

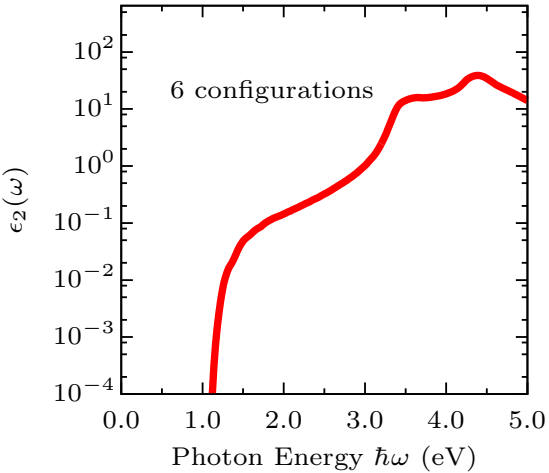
DFT-LDA calculations + quantum nuclear effects, Method: ISMC (8×8×8 supercell)



M. Zacharias, C. E. Patrick, F. Giustino, Phys. Rev. Lett. 115, 177401 (2015)

Convergence test with configurational sampling

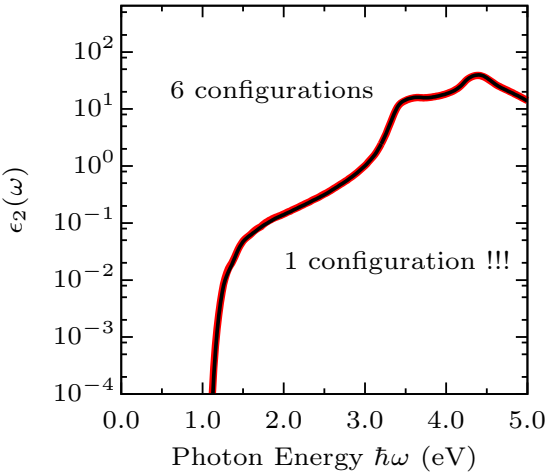
DFT-LDA calculations + quantum nuclear effects, Method: ISMC (8×8×8 supercell)



M. Zacharias, C. E. Patrick, F. Giustino, Phys. Rev. Lett. 115, 177401 (2015)

Convergence test with configurational sampling

DFT-LDA calculations + quantum nuclear effects, Method: ISMC (8×8×8 supercell)



M. Zacharias, C. E. Patrick, F. Giustino, Phys. Rev. Lett. 115, 177401 (2015)

The special displacement method (SDM) and ZG displacements

Original observation for Zacharias-Giustino (ZG) displacements $\Delta\tau^{\mathrm{ZG}}$:

1. Exact Williams-Lax (WL) dielectric function:

$$\epsilon_2^{\mathrm{WL}}(\omega;T) = \epsilon_2(\omega) + \frac{1}{2}\sum_{\nu}\frac{\partial^2\epsilon_2^x(\omega)}{\partial x_\nu^2}\sigma_{\nu,T}^2 + \mathcal{O}(\sigma^4)$$

2. One configuration with $x_\nu = \sigma_{\nu,T}$:

$$\epsilon_2^{\mathrm{ZG}}(\omega;T) = \epsilon_2(\omega) + \frac{1}{2}\sum_{\nu\mu} S_\nu S_\mu \frac{\partial^2\epsilon_2^x(\omega)}{\partial x_\nu \partial x_\mu}\sigma_{\nu,T}\sigma_{\mu,T} + \mathcal{O}(\sigma^4)$$

Special set of signs: $\{S_\nu\} = \{+\,-\,+\,-\,+\,-\,\cdots\}$ $\quad S_\nu = (-1)^{\nu-1}$

3. We can prove:

$$\lim_{N_p\to\infty} \epsilon_2^{\mathrm{ZG}}(\omega;T) = \epsilon_2^{\mathrm{WL}}(\omega;T) \quad \text{if} \quad \Delta\tau_{\kappa\alpha}^{\mathrm{ZG}} = (M_0/M_\kappa)^{\frac{1}{2}} \sum_{\nu} S_\nu\, e_{\kappa\alpha,\nu}\, \sigma_{\nu,T}$$

M. Zacharias, F. Giustino, Phys. Rev. B 94, 075125 (2016)

The special displacement method (SDM) and ZG displacements

Original observation for Zacharias-Giustino (ZG) displacements $\Delta\tau^{\rm ZG}$:

1. Exact Williams-Lax (WL) dielectric function:

$$\epsilon_2^{\rm SC}(\omega;T) = \prod_\nu \int dx_\nu \frac{\exp(-x_\nu^2/2\sigma_{\nu,T}^2)}{\sqrt{2\pi\sigma_{\nu,T}^2}} \epsilon_2^x(\omega)$$

2. One configuration with $x_\nu = \sigma_{\nu,T}$:

$$\epsilon_2^{\rm ZG}(\omega;T) = \epsilon_2(\omega) + \frac{1}{2}\sum_{\nu\mu} S_\nu S_\mu \frac{\partial^2\epsilon_2^x(\omega)}{\partial x_\nu \partial x_\mu} \sigma_{\nu,T}\sigma_{\mu,T} + \mathcal{O}(\sigma^4)$$

Special set of signs: $\{S_\nu\} = \{+\,-\,+\,-\,+\,-\,\cdots\}$ $\quad S_\nu = (-1)^{\nu-1}$

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M. Zacharias, F. Giustino, Phys. Rev. B 94, 075125 (2016)

The special displacement method (SDM) and ZG displacements

Original observation for Zacharias-Giustino (ZG) displacements $\Delta\tau^{\mathrm{ZG}}$:

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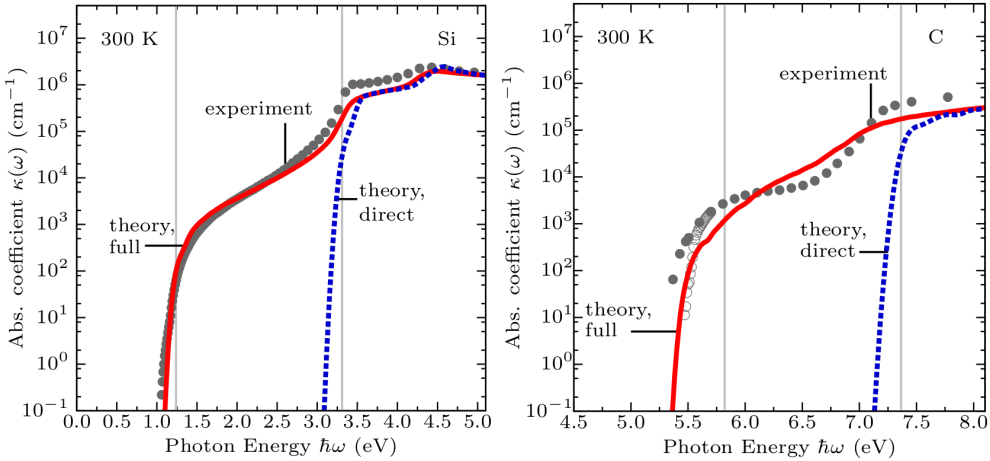
M. Zacharias, F. Giustino, Phys. Rev. B 94, 075125 (2016)

Silicon and diamond absorption spectra with the SDM

DFT-LDA calculations + quantum nuclear effects, Method: SDM (8×8×8 supercell)

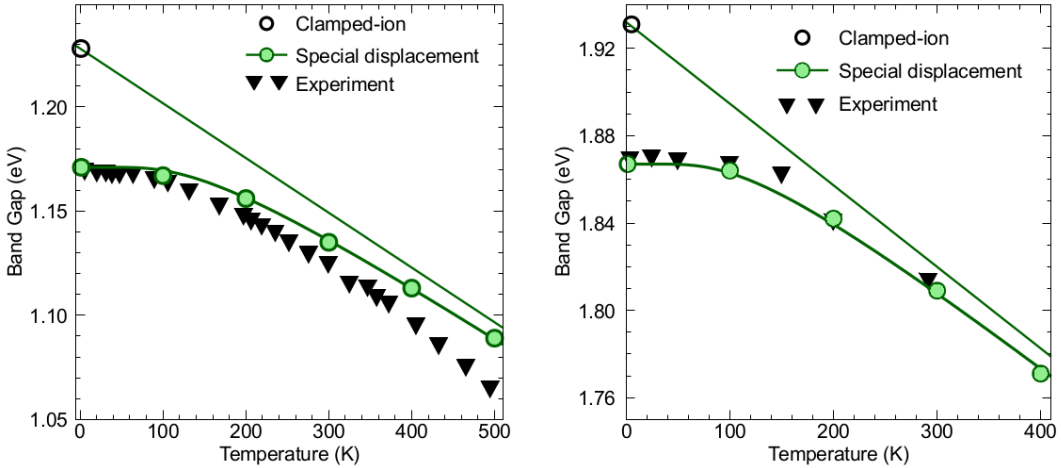


M. Zacharias, F. Giustino, Phys. Rev. B 94, 075125 (2016)

(see tutorial `exercise4`)

Temperature-dependent band gaps

Temperature dependent band gaps of **Si** (ZPR $= 57$ meV) and **MoS$_2$** (ZPR $= 65$ meV).



M. Zacharias, F. Giustino, Phys. Rev. Res. 2, 013357 (2020)

Relations connecting the SDM and Perturbative methods

- Optical spectra (Hall-Bardeen-Blat (HBB) theory):

$$\frac{\partial^2 \epsilon_2^x}{\partial x_\nu^2} \propto \frac{2}{l_\nu^2}\frac{1}{\omega^2}\sum_{cv}\left|\sum_n{}' \left[\frac{p_{cn}\, g_{n\nu\nu}}{\varepsilon_v - \varepsilon_n} + \frac{g_{cn\nu}\, p_{n\nu}}{\varepsilon_c - \varepsilon_n}\right]\right|^2 \delta\left(\varepsilon_c - \varepsilon_v - \hbar\omega\right)$$

- Temperature-dependent band structures (Allen-Heine theory):

$$\frac{\partial^2 \varepsilon_c^x}{\partial x_\nu^2} = \frac{2}{l_\nu^2}\left[\sum_n{}' \frac{|g_{cn\nu}|^2}{\varepsilon_c - \varepsilon_n} + h_{cv\nu\nu}\right],$$

Nonperturbative methods:

1. miss $\hbar\omega_\nu$ in the denominator and $\delta()$ (ok if $\hbar\omega_\nu << \varepsilon_g$)
2. capture all coefficients $\frac{\partial^{2n}\epsilon_2^x}{\partial x_\nu^{2n}}$; thus *electron-multi-phonon* interactions
3. includes off-diagonal Debye-Waller contribution, no rigid-ion approx.

Reciprocal space formulation of the SDM

SDM: Gives the set of atomic displacements (ZG displacements) that best incorporate the effect of electron-phonon coupling in ab-initio nonperturbative calculations:

$$\Delta\boldsymbol{\tau}_{p\kappa}^{\mathrm{ZG}} = \left[\frac{M_0}{N_p M_\kappa}\right]^{\frac{1}{2}} 2 \sum_{\mathbf{q}\in\mathcal{B},\nu} S_{\mathbf{q}\nu}\, \mathrm{Re}\left[e^{i\mathbf{q}\cdot\mathbf{R}_p}\mathbf{e}_{\kappa,\nu}(\mathbf{q})\right]\sigma_{\mathbf{q}\nu,T}$$

where

- $\sigma^2_{\mathbf{q}\nu,T} = (2n_{\mathbf{q}\nu,T}+1)\hbar/(2M_0\omega_{\mathbf{q}\nu})$ with $n_{\mathbf{q}\nu,T} = [\exp(\hbar\omega_{\mathbf{q}\nu}/k_{\mathrm{B}}T)-1]^{-1}$
- $\omega_{\mathbf{q}\nu} \longrightarrow$ phonon frequencies
- $\mathbf{e}_{\kappa,\nu}(\mathbf{q}) \longrightarrow$ phonon polarization vectors
- $S_{\mathbf{q}\nu} \longrightarrow$ signs of normal coordinates

This equation is implemented in the `EPW/ZG` module of `Quantum Espresso`.

M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020) and H. Lee, *et al* npj Comput. Mater. 9, 156 (2023)

Compute and minimize the function $E(\{S_{\mathbf{q}\nu}\}, T)$

Find the best ZG displacements for a given *supercell size* and *temperature* by setting `compute_error = .true.`, `error_thresh = 0.2` (see tutorial `exercise1`) so that the function:

$$E(\{S_{\mathbf{q}\nu}\}, T) = \sum_{\substack{\kappa\alpha \\ \kappa'\alpha'}} \frac{\left| \sum_{\substack{\mathbf{q}\in\mathcal{B} \\ \nu<\nu'}} \Re[e^*_{\kappa\alpha,\nu}(\mathbf{q}) e_{\kappa'\alpha',\nu'}(\mathbf{q})] \sigma_{\mathbf{q}\nu,T} \sigma_{\mathbf{q}\nu',T} S_{\mathbf{q}\nu} S_{\mathbf{q}\nu'} \right|}{\left| \sum_{\substack{\mathbf{q}\in\mathcal{B} \\ \nu}} \Re[e^*_{\kappa\alpha,\nu}(\mathbf{q}) e_{\kappa'\alpha',\nu}(\mathbf{q})] \sigma^2_{\mathbf{q}\nu,T} \right|}$$

is lower than `error_thresh` based on the choice of $\{S_{\mathbf{q}\nu}\}$.

All quantities in $E(\{S_{\mathbf{q}\nu}\})$ can be computed from DFPT;
no extra DFT calculations are required to find the optimum ZG configuration.

Reciprocal space formulation of the SDM

Key findings due to periodicity of solids:

- Linear order derivatives vanish in a supercell calculation:

$$\frac{\partial O^{\{\tau\}}}{\partial z_{\mathbf{q}\nu}} = 0 \text{ if } \mathbf{q} \in \mathcal{B}.$$

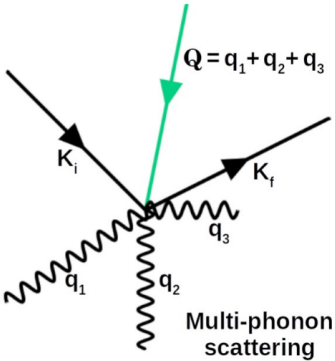
- All second order derivatives with $\mathbf{q} \neq \mathbf{q}'$ vanish in a supercell calculation:

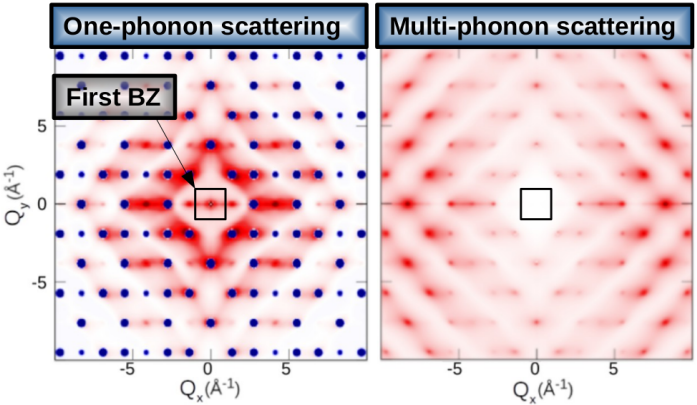
$$\frac{\partial^2 O^{\{\tau\}}}{\partial z_{\mathbf{q}\nu} \partial z_{\mathbf{q}'\nu'}} = 0 \text{ if } \mathbf{q} \neq \mathbf{q}'.$$

This simplifies **A LOT** the procedure for minimizing the error coming from the cross-coupling terms.

Physical meaning of minimizing $E(\{S_{\mathbf{q}\nu}\}, T)$

ZG displacements give the best collection of scatterers that best reproduce *phonon-induced inelastic scattering patterns*: **Black Phosphorus**

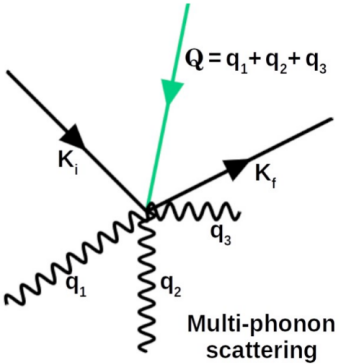


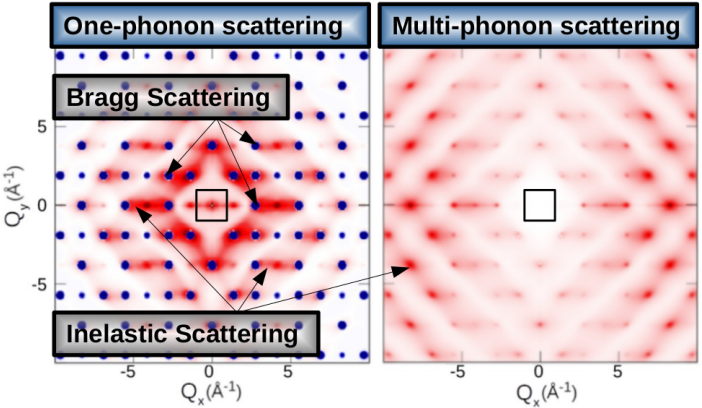


M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, Phys. Rev. Lett. 127, 207401 (2021)
M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, Phys. Rev. B 104, 205109 (2021)

Physical meaning of minimizing $E(\{S_{\mathbf{q}\nu}\}, T)$

ZG displacements give the best collection of scatterers that best reproduce *phonon-induced inelastic scattering patterns*: **Black Phosphorus**

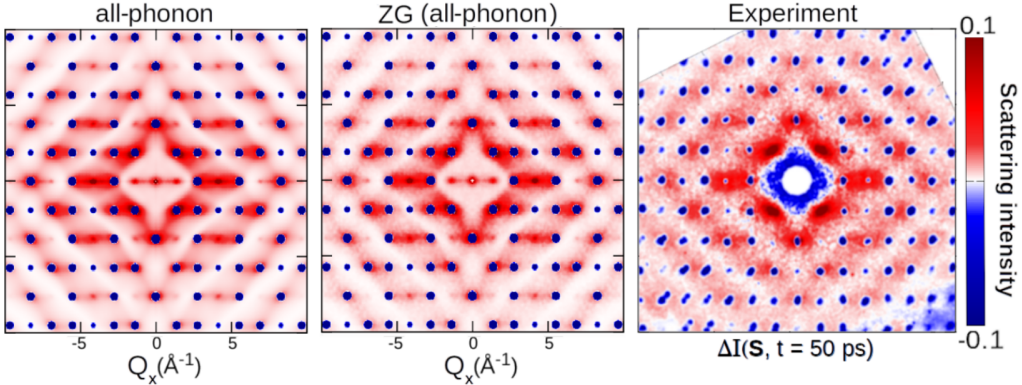




M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, Phys. Rev. Lett. 127, 207401 (2021)
M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, Phys. Rev. B 104, 205109 (2021)

Physical meaning of minimizing $E(\{S_{\mathbf{q}\nu}\}, T)$

ZG displacements give the best collection of scatterers that best reproduce *phonon-induced inelastic scattering patterns*: $I_{\mathrm{ZG}}(\mathbf{Q}, T) = \left| \sum_{p\kappa} f_\kappa(\mathbf{Q}) e^{i\mathbf{Q}\cdot\left[\mathbf{R}_p + \boldsymbol{\tau}_\kappa + \Delta\boldsymbol{\tau}_{p\kappa}^{\mathrm{ZG}}\right]} \right|^2$

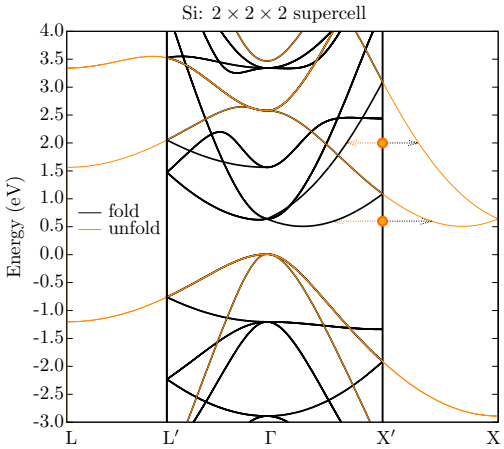


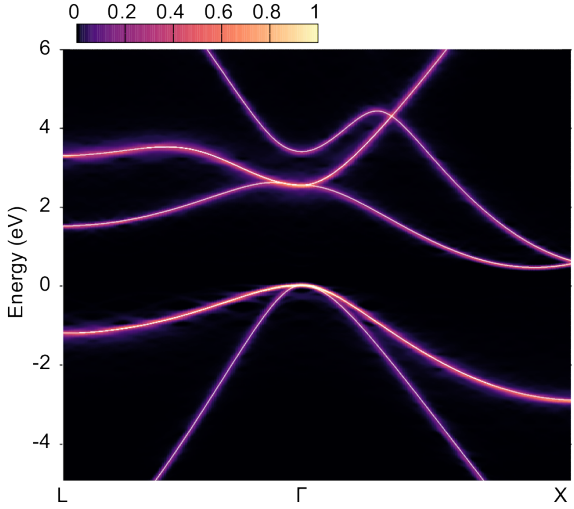
Someone can calculate diffuse scattering maps using `ZG.x` and `disca.x` of QE (see tutorial `exercise5`).

M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, Phys. Rev. Lett. 127, 207401 (2021)
M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, Phys. Rev. B 104, 205109 (2021)

Band structure unfolding

Temperature-dependent band structures
with the band structure unfolding technique
as implemented in `bands_unfold.x` of QE.





V. Popescu, A. Zunger, Phys. Rev. B 85, 085201 (2012) M. Zacharias, F. Giustino, Phys. Rev. Res. 2, 013357 (2020)

Band structure unfolding

Temperature-dependent band structures with the band structure unfolding technique

Goal is to evaluate the electron spectral function:

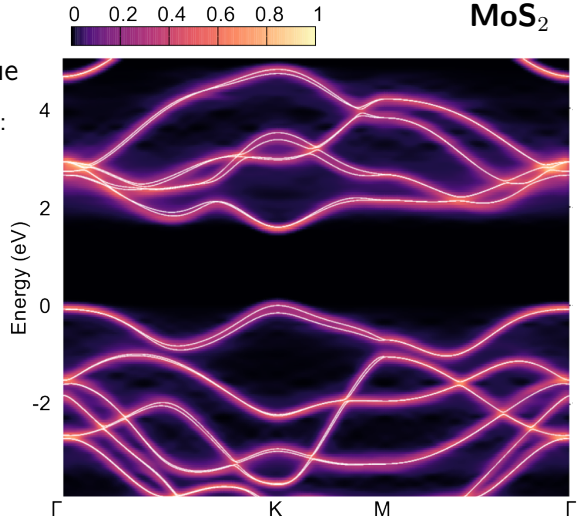
$$A_{\mathbf{k}}(\varepsilon;T) = \sum_{m\mathbf{K}} P_{m\mathbf{K},\mathbf{k}}(T)\,\delta[\varepsilon - \varepsilon_{m\mathbf{K}}(T)],$$

where $P_{m\mathbf{K},\mathbf{k}}(T)$ are temperature-dependent spectral weights evaluated as:

$$P_{m\mathbf{K},\mathbf{k}}(T) = \sum_{\mathbf{g}} |c^{\mathrm{ZG}}_{m\mathbf{K}}(\mathbf{g}+\mathbf{k}-\mathbf{K};T)|^2.$$

This is implemented in `bands_unfold.x` for NC, US, and PAW pseudopotentials. (see tutorial `exercise2`)

V. Popescu, A. Zunger, Phys. Rev. B 85, 085201 (2012)
P. V. C. Medeiros, S. Stafström, J. Björk, Phys. Rev. B 89, 041407(R) (2014)

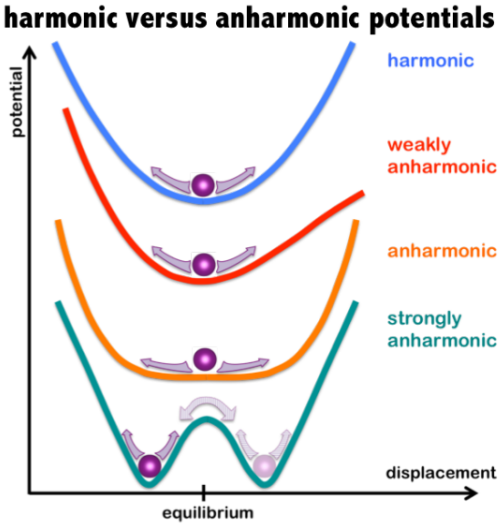


M. Zacharias, F. Giustino, Phys. Rev. Res. 2, 013357 (2020)

Anharmonicity

Exploring anharmonicity via the A-SDM.

Accounting for anharmonicity in first-principles calculations



C. Katan et al., Nature Materials, 17, 377–379 (2018)

Anharmonic PES:
Harmonic approaches fail to calculate stable phonons.

Current state-of-the-art methods:
TDEP: O. Hellman *et al.*,
Phys. Rev. B 84, 180301(R) (2011)
SSCHA: I. Errea *et al.*,
Phys. Rev. B 89, 064302 (2014)
PT: T. Tadano, S. Tsuneyuki,
Phys. Rev. B 92, 054301 (2015)

or upgrade the special displacement method (A-SDM) ...

Anharmonicity within the Self-Consistent Phonon (SCP) theory

We introduce an effective harmonic Hamiltonian that drives nuclear vibrations:

$$H_{\text{eff}} = \sum_{\nu} \left(U_0 - \frac{\hbar^2}{2M_0} \frac{\partial^2}{\partial x_\nu^2} + \frac{1}{2} M_0 \omega_\nu^2 x_\nu^2 \right)$$

and a perturbation to this Hamiltonian that accounts for anharmonicity with all higher-order terms:

$$\begin{aligned} H' &= \sum_{\nu} \frac{\partial \hat{U}}{\partial x_\nu} x_\nu + \left[\frac{1}{2} \sum_{\nu\nu'} \frac{\partial^2 \hat{U}}{\partial x_\nu \partial x_{\nu'}} x_\nu x_{\nu'} - \sum_{\nu} \frac{1}{2} M_0 \omega_\nu^2 x_\nu^2 \right] + \frac{1}{3!} \sum_{\nu\nu'\nu''} \frac{\partial^3 \hat{U}}{\partial x_\nu \partial x_{\nu'} \partial x_{\nu''}} x_\nu x_{\nu'} x_{\nu''} \\ &+ \frac{1}{4!} \sum_{\nu\nu'\nu''\nu'''} \frac{\partial^4 \hat{U}}{\partial x_\nu \partial x_{\nu'} \partial x_{\nu''} \partial x_{\nu'''}} x_\nu x_{\nu'} x_{\nu''} x_{\nu'''} + \cdots \end{aligned}$$

To first order in perturbation theory we have the correction:

$$\langle \Delta E^{(1)} \rangle_T = \prod_{\nu} \int \frac{dx_\nu}{\sigma_\nu \sqrt{2\pi}} e^{-\frac{x_\nu^2}{2\sigma_\nu^2}} H' = \left[\frac{1}{2} \sum_{\nu} \frac{\partial^2 H}{\partial x_\nu^2} \sigma_\nu^2 - \frac{1}{2} M_0 \omega_\nu^2 \sigma_\nu^2 \right] + \frac{1}{4!} \sum_{\nu\nu'} \frac{\partial^4 H}{\partial x_\nu^2 \partial x_{\nu'}^2} \sigma_\nu^2 \sigma_{\nu'}^2 + \cdots$$

(All first-order diagrams, including the loop (quartic) diagram which comes first in perturbation theory)

Anharmonicity within the Self-Consistent Phonon (SCP) theory

1. Minimize the (trial) free energy of the system with respect to $C_{p\kappa\alpha,p'\kappa'\alpha'}(T)$ based on the GB inequality:

$$F(T) = \langle U \rangle_T - U_{\rm h}(T) + F_{\rm vib}(T)$$

$$F(T) = \langle U \rangle_T - \frac{M_0}{2} \sum_{\mathbf{q}\nu} \omega^2_{\mathbf{q}\nu} \sigma^2_{\mathbf{q}\nu,T} + \sum_{\mathbf{q}\nu} \left[\frac{\hbar\omega_{\mathbf{q}\nu}}{2} - k_{\rm B}T \ln[1 + n_{\mathbf{q}\nu,T}] \right], \text{ so that } \boxed{\frac{\partial F(T)}{\partial C_{\kappa\alpha,\kappa'\alpha'}} = 0}$$

2. We can prove:

$$\frac{\partial F(T)}{\partial C_{\kappa\alpha,\kappa'\alpha'}} = \frac{\partial \langle U \rangle_T}{\partial C_{\kappa\alpha,\kappa'\alpha'}} - \frac{\partial U_{\rm h}(T)}{\partial C_{\kappa\alpha,\kappa'\alpha'}} + \frac{\partial F_{\rm vib}(T)}{\partial C_{\kappa\alpha,\kappa'\alpha'}} \propto \sum_{\substack{\kappa''\alpha'' \\ \kappa'''\alpha'''}} [\cdots] \left[\left\langle \frac{\partial^2 U}{\partial \tau_{\kappa''\alpha''} \partial \tau_{\kappa'''\alpha'''}} \right\rangle_T - C_{\kappa''\alpha'',\kappa'''\alpha'''} \right]$$

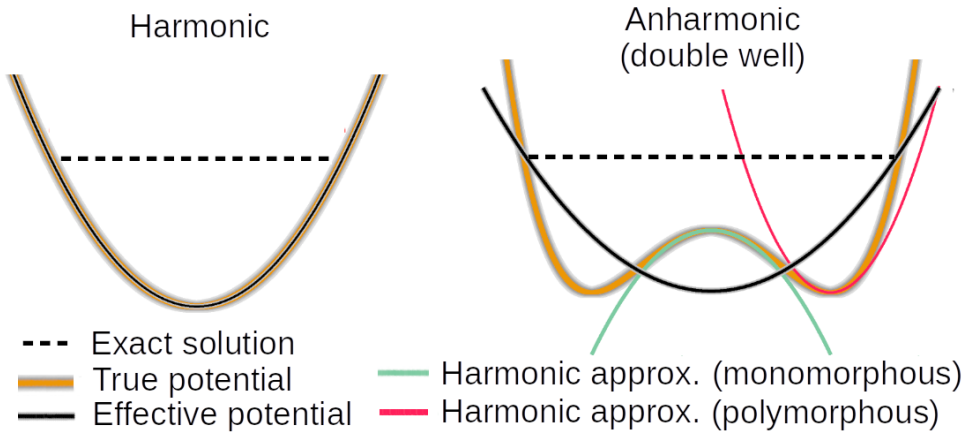
3. Compute temperature-dependent effective IFCs:

$$C_{p\kappa\alpha,p'\kappa'\alpha'}(T) = \left\langle \frac{\partial^2 U^{\{\tau\}}}{\partial \tau_{p\kappa\alpha} \partial \tau_{p'\kappa'\alpha'}} \right\rangle_T ,$$

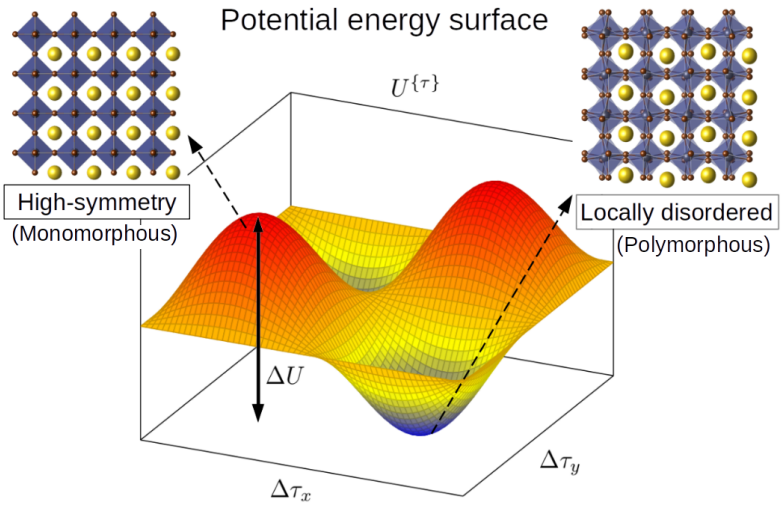
iteratively until self-consistency is obtained.

M. Zacharias, G. Volonakis, F. Giustino, J. Even Phys. Rev. B 108, 035155 (2023)
D. Hooton, LI. A new treatment of anharmonicity in lattice thermodynamics: I, Philos. Mag. J. Sci. 46, 422 (1955)

Schematic illustration of an effective potential



Starting point: Ground-state locally disordered structure



Monomorphous, Polymorphous: X-G. Zhao, G. M. Dalpian, Z. Wang, A. Zunger Phys. Rev. B 101, 155137 (2020)

SCPs with the A-SDM

Compute temperature-dependent effective IFCs

$$C_{p\kappa\alpha,p'\kappa'\alpha'}(T) = \left\langle \frac{\partial^2 U^{\{\tau\}}}{\partial\tau_{p\kappa\alpha}\partial\tau_{p'\kappa'\alpha'}} \right\rangle_T \simeq \frac{\partial^2 U^{\{\tau^{\mathrm{ZG}}\}}}{\partial\tau_{p\kappa\alpha}\partial\tau_{p'\kappa'\alpha'}},$$

iteratively until self-consistent phonons are obtained. This involves:

1. Compute harmonic $C_{p\kappa\alpha,p'\kappa'\alpha'}$ of the polymorphous structure using finite differences, enforce symmetries, and obtain initial $\{\omega_{\mathbf{q}\nu}/e_{\kappa\alpha,\nu}(\mathbf{q})\}_{\mathrm{Poly-SYM}}$

Stable phonons **but no** temperature dependence

SCPs with the A-SDM

Compute temperature-dependent effective IFCs

$$C_{p\kappa\alpha,p'\kappa'\alpha'}(T) = \left\langle \frac{\partial^2 U^{\{\tau\}}}{\partial\tau_{p\kappa\alpha}\partial\tau_{p'\kappa'\alpha'}} \right\rangle_T \simeq \frac{\partial^2 U^{\{\tau^{\mathrm{ZG}}\}}}{\partial\tau_{p\kappa\alpha}\partial\tau_{p'\kappa'\alpha'}},$$

iteratively until self-consistent phonons are obtained. This involves:

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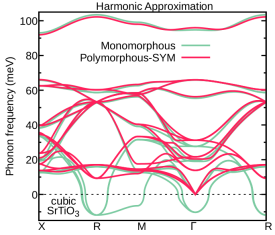


Stable phonons **but no** temperature dependence

SCPs with the A-SDM

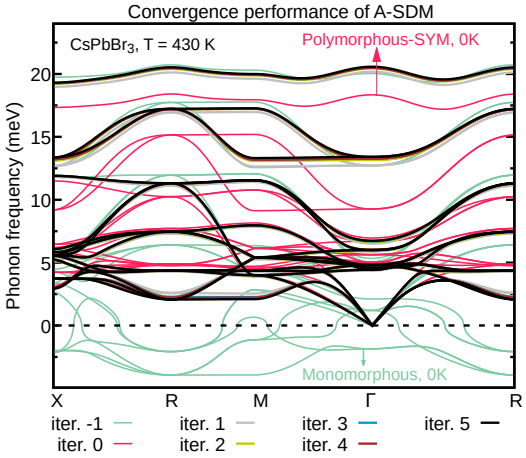
Compute temperature-dependent effective IFCs

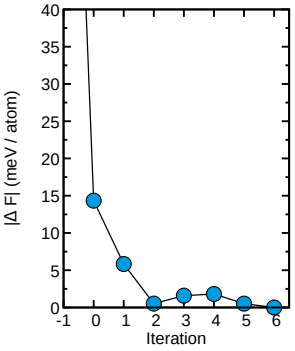
$$C_{p\kappa\alpha,p'\kappa'\alpha'}(T) = \left\langle \frac{\partial^2 U^{\{\tau\}}}{\partial\tau_{p\kappa\alpha}\partial\tau_{p'\kappa'\alpha'}} \right\rangle_T \simeq \frac{\partial^2 U^{\{\tau^{\mathrm{ZG}}\}}}{\partial\tau_{p\kappa\alpha}\partial\tau_{p'\kappa'\alpha'}},$$

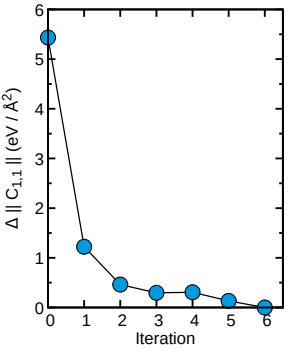
iteratively until self-consistent phonons are obtained. This involves:

1. Compute harmonic $C_{p\kappa\alpha,p'\kappa'\alpha'}$ of the polymorphous structure using finite differences, enforce symmetries, and obtain initial $\{\omega_{\mathbf{q}\nu}/e_{\kappa\alpha,\nu}(\mathbf{q})\}_{\mathrm{Poly-SYM}}$
2. Generate $\Delta\tau^{\mathrm{ZG}}$
3. Compute $C_{p\kappa\alpha,p'\kappa'\alpha'}(T)$ using finite differences
4. Enforce crystal symmetries to $C_{p\kappa\alpha,p'\kappa'\alpha'}(T)$
5. Calculate T-dependent $\boxed{\{\omega_{\mathbf{q}\nu}/\mathbf{e}_{\kappa\alpha,\nu}(\mathbf{q})\}_{\mathbf{A-SDM}}}$
6. Repeat steps 3-5 until self-consistency is achieved (with iterative mixing)

A-SDM convergence performance: $CsPbBr_3$

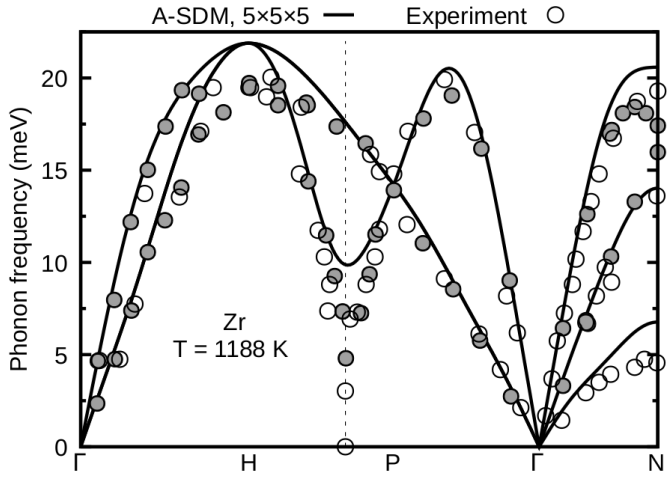






M. Zacharias, G. Volonakis, F. Giustino, J. Even Phys. Rev. B 108, 035155 (2023) see tutorial `exerciseCsPbBr3`

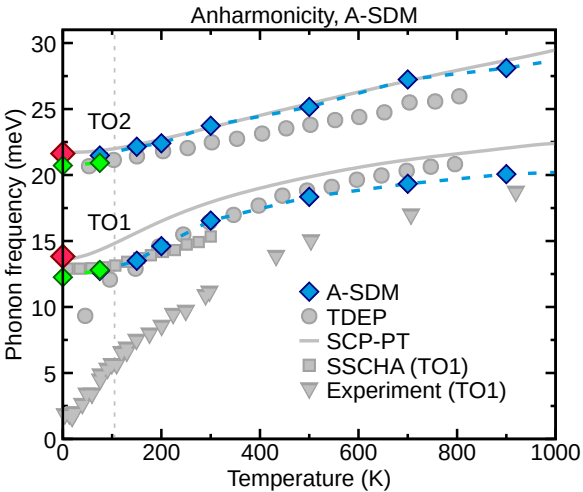
A-SDM validation: Zr (compare with experiment)



see tutorial `exercise3`

M. Zacharias, G. Volonakis, F. Giustino, J. Even Phys. Rev. B 108, 035155 (2023)

A-SDM validation: $SrTiO_3$ (compare with other approaches)

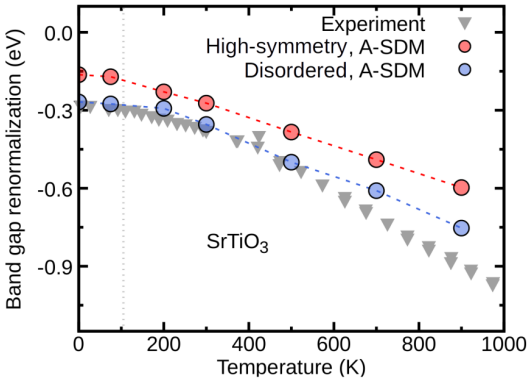


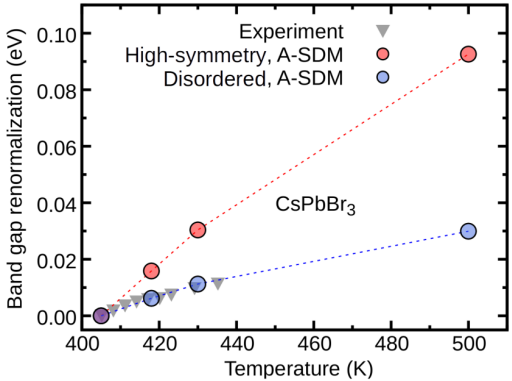
A-SDM data: M. Zacharias, G. Volonakis, F. Giustino, J. Even Phys. Rev. B 108, 035155 (2023)

ALAMODE and TDEP data: T. Tadano, S. Tsuneyuki, PRB 92 (2015) SSCHA data: C. Verdi, *et al*, PRM 7 (2023)

Application of the A-SDM: polymorphous perovskites

$$\text{Allen} - \text{Heine theory} : \Delta\varepsilon_c(T) = \sum\nolimits_{\nu} \left[\sum_{n \neq c} \frac{|g_{cn\nu}|^2}{\varepsilon_c - \varepsilon_n} + h_{c\nu\nu} \right] (2n_{\nu,T} + 1)$$



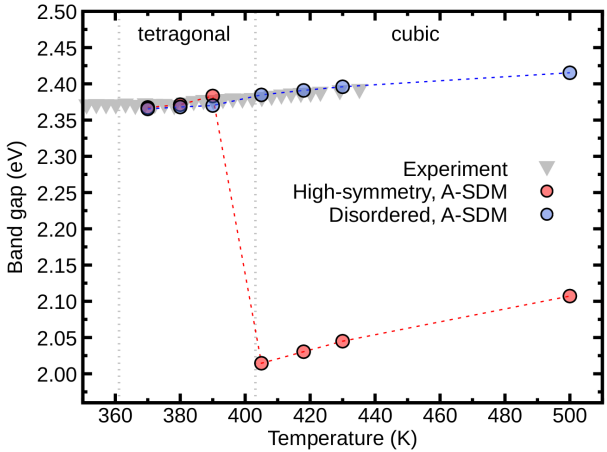


Experiment $SrTiO_3$: D. J. Kok, et al. Phys. Stat. Solidi 212, 1880, (2015) (see tutorial `exerciseCsPbBr3`)

Experiment $CsPbBr_3$: G. Mannino, et al. J. Phys. Chem. Lett. 11, 2490 (2020)

Theory: M. Zacharias, G. Volonakis, F. Giustino, J. Even npj Comput. Mater. 9, 153 (2023)

Application of the A-SDM: polymorphous $CsPbBr_3$

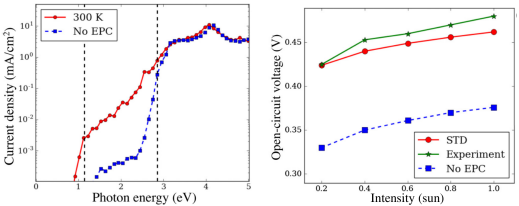


Experiment $CsPbBr_3$: G. Mannino, et al. J. Phys. Chem. Lett. 11, 2490 (2020)

Theory: M. Zacharias, G. Volonakis, F. Giustino, J. Even npj Comput. Mater. 9, 153 (2023)

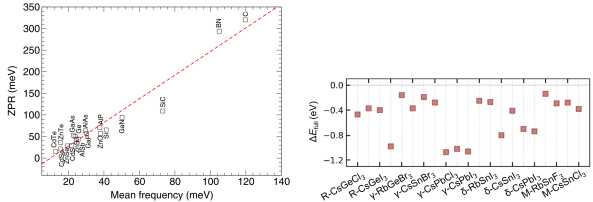
Applications of the SDM

Phonon-assisted photocurrent in large solar-cell devices



M. Palsgaard, *et al*, PRA 10, 014026 (2018)

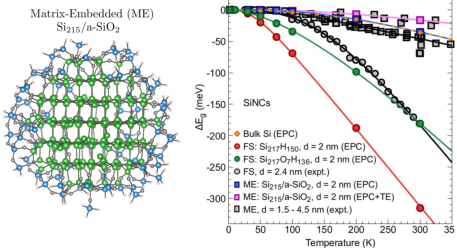
Zero-point renormalization within GW and Hybrid functionals



F. Karsai, *et al*, NJP 20 123008 (2018)

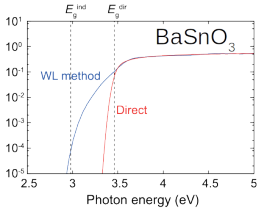
H. Wang, *et al*, npj CM 8 237 (2022)

Band gap renormalization of nanostructures



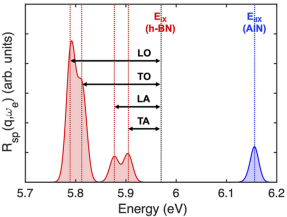
M. Zacharias, *et al*, PRB 101, 245122 (2020)

Indirect optical absorption in $BaSnO_3$



Y. Kang, *et al*, APL 112 (2018)

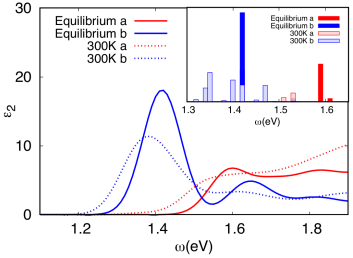
Phonon-assisted emission spectrum of h-BN and AlN



D. A. Laleyan, W. Lee, *et al* APL Mater 11 (2023)

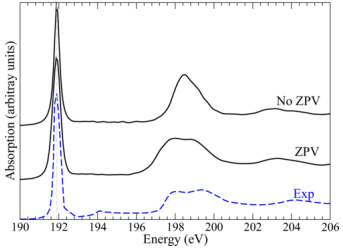
Applications of the SDM

Exciton-phonon coupling in 2D GeSe



T. A. Huang, *et al*, JPCL 12 (2021)

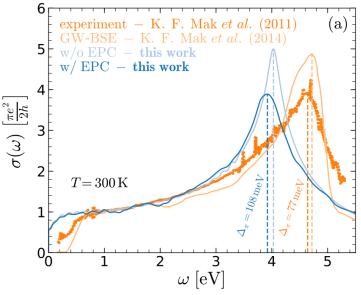
Exciton-phonon coupling in h-BN



F. Karsai, *et al*, PRB 98, 235205 (2018)

https://www.vasp.at/wiki/ (see `PHON_NSTRUCT` flag)

Optical conductivity in graphene (pristine and doped)



D. Novko & M. Kralj, npj 2D mater. appl. 48 (2019)

Take home messages ...

1. The SDM is a very simple and efficient methodology for capturing anharmonicity and electron-phonon coupling effects in *ab initio* calculations. Tutorials and input flags available in `https://docs.epw-code.org/doc/`.

2. The SDM is not simply a numerical trick, but encloses important physics.

3. SDM potential for other temperature-dependent observables, e.g. conductivity, tunnelling spectra, exciton spectra, etc ...

4. The A-SDM compares well with TDEP, SSCHA, or ALAMODE results for the evaluation of second-order effective IFCs (all rely on the SCP theory).

5. Temperature-dependent (anharmonic) IFCs with `EPW` are within reach.

Acknowledgements

THANK YOU !!!

Funded by the
European Union

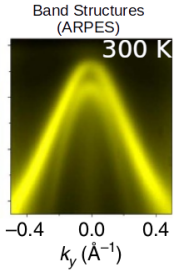
This research was also funded by the European Union (project ULTRA-2DPK / HORIZON-MSCA-2022-PF-01 / Grant Agreement No. 101106654). Views and opinions expressed are however those of the authors only and do not necessarily reflect those of the European Union or the European Commission. Neither the European Union nor the granting authority can be held responsible for them.

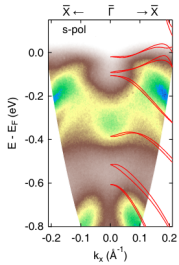
Reference list

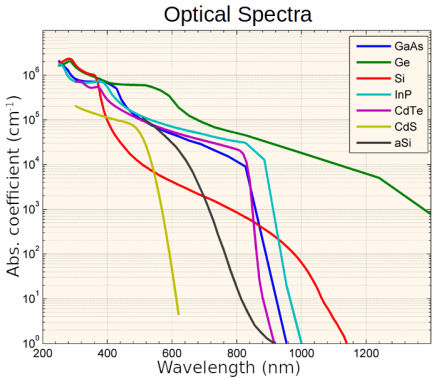
1. C. E. Patrick, F. Giustino, J. Phys. Condens. Matter 26, 365503 (2014)
2. M. Zacharias, F. Giustino, Phys. Rev. B 94, 075125 (2016)
3. M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020)
4. D. Hooton, LI. A new treatment of anharmonicity in lattice thermodynamics: I, Philos. Mag. J. Sci. 46, 422 (1955)
5. M. Zacharias, G. Volonakis, F. Giustino, J. Even Phys. Rev. B 108, 035155 (2023)
6. R. Bianco, I. Errea, L. Paulatto, M. Calandra, F. Mauri Phys. Rev. B 96 (2017)
7. H. Lee, *et al* npj Comput. Mater. 9, 156 (2023)

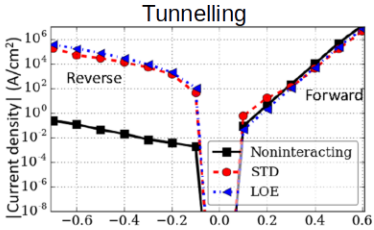
Nonperturbative Approaches - Literature III

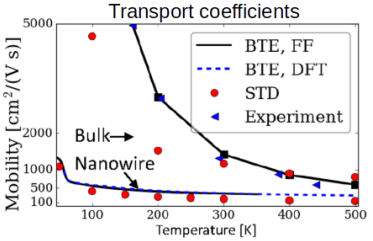
All nonperturbative approaches can be upgraded
to evaluate any property written as a **Fermi-Golden Rule**, e.g.:







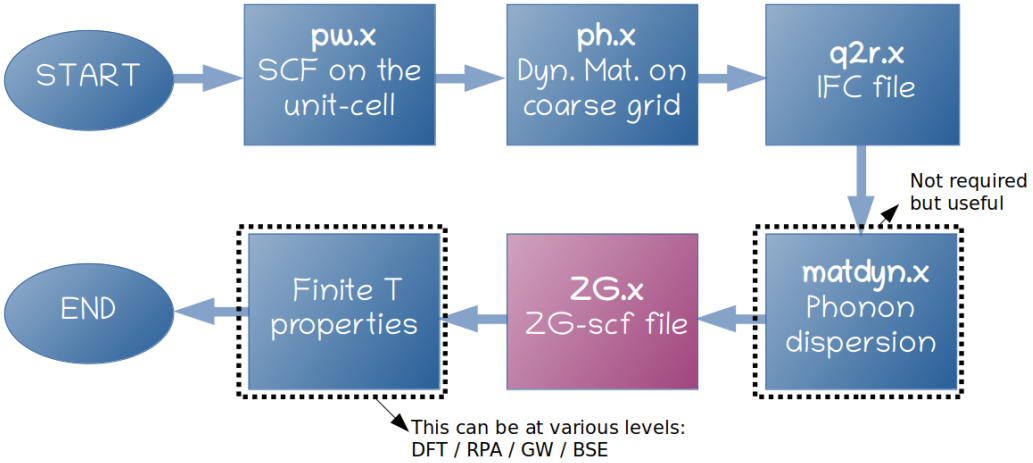




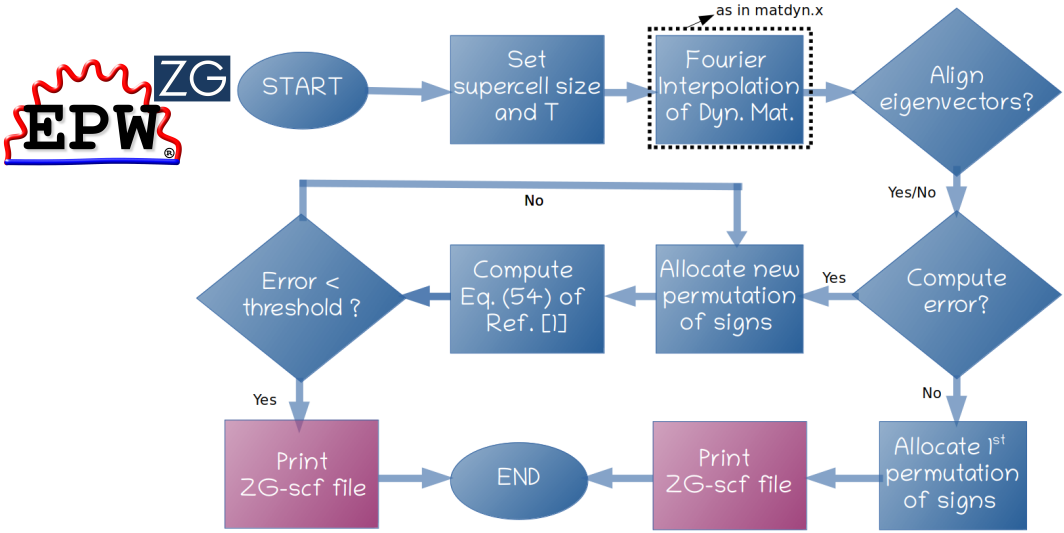
Refs: P. Hein *et al.* J. Phys.: Condens. Matter 32 345503 (2020)

P. Chen *et al.* Nat. Commun. 6, 8943 (2015) , pveducation.org , T. Gunst *et al.* Phys. Rev. B 96, 161404(R) (2017)

Appendix: Flowchart for ab-initio calculations with the SDM

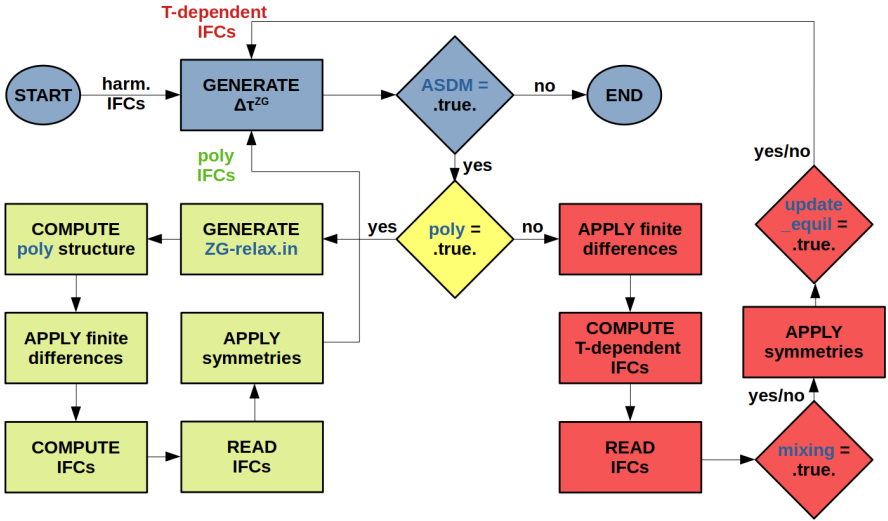


Appendix: Flowchart for ZG.x



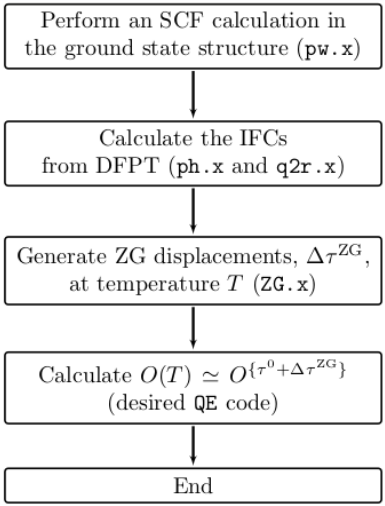
Ref. [1]: M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020)

Appendix: Flowchart for the A-SDM in ZG.x



M. Zacharias, G. Volonakis, F. Giustino, J. Even Phys. Rev. B 108, 035155 (2023)

Flowchart for ab-initio calculations with the SDM



Tutorials and description of input flags available in

Appendix: Input file for ZG.x (similar structure to matdyn.x)

```
--
&input
  flfrc='si.444.fc',
  asr='simple', amass(1)=28.0855, atm_zg(1) = 'Si',
  flscf = 'si.scf.in'
  T = 0.00,
  dim1 = 5, dim2 = 5, dim3 = 5
  compute_error = .true., synch = .true., error_thresh = 0.2
  incl_qA = .false.
/
```

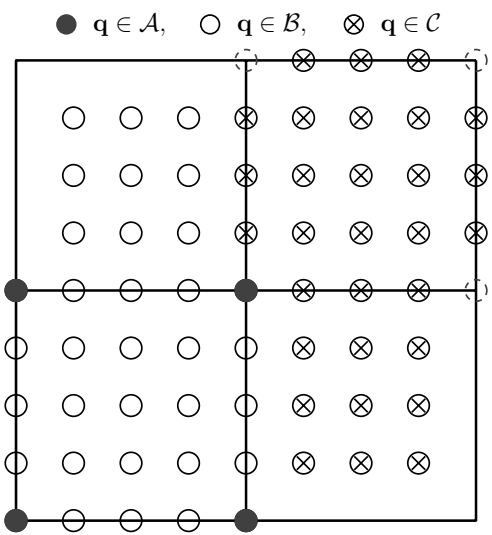
Tutorials and description of the input flags are available online in https://docs.epw-code.org/doc/.

Appendix: Things to have in mind when applying the SDM via ZG.x:

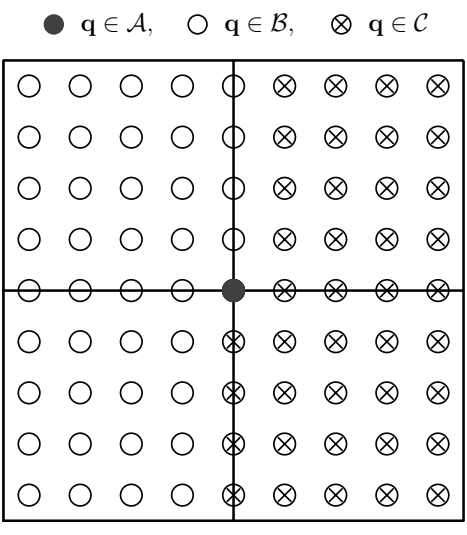
- Make sure that the phonon dispersion is correct. For *anharmonicity* one can upgrade the IFC file using the A-SDM.
- **q**-grid for phonons should not be necessarily the same with the supercell size. Use a coarse **q**-grid and generate any size of ZG configurations.
- Achive convergence of the T-dependent observable with the supercell size.
- Set `error_thresh` (< 0.4).
- Check the anisotropic displacement tensor data at the end of the output `ZG_XXX.out` (as in `exercise1`).
- Pointless to minimize the error function for systems with many atoms (> 15) in the unit-cell (set `compute_error = .false.`).

Partitioning of $\mathbf{q}$ into sets $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$

$8\times8\times1$ $\mathbf{q}$-grid

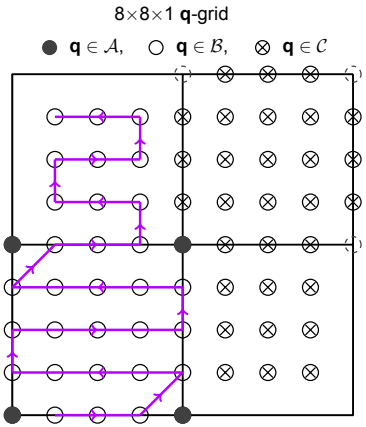


$9\times9\times1$ $\mathbf{q}$-grid



Smooth gauge of $\mathbf{e}_{\kappa,\nu}(\mathbf{q})$ along a path in reciprocal space

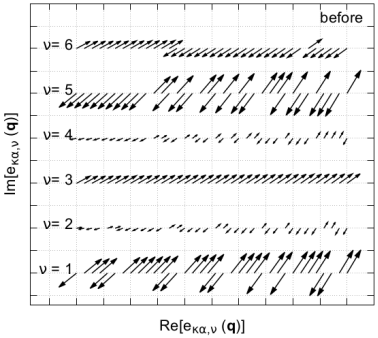
Apply a smooth gauge by setting: `synch = .true.`

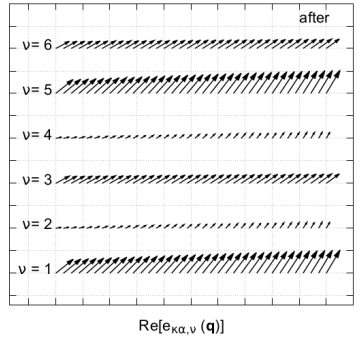


We apply the transformation:

$$e'_{\kappa\alpha,\nu}(\mathbf{q}+\Delta\mathbf{q}) = \sum_{\nu'} U_{\nu\nu'} e_{\kappa\alpha,\nu'}(\mathbf{q}+\Delta\mathbf{q}),$$

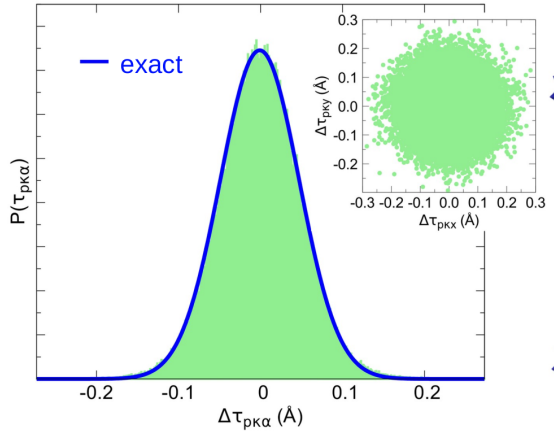
so that $e_{\kappa\alpha,\nu}(\mathbf{q})$ and $e_{\kappa\alpha,\nu}(\mathbf{q}+\Delta\mathbf{q})$ are as similar as possible.

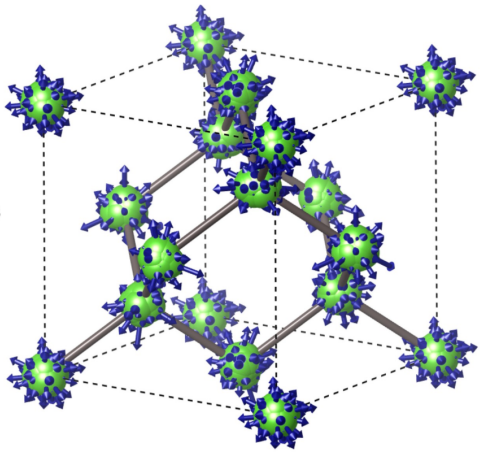




Physical meaning of minimizing $E(\{S_{\mathbf{q}\nu}\}, T)$

Gives the correct quantum mechanical probability distribution of nuclei displacements and the anisotropic displacement tensor / thermal ellipsoids. **Silicon**

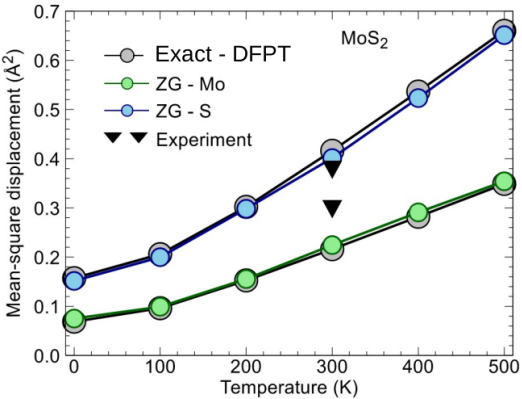


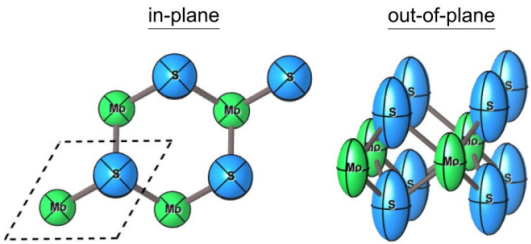


M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020)

Physical meaning of minimizing $E(\{S_{\mathbf{q}\nu}\}, T)$

Gives the correct quantum mechanical probability distribution of nuclei displacements and the anisotropic displacement tensor / thermal ellipsoids. **MoS_2**

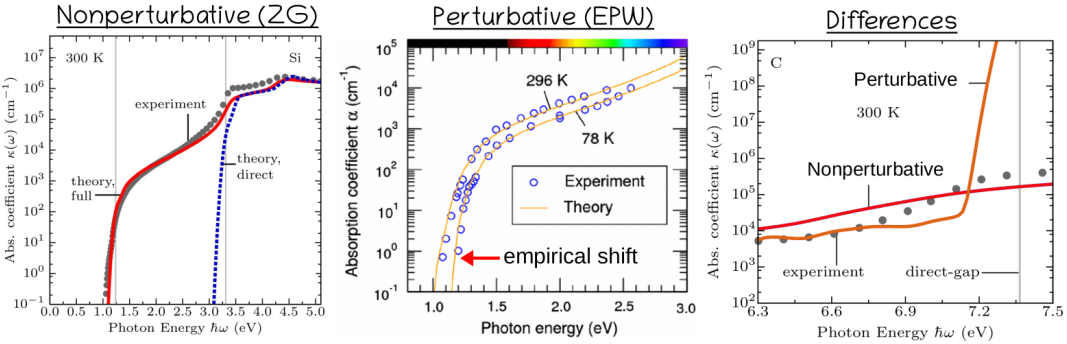




Thermal Ellipsoids of MoS_2

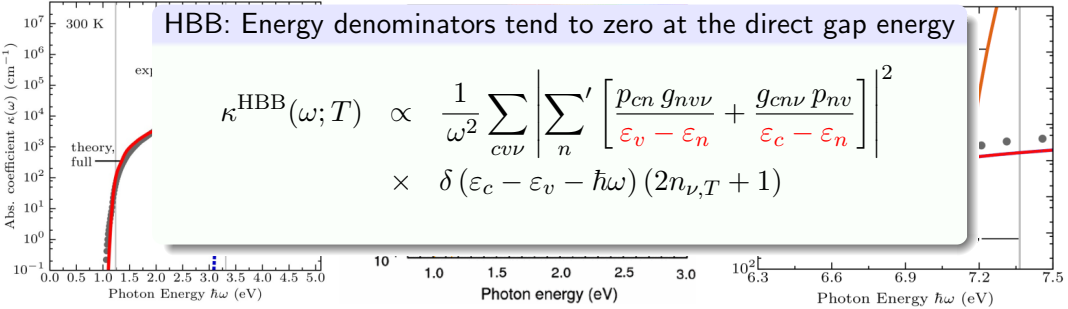
M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020)

Nonperturbative vs Perturbative: Divergence in optical spectra



Nonperturbative vs Perturbative: Divergence in optical spectra

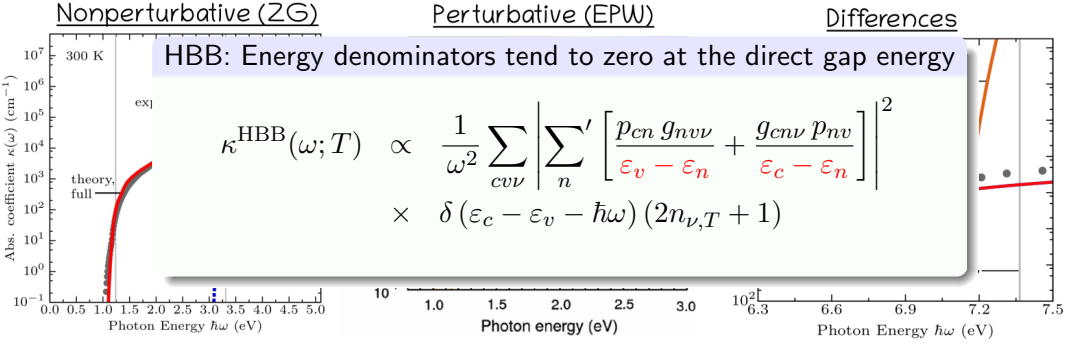
Nonperturbative (ZG) | Perturbative (EPW) | Differences



HBB: Energy denominators tend to zero at the direct gap energy

$$\kappa^{\mathrm{HBB}}(\omega;T) \propto \frac{1}{\omega^2}\sum_{cv\nu}\left|\sum_{n}{}'\left[\frac{p_{cn}\,g_{nv\nu}}{\varepsilon_v-\varepsilon_n}+\frac{g_{cn\nu}\,p_{nv}}{\varepsilon_c-\varepsilon_n}\right]\right|^2 \times \delta\left(\varepsilon_c-\varepsilon_v-\hbar\omega\right)\left(2n_{\nu,T}+1\right)$$

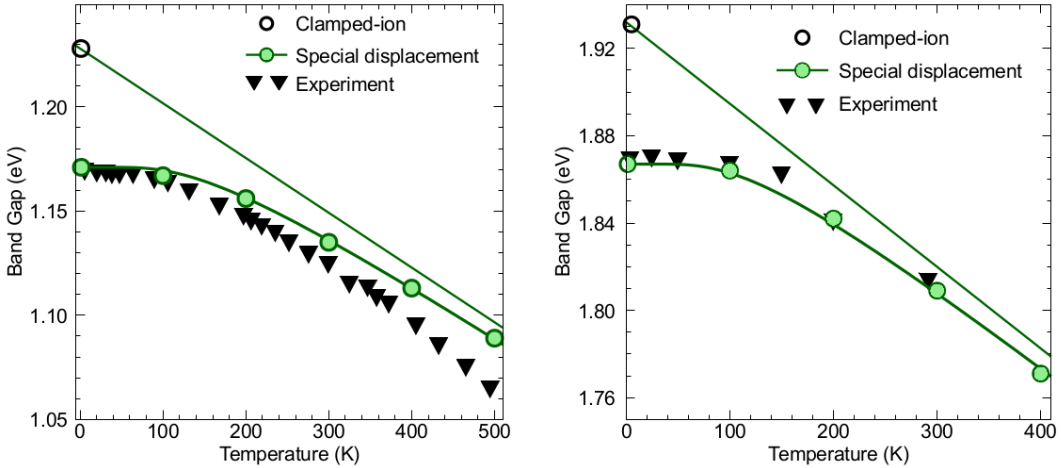
Nonperturbative vs Perturbative: Divergence in optical spectra



- ZG gives the full spectrum → all terms in perturbation theory: ✓
  $\kappa^{\mathrm{ZG}}(\omega;T) = \kappa^{\mathrm{HBB}}(\omega;T)$ + direct absorp. + higher ph. assisted processes + mix terms + band gap renorm.
- Straightforward to implement on top of any electronic structure code. ✓
- ZG requires supercells → EPW elegance of unit-cell calculations. ✗
- ZG misses non-adiabatic (e.g. ph. frequencies in the denominators) and dynamical effects. ✗
- Divergence is solved with Quasi-Degenerate Perturbation Theory (QDPT) → Sat.6.Tawari ✓

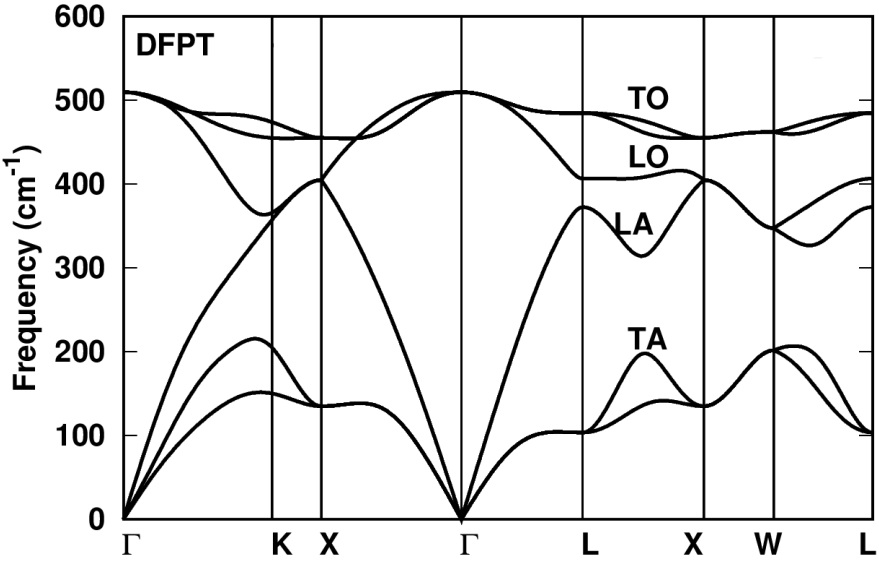
Applications of the SDM (Zero-point renormalization - ZPR)

Temperature dependent band gaps of **Si** (ZPR $= 57$ meV) and **MoS$_2$** (ZPR $= 65$ meV).

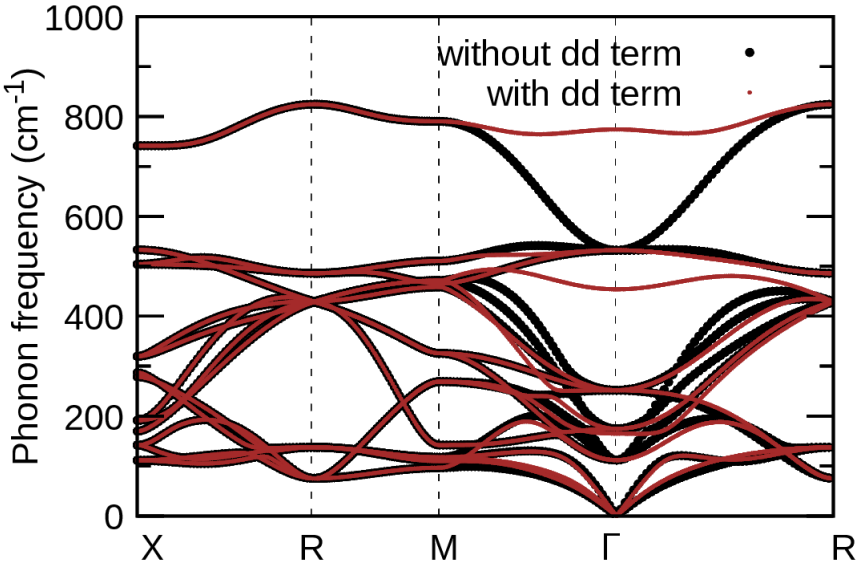


M. Zacharias, F. Giustino, Phys. Rev. Res. 2, 013357 (2020)

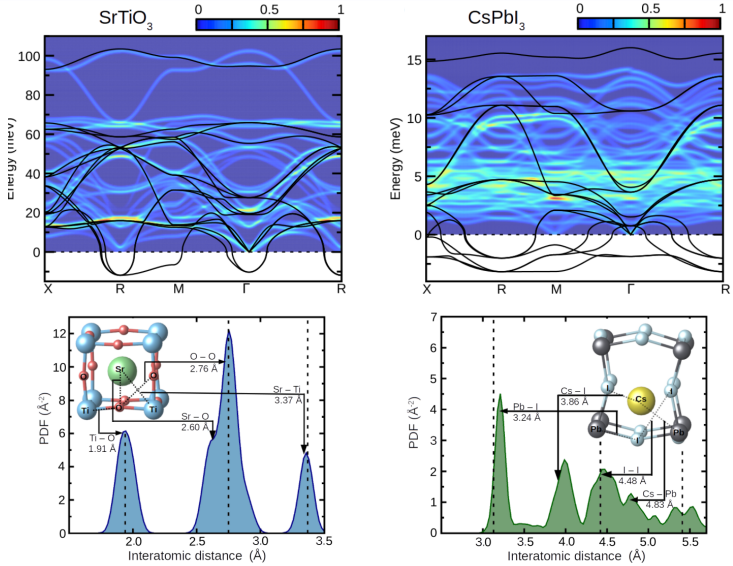
Phonon dispersion of silicon



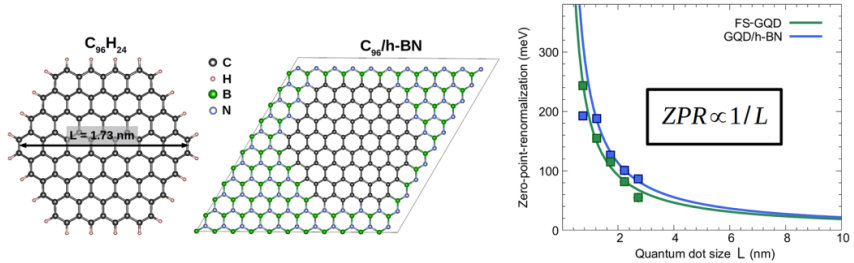
A-SDM phonon dispersion of $SrTiO_3$ (incl_epsil = .true.)



Systems with local disorder (phonon unfolding as in exercise6)



The SDM for nanostructures



M. Zacharias, P. C. Kelires, J. Phys. Chem. Lett. 12, 9940 (2021)

Remark: Energy level degeneracies in the SDM calculations.

- For periodic systems degeneracies should be preserved at finite temperatures (consequence of the harmonic approximation).

  Treatment: if degeneracy splitting exist due to numerical artefacts, take the average of the energy levels.

- For non-periodic systems (molecules, clusters, etc ..) degeneracies are **not** preserved at finite temperatures.
  (either in the harmonic approximation or beyond).

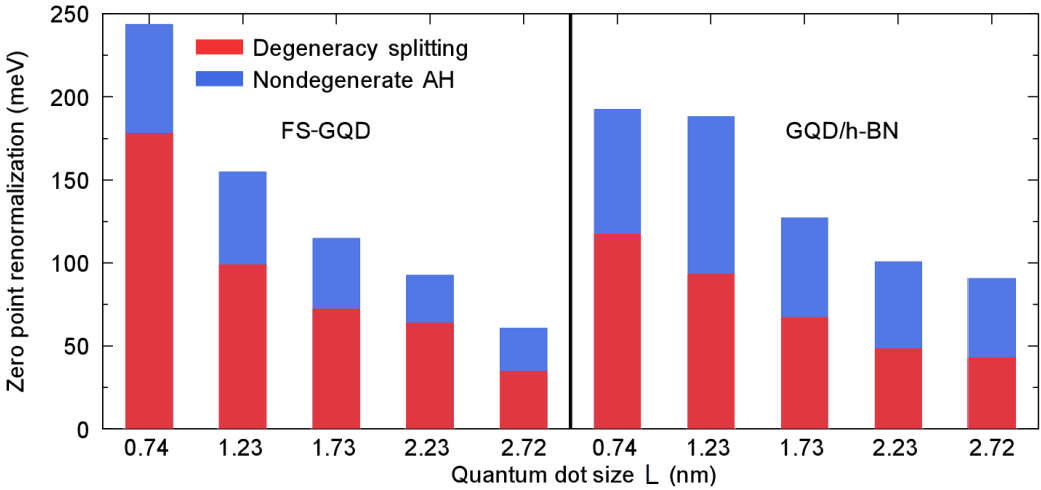
New linear term added to AH from degenerate perturb. theory:

$$\Delta\varepsilon^{\pm}_{c_1,T} = \pm \left| \sum_{\nu} (g_{c_1 c_1 \nu} - g_{c_2 c_2 \nu}) \frac{\sigma_{\nu,T}}{\sqrt{2\pi}} \right| + {\sum_{\nu\beta}}' \left[\frac{|g_{c_1 \beta \nu}|^2}{\varepsilon_{c_1} - \varepsilon_{\beta}} + h_{c_1 \nu} \right] \sigma^2_{\nu,T}.$$

M. Zacharias, P. C. Kelires, J. Phys. Chem. Lett. 12, 9940 (2021)

Remark: Energy level degeneracies of GQDs in the SDM.

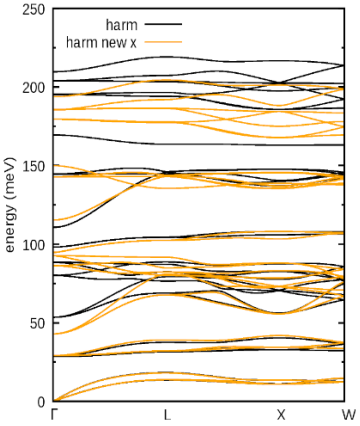
M. Zacharias, P. C. Kelires, J. Phys. Chem. Lett. 12, 9940 (2021)

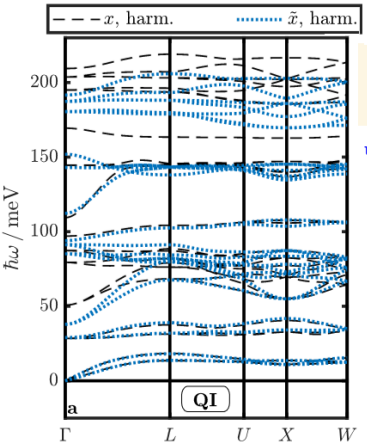


A-SDM for hydrides: $BaSiH_8$, T = 0 K, 2×2×2 supercells

Anharmonic quantum ionic effects with A-SDM: minimize free energy w.r.t internal nuclei coordinates

SSCHA calculations: Lucrezi R. et al, Commun. Phys. 6, 298 (2023).






```
ATOMIC_POSITIONS (crystal_sg)
Ba  4b
Si  4a
H   32f 0.1482757992
```

```
update_equil = .true.
```

$$\tau^{\text{new}}_{p\kappa\alpha}(T) = \tau_{p\kappa\alpha}(T) + C^{-1}_{p\kappa\alpha,p\kappa\alpha}(T) F^{\{\tau^{\text{SDM}}\}}_{p\kappa\alpha}$$

A-SDM for hydrides: $BaSiH_8$, T = 0 K, 2×2×2 supercells

Anharmonic effects form third order IFCs (static bubble diagram).
SSCHA calculations: Lucrezi R. et al, Commun. Phys. 6, 298 (2023).