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Temperature and zero-point motion effects on the electronic band structure

X. Gonze
Université Catholique de Louvain,
Louvain-la-neuve, Belgium

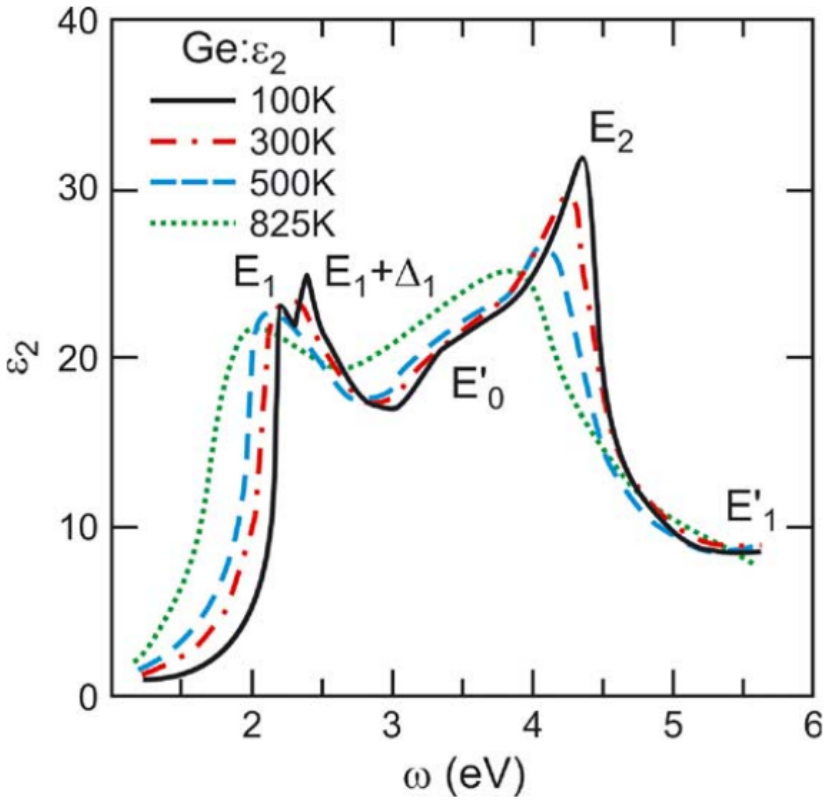
Collaborators :
P. Boulanger (CEA-Grenoble), S. Poncé (UCL)
M. Côté, G. Antonius (U. Montréal)
+ help from A. Marini, E. Canuccia for the QE+YAMBO/ABINIT comparison
+ discussions with F. Giustino

Temperature dependence of electronic/optical properties

The electrical and optical properties clearly depend on temperature...

- peaks shift in energy

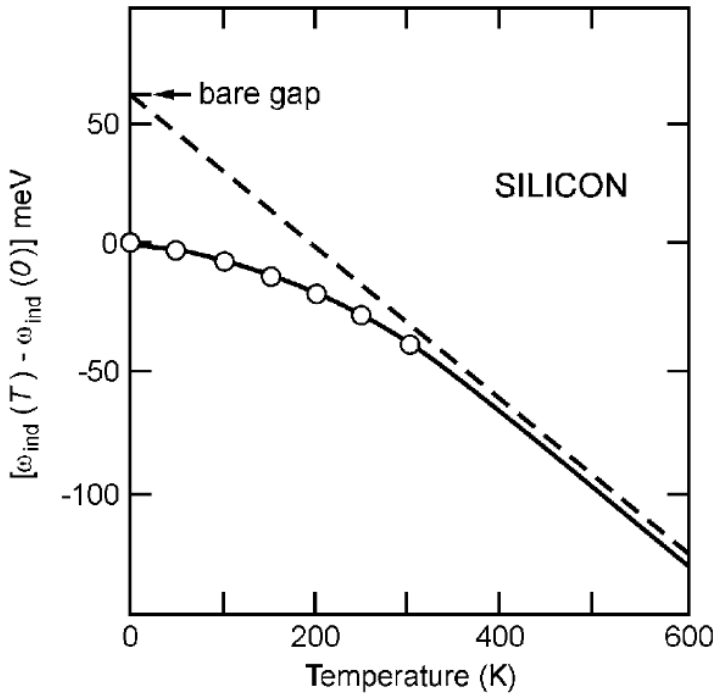
- peaks broaden with increasing temperature : decreased electron lifetime.

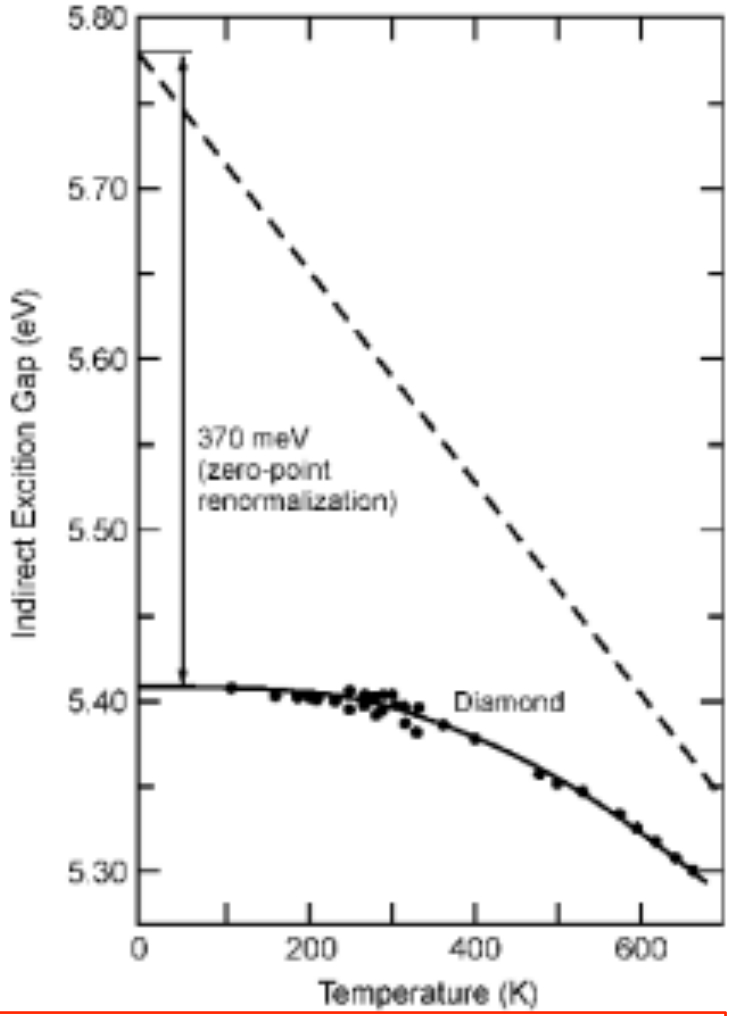


L. Viña, S. Logothetidis and M. Cardona, *Phys. Rev. B* **30**, 1979 (1984)

Even at 0 Kelvin ...

... vibrational effects are important, because of Zero Point motion (ZPM).



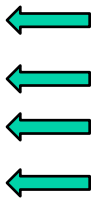


From
M. Cardona, *Solid State Comm.* **133**, 3 (2005)

The ZPM renormalization is important ! We must also calculate it.

Vertex correction... And beyond ?

	scGW RPA	scGW *e-h*	EXP
Ge	0.95	0.81	0.74
Si	1.41	1.24	1.17
GaAs	1.85	1.62	1.52
SiC	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	3.44
ZnS	4.15	3.60	3.91
C	6.18	5.79	5.48
BN	7.14	6.59	≈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



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

For materials with lighter atoms, remaining discrepancy 0.1 eV ... 0.4 eV
Due to phonons, at least partly !

Outline

(1) Motivation

(2) Brief review of first-principles phonon methodology

(3) The Allen-Heine-Cardona approach (AHC)

(4) Corrections beyond the rigid-ion approximation

(5) Application to diamond

... Work in progress ...

X. G., P. Boulanger and M. Côté. *Ann. Phys. (Berlin)* 523, 168-178 (2011).

G. Antonius, S. Poncé, X. G. and M. Côté, in preparation

The present theoretical approach : keywords

Density Functional Theory

(from QM and EM to *total energies* of solids, molecules, nanosystems ...)

Plane Waves / Pseudopotentials

(representation on a computer)

ABINIT

(the actual software)

Density Functional Perturbation Theory /Linear Response

(derivatives of total energy - dynamical matrices, phonon band structures, ...)

Brief review of phonon methodology

Density functional theory ...

The electronic energy can be obtained by the minimisation of

$$E_{el}\{\psi_\alpha\} = \sum_{\alpha}^{occ} \langle \psi_\alpha | \hat{T} + \hat{V}_{nucl} | \psi_\alpha \rangle + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} dr\, dr' + E_{xc}[\rho]$$

under constraints of orthonormalization $\langle \psi_\alpha | \psi_\beta \rangle = \delta_{\alpha\beta}$
for the occupied orbitals (independent-particle system).

The density is given by $\rho(\vec{r}) = \sum_{\alpha}^{occ} \psi_\alpha^*(\vec{r})\psi_\alpha(\vec{r})$

Approximation needed for $E_{xc}[\rho]$

The eigenfunctions also obey $\hat{H}|\psi_\alpha\rangle = \varepsilon_\alpha |\psi_\alpha\rangle$

where $\hat{H} = \hat{T} + \hat{V}_{nucl} + \int \frac{\rho(r')}{|r-r'|} dr' + \frac{\delta E_{xc}}{\delta \rho(r)}$ (Kohn-Sham equation)

$$\hat{V}_{nucl} = \sum_{\kappa} V_\kappa (r - R_\kappa)$$

Interatomic Force Constants - IFC (I)

Expansion of the total energy of a (periodic) crystal with respect to small deviations of atomic positions from the equilibrium ones (second-order):

$$E_{tot}\left(\left\{\Delta\vec{R}\right\}\right) = E_{tot}^{(0)} + \sum_{a\kappa\alpha} \sum_{a'\kappa'\alpha'} \frac{1}{2}\left(\frac{\partial^2 E_{tot}}{\partial R^a_{\kappa\alpha}\partial R^{a'}_{\kappa'\alpha'}}\right) \Delta R^a_{\kappa\alpha}\ \Delta R^{a'}_{\kappa'\alpha'}$$

where $\Delta R^a_{k\alpha}$ is the displacement along direction α of the atom k in the cell labeled a, from its equilibrium position $\vec{R}_k + \vec{R}_a$

The matrix of IFC's is defined as

$$C_{\kappa\alpha,\kappa'\alpha'}(a,a') = \frac{\partial^2 E_{tot}}{\partial R^a_{\kappa\alpha}\partial R^{a'}_{\kappa'\alpha'}}$$

Interatomic Force Constants (II)

Its Fourier Transform (using translational invariance)

$$\tilde{C}_{\kappa\alpha,\kappa'\alpha'}(\vec{q}) = \sum_{a'} C_{\kappa\alpha,\kappa'\alpha'}(0,a')\, e^{i\vec{q}.\vec{R}_{a'}}$$

allows one to compute phonon frequencies and eigenvectors as solution of the following generalized eigenvalue problem:

$$\sum_{\kappa'\alpha'} \tilde{C}_{\kappa\alpha,\kappa'\alpha'}(\vec{q}).\xi_{\kappa'\alpha'}(m\vec{q}) = M_{\kappa}.\,\omega^2_{m\vec{q}}\,.\,\xi_{\kappa\alpha}(m\vec{q})$$

phonon displacement pattern

masses

square of phonon frequencies

Note : If the eigenvalue is negative (imaginary frequency), the system is unstable against spontaneous deformation

How to get second derivatives of the energy ?
Density Functional Perturbation Theory !

General framework of perturbation theory

* $A(\lambda) = A^{(0)} + \lambda A^{(1)} + \lambda^2 A^{(2)} + \lambda^3 A^{(3)} \ldots$
* $E\{\psi;\ V_{\text{nucl}}\}$

Hypothesis : we know $V_{nucl}(\lambda) = V_{nucl}^{(0)} + \lambda V_{nucl}^{(1)} + \lambda^2 V_{nucl}^{(2)} + \ldots$

through all orders, as well as $\psi^{(0)}$, $n^{(0)}$, $E^{(0)}$

We would like to calculate

$E^{(1)}$, $E^{(2)}$, $E^{(3)} \ldots$

$\rho_\alpha^{(1)}$, $\rho_\alpha^{(2)}$, $\rho_\alpha^{(3)}$ ...

$\psi_\alpha^{(1)}$, $\psi_\alpha^{(2)}$, $\psi_\alpha^{(3)}$ ...

$\varepsilon_\alpha^{(1)}$, $\varepsilon_\alpha^{(2)}$, $\varepsilon_\alpha^{(3)}$ ...

Linear-response

The unperturbed quantities $\psi^{(0)}, \hat{H}^{(0)}, \varepsilon_\alpha^{(0)}$ must be precomputed

Also, $\hat{V}^{(1)}_{\text{nucl}}$ must be available.

Then, $\psi^{(1)}$ can be found by solving self-consistently

$$\hat{H}^{(0)} - \varepsilon_\alpha^{(0)} \left| \psi_\alpha^{(1)} \right\rangle = -P_{\text{unocc}} \hat{H}^{(1)} \left| \psi_\alpha^{(0)} \right\rangle$$

with $$\hat{H}^{(1)} = \hat{V}^{(1)}_{\text{nucl}} + \int \left(\frac{1}{|\vec{r}-\vec{r}'|} + \frac{\delta^2 E_{xc}}{\delta\rho(\vec{r})\delta\rho(\vec{r}')} \right) \rho^{(1)}(\vec{r}')\, d\vec{r}'$$

$$\rho^{(1)}(\vec{r}) = \sum_\alpha^{occ} \psi_\alpha^{(1)*}(\vec{r})\psi_\alpha^{(0)}(\vec{r}) + \psi_\alpha^{(0)*}(\vec{r})\psi_\alpha^{(1)}(\vec{r})$$

under constraint $$\left\langle \psi_\alpha^{(0)} \middle| \psi_\beta^{(1)} \right\rangle = 0$$

Late '80 + early '90 Baroni, Gianozzi, Testa, XG, Savrasov ...

Alternative approach : frozen-phonon ...

But DFPT is much more efficient : allows to treat efficiently all wavevectors.

See the Review of Modern Physics 73, 515 (2001)

by S. Baroni, S. De Gironcoli, A. Dal Corso, and P. Giannozzi.

The Allen-Heine-Cardona approach

Long history of the theory of T-dependent effects

In a semi-empirical context :

Work from the '50, based on 2nd order perturbation theory treatment of the electron-phonon effect

+ empirical psps/tight-binding :

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)

...

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

Long history of the theory of T-dependent effects

First-principles context :

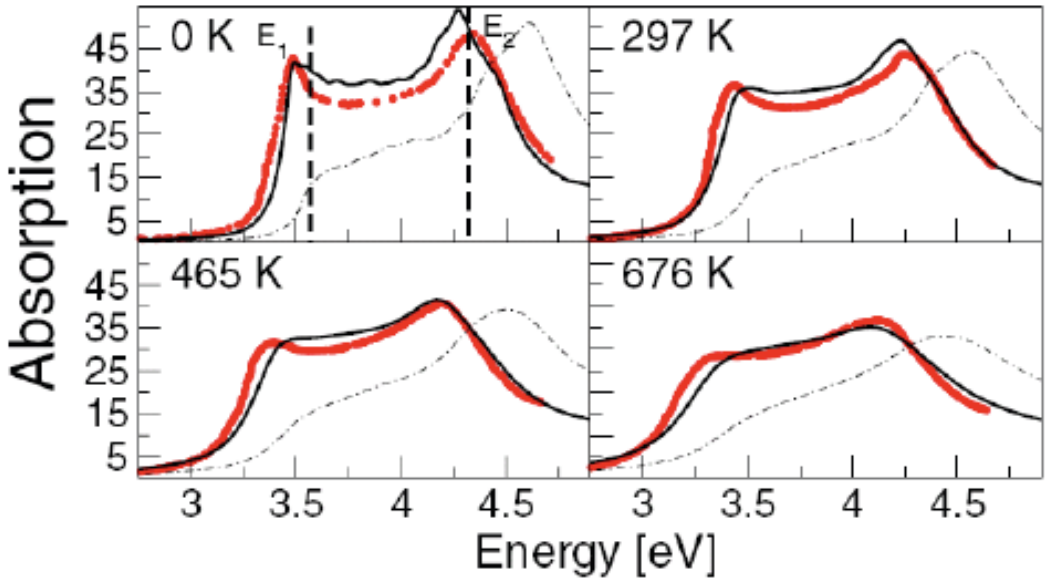
R. D. King-Smith, R. J. Needs, V. Heine and M. J. Hodgson.
Europhysics Letters **10, 569 (1989)**

A. Marini, Phys. Rev. Lett. **101, 106405 (2008)**

F. Giustino, S. Louie, M. Cohen, Phys. Rev. Lett. **105, 265501 (2010)**

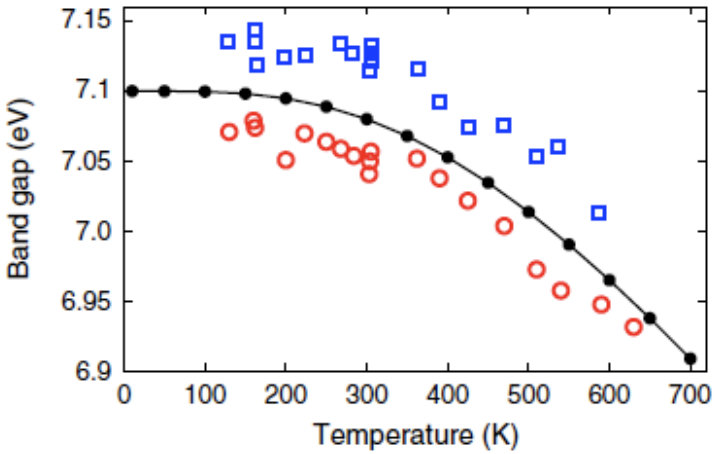
E. Canuccia and A. Marini, Phys. Rev. Lett. **107, 255501 (2011)**
E. Canuccia and A. Marini, Eur. Phys. J. B **85, 320 (2012)**

Applications of AHC theory



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

Silicon. Marini PRL (2008)
Excellent agremeent with exp.
Mostly broadening effect,
imaginary part of the Fan term
(not discussed in this talk)



Giustino, Louie, Cohen, PRL105, 265501 (2010)

Diamond. Direct gap at Gamma. ZPM 615 meV
Excellent agremeent with exp. T-dep
To be compared with Cardona estimation of
370 meV for the indirect exciton gap ... ?!?

ZPM confirmed by
Canuccia & Marini, Eur. Phys. J. B **85, 320 (2012)**

Allen-Heine-Cardona theory

Second-order (time-dependent) perturbation theory
(no average contribution from first order).

If one neglects the phonon frequencies with respect to the electronic gap :

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

+ occupation number from BE statistics

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

"Phonon mode factor"

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

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

$$\varepsilon_n = \langle \phi_n | \hat{H} | \phi_n \rangle \qquad \hat{H} = \hat{T} + \hat{V}_{\text{nucl}} + \int \frac{\rho(r')}{|r-r'|} dr' + \frac{dE_{xc}}{d\rho(r)}$$

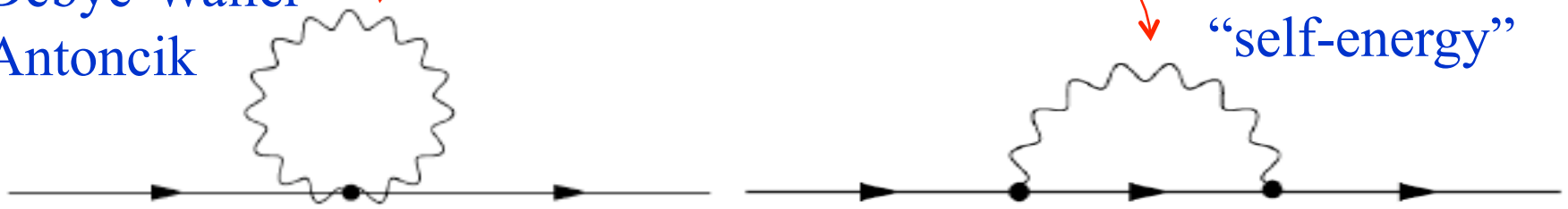
Hellman-Feynman theorem : $\varepsilon_n^{(1)} = \langle \phi_n^{(0)} | \hat{H}^{(1)} | \phi_n^{(0)} \rangle$

One more derivative :

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

Debye-Waller
Antoncik

Fan
"self-energy"



In AHC, $|\phi_n^{(1)}\rangle$ obtained by sum-over-states $|\phi_n^{(1)}\rangle = \sum_{m \neq n} |\phi_m^{(0)}\rangle \frac{\langle \phi_m^{(0)} | \hat{H}^{(1)} | \phi_n^{(0)} \rangle}{\varepsilon_n - \varepsilon_m}$

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 ! $\qquad \frac{\partial^2\hat{V}_{nucl}}{\partial R_{\kappa a}\partial R_{\kappa' b}}=0 \text{ for } \kappa\neq\kappa'$

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

Moreover, invariance under pure translations

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

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

The AHC theory : Fan term and site-diagonal Debye-Waller term

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

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

$$\frac{\partial \varepsilon_{\vec{k}n}(DW^{diag})}{\partial n_{\vec{q}j}} = -\frac{1}{\omega_{\vec{q}j}} \Re \sum_{\kappa a \kappa' b n'} \frac{\left\langle \phi_{\vec{k}n} \middle| \nabla_{\kappa a} V_{\kappa} \middle| \phi_{\vec{k}n'} \right\rangle \left\langle \phi_{\vec{k}n'} \middle| \nabla_{\kappa' b} V_{\kappa'} \middle| \phi_{\vec{k}n} \right\rangle}{\varepsilon_{\vec{k}n} - \varepsilon_{\vec{k}n'}} \times \frac{1}{2} \left(\frac{\xi_{\kappa a}(\vec{q}j) \xi_{\kappa b}(-\vec{q}j)}{M_{\kappa}} + \frac{\xi_{\kappa' a}(\vec{q}j) \xi_{\kappa' b}(-\vec{q}j)}{M_{\kappa'}} \right)$$

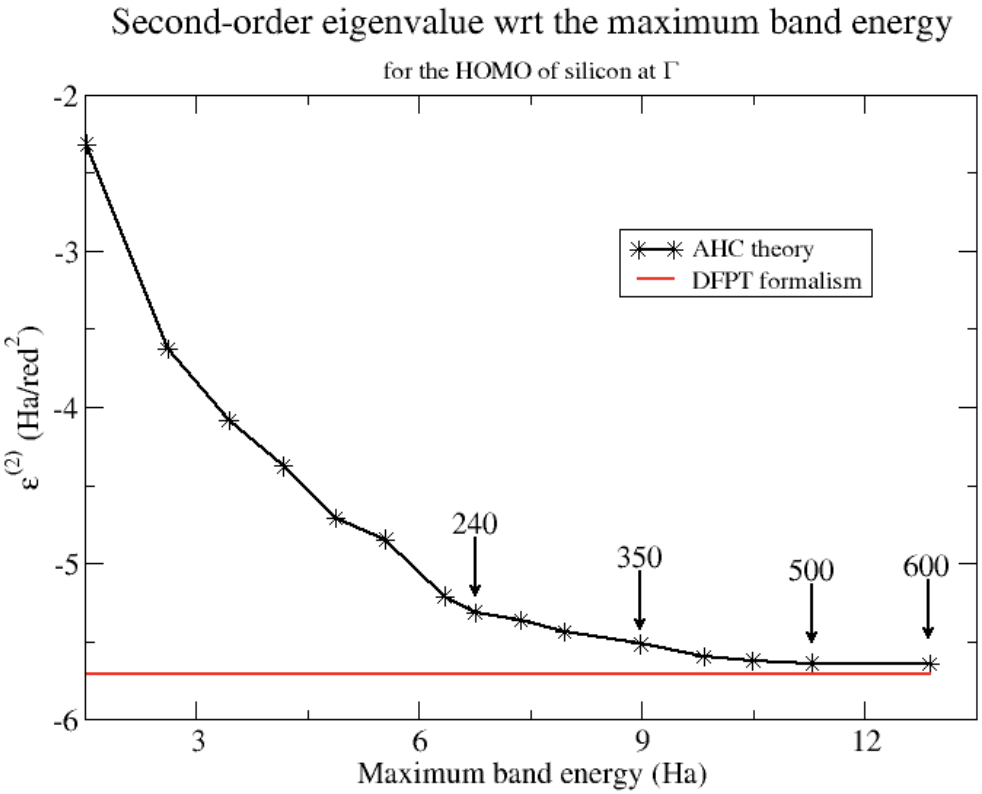
Good : only first-order electron-phonon matrix elements are needed
(+ standard ingredients from first-principles phonon/band structure calculations)

Bad : (1) summation over a large number of unoccupied states n'
(2) neglect of non-site-diagonal Debye-Waller term, while
the rigid-ion approx. is not valid for first-principles calculations
(3) DFT first-principles calculations, while MBPT should be used

Implementation

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

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



For converged calculations
for silicon :

sum over states 125 h
DFPT 17h

X. G., P. Boulanger and M. Côté. *Ann. Phys. (Berlin)* 523, 168-178 (2011).

Beyond the rigid-ion approximation

... + non-site-diagonal Debye-Waller term ?

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

$$\frac{\partial \varepsilon_{\vec{k}n}(DW^{non-diag})}{\partial n_{\vec{q}j}} = \frac{1}{2\omega_{\vec{q}j}} \sum_{\kappa a \kappa' b} \left\langle \phi_{\vec{k}n} \middle| \nabla_{\kappa a} \nabla_{\kappa' b} H \middle| \phi_{\vec{k}n} \right\rangle \times \left[\frac{\xi_{\kappa a}(\vec{q}j)\xi_{\kappa' b}(-\vec{q}j)}{\sqrt{M_\kappa M_{\kappa'}}} e^{iq.(R_{\kappa' b} - R_{\kappa a})} - \frac{1}{2}\left(\frac{\xi_{\kappa a}(\vec{q}j)\xi_{\kappa b}(-\vec{q}j)}{M_\kappa} + \frac{\xi_{\kappa' a}(\vec{q}j)\xi_{\kappa' b}(-\vec{q}j)}{M_{\kappa'}} \right) \right]$$

This term vanishes indeed for $\kappa = \kappa'$

Is it an important contribution to the temperature effect ?
Quite difficult to compute from first principles for a solid ...
not present in the DFPT for phonons !

Phonon population effect: dimers

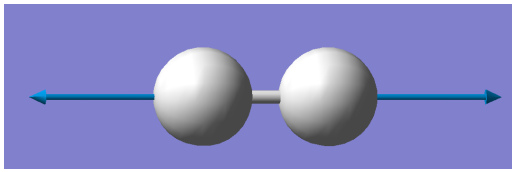
Diatomic molecules are the simplest system to study the temperature dependence of their eigenvalues. This simplicity stems from the fact that they have discrete levels, well described with the theory of the molecular orbitals, and, especially, only one relevant vibration mode.

(The 6 modes decouple as 3 translations, 2 rotations and the stretch mode.)

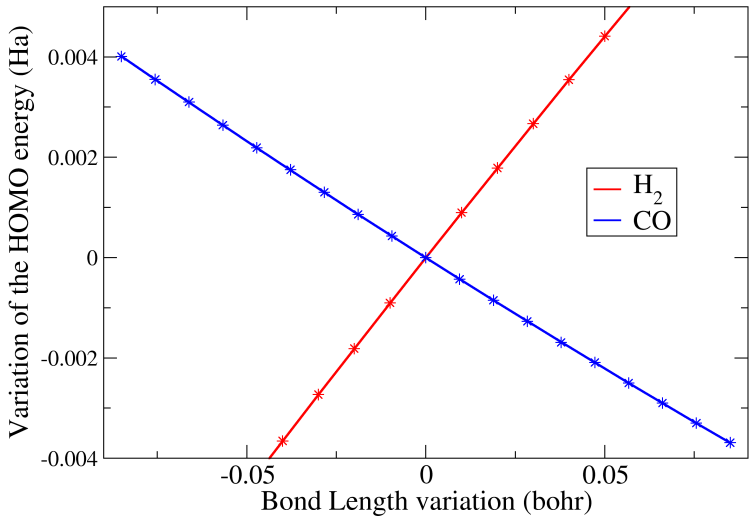
We can write the eigenenergies of the electronic states as a Taylor series on the bond length:

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

=> A "frozen-phonon" approach can deliver $\partial^2 \varepsilon_n / \partial R^2$ for reference



Variation of the HOMO energy wrt bond length



Beyond the rigid-ion approximation

The case of diatomic molecules is simple enough, that we can also evaluate directly the importance of the non-diagonal Debye-Waller term.

$$\frac{\partial \varepsilon_n(Fan+DDW)}{\partial n_{str}} = \frac{-1}{\omega_{str}}\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\Re\sum_{n'}\frac{\langle\phi_n|\partial H/\partial R_1|\phi_{n'}\rangle\langle\phi_{n'}|\partial H/\partial R_2|\phi_n\rangle}{\varepsilon_n-\varepsilon_{n'}}$$

$$\frac{\partial \varepsilon_n(NDDW)}{\partial n_{str}} = \frac{-1}{2\omega_{str}}\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\langle\phi_n|\partial^2 H/\partial R_1\partial R_2|\phi_n\rangle$$

Does not cancel, unlike with rigid-ion hypothesis !
Only Hartree + xc contribution

For the hydrogen dimer :

$$\left(\frac{\partial^2 E_{HOMO}}{\partial R^2}\right)^{Fan+diagDW} = -0.154 \ \frac{\text{Ha}}{\text{bohr}^2} \qquad \left(\frac{\partial^2 E_{HOMO}}{\partial R^2}\right)^{all\ contribs} = -0.070 \ \frac{\text{Ha}}{\text{bohr}^2}$$

A large difference : a factor of 2 !

Small molecules

Excellent agreement

AHC

		DDW + FAN	NDDW	Total	Frozen Phonon
H_2	HOMO	−0.1537792	0.0834663	−0.0703129	−0.0703087
	LUMO	−0.0038501	0.0054309	0.0015809	0.0015819
	LUMO-HOMO	0.1499292	−0.0780350	0.0718938	0.0718906
N_2	HOMO	−0.1434389	0.1248886	−0.0185503	−0.0188289
	LUMO	0.1230293	0.0967334	0.2197626	0.2197722
	LUMO-HOMO	0.2664682	−0.0281553	0.2383129	0.2386011
CO	HOMO	−0.0128687	0.0577108	0.0448420	0.0448244
	LUMO	0.0853891	0.0722377	0.1576268	0.1575478
	LUMO-HOMO	0.0982578	0.0145269	0.1127847	0.1127233
LiF	HOMO	−0.0396112	0.0108321	−0.0287791	−0.0284375
	LUMO	−0.0018114	−0.0033077	−0.0051191	−0.0051438
	LUMO-HOMO	0.0377998	−0.0141397	0.0236600	0.0232938

The Non-Diagonal DW term is a sizeable contribution to the total :
equal in size but opposite for H2, 10-15% for N2 and CO, 50% for LiF.

X. G., P. Boulanger and M. Côté. *Ann. Phys. (Berlin)* 523, 168-178 (2011).

Application to diamond

Solids

-Large number of vibration modes (full Brillouin Zone)
-Still one can focus on the contribution of selected, commensurate vibration modes
- e.g. Zero-point motion correction to the HOMO eigenenergy (meV) :

	DDW+Fan (=AHC)	NDDW	Finite-differences
Gamma	23.5	4.7	28.1
L	178.2	1.8	180.1
X	19.7	1.1	20.7
2/3 L	225.6	1.5	227.6

So, the NDDW can be as much as 20%, but as small as 1%.
Apparently, always the same order of magnitude (< 5 meV), while the DDW+Fan can vary widely, and especially diverge near critical points (see next slides).
G. Antonius, S. Poncé, X. G. and M. Côté, in preparation

Numerical study : ZPM in diamond

-Target numerical accuracy 10 meV
-Direct band gap at Gamma (like Giustino, Marini)
-Converged number of plane waves (30 ... 40 Hartree)
-k point sampling : 6x6x6 is sufficient for the generation of the first-order H

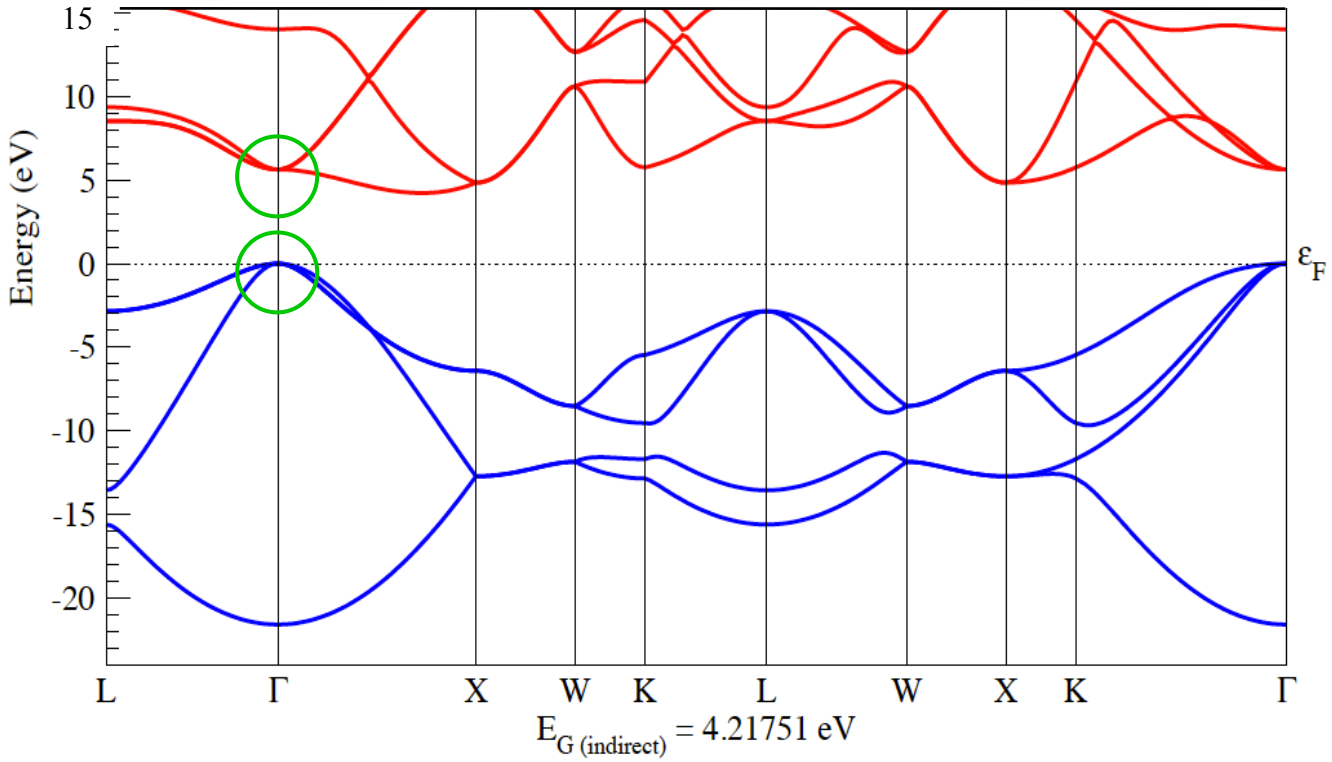
-Sampling on the q phonon wavevectors for the Fan term is a big issue !

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

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

Intraband contributions
diverge due to the denominator !

The strong divergence for small q

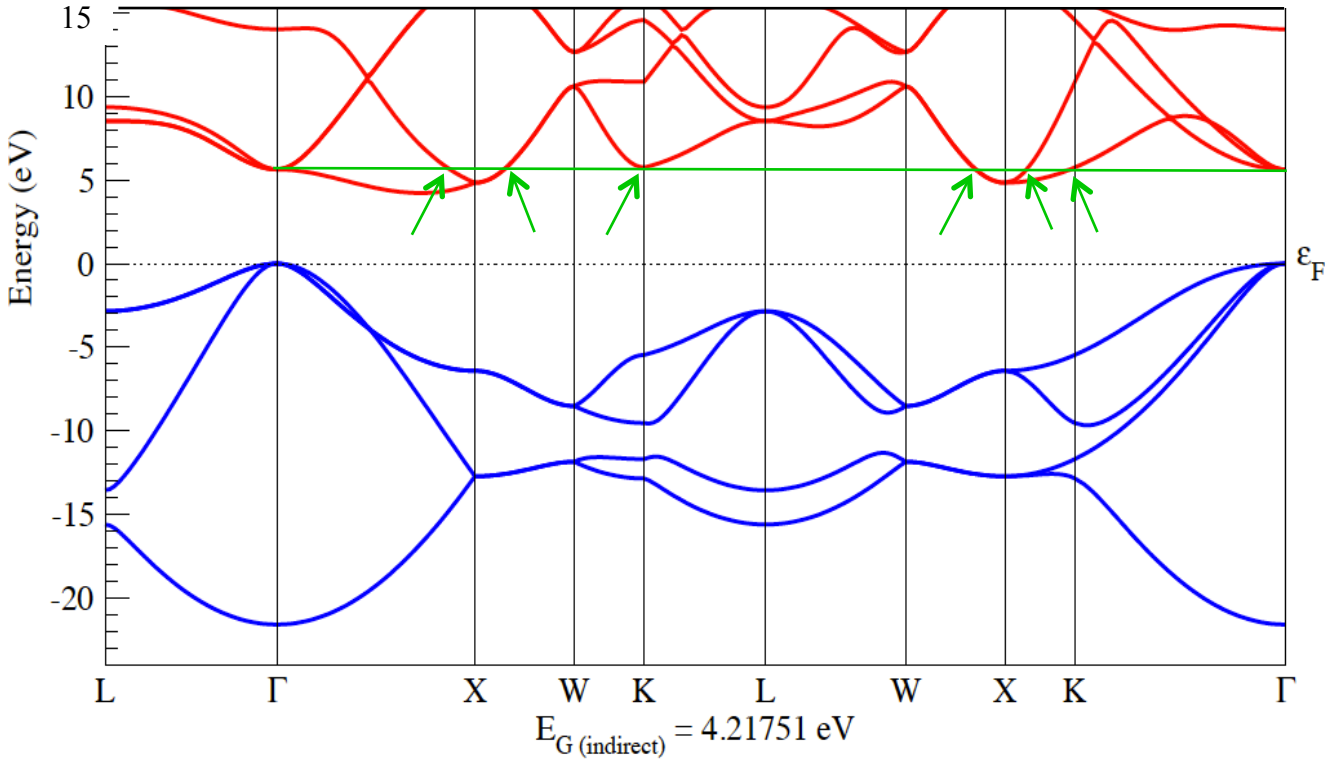


$$\lim_{\vec{q}\to 0} \frac{\partial \varepsilon_{\Gamma n}(Fan)}{\partial n_{\vec{q}j}} = \lim_{\vec{q}\to 0} \frac{1}{\omega_{\vec{q}j}} \frac{f(\vec{q}jn)}{\varepsilon_{\Gamma n} - \varepsilon_{\vec{q}n}}$$

Acoustic modes : Fan/DDW contribs cancel each other $f(\vec{q}jn) \to 0$

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

Divergences on isoenergetic surface



Set of isoenergetic wavevectors

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

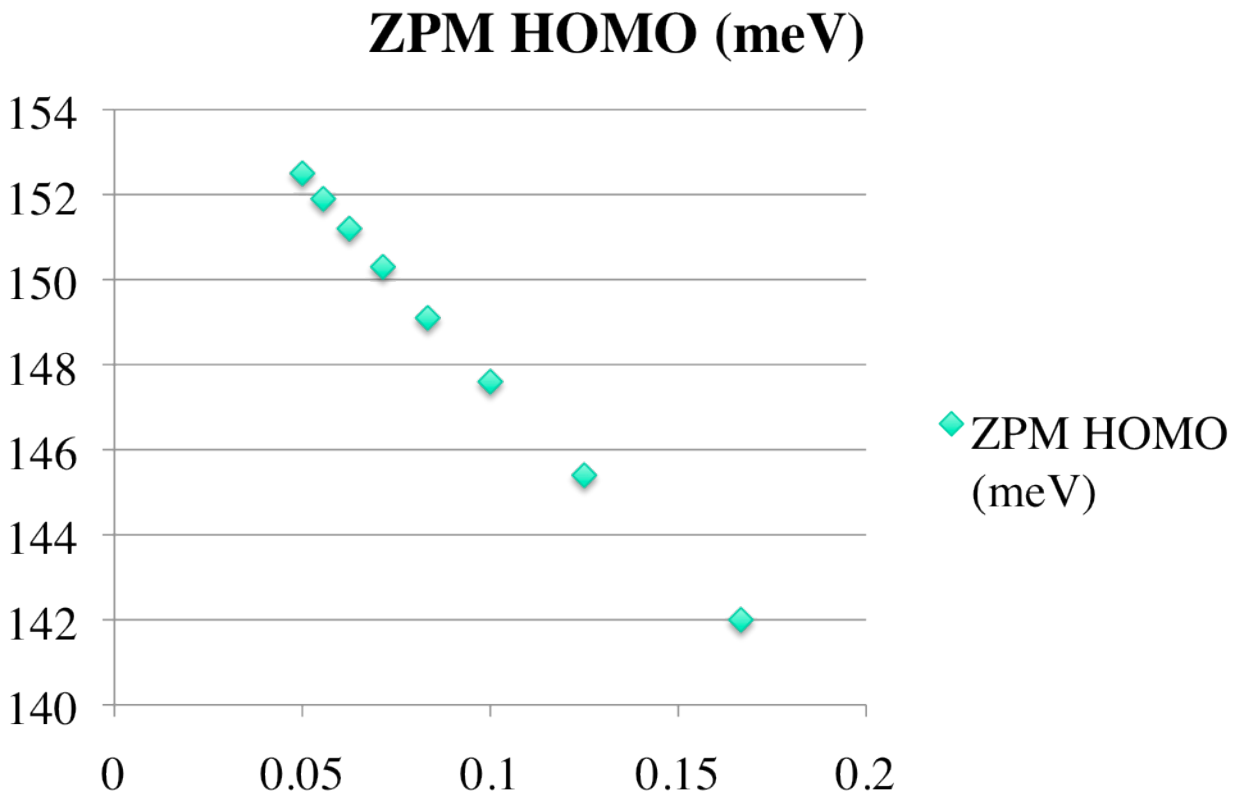
Only for the ZPM of the conduction state

q grid convergence : slow / fluctuations

q grid	#q in IBZ	ZPM HOMO (meV)	ZPM LUMO (meV)	ZPM gap (meV)
6x6x6 x4s	28	142.0	-414.8	-556.2
8x8x8 x4s	60	145.4	Non sense*	
10x10x10 x4s	110	147.6	-292.3	-439.9
12x12x12 x4s	182	149.1	-266.2	-415.3
14x14x14 x4s	280	150.3	Non sense*	
16x16x16 x4s	408	151.2	-293.2	-444.3
18x18x18 x4s	570	151.9	-280.9	-432.8
20x20x20 x4s	770	152.6	-241.3	-393.8

*Variations become wider ...

Convergence wrt to q sampling



Convergence like 1/Nq for q point grids Nq*Nq*Nq
Confirm theoretical understanding

Smoothing the denominator

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

... dramatically helps the convergence

Take imaginary part to be 100 meV (as done by Giustino) :

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

Converged within 10 meV ! But ... not to the value of Giustino et al (-615 meV)

More tests ...

-Three different pseudopotentials (TM, two UPF) including the one from Giustino. At 28x28x28 x4s grid.

Pseudo	ZPM HOMO (meV)	ZPM LUMO (meV)	ZPM gap (meV)
Troullier-Martins (own psp)	141.7	-269.1	-410.8
Berkeley 2005.UPF (from FG)	145.3	-268.1	-413.4
pz-vbc.UPF (from AM)	146.0	-250.9	-396.9

-Computed the ZPM shift from 2-atom primitive cell, 8-atom conventional cell, 16-atom supercell : perfect consistency.

-Compared with finite difference calculations for selected phonon wavevectors (shown previously)

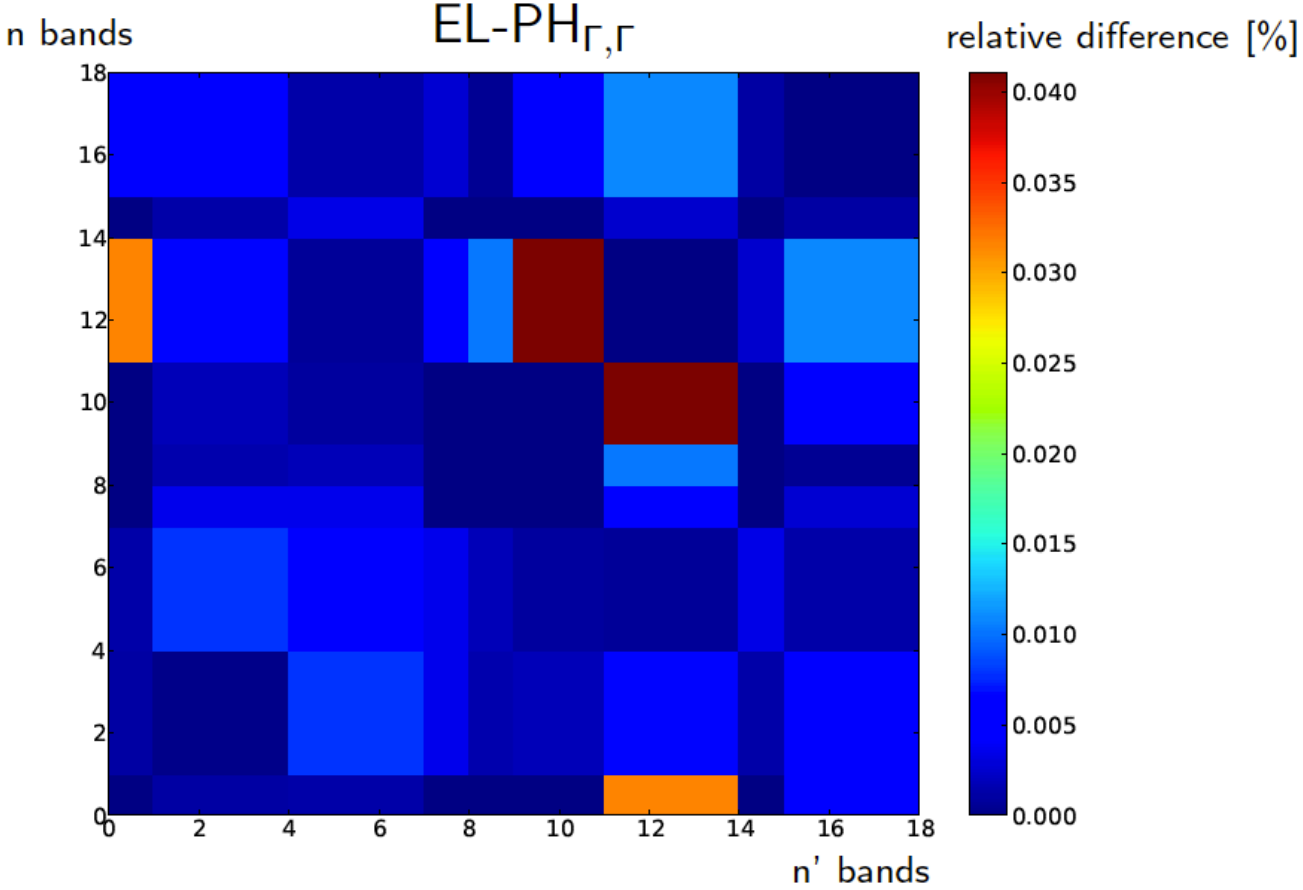
External checks : QE+YAMBO vs ABINIT

	Abinit 6.12.0	QE 4.0.5
Psp	C.pz-vbc.UPF	C.pz-vbc.UPF
ngkpt	4x4x4 (unshifted)	4x4x4 (unshifted)
ecut	20 Ha	40 Ry
acell/alat	6.67099831 Bohr	6.67099831 Bohr
kinetic energy [Ha]	8.33446183	-
one-electron contribution [Ha]	-	4.21636207
hartree contribution [Ha]	0.91317776	0.91318102
xc contribution [Ha]	-3.55327422	-3.55327531
ewald contribution [Ha]	-12.91992063	-12.91992071
PspCore energy [Ha]	-0.01765764	-
Loc. psp. energy [Ha]	-5.25551335	-
NL psp energy [Ha]	1.15507512	-
total energy [Ha]	**-11.34365**113	**-11.34365**292
	diff of 9E-7 Ha per at.	
Phonon freq [cm-1]	546.28 (2x)	546.30 (2x)
at q = 0.5 0.0 0.0	1118.32	1118.35
	1283.14	1283.16
	1292.81 (2x)	1292.83 (2x)

External checks : el-ph matrix element

The electron-phonon matrix elements EL-PH=$G^{\vec{q}}_{n,n',k}$ is an important quantity that enters in the computation of the ZPR:

$$G^{\vec{q}}_{n,n',k} = \sum_{m,R} \sum_{\kappa,\alpha} \sqrt{\frac{1}{2M_\kappa \omega_{\vec{q},m} N}} e^{iq \cdot x_{\kappa,\alpha}(R)} \xi^m_{\kappa,\alpha}(\vec{q}) \left\langle \Psi_{n,k+\vec{q}} \left| \frac{\partial V}{\partial x_{\kappa,\alpha}(R)} \right| \Psi_{n',k} \right\rangle$$



External checks : ZPM (not fully converged)

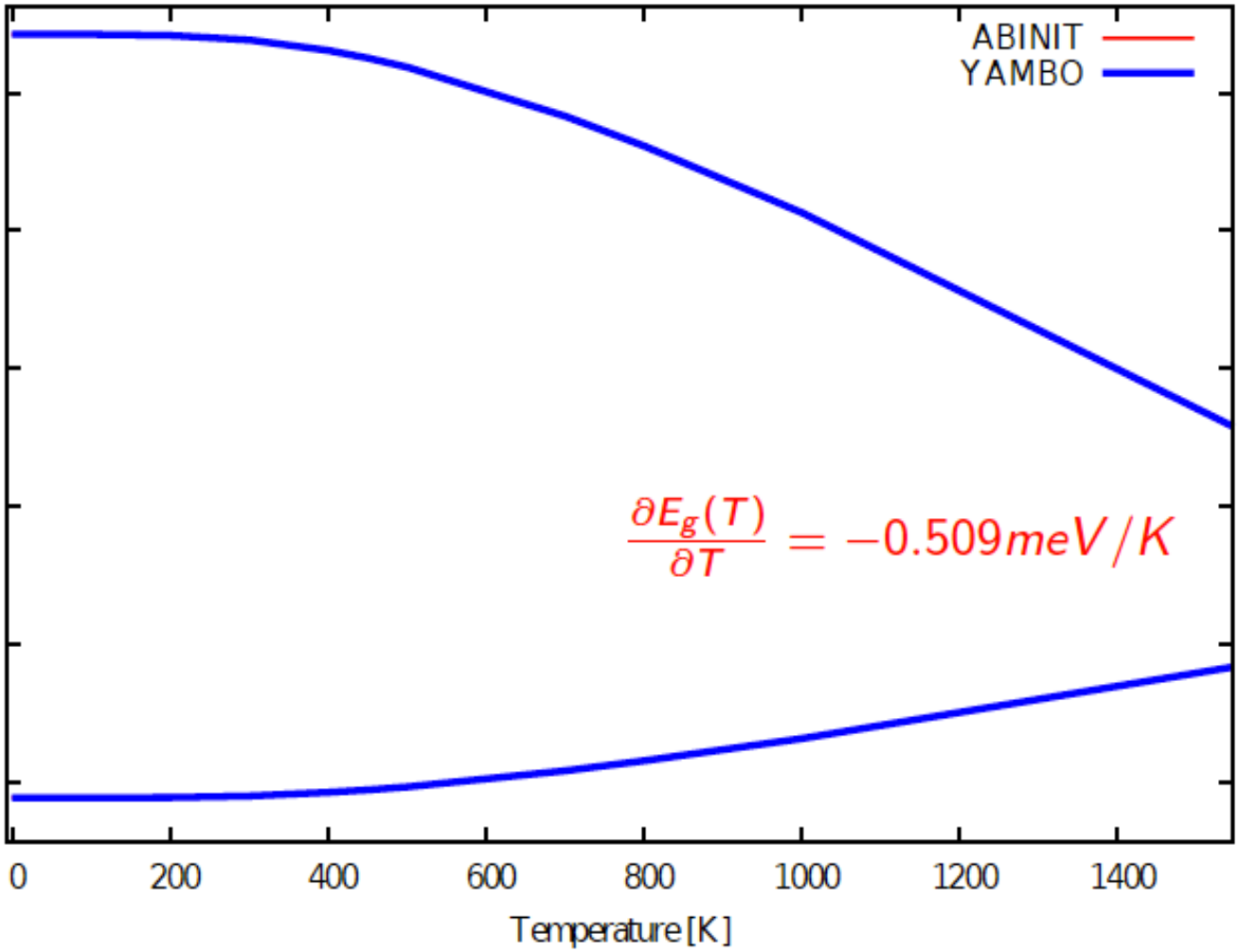
K-point	Band	Abinit 6.12.0 ZPR (eV)	Yambo 3.2.4 rev 786 ZPR (eV)
Γ	1	−0.0629	−0.0628
	2-3-4	0.1864	0.1866
	5-6-7	−0.2791	−0.2797
	8	−0.1606	−0.1630
	9	−0.0056	−0.0082

With a 10x10x10 q-point grid and 100 bands, near perfect agreement between ABINIT and YAMBO : 0.465 eV for the ZPM of the HOMO-LUMO gap ?!?

Sublety : published results with YAMBO do not use a regular grid, but a random sampling.
But results with EPW (F. Giustino) use a regular grid !

?????????

External checks : temperature dependence



Summary

-Electronic levels and optical properties depends on vibrational effects ...
Allen, Heine, Cardona formalism.

-The thermal expansion contribution is easily calculated using DFT + finite differences, but only a very small contribution

- The non-diagonal Debye-Waller term was shown to be non-negligible for several dimers (50% !). Apparently, its relative effect on the temperature dependence of the electronic bands in diamond is much smaller (1-2%).

- The calculation of the phonon population contribution for systems with many vibration modes can be done efficiently within DFPT + the rigid-ion approximation. Very difficult q point convergence !

Perspectives

- Code comparison is important ! But the discrepancy is not yet understood ...

- Of course : DFT (DFPT) calculation => One should try GW !

- Need broadening parameter (100 meV), of course non ab initio.

- Treatment of AHC : static phonons ... The later work by E. Canuccia & A. Marini includes dynamical effects ... Spectral function exhibit peaks, but the weight can be much smaller than 1...

- Link with the approach by Eiguren & Draxl ?