Density Functional Perturbation Theory

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Properties of solids from DFT

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

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

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

“Classic” References :

The Kohn-Sham orbitals and eigenvalues

Non-interacting electrons in the Kohn-Sham potential:

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

Density

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

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

Hartree potential   Exchange-correlation potential

To be solved self-consistently!

Note. At self-consistency, supposing XC functional to be exact:
- the KS density = the exact density,
- the KS electronic energy = the exact electronic energy,
- but KS wavefunctions and eigenenergies correspond to a fictitious set of independent electrons, so they do not correspond to any exact quantity.
Minimum principle for the energy

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

\[ E_{KS} \left[ \{ \psi_i \} \right] = \sum_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{ext}(r)n(r)dr + \frac{1}{2} \int \frac{n(r_1)n(r_2)}{|r_1 - r_2|} dr_1dr_2 + E_{xc}[n] \]

under constraints of orthonormalization

\[ \langle \psi_i | \psi_j \rangle = \delta_{ij} \]

for the occupied orbitals.
The XC energy

To be approximated!
Exact result: the XC energy can be expressed as

\[ E_{\text{xc}}[n] = \int n(r_1) \epsilon_{\text{xc}}(r_1; n) \, dr_1 \]

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 »)

\[ \epsilon_{\text{xc}}^{\text{LDA}}(r_1; n) = \epsilon_{\text{xc}}^{\text{hom}}(n(r_1)) \]
\[ E_{\text{xc}}^{\text{LDA}}[n] = \int n(r_1) \epsilon_{\text{xc}}^{\text{LDA}}(n(r_1)) \, dr_1 \]

Generalized gradient approximations (GGA)

\[ E_{\text{xc}}^{\text{GGA}}[n] = \int n(r_1) \epsilon_{\text{xc}}^{\text{GGA}}(n(r_1), |\nabla n(r_1)|) \, dr_1 \]

In this talk, GGA = « PBE »

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

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Material properties from total energy derivatives: phonons
Changing atomic positions

Born-Oppenheimer approximation ...

\[ R_{\kappa\alpha}^a = R_{\alpha}^a + \tau_{\kappa\alpha} + u_{\kappa\alpha}^a \]

cell  \quad equilibrium atomic position  \quad displacement
Phonon frequencies from force constants

Matrix of interatomic force constants:

\[ C_{k\alpha,k'\alpha'}(a,a') = \frac{\partial^2 E_{BO}}{\partial R_{k\alpha} \partial R_{k'\alpha'}} \]

Fourier Transform (using translational invariance):

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

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

\[ \sum_{k'\alpha'} \tilde{C}_{k\alpha,k'\alpha'}(\tilde{q}) \cdot u_{m\tilde{q}}(k'\alpha') = M_k \cdot \omega^2_{m\tilde{q}} \cdot u_{m\tilde{q}}(k\alpha) \]

How to get second derivatives of the energy?
Density Functional Perturbation Theory...
Phonons: exp vs theory

**Zircon**

Diamond


Challenges for periodic materials?

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

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

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

Even for phonons at zero wavevector (Gamma), treating LO-TO splitting
   (longitudinal optic – transverse optic)
Perturbations (adiabatic)
Why perturbations?

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

Consider:

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

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

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

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

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

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

* Variation of energy and density around fixed potential

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

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

* Perturbations (assumed known through all orders)

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

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

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

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

small
parameter
'polarisation'
of the phonon
phonon
wavevector
How to get energy derivatives?

\[ E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots \]
\[ \psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \ldots \]

* Finite Differences

Compare \[ E \{\psi; V_{\text{ext}}\} \] and \[ E' \{\psi'; V'_{\text{ext}}\} \]

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

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

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

\[ \frac{dE}{d\lambda} = \frac{\partial E}{\partial V_{\text{ext}}} \frac{\partial V_{\text{ext}}}{\partial \lambda} + \frac{\partial E}{\partial \psi} \cdot \frac{\partial \psi}{\partial \lambda} = \frac{\partial E}{\partial V_{\text{ext}}} V^{(1)}_{\text{ext}} \]

In order to get \( E^{(1)} \) we do not need \( \psi^{(1)} \)
General framework of perturbation theory

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

* \( E\{\psi; V_{ext}\} \)

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

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

Should calculate:

2\textsuperscript{nd} order derivatives of BO energy:
- dynamical matrix, dielectric susceptibility, elastic constants, …
- \( \psi^{(1)}_\alpha, \psi^{(2)}_\alpha, \psi^{(3)}_\alpha \ldots \)
- \( \epsilon^{(1)}_\alpha, \epsilon^{(2)}_\alpha, \epsilon^{(3)}_\alpha \ldots \)
- \( \rho^{(1)}_\alpha, \rho^{(2)}_\alpha, \rho^{(3)}_\alpha \ldots \)

will be needed for T-dependence of electronic structure
Ordinary quantum mechanics
Perturbation theory for ordinary quantum mechanics

\[(\hat{H} - \varepsilon_{\alpha}) \left| \psi_{\alpha} \right\rangle = 0 \]  
(Schrödinger equation)

\[\left\langle \psi_{\alpha} \right| \psi_{\alpha} \left\rangle = 1 \]  
(normalisation condition)

\[\left\langle \psi_{\alpha} \right| \hat{H} - \varepsilon_{\alpha} \left| \psi_{\alpha} \right\rangle = 0 \]

or \[\varepsilon_{\alpha} = \left\langle \psi_{\alpha} \right| \hat{H} \left| \psi_{\alpha} \right\rangle \]  
(expectation value)

Hamiltonian supposed known through all orders

\[\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \lambda^2 \hat{H}^{(2)} + ... = \sum_n \lambda^n \hat{H}^{(n)}\]
Perturbation expansion of the Schrödinger Eq.

Suppose
\[ \hat{H}(\lambda) \left| \psi_n(\lambda) \right\rangle = \varepsilon_n \left| \psi_n(\lambda) \right\rangle \quad \text{valid for all } \lambda \]

with
\[
\begin{align*}
\hat{H}(\lambda) &= \hat{H}(0) + \lambda \hat{H}(1) \\
\psi_n(\lambda) &= \psi_n(0) + \lambda \psi_n(1) + \lambda^2 \psi_n(2) + \ldots \\
\varepsilon_n(\lambda) &= \varepsilon_n(0) + \lambda \varepsilon_n(1) + \lambda^2 \varepsilon_n(2) + \ldots
\end{align*}
\]

One expands the Schrödinger equation:

\[
\begin{align*}
\hat{H}(0) \left| \psi_n^{(0)} \right\rangle + \lambda \left( \hat{H}(1) \left| \psi_n^{(0)} \right\rangle + \hat{H}(0) \left| \psi_n^{(1)} \right\rangle \right) + \lambda^2 \left( \hat{H}(1) \left| \psi_n^{(1)} \right\rangle + \hat{H}(0) \left| \psi_n^{(2)} \right\rangle \right) + \ldots \\
= \varepsilon_n^{(0)} \left| \psi_n^{(0)} \right\rangle + \lambda \left( \varepsilon_n^{(1)} \left| \psi_n^{(0)} \right\rangle + \varepsilon_n^{(0)} \left| \psi_n^{(1)} \right\rangle \right) + \lambda^2 \left( \varepsilon_n^{(2)} \left| \psi_n^{(0)} \right\rangle + \varepsilon_n^{(1)} \left| \psi_n^{(1)} \right\rangle + \varepsilon_n^{(0)} \left| \psi_n^{(2)} \right\rangle \right) + \ldots
\end{align*}
\]
Perturbation expansion of the Schrödinger Eq.

\[ \hat{H}^{(0)} | \psi_{n}^{(0)} \rangle + \lambda \left( \hat{H}^{(1)} | \psi_{n}^{(0)} \rangle + \hat{H}^{(0)} | \psi_{n}^{(1)} \rangle \right) + \lambda^2 \left( \hat{H}^{(1)} | \psi_{n}^{(1)} \rangle + \hat{H}^{(0)} | \psi_{n}^{(2)} \rangle \right) + ... \]

\[ = \epsilon_{n}^{(0)} | \psi_{n}^{(0)} \rangle + \lambda \left( \epsilon_{n}^{(1)} | \psi_{n}^{(0)} \rangle + \epsilon_{n}^{(0)} | \psi_{n}^{(1)} \rangle \right) + \lambda^2 \left( \epsilon_{n}^{(2)} | \psi_{n}^{(0)} \rangle + \epsilon_{n}^{(1)} | \psi_{n}^{(1)} \rangle + \epsilon_{n}^{(0)} | \psi_{n}^{(2)} \rangle \right) + ... \]

In \( \lambda = 0 \), one gets

\[ \hat{H}^{(0)} | \psi_{n}^{(0)} \rangle = \epsilon_{n}^{(0)} | \psi_{n}^{(0)} \rangle \]

no surprise …

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

\[ \Rightarrow \hat{H}^{(1)} | \psi_{n}^{(0)} \rangle + \hat{H}^{(0)} | \psi_{n}^{(1)} \rangle = \epsilon_{n}^{(1)} | \psi_{n}^{(0)} \rangle + \epsilon_{n}^{(0)} | \psi_{n}^{(1)} \rangle \]

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

\[ \Rightarrow \hat{H}^{(1)} | \psi_{n}^{(1)} \rangle + \hat{H}^{(0)} | \psi_{n}^{(2)} \rangle = \epsilon_{n}^{(2)} | \psi_{n}^{(0)} \rangle + \epsilon_{n}^{(1)} | \psi_{n}^{(1)} \rangle + \epsilon_{n}^{(0)} | \psi_{n}^{(2)} \rangle \]
Perturbation expansion of the normalisation

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

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

Same technique than for Schrödinger equation, one deduces:

\[
\begin{align*}
\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle &= 1 \\
\langle \psi_n^{(1)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle &= 0 \\
\langle \psi_n^{(2)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle &= 0
\end{align*}
\]

no surprise …
Hellmann & Feynman theorem: $\mathcal{E}_n^{(1)}$

Start from first-order Schrödinger equation

$$\hat{H}^{(1)}\ket{\psi_n^{(0)}} + \hat{H}^{(0)}\ket{\psi_n^{(1)}} = \mathcal{E}_n^{(1)}\ket{\psi_n^{(0)}} + \mathcal{E}_n^{(0)}\ket{\psi_n^{(1)}}$$

Premultiply by $\bra{\psi_n^{(0)}}$

$$\bra{\psi_n^{(0)}}\hat{H}^{(1)}\ket{\psi_n^{(0)}} + \bra{\psi_n^{(0)}}\hat{H}^{(0)}\ket{\psi_n^{(1)}} = \mathcal{E}_n^{(1)}\bra{\psi_n^{(0)}}\psi_n^{(0)}\ket{\psi_n^{(0)}} + \mathcal{E}_n^{(0)}\bra{\psi_n^{(0)}}\psi_n^{(1)}\ket{\psi_n^{(0)}}$$

$$\bra{\psi_n^{(0)}}\hat{H}^{(1)}\ket{\psi_n^{(0)}} = 1$$

So: $\mathcal{E}_n^{(1)} = \bra{\psi_n^{(0)}}\hat{H}^{(1)}\ket{\psi_n^{(0)}} = \text{Hellmann & Feynman theorem}$

- $\psi_n^{(0)}$ and $\hat{H}^{(1)}$ supposed known
- $\psi_n^{(1)}$ not needed
- $\bra{\psi_n^{(0)}}\hat{H}^{(1)}\ket{\psi_n^{(0)}}$ = expectation of the Hamiltonian for the non-perturbed wavef.
Second-order derivative of total energy $\varepsilon^{(2)}_\alpha$

Start from second-order Schrödinger equation

$$\hat{H}^{(1)}|\psi^{(1)}_n\rangle + \hat{H}^{(0)}|\psi^{(2)}_n\rangle = \varepsilon^{(2)}_n|\psi^{(0)}_n\rangle + \varepsilon^{(1)}_n|\psi^{(1)}_n\rangle + \varepsilon^{(0)}_n|\psi^{(2)}_n\rangle$$

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

$$\varepsilon^{(2)}_\alpha = \langle \psi^{(0)}_\alpha | \hat{H}^{(1)} - \varepsilon^{(1)}_\alpha | \psi^{(1)}_\alpha \rangle \quad \text{or} \quad \varepsilon^{(2)}_\alpha = \langle \psi^{(1)}_\alpha | \hat{H}^{(1)} - \varepsilon^{(1)}_\alpha | \psi^{(0)}_\alpha \rangle$$

Both can be combined:

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

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

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

No knowledge of $\psi^{(2)}_\alpha$ is needed, but needs $\psi^{(1)}_\alpha$! How to get it?
In search of $|\psi_n^{(1)}\rangle$

Again first-order Schrödinger equation:

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

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

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

(called Sternheimer equation)

Equivalence with matrix equation (system of linear equations)

$$
A \cdot x = y
$$

usually solved by $x = A^{-1} y$ if $A^{-1}$ exist.
Variational Principle for the lowest $\varepsilon^{(2)}$ (Hylleraas principle)

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

with the following constraint on $|\psi^{(1)}_n\rangle$

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

Allows to recover Sternheimer’s equation:

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

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

Equivalence of:

* Minimization of $\varepsilon^{(2)}_n$
* Sternheimer equation
* also … sum over states … Green’s function …
Computation of $\varepsilon_\alpha^{(3)}$ (I)

Starting from

$$
(\hat{H}^{(0)} - \varepsilon^{(0)}_\alpha)\ket{\psi^{(3)}_\alpha} + (\hat{H}^{(1)} - \varepsilon^{(1)}_\alpha)\ket{\psi^{(2)}_\alpha} + (\hat{H}^{(2)} - \varepsilon^{(2)}_\alpha)\ket{\psi^{(1)}_\alpha} + (\hat{H}^{(3)} - \varepsilon^{(3)}_\alpha)\ket{\psi^{(0)}_\alpha} = 0
$$

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

$$
\varepsilon^{(3)}_\alpha = \begin{align*}
\langle \psi^{(0)}_\alpha | \hat{H}^{(3)} | \psi^{(0)}_\alpha \rangle \\
+ \langle \psi^{(0)}_\alpha | \hat{H}^{(2)} - \varepsilon^{(2)}_\alpha | \psi^{(1)}_\alpha \rangle \\
+ \langle \psi^{(0)}_\alpha | \hat{H}^{(1)} - \varepsilon^{(1)}_\alpha | \psi^{(2)}_\alpha \rangle
\end{align*}
$$

⚠️ $\psi^{(2)}_\alpha$ is needed in this formula
The computation of $\varepsilon^{(3)}_\alpha$  (II)

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

\[
0 = \langle \psi^{(0)}_\alpha | \hat{H}^{(3)} - \varepsilon^{(3)}_\alpha | \psi^{(0)}_\alpha \rangle + \langle \psi^{(1)}_\alpha | \hat{H}^{(2)} - \varepsilon^{(2)}_\alpha | \psi^{(0)}_\alpha \rangle + \langle \psi^{(2)}_\alpha | \hat{H}^{(1)} - \varepsilon^{(1)}_\alpha | \psi^{(0)}_\alpha \rangle + \langle \psi^{(3)}_\alpha | \hat{H}^{(0)} - \varepsilon^{(0)}_\alpha | \psi^{(0)}_\alpha \rangle \\
+ \langle \psi^{(0)}_\alpha | \hat{H}^{(2)} - \varepsilon^{(2)}_\alpha | \psi^{(1)}_\alpha \rangle + \langle \psi^{(1)}_\alpha | \hat{H}^{(1)} - \varepsilon^{(1)}_\alpha | \psi^{(1)}_\alpha \rangle + \langle \psi^{(2)}_\alpha | \hat{H}^{(0)} - \varepsilon^{(0)}_\alpha | \psi^{(1)}_\alpha \rangle \\
+ \langle \psi^{(0)}_\alpha | \hat{H}^{(1)} - \varepsilon^{(1)}_\alpha | \psi^{(2)}_\alpha \rangle + \langle \psi^{(1)}_\alpha | \hat{H}^{(0)} - \varepsilon^{(0)}_\alpha | \psi^{(2)}_\alpha \rangle \\
+ \langle \psi^{(0)}_\alpha | \hat{H}^{(0)} - \varepsilon^{(0)}_\alpha | \psi^{(3)}_\alpha \rangle
\]

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:

\[
\varepsilon^{(3)}_\alpha = \langle \psi^{(0)}_\alpha | \hat{H}^{(3)} | \psi^{(0)}_\alpha \rangle + \langle \psi^{(1)}_\alpha | \hat{H}^{(2)} | \psi^{(0)}_\alpha \rangle \\
+ \langle \psi^{(0)}_\alpha | \hat{H}^{(2)} | \psi^{(1)}_\alpha \rangle + \langle \psi^{(1)}_\alpha | \hat{H}^{(1)} - \varepsilon^{(1)}_\alpha | \psi^{(1)}_\alpha \rangle
\]

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

\[\triangle \psi^{(2)}_\alpha\] is not needed in this formula

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Dynamical matrices from density-functional perturbation theory (DFPT)
Density functional perturbation theory

Without going into the formulas, there exist expressions:

\[ E^{(0)} \{ \psi_{\alpha}^{(0)} \} \] variational with respect to \( \psi_{\alpha}^{(0)} \)

\[ E^{(1)} \{ \psi_{\alpha}^{(0)} \} \]

\[ E^{(2)} \{ \psi_{\alpha}^{(0)}, \psi_{\alpha}^{(1)} \} \] variational with respect to \( \psi_{\alpha}^{(1)} \)

\[ E^{(3)} \{ \psi_{\alpha}^{(0)}, \psi_{\alpha}^{(1)} \} \]

\[ E^{(4)} \{ \psi_{\alpha}^{(0)}, \psi_{\alpha}^{(1)}, \psi_{\alpha}^{(2)} \} \] variational with respect to \( \psi_{\alpha}^{(2)} \)

\[ E^{(5)} \{ \psi_{\alpha}^{(0)}, \psi_{\alpha}^{(1)}, \psi_{\alpha}^{(2)} \} \]

+ knowledge of \( \{ \psi_{\alpha}^{(0)} \} \) allows one to obtain \( \rho^{(0)}, H^{(0)}, \varepsilon_{\alpha}^{(0)} \)

knowledge of \( \{ \psi_{\alpha}^{(0)}, \psi_{\alpha}^{(1)} \} \) allows one to obtain \( \rho^{(1)}, H^{(1)}, \varepsilon_{\alpha}^{(1)} \)

knowledge of \( \{ \psi_{\alpha}^{(0)}, \psi_{\alpha}^{(1)}, \psi_{\alpha}^{(2)} \} \) allows one to obtain \( \rho^{(2)}, H^{(2)}, \varepsilon_{\alpha}^{(2)} \)

Need \( \psi_{\alpha}^{(2)} \) unlike in ordinary QM
Basic equations in DFT

Solve self-consistently Kohn-Sham equation

\[
\hat{H} |\psi_n\rangle = \varepsilon_n |\psi_n\rangle
\]

\[
\hat{H} = \hat{T} + \hat{V} + \hat{V}_{Hxc}[\rho]
\]

\[
\rho(\vec{r}) = \sum_n^{occ} \psi_n^*(\vec{r})\psi_n(\vec{r})
\]

or minimize

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

What is \( \hat{V} \)?

\[
\hat{V}(\vec{r}) = \sum_{a\kappa} \frac{Z_\kappa}{|\vec{r} - \vec{R}_a^\kappa|}
\]
Basic equations in DFPT

Solve self-consistently Sternheimer equation

\[
\begin{aligned}
(H^{(0)} - \epsilon_n^{(0)}) \psi_n^{(1)} &= - (H^{(1)} - \epsilon_n^{(1)}) \psi_n^{(0)} \\
H^{(1)} &= \hat{V}^{(1)} + \int \frac{\delta^2 E_{Hxc}}{\delta \rho(r) \delta \rho(r')} \rho^{(1)}(r') \, dr' \\
\epsilon_n^{(1)} &= \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle \\
\rho^{(1)}(r) &= \sum_n \psi_n^{(1)*}(r) \psi_n^{(0)}(r) + \psi_n^{(0)*}(r) \psi_n^{(1)}(r) \\
0 &= \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle \text{ for } m \in \text{occupied set}
\end{aligned}
\]

or minimize

\[
E_{el}^{(2)} \{ \psi^{(1)}, \psi^{(0)} \} = \sum_n \langle \psi_n^{(0)} | H^{(0)} - \epsilon_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(1)} | \hat{V}^{(1)} | \psi_n^{(0)} \rangle \\
+ \langle \psi_n^{(0)} | \hat{V}^{(1)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(1)} | \hat{V}^{(2)} | \psi_n^{(0)} \rangle \\
+ \frac{1}{2} \int \int \frac{\delta^2 E_{Hxc}}{\delta \rho(r) \delta \rho(r')} \rho^{(1)}(r) \rho^{(1)}(r') \, dr \, dr'
\]

What is \( \hat{V}^{(1)} \), \( \hat{V}^{(2)} \)?
The potential and its 1\textsuperscript{st} derivative

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

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

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

Generalisation to pseudopotentials can be worked out ...

Collective displacement with wavevector $\vec{q}$

\[
V_{\vec{q}, \kappa, \alpha}^{(1)}(\vec{r}) = \sum_a e^{i\vec{q} \cdot \vec{R}_a} \frac{\partial V(\vec{r})}{\partial R_{\kappa \alpha}^a}
\]
Factorization of the phase

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

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

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

\[ \rho^{(1)}(\vec{r}+\vec{R}_a) = e^{i\vec{q} \cdot \vec{R}_a} \rho^{(1)}(\vec{r}) \]
\[ \psi_{m,k,\tilde{q}}^{(1)}(\vec{r}+\vec{R}_a) = e^{i(\vec{k}+\vec{q}) \cdot \vec{R}_a} \psi_{m,k,\tilde{q}}^{(1)}(\vec{r}) \]

Now, define related periodic quantities

\[ \tilde{\rho}^{(1)}(\vec{r}) = e^{-i\vec{q} \cdot \vec{r}} \rho^{(1)}(\vec{r}) \]
\[ u^{(1)}_{m,k,\tilde{q}}(\vec{r}) = (N\Omega_0)^{1/2} e^{-i(\vec{k}+\vec{q}) \cdot \vec{r}} \psi_{m,k,\tilde{q}}^{(1)}(\vec{r}) \]

In equations of DFPT, only these periodic quantities appear:

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

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

How to get $E^{j_1j_2}$ from $\psi^{(0)}_\alpha$, $\psi^{j_1}_\alpha$, $\psi^{j_2}_\alpha$?

$$E^{(2)}_{el} \{ \psi^{(I)} ; \psi^{(0)} \} = \sum_n^{occ} \left\langle \psi_n^{(I)} \right| \hat{H}^{(0)} - \epsilon_n^{(0)} \left| \psi_n^{(I)} \right\rangle + \left\langle \psi_n^{(0)} \right| \hat{V}^{(1)} \left| \psi_n^{(0)} \right\rangle$$

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

$$+ \frac{1}{2} \iint \frac{\delta^2 E_{Hxc}}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')} \rho^{(1)}(\vec{r}) \rho^{(1)}(\vec{r}') \, d\vec{r} \, d\vec{r}'$$

Generalization to $E^{j_1j_2}_{el} = \frac{1}{2} \left( \tilde{E}_{el}^{j_1j_2} + \tilde{E}_{el}^{j_2j_1} \right)$

with

$$\tilde{E}_{el}^{j_1j_2} \{ \psi^{j_1} , \psi^{j_2} ; \psi^{(0)} \} = \sum_n^{occ} \left\langle \psi_n^{j_1} \right| \hat{H}^{(0)} - \epsilon_n^{(0)} \left| \psi_n^{j_2} \right\rangle + \left\langle \psi_n^{j_2} \right| \hat{V}^{j_1j_2} \left| \psi_n^{(0)} \right\rangle$$

$$+ \left\langle \psi_n^{j_1} \right| \hat{V}^{j_1j_2} \left| \psi_n^{(0)} \right\rangle + \left\langle \psi_n^{j_2} \right| \hat{V}^{j_2j_1} \left| \psi_n^{(0)} \right\rangle$$

$$+ \frac{1}{2} \iint \frac{\delta^2 E_{Hxc}}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')} \rho^{j_1}(\vec{r}) \rho^{j_2}(\vec{r}') \, d\vec{r} \, d\vec{r}'$$

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

$$E^{j_1j_2}_{el} \{ \psi^{j_1} ; \psi^{(0)} \} = \sum_n^{occ} \left\langle \psi_n^{j_1} \right| \hat{V}^{j_2} \left| \psi_n^{(0)} \right\rangle + \left\langle \psi_n^{j_2} \right| \hat{V}^{j_1j_2} \left| \psi_n^{(0)} \right\rangle$$

Independent of $\psi^{j_2}$
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 $E^{j_1 j_2}$ from $\psi_n^{(0)}, \psi_n^{j_1}, \psi_n^{j_2}$
   - Enddo

4. Post-processing: from ‘bare’ $E^{j_1 j_2}$ to physical properties
Phonon band structures from DFPT
Phonon band structure

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

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

Full band structure needs values for many wavevectors ...

SiO$_2$ alpha-quartz

Fourier Interpolation

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

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

IFCs are generated by

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

= Fourier interpolation of dynamical matrices.
Numerical Fourier Interpolation

Key of the interpolation: replace the integral

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

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

Grid of \((l,m,n)\) points

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

Numerical Fourier Interpolation
Fourier interpolation : Silicon

![Graph showing frequency vs. q-points for 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

- ▲ = dipole-dipole
- ▼ = short-range

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

\[
\tilde{C}^{na}_{\kappa\alpha, \kappa', \beta}(\tilde{q} \to 0) = \frac{4\pi e^2}{\Omega_0} \sum_{\gamma} Z^{*}_{\kappa, \alpha \gamma} q_{\gamma} \sum_{\nu} Z^{*}_{\kappa', \beta \nu} q_{\nu} \sum_{\gamma, \nu} q_{\gamma} \varepsilon_{\gamma \nu}^{\infty} q_{\nu}
\]

\[
Z^{*}_{\kappa, \alpha \beta} = \Omega_0 \frac{\partial P_{\alpha}}{\partial u_{\kappa, \beta}} \bigg|_{\delta \tilde{E}=0} = \frac{\partial F_{\kappa \beta}}{\partial \varepsilon_{\beta}}
\]

Born effective charge tensor for atom \( \kappa \)

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

\[
\varepsilon_{\gamma \nu}^{\infty} = \delta_{\gamma \nu} + 4\pi \frac{\partial P_{\gamma}}{\partial \varepsilon_{\nu}}
\]

electronic dielectric tensor

(electronic contribution to the screening of the charges)

Both can be linked to a second derivative of total energy
Dielectric properties from DFPT
Treatment of homogeneous electric field

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

One needs, for linear response:

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

Solution:

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

+ the derivative with respect to $k$

The treatment of homogeneous electric field is thus mapped onto the original periodic system.
Dielectric tensor: electronic part

\[ \varepsilon_{\gamma\nu}^\infty = \delta_{\gamma\nu} + 4\pi \frac{\partial P^\gamma}{\partial \varepsilon^\nu} \]

electronic dielectric tensor

(Proportionality coefficient between polarisation and electric field)

Linked to a second derivative of total energy

\[ P^\gamma = -\frac{1}{V} \frac{\partial E}{\partial \varepsilon^\gamma} \quad \varepsilon_{\gamma\nu}^\infty = \delta_{\gamma\nu} - \frac{4\pi}{V} \frac{\partial^2 E}{\partial \varepsilon^\gamma \partial \varepsilon^\nu} \]
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 \( \kappa \)

A mixed second derivative of total energy

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

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

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

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

Enforce sum-rules

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

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

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

Add the dipole-dipole part for that Q-point

Diagonalize dynamical matrix to find phonon frequencies
Phonon dispersion curves of ZrO$_2$

ZrO$_2$ in the cubic structure at the equilibrium lattice constant $a_0 = 5.13$ Å.

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


DFPT (Linear-response)

with 

\[
\begin{align*}
Z_\text{Zr}^* &= 5.75 \\
Z_\text{0}^* &= -2.86 \\
\varepsilon_\infty &= 5.75
\end{align*}
\]

LO - TO splitting 11.99 THz  
Non-polar mode is OK

Phonon dispersion relations.

(a) Ideal cubic phase: unstable.

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

**Analysis of instabilities**

MgSiO$_3$  
CUBIC  
(5at/cell)

Phonon dispersion relations.

(a) Ideal cubic phase: unstable.

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

ORTHORHOMBIC  
(20at/cell)
Electric field - atomic displacement coupling

Frequency-dependent dielectric tensor in the IR range

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

Infrared (IR) reflectivity

\[ R_k(\omega) = \left| \frac{\varepsilon_{kk}^{1/2}(\omega) - 1}{\varepsilon_{kk}^{1/2}(\omega) + 1} \right| \]

Infrared reflectivity of lithium iodate

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

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

\[ \Delta (\epsilon^{-1})_{ij} \Delta = \sum_k r_{ijk} \epsilon_k \]

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNbO(_3)</td>
<td></td>
<td></td>
<td>9.67</td>
<td>8.6</td>
<td>13.8</td>
<td>8</td>
</tr>
<tr>
<td>PbTiO(_3)</td>
<td></td>
<td></td>
<td>8.98</td>
<td>5.88</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>BaTiO(_3)</td>
<td></td>
<td></td>
<td>8.91</td>
<td>22.27</td>
<td>10.2</td>
<td>8</td>
</tr>
<tr>
<td>LiIO(_3)</td>
<td></td>
<td></td>
<td>6.75</td>
<td>10.22</td>
<td>0.82</td>
<td>6.60</td>
</tr>
</tbody>
</table>

Exp. [11] 4.1 ± 0.6 6.4 ± 1 1.4 ± 0.2 3.3 ± 0.7
Exp. [42] 5.8 ± 1.2

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

\[ D_i = \sum_j e_{ij} \eta_j + \sum_j e_{ij} \varepsilon_j \]

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

\( \text{LiIO}_3 \)

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

<table>
<thead>
<tr>
<th>Piezoelectric tensor (C/m²)</th>
<th>( e_{13} )</th>
<th>( e_{33} )</th>
<th>( e_{41} )</th>
<th>( e_{42} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA (this work)</td>
<td>1.14</td>
<td>1.54</td>
<td>-0.13</td>
<td>1.26</td>
</tr>
<tr>
<td>GGA (this work)</td>
<td>0.92</td>
<td>1.28</td>
<td>-0.07</td>
<td>1.10</td>
</tr>
<tr>
<td>Exp. [51]</td>
<td>0.65</td>
<td>0.97</td>
<td>0.10</td>
<td>0.89</td>
</tr>
</tbody>
</table>

Raman scattering intensities

LiI\textsubscript{3}O

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

B. Van Troeye, Y. Gillet, S. Poncé and XG, Optical Materials 36, 1494 (2014)
Thermodynamic properties from DFPT
Statistical physics: phonons = bosons

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

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

Internal energy

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

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

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

\( m = \) 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 \( F \):

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

Vibrational contribution to \( C_v \):

\[ C_v = 3n_{at}N k_B \int_0^{\omega_{\text{max}}} \left( \frac{\omega}{2k_BT} \right)^2 \text{csch}^2 \left( \frac{\omega}{2k_BT} \right) g(\omega) d\omega \]
Ab initio thermal expansion

\[ \alpha(T) = \frac{V}{3B} \sum_{\tilde{q}, m} \frac{1}{\hbar \omega_{\tilde{q}, m}} \gamma_{\tilde{q}, m} \left( \frac{\partial n(\omega_{\tilde{q}, m})}{\partial T} \right) \]

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

Alternative path: minimisation of free energy
Ab initio thermal expansion

Linear thermal expansion coefficient of bulk silicon

Linear thermal expansion coefficient of bulk germanium

G.-M. Rignanese, J.-P. Michenaud and XG
Phonons : LDA ? GGA ?
... 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 :

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

Thermal expansion and T-dependent bulk modulus of copper

Phonons in weakly bonded systems
Layered materials

For the last decade: interest in layered and other nanostructured materials. Graphene, transition metal dichalcogenides, etc …
- Interesting transport properties
- Topological materials
- Li or Na insertion in layered materials
Weak bonding : LDA ? GGA ? Beyond ?

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

\[
E_{xc} [n] = \int n(r_1) \epsilon_{xc}(r_1; n) \, dr_1
\]

\[
E_{xc}^{\text{LDA}} [n] = \int n(r_1) \epsilon_{xc}^{\text{LDA}} (n(r_1)) \, dr_1
\]

\[
E_{xc}^{\text{GGA}} [n] = \int n(r_1) \epsilon_{xc}^{\text{GGA}} (n(r_1), |\nabla n(r_1)|) \, dr_1
\]

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

⇒ New (classes of) functionals
DFT-vDW-DF ; DFT-vDW-WF ; DFT-D2, -D3, -D3(BJ) ; …
**DFT+D3(BJ)**

Interlayer parameter $d$ (nm)

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

Primitive cell volume (nm$^3$)

- [Pbca - 4 Benzene rings]
  - GGA(PBE) $>0.600$
  - +D3(BJ) 0.455
  - Exp. 0.4625
Phonons in benzene crystal

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

// Difference in molecule: anharmonic effects

CEA Bruyères, January 24, 2019
Temperature dependence of the electronic gap
Temperature dependence of electronic and optical properties

Bulk Silicon

peaks shift

peaks broaden

Diamond : zero-point motion effect

0.37 eV for the indirect band gap


How to compute it?
Allen-Heine-Cardona theory

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

Debye-Waller Antoncik

Fan “self-energy”

Electron-phonon interaction

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

\[
\frac{\partial \varepsilon_{kn}}{\partial n_{\tilde{q}j}} = \left( \frac{\partial \varepsilon_{kn} (Fan)}{\partial n_{\tilde{q}j}} \right) + \left( \frac{\partial \varepsilon_{kn} (DWR)}{\partial n_{\tilde{q}j}} \right)
\]

\[
\frac{\partial \varepsilon_{kn} (Fan)}{\partial n_{\tilde{q}j}} = \frac{1}{\omega_{\tilde{q}j}} \Re \sum_{\kappa\kappa'bn'} \langle \phi_{kn} | \nabla_{\kappa a} H_{\kappa} | \phi_{k+\tilde{q}n'} \rangle \langle \phi_{k+\tilde{q}n'} | \nabla_{\kappa' b} H_{\kappa'} | \phi_{kn} \rangle \frac{\xi_{\kappa a} (\tilde{q}j) \xi_{\kappa' b} (-\tilde{q}j)}{\sqrt{M_{\kappa} M_{\kappa'}}} e^{i\tilde{q}_a (R_{\kappa' b} - R_{\tilde{q}a})} 
\]

\[
\frac{\partial \varepsilon_{kn} (DWR)}{\partial n_{\tilde{q}j}} = -\frac{1}{\omega_{\tilde{q}j}} \Re \sum_{\kappa\kappa'bn'} \langle \phi_{kn} | \nabla_{\kappa a} H_{\kappa} | \phi_{k+\tilde{q}n'} \rangle \langle \phi_{k+\tilde{q}n'} | \nabla_{\kappa' b} H_{\kappa'} | \phi_{kn} \rangle \frac{\varepsilon_{kn} - \varepsilon_{k+\tilde{q}n'}}{\sqrt{M_{\kappa} M_{\kappa'}}}
\]

\[
\times \frac{1}{2} \left( \frac{\xi_{\kappa a} (\tilde{q}j) \xi_{\kappa b} (-\tilde{q}j)}{M_{\kappa}} + \frac{\xi_{\kappa' a} (\tilde{q}j) \xi_{\kappa' b} (-\tilde{q}j)}{M_{\kappa'}} \right)
\]

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

Temperature-dependence of the gaps in diamond [meV]

DFT T-dependent band structure

Diamond 0 Kelvin  
(incl. Zero-point motion)

Note the widening of the bands = lifetime

---

DFT T-dependent band structure

Diamond 300 Kelvin

Note the widening of the bands = lifetime

DFT T-dependent band structure

Diamond 900 Kelvin

Note the widening of the bands = lifetime

DFT T-dependent band structure

Diamond 1500 Kelvin

Note the widening of the bands = lifetime

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

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

Zero-point motion in DFT+GW: 0.63 eV for the direct gap, in agreement with experiments

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

In red: ZPR from adiabatic supercell calculations. Wide spread of discrepancies

In blue: ZPR from non-adiabatic AHC calculations. Much better agreement, within 20% except for two materials

Band gap: comparison with experiment

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

Squares: scGW$_{e\text{h}}$ (self-consistent GW with electron-hole interaction). Slight overestimation, except ZnS, ZnO, CdS.

In blue: scGW$_{e\text{h}}$ + ZPR from non-adiabatic AHC calculations or Exp. Within 4% except for 3 materials

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