

Density-functional Perturbation Theory: phonons, thermodynamic properties ...

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Properties of solids from DFT

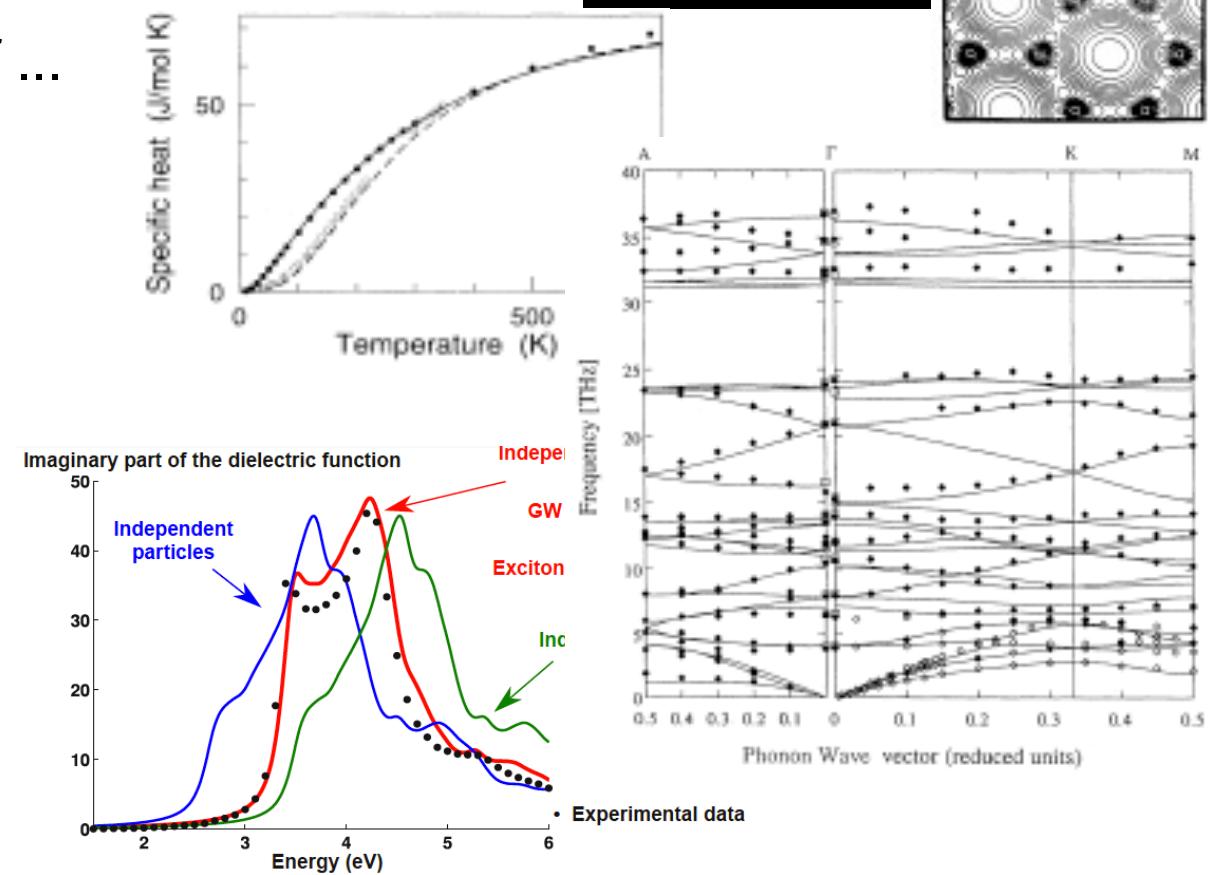
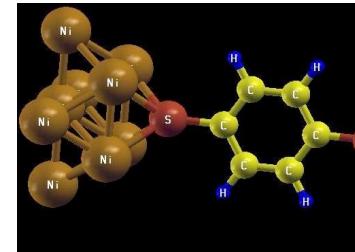
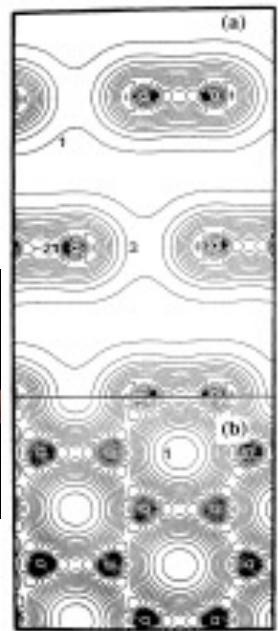
Computation of ...

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. Phonons : LDA ? GGA ? Weak bond systems ?

“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)

Kohn-Sham equation+self-consistency

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

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

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 **minimisation** of

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

Hartree energy

Exchange-
correlation
energy

under constraints of orthonormalization

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad \text{for occupied orbitals.}$$

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 »)

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

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

Generalized gradient approximations (GGA)

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

Here, GGA = « PBE »

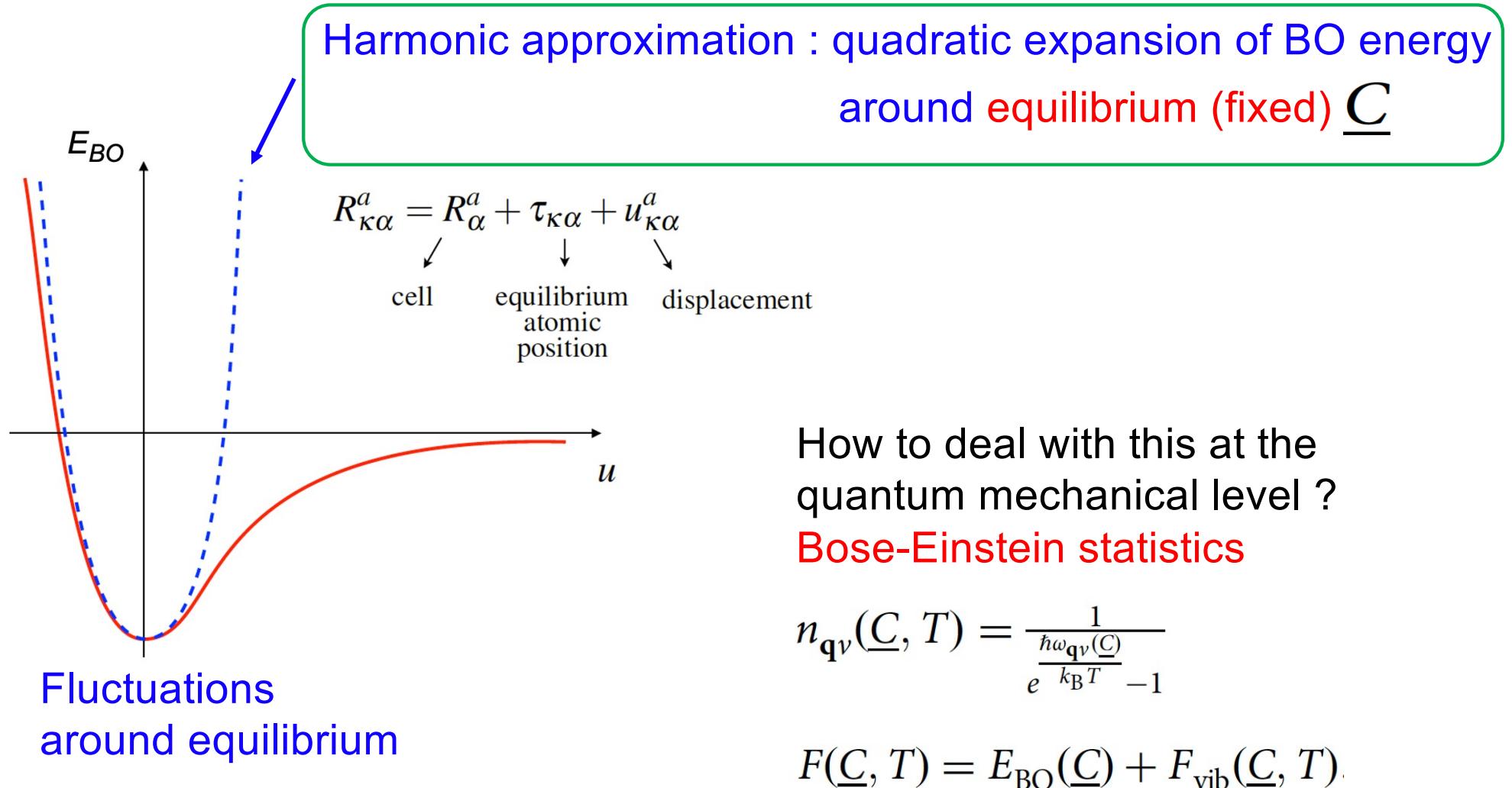
Perdew, Burke and Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)

Beyond GGA : hybrids, mGGA,
+ van der Waals xc functionals

Material properties from total energy derivatives : phonons

Changing atomic positions

Goal : include the phonons in the energy => free energy



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) :

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

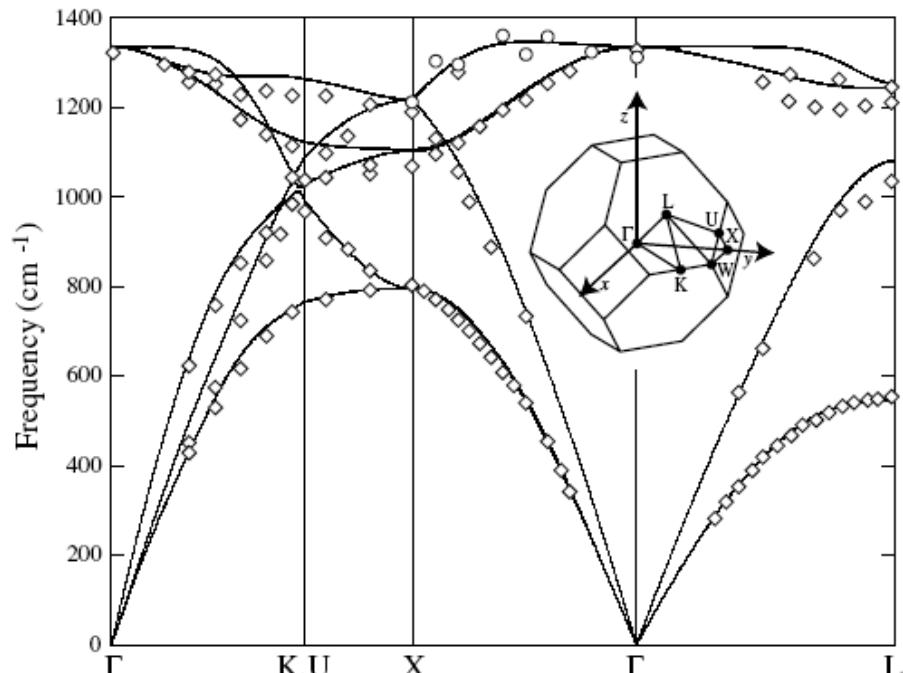
Computation of phonon frequencies and eigenvectors =
solution of generalized eigenvalue problem

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

↑
phonon displacement pattern ↑
 masses ↑
 square of
 phonon frequencies

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

Phonons : exp vs theory

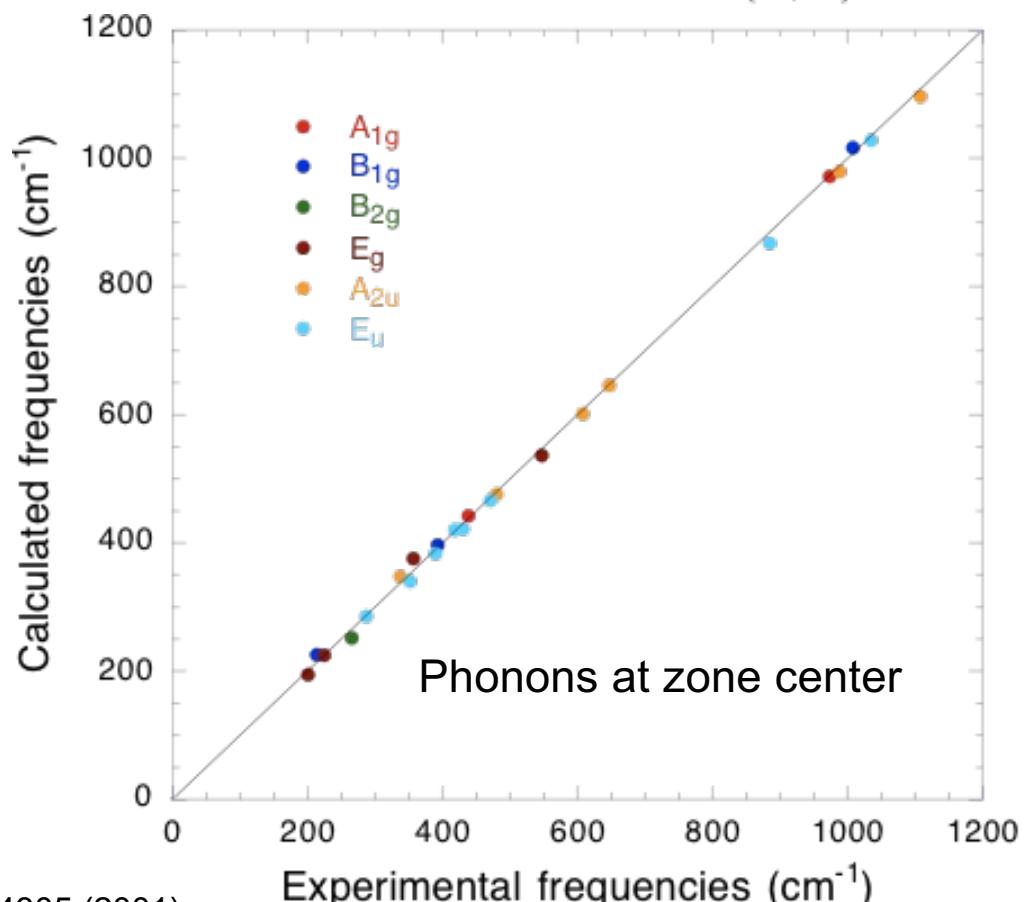


Diamond

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

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

Zircon



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, magnetic 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.

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

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

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 : $\frac{\partial E}{\partial \psi} = 0$

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

\Downarrow
 $0 \quad \psi^{(1)}$

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

General framework of perturbation theory

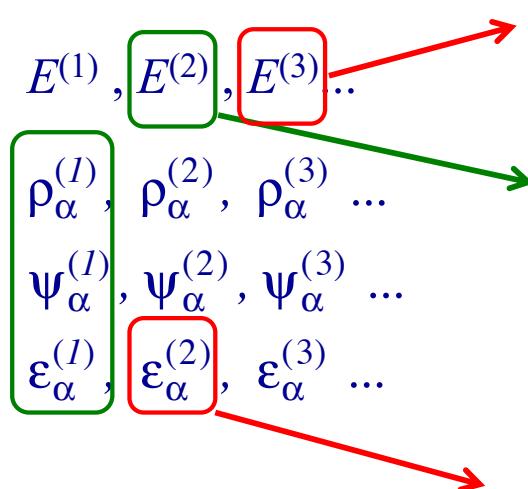
- * $A(\lambda) = A^{(0)} + \lambda A^{(1)} + \lambda^2 A^{(2)} + \lambda^3 A^{(3)} \dots$

- * $E\{\Psi; V_{ext}\}$

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 :



3rd order derivatives of BO energy :
many non-linear effects

2nd order derivatives of BO energy :
dynamical matrix, dielectric susceptibility,
elastic constants, ...

needed for
T-dependence of
electronic structure

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 Schrödinger equation

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

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

Expand 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 Schrödinger equation

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

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

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

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

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

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

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 : $\varepsilon_n^{(1)}$

Start from first-order Schrödinger equation

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

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

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

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

$\varepsilon_n^{(1)}$ 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 $\varepsilon_{\alpha}^{(2)}$

Start from second-order Schrödinger equation

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

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

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

Both can be combined :

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

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 :

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

known known

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

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

Equivalence with matrix equation (system of linear equations)

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

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

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

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

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 :

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

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

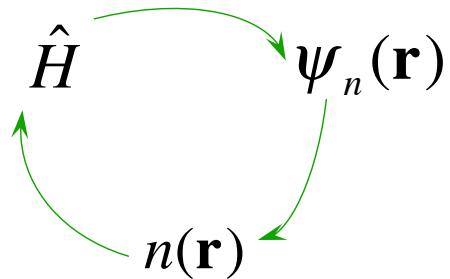
Equivalence of : * Minimization of $\varepsilon_n^{(2)}$
* Sternheimer equation
* also ... sum over states ... Green's function ...

Generalisation: Density-functional perturbation theory (DFPT)

Basic equations in DFT

Solve self-consistently Kohn-Sham equation

$$\left\{ \begin{array}{l} \hat{H} |\Psi_n\rangle = \varepsilon_n |\Psi_n\rangle \\ \hat{H} = \hat{T} + \hat{V} + V_{Hxc}[n] \\ n(\vec{r}) = \sum_n^{occ} \Psi_n^*(\vec{r}) \Psi_n(\vec{r}) \end{array} \right.$$



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

or minimize

$$E_{el}\{\Psi\} = \sum_n^{occ} \langle \Psi_n | \hat{T} + \hat{V} | \Psi_n \rangle + E_{Hxc}[n]$$

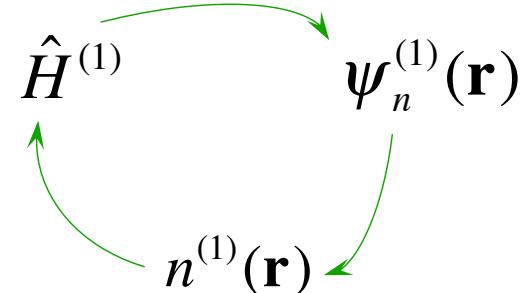
What is \hat{V} ?

$$\hat{V}(\vec{r}) = \sum_{ak} -\frac{Z_k}{|\vec{r} - \vec{R}_k^a|}$$

Basic equations in DFPT

Solve self-consistently Sternheimer equation

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



or minimize

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

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

The potential and its 1st derivative

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

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

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

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 : $V^{(I)}(\vec{r} + \vec{R}_a) = e^{i\vec{q}\cdot\vec{R}_a} V^{(I)}(\vec{r})$

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

$$n^{(I)}(\vec{r} + \vec{R}_a) = e^{i\vec{q}\cdot\vec{R}_a} n^{(I)}(\vec{r}) \quad \psi_{m,\vec{k},\vec{q}}^{(I)}(\vec{r} + \vec{R}_a) = e^{i(\vec{k} + \vec{q})\cdot\vec{R}_a} \psi_{m,\vec{k},\vec{q}}^{(I)}(\vec{r})$$

Now, define related periodic quantities

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

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 $\Psi_\alpha^{(0)}, \Psi_\alpha^{j_1}, \Psi_\alpha^{j_2}$?

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

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

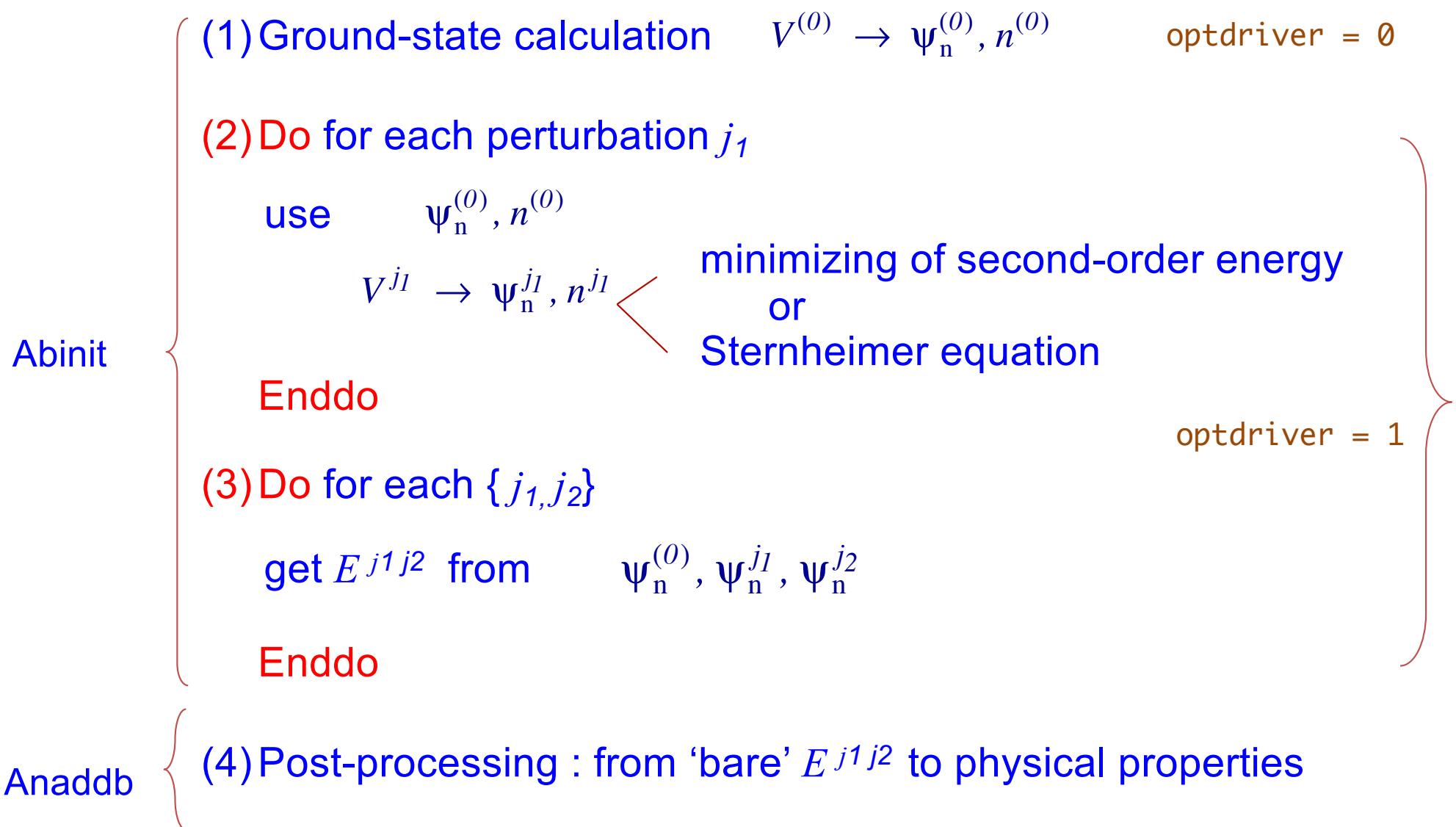
with $\tilde{E}_{el}^{j_1 j_2} \left\{ \Psi^{j_1}, \Psi^{j_2}; \Psi^{(0)} \right\} = \sum_n^{occ} \left\langle \Psi_n^{j_1} \left| \hat{H}^{(0)} - \epsilon_n^{(0)} \right| \Psi_n^{j_2} \right\rangle + \left\langle \Psi_n^{j_1} \left| \hat{V}^{j_2} \right| \Psi_n^{(0)} \right\rangle \\ + \left\langle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

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



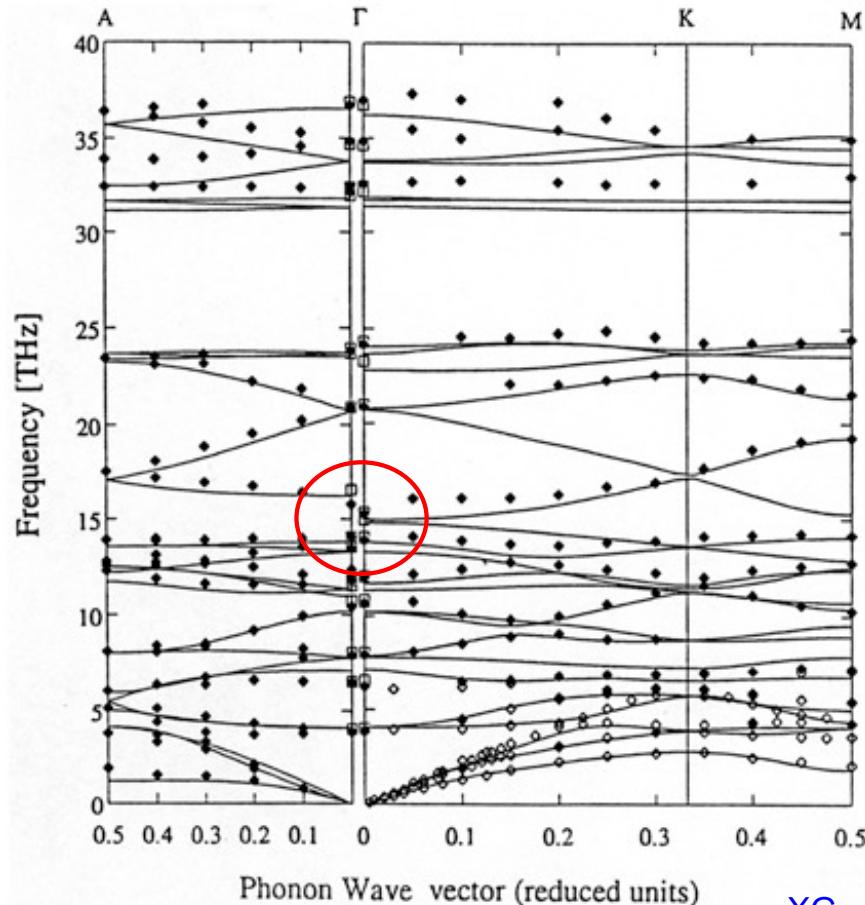
Phonon band structures from DFPT

Phonon band structure

From DFPT : straightforward, although lengthy (self-consistent calculation)

to compute $\tilde{C}_{k\alpha,k'\beta}(\vec{q})$ for one wavevector :

Full phonon band structure needs values for many wavevectors ...

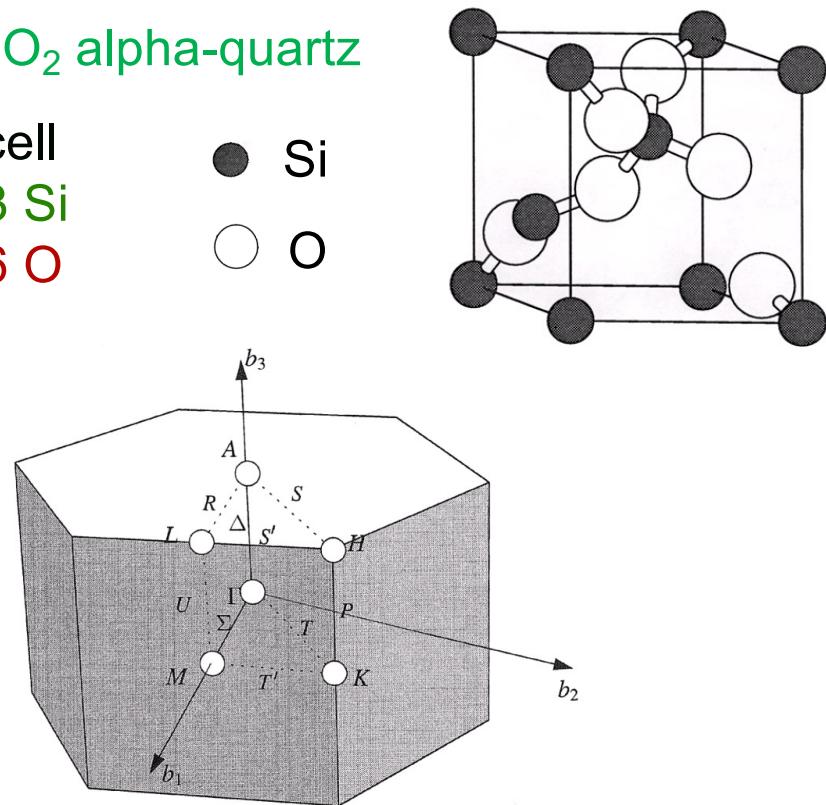


SiO_2 alpha-quartz

cell

3 Si

6 O



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.

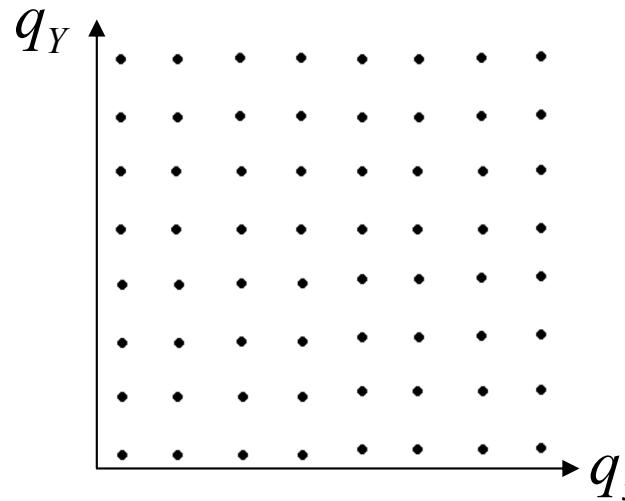
Numerical Fourier Interpolation

Key of the interpolation : replace the integral

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

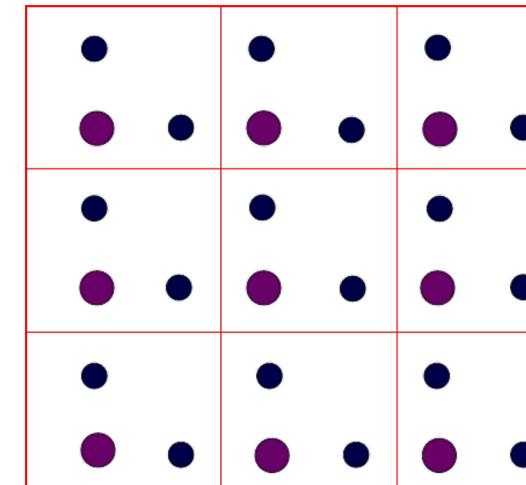
by summation on a few wavevectors (=“q-points”).

Grid of (l,m,n) points in q space

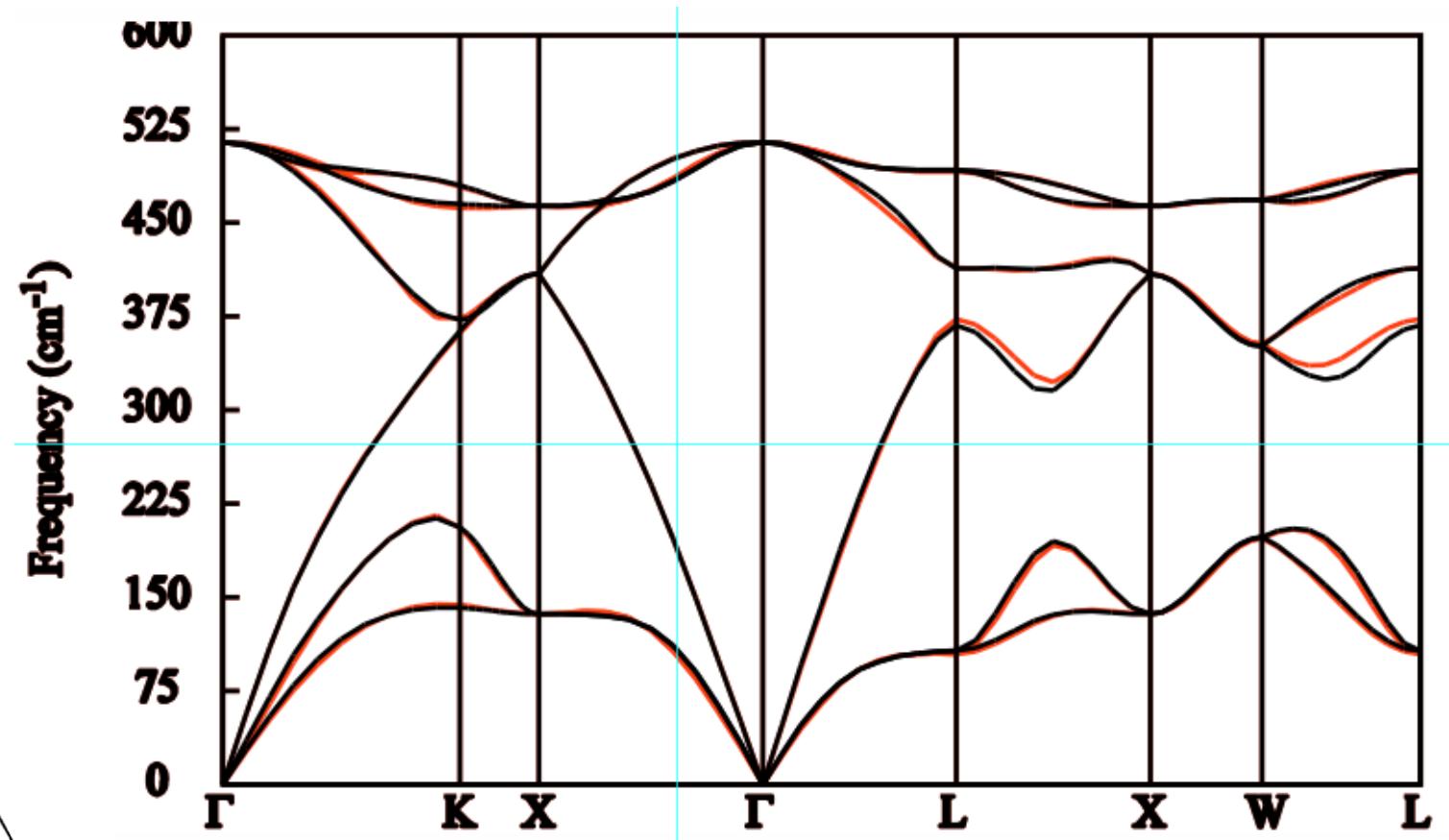
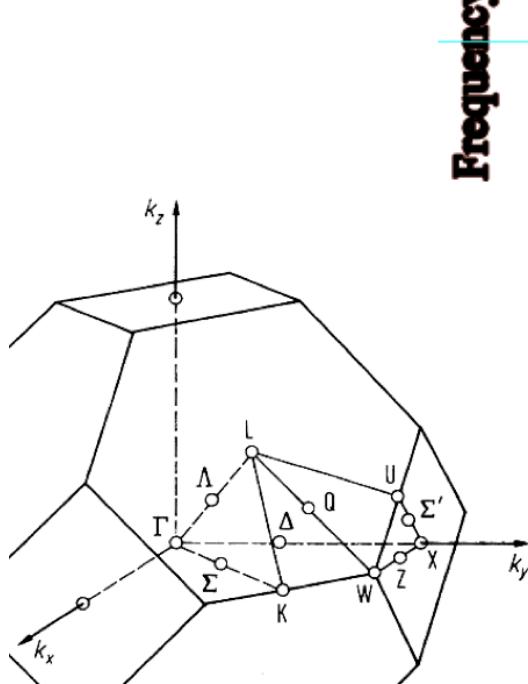


IFCs in box of (l,m,n) periodic cells

Fourier



Fourier interpolation : Silicon



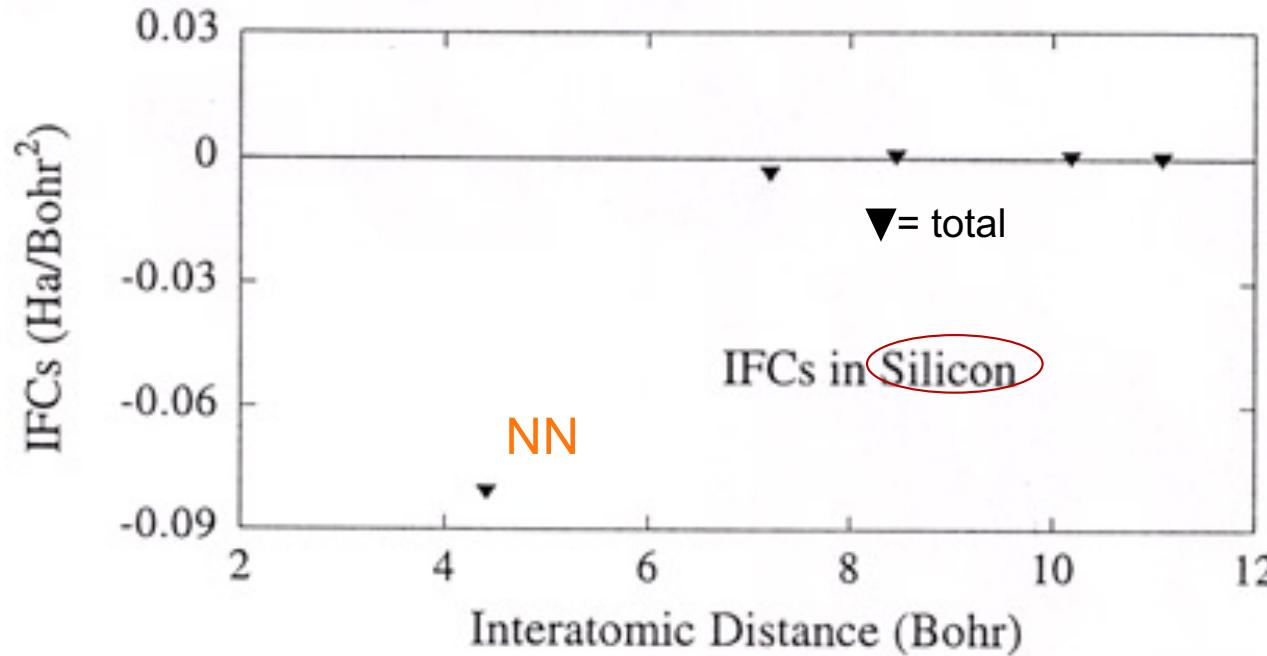
- Real space IFCs calculated from 10 q-points
- Real space IFCs calculated from 18 q-points

Then, dynamical matrices from IFCs, and diagonalization

Interatomic force constants for silicon

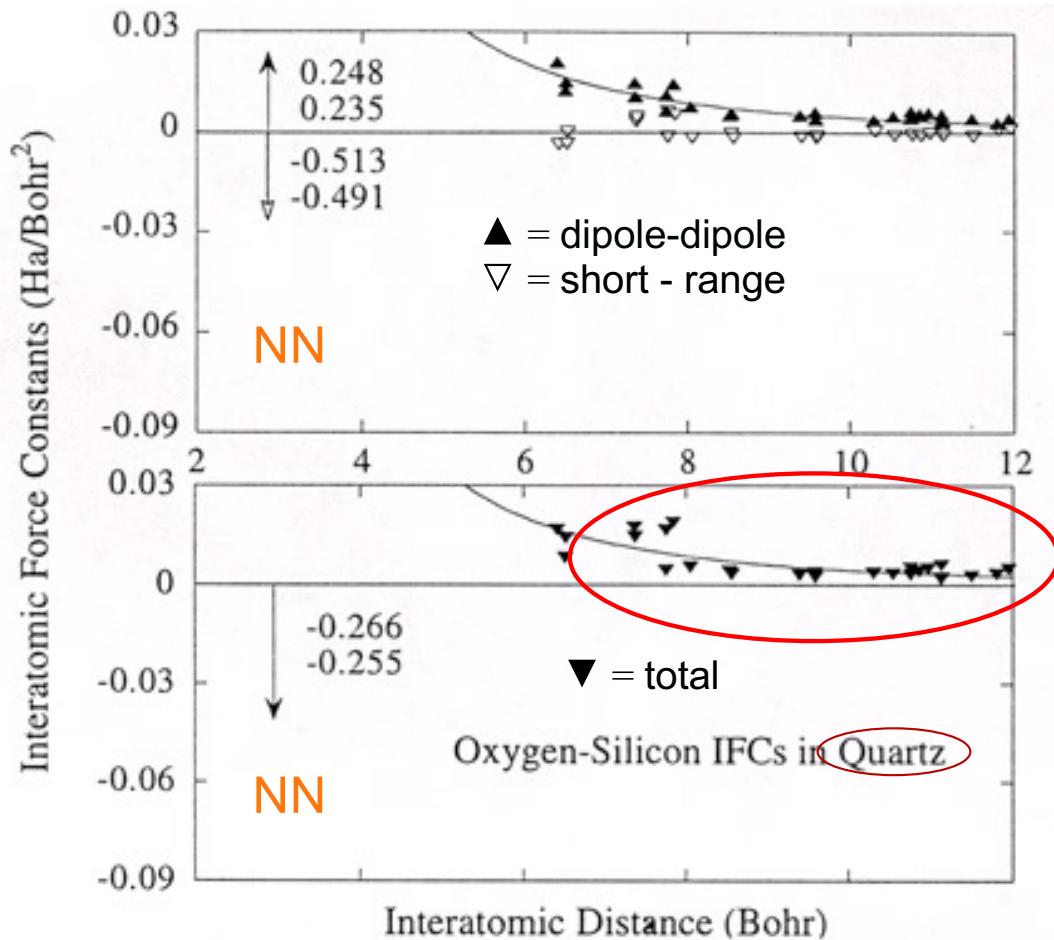
For Si, IFCs are short ranged, i.e. falling to zero quickly after the nearest-neighbors (NN).

Plot of longitudinal IFCs between nuclei pairs

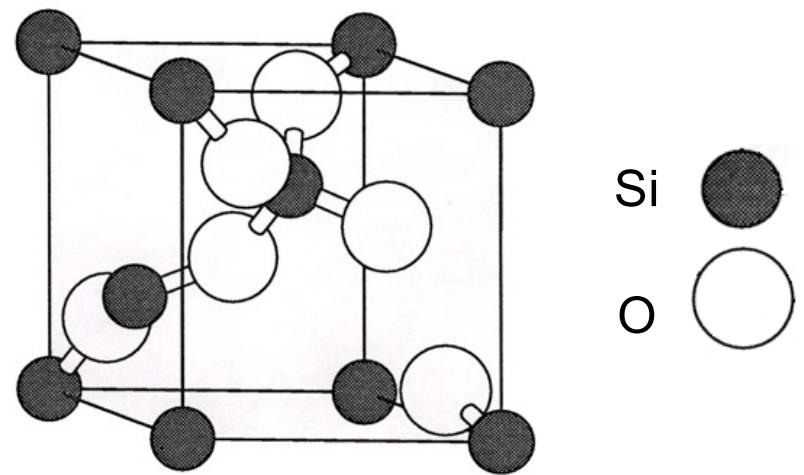


XG, *Adv. in Quantum Chemistry* 33, 225 (1999)

Interatomic force constants for silica quartz



SiO_2 Quartz
3 Si
6 O



Long-ranged
interatomic forces !

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

Understanding the long-range behaviour

When an 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 IFCs.

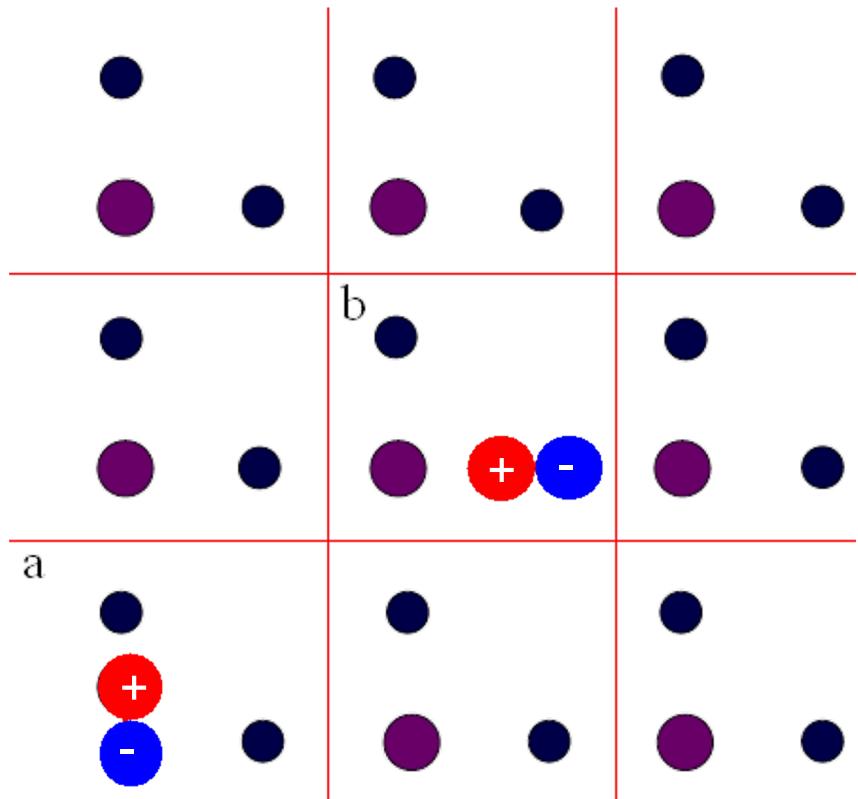
Suppose : homogeneous material with isotropic dielectric tensor $\epsilon \delta_{\alpha\beta}$, ions with charges Z_k and $Z_{k'}$, then

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

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

Long range decay
of the IFCs : $1/d^3$

Effect in reciprocal space ?



Effect of the long-range interaction

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

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

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

Born effective charge tensor for atom κ

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

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

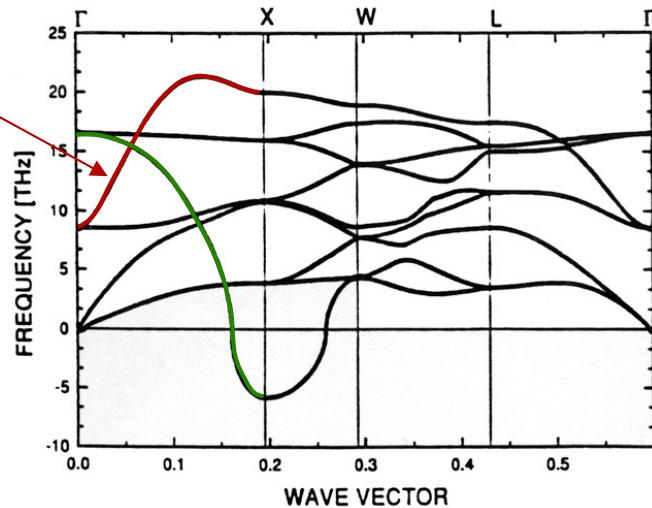
electronic dielectric tensor

(Electronic contribution to the screening of the charges)

Both linked to a second derivative of total energy: DFPT !

Phonon dispersion curves of ZrO_2

Wrong behaviour



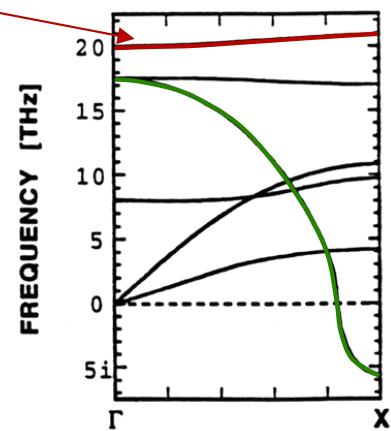
ZrO_2 in the cubic structure at the equilibrium
lattice constant $a_0 = 5.13 \text{ \AA}$.

High - temperature : Fluorite structure
($Fm\bar{3}m$, 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))

Correct behaviour



DFPT (Linear-response)
with $Z_{\text{Zr}}^* = 5.75$
 $Z_0^* = -2.86$
 $\epsilon_\infty = 5.75$

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

MgSiO₃

CUBIC

(5at/cell)

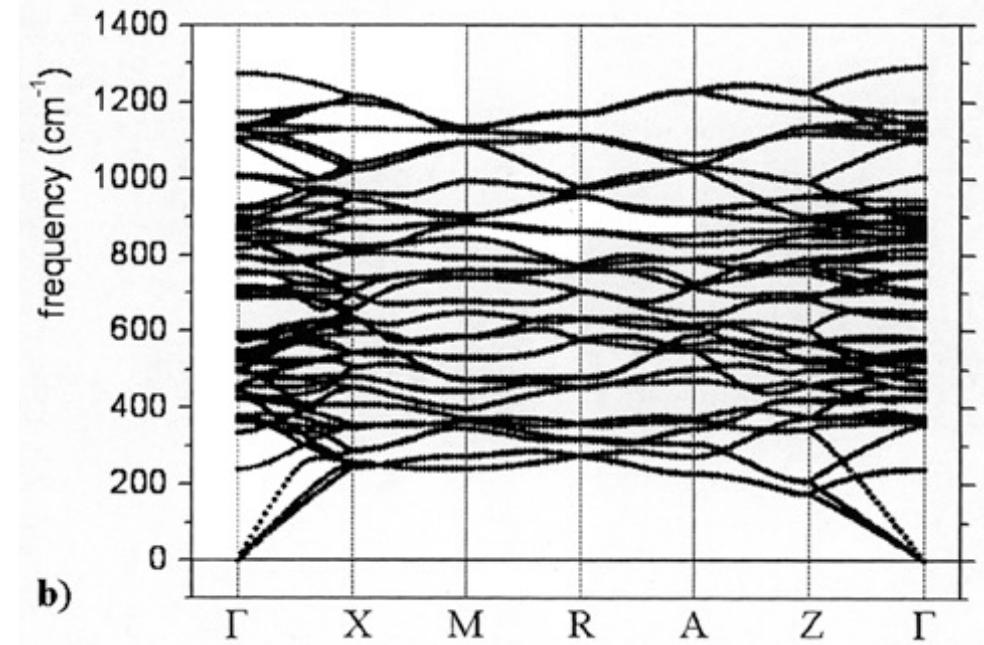
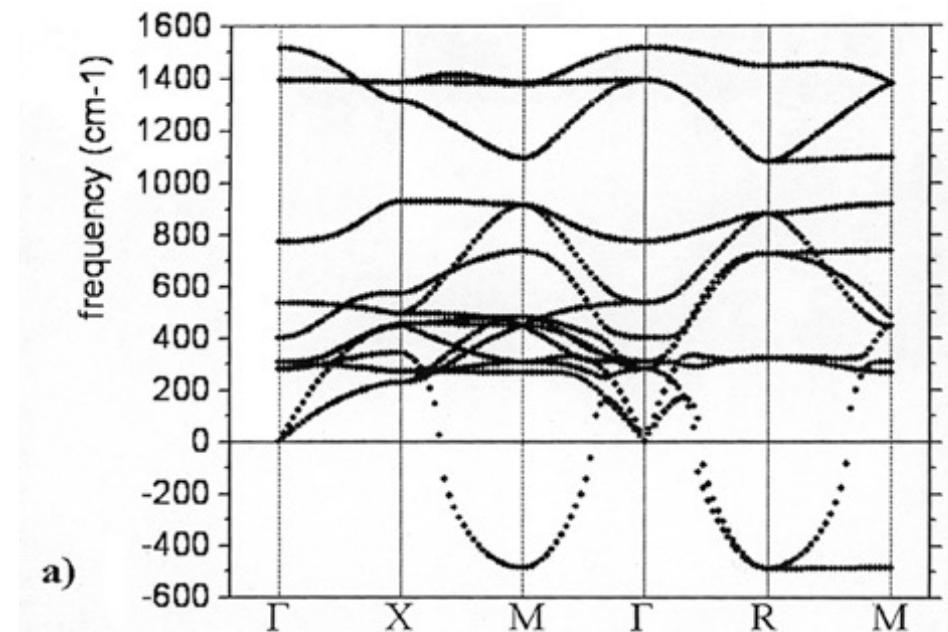
Phonon dispersion relations.

(a) Ideal cubic phase : unstable.

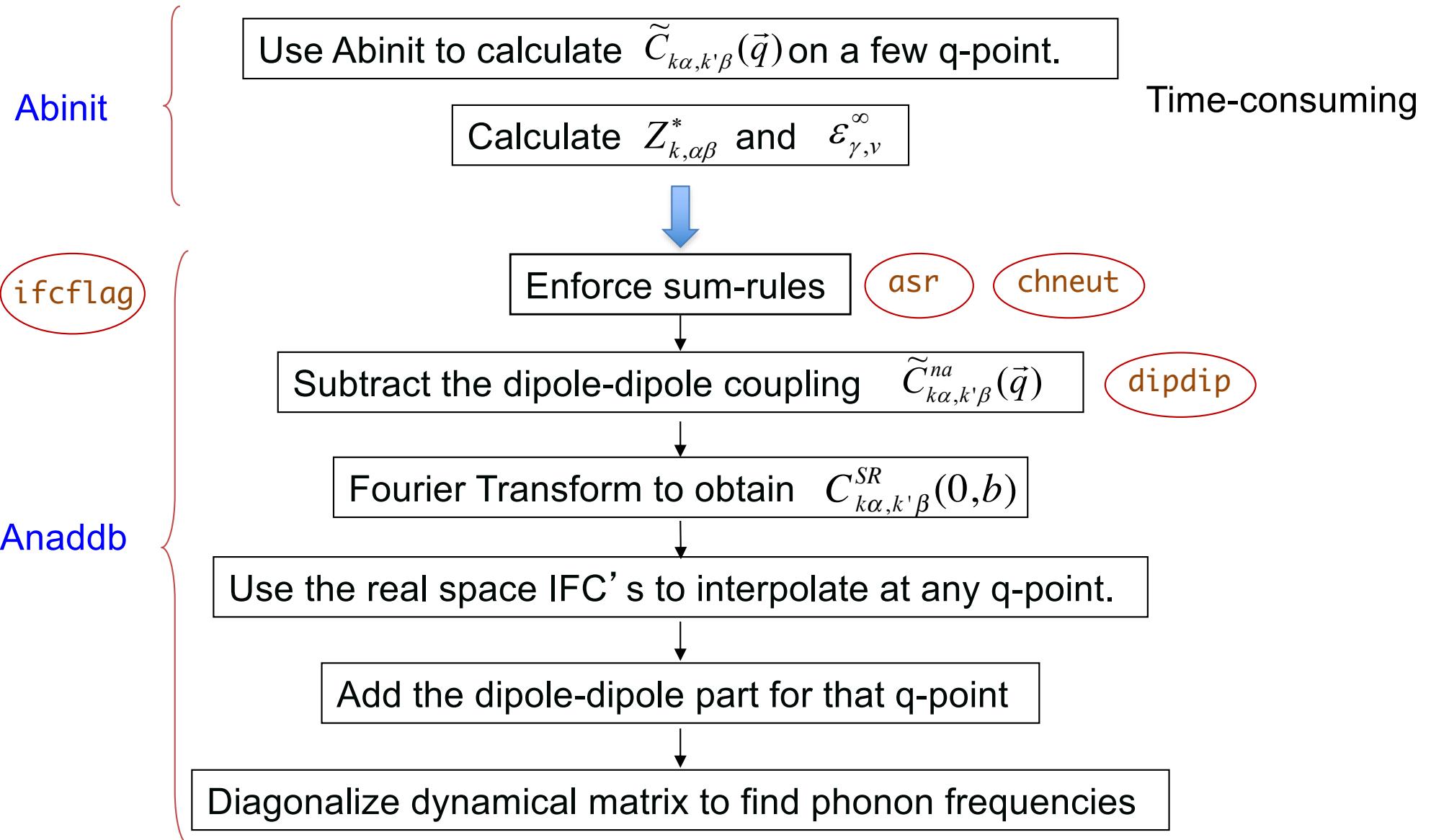
(b) Condensations of the unstable phonon modes generate a (meta) stable orthorhombic phase

ORTHORHOMBIC

(20at/cell)



Interpolation Scheme



Dielectric properties from DFPT

Treatment of homogeneous electric field

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

One needs, for DFPT - linear response :

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

↑ conduction state ↑ valence state ↑ projection on conduction states

periodic part
of Bloch wf

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

+ derivative with respect to k obtained within DFPT

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

Dielectric tensor : electronic part

$$\varepsilon_{\gamma\nu}^{\infty} = \delta_{\gamma\nu} + 4\pi \frac{\partial P_{\gamma}}{\partial \mathcal{E}_{\nu}}$$

electronic dielectric tensor

(Proportionality coefficient between polarisation and electric field)

Linked to a second derivative of total energy

$$P_{\gamma} = -\frac{1}{V} \frac{\partial E}{\partial \mathcal{E}_{\gamma}}$$

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

Born effective charges

$$Z_{\kappa,\alpha\beta}^* = -\frac{\Omega_0}{V} \frac{\partial^2 E}{\partial \mathcal{E}_\alpha \partial u_{\kappa,\beta}}$$

Born effective charge tensor for atom κ

A mixed second derivative of total energy

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

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

Electric field - atomic displacement coupling

Frequency - dependent dielectric tensor in the IR range

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

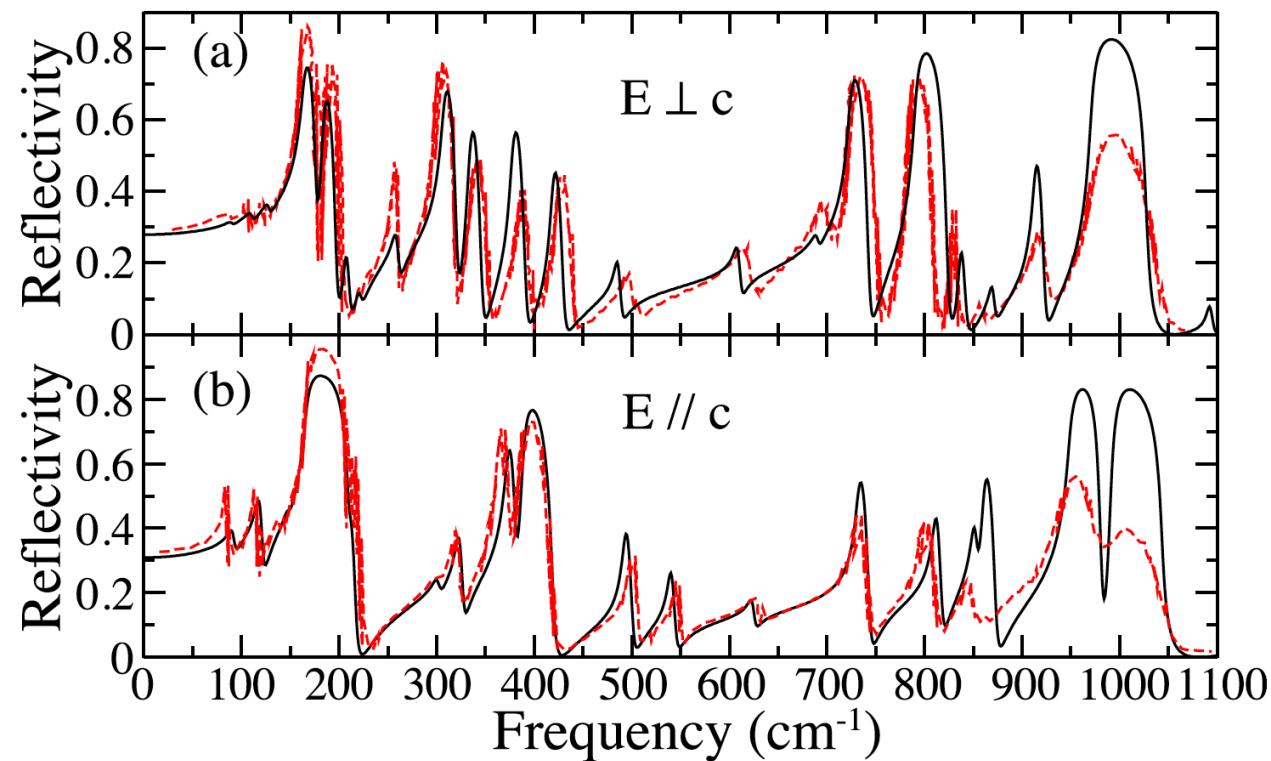
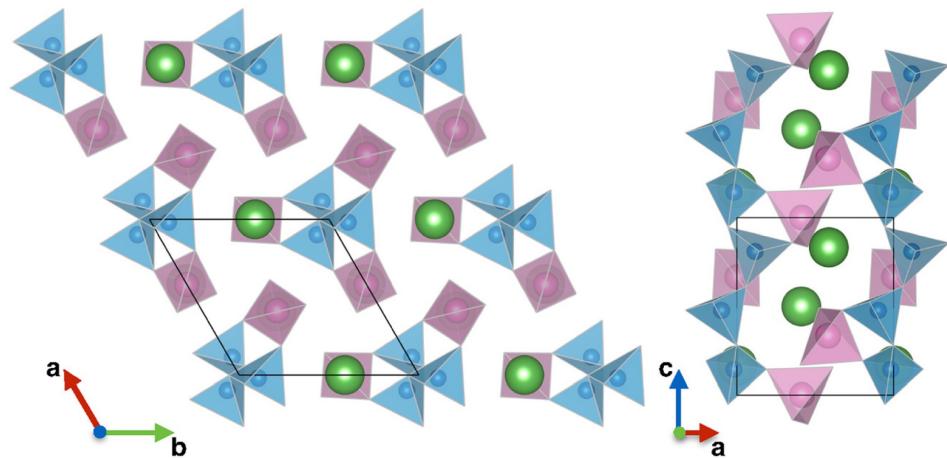
Infrared (IR) reflectivity

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

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

Infrared reflectivity of LaBGeO₅

R. Shaltaf, H.K. Juwhari, B. Hamad, J. Khalifeh,
G.-M. Rignanese, and X. Gonze,
J. of Applied Physics 115, 074103 (2014)



Thermodynamic properties from DFPT

Statistical physics : phonons = bosons

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

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

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.

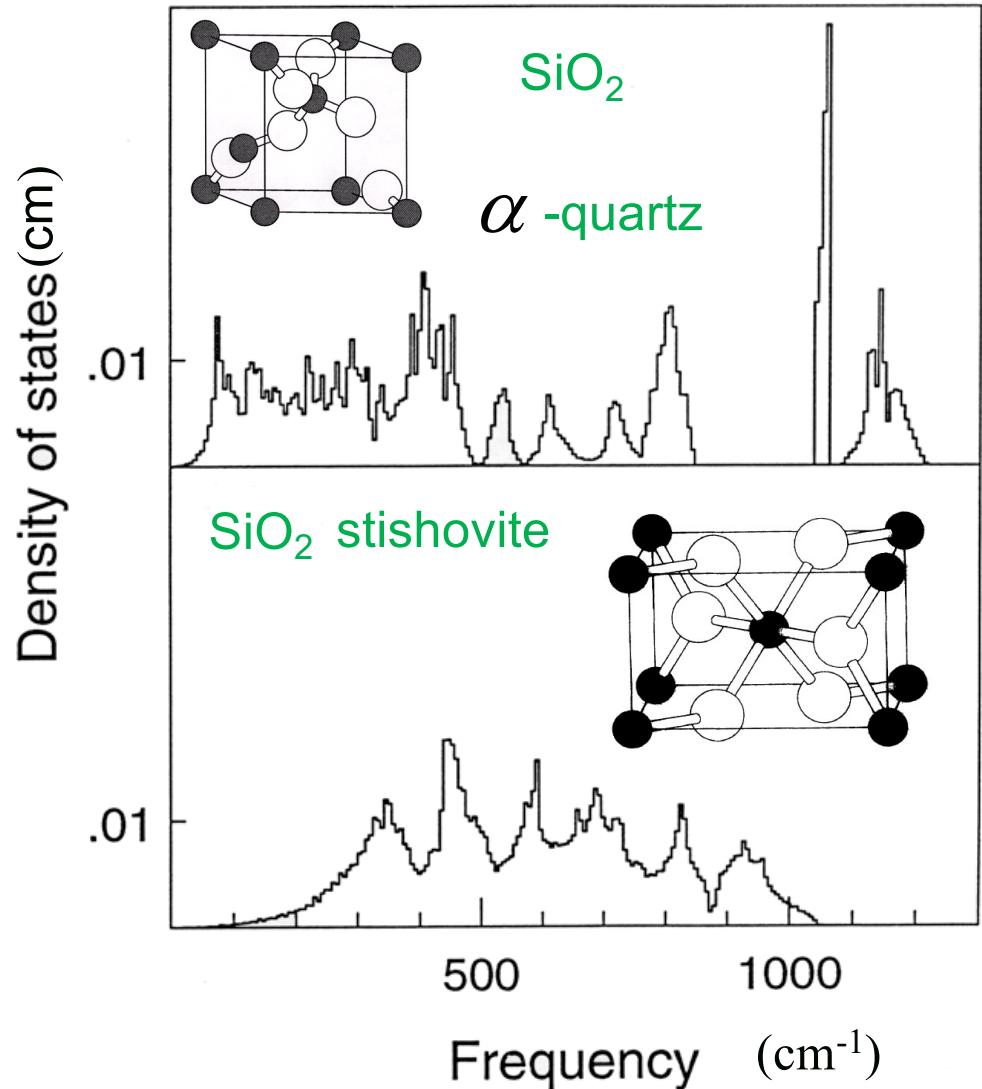
Phonon density of states

● Si
○ O

For each frequency channel,
counts 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)



Helmholtz free energy and specific heat

$$F = U - TS$$

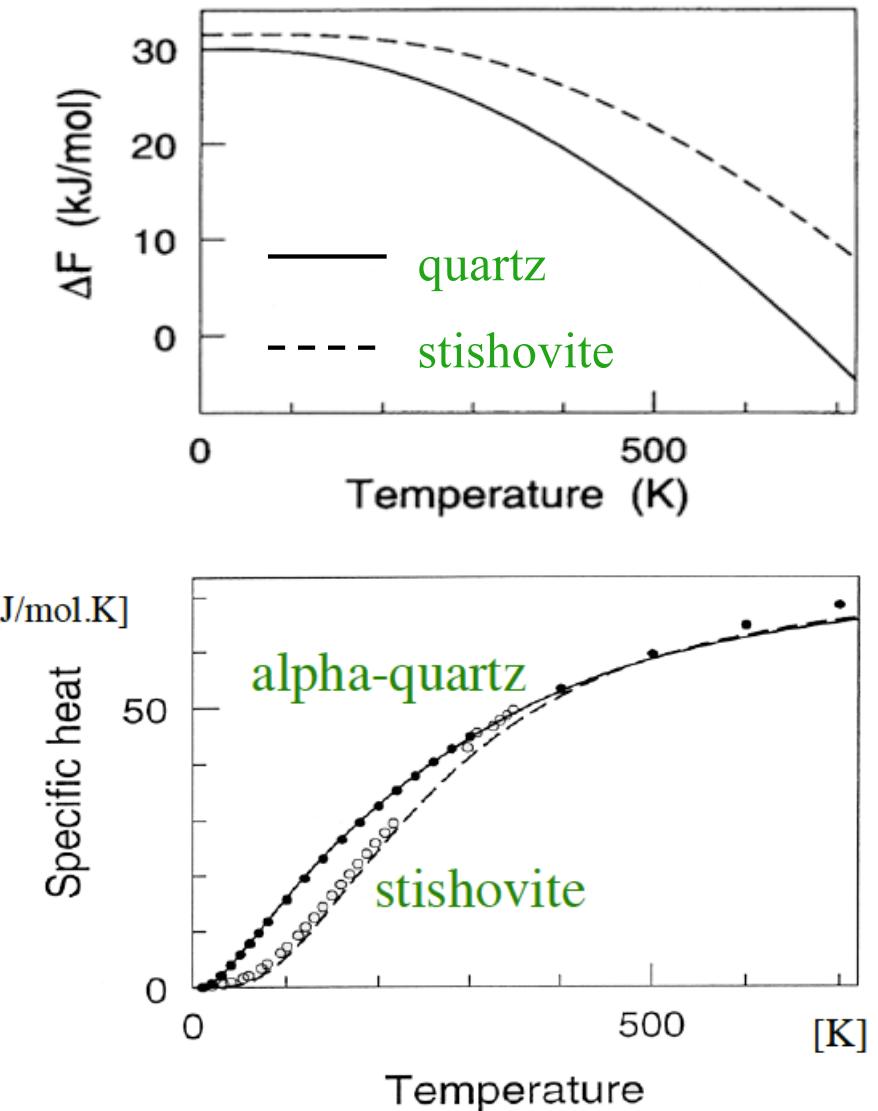
$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V$$

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 C_V :

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



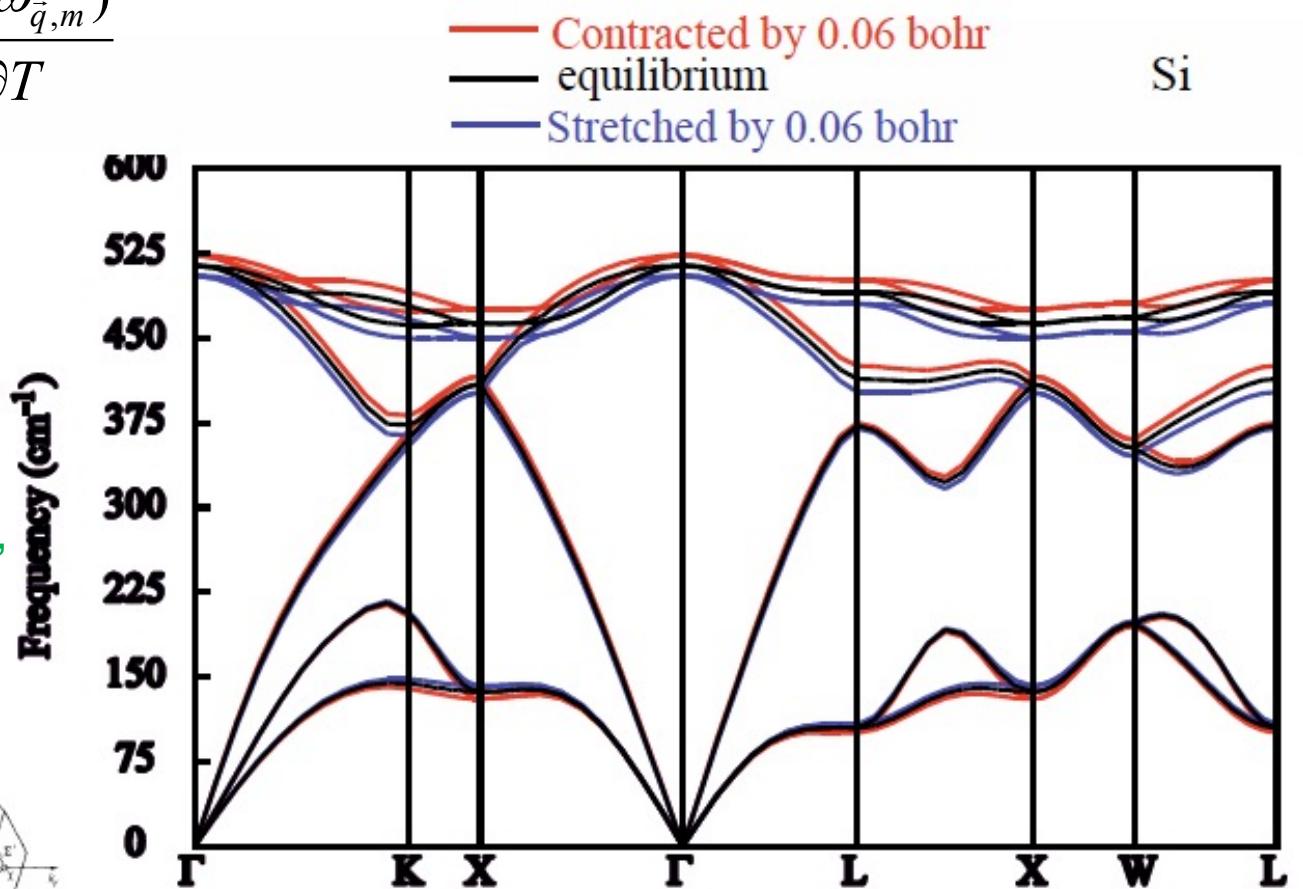
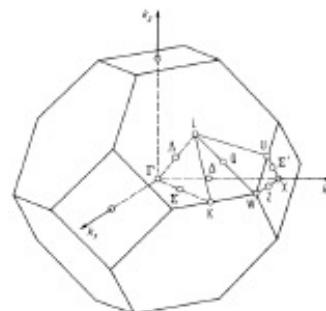
Ab initio thermal expansion

Grüneisen approach :

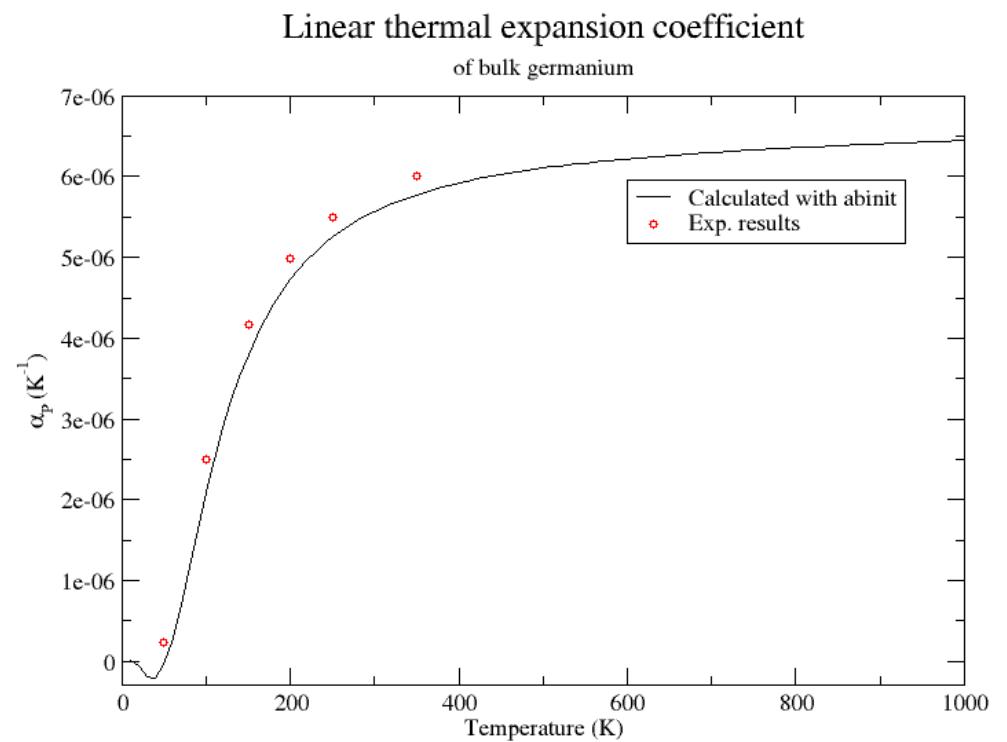
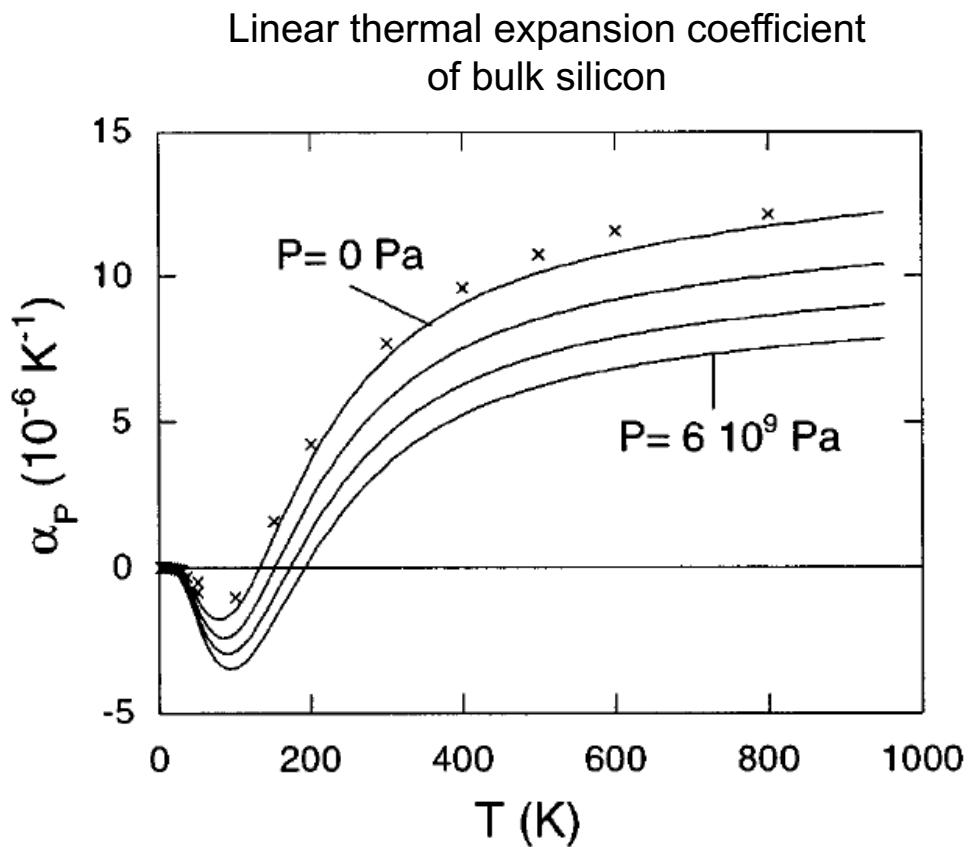
$$\gamma_{m,\vec{q}} = -\frac{\partial(\ln \omega_{m,\vec{q}})}{\partial(\ln V)}$$

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

More accurate approach :
minimisation of free energy
“quasi-harmonic approximation”



Ab initio thermal expansion



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

Phonons : LDA ? GGA ?

Weak bond systems ?

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 :

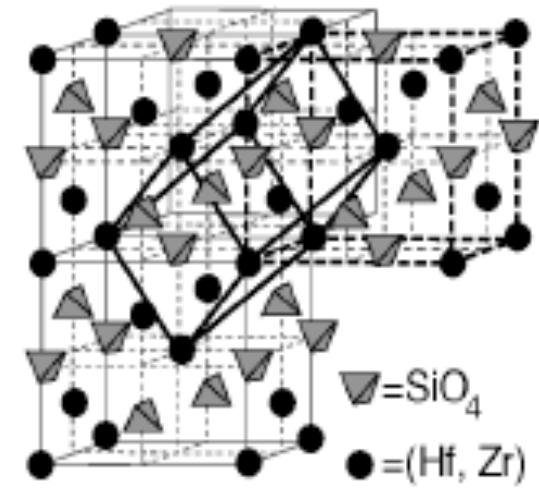
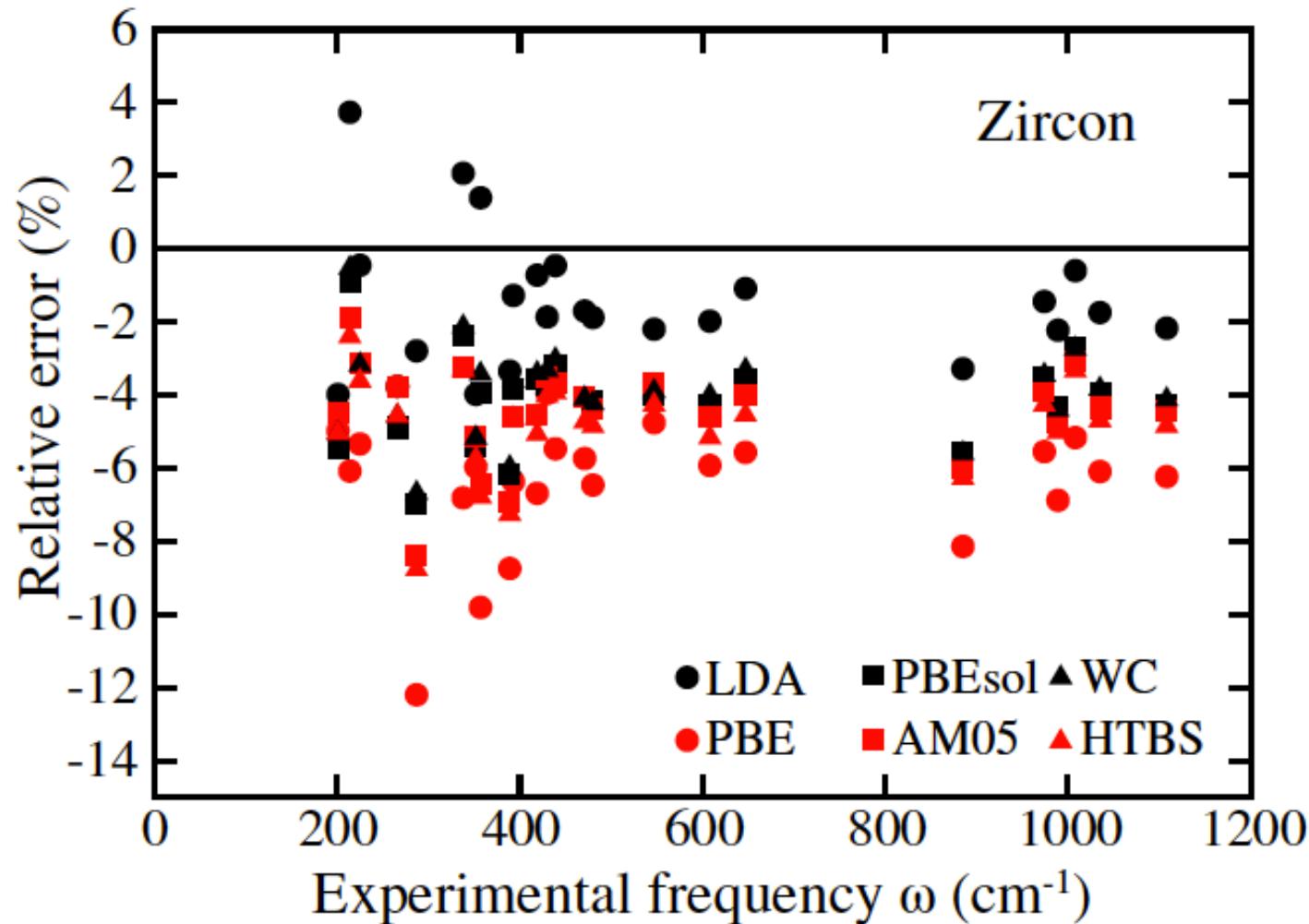
L. He et al, Phys. Rev. B89, 064305 (2014)

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 than GGA ... Compensation of errors !

Gamma phonons of zircon

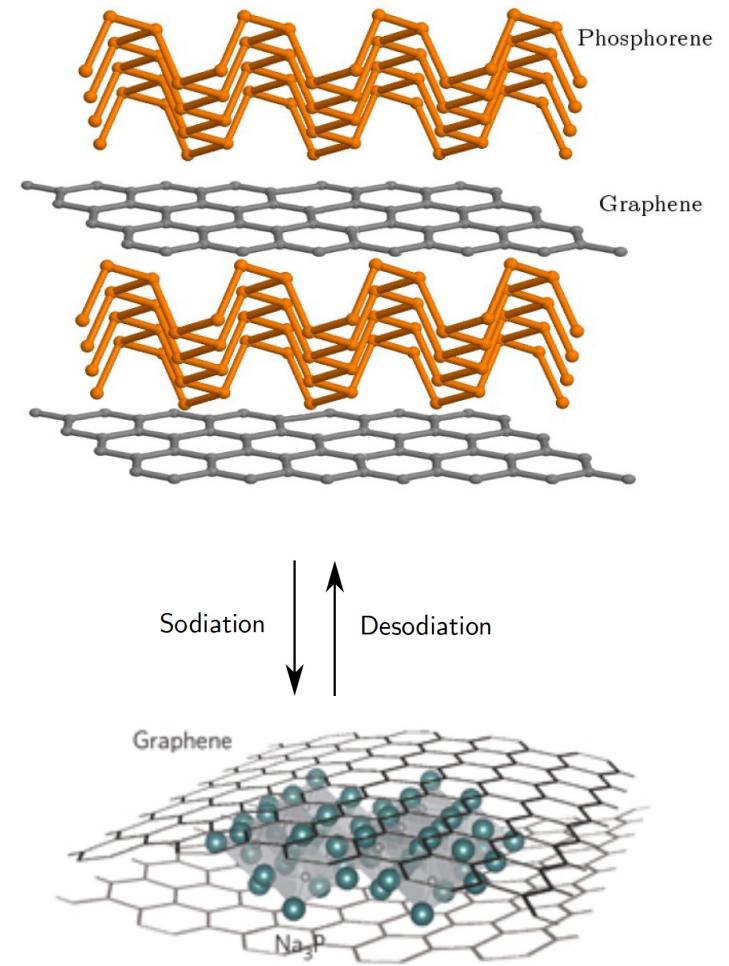
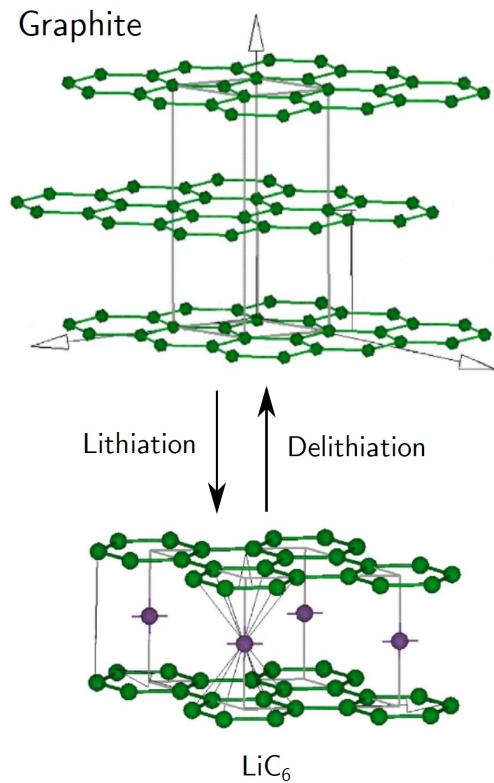


L. He et al, Phys. Rev. B89, 064305 (2014)

Layered materials

For the last 15 years : 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 ...

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

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

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

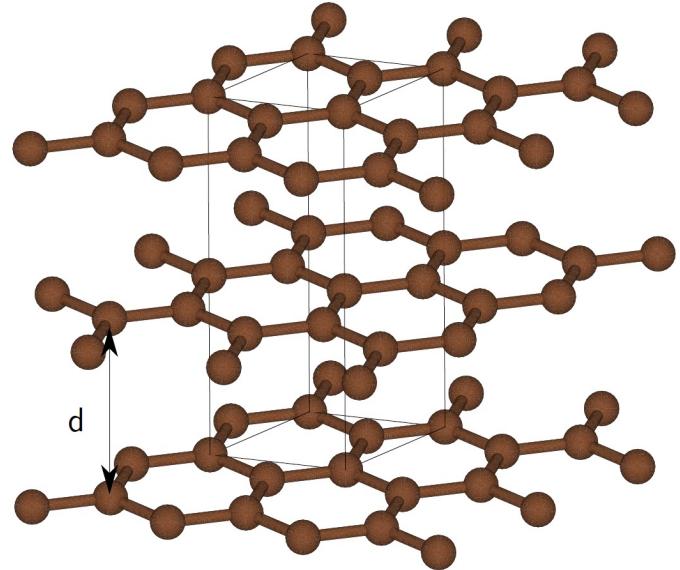
Van der waals : intrinsically non-local,
long range electron-electron correlation

→ New (classes of) functionals

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

Abinit DFPT

DFT+D3(BJ)



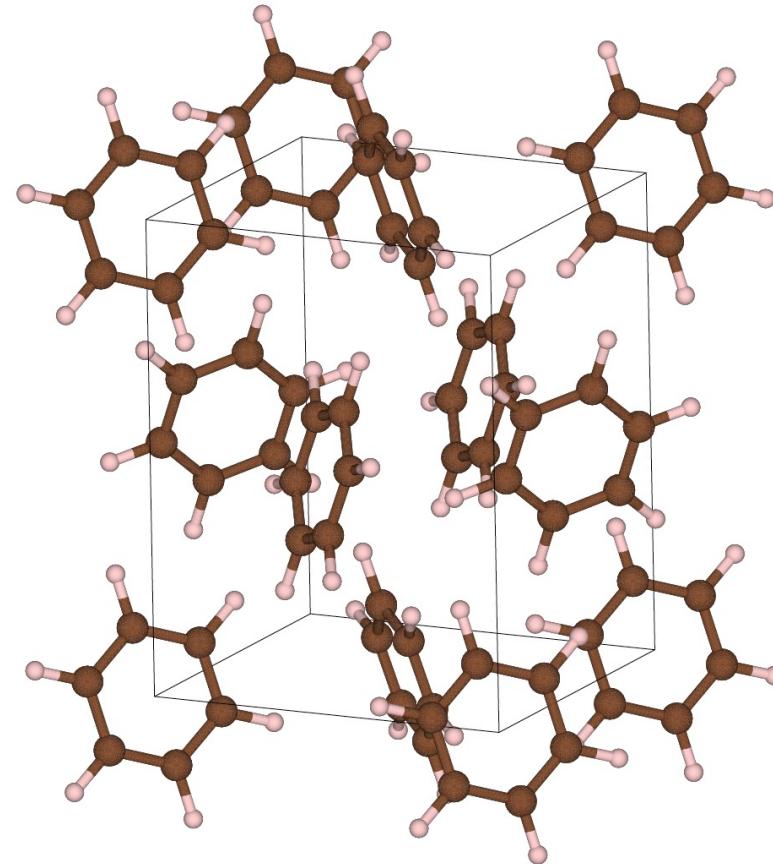
Graphite

Interlayer parameter d (nm)

GGA(PBE) 0.44

+D3(BJ) 0.337

Exp. 0.334



Benzene crystal

[Pbca - 4 Benzene rings]

Primitive cell volume (nm³)

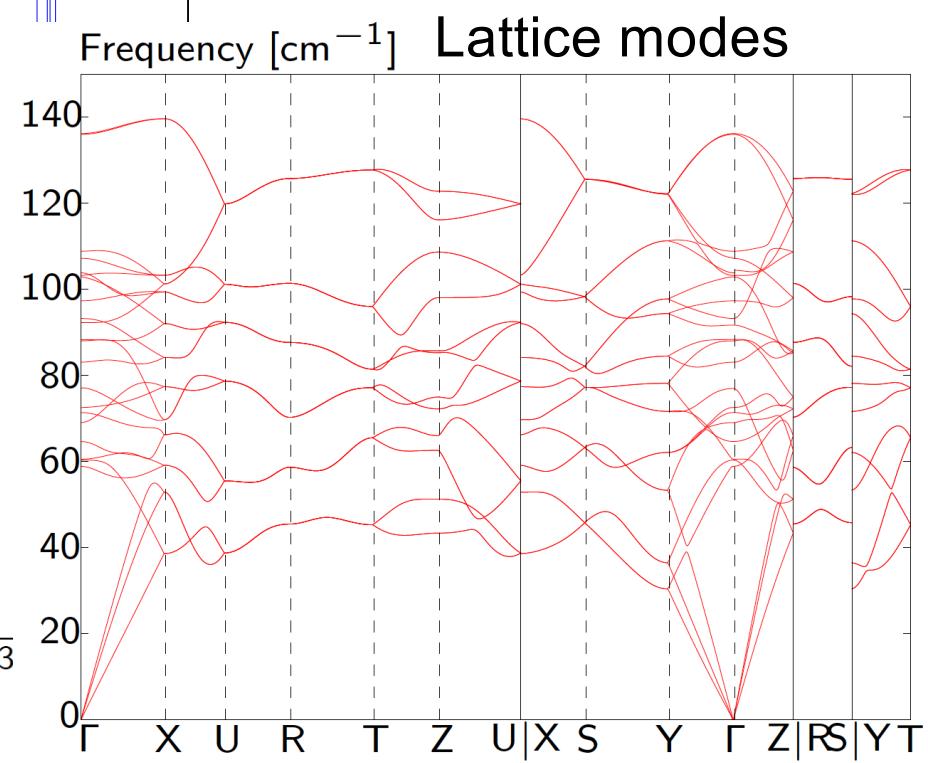
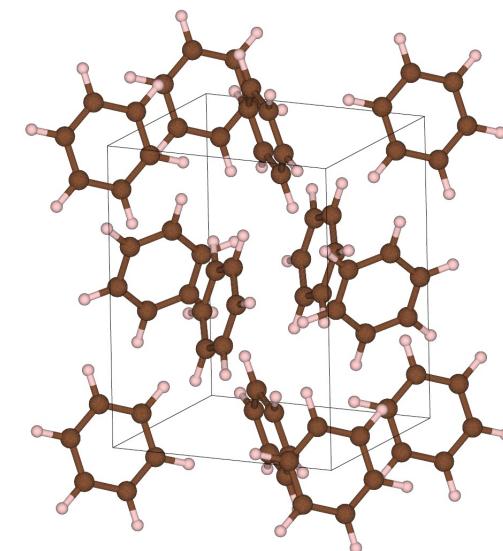
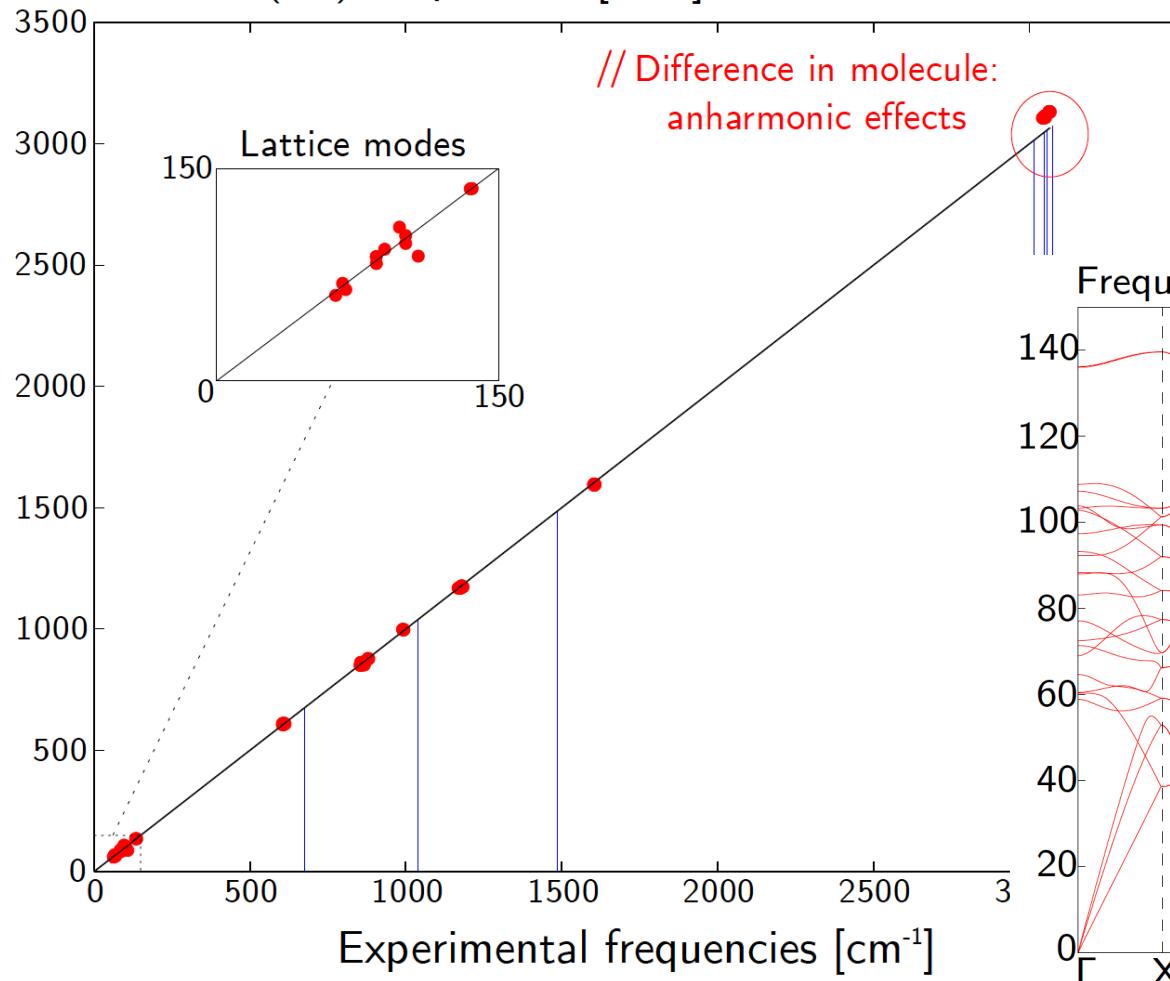
GGA(PBE) >0.600

+D3(BJ) 0.455

Exp. 0.4625

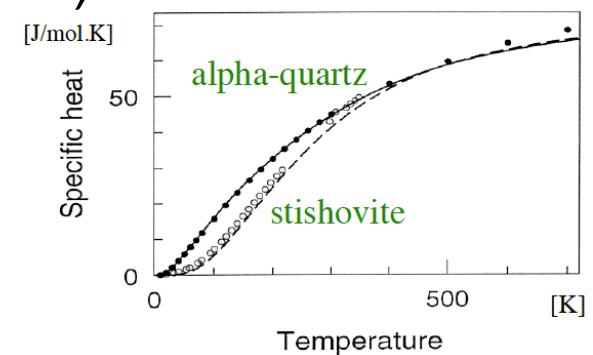
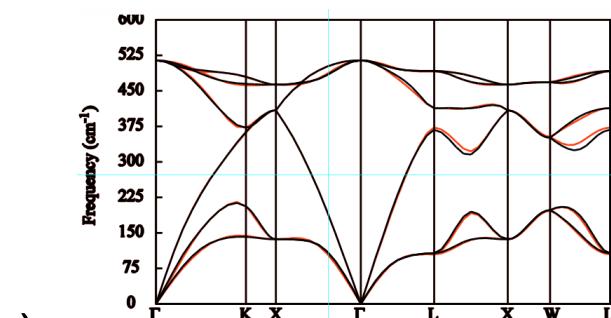
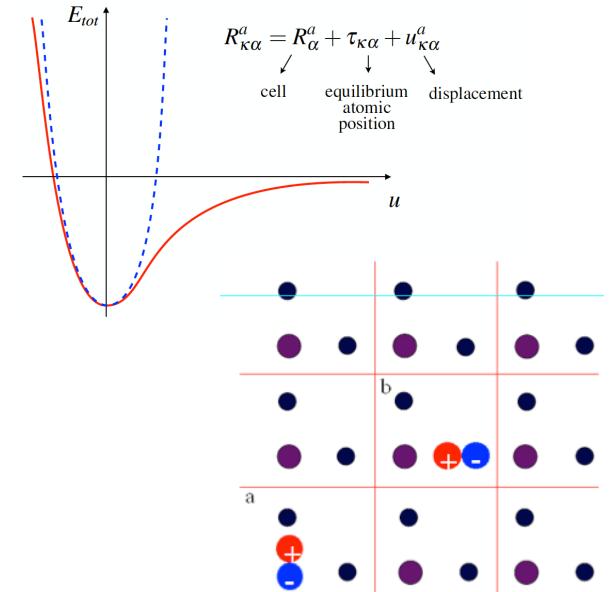
Phonons in benzene crystal

Phonons at Gamma
DFT-D3(BJ) frequencies [cm^{-1}]



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.
- Fourier interpolation + treatment of
dipole-dipole interaction = effective interpolation
of dynamical matrices => phonon band structures.
- Phonon band structures easily
computed for insulators, metals, ...
- Treatment of homogeneous electric field
- Thermodynamics (specific heat, thermal expansion ...)
- Impact of XC functionals (LDA, GGA)
- vdW functionals : OK for DFPT in
weakly bonded systems



Supplementary slides

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

Starting from

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

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

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

⚠ $\Psi_{\alpha}^{(2)}$ is needed in this formula

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

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

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

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

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

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

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

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

Density functional perturbation theory

Without going into the formulas, there exist expressions :

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

variational with respect to $\Psi_{\alpha}^{(0)}$

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

variational with respect to $\Psi_{\alpha}^{(1)}$

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

variational with respect to $\Psi_{\alpha}^{(1)}$

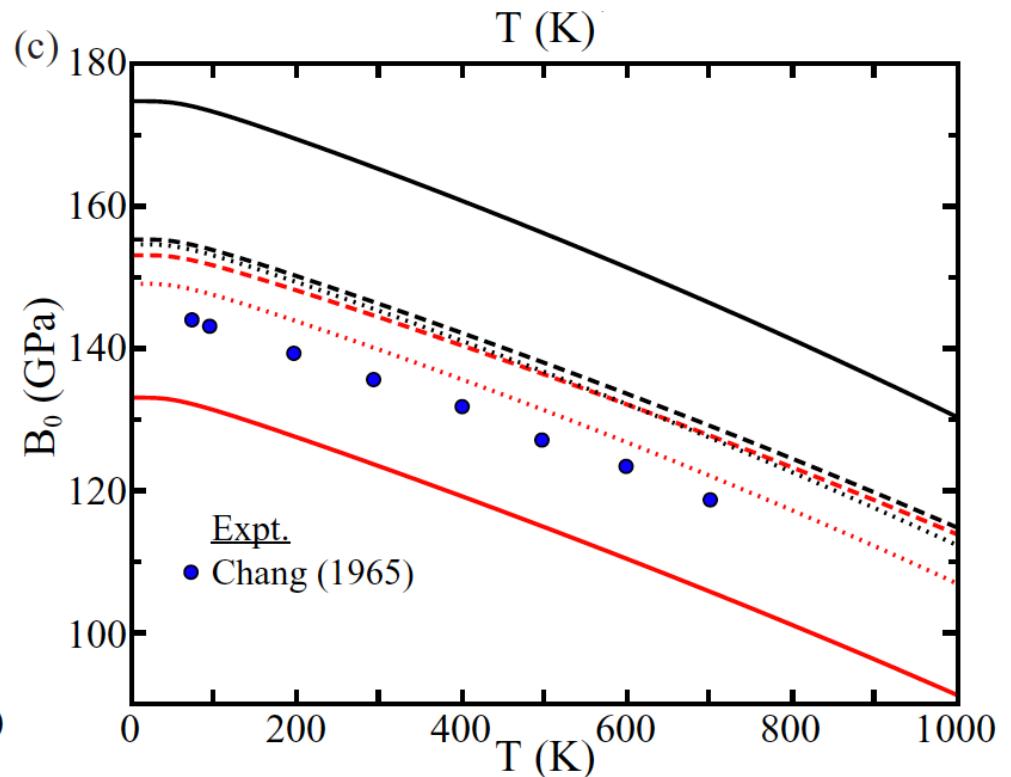
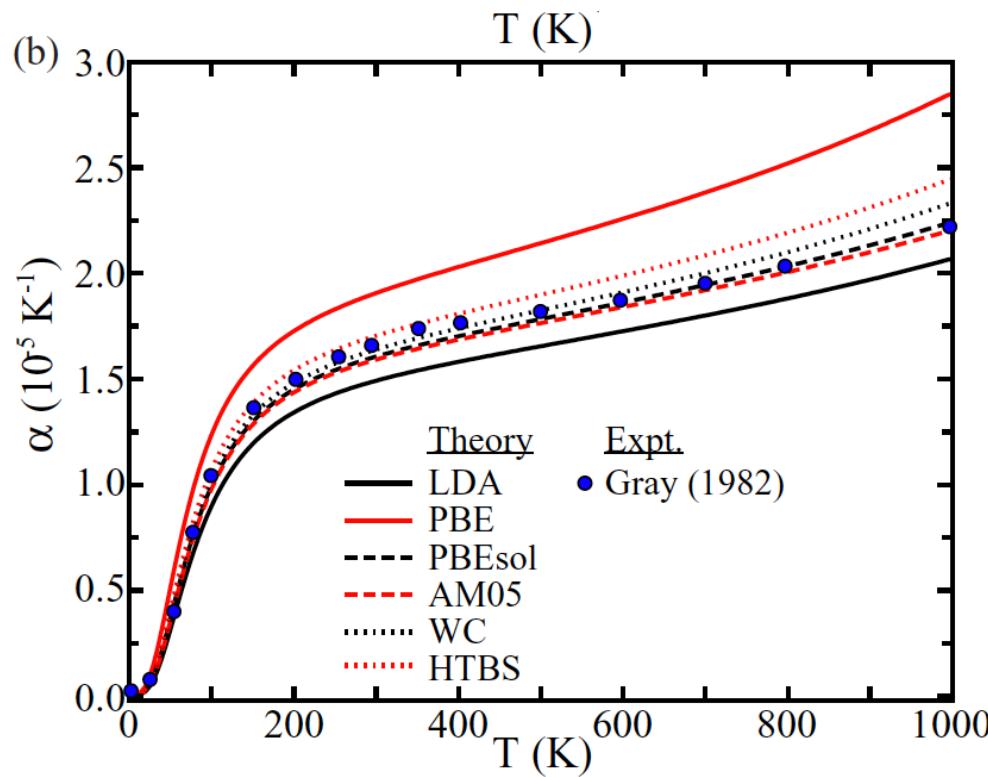
$$E^{(3)} \left\{ \Psi_{\alpha}^{(0)}; \Psi_{\alpha}^{(1)} \right\}$$

$$E^{(4)} \left\{ \Psi_{\alpha}^{(0)}; \Psi_{\alpha}^{(1)}; \Psi_{\alpha}^{(2)} \right\}$$
 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 $n^{(0)}, H^{(0)}, \varepsilon_{\alpha}^{(0)}$
- knowledge of $\left\{ \Psi_{\alpha}^{(0)}; \Psi_{\alpha}^{(1)} \right\}$ allows one to obtain $n^{(1)}, H^{(1)}, \varepsilon_{\alpha}^{(I)}$
- knowledge of $\left\{ \Psi_{\alpha}^{(0)}; \Psi_{\alpha}^{(1)}; \Psi_{\alpha}^{(2)} \right\}$ allows one to obtain $n^{(2)}, H^{(2)}, \varepsilon_{\alpha}^{(2)}$
Need $\Psi_{\alpha}^{(2)}$ unlike in ordinary QM

Thermal expansion and T-dependent bulk modulus of copper



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