Electronic structure of solids : temperature dependence and zero-point motion effect

X. Gonze, Université catholique de Louvain, Belgium

Collaborators :
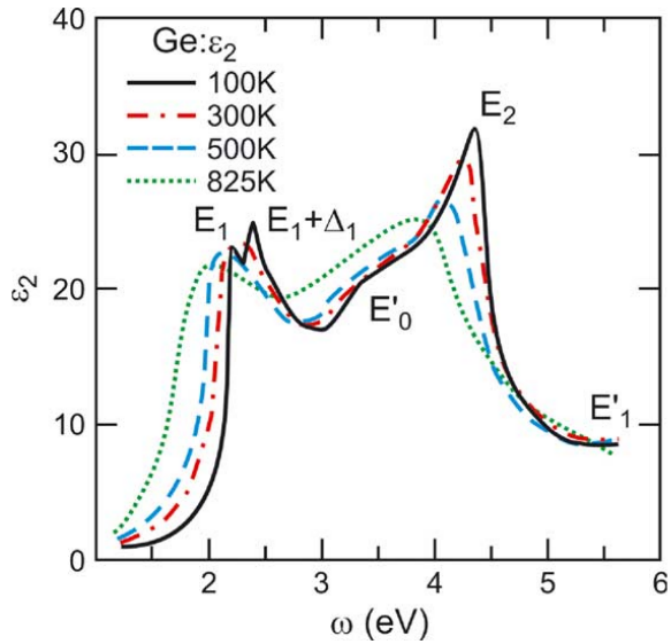S. Poncé, Y. Gillet, J. Laflamme, U.C. Louvain, Belgium
G. Antonius, M. Côté, U. de Montréal, Canada
A. Marini, CNR Italy
P. Boulanger, CEA Grenoble

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Temperature dependence of electronic/optical properties
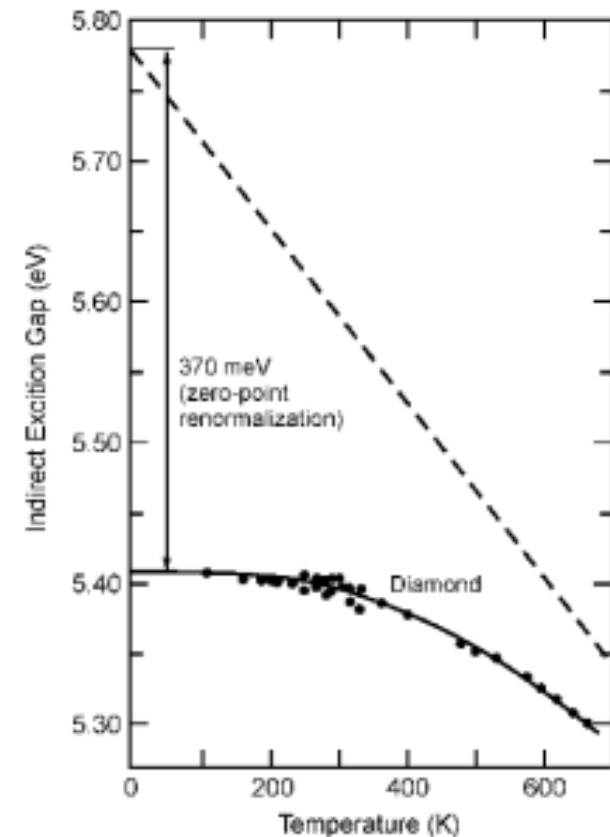

L. Viña, S. Logothetidis and M. Cardona,
Phys. Rev. B **30**, 1979 (1984)

- peaks shift in energy
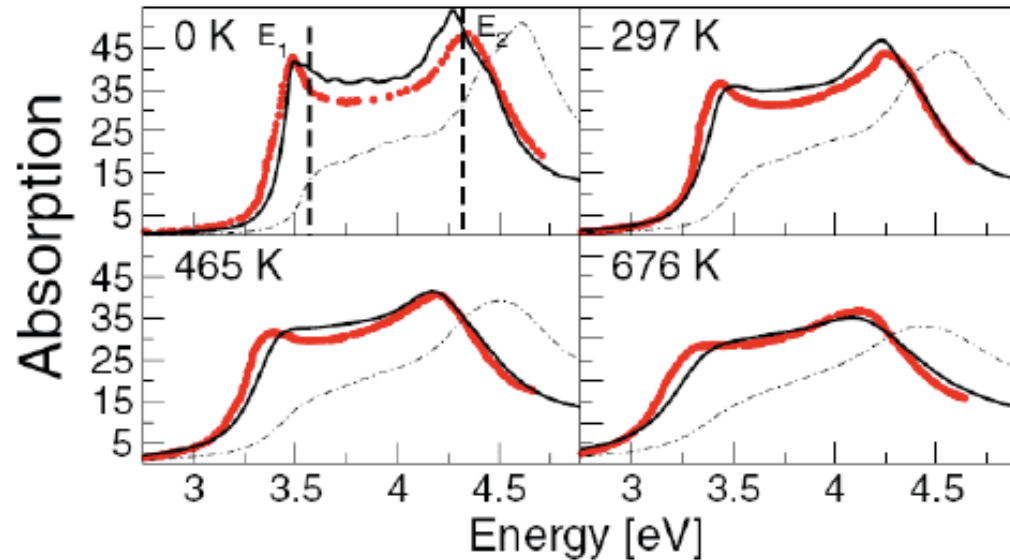- peaks broaden with increasing temperature : decreased electron lifetime

- even at 0K, vibrational effects are important, due to Zero-Point Motion

Usually, not taken into account in First-principles calculations !

M. Cardona, *Solid State Comm.* **133**, 3 (2005)

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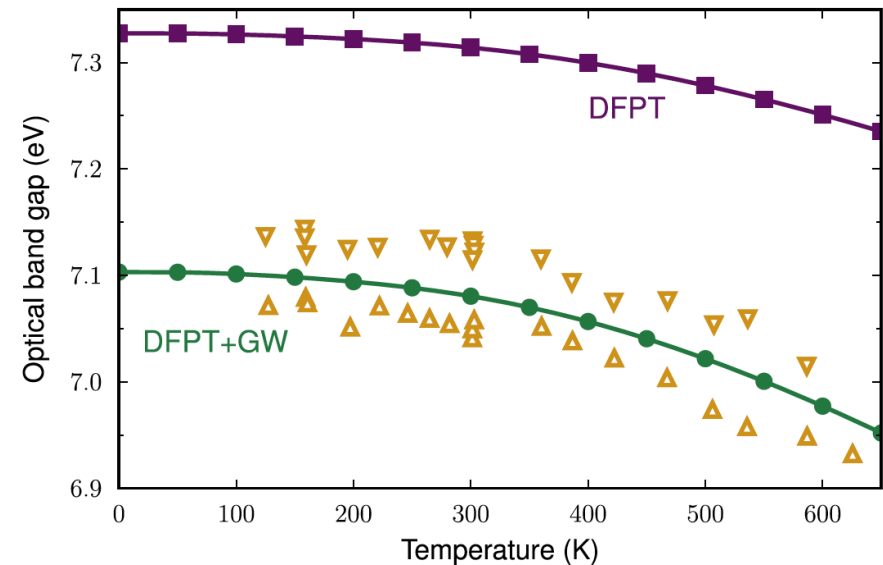# Allen-Heine-Cardona theory + first-principles

A. Marini, *Physical Review Letters* 101, 106405 (2008)

Optical absorption of Silicon.
Excellent agremeent with Exp.
Mostly broadening effect,
imaginary part of the Fan term
(not discussed in this talk)

Diamond Zero-point motion
in DFT : 0.4 eV for the direct gap

Diamond Zero-point motion
in DFT+GW : 0.63 eV for the direct gap,
in agreement with experiments

G. Antonius, S. Poncé, P. Boulanger, M. Côté & XG, Phys. Rev. Lett. 112, 215501 (2014)

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Overview

1. Motivation
2. Thermal expansion and phonon population effects
3. Ab initio Allen-Heine-Cardona (AHC) theory
4. Temperature effects with GW electronic structure
5. Breakdown of the adiabatic AHC theory
   for infra-red active materials
6. Many-body perturbation theory with vibrational effects

References :

(1) X. Gonze, P. Boulanger and M. Côté, *Ann. Phys* 523, 168 (2011)
(2) S. Poncé *et al, Comput. Materials Science* 83, 341 (2014)
(3) G. Antonius, S. Poncé, P. Boulanger, M. Côté and X. Gonze, *Phys. Rev. Lett.*112, 215501 (2014)
(4) S. Poncé *et al, Phys. Rev. B*. 90, 214304 (2014)
(5) A. Marini, S. Poncé and X. Gonze, *Phys. Rev. B* 91, 224310 (2015)
(6) S. Poncé *et al, J. Phys. Chem* 143, 102813 (2015)
(7) G. Antonius *et al, Phys. Rev. B* 92, 085137 (2015)
(8) XG et al , Comput. Phys. Comm. 205, 106 (2016)

Note : For the assessment of the size rigid-ion effects, not mentioned in this talk, see (1) and (4)

Thermal expansion and phonon population effects

Divide and conquer …

Constant-pressure temperature dependence of the electronic eigenenergies : two contributions

$$\left(\frac{\partial \varepsilon_{n\vec{k}}}{\partial T}\right)_P = \boxed{\left(\frac{\partial \varepsilon_{n\vec{k}}}{\partial T}\right)_V} + \boxed{\left(\frac{\partial \varepsilon_{n\vec{k}}}{\partial \ln V}\right)_T} \left(\frac{\partial \ln V}{\partial T}\right)_P$$

Constant volume

Constant temperature

$= \alpha_P(T)$

Thermal expansion coefficient

Contribution of the phonon population, i.e. the vibrations of the atomic nuclei, at constant volume
+
Contribution of the thermal expansion, i.e. the change in volume of the sample, at constant temperature

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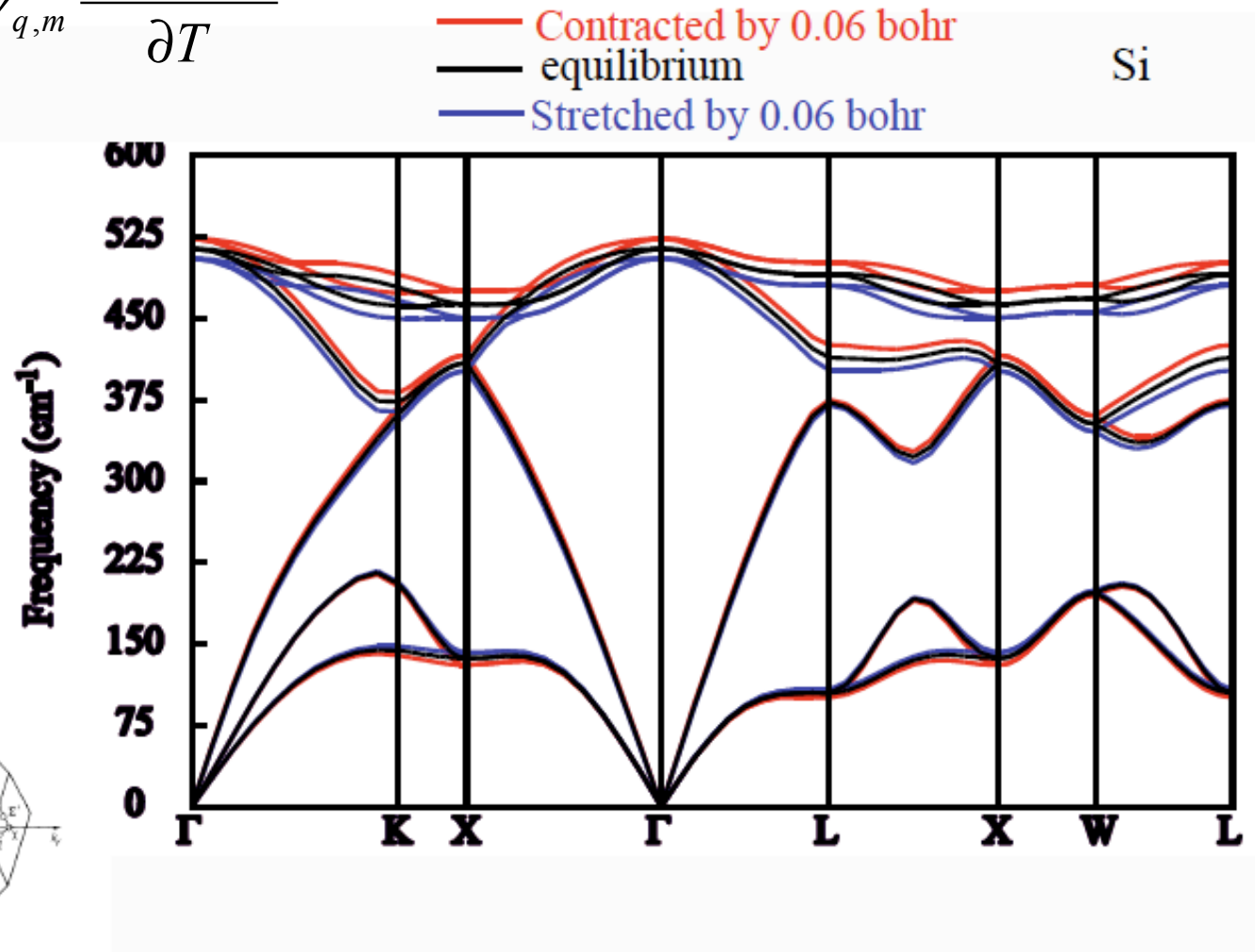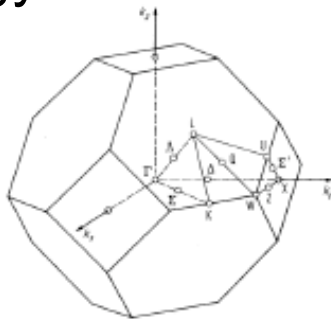Université catholique de Louvain

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Ab initio thermal expansion

$$\alpha(T) = \frac{V}{3B} \sum_{q,m} \frac{1}{\omega_{q,m}} \gamma_{q,m} \frac{\partial n(\omega_{q,m})}{\partial T}$$

Mode-Grüneisen parameters

$$\gamma_{m,q} = -\frac{\partial(\ln \omega_{m,q})}{\partial(\ln V)}$$

Alternative path : minimisation of free energy

Contracted by 0.06 bohr
equilibrium
Stretched by 0.06 bohr

Si

Ab initio thermal expansion

Linear thermal expansion coefficient of bulk silicon
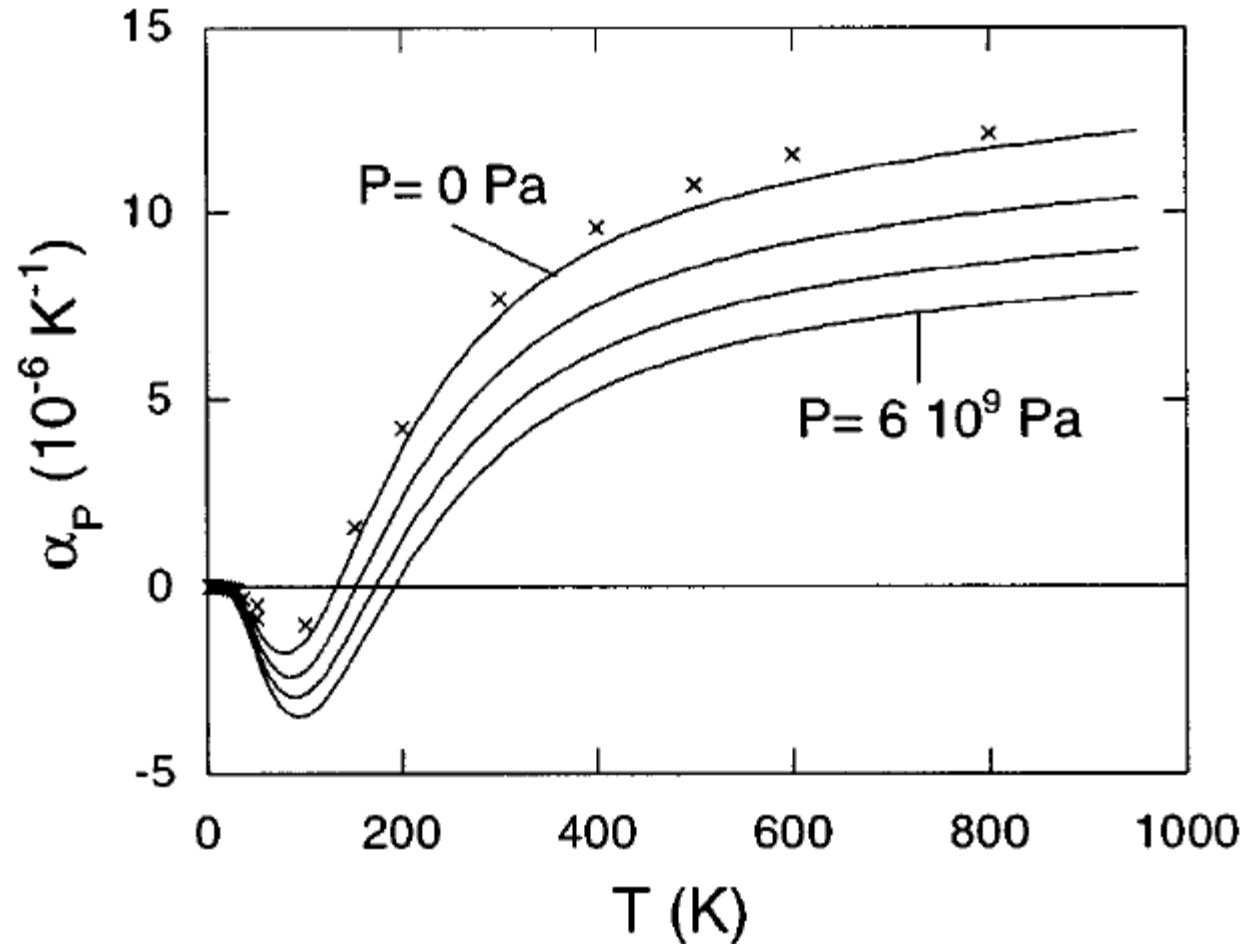
G.-M. Rignanese, J.-P. Michenaud and XG *Phys. Rev. B* 53, 4488 (1996)

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Thermal expansion contribution to the gap of Si

- Calculation
* Exp

y-axis: $-\Delta\varepsilon_{gap}$ (eV)
x-axis: Temperature (K)
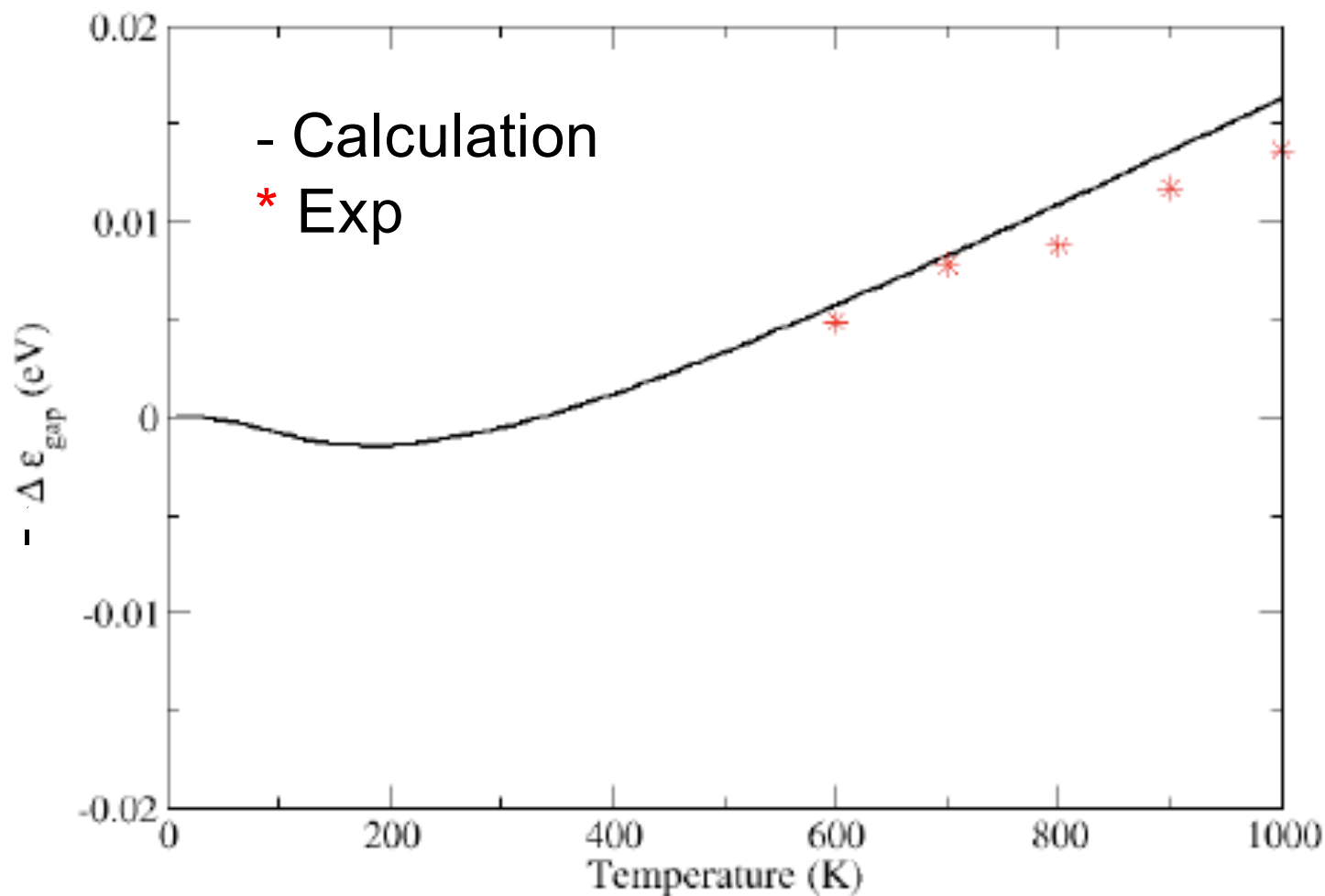
But **total** exper. change between 0K and 300K = 0.06 eV !
...Thermal expansion contribution is negligible (for Si) ...

Phonon population effects

Different levels of approximation :

-dynamics of the nuclei … classical … quantum ?

-harmonic treatment of vibrations or anharmonicities ?

-adiabatic decoupling of nuclei and electronic dynamic, or non-adiabatic corrections ?

-independent electronic quasi-particles (DFT or GW), or many-body approach with spectral functions ?

… At least 5 first-principle methodologies :

(1) Time-average

(2) Thermal average

(3) Harmonic approximation + thermal average

(4) Diagrammatic approach (Allen-Heine-Cardona)

(5) Exact factorization (H. Gross and co-workers)

Nuclear dynamics : dimers

Diatomic molecules = simplest system to study temperature dependence of eigenvalues.

- discrete levels, well described with the theory of the molecular orbitals
- only one relevant vibration mode.
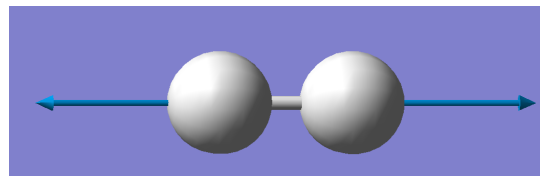
(6 modes decouple as 3 translations, 2 rotations + the stretch.)

Average eigenenergies in the BO approx.

Variation of the HOMO energy wrt bond length

Electronic eigenenergies,
function of the bond length $\varepsilon_n(\Delta R)$ =>

(1) Time-average of eigenenergies
from Molecular Dynamics trajectories,
$\Delta R(t)$ at average T, with

$$\varepsilon_n(T) = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} \varepsilon_n(\Delta R(t))\, dt$$

Pros : well-defined procedure ; compatible with current implementations
and computing capabilities ; $\varepsilon_n(\Delta R(t))$ from DFT or GW ;
anharmonicities
Cons : if classical dynamics => no zero-point motion ; adiabatic
(vibrations, but no exchange of energy !) ; hard for solids (supercell)
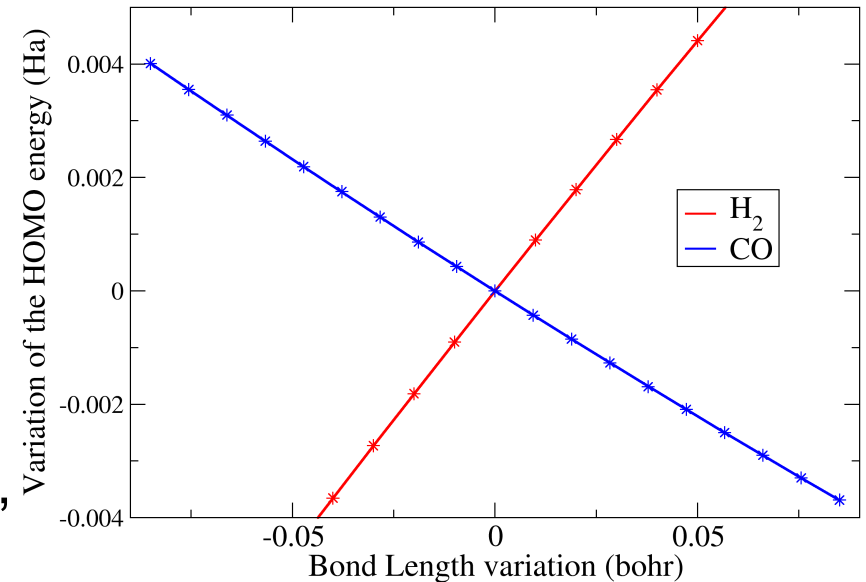
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Average eigenenergies in the BO approx.

Variation of the HOMO energy wrt bond length

Electronic eigenenergies function of the bond length $\varepsilon_n(\Delta R)$

(2) Thermal average with accurate quantum vibrational states,

$$\varepsilon_n(T) = \frac{1}{Z} \sum_m e^{-\frac{E_{ph}(m)}{k_B T}} \left(\int \chi_m^*(\Delta R) \varepsilon_n(\Delta R) \chi_m(\Delta R) d\Delta R \right) \qquad Z = \sum_m e^{-\frac{E_{ph}(m)}{k_B T}}$$

Pros : zero-point motion ; $\varepsilon_n(\Delta R(t))$ from DFT or GW ; anharmonicities

Cons : hard to sample more than a few vibrational degrees of freedom ; adiabatic (vibrations, but no exchange of energy !)
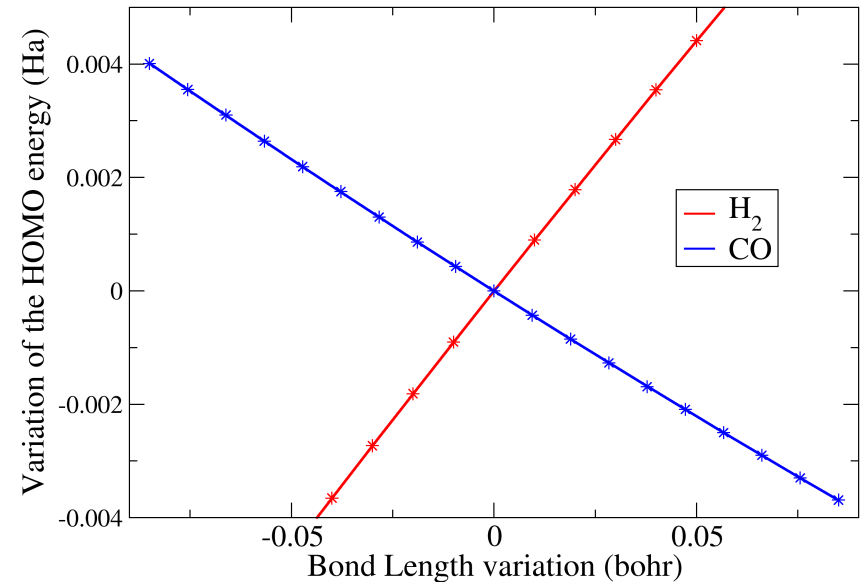
Average eigenenergies : BO and harmonic approx.

(3) Thermal average with quantum vibrational states in the harmonic approximation, and expansion of $\varepsilon_n(\Delta R)$ to second order

$$E_{ph}(m) = \hbar\omega(m + \frac{1}{2})$$

$$n_{vib}(T) = \frac{1}{e^{-\frac{\hbar\omega}{k_B T}} - 1}$$

T-dependent phonon occupation number (Bose-Einstein)

$$\varepsilon_n = \varepsilon_n^0 + \frac{\partial \varepsilon_n}{\partial R}\Delta R + \frac{1}{2}\frac{\partial^2 \varepsilon_n}{\partial R^2}\Delta R^2$$

$$\delta\varepsilon_n(T) = \frac{\partial \varepsilon_n}{\partial n_{vib}}\left(n_{vib}(T) + \frac{1}{2}\right)$$

Pros : zero-point motion ; $\varepsilon_n(\Delta R)$ from DFT or GW ; tractable … for molecules …

Cons : hard for solids (supercells) ; no anharmonicities ; adiabatic (vibrations, but no exchange of energy !)

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Ab initio Allen-Heine-Cardona theory

Long history of the theory of T-dependent effects

In a **semi-empirical** context (empirical pseudopotential, tight-binding) ...

Work from the '50 :

H. Y. Fan. Phys. Rev. **78, 808 (1950)** ; **82, 900 (1951)**

E. Antoncik. Czechosl. Journ. Phys. **5, 449 (1955)**. Debye-Waller contribution.

H. Brooks. Adv. Electron **7, 85 (1955)** + Yu (PhD thesis, unpubl., Brooks supervisor)

Fan   Debye-Waller

Within 2nd order perturbation theory treatment

of electron-phonon effect, both contributions are needed (of course !).

Unification by :

Allen + Heine, J. Phys. C **9, 2305 (1976).**

Allen + Cardona, Phys. Rev. B **24, 7479 (1981)** ; **27, 4760 (1983).**

=> the Allen-Heine-Cardona (AHC) theory

Allen-Heine-Cardona (AHC) formalism

Second-order (time-dependent) perturbation theory
(no average contribution from first order)
For solids (phonons have cristalline momentum)

If adiabatic BO ... neglect the phonon frequencies with respect to the electronic gap, no transfer of energy :

$$\delta\varepsilon_{\vec{k}n}(T, V = const) = \frac{1}{N_{\vec{q}}}\sum_{\vec{q}j}\frac{\partial\varepsilon_{\vec{k}n}}{\partial n_{\vec{q}j}}\left(\left\langle\hat{n}_{\vec{q}j}\right\rangle(T) + \frac{1}{2}\right)$$

+ occupation number from Bose-Einstein statistics

$$\frac{\partial\varepsilon_{\vec{k}n}}{\partial n_{\vec{q}j}} = \frac{1}{2\omega_{\vec{q}j}}\sum_{\kappa a\kappa'b}\frac{\partial^2\varepsilon_{\vec{k}n}}{\partial R_{\kappa a}\partial R_{\kappa'b}}\frac{\xi_{\kappa a}(\vec{q}j)\xi_{\kappa'b}(-\vec{q}j)}{\sqrt{M_{\kappa}M_{\kappa'}}}e^{iq.(R_{\kappa'b}-R_{\kappa a})}$$

Electron-phonon coupling energy (EPCE)

"Phonon mode factor"

$\xi_{\kappa a}(\vec{q}j)$ phonon eigenmodes, κ = atom label, a=x, y, or z

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Eigenvalue changes $\left(\dfrac{\partial^2 \varepsilon_{\vec{k}n}}{\partial R_{\kappa a}\partial R_{\kappa' b}}\right)$ **?**

$$\varepsilon_{\vec{k}n} = \left\langle \phi_{\vec{k}n} \left| \hat{H}_{\vec{k}} \right| \phi_{\vec{k}n} \right\rangle \qquad \hat{H} = \hat{T} + \hat{V}_{\text{nucl}} + \int \frac{\rho(r')}{|r-r'|}dr' + \frac{dE_{xc}}{d\rho(r)}$$
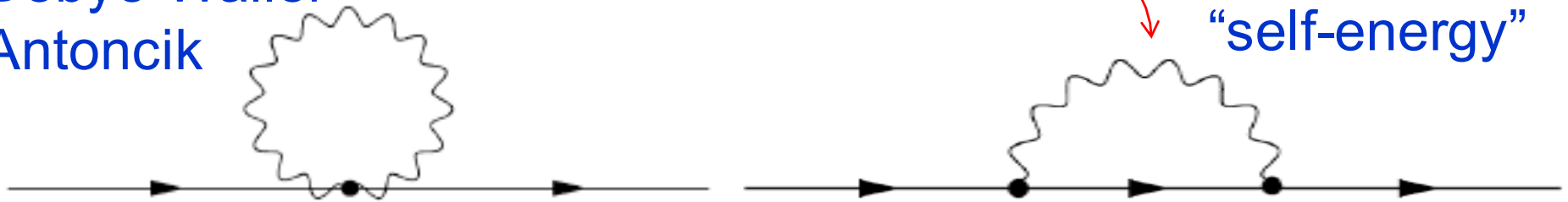
Hellman-Feynman theorem : $\quad \varepsilon_{\vec{k}n}^{(1)} = \left\langle \phi_{\vec{k}n}^{(0)} \left| \hat{H}_{\vec{k}}^{(1)} \right| \phi_{\vec{k}n}^{(0)} \right\rangle$

One more derivative :

$$\varepsilon_{\vec{k}n}^{(2)} = \boxed{\left\langle \phi_{\vec{k}n}^{(0)} \left| \hat{H}_{\vec{k}}^{(2)} \right| \phi_{\vec{k}n}^{(0)} \right\rangle} + \boxed{\frac{1}{2}\left(\left\langle \phi_{\vec{k}n}^{(0)} \left| \hat{H}_{\vec{k}+\vec{q}}^{(1)} \right| \phi_{\vec{k}\vec{q}n}^{(1)} \right\rangle + (c.c) \right)}$$

Debye-Waller
Antoncik

Fan
"self-energy"

In AHC, $\left| \phi_n^{(1)} \right\rangle$ obtained by <u>sum-over-states</u> $\quad \left| \phi_n^{(1)} \right\rangle = \sum_{m \neq n} \left| \phi_m^{(0)} \right\rangle \dfrac{\left\langle \phi_m^{(0)} \left| \hat{H}^{(1)} \right| \phi_n^{(0)} \right\rangle}{\varepsilon_n - \varepsilon_m}$

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Derivatives of the Hamiltonian ?

$$\hat{H} = \hat{T} + \hat{V}_{nucl} + \int \frac{\rho(r')}{|r-r'|} dr' + \frac{dE_{xc}}{d\rho(r)} \qquad \hat{V}_{nucl} = \sum_{\kappa} V_{\kappa}(r-R_{\kappa})$$

In AHC, use of semi-empirical pseudopotential => rigid-ion approximation

Upon infinitesimal displacements of the nuclei,
the rearrangement of electrons due to the perturbation is ignored

$\Rightarrow \hat{H}^{(2)}$ pure site-diagonal ! $\dfrac{\partial^2 \hat{V}_{nucl}}{\partial R_{\kappa a} \partial R_{\kappa' b}} = 0$ for $\kappa \neq \kappa'$

$\Rightarrow$ Debye-Waller contribution pure site-diagonal !

Moreover, invariance under pure translations

$$0 = \varepsilon_n^{(2)} = \left\langle \phi_n^{(0)} \middle| \hat{H}_{transl}^{(2)} \middle| \phi_n^{(0)} \right\rangle + \frac{1}{2}\left(\left\langle \phi_n^{(0)} \middle| \hat{H}_{transl}^{(1)} \middle| \phi_n^{(1)} \right\rangle + (c.c) \right)$$

$\Rightarrow$ Reformulation of the Debye-Waller term.

Ad. AHC = Ad. Fan + rigid-ion Debye-Waller

$$\frac{\partial \varepsilon_{\vec{k}n}}{\partial n_{\vec{q}j}} = \left(\frac{\partial \varepsilon_{\vec{k}n}(Fan)}{\partial n_{\vec{q}j}} \right) + \left(\frac{\partial \varepsilon_{\vec{k}n}(DW^{RIA})}{\partial n_{\vec{q}j}} \right)$$

$$\frac{\partial \varepsilon_{\vec{k}n}(Fan)}{\partial n_{\vec{q}j}} = \frac{1}{\omega_{\vec{q}j}} \Re \sum_{\kappa a \kappa' b n'} \frac{\langle \phi_{\vec{k}n} | \nabla_{\kappa a} H_\kappa | \phi_{\vec{k}+\vec{q}n'} \rangle \langle \phi_{\vec{k}+\vec{q}n'} | \nabla_{\kappa' b} H_{\kappa'} | \phi_{\vec{k}n} \rangle}{\varepsilon_{\vec{k}n} - \varepsilon_{\vec{k}+\vec{q}n'}} \frac{\xi_{\kappa a}(\vec{q}j)\xi_{\kappa' b}(-\vec{q}j)}{\sqrt{M_\kappa M_{\kappa'}}} e^{iq.(R_{\kappa' b} - R_{\kappa a})}$$

$$\frac{\partial \varepsilon_{\vec{k}n}(DW^{RIA})}{\partial n_{\vec{q}j}} = -\frac{1}{\omega_{\vec{q}j}} \Re \sum_{\kappa a \kappa' b n'} \frac{\langle \phi_{\vec{k}n} | \nabla_{\kappa a} H_\kappa | \phi_{\vec{k}n'} \rangle \langle \phi_{\vec{k}n'} | \nabla_{\kappa' b} H_{\kappa'} | \phi_{\vec{k}n} \rangle}{\varepsilon_{\vec{k}n} - \varepsilon_{\vec{k}n'}}$$

$$\times \frac{1}{2} \left(\frac{\xi_{\kappa a}(\vec{q}j)\xi_{\kappa b}(-\vec{q}j)}{M_\kappa} + \frac{\xi_{\kappa' a}(\vec{q}j)\xi_{\kappa' b}(-\vec{q}j)}{M_{\kappa'}} \right)$$

Good : only first-order electron-phonon matrix elements are needed (+ standard ingredients from first-principles phonon/band structure calculations) ; no supercell calculations

Bad : (1) summation over a large number of unoccupied states n'
(2) is the rigid-ion approx. valid for first-principles calculations ?
(3) If first-principles calculations : DFT electron-phonon matrix elements, as well as eigenenergies, while MBPT should be used
(4) Adiabatic approx. : phonon frequencies neglected in denominator

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Implementation

Sum over state present in the AHC formalism, replaced by the use of
Density-Functional Perturbation Theory quantities
=> large gain in speed.

$$\left|\phi_n^{(1)}\right\rangle = \sum_{m\neq n}\left|\phi_m^{(0)}\right\rangle\frac{\left\langle\phi_m^{(0)}\left|\hat{H}^{(1)}\right|\phi_n^{(0)}\right\rangle}{\varepsilon_n - \varepsilon_m}$$

Second-order eigenvalue wrt the maximum band energy
for the HOMO of silicon at Γ

For converged calculations
for silicon :
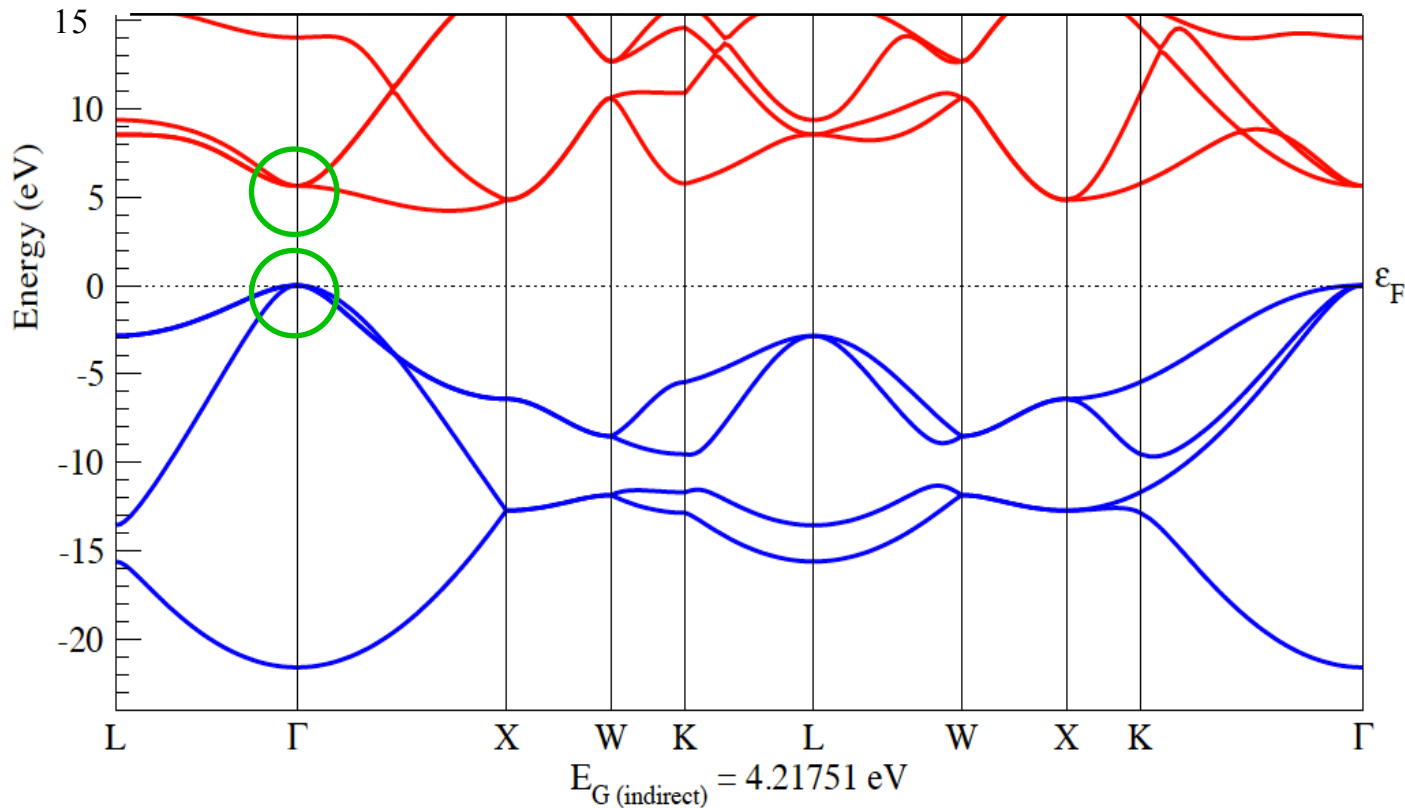   sum over states 125 h
    DFPT   17h
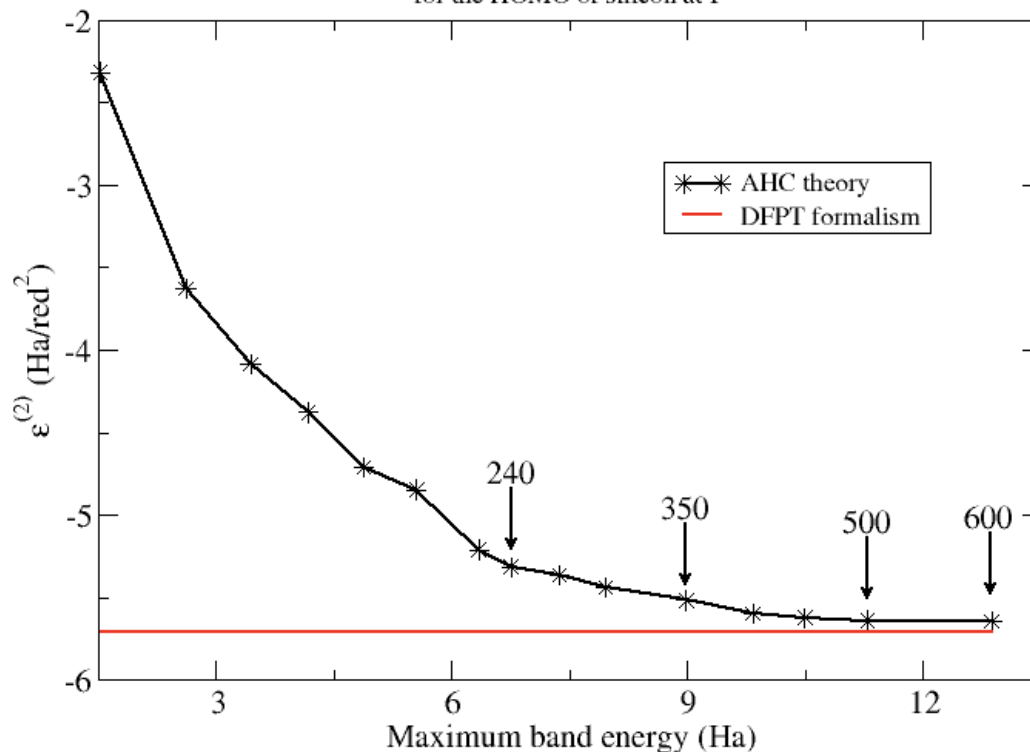
Numerical study : ZPR in diamond

-Implementation in ABINIT (www.abinit.org)
-Plane wave + pseudopotential methodology
-Converged number of plane waves (30 ... 40 Hartree)
-k point sampling : 6x6x6 is sufficient for the generation of the first-order Hamiltonian
-Sampling on the q phonon wavevectors for the Fan term is a big issue !

$$\delta\varepsilon_{\Gamma n}^{ZPM} = \frac{1}{N_{\vec{q}}}\sum_{\vec{q}j}\frac{\partial\varepsilon_{\Gamma n}}{\partial n_{\vec{q}j}}\frac{1}{2}$$

$$\frac{\partial\varepsilon_{\Gamma n}(Fan)}{\partial n_{\vec{q}j}} = \frac{1}{\omega_{\vec{q}j}}\Re\sum_{\kappa a\kappa' b n'}\frac{\langle\phi_{\Gamma n}|\nabla_{\kappa a}H_{\kappa}|\phi_{\vec{q}n'}\rangle\langle\phi_{\vec{q}n'}|\nabla_{\kappa' b}H_{\kappa'}|\phi_{\Gamma n}\rangle}{\varepsilon_{\Gamma n}-\varepsilon_{\vec{q}n'}}\frac{\xi_{\kappa a}(\vec{q}j)\xi_{\kappa' b}(-\vec{q}j)}{\sqrt{M_{\kappa}M_{\kappa'}}}e^{iq.(R_{\kappa' b}-R_{\kappa a})}$$

Indeed (1) interband contributions have strong variations
        (2) intraband contributions diverge due to the denominator !

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Intraband divergence for small q

$E_{G\,(indirect)} = 4.21751$ eV

$$\lim_{\vec{q}\to 0} \frac{\partial \varepsilon_{\Gamma n}(Fan)}{\partial n_{\vec{q}j}} = \lim_{\vec{q}\to 0} \frac{1}{\omega_{\vec{q}j}} \frac{f(\vec{q}jn)}{\varepsilon_{\Gamma n} - \varepsilon_{\vec{q}n}}$$

Optic modes : $\displaystyle\lim_{\vec{q}\to 0} \frac{\partial \varepsilon_{\Gamma n}(Fan)}{\partial n_{\vec{q}j}} \propto \frac{1}{q^2}$

However, for acoustic modes, Fan/DDW contribs cancel each other

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Intraband divergence on isoenergetic surface
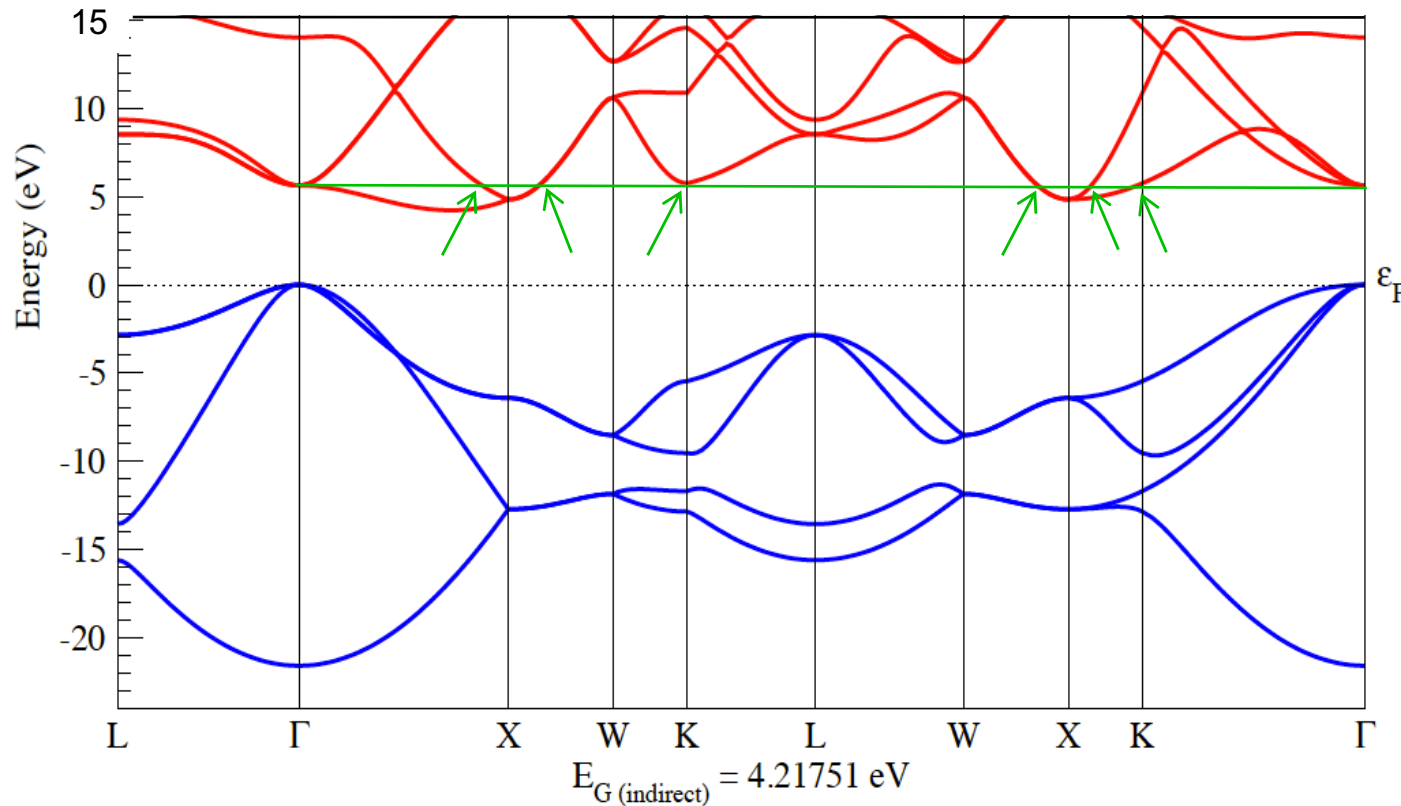
Set of isoenergetic wavevectors

$E_{G \text{ (indirect)}} = 4.21751$ eV

$$\lim_{\vec{q} \to \vec{q}_{iso}} \frac{\partial \varepsilon_{\Gamma n}(Fan)}{\partial n_{\vec{q}j}} = \lim_{\vec{q} \to \vec{q}_{iso}} \frac{1}{\omega_{\vec{q}j}} \frac{f(\vec{q}jn)}{\varepsilon_{\Gamma n} - \varepsilon_{\vec{q}n}} \propto \frac{1}{\nabla_{\vec{q}} \varepsilon_{\vec{q}n}\big|_{\vec{q}_{iso}} . (\vec{q} - \vec{q}_{iso})}$$

Problem only for the ZPR of the conduction state

Phonon wavevector integration

$$\delta \varepsilon_{\vec{k}n}(T, V = const) =$$

$$\frac{1}{N_{\vec{q}}} \sum_{\vec{q}j} \frac{\partial \varepsilon_{\vec{k}n}}{\partial n_{\vec{q}j}} \left(\langle \hat{n}_{\vec{q}j} \rangle (T) + \frac{1}{2} \right)$$

G. Antonius, S. Poncé, P. Boulanger,
M. Côté & XG,
Phys. Rev. Lett. 112, 215501 (2014)

Bottom of conduction Band at Gamma

Top of valence band

Legend:
— Perturbative DFT
● Finite differences

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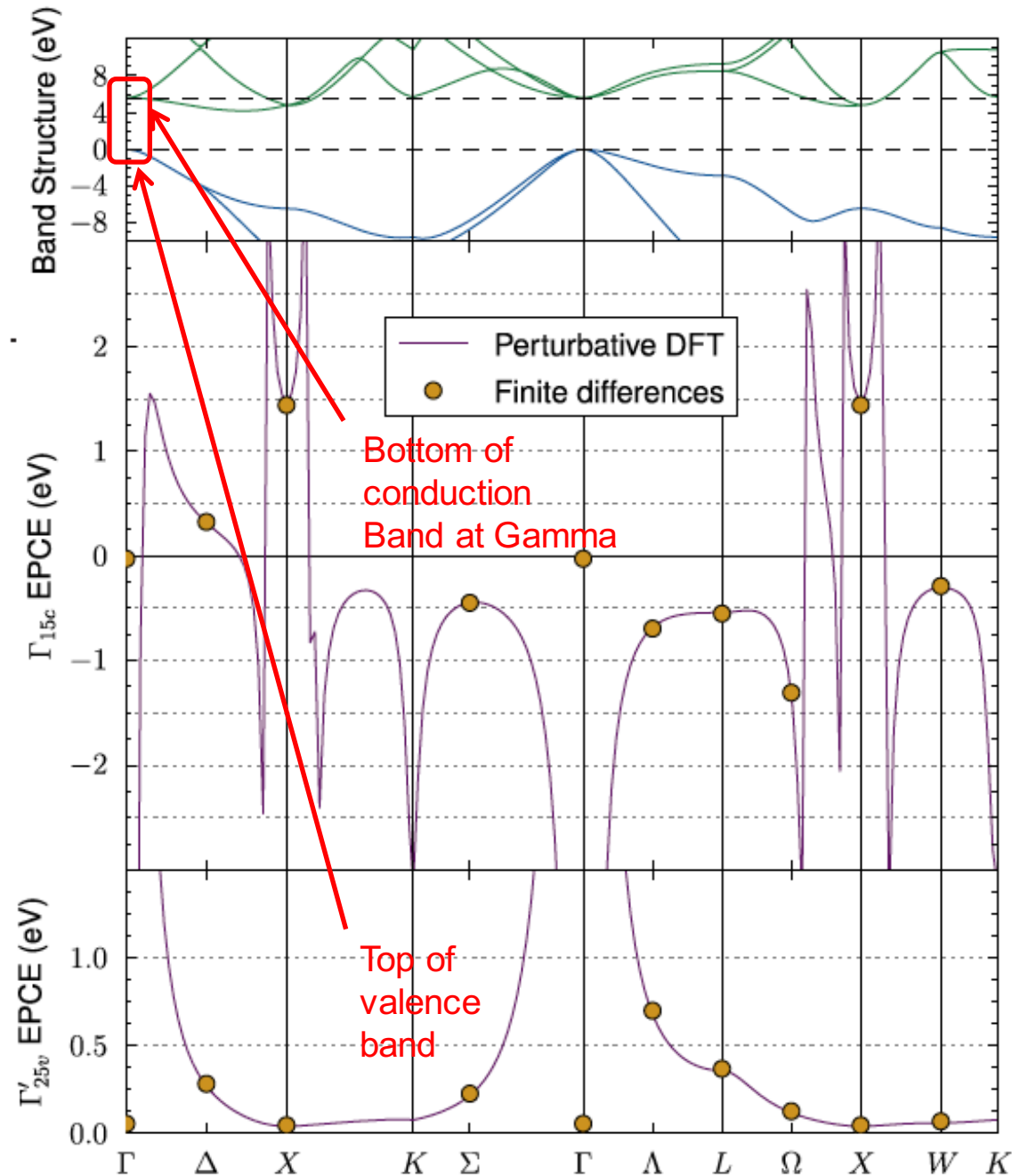
Rate of convergence
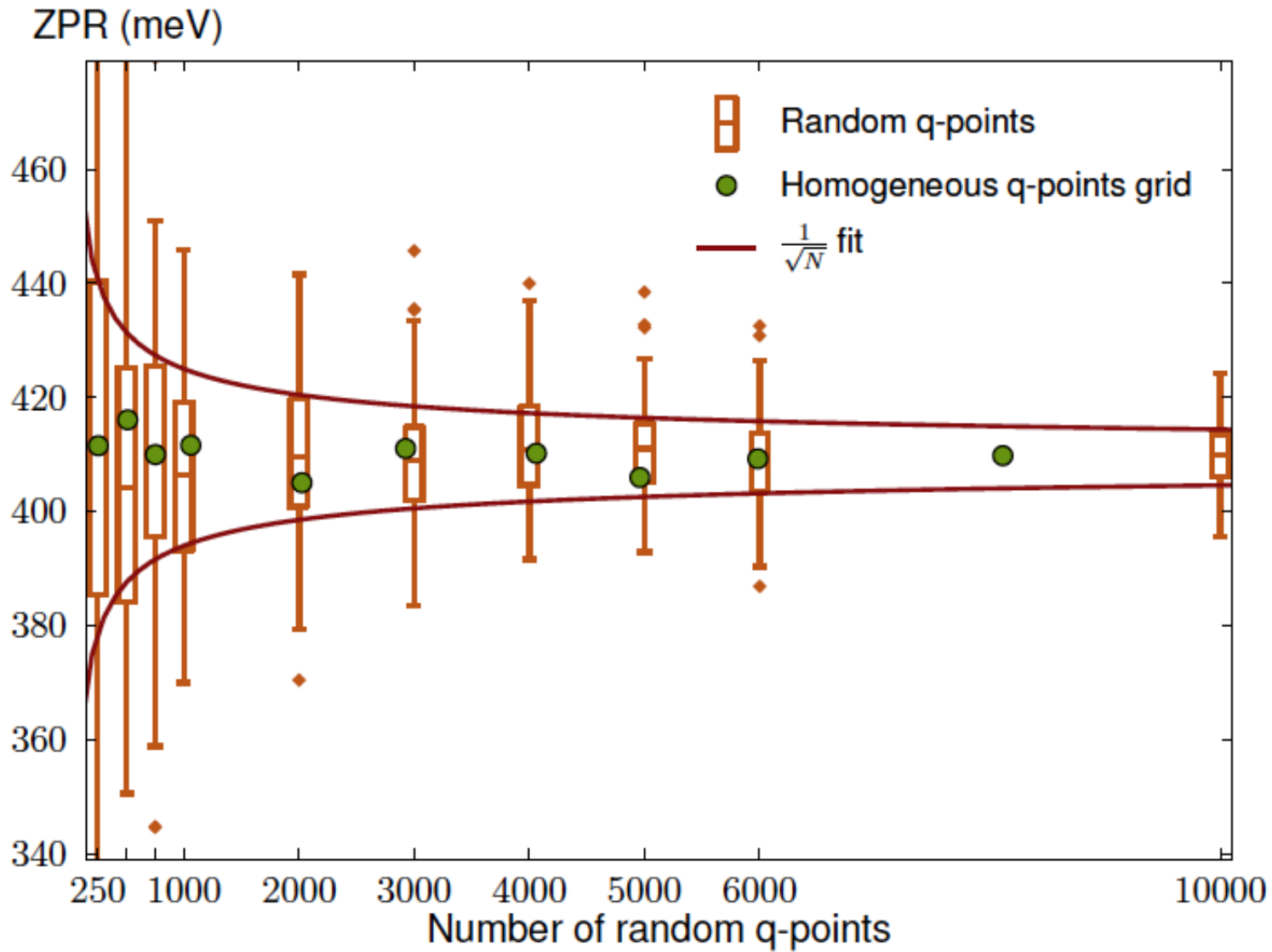
S. Poncé *et al, Comput. Materials Science* 83, 341 (2014)

Smoothing the denominator

$$\frac{\partial \varepsilon_{\Gamma n}(Fan)}{\partial n_{\vec{q}j}} = \frac{1}{\omega_{\vec{q}j}} \Re \sum_{\kappa a \kappa' b n'} \frac{\langle \phi_{\Gamma n} | \nabla_{\kappa a} H_\kappa | \phi_{\vec{q}n'} \rangle \langle \phi_{\vec{q}n'} | \nabla_{\kappa' b} H_{\kappa'} | \phi_{\Gamma n} \rangle}{\varepsilon_{\Gamma n} - \varepsilon_{\vec{q}n'} \boxed{+ i\delta}} \frac{\xi_{\kappa a}(\vec{q}j)\xi_{\kappa' b}(-\vec{q}j)}{\sqrt{M_\kappa M_{\kappa'}}} e^{iq.(R_{\kappa' b} - R_{\kappa a})}$$

... dramatically helps the convergence … to a (slightly) different value …
If imaginary part = 100 meV :

q grid	#q in IBZ	ZPM HOMO (meV)	ZPM LUMO (meV)	ZPM gap (meV)
8x8x8 x4s	60	140.5	-181.9	-322.4
12x12x12 x4s	182	141.7	-293.1	-434.8
16x16x16 x4s	408	141.7	-273.9	-415.6
20x20x20 x4s	770	141.7	-260.1	-401.8
24x24x24 x4s	1300	141.7	-257.5	-399.2
28x28x28 x4s	2030	141.7	-269.1	-410.8
32x32x32 x4s	2992	141.7	-271.8	-413.5

Changing the imaginary delta

$$\frac{f(\vec{q}jn)}{\varepsilon_{\Gamma n} - \varepsilon_{\vec{q}n} + i\delta}$$

For very large q-wavevector sampling, rate of convergence understood,
+ correspond to expectations !
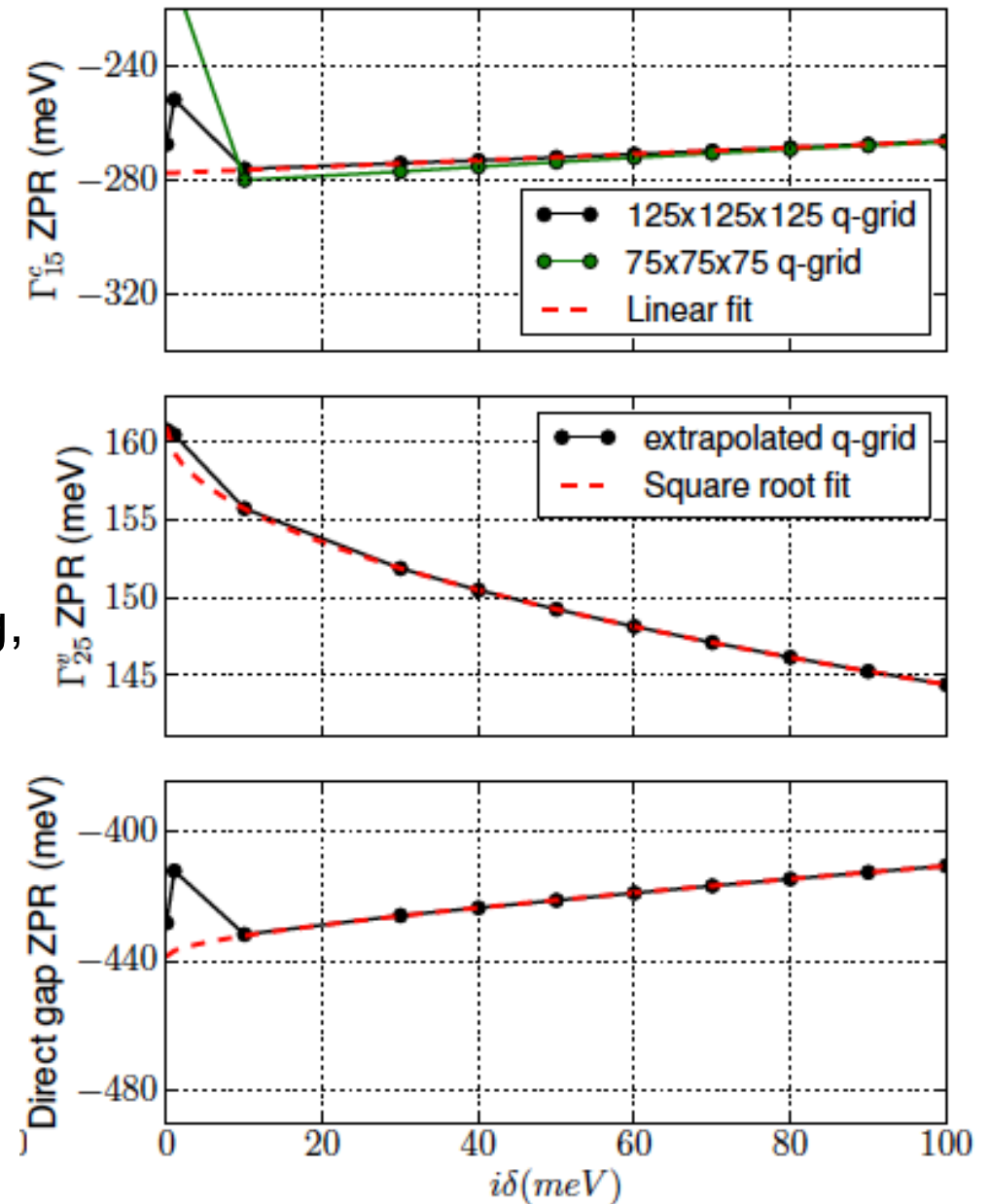
Cross-checking

Independent implementations (without the Sternheimer trick, though)
-Quantum/Espresso + EPW => 0.6 eV … ?! *(Giustino, PRL105, 265501 (2010))*
-Quantum/Espresso + Yambo => initially 0.6 eV, but after debugging,
excellent agreement with ABINIT … 0.4 eV !

Band	Fan + DDW	
	ABINIT 7.3.2 SEq/ 300 bands	Yambo 3.4.0 300 bands
1	−61.75	−61.87
2–3–4	140.54	140.70
5–6–7	−260.63	−259.40
8	−232.37	−230.40
9	−43.86	−43.95
ZPR Band gap	-401.17 meV	-400.10 meV

S. Poncé *et al, Comput. Materials Science* 83, 341 (2014)

DFT+AHC T-dependent bandgap : diamond

Temperature-dependence of the gaps in diamond [meV]

Legend:
- Diamond direct-gap (red line)
- Diamond indirect-gap (black line)
- Clark 1964 (black dots)
- Logothetidis 1992 (1st) (red diamonds)
- Logothetidis 1992 (2nd) (blue squares)
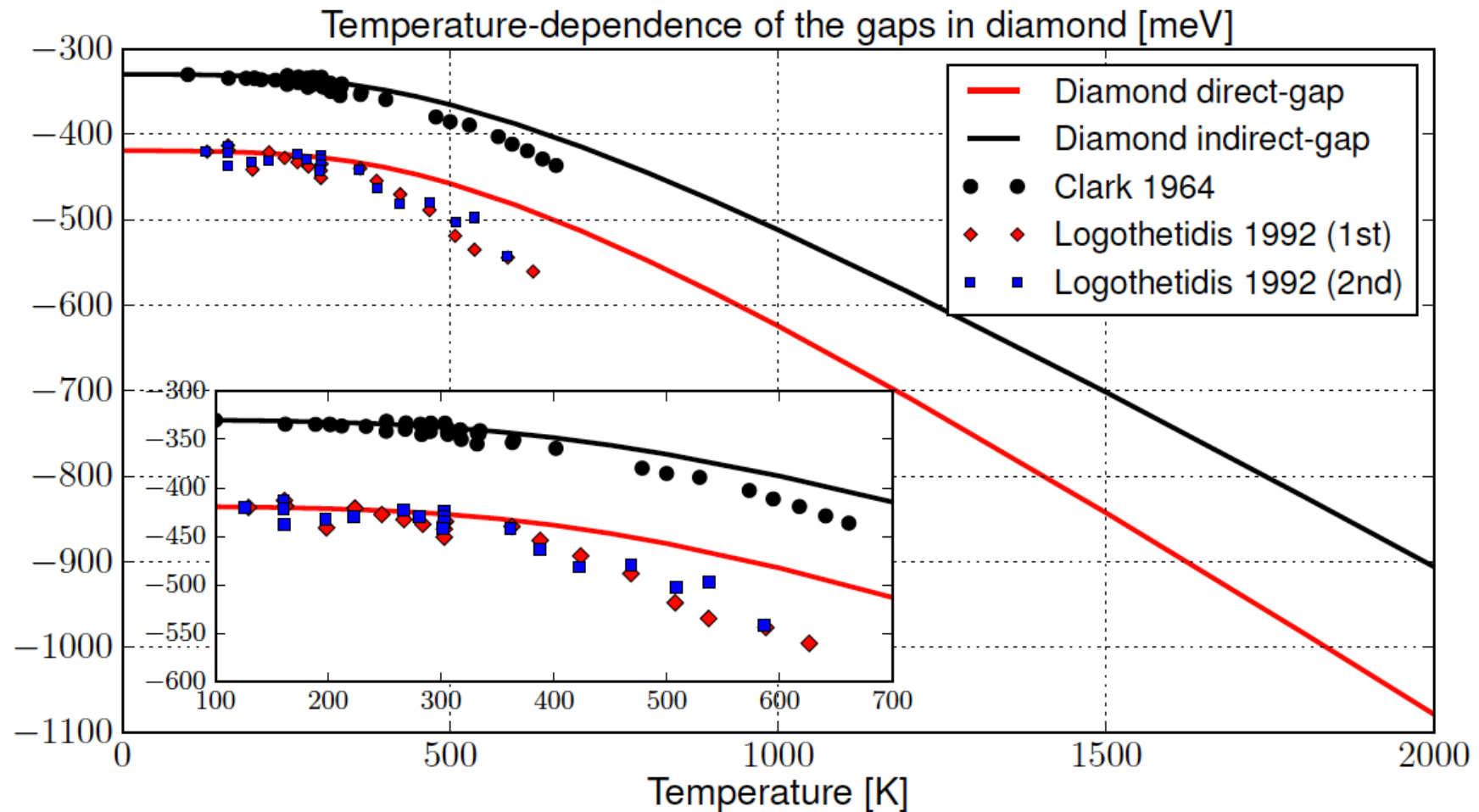
Not bad, but still too small effect … ?!

Hefei, June 18, 2016

DFT T-dependent band structure
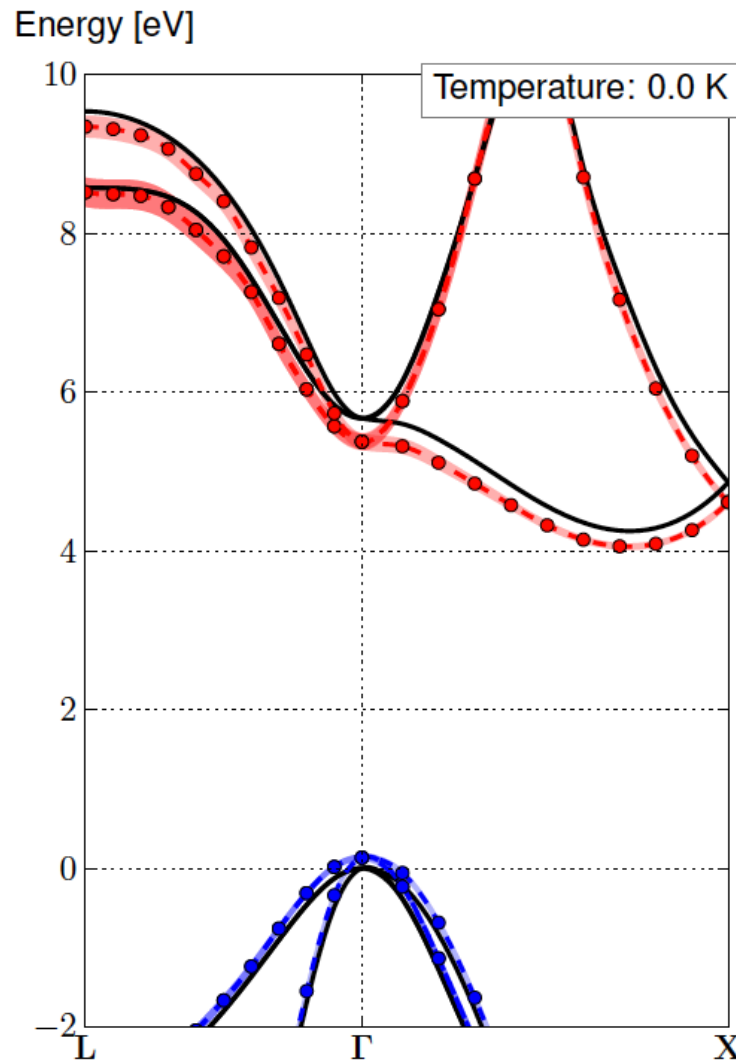
Diamond 0 Kelvin
(incl. Zero-point motion)

Note the widening of
the bands = lifetime

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DFT T-dependent band structure
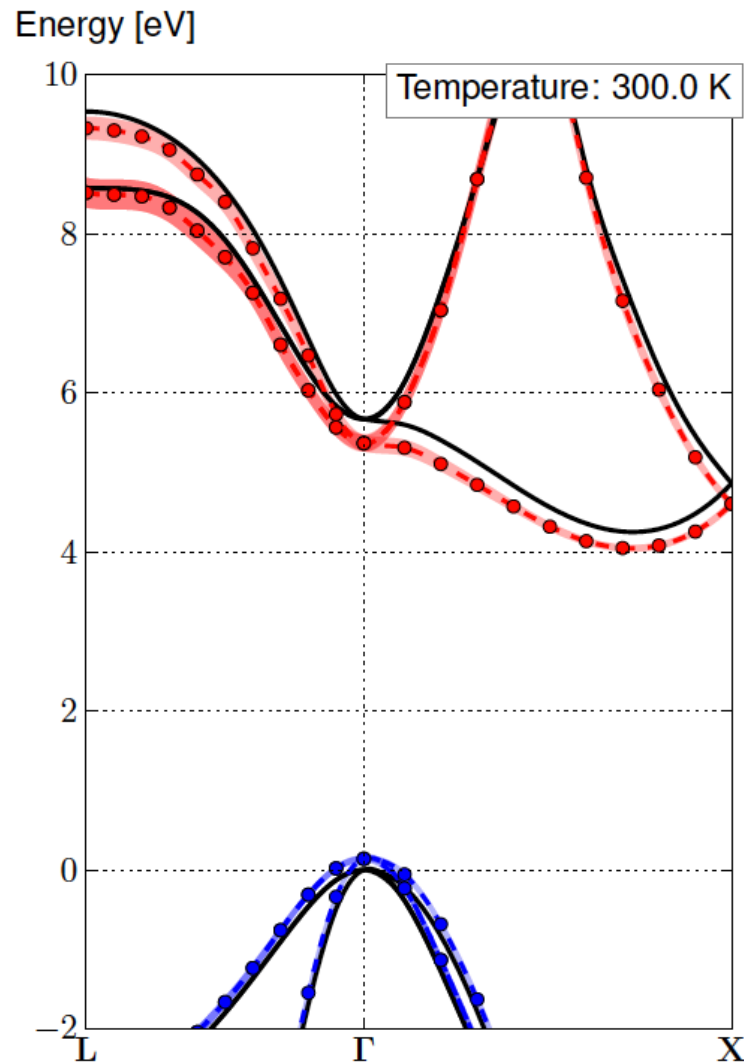
Diamond 300 Kelvin

Note the widening of
the bands = lifetime

S. Poncé, Y. Gillet, J. Laflamme Janssen, A. Marini, M. Verstraete & XG, J. Chem. Phys. 143, 102813 (2015)

DFT T-dependent band structure
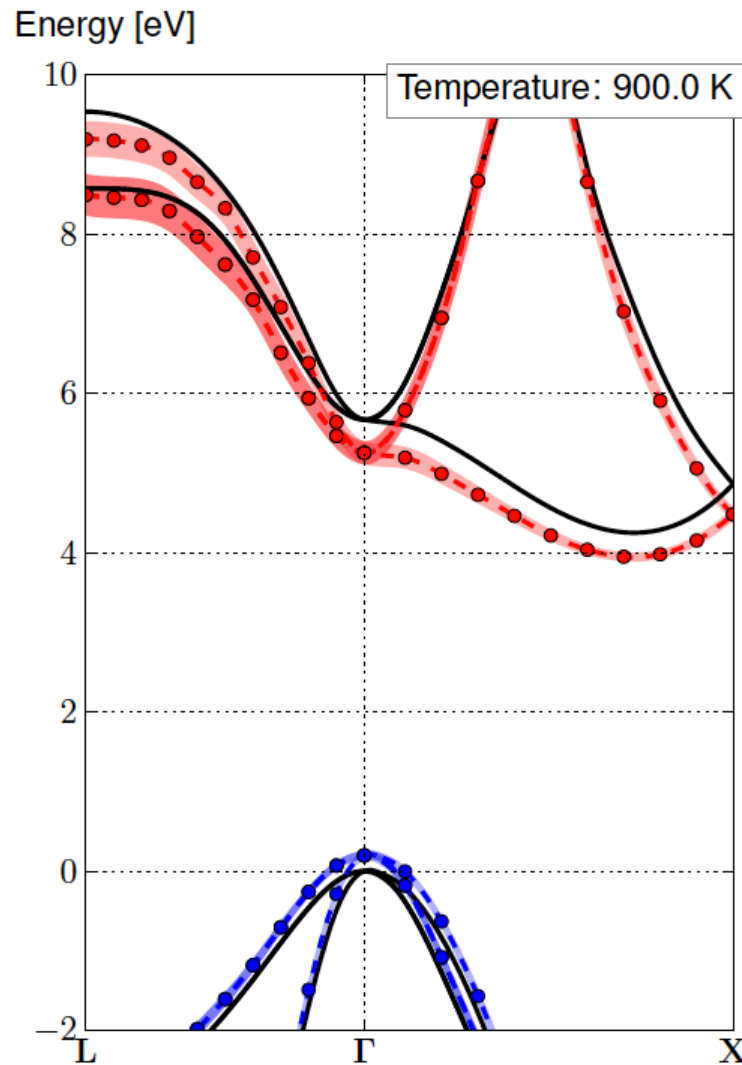
Diamond 900 Kelvin

Note the widening of the bands = lifetime

S. Poncé, Y. Gillet, J. Laflamme Janssen, A. Marini, M. Verstraete & XG, J. Chem. Phys. 143, 102813 (2015)

DFT T-dependent band structure
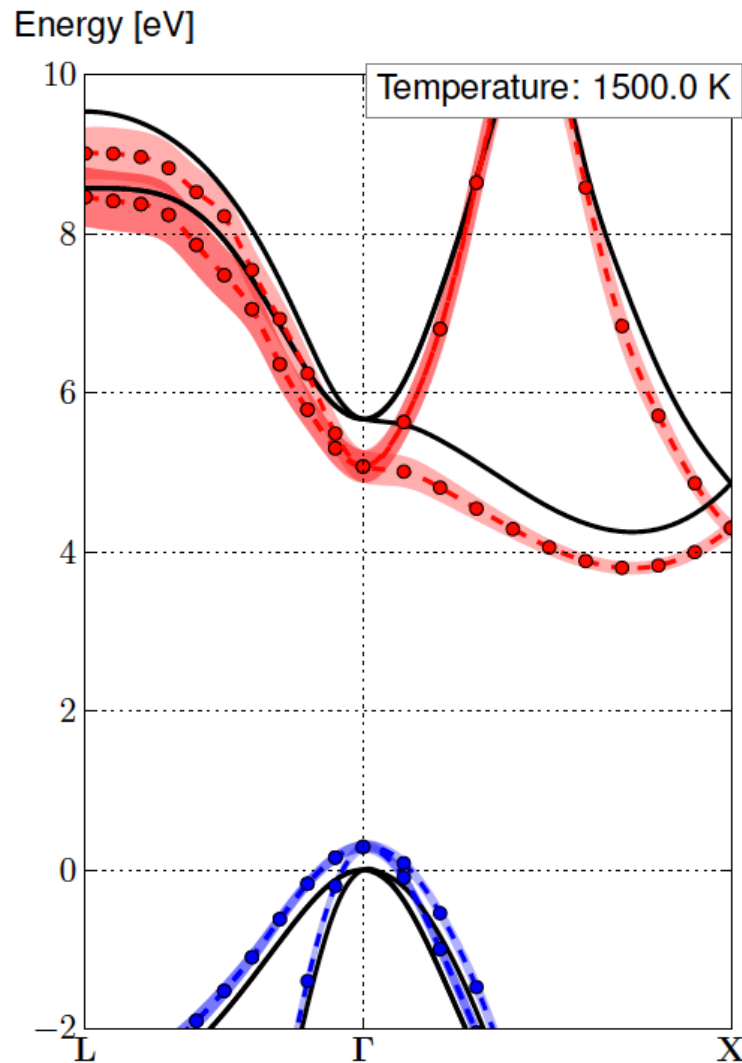
Diamond 1500 Kelvin

Note the widening of
the bands = lifetime

S. Poncé, Y. Gillet, J. Laflamme Janssen, A. Marini, M. Verstraete & XG, J. Chem. Phys. 143, 102813 (2015)

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Temperature effects with GW electronic structure

GW energies + frozen-phonon in supercells

$$\delta \varepsilon_{\vec{k}n}(T, V = const) = \frac{1}{N_{\vec{q}}} \sum_{\vec{q}j} \frac{\partial \varepsilon_{\vec{k}n}}{\partial n_{\vec{q}j}} \left(\left\langle \hat{n}_{\vec{q}j} \right\rangle (T) + \frac{1}{2} \right)$$

+ occupation number from Bose-Einstein statistics

$$\frac{\partial \varepsilon_{\vec{k}n}}{\partial n_{\vec{q}j}} = \frac{1}{2\omega_{\vec{q}j}} \sum_{\kappa a \kappa' b} \frac{\partial^2 \varepsilon_{\vec{k}n}}{\partial R_{\kappa a} \partial R_{\kappa' b}} \frac{\xi_{\kappa a}(\vec{q}j)\xi_{\kappa' b}(-\vec{q}j)}{\sqrt{M_\kappa M_{\kappa'}}} e^{iq.(R_{\kappa' b} - R_{\kappa a})}$$

Finite-difference evaluation of the derivatives of the GW electronic energies wrt phonons, using supercells

G. Antonius, S. Poncé, P. Boulanger, M. Côté & XG, *Phys. Rev. Lett.* 112, 215501 (2014)

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Electron-phonon coupling energies

EPCE $\dfrac{\partial \varepsilon_{\vec{k}n}}{\partial n_{\vec{q}j}}$ from DFT, G0W0 and scGW

Significantly larger decrease of the gap within G0W0 and scGW compared to DFT

G0W0 and scGW very close to each other

G. Antonius, S. Poncé, P. Boulanger, M. Côté & XG,
Phys. Rev. Lett. 112, 215501 (2014)

Bottom of conduction Band at Gamma

Top of valence band

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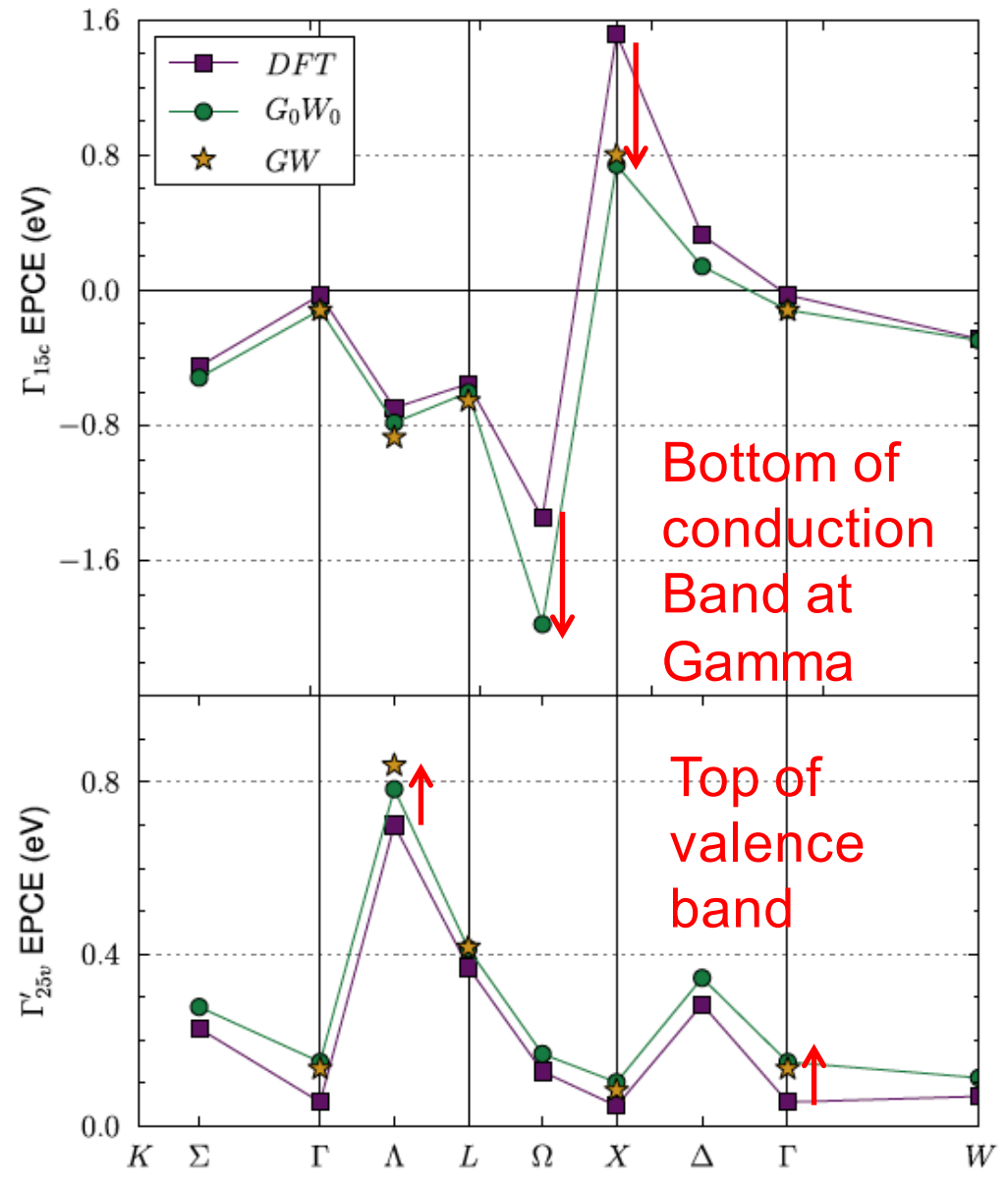
DFT + perturbative phonons + GW + frozen-phonon in supercells
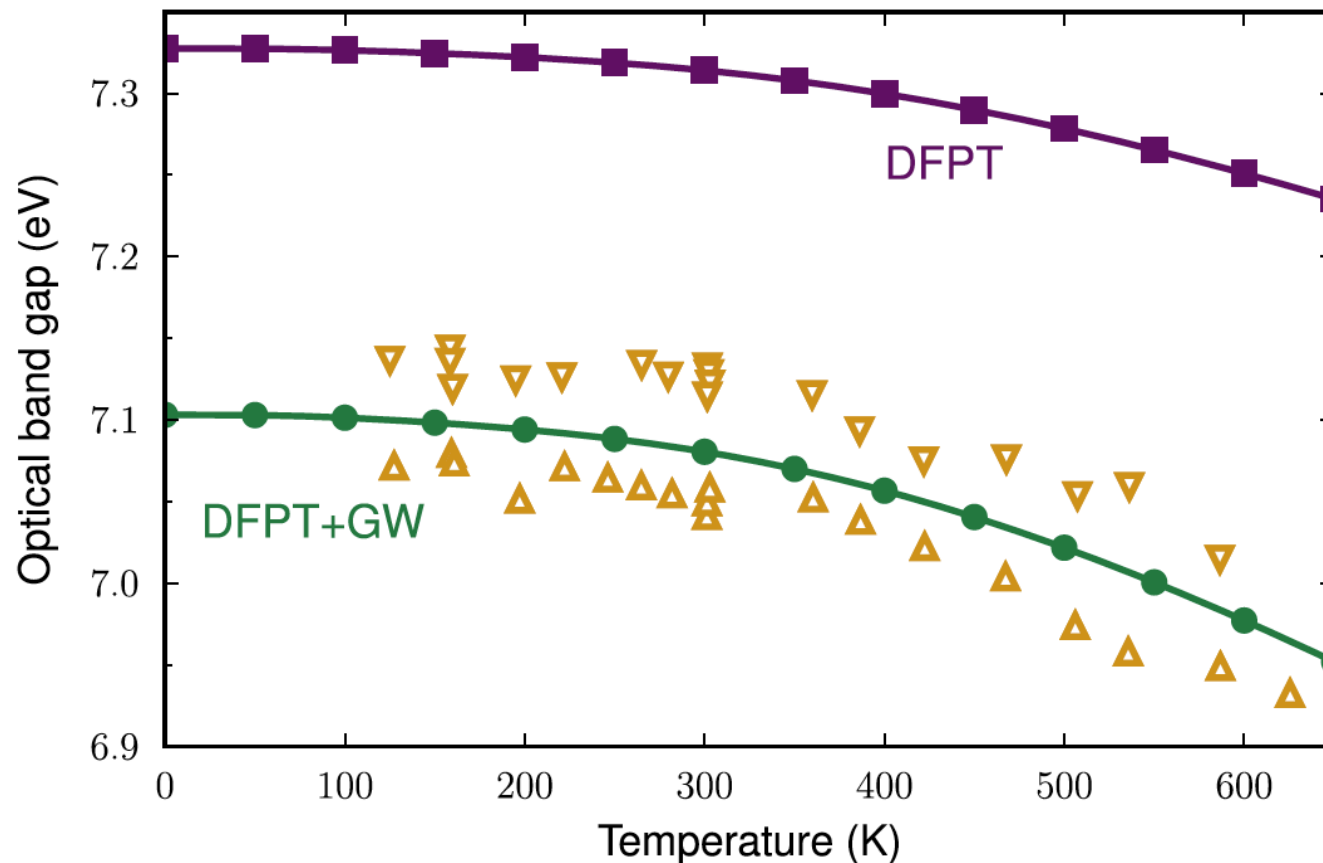
Zero-point motion in DFT :
0.4 eV
for the direct gap

Zero-point motion in DFT+GW :
0.63 eV
for the direct gap, in agreement with experiments

G. Antonius, S. Poncé, P. Boulanger, M. Côté & XG, *Phys. Rev. Lett.* 112, 215501 (2014)

Breakdown of the adiabatic AHC theory for infra-red active materials

Boron nitride renormalization of gap
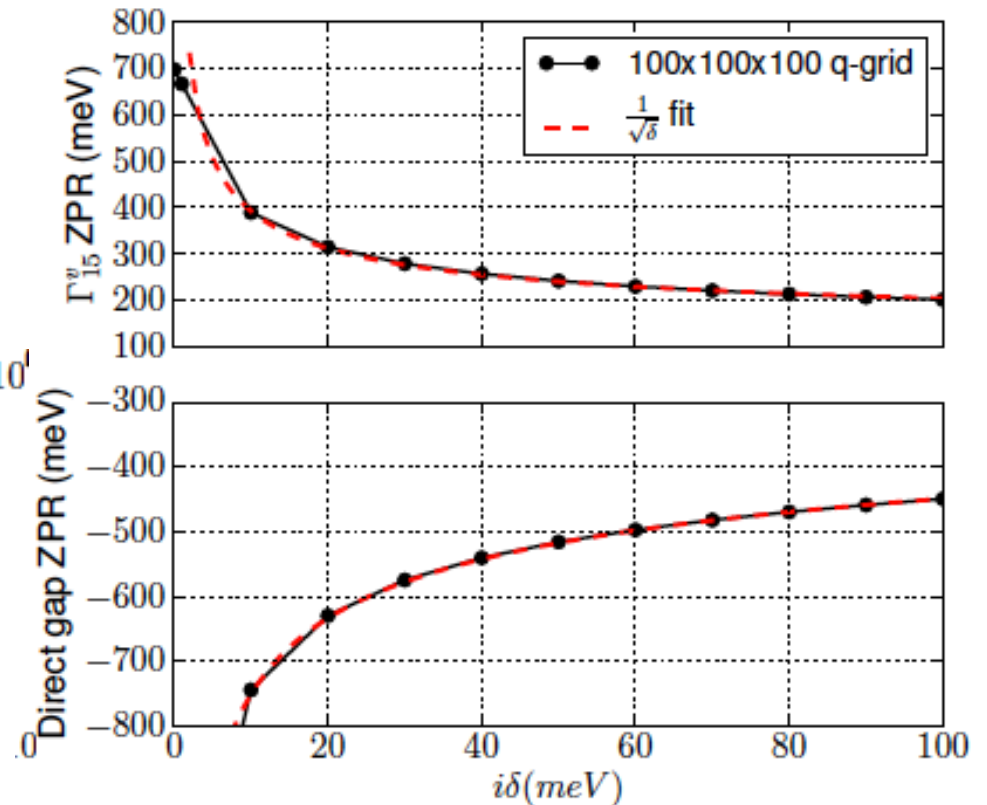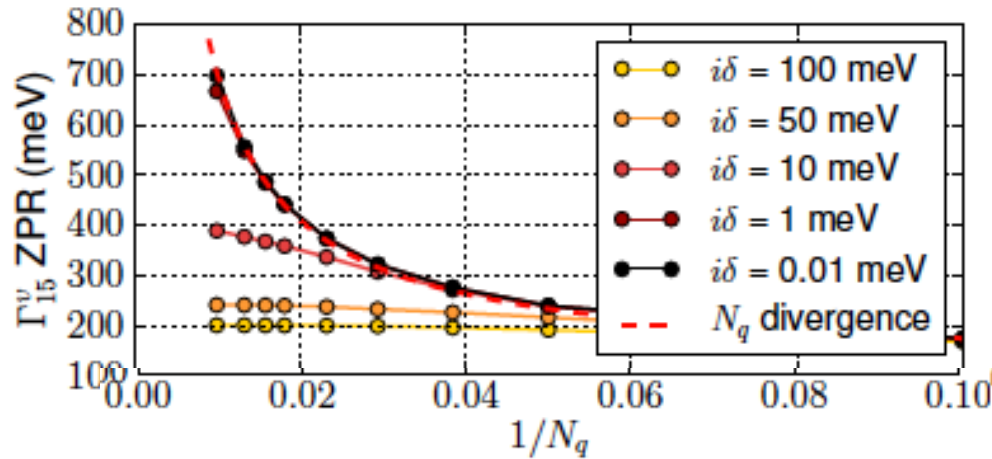
when the imaginary delta
tends to zero,
the ZPR diverges !

… such a divergence is confirmed
  by a « post-mortem » analysis …

Electric field with IR-active optic modes

Collective displacement with wavevector $|\mathbf{q}| \to 0$

$$H_{\mathbf{q}}^{(1)} = \overline{V}_{ext,\mathbf{q}}^{(1)} + \overline{V}_{H,\mathbf{q}}^{(1)} + \overline{V}_{xc,\mathbf{q}}^{(1)}$$

$$\overline{V}_{ext,\mathbf{q}}^{(1)}(\mathbf{G}) = \frac{-i}{\Omega_0}(\mathbf{G}+\mathbf{q})_\alpha e^{-i(G+q).\tau} v_\kappa(\mathbf{G}+\mathbf{q})$$

$$v_\kappa(\mathbf{q} \to 0) = -\frac{4\pi Z_\kappa}{q^2} + C_\kappa + O(q^2)$$

$$\overline{V}_{H,\mathbf{q}}^{(1)}(\mathbf{G}) = 4\pi \frac{\overline{n}_{\mathbf{q}}^{(1)}}{|\mathbf{G}+\mathbf{q}|^2}$$

$$\overline{n}_{\mathbf{q}}^{(1)} \propto |\mathbf{q}| \quad \text{when} \quad |\mathbf{q}| \to 0$$

Both the "external" and Hartree potentials can diverge like 1/q.

Definition of the polarization of a phonon mode :
$$P_\alpha^{(1)}(\mathbf{q}j) = \sum_{\kappa\beta} Z_{\kappa,\alpha\beta}^* \xi_{\kappa\beta}(\mathbf{q}j)$$

$$Z_{\kappa,\alpha\beta}^* = \Omega_0 \left.\frac{\partial P_\alpha}{\partial u_{\kappa,\beta}}\right|_{\delta\vec{E}=0}$$

Born effective charge tensor for atom κ

Associated electric field
$$E_\alpha = -\frac{4\pi}{\Omega_0} \frac{\sum_\delta P_\delta^{(1)}(\mathbf{q}j)q_\delta}{\sum_{\gamma\delta} q_\gamma \varepsilon_{\gamma\delta} q_\delta} = iH_{\mathbf{q}}^{(1)}(\mathbf{G}=0)$$

AHC with IR-active optic modes

$$\frac{\partial \varepsilon_{\Gamma n}(Fan)}{\partial n_{\vec{q}j}} = \frac{1}{\omega_{\vec{q}j}} \Re \sum_{\kappa a \kappa' b n'} \frac{\langle \phi_{\Gamma n} | \nabla_{\kappa a} H_{\kappa} | \phi_{\vec{q}n'} \rangle \langle \phi_{\vec{q}n'} | \nabla_{\kappa' b} H_{\kappa'} | \phi_{\Gamma n} \rangle}{\varepsilon_{\Gamma n} - \varepsilon_{\vec{q}n'}} \frac{\xi_{\kappa a}(\vec{q}j)\xi_{\kappa' b}(-\vec{q}j)}{\sqrt{M_{\kappa} M_{\kappa'}}} e^{iq.(R_{\kappa' b} - R_{\kappa a})}$$

$$H_{\vec{q}}^{(1)} = \sum_{\kappa a} \nabla_{\kappa a} H_{\kappa} \xi_{\kappa a}(\vec{q}j)$$ diverges like $\boxed{1/q}$ for polar optic modes.

At band extrema, the denominator diverges like $\boxed{1/q^2}$.

For non-polar modes, divergence like $\boxed{1/q^2}$, can be integrated …

For polar optic modes, divergence like $\boxed{1/q^4}$, cannot be integrated …

The adiabatic AHC theory breaks down for materials
with IR-active optic modes. Also harmonic thermal average method !

[Note : In gapped systems, only elemental solids do not have IR-active modes]

S. Poncé, Y. Gillet, J. Laflamme Janssen, A. Marini, M. Verstraete & XG, J. Chem. Phys. 143, 102813 (2015)

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Non-adiabatic AHC theory

Beyond Rayleigh-Schrödinger perturbation theory … MBPT !

Fan self-energy :

$$\Sigma_{\lambda\lambda'}^{Fan}(\omega) = \sum_\nu \frac{1}{2\omega_\nu} \sum_{\lambda''} \langle\psi_\lambda| H_\nu^{(1)} |\psi_{\lambda''}\rangle \langle\psi_{\lambda''}| H_\nu^{(1)*} |\psi_{\lambda'}\rangle$$

$$\left[\frac{n_\nu(T) + f_{\lambda''}(T)}{\omega - \varepsilon_{\lambda''}^0 \boxed{+ \omega_\nu} + i\eta\,\mathrm{sgn}(\omega)} + \frac{n_\nu(T) + 1 - f_{\lambda''}(T)}{\omega - \varepsilon_{\lambda''}^0 \boxed{- \omega_\nu} + i\eta\,\mathrm{sgn}(\omega)} \right]$$

This yields a renormalizable theory !

Different levels :

On-the-mass shell approximation

Quasi-particle approximation

$$\varepsilon_\lambda = \varepsilon_\lambda^0 + \Sigma_\lambda^{ep}(\varepsilon_\lambda^0)$$

$$\varepsilon_\lambda = \varepsilon_\lambda^0 + \Sigma_\lambda^{ep}(\varepsilon_\lambda) \qquad \varepsilon_\lambda = \varepsilon_\lambda^0 + Z_\lambda \Sigma_\lambda^{ep}(\varepsilon_\lambda^0)$$

$$Z_\lambda = \left(1 - \mathfrak{Re}\frac{\partial \Sigma_\lambda^{ep}(\omega)}{\partial\omega}\Big|_{\omega=\varepsilon_\lambda^0} \right)^{-1}$$

Or even spectral functions

$$A_\lambda(\omega) = \frac{1}{\pi} \frac{|\mathfrak{Im}\Sigma_\lambda^{ep}(\omega)|}{[\omega - \varepsilon_\lambda^0 - \mathfrak{Re}\Sigma_\lambda^{ep}(\omega)]^2 + \mathfrak{Im}\Sigma_\lambda^{ep}(\omega)^2}$$
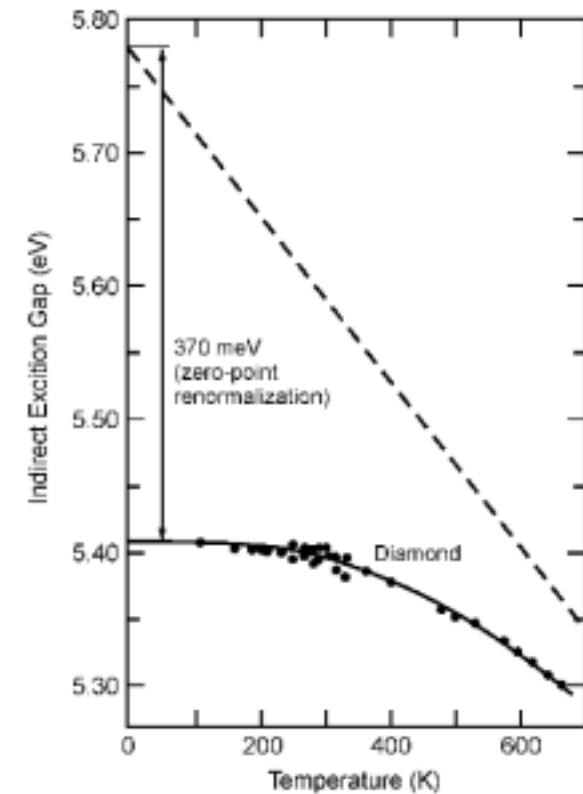
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T-dependent bandgaps for several insulators

Zero-temperature limit
and
High-temperature linear slope

$$\varepsilon_\lambda = \varepsilon_\lambda^0 + \Sigma_\lambda^{ep}(\varepsilon_\lambda^0)$$

S. Poncé, Y. Gillet, J. Laflamme Janssen, A. Marini,
M. Verstraete & XG, J. Chem. Phys. 143, 102813 (2015)

Compounds	Gap	ZPR [meV]			$(dGap/dT)_{T\to\infty}$ [meV/K]	
		Static	Non-adiabatic	Experimental	Non-adiabatic	Experimental
α-AlN	$\mathbf{\Gamma - \Gamma}$	-	-377.7	-239[62]		-0.83[53,55,62]
β-AlN	$\mathbf{\Gamma - \Gamma}$	-	-413.6		-0.763	
	$\mathbf{\Gamma - X}$	-	-334.4		-0.521	
c-BN	$\mathbf{\Gamma - \Gamma}$	-	-502.0		-0.639	
	$\mathbf{\Gamma - X}$	-	-405.6		-0.521	
C	$\mathbf{\Gamma - \Gamma}$	-438.6	-415.8	-320[52],-450[52]	-0.504	-0.60[52], -0.69[52]
	$\mathbf{\Gamma - 0.727X}$	-379.3	-329.8	-364[53]	-0.435	-0.54[53]
Si	$\mathbf{\Gamma - \Gamma}$	-47.1	-42.1		-0.147	
	$\mathbf{\Gamma - 0.848X}$	-64.3	-56.2	-62[53],-64[53]	-0.255	-0.32[58,59]

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Dynamical ep renormalisation for 4 solids

On top of DFT : from static AHC (delta=0.1 eV), to position of peak maximum

		$\Sigma^{stat}(\varepsilon^0)$	$\Sigma^{dyn}(\varepsilon^0)$	Z	$Z\Sigma^{dyn}(\varepsilon^0)$	$\Sigma^{dyn}(\varepsilon)$	$\Delta A(\varepsilon)$
C	VB	0.134	0.126	0.931	0.118	0.118	0.118
	CB	-0.238	-0.240	1.007	-0.242	-0.240	-0.247
	Gap	-0.372	-0.366	-	-0.359	-0.358	-0.365
BN	VB	0.198	0.173	0.823	0.143	0.147	0.147
	CB	-0.190	-0.196	1.020	-0.200	-0.197	-0.208
	Gap	-0.388	-0.370	-	-0.343	-0.344	-0.355
MgO	VB	0.197	0.198	0.734	0.145	0.145	0.147
	CB	-0.153	-0.143	0.870	-0.125	-0.127	-0.127
	Gap	-0.350	-0.341	-	-0.270	-0.272	-0.274
LiF	VB	0.398	0.446	0.596	0.266	0.254	0.256
	CB	-0.279	-0.273	0.746	-0.204	-0.211	-0.211
	Gap	-0.677	-0.718	-	-0.469	-0.464	-0.467

$$Z_\lambda = \left(1 - \mathfrak{Re}\frac{\partial \Sigma_\lambda^{ep}(\omega)}{\partial \omega}\Big|_{\omega=\varepsilon_\lambda^0}\right)^{-1}$$

From peak max of spectral function

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Advertimsement for ABINIT v8.0.7

ABINIT v8.0.x recently made available (1 year of cleaning and new devs).

New features (or much improved features) :
-Temperature-dependence of the electronic structure
-Dynamical-Mean Field Theory (CT-QMC solver and TRIQS library)
-Van der Waals (DFT-Dx , also including phonons)
-Improved Bethe-Salpeter (recursion, direct diago, CG + interpolation)
-PIMD
-Pseudos and PAW atomic data : well-tested tables (see Lejaeghere et al 2016)

In addition to already existing features :
-DFPT (with NC and PAW) also for direct eval of effective masses
-GW
-Finite electric field + Berry phase
-…

See http://www.abinit.org , including the tutorial, and
XG et al , Comput. Phys. Comm. 205, 106 (2016)

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A few more data - all within DFT - …

…Not of equivalent quality … Different approximations ...

Big shifts :

CH_4 crystal	1.7 eV	
NH_3 crystal	1.0 eV	
Ice	1.5 eV	
HF crystal	1.6 eV	(Montserrat et al, 2015)
Helium (at 25 TPa)	2.0 eV	(Montserrat et al, 2014)

Medium shifts :

Helium (at 0 GPa)	0.40 eV	(Montserrat, Conduit, Needs, 2013)
$LiNbO_3$	0.41 eV	(Friedrich et al, 2015)
Polyethylene	0.28 eV	(Canuccia & Marini, 2012)

Small shifts :

LiH	0.04 eV	
LiD	0.03 eV	(Montserrat, Drummond, Needs, 2013)
GaN	0.13 eV	(Kawai et al, 2013)
GaN	0.15 eV	(Nery & Allen, arXiv:1603.04269, 2016)
Trans-polyacetylene	0.04 eV	(Canuccia & Marini, 2012)

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Many-body theory with vibrational effects

Motivation

Incoherent many-body approaches !

Either :

MBPT for electrons and EPCE (GW) +

      static treatment of self-energy due to ep coupling

Or :

DFT for electrons and EPCE +

      dynamical treatment of self-energy due to ep coupling

Need a unified theory.

In particular : avoid possible double counting,

because phonons are already determined self-consistently,

with screening. And the EPCE is also screened by electrons !

$$\Sigma_{\lambda\lambda'}^{Fan}(\omega) = \sum_{\nu} \frac{1}{2\omega_\nu} \sum_{\lambda''} \langle \psi_\lambda | H_\nu^{(1)} | \psi_{\lambda''} \rangle \langle \psi_{\lambda''} | H_\nu^{(1)*} | \psi_{\lambda'} \rangle$$

$$\left[\frac{n_\nu(T) + f_{\lambda''}(T)}{\omega - \varepsilon_{\lambda''}^0 \boxed{+\omega_\nu} + i\eta \,\mathrm{sgn}(\omega)} + \frac{n_\nu(T) + 1 - f_{\lambda''}(T)}{\omega - \varepsilon_{\lambda''}^0 \boxed{-\omega_\nu} + i\eta \,\mathrm{sgn}(\omega)} \right]$$

$$H_{\vec{q}}^{(1)} = \bar{V}_{ext,\vec{q}}^{(1)} + \bar{V}_{H,\vec{q}}^{(1)} + \bar{V}_{xc,\vec{q}}^{(1)}$$

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Outline

For details see :

A. Marini, S. Poncé and XG, Phys. Rev. B 91, 224310 (2015)

$$\hat{H}(\mathbf{R}) = \hat{H}_e + \hat{H}_n(\mathbf{R}) + \hat{W}_{e\text{-}n}(\mathbf{R})$$

$$\hat{H}_e = \hat{T}_e + \hat{W}_{e\text{-}e}$$

$$\hat{H}_n(\mathbf{R}) = \hat{T}_n + \hat{W}_{n\text{-}n}(\mathbf{R})$$

We would like :

$$\hat{H}(\mathbf{R}) = \hat{H}_0(\mathbf{R}) + \Delta\hat{H}(\mathbf{R})$$

$$\hat{H}_0(\mathbf{R}) = \sum_{n\mathbf{k}} \epsilon_{n\mathbf{k}} \hat{c}_{n\mathbf{k}}^\dagger \hat{c}_{n\mathbf{k}} + \sum_{\mathbf{q}\lambda} \omega_{\mathbf{q}\lambda} \left(\hat{b}_{\mathbf{q}\lambda}^\dagger \hat{b}_{\mathbf{q}\lambda} + \frac{1}{2} \right)$$

With physically meaningful « bare »
electronic and phononic eigenenergies …

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Choosing a reference system

Definition of the reference Hamiltonian (e.g. from DFT, but not mandatory)
- equilibrium atomic positions
- reference interatomic force constants

$$\widehat{H}_0(\mathbf{R}) = \widehat{T}_e + \widehat{T}_n + \widehat{W}_{e\text{-}n}(\overline{\mathbf{R}}) + \widehat{W}_{n\text{-}n}(\overline{\mathbf{R}}) + \Delta\widehat{W}_{n\text{-}n}^{\text{ref}}(\mathbf{R})$$

where $\widehat{W}_{e\text{-}n}$ and $\widehat{W}_{n\text{-}n}$ are evaluated at the equilibrium geometry

$$\Delta\widehat{W}_{n\text{-}n}^{\text{ref}}(\mathbf{R}) = \frac{1}{2}\sum_{ls\alpha,l's'\beta}\overline{\partial^2_{R_{ls\alpha}R_{l's'\beta}}E^{\text{BO}}(\mathbf{R})}\Delta\widehat{R}_{ls\alpha}\Delta\widehat{R}_{l's'\beta}$$
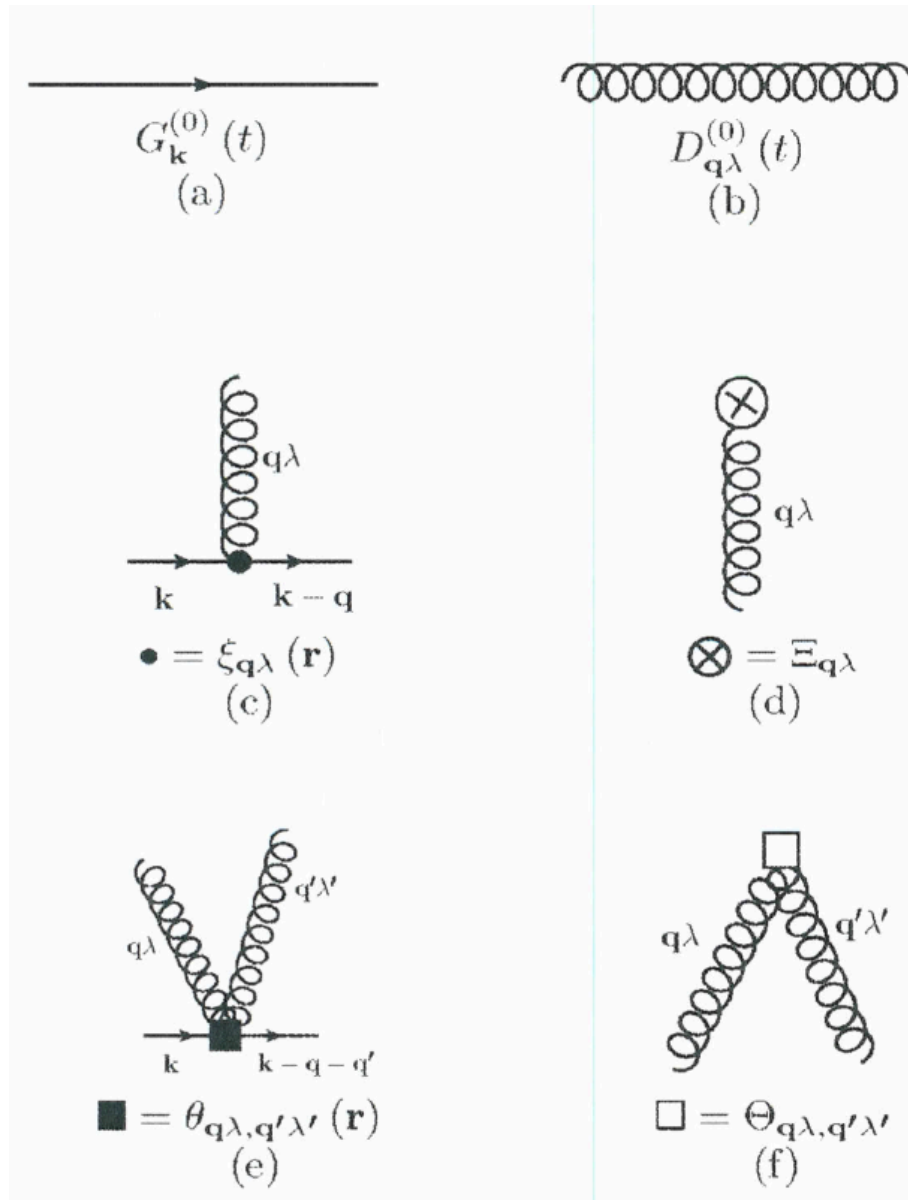
Remaining terms, up to 2$^{\text{nd}}$ order in atomic displacement operator

$$\Delta\widehat{H}(\mathbf{R}) = \widehat{W}_{e\text{-}e} + \Delta\widehat{H}^{(1)}(\mathbf{R}) + \Delta\widehat{H}^{(2)}(\mathbf{R})$$
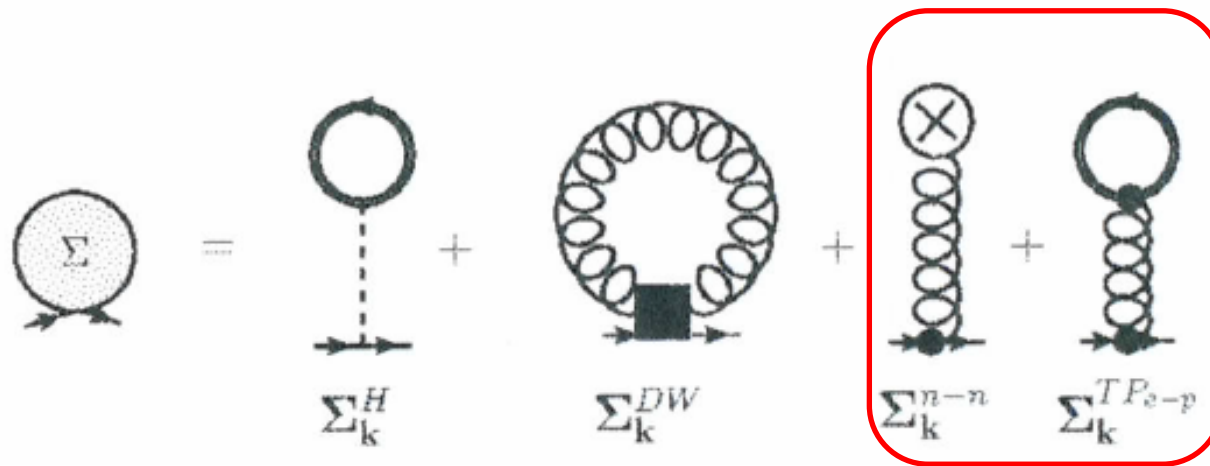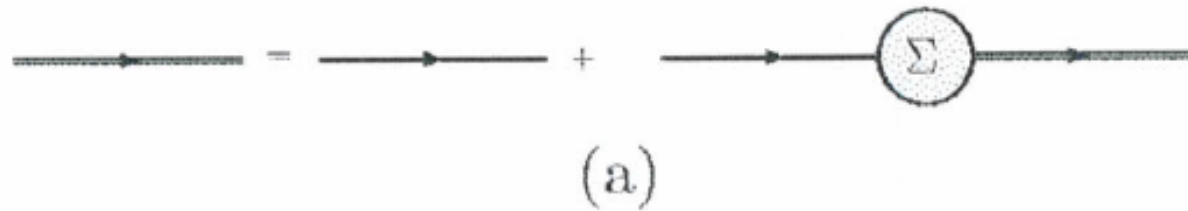
$$\Delta\widehat{H}^{(1)}(\mathbf{R}) \equiv \sum_{ls\alpha}\overline{\partial_{R_{ls\alpha}}[W_{e\text{-}n}(\mathbf{R}) + W_{n\text{-}n}(\mathbf{R})]}\Delta\widehat{R}_{ls\alpha}$$

$$\Delta\widehat{H}^{(2)}(\mathbf{R}) \equiv \frac{1}{2}\sum_{ls\alpha,l's'\beta}\overline{\partial^2_{R_{ls\alpha}R_{l's'\beta}}[W_{e\text{-}n}(\mathbf{R}) + W_{n\text{-}n}(\mathbf{R})]}$$
$$\times\Delta\widehat{R}_{ls\alpha}\Delta\widehat{R}_{l's'\beta} - \Delta\widehat{W}_{n\text{-}n}^{\text{ref}}(\mathbf{R}). \qquad ($$

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Diagrammatic representation

Lowest-order electronic self-energy

In general, non-zero !
They cancel each other
when the equilibrium geometry
is coherent with the level
of approximation

Next-order electronic self-energy

Result :
- after suppression of the tad-pole and 1st order phonon (suppose correct geometry)
- at the GW level

FIG. 10. The Dyson equation at the GW level in the electron-electron and electron-phonon interaction. The electron-phonon diagram is known as Fan self-energy and its vertex (represented by the circled dot) represents a dressed electron-phonon interaction [see Eq. (76)]. The wiggled line is a dressed electron-electron interaction [see Eq. (77)]. The most important aspect of this diagram is that, as long as only skeleton diagrams are included, the second-order electron-phonon interaction, and consequently the DW diagram, is not screened.
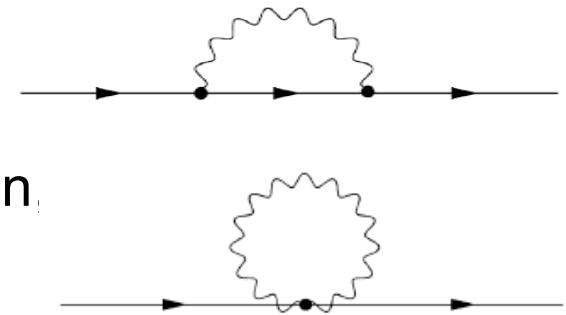
Confirmation of the screening of the 1st order electron-phonon vertex`
Of course, the screening « flavor » differs from the DFT one …
Screening of the DW diagram comes from self-consistency !

Summary

- Integration over the phonon degrees of freedom yields thermodynamic quantities, thermal expansion, T-dependent electronic structure

-Many effects are to be taken into account :
thermal expansion, Fan, Debye-Waller, dynamical self-energy, anharmonicities, non-rigid ion behaviour, delicate sampling of the phonon Brillouin zone, accurate starting electronic structure (GW), accurate electron-phonon coupling (GW) …
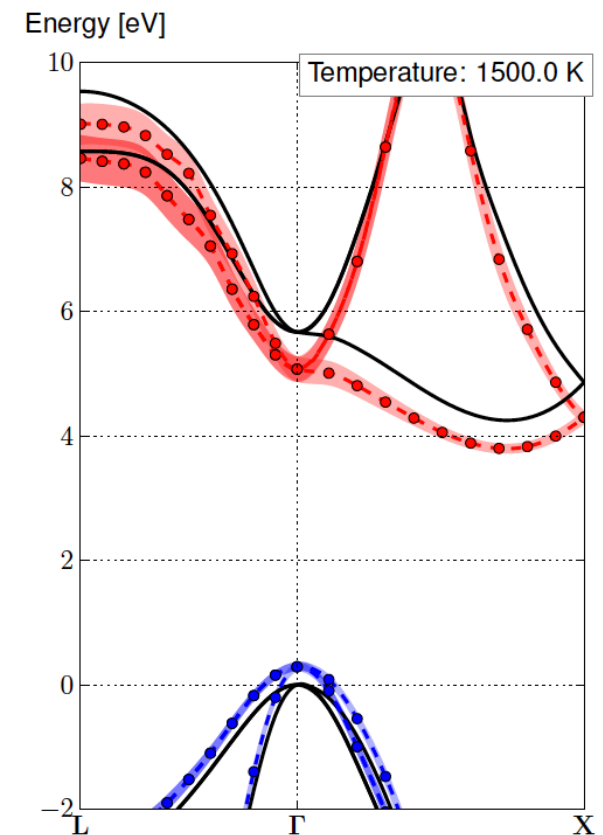
-The static AHC (Fan + Debye-Waller) breaks down for infra-red active solids

-Still lot of work to do to improve our tools !

-Unified MBPT of electron, phonons and electron-phonon coupling

Energy [eV]

Temperature: 1500.0 K

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