2023 Virtual School on Many-Body Calculations using EPW and BerkeleyGW

June 5-9 2023

Lecture Wed.2

The Special Displacement Method

Marios Zacharias

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

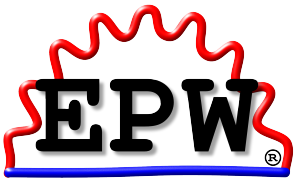
Univ. Rennes

Lecture Summary

- Nonperturbative approaches to electron-phonon coupling
- From the stochastic framework to deterministic
- The special displacement method (SDM):
  1. Theory
  2. Physical interpretation
  3. Applications
- Self-consistent anharmonic special displacements (A-SDM):
  1. Theory
  2. Validation and applications

Codes for perturbative and nonperturbative calculations

Calculation of temperature-dependent properties using, e.g.:

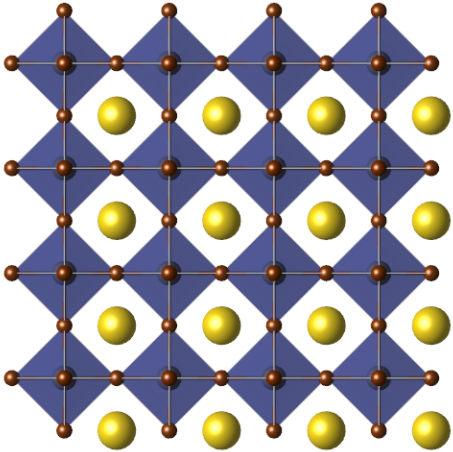


$g_{mn,\nu}(\mathbf{k},\mathbf{q})$ from DFPT in the unit-cell

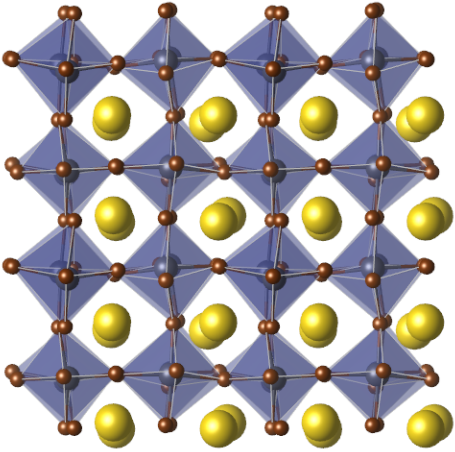
Displaced nuclei in large supercells; $g_{mn,\nu}(\mathbf{k},\mathbf{q})$ is not explicitly evaluated

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

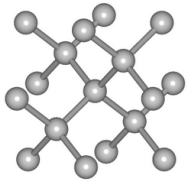
High-symmetry configuration
(and static-equilibrium)



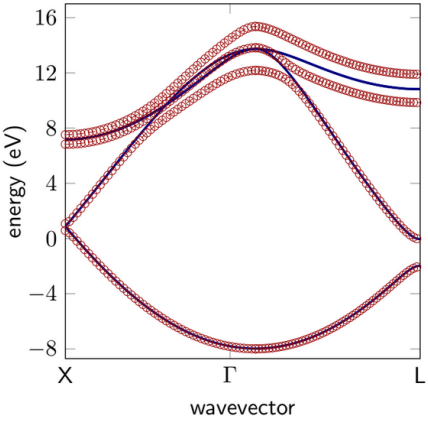
ZG configuration

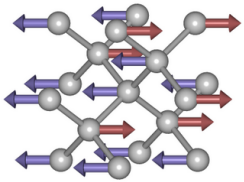


Slide 4 from Giustino Mon.1



diamond

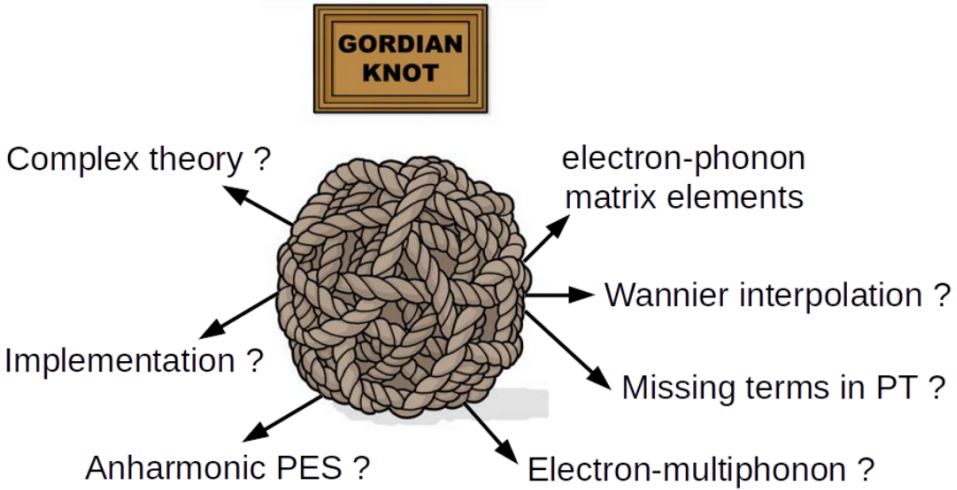




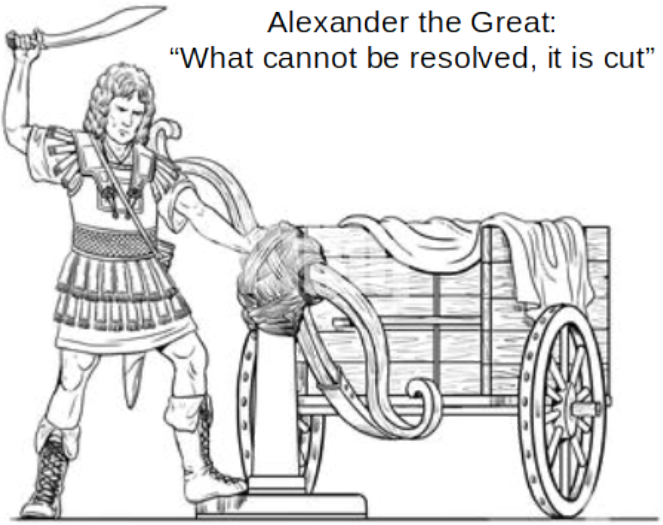
Γ-point optical mode

0.015 Å C-displacement

Why useful ? (Compared to perturbative approaches)



Why useful ?



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)

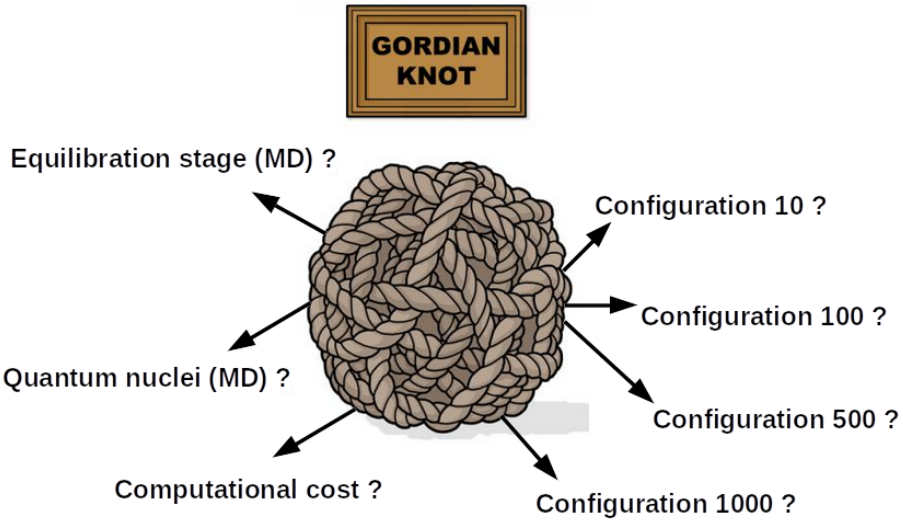
Special Displacement Method (SDM):

- 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 arXiv:2212.10633

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

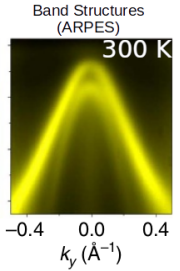
- R. B. Capaz, C. D. Spataru, P. Tangney, M. L. Cohen, S. G. Louie, Phys. Rev. Lett. 94, 036801 (2005)
- G. Antonius, S. Poncé, P. Boulanger, M. Côté, X. Gonze, Phys. Rev. Lett. 112, 215501 (2014)
- B. Monserrat, J. Phys.: Condens. Matter 30, 083001 (2018)

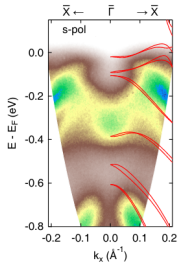
Why useful ? (compared to MD or MC)

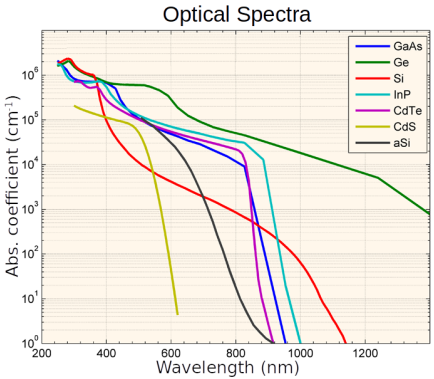


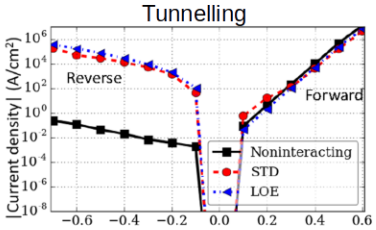
Nonperturbative Approaches - Literature III

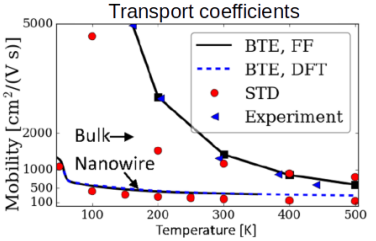
All nonperturbative approaches can be upgraded
to evaluate any property written as a **Fermi-Golden Rule**, e.g.:







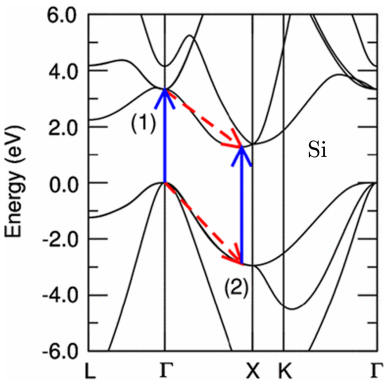




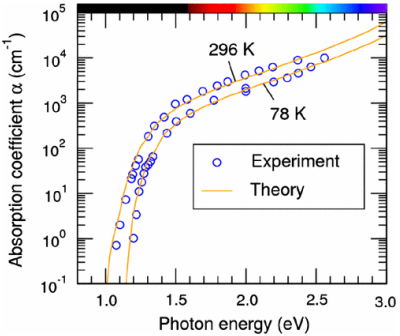
Refs: P. Hein *et al.* J. Phys.: Condens. Matter 32 345503 (2020)

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

Phonon-assisted optical spectra



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

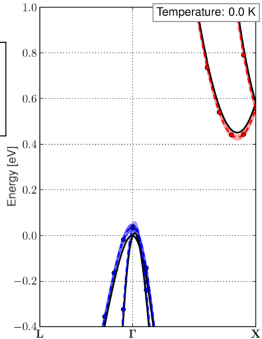
Temperature-dependence of the energy levels in the Allen-Heine theory:

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

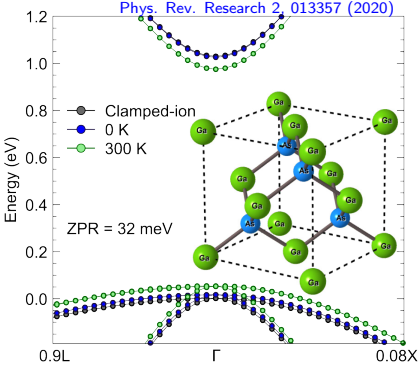
Perturbative first-principles applications:

- 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)
- H. Kawai, *et al*, PRB 89, 085202 (2014)
- 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)
- 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:

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

- M. Zacharias, C. E. Patrick, F. Giustino, Phys. Rev. Lett. 115, 177401 (2015)
- M. Zacharias, F. Giustino, Phys. Rev. B 94, 075125 (2016); DPhil Thesis , University of Oxford (2017)

Williams-Lax Theory

1. Herzberg-Teller rate as the starting point:

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

2. Semiclassical approximation for 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); DPhil Thesis , University of Oxford (2017)

Williams-Lax Theory

1. Herzberg-Teller rate as the starting point:

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

2. Semiclassical approximation for 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:

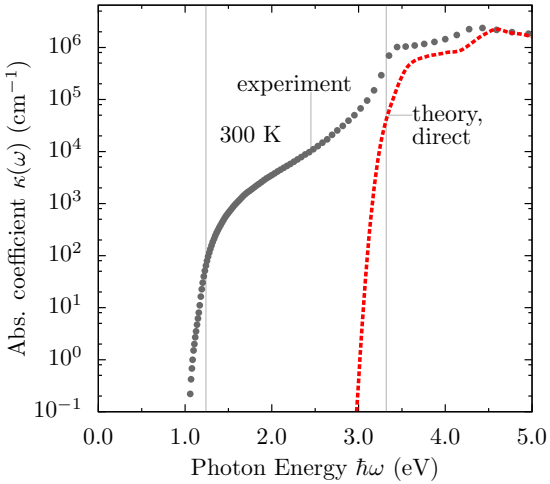
$$\epsilon_2^x(\omega) \propto \frac{1}{\omega^2} \sum_{cv} |p^x_{cv}|^2 \delta(\varepsilon^x_c - \varepsilon^x_v - \hbar\omega)$$

Interpretation: Weighted average of the spectra calculated with the nuclei fixed in a variety of configurations.

- M. Zacharias, C. E. Patrick, F. Giustino, Phys. Rev. Lett. 115, 177401 (2015)
- M. Zacharias, F. Giustino, Phys. Rev. B 94, 075125 (2016); DPhil Thesis , University of Oxford (2017)

Silicon optical absorption in the Williams-Lax theory

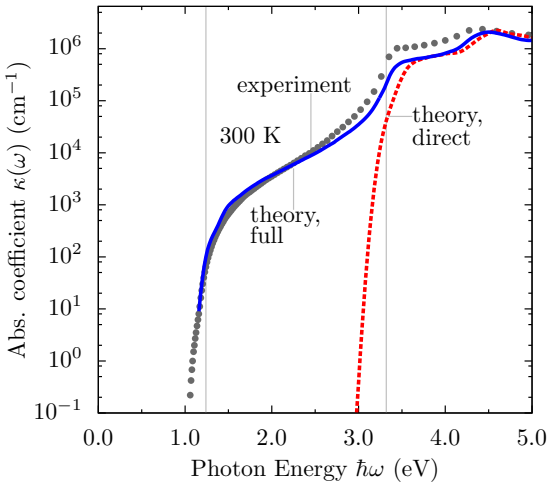
DFT-LDA calculations with nuclei at equilibrium



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

Silicon optical absorption in the Williams-Lax theory

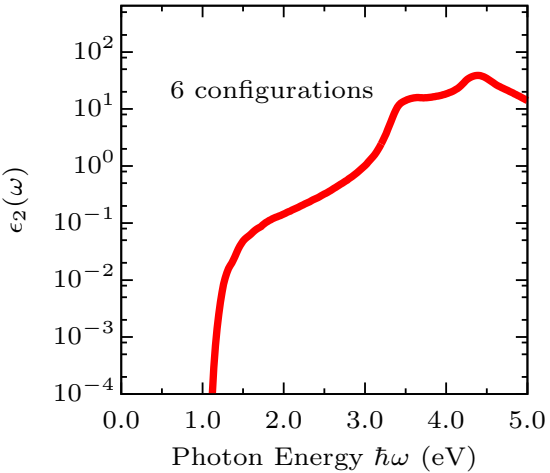
DFT-LDA calculations + quantum nuclear effects, Method: ISMC (8×8×8 supercell)



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

Convergence test with configurational sampling

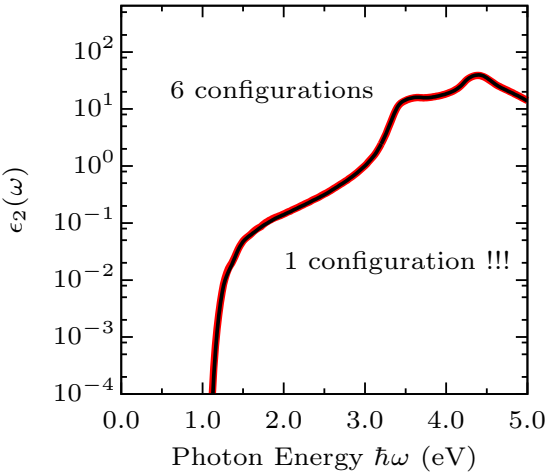
DFT-LDA calculations + quantum nuclear effects, Method: ISMC (8×8×8 supercell)



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 $\Delta\tau^{\rm ZG}$:

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

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

2. One configuration:

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

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

3. We can prove:

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

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:

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

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

3. We can prove:

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

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:

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

2. One configuration:

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

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

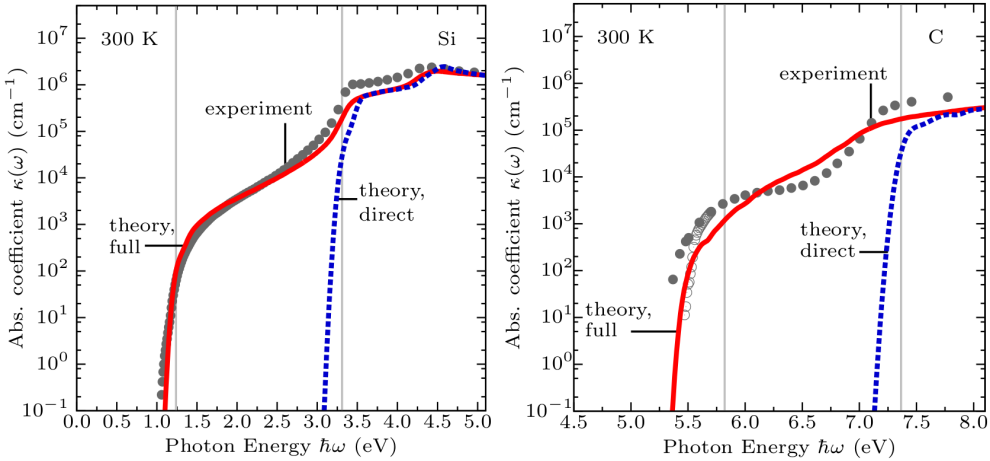
3. We can prove:

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

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

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`)

Relations connecting the SDM and Perturbative methods

- Optical spectra:

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

- Temperature-dependent band structures:

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

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:

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

where

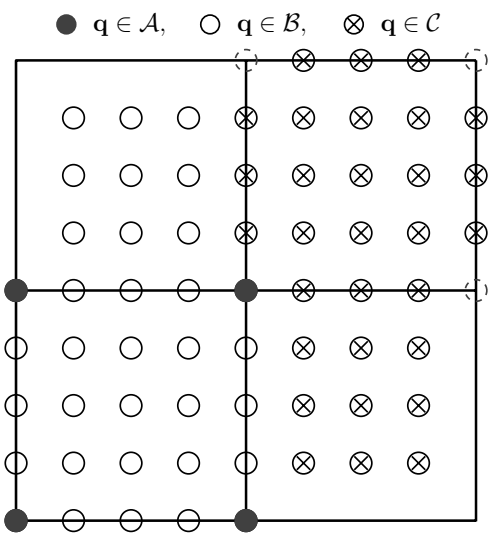
- $\sigma^2_{\mathbf{q}\nu,T} = (2n_{\mathbf{q}\nu,T}+1)\hbar/(2M_{\mathrm{p}}\omega_{\mathbf{q}\nu})$ with $n_{\mathbf{q}\nu,T} = [\exp(\hbar\omega_{\mathbf{q}\nu}/k_{\mathrm{B}}T)-1]^{-1}$
- $\omega_{\mathbf{q}\nu} \longrightarrow$ phonon frequencies
- $\mathbf{e}_{\kappa,\nu}(\mathbf{q}) \longrightarrow$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

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

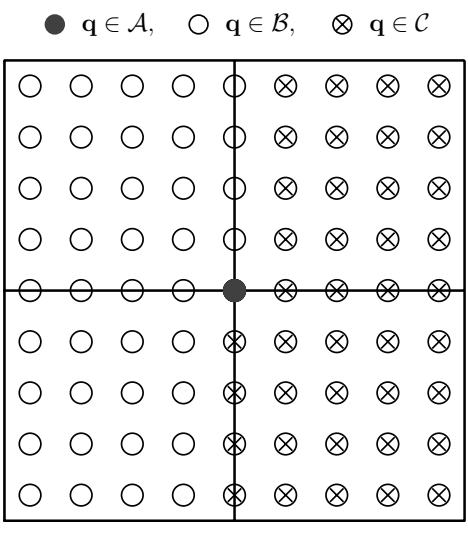
M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020) and H. Lee, *et al* arXiv:2302.08085

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



Reciprocal space formulation of the SDM

Key findings from our theory 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.

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 = 0.05` (see tutorial `exercise1`) so that the function:

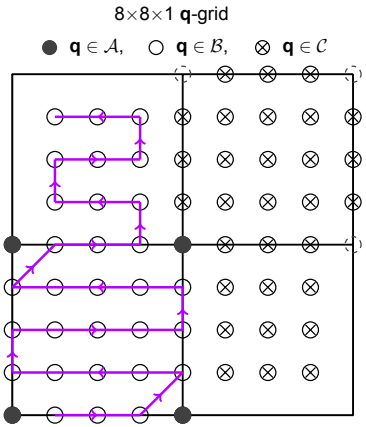
$$E(\{S_{\mathbf{q}\nu}\}, T) = \sum_{\substack{\kappa\alpha \\ \kappa'\alpha'}} \frac{\left| \sum_{\substack{\mathbf{q}\in\mathcal{B} \\ \nu<\nu'}} \Re[e^*_{\kappa\alpha,\nu}(\mathbf{q}) e_{\kappa'\alpha',\nu'}(\mathbf{q})] \sigma_{\mathbf{q}\nu,T} \sigma_{\mathbf{q}\nu',T} S_{\mathbf{q}\nu} S_{\mathbf{q}\nu'}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

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.

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

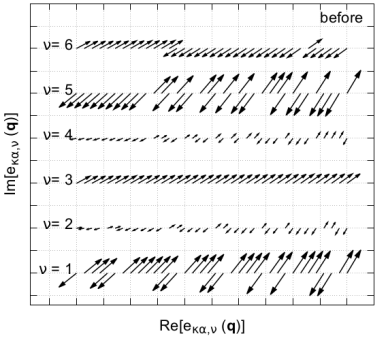
Apply a smooth gauge by setting: `synch = .true.`

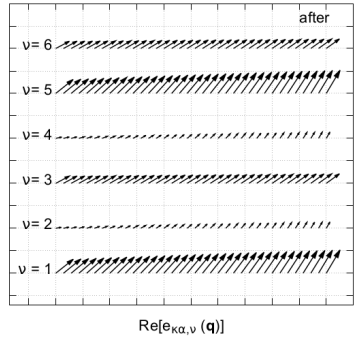


We apply the transformation:

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

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

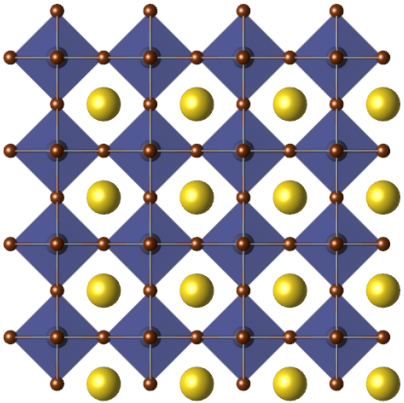




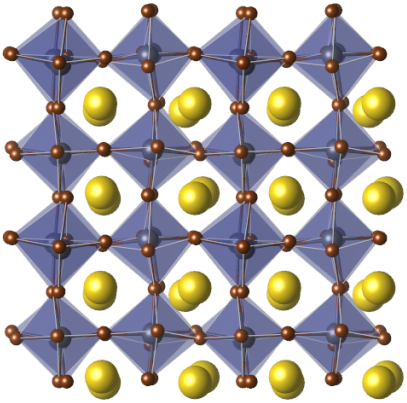
Physical meaning of minimizing $E(\{S_{\mathbf{q}\nu}\}, T)$

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

High-symmetry configuration
(and static-equilibrium)

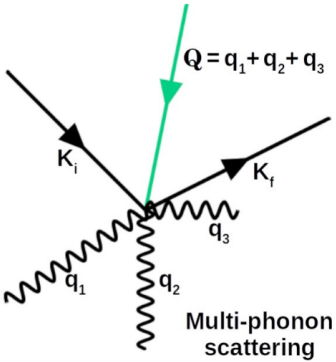


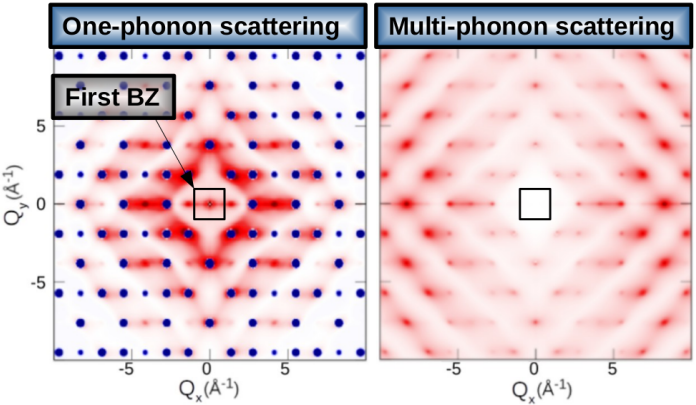
ZG configuration



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**

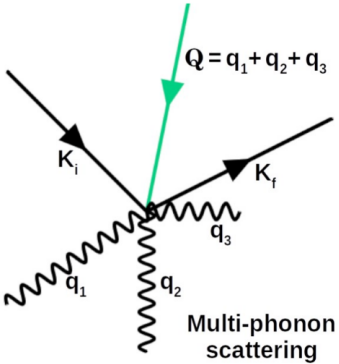


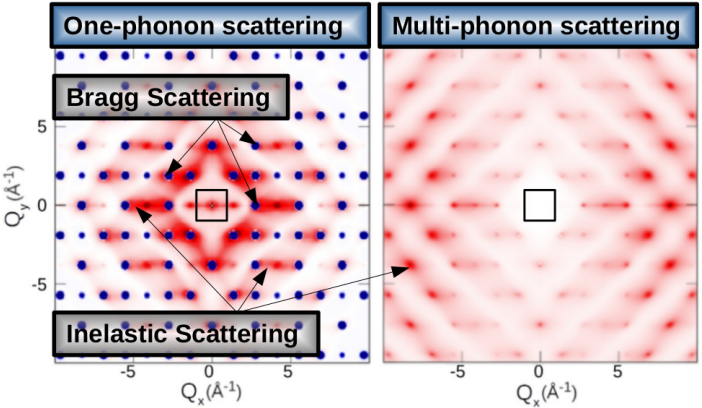


M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, Phys. Rev. Lett. 127, 207401 (2021)
M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, Phys. Rev. B 104, 205109 (2021)

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**

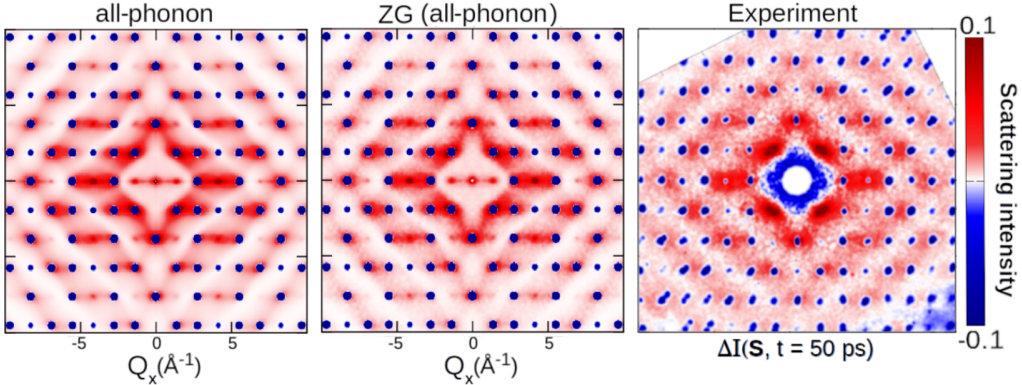




M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, Phys. Rev. Lett. 127, 207401 (2021)
M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, Phys. Rev. B 104, 205109 (2021)

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*: $I_{\mathrm{ZG}}(\mathbf{Q}, T) = \left| \sum_{p\kappa} f_\kappa(\mathbf{Q}) e^{i\mathbf{Q}\cdot\left[\mathbf{R}_p + \boldsymbol{\tau}_\kappa + \Delta\boldsymbol{\tau}_{p\kappa}^{\mathrm{ZG}}\right]} \right|^2$

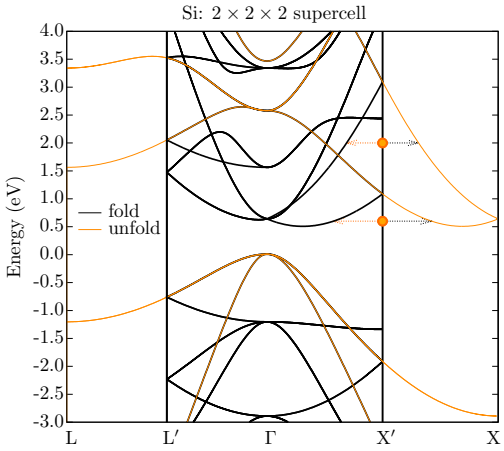


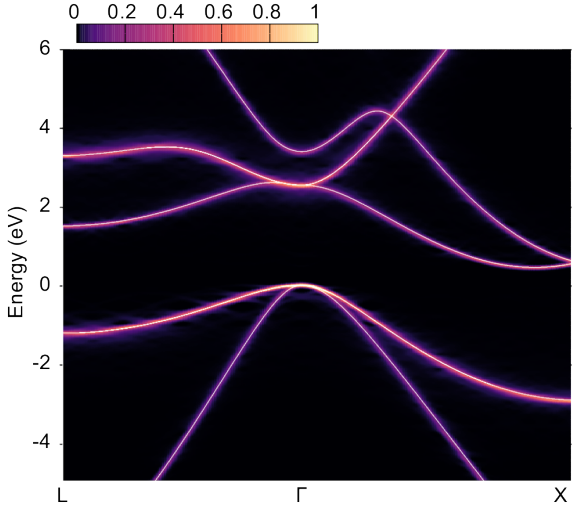
Someone can calculate diffuse scattering maps using `ZG.x` and `disca.x` of QE (see tutorial `exercise5`).

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)

Applications of the SDM

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)

Applications of the SDM

Temperature-dependent band structures with the band structure unfolding technique

Goal is to evaluate the electron spectral function:

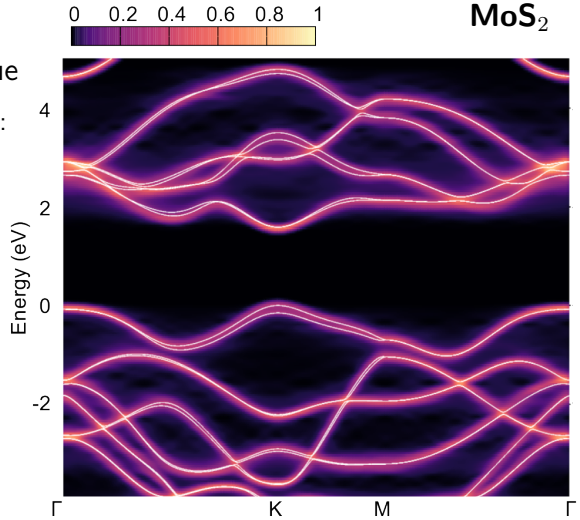
$$A_{\mathbf{k}}(\varepsilon;T) = \sum_{m\mathbf{K}} P_{m\mathbf{K},\mathbf{k}}(T)\,\delta[\varepsilon - \varepsilon_{m\mathbf{K}}(T)],$$

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`)

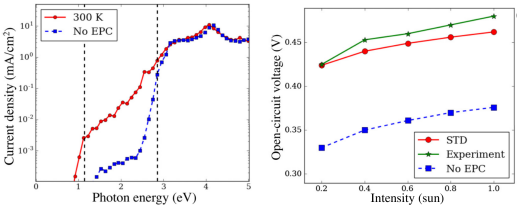
V. Popescu, A. Zunger, Phys. Rev. B 85, 085201 (2012)
P. V. C. Medeiros, S. Stafström, J. Björk, Phys. Rev. B 89, 041407(R) (2014)



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

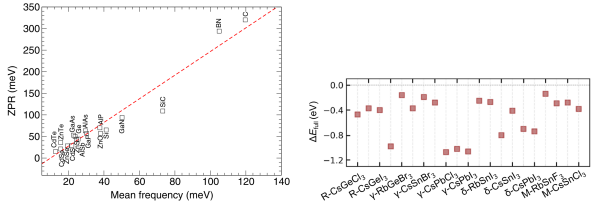
Applications of the SDM

Phonon-assisted photocurrent in large solar-cell devices



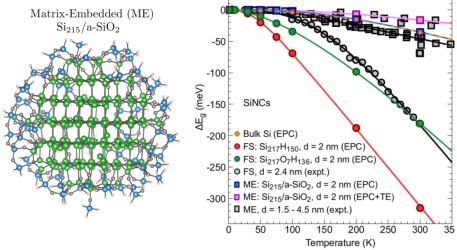
M. Palsgaard, *et al*, PRA 10, 014026 (2018)

Zero-point renormalization within GW and Hybrid functionals



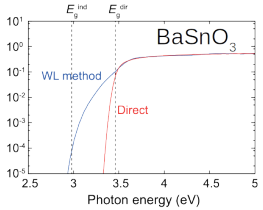
F. Karsai, *et al*, NJP 20 123008 (2018) H. Wang, *et al*, npj CM 8 237 (2022)

Band gap renormalization of nanostructures



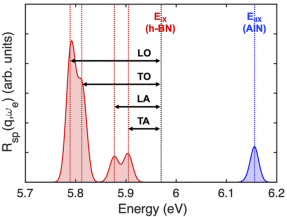
M. Zacharias, *et al*, PRB 101, 245122 (2020)

Indirect optical absorption in $BaSnO_3$



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

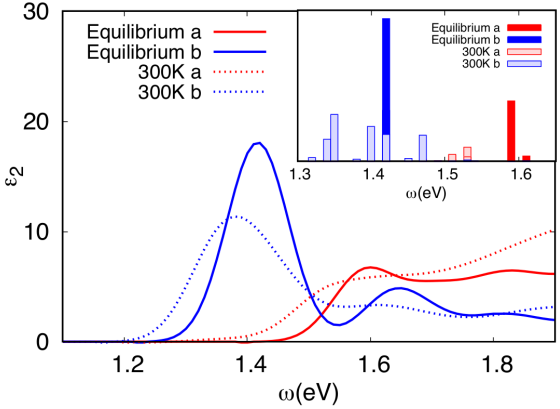
Phonon-assisted emission spectrum of h-BN and AlN



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

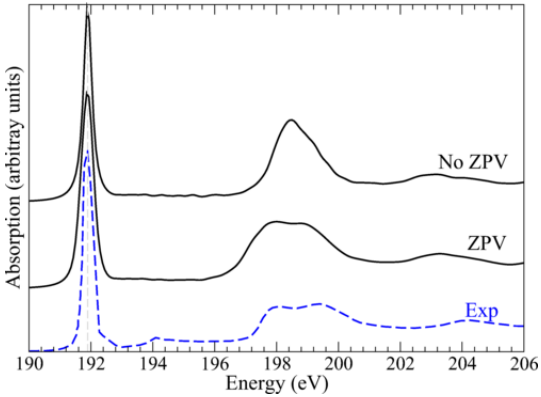
Applications of the SDM

Exciton-phonon coupling in 2D GeSe



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

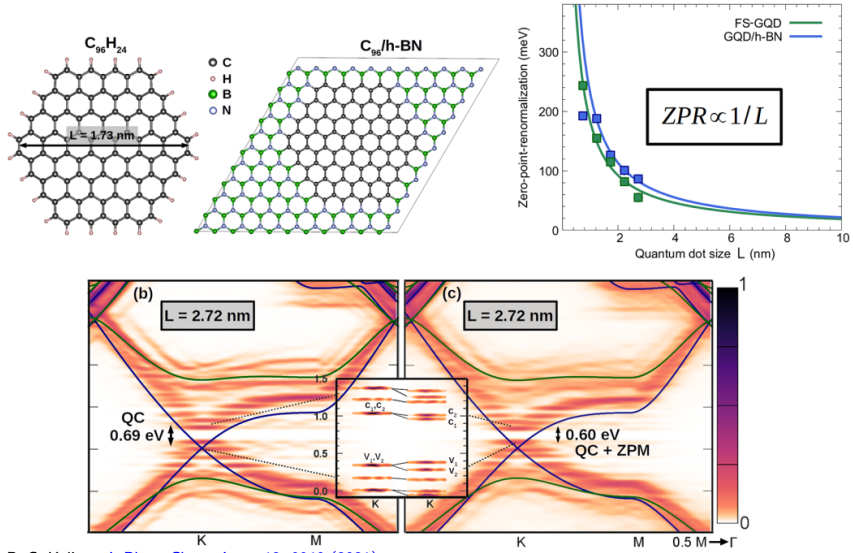
Exciton-phonon coupling in h-BN



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

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

The SDM for nanostructures

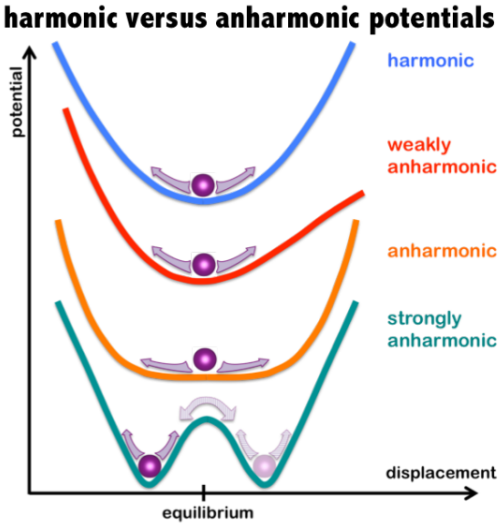


M. Zacharias, P. C. Kelires, J. Phys. Chem. Lett. 12, 9940 (2021)

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 (SDM) ...

Anharmonicity within the Self-Consistent Phonon (SCP) theory

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. The proof involves:

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

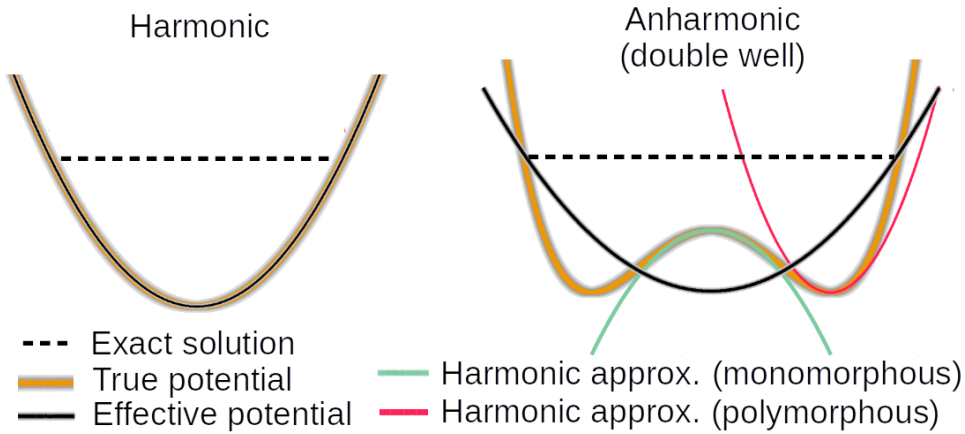
$$\begin{aligned} F(T) &= \langle U\rangle_T - U_{\rm h}(T) + F_{\rm vib}(T) \\ F(T) &= \langle U\rangle_T - \frac{M_0}{2}\sum_{\mathbf{q}\nu}\omega^2_{\mathbf{q}\nu}\sigma^2_{\mathbf{q}\nu,T} + \sum_{\mathbf{q}\nu}\left[\frac{\hbar\omega_{\mathbf{q}\nu}}{2} - k_{\rm B}T\ln[1+n_{\mathbf{q}\nu,T}]\right],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

2. We can prove:

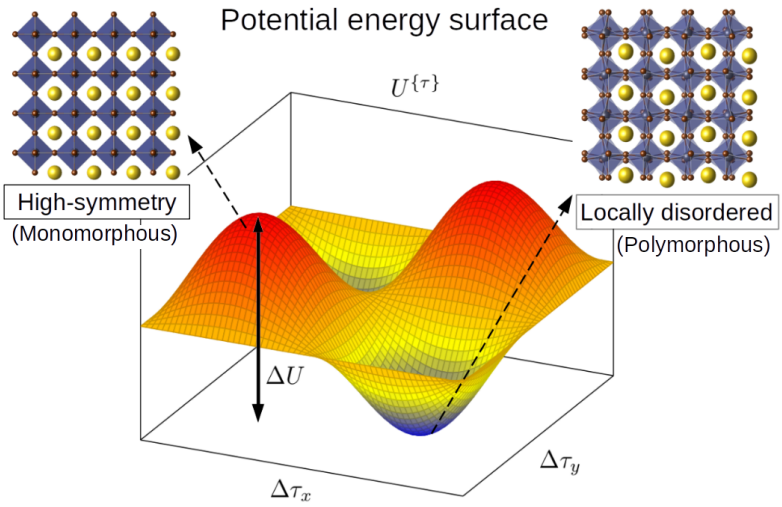
$$\frac{\partial F(T)}{\partial C_{\kappa\alpha,\kappa'\alpha'}} = \frac{\partial \langle U\rangle_T}{\partial C_{\kappa\alpha,\kappa'\alpha'}} - \frac{\partial U_{\rm h}(T)}{\partial C_{\kappa\alpha,\kappa'\alpha'}} + \frac{\partial F_{\rm vib}(T)}{\partial C_{\kappa\alpha,\kappa'\alpha'}} \propto \sum_{\substack{\kappa''\alpha''\\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

M. Zacharias, G. Volonakis, F. Giustino, J. Even arXiv:2212.10633

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 structue 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

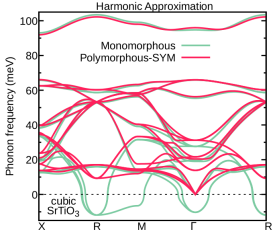
SCPs with the A-SDM

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:

1. Compute harmonic $C_{p\kappa\alpha,p'\kappa'\alpha'}$ of the polymorphous structue 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

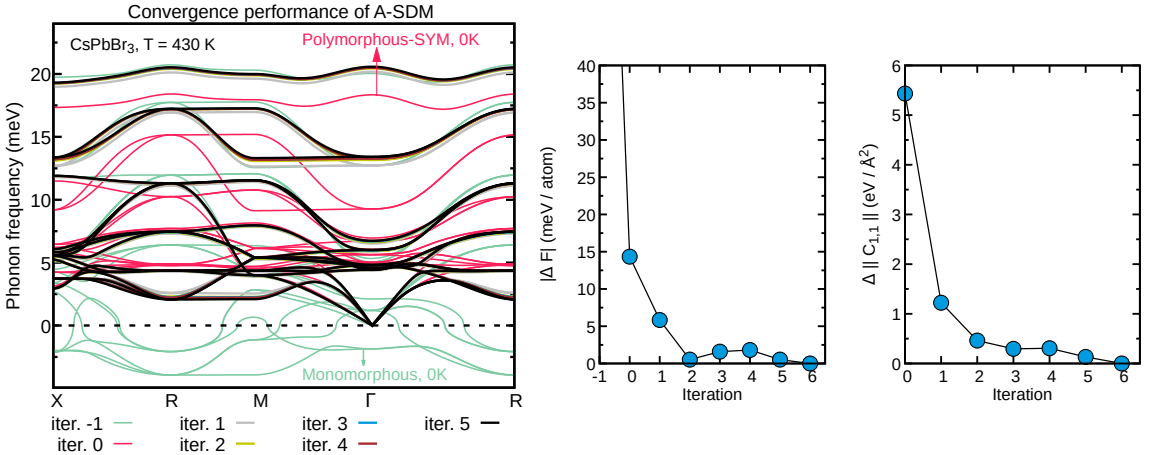
Compute temperature-dependent effective IFCs

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

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

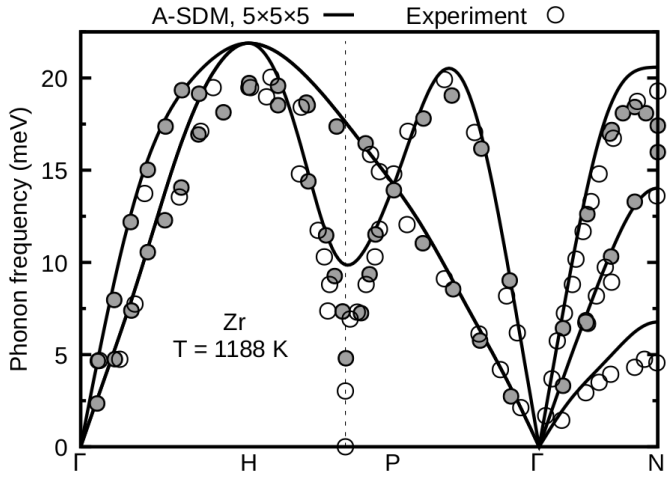
1. Compute harmonic $C_{p\kappa\alpha,p'\kappa'\alpha'}$ of the polymorphous structure using finite differences, enforce symmetries, and obtain initial $\{\omega_{\mathbf{q}\nu}/e_{\kappa\alpha,\nu}(\mathbf{q})\}_{\mathrm{Poly-SYM}}$
2. Generate $\Delta\tau^{\mathrm{ZG}}$
3. Compute $C_{p\kappa\alpha,p'\kappa'\alpha'}(T)$ 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 arXiv:2212.10633

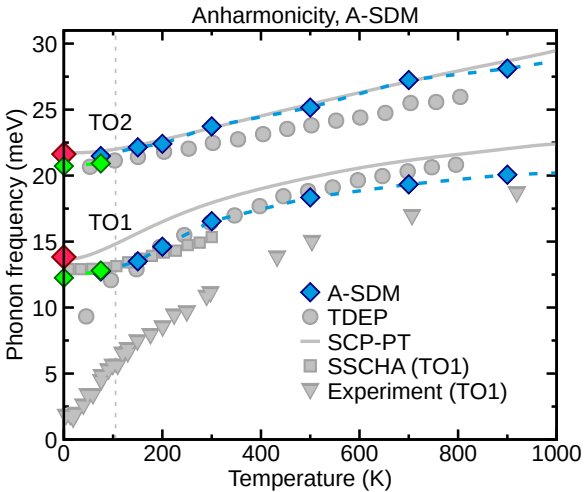
A-SDM validation: Zr (compare with experiment)



see tutorial `exercise3`

M. Zacharias, G. Volonakis, F. Giustino, J. Even arXiv:2212.10633

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

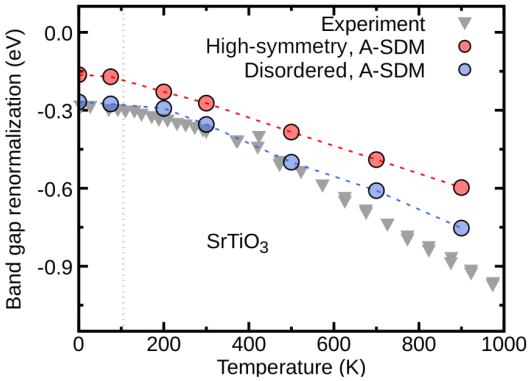


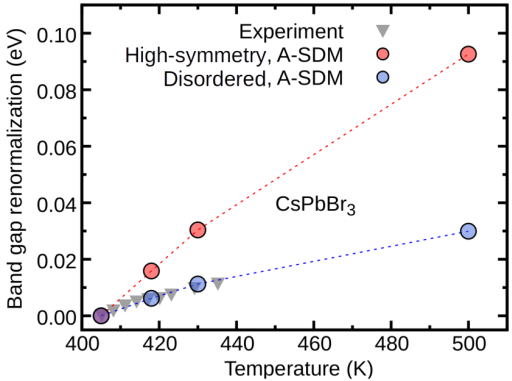
A-SDM data: M. Zacharias, G. Volonakis, F. Giustino, J. Even arXiv:2212.10633,

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

Application of the A-SDM: perovskite polymorphs

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



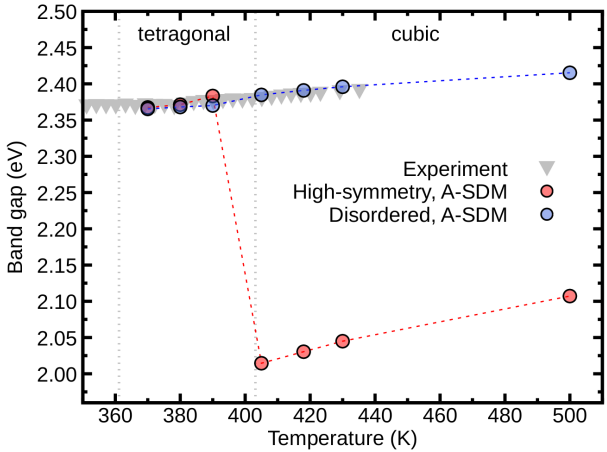


Experiment $SrTiO_3$: D. J. Kok, et al. Phys. Stat. Solidi 212, 1880, (2015)

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

Theory: M. Zacharias, G. Volonakis, F. Giustino, J. Even arXiv:2302.09625

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 arXiv:2302.09625

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://epwdoc.gitlab.io`.

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 SCP-PT 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. M. Zacharias, G. Volonakis, F. Giustino, J. Even arXiv:2212.10633
5. R. Bianco, I. Errea, L. Paulatto, M. Calandra, F. Mauri Phys. Rev. B 96 (2017)
6. H. Lee, *et al* arXiv:2302.08085

Williams-Lax Theory

1. Herzberg-Teller rate as the starting point:

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

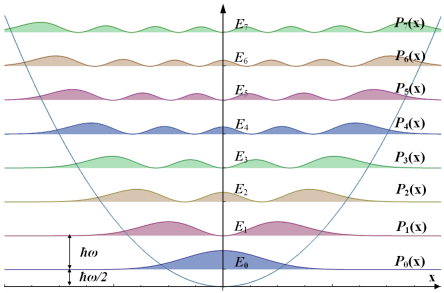
Williams-Lax Theory

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:

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

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

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

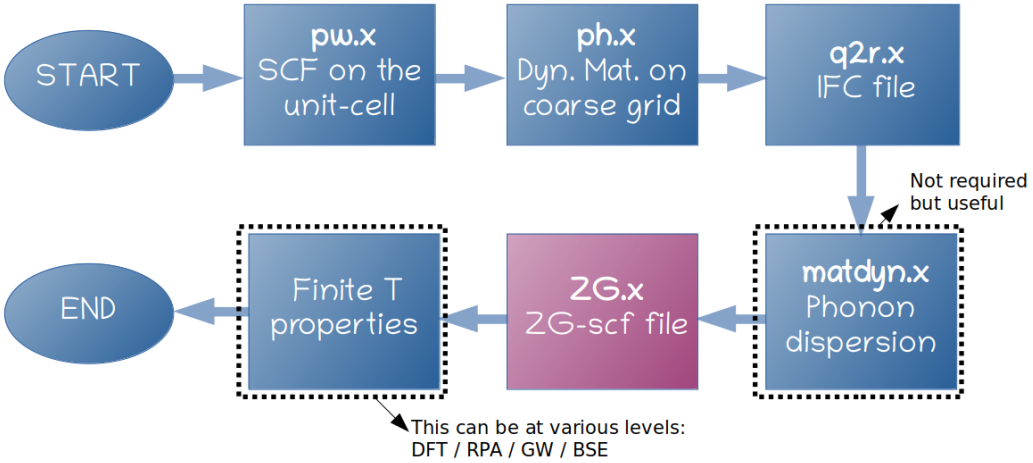
3. Thermal average, Harmonic approximation, and Mehler's formula:

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

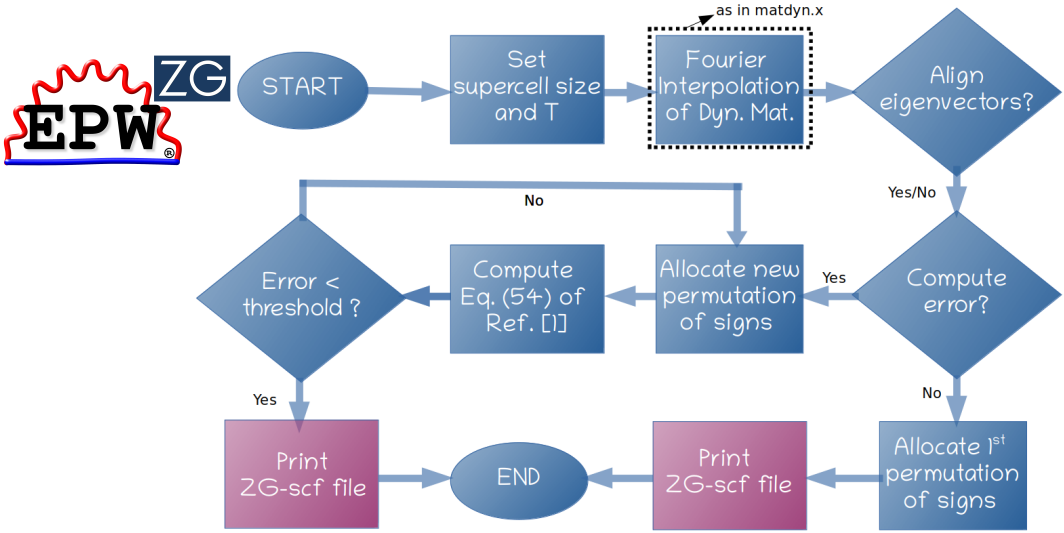
wtih $\sigma^2_{\nu,T}=(2n_{\nu,T}+1)\,l^2_\nu$.

- 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)

Appendix: Flowchart for ab-initio calculations with the SDM

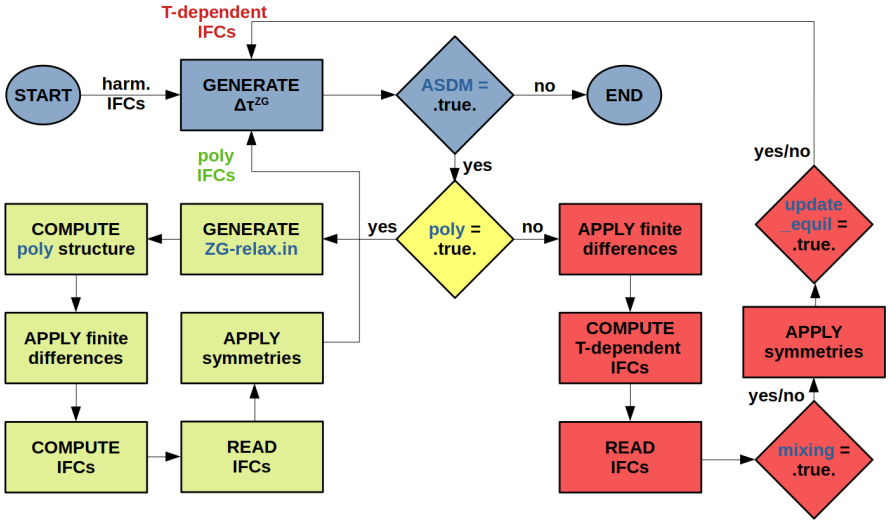


Appendix: Flowchart for ZG.x



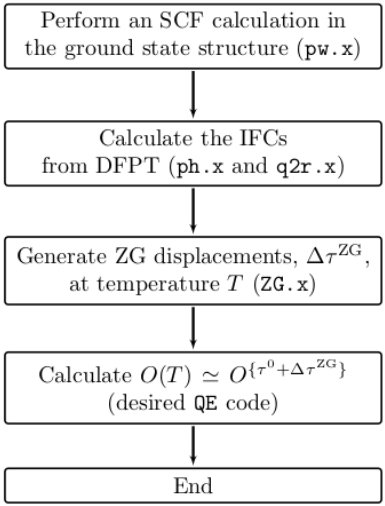
Ref. [1]: M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020)

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



M. Zacharias, G. Volonakis, F. Giustino, J. Even arXiv:2212.10633

Flowchart for ab-initio calculations with the SDM



Tutorials and description of input flags available in `https://epwdoc.gitlab.io`.

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 = 0.05
  incl_qA = .false.
/
```

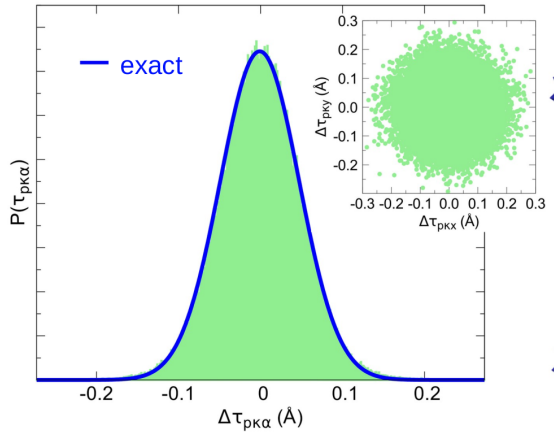
Tutorials and description of the input flags are available online in https://epwdoc.gitlab.io.

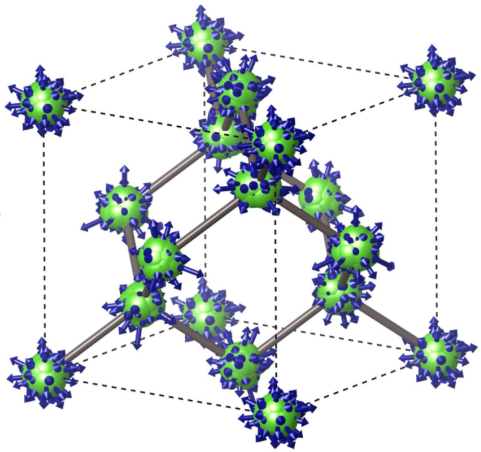
Appendix: Things to have in mind when applying the SDM via ZG.x:

- Make sure that the phonon dispersion is correct. For *anharmonicity* one can upgrade the IFC file using the A-SDM or the methods.
- **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.
- Make sure `error_thresh` is small (< 0.1).
- 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.`).

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**

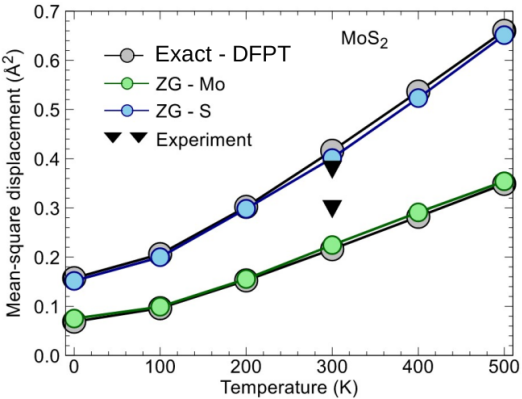


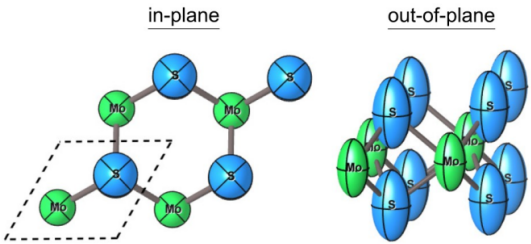


M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020)

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**

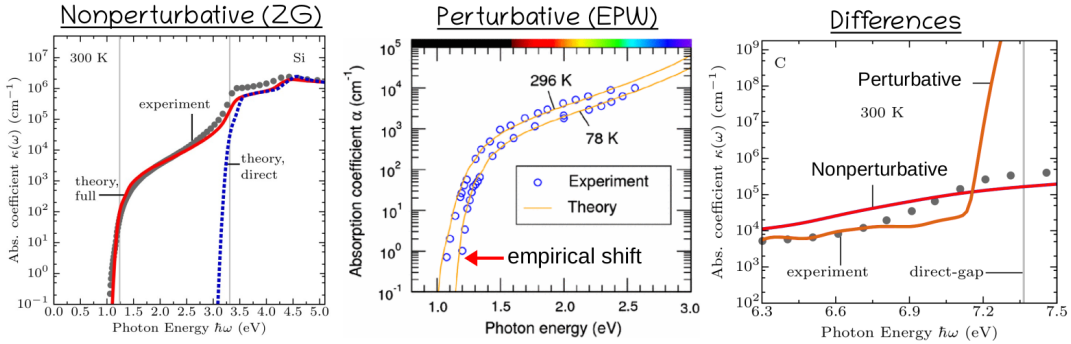




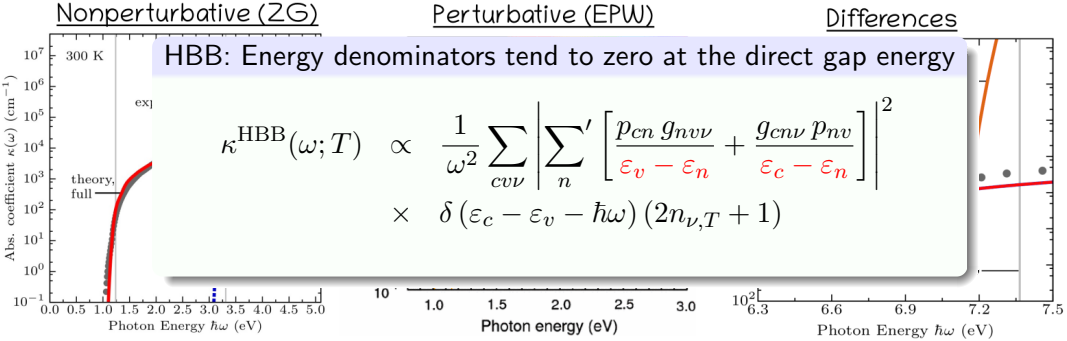
Thermal Ellipsoids of MoS_2

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

Nonperturbative vs Perturbative: Divergence in optical spectra



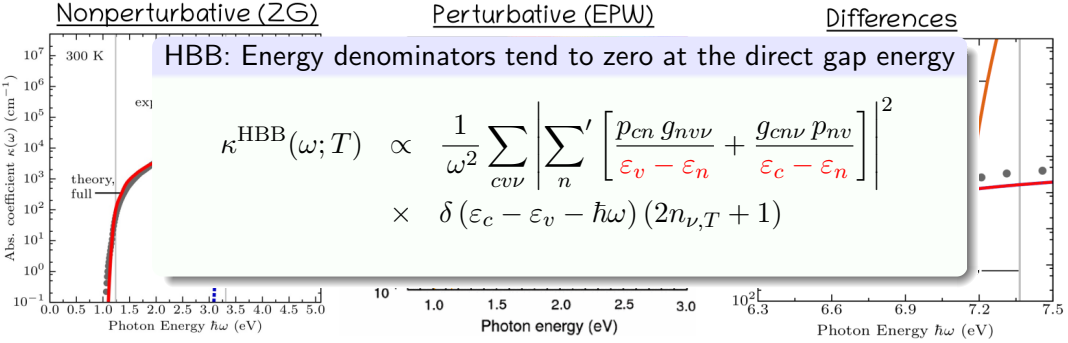
Nonperturbative vs Perturbative: Divergence in optical spectra



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

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

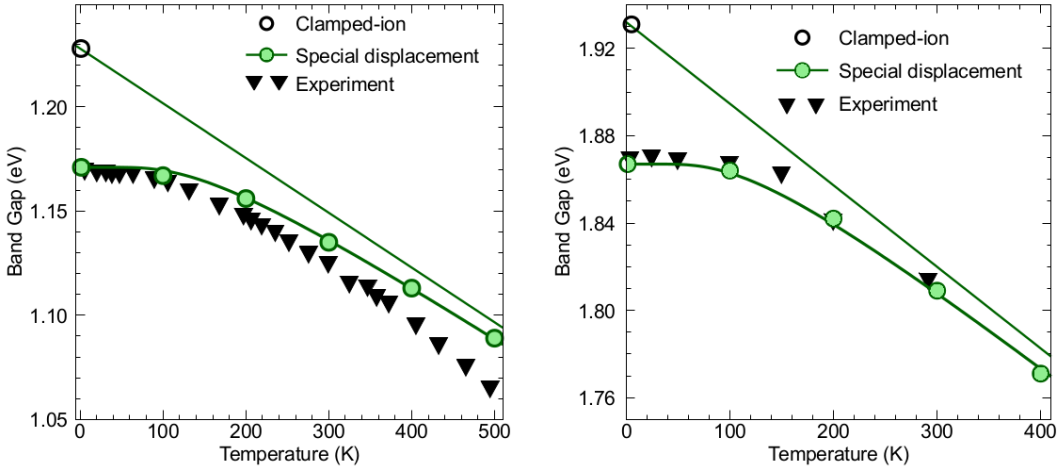
Nonperturbative vs Perturbative: Divergence in optical spectra



- 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. ✗

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)

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).

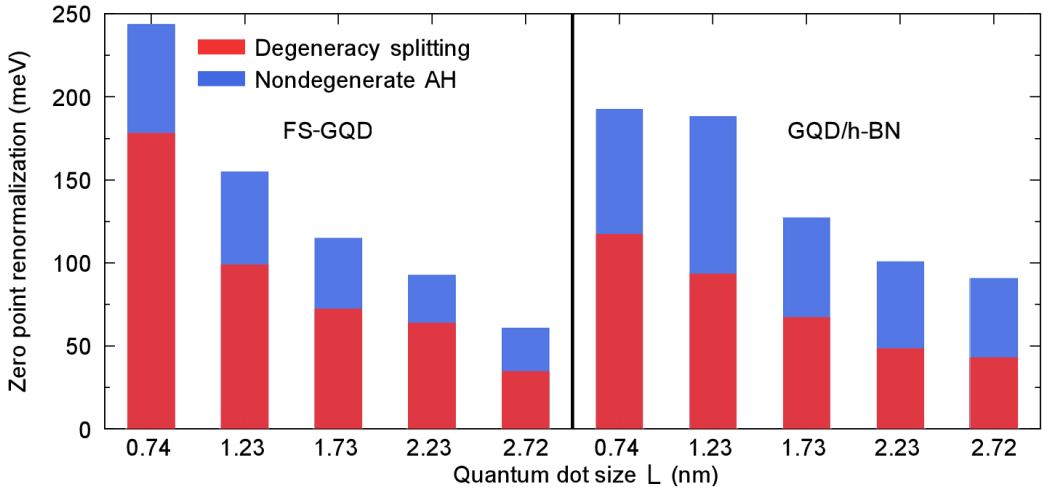
New linear term added to AH from degenerate perturb. theory:

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

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

Remark: Energy level degeneracies of GQDs in the SDM calculations

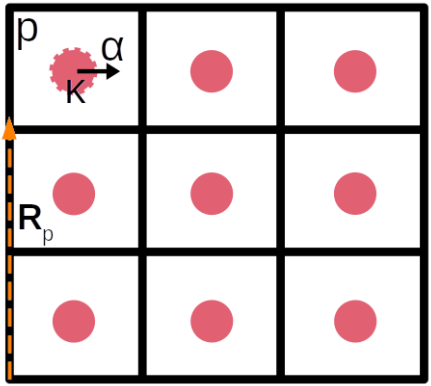
M. Zacharias, P.C. Kelires, J. Phys. Chem. Lett. 12, 9940 (2021)



Phonons from first-principles

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

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:

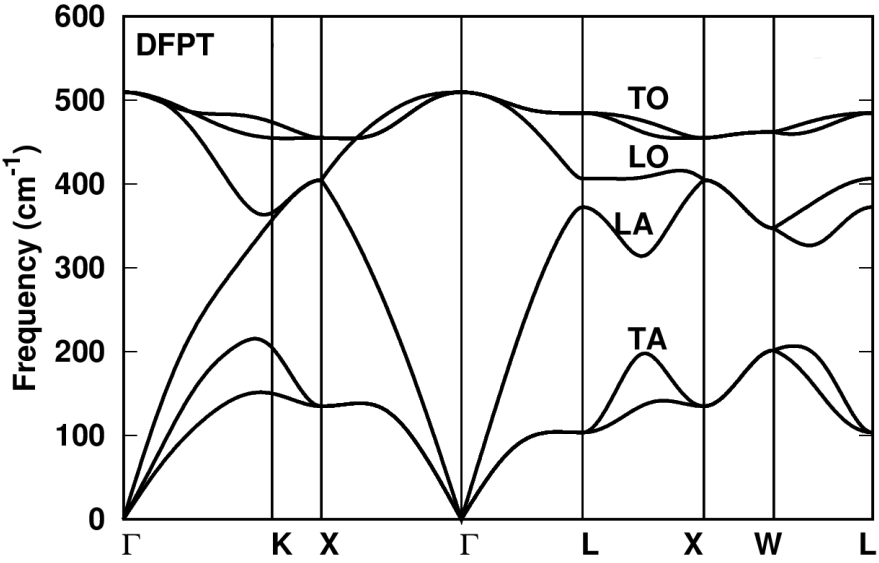
$$\sum_{\kappa'\alpha'} D_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}) e_{\kappa'\alpha',\nu}(\mathbf{q}) = \omega^2_{\mathbf{q}\nu} e_{\kappa\alpha,\nu}(\mathbf{q})$$

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

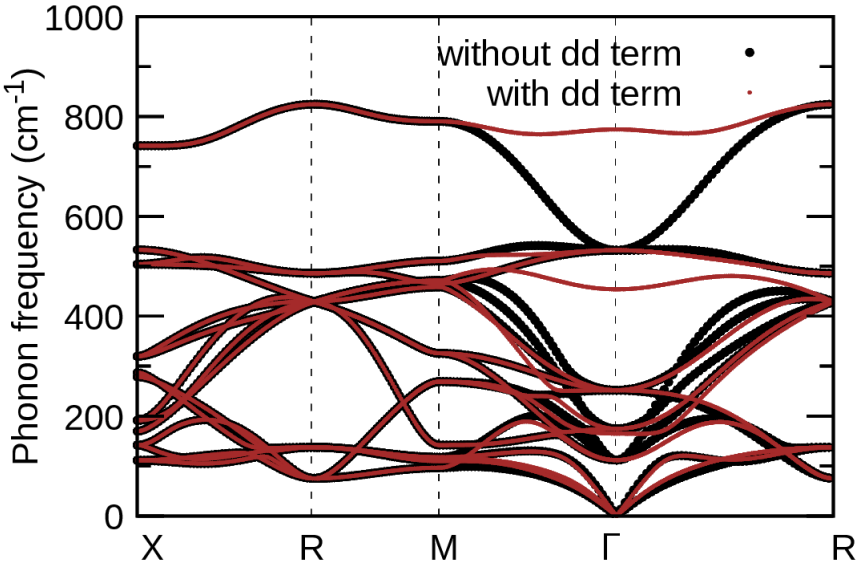
5. For polar materials include the dipole-dipole interaction term:

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

Phonon dispersion of silicon



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



Systems with local disorder (phonon unfolding as in exercise6)