

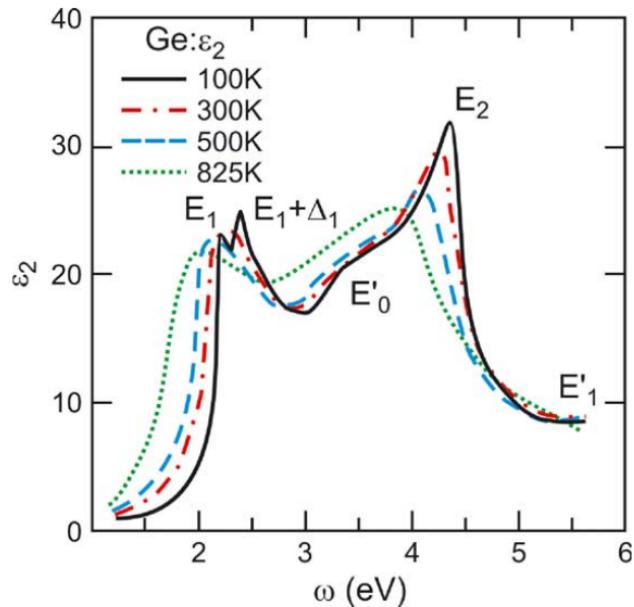
# Vibrational effects in electronic structure: temperature dependence and zero-point motion

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P. Boulanger, [CEA Grenoble](#) JP Nery, Ph. Allen, [Stony Brook, USA](#)

# T-dependence of electronic/optical properties

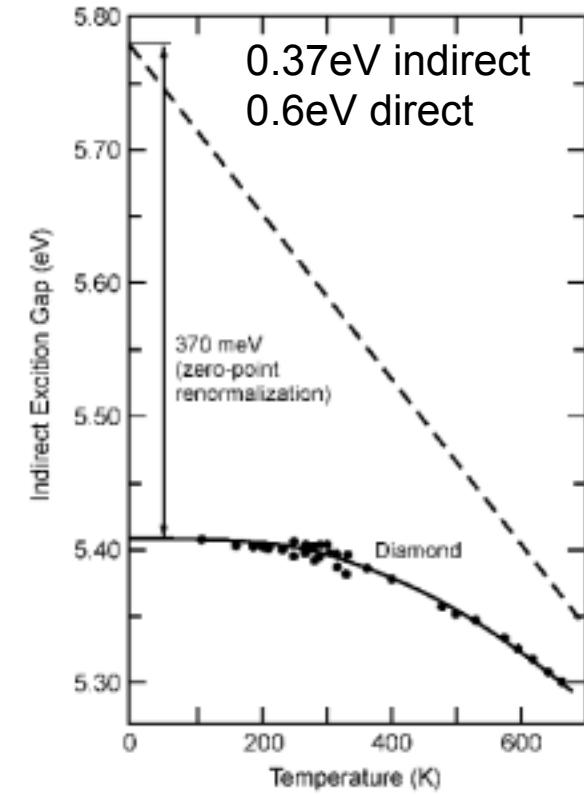


- peaks **shift** in energy
- peaks **broaden** with increasing temperature : decreased electron lifetime

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

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

Usually, not included in first-principles  
(DFT or beyond) calculations !



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

# Overview

1. Thermal expansion and phonon population effects
2. First-principles Allen-Heine-Cardona (AHC) theory
3. Breakdown of the adiabatic quadratic approximation for infra-red active materials
4. Zero-point renormalization (ZPR) : theory vs experiment
5. The physics of the ZPR in infra-red active materials

References :

- X. Gonze, P. Boulanger and M. Côté, *Ann. Phys.* 523, 168 (2011)  
S. Poncé *et al*, *Comput. Materials Science* 83, 341 (2014)  
G. Antonius, S. Poncé, P. Boulanger, M. Côté and X. Gonze, *Phys. Rev. Lett.* 112, 215501 (2014)  
S. Poncé *et al*, *Phys. Rev. B* 90, 214304 (2014)  
S. Poncé *et al*, *J. Phys. Chem* 143, 102813 (2015)  
G. Antonius *et al*, *Phys. Rev. B* 92, 085137 (2015)  
J.-P. Néry, P.B. Allen, G. Antonius, L. Reining, A. Miglio, and X. Gonze *Phys. Rev. B* 97, 115145 (2018)  
A. Miglio, M. Giantomassi, Y. Gillet, G. Antonius, Y.-H. Chan, V. Brousseau, M. Côté and X. Gonze,  
*submitted*

Also : *Many-body perturbation theory approach to the electron-phonon interaction with density-functional theory as a starting point*, A. Marini, S. Poncé and X. Gonze, *Phys. Rev. B* 91, 224310 (2015)

# Thermal expansion and phonon population effects

# Divide and conquer ...

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

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

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**

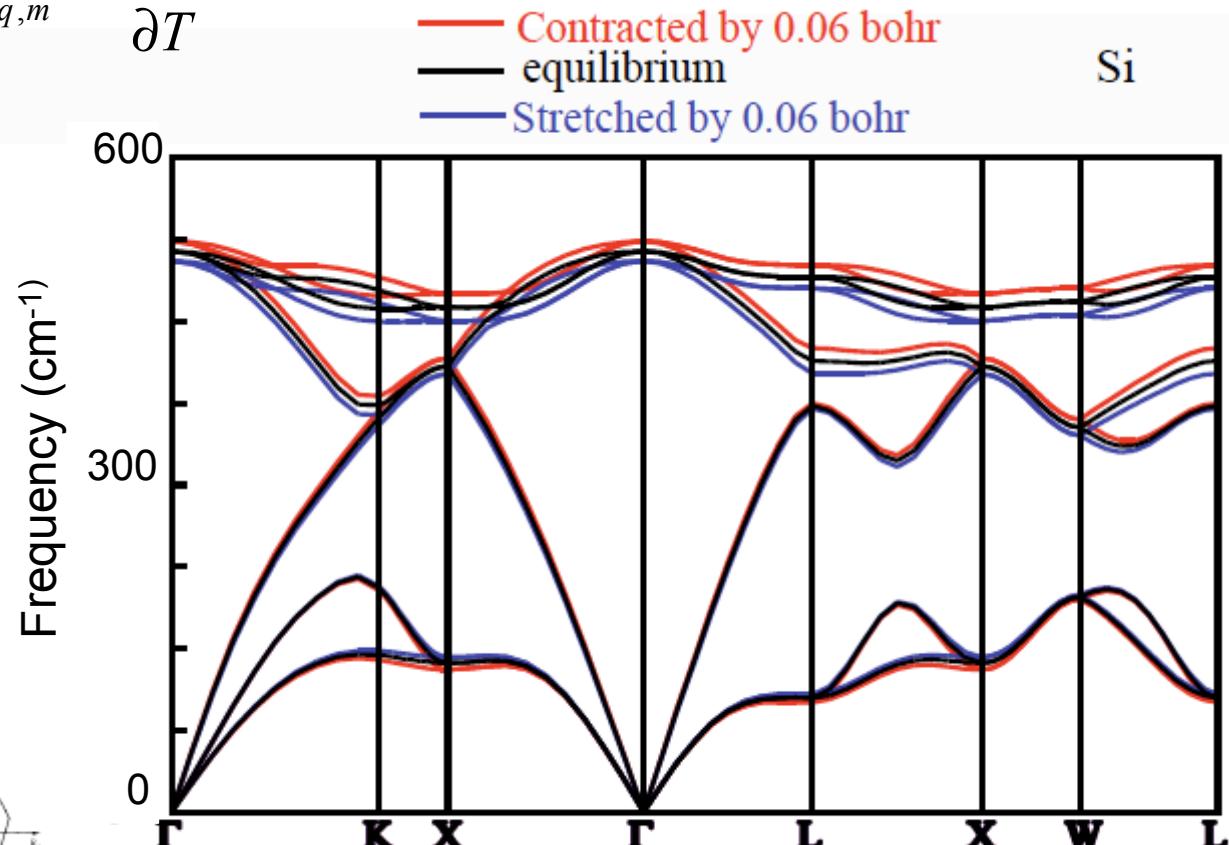
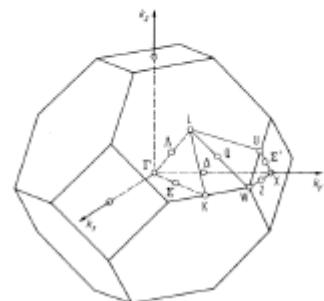
# Ab initio thermal expansion

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

Mode-Grüneisen parameters

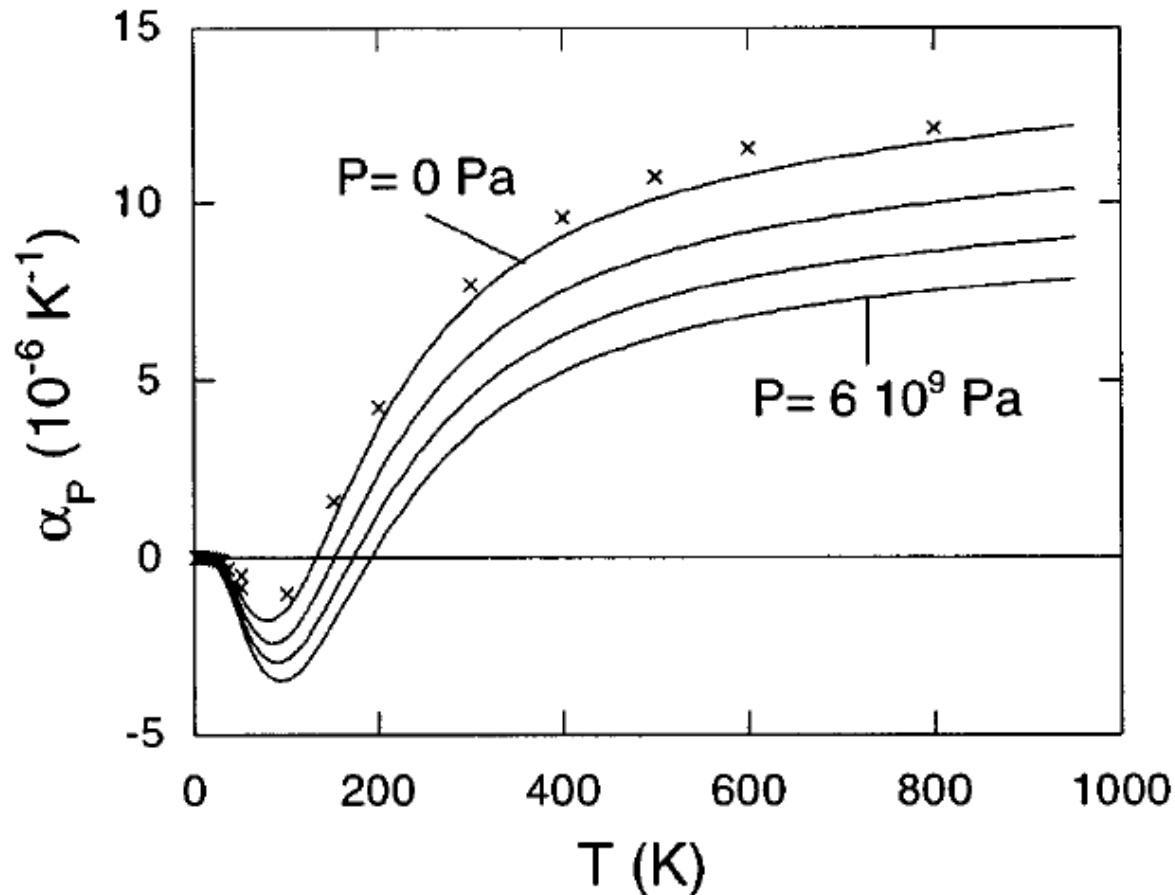
$$\gamma_{m,q} = -\frac{\partial(\ln \omega_{m,q})}{\partial(\ln V)}$$

Alternative path : minimisation of free energy



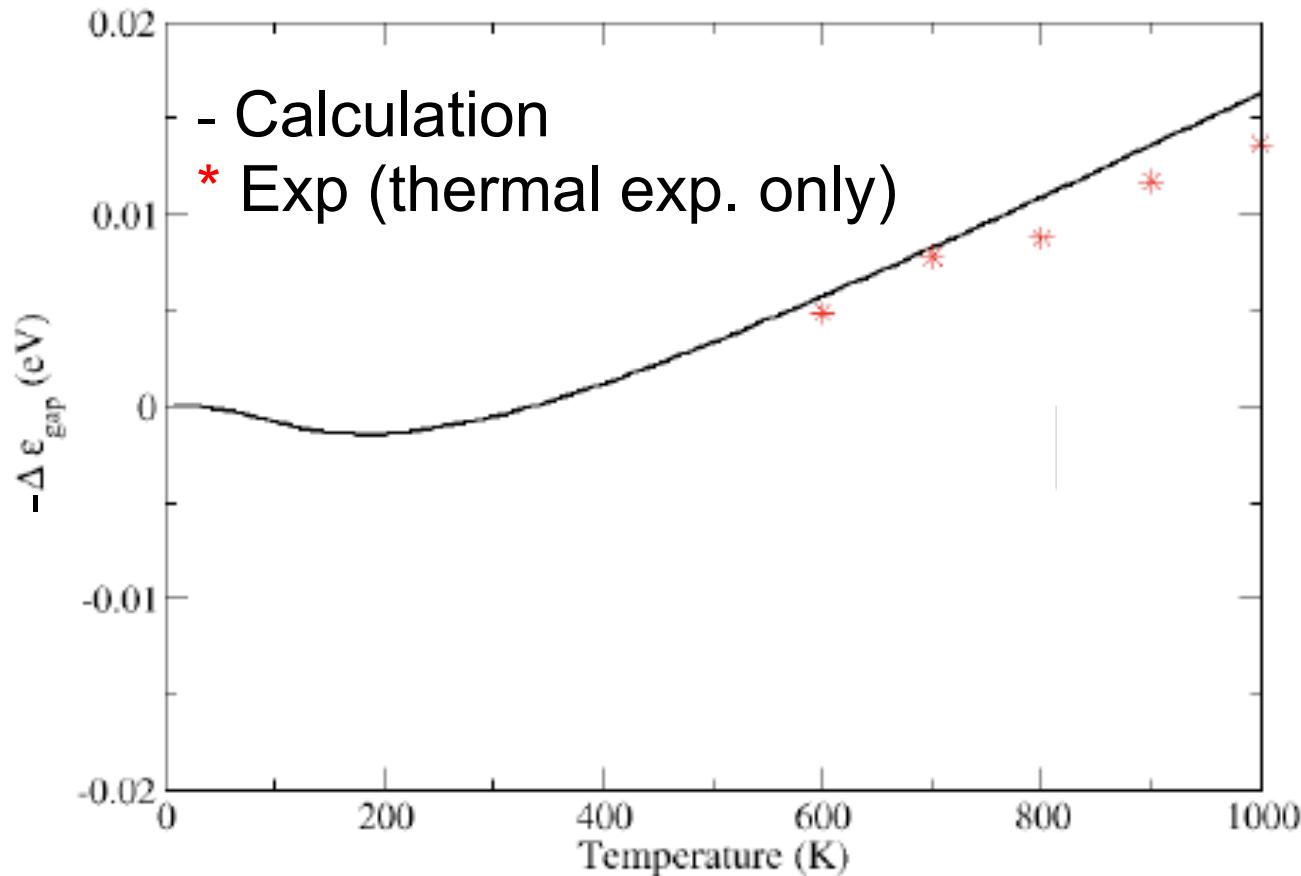
# Ab initio thermal expansion

Linear thermal expansion coefficient of bulk silicon



G.-M. Rignanese, J.-P. Michenaud and XG *Phys. Rev. B* 53, 4488 (1996)

# Thermal expansion contribution to the gap of Si



But total exp. change between 0K and 300K = 0.06 eV !

...Thermal expansion contribution is negligible (for Si) ...

NOT always the case, can be of same size : black phosphorus (Villegas, et al, Nanolett. 16, 5095 (2016)),  $\text{Bi}_2\text{Se}_3$  family (Monserrat & Vanderbilt, PRL117, 226801 (2016)).

# 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-principles 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)

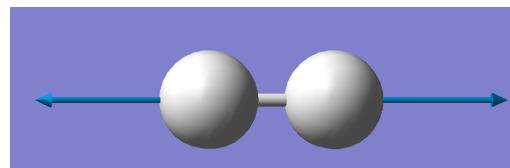
# Phonon population effects in solids

Concepts ...

... can be explained with diatomic molecules

Simple :

- discrete levels, simple molecular orbitals
- only one relevant vibration mode.



(6 modes decouple as 3 translations, 2 rotations + the stretch.)

# Average eigenenergies in the BO approx.

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

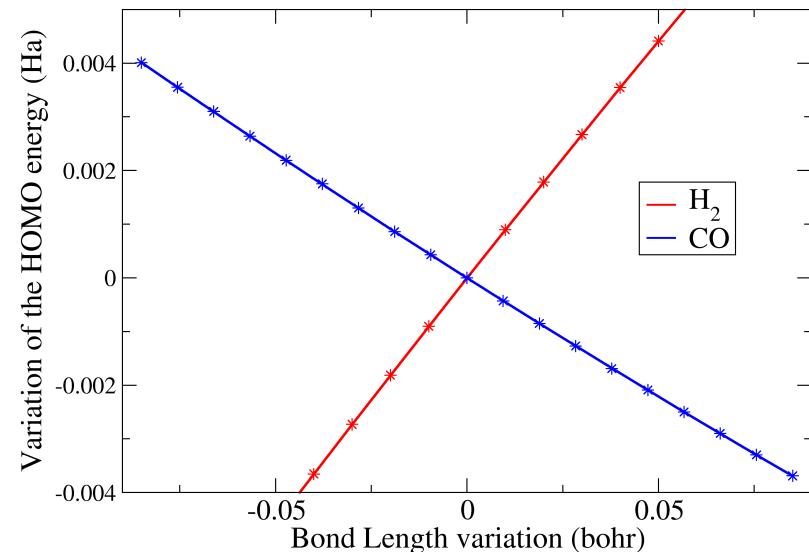
- (1) Time-average of eigenenergies  
from Molecular Dynamics trajectories,  
 $\Delta R(t)$  at average T, with

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

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)  
also supercell mix eigenstates, need unfolding

Variation of the HOMO energy wrt bond length



# Average eigenenergies in the BO approx.

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

(2) Thermal average with accurate  
quantum vibrational states,

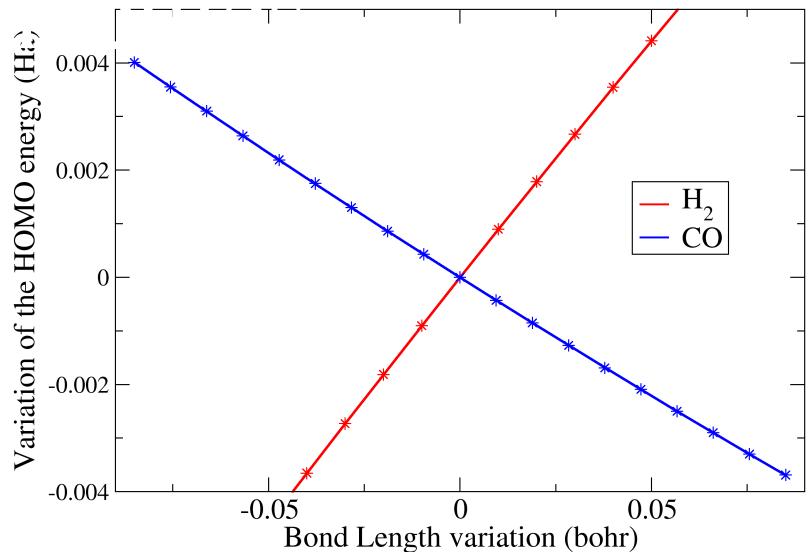
$$\varepsilon_n(T) = \frac{1}{Z} \sum_m e^{-\frac{E_{ph}(m)}{k_B T}} \left( \int \chi_m^*(\Delta R) \varepsilon_n(\Delta R) \chi_m(\Delta R) d\Delta R \right) \quad Z = \sum_m e^{-\frac{E_{ph}(m)}{k_B T}}$$

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 !); hard for solids  
(supercell), also supercell mix eigenstates, need unfolding

Alternative: one very large supercell with prepared atomic displacements

Variation of the HOMO energy wrt bond length



# 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)

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

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

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 !); supercell mix  
eigenstates, need unfolding

# First-principles 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**.

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



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.

Used for semi-empirical calculations in the '80s

# Allen-Heine-Cardona (AHC) formalism

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

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

Second-order (time-dependent) perturbation theory

(no average contribution from first order)

\* Formulas for solids (phonons have crystalline momentum)

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

$$\delta\epsilon_{\vec{k}n}(T, V = \text{const}) = \frac{1}{N_{\vec{q}}} \sum_{\vec{q}j} \frac{\partial\epsilon_{\vec{k}n}}{\partial n_{\vec{q}j}} \left( n_{\vec{q}j}(T) + \frac{1}{2} \right) \quad \text{occupation number from Bose-Einstein statistics}$$

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

Electron-phonon coupling energy (EPCE)

“Phonon mode factor”

$\xi_{\kappa a}(\vec{q}j)$  phonon eigenmodes

$\kappa$  = atom label

$a=x, y, \text{ or } z$

# Eigenvalue changes

$$\left( \frac{\partial^2 \epsilon_{\vec{k}n}}{\partial R_{\kappa a} \partial R_{\kappa' b}} \right) ?$$

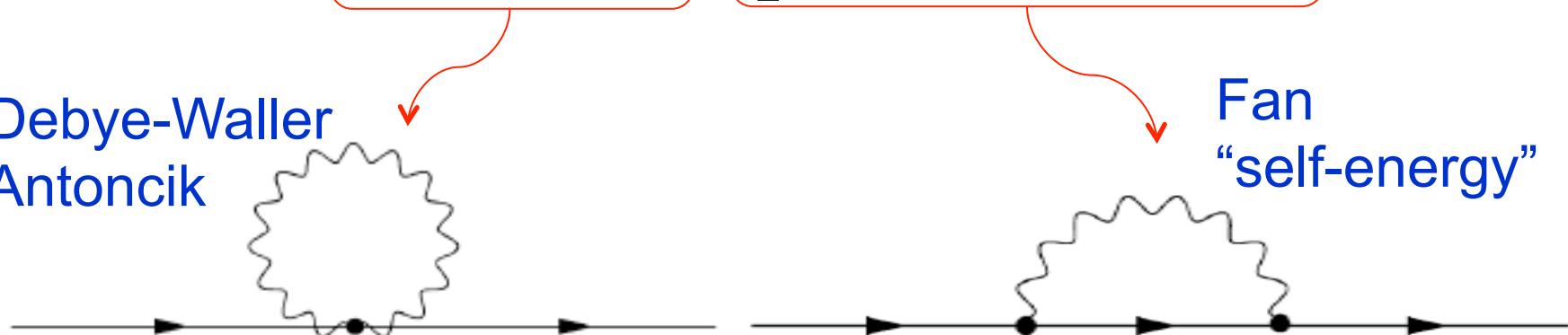
$$\epsilon_{\vec{k}n} = \langle \phi_{\vec{k}n} | \hat{H}_{\vec{k}} | \phi_{\vec{k}n} \rangle \quad \hat{H} = \hat{T} + \hat{V}_{\text{nucl}} + \int \frac{\rho(r')}{|r-r'|} dr' + \frac{dE_{xc}}{d\rho(r)}$$

Hellman-Feynman theorem :  $\epsilon_{\vec{k}n}^{(1)} = \langle \phi_{\vec{k}n}^{(0)} | \hat{H}_{\vec{k}}^{(1)} | \phi_{\vec{k}n}^{(0)} \rangle$

One more derivative :

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

Debye-Waller  
Antoncik

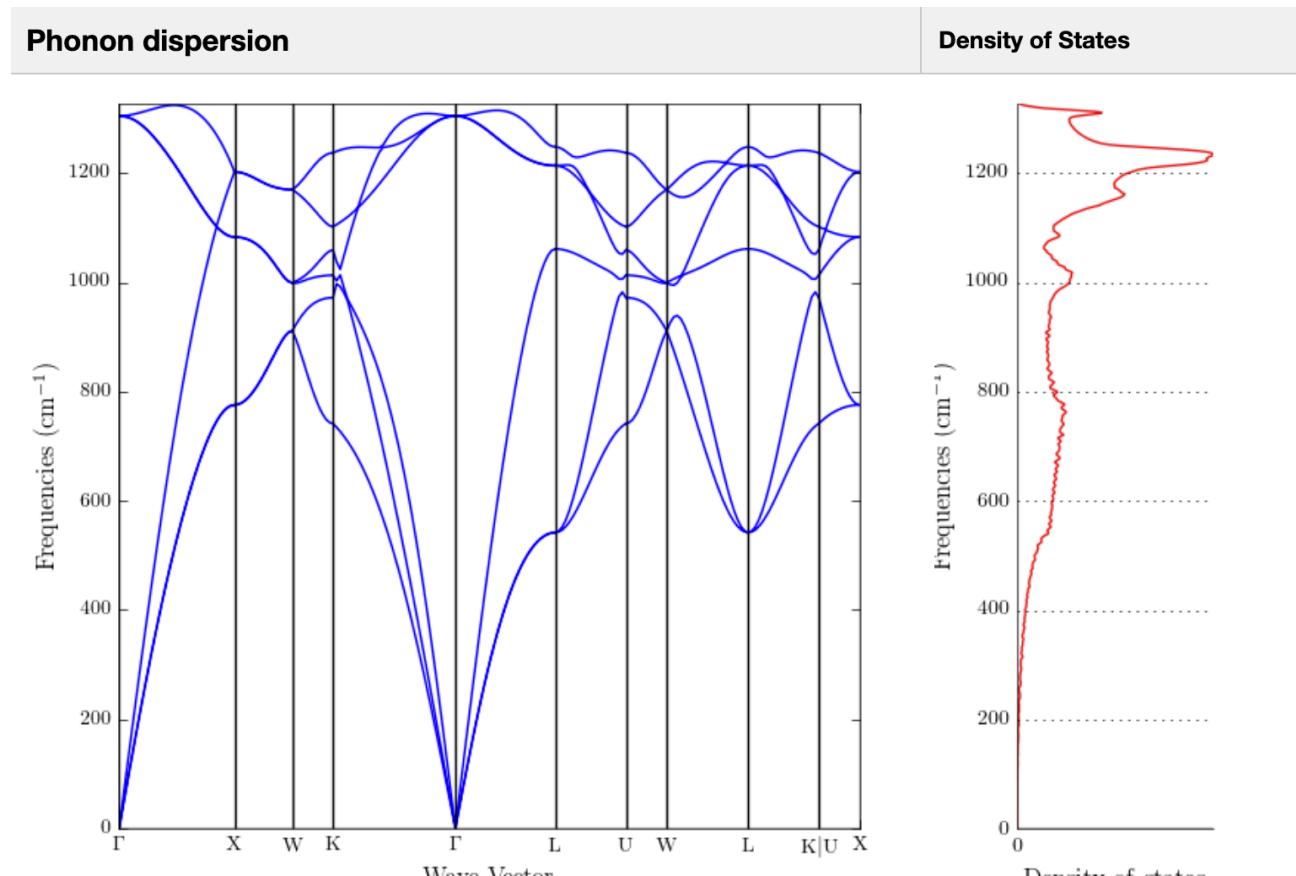


# First-principles implementation

- Density-Functional Theory (later, GW results will be shown as well)
- Implementation in ABINIT ([www.abinit.org](http://www.abinit.org))
- Plane wave + pseudopotential methodology
- Converged number of plane waves (for diamond 30 ... 40 Hartree)
- k point sampling (for diamond 6x6x6 sufficient for first-order Hamiltonian)
- Density Functional Perturbation Theory for phonons => no sum on conduction bands, no supercell

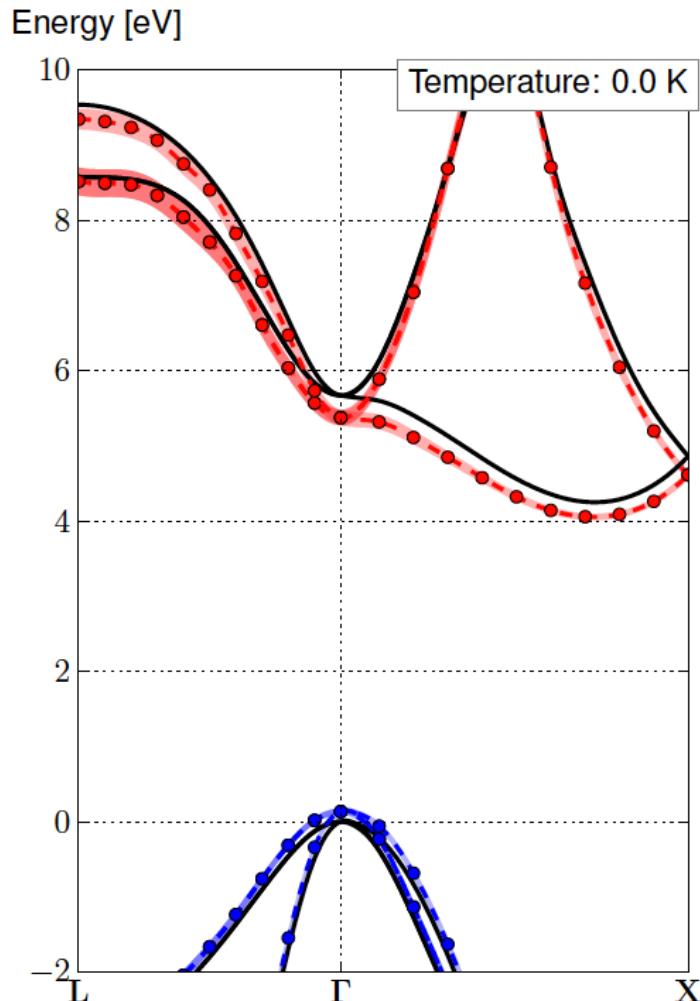
Technology used in the Materials project (<http://materialsproject.org>)  
>1500 phonon band structures from ABINIT freely available

# ABINIT phonons uploaded in Materials Project



Warning! These calculations were performed using a PBEsol exchange correlation functional in the framework of DFPT using the Abinit code. Please see the [wiki](#) for more info. ×

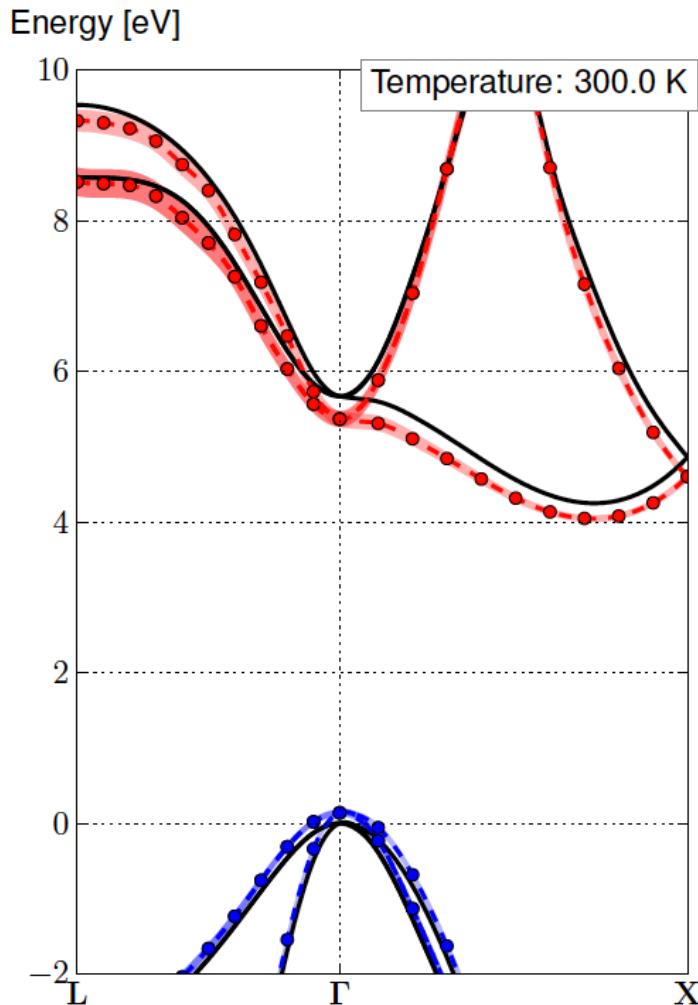
# DFT T-dependent band structure



Diamond 0 Kelvin  
(incl. Zero-point motion)

Note the widening of  
the bands = lifetime

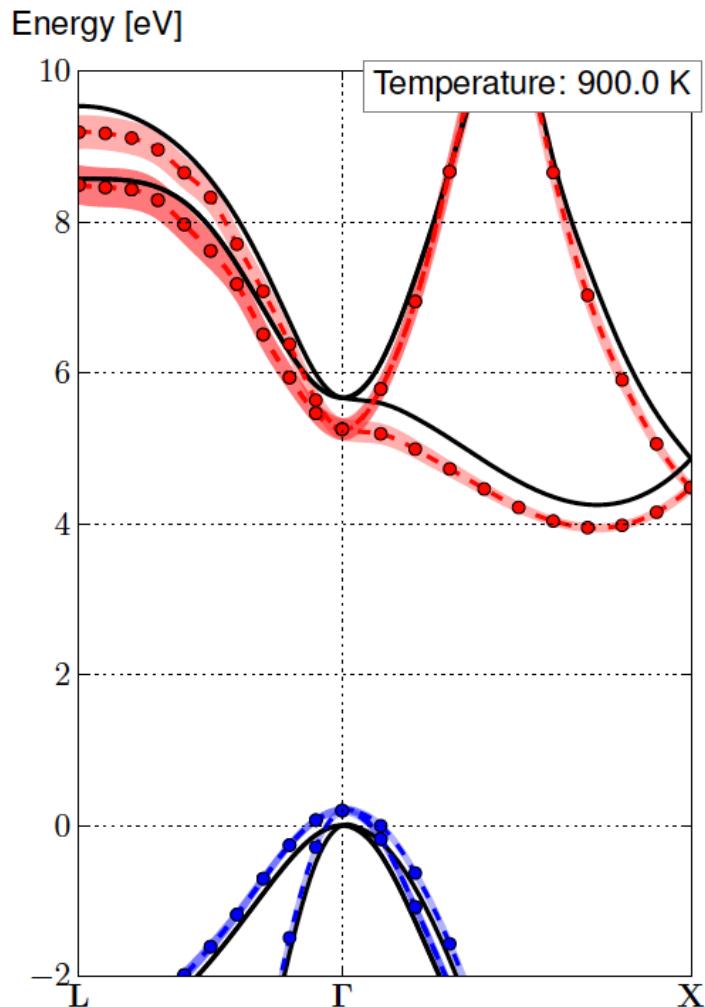
# DFT T-dependent band structure



Diamond 300 Kelvin

Note the widening of  
the bands = lifetime

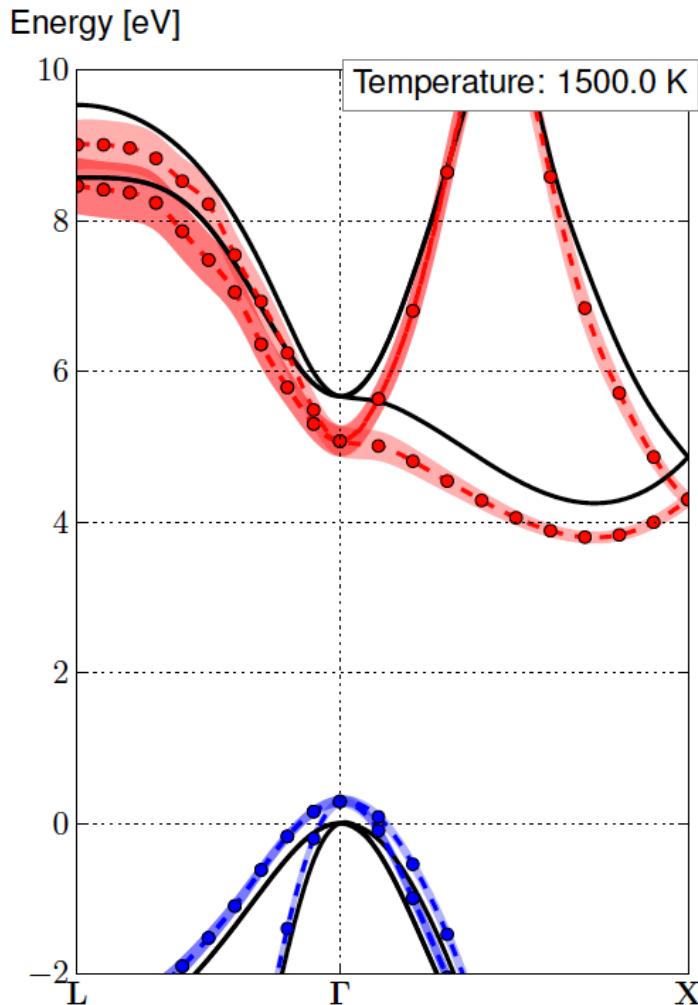
# DFT T-dependent band structure



Diamond 900 Kelvin

Note the widening of  
the bands = lifetime

# DFT T-dependent band structure



Diamond 1500 Kelvin

Note the widening of  
the bands = lifetime

# First-principles implementation

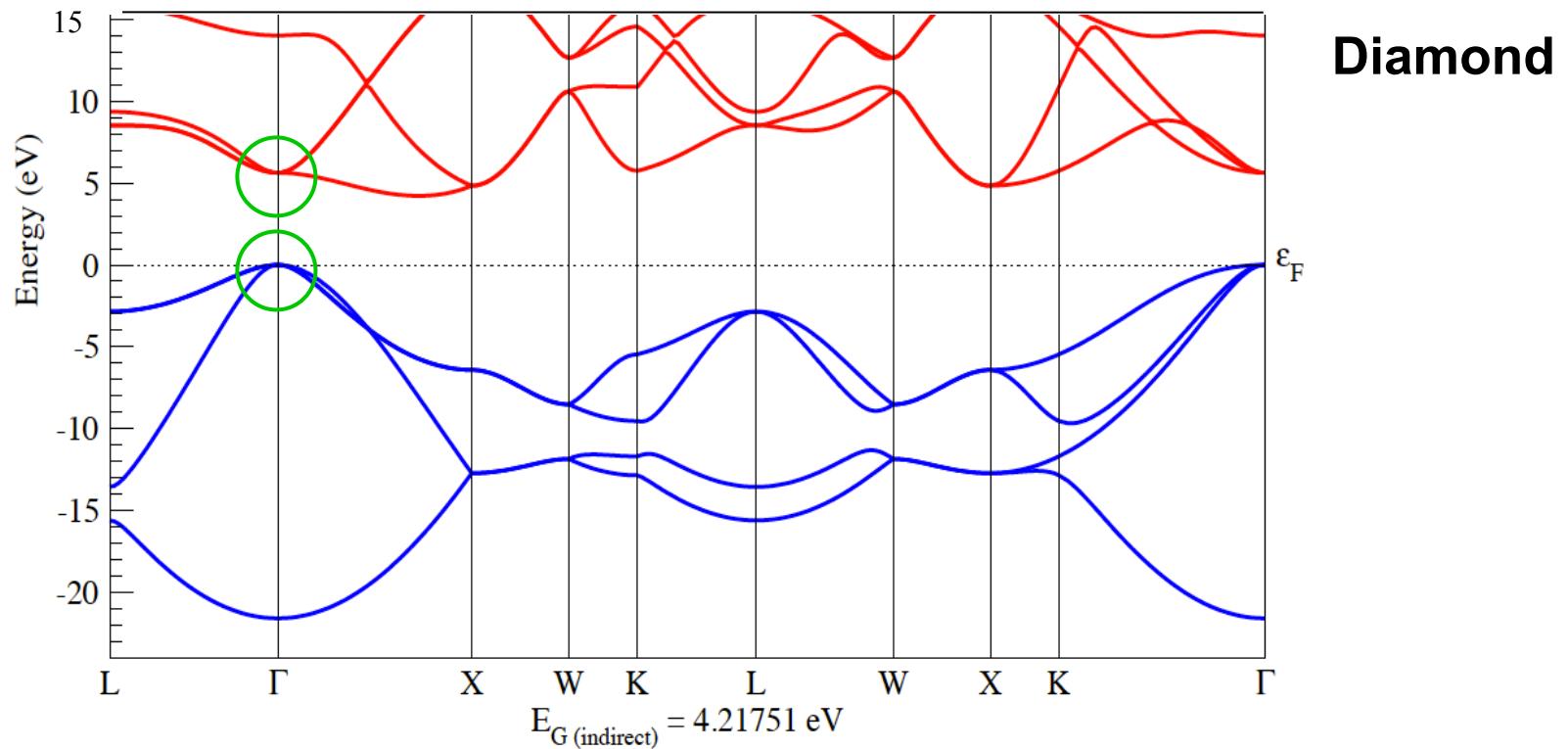
- Density-Functional Theory (later, GW results will be shown as well)
- Implementation in ABINIT ([www.abinit.org](http://www.abinit.org))
- Plane wave + pseudopotential methodology
- Converged number of plane waves (for diamond 30 ... 40 Hartree)
- $k$  point sampling (for diamond 6x6x6 sufficient for first-order Hamiltonian)
- Density Functional Perturbation Theory **for phonons** => no sum on conduction bands, no supercell need ; reformulation of the Debye-Waller term thanks to the rigid-ion approximation
- Sampling on the  $q$  phonon wavevectors for the Fan term is a big issue !

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

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

Indeed intraband contributions **diverge** due to the denominator !  
Still, can be **integrated out** ... for diamond ...

# Intraband divergence for small q



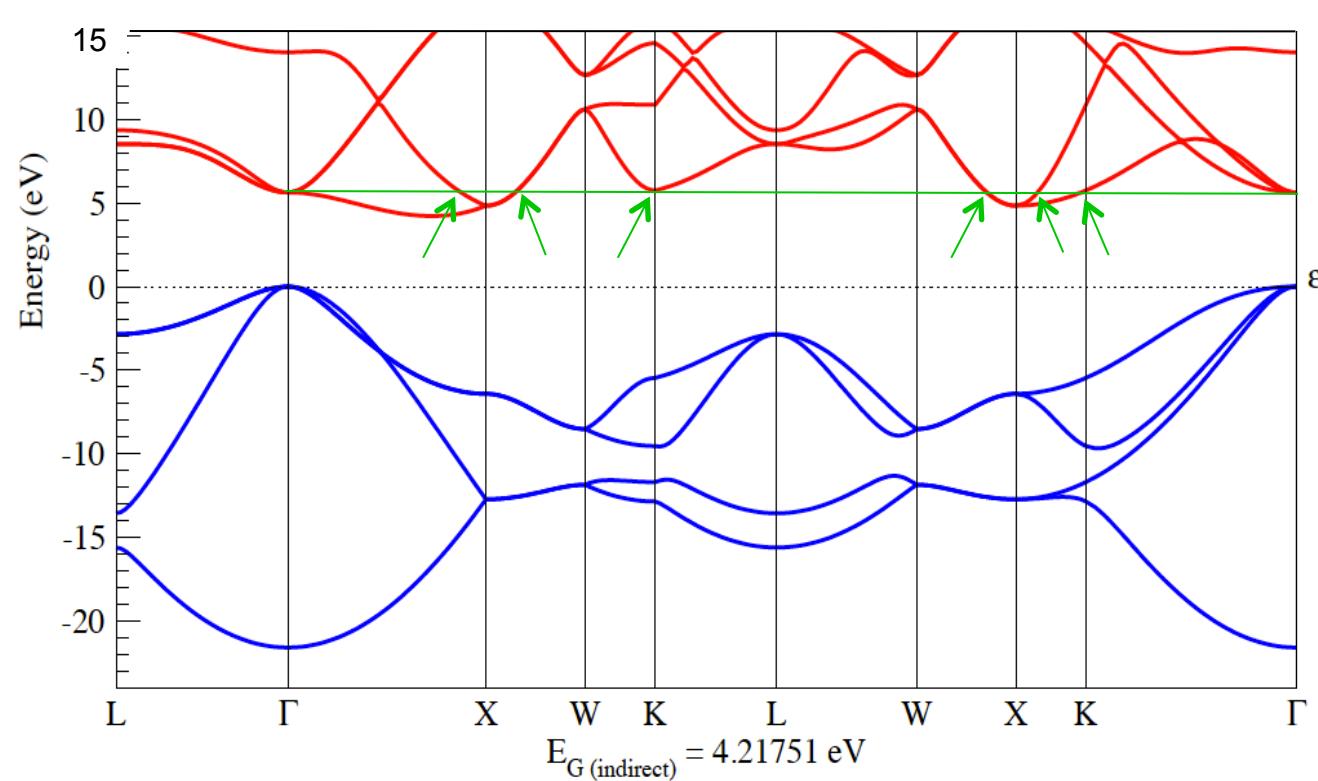
$$\lim_{\vec{q} \rightarrow 0} \frac{\partial \epsilon_{\Gamma n}(Fan)}{\partial n_{\vec{q}j}} = \lim_{\vec{q} \rightarrow 0} \frac{1}{\omega_{\vec{q}j}} \frac{f(\vec{q}jn)}{\epsilon_{\Gamma n} - \epsilon_{\vec{q}n}}$$

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

Can be integrated in 3D !

+ For acoustic modes, Fan/DDW contribs cancel each other

# Divergences on isoenergetic surface



**Diamond**  
Set of  
isoenergetic  
wavevectors

$$\lim_{\vec{q} \rightarrow \vec{q}_{iso}} \frac{\partial \epsilon_{\Gamma n}(Fan)}{\partial n_{\vec{q}j}} = \lim_{\vec{q} \rightarrow \vec{q}_{iso}} \frac{1}{\omega_{\vec{q}j}} \frac{f(\vec{q}jn)}{\epsilon_{\Gamma n} - \epsilon_{\vec{q}n}} \propto \frac{1}{\nabla_{\vec{q}} \epsilon_{\vec{q}n} \Big|_{\vec{q}_{iso}} \cdot (\vec{q} - \vec{q}_{iso})}$$

Can be integrated !  
Such problem occurs only off the extrema

# Smoothing the denominator

Standard recipe in AHC works in the 80s: C, but also Si, III-V compounds ...

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

... dramatically helps the convergence ... to a (slightly) different value ...

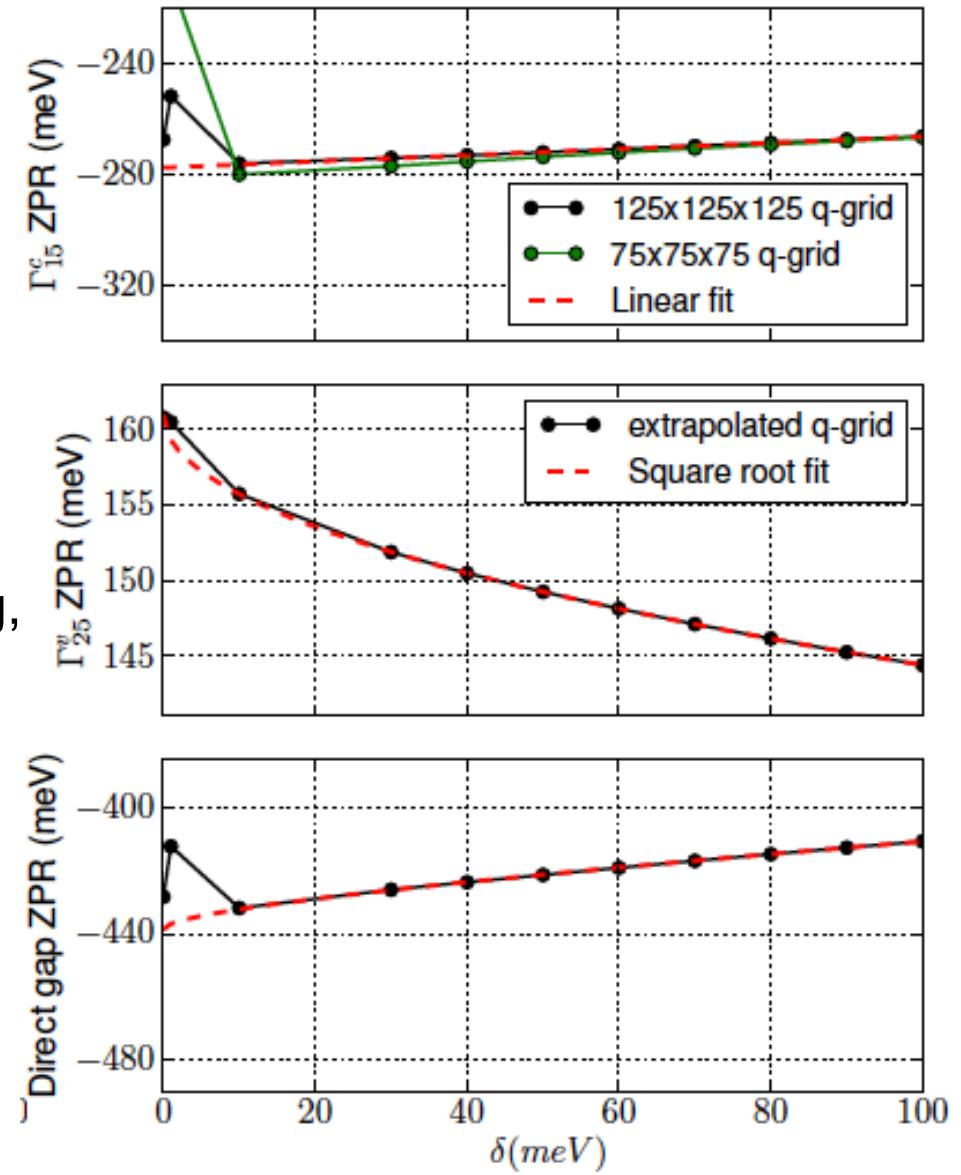
If imaginary part = 100 meV (considering direct gap at Gamma) :

q grid	#q in IBZ	ZPR VBM (meV)	ZPR CBM (meV)	ZPR 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

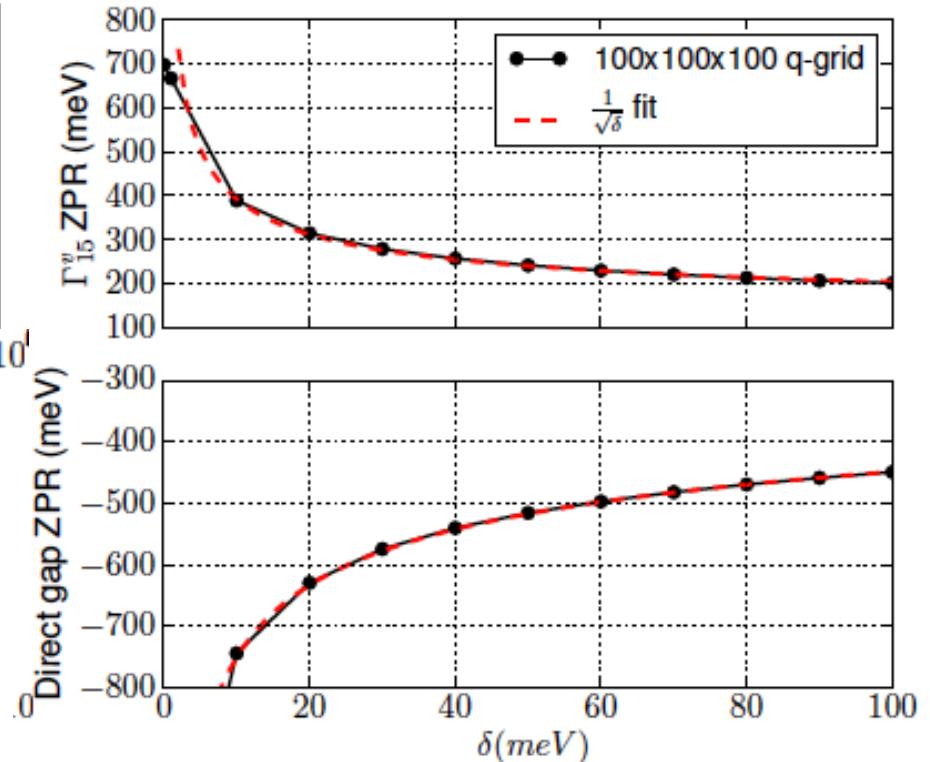
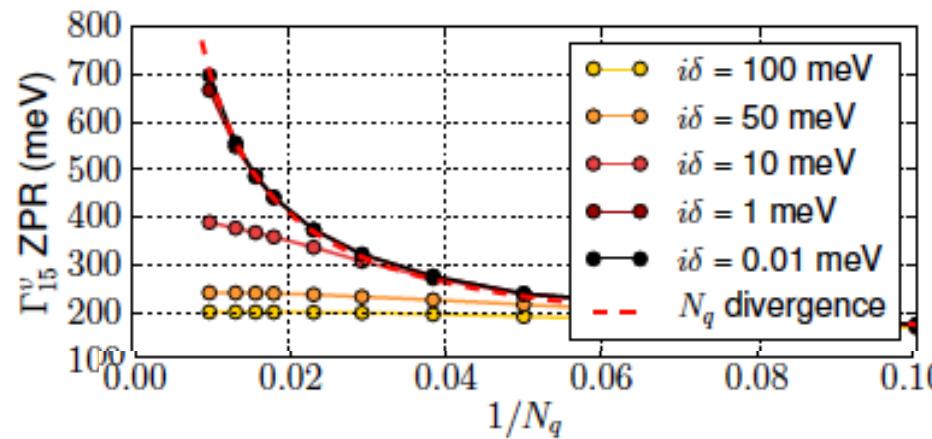
$$\frac{f(\vec{q}jn)}{\epsilon_{\Gamma n} - \epsilon_{\vec{q}n} + i\delta}$$

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



# **Breakdown of the adiabatic quadratic approximation 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  $|\mathbf{q}| \rightarrow 0$        $\mathbf{G} = 0$

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

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

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

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

$$\bar{n}_{\mathbf{q}}^{(1)} \propto \boxed{|\mathbf{q}|} \text{ when } |\mathbf{q}| \rightarrow 0$$

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  $\kappa$

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

# Quadratic approx. with IR-active optic modes

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

Twice  $H_{\vec{q}}^{(1)} = \sum_{\kappa a} \nabla_{\kappa a} H_{\kappa} \xi_{\kappa a}(\vec{q}j)$ , each diverges like  $1/q^2$  for polar optic modes.

At band extrema, the denominator induces a  $1/q^2$  divergence .

For polar optic modes : total divergence is like  $1/q^4$ , cannot be integrated !

The adiabatic quadratic approximation breaks down for materials with IR-active optic modes.

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

# Dynamical AHC theory

Beyond adiabatic perturbation theory ... Many-body perturbation theory !  
Fan self-energy (also called Migdal self-energy) :

$$\Sigma_{\lambda\lambda'}^{Fan}(\omega) = \sum_{\nu} \frac{1}{2\omega_{\nu}} \sum_{\lambda''} \langle \psi_{\lambda} | H_{\nu}^{(1)} | \psi_{\lambda''} \rangle \langle \psi_{\lambda''} | H_{\nu}^{(1)*} | \psi_{\lambda'} \rangle$$
$$\left[ \frac{n_{\nu}(T) + f_{\lambda''}(T)}{\omega - \varepsilon_{\lambda''}^0 + \omega_{\nu} + i\eta \operatorname{sgn}(\omega)} + \frac{n_{\nu}(T) + 1 - f_{\lambda''}(T)}{\omega - \varepsilon_{\lambda''}^0 - \omega_{\nu} + i\eta \operatorname{sgn}(\omega)} \right]$$

→ **integrable divergences !**

Different levels :

On-the-mass shell approximation       $\varepsilon_{\lambda} = \varepsilon_{\lambda}^0 + \Sigma_{\lambda}^{ep}(\varepsilon_{\lambda}^0)$

Quasi-particle approximation       $\varepsilon_{\lambda} = \varepsilon_{\lambda}^0 + \Sigma_{\lambda}^{ep}(\varepsilon_{\lambda})$        $\varepsilon_{\lambda} = \varepsilon_{\lambda}^0 + Z_{\lambda} \Sigma_{\lambda}^{ep}(\varepsilon_{\lambda}^0)$

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

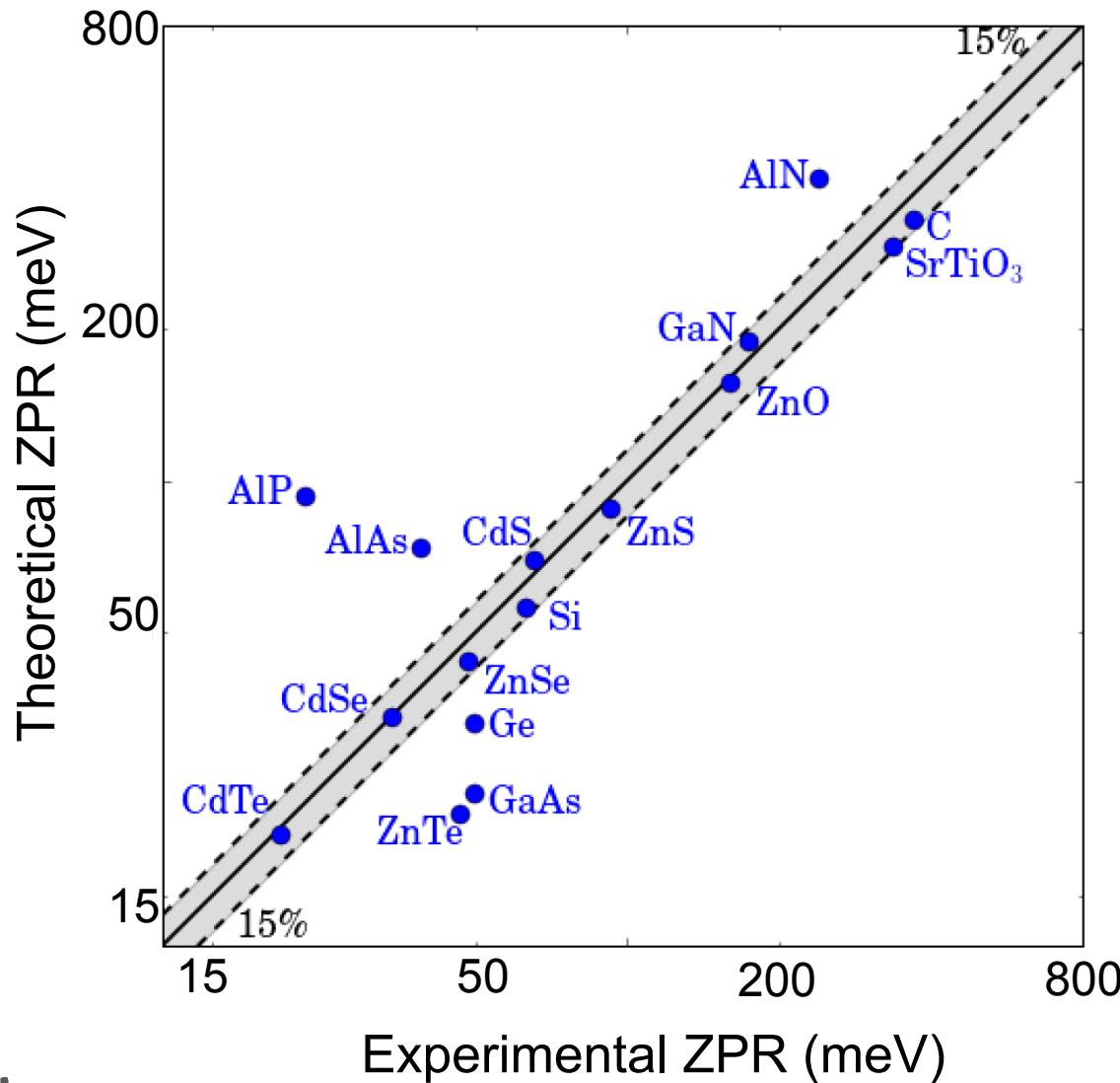
Or even spectral functions

$$A_{\lambda}(\omega) = \frac{1}{\pi} \frac{|\Im \Sigma_{\lambda}^{ep}(\omega)|}{[\omega - \varepsilon_{\lambda}^0 - \Re \Sigma_{\lambda}^{ep}(\omega)]^2 + |\Im \Sigma_{\lambda}^{ep}(\omega)|^2}$$

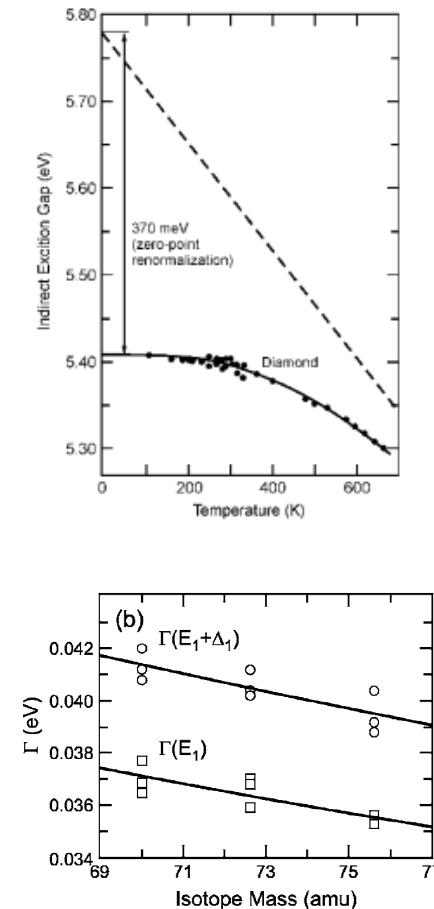
S. Poncé, Y. Gillet, J. Laflamme Janssen, A. Marini,  
M. Verstraete & XG, J. Chem. Phys. 143, 102813 (2015)

# Zero-point renormalization: theory vs experiment

# Non-adiabatic AHC theory vs experiment

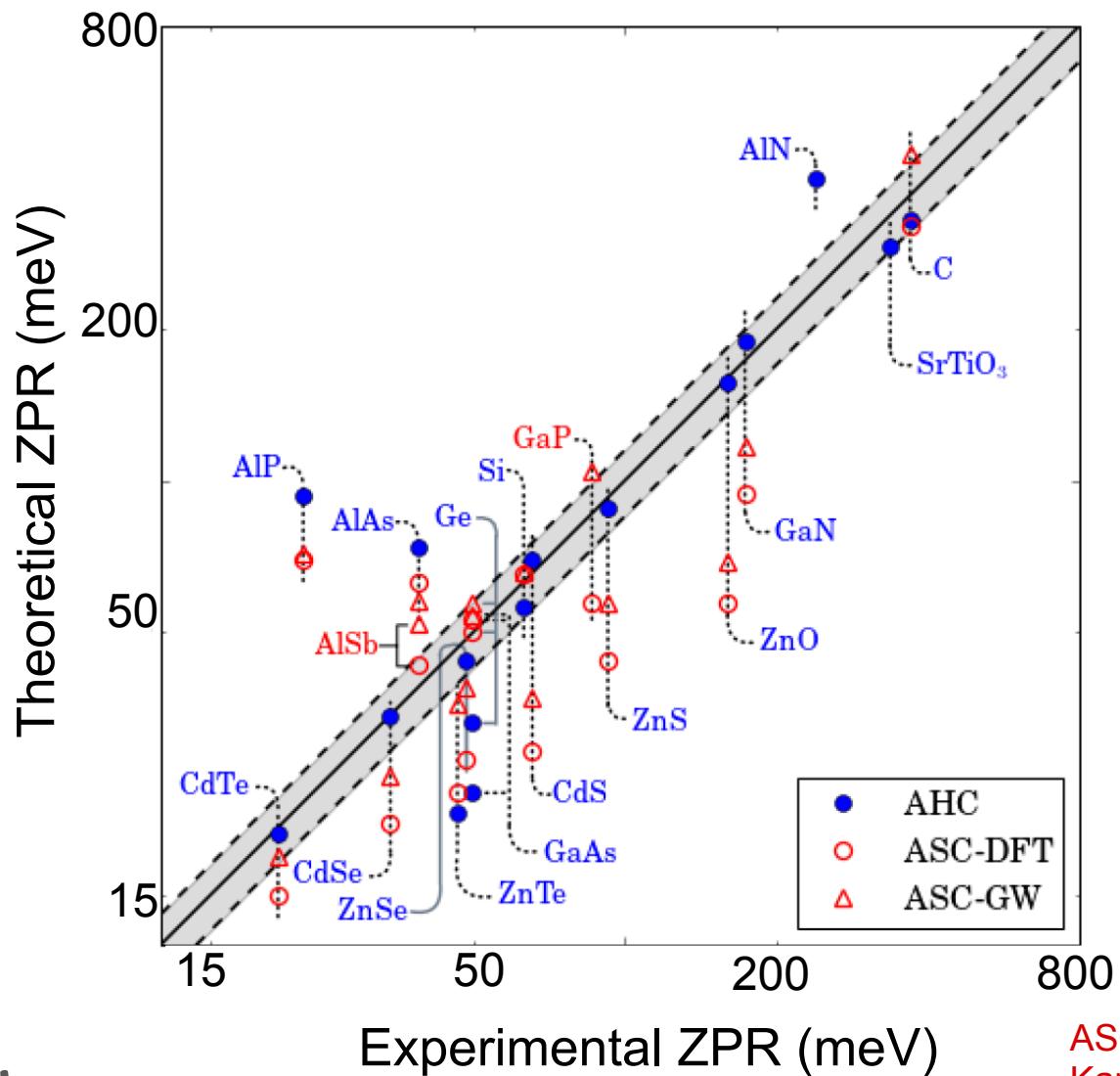


ZPR of the band gap  
Two different exp techniques



$$E_M = E_\infty + BM^{-1/2}$$

# What about other theories ?

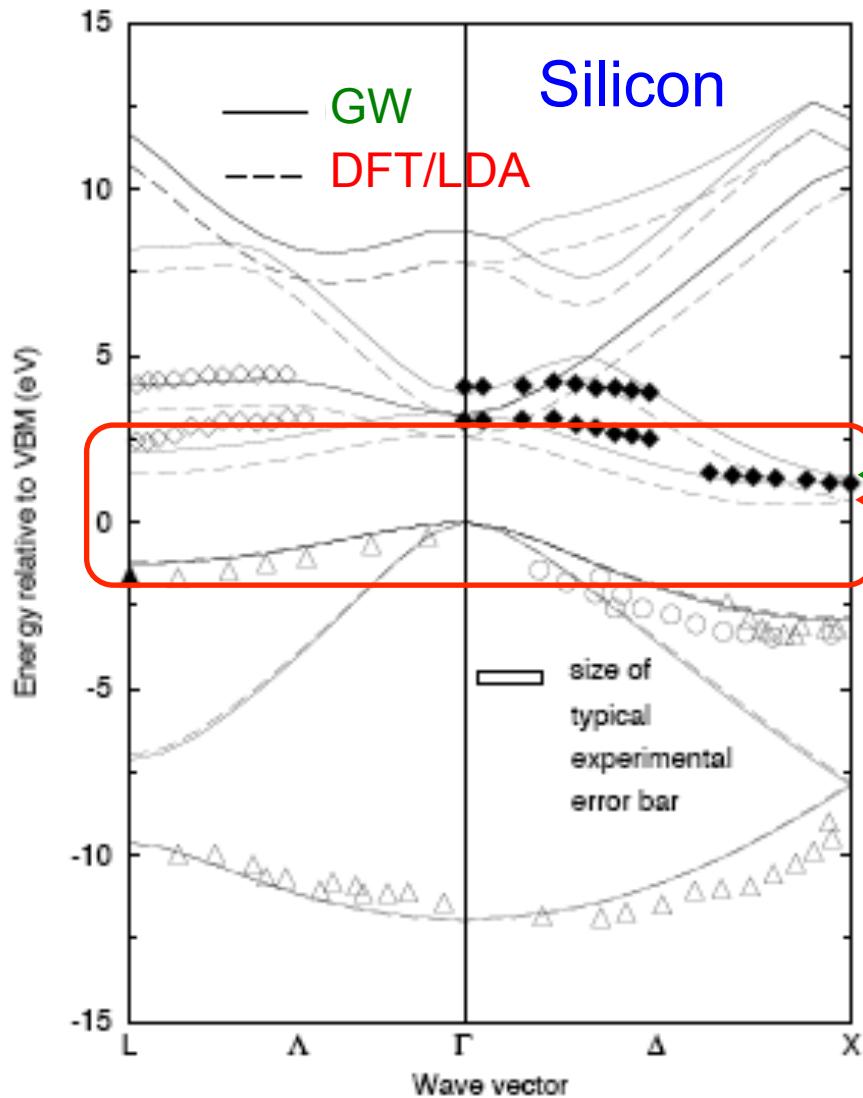


ASC= Adiabatic SuperCell,  
based on DFT (PBE)  
or on GW -in principle more  
accurate than DFT.

For both ASC types, less than  
one third of points fall inside  
15% zone

ASC results from  
Karsai et al, *New J. Phys.*, **20**, 123008 (2018)

# The DFT bandgap problem



Comparison of DFT/LDA and Many-Body Perturbation Theory GW band structures with photoemission and inverse photoemission experiments for Silicon.

$$E_g(\text{exp}) = 1.17 \text{ eV}$$

$$E_g(\text{GW}) = 1.2 \text{ eV}$$

$$E_g(\text{DFT/LDA}) = 0.6 \text{ eV}$$

Problem !

From "Quasiparticle calculations in solids",  
by Aulbur WG, Jonsson L, Wilkins JW,

Solid State Physics 54, 1-218 (2000)

# $G_0W_0$ + self-consistency + vertex (+e-h)...?

	scGW RPA	scGW <i>e-h</i>	EXP
Ge	0.95	0.81	<u>0.74</u>
Si	1.41	1.24	<u>1.17</u>
GaAs	1.85	1.62	<u>1.52</u>
<i>SiC</i>	2.88	2.53	2.40
CdS	2.87	2.39	2.42
AlP	2.90	2.57	2.45
GaN	3.82	3.27	3.20
ZnO	3.8	3.2	<u>3.44</u>
ZnS	4.15	3.60	<u>3.91</u>
C	6.18	5.79	5.48
BN	7.14	6.59	$\approx 6.25$
MgO	9.16	8.12	7.83
LiF	15.9	14.5	14.20
Ar	14.9	13.9	14.20
Ne	22.1	21.4	21.70

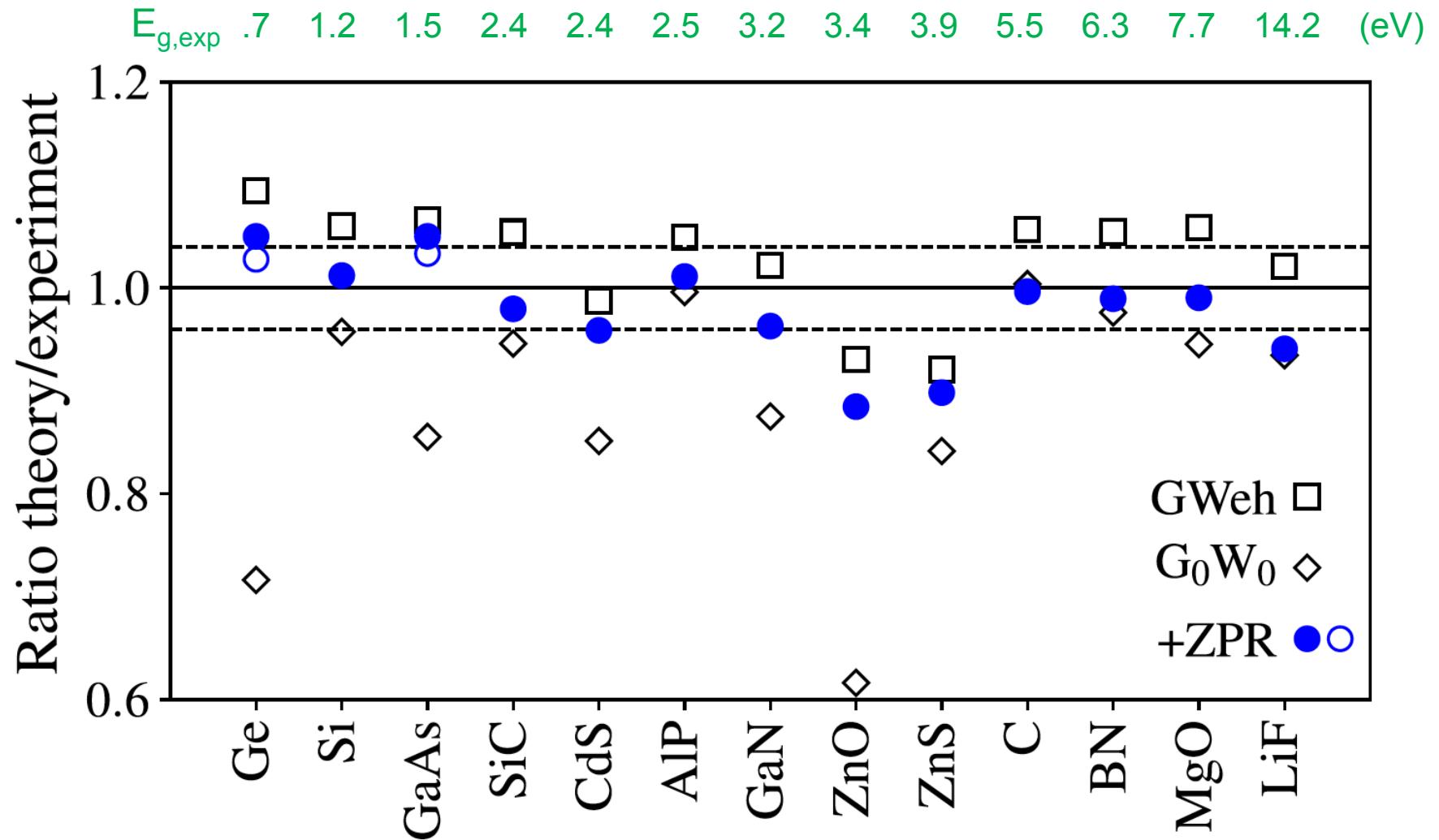
scGW RPA vs EXP  
Diff. 0.1 eV ... 1.4 eV

scGW + e-h is even better ...  
Remaining discrepancy  
0.1 eV ... 0.4 eV

Due to phonons, at least partly !

From Shishkin, Marsman, Kresse,  
PRL 99, 246403 (2007)

# Band gap : theory vs experiment



# The physics of the zero-point renormalization in IR-active materials

# Try Fröhlich Hamiltonian ...

Approximations ... (*Fröhlich, Proc. R. Soc. Lond. A 215, 291 (1952), Adv. Phys. 3,325 (1954)*).

One (c or v) electronic band with only one LO phonon branch. Moreover :

- (1) el-ph coupling = macroscopically screened Coulomb;
- (2) parabolic (c or v) band with effective mass ;
- (3) only intraband electronic contributions;
- (4) phonon energy constant with respect to wavevector q.

Hypotheses (1-4) **CORRECT** for  $q@0$ , but extended to full BZ and beyond.

**NO Debye-Waller, no TO, no acoustic branches ! Long history (large polarons)...**

For non-degenerate isotropic c or v band extrema + isotropic material :

$$\alpha = \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \left( \frac{m^*}{2\omega_{LO}} \right)^{1/2}$$

Lowest-order perturbation theory

$$\text{ZPR}^{Fr} = -\alpha \omega_{LO}$$

# Fröhlich Hamiltonian

Approximations ... (*Fröhlich, Proc. R. Soc. Lond. A 215, 291 (1952), Adv. Phys. 3,325 (1954)*).

One (c or v) electronic band with only one LO phonon branch...

$$\hat{H}^{Fr} = \hat{H}_{el}^{Fr} + \hat{H}_{ph}^{Fr} + \hat{H}_{EPI}^{Fr}$$

$$\hat{H}_{el}^{Fr} = \sum_{\mathbf{k}} \frac{\mathbf{k}^2}{2m^*} \hat{c}_{\mathbf{k}}^+ \hat{c}_{\mathbf{k}}$$

$$\hat{H}_{ph}^{Fr} = \sum_{\mathbf{q}} \omega_{LO} \hat{a}_{\mathbf{q}}^+ \hat{a}_{\mathbf{q}}$$

$$\hat{H}_{EPI}^{Fr} = \sum_{\mathbf{q}, \mathbf{k}} g^{Fr}(\mathbf{q}) \hat{c}_{\mathbf{k}+\mathbf{q}}^+ \hat{c}_{\mathbf{k}} (\hat{a}_{\mathbf{q}} + \hat{a}_{-\mathbf{q}}^+)$$

$$g^{Fr}(\mathbf{q}) = \frac{i}{q} \left[ \frac{2\pi\omega_{LO}}{V_{BvK}} \left( \frac{1}{\epsilon^\infty} - \frac{1}{\epsilon^0} \right) \right]^{1/2}$$

Lowest-order perturbation theory

$$\text{ZPR}^{Fr} = -\alpha \omega_{LO}$$

$$\alpha = \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \left( \frac{m^*}{2\omega_{LO}} \right)^{1/2}$$

# Generalisation of Fröhlich Hamiltonian

Here, lowest-order PT generalized to **degenerate & anisotropic** extrema + **anisotropic** materials + **multiple phonon** branches, still with hypotheses (1-4)  
 $(Z^*, m^*, \text{dynamical matrix at } \Gamma \dots \text{ from 1st-principles})$

$$\hat{H}^{gFr} = \hat{H}_{el}^{gFr} + \hat{H}_{ph}^{gFr} + \hat{H}_{EPI}^{gFr}$$

$$\hat{H}_{el}^{gFr} = \sum_{\mathbf{k}n} \frac{k^2}{2m_n^*(\hat{\mathbf{k}})} \hat{c}_{\mathbf{k}n}^+ \hat{c}_{\mathbf{k}n}$$

$$\hat{H}_{ph}^{gFr} = \sum_{\mathbf{q}j} \omega_{j0}(\hat{\mathbf{q}}) \hat{a}_{\mathbf{q}j}^+ \hat{a}_{\mathbf{q}j}$$

$$\hat{H}_{EPI}^{gFr} = \sum_{\mathbf{q}j, \mathbf{k}n'n} g^{gFr}(\mathbf{q}j, \mathbf{k}n'n) \hat{c}_{\mathbf{k}+\mathbf{q}n'}^+ \hat{c}_{\mathbf{k}n} (\hat{a}_{\mathbf{q}j} + \hat{a}_{-\mathbf{q}j}^+)$$

$$g^{gFr}(\mathbf{q}j, \mathbf{k}n'n) = \frac{i}{q} \frac{4\pi}{\Omega_0} \left( \frac{1}{2\omega_{j0}(\hat{\mathbf{q}})} \right)^{1/2} \frac{\hat{\mathbf{q}} \cdot \mathbf{p}_j(\hat{\mathbf{q}})}{\epsilon^\infty(\hat{\mathbf{q}})} \sum_m s_{n'm}(\hat{\mathbf{k}}') (s_{nm}(\hat{\mathbf{k}}))^*$$

Lowest-order perturbation theory

$$\text{ZPR}_c^{gFr} = - \sum_{jn} \frac{1}{\sqrt{2}\Omega_0 n_d} \int_{4\pi} d\hat{\mathbf{q}} (m_n^*(\hat{\mathbf{q}}))^{1/2} (\omega_{j0}(\hat{\mathbf{q}}))^{-3/2} \left( \frac{\hat{\mathbf{q}} \cdot \mathbf{p}_j(\hat{\mathbf{q}})}{\epsilon^\infty(\hat{\mathbf{q}})} \right)^2$$

# Strongly IR active materials: oxides

Material	Gap ZPR (meV)		
	AHC (meV)	gFr (meV)	gFr/AHC
BaO	-271	-358	<b>1.32</b>
SrO	-326	-370	<b>1.13</b>
CaO	-371	-377	<b>1.11</b>
TiO <sub>2</sub>	-337	-371	<b>1.10</b>
Li <sub>2</sub> O	-573	-536	<b>0.94</b>
ZnO	-157	-144	<b>0.92</b>
MgO	-524	-464	<b>0.89</b>
SnO <sub>2</sub>	-215	-191	<b>0.89</b>
SrTiO <sub>3</sub>	-290	-255	<b>0.88</b>
SiO <sub>2</sub>	-573	-459	<b>0.80</b>
BeO	-699	-480	<b>0.69</b>

# Weakly IR active materials

Material	Gap ZPR (meV)		
	AHC (meV)	gFr (meV)	gFr/AHC
CdTe	-20	-16	<b>0.80</b>
CdS	-70	-54	<b>0.77</b>
CdSe	-34	-26	<b>0.76</b>
ZnSe	-44	-30	<b>0.68</b>
ZnTe	-22	-15	<b>0.68</b>
ZnS	-88	-59	<b>0.67</b>
GaN-zb	-176	-107	<b>0.61</b>
GaN-w	-189	-111	<b>0.59</b>
AlN	-399	-231	<b>0.58</b>
SiC	-179	-91	<b>0.51</b>
BN	-406	-162	<b>0.40</b>
AlP	-93	-35	<b>0.38</b>
AlAs	-74	-21	<b>0.28</b>
GaAs	-24	-5	<b>0.21</b>

# Why are LO phonon frequencies so important ?

$$\text{ZPR}^{Fr} = -\alpha \omega_{LO}$$

$$\alpha = \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \left( \frac{m^*}{2\omega_{LO}} \right)^{1/2}$$

Crucial dynamical effects !

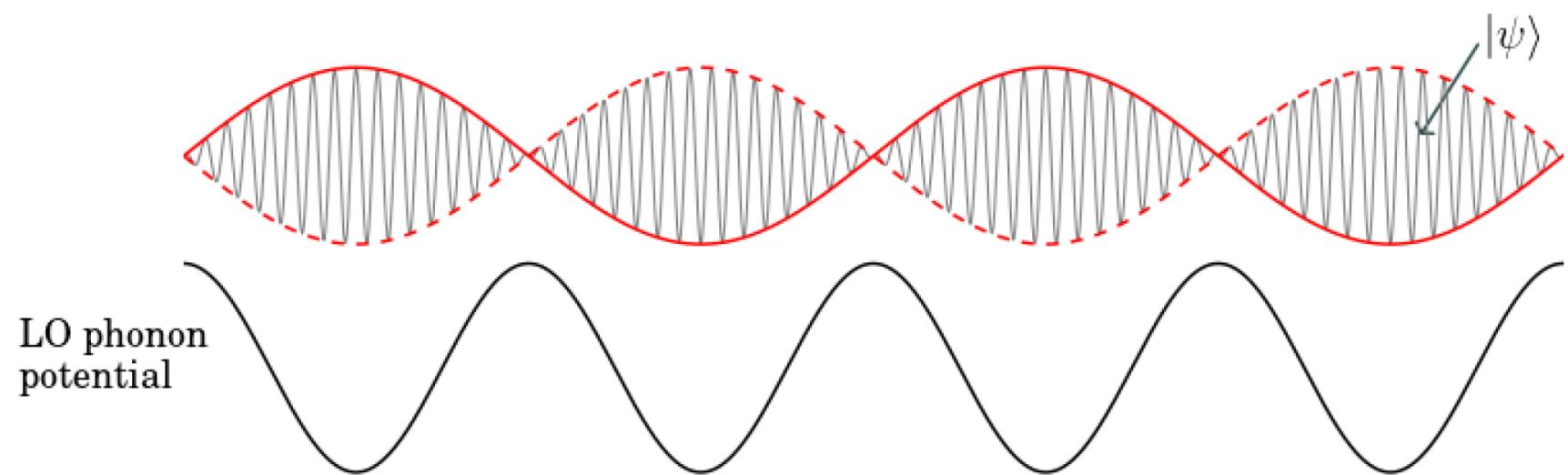
“Slow electrons + fast phonons” = “polarons”

# Adiabatic approximation: fast electrons

$$\Sigma_{\mathbf{q}\nu} \propto \frac{1}{\varepsilon_{\mathbf{k}n}^0 - \varepsilon_{\mathbf{k}+\mathbf{q}n}^0 \pm \omega_{\mathbf{q}\nu}}, \quad \text{where } \varepsilon_{\mathbf{k}n}^0 - \varepsilon_{\mathbf{k}+\mathbf{q}n}^0 = \Delta\varepsilon^0 \sim \frac{q^2}{2m^*}$$

Combine states  $|\mathbf{k}n\rangle$  and  $|\mathbf{k} + \mathbf{q}n\rangle$ :

Static (adiabatic) case

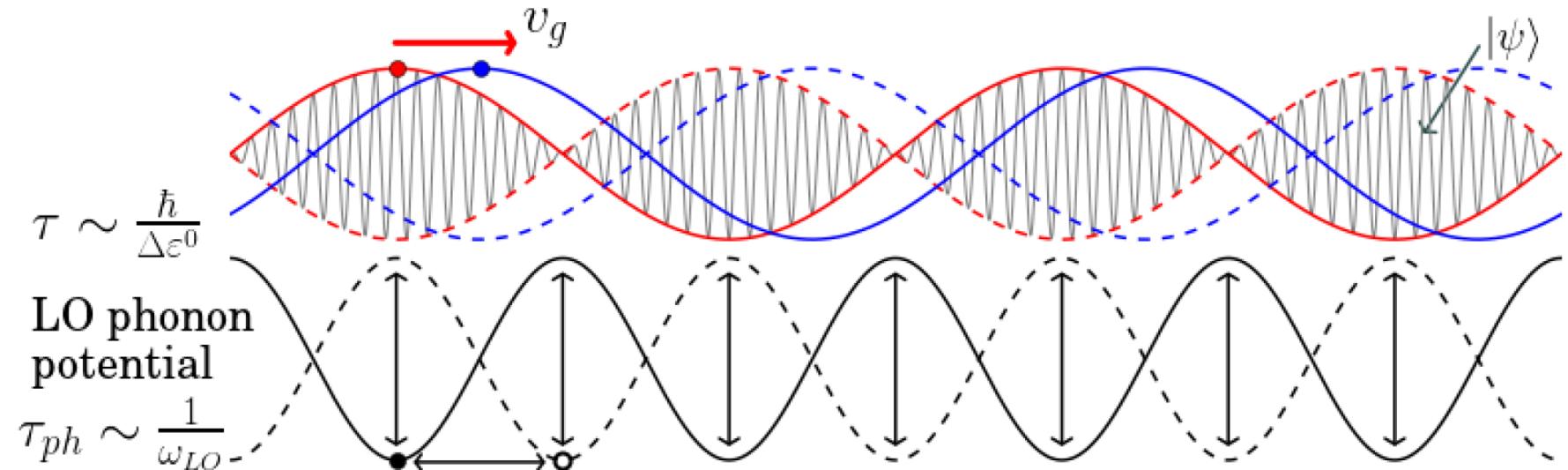


# Are electrons always fast ?

$$\Sigma_{\mathbf{q}\nu} \propto \frac{1}{\varepsilon_{\mathbf{k}n}^0 - \varepsilon_{\mathbf{k}+\mathbf{q}n}^0 \pm \omega_{\mathbf{q}\nu}}, \quad \text{where } \varepsilon_{\mathbf{k}n}^0 - \varepsilon_{\mathbf{k}+\mathbf{q}n}^0 = \Delta\varepsilon^0 \sim \frac{q^2}{2m^*}$$

Combine states  $|\mathbf{k}n\rangle$  and  $|\mathbf{k} + \mathbf{q}n\rangle$ :

Dynamical (non-adiabatic) case

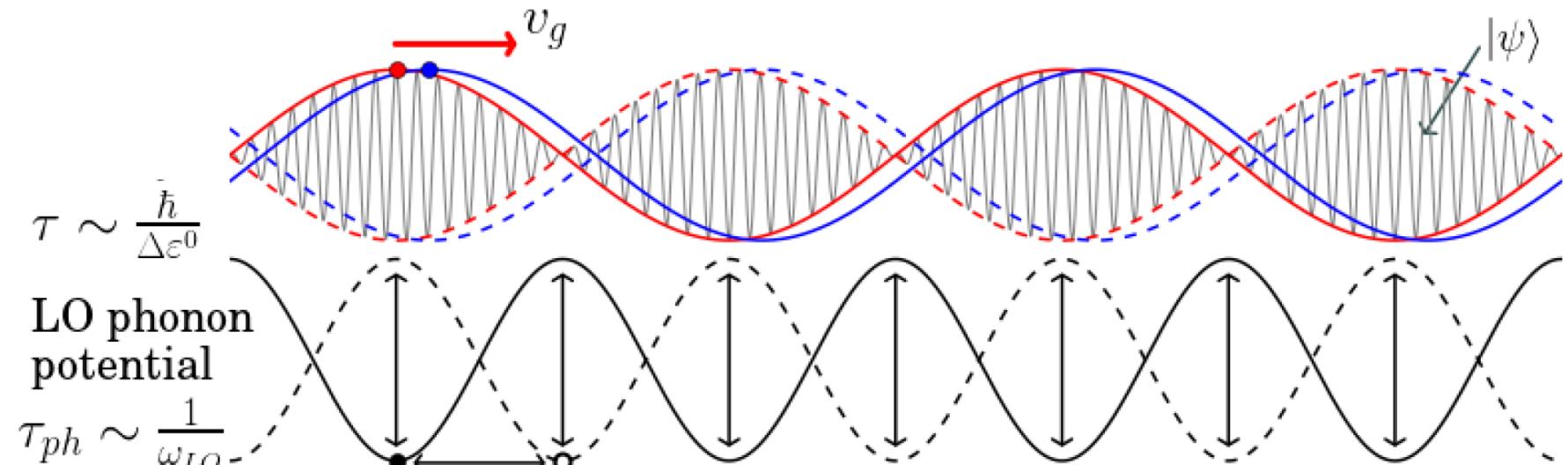


# Are electrons always fast ?

$$\Sigma_{\mathbf{q}\nu} \propto \frac{1}{\varepsilon_{\mathbf{k}n}^0 - \varepsilon_{\mathbf{k}+\mathbf{q}n}^0 \pm \omega_{\mathbf{q}\nu}}, \quad \text{where } \varepsilon_{\mathbf{k}n}^0 - \varepsilon_{\mathbf{k}+\mathbf{q}n}^0 = \Delta\varepsilon^0 \sim \frac{q^2}{2m^*}$$

Combine states  $|\mathbf{k}n\rangle$  and  $|\mathbf{k} + \mathbf{q}n\rangle$ :

Dynamical (non-adiabatic) case



When  $\tau > \tau_{ph}$  : electron has no time to adjust

At variance with adiabatic hypothesis, in IR-active materials, LO phonons are faster than the added electron (or the hole) => polarons

# Summary

- Many effects : Fan, Debye-Waller, dynamical self-energy, accurate starting electronic structure (GW) and el-ph coupling (GW) ... but also thermal expansion, anharmonicities, non-rigid ion behaviour ... (not presented here)
- Sampling phonon wavevector (= supercell size) is a serious issue
- Adiabatic quadratic approximation breaks down for infra-red active solids (both for AHC and supercell case), while inclusion of dynamical effects remove divergences
- Fröhlich Hamiltonian captures well the main features of first-principle results for IR-active materials !
- Crucial dynamical effects !  
“Slow electrons + fast phonons” = “polarons”

