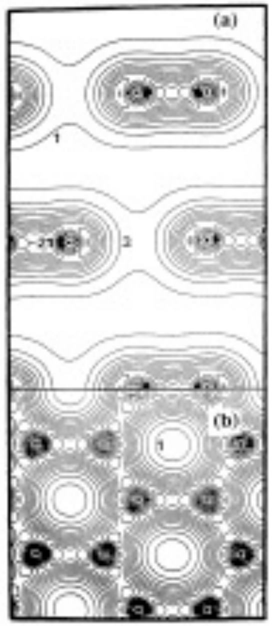
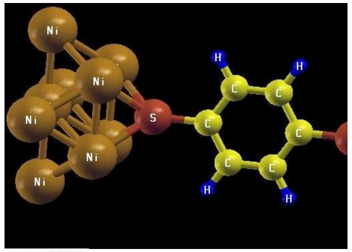
▫Advanced Materials Modeling DFPT and phonons

- \+ Material properties as derivatives of total energy
- \+ Perturbations (adiabatic)
- \+ Ordinary quantum mechanics
- \+ Density Functional Perturbation Theory
- \+ Phonon band structures
- \+ Thermodynamical properties
- \+ Electron-phonon effects on electronic energies
- \+ Electron-phonon effects on transport properties

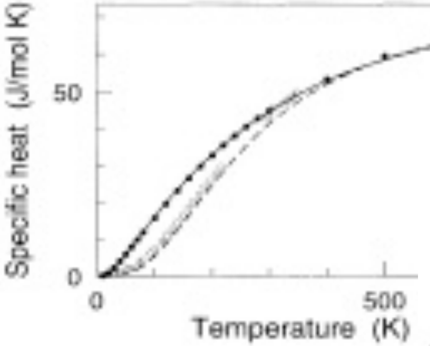
Properties of solids from DFT

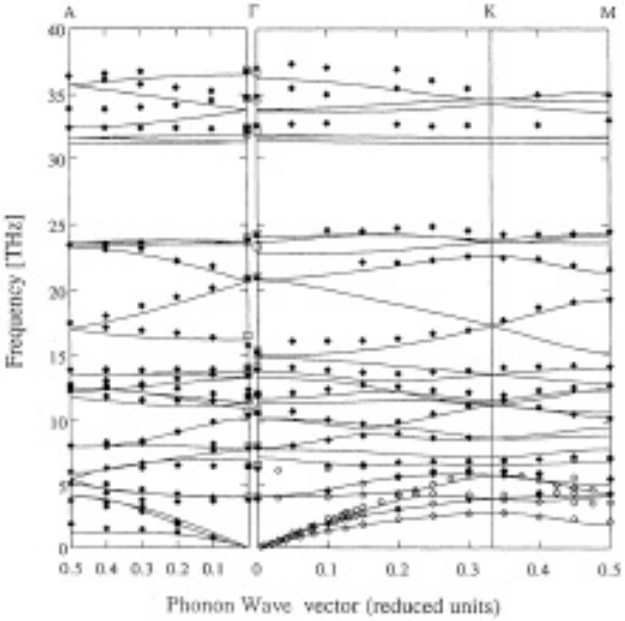


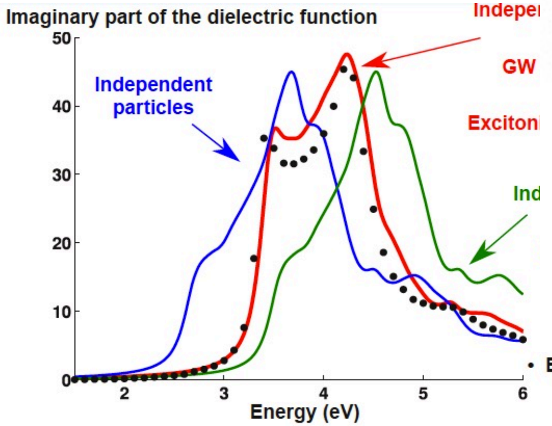
Computation of ...
- interatomic distances, angles, total energies
- electronic charge densities, electronic energies



A basis for the computation of ...
- chemical reactions
- electronic transport
- vibrational properties
- thermal capacity
- dielectric response
- optical response
- superconductivity
- surface properties
- spectroscopic responses
- ...

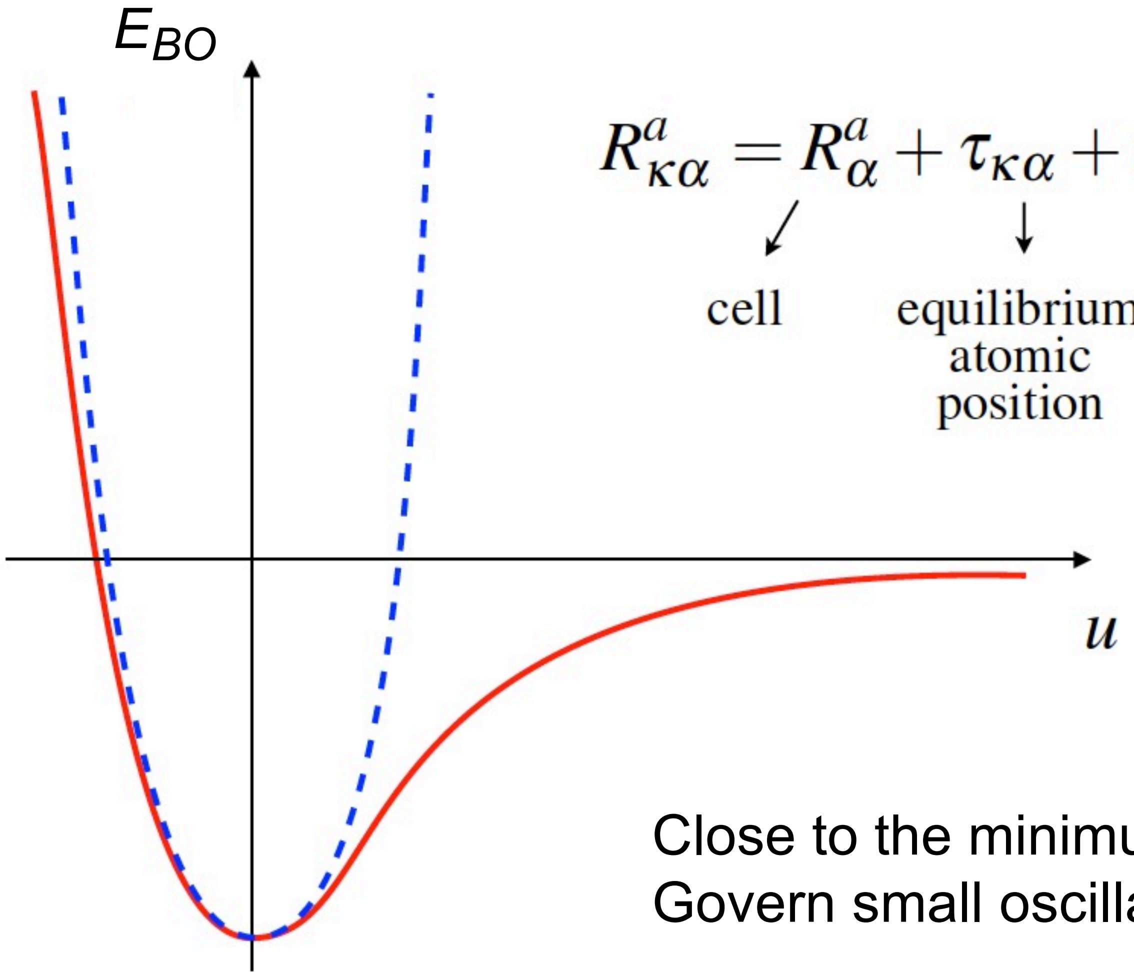






Changing atomic positions

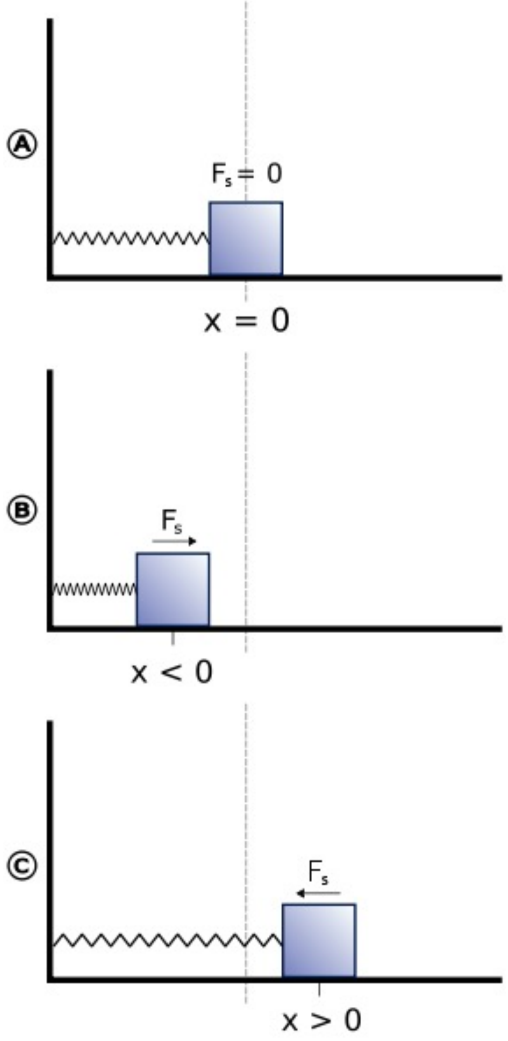
Born-Oppenheimer approximation …



$$R^a_{\kappa\alpha} = \underset{\substack{\swarrow \\ \text{cell}}}{R^a_\alpha} + \underset{\substack{\downarrow \\ \text{equilibrium} \\ \text{atomic} \\ \text{position}}}{\tau_{\kappa\alpha}} + \underset{\substack{\searrow \\ \text{displacement}}}{u^a_{\kappa\alpha}}$$

Close to the minimum : parabola
Govern small oscillations

Harmonic oscillator



Classical mechanics

Potential : $V(x) = \frac{1}{2}kx^2$

Restoring force: $F(x) = -kx$

$$\boxed{-kx = m\frac{d^2x}{dt^2}}$$

Solution : $x(t) = A\sin(\omega t) + B\cos(\omega t)$

with $\omega = \sqrt{k/m}$

Phonon frequencies from force constants

Matrix of interatomic force constants :

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

Fourier Transform (using translational invariance) :

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

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

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

phonon displacement pattern

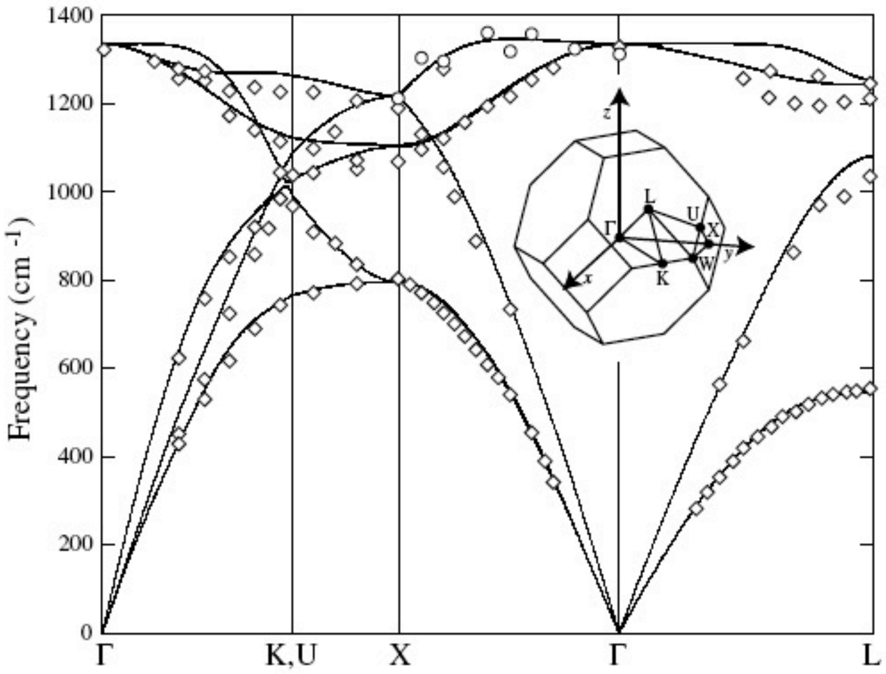
masses

square of phonon frequencies

How to get second derivatives of the energy ?

Density Functional Perturbation Theory...

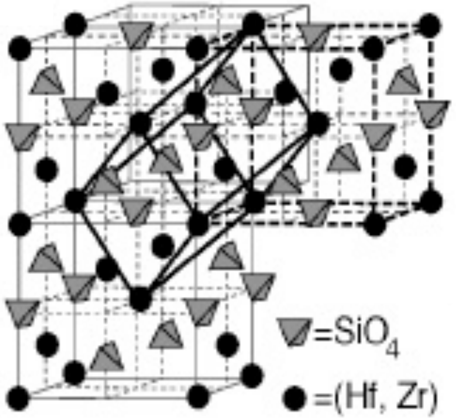
Phonons : exp vs theory

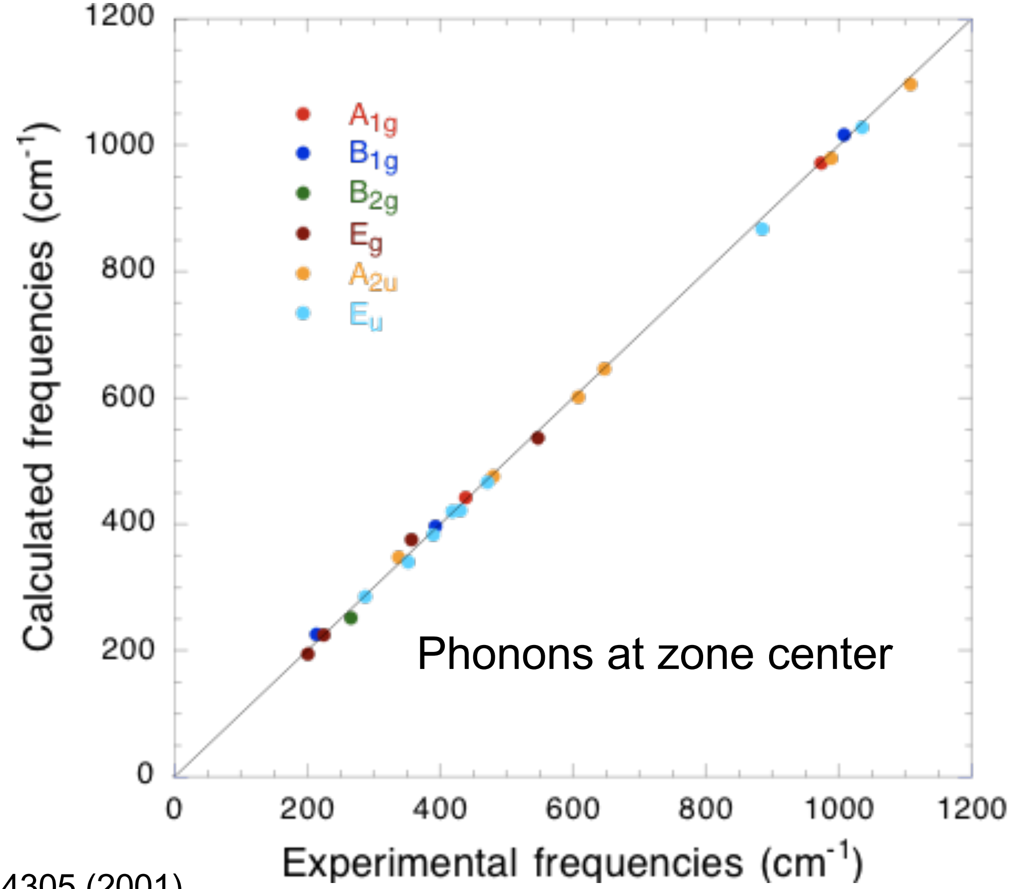


Diamond

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

Zircon





Phonons at zone center

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

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

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

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

- Perturbations (assumed known through all orders)

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

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

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

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

small parameter

'polarisation' of the phonon

phonon wavevector

How to get energy derivatives ?

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots \qquad \psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \ldots$$

- Finite Differences

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

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

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

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

$$\frac{dE}{d\lambda} = \frac{\partial E}{\partial V_{ext}} \frac{\partial V_{ext}}{\partial \lambda} + \underset{\overset{\parallel}{0}}{\frac{\partial E}{\partial \psi}} \cdot \underset{\downarrow\, \psi^{(1)}}{\frac{\partial \psi}{\partial \lambda}} = \frac{\partial E}{\partial V_{ext}} V_{ext}^{(1)}$$

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

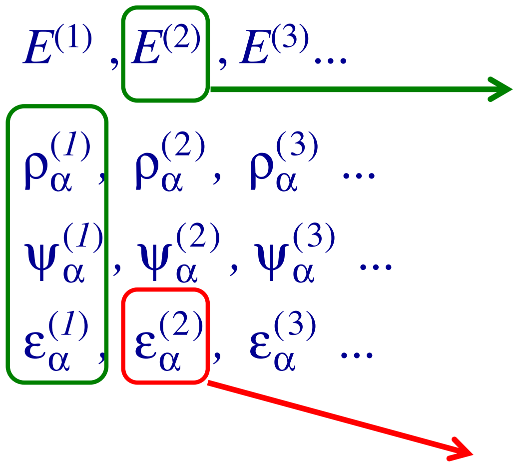
General framework of perturbation theory

- * $A\left(\lambda\right) = A^{(0)} + \lambda A^{(1)} + \lambda^2 A^{(2)} + \lambda^3 A^{(3)} \ldots$
- * $E\left\{\psi;\ V_{ext}\right\}$

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

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

Should calculate :



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

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

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

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

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

will be needed for T-dependence of electronic structure

Skoltech

Ordinary quantum mechanics

Perturbation theory for ordinary quantum mechanics

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

$\langle\psi_\alpha|\psi_\alpha\rangle = 1$ (normalisation condition)

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

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

Hamiltonian supposed known through all orders

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

Perturbation expansion of Schrödinger equation

Suppose $\hat{\mathrm{H}}(\lambda)\,\left|\psi_{\mathrm{n}}(\lambda)\right\rangle = \varepsilon_{\mathrm{n}}(\lambda)\left|\psi_{\mathrm{n}}(\lambda)\right\rangle$ valid for all λ

with
$$\begin{cases} \hat{\mathrm{H}}(\lambda) = \hat{\mathrm{H}}^{(0)} + \lambda\,\hat{\mathrm{H}}^{(1)} \\ \psi_{\mathrm{n}}(\lambda) = \psi_{\mathrm{n}}^{(0)} + \lambda\psi_{\mathrm{n}}^{(1)} + \lambda^2\psi_{\mathrm{n}}^{(2)} + \ldots \\ \varepsilon_{\mathrm{n}}(\lambda) = \varepsilon_{\mathrm{n}}^{(0)} + \lambda\,\varepsilon_{\mathrm{n}}^{(1)} + \lambda^2\varepsilon_{\mathrm{n}}^{(2)} + \ldots \end{cases}$$

Expand Schrödinger equation:

$$\hat{\mathrm{H}}^{(0)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle + \lambda\left(\hat{\mathrm{H}}^{(1)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle + \hat{\mathrm{H}}^{(0)}\left|\psi_{\mathrm{n}}^{(1)}\right\rangle\right) + \lambda^2\left(\hat{\mathrm{H}}^{(1)}\left|\psi_{\mathrm{n}}^{(1)}\right\rangle + \hat{\mathrm{H}}^{(0)}\left|\psi_{\mathrm{n}}^{(2)}\right\rangle\right) + \ldots$$
$$= \varepsilon_{\mathrm{n}}^{(0)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle + \lambda\left(\varepsilon_{\mathrm{n}}^{(1)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle + \varepsilon_{\mathrm{n}}^{(0)}\left|\psi_{\mathrm{n}}^{(1)}\right\rangle\right) + \lambda^2\left(\varepsilon_{\mathrm{n}}^{(2)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle + \varepsilon_{\mathrm{n}}^{(1)}\left|\psi_{\mathrm{n}}^{(1)}\right\rangle + \varepsilon_{\mathrm{n}}^{(0)}\left|\psi_{\mathrm{n}}^{(2)}\right\rangle\right) + \ldots$$

Perturbation expansion of Schrödinger equation

$$\hat{\mathrm{H}}^{(0)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle + \lambda\left(\hat{\mathrm{H}}^{(1)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle + \hat{\mathrm{H}}^{(0)}\left|\psi_{\mathrm{n}}^{(1)}\right\rangle\right) + \lambda^{2}\left(\hat{\mathrm{H}}^{(1)}\left|\psi_{\mathrm{n}}^{(1)}\right\rangle + \hat{\mathrm{H}}^{(0)}\left|\psi_{\mathrm{n}}^{(2)}\right\rangle\right) + \ldots$$

$$= \varepsilon_{\mathrm{n}}^{(0)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle + \lambda\left(\varepsilon_{\mathrm{n}}^{(1)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle + \varepsilon_{\mathrm{n}}^{(0)}\left|\psi_{\mathrm{n}}^{(1)}\right\rangle\right) + \lambda^{2}\left(\varepsilon_{\mathrm{n}}^{(2)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle + \varepsilon_{\mathrm{n}}^{(1)}\left|\psi_{\mathrm{n}}^{(1)}\right\rangle + \varepsilon_{\mathrm{n}}^{(0)}\left|\psi_{\mathrm{n}}^{(2)}\right\rangle\right) + \ldots$$

If $\lambda = 0$, one gets $\hat{\mathrm{H}}^{(0)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle = \varepsilon_{\mathrm{n}}^{(0)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle$ no surprise …

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

=> $\hat{\mathrm{H}}^{(1)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle + \hat{\mathrm{H}}^{(0)}\left|\psi_{\mathrm{n}}^{(1)}\right\rangle = \varepsilon_{\mathrm{n}}^{(1)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle + \varepsilon_{\mathrm{n}}^{(0)}\left|\psi_{\mathrm{n}}^{(1)}\right\rangle$

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

=> $\hat{\mathrm{H}}^{(1)}\left|\psi_{\mathrm{n}}^{(1)}\right\rangle + \hat{\mathrm{H}}^{(0)}\left|\psi_{\mathrm{n}}^{(2)}\right\rangle = \varepsilon_{\mathrm{n}}^{(2)}\left|\psi_{\mathrm{n}}^{(0)}\right\rangle + \varepsilon_{\mathrm{n}}^{(1)}\left|\psi_{\mathrm{n}}^{(1)}\right\rangle + \varepsilon_{\mathrm{n}}^{(0)}\left|\psi_{\mathrm{n}}^{(2)}\right\rangle$

Perturbation expansion of the normalisation

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

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

Same technique than for Schrödinger equation, one deduces :

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

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

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

no surprise …

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

Start from first-order Schrödinger equation

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

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

$$\left\langle\psi_n^{(0)}\middle|\hat{H}^{(1)}\middle|\psi_n^{(0)}\right\rangle + \underbrace{\left\langle\underbrace{\psi_n^{(0)}\middle|\hat{H}^{(0)}}_{\substack{\parallel \\ \left\langle\psi_n^{(0)}\middle|\varepsilon_n^{(0)}\right.}}\middle|\psi_n^{(1)}\right\rangle}_{} = \varepsilon_n^{(1)}\underbrace{\left\langle\psi_n^{(0)}\middle|\psi_n^{(0)}\right\rangle}_{=1} + \underbrace{\varepsilon_n^{(0)}\left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle}_{}$$

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

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

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

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

Start from second-order Schrödinger equation

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

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

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

Both can be combined :

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

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

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

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 :

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

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

$$\left(\underline{\hat{H}^{(0)} - \varepsilon_n^{(0)}}\right)\boxed{|\psi_n^{(1)}\rangle} = -\underline{\left(\hat{H}^{(1)} - \varepsilon_n^{(1)}\right)|\psi_n^{(0)}}\rangle$$

(called **Sternheimer equation**)

Equivalence with matrix equation (systeme of linear equations)

$$\underline{\underline{A}} \,.\, \underline{x} = \underline{y}$$

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

Generalisation: Density-functional perturbation theory (DFPT)

Basic equations in DFT

Solve self-consistently Kohn-Sham equation

$$\left\{\begin{aligned} &\hat{H}\left|\psi_n\right\rangle = \varepsilon_n\left|\psi_n\right\rangle \\ &\hat{H} = \hat{T} + \hat{V} + \hat{V}_{Hxc}[\mathrm{n}] \\ &\mathrm{n}(\vec{r}) = \sum_{\mathrm{n}}^{occ} \psi_{\mathrm{n}}^{*}(\vec{r})\psi_{\mathrm{n}}(\vec{r}) \end{aligned}\right.$$

$$\begin{tikzcd} \hat{H} \arrow[rr, bend left] & & \psi_n(\mathbf{r}) \arrow[dl, bend left] \\ & n(\mathbf{r}) \arrow[ul, bend left] & \end{tikzcd}$$

$$\delta_{\mathrm{mn}} = \left\langle \psi_{\mathrm{m}} \middle| \psi_{\mathrm{n}} \right\rangle \text{for m,n} \in \text{occupied set}$$

or minimize

$$E_{el}\{\psi\} = \sum_{\mathrm{n}}^{occ} \left\langle \psi_{\mathrm{n}} \middle| \hat{T} + \hat{V} \middle| \psi_{\mathrm{n}} \right\rangle + E_{Hxc}[\mathrm{n}]$$

What is $\hat{V}$?

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

Basic equations in DFPT

Solve self-consistently Sternheimer equation

$$\left\{\begin{aligned}
&(\hat{H}^{(0)}-\varepsilon_n^{(0)})\left|\psi_n^{(1)}\right\rangle = -(\hat{H}^{(1)}-\varepsilon_n^{(1)})\left|\psi_n^{(0)}\right\rangle \\
&\qquad \varepsilon_n^{(1)} = \left\langle\psi_n^{(0)}\middle|\hat{H}^{(1)}\middle|\psi_n^{(0)}\right\rangle \\
&\qquad \hat{H}^{(1)} = \hat{V}^{(1)} + \int \frac{\delta^2 E_{Hxc}}{\delta\rho(r)\delta\rho(r')} n^{(1)}(r')\,dr' \\
&n^{(1)}(\vec{r}) = \sum_n^{occ} \psi_n^{(1)*}(\vec{r})\psi_n^{(0)}(\vec{r}) + \psi_n^{(0)*}(\vec{r})\psi_n^{(1)}(\vec{r})
\end{aligned}\right.$$

$$0 = \left\langle\psi_m^{(0)}\middle|\psi_n^{(1)}\right\rangle \text{for m} \in \text{occupied set}$$

$$\begin{tikzcd}
\hat{H}^{(1)} \arrow[rr, bend left] & & \psi_n^{(1)}(\mathbf{r}) \arrow[dl, bend left] \\
& n^{(1)}(\mathbf{r}) \arrow[ul, bend left] &
\end{tikzcd}$$

or minimize

$$\begin{aligned}
E_{el}^{(2)}\left\{\psi^{(1)};\psi^{(0)}\right\} = \sum_n^{occ} & \left\langle\psi_n^{(1)}\middle|\hat{H}^{(0)}-\varepsilon_n^{(0)}\middle|\psi_n^{(1)}\right\rangle + \left\langle\psi_n^{(1)}\middle|\hat{V}^{(1)}\middle|\psi_n^{(0)}\right\rangle \\
& + \left\langle\psi_n^{(0)}\middle|\hat{V}^{(1)}\middle|\psi_n^{(1)}\right\rangle + \left\langle\psi_n^{(0)}\middle|\hat{V}^{(2)}\middle|\psi_n^{(0)}\right\rangle \\
& + \frac{1}{2}\iint \frac{\delta^2 E_{Hxc}}{\delta\rho(\vec{r})\delta\rho(\vec{r}')}\, n^{(1)}(\vec{r})\, n^{(1)}(\vec{r}')\, d\vec{r}\, d\vec{r}'
\end{aligned}$$

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

The potential and its 1st derivative

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

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

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

Generalisation to pseudopotentials can be worked out ...

Collective displacement with wavevector $\vec{q}$

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

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 : $V^{(1)}(\vec{r}+\vec{R}_a) = e^{i\vec{q}.\vec{R}_a} V^{(1)}(\vec{r})$

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

$$\mathrm{n}^{(1)}(\vec{r}+\vec{R}_a) = e^{i\vec{q}.\vec{R}_a}\, \mathrm{n}^{(1)}(\vec{r}) \qquad \psi^{(1)}_{m,\vec{k},\vec{q}}(\vec{r}+\vec{R}_a) = e^{i(\vec{\mathrm{k}}+\vec{q})\vec{R}_a}\, \psi^{(1)}_{m,\vec{k},\vec{q}}(\vec{r})$$

Now, define related periodic quantities

$$\bar{\mathrm{n}}^{(1)}(\vec{r}) = e^{-i\vec{q}\,\vec{r}}\, \mathrm{n}^{(1)}(\vec{r}) \qquad u^{(1)}_{m,\vec{k},\vec{q}}(\vec{r}) = (N\Omega_0)^{1/2}\, e^{-i(\vec{\mathrm{k}}+\vec{q})\vec{r}}\, \psi^{(1)}_{m,\vec{k},\vec{q}}(\vec{r})$$

In equations of DFPT, only these periodic quantities appear:

phases $e^{-i\vec{q}.\vec{r}}$ and $e^{-i(\vec{k}+\vec{q})\vec{r}}$ 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 $E^{j1\,j2}$ from $\psi_\alpha^{(0)}, \psi_\alpha^{j_1}, \psi_\alpha^{j_2}$?

$$E_{el}^{(2)}\left\{\psi^{(1)};\psi^{(0)}\right\} = \sum_{n}^{occ}\left\langle\psi_n^{(1)}\middle|\hat{H}^{(0)}\text{-}\varepsilon_n^{(0)}\middle|\psi_n^{(1)}\right\rangle+\left\langle\psi_n^{(1)}\middle|\hat{V}^{(1)}\middle|\psi_n^{(0)}\right\rangle$$
$$+\left\langle\psi_n^{(0)}\middle|\hat{V}^{(1)}\middle|\psi_n^{(1)}\right\rangle+\left\langle\psi_n^{(0)}\middle|\hat{V}^{(2)}\middle|\psi_n^{(0)}\right\rangle$$
$$+\ \frac{1}{2}\iint\frac{\delta^2 E_{Hxc}}{\delta\rho(\vec{r})\delta\rho(\vec{r}')}\,n^{(1)}(\vec{r})\,n^{(1)}(\vec{r}')\,d\vec{r}\,d\vec{r}'$$

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

with $\tilde{E}_{el}^{j_1 j_2}\left\{\psi^{j_1},\psi^{j_2};\psi^{(0)}\right\} = \sum_{n}^{occ}\left\langle\psi_n^{j_1}\middle|\hat{H}^{(0)}\text{-}\varepsilon_n^{(0)}\middle|\psi_n^{j_2}\right\rangle+\left\langle\psi_n^{j_1}\middle|\hat{V}^{j_2}\middle|\psi_n^{(0)}\right\rangle$

$$+\left\langle\psi_n^{(0)}\middle|\hat{V}^{j_1}\middle|\psi_n^{j_2}\right\rangle+\left\langle\psi_n^{(0)}\middle|\hat{V}^{j_1 j_2}\middle|\psi_n^{(0)}\right\rangle$$
$$+\ \frac{1}{2}\iint\frac{\delta^2 E_{Hxc}}{\delta\rho(\vec{r})\delta\rho(\vec{r}')}\,n^{j_1}(\vec{r})\,n^{j_2}(\vec{r}')\,d\vec{r}\,d\vec{r}'$$

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

$$E_{el}^{j_1 j_2}\left\{\psi^{j_1};\psi^{(0)}\right\} = \sum_{n}^{occ}\left\langle\psi_n^{j_1}\middle|\hat{V}^{j_2}\middle|\psi_n^{(0)}\right\rangle+\left\langle\psi_n^{(0)}\middle|\hat{V}^{j_1 j_2}\middle|\psi_n^{(0)}\right\rangle$$

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

$V^{j_1} \rightarrow \psi_n^{j_1}, n^{j_1}$

using minimization of second-order energy
or
Sternheimer equation

Enddo

(3) Do for each { j_1, j_2 }

get $E^{j1\,j2}$ from $\psi_n^{(0)}, \psi_n^{j_1}, \psi_n^{j_2}$

Enddo

(4) Post-processing : from ‘bare’ $E^{j1\,j2}$ to physical properties

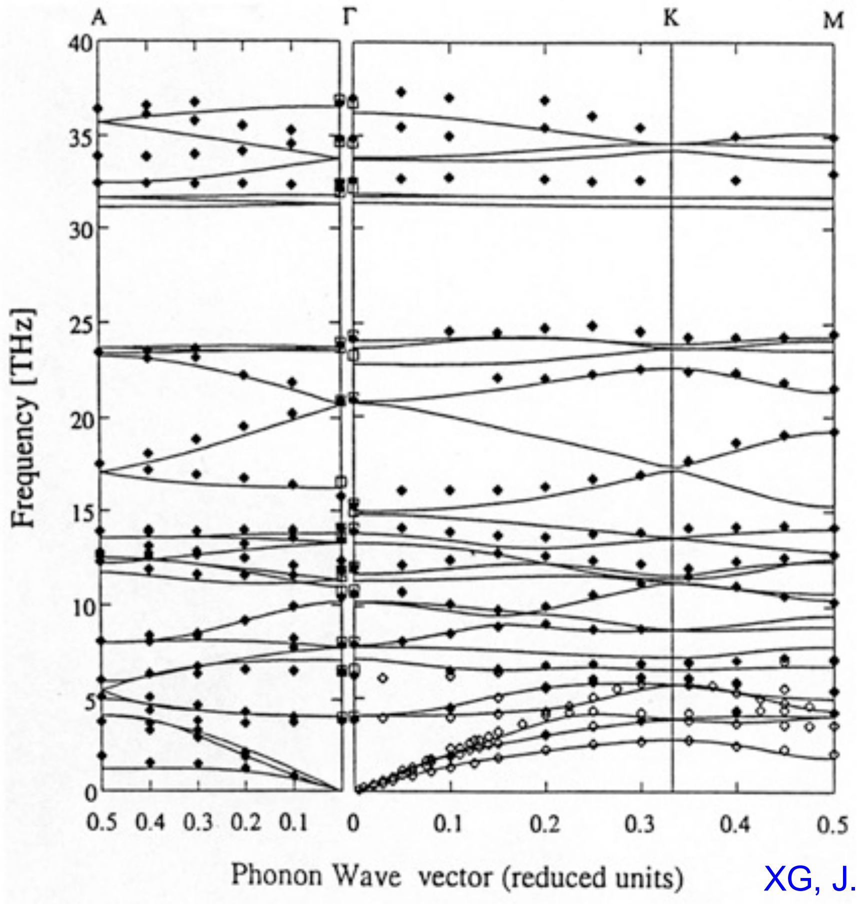
Phonon band structures from DFPT

Phonon band structure

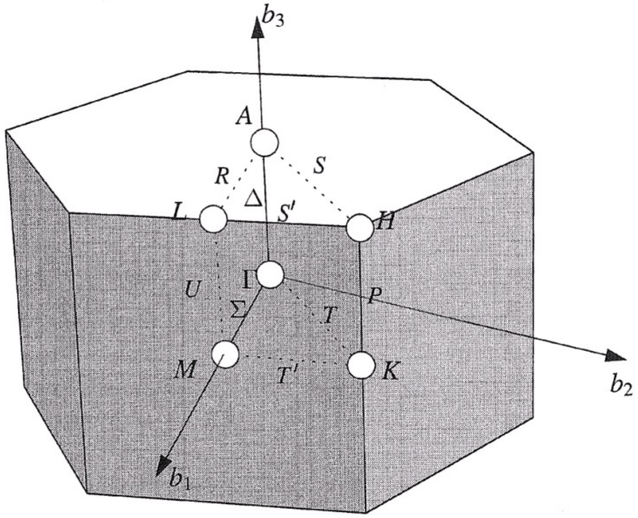
From DFPT : straightforward, although lengthy (self-consistent calculation) to compute, for one wavevector :

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

Full band structure needs values for many wavevectors ...



SiO$_2$ 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

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

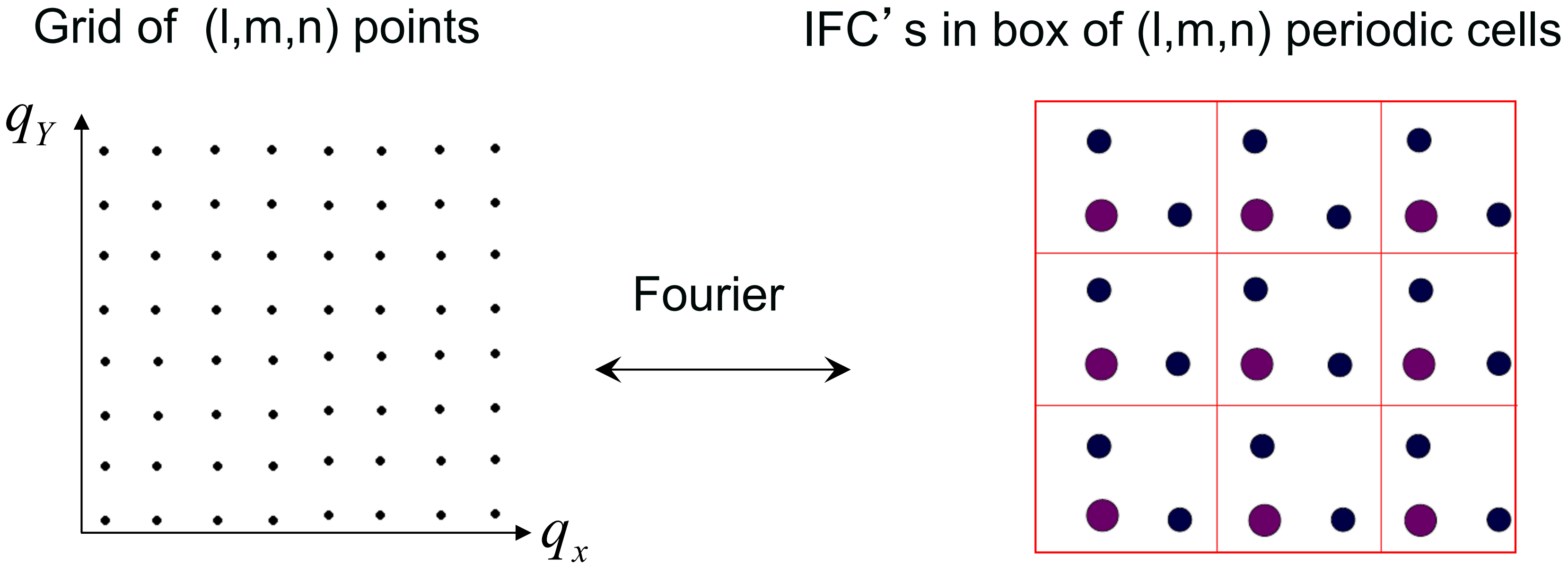
= Fourier interpolation of dynamical matrices.

Numerical Fourier Interpolation

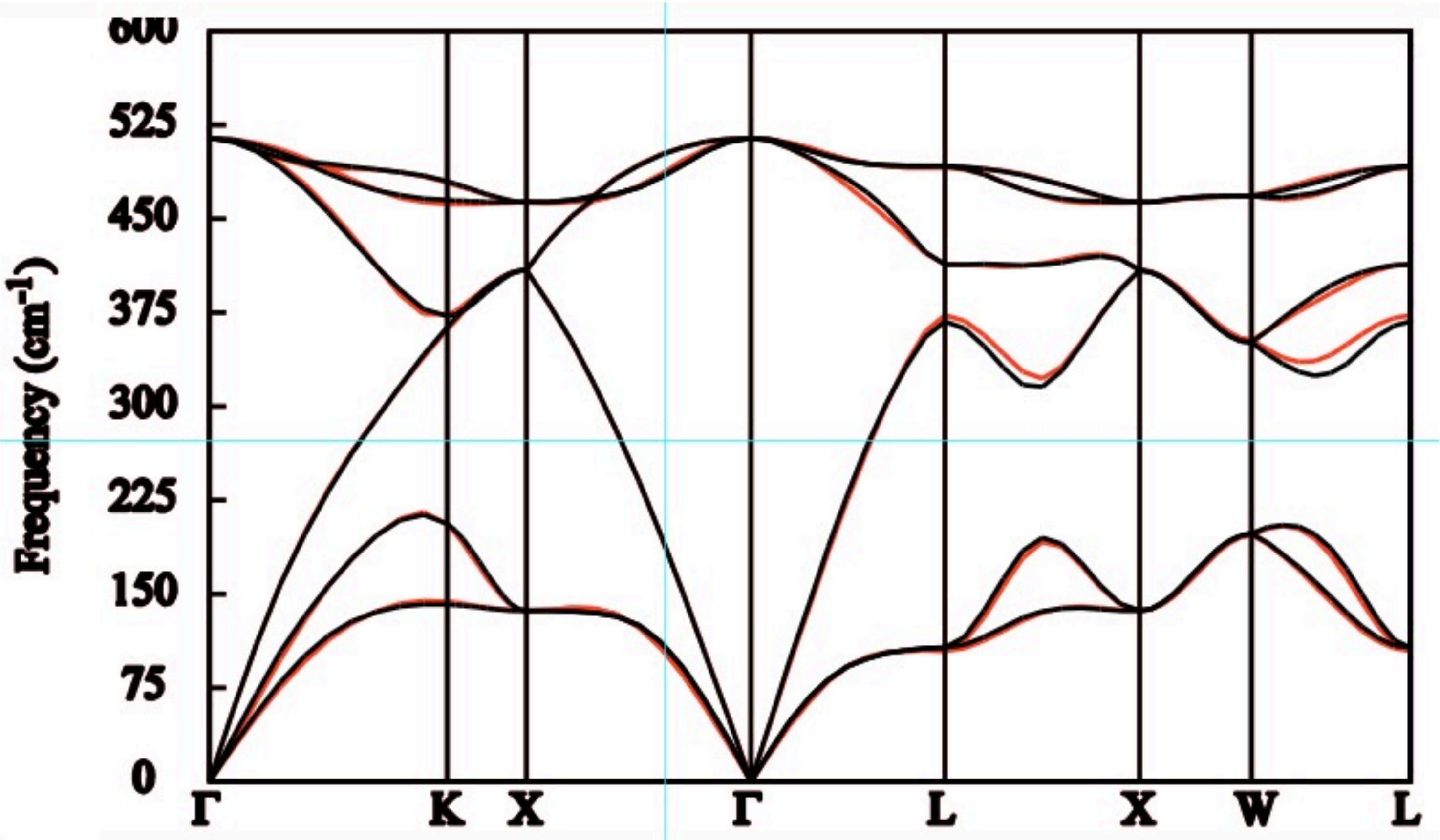
Key of the interpolation : replace the integral

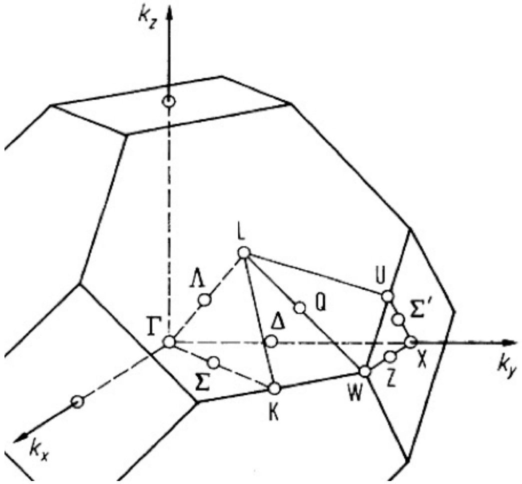
$$C_{\kappa\alpha,\kappa'\beta}(0,b)=\frac{(2\pi)^3}{\Omega_0}\int_{BZ}\tilde{C}_{\kappa\alpha,\kappa'\beta}(\vec{q})e^{-i\vec{q}\cdot\vec{R}^b}\,d\vec{q}$$

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



Fourier interpolation : Silicon



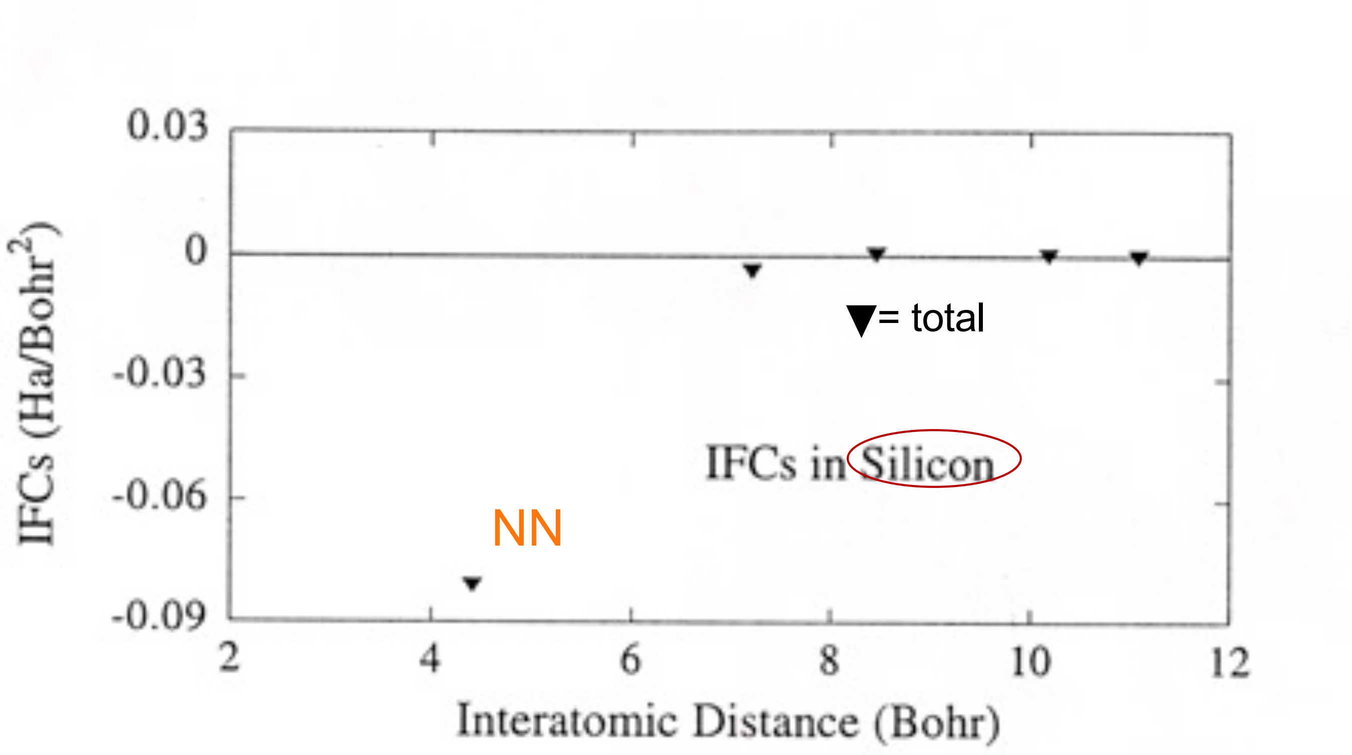


—— Real space IFC's calculated with 10 q-points

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

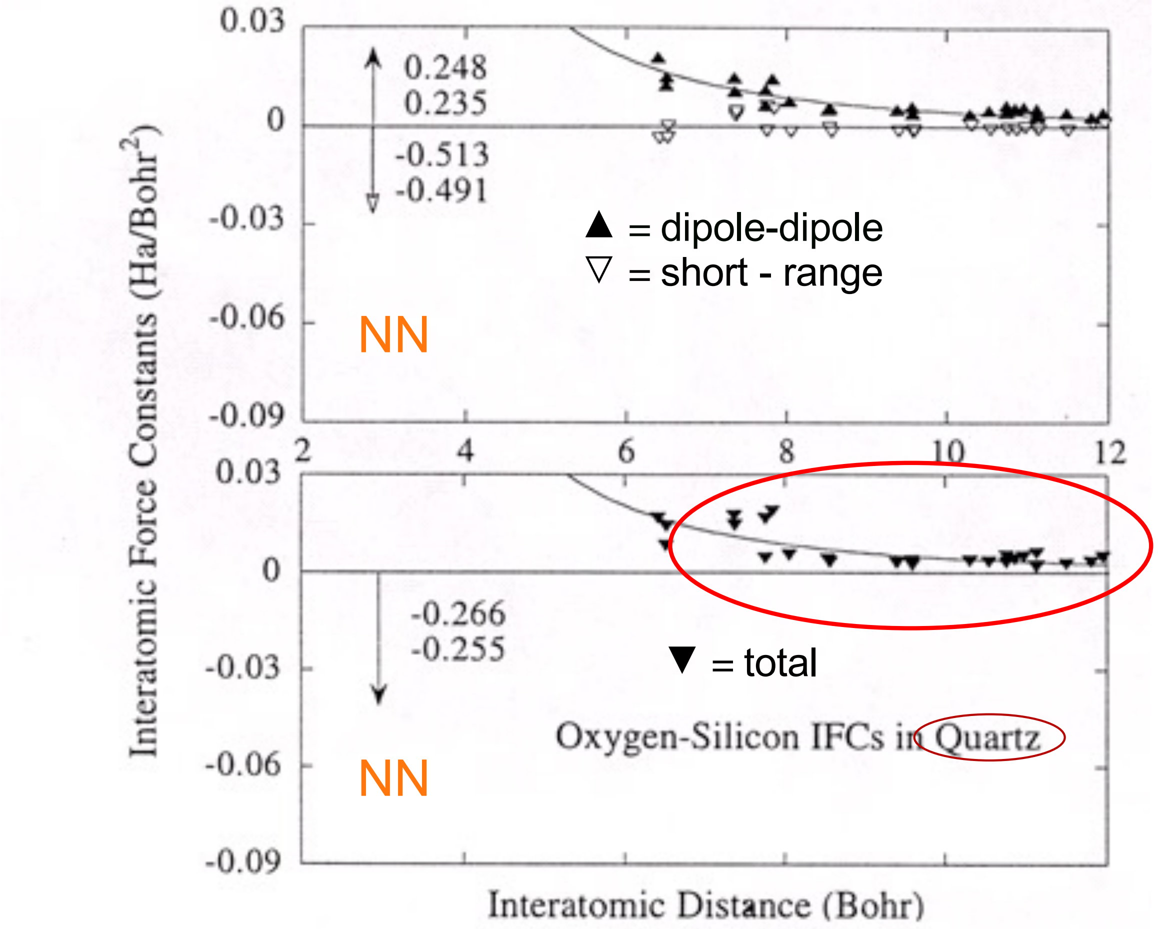
Interatomic force constants for silicon

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

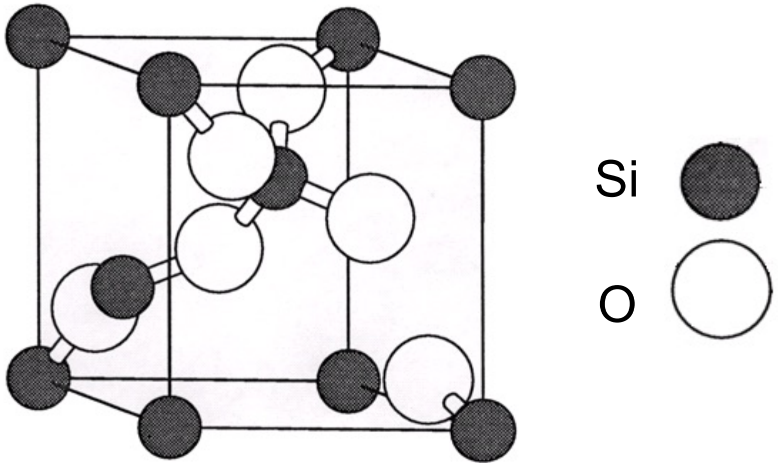


XG, *Adv. in Quantum Chemistry* 33, 225 (1999)

Interatomic force constants for silica quartz



Quartz
3 Si
6 O



Long-ranged interatomic forces !

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

Understanding the long-range behaviour

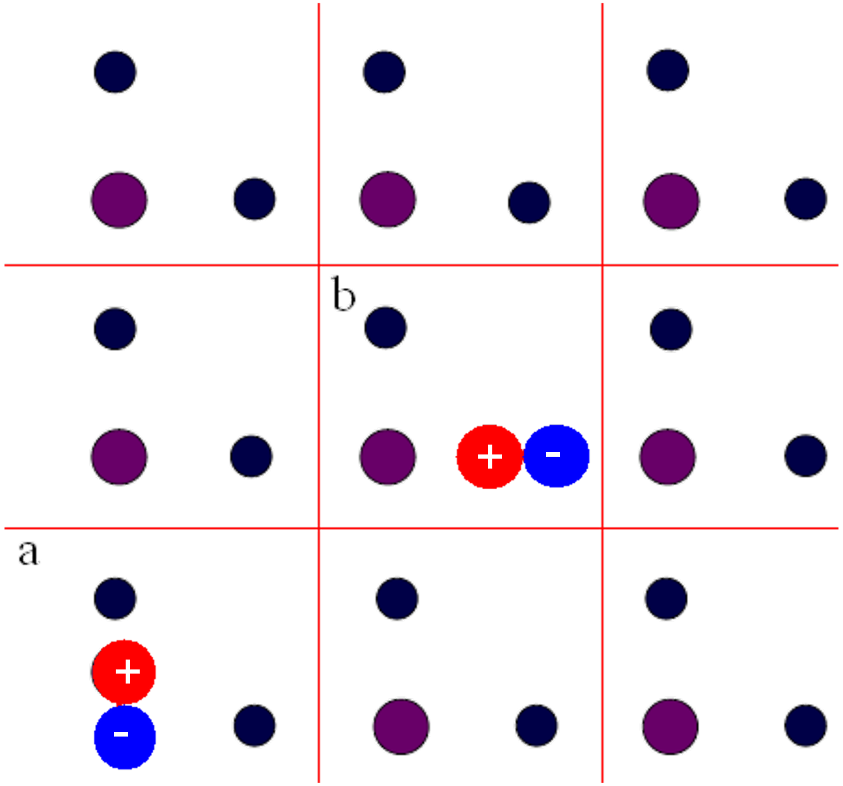
When a ion with charge Z is displaced from its equilibrium position, a dipolar electric field is created. Its effect on other ions is described by a dipole - dipole interaction appearing in IFC's.

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

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

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

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

$$\boxed{\tilde{C}^{na}_{\kappa\alpha,\kappa'\beta}(\vec{q}\to 0) = \frac{4\pi e^2}{\Omega_0}\,\frac{\sum_{\gamma} Z^*_{\kappa,\alpha\gamma} q_\gamma \sum_{\nu} Z^*_{\kappa',\beta\nu} q_\nu}{\sum_{\gamma,\nu} q_\gamma \varepsilon^\infty_{\gamma\nu} q_\nu}}$$

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

Born effective charge tensor for atom κ

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

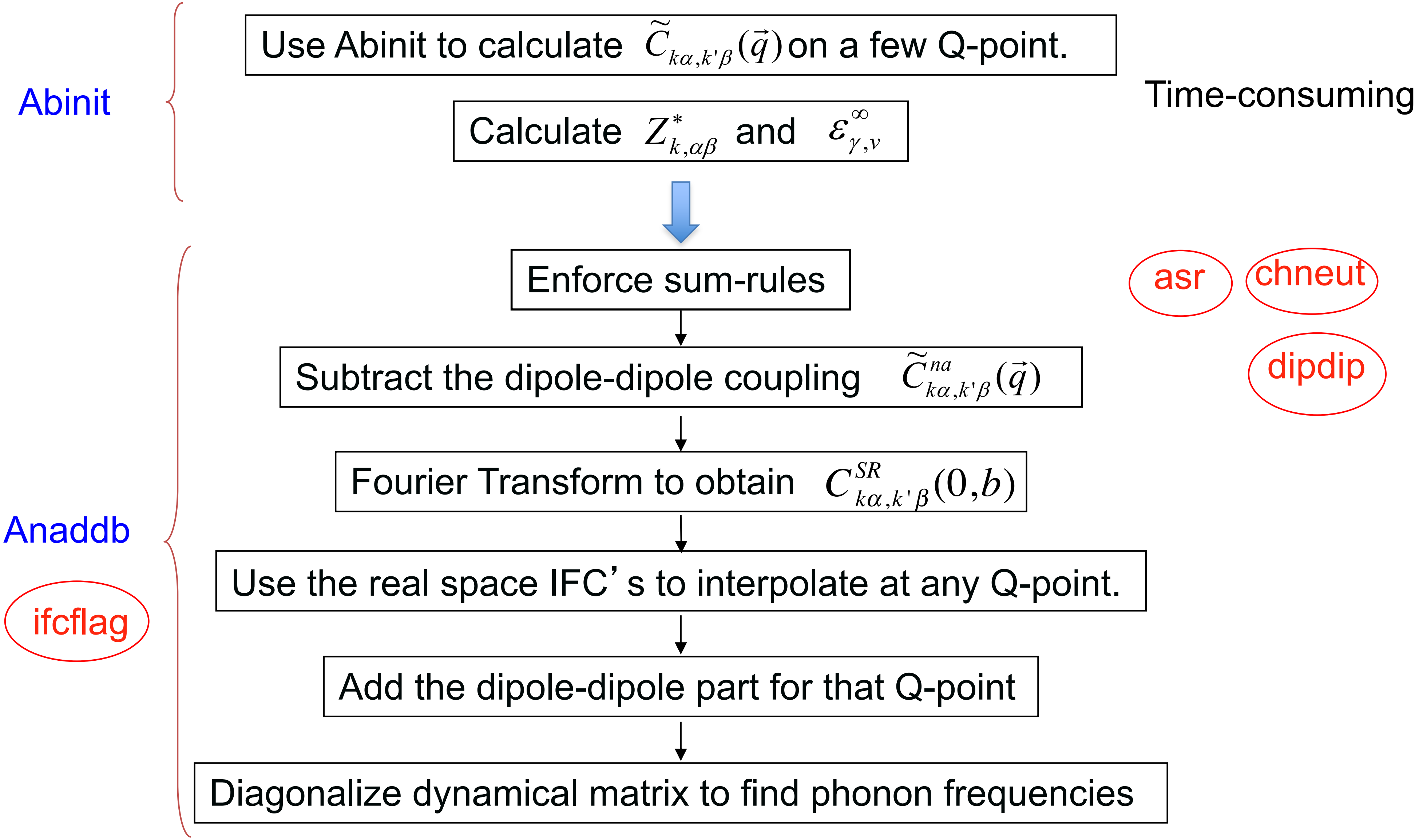
$$\varepsilon^\infty_{\gamma\nu} = \delta_{\gamma\nu} + 4\pi \frac{\partial P_\gamma}{\partial \mathcal{E}_\nu}$$

electronic dielectric tensor

(electronic contribution to the screening of the charges)

Both can be linked to a second derivative of total energy

Interpolation Scheme



Abinit

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

Calculate $Z^{*}_{k,\alpha\beta}$ and $\varepsilon^{\infty}_{\gamma,\nu}$

Time-consuming

Anaddb

Enforce sum-rules

asr

chneut

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

dipdip

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

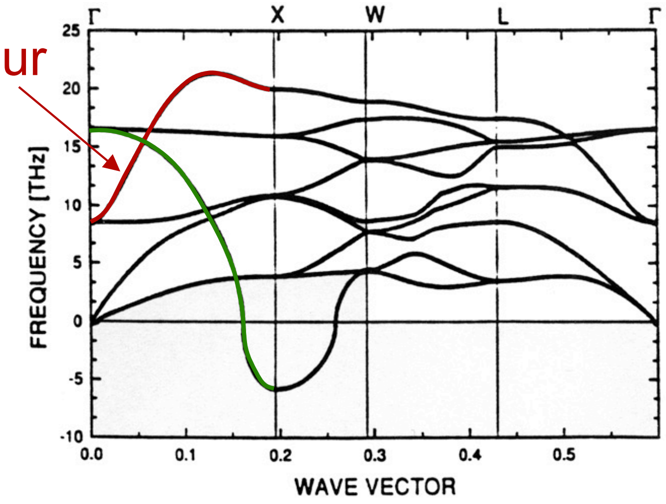
Use the real space IFC's to interpolate at any Q-point.

ifcflag

Add the dipole-dipole part for that Q-point

Diagonalize dynamical matrix to find phonon frequencies

Phonon dispersion curves of ZrO_2



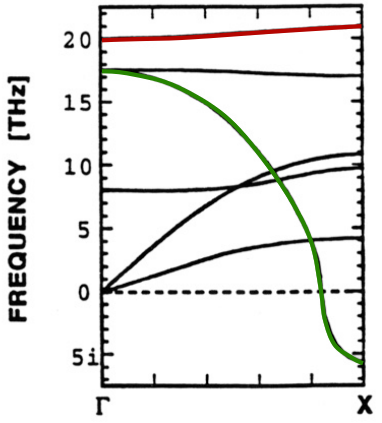
Wrong behaviour

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))

ZrO_2 in the cubic structure at the equilibrium lattice constant a_0 = 5.13 Å.



DFPT (Linear-response)

with Z^*_{Zr} = 5.75
Z^*_{O} = -2.86
ε_∞ = 5.75

LO - TO splitting 11.99 THz

Non-polar mode is OK

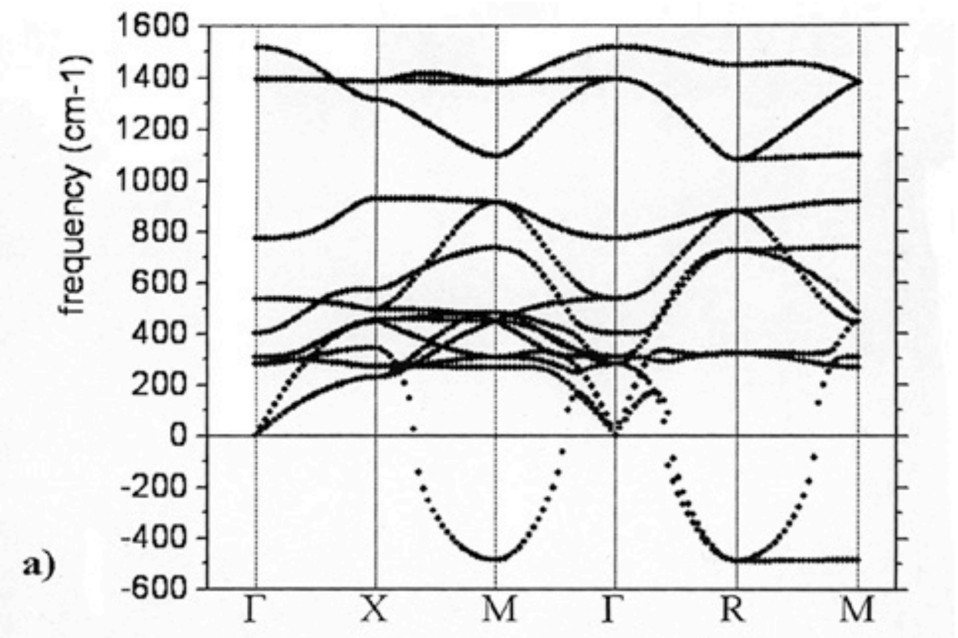
(From Detraux F., Ghosez Ph. and Gonze X., *Phys. Rev. Lett.* 81, 3297 (1998) - Comment to the Parlinski & al paper)

Analysis of instabilities

$MgSiO_3$

CUBIC

(5at/cell)



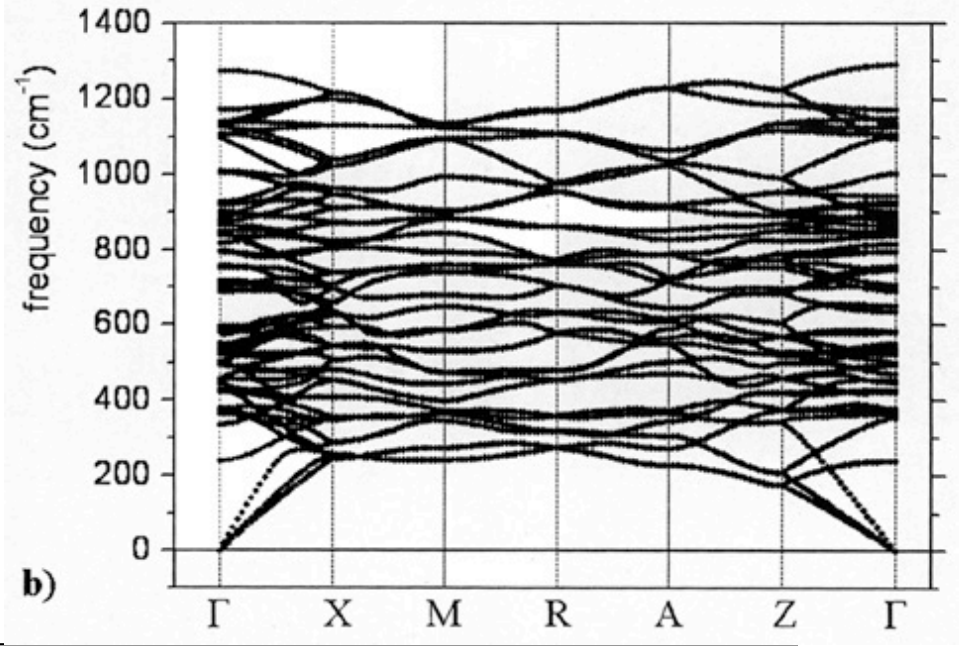
Phonon dispersion relations.

(a) Ideal cubic phase : unstable.

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

ORTHORHOMBIC

(20at/cell)



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

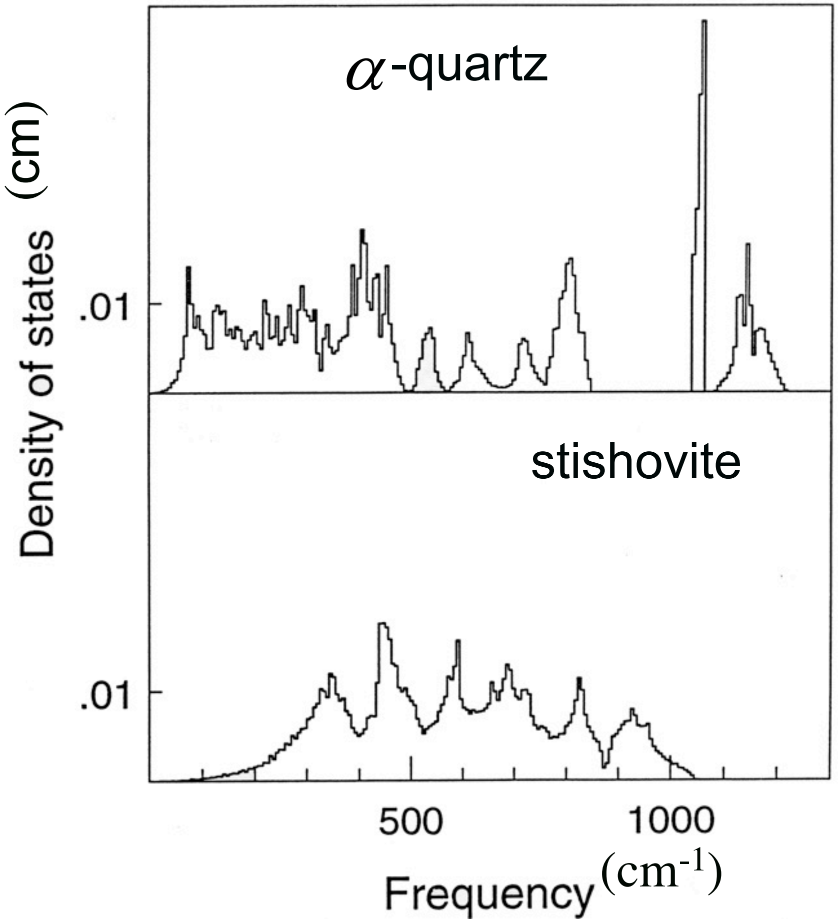
For each frequency channel, count the "number" of phonon modes

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

m = index of pattern of vibration,

$\vec{q}$ = a crystalline momentum

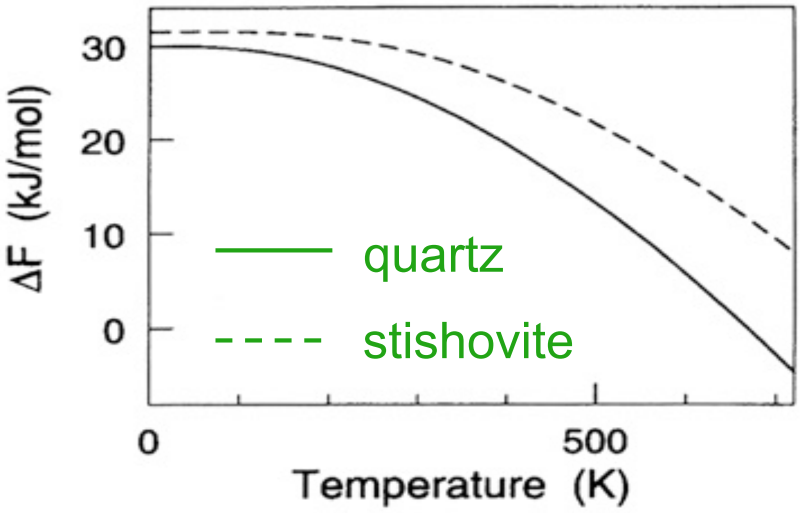
(=> velocity of the vibrational wave)



Helmoltz free energy and specific heat

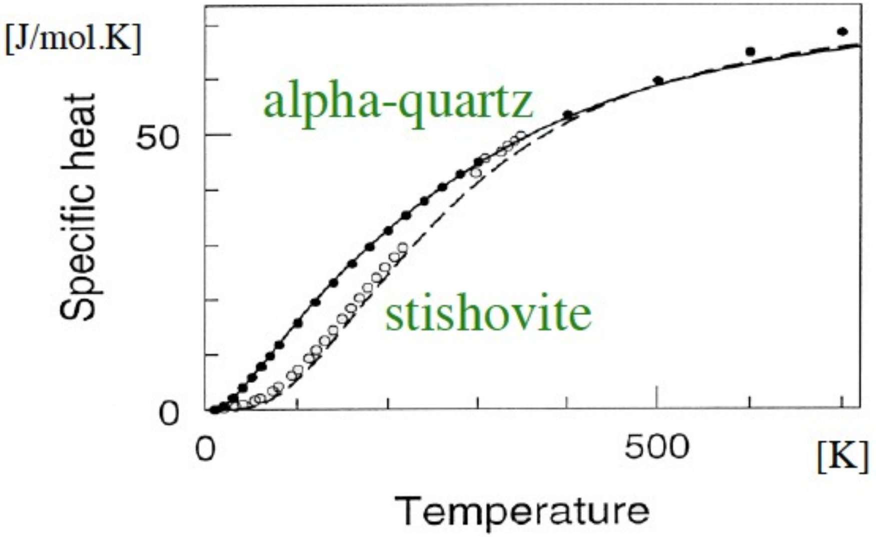
$$F = U - TS$$

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



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 :

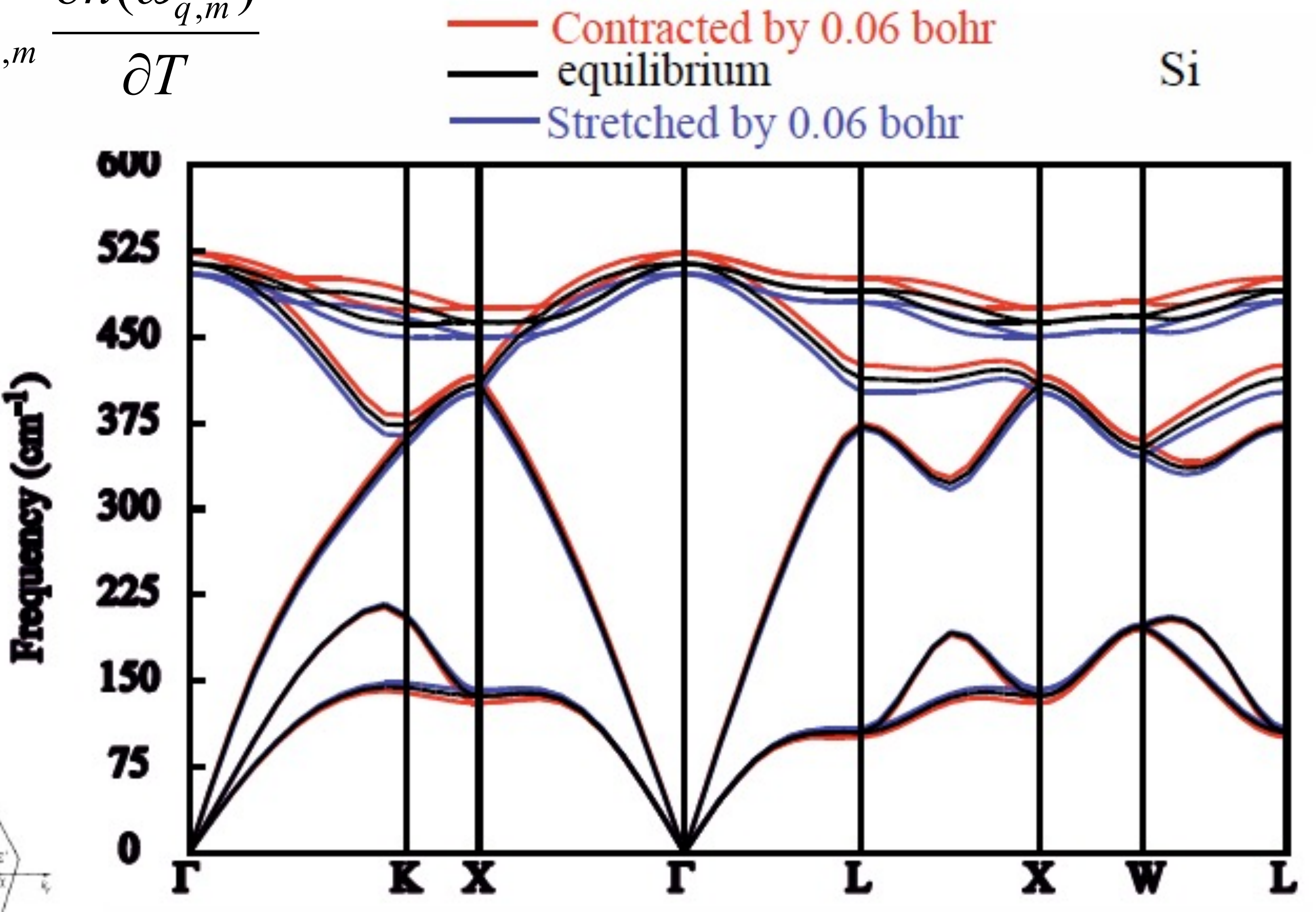
$$C_V = 3n_{at}N\ k_B \int_0^{\omega_{\max}} \left(\frac{\omega}{2k_B T}\right)^2 \operatorname{csch}^2\left(\frac{\omega}{2k_B T}\right) g(\omega)d\omega$$

Ab initio thermal expansion

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

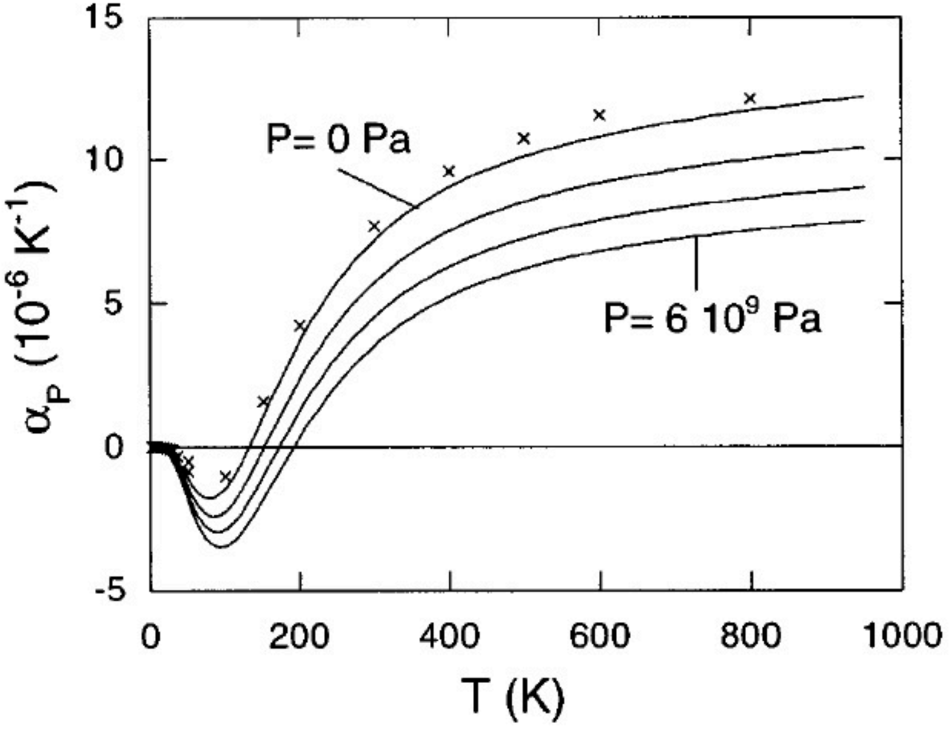
$$\gamma_{m,\vec{q}} = -\frac{\partial(\ln\omega_{m,\vec{q}})}{\partial(\ln V)}$$

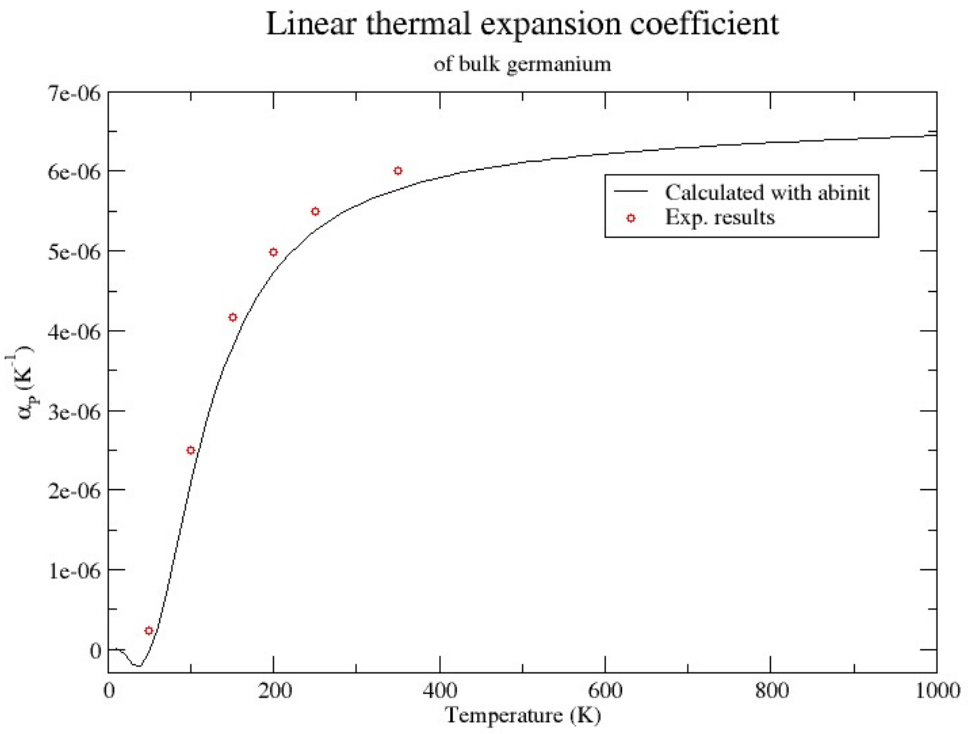
Alternative path : minimisation of free energy



Ab initio thermal expansion

Linear thermal expansion coefficient
of bulk silicon



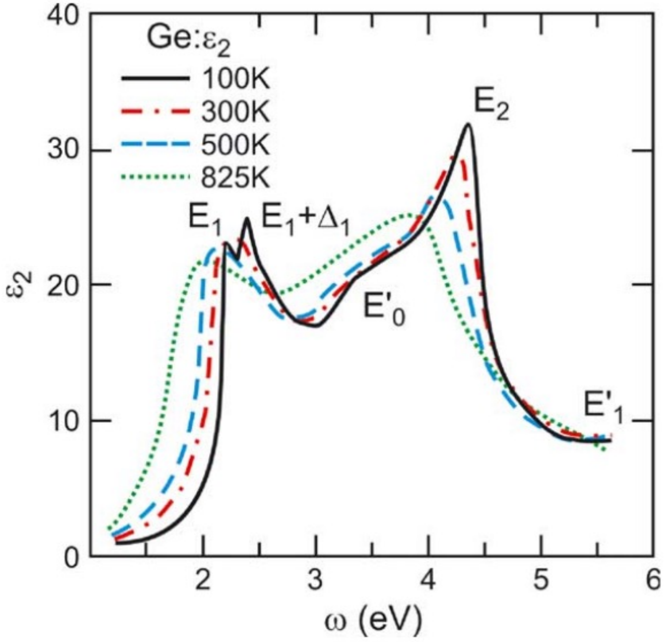


G.-M. Rignanese, J.-P. Michenaud and XG
Phys. Rev. B 53, 4488 (1996)

Electron-phonon effects on electronic energies

T-dependence of electronic/optical properties

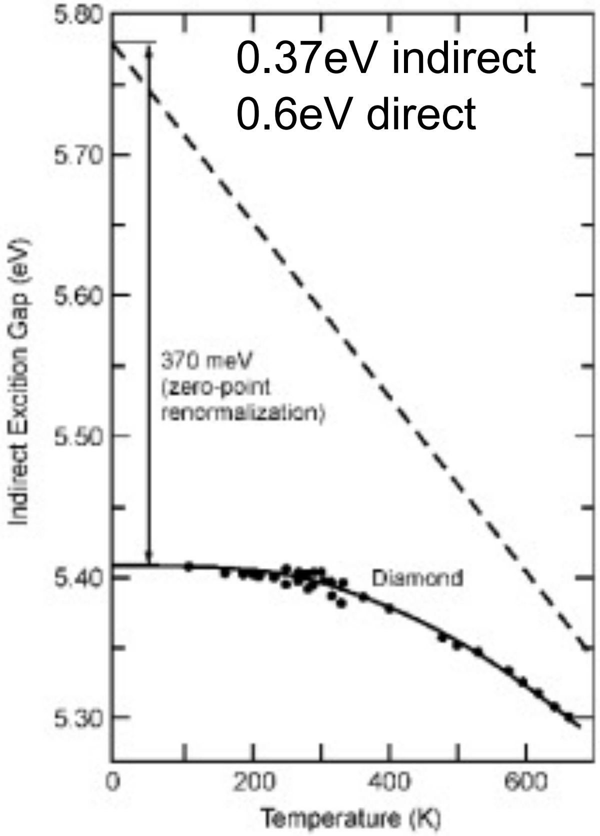
- peaks shift in energy
- peaks broaden with increasing temperature : decreased electron lifetime



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

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

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



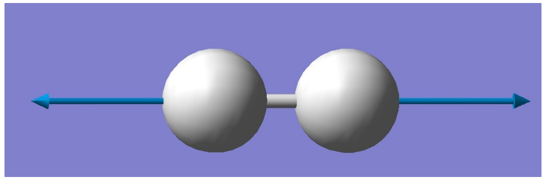
0.37eV indirect
0.6eV direct

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

Phonon population effects in solids

Concepts …
... can be explained with diatomic molecules

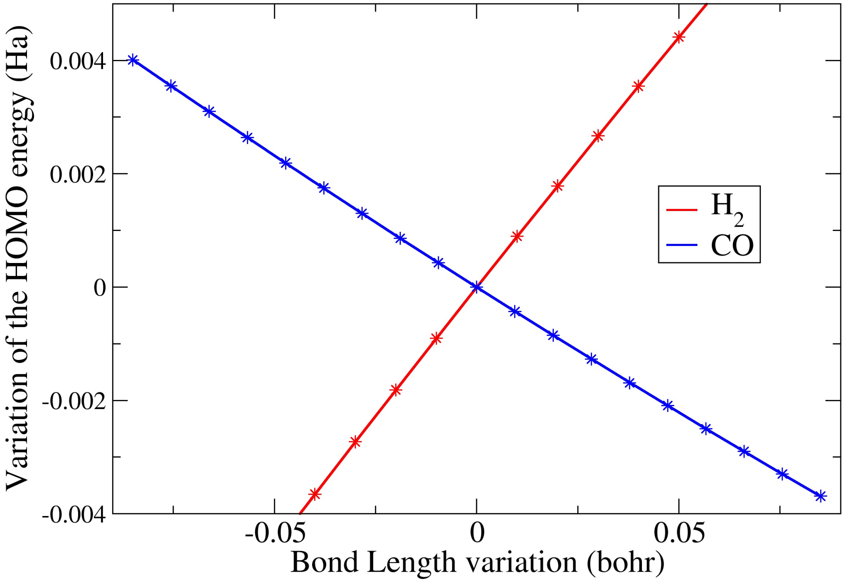
Simple :
-discrete levels, simple molecular orbitals
-only one relevant vibration mode.



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

Average eigenenergies in the BO approx.

Variation of the HOMO energy wrt bond length



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

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

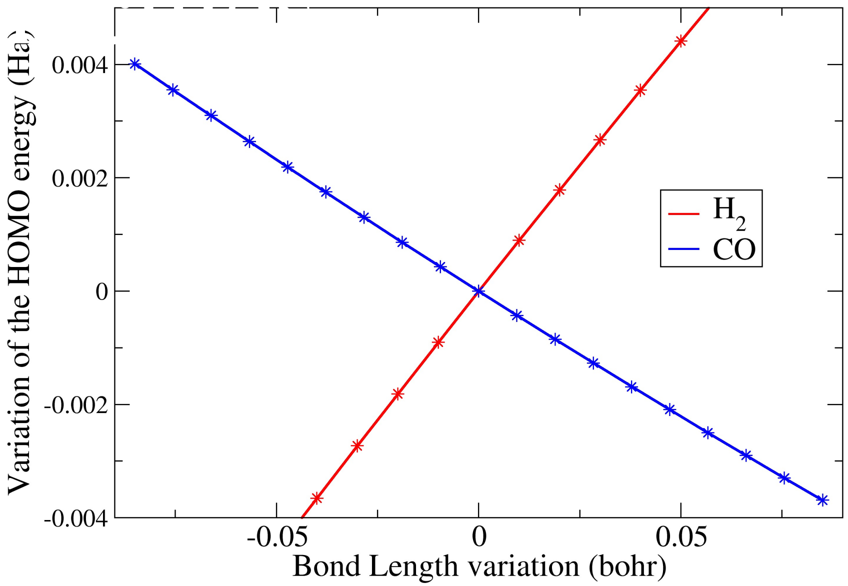
$$\varepsilon_n(T) = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} \varepsilon_n(\Delta R(t))\, dt$$

Pros : well-defined procedure ; compatible with current implementations and computing capabilities ; $\varepsilon_n(\Delta R(t))$ from DFT or GW ; anharmonicities

Cons : if classical dynamics => no zero-point motion ; adiabatic (vibrations, but no exchange of energy !) ; hard for solids (supercell) also supercell mix eigenstates, need unfolding

Average eigenenergies in the BO approx.

Variation of the HOMO energy wrt bond length



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

(2) Thermal average with accurate quantum vibrational states,

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

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

Cons : hard to sample more than a few vibrational degrees of freedom ;
adiabatic (vibrations, but no exchange of energy !); hard for solids (supercell), also supercell mix eigenstates, need unfolding

Alternative: one very large supercell with prepared atomic displacements

Average eigenenergies : BO and harmonic approx.

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

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

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

T-dependent phonon occupation number (Bose-Einstein)

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

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

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

Cons : hard for solids (supercells) ; no anharmonicities ; adiabatic (vibrations, but no exchange of energy !); supercell mix eigenstates, need unfolding

Allen-Heine-Cardona (AHC) formalism

Allen + Heine, *J. Phys. C* **9, 2305 (1976).** *Allen + Cardona*, *Phys. Rev. B* **24, 7479 (1981) ; 27, 4760 (1983).**

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

* Formulas for solids (phonons have crystalline momentum)

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

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

occupation number from Bose-Einstein statistics

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

Electron-phonon coupling energy (EPCE)

"Phonon mode factor"

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

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

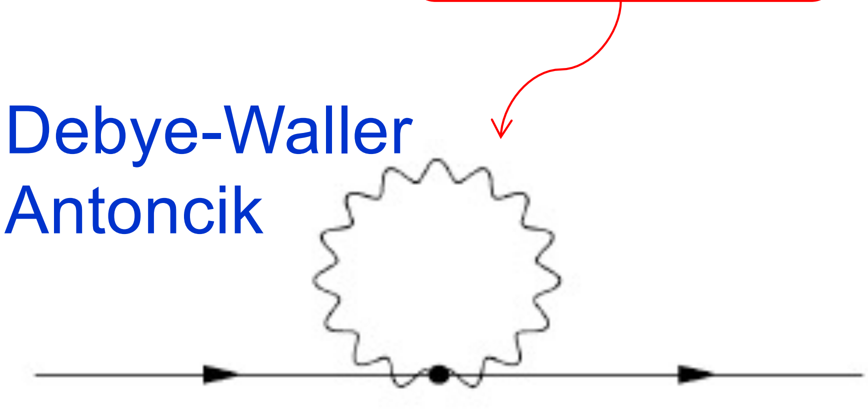
$$\varepsilon_{\vec{k}n} = \left\langle \phi_{\vec{k}n} \middle| \hat{H}_{\vec{k}} \middle| \phi_{\vec{k}n} \right\rangle \qquad \hat{H} = \hat{T} + \hat{V}_{\text{nucl}} + \int \frac{\rho(r')}{|r-r'|} dr' + \frac{dE_{xc}}{d\rho(r)}$$

Hellman-Feynman theorem : $\varepsilon^{(1)}_{\vec{k}n} = \left\langle \phi^{(0)}_{\vec{k}n} \middle| \hat{H}^{(1)}_{\vec{k}} \middle| \phi^{(0)}_{\vec{k}n} \right\rangle$

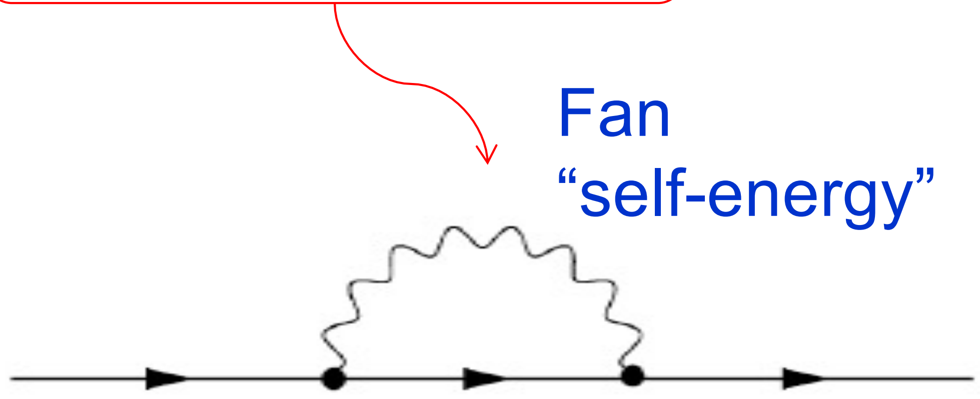
One more derivative :

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

Debye-Waller
Antoncik



Fan
“self-energy”



Non-adiabatic AHC theory

Beyond adiabatic perturbation theory … Many-body perturbation theory !

Fan self-energy (also called Migdal self-energy) :

$$\Sigma^{Fan}_{\lambda\lambda'}(\omega) = \sum_{\nu} \frac{1}{2\omega_\nu} \sum_{\lambda''} \langle\psi_\lambda|\, H^{(1)}_{\nu}\, |\psi_{\lambda''}\rangle \langle\psi_{\lambda''}|\, H^{(1)*}_{\nu}\, |\psi_{\lambda'}\rangle$$

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

Different levels :

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

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

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

Or even spectral functions

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

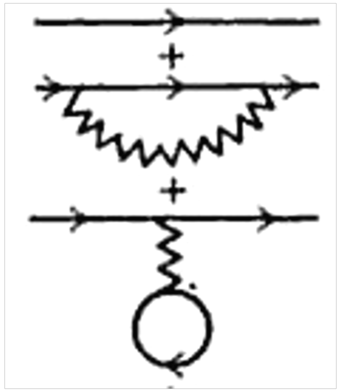
S. Poncé, Y. Gillet, J. Laflamme Janssen, A. Marini,
M. Verstraete & XG, J. Chem. Phys. 143, 102813 (2015)

Reminder : Many-body perturbation theory

Historically older than DFT (from the 40-50’s) !
Big names : Feynman, Schwinger, Hubbard, Hedin, Lundqvist
Heavy formalism ! Not amenable to 1-hour presentation …
Diagrammatic representation of perturbative terms
Based on Green’s functions = propagators

1-particle

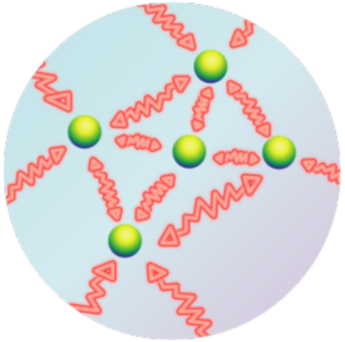
$G(\mathbf{r},t;\mathbf{r}',t')$

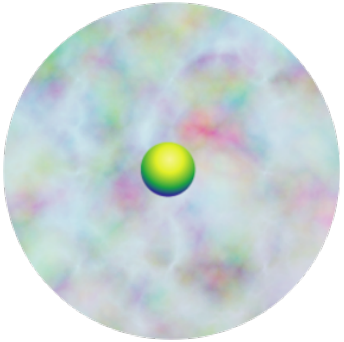


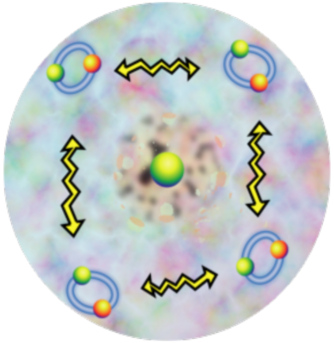
Propagation without Coulomb interactions
+
Propagation with polarization of medium
+
Propagation with mean-field electrostatic interaction with other electrons

Skoltech

Reminder : GW approximation


Wavefunctions


DFT


GW

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

DFT

$$\left(-\frac{1}{2}\nabla^2+V_{ext}(\mathbf{r})+V_H(\mathbf{r})\right)\psi_i(\mathbf{r})+\int\boxed{\Sigma(\mathbf{r},\mathbf{r}';\varepsilon_i^{QP})}\psi_i(\mathbf{r}')d\mathbf{r}'=\varepsilon_i^{QP}\psi_i(\mathbf{r})$$

$$\boxed{\Sigma(\mathbf{r},\mathbf{r}';\omega)}=\lim_{\delta\to 0+}\frac{i}{2\pi}\int d\omega' e^{i\omega'\delta}\boxed{G}(\mathbf{r},\mathbf{r}';\omega+\omega')\boxed{W}(\mathbf{r},\mathbf{r}';\omega')$$

GW

Self energy

Green’s function

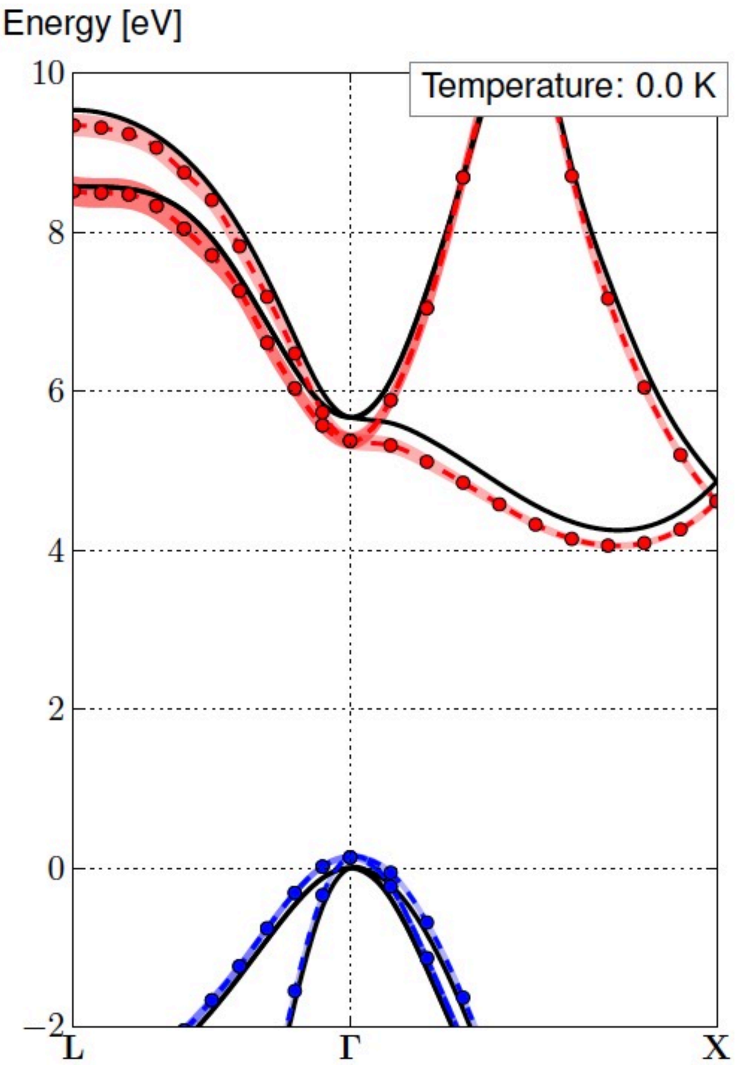
Screened interaction

Reminder : Linearized quasi-particle equation

$$\boxed{\varepsilon_i^{QP} = \varepsilon_i^{KS} + Z_i \left\langle \psi_i^{KS} \middle| \Sigma(\varepsilon_i^{KS}) - V_{xc} \middle| \psi_i^{KS} \right\rangle}$$

with $Z_i^{-1} = 1 - \left\langle \psi_i^{KS} \middle| \left.\frac{\partial \Sigma}{\partial \varepsilon}\right|_{\varepsilon_i^{KS}} \middle| \psi_i^{KS} \right\rangle$

DFT T-dependent band structure

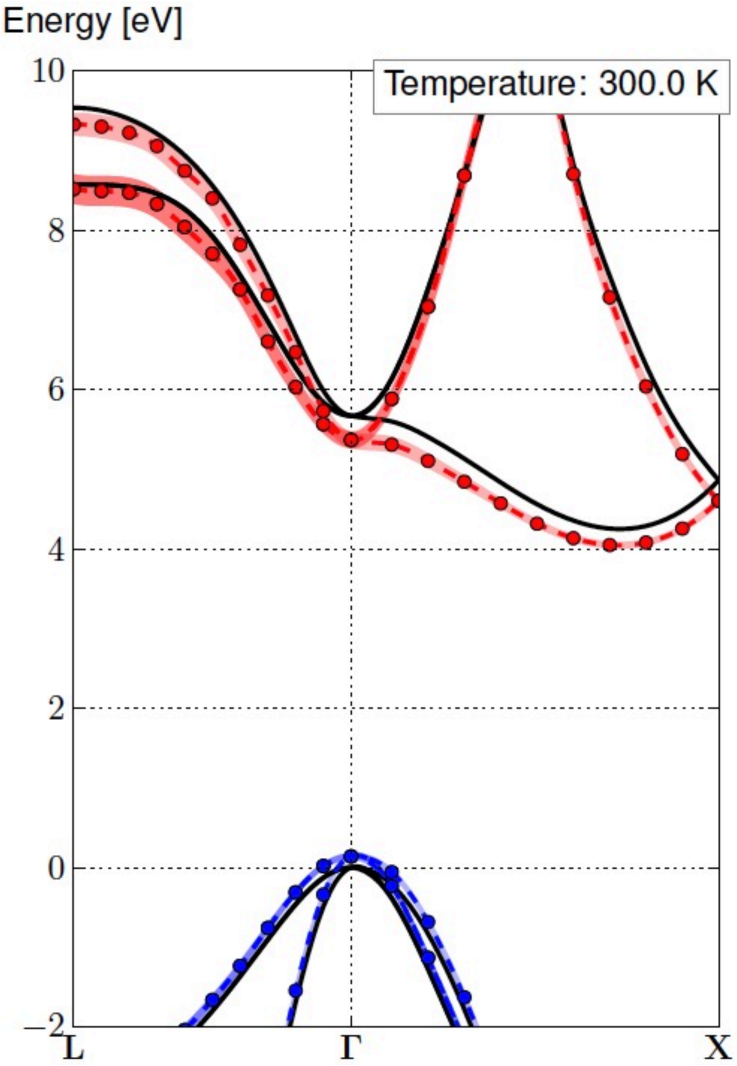


Diamond 0 Kelvin
(incl. Zero-point motion)

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

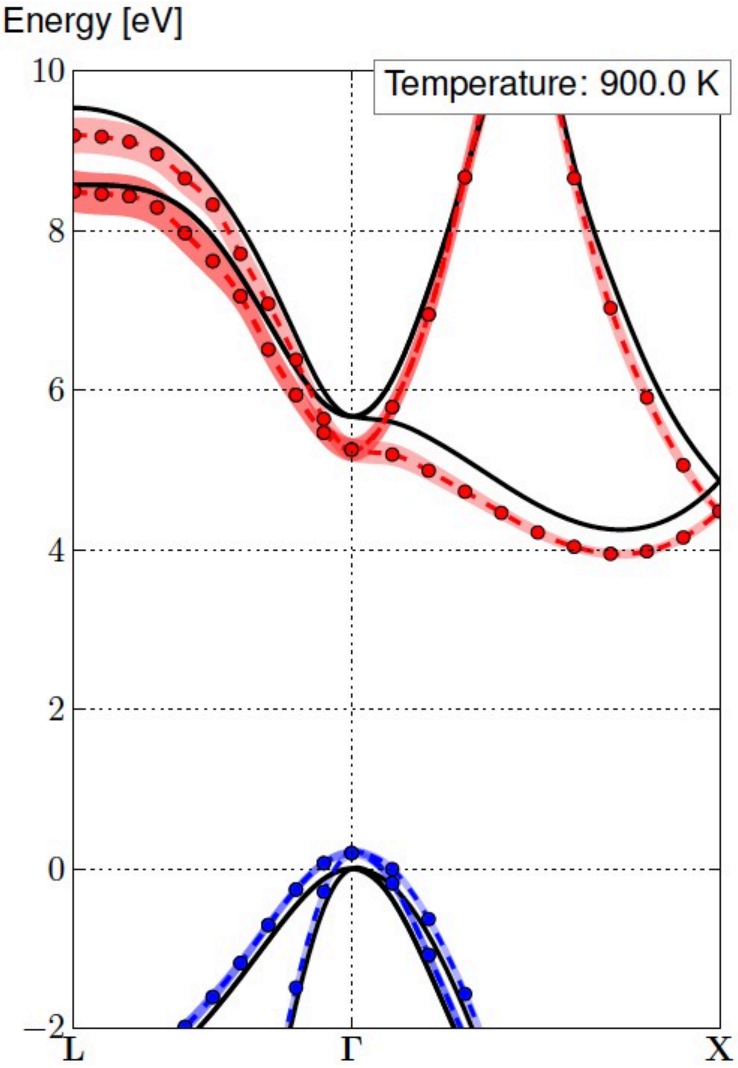


Diamond 300 Kelvin

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

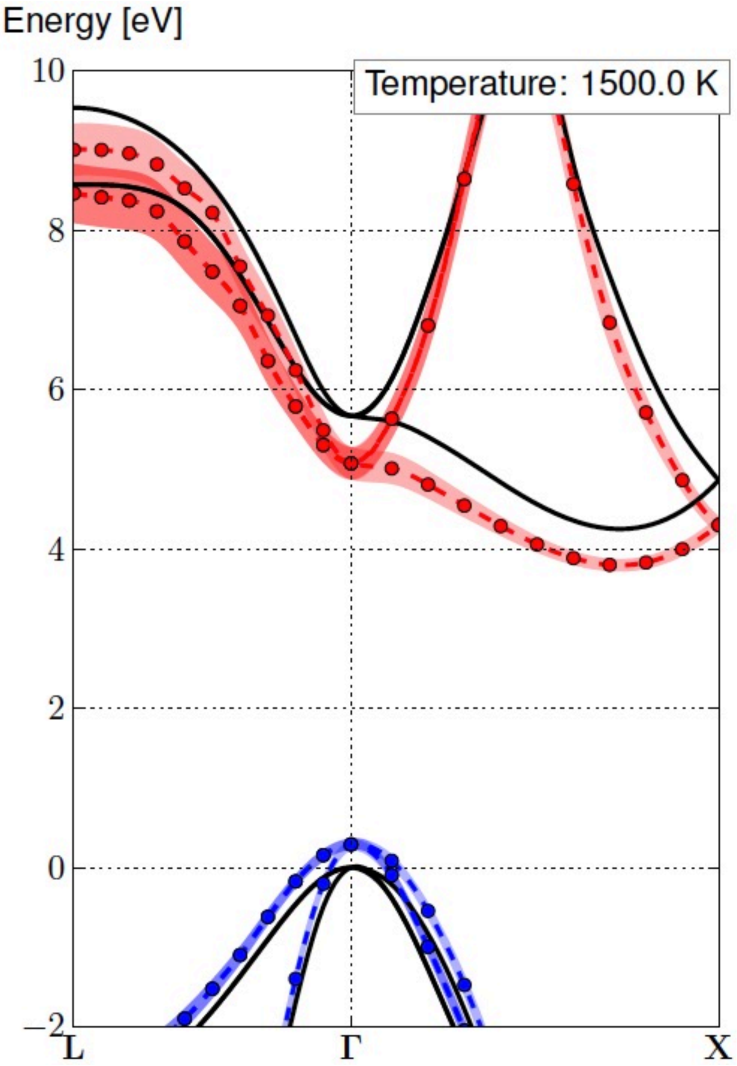


Diamond 900 Kelvin

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

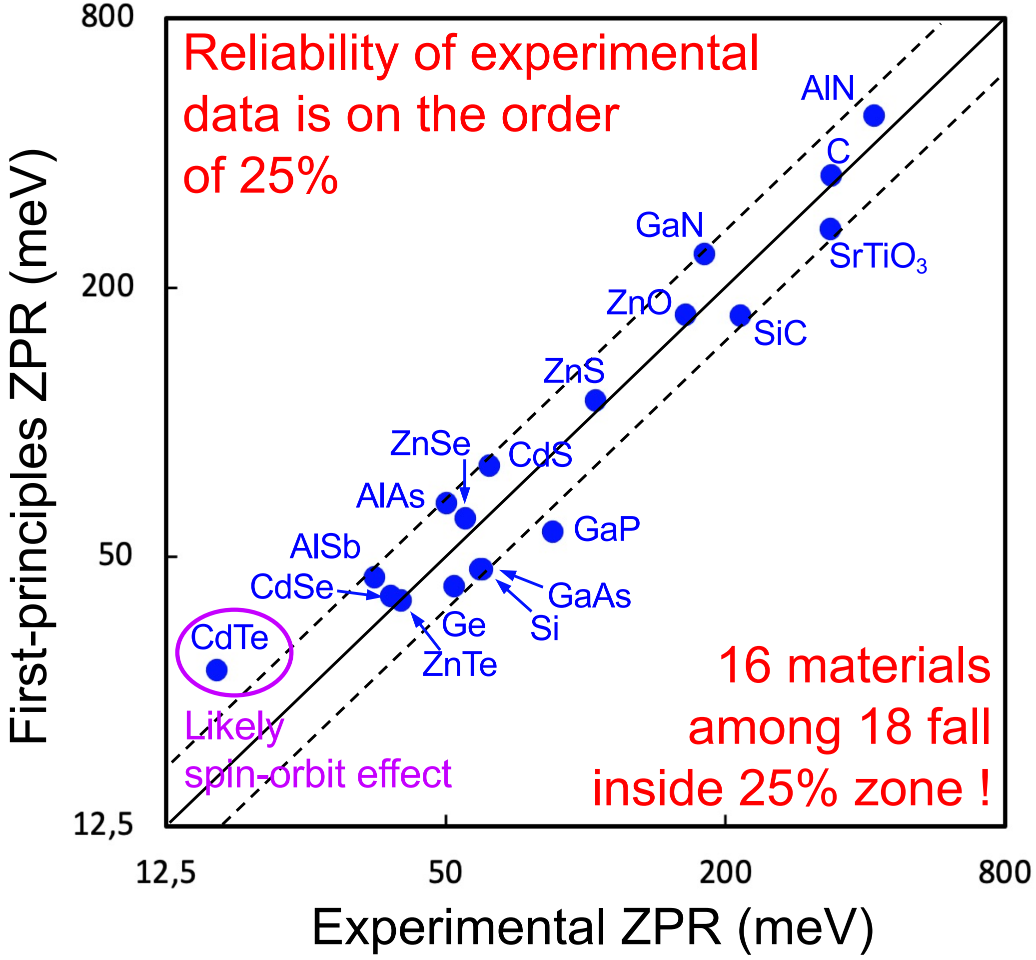


Diamond 1500 Kelvin

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)

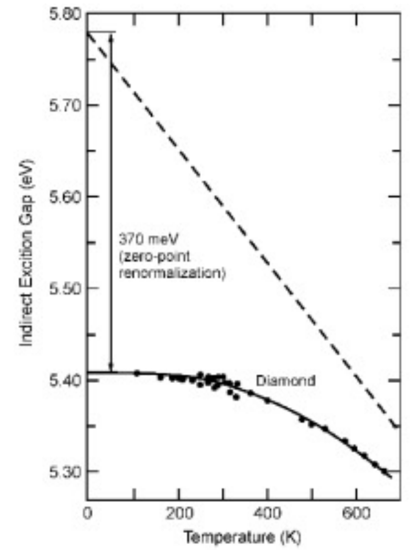
Non-adiabatic AHC theory vs experiment

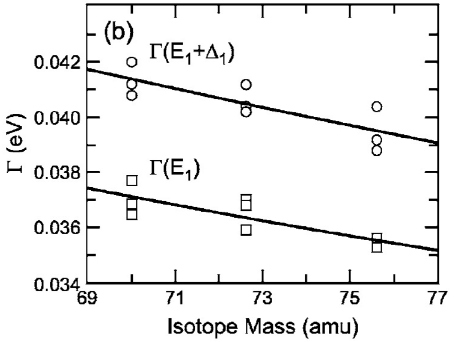


Reliability of experimental data is on the order of 25%

16 materials among 18 fall inside 25% zone !

ZPR of the band gap
Two different exp techniques



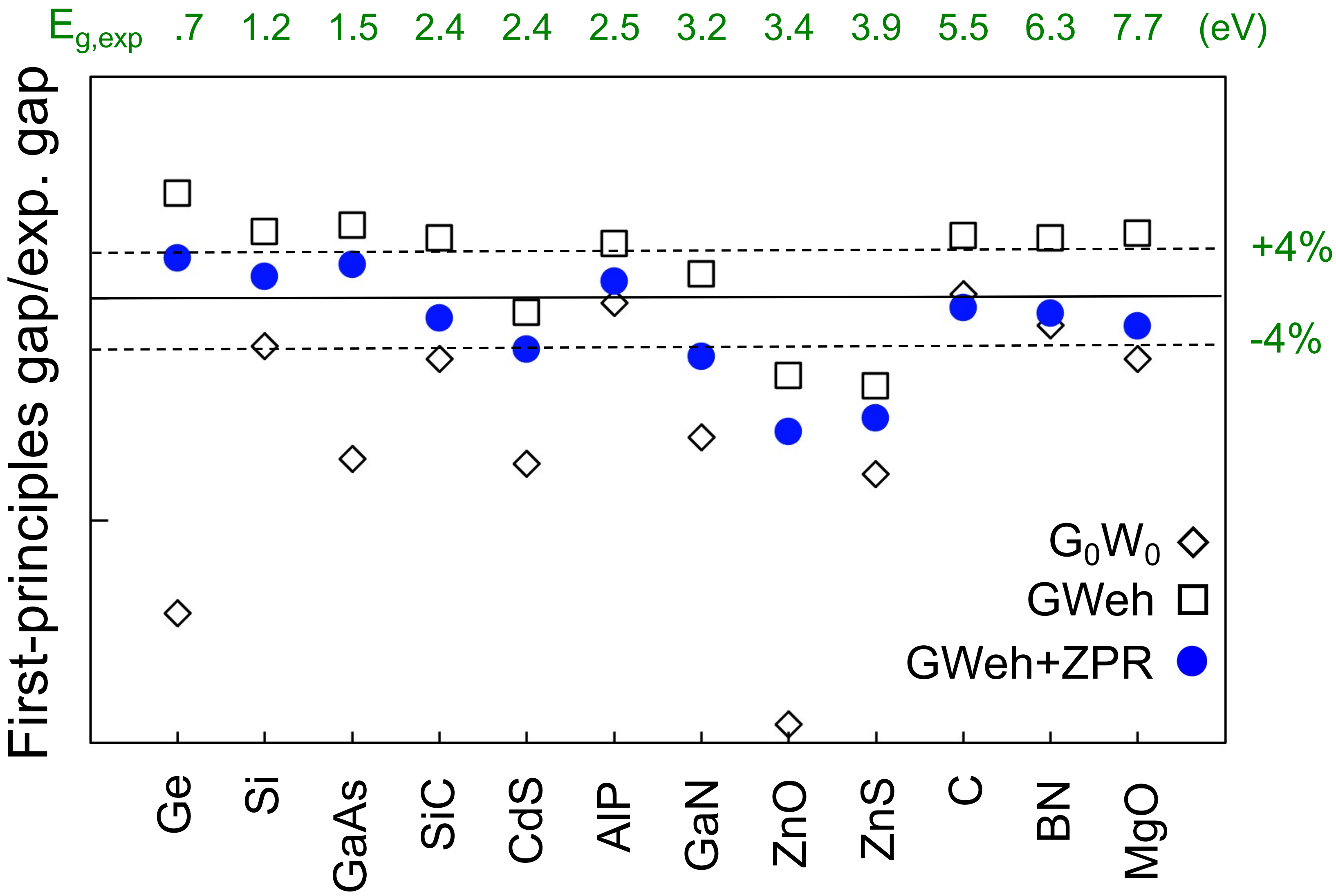


$$E_M = E_\infty + B M^{-1/2}$$

Miglio, Brousseau, Godbout, Côté, Antonius, Chan, Louie,
Giantomassi and XG, *npj Comput Materials 6, 167,2020*

Cardona & Thewalt, *Rev. Mod. Phys.*, **77**, 1173 (2005)

Band gap : theory vs experiment



Miglio, Brousseau, Godbout, Côté, Antonius, Chan, Louie, Giantomassi and XG, *npj Comput Materials 6, 167,2020*

Electron-phonon effects on transport properties

Transport properties

For a metal, Ohm's law : $\mathbf{j} = \sigma \mathbf{E}$

How to compute the conductivity tensor σ ?

Conductivity in doped semiconductors.

Suppose we now the density of carriers (n_e or n_h).

$$\sigma = n_e \mu_e + n_h \mu_h$$

How to compute the mobility tensors μ_e and μ_h ?

Seebeck coefficient in thermoelectrics.

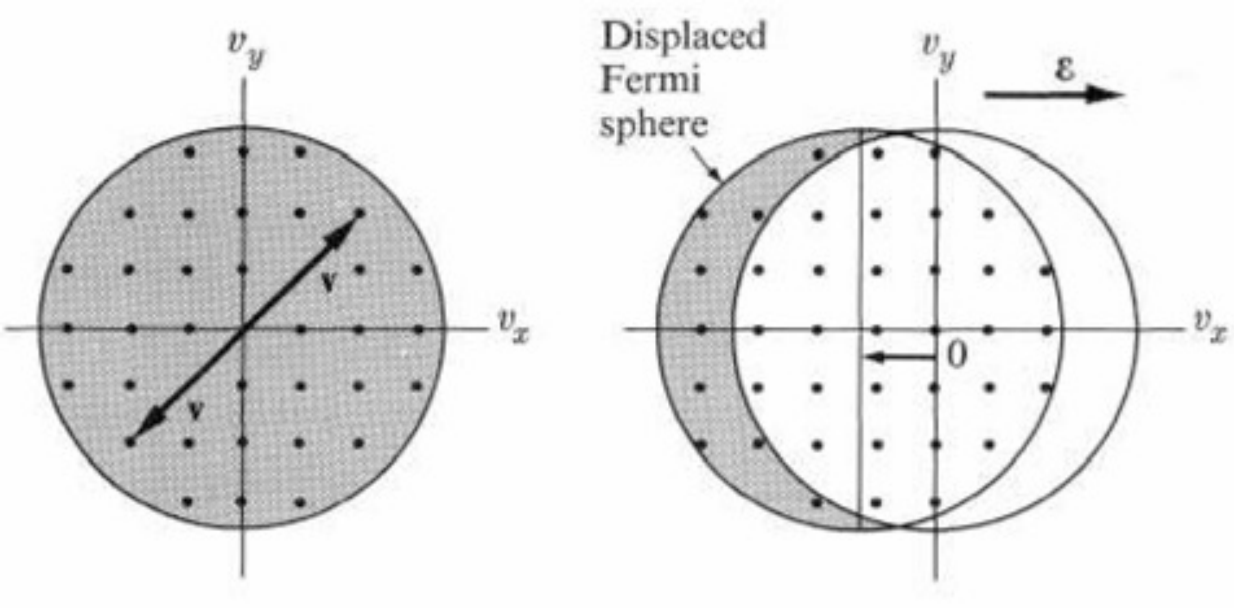
A difference of temperature creates a difference of electric potential.

$$\Delta V = S.\Delta T$$

Superconducting critical temperature T_c

Resistivity of a normal metal drops to 0 below the critical temperature

Effect of a steady electric field on a metal



Fermi surface shift due to electric field

Group velocity of an electronic state : $v_{n\mathbf{k},\alpha} = \frac{1}{\hbar}\frac{\partial \varepsilon_{n\mathbf{k}}}{\partial k_\alpha} = \left\langle u_{n\mathbf{k}} \middle| \frac{\hat{p}_\alpha}{m_e} \middle| u_{n\mathbf{k}} \right\rangle$

Without electric field: cancellation of velocities between opposite momentum electrons => no net current
With electric field: unbalance => net current

Boltzmann transport equation

Ensemble of particles distributed in space and evolving in time.

Distribution function $f(\mathbf{r},\mathbf{p},t)$

How this distribution evolve with time ?

$$\frac{df}{dt} = \left(\frac{\partial f}{\partial t}\right)_{force} + \left(\frac{\partial f}{\partial t}\right)_{diffusion} + \left(\frac{\partial f}{\partial t}\right)_{collisions}$$

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m}.\nabla f + \mathbf{F}.\frac{\partial f}{\partial \mathbf{p}} = \left(\frac{\partial f}{\partial t}\right)_{collisions}$$

In steady state, and with homogeneous medium

$$\boxed{\mathbf{F}\frac{\partial f}{\partial \mathbf{p}} = \left(\frac{\partial f}{\partial t}\right)_{collisions}}$$

Electronic Boltzmann transport equation

Hypotheses : steady state, homogeneous medium, small electric field, electron-phonon collisions.

$f_{n\mathbf{k}}$ occupation number for state $n\mathbf{k}$

$$\mathbf{F}\frac{\partial f}{\partial \mathbf{p}} = \left(\frac{\partial f}{\partial t}\right)_{collisions}$$ becomes

$$-ev_{n\mathbf{k},\beta}\frac{\partial f^0_{n\mathbf{k}}}{\partial \varepsilon_{n\mathbf{k}}} = \sum_m \int \frac{d\mathbf{q}}{\Omega_{BZ}}\left[\tau^{-1}_{m\mathbf{k+q}\rightarrow n\mathbf{k}}\frac{\partial f_{m\mathbf{k+q}}}{\partial E} - \tau^{-1}_{n\mathbf{k}\rightarrow m\mathbf{k+q}}\frac{\partial f_{n\mathbf{k}}}{\partial E}\right]$$

with the Fermi-Dirac distribution $f^0_{n\mathbf{k}} = \dfrac{1}{\mathrm{e}^{\left(\varepsilon_{n\mathbf{k}}-\varepsilon_F\right)/k_BT}+1}$

and $\tau^{-1}_{n\mathbf{k}\rightarrow m\mathbf{k+q}}$ is the electron-phonon partial decay rate

Electronic partial decay rate

Electronic partial decay rate due to electron-phonon interaction

$$\tau^{-1}_{n\mathbf{k}\to m\mathbf{k+q}} = \sum_{\nu} \frac{2\pi}{\hbar}\left|g_{mnj}(\mathbf{k},\mathbf{q})\right|^2$$

$$\left[\left(n_{j\mathbf{q}} + f^{0}_{m\mathbf{k+q}}\right)\delta\left(\Delta\varepsilon^{nm}_{\mathbf{k,k+q}} + \hbar\omega_{j\mathbf{q}}\right) + \left(n_{j\mathbf{q}} + 1 - f^{0}_{m\mathbf{k+q}}\right)\delta\left(\Delta\varepsilon^{nm}_{\mathbf{k,k+q}} - \hbar\omega_{j\mathbf{q}}\right)\right]$$

with the electron-phonon matrix element obtained from DFPT

$$g_{mnj}(\mathbf{k},\mathbf{q}) = \left\langle u_{m\mathbf{k+q}} \middle| \Delta_{\mathbf{q}\nu} V_{KS} \middle| u_{n\mathbf{k}} \right\rangle$$

$$\Delta_{j\mathbf{q}} V_{KS} = \frac{1}{\sqrt{2\omega_{j\mathbf{q}}}} \sum_{p\kappa\alpha} \frac{\partial V_{KS}}{\partial R_{\kappa\alpha}} \frac{\xi_{\kappa\alpha,j}(\mathbf{q})}{\sqrt{M_{\kappa}}} e^{i\mathbf{q}\mathbf{R}_p}$$

This is connected to the imaginary part of the Fan self-energy.

Imaginary part of the Fan self-energy

Fan self-energy (also called Migdal self-energy) :

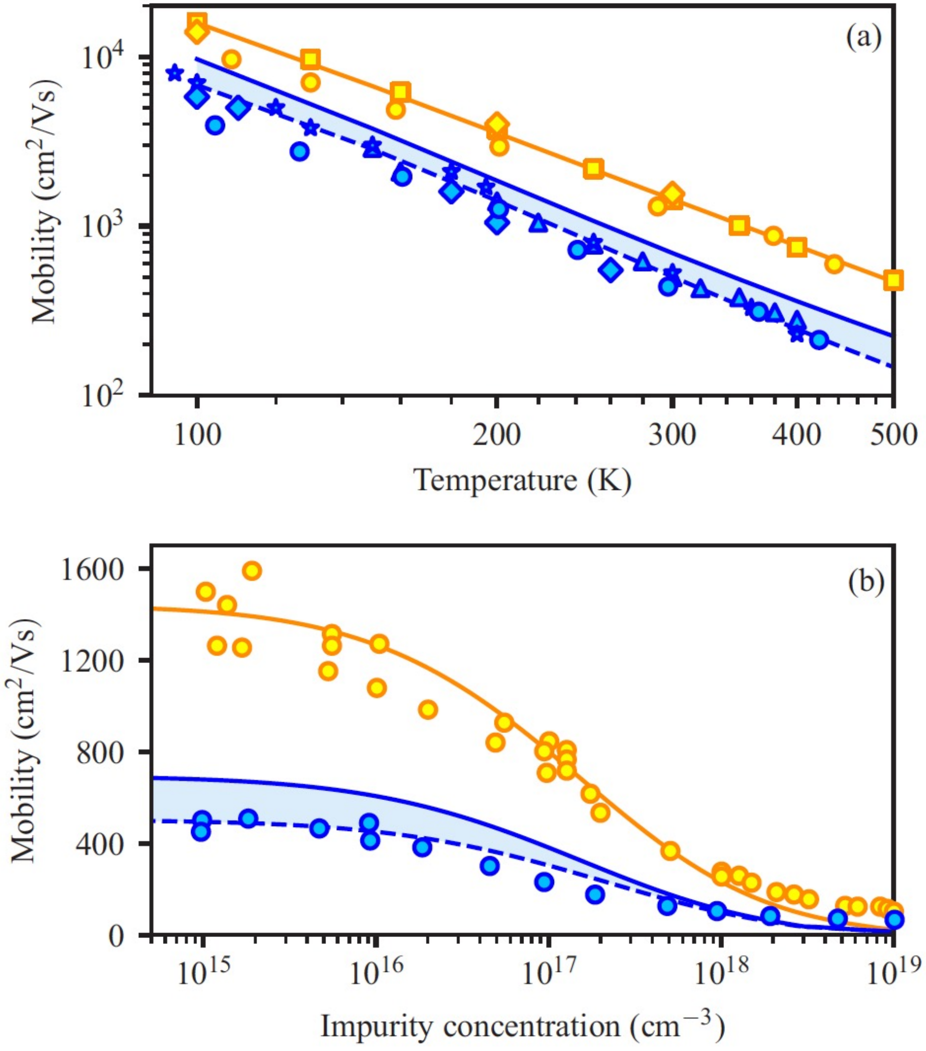
$$\Sigma^{Fan}_{\lambda\lambda'}(\omega) = \sum_{\nu} \frac{1}{2\omega_\nu} \sum_{\lambda''} \langle\psi_\lambda|\, H_\nu^{(1)} \,|\psi_{\lambda''}\rangle \langle\psi_{\lambda''}|\, H_\nu^{(1)*} \,|\psi_{\lambda'}\rangle \left[\frac{n_\nu(T) + f_{\lambda''}(T)}{\omega - \varepsilon^0_{\lambda''} \boxed{+\,\omega_\nu}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

where

$$\boxed{\lim_{\substack{\delta^+\to 0\\ \delta^+>0}} \frac{1}{\omega_{mn} - \omega - i\delta^+} = \frac{1}{\omega_{mn} - \omega} + i\pi\delta(\omega_{mn} - \omega)}$$

$$\boxed{\lim_{\substack{\delta^+\to 0\\ \delta^+>0}} \frac{1}{\omega_{mn} + \omega + i\delta^+} = \frac{1}{\omega_{mn} + \omega} - i\pi\delta(\omega_{mn} + \omega)}$$

Mobility in Silicon

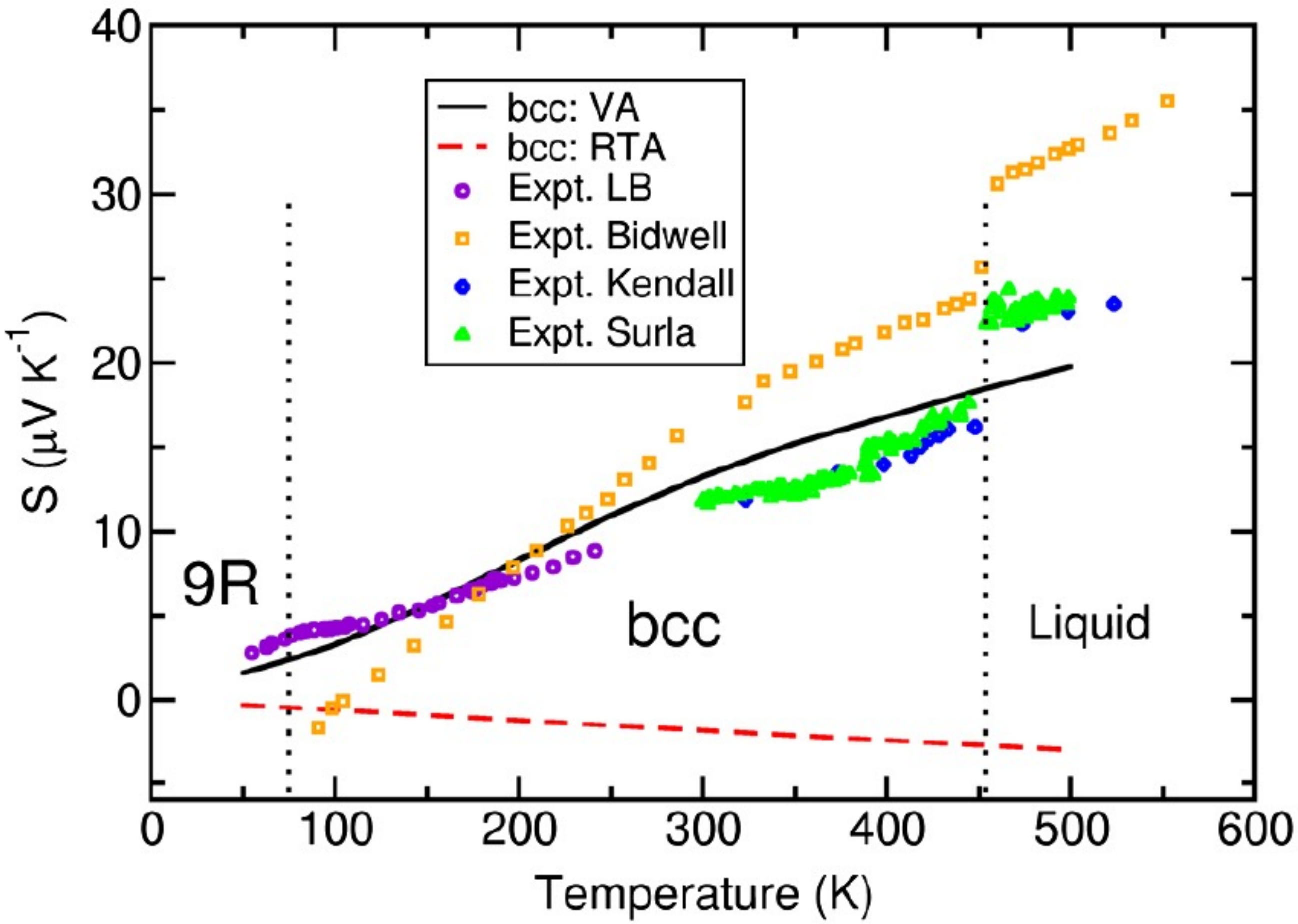


Orange : electrons
Blue : holes

Lines : Theory
Signs : Experiment

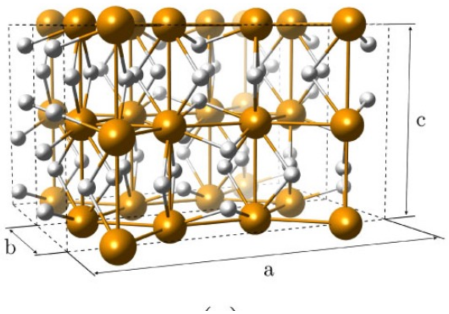
S. Poncé, E.R. Margine and F. Giustino, Phys. Rev. B 97, 121201(R) (2018)

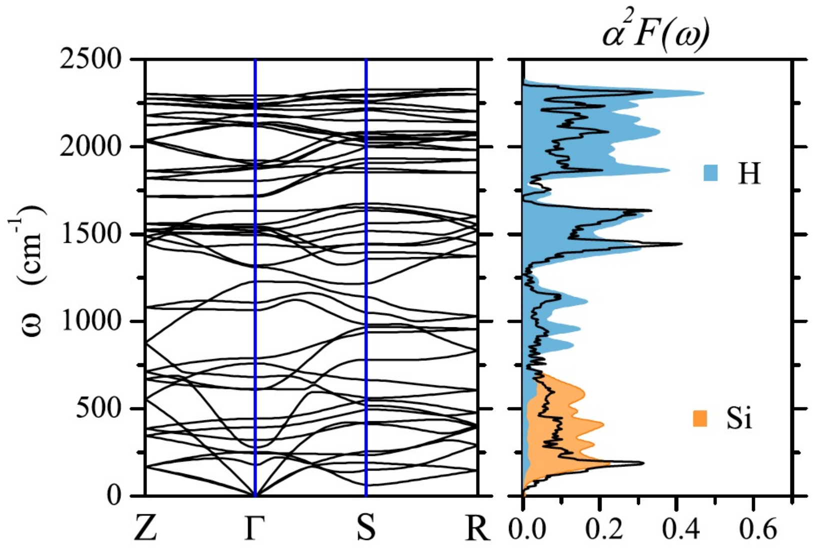
Seebeck coefficient of Li



Bin Xu and M. Verstraete, Phys. Rev. Lett. 112, 196693 (2014)

Pressure-dependent superconducting temperature of disilane





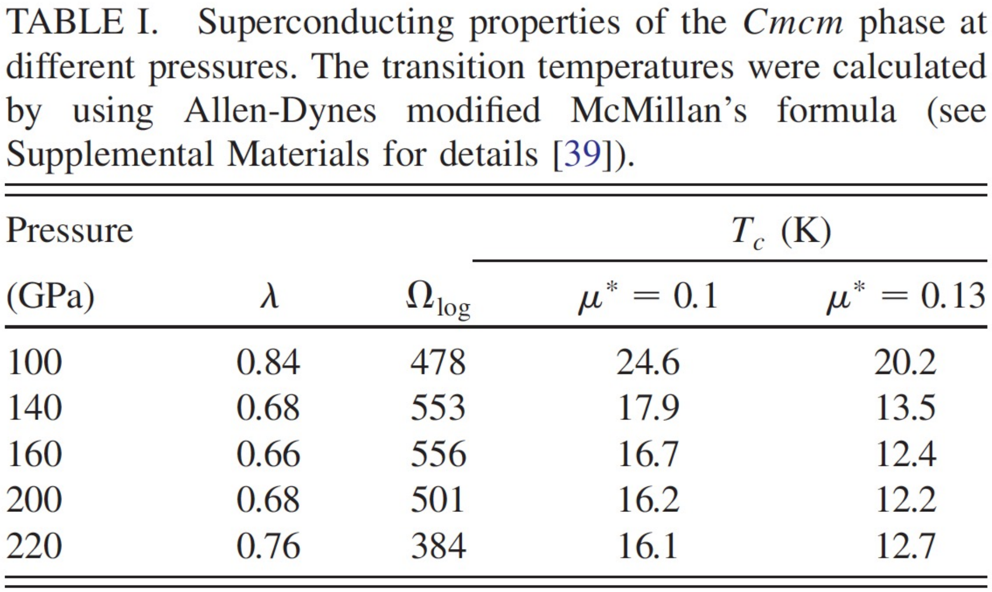


TABLE I. Superconducting properties of the *Cmcm* phase at different pressures. The transition temperatures were calculated by using Allen-Dynes modified McMillan's formula (see Supplemental Materials for details [39]).

Pressure (GPa)	λ	$\Omega_{\log}$	T_c (K) $\mu^* = 0.1$	T_c (K) $\mu^* = 0.13$
100	0.84	478	24.6	20.2
140	0.68	553	17.9	13.5
160	0.66	556	16.7	12.4
200	0.68	501	16.2	12.2
220	0.76	384	16.1	12.7

J. Flores-Livas et al, Phys. Rev. Lett. 108, 117004 (2012)

Supplementary slides

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 ...

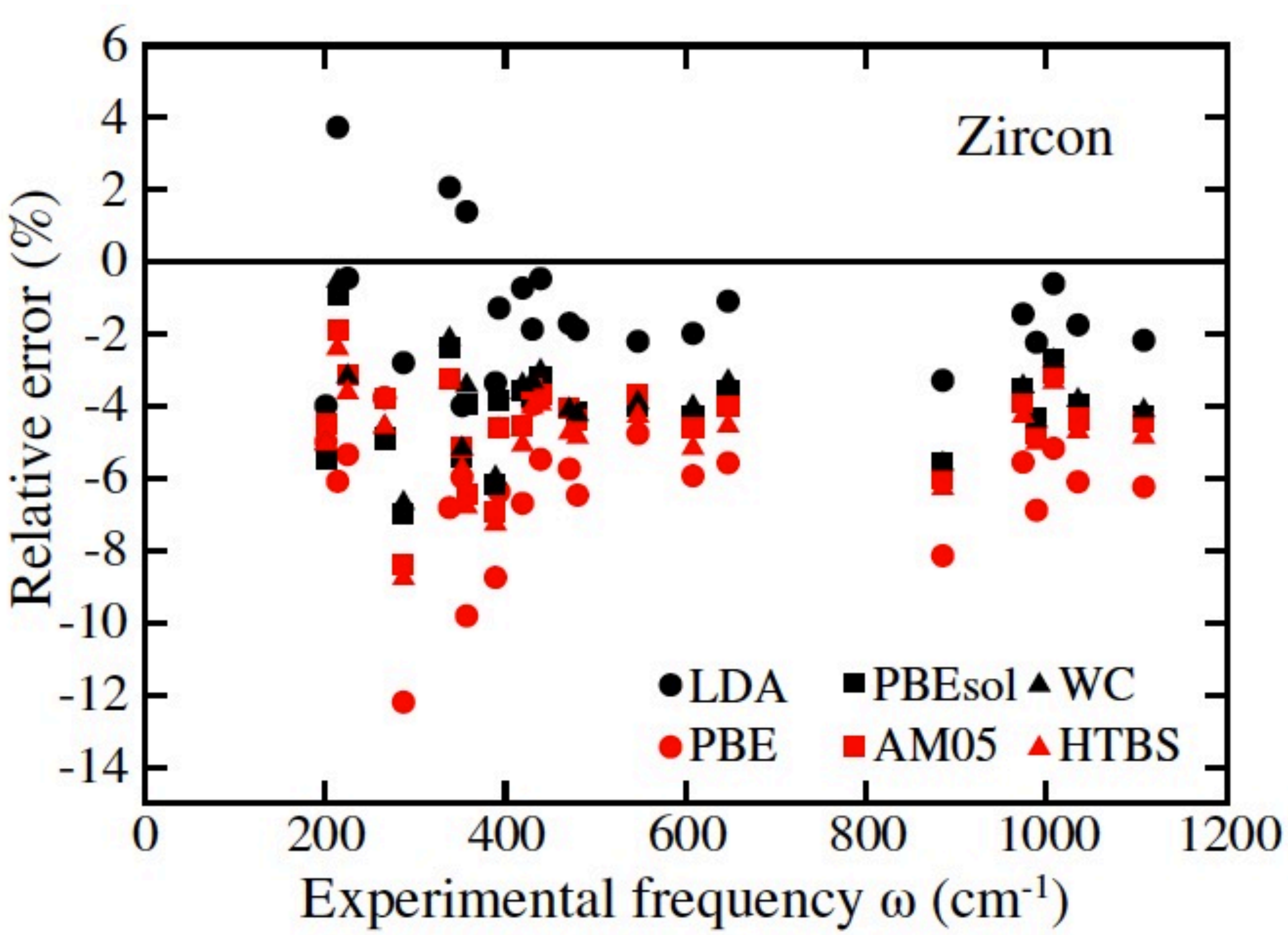
Effect of the choice of XC flavor on
phonon frequencies, dielectric tensor, Born effective charges ?

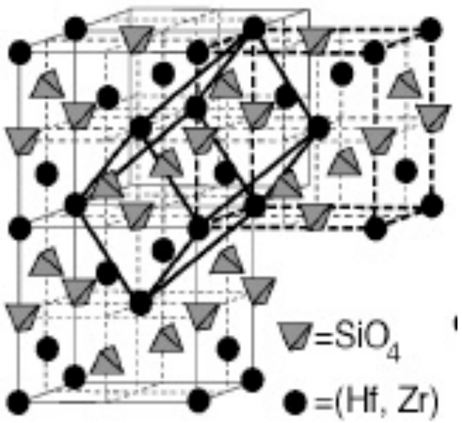
Exhaustive study :
L. He et al, Phys. Rev. B89, 064305 (2014)

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 ...

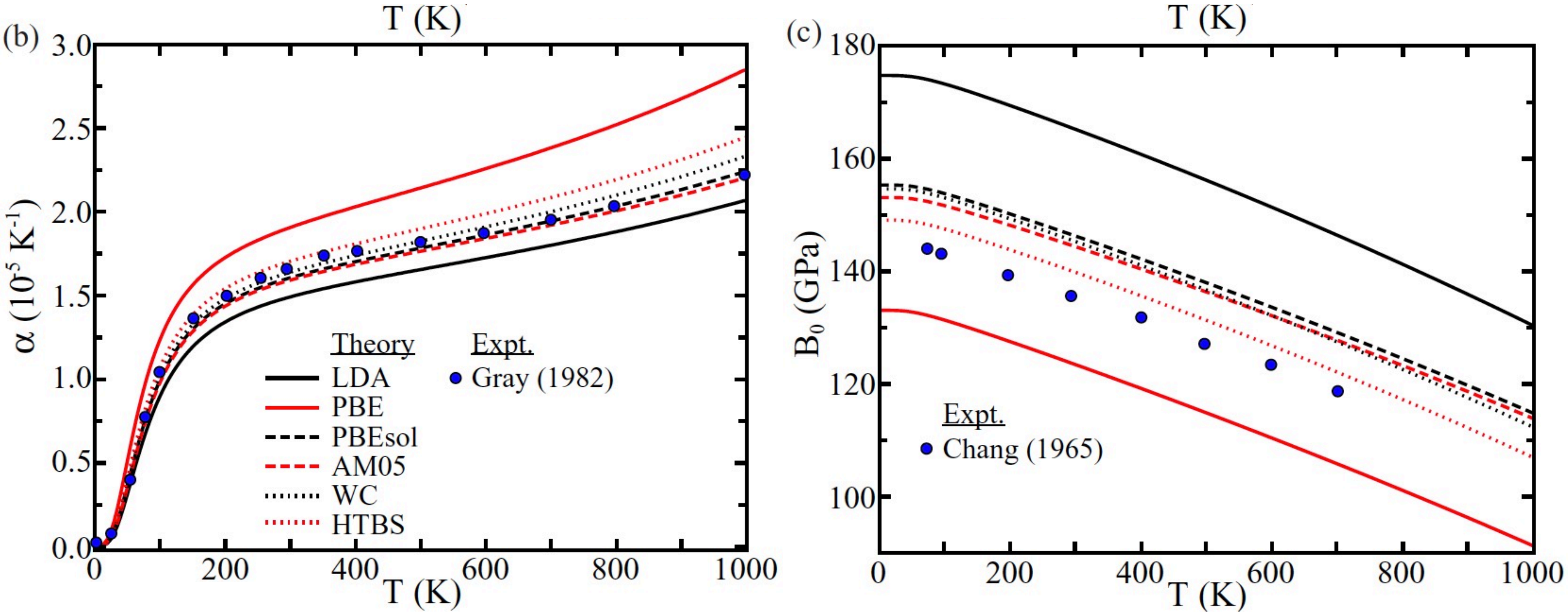
Gamma phonons of zircon





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)

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

Starting from

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

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

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

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

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

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

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

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:

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

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

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

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 :

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

$$=> \quad (\hat{H}^{(0)} - \varepsilon^{(0)}) |\psi^{(1)}\rangle + (\hat{H}^{(1)} - \varepsilon^{(1)}) |\psi^{(0)}\rangle = 0$$

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

Density functional perturbation theory

Without going into the formulas, there exist expressions :

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

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

$E^{(2)}\left\{\psi_\alpha^{(0)};\psi_\alpha^{(1)}\right\}$ 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 $n^{(1)}, H^{(1)}, \varepsilon_\alpha^{(1)}$

knowledge of $\left\{\psi_\alpha^{(0)};\psi_\alpha^{(1)};\psi_\alpha^{(2)}\right\}$ allows one to obtain $n^{(2)}, H^{(2)}, \boxed{\varepsilon_\alpha^{(2)}}$

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

Divide and conquer …

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

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

Constant volume

Constant temperature

$$= \alpha_P(T)$$

Thermal expansion coefficient

Contribution of the phonon population, i.e. the vibrations of the atomic nuclei, at constant volume

\+

Contribution of the thermal expansion, i.e. the change in volume of the sample, at constant temperature