

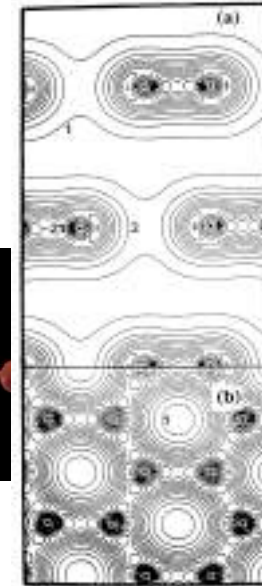
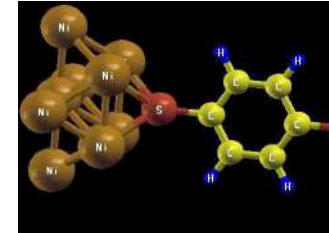
Density Functional Perturbation Theory

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Properties of solids from DFT

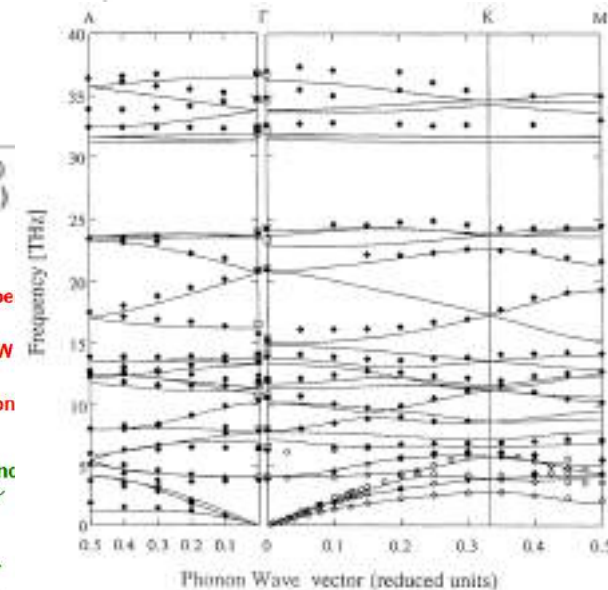
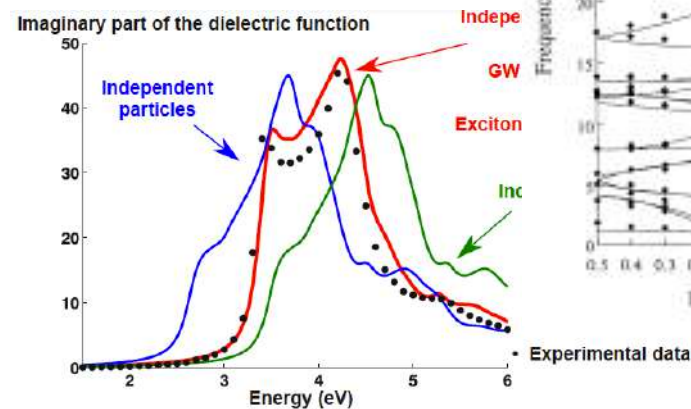
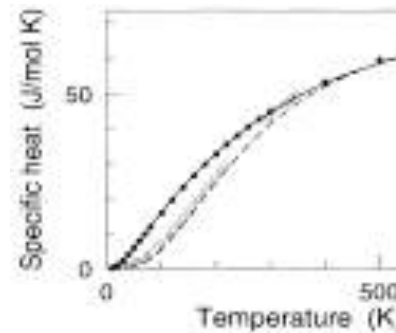
Computation of ...

interatomic distances, angles, total energies
 electronic charge densities, electronic energies



A basis for the computation of ...

chemical reactions
 electronic transport
 vibrational properties
 thermal capacity
 dielectric response
 optical response
 superconductivity
 surface properties
 spectroscopic responses
 ...



Overview

1. A brief reminder : Density Functional Theory
2. Material properties from total energy derivatives : phonons
3. Perturbations (adiabatic)
4. Perturbation Theory : « ordinary » quantum mechanics
5. Density-Functional Perturbation Theory (DFPT)
6. Phonon band structures from DFPT
7. Dielectric properties from DFPT
8. Thermodynamic properties from DFPT
9. LDA / GGA / Van der Waals
10. Temperature dependence of the electronic structure

“Classic” References :

- S. Baroni, P. Giannozzi and A. Testa, *Phys. Rev. Lett.* **58**, 1861 (1987)
- X. Gonze & J.-P. Vigneron, *Phys. Rev. B* **39**, 13120 (1989)
- X. Gonze, *Phys. Rev. A* **52**, 1096 (1995)
- S. de Gironcoli, *Phys. Rev. B* **51**, 6773 (1995)
- X. Gonze, *Phys. Rev. B* **55**, 10337 (1997)
- X. Gonze & C. Lee, *Phys. Rev. B* **55**, 10355 (1997)
- S. Baroni, et al., *Rev. Mod. Phys.* **73**, 515 (2001)

The Kohn-Sham orbitals and eigenvalues

Non-interacting electrons in the Kohn-Sham potential :

$$\left(-\frac{1}{2} \nabla^2 + V_{\text{KS}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

Density $n(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$

$$V_{\text{KS}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1 + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}$$

Hartree potential

Exchange-correlation potential

To be solved self-consistently !

Note. At self-consistency, supposing XC functional to be exact :

- the KS **density** = the exact density,
- the KS **electronic energy** = the exact electronic energy
- but KS **wavefunctions** and **eigenenergies** correspond to a **fictitious** set of independent electrons, so they **do not** correspond to any exact quantity.

Minimum principle for the energy

Variational principle for non-interacting electrons :
solution of KS self-consistent system of equations
is equivalent to the **minimisation** of

$$E_{\text{KS}}[\{\psi_i\}] = \sum_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}}[n]$$

under constraints of orthonormalization $\langle \psi_i | \psi_j \rangle = \delta_{ij}$
for the occupied orbitals.

The XC energy

To be approximated !

Exact result : the XC energy can be expressed as

$$E_{xc} [n] = \int n(\mathbf{r}_1) \epsilon_{xc}(\mathbf{r}_1; n) d\mathbf{r}_1$$

Local density approximation (LDA) :

- local XC energy per particle only depends on local density
- and is equal to the local XC energy per particle of an homogeneous electron gas of same density (« jellium »)

$$\epsilon_{xc}^{LDA}(\mathbf{r}_1; n) = \epsilon_{xc}^{hom}(n(\mathbf{r}_1))$$

$$E_{xc}^{LDA} [n] = \int n(\mathbf{r}_1) \epsilon_{xc}^{LDA}(n(\mathbf{r}_1)) d\mathbf{r}_1$$

Generalized gradient approximations (GGA)

$$E_{xc}^{GGA} [n] = \int n(\mathbf{r}_1) \epsilon_{xc}^{GGA}(n(\mathbf{r}_1), |\nabla n(\mathbf{r}_1)|) d\mathbf{r}_1$$

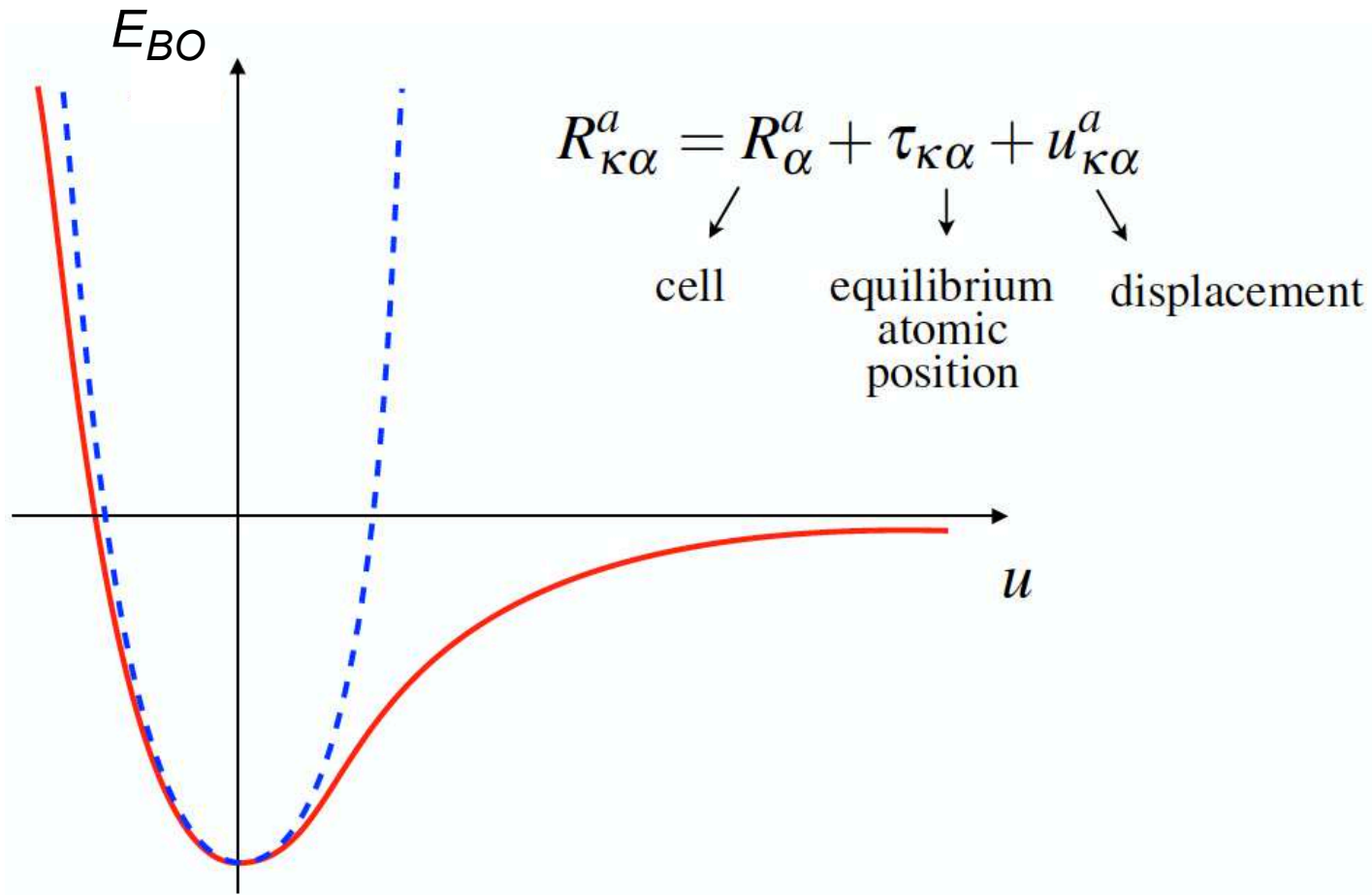
In this talk, GGA = « PBE »

Perdew, Burke and Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)

Material properties from total energy derivatives : phonons

Changing atomic positions

Born-Oppenheimer approximation ...



Phonon frequencies from force constants

Matrix of interatomic force constants :

$$C_{\kappa\alpha,\kappa'\alpha'}(a,a') = \frac{\partial^2 E_{BO}}{\partial R_{\kappa\alpha}^a \partial R_{\kappa'\alpha'}^{a'}}$$

Fourier Transform (using translational invariance) :

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

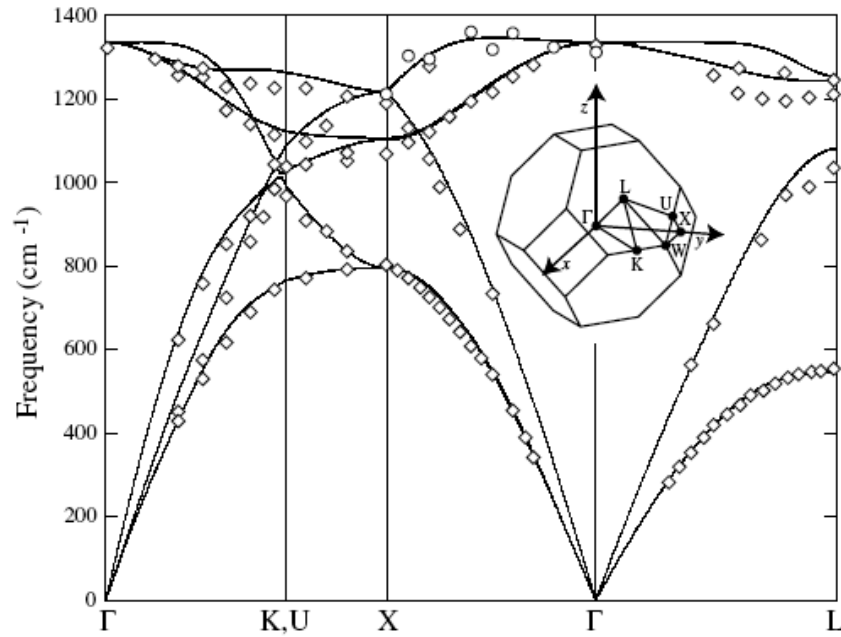
Computation of phonon frequencies and eigenvectors = solution of generalized eigenvalue problem

$$\sum_{k'\alpha'} \tilde{C}_{\kappa\alpha,k'\alpha'}(\vec{q}) \cdot u_{m\vec{q}}(k'\alpha') = M_k \cdot \omega_{m\vec{q}}^2 \cdot u_{m\vec{q}}(k\alpha)$$

↑ phonon displacement pattern
 ↑ masses
 ↑ square of phonon frequencies

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

Phonons : exp vs theory

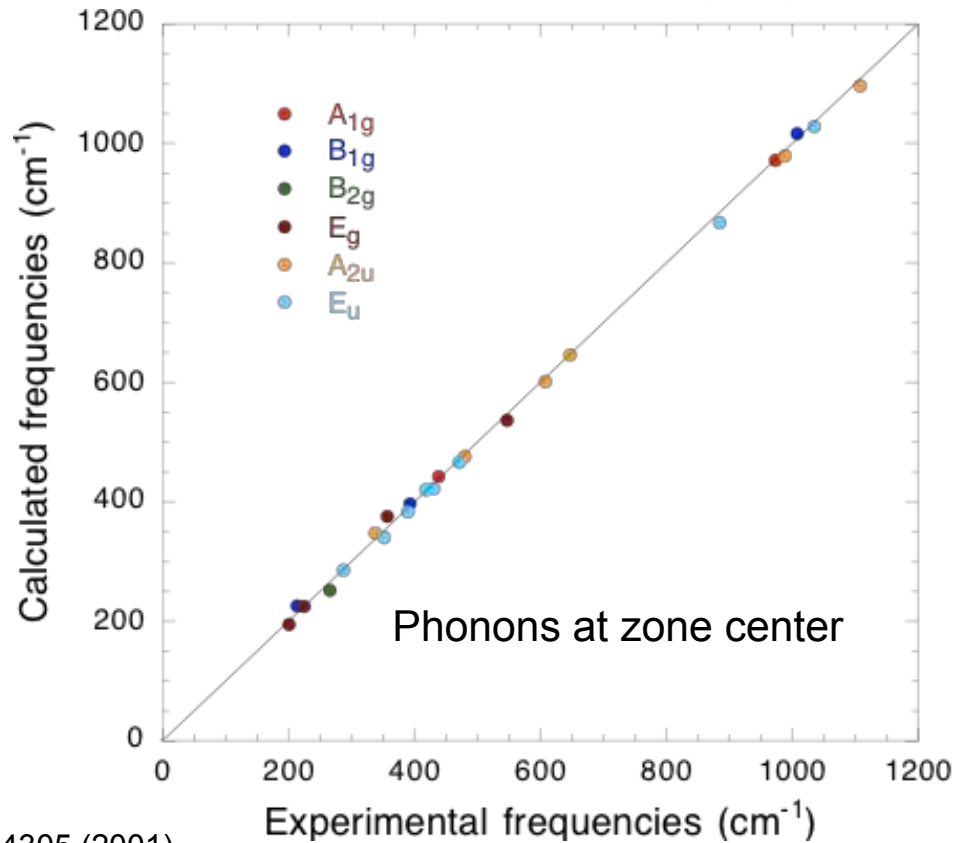
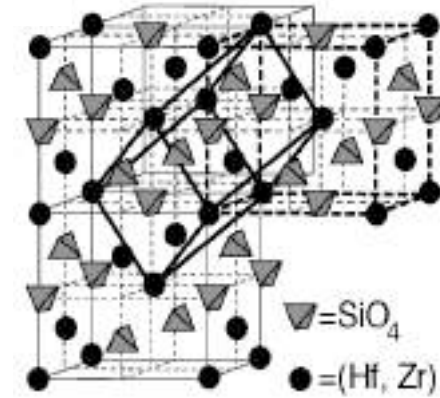


Diamond

XG, G.-M. Rignanese and R. Caracas.
Zeit. Kristall. 220, 458-472 (2005)

Rignanese, XG and Pasquarello. *Phys. Rev. B* 63, 104305 (2001)

Zircon



Phonons at zone center

Challenges for periodic materials ?

In addition of being able to compute derivatives of BO energy :

Treating phonons of **different wavelengths** ?
(Not only periodic ones)

Treating **electric field** ?
Electric field => linear potential,
incompatible with periodicity

Even for phonons at zero wavevector (Gamma),
treating **LO-TO splitting**
(longitudinal optic – transverse optic)

Perturbations (adiabatic)

Why perturbations ?

Many physical properties = derivatives of total energy
(or suitable thermodynamic potential) with respect to perturbations.

Consider :

- atomic displacements (phonons)
- dilatation/contraction of primitive cell
- homogeneous external field (electric field ...)

Derivatives of total energy (electronic part + nuclei-nuclei interaction) :

1st order derivatives : forces, stresses, dipole moment ...

2nd order derivatives : dynamical matrix, elastic constants, dielectric susceptibility
atomic polar tensors or Born effective charge tensors
piezoelectricity, internal strains

3rd order derivatives : non-linear dielectric susceptibility, Raman susceptibilities
electro-optic effect, phonon - phonon interaction, Grüneisen parameters, ...

Further properties obtained by integration over phononic degrees of freedom :
entropy, thermal expansion, phonon-limited thermal conductivity ...

Perturbations

- * Variation of energy and density around fixed potential

$$E_{el}(\lambda) = \sum_{\alpha, occ} \langle \psi_{\alpha}(\lambda) | \hat{T} + \hat{V}_{ext}(\lambda) | \psi_{\alpha}(\lambda) \rangle + E_{Hxc}[\rho(\lambda)]$$

$$\rho(\vec{r}; \lambda) = \sum_{\alpha, occ} \psi_{\alpha}^*(\vec{r}; \lambda) \psi_{\alpha}(\vec{r}; \lambda)$$

- * Perturbations (assumed known through all orders)

$$\hat{V}_{ext}(\lambda) = \hat{V}_{ext}^{(0)} + \lambda \hat{V}_{ext}^{(1)} + \lambda^2 \hat{V}_{ext}^{(2)} + \dots$$

i.e. : to investigate phonons, parameter of perturbation governs linearly nuclei displacement, but change of potential is non-linear in this parameter.

$$\Delta V_{ph}(\vec{r}) = \sum_{\kappa: \text{nuclei+cell}} V_{\kappa}(\vec{r} - (\vec{R}_{\kappa}^{(0)} + \vec{u}_{\kappa})) - V_{\kappa}(\vec{r} - \vec{R}_{\kappa}^{(0)})$$

$$\vec{u}_{\kappa} = \lambda \vec{e}_{\kappa} \cos(\vec{q} \cdot \vec{R}_{\kappa}^{(0)})$$

small parameter
 'polarisation' of the phonon
 phonon wavevector

How to get energy derivatives ?

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \quad \psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \dots$$

- * **Finite Differences**

Compare $E \{ \psi; V_{ext} \}$ and $E' \{ \psi'; V'_{ext} \}$

'Direct' Approach (Frozen phonons ... Supercells ...)
[Note problem with commensurability]

- * **Hellman - Feynman theorem (for $E^{(1)}$)**

Due to variational character : $\frac{\partial E}{\partial \psi} = 0$

$$\frac{dE}{d\lambda} = \frac{\partial E}{\partial V_{ext}} \frac{\partial V_{ext}}{\partial \lambda} + \frac{\partial E}{\partial \psi} \cdot \frac{\partial \psi}{\partial \lambda} = \frac{\partial E}{\partial V_{ext}} V_{ext}^{(1)}$$

\parallel
 0 $\psi^{(1)}$

In order to get $E^{(1)}$ we do not need $\psi^{(1)}$

General framework of perturbation theory

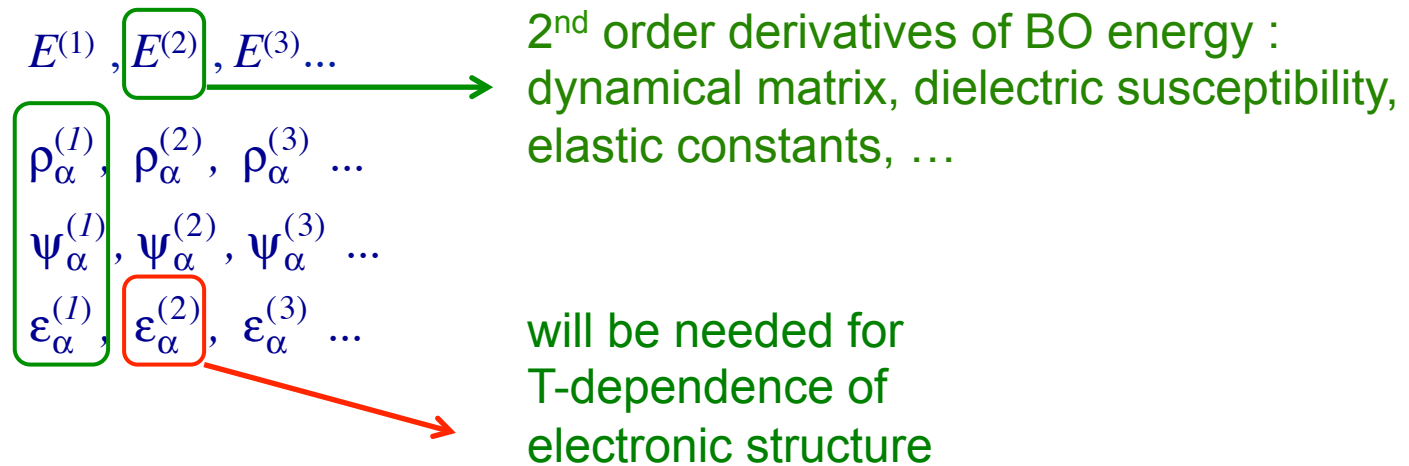
* $A(\lambda) = A^{(0)} + \lambda A^{(1)} + \lambda^2 A^{(2)} + \lambda^3 A^{(3)} \dots$

* $E\{\psi; V_{ext}\}$

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

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

Should calculate :



Ordinary quantum mechanics

Perturbation theory for ordinary quantum mechanics

$$(\hat{H} - \varepsilon_\alpha) |\psi_\alpha\rangle = 0 \quad (\text{Schrödinger equation})$$

$$\langle \psi_\alpha | \psi_\alpha \rangle = 1 \quad (\text{normalisation condition})$$

$$\langle \psi_\alpha | \hat{H} - \varepsilon_\alpha | \psi_\alpha \rangle = 0$$

$$\text{or } \varepsilon_\alpha = \langle \psi_\alpha | \hat{H} | \psi_\alpha \rangle \quad (\text{expectation value})$$

Hamiltonian supposed known through all orders

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \lambda^2 \hat{H}^{(2)} + \dots = \sum_n \lambda^n \hat{H}^{(n)}$$

Perturbation expansion of the Schrödinger Eq.

Suppose $\hat{H}(\lambda) |\psi_n(\lambda)\rangle = \varepsilon_n |\psi_n(\lambda)\rangle$ valid for all λ

with
$$\begin{cases} \hat{H}(\lambda) = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} \\ \psi_n(\lambda) = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots \\ \varepsilon_n(\lambda) = \varepsilon_n^{(0)} + \lambda \varepsilon_n^{(1)} + \lambda^2 \varepsilon_n^{(2)} + \dots \end{cases}$$

One expands the Schrödinger equation:

$$\begin{aligned} & \hat{H}^{(0)} |\psi_n^{(0)}\rangle + \lambda \left(\hat{H}^{(1)} |\psi_n^{(0)}\rangle + \hat{H}^{(0)} |\psi_n^{(1)}\rangle \right) + \lambda^2 \left(\hat{H}^{(1)} |\psi_n^{(1)}\rangle + \hat{H}^{(0)} |\psi_n^{(2)}\rangle \right) + \dots \\ &= \varepsilon_n^{(0)} |\psi_n^{(0)}\rangle + \lambda \left(\varepsilon_n^{(1)} |\psi_n^{(0)}\rangle + \varepsilon_n^{(0)} |\psi_n^{(1)}\rangle \right) + \lambda^2 \left(\varepsilon_n^{(2)} |\psi_n^{(0)}\rangle + \varepsilon_n^{(1)} |\psi_n^{(1)}\rangle + \varepsilon_n^{(0)} |\psi_n^{(2)}\rangle \right) + \dots \end{aligned}$$

Perturbation expansion of the Schrödinger Eq.

$$\begin{aligned} & \hat{H}^{(0)}|\psi_n^{(0)}\rangle + \lambda \left(\hat{H}^{(1)}|\psi_n^{(0)}\rangle + \hat{H}^{(0)}|\psi_n^{(1)}\rangle \right) + \lambda^2 \left(\hat{H}^{(1)}|\psi_n^{(1)}\rangle + \hat{H}^{(0)}|\psi_n^{(2)}\rangle \right) + \dots \\ & = \epsilon_n^{(0)}|\psi_n^{(0)}\rangle + \lambda \left(\epsilon_n^{(1)}|\psi_n^{(0)}\rangle + \epsilon_n^{(0)}|\psi_n^{(1)}\rangle \right) + \lambda^2 \left(\epsilon_n^{(2)}|\psi_n^{(0)}\rangle + \epsilon_n^{(1)}|\psi_n^{(1)}\rangle + \epsilon_n^{(0)}|\psi_n^{(2)}\rangle \right) + \dots \end{aligned}$$

In $\lambda = 0$, one gets $\hat{H}^{(0)}|\psi_n^{(0)}\rangle = \epsilon_n^{(0)}|\psi_n^{(0)}\rangle$ no surprise ...

Derivative with respect to λ , then $\lambda = 0$ (=first order of perturbation)

$$\Rightarrow \hat{H}^{(1)}|\psi_n^{(0)}\rangle + \hat{H}^{(0)}|\psi_n^{(1)}\rangle = \epsilon_n^{(1)}|\psi_n^{(0)}\rangle + \epsilon_n^{(0)}|\psi_n^{(1)}\rangle$$

2 derivatives with respect to λ , then $\lambda = 0$ (=second order of perturbation)

$$\Rightarrow \hat{H}^{(1)}|\psi_n^{(1)}\rangle + \hat{H}^{(0)}|\psi_n^{(2)}\rangle = \epsilon_n^{(2)}|\psi_n^{(0)}\rangle + \epsilon_n^{(1)}|\psi_n^{(1)}\rangle + \epsilon_n^{(0)}|\psi_n^{(2)}\rangle$$

Perturbation expansion of the normalisation

If $\forall \lambda : \langle \psi_n(\lambda) | \psi_n(\lambda) \rangle = 1$

with $\psi_n(\lambda) = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots$

Same technique than for Schrödinger equation, one deduces :

$$\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1$$

$$\langle \psi_n^{(1)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$$

$$\langle \psi_n^{(2)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle = 0$$

no surprise ...

Hellmann & Feynman theorem : $\epsilon_n^{(1)}$

Start from first-order Schrödinger equation

$$\hat{H}^{(1)} |\psi_n^{(0)}\rangle + \hat{H}^{(0)} |\psi_n^{(1)}\rangle = \epsilon_n^{(1)} |\psi_n^{(0)}\rangle + \epsilon_n^{(0)} |\psi_n^{(1)}\rangle$$

Premultiply by $\langle \psi_n^{(0)} |$

$$\langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle + \underbrace{\langle \psi_n^{(0)} | \hat{H}^{(0)} | \psi_n^{(1)} \rangle}_{\langle \psi_n^{(0)} | \epsilon_n^{(0)} \rangle} = \epsilon_n^{(1)} \underbrace{\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle}_{=1} + \epsilon_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle$$

So : $\boxed{\epsilon_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle}$ = Hellmann & Feynman theorem

$\epsilon_n^{(1)}$ OK!

- $\psi_n^{(0)}$ and $\hat{H}^{(1)}$ supposed known
- $\psi_n^{(1)}$ not needed
- $\langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle$ = expectation of the Hamiltonian for the non-perturbed wavef.

Second-order derivative of total energy $\epsilon_{\alpha}^{(2)}$

Start from second-order Schrödinger equation

$$\hat{H}^{(1)}|\psi_n^{(1)}\rangle + \hat{H}^{(0)}|\psi_n^{(2)}\rangle = \epsilon_n^{(2)}|\psi_n^{(0)}\rangle + \epsilon_n^{(1)}|\psi_n^{(1)}\rangle + \epsilon_n^{(0)}|\psi_n^{(2)}\rangle$$

Premultiply by $\langle\psi_n^{(0)}|$

$$\epsilon_{\alpha}^{(2)} = \langle\psi_{\alpha}^{(0)}|\hat{H}^{(1)} - \epsilon_{\alpha}^{(1)}|\psi_{\alpha}^{(1)}\rangle \text{ or } \epsilon_{\alpha}^{(2)} = \langle\psi_{\alpha}^{(1)}|\hat{H}^{(1)} - \epsilon_{\alpha}^{(1)}|\psi_{\alpha}^{(0)}\rangle$$

Both can be combined :

$$\epsilon_{\alpha}^{(2)} = \frac{1}{2} \left(\langle\psi_{\alpha}^{(0)}|\hat{H}^{(1)} - \epsilon_{\alpha}^{(1)}|\psi_{\alpha}^{(1)}\rangle + \langle\psi_{\alpha}^{(1)}|\hat{H}^{(1)} - \epsilon_{\alpha}^{(1)}|\psi_{\alpha}^{(0)}\rangle \right)$$

and, using $\langle\psi_n^{(1)}|\psi_n^{(0)}\rangle + \langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = 0$

$$= \frac{1}{2} \left(\langle\psi_{\alpha}^{(0)}|\hat{H}^{(1)}|\psi_{\alpha}^{(1)}\rangle + \langle\psi_{\alpha}^{(1)}|\hat{H}^{(1)}|\psi_{\alpha}^{(0)}\rangle \right)$$

No knowledge of $\psi_{\alpha}^{(2)}$ is needed, but needs $\psi_{\alpha}^{(1)}$! How to get it ?

In search of $|\psi_n^{(1)}\rangle$

Again first-order Schrödinger equation :

$$\underbrace{\hat{H}^{(1)} |\psi_n^{(0)}\rangle + \hat{H}^{(0)} |\psi_n^{(1)}\rangle}_{\text{known}} = \underbrace{\epsilon_n^{(1)} |\psi_n^{(0)}\rangle + \epsilon_n^{(0)} |\psi_n^{(1)}\rangle}_{\text{known}}$$

Terms containing $|\psi_n^{(1)}\rangle$ are gathered :

$$\underbrace{(\hat{H}^{(0)} - \epsilon_n^{(0)})}_{\text{known}} |\psi_n^{(1)}\rangle = - \underbrace{(\hat{H}^{(1)} - \epsilon_n^{(1)})}_{\text{known}} |\psi_n^{(0)}\rangle \quad (\text{called Sternheimer equation})$$

Equivalence with matrix equation (systeme of linear equations)

$$\underline{\underline{A}} \cdot \underline{\underline{x}} = \underline{\underline{y}}$$

usually solved by $\underline{\underline{x}} = \underline{\underline{A}}^{-1} \underline{\underline{y}}$ if $\underline{\underline{A}}^{-1}$ exist.

Variational Principle for the lowest $\epsilon_{\alpha}^{(2)}$ (Hylleraas principle)

$$\epsilon^{(2)} = \min_{\psi^{(1)}} \left\{ \langle \psi^{(1)} | \hat{H}^{(1)} | \psi^{(0)} \rangle + \langle \psi^{(1)} | \hat{H}^{(0)} - \epsilon^{(0)} | \psi^{(1)} \rangle + \langle \psi^{(0)} | \hat{H}^{(2)} | \psi^{(0)} \rangle + \langle \psi^{(0)} | \hat{H}^{(1)} | \psi^{(1)} \rangle \right\}$$

with the following constraint on $|\psi_n^{(1)}\rangle$:

$$\langle \psi^{(0)} | \psi^{(1)} \rangle + \langle \psi^{(1)} | \psi^{(0)} \rangle = 0$$

Allows to recover Sternheimer's equation :

$$\frac{\delta}{\delta \psi^{(1)}} [\dots] = 0 \quad + \text{Lagrange multiplier}$$

$$\Rightarrow (\hat{H}^{(0)} - \epsilon^{(0)}) | \psi^{(1)} \rangle + (\hat{H}^{(1)} - \epsilon^{(1)}) | \psi^{(0)} \rangle = 0$$

Equivalence of :

- * Minimization of $\epsilon_n^{(2)}$
- * Sternheimer equation
- * also ... sum over states ... Green's function ...

Computation of $\epsilon_{\alpha}^{(3)}$ (I)

Starting from

$$(\hat{H}^{(0)} - \epsilon_{\alpha}^{(0)})|\psi_{\alpha}^{(3)}\rangle + (\hat{H}^{(1)} - \epsilon_{\alpha}^{(1)})|\psi_{\alpha}^{(2)}\rangle + (\hat{H}^{(2)} - \epsilon_{\alpha}^{(2)})|\psi_{\alpha}^{(1)}\rangle + (\hat{H}^{(3)} - \epsilon_{\alpha}^{(3)})|\psi_{\alpha}^{(0)}\rangle = 0$$

Premultiply by $\langle\psi_{\alpha}^{(0)}|$ gives

$$\begin{aligned}\epsilon_{\alpha}^{(3)} &= \langle\psi_{\alpha}^{(0)}|\hat{H}^{(3)}|\psi_{\alpha}^{(0)}\rangle \\ &+ \langle\psi_{\alpha}^{(0)}|\hat{H}^{(2)} - \epsilon_{\alpha}^{(2)}|\psi_{\alpha}^{(1)}\rangle \\ &+ \langle\psi_{\alpha}^{(0)}|\hat{H}^{(1)} - \epsilon_{\alpha}^{(1)}|\psi_{\alpha}^{(2)}\rangle\end{aligned}$$

$\triangle \psi_{\alpha}^{(2)}$ is needed in this formula

The computation of $\epsilon_\alpha^{(3)}$ (II)

However, perturbation expansion of $0 = \langle \psi_\alpha | \hat{H} - \epsilon_\alpha | \psi_\alpha \rangle$ at third order gives:

$$\begin{aligned}
 0 = & \langle \psi_\alpha^{(0)} | \hat{H}^{(3)} - \epsilon_\alpha^{(3)} | \psi_\alpha^{(0)} \rangle + \langle \psi_\alpha^{(1)} | \hat{H}^{(2)} - \epsilon_\alpha^{(2)} | \psi_\alpha^{(0)} \rangle + \langle \psi_\alpha^{(2)} | \hat{H}^{(1)} - \epsilon_\alpha^{(1)} | \psi_\alpha^{(0)} \rangle + \langle \psi_\alpha^{(3)} | \hat{H}^{(0)} - \epsilon_\alpha^{(0)} | \psi_\alpha^{(0)} \rangle \\
 & + \langle \psi_\alpha^{(0)} | \hat{H}^{(2)} - \epsilon_\alpha^{(2)} | \psi_\alpha^{(1)} \rangle + \langle \psi_\alpha^{(1)} | \hat{H}^{(1)} - \epsilon_\alpha^{(1)} | \psi_\alpha^{(1)} \rangle + \langle \psi_\alpha^{(2)} | \hat{H}^{(0)} - \epsilon_\alpha^{(0)} | \psi_\alpha^{(1)} \rangle \\
 & + \langle \psi_\alpha^{(0)} | \hat{H}^{(1)} - \epsilon_\alpha^{(1)} | \psi_\alpha^{(2)} \rangle + \langle \psi_\alpha^{(1)} | \hat{H}^{(0)} - \epsilon_\alpha^{(0)} | \psi_\alpha^{(2)} \rangle \\
 & + \langle \psi_\alpha^{(0)} | \hat{H}^{(0)} - \epsilon_\alpha^{(0)} | \psi_\alpha^{(3)} \rangle
 \end{aligned}$$

The sum of terms in a row or in a column vanishes ! (Exercise !)

Suppress 2 last columns and 2 last rows, rearrange the equation, and get:

$$\begin{aligned}
 \epsilon_\alpha^{(3)} = & \langle \psi_\alpha^{(0)} | \hat{H}^{(3)} | \psi_\alpha^{(0)} \rangle + \langle \psi_\alpha^{(1)} | \hat{H}^{(2)} | \psi_\alpha^{(0)} \rangle \\
 & + \langle \psi_\alpha^{(0)} | \hat{H}^{(2)} | \psi_\alpha^{(1)} \rangle + \langle \psi_\alpha^{(1)} | \hat{H}^{(1)} - \epsilon_\alpha^{(1)} | \psi_\alpha^{(1)} \rangle
 \end{aligned}$$

[We have used $\langle \psi_\alpha^{(0)} | \psi_\alpha^{(0)} \rangle = 1$ and $\langle \psi_\alpha^{(0)} | \psi_\alpha^{(1)} \rangle + \langle \psi_\alpha^{(1)} | \psi_\alpha^{(0)} \rangle = 0$]

$\triangle \psi_\alpha^{(2)}$ is not needed in this formula

Dynamical matrices from density-functional perturbation theory (DFPT)

Density functional perturbation theory

Without going into the formulas, there exist expressions :

$$E^{(0)} \left\{ \Psi_{\alpha}^{(0)} \right\} \quad \text{variational with respect to } \Psi_{\alpha}^{(0)}$$

$$E^{(1)} \left\{ \Psi_{\alpha}^{(0)} \right\}$$

$$E^{(2)} \left\{ \Psi_{\alpha}^{(0)}; \Psi_{\alpha}^{(1)} \right\} \quad \text{variational with respect to } \Psi_{\alpha}^{(1)}$$

$$E^{(3)} \left\{ \Psi_{\alpha}^{(0)}; \Psi_{\alpha}^{(1)} \right\}$$

$$E^{(4)} \left\{ \Psi_{\alpha}^{(0)}; \Psi_{\alpha}^{(1)}; \Psi_{\alpha}^{(2)} \right\} \quad \text{variational with respect to } \Psi_{\alpha}^{(2)}$$

$$E^{(5)} \left\{ \Psi_{\alpha}^{(0)}; \Psi_{\alpha}^{(1)}; \Psi_{\alpha}^{(2)} \right\}$$

+ knowledge of $\left\{ \Psi_{\alpha}^{(0)} \right\}$ allows one to obtain $\rho^{(0)}, H^{(0)}, \epsilon_{\alpha}^{(0)}$

knowledge of $\left\{ \Psi_{\alpha}^{(0)}; \Psi_{\alpha}^{(1)} \right\}$ allows one to obtain $\rho^{(1)}, H^{(1)}, \epsilon_{\alpha}^{(1)}$

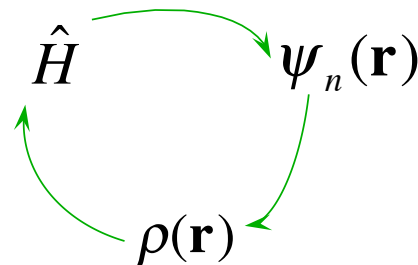
knowledge of $\left\{ \Psi_{\alpha}^{(0)}; \Psi_{\alpha}^{(1)}; \Psi_{\alpha}^{(2)} \right\}$ allows one to obtain $\rho^{(2)}, H^{(2)}, \epsilon_{\alpha}^{(2)}$

Need $\Psi_{\alpha}^{(2)}$ unlike in ordinary QM

Basic equations in DFT

Solve self-consistently Kohn-Sham equation

$$\left\{ \begin{array}{l} \hat{H} |\psi_n\rangle = \epsilon_n |\psi_n\rangle \\ \hat{H} = \hat{T} + \hat{V} + \hat{V}_{Hxc}[\rho] \\ \rho(\vec{r}) = \sum_n^{occ} \psi_n^*(\vec{r}) \psi_n(\vec{r}) \end{array} \right.$$



$$\delta_{mn} = \langle \psi_m | \psi_n \rangle \text{ for } m, n \in \text{occupied set}$$

or minimize

$$E_{el} \{ \psi \} = \sum_n^{occ} \langle \psi_n | \hat{T} + \hat{V} | \psi_n \rangle + E_{Hxc}[\rho]$$

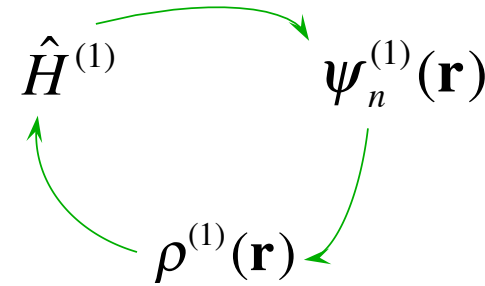
What is \hat{V} ?

$$\hat{V}(\vec{r}) = \sum_{a\kappa} -\frac{Z_\kappa}{|\vec{r} - \vec{R}_\kappa^a|}$$

Basic equations in DFPT

Solve self-consistently Sternheimer equation

$$\left\{ \begin{array}{l} (\hat{H}^{(0)} - \epsilon_n^{(0)}) |\psi_n^{(1)}\rangle = - (\hat{H}^{(1)} - \epsilon_n^{(1)}) |\psi_n^{(0)}\rangle \\ \hat{H}^{(1)} = \hat{V}^{(1)} + \int \frac{\delta^2 E_{Hxc}}{\delta \rho(r) \delta \rho(r')} \rho^{(1)}(r') dr' \\ \epsilon_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle \\ \rho^{(1)}(\vec{r}) = \sum_n^{occ} \psi_n^{(1)*}(\vec{r}) \psi_n^{(0)}(\vec{r}) + \psi_n^{(0)*}(\vec{r}) \psi_n^{(1)}(\vec{r}) \quad 0 = \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle \text{ for } m \in \text{occupied set} \end{array} \right.$$



or minimize

$$E_{el}^{(2)} \{ \psi^{(1)}; \psi^{(0)} \} = \sum_n^{occ} \langle \psi_n^{(1)} | \hat{H}^{(0)} - \epsilon_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(1)} | \hat{V}^{(1)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(0)} | \hat{V}^{(1)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(0)} | \hat{V}^{(2)} | \psi_n^{(0)} \rangle + \frac{1}{2} \iint \frac{\delta^2 E_{Hxc}}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')} \rho^{(1)}(\vec{r}) \rho^{(1)}(\vec{r}') d\vec{r} d\vec{r}'$$

What is $\hat{V}^{(1)}$, $\hat{V}^{(2)}$?

The potential and its 1st derivative

Derivative with respect to $R_{\kappa\alpha}^a$

$$V^{(0)}(\vec{r}) = \sum_{\kappa} -\frac{Z_{\kappa}}{|\vec{r}-\vec{R}_{\kappa}^a|}$$

$$V^{(1)}(\vec{r}) = \frac{\partial V(\vec{r})}{\partial R_{\kappa,\alpha}^a} = \frac{Z_{\kappa}}{|\vec{r}-\vec{R}_{\kappa}^a|^2} \cdot \frac{\partial |\vec{r}-\vec{R}_{\kappa}^a|}{\partial u_{\kappa,\alpha}^a} = -\frac{Z_{\kappa}}{|\vec{r}-\vec{R}_{\kappa}^a|^3} \cdot (\vec{r}-\vec{R}_{\kappa}^a)_{\alpha}$$

Generalisation to pseudopotentials can be worked out ...

Collective displacement with wavevector \vec{q}

$$V_{\vec{q},\kappa,\alpha}^{(1)}(\vec{r}) = \sum_a e^{i\vec{q}\vec{R}_a} \frac{\partial V(\vec{r})}{\partial R_{\kappa,\alpha}^a}$$

Factorization of the phase

Suppose unperturbed system periodic $V^{(0)}(\vec{r}+\vec{R}_a) = V^{(0)}(\vec{r})$

If perturbation characterized by a wavevector : $V^{(1)}(\vec{r}+\vec{R}_a) = e^{i\vec{q}\cdot\vec{R}_a} V^{(1)}(\vec{r})$

all responses, at linear order, will be characterized by a wavevector :

$$\rho^{(1)}(\vec{r}+\vec{R}_a) = e^{i\vec{q}\cdot\vec{R}_a} \rho^{(1)}(\vec{r}) \quad \Psi_{m,\vec{k},\vec{q}}^{(1)}(\vec{r}+\vec{R}_a) = e^{i(\vec{k}+\vec{q})\cdot\vec{R}_a} \Psi_{m,\vec{k},\vec{q}}^{(1)}(\vec{r})$$

Now, define related periodic quantities

$$\bar{\rho}^{(1)}(\vec{r}) = e^{-i\vec{q}\cdot\vec{r}} \rho^{(1)}(\vec{r}) \quad u_{m,\vec{k},\vec{q}}^{(1)}(\vec{r}) = (N\Omega_0)^{1/2} e^{-i(\vec{k}+\vec{q})\cdot\vec{r}} \Psi_{m,\vec{k},\vec{q}}^{(1)}(\vec{r})$$

In equations of DFPT, only these periodic quantities appear:

phases $e^{-i\vec{q}\cdot\vec{r}}$ and $e^{-i(\vec{k}+\vec{q})\cdot\vec{r}}$ can be factorized

Treatment of perturbations **incommensurate** with unperturbed system periodicity is thus mapped onto the **original periodic system**.

Computing mixed derivatives

How to get $E^{j_1 j_2}$ from $\Psi_\alpha^{(0)}$, $\Psi_\alpha^{j_1}$, $\Psi_\alpha^{j_2}$?

$$E_{el}^{(2)} \left\{ \Psi^{(1)}; \Psi^{(0)} \right\} = \sum_n^{occ} \left\langle \Psi_n^{(1)} \left| \hat{H}^{(0)} - \epsilon_n^{(0)} \right| \Psi_n^{(1)} \right\rangle + \left\langle \Psi_n^{(1)} \left| \hat{V}^{(1)} \right| \Psi_n^{(0)} \right\rangle \\ + \left\langle \Psi_n^{(0)} \left| \hat{V}^{(1)} \right| \Psi_n^{(1)} \right\rangle + \left\langle \Psi_n^{(0)} \left| \hat{V}^{(2)} \right| \Psi_n^{(0)} \right\rangle \\ + \frac{1}{2} \iint \frac{\delta^2 E_{Hxc}}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')} \rho^{(1)}(\vec{r}) \rho^{(1)}(\vec{r}') d\vec{r} d\vec{r}'$$

Generalization to $E_{el}^{j_1 j_2} = \frac{1}{2} \left(\tilde{E}_{el}^{j_1 j_2} + \tilde{E}_{el}^{j_2 j_1} \right)$

$$\text{with } \tilde{E}_{el}^{j_1 j_2} \left\{ \Psi^{j_1}, \Psi^{j_2}; \Psi^{(0)} \right\} = \sum_n^{occ} \left\langle \Psi_n^{j_1} \left| \hat{H}^{(0)} - \epsilon_n^{(0)} \right| \Psi_n^{j_2} \right\rangle + \left\langle \Psi_n^{j_1} \left| \hat{V}^{j_2} \right| \Psi_n^{(0)} \right\rangle \\ + \left\langle \Psi_n^{(0)} \left| \hat{V}^{j_1} \right| \Psi_n^{j_2} \right\rangle + \left\langle \Psi_n^{(0)} \left| \hat{V}^{j_1 j_2} \right| \Psi_n^{(0)} \right\rangle \\ + \frac{1}{2} \iint \frac{\delta^2 E_{Hxc}}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')} \rho^{j_1}(\vec{r}) \rho^{j_2}(\vec{r}') d\vec{r} d\vec{r}'$$

being a stationary expression, leading to the non-stationary expression

$$E_{el}^{j_1 j_2} \left\{ \Psi^{j_1}; \Psi^{(0)} \right\} = \sum_n^{occ} \left\langle \Psi_n^{j_1} \left| \hat{V}^{j_2} \right| \Psi_n^{(0)} \right\rangle + \left\langle \Psi_n^{(0)} \left| \hat{V}^{j_1 j_2} \right| \Psi_n^{(0)} \right\rangle$$

Independent of Ψ^{j_2}

Order of calculations in DFPT

(1) Ground-state calculation $V^{(0)} \rightarrow \psi_n^{(0)}, n^{(0)}$

(2) Do for each perturbation j_1

use $\psi_n^{(0)}, n^{(0)}$

$V^{j_1} \rightarrow \psi_n^{j_1}, n^{j_1}$ $\left\langle \begin{array}{l} \text{using minimization of second-order energy} \\ \text{or} \\ \text{Sternheimer equation} \end{array} \right.$

Enddo

(3) Do for each $\{j_1, j_2\}$

get $E^{j_1 j_2}$ from $\psi_n^{(0)}, \psi_n^{j_1}, \psi_n^{j_2}$

Enddo

(4) Post-processing : from 'bare' $E^{j_1 j_2}$ to physical properties

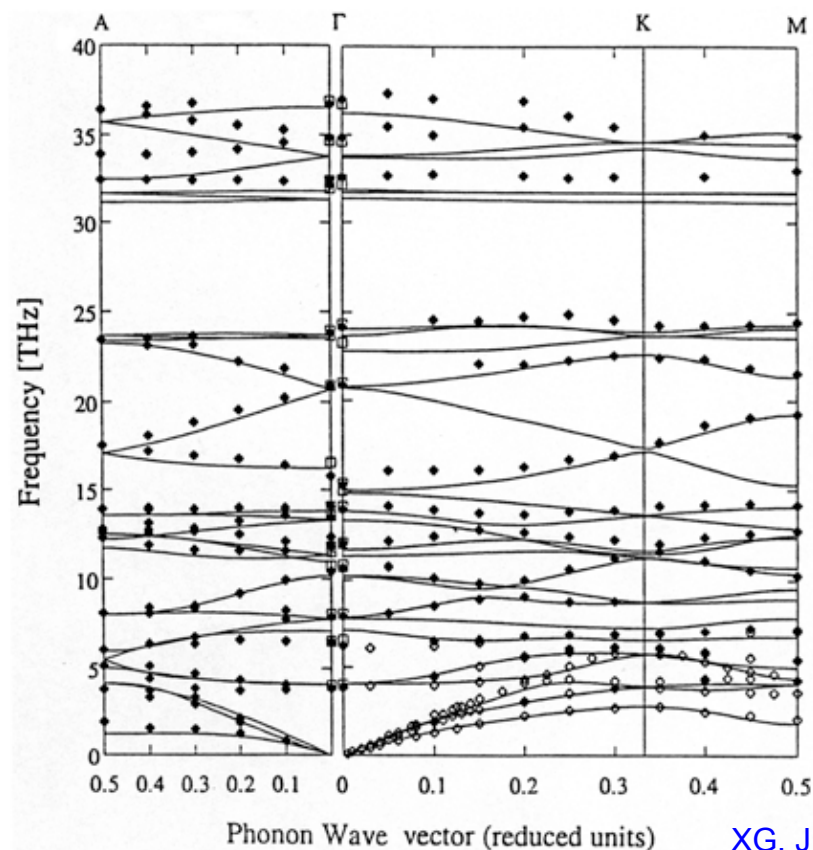
Phonon band structures from DFPT

Phonon band structure

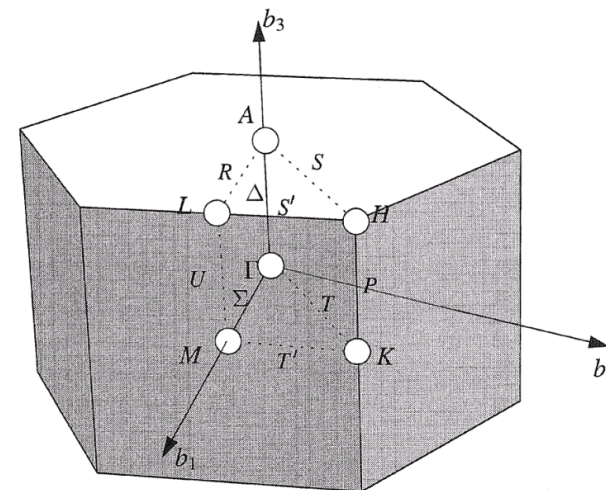
From DFPT : straightforward, although lengthy (self-consistent calculation) to compute, for one wavevector :

$$\tilde{C}_{k\alpha,k'\beta}(\vec{q})$$

Full band structure needs values for many wavevectors ...



SiO₂ alpha-quartz



XG, J.-C.Charlier, D.C.Allan, M.P.Teter, *Phys. Rev. B* 50, 13055 (1994)

Fourier Interpolation

If IFCs were available, dynamical matrices could be obtained easily for **any** number of wavevectors

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}(\vec{q}) = \sum_b C_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\vec{q}\cdot\vec{R}^b}$$

IFCs are generated by

$$C_{\kappa\alpha,\kappa'\beta}(0,b) = \frac{(2\pi)^3}{\Omega_0} \int_{BZ} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\vec{q}) e^{-i\vec{q}\cdot\vec{R}^b} d\vec{q}$$

= **Fourier interpolation** of dynamical matrices.

Numerical Fourier Interpolation

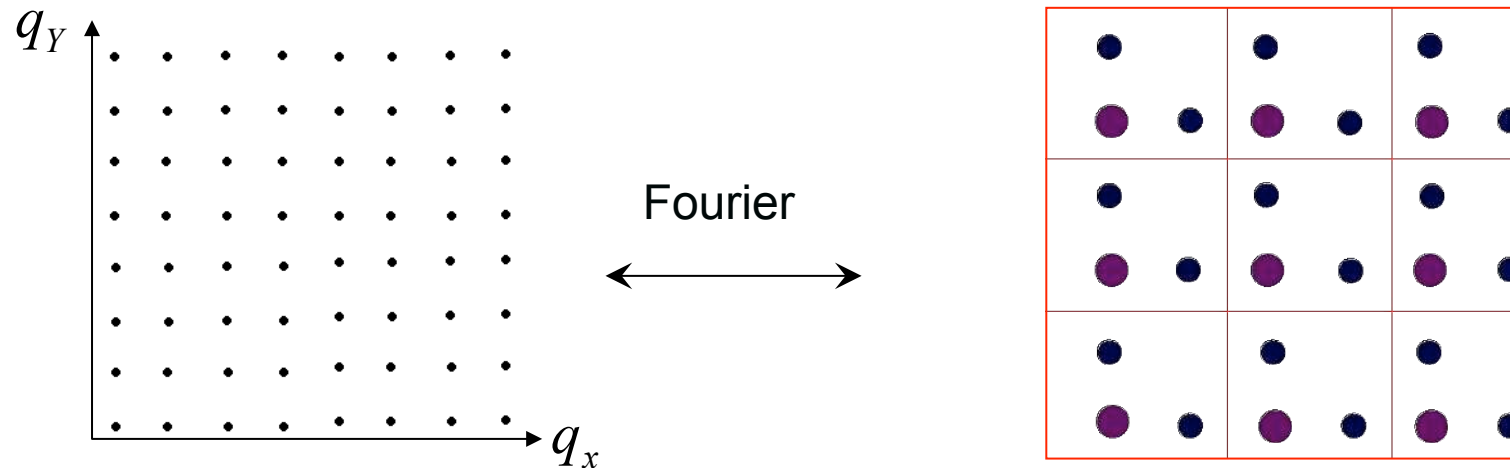
Key of the interpolation : replace the integral

$$C_{\kappa\alpha,\kappa'\beta}(0,b) = \frac{(2\pi)^3}{\Omega_0} \int_{BZ} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\vec{q}) e^{-i\vec{q}\cdot\vec{R}^b} d\vec{q}$$

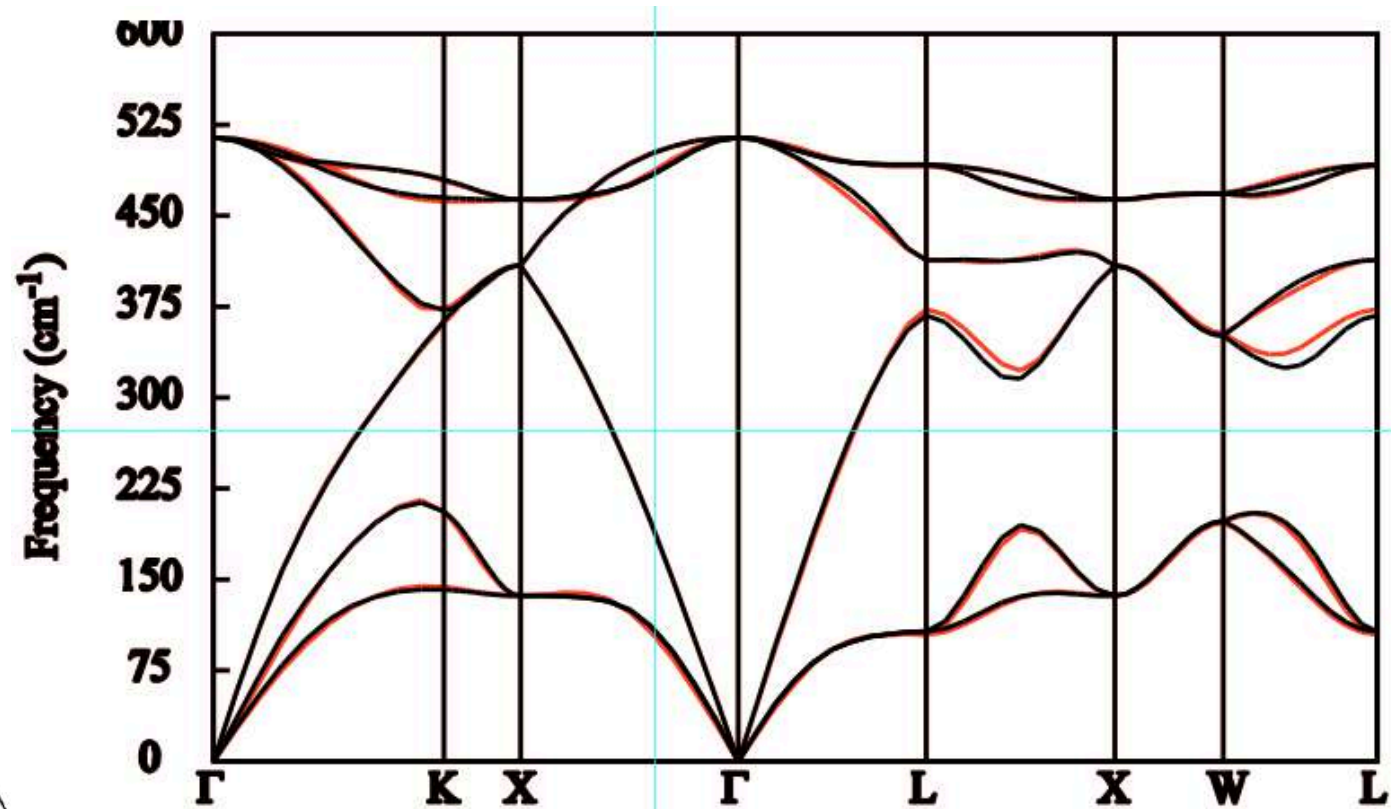
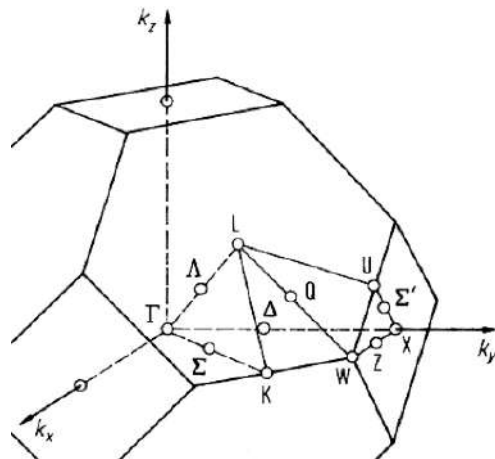
by summation on a few wavevectors (=“q-points”).

Grid of (l,m,n) points

IFC' s in box of (l,m,n) periodic cells



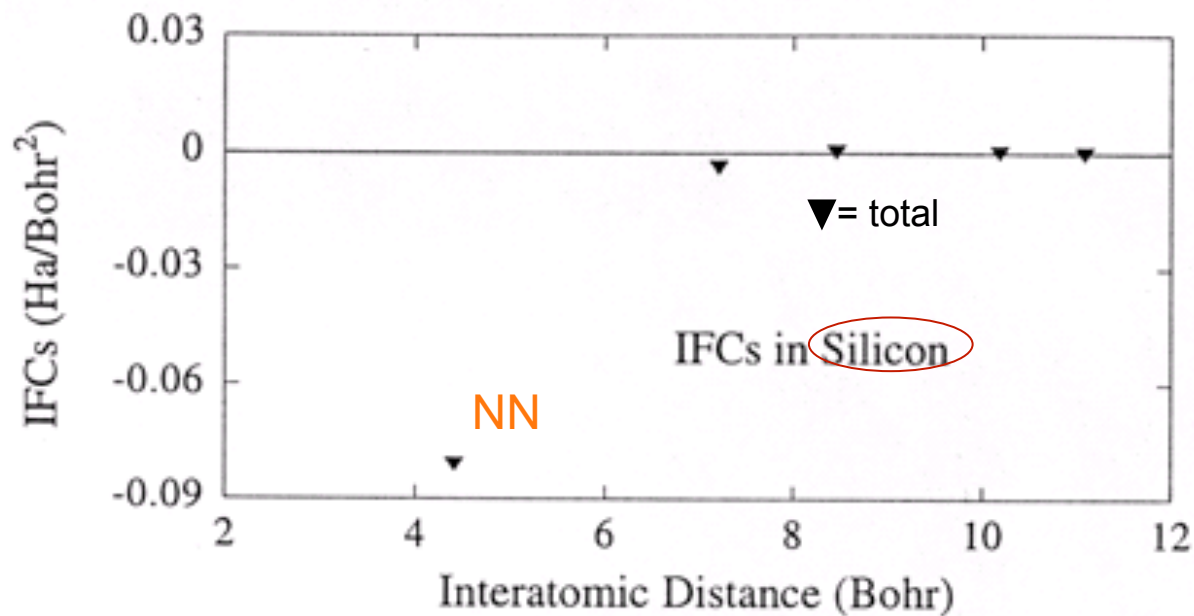
Fourier interpolation : Silicon



- Real space IFC's calculated with 10 q-points
- Real space IFC's calculated with 18 q-points

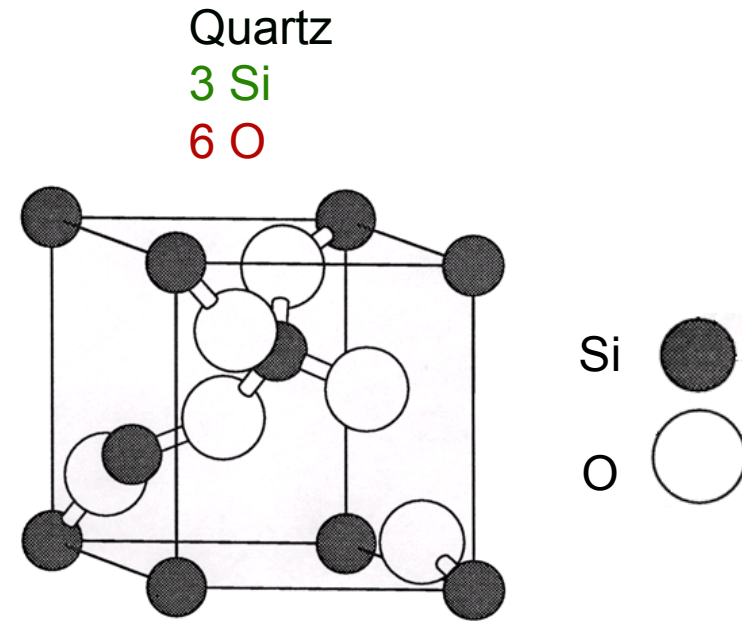
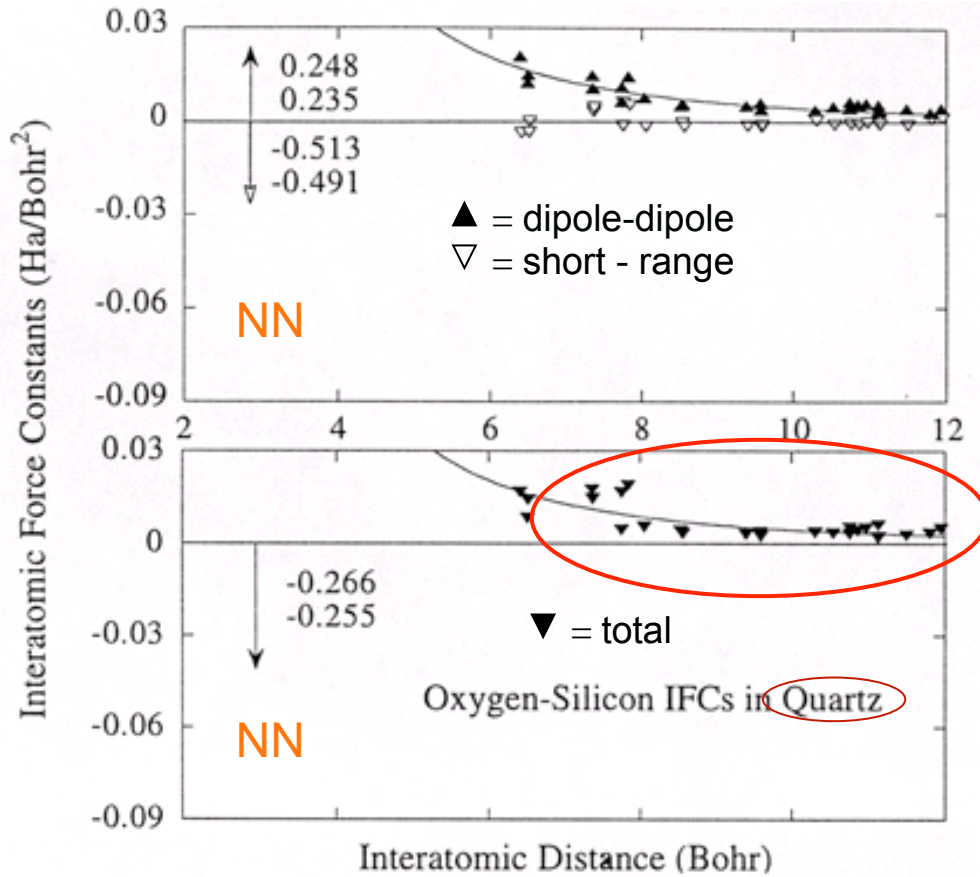
Interatomic force constants for silicon

IFC's are short range, i.e. falling to zero quickly after the nearest-neighbors (NN).



XG, *Adv. in Quantum Chemistry* 33, 225 (1999)

Interatomic force constants for silica quartz



Long-ranged
interatomic forces !

XG, *Adv. in Quantum Chemistry* 33, 225 (1999)

Understanding the long-range behaviour

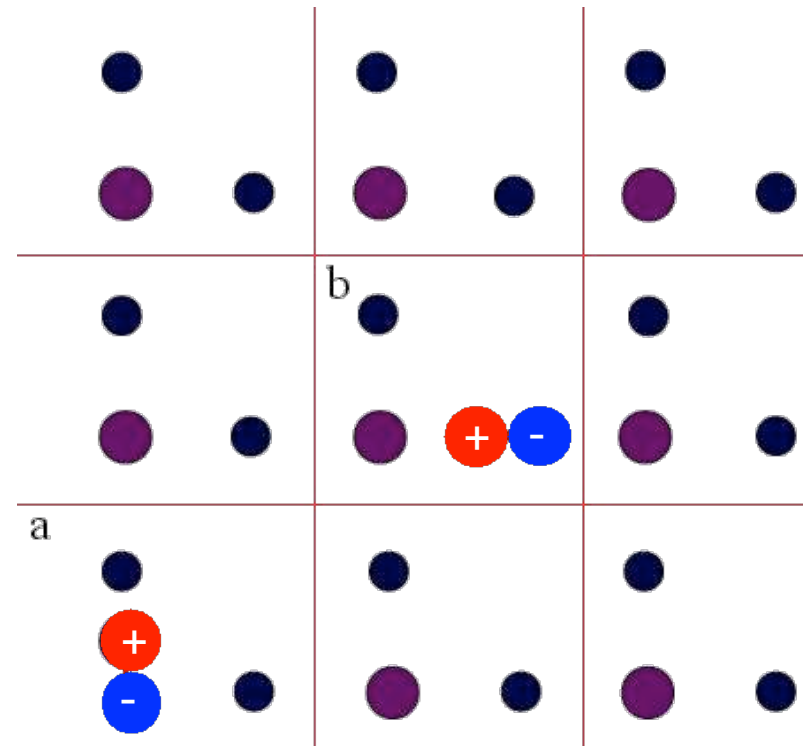
When a ion with charge Z is displaced from its equilibrium position, a **dipolar electric field** is created. Its effect on other ions is described by a **dipole - dipole interaction** appearing in IFC's.

Suppose : homogeneous material with isotropic dielectric tensor $\epsilon\delta_{\alpha\beta}$, ions with charges Z_k and $Z_{k'}$, then

$$C_{k\alpha,k'\beta}(0,b) = \frac{Z_k Z_{k'}}{\epsilon} \left(\frac{\delta_{\alpha\beta}}{d^3} - 3 \frac{d_\alpha d_\beta}{d^5} \right)$$

$$d = r_k^0 - r_{k'}^a = R^a + \tau_{k'} - \tau_k$$

Long range decay
of the IFC's : $1/d^3$



Effect of the long-range interaction

The dynamical matrix exhibit a non-analytical (na) behavior, mediated by the long-wavelength electric field

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}^{na}(\vec{q} \rightarrow 0) = \frac{4\pi e^2}{\Omega_0} \frac{\sum_{\gamma} Z_{\kappa,\alpha\gamma}^* q_{\gamma} \sum_{\nu} Z_{\kappa',\beta\nu}^* q_{\nu}}{\sum_{\gamma,\nu} q_{\gamma} \epsilon_{\gamma\nu}^{\infty} q_{\nu}}$$

$$Z_{\kappa,\alpha\beta}^* = \Omega_0 \left. \frac{\partial P_{\alpha}}{\partial u_{\kappa,\beta}} \right|_{\delta\vec{E}=0} = \frac{\partial F_{\kappa\beta}}{\partial \mathcal{E}_{\beta}} \quad \text{Born effective charge tensor for atom } \kappa$$

(Proportionality coefficient between polarisation and displacement, also between force and electric field)

$$\epsilon_{\gamma\nu}^{\infty} = \delta_{\gamma\nu} + 4\pi \frac{\partial P_{\gamma}}{\partial \mathcal{E}_{\nu}} \quad \text{electronic dielectric tensor}$$

(electronic contribution to the screening of the charges)

Both can be linked to a second derivative of total energy

Dielectric properties from DFPT

Treatment of homogeneous electric field

$$V_{\text{ext}}^{(1)} = \vec{\mathcal{E}} \cdot \vec{r} \quad \text{breaks the periodic boundary conditions !}$$

One needs, for linear response :

$$\langle u_{c,k} | \vec{r} | u_{v,k} \rangle \quad \text{or} \quad P_{ck} \left[\vec{r} | u_{v,k} \rangle \right]$$

↑ conduction state
↑ valence state
↑ projection on conduction states

periodic part of Bloch wf

Solution :

$$P_{ck} \left[\vec{r} | u_{v,k} \rangle \right] = P_{ck} \left[-i \nabla_{\vec{k}} | u_{v,\vec{k}} \rangle \right]$$

+ the derivative with respect to k
can be computed within DFPT

The treatment of homogeneous electric field is thus mapped onto the **original periodic system**.

Dielectric tensor : electronic part

$$\epsilon_{\gamma\nu}^{\infty} = \delta_{\gamma\nu} + 4\pi \frac{\partial P_{\gamma}}{\partial \mathcal{E}_{\nu}} \quad \text{electronic dielectric tensor}$$

(Proportionality coefficient between polarisation and electric field)

Linked to a second derivative of total energy

$$P_{\gamma} = -\frac{1}{V} \frac{\partial E}{\partial \mathcal{E}_{\gamma}} \quad \epsilon_{\gamma\nu}^{\infty} = \delta_{\gamma\nu} - \frac{4\pi}{V} \frac{\partial^2 E}{\partial \mathcal{E}_{\gamma} \partial \mathcal{E}_{\nu}}$$

Born effective charges

$$Z_{\kappa,\alpha\beta}^* = -\frac{\Omega_0}{V} \frac{\partial^2 E}{\partial \mathcal{E}_\alpha \partial u_{\kappa,\beta}} \quad \text{Born effective charge tensor for atom } \kappa$$

A mixed second derivative of total energy

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

Proportionality coefficient between polarisation and displacement, also between force and electric field

Interpolation Scheme

Abinit

Use Abinit to calculate $\tilde{C}_{k\alpha,k'\beta}(\vec{q})$ on a few Q-point.

Time-consuming

Calculate $Z_{k,\alpha\beta}^*$ and $\epsilon_{\gamma,\nu}^\infty$



Enforce sum-rules

asr

chneut

Subtract the dipole-dipole coupling $\tilde{C}_{k\alpha,k'\beta}^{na}(\vec{q})$

dipdip

Fourier Transform to obtain $C_{k\alpha,k'\beta}^{SR}(0,b)$

Anadbb

Use the real space IFC's to interpolate at any Q-point.

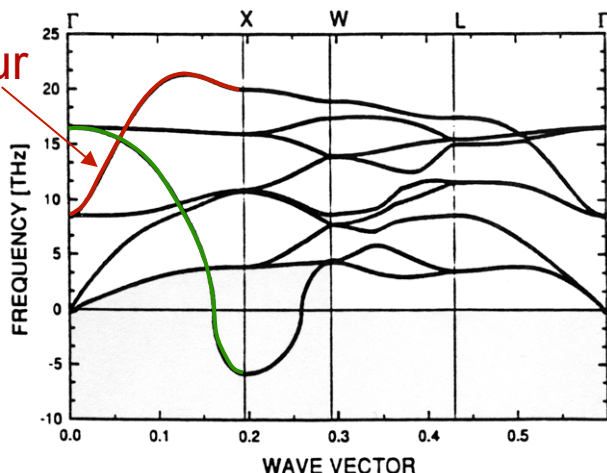
ifcflag

Add the dipole-dipole part for that Q-point

Diagonalize dynamical matrix to find phonon frequencies

Phonon dispersion curves of ZrO₂

Wrong behaviour

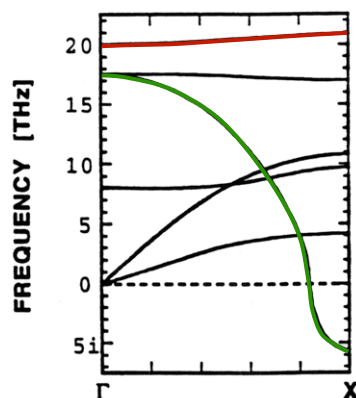


High - temperature : Fluorite structure
($F_{m\bar{3}m}$, one formula unit per cell)

Supercell calculation + interpolation
⚠ Long-range dipole-dipole interaction not taken into account

(From Parlinski K., Li Z.Q., and Kawazoe Y., *Phys. Rev. Lett.* 78, 4063 (1997))

ZrO₂ in the cubic structure at the equilibrium lattice constant $a_0 = 5.13 \text{ \AA}$.



DFPT (Linear-response)

with $Z_{Zr}^* = 5.75$

$Z_O^* = -2.86$

$\epsilon_\infty = 5.75$

LO - TO splitting 11.99 THz

Non-polar mode is OK

(From Detraux F., Ghosez Ph. and Gonze X., *Phys. Rev. Lett.* 81, 3297 (1998) - Comment to the Parlinski & al paper)

Analysis of instabilities



CUBIC

(5at/cell)

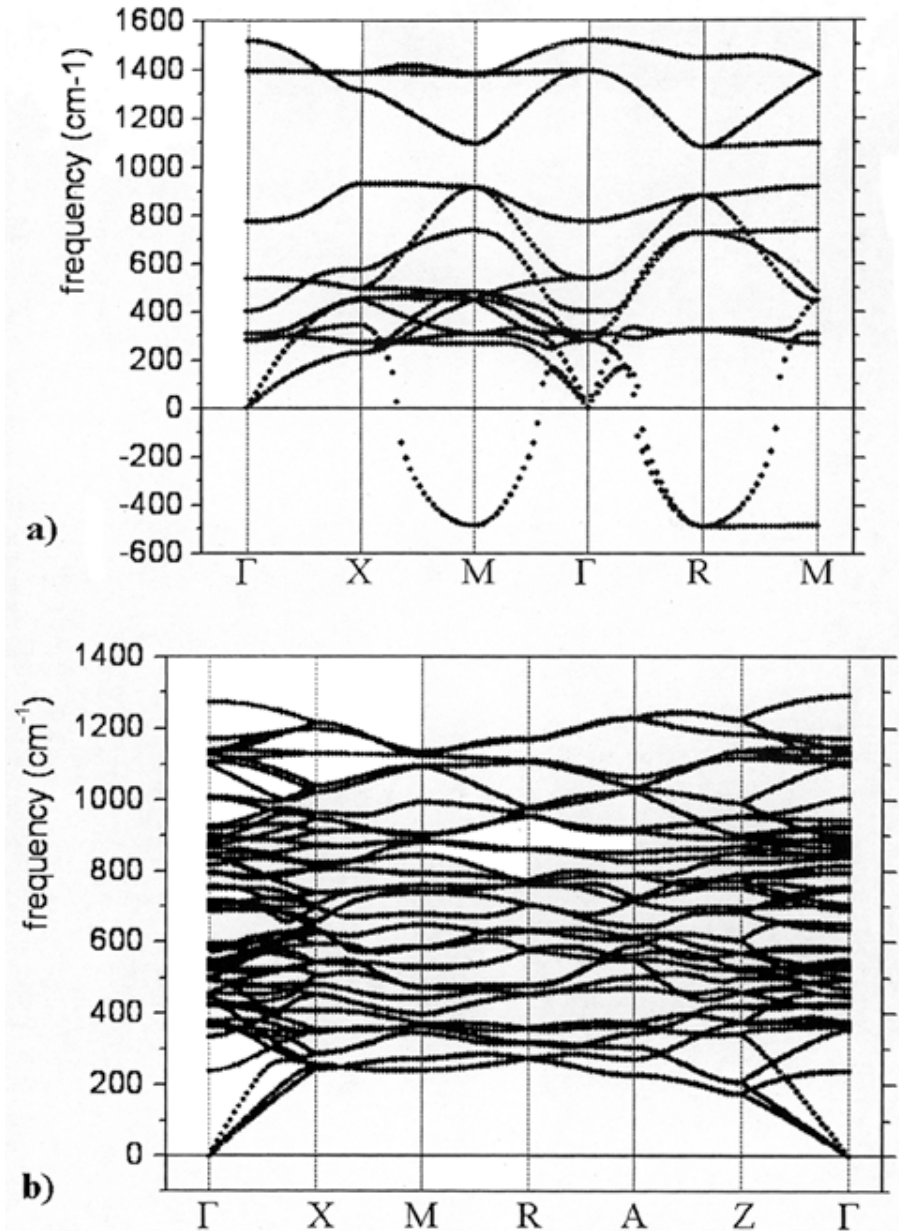
Phonon dispersion relations.

(a) Ideal cubic phase : unstable.

(b) Condensations of the unstable phonon modes generate a (meta) stable orthorhombic phase

ORTHORHOMBIC

(20at/cell)



Electric field - atomic displacement coupling

Frequency - dependent dielectric tensor in the IR range

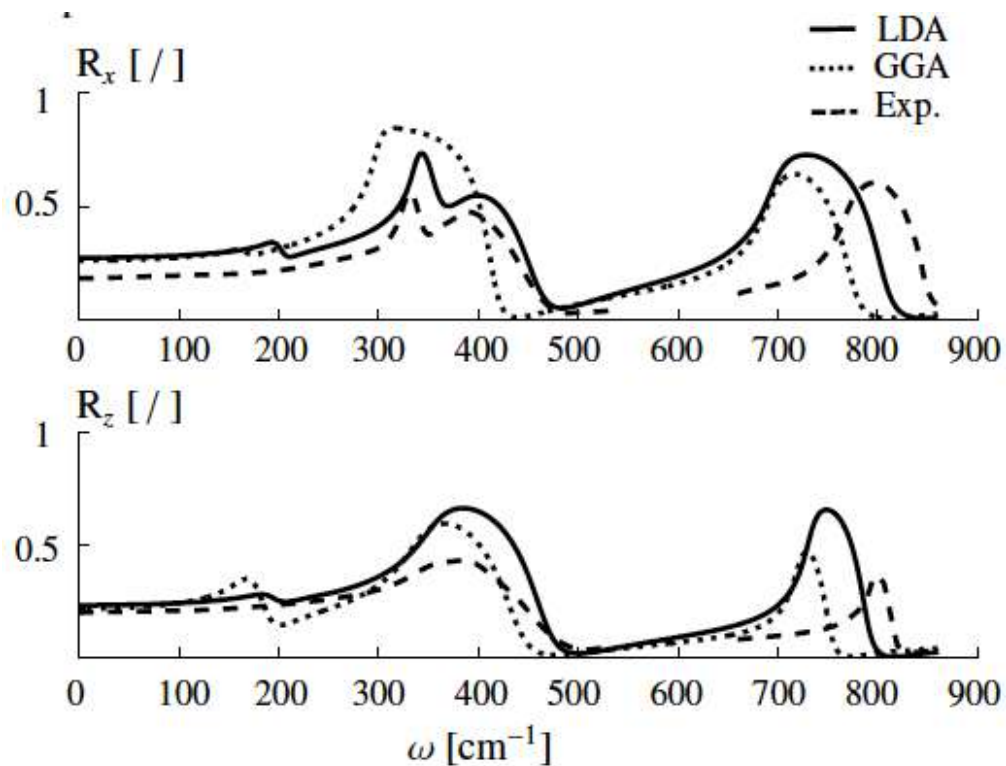
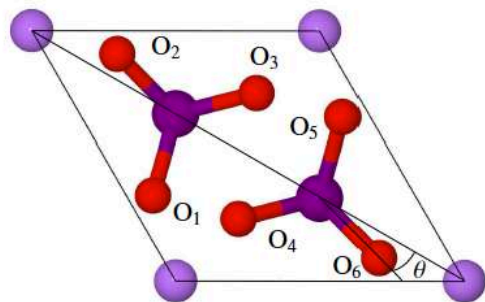
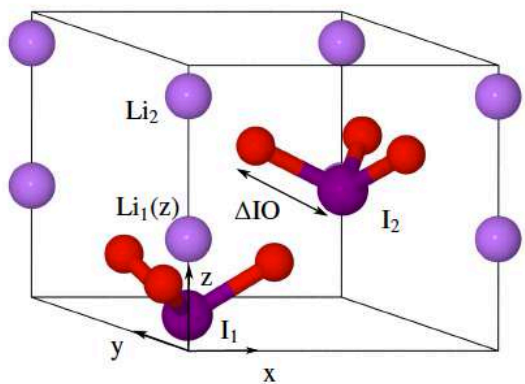
$$\epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}^{\infty} + \sum_m \frac{\left[\sum_{\kappa\gamma} Z_{\kappa,\alpha\gamma}^* u_{m\vec{q}=0}^*(\kappa\gamma) \right] \left[\sum_{\kappa'\gamma'} Z_{\kappa',\beta\gamma}^* u_{m\vec{q}=0}(\kappa'\gamma') \right]}{\omega^2 - \omega_{mq=0}^2}$$

Infrared (IR) reflectivity

$$R_k(\omega) = \left| \frac{\epsilon_{kk}^{1/2}(\omega) - 1}{\epsilon_{kk}^{1/2}(\omega) + 1} \right|^2$$

XG & C. Lee, *Phys. Rev. B.* 55, 10355 (1997)

Infrared reflectivity of lithium iodate



B. Van Troeye, Y. Gillet, S. Poncé and XG, *Optical Materials* 36, 1494 (2014)

Electro-optic coefficients

$$\Delta(\epsilon^{-1})_{ij} \triangleq \sum_k r_{ijk} \mathcal{E}_k$$

Computed from DFPT from 3rd derivatives of electric enthalpy with respect to electric fields and atomic displacements

		Electro-optic coefficients (pm/V)				
		r_{31}^S	r_{33}^S	r_{22}^S	r_{51}^S	
LiNbO ₃	LDA [24]	9.67	26.93	4.55	14.93	
	Exp. [1]	8.6	30.8	3.4	28	
PbTiO ₃	LDA [24]	8.98	5.88		30.53	
	Exp. [46]	13.8	5.9			
BaTiO ₃	LDA [24]	8.91	22.27			
	Exp. [47]	10.2	40.6			
	Exp. [1]	8	28			
LiIO ₃		r_{31}^S	r_{33}^S	ω	r_{41}^S	r_{42}^S
Tot.		6.75	10.22		0.82	6.60
Exp. [11]		4.1 ± 0.6	6.4 ± 1		1.4 ± 0.2	3.3 ± 0.7
Exp. [42]		5.8 ± 1.2				

B. Van Troeye, Y. Gillet, S. Poncé and XG, *Optical Materials* 36, 1494 (2014)

Piezoelectric coefficients

$$D_i = \sum_j e_{ij} \eta_j + \sum_j \epsilon_{ij} \mathcal{E}_j$$

Computed from DFPT as a mixed 2nd derivative of electric enthalpy with respect to strain perturbation and electric field

LiIO_3

Computed piezoelectric tensors for both LDA and GGA functionals as well as experimental data available.

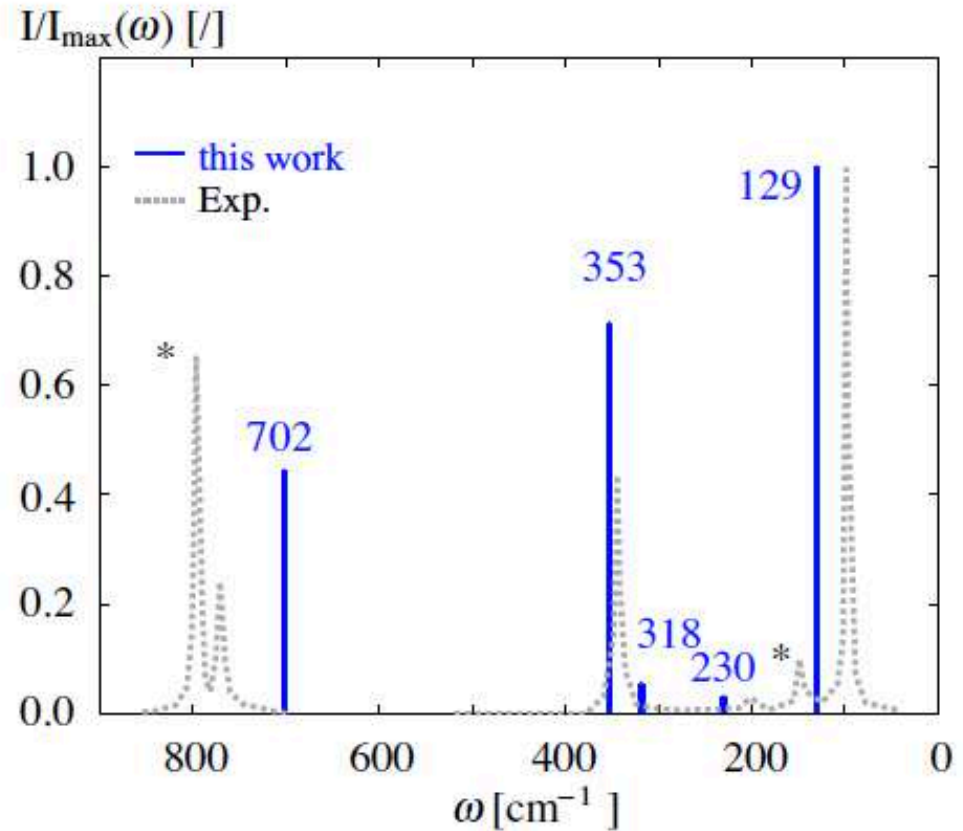
	Piezoelectric tensor (C/m ²)			
	e_{13}	e_{33}	e_{41}	e_{42}
LDA (this work)	1.14	1.54	-0.13	1.26
GGA (this work)	0.92	1.28	-0.07	1.10
Exp. [51]	0.65	0.97	0.10	0.89

B. Van Troeye, Y. Gillet, S. Poncé and XG, *Optical Materials* 36, 1494 (2014)

Raman scattering intensities



Computed from DFPT
as a mixed 3rd derivative
of electric enthalpy
with respect to electric field and
two atomic displacements



(a) Raman spectrum for the X(YX)Y configuration (Blue) E_2 modes.

B. Van Troeye, Y. Gillet, S. Poncé and XG,
Optical Materials 36, 1494 (2014)

Thermodynamic properties from DFPT

Statistical physics : phonons = bosons

Harmonic approximation :
phonons are independent particles,
obeying Bose-Einstein statistics

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

Internal energy

$$U_{phon} = \int_0^{\omega_{max}} \hbar\omega \left(n(\omega) + \frac{1}{2} \right) g(\omega) d\omega$$

Energy of the harmonic oscillator

Phonon density of states

All vibrational contributions to thermodynamic properties, in the harmonic approximation, can be calculated in this manner.

Phonon density of states

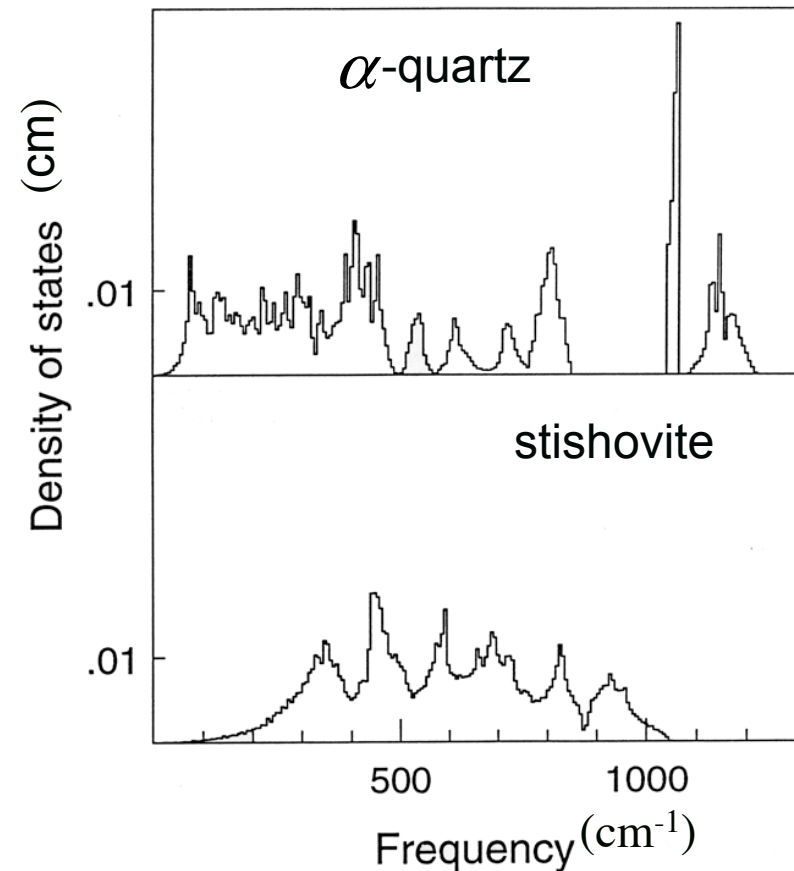
For each frequency channel,
count the “number” of
phonon modes

$$g_{norm}(\omega) = \frac{1}{3n_{at}N} \sum_{mq} \delta(\omega - \omega_{mq})$$

m = index of pattern of vibration,

\vec{q} = a crystalline momentum

(=> velocity of the vibrational wave)



Helmoltz free energy and specific heat

$$F = U - TS$$

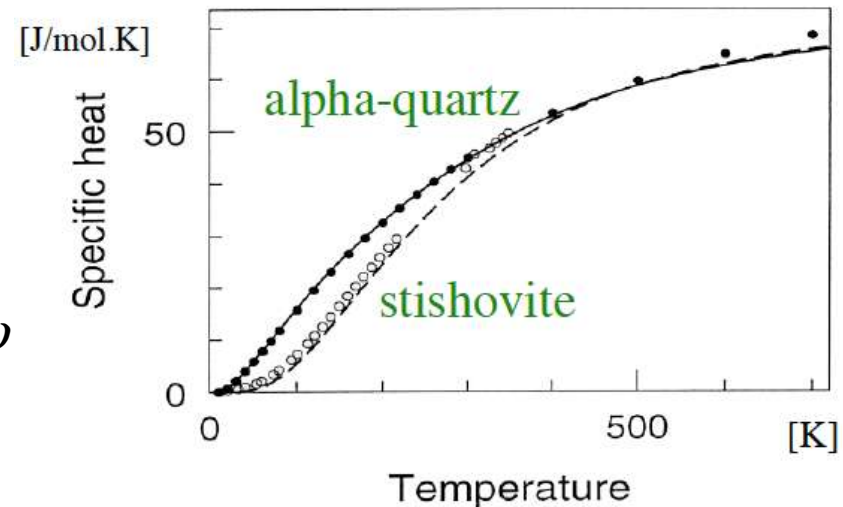
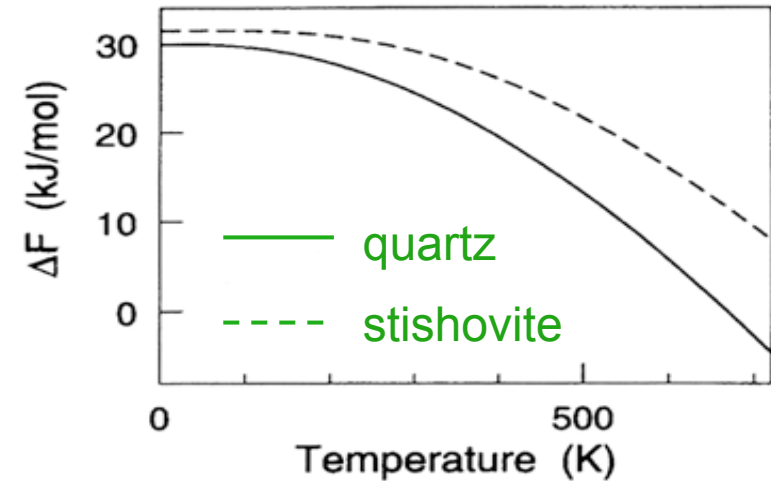
$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V$$

Vibrational contribution to F :

$$\Delta F = 3n_{at} N k_B T \int_0^{\omega_{max}} \ln \left\{ 2 \sinh \left(\frac{\omega}{2k_B T} \right) \right\} g(\omega) d\omega$$

Vibrational contribution to Cv :

$$C_V = 3n_{at} N k_B \int_0^{\omega_{max}} \left(\frac{\omega}{2k_B T} \right)^2 \operatorname{csch}^2 \left(\frac{\omega}{2k_B T} \right) g(\omega) d\omega$$

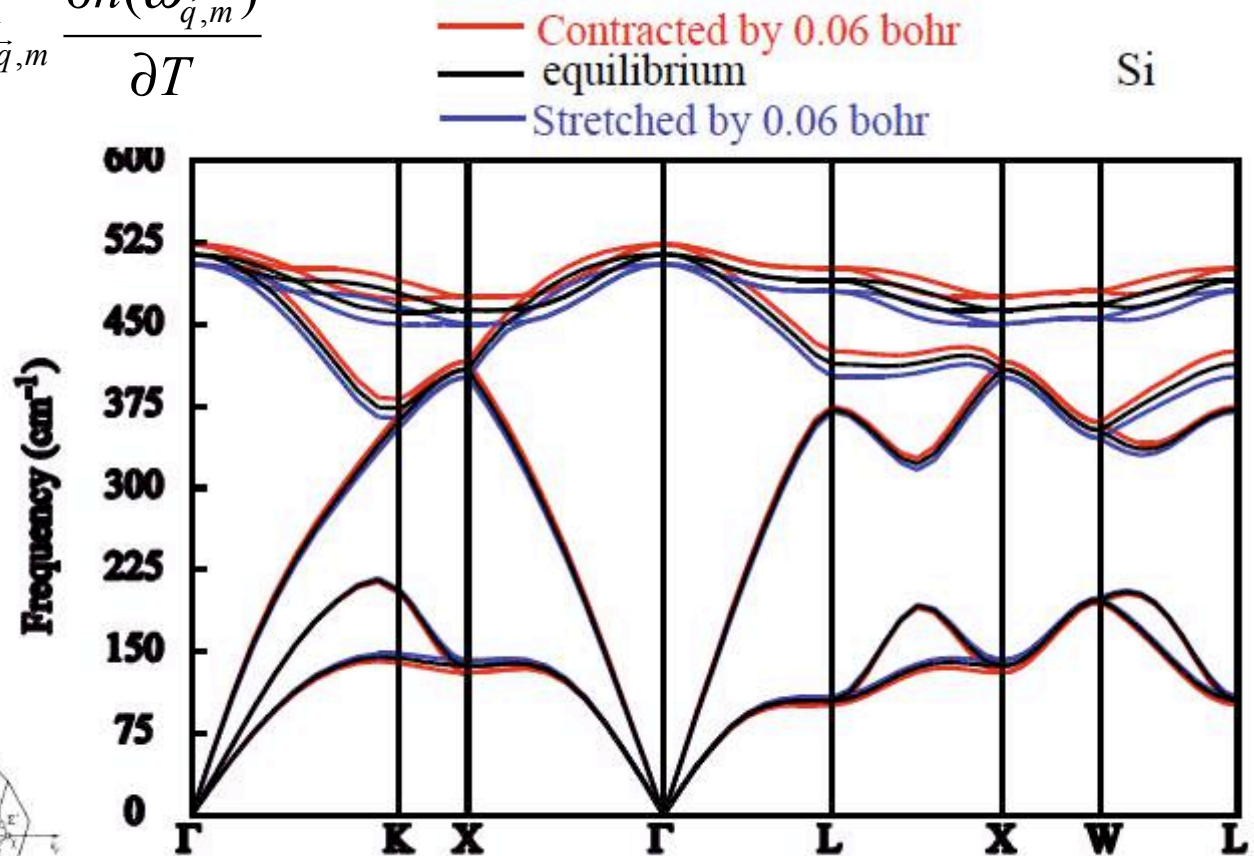
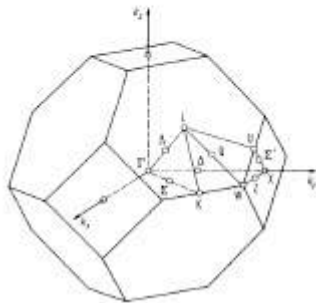


Ab initio thermal expansion

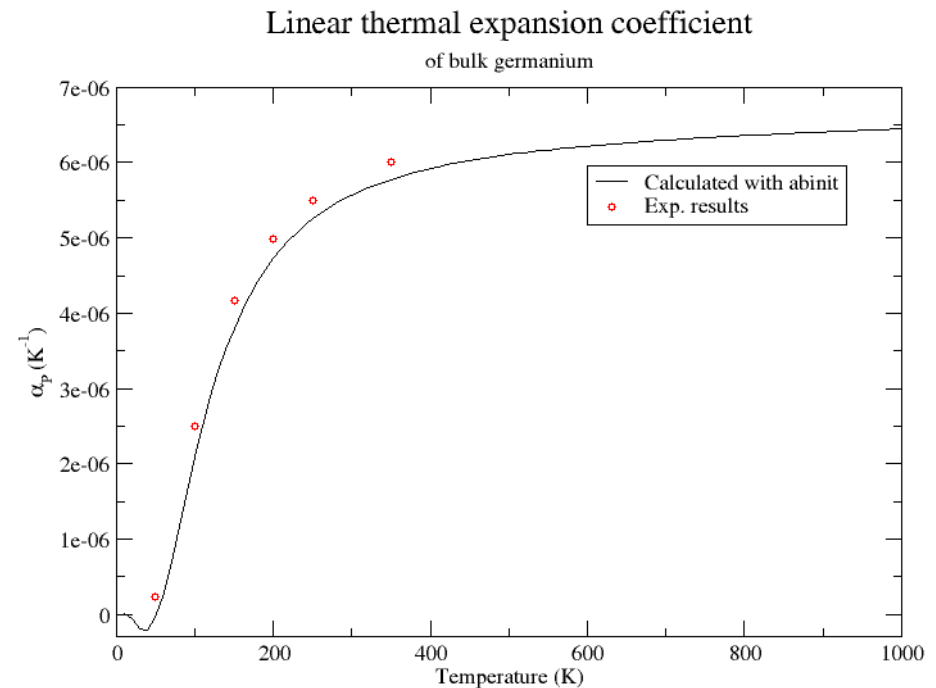
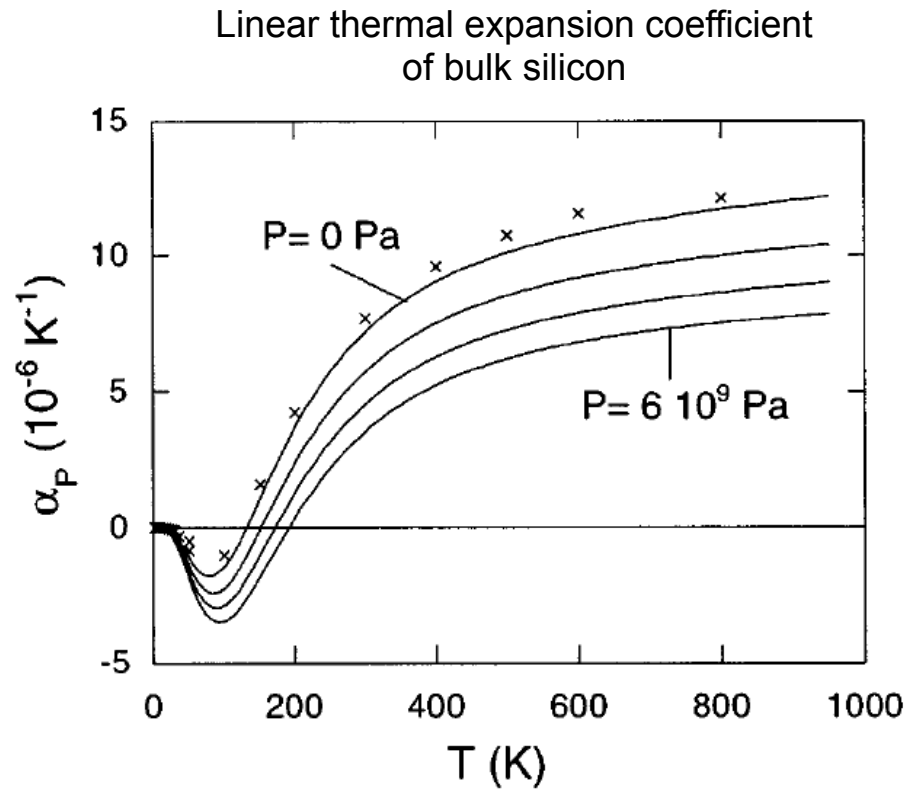
$$\alpha(T) = \frac{V}{3B} \sum_{\bar{q},m} \frac{1}{\hbar \omega_{\bar{q},m}} \gamma_{\bar{q},m} \frac{\partial n(\omega_{\bar{q},m})}{\partial T}$$

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

Alternative path :
minimisation of
free energy



Ab initio thermal expansion



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

Phonons : LDA ? GGA ?

DFPT : use it with LDA ? GGA-PBE ... ?

- ... Lattice parameters from LDA are usually underestimated
- ... GGA exists in many different flavors (e.g. PBE, PBEsol, AM05, ...),
PBE tends to overestimate, PBEsol is better, etc ...

Effect of the choice of **XC flavor** on
phonon frequencies, dielectric tensor, Born effective charges ?

Exhaustive study :

L. He et al, Phys. Rev. B89, 064305 (2014)

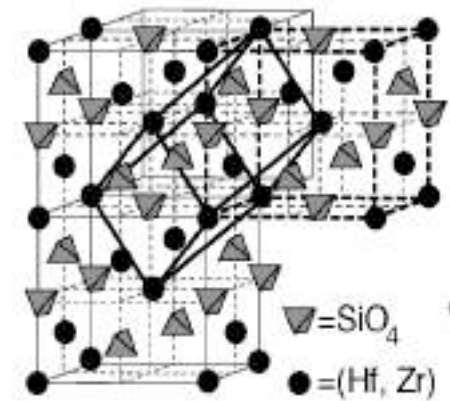
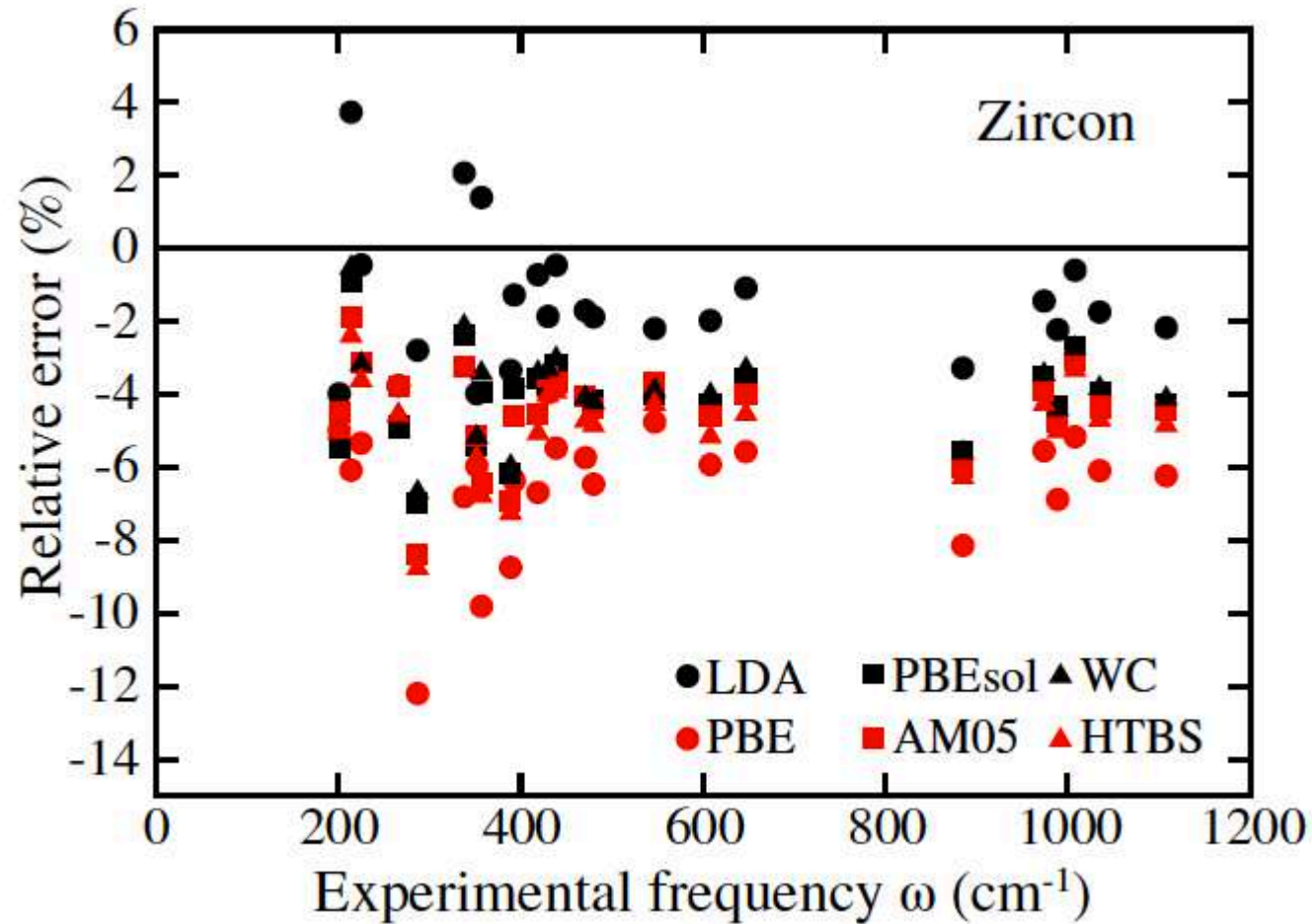
Studied (cf LibXC) :

LDA, PBE, PBEsol, AM05, WC, HTBS

for Si, quartz, stishovite, zircon, periclase (MgO), copper

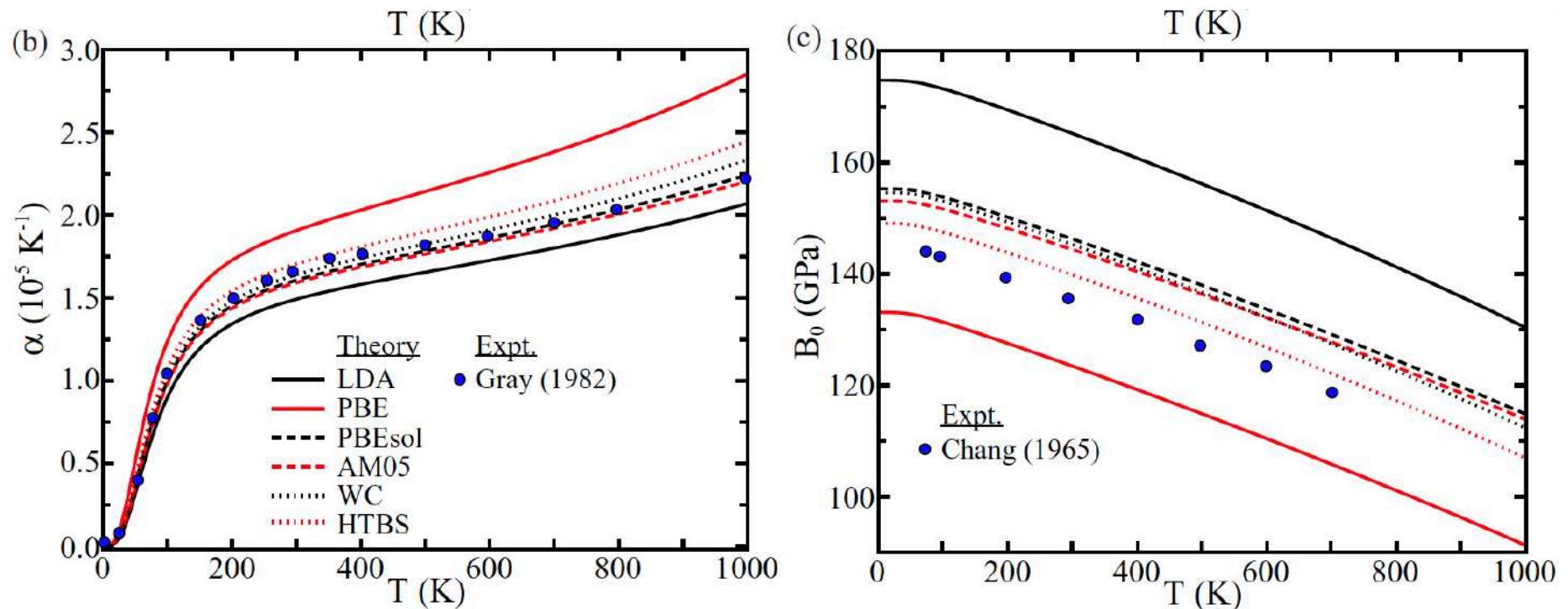
Message : in general, at relaxed atomic parameters, LDA performs better ...

Gamma phonons of zircon



L. He et al, Phys. Rev. B89, 064305 (2014)

Thermal expansion and T-dependent bulk modulus of copper



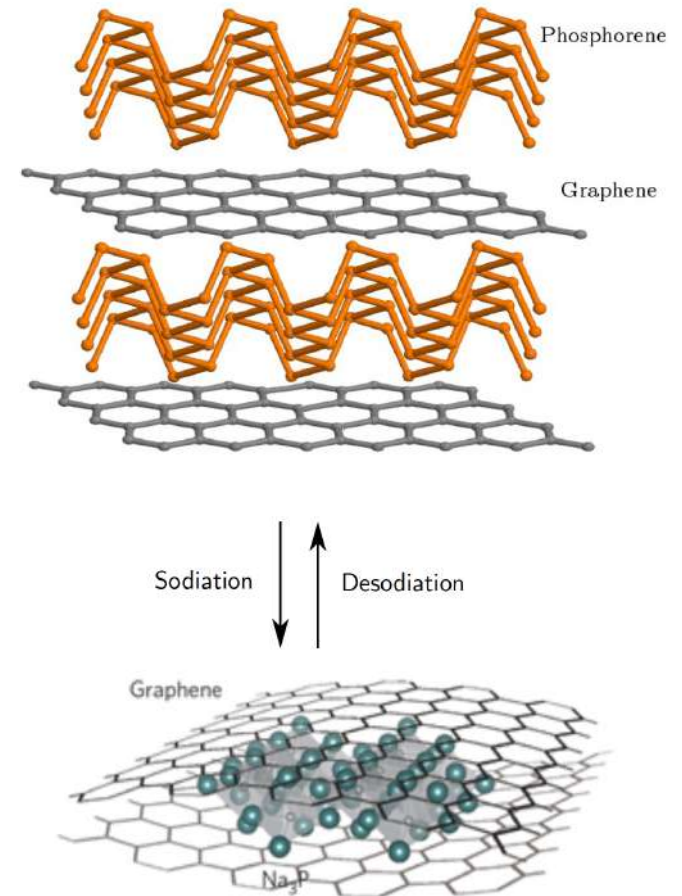
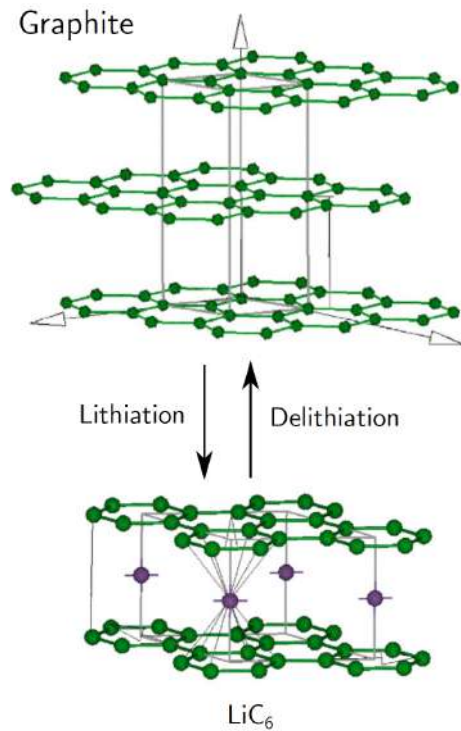
L. He et al, Phys. Rev. B89, 064305 (2014)

Phonons in weakly bonded systems

Layered materials

For the last decade : interest in layered and other nanostructured materials. Graphene, transition metal dichalcogenides, etc ...

- Interesting transport properties
- Topological materials
- Li or Na insertion in layered materials



Weak bonding : LDA ? GGA ? Beyond ?

Local Density Approximation and Generalized Gradient Approximation only rely on local density, gradients, etc ...

$$E_{xc} [n] = \int n(\mathbf{r}_1) \varepsilon_{xc}(\mathbf{r}_1; n) d\mathbf{r}_1$$

$$E_{xc}^{\text{LDA}} [n] = \int n(\mathbf{r}_1) \varepsilon_{xc}^{\text{LDA}}(n(\mathbf{r}_1)) d\mathbf{r}_1$$

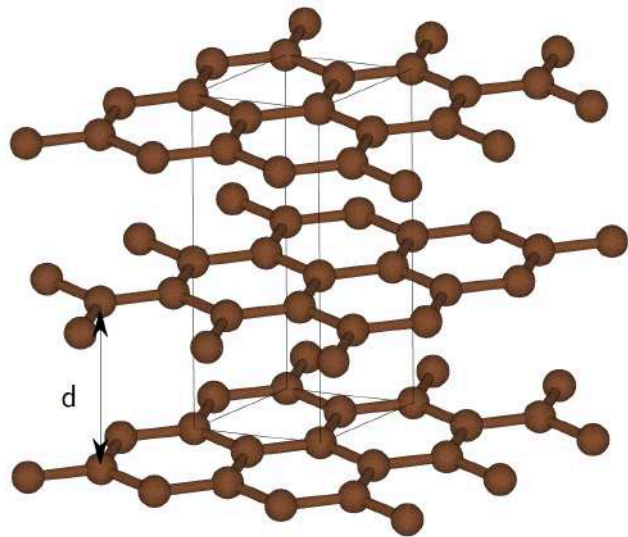
$$E_{xc}^{\text{GGA}} [n] = \int n(\mathbf{r}_1) \varepsilon_{xc}^{\text{GGA}}(n(\mathbf{r}_1), |\nabla n(\mathbf{r}_1)|) d\mathbf{r}_1$$

Van der waals : intrinsically non-local,
long range electron-electron correlation

→ New (classes of) functionals

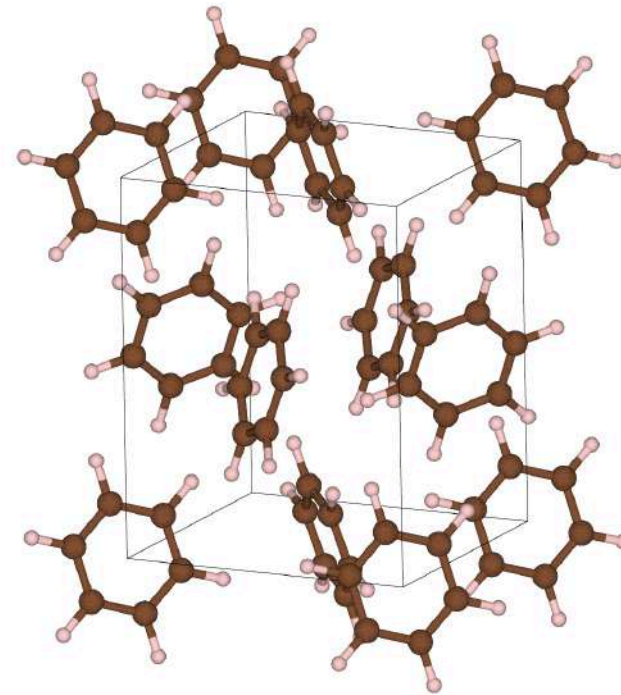
DFT-vDW-DF ; DFT-vDW-WF ; DFT-D2, -D3, -D3(BJ) ; ...

DFT+D3(BJ)



Interlayer parameter d (nm)

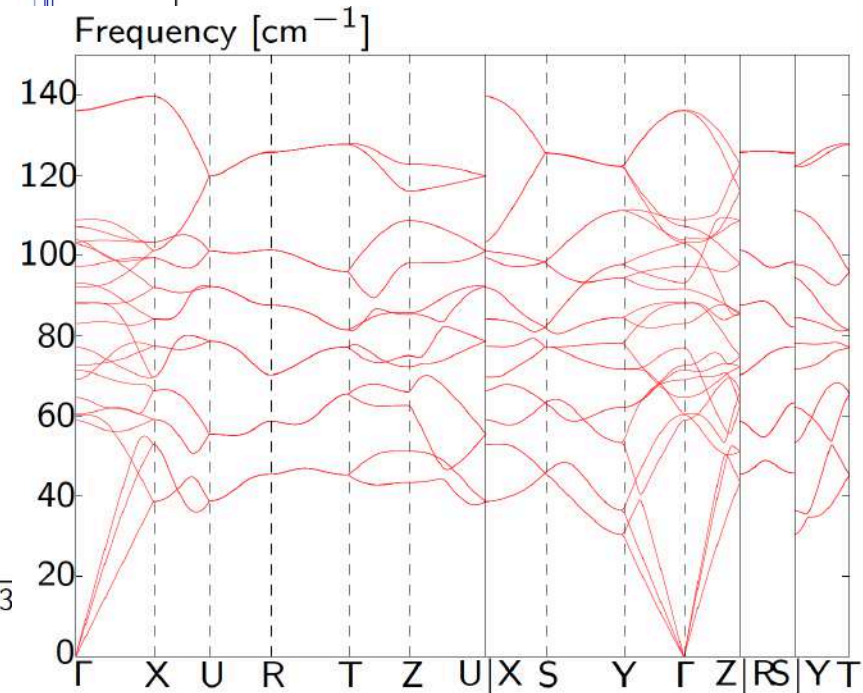
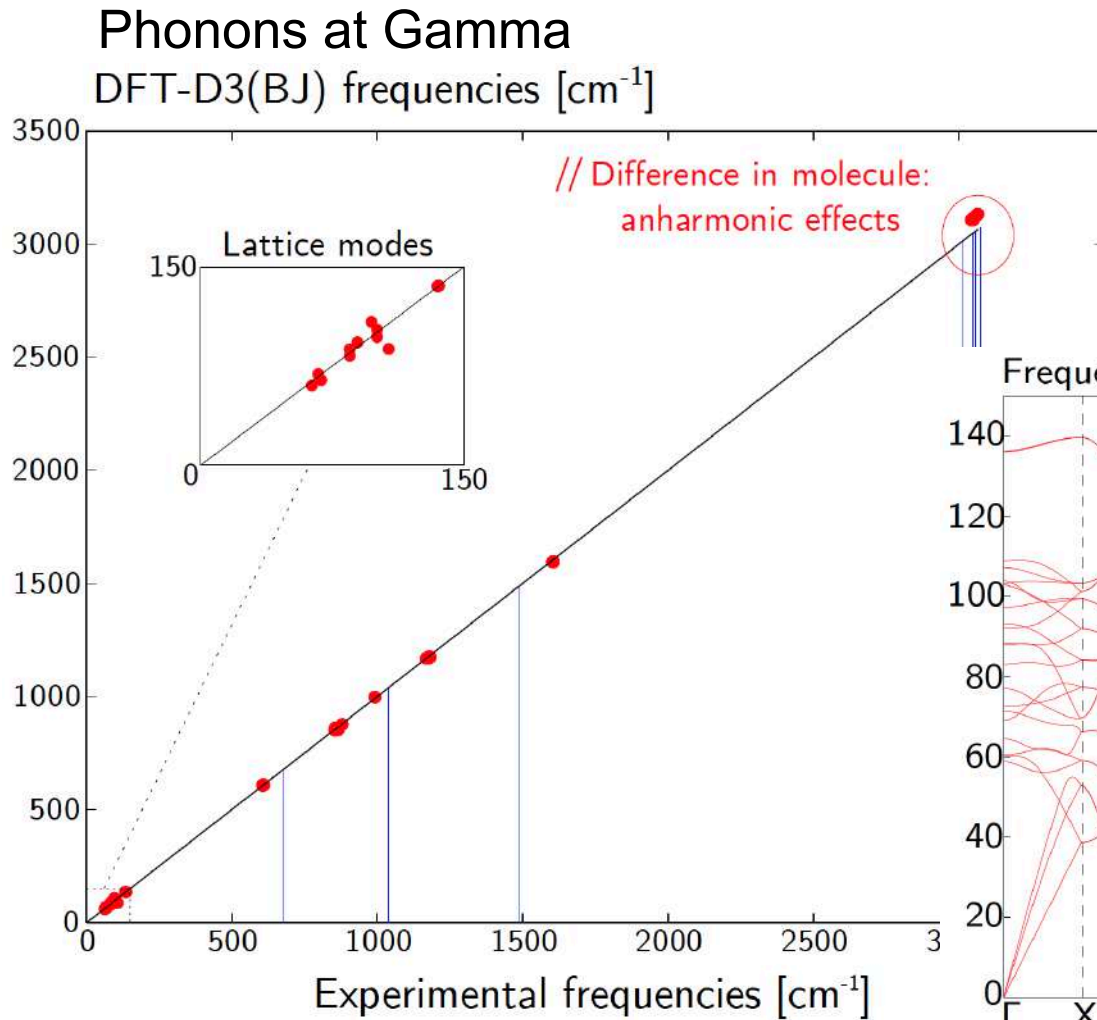
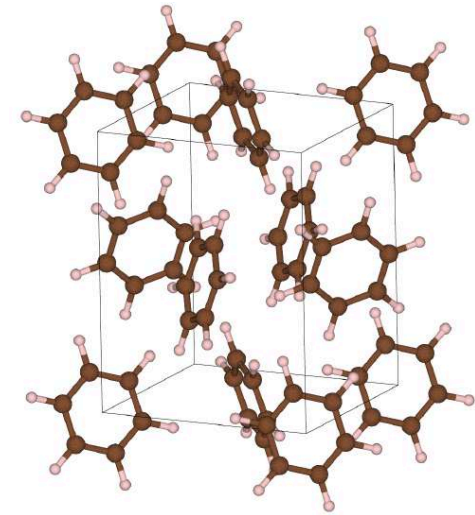
GGA(PBE)	0.44
+D3(BJ)	0.337
Exp.	0.334



Primitive cell volume (nm³)
[Pbca - 4 Benzene rings]

GGA(PBE)	>0.600
+D3(BJ)	0.455
Exp.	0.4625

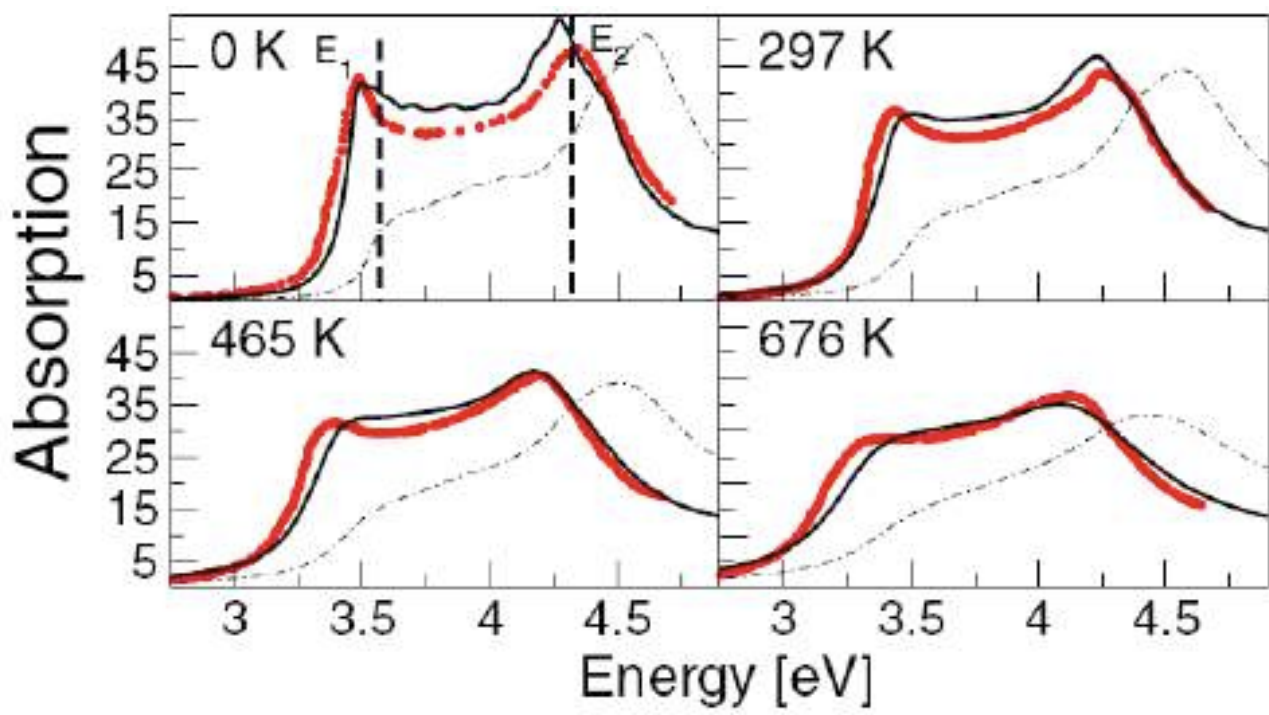
Phonons in benzene crystal



Temperature dependence of the electronic gap

Temperature dependence of electronic and optical properties

Bulk Silicon

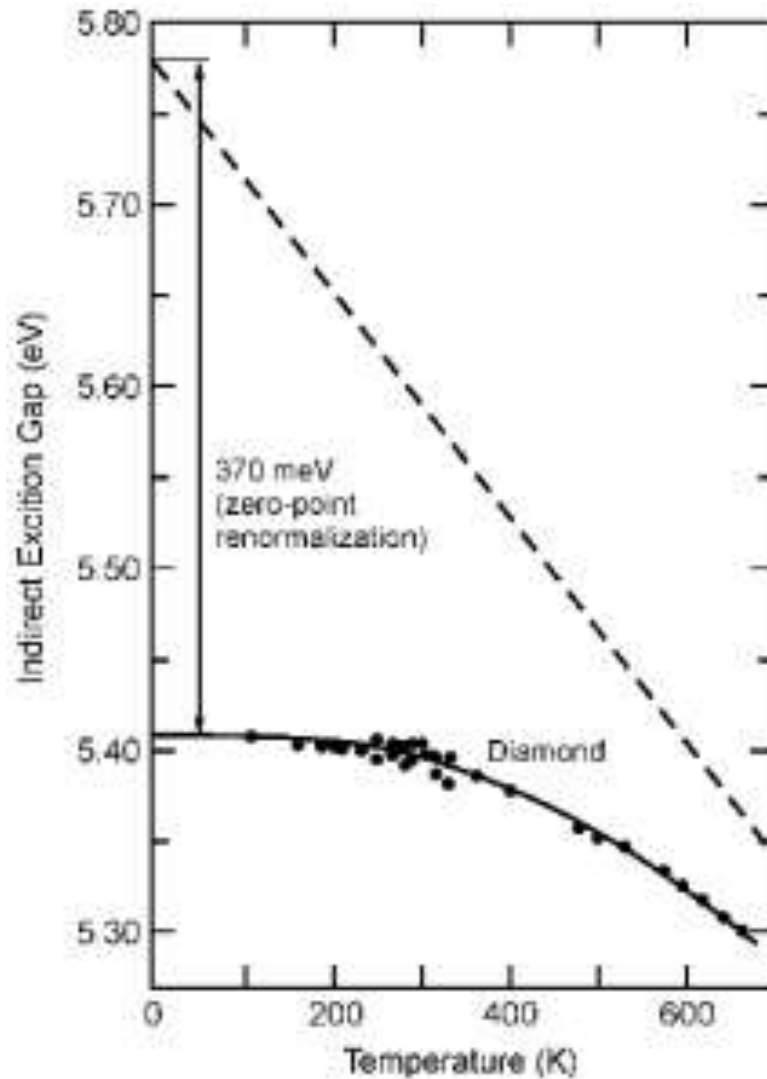


peaks **shift**

peaks **broaden**

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

Diamond : zero-point motion effect



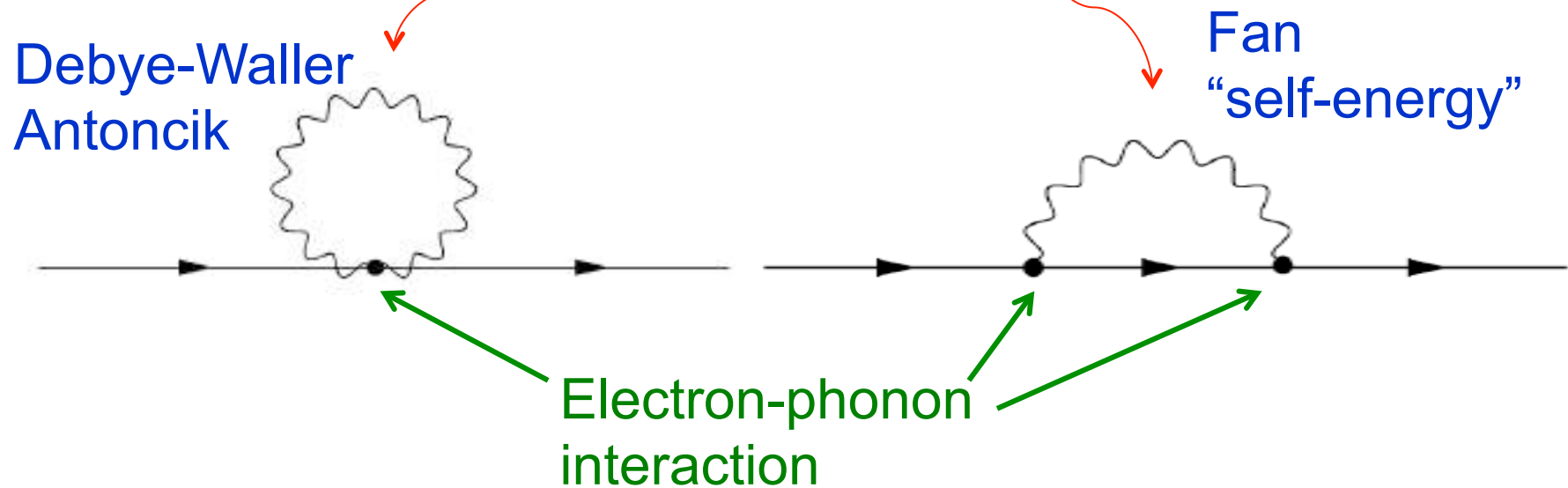
0.37 eV
for the indirect band gap

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

How to compute it ?

Allen-Heine-Cardona theory

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



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

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

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

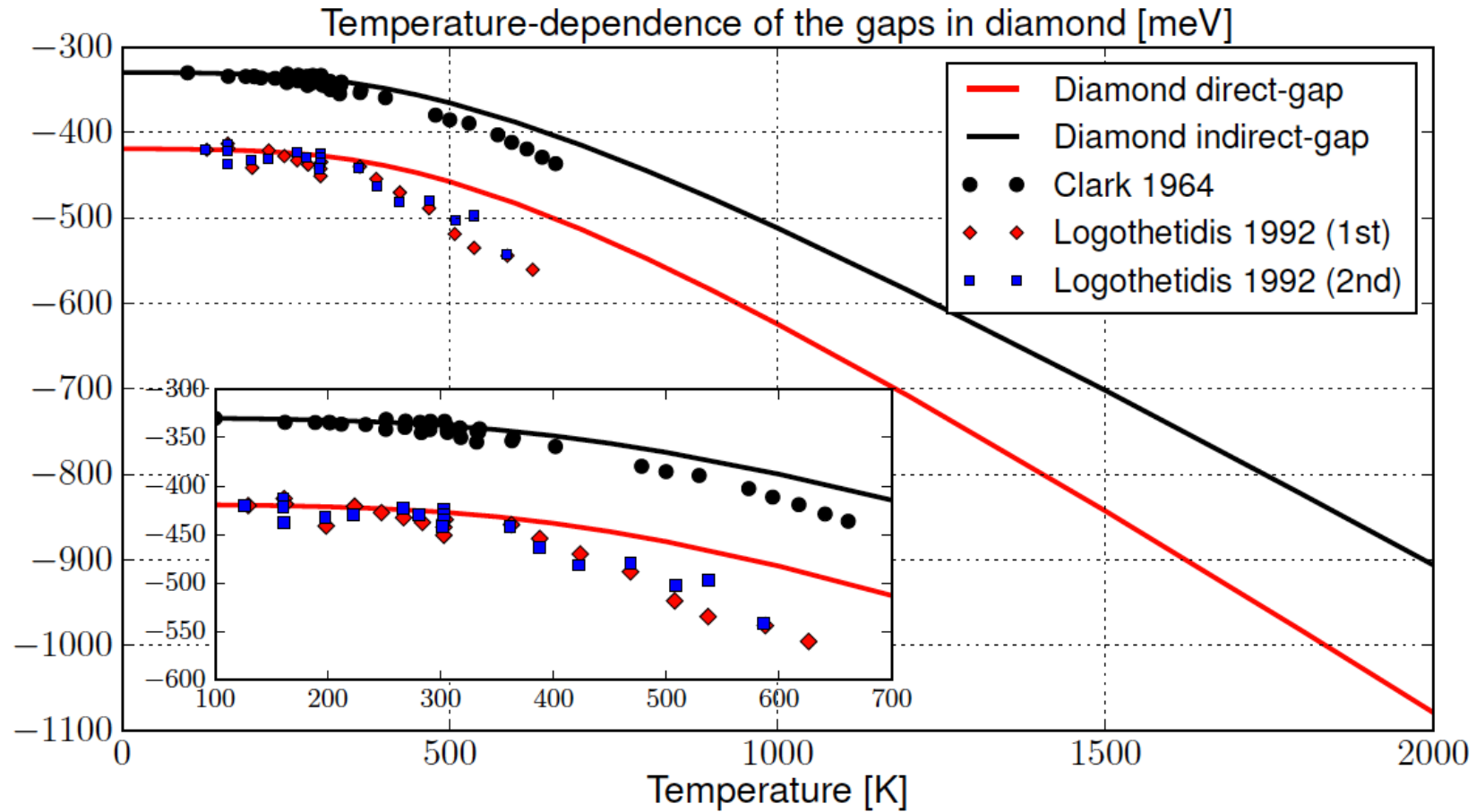
$$\frac{\partial \varepsilon_{\bar{k}n}}{\partial n_{\bar{q}j}} = \left(\frac{\partial \varepsilon_{\bar{k}n} (Fan)}{\partial n_{\bar{q}j}} \right) + \left(\frac{\partial \varepsilon_{\bar{k}n} (DW^{RIA})}{\partial n_{\bar{q}j}} \right)$$

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

$$\begin{aligned} \frac{\partial \varepsilon_{\bar{k}n} (DW^{RIA})}{\partial n_{\bar{q}j}} = & -\frac{1}{\omega_{\bar{q}j}} \Re \sum_{\kappa a \kappa' b n'} \frac{\langle \phi_{\bar{k}n} | \nabla_{\kappa a} H_{\kappa} | \phi_{\bar{k}n'} \rangle \langle \phi_{\bar{k}n'} | \nabla_{\kappa' b} H_{\kappa'} | \phi_{\bar{k}n} \rangle}{\varepsilon_{\bar{k}n} - \varepsilon_{\bar{k}n'}} \\ & \times \frac{1}{2} \left(\frac{\xi_{\kappa a}(\bar{q}j) \xi_{\kappa b}(-\bar{q}j)}{M_{\kappa}} + \frac{\xi_{\kappa' a}(\bar{q}j) \xi_{\kappa' b}(-\bar{q}j)}{M_{\kappa'}} \right) \end{aligned}$$

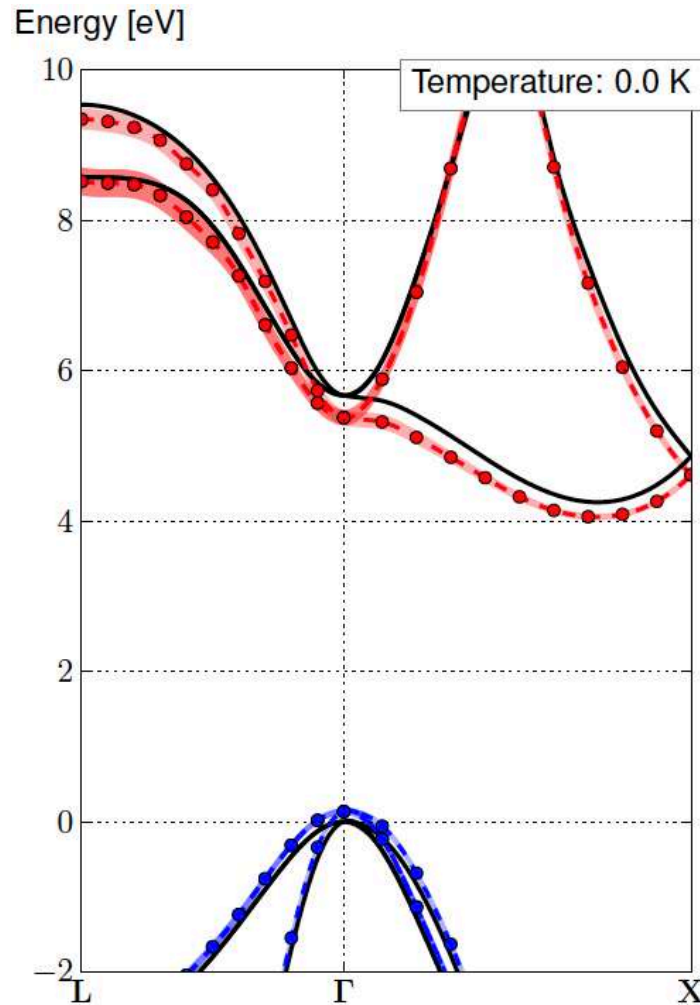
Good : only **first-order** electron-phonon matrix elements are needed (+ standard ingredients from first-principles phonon/band structure calculations) ; **no supercell calculations**

DFT T-dependent bandgaps : diamond



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

DFT T-dependent band structure

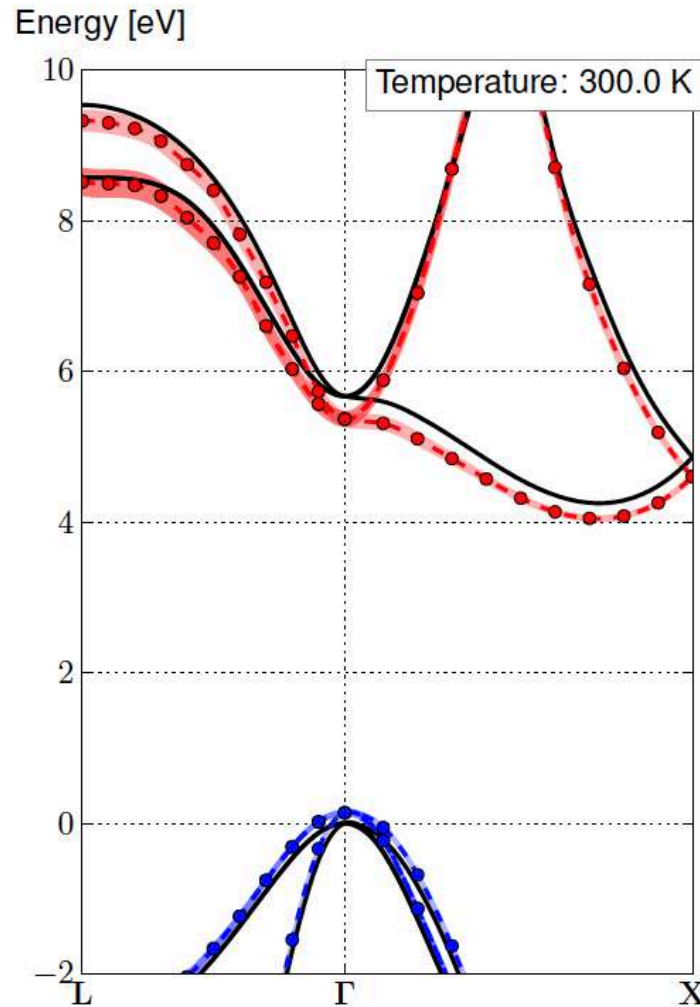


Diamond 0 Kelvin
(incl. Zero-point motion)

Note the widening of
the bands = lifetime

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

DFT T-dependent band structure

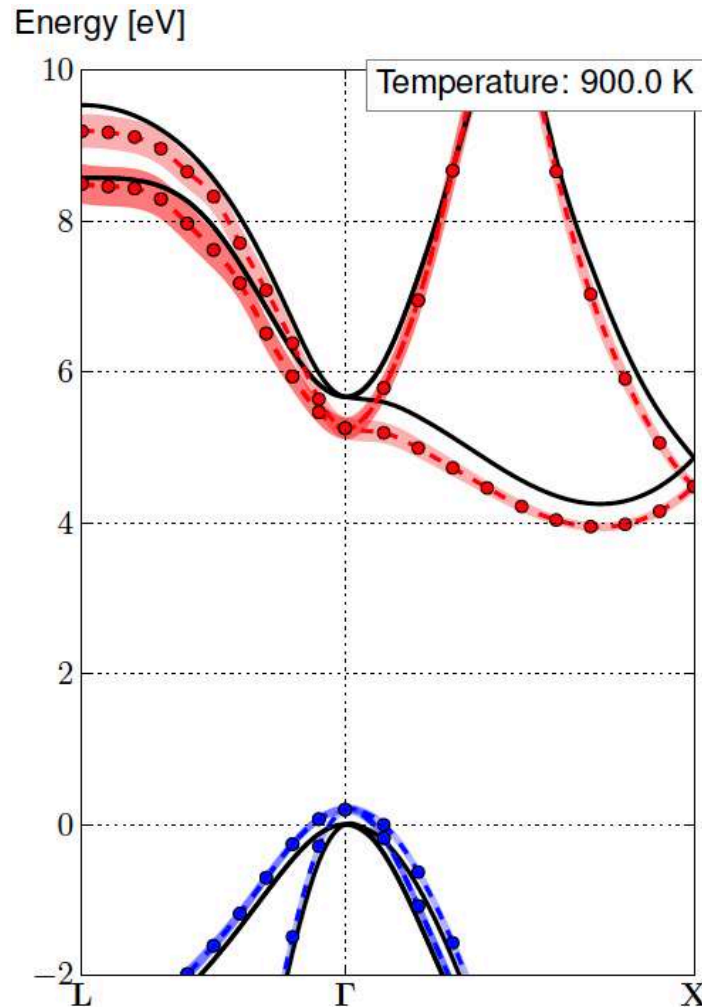


Diamond 300 Kelvin

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

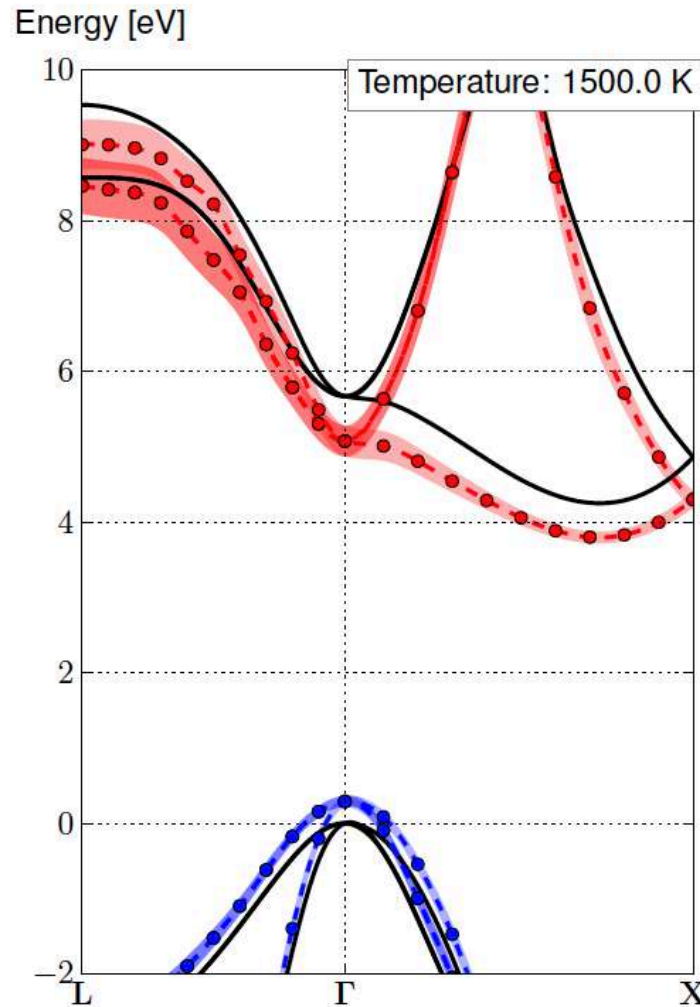


Diamond 900 Kelvin

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

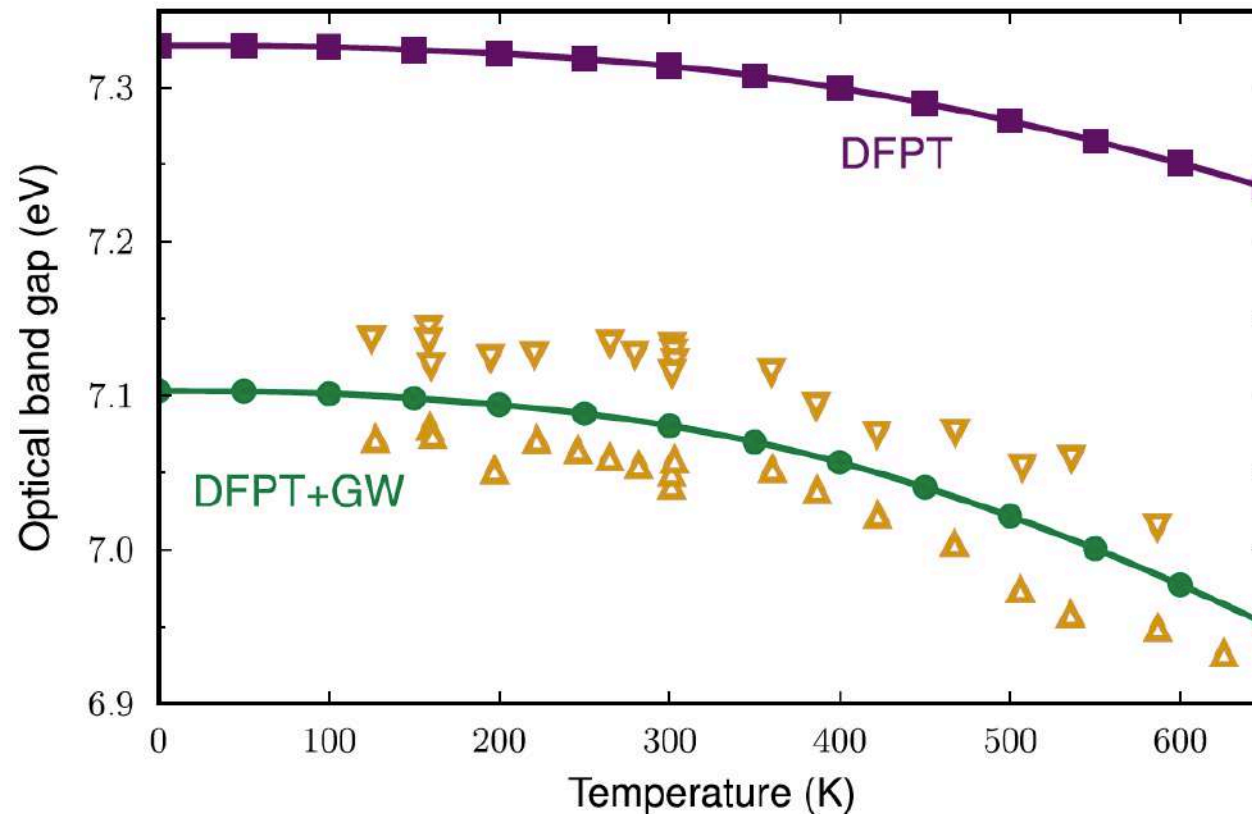


Diamond 1500 Kelvin

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)

DFT + perturbative phonons + GW + frozen-phonon in supercells

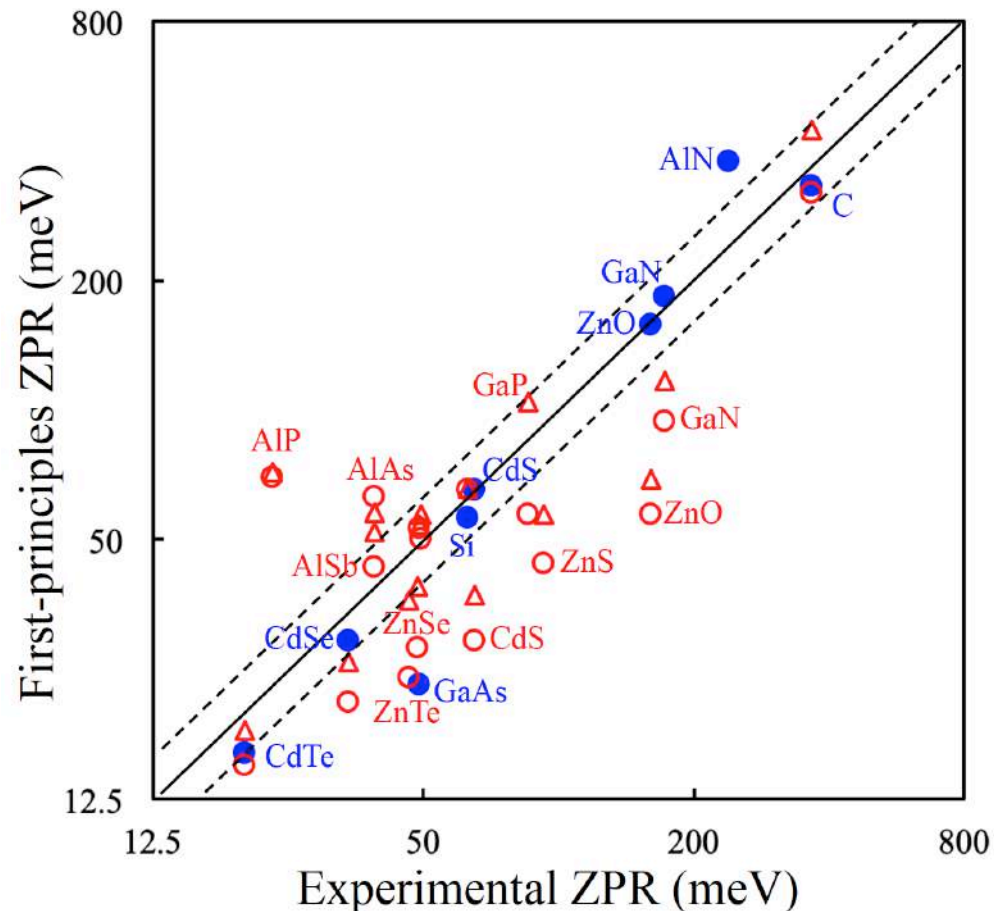


Zero-point motion
in DFT :
0.4 eV
for the direct gap

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)

ZPR for 28 materials: importance of non-adiabatic effects for IR active materials



In **red**: ZPR from adiabatic supercell calculations.

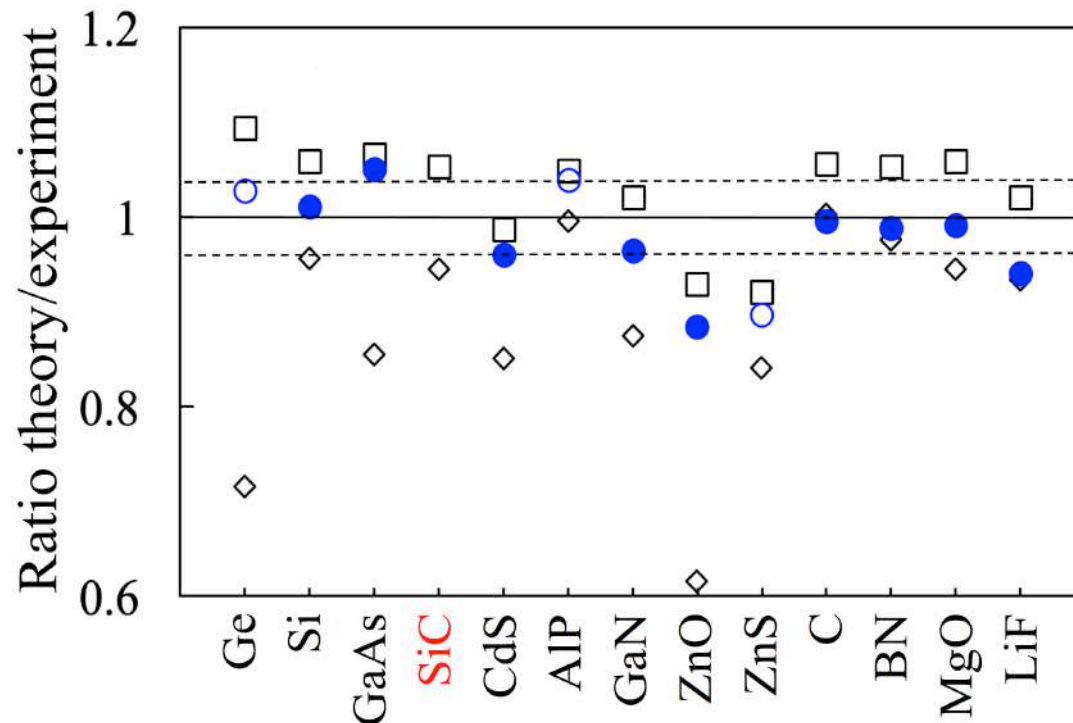
Wide spread of discrepancies

In **blue**: ZPR from non-adiabatic AHC calculations.

Much better agreement, within 20% except for two materials

A. Miglio, V. Brousseau, M. Côté, G. Antonius, Y.-H. Chan, M. Glantomassi & XG, in preparation

Band gap: comparison with experiment



Lozanges: G_0W_0
(non-self-consistent GW)
up to 40% underestimation

Squares: scGW eh
(self-consistent GW with
electron-hole interaction).
Slight overestimation,
except ZnS, ZnO, CdS.

In blue: scGW eh + ZPR
from non-adiabatic AHC
calculations or Exp.

Within 4% except for 3
materials

A. Miglio, V. Brousseau, M. Côté, G. Antonius, Y.-H. Chan, M. Glantomassi & XG, in preparation

Summary

- Phonon eigenmodes and frequencies: solutions of eigenproblem from dynamical matrices
- **Density-Functional Perturbation Theory** : ideal for accurate computation of dynamical matrices
- **Interatomic force constants** for polar insulators: long ranged due to dipole-dipole interaction
- Response to homogeneous electric field within DFPT => **dielectric tens., Born eff. charges, piezoelectricity.**
- Fourier interpolation + treatment of dipole-dipole interaction = effective interpolation of dynamical matrices => **phonon band structures.**
- Phonon band structures easily computed for insulators, metals, ...
- Third-order properties are also accessed : **electro-optic, Raman, ...**
- Thermodynamics (**specific heat, thermal expansion ...**)
- New functionals : OK for DFPT in weakly bonded systems
- Gap: temperature dependence, zero-point renormalization.

