Temperature-dependent optical spectra and band structures using the special configuration method

theory and methods

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Outline

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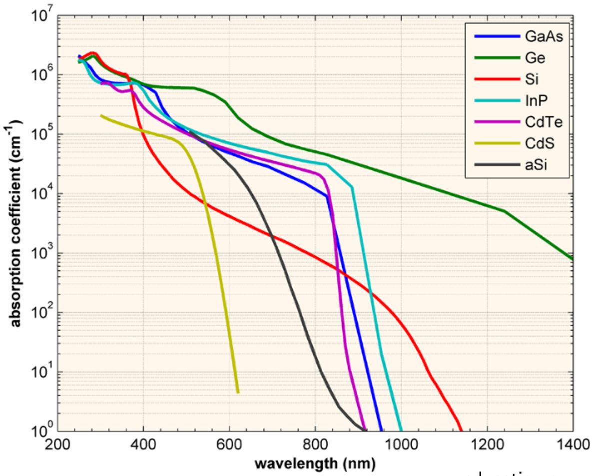
Outline

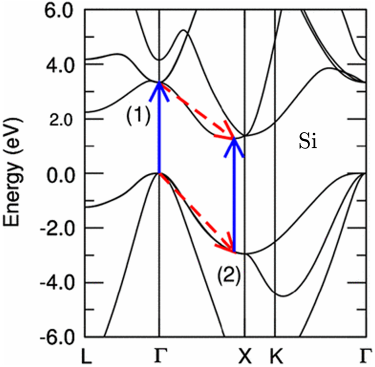
1. Standard theory of indirect optical absorption and Allen-Heine theories.
2. Williams-Lax theory and main approximation.
3. Special ZG-configuration.
4. Full T-dependent band structures.

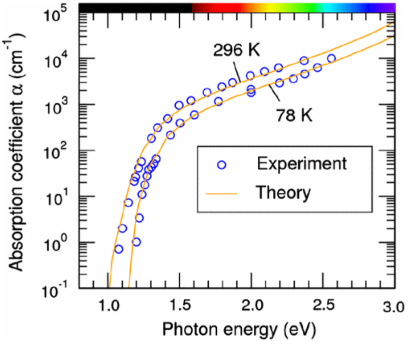
- Quantum nuclear effects on the optical properties of solids



- pveducation.org

HBB theory of phonon-assisted optical absorption





J. Noffsinger *et al.*, PRL, **108**, 167402, 2012

Phonon-assisted transition rate - HBB theory

$$\mathrm{I}_{u\to c}(\omega) \propto \sum_{\nu} \left| \sum_{n\neq c} \frac{p_{un} g_{nc,\nu}}{\epsilon_n - \epsilon_u - \hbar\omega} + \sum_{n\neq u} \frac{g_{un,\nu} p_{nc}}{\epsilon_n - \epsilon_u \pm \hbar\Omega_\nu} \right|^2 \delta(\epsilon_c - \epsilon_u \pm \hbar\Omega_\nu - \hbar\omega)$$

L. Hall, J. Bardeen, and F. Blatt, Phys. Rev. **95**, 559 (1954)

AH theory of the T dependence of the band structure

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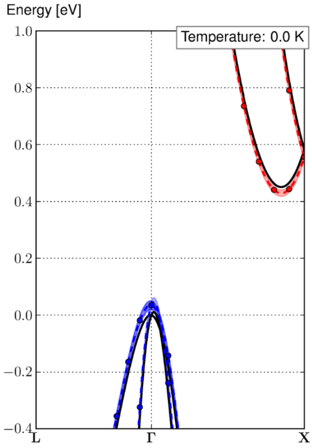
Temperature dependence of the energy levels

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

P. B. Allen and V. Heine, J. Phys. C **9**, 2305 (1976)

First-principles implementations:

A. Marini, Phys. Rev. Lett. **101**, 106405 (2008)
F. Giustino *et al.*, Phys. Rev. Lett. **105**, 265501 (2010)
X. Gonze *et al.*, Ann. Phys. **523**, 168 (2011)
E. Cannuccia *et al.*, Phys. Rev. Lett. **107**, 255501 (2011)
S. Poncé *et al.*, Phys. Rev. B **90**, 214304 (2014).
S. Poncé *et al.*, Comput. Mater. Science **83**, 341 (2014)
G. Antonius *et al.*, Phys. Rev. Lett. **112**, 215501 (2014)
B. Monserrat *et al.*, Phys. Rev. B **89**, 214304 (2014)
J. H. Lloyd-Williams *et al.*, Phys. Rev. B **92** (2015)
S. Poncé *et al.*,J. Chem. Phys. **143** (2015)
B. Monserrat, Phys. Rev. B **93**, 014302 (2016)



(a) Si band structure renormalization

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

Williams-Lax theory

WL theory

1. Herzberg-Teller rate as the starting point:

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

Williams-Lax theory

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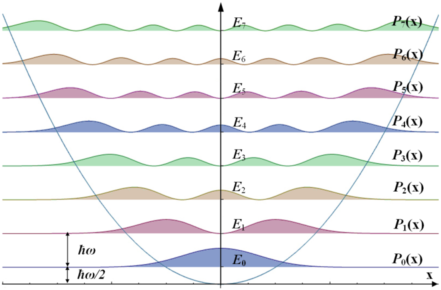
2. Classical approximation: replace $E_{\beta m}$ with the A-PES.

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



Williams-Lax theory

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

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

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

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 and F. Giustino, Nat. Commun. 4, 2006 (2013)
C. E. Patrick and F. Giustino, J. Phys. Condens. Matter 26, 365503 (2014)

WL theory

4. Make contact wth DFT. We write for the A-PES:

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

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

Williams-Lax theory

WL theory

4. Make contact wth DFT. We write for the A-PES:

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

5. Imaginary part of the dielectric function at 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 IP picture: $\epsilon_2^x(\omega) \propto \frac{1}{\omega^2} \sum_{v,c} |p^x_{cv}|^2 \delta(\varepsilon^x_c - \varepsilon^x_v - \hbar\omega)$

M. Zacharias, C. E. Patrick, and F. Giustino, Phys. Rev. Lett. **115**, 177401 (2015)
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Williams-Lax theory

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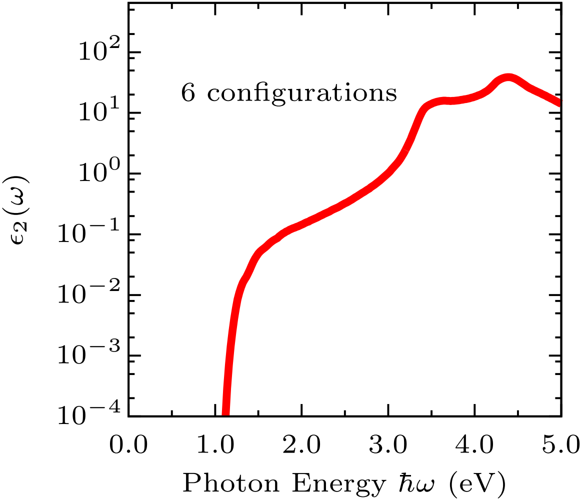
Interpretation: Weighted average of the spectra calculated with the nuclei fixed in a variety of configurations.

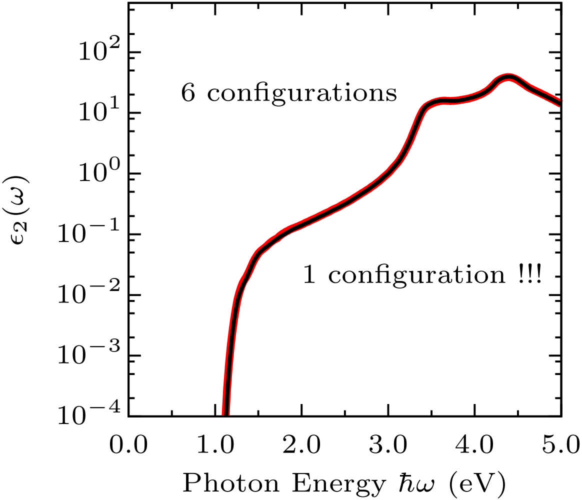
M. Zacharias, C. E. Patrick, and F. Giustino, Phys. Rev. Lett. **115**, 177401 (2015)
M. Zacharias and F. Giustino, Phys. Rev. B **94**, 075125 (2016)

Optical spectra of Si, 8×8×8 supercell



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

Optical spectra of Si, 8×8×8 supercell



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

One-shot frozen-phonon calculations

Special ZG-configuration

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

2. One config.: $\epsilon_2^{\mathrm{1C-ZG}}(\omega; T) = \epsilon_2(\omega) + \frac{1}{2}\sum_{\nu\mu} s_\nu s_\mu \frac{\partial^2 \epsilon_2^{x}(\omega)}{\partial x_\nu \partial x_\mu}\sigma_{\nu,T}\sigma_{\mu,T} + \mathcal{O}(\sigma^4)$

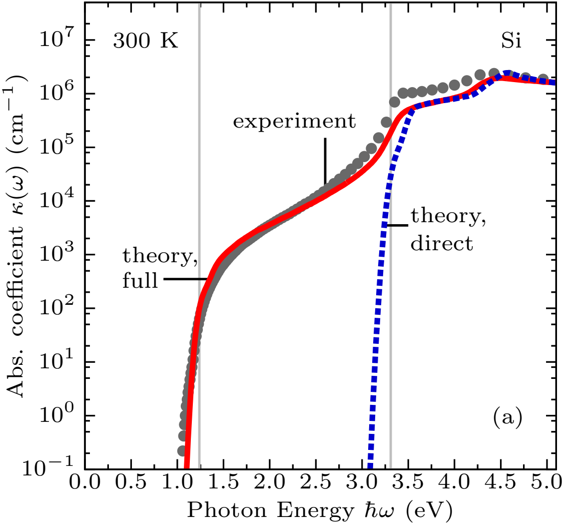
   Special set of signs: $\{+ \; - \; + \; - \; + \; - \; \cdots\}$

3. We can prove:

$$\lim_{N\to\infty} \epsilon_2^{\mathrm{1C-ZG}}(\omega; T) = \epsilon_2^{\mathrm{WL}}(\omega; T)$$

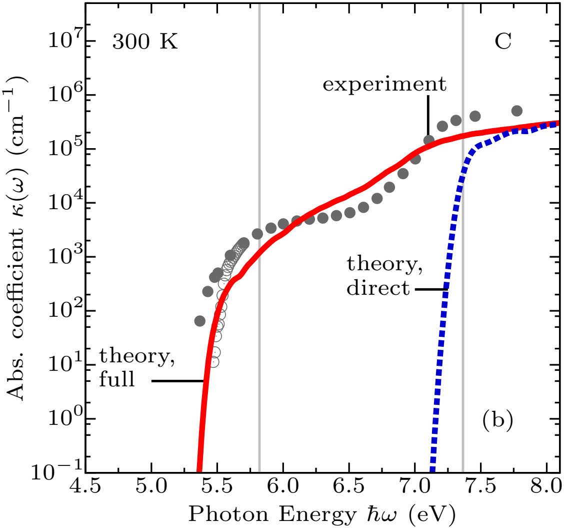
M. Zacharias and F. Giustino, Phys. Rev. B **94**, 075125 (2016)

WL spectrum (ZG-configuration) - experiment: Si



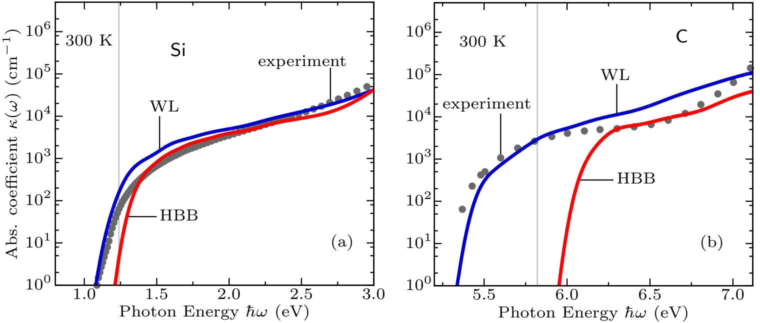
M. Zacharias and F. Giustino, Phys. Rev. B **94**, 075125 (2016)

WL spectrum (ZG-configuration) - experiment: C



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

Williams Lax (WL) vs Hall Bardeen and Blatt (HBB)



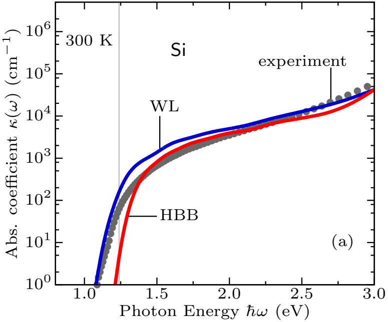
HBB vs WL

$$\epsilon_2^{\mathrm{aHBB}}(\omega; T) \propto \frac{1}{\omega^2} \sum_{cv\nu} \left| \sum_n{}' \left[\frac{p_{cn}\, g_{nv\nu}}{\varepsilon_v - \varepsilon_n} + \frac{g_{cn\nu}\, p_{nv}}{\varepsilon_c - \varepsilon_n} \right] \right|^2$$

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

vs

Connection of WL, HBB and AH theories

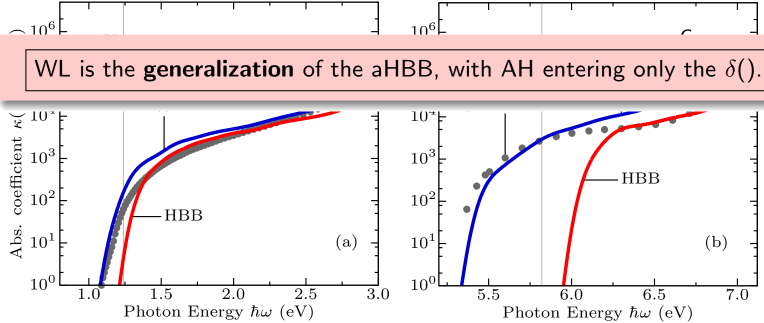


HBB vs WL

$$\epsilon_2^{\mathrm{WL}}(\omega;T) \propto \frac{1}{\omega^2}\sum_{cv\nu}\left|\sum_n{}' \left[\frac{p_{cn}\,g_{nv\nu}}{\varepsilon_v-\varepsilon_n}+\frac{g_{cn\nu}\,p_{nv}}{\varepsilon_c-\varepsilon_n}\right]\right|^2$$

$$\times \frac{1}{\sqrt{2\pi}\Gamma_{cv}} \exp\left[-\frac{\left(\varepsilon_{c,T}^{\mathrm{AH}}-\varepsilon_{v,T}^{\mathrm{AH}}-\hbar\omega\right)^2}{2\,\Gamma_{cv}^2}\right](2n_{\nu,T}+1)$$

Connection of WL, HBB and AH theories



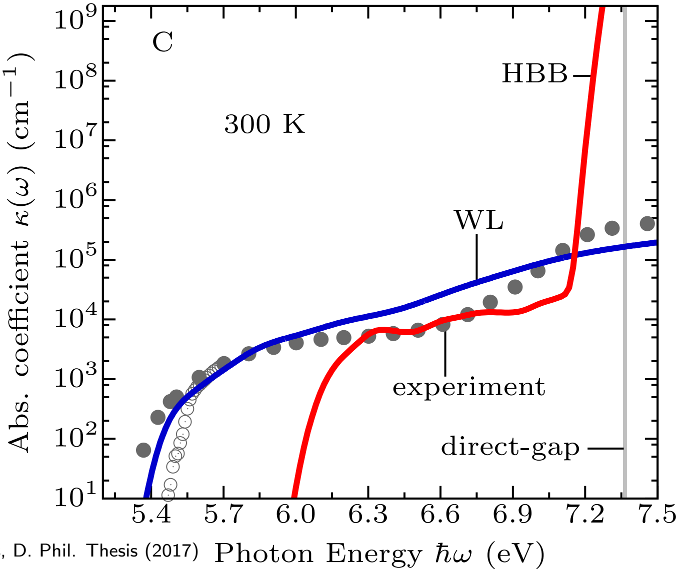
WL is the **generalization** of the aHBB, with AH entering only the $\delta()$.

HBB vs WL

$$\epsilon_2^{\mathrm{WL}}(\omega; T) \propto \frac{1}{\omega^2}\sum_{cv\nu}\left|\sum_n{}'\left[\frac{p_{cn}\, g_{nv\nu}}{\varepsilon_v-\varepsilon_n}+\frac{g_{cn\nu}\, p_{nv}}{\varepsilon_c-\varepsilon_n}\right]\right|^2$$

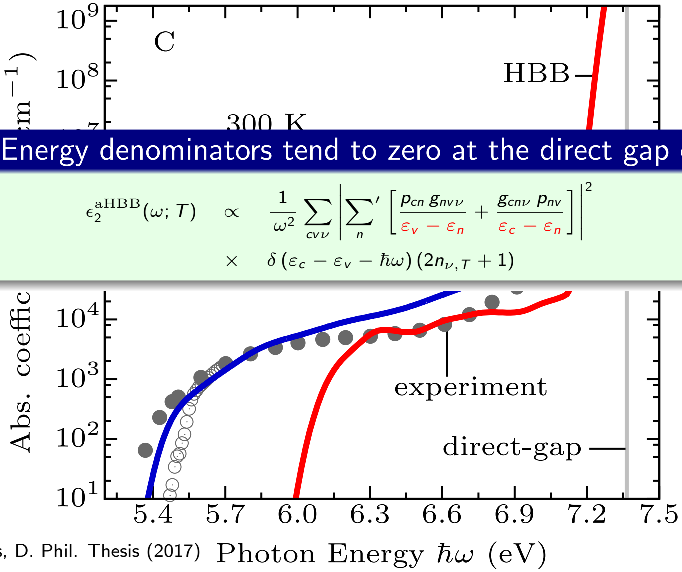
$$\times \frac{1}{\sqrt{2\pi}\Gamma_{cv}}\exp\left[-\frac{\left(\varepsilon_{c,T}^{\mathrm{AH}}-\varepsilon_{v,T}^{\mathrm{AH}}-\hbar\omega\right)^2}{2\,\Gamma_{cv}^2}\right](2n_{\nu,T}+1)$$

HBB divergence at the direct gap



M. Zacharias, D. Phil. Thesis (2017)

HBB divergence at the direct gap

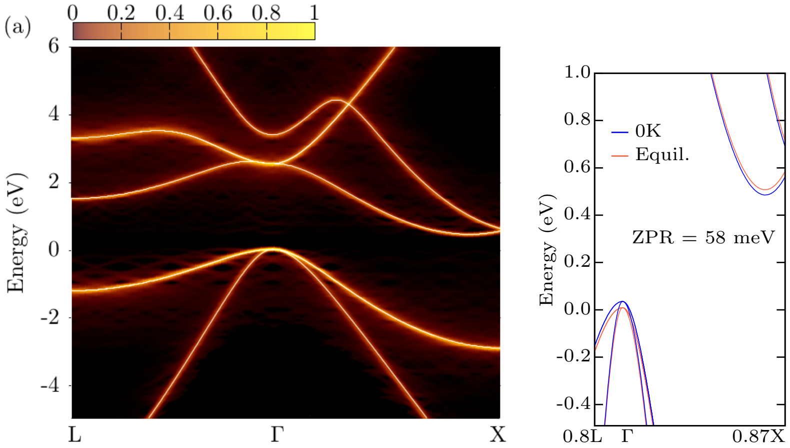


HBB: Energy denominators tend to zero at the direct gap energy

$$\epsilon_2^{\mathrm{aHBB}}(\omega;T) \propto \frac{1}{\omega^2}\sum_{cv\nu}\left|{\sum_n}'\left[\frac{p_{cn}\,g_{nv\nu}}{\varepsilon_v-\varepsilon_n}+\frac{g_{cn\nu}\,p_{nv}}{\varepsilon_c-\varepsilon_n}\right]\right|^2 \times \delta\left(\varepsilon_c-\varepsilon_v-\hbar\omega\right)\left(2n_{\nu,T}+1\right)$$

M. Zacharias, D. Phil. Thesis (2017)

T-dependent band structures of Si, 8×8×8, 0 K

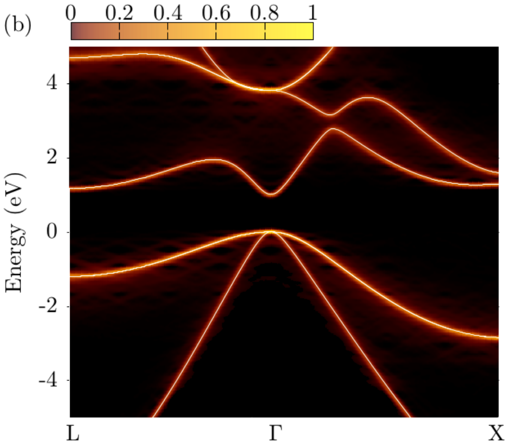


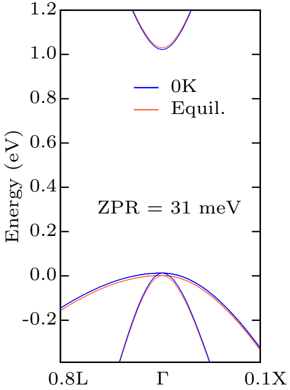
ZPR in good agreement with other theoretical results (AH theory) and experiment

M. Zacharias and F. Giustino, unpublished

V. Popescu and A. Zunger, Phys. Rev. B 85, 085201, 2012 → unfolding from supercell calculations

T-dependent band structures of GaAs, 8×8×8, 0 K





ZPR in good agreement with other theoretical results (AH theory) and experiment

M. Zacharias and F. Giustino, unpublished

V. Popescu and A. Zunger, Phys. Rev. B 85, 085201, 2012 → unfolding from supercell calculations

Unit cell formulation for the special ZG-configuration

Expression that leads to the deterministic choice

1. Using translational inveriance of the lattice we can prove:

$$\sum_{\substack{\mathbf{q} \\ \nu\neq\nu'}} \frac{\partial^2 \epsilon_2^x}{\partial x_{\mathbf{q}\nu}\partial x_{\mathbf{q}\nu'}} \sigma_{\mathbf{q}\nu,T}\sigma_{\mathbf{q}\nu',T} \propto \sum_{\substack{\mathbf{q} \\ \nu\neq\nu'}} s_{\mathbf{q}\nu} s_{\mathbf{q}\nu'} \Re[e^{\nu}_{\kappa\alpha}(\mathbf{q}) e^{\nu'*}_{\kappa'\alpha'}(\mathbf{q})] \sigma_{\mathbf{q}\nu,T}\sigma_{\mathbf{q}\nu',T}$$

   All terms are known. Under what conditions the R.H.S. reduces to zero ?

2. The coupling between different branches constitutes a combinatorial problem.

3. Our choice of signs is rigorously verified.

Connection to Debye-Waller factor

Probability distribution

1. Using quantum mechanics we can prove:

$$P(\Delta\tau_{p\kappa\alpha}) = \frac{1}{\sqrt{2\pi}\sigma_{\mathrm{DW}}}\exp\left(-\frac{\Delta\tau^2_{p\kappa\alpha}}{2\sigma^2_{\mathrm{DW}}}\right)$$

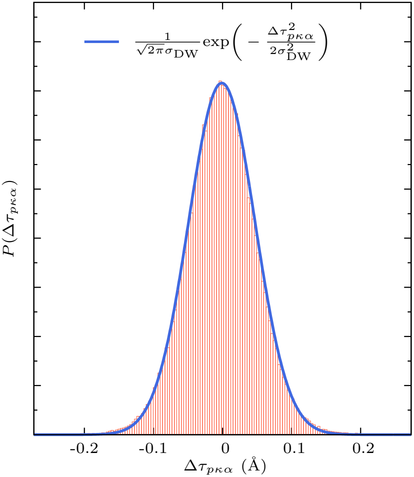
where the Debye-Waller factor:

$$\sigma^2_{\mathrm{DW}} = \langle\Delta\tau^2_{p\kappa\alpha}\rangle = \frac{2M_0}{N_p M_\kappa}\sum_{\mathbf{q},\nu}|e^{\nu}_{\kappa\alpha}(\mathbf{q})|^2\sigma^2_{\mathbf{q}\nu,T}$$

2. Mean-square vibrational amplitude of the nuclei:

$$\sum_p \frac{\Delta\tau^2_{p\kappa\alpha}}{N_p} = \frac{2M_0}{N_p M_\kappa}\sum_{\substack{\mathbf{q}\\ \nu\nu'}} s_{\mathbf{q}\nu}s_{\mathbf{q}\nu'}\Re[e^{\nu}_{\kappa\alpha}(\mathbf{q})e^{\nu'*}_{\kappa\alpha}(\mathbf{q})]\sigma_{\mathbf{q}\nu,T}\sigma_{\mathbf{q}\nu',T}$$

tends to the exact σ^2_{DW} for $\lim_{N_p\to\infty}$



M. Zacharias and F. Giustino, unpublished

General procedure

DFPT $\rightarrow$ ZG $\rightarrow$ Optical properties

1. Converged calculation of phonons using DFPT.
2. Generate the special configuration at the required supercell size (implemented).
3. Calculate optical spectra at different levels of approximation.
4. Calculate T-dependent band structures using the unfolding procedure (implemented for norm-conserving and ultasoft pseudos with spin-orbit coupling)

Advantages

Advantages of the special ZG-configuration method

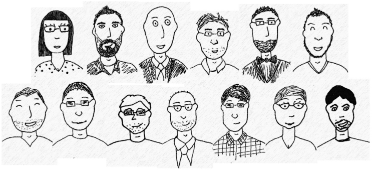
1. Easy to implement on top of any electronic structure package.
2. Includes el-ph coupling by just displacing atoms from equilibrium positions.
3. No divergence at the direct gap.
4. Captures at the same time ph-assisted transitions and zero-point renormalization.

Future directions

1. Understand how to cure divergence of the HBB spectra using a perturbative approach.
2. Predictive calculations of the optical spectra of new compounds.
3. Changes on phonon assisted optical properties beyond the independent particle picture (GW-BSE).
4. Investigate effects of anharmonicity

Acknowledgements

Giustino's Group in Oxford



Supervisor
Feliciano Giustino

THANK YOU !!!

Connection of WL to HBB and AH theories

$$\epsilon_2(\omega;x) = \frac{2\pi}{m_e N_e}\frac{\omega_\mathrm{p}^2}{\omega^2}\sum_{cv}|p_{cv}^x|^2\delta(\varepsilon_{cv} - \Delta\varepsilon_{cv}^x - \hbar\omega) \to \delta(\epsilon+\eta) = \sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\left.\frac{\partial^n\delta}{\partial\epsilon^n}\right|_\epsilon \eta^n$$

For an indirect gap material (only single-phonon processes)

$$\epsilon_2^{\mathrm{WL-sp}}(\omega;T) = \frac{2\pi}{m_\mathrm{e} N_\mathrm{e}}\frac{\omega_\mathrm{p}^2}{\omega^2}\sum_{cv\nu}\left|\sum_n{}' \left[\frac{p_{cn}\,g_{nv\nu}}{\varepsilon_v - \varepsilon_n} + \frac{g_{cn\nu}\,p_{nv}}{\varepsilon_c - \varepsilon_n}\right]\right|^2$$
$$\times \frac{1}{\sqrt{2\pi}\Gamma_{cv}}\exp\left[-\frac{\left(\varepsilon_{c,T}^{\mathrm{AH}} - \varepsilon_{v,T}^{\mathrm{AH}} - \hbar\omega\right)^2}{2\,\Gamma_{cv}^2}\right](2n_{\nu,T}+1)$$

where

$$\Gamma_{cv} = \left[\sum\nolimits_\nu |g_{cc\nu} - g_{vv\nu}|^2\,(2n_{\nu,T}+1)\right]^{1/2}$$

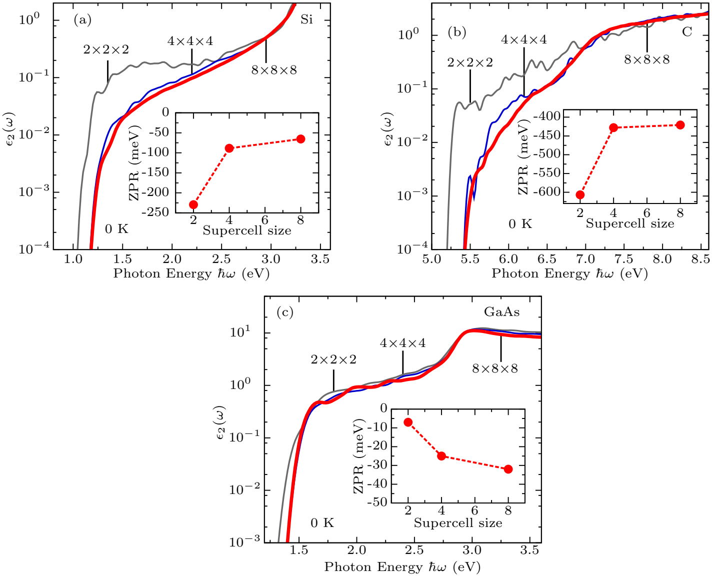
is the width of the optical transition

WL is the **generalization** of the aHBB, with AH entering only the delta function.

Similar expression for a direct gap material.

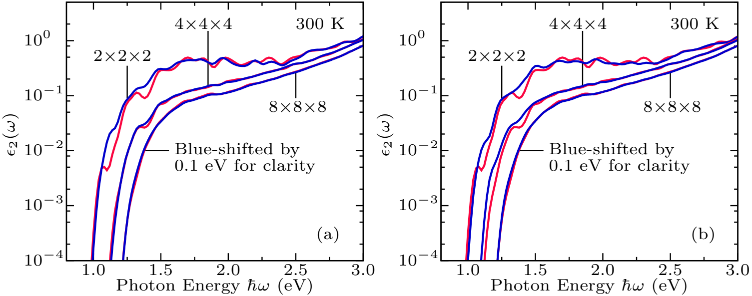
M. Zacharias and F. Giustino, Phys. Rev. B **94**, 075125 (2016)

One-shot spectra: Silicon - Diamond - GaAs



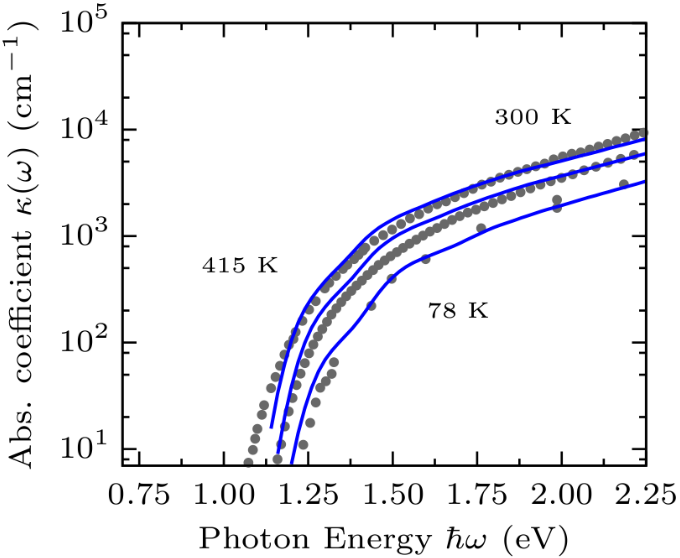
M. Zacharias and F. Giustino, Phys. Rev. B **94**, 075125 (2016)

Deterministic sampling



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

Temperature dependent absorption coefficient



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

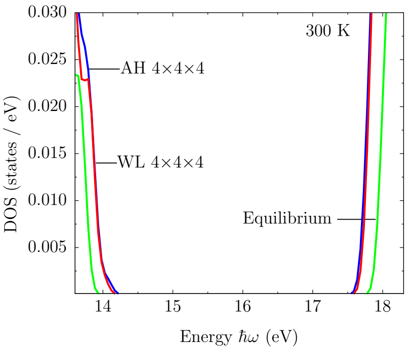
Multiphonon contributions to band gap:

AH theory, take thermal average:

$$\epsilon^{\mathrm{AH}}_{n,T} = \epsilon_n + \frac{1}{2}\sum_{\nu}\frac{\partial^2\epsilon^x_n}{\partial x^2_\nu}\sigma^2_{\nu,T} + \frac{3}{4!}\sum_{\mu\neq\nu}\frac{\partial^4\epsilon^x_n}{\partial x^2_\mu\partial x^2_\nu}\sigma^2_{\mu,T}\sigma^2_{\nu,T} + \frac{3}{4!}\sum_{\nu}\frac{\partial^4\epsilon^x_n}{\partial x^4_\nu}\sigma^4_{\nu,T} + \mathcal{O}(\sigma^6).$$

Optimum configuration and limit of $N\to\infty$, we find:

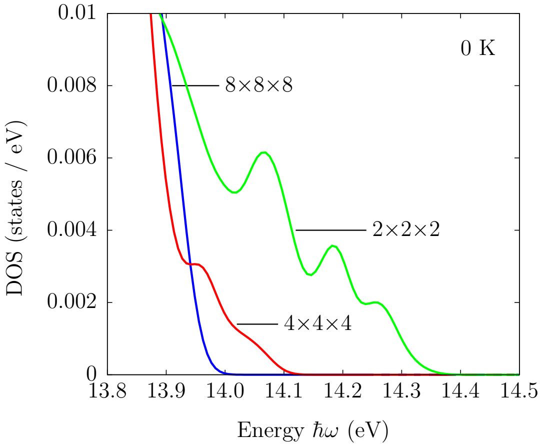
$$\epsilon^{\mathrm{1C}}_{n,T} = \epsilon_n + \frac{1}{2}\sum_{\nu}\frac{\partial^2\epsilon^x_n}{\partial x^2_\nu}\sigma^2_{\nu,T} + \frac{3}{4!}\sum_{\mu\neq\nu}\frac{\partial^4\epsilon^x_n}{\partial x^2_\mu\partial x^2_\nu}\sigma^2_{\mu,T}\sigma^2_{\nu,T} + \frac{1}{4!}\sum_{\nu}\frac{\partial^4\epsilon^x_n}{\partial x^4_\nu}\sigma^4_{\nu,T} + \mathcal{O}(\sigma^6).$$



Degeneracies in supercell calculations:

Spurious contribution from **degeneracies**

vanishes in the thermodynamic limit:

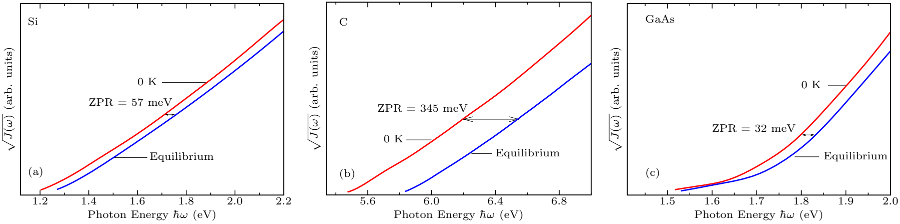


Calculate ZPR form Williams-Lax Joint DOS:

$$J(\omega; T) = \sum_{cv} \delta\left(\varepsilon^{\mathrm{AH}}_{cv,T} - \hbar\omega\right) + \mathcal{O}(\sigma^4)$$

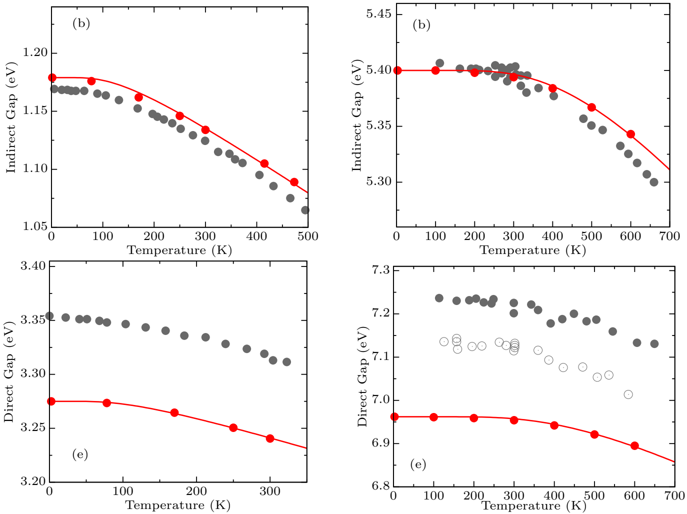
with $J(\omega, T)^{1/2} = \mathrm{const} \times (\hbar\omega - E_{\mathrm{g},T})$

ZPR from the horizontal offset between the curves $J(\omega)^{1/2}$ and $J(\omega, T = 0)^{1/2}$.



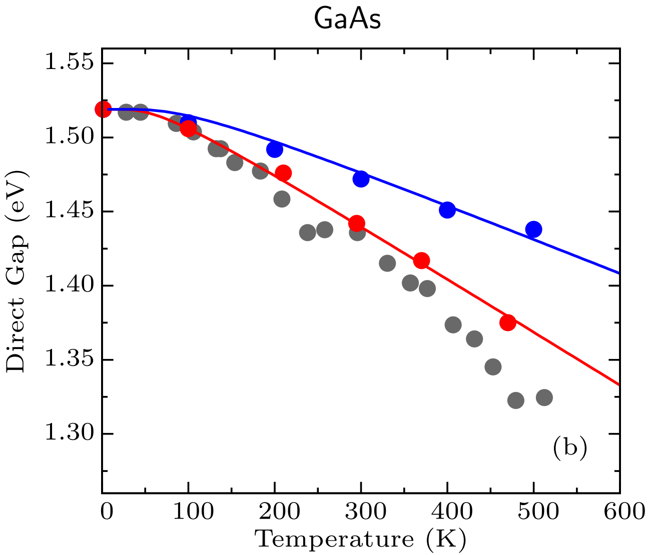
Band gap renormalization: Silicon - Diamond

Silicon | Diamond



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

Band gap renormalization: GaAs



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

Theory for the special configuration

Williams-Lax using the conventional reciprocal space formulation

1. Atomic displacements $\Delta\tau_{p\kappa\alpha}$ in terms of normal coordinates $z_{\mathbf{q}\nu}$:

$$\Delta\tau_{p\kappa\alpha} = \left(\frac{M_0}{M_\kappa N_p}\right)^{1/2} \sum_{\mathbf{q}\nu} e^{i\mathbf{q}\cdot\mathbf{R}_p} e^{\nu}_{\kappa\alpha}(\mathbf{q}) z_{\mathbf{q}\nu}\,, \quad \text{with} \quad z_{\mathbf{q}\nu} = x_{\mathbf{q}\nu} + iy_{\mathbf{q}\nu}$$

which we can re-write in terms of sets A and B:

$$\Delta\tau_{p\kappa\alpha} = \left(\frac{M_0}{M_\kappa N_p}\right)^{1/2} \left\{ \sum_{\mathbf{q}\in A,\nu} e^{\nu}_{\kappa\alpha}(\mathbf{q}) x_{\mathbf{q}\nu} \cos(\mathbf{q}\cdot\mathbf{R}_p) + 2\Re\left[\sum_{\mathbf{q}\in B,\nu} e^{i\mathbf{q}\cdot\mathbf{R}_p} e^{\nu}_{\kappa\alpha}(\mathbf{q})(x_{\mathbf{q}\nu} + iy_{\mathbf{q}\nu})\right]\right\}$$

2. The WL dielectric function is:

$$\epsilon_2^{\mathrm{WL}}(\omega;T) = \left(\prod_{\mathbf{q}\in A,\nu} \int \frac{dx_{\mathbf{q}\nu}}{\sqrt{2\pi}\sigma_{\nu\mathbf{q},T}} e^{-x^2_{\mathbf{q}\nu}/2\sigma^2_{\nu\mathbf{q},T}} \prod_{\mathbf{q}\in B,\nu} \int\int \frac{dx_{\mathbf{q}\nu}\,dy_{\mathbf{q}\nu}}{\sqrt{2\pi}\sigma_{\nu\mathbf{q},T}} e^{-(x^2_{\mathbf{q}\nu}+y^2_{\mathbf{q}\nu})/2\sigma^2_{\nu\mathbf{q},T}} \right) \epsilon_2^{\{\tau\}}(\omega)$$

where $\sigma_{\nu\mathbf{q},T} = l^2_{\mathbf{q}\nu}(2n_{\mathbf{q}\nu,T}+1)$

Theory for the special configuration

Williams-Lax using the conventional reciprocal space formulation

3. Expand the $\epsilon_2^{\{\tau\}}(\omega)$ around $\Delta\tau_{p\kappa\alpha}$ to find

$$\epsilon_2^{\{\tau\}}(\omega) = \epsilon_2^0(\omega) + \sum_{\mathbf{q}\nu} \frac{\partial \epsilon_2^{\{\tau\}}(\omega)}{\partial z_{\mathbf{q}\nu}} z_{\mathbf{q}\nu} + \frac{1}{2} \sum_{\mathbf{q}\nu,\mathbf{q}'\nu'} \frac{\partial^2 \epsilon_2^{\{\tau\}}(\omega)}{\partial z_{\mathbf{q}\nu} \partial z_{\mathbf{q}'\nu'}} z_{\mathbf{q}\nu} z_{\mathbf{q}'\nu'}$$

and perform the integration:

$$\epsilon_2^{\mathrm{WL}}(\omega, T) = \epsilon_2^0(\omega) + \frac{1}{2} \sum_{\mathbf{q}\in A,\nu} \frac{\partial^2 \epsilon_2^{\{\tau\}}(\omega)}{\partial x_{\mathbf{q}\nu}^2} \sigma_{\mathbf{q}\nu,T}^2 + \frac{1}{2} \sum_{\mathbf{q}\in B,\nu} \left[\frac{\partial^2 \epsilon_2^{\{\tau\}}(\omega)}{\partial x_{\mathbf{q}\nu}^2} + \frac{\partial^2 \epsilon_2^{\{\tau\}}(\omega)}{\partial y_{\mathbf{q}\nu}^2} \right] \sigma_{\mathbf{q}\nu,T}^2 .$$

4. For practical calculations the goal is to find the set of normal coordinates $\{z_{\mathbf{q}\nu}\}$ or $\{x_{\mathbf{q}\nu}, y_{\mathbf{q}\nu}\}$ that results to the exact $\epsilon_2^{\mathrm{WL}}(\omega, T)$.

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Theory for the special configuration

Examine the coupling coefficients

1. The linear coupling coefficients:

$$\frac{\partial \epsilon_2^{\{\tau\}}}{\partial z_{\mathbf{q}\nu}} = N_p^{-1/2} \sum_{p\kappa\alpha} \left(\frac{M_0}{M_\kappa}\right)^{1/2} e^{i\mathbf{q}\cdot\mathbf{R}_p} e_{\kappa\alpha}^{\nu}(\mathbf{q}) \frac{\partial \epsilon_2^{\{\tau\}}}{\partial \Delta\tau_{p\kappa\alpha}}.$$

   Translational invariance of the lattice to re-write:

$$\frac{\partial \epsilon_2^{\{\tau\}}}{\partial z_{\mathbf{q}\nu}} = N_p^{-1/2} \sum_{\kappa\alpha} \left(\frac{M_0}{M_\kappa}\right)^{1/2} e_{\kappa\alpha}^{\nu}(\mathbf{q}) \frac{\partial \epsilon_2^{\{\tau\}}}{\partial \Delta\tau_{1\kappa\alpha}} \boxed{\sum_p e^{i\mathbf{q}\cdot\mathbf{R}_p}},$$

2. Using the sum-rule $\sum_{\mathbf{q}} e^{i(\mathbf{R}_p - \mathbf{R}_{p'})\cdot\mathbf{q}} = N_p \delta_{pp'}$ we obtain:

$$\frac{\partial \epsilon_2^{\{\tau\}}}{\partial z_{\mathbf{q}\nu}} = \begin{cases} N_p^{1/2} \sum_{\kappa\alpha} \left(\frac{M_0}{M_\kappa}\right)^{1/2} e_{\kappa\alpha}^{\nu}(\mathbf{q}) \frac{\partial \epsilon_2^{\{\tau\}}}{\partial \Delta\tau_{1\kappa\alpha}}, & \mathbf{q} \in A. \\ 0, & \mathbf{q} \in B. \end{cases}$$

Theory for the special configuration

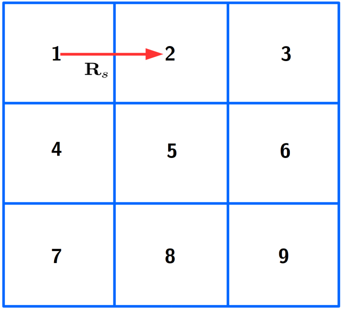
Examine the coupling coefficients

3. Similar concept for the quadratic coupling coefficients:

$$\frac{\partial^2 \epsilon_2^{\{\tau\}}}{\partial z_{\mathbf{q}\nu} \partial z_{\mathbf{q}'\nu'}} = \sum_{\substack{p\kappa\alpha \\ p'\kappa'\alpha'}} \frac{M_0 N_p^{-1}}{(M_\kappa M_{\kappa'})^{\frac{1}{2}}} \frac{\partial^2 \epsilon_2^{\{\tau\}}}{\partial \Delta\tau_{p\kappa\alpha} \partial \Delta\tau_{p'\kappa'\alpha'}} e^{i\mathbf{q}\cdot\mathbf{R}_p} e^{i\mathbf{q}'\cdot\mathbf{R}_{p'}} e^{\nu}_{\kappa\alpha}(\mathbf{q}) e^{\nu'}_{\kappa'\alpha'}(\mathbf{q}')$$

4. Translational invariance of the lattice, same coefs. for every pair (p, p'), when $\mathbf{R}_p + \mathbf{R}_s = \mathbf{R}_{p'}$:

2D case for $N_p = 9$



Always Np pairs

(1,2), (2,3), (3,1)
(4,5), (5,6), (6,4)
(7,8), (8,9), (9,7)

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Examine the electron-phonon coupling coefficients

3. Similar concept for the quadratic electron-phonon coupling coefficients:

$$\frac{\partial^2 \epsilon_2^{\{\tau\}}}{\partial z_{\mathbf{q}\nu} \partial z_{\mathbf{q}'\nu'}} = \sum_{\substack{p\kappa\alpha \\ p'\kappa'\alpha'}} \frac{M_0 N_p^{-1}}{(M_\kappa M_{\kappa'})^{\frac{1}{2}}} \frac{\partial^2 \epsilon_2^{\{\tau\}}}{\partial \Delta\tau_{p\kappa\alpha} \partial \Delta\tau_{p'\kappa'\alpha'}} e^{i\mathbf{q}\cdot\mathbf{R}_p} e^{i\mathbf{q}'\cdot\mathbf{R}_{p'}} e_{\kappa\alpha}^{\nu}(\mathbf{q}) e_{\kappa'\alpha'}^{\nu'}(\mathbf{q}')$$

4. Translational invariance of the lattice, same coefs. for every pair (p, p'), when $\mathbf{R}_p + \mathbf{R}_s = \mathbf{R}_{p'}$:

$$\frac{\partial^2 \epsilon_2^{\{\tau\}}}{\partial z_{\mathbf{q}\nu} \partial z_{\mathbf{q}'\nu'}} = \sum_{\substack{\kappa\alpha \\ \kappa'\alpha'}} \frac{M_0 N_p^{-1}}{(M_\kappa M_{\kappa'})^{\frac{1}{2}}} \sum_{s=0}^{N_p-1} \frac{\partial^2 \epsilon_2^{\{\tau\}}}{\partial \Delta\tau_{1\kappa\alpha} \partial \Delta\tau_{(1+s)\kappa'\alpha'}} e^{i\mathbf{q}'\cdot\mathbf{R}_s} e_{\kappa\alpha}^{\nu}(\mathbf{q}) e_{\kappa'\alpha'}^{\nu'}(\mathbf{q}') \boxed{\sum_p e^{i(\mathbf{q}+\mathbf{q}')\cdot\mathbf{R}_p}}$$

Using the sum rule as before:

$$\frac{\partial^2 \epsilon_2^{\{\tau\}}}{\partial z_{\mathbf{q}\nu} \partial z_{\mathbf{q}'\nu'}} = \sum_{\substack{\kappa\alpha \\ \kappa'\alpha'}} \frac{M_0}{(M_\kappa M_{\kappa'})^{\frac{1}{2}}} \sum_{s=0}^{N_p-1} \frac{\partial^2 \epsilon_2^{\{\tau\}}}{\partial \Delta\tau_{1\kappa\alpha} \partial \Delta\tau_{(1+s)\kappa'\alpha'}} e^{i\mathbf{q}'\cdot\mathbf{R}_s} \delta_{\mathbf{q},-\mathbf{q}'} e_{\kappa\alpha}^{\nu}(\mathbf{q}) e_{\kappa'\alpha'}^{\nu'}(\mathbf{q}')$$

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Theory for the special configuration

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Special configuration

1. Due to translational inveriance of the lattice we are finally left with:

$$\epsilon_2^{\{\tau\}} = \epsilon_2^0 + \sum_{\mathbf{q}\in A,\nu} \frac{\partial \epsilon_2^{\{\tau\}}}{\partial x_{\mathbf{q}\nu}} x_{\mathbf{q}\nu} + \sum_{\mathbf{q}\in A,\nu\nu'} \frac{\partial^2 \epsilon_2^{\{\tau\}}}{\partial x_{\mathbf{q}\nu}\partial x_{\mathbf{q}\nu'}} x_{\mathbf{q}\nu} x_{\mathbf{q}\nu'} + 4\Re \sum_{\mathbf{q}\in B,\nu\nu'} \frac{\partial^2 \epsilon_2^{\{\tau\}}}{\partial z_{\mathbf{q}\nu}\partial z^*_{\mathbf{q}\nu'}} z_{\mathbf{q}\nu} z^*_{\mathbf{q}\nu'}$$

Theory for the special configuration

Special configuration

1. Due to translational inveriance of the lattice we are finally left with:

$$\epsilon_2^{\{\tau\}} = \epsilon_2^0 + \sum_{\mathbf{q}\in A,\nu} \frac{\partial \epsilon_2^{\{\tau\}}}{\partial x_{\mathbf{q}\nu}} x_{\mathbf{q}\nu} + \sum_{\mathbf{q}\in A,\nu\nu'} \frac{\partial^2 \epsilon_2^{\{\tau\}}}{\partial x_{\mathbf{q}\nu}\partial x_{\mathbf{q}\nu'}} x_{\mathbf{q}\nu} x_{\mathbf{q}\nu'} + 4\Re \sum_{\mathbf{q}\in B,\nu\nu'} \frac{\partial^2 \epsilon_2^{\{\tau\}}}{\partial z_{\mathbf{q}\nu}\partial z^*_{\mathbf{q}\nu'}} z_{\mathbf{q}\nu} z^*_{\mathbf{q}\nu'}$$

The contribution from modes with $\mathbf{q} \in A$ vanishes for $N_p \to \infty$

M. Zacharias and F. Giustino, unpublished

Theory for the special configuration

Special configuration

1. Due to translational inveriance of the lattice we are finally left with:

$$\epsilon_2^{\{\tau\}} = \epsilon_2^0 + \sum_{\mathbf{q}\in A,\nu} \frac{\partial \epsilon_2^{\{\tau\}}}{\partial x_{\mathbf{q}\nu}} x_{\mathbf{q}\nu} + \sum_{\mathbf{q}\in A,\nu\nu'} \frac{\partial^2 \epsilon_2^{\{\tau\}}}{\partial x_{\mathbf{q}\nu}\partial x_{\mathbf{q}\nu'}} x_{\mathbf{q}\nu} x_{\mathbf{q}\nu'} + 4\Re \sum_{\mathbf{q}\in B,\nu\nu'} \frac{\partial^2 \epsilon_2^{\{\tau\}}}{\partial z_{\mathbf{q}\nu}\partial z^*_{\mathbf{q}\nu'}} z_{\mathbf{q}\nu} z^*_{\mathbf{q}\nu'}$$

   The contribution from modes with $\mathbf{q} \in A$ vanishes for $N_p \to \infty$

2. Eliminate the error from the last term and modes with $\nu \neq \nu'$:

$$4\Re \sum_{\substack{\mathbf{q}\in B \\ \nu\neq\nu'}} \frac{\partial^2 \epsilon_2^{x}}{\partial z_{\mathbf{q}\nu}\partial z^*_{\mathbf{q}\nu'}} z_{\mathbf{q}\nu} z^*_{\mathbf{q}\nu'} \propto \sum_{\mathbf{q}\in B} \sum_{\nu\neq\nu'} \Re[e^{\nu}_{\kappa\alpha}(\mathbf{q}) e^{\nu' *}_{\kappa'\alpha'}(\mathbf{q}) z_{\mathbf{q}\nu} z^*_{\mathbf{q}\nu'}]$$

   All terms are known. Under what conditions the R.H.S. reduces to zero ?

3. The coupling between different branches constitutes a combinatorial problem.

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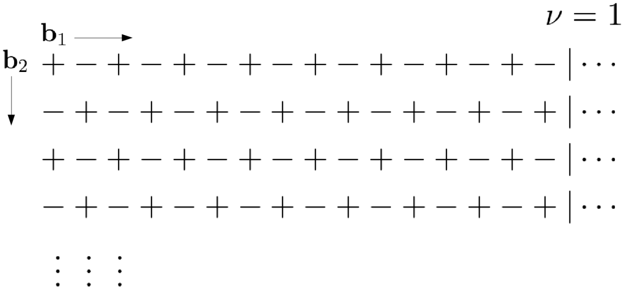
Theory for the special configuration



Choice of signs

For the rest branches ν we make simple permutations of the above signs. This choice gives:

$$\lim_{N_p \to \infty} \sum_{\mathbf{q} \in B} \sum_{\nu \neq \nu'} \Re[e^{\nu}_{\kappa\alpha}(\mathbf{q}) e^{\nu' *}_{\kappa'\alpha'}(\mathbf{q}) z_{\mathbf{q}\nu} z^{*}_{\mathbf{q}\nu'}] = 0$$

for $|z_{\mathbf{q}\nu}| = \sigma_{\mathbf{q}\nu,T}$. This is becuase $\lim_{\Delta\mathbf{q} \to 0} D^{\rm dm}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q} + \Delta\mathbf{q}) = D^{\rm dm}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q})$.