2021 Virtual School on Electron-Phonon Physics and the EPW code

June 14-18 2021

Lecture Fri.6

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. Implementation and structure of the `ZG` code
  3. Applications

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, FHI-aims → 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:

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

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, arXiv:2104.11065

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)

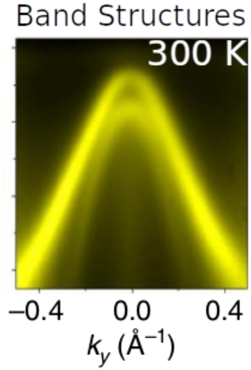
Special Displacement Method (SDM):

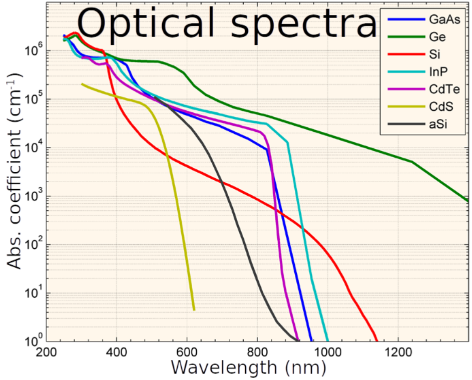
- M. Zacharias, F. Giustino, Phys. Rev. B 94, 075125 (2016)
- F. Karsai, M. Engel, E. Flage-Larsen, G. Kresse, New J. Phys. 20 123008 (2018)
- M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020)

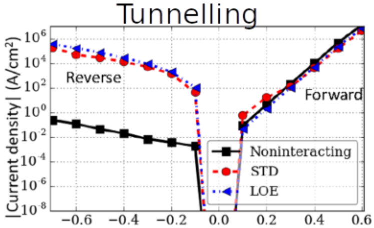
Other supercell approaches: Finite Differences (FD):

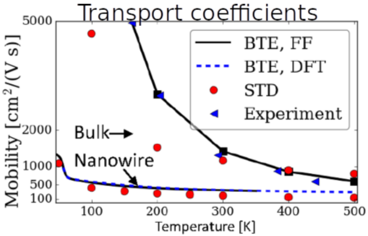
- R. B. Capaz, C. D. Spataru, P. Tangney, M. L. Cohen, S. G. Louie, Phys. Rev. Lett. 94, 036801 (2005)
- G. Antonius, S. Poncé, P. Boulanger, M. Côté, X. Gonze, Phys. Rev. Lett. 112, 215501 (2014)
- B. Monserrat, J. Phys.: Condens. Matter 30, 083001 (2018)

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

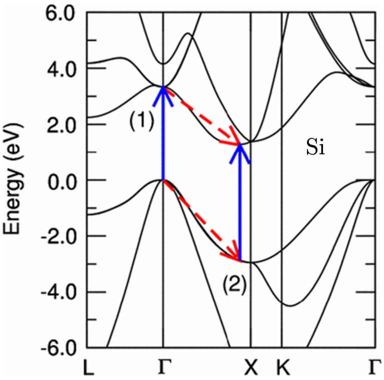




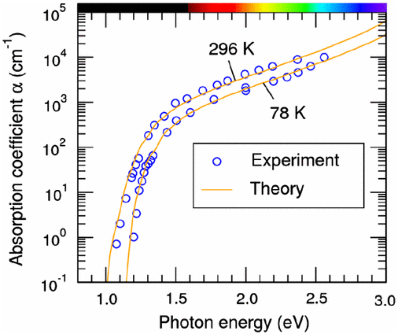




Refs: pveducation.org , P. Chen *et al.* Nat. Commun. 6, 8943 (2015) , T. Gunst *et al.* Phys. Rev. B 96, 161404(R) (2017)



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:

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

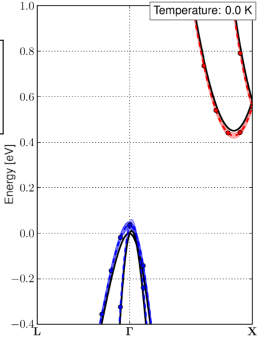
Temperature-dependence of the energy levels in the Allen-Heine theory:

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

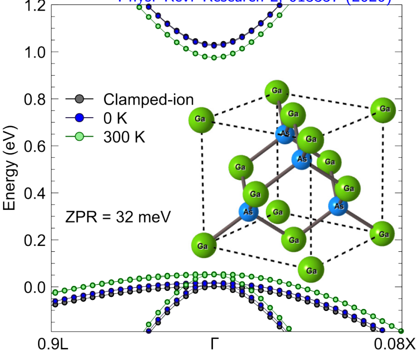
Perturbative first-principles applications:

- 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)

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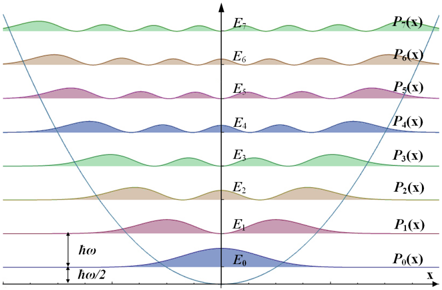
2. Semiclassical approximation: replace $E_{\beta m}$ with the adiabatic potential energy surface E^x_β:

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



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

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

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)

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

$$\lim_{N_e \to \infty} E_\beta^x - E_0^x = \varepsilon_c^x - \varepsilon_v^x$$

- 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

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

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

   and in the indipendent-particle picture:

$$\epsilon_2^x(\omega) \propto \frac{1}{\omega^2} \sum_{cv} |p_{cv}^x|^2 \delta(\varepsilon_c^x - \varepsilon_v^x - \hbar\omega)$$

- M. Zacharias, C. E. Patrick, F. Giustino, Phys. Rev. Lett. 115, 177401 (2015)
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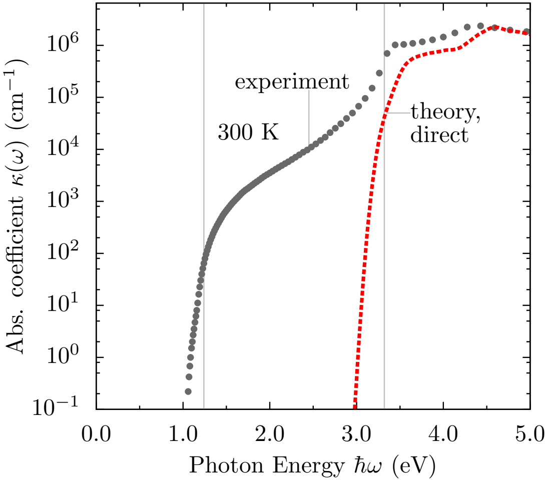
Interpretation: Weighted average of the spectra calculated with the nuclei fixed in a variety of configurations.

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

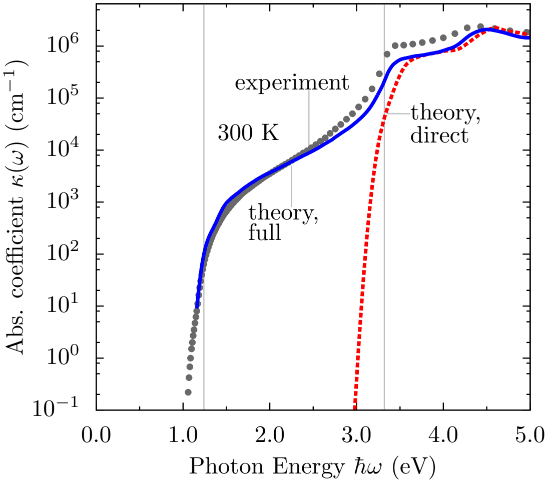
Silicon optical absorption in the Williams-Lax theory

DFT-LDA calculations with nuclei at equilibirum



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

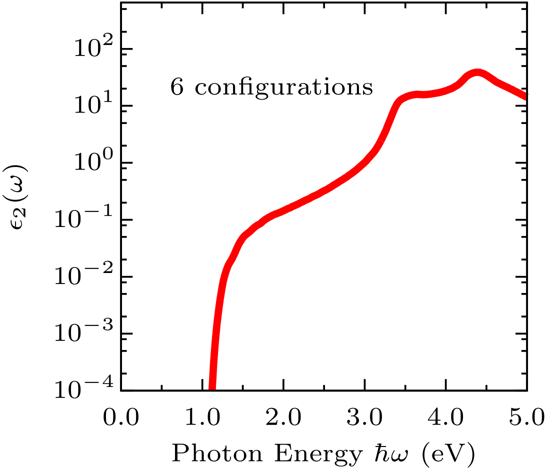
DFT-LDA calculations + quantum nuclear effects, Method: ISMC (8×8×8 supercell)



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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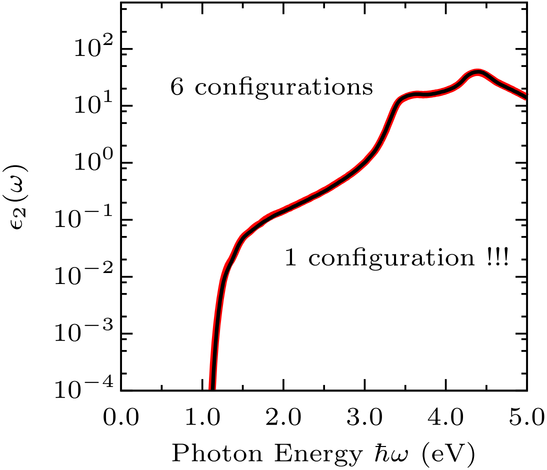


M. Zacharias, C. E. Patrick, F. Giustino, Phys. Rev. Lett. 115, 177401 (2015)

The special displacement method (SDM) and ZG displacements

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

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:

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

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

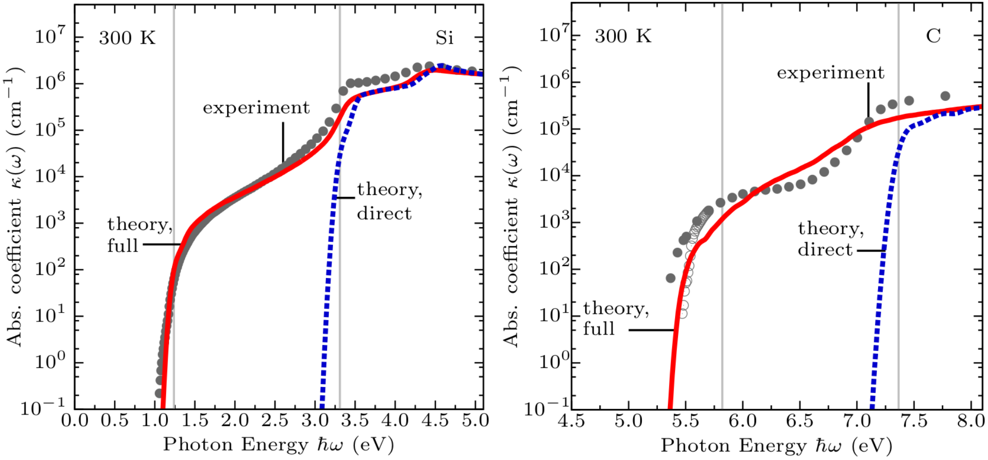
3. We can prove:

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

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:

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

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

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:

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

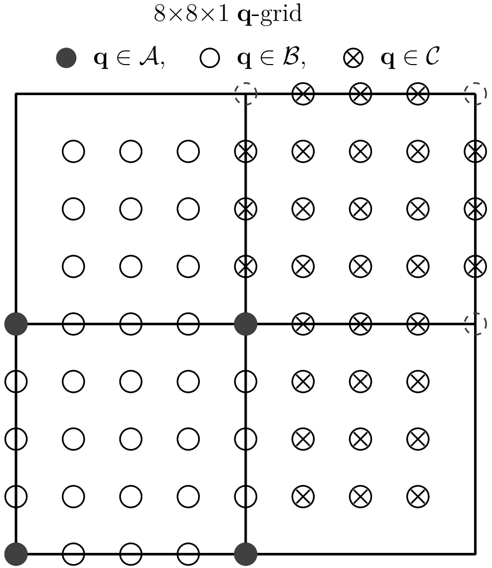
where

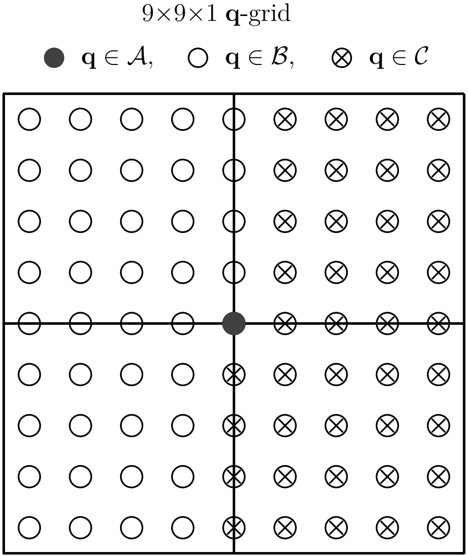
- $\sigma^2_{\mathbf{q}\nu,T} = (2n_{\mathbf{q}\nu,T}+1)\hbar/(2M_{\mathrm{p}}\omega_{\mathbf{q}\nu})$ with $n_{\mathbf{q}\nu,T} = [\exp(\hbar\omega_{\mathbf{q}\nu}/k_{\mathrm{B}}T)-1]^{-1}$
- $\omega_{\mathbf{q}\nu} \longrightarrow$ phonon frequencies
- $\mathbf{e}_{\kappa,\nu}(\mathbf{q}) \longrightarrow$ 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.6.Zacharias.pdf`).

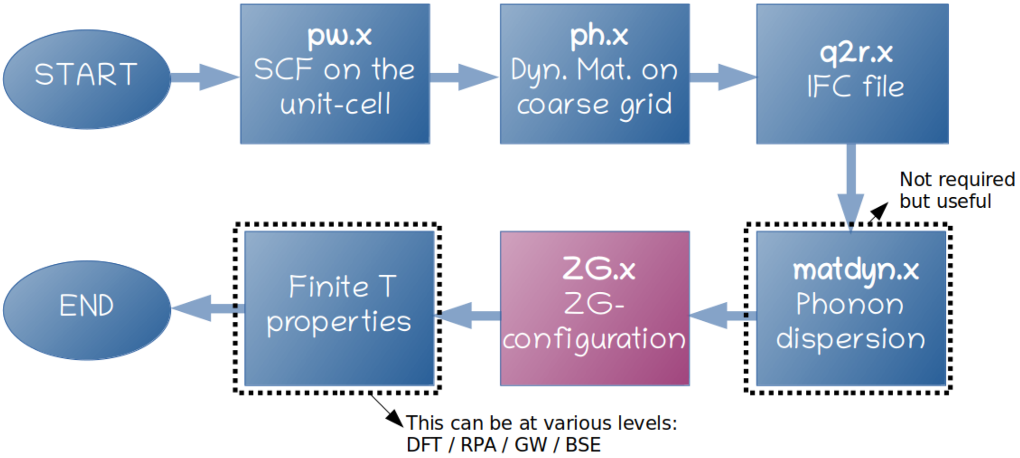
M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020)

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

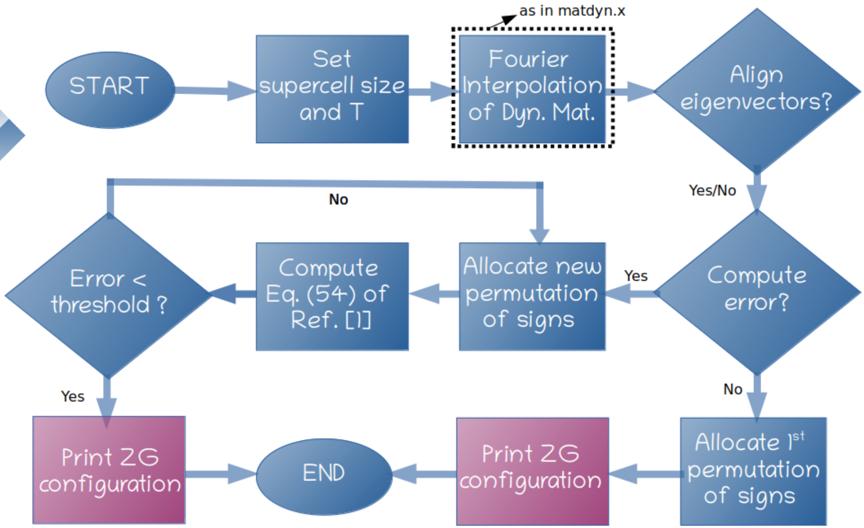




Flowchart for ab-initio calculations with ZG configurations



Flowchart for ZG.x



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

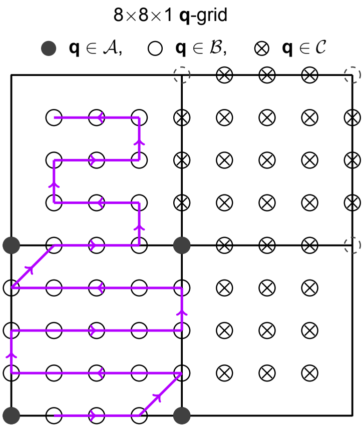
Smooth gauge of $\mathbf{e}_{\kappa,\nu}(\mathbf{q})$ along a path in reciprocal space

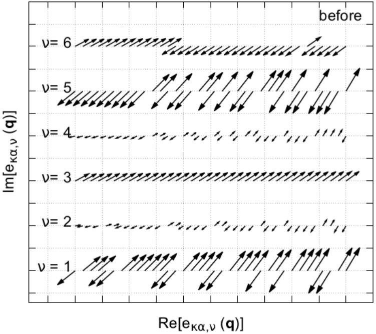
Apply a smooth gauge by setting: `synch = .true.`

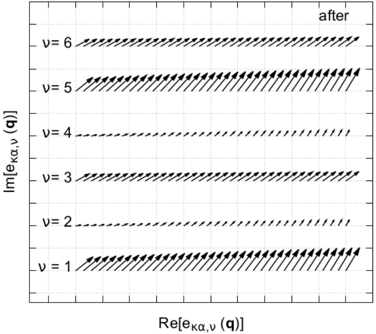
We apply the transformation:

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

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







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.

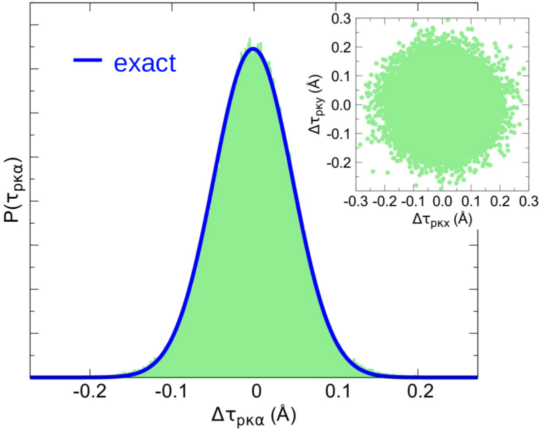
Example input file for ZG.x (similar structure to matdyn.x)

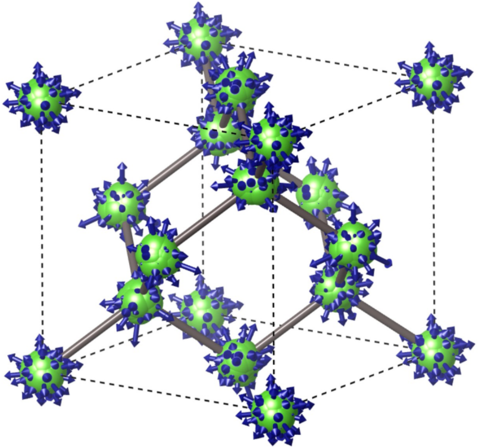
```
--
   &input
   flfrc='si.444.fc',
   asr='simple', amass(1)=28.0855, atm_zg(1) = 'Si',
   T = 0.00,
   dim1 = 5, dim2 = 5, dim3 = 5
   synch = .true.,
   compute_error = .true., error_thresh = 0.05, niters = 30000
   incl_qA = .false.
/
```

More details about the input flags are available in the file tuto_Fri6_flags.pdf which can be found, together with the tutorial, in Fri.6.Zacharias.tar.

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)

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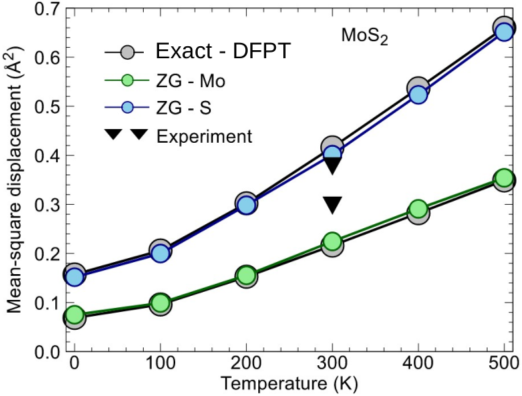
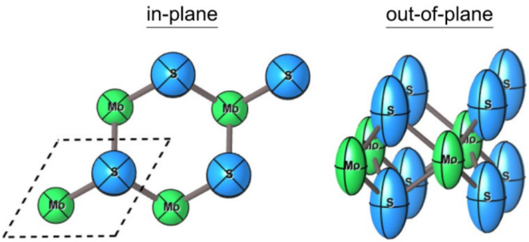




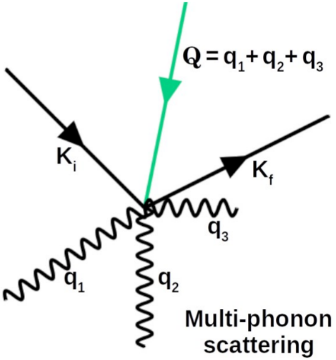
Thermal Ellipsoids of MoS$_2$

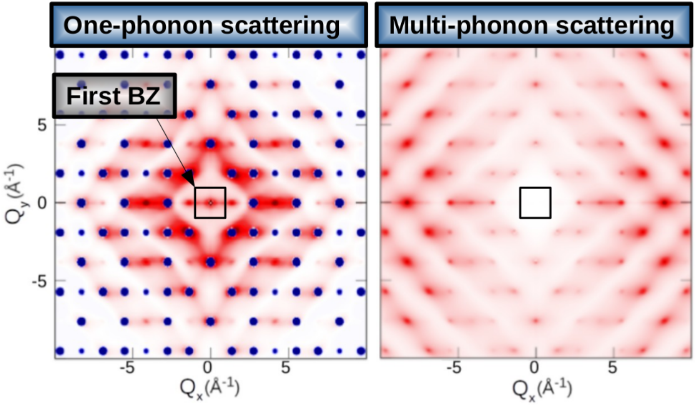
M. Zacharias, F. Giustino, Phys. Rev. Research 2, 013357 (2020)

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*:

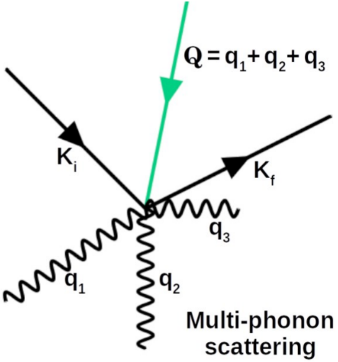
Black Phosphorus

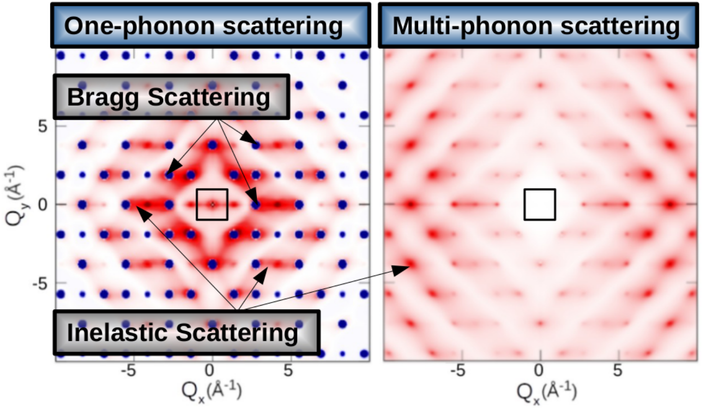




M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, arXiv:2103.10108, (2021)
M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, arXiv:2104.07900, (2021)

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

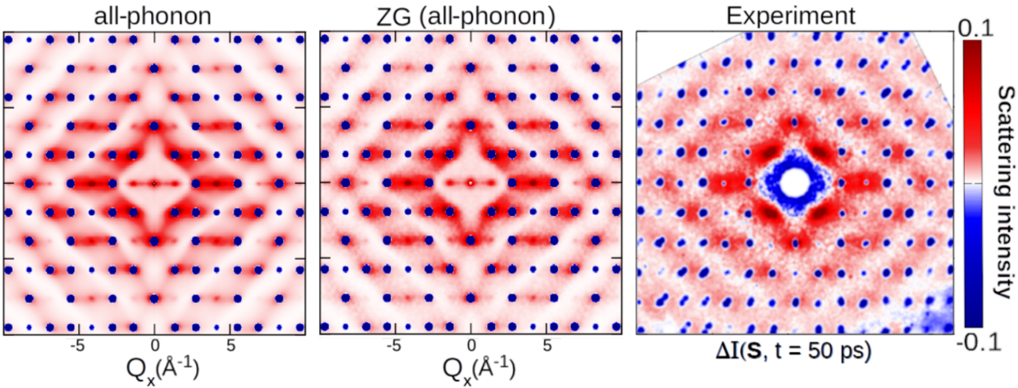




M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, arXiv:2103.10108, (2021)
M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, arXiv:2104.07900, (2021)

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

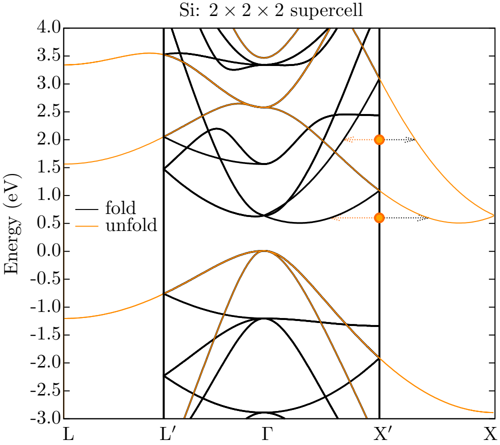


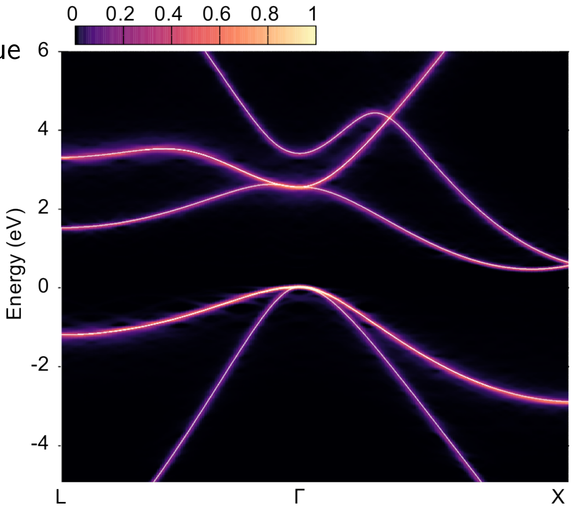
We will show how to calculate diffraction maps using `ZG.x` and `disca.x` (see tutorial `exercise4`).

M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, arXiv:2103.10108, (2021)
M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. Kelires, R. Ernstorfer, arXiv:2104.07900, (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)

Temperature-dependent band structures
with the band structure unfolding technique

Goal is to evaluate the electron spectral function:

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

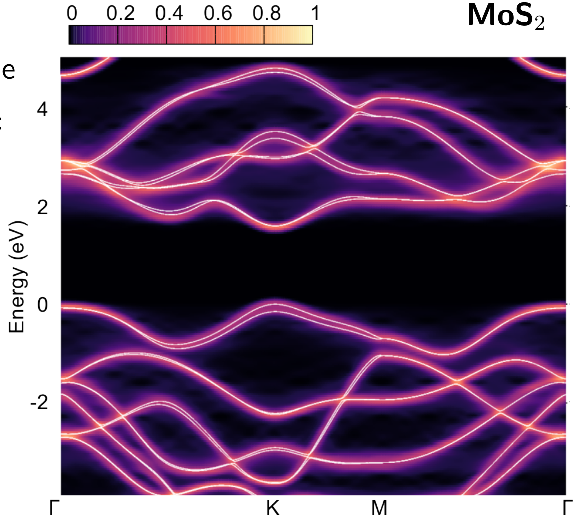
where $P_{m\mathbf{K},\mathbf{k}}(T)$ are temperature-dependent spectral weights evaluated as:

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

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)

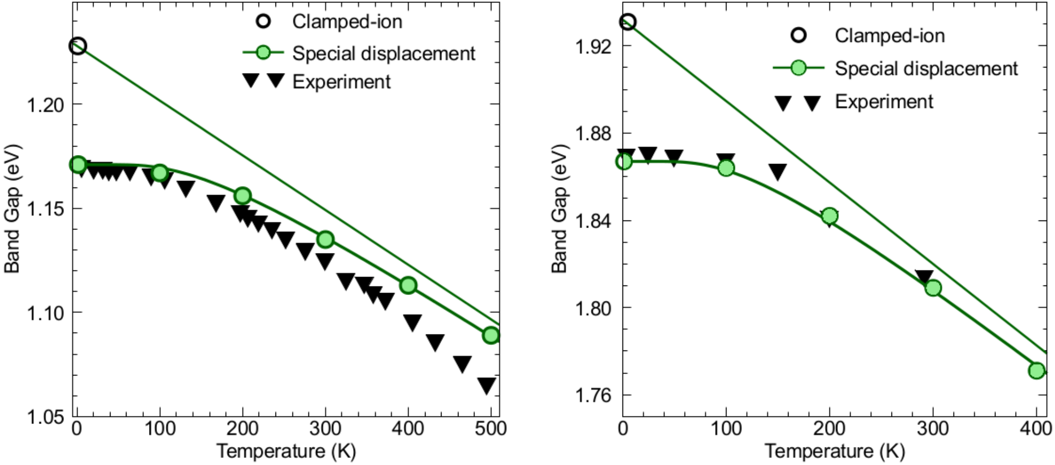
MoS_2



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

Applications of SDM

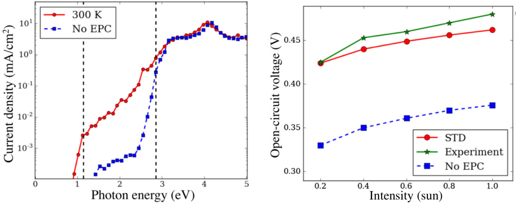
Temperature dependent band gaps of **Si** (ZPR $= 57$ meV) and **MoS_2** (ZPR $= 65$ meV).



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

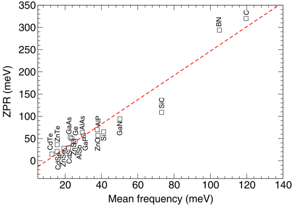
Applications of SDM

Phonon-assisted photocurrent in large solar-cell devices



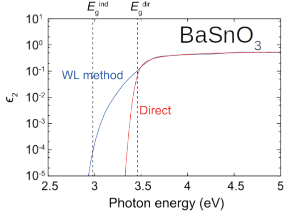
M. Palsgaard, *et al*, PRA 10, 014026 (2018)

Zero-point renormalization within GW



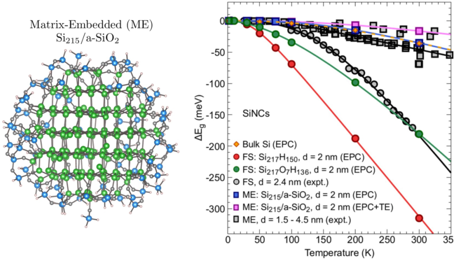
F. Karsai, *et al*, NJP 20 123008 (2018)

Indirect optical absorption in $BaSnO_3$



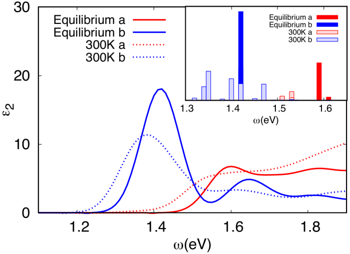
Y. Kang, *et al*, APL 112 (2018)

Band gap renormalization of nanostructures



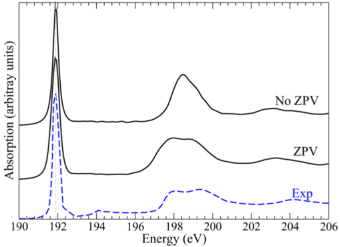
M. Zacharias, *et al*, PRB 101, 245122 (2020)

Exciton-phonon coupling in 2D GeSe



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

Exciton-phonon coupling in h-BN



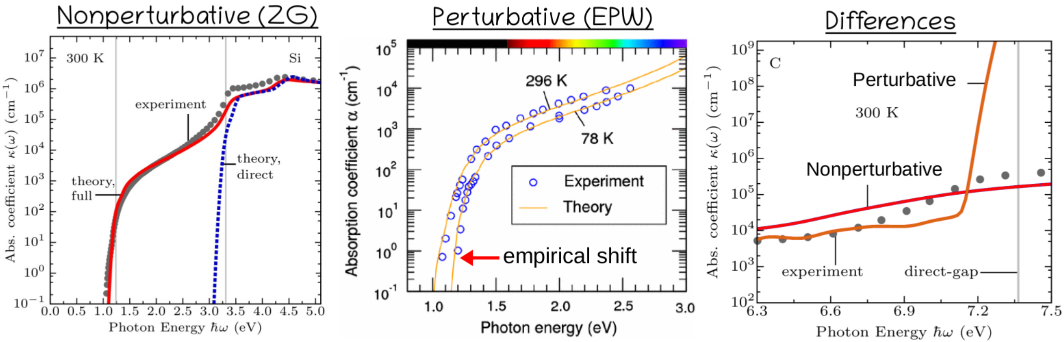
F. Karsai, *et al*, PRB 98, 235205 (2018)

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

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

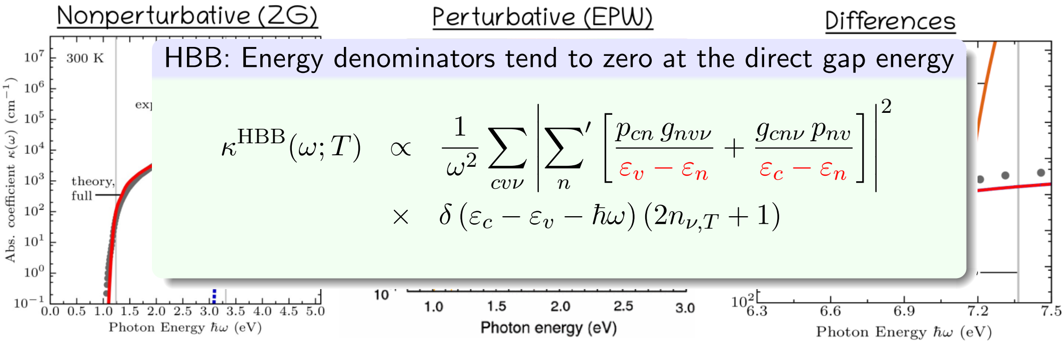
  O. Hellman *et al.*, Phys. Rev. B 84, 180301(R) (2011)

  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_configuration.dat` (as in `exercise1`).



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

Final remark: Nonperturbative vs Perturbative



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

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

$$\times\ \delta\left(\varepsilon_c-\varepsilon_v-\hbar\omega\right)\left(2n_{\nu,T}+1\right)$$

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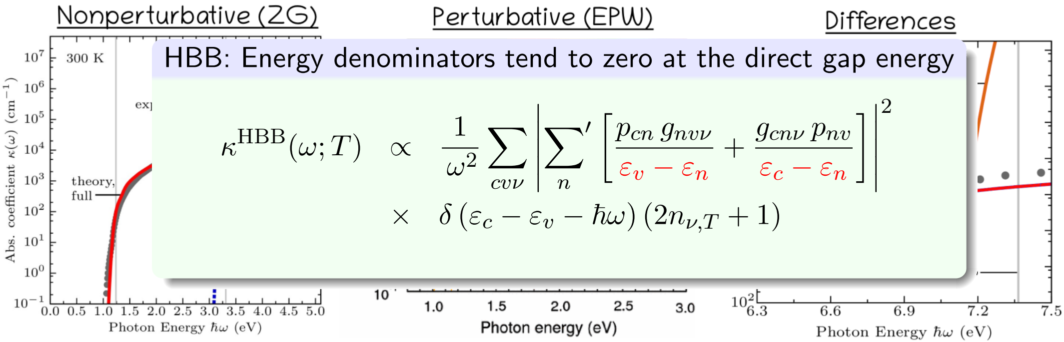
Final remark: Nonperturbative vs Perturbative



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- ZG gives the full spectrum → all terms in perturbation theory: ✓
  $\kappa^{\text{ZG}}(\omega;T) = \kappa^{\text{HBB}}(\omega;T)$ + 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`.