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Lecture Fri.1

The Special Displacement Method

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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

Codes for perturbative and nonperturbative calculations

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

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

VASP, ZG, i-PI, The ab initio molecular simulations package FHI-aims (FHI-vibes) → Displaced nuclei in large supercells; $g_{mn,\nu}(\mathbf{k},\mathbf{q})$ is not explicitly evaluated

Nonperturbative Approaches - Literature I

Common goal is to evaluate the observable $\mathcal{O}$ at finite 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)
- A. Kundu, M. Govoni, H. Yang, M. Ceriotti, F. Gygi, G. Galli, Phys. Rev. Materials 5, L070801 (2021)

Molecular Dynamics (MD):

- 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)
- M. Zacharias, M. Scheffler, C. Carbogno, Phys. Rev. B 102, 045126 (2020)

Nonperturbative Approaches - Literature II

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

Quantum Monte Carlo (QMC):

- R. J. Hunt, B. Monserrat, V. Zólyomi, N. D. Drummond, Phys. Rev. B 101, 205115 (2020)
- V. Gorelov, D. M. Ceperley, M. Holzmann, C. Pierleoni, J. Chem. Phys. 153, 234117 (2020)

Thermal Lines (TL):

- B. Monserrat, Phys. Rev. B 93, 014302 (2016)
- B. Monserrat, Phys. Rev. B 93, 100301(R) (2016)

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)

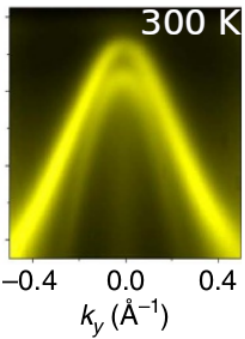
Other supercell approaches: Finite Differences (FD):

- 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)

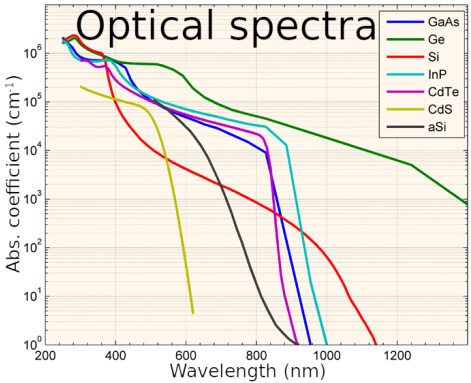
Nonperturbative Approaches - Literature III

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

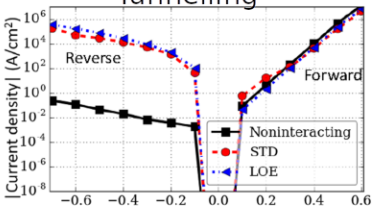
Band Structures



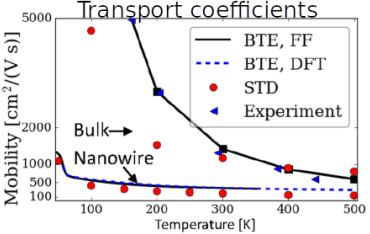
Optical spectra



Tunnelling

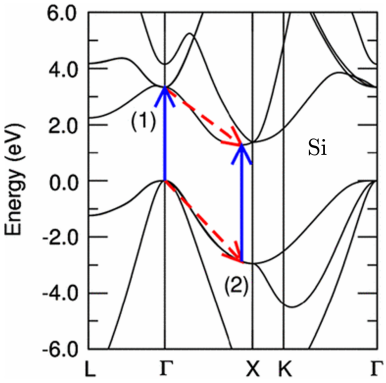


Transport coefficients

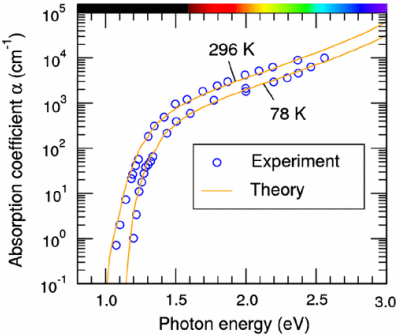


Refs: pveducation.org , P. Chen *et al.* Nat. Commun. 6, 8943 (2015) , T. Gunst *et al.* Phys. Rev. B 96, 161404(R) (2017)

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

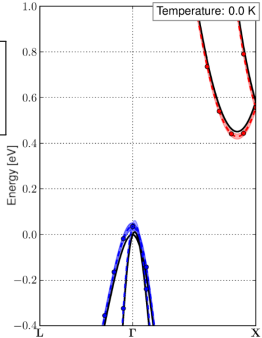
Temperature-dependence of the energy levels in the Allen-Heine theory:

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

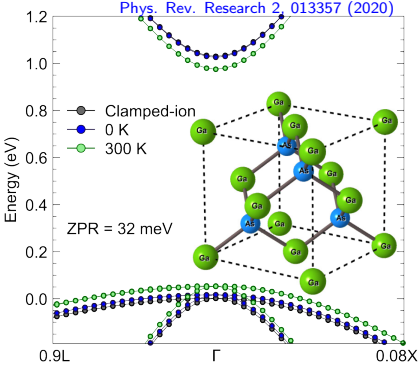
Perturbative first-principles applications:

- 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*, arXiv:2205.04265

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:

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

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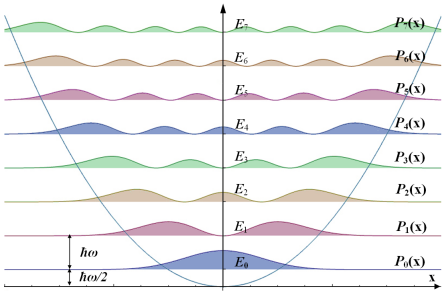
2. Semiclassical approximation: replace $E_{\beta m}$ with the adiabatic potential energy surface E^x_β:

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



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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)

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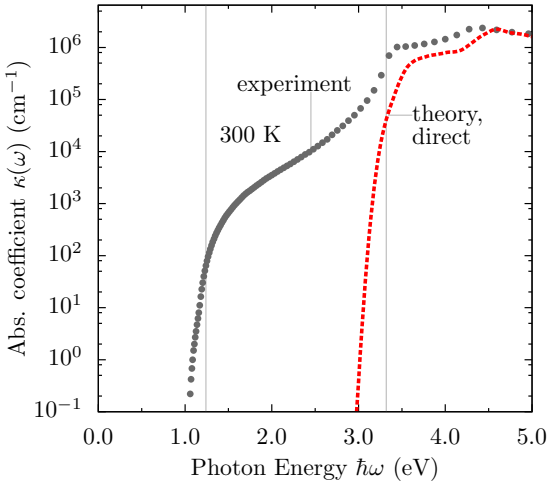
Interpretation: Weighted average of the spectra calculated with the nuclei fixed in a variety of configurations.

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

Silicon optical absorption in the Williams-Lax theory

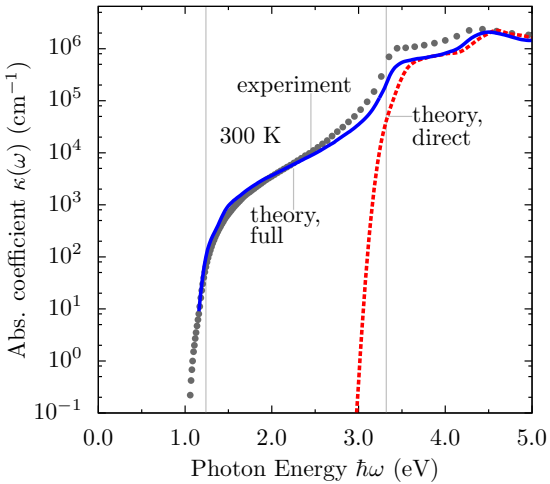
DFT-LDA calculations with nuclei at equilibirum



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

Silicon optical absorption in the Williams-Lax theory

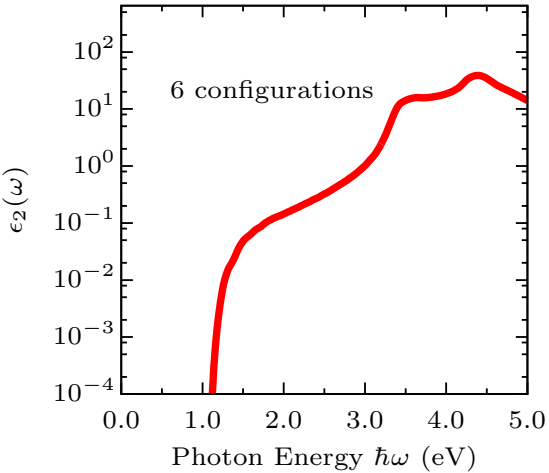
DFT-LDA calculations + quantum nuclear effects, Method: ISMC (8×8×8 supercell)



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)

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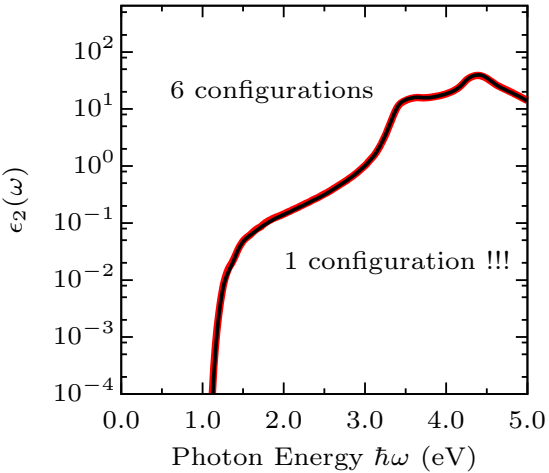


M. Zacharias, C. E. Patrick, F. Giustino, Phys. Rev. Lett. 115, 177401 (2015)

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: $\boxed{\{S_\nu\} = \{+\ -\ +\ -\ +\ -\ \cdots\}}$ $S_\nu = (-1)^{\nu-1}$

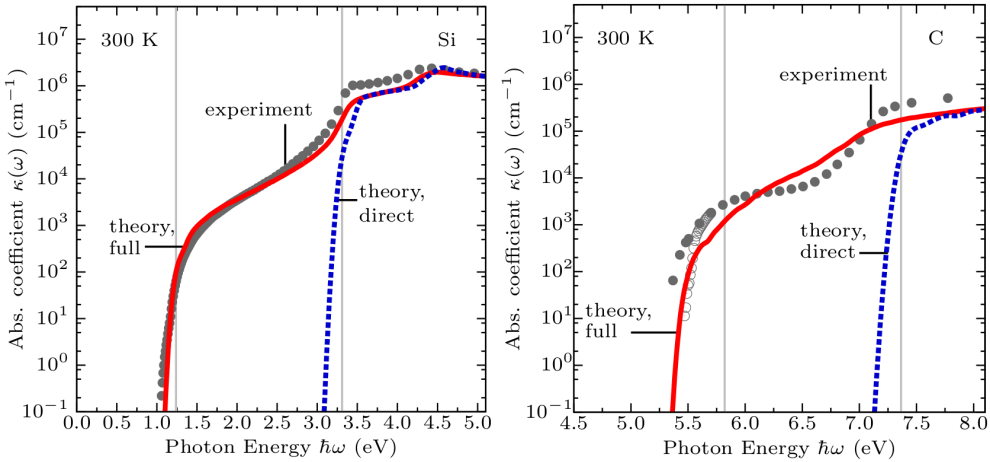
3. We can prove:

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

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

Silicon and diamond absorption spectra with SDM

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



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

Relations connecting Nonperturbative 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 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

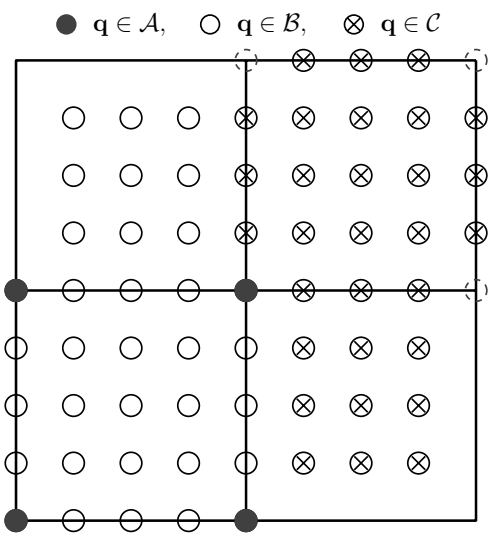
- $\sigma^2_{\mathbf{q}\nu,T} = (2n_{\mathbf{q}\nu,T}+1)\hbar/(2M_{\mathrm{p}}\omega_{\mathbf{q}\nu})$ with $n_{\mathbf{q}\nu,T} = [\exp(\hbar\omega_{\mathbf{q}\nu}/k_{\mathrm{B}}T)-1]^{-1}$
- $\omega_{\mathbf{q}\nu} \longrightarrow$ phonon frequencies
- $\mathbf{e}_{\kappa,\nu}(\mathbf{q}) \longrightarrow$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

This equation is implemented in the `ZG.x` code (see tutorial `Fri.3.Zacharias.pdf`).

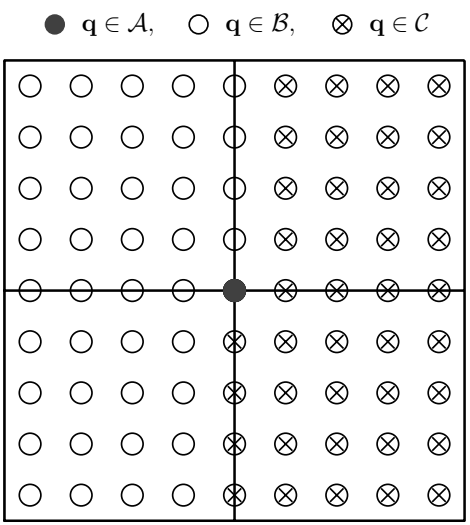
M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020)

Partitioning of $\mathbf{q}$-points 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 SDM

Key findings from our theory due to periodicity of solids:

- Linear order derivatives vanish in a supercell calculation:

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

Contribution from linear derivatives when $\mathbf{q} \in \mathcal{A}$ do not survive in the large supercell limit

- 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 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`
so that the function:

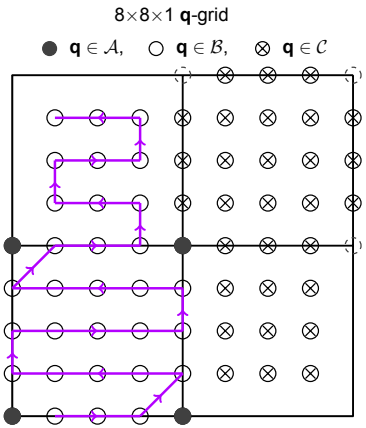
$$E(\{S_{\mathbf{q}\nu}\}, T) = \sum_{\substack{\kappa\alpha \\ \kappa'\alpha'}} \frac{\left| \sum_{\substack{\mathbf{q}\in\mathcal{B} \\ \nu<\nu'}} \Re[e^*_{\kappa\alpha,\nu}(\mathbf{q}) e_{\kappa'\alpha',\nu'}(\mathbf{q})] \sigma_{\mathbf{q}\nu,T} \sigma_{\mathbf{q}\nu',T} S_{\mathbf{q}\nu} S_{\mathbf{q}\nu'}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

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 caclualtions are required to find the optimum ZG configuration.

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

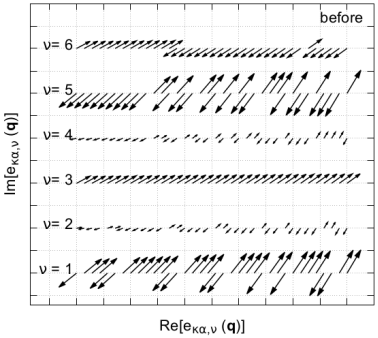
Apply a smooth gauge by setting: `synch = .true.`

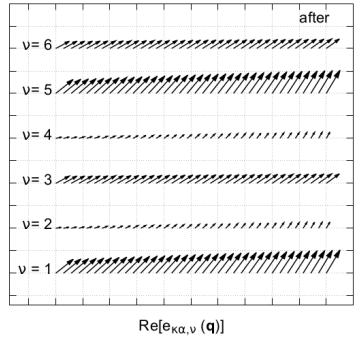


We apply the transformation:

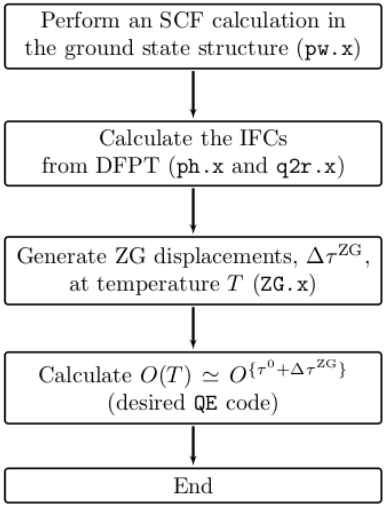
$$e'_{\kappa\alpha,\nu}(\mathbf{q}+\Delta\mathbf{q}) = \sum_{\nu'} U_{\nu\nu'} e_{\kappa\alpha,\nu'}(\mathbf{q}+\Delta\mathbf{q}),$$

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



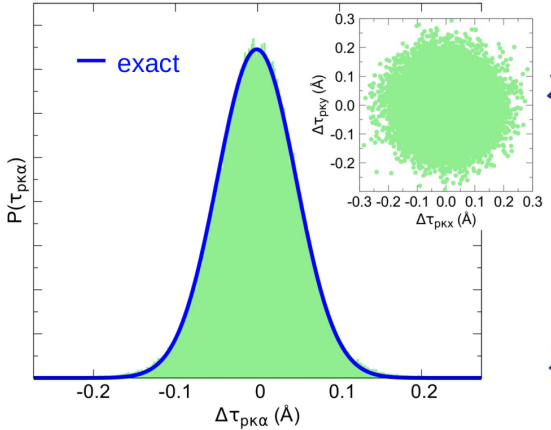


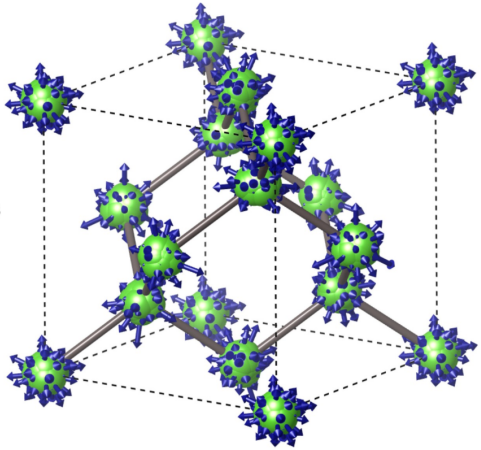
Flowchart for ab-initio calculations with ZG configurations



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.

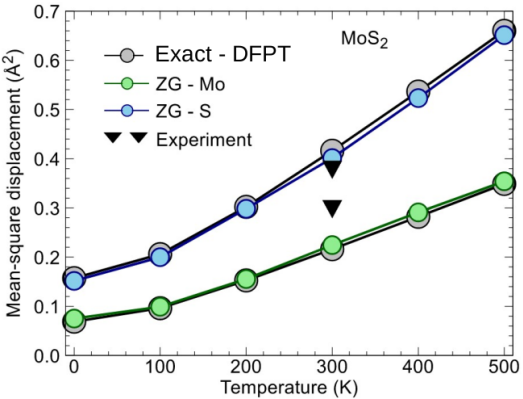


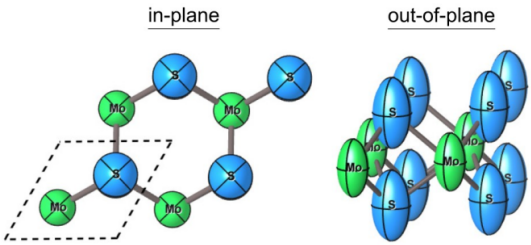


M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020)

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.



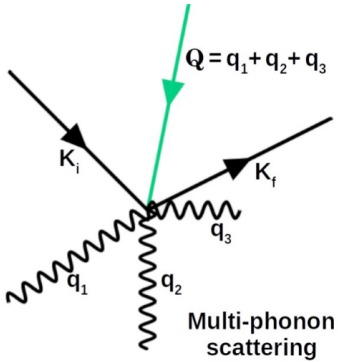


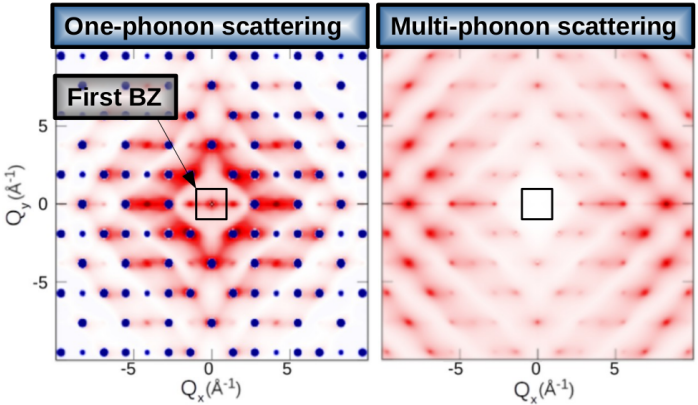
Thermal Ellipsoids of MoS_2

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

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**

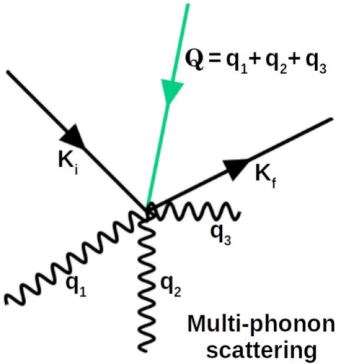


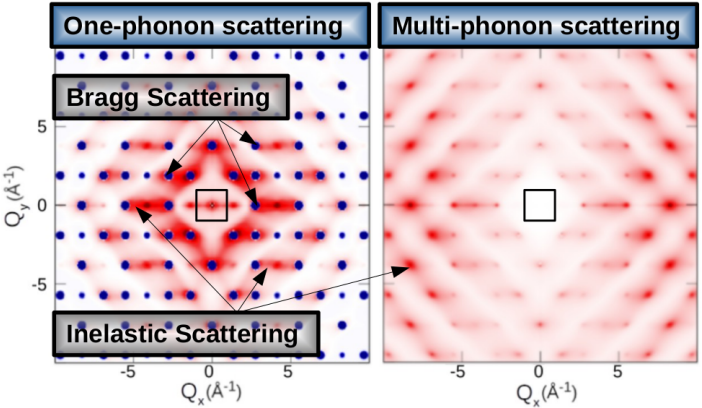


M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, Phys. Rev. Lett. 127, 207401 (2021)
M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, Phys. Rev. B 104, 205109 (2021)

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**

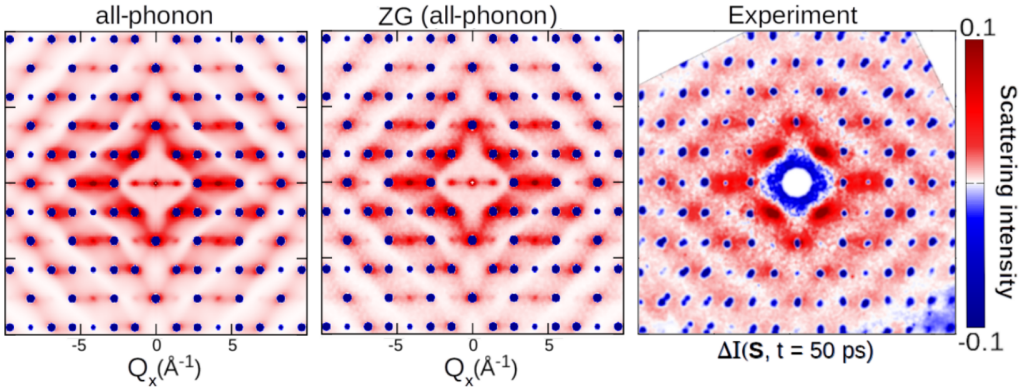




M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, Phys. Rev. Lett. 127, 207401 (2021)
M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, Phys. Rev. B 104, 205109 (2021)

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

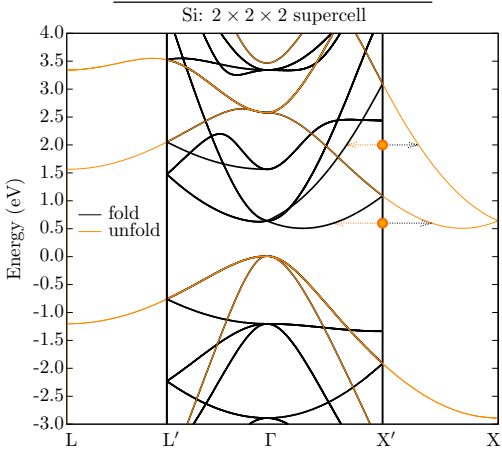


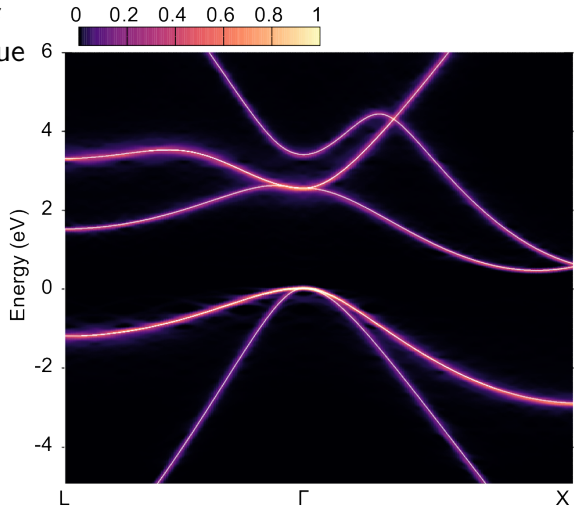
We will show how to calculate diffraction maps using `ZG.x` and `disca.x` (see tutorial `exercise4`).

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 SDM

Temperature-dependent band structures
with the band structure unfolding technique





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

Applications of SDM

Temperature-dependent band structures with the band structure unfolding technique

Goal is to evaluate the electron spectral function:

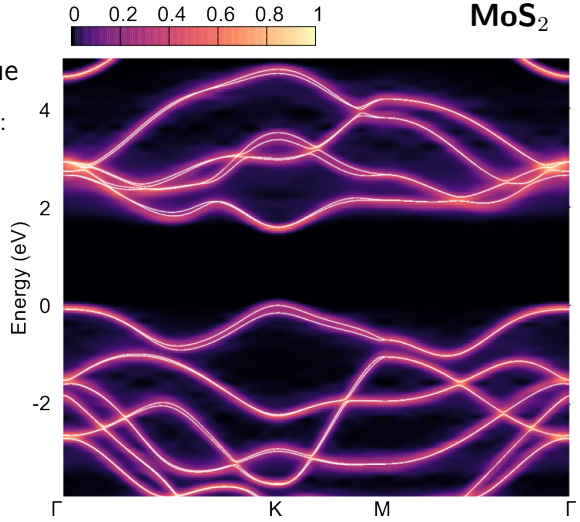
$$A_{\mathbf{k}}(\varepsilon;T) = \sum_{m\mathbf{K}} P_{m\mathbf{K},\mathbf{k}}(T)\,\delta[\varepsilon - \varepsilon_{m\mathbf{K}}(T)],$$

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`)

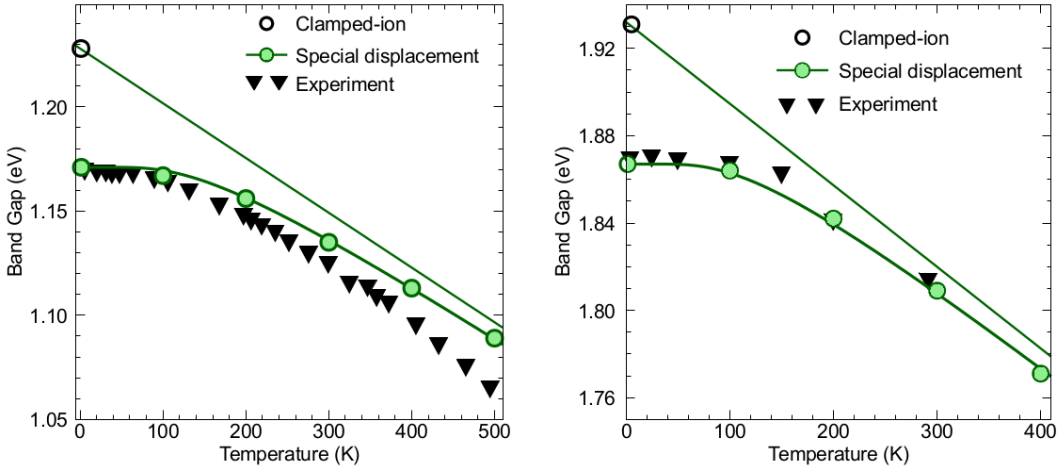
V. Popescu, A. Zunger, Phys. Rev. B 85, 085201 (2012)
P. V. C. Medeiros, S. Stafström, J. Björk, Phys. Rev. B 89, 041407(R) (2014)



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

Applications of SDM

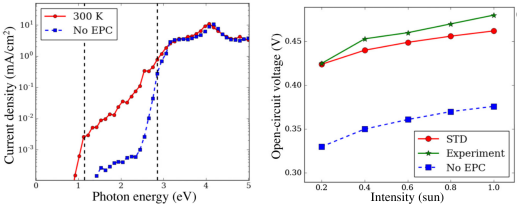
Temperature dependent band gaps of **Si** (ZPR $= 57$ meV) and **MoS$_2$** (ZPR $= 65$ meV).



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

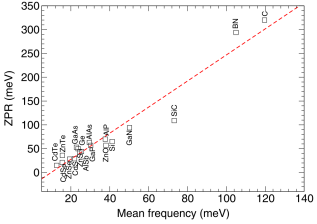
Applications of SDM

Phonon-assisted photocurrent in large solar-cell devices



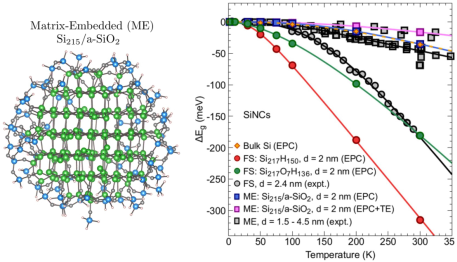
M. Palsgaard, *et al*, PRA 10, 014026 (2018)

Zero-point renormalization within GW



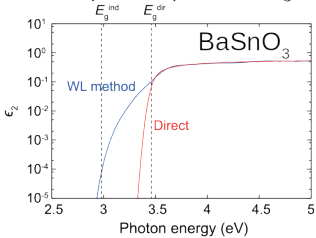
F. Karsai, *et al*, NJP 20 123008 (2018)

Band gap renormalization of nanostructures



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

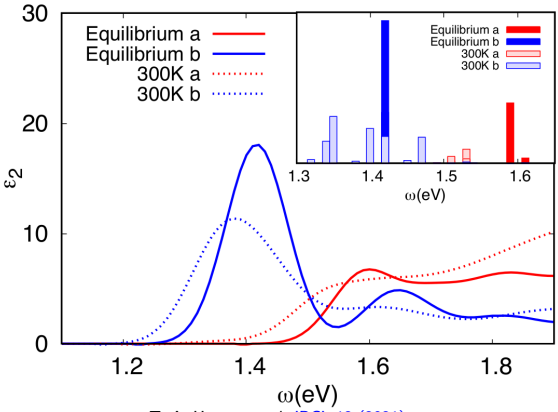
Indirect optical absorption in $BaSnO_3$



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

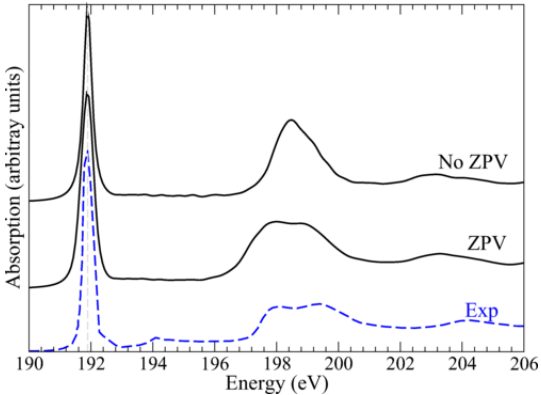
Applications of SDM

Exciton-phonon coupling in 2D GeSe



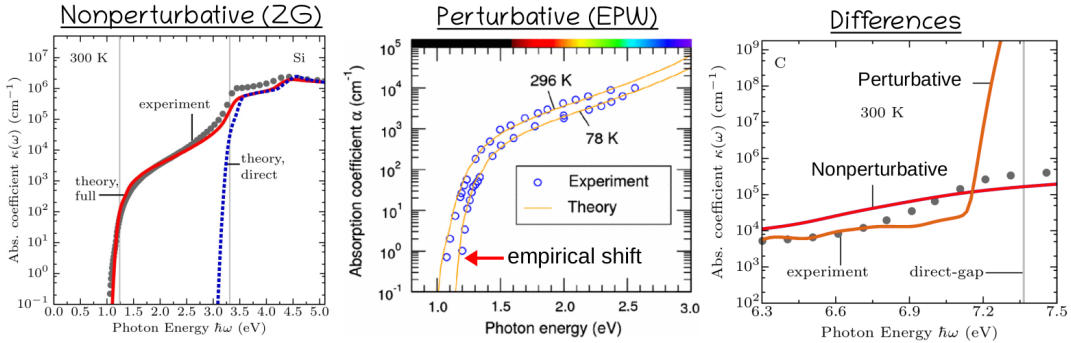
T. A. Huang, *et al*, JPCL 12 (2021)

Exciton-phonon coupling in h-BN



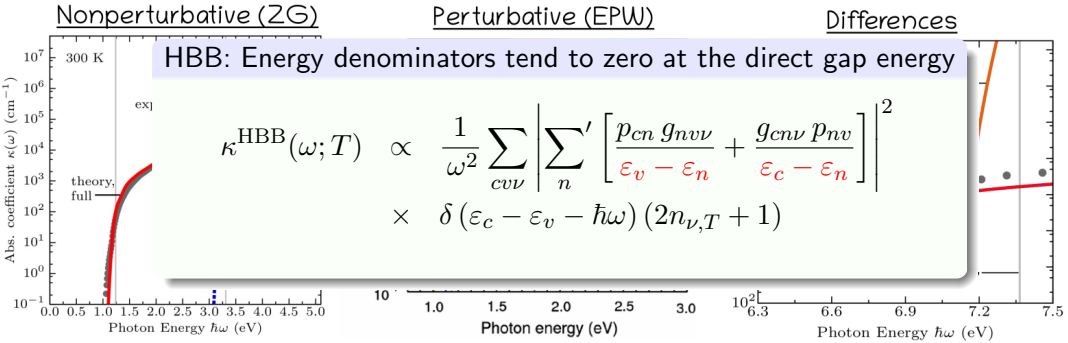
F. Karsai, *et al*, PRB 98, 235205 (2018)

Nonperturbative vs Perturbative



To learn calculating optical spectra using the ZG configuration see `exercise3`.

Nonperturbative vs Perturbative



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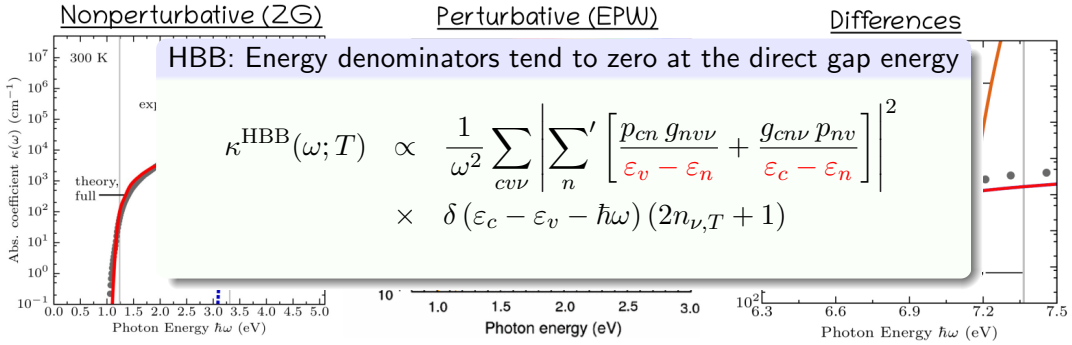
Nonperturbative vs Perturbative



- 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. ✗

To learn calculating optical spectra using the ZG configuration see `exercise3`.

Final remark: Energy level degeneracies in 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).

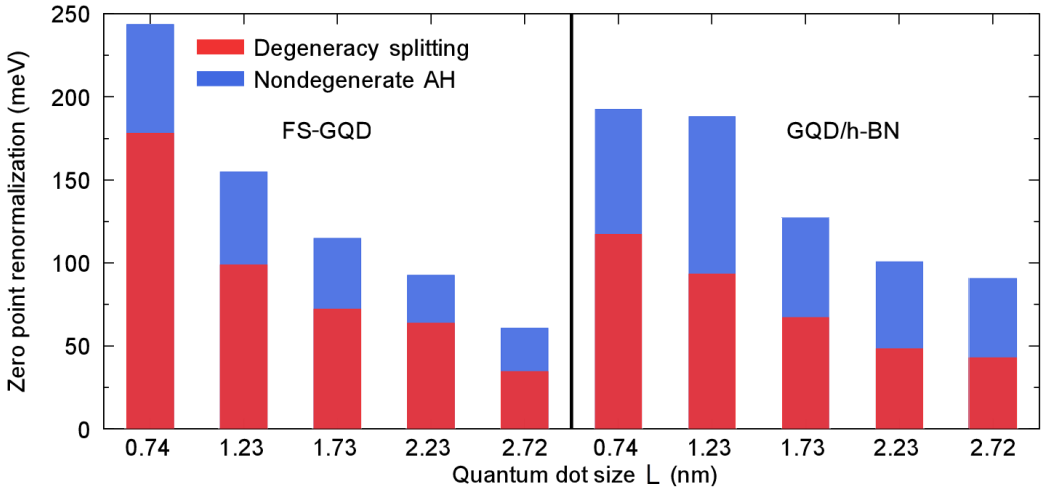
New linear term added to AH from degenerate perturb. theory:

$$\Delta\varepsilon^{\pm}_{c_1,T} = \pm \left| \sum_{\nu} (g_{c_1c_1\nu} - g_{c_2c_2\nu}) \frac{\sigma_{\nu,T}}{\sqrt{2\pi}} \right| + \sum_{\nu\beta}{}' \left[\frac{|g_{c_1\beta\nu}|^2}{\varepsilon_{c_1} - \varepsilon_{\beta}} + h_{c_1\nu} \right] \sigma^2_{\nu,T}.$$

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

Final remark: Energy level degeneracies in SDM calculations.

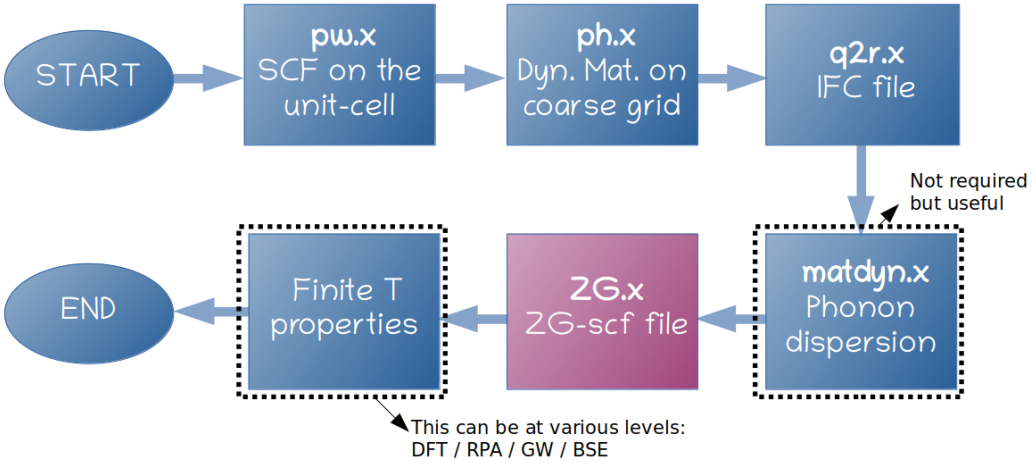
M. Zacharias, P. C. Kelires, J. Phys. Chem. Lett. 12, 9940 (2021)



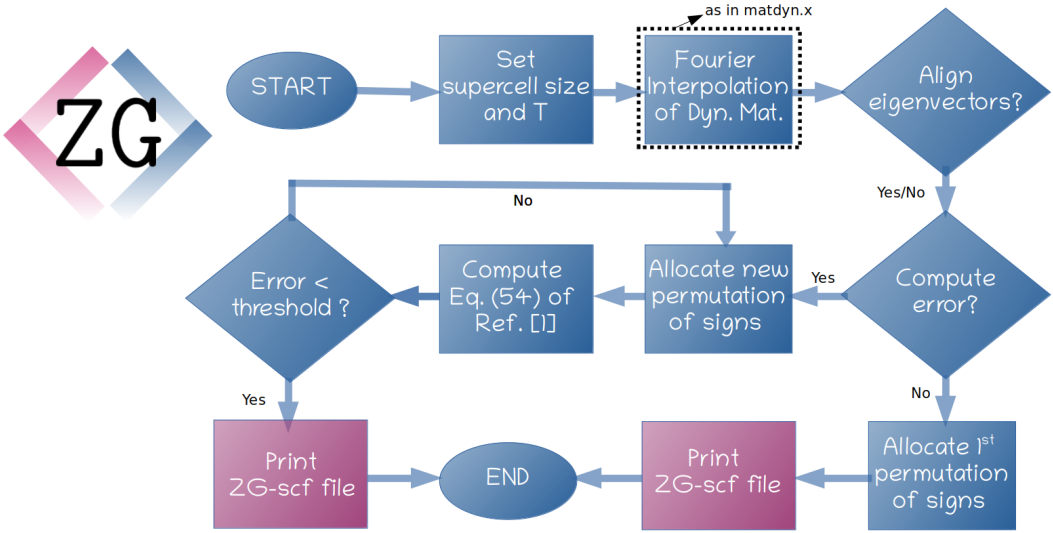
Reference list

1. F. E. Williams, Phys. Rev. 82, 281 (1951)
2. M. Lax, J. Chem. Phys. 20, 1752 (1952)
3. C. E. Patrick, F. Giustino, J. Phys. Condens. Matter 26, 365503 (2014)
4. M. Zacharias, F. Giustino, Phys. Rev. B 94, 075125 (2016)
5. M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020)

Appendix: Flowchart for ab-initio calculations with SDM



Appendix: Flowchart for ZG.x



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

Appendix: Example 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 SDM via `ZG.x`

- Make sure that the phonon dispersion is correct. For *anharmonicity* one can upgrade the IFC file using the methods:

  O. Hellman *et al.*, Phys. Rev. B 84, 180301(R) (2011)

  I. Errea *et al.*, Phys. Rev. B 89, 064302 (2014)

- **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.`).