Temperature dependence of electronic eigenenergies in the adiabatic harmonic approximation

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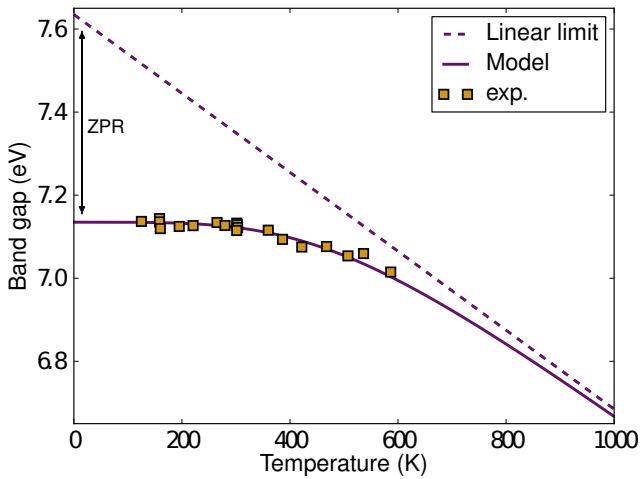
Study of the temperature dependence

The electron-phonon coupling can be probe experimentally by measuring the zero-point motion (ZPR).
For example, the direct bandgap diamond:



S. Logothetidis, J. Petalas, H. M. Polatoglou and D. Fuchs, Phys. Rev. B **46**, 4483 (1992)

The ZPR lies between 400 meV and 600 meV according to the analysis of various authors.

First-principles temperature dependence of eigenenergies

It can be computed by 3 types of methods

- Molecular Dynamics (MD)
  - ✓ Includes effects beyond the harmonic approx.
  - ✗ Normal MD delivers a Boltzmann statistic for phonons → no ZPR
  - ✓ But Path-Integral Molecular Dynamics (PIMD) does include Bose-Einstein statistics → ZPR is observed
  - ✗ Needs supercell for solids (molecules ok)
- Frozen-Phonon (FP)
  - ✓ Includes effects beyond the harmonic approx.
  - ✗ Supercell is required
- Diagrammatic method of many-body perturbation theory (AHC)
  - ✓ Only primitive cell is required (DFPT based)
  - ✗ Harmonic approximation
  - ✗ Rigid-ion approximation

In the first-principles context

- PIMD and FP are equivalent within the adiabatic approximation
- AHC is equivalent ONLY when the rigid-ion approximation is valid
  - NRIA terms seem large in molecules
    X. Gonze *et al.* Ann. Phys. **523**, 168 (2011)
  - NIRA terms seem small in solids
    G. Antonius *et al.* Phys. Rev. Lett. **112**, 215501 (2014)

Brook's theorem: 3 equivalences

Brooks theorem states that *"the shift in an electronic eigenenergy due to the electron-phonon interaction, when a phonon is added in a phononic mode, is equivalent to the shift in the m phonon mode eigenfrequency when an electron is placed in the n level, also caused by the electron-phonon interaction"*.

$$\boxed{\frac{\partial \varepsilon_n}{\partial n_m} = \frac{\partial \omega_m}{\partial f_n}}$$

H. Brooks, Adv. Electron El. Phys. **7**, 85 (1955)

P. B. Allen *et al.*, Z. Phys. B Con. Mat. **37**, 33 (1980)

R. D. King-Smith *et al.*, Europhys. Lett. **10**, 569 (1989)

Brook's theorem: 3 equivalences

- $\varepsilon_n(T) \triangleq \langle \tilde{\varepsilon}_n[z\mathbf{U}] \rangle (T)$
  $= \sum_m^{3N} \frac{1}{\mathcal{Z}_m} \sum_{s_m} e^{\frac{-(s_m+1/2)\omega_m}{k_B T}} \int \chi^*_{m,s_m}(z) \tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}] \chi_{m,s_m}(z) dz$
- $\tilde{\varepsilon}_n[z\mathbf{U}]$ can be Taylor expanded
- $\Delta\varepsilon_n(T) \triangleq \varepsilon_n(T) - \tilde{\varepsilon}_n[0] = \sum_m^{3N} \frac{1}{2\omega_m} \frac{d^2}{dz^2} \tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}]\Big|_{z=0} \left(n_m(T) + \frac{1}{2}\right)$
- $\frac{\partial \varepsilon_n}{\partial n_m} = \frac{1}{2\omega_m} \frac{d^2}{dz^2} \tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}]\Big|_{z=0}$
- Therefore $\boxed{\Delta\varepsilon_n(T) = \sum_m^{3N} \frac{\partial \varepsilon_n}{\partial n_m} \left(n_m(T) + \frac{1}{2}\right)}$

Brook's theorem: 3 equivalences

- Janak's theorem: $\varepsilon_n = \frac{\partial E^{BO}}{\partial f_n}$ [Janak, Phys. Rev. B **18**, 7165 (1978)]
- + total energy with phonon energy at harmonic level $E(T) = E^{BO} + \sum_m^{3N} \omega_m \left(n_m(T) + \frac{1}{2}\right)$ does not work !
- Helmholtz free energy $F(T) \triangleq E(T) - TS_{\text{vib}}(T)$ is required
- + extension of Janak to finite temperature phonon $\varepsilon_n(T) = \frac{\partial F(T)}{\partial f_n}$
- Does work and gives $\boxed{\Delta\varepsilon_n(T) = \sum_m^{3N} \frac{\partial \omega_m}{\partial f_n} \left(n_m(T) + \frac{1}{2}\right)}$

Brook's theorem: 3 equivalences

Brook's theorem:

$$\frac{\partial \varepsilon_n}{\partial n_m} = \frac{1}{2\omega_m} \frac{d^2}{dz^2} \tilde{\varepsilon}_n[z\mathbf{U}_{m,\kappa}]\Big|_{z=0}$$
$$= \frac{1}{2\omega_m} \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} U^*_{m,\kappa'\gamma} \frac{\partial^2 \varepsilon_n}{\partial R_{\kappa\alpha} \partial R_{\kappa'\gamma}} U_{m,\kappa\alpha} = \frac{\partial \omega_m}{\partial f_n}$$

More information in S. Poncé *et al.*, Phys. Rev. B **90**, 214304 (2014)

Temperature-dependence in the adiabatic harmonic approximation

For periodic solids

$$\Delta\varepsilon_{n\mathbf{k}}(T) = \frac{1}{N_q}\sum_{\mathbf{q}}\sum_{m}^{3N}\frac{\partial\varepsilon_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}}\left(n_{m\mathbf{q}}(T)+\frac{1}{2}\right)$$

$$\frac{\partial\varepsilon_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} = \frac{1}{2\omega_{m\mathbf{q}}}\sum_{\substack{\kappa\alpha\\ \kappa'\gamma}}\sum_{ll'}\frac{\partial^2\varepsilon_{n\mathbf{k}}}{\partial R_{l\kappa\alpha}\partial R_{l'\kappa'\gamma}}e^{-i\mathbf{q}\cdot(\mathbf{R}_l-\mathbf{R}_{l'})}U^*_{m,\kappa'\gamma}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})$$

$$\varepsilon_{n\mathbf{k}} = \left\langle u^{(0)}_{n\mathbf{k}}\middle|\,\hat{H}_{\mathbf{k},\mathbf{k}}\,\middle|u^{(0)}_{n\mathbf{k}}\right\rangle$$

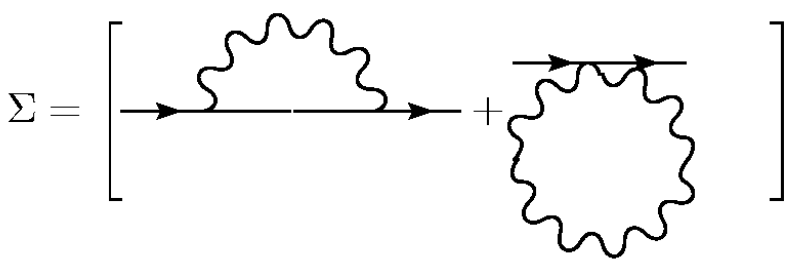
$\left\langle u^{(0)}_{n\mathbf{k}}\middle|\,\frac{\partial^2\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(-\mathbf{q})\partial R_{\kappa'\gamma}(\mathbf{q})}\,\middle|u^{(0)}_{n\mathbf{k}}\right\rangle$ is very difficult to compute

Temperature-dependence in the adiabatic harmonic approximation

The Allan-Heine-Cardona (AHC) theory using the rigid-ion approximation:

$$\Delta\varepsilon_{n\mathbf{k}}^{(\text{static,RIA})}(T) = \frac{1}{N_q}\sum_{\mathbf{q}}\sum_{m}^{3N}\left(n_{m\mathbf{q}}(T)+\frac{1}{2}\right)\frac{1}{2\omega_{m\mathbf{q}}}\sum_{\substack{\kappa\alpha\\ \kappa'\gamma}}\underbrace{\left\langle u_{n\mathbf{k}}^{(1)}(\mathbf{q})\middle|\hat{H}_{\mathbf{k},\mathbf{k}}^{(1)}(\mathbf{q})\middle|u_{n\mathbf{k}}^{(0)}\right\rangle U^*_{m,\kappa'\gamma}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})}_{\text{Fan}}$$

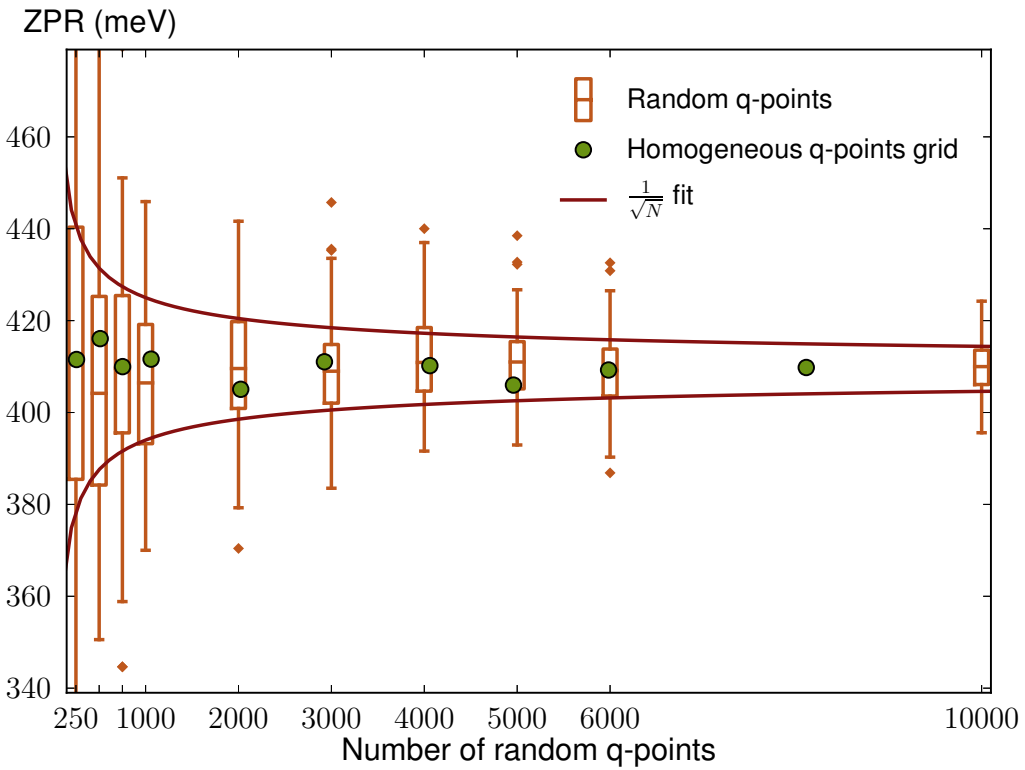
$$-\underbrace{\frac{1}{2}\left\langle u_{n\mathbf{k}}^{(1)}(\mathbf{\Gamma})\middle|\hat{H}_{\mathbf{k},\mathbf{k}}^{(1)}(\mathbf{\Gamma})\middle|u_{n\mathbf{k}}^{(0)}\right\rangle\left(U^*_{m,\kappa\gamma}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})+U^*_{m,\kappa'\gamma}(\mathbf{q})U_{m,\kappa'\alpha}(\mathbf{q})\right)}_{\text{Debye-Waller (DW) within RIA}}.$$



Fan DW

ZPR of diamond using Abinit

The ZPR of the direct bandgap of diamond converges to 409 meV but integration over **q**-grid requires a huge sampling.



See S. Poncé *et al.*, Comput. Mater. Sci. **83**, 341 (2014)

Non rigid-ion (NRIA) terms

$$\frac{\partial \varepsilon_{n\mathbf{k}}^{\mathrm{DW_{NRIA}}}}{\partial n_{m\mathbf{q}}} = \frac{1}{2\omega_{m\mathbf{q}}} \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} \left(\mathcal{D}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}) U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}) - \frac{1}{2} \mathcal{D}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{\Gamma}) \left(U^*_{m,\kappa\gamma}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}) + U^*_{m,\kappa'\gamma}(\mathbf{q}) U_{m,\kappa'\alpha}(\mathbf{q}) \right) \right)$$

with the DW term

$$\mathcal{D}_{\substack{\kappa\alpha \\ \kappa'\gamma}}(\mathbf{q}) \triangleq \left\langle u^{(0)}_{n\mathbf{k}} \middle| \frac{\partial^2 \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(-\mathbf{q}) \partial R_{\kappa'\gamma}(\mathbf{q})} \middle| u^{(0)}_{n\mathbf{k}} \right\rangle$$

Temperature-dependence from FP

$$\Delta\varepsilon_{n\mathbf{k}}(T) = \frac{1}{N_q}\sum_{\mathbf{q}}\sum_{m}^{3N}\frac{\partial\varepsilon_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}}\left(n_{m\mathbf{q}}(T)+\frac{1}{2}\right)$$

$$\frac{\partial\varepsilon_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} = \frac{1}{2\omega_{m\mathbf{q}}}\left(\frac{\partial^2}{\partial h^2}\varepsilon_{n\mathbf{k}}\left[\left\{R_{l\kappa'\alpha}+hv_{lm,\kappa'\alpha}(\mathbf{q})\right\}\right]\Big|_{h=0} + \frac{\partial^2}{\partial h^2}\varepsilon_{n\mathbf{k}}\left[\left\{R_{l\kappa'\alpha}+hw_{lm,\kappa'\alpha}(\mathbf{q})\right\}\right]\Big|_{h=0}\right)$$

The NRIA contribution can be computed separately using FP, knowing that

$$\frac{\partial\varepsilon_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} = \frac{\partial\varepsilon_{n\mathbf{k}}^{\mathrm{FAN}}}{\partial n_{m\mathbf{q}}} + \frac{\partial\varepsilon_{n\mathbf{k}}^{\mathrm{DW_{RIA}}}}{\partial n_{m\mathbf{q}}} + \frac{\partial\varepsilon_{n\mathbf{k}}^{\mathrm{DW_{NRIA}}}}{\partial n_{m\mathbf{q}}}$$

$$\frac{\partial\varepsilon_{n\mathbf{k}}^{\mathrm{DW_{NRIA}}}}{\partial n_{m\mathbf{q}}} = \frac{1}{2\omega_{m\mathbf{q}}}\left(\frac{\partial^2}{\partial h^2}\left\langle u_{n\mathbf{k}}^{(0)}\middle|\hat{H}_{\mathbf{k},\mathbf{k}}\left[\left\{R_{l\kappa'\alpha}+hv_{lm,\kappa'\alpha}(\mathbf{q})\right\}\right]+\hat{H}_{\mathbf{k},\mathbf{k}}\left[\left\{R_{l\kappa'\alpha}+hw_{lm,\kappa'\alpha}(\mathbf{q})\right\}\right]\middle|u_{n\mathbf{k}}^{(0)}\right\rangle\Big|_{h=0}\right.$$
$$\left. - \sum_{\gamma}\frac{\partial^2}{\partial S_\gamma\,\partial T_\gamma}\left\langle u_{n\mathbf{k}}^{(0)}\middle|\hat{V}_{\mathrm{Hxc}}\left[\left\{R_{l\kappa'\alpha}+S_\gamma U^*_{m,\kappa'\gamma}(\mathbf{q})U_{m,\kappa'\alpha}(\mathbf{q})+T_\gamma\delta_{\alpha\gamma}\right\}\right]\middle|u_{n\mathbf{k}}^{(0)}\right\rangle\Big|_{S_\gamma,T_\gamma=0}\right),$$

Comparison between the AHC/DFPT and FP results for molecules

NRIA terms are huge in molecules

		sum AHC Ha/bohr^2	DW_{NRIA} Ha/bohr^2	% NRIA	sum both Ha/bohr^2	FP Ha/bohr^2	diff. μHa/bohr^2
H_2	HOMO	−0.153 779	0.083 466	119	−0.070 313	−0.070 309	−4.2
	LUMO	−0.003 850	0.005 431	343	0.001 581	0.001 582	1.0
N_2	HOMO	−0.143 439	0.124 889	673	−0.018 550	−0.018 829	278.6
	LUMO	0.123 029	0.096 733	44	0.219 763	0.219 772	−9.6
CO	HOMO	−0.012 869	0.057 711	129	0.044 842	0.044 824	17.6
	LUMO	0.085 389	0.072 238	46	0.157 627	0.157 548	79.0
LiF	HOMO	−0.039 611	0.010 832	38	−0.028 779	−0.028 437	−341.6
	LUMO	−0.001 811	−0.003 308	65	−0.005 119	−0.005 144	24.7

X. Gonze *et al.* Ann. Phys. **523**, 168 (2011)

Comparison between the AHC/DFPT and FP results for diamond

NRIA terms are much smaller in solids

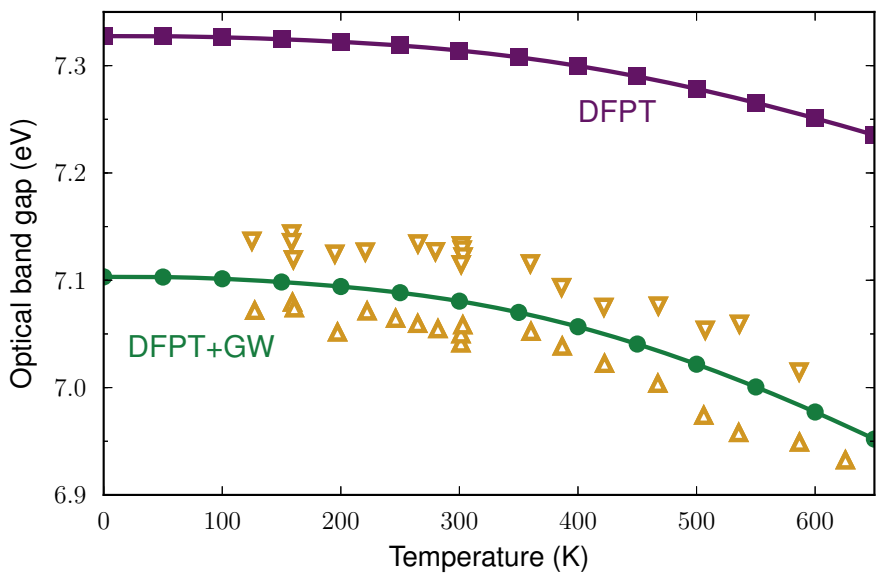
		AHC [meV]			NRIA [meV]		sum all	FP	diff.
q	k	Fan	DW_{RIA}	sumAHC	DW_{NRIA}	% NRIA	[meV]	[meV]	[μeV]
Γ	Γ_1	−32.817	20.287	−12.531	1.450	13.09	−11.081	−11.081	0.308
	$\Gamma_{25'}$	−332.426	357.256	24.830	3.598	12.66	28.428	28.429	−0.638
	Γ_{15}	−330.436	316.202	−14.234	0.385	2.78	−13.849	−13.850	0.338
	$\Gamma_{2'}$	−63.309	32.376	−30.933	0.300	0.98	−30.633	−30.633	0.748
	$L_{2'}$	−67.860	46.878	−20.981	2.282	12.20	−18.699	−18.700	0.554
	L_1	−146.081	129.477	−16.604	1.133	7.32	−15.471	−15.471	0.367
	$L_{3'}$	−311.231	321.329	10.098	2.961	22.67	13.059	13.059	−0.307
	L_3	−473.011	292.467	−180.546	0.156	0.09	−180.390	−180.394	6.977
L	Γ_1	−116.428	62.697	−53.731	0.907	1.72	−52.826	−52.824	1.104
	$\Gamma_{25'}$	−922.824	1104.105	181.281	2.295	1.25	183.576	183.577	−1.017
	Γ_{15}	−1250.808	977.226	−273.582	−1.006	0.37	−274.588	−274.588	0.244
	$\Gamma_{2'}$	−407.602	100.058	−307.544	−1.848	0.60	−309.392	−309.397	5.131
	$L_{2'}$	−234.235	144.878	−89.357	1.486	1.69	−87.871	−87.873	1.542
	L_1	−620.707	400.150	−220.557	0.507	0.23	−220.050	−220.052	2.359
	$L_{3'}$	−1018.979	993.070	−25.909	1.742	7.21	−24.167	−24.167	−0.210
	L_3	−740.682	903.868	163.186	−1.093	0.67	162.093	162.093	−0.142

See S. Poncé *et al.*, Comput. Mater. Sci. **83**, 341 (2014)

ZPR of diamond using Abinit

The Abinit results with AHC do not reproduce experiment well ... and it should not !

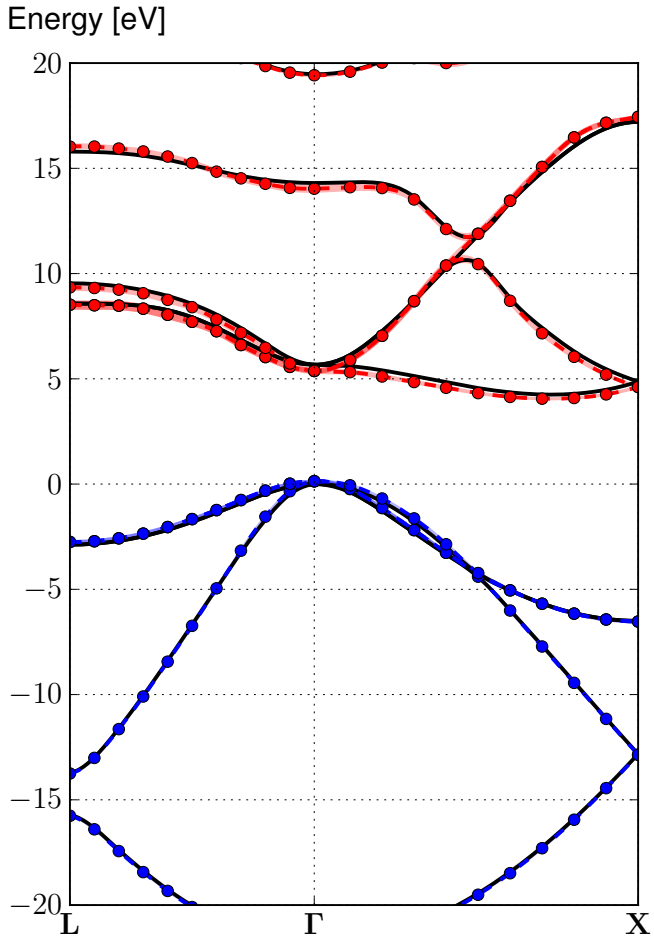
- Calculation made on a 32x32x32 **q**-grid with DFPT AHC leads to -404 meV gap renormalization.
- Many-body G_0W_0 correction: -209 meV on the ZPM



See G. Antonius *et al.* Phys. Rev. Lett. **112**, 215501 (2014)

The renormalized electronic bandstructure of diamond

- The non-adiabatic ZPR is integrated over a 55x55x55 **q**-point grid (4060 qpt in IBZ) with $i\delta = 10\ meV$
- Abinit-7.10.x can now compute:
  - the static ZPR (AHC)
  - the non-adiabatic ZPR
  - the phonon-induced lifetime broadening in the static limit
  - the temperature-dependence of all the above-mentioned quantities



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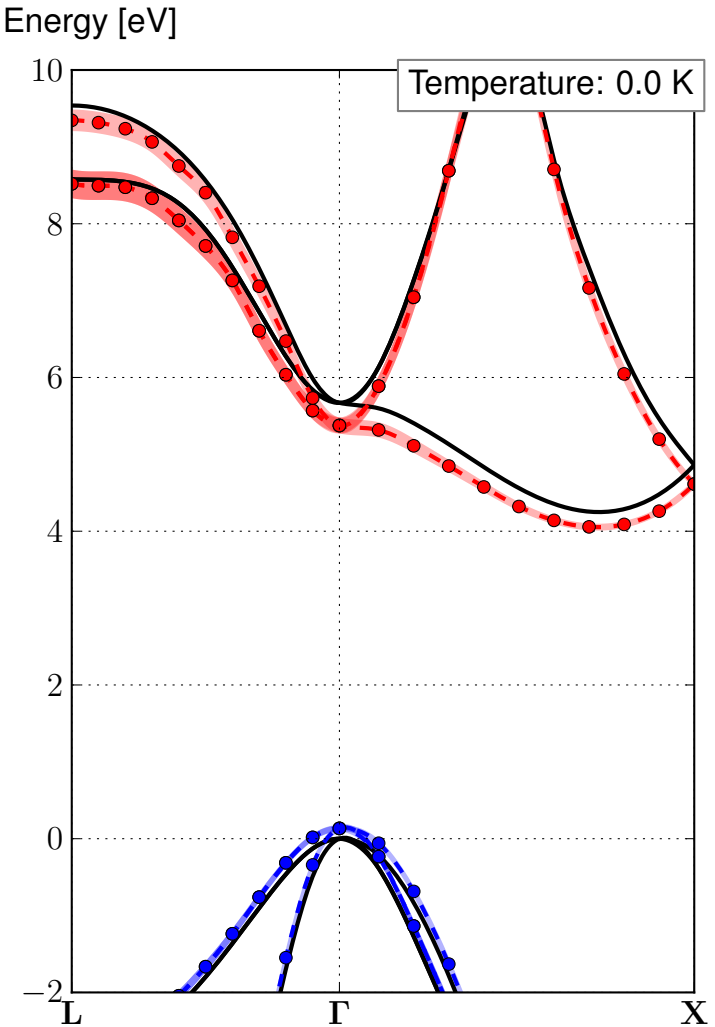

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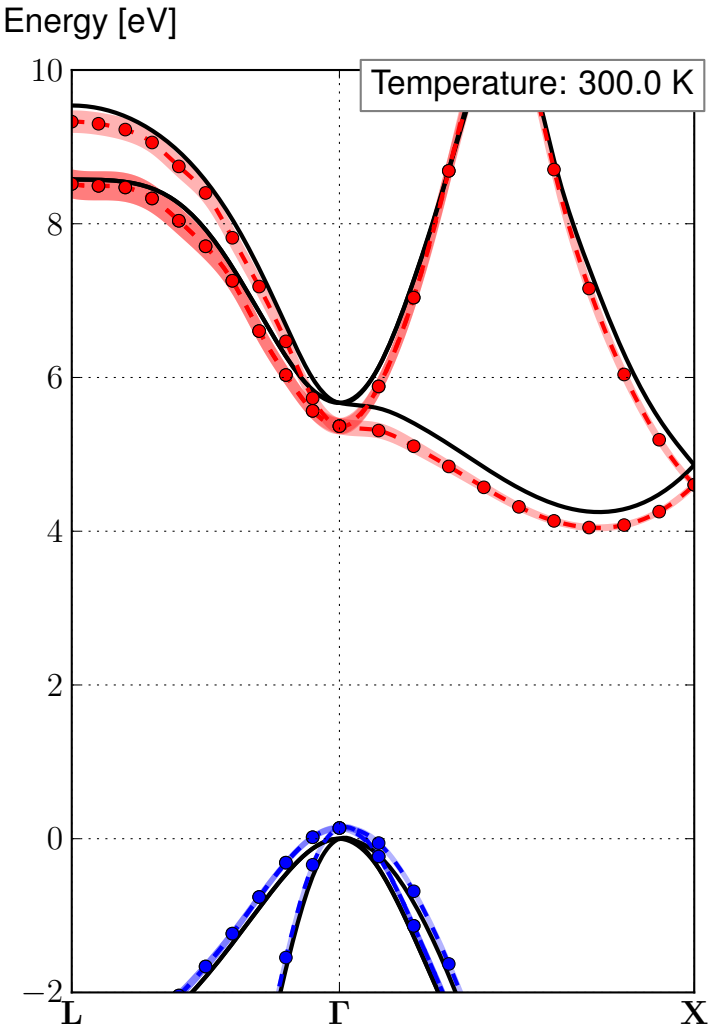

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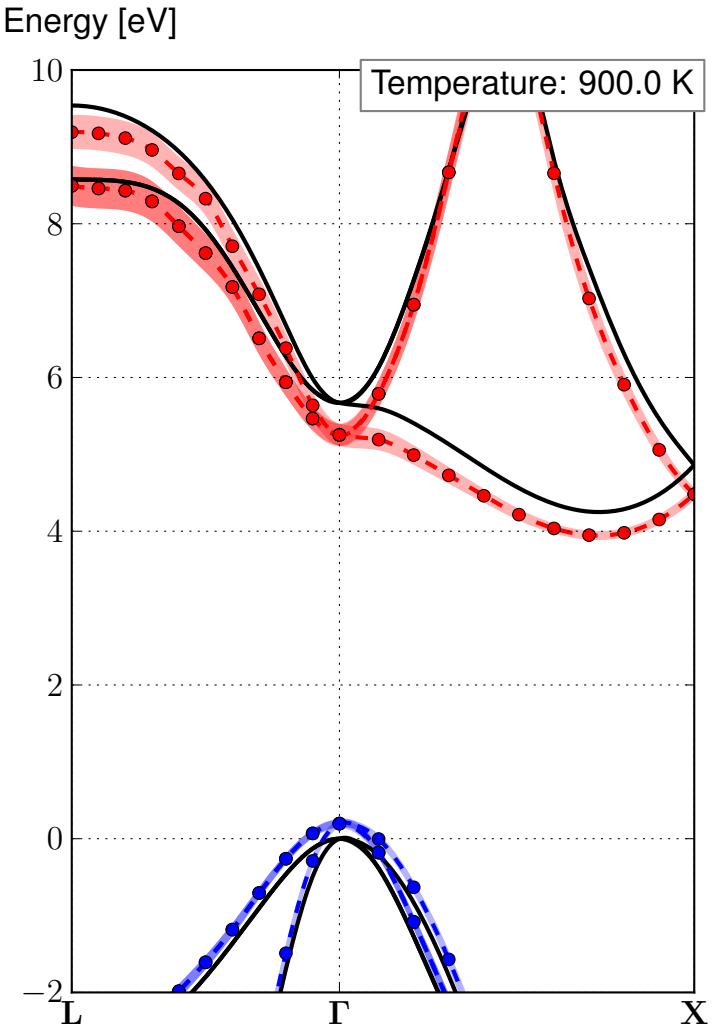

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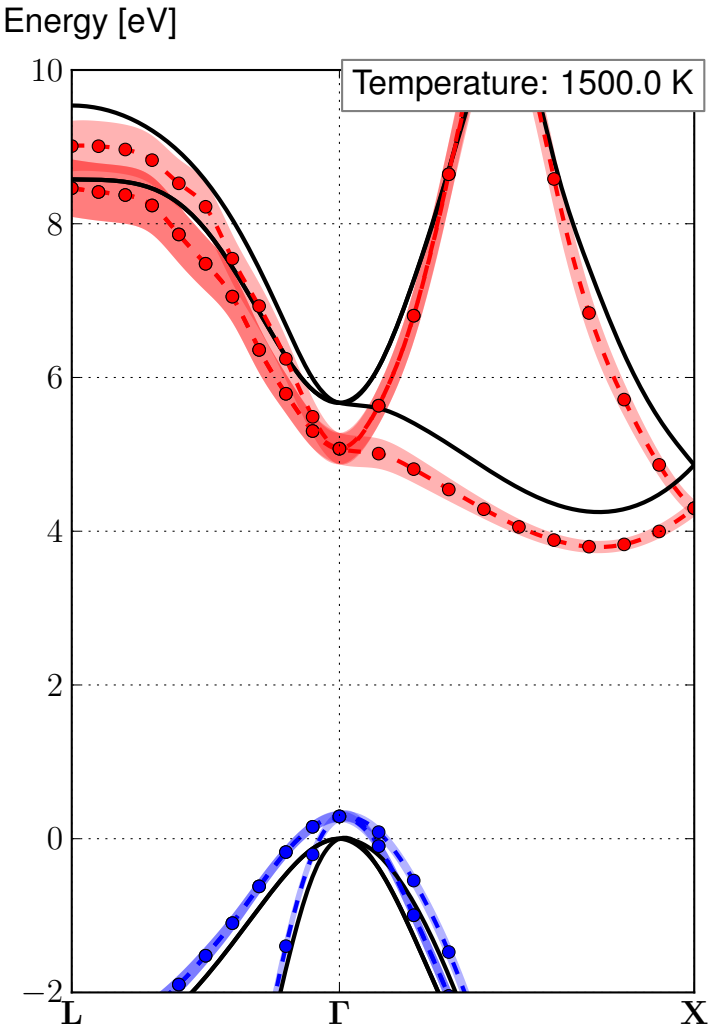
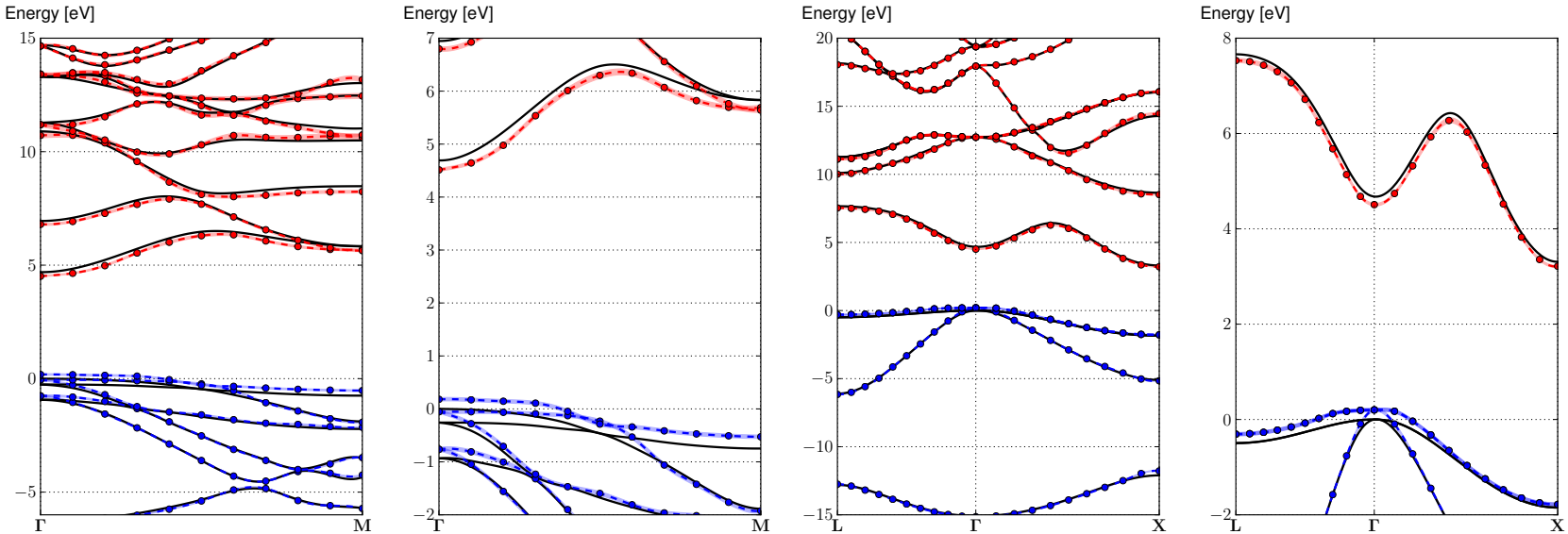


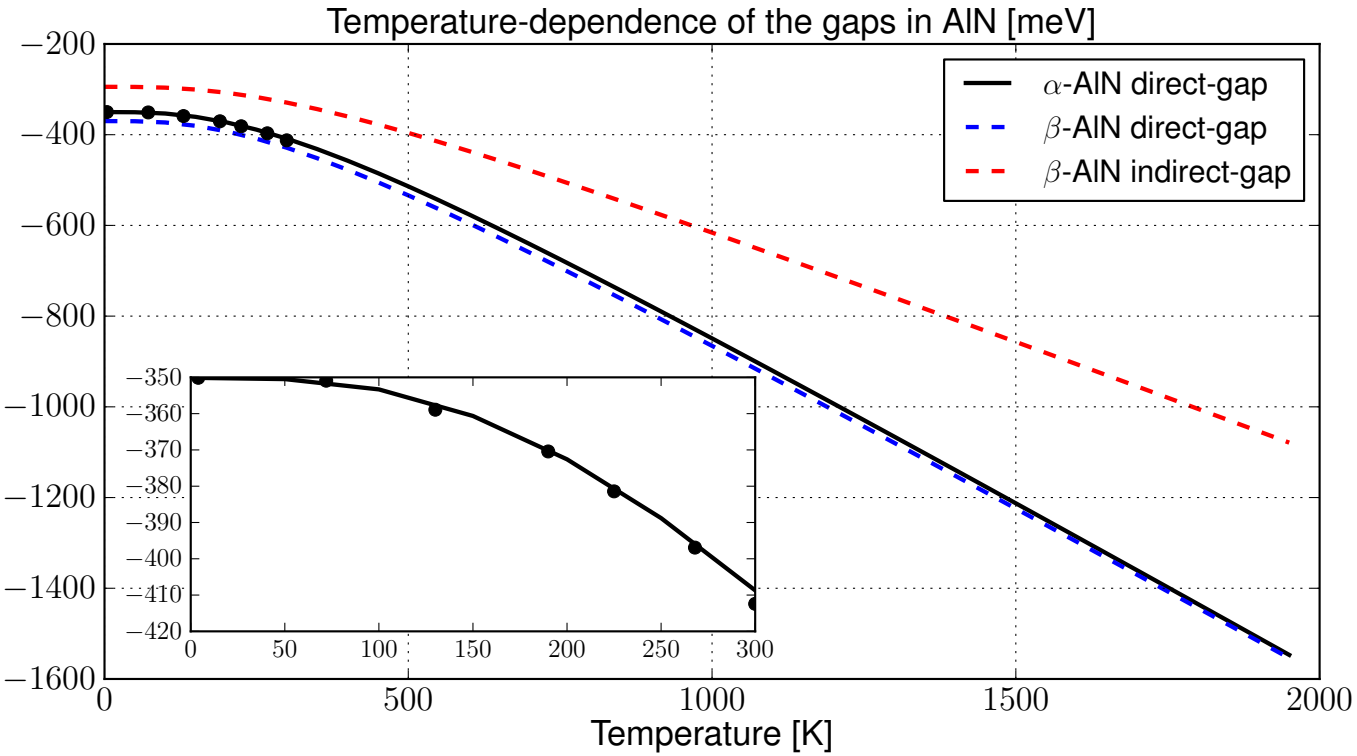
BS of α- and β-Aluminum Nitride



α-AlN at 0K. Zoom. β-AlN at 0K. Zoom.

Figure : Electronic bandstructure (plain black line), renormalisation (dashed line) and phonon-induced broadening (envelope around the dashed line) at 0 K for the AlN phases, where the dots are the actual renormalization calculation. The non-adiabatic ZPR is integrated on a (a) 26x26x26 **q**-point grid ($i\delta$=10 meV) and on a (c) 63x63x63 **q**-point grid ($i\delta$=50 meV).

Temperature dependence in α- and β-Aluminum Nitride

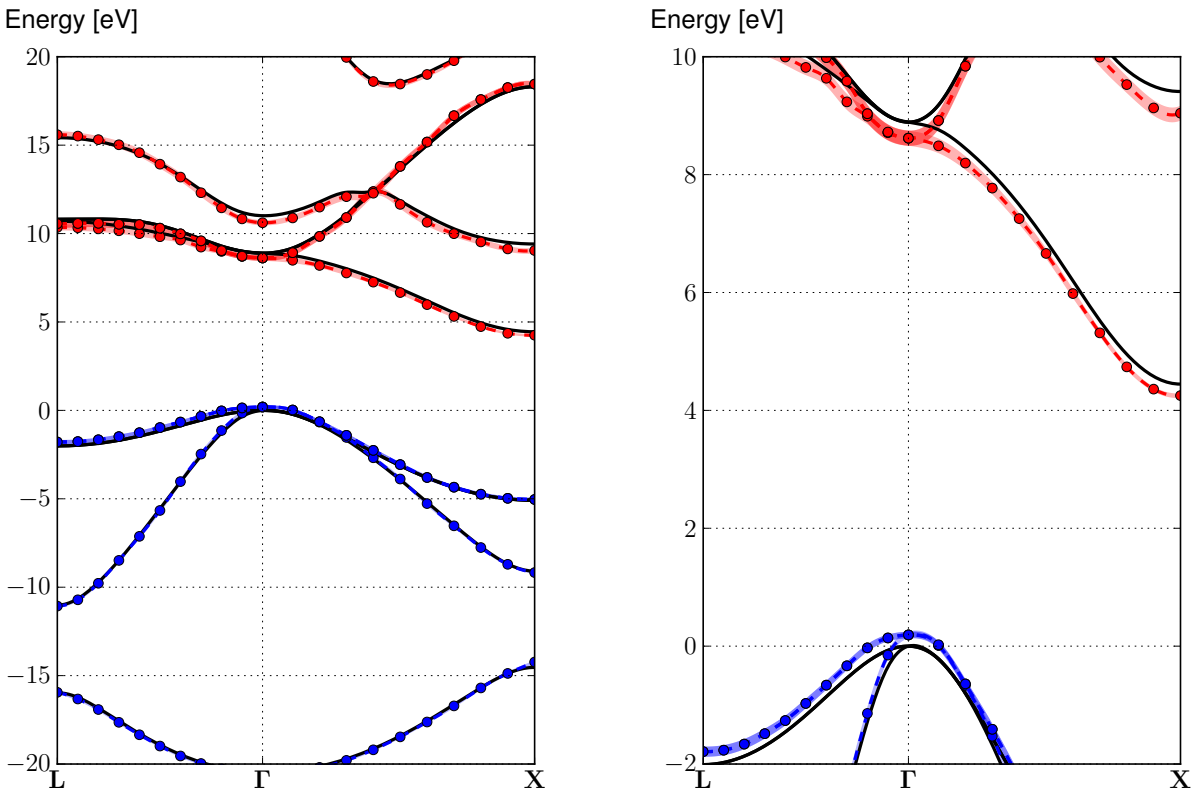


Exp. are shifted to match with the theoretical one at 4 K.

- The slopes at high temperature are -0.74, -0.49 and -0.73 meV/K for the direct gap of α-AlN, the indirect bandgap of β-AlN and the direct bandgap of β-AlN, respectively.

Exp: D. Brunner *et al.*, J. Appl. Phys. **82**, 5090 (1997).

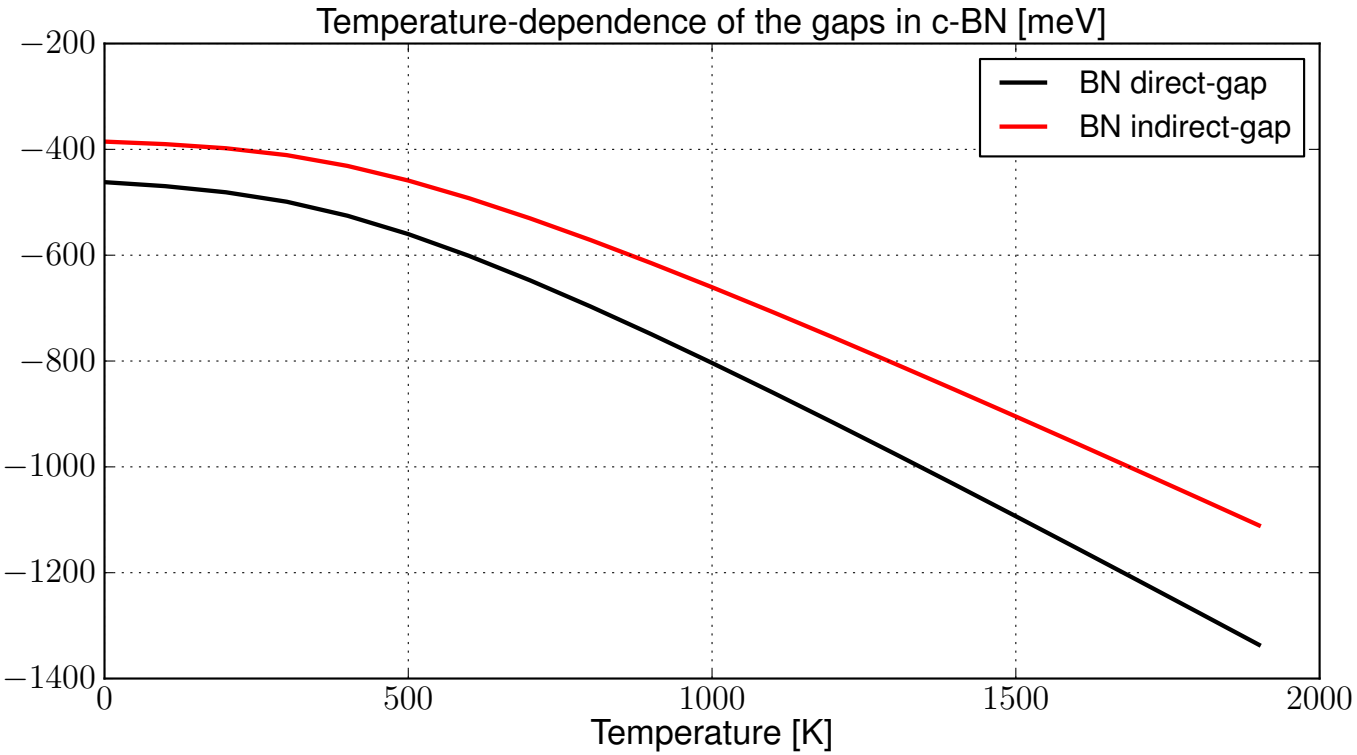
BS of cubic Boron Nitride



c-BN at 0K. Zoom.

Figure : Electronic bandstructure (plain black line), renormalisation (dashed line) and phonon-induced broadening (envelope around the dashed line) at 0K using the non-adiabatic ZPR integrated on a 63x63x63 **q**-point grid ($i\delta$=10 meV) for c-BN, where the dots are the actual renormalization calculation.

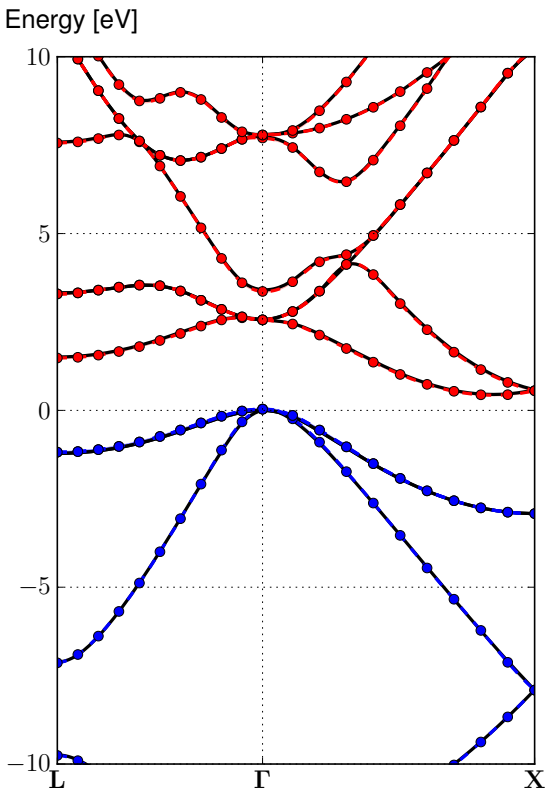
Temperature dependence in cubic Boron Nitride



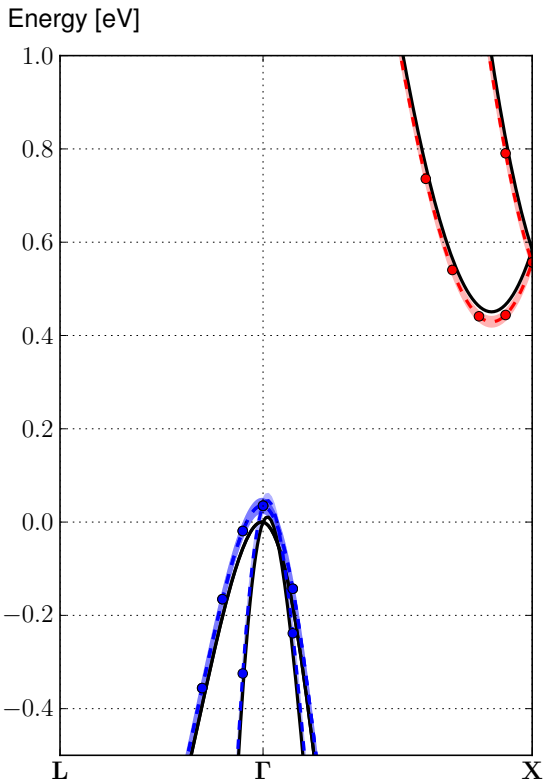
No experiment !

- The slopes at high temperature is -0.59 meV/K for the direct gap of c-BN and -0.50 meV/K for the indirect one.

BS of cubic Silicon



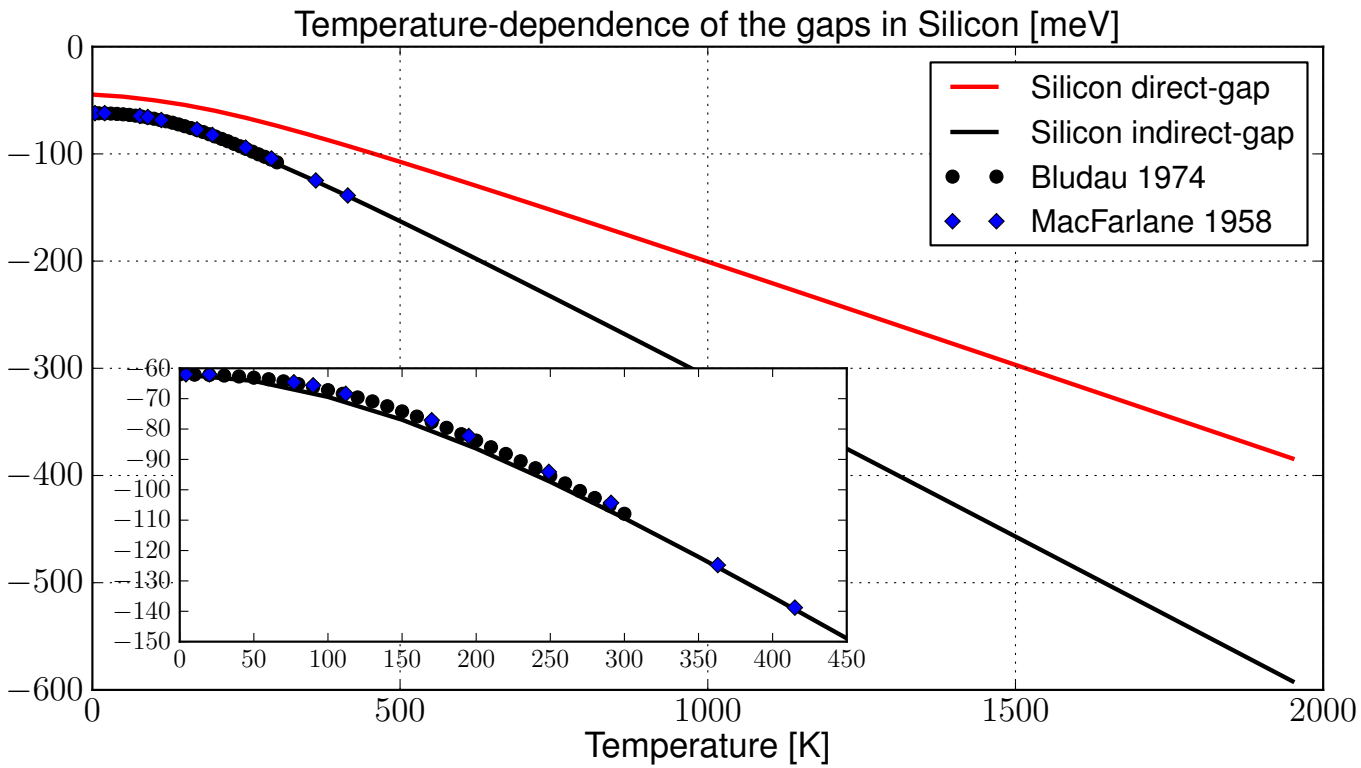
Silicon at 0K.



Zoom.

Figure : Electronic bandstructure (plain black line), renormalisation (dashed line) and phonon-induced broadening (envelope around the dashed line) at 0K using the non-adiabatic ZPR integrated on a 55x55x55 **q**-point grid ($i\delta$=10 meV) for silicon, where the dots are the actual renormalization calculation.

Temperature dependence in Silicon



Exp. are shifted to match with the theoretical one at 4 K.

- The slopes at high temperature is -0.19 meV/K for the direct gap of silicon and -0.30 meV/K for the indirect one.

Exp: W. Bludau *et al.*, J. Appl. Phys. **45**, 1846 (1974).

G. Macfarlane *et al.*, Phys. Rev. **111**, 1245 (1958).

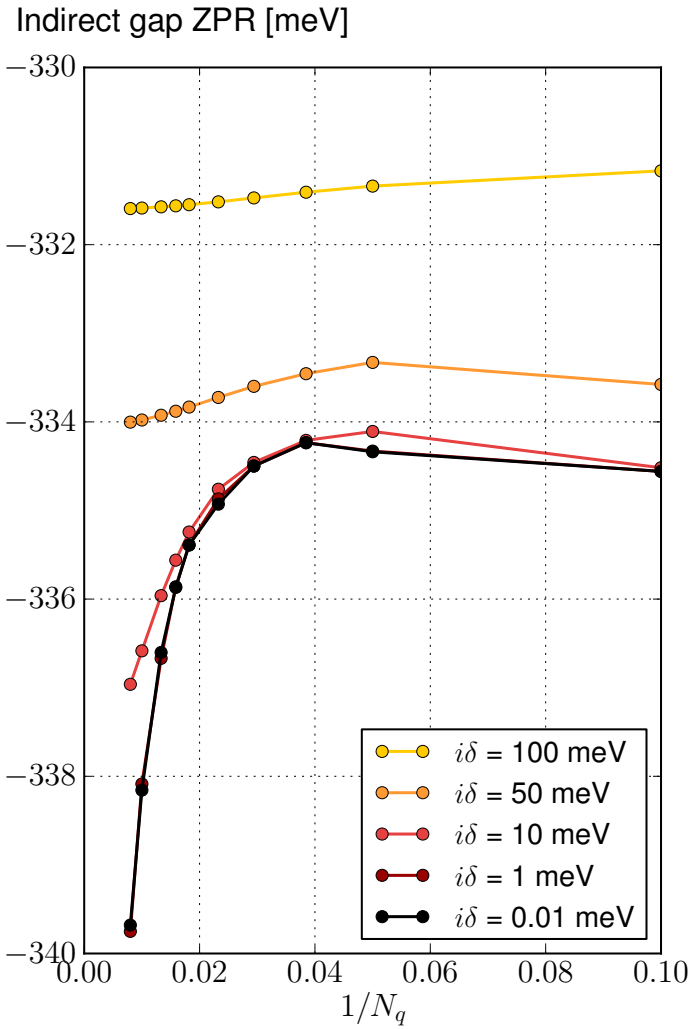
Summary of ZPR

			ZPR [meV]		
	q-grid	Gap	Static	Non-adiabatic	Exp.
α-AlN	34x34x34	$\mathbf{\Gamma} - \mathbf{\Gamma}$	-429±58 (50)	-369 (0.01)	-239
β-AlN	63x63x63	$\mathbf{\Gamma} - \mathbf{\Gamma}$	-427±59 (50)	-386 (10)	
		$\mathbf{\Gamma} - \mathbf{X}$	-352±54 (50)	-311 (0.01)	
$Ba_3Si_6O_{12}N_2$	4x4x4	$\mathbf{\Gamma} - \mathbf{\Gamma}$	-149 (100)	-321 (100)	
		$\mathbf{A} - \mathbf{\Gamma}$	-379 (100)	-330 (100)	
$Ba_3Si_6O_9N_4$	4x4x4	$\mathbf{\Gamma} - \mathbf{\Gamma}$	-129 (100)	-225 (100)	
		$\mathbf{M} - \mathbf{\Gamma}$	-324 (100)	-327 (100)	
c-BN	63x63x63	$\mathbf{\Gamma} - \mathbf{\Gamma}$	-514±157 (50)	-461 (50)	
		$\mathbf{\Gamma} - \mathbf{X}$	-470±67 (50)	-385 (0.01)	
C	125x125x125	$\mathbf{\Gamma} - \mathbf{\Gamma}$	-421±118 (50)	-409 (50)	-320
					-450
		$\mathbf{\Gamma} - \frac{2}{3}\mathbf{X}$	-366±60 (50)	-334 (50)	-364
Si	63x63x63	$\mathbf{\Gamma} - \mathbf{\Gamma}$	-43±26 (50)	-42 (50)	
		$\mathbf{\Gamma} - \frac{2}{3}\mathbf{X}$	-61±30 (50)	-59 (50)	-62
					-64

For experimental ref. see S. Poncé PhD thesis.

Open question: divergence in $\hat{H}^{(1)}_{\mathbf{q}}$

- The indirect bandgap of diamond using non-adiabatic AHC theory diverges with increasing **q**-grid for vanishing $i\delta$.
- Largest **q**-grid is a 125x125x125 one.
- Actually such divergence comes from $\hat{H}^{(1)}_{\mathbf{q}}$.



Open question: divergence in $\varepsilon^{(1)}_{n\mathbf{q}}$

From X. Gonze, Phys. Rev. B **55**, 10337 (1997):

- $H^{(1)}_{\mathbf{q}} = v^{(1)}_{psp,\mathbf{q}} + v^{(1)}_{H,\mathbf{q}} + v^{(1)}_{xc,\mathbf{q}}$.
- Numerical tests on diamond show that both $v^{(1)}_{psp,\mathbf{q}}$ and $v^{(1)}_{H,\mathbf{q}}$ diverge with an opposite sign and that $v^{(1)}_{xc,\mathbf{q}}$ does not.
- The cancellation is not exact for small $\mathbf{q}$ and the sum still diverges.
- $v^{(1)}_{psp,\mathbf{q}}(\mathbf{G}) = \frac{-i}{\Omega_0}(\mathbf{G}+\mathbf{q})_\alpha e^{-i(\mathbf{G}+\mathbf{q})\cdot\tau_\kappa} v^{loc}_\kappa(\mathbf{G}+\mathbf{q})$.
- $v^{loc}_\kappa(\mathbf{K}\to 0) = -\frac{4\pi Z_\kappa}{K^2} + C_\kappa + O(K^2)$.
- $v^{(1)}_{H,\mathbf{q}}(\mathbf{G}) = 4\pi \frac{n^{(1)}_{\mathbf{q}}}{|\mathbf{G}+\mathbf{q}|^2}$ with $n^{(1)}_{\mathbf{q}} \propto \mathbf{q}$.
- How to prove mathematically that the two terms should cancel?
- How to make a Taylor expansion in $\mathbf{q}$ of the two terms to find out if the leading coefficients cancel out?

Conclusions

- 3 methods to compute the ZPR.
- 3 equivalences of the Brook's theorem.
- Verifications & Validation of AHC vs FP.
- The NRIA terms are large in molecules but not so much in solids.
- GW adds a significant electron-phonon coupling contribution.
- New capabilities of Abinit: static & non-adiabatic temp. dep. + static lifetime over BS.
- 5 semiconductors have been studied (α-,β-AlN, C, c-BN, Si)

Theory of bandgap temperature dependence

The Allan-Heine-Cardona (AHC) theory using the translation invariance and the rigid-ion approximation:

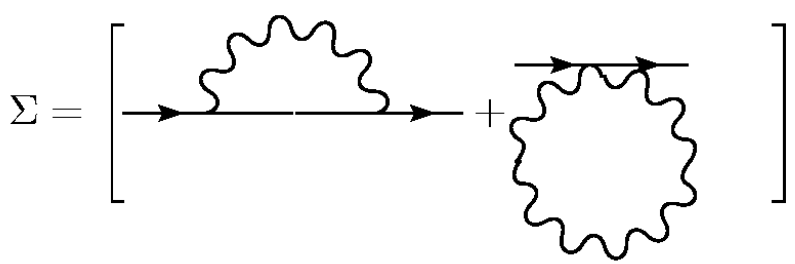
$$\Delta\varepsilon_{n\mathbf{k}}^{(\text{static,RIA})}(T) = \frac{1}{N_q}\sum_{\mathbf{q}}\sum_{m}^{3N}\left(n_{m\mathbf{q}}(T)+\frac{1}{2}\right)\frac{1}{2\omega_{m\mathbf{q}}}\sum_{\substack{\kappa\alpha\\ \kappa'\gamma}}\left[\sum_{n'=1}^{M}{}' \frac{\left\langle u_{n\mathbf{k}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(-\mathbf{q})}\middle|u_{n'\mathbf{k}+\mathbf{q}}^{(0)}\right\rangle\left\langle u_{n'\mathbf{k}+\mathbf{q}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle}{\varepsilon_{n\mathbf{k}}^{(0)}-\varepsilon_{n'\mathbf{k}+\mathbf{q}}^{(0)}+i\delta}\right.$$

$$\left.+\left\langle P_{c\mathbf{k}+\mathbf{q}}\frac{\partial u_{n\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{q})}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle\right]U_{m,\kappa'\gamma}^{*}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q}) - \frac{1}{2}\left[\sum_{n'=1}^{M}{}' \frac{\left\langle u_{n\mathbf{k}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{\Gamma})}\middle|u_{n'\mathbf{k}}^{(0)}\right\rangle\left\langle u_{n'\mathbf{k}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{\Gamma})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle}{\varepsilon_{n\mathbf{k}}^{(0)}-\varepsilon_{n'\mathbf{k}}^{(0)}+i\delta}\right.$$

$$\left.+\left\langle P_{c\mathbf{k}}\frac{\partial u_{n\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{\Gamma})}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{\Gamma})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle\right]\left(U_{m,\kappa\gamma}^{*}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})+U_{m,\kappa'\gamma}^{*}(\mathbf{q})U_{m,\kappa'\alpha}(\mathbf{q})\right).$$

Fan

Diagonal Debye-Waller (DDW) within RIA



Fan DDW

Dynamical Fan self-energy beyond the Rayleigh-Schrödinger perturbation theory

$$\Delta\varepsilon_{n\mathbf{k}}^{(\text{non-adiabatic,RIA})}(T) = \Re\frac{1}{N_q}\sum_{\mathbf{q}}\sum_{m}^{3N}\frac{1}{2\omega_{m\mathbf{q}}}\sum_{\substack{\kappa\alpha\\ \kappa'\gamma}}$$

$$\left[\sum_{n'=1}^{M}\left\langle u_{n\mathbf{k}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(-\mathbf{q})}\middle|u_{n'\mathbf{k}+\mathbf{q}}^{(0)}\right\rangle\left\langle u_{n'\mathbf{k}+\mathbf{q}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle\right.$$

$$\left(\frac{n_{m\mathbf{q}}(T)+f_{n'\mathbf{k}+\mathbf{q}}}{\omega-\varepsilon_{n'\mathbf{k}+\mathbf{q}}^{(0)}+\omega_{m\mathbf{q}}(T)+i\delta\,\mathrm{sgn}(\varepsilon_{n\mathbf{k}})}+\frac{n_{m\mathbf{q}}(T)+1-f_{n'\mathbf{k}+\mathbf{q}}}{\omega-\varepsilon_{n'\mathbf{k}+\mathbf{q}}^{(0)}-\omega_{m\mathbf{q}}+i\delta\,\mathrm{sgn}(\varepsilon_{n\mathbf{k}})}\right)$$

$$\left.+\left\langle P_{c\mathbf{k}+\mathbf{q}}\frac{\partial u_{n\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{q})}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle\left(n_{m\mathbf{q}}(T)+\frac{1}{2}\right)\right]$$

$$U_{m,\kappa'\gamma}^{*}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})$$

$$-\frac{1}{2}\left[\sum_{n'=1}^{M}\frac{\left\langle u_{n\mathbf{k}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{\Gamma})}\middle|u_{n'\mathbf{k}}^{(0)}\right\rangle\left\langle u_{n'\mathbf{k}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{\Gamma})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle}{\varepsilon_{n\mathbf{k}}^{(0)}-\varepsilon_{n'\mathbf{k}}^{(0)}+i\delta}\right.$$

$$\left.\left.+\left\langle P_{c\mathbf{k}}\frac{\partial u_{n\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{\Gamma})}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{\Gamma})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle\right]\left(U_{m,\kappa\gamma}^{*}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})+U_{m,\kappa'\gamma}^{*}(\mathbf{q})U_{m,\kappa'\alpha}(\mathbf{q})\right),$$

Phonon-induced lifetime broadening in the adiabatic limit

By taking the adiabatic limit ($\omega_{m\mathbf{q}} << \omega - \varepsilon_{n'\mathbf{k}+\mathbf{q}}$) of the imaginary part of the previous equation, we obtain

$$\frac{1}{2\tau_{n\mathbf{k}}^{(\text{static,RIA})}} = \frac{\pi}{N_q} \sum_{\mathbf{q}} \sum_{m}^{3N} \frac{1}{2\omega_{m\mathbf{q}}} \left(n_{m\mathbf{q}}(T) + \frac{1}{2} \right) \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} \sum_{n'=1}^{M}{}' \left\langle u_{n\mathbf{k}}^{(0)} \middle| \frac{\partial \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(-\mathbf{q})} \middle| u_{n'\mathbf{k}+\mathbf{q}}^{(0)} \right\rangle \left\langle u_{n'\mathbf{k}+\mathbf{q}}^{(0)} \middle| \frac{\partial \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})} \middle| u_{n\mathbf{k}}^{(0)} \right\rangle \delta(\varepsilon_{n\mathbf{k}}^{(0)} - \varepsilon_{n'\mathbf{k}+\mathbf{q}}^{(0)}) U_{m,\kappa'\gamma}^{*}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}).$$