

CECAM Tutorial: “Dynamical, dielectric and magnetic properties of solids with ABINIT”

Lyon, 12-16 may 2014

Basics of density functional perturbation theory

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Born-Oppenheimer approximation

- Quantum treatment for electrons → **Kohn-Sham equation**

$$E_{el}[\rho] = \sum_v \langle \psi_v | T + V_{ext} | \psi_v \rangle + E_{Hxc}[\rho]$$

$$\rho(\mathbf{r}) = \sum_v \psi_v^*(\mathbf{r}) \psi_v(\mathbf{r})$$

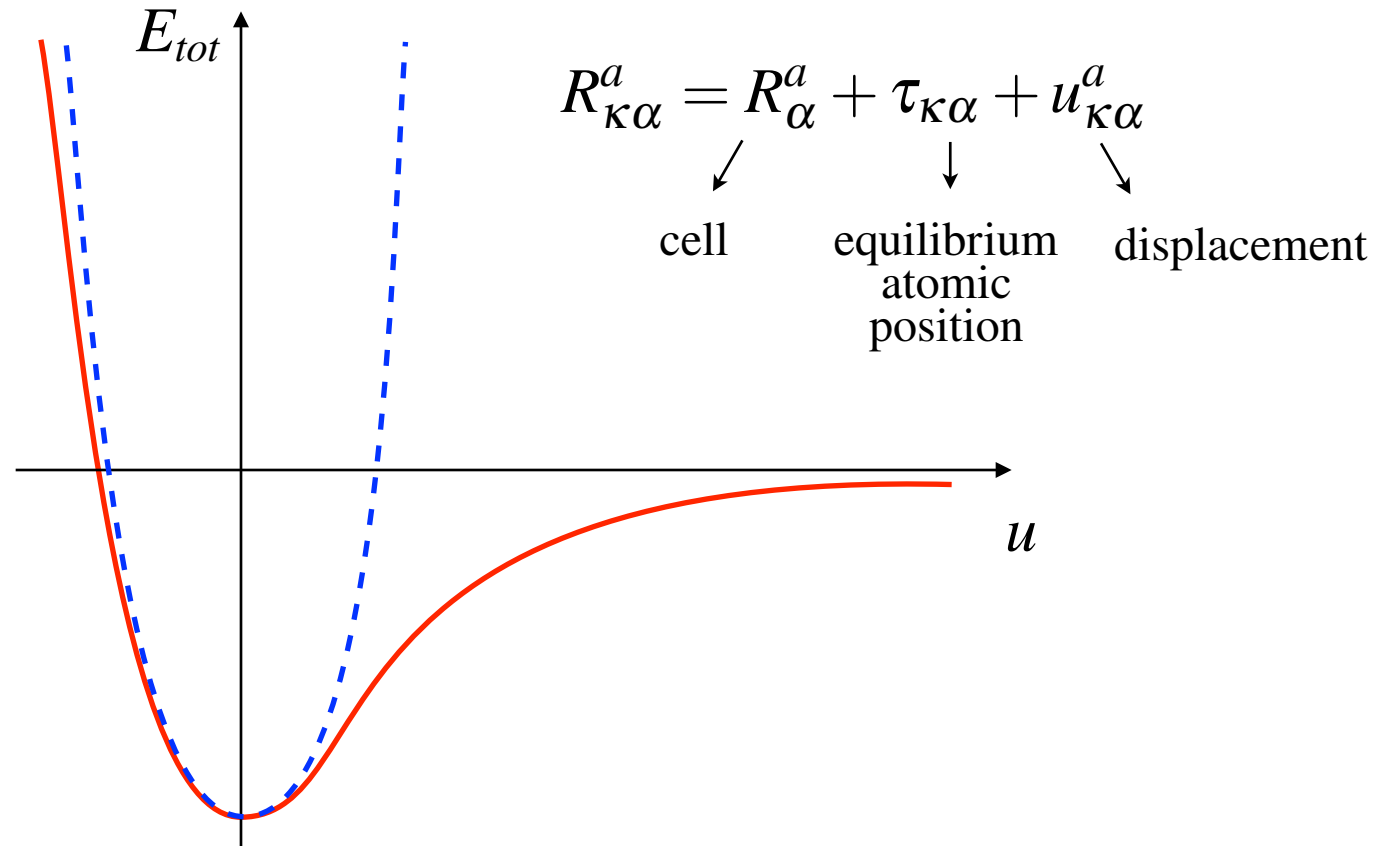
$$\left[-\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + V_{Hxc}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

- Classical treatment for nuclei → **Newton equation**

$$\begin{array}{c}
 \text{unit cell} \\
 \uparrow \\
 F_{\kappa\alpha}^a = - \left. \frac{\partial E_{tot}}{\partial R_{\kappa\alpha}^a} \right|_{\{\mathbf{R}\}} = M_{\kappa} \frac{d^2 R_{\kappa\alpha}^a}{dt^2} \\
 \swarrow \quad \searrow \\
 \text{atom} \quad \text{direction} \\
 (\alpha=1,2,3)
 \end{array}$$

$$E_{tot} = E_{ion} + E_{el}$$

Harmonic approximation



$$E_{tot}(\{\mathbf{u}\}) = E_{tot}^{(0)} + \sum_{a\kappa\alpha} \sum_{a'\kappa'\alpha'} \frac{1}{2} \left(\frac{\partial^2 E_{tot}}{\partial u_{\kappa\alpha}^a \partial u_{\kappa'\alpha'}^{a'}} \right) u_{\kappa\alpha}^a u_{\kappa'\alpha'}^{a'}$$

Phonons

- The matrix of **interatomic force constants** (IFCs) is defined as

$$C_{\kappa\alpha, \kappa'\alpha'}(a, a') = \left(\frac{\partial^2 E_{tot}}{\partial u_{\kappa\alpha}^a \partial u_{\kappa'\alpha'}^{a'}} \right)$$

- Its Fourier transform (using translational invariance)

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

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

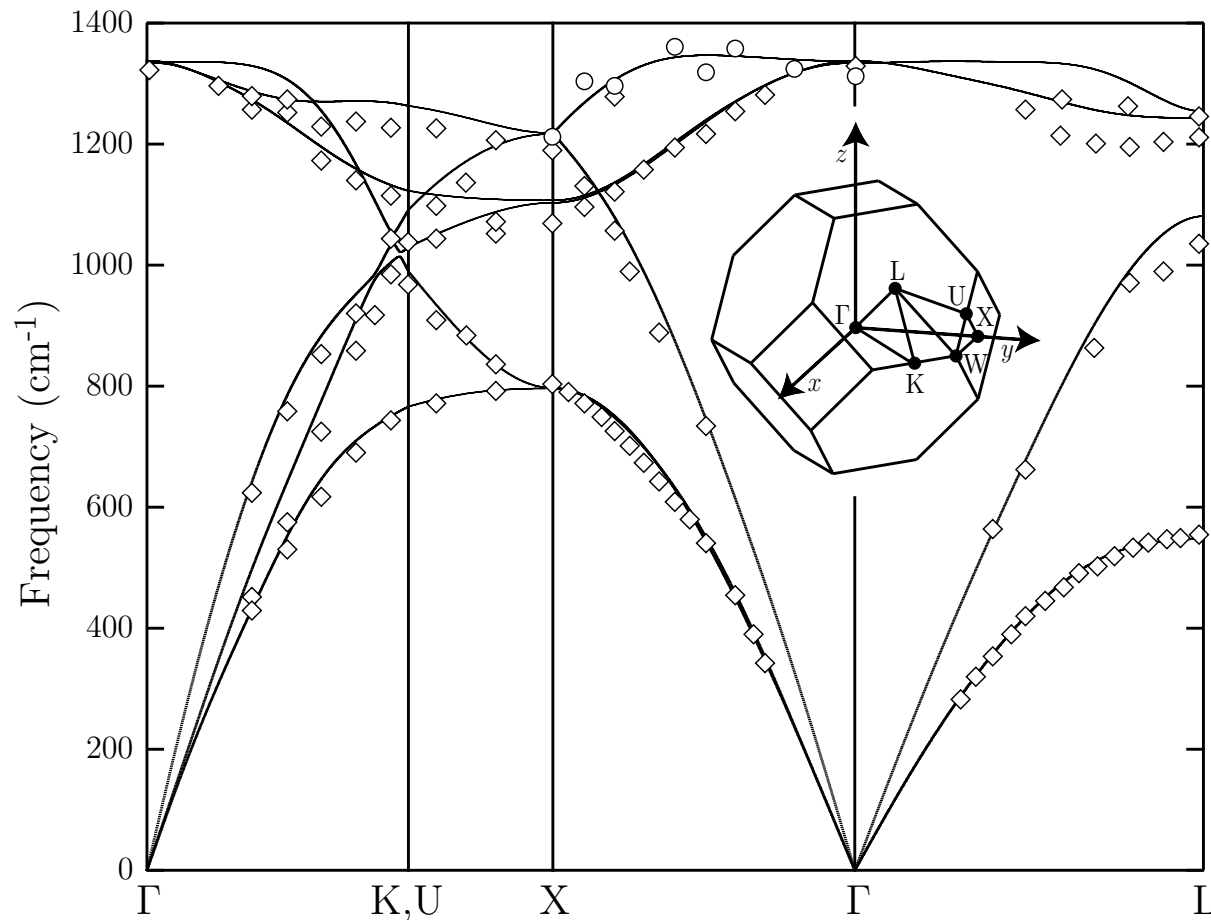
$$\sum_{\kappa'\alpha'} \tilde{C}_{\kappa\alpha, \kappa'\alpha'}(\mathbf{q}) U_{m\mathbf{q}}(\kappa'\alpha') = M_{\kappa} \omega_{m\mathbf{q}}^2 U_{m\mathbf{q}}(\kappa\alpha)$$

\swarrow
 phonon
displacement
pattern

\downarrow
 masses

\searrow
 square of
phonon
frequencies

Example: Diamond



Theory vs. Experiment

[X. Gonze, GMR, and R. Caracas, *Z. Kristallogr.* **220**, 458 (2000)]

Total energy derivatives

- In fact, many physical properties are derivatives of the total energy (or a suitable thermodynamic potential) with respect to external perturbations.
- Possible perturbations include:
 - ★ atomic displacements,
 - ★ expansion or contraction of the primitive cell,
 - ★ homogeneous external field (electric or magnetic),
 - ★ alchemical change
 - ★ ...

Total energy derivatives

- Related derivatives of the total energy ($E_{el} + E_{ion}$)
 - ★ 1st order: forces, stress, dipole moment, ...
 - ★ 2nd order: dynamical matrix, elastic constants, dielectric susceptibility, Born effective charge tensors, piezoelectricity, internal strains
 - ★ 3rd order: non-linear dielectric susceptibility, phonon-phonon interaction, Grüneisen parameters, ...
- Further properties can be obtained by integration over phononic degrees of freedom (e.g., entropy, thermal expansion, ...)

Total energy derivatives

- These derivatives can be obtained from
 - ★ direct approaches:
 - finite differences (e.g. frozen phonons)
 - molecular-dynamics spectral analysis methods
 - ★ perturbative approaches
- The former have a series of limitations (problems with commensurability, difficulty to decouple the responses to perturbations of different wavelength, ...). On the other hand, the latter show a lot of flexibility which makes it very attractive for practical calculations.

Outline

Perturbation Theory

Density Functional Perturbation Theory

Atomic displacements and

homogeneous electric field

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Perturbation Theory

Density Functional Perturbation Theory

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Reference and perturbed systems

- Let us assume that all the solutions are known for a **reference** system for which the one-body **Schrödinger equation** is:

$$H^{(0)} \left| \psi_i^{(0)} \right\rangle = \varepsilon_i^{(0)} \left| \psi_i^{(0)} \right\rangle$$

with the normalization condition:

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

- Let us now introduce a perturbation of the external potential characterized by a small parameter λ :

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

known at all orders.

Reference and perturbed systems

- We now want to solve the **perturbed Schrödinger equation**:

$$H(\lambda)|\psi_i(\lambda)\rangle = \varepsilon_i(\lambda)|\psi_i(\lambda)\rangle$$

with the normalization condition:

$$\langle \psi_i(\lambda) | \psi_i(\lambda) \rangle = 1$$

- Idea: all the quantities ($X=H, \varepsilon_i, \psi_i$) are written as a perturbation series with respect to the parameter λ :

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

$$\text{with } X^{(n)} = \frac{1}{n!} \left. \frac{d^n X}{d\lambda^n} \right|_{\lambda=0}$$

Expansion of the Schrödinger equation

- Starting from:

$$H(\lambda)|\psi_i(\lambda)\rangle = \varepsilon_i(\lambda)|\psi_i(\lambda)\rangle \quad \forall \lambda$$

and inserting:

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

$$|\psi_i(\lambda)\rangle = |\psi_i^{(0)}\rangle + \lambda |\psi_i^{(1)}\rangle + \lambda^2 |\psi_i^{(2)}\rangle + \dots$$

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

we get:

$$\left(H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \dots \right) \left(|\psi_i^{(0)}\rangle + \lambda |\psi_i^{(1)}\rangle + \lambda^2 |\psi_i^{(2)}\rangle + \dots \right) = \left(\varepsilon_i^{(0)} + \lambda \varepsilon_i^{(1)} + \lambda^2 \varepsilon_i^{(2)} + \dots \right) \left(|\psi_i^{(0)}\rangle + \lambda |\psi_i^{(1)}\rangle + \lambda^2 |\psi_i^{(2)}\rangle + \dots \right)$$

Expansion of the Schrödinger equation

- This can be rewritten as:

$$H^{(0)} |\psi_i^{(0)}\rangle$$

$$+ \lambda \left(H^{(0)} |\psi_i^{(1)}\rangle + H^{(1)} |\psi_i^{(0)}\rangle \right)$$

$$+ \lambda^2 \left(H^{(0)} |\psi_i^{(2)}\rangle + H^{(1)} |\psi_i^{(1)}\rangle + H^{(2)} |\psi_i^{(0)}\rangle \right)$$

$$+ \dots =$$

$$\varepsilon_i^{(0)} |\psi_i^{(0)}\rangle$$

$$+ \lambda \left(\varepsilon_i^{(0)} |\psi_i^{(1)}\rangle + \varepsilon_i^{(1)} |\psi_i^{(0)}\rangle \right)$$

$$+ \lambda^2 \left(\varepsilon_i^{(0)} |\psi_i^{(2)}\rangle + \varepsilon_i^{(1)} |\psi_i^{(1)}\rangle + \varepsilon_i^{(2)} |\psi_i^{(0)}\rangle \right)$$

$$+ \dots$$

setting $\lambda=0$

deriving w.r.t. λ
and setting $\lambda=0$

deriving twice
w.r.t. λ and
setting $\lambda=0$

Expansion of the Schrödinger equation

- Finally, we have that:

$$H^{(0)} |\psi_i^{(0)}\rangle = \varepsilon_i^{(0)} |\psi_i^{(0)}\rangle \quad 0^{\text{th}} \text{ order}$$

$$H^{(0)} |\psi_i^{(1)}\rangle + H^{(1)} |\psi_i^{(0)}\rangle = \varepsilon_i^{(0)} |\psi_i^{(1)}\rangle + \varepsilon_i^{(1)} |\psi_i^{(0)}\rangle \quad 1^{\text{st}} \text{ order}$$

$$H^{(0)} |\psi_i^{(2)}\rangle + H^{(1)} |\psi_i^{(1)}\rangle + H^{(2)} |\psi_i^{(0)}\rangle = \varepsilon_i^{(0)} |\psi_i^{(2)}\rangle + \varepsilon_i^{(1)} |\psi_i^{(1)}\rangle + \varepsilon_i^{(2)} |\psi_i^{(0)}\rangle \quad 2^{\text{nd}} \text{ order}$$

...

Expansion of the normalization condition

- Starting from:

$$\langle \psi_i(\lambda) | \psi_i(\lambda) \rangle = 1 \quad \forall \lambda$$

and inserting:

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

we get:

$$\begin{aligned} & \langle \psi_i^{(0)} | \psi_i^{(0)} \rangle \\ & + \lambda \left(\langle \psi_i^{(0)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(1)} | \psi_i^{(0)} \rangle \right) \\ & + \lambda^2 \left(\langle \psi_i^{(0)} | \psi_i^{(2)} \rangle + \langle \psi_i^{(1)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(2)} | \psi_i^{(0)} \rangle \right) \\ & + \dots = 1 \end{aligned}$$

Expansion of the normalization condition

- Finally, we have that

$$\langle \psi_i^{(0)} | \psi_i^{(0)} \rangle = 1 \quad 0^{\text{th}} \text{ order}$$

$$\langle \psi_i^{(0)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(1)} | \psi_i^{(0)} \rangle = 0 \quad 1^{\text{st}} \text{ order}$$

$$\langle \psi_i^{(0)} | \psi_i^{(2)} \rangle + \langle \psi_i^{(1)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(2)} | \psi_i^{(0)} \rangle = 0 \quad 2^{\text{nd}} \text{ order}$$

...

1st order corrections to the energies

- Starting from the 1st order of the Schrödinger equation

$$H^{(0)}|\psi_i^{(1)}\rangle + H^{(1)}|\psi_i^{(0)}\rangle = \varepsilon_i^{(0)}|\psi_i^{(1)}\rangle + \varepsilon_i^{(1)}|\psi_i^{(0)}\rangle$$

and premultiplying by $\langle\psi_i^{(0)}|$, we get:

$$\underbrace{\langle\psi_i^{(0)}|H^{(0)}|\psi_i^{(1)}\rangle}_{\varepsilon_i^{(0)}\langle\psi_i^{(0)}|\psi_i^{(1)}\rangle} + \langle\psi_i^{(0)}|H^{(1)}|\psi_i^{(0)}\rangle = \varepsilon_i^{(0)}\langle\psi_i^{(0)}|\psi_i^{(1)}\rangle + \varepsilon_i^{(1)}\underbrace{\langle\psi_i^{(0)}|\psi_i^{(0)}\rangle}_1$$

and thus, finally, we have the **Hellman-Feynman theorem**:

$$\varepsilon_i^{(1)} = \langle\psi_i^{(0)}|H^{(1)}|\psi_i^{(0)}\rangle$$

- The 0th order wavefunctions are thus the only required ingredient to obtain the 1st order corrections to the energies.

2nd order corrections to the energies

- Starting from the 2nd order of the Schrödinger equation

$$H^{(0)}|\psi_i^{(2)}\rangle + H^{(1)}|\psi_i^{(1)}\rangle + H^{(2)}|\psi_i^{(0)}\rangle = \varepsilon_i^{(0)}|\psi_i^{(2)}\rangle + \varepsilon_i^{(1)}|\psi_i^{(1)}\rangle + \varepsilon_i^{(2)}|\psi_i^{(0)}\rangle$$

and premultiplying by $\langle\psi_i^{(0)}|$, we get:

$$\underbrace{\varepsilon_i^{(0)}\langle\psi_i^{(0)}|\psi_i^{(2)}\rangle}_{\langle\psi_i^{(0)}|H^{(0)}|\psi_i^{(2)}\rangle} + \langle\psi_i^{(0)}|H^{(1)}|\psi_i^{(1)}\rangle + \langle\psi_i^{(0)}|H^{(2)}|\psi_i^{(0)}\rangle = \varepsilon_i^{(0)}\langle\psi_i^{(0)}|\psi_i^{(2)}\rangle + \varepsilon_i^{(1)}\langle\psi_i^{(0)}|\psi_i^{(1)}\rangle + \underbrace{\varepsilon_i^{(2)}\langle\psi_i^{(0)}|\psi_i^{(0)}\rangle}_1$$

and thus, finally, we have:

$$\varepsilon_i^{(2)} = \langle\psi_i^{(0)}|H^{(2)}|\psi_i^{(0)}\rangle + \langle\psi_i^{(0)}|H^{(1)} - \varepsilon_i^{(1)}|\psi_i^{(1)}\rangle$$

2nd order corrections to the energies

- Since the energies are real, we can write that:

$$\begin{aligned}\varepsilon_i^{(2)} &= \langle \psi_i^{(0)} | H^{(2)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(0)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(1)} \rangle \\ &= \langle \psi_i^{(0)} | H^{(2)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(1)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(0)} \rangle\end{aligned}$$

or, combining both equalities:

$$\begin{aligned}\varepsilon_i^{(2)} &= \langle \psi_i^{(0)} | H^{(2)} | \psi_i^{(0)} \rangle \\ &\quad + \frac{1}{2} \left(\langle \psi_i^{(0)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(1)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(0)} \rangle \right)\end{aligned}$$

- Using the expansion of the normalization condition at 1st order, we can finally write that:

$$\varepsilon_i^{(2)} = \langle \psi_i^{(0)} | H^{(2)} | \psi_i^{(0)} \rangle + \frac{1}{2} \left(\langle \psi_i^{(0)} | H^{(1)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(1)} | H^{(1)} | \psi_i^{(0)} \rangle \right)$$

- To obtain the 2nd order corrections to the energies, the only required ingredients are the 0th and 1st order wavefunctions.

1st order corrections to the wavefunctions

- The 1st order of the Schrödinger equation

$$H^{(0)}|\psi_i^{(1)}\rangle + H^{(1)}|\psi_i^{(0)}\rangle = \varepsilon_i^{(0)}|\psi_i^{(1)}\rangle + \varepsilon_i^{(1)}|\psi_i^{(0)}\rangle$$

can be rewritten gathering the terms containing $|\psi_i^{(1)}\rangle$:

$$\left(H^{(0)} - \varepsilon_i^{(0)}\right)|\psi_i^{(1)}\rangle = -\left(H^{(1)} - \varepsilon_i^{(1)}\right)|\psi_i^{(0)}\rangle$$

producing the so-called **Sternheimer equation**.

- In order to get $|\psi_i^{(1)}\rangle$ one would like to invert the $(H^{(0)} - \varepsilon_i^{(0)})$ operator, but it cannot be done as such since $\varepsilon_i^{(0)}$ is an eigenvalue of $H^{(0)}$. The problem can be solved by expressing the 1st order wavefunction as a linear combination of the 0th order ones:

$$|\psi_i^{(1)}\rangle = \sum_j c_{ij}^{(1)}|\psi_j^{(0)}\rangle$$

1st order corrections to the wavefunctions

- We separate the 0th order wavefunctions into two subsets:

- ★ those associated to $\varepsilon_i^{(0)} : j \in I$ if $H^{(0)} |\psi_j^{(0)}\rangle = \varepsilon_i^{(0)} |\psi_j^{(0)}\rangle$
(just $|\psi_i^{(0)}\rangle$ if the energy is non-degenerate)

- ★ those that belong to the subspace that is orthogonal: $j \in I^\perp$

$$|\psi_i^{(1)}\rangle = \sum_j c_{ij}^{(1)} |\psi_j^{(0)}\rangle = \sum_{j \in I} c_{ij}^{(1)} |\psi_j^{(0)}\rangle + \sum_{j \in I^\perp} c_{ij}^{(1)} |\psi_j^{(0)}\rangle$$

- The Sternheimer equation can thus be rewritten as:

$$\begin{aligned} \left(H^{(0)} - \varepsilon_i^{(0)} \right) |\psi_i^{(1)}\rangle &= \sum_j c_{ij}^{(1)} \left(H^{(0)} - \varepsilon_i^{(0)} \right) |\psi_j^{(0)}\rangle \\ &= \sum_{j \in I^\perp} c_{ij}^{(1)} \left(\varepsilon_j^{(0)} - \varepsilon_i^{(0)} \right) |\psi_j^{(0)}\rangle \\ &= - \left(H^{(1)} - \varepsilon_i^{(1)} \right) |\psi_i^{(0)}\rangle \end{aligned}$$

1st order corrections to the wavefunctions

- Premultiplying by $\langle \psi_k^{(0)} |$ with $k \in I^\perp$, we get:

$$\sum_{j \in I^\perp} c_{ij}^{(1)} \left(\epsilon_j^{(0)} - \epsilon_i^{(0)} \right) \underbrace{\langle \psi_k^{(0)} | \psi_j^{(0)} \rangle}_{\delta_{kj}} = - \langle \psi_k^{(0)} | H^{(1)} - \epsilon_i^{(1)} | \psi_i^{(0)} \rangle$$

$\langle \psi_k^{(0)} | \psi_i^{(0)} \rangle = 0$
since $k \in I^\perp$

$$c_{ik}^{(1)} \left(\epsilon_k^{(0)} - \epsilon_i^{(0)} \right) = - \langle \psi_k^{(0)} | H^{(1)} | \psi_i^{(0)} \rangle$$

and, thus:

$$c_{ij}^{(1)} = \frac{1}{\epsilon_i^{(0)} - \epsilon_j^{(0)}} \langle \psi_j^{(0)} | H^{(1)} | \psi_i^{(0)} \rangle \quad \text{for } j \in I^\perp$$

1st order corrections to the wavefunctions

- Premultiplying by $\langle \psi_k^{(0)} |$ with $k \in I$, we get:

$$\sum_{j \in I^\perp} c_{ij}^{(1)} \left(\epsilon_j^{(0)} - \epsilon_i^{(0)} \right) \underbrace{\langle \psi_k^{(0)} | \psi_j^{(0)} \rangle}_0 = - \langle \psi_k^{(0)} | H^{(1)} - \epsilon_i^{(1)} | \psi_i^{(0)} \rangle$$

$\langle \psi_k^{(0)} | \psi_i^{(0)} \rangle = \delta_{ki}$
since $k \in I$

$$\epsilon_k^{(1)} \delta_{ki} = \langle \psi_k^{(0)} | H^{(1)} | \psi_i^{(0)} \rangle$$

- For $k = i$, it is nothing but the Hellmann-Feynman theorem.
But, it does not provide any information on the $c_{ij}^{(1)}$ for $j \in I$.
- In fact, there is a gauge freedom that allows to choose them equal to zero.

1st order corrections to the wavefunctions

- Finally, we can write the so-called **sum over states** expression:

$$|\psi_i^{(1)}\rangle = \sum_{j \in I^\perp} |\psi_j^{(0)}\rangle \frac{1}{\epsilon_i^{(0)} - \epsilon_j^{(0)}} \langle \psi_j^{(0)} | H^{(1)} | \psi_i^{(0)} \rangle$$

which requires the knowledge of all the 0th order wavefunctions and energies.

- Instead, if we define the projector P_{I^\perp} onto the subspace I^\perp by:

$$P_{I^\perp} = \sum_{j \in I^\perp} |\psi_j^{(0)}\rangle \langle \psi_j^{(0)}|$$

we can rewrite the Sterheimer equation in that subspace:

$$P_{I^\perp} \left(H^{(0)} - \epsilon_i^{(0)} \right) P_{I^\perp} |\psi_i^{(1)}\rangle = -P_{I^\perp} H^{(1)} |\psi_i^{(0)}\rangle$$

1st order corrections to the wavefunctions

- In this form, the singularity has disappeared and it can thus be inverted:

$$P_{I^\perp} |\psi_i^{(1)}\rangle = - \left[P_{I^\perp} \left(H^{(0)} - \varepsilon_i^{(0)} \right) P_{I^\perp} \right]^{-1} H^{(1)} |\psi_i^{(0)}\rangle$$

and defining the Green's function in the subspace I^\perp as:

$$G_{I^\perp}(\varepsilon) = \left[P_{I^\perp} \left(\varepsilon - H^{(0)} \right) P_{I^\perp} \right]^{-1}$$

we can write:

$$P_{I^\perp} |\psi_i^{(1)}\rangle = G_{I^\perp}(\varepsilon_i^{(0)}) H^{(1)} |\psi_i^{(0)}\rangle$$

- This is the **Green's function technique** for dealing with the Sternheimer equation.

2nd order corrections to the energies

- The sum over states expression for the 1st order wavefunctions:

$$|\psi_i^{(1)}\rangle = \sum_{j \in I^\perp} |\psi_j^{(0)}\rangle \frac{1}{\epsilon_i^{(0)} - \epsilon_j^{(0)}} \langle \psi_j^{(0)} | H^{(1)} | \psi_i^{(0)} \rangle$$

can be inserted in the 2nd order corrections to the energies:

$$\epsilon_i^{(2)} = \langle \psi_i^{(0)} | H^{(2)} | \psi_i^{(0)} \rangle + \frac{1}{2} \left(\langle \psi_i^{(0)} | H^{(1)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(1)} | H^{(1)} | \psi_i^{(0)} \rangle \right)$$

leading to:

$$\begin{aligned} \epsilon_i^{(2)} = & \langle \psi_i^{(0)} | H^{(2)} | \psi_i^{(0)} \rangle \\ & + \sum_{j \in I^\perp} \langle \psi_i^{(0)} | H^{(1)} | \psi_j^{(0)} \rangle \frac{1}{\epsilon_i^{(0)} - \epsilon_j^{(0)}} \langle \psi_j^{(0)} | H^{(1)} | \psi_i^{(0)} \rangle \end{aligned}$$

2nd order corrections to the energies

- Alternatively, we can write that:

$$\langle \psi_i(\lambda) | H(\lambda) - \varepsilon_i(\lambda) | \psi_i(\lambda) \rangle = 0 \quad \forall \lambda$$

and the perturbation expansion at the 2nd order gives:

$$\begin{aligned} & \langle \psi_i^{(0)} | H^{(0)} - \varepsilon_i^{(0)} | \psi_i^{(2)} \rangle \\ + & \langle \psi_i^{(0)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(1)} | H^{(0)} - \varepsilon_i^{(0)} | \psi_i^{(1)} \rangle \\ + & \langle \psi_i^{(0)} | H^{(2)} - \varepsilon_i^{(2)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(1)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(2)} | H^{(0)} - \varepsilon_i^{(0)} | \psi_i^{(0)} \rangle = 0 \end{aligned}$$

- It can be shown that the sum of the terms in a row or in column vanishes! Getting rid of the first row and the last column, we get another expression for the 2nd order corrections to the energies:

$$\begin{aligned} \varepsilon_i^{(2)} = & \langle \psi_i^{(0)} | H^{(2)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(1)} | H^{(0)} - \varepsilon_i^{(0)} | \psi_i^{(1)} \rangle \\ & + \langle \psi_i^{(0)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(1)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(0)} \rangle \end{aligned}$$

2nd order corrections to the energies

- Actually, a number of other expressions exist for the 2nd order corrections to the energies.
- However, it can be demonstrated that this expression is variational in the sense that the 2nd order corrections to the energies can be obtained by minimizing it with respect to $\psi_i^{(1)}$:

$$\varepsilon_i^{(2)} = \min_{\psi_i^{(1)}} \left\{ \langle \psi_i^{(0)} | H^{(2)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(1)} | H^{(0)} - \varepsilon_i^{(0)} | \psi_i^{(1)} \rangle \right. \\ \left. + \langle \psi_i^{(0)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(1)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(0)} \rangle \right\}$$

under the constraint that:

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

3rd order corrections to the energies

- Starting from the 3rd order of the Schrödinger equation

$$H^{(0)}|\psi_i^{(3)}\rangle + H^{(1)}|\psi_i^{(2)}\rangle + H^{(2)}|\psi_i^{(1)}\rangle + H^{(3)}|\psi_i^{(0)}\rangle = \varepsilon_i^{(0)}|\psi_i^{(3)}\rangle + \varepsilon_i^{(1)}|\psi_i^{(2)}\rangle + \varepsilon_i^{(2)}|\psi_i^{(1)}\rangle + \varepsilon_i^{(3)}|\psi_i^{(0)}\rangle$$

and premultiplying by $\langle\psi_i^{(0)}|$, we get:

$$\begin{aligned} & \varepsilon_i^{(0)} \langle\psi_i^{(0)}|\psi_i^{(3)}\rangle \\ & \overbrace{\langle\psi_i^{(0)}|H^{(0)}|\psi_i^{(3)}\rangle} + \langle\psi_i^{(0)}|H^{(1)}|\psi_i^{(2)}\rangle \\ & + \langle\psi_i^{(0)}|H^{(2)}|\psi_i^{(1)}\rangle + \langle\psi_i^{(0)}|H^{(3)}|\psi_i^{(0)}\rangle \\ & = \varepsilon_i^{(0)} \langle\psi_i^{(0)}|\psi_i^{(3)}\rangle + \varepsilon_i^{(1)} \langle\psi_i^{(0)}|\psi_i^{(2)}\rangle \\ & + \varepsilon_i^{(2)} \langle\psi_i^{(0)}|\psi_i^{(1)}\rangle + \varepsilon_i^{(3)} \underbrace{\langle\psi_i^{(0)}|\psi_i^{(0)}\rangle}_1 \end{aligned}$$

3rd order corrections to the energies

- Finally, we we can write:

$$\begin{aligned}\varepsilon_i^{(3)} = & \langle \psi_i^{(0)} | H^{(3)} | \psi_i^{(0)} \rangle \\ & + \langle \psi_i^{(0)} | H^{(2)} - \varepsilon_i^{(2)} | \psi_i^{(1)} \rangle \\ & + \langle \psi_i^{(0)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(2)} \rangle\end{aligned}$$

- This expression of the 3rd order corrections to the energies requires to know the wavefunctions up to the 2nd order.

3rd order corrections to the energies

- Alternatively, we can write that:

$$\langle \psi_i(\lambda) | H(\lambda) - \varepsilon_i(\lambda) | \psi_i(\lambda) \rangle = 0 \quad \forall \lambda$$

and the perturbation expansion at the 3rd order gives:

$$\begin{aligned} & \langle \psi_i^{(0)} | H^{(0)} - \varepsilon_i^{(0)} | \psi_i^{(3)} \rangle \\ & + \langle \psi_i^{(0)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(2)} \rangle + \langle \psi_i^{(1)} | H^{(0)} - \varepsilon_i^{(0)} | \psi_i^{(2)} \rangle \\ & + \langle \psi_i^{(0)} | H^{(2)} - \varepsilon_i^{(2)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(1)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(2)} | H^{(0)} - \varepsilon_i^{(0)} | \psi_i^{(1)} \rangle \\ & + \langle \psi_i^{(0)} | H^{(3)} - \varepsilon_i^{(3)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(1)} | H^{(2)} - \varepsilon_i^{(2)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(2)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(3)} | H^{(0)} - \varepsilon_i^{(0)} | \psi_i^{(0)} \rangle = 0 \end{aligned}$$

- Again, the sum of the terms in a row or in column vanishes. So, getting rid of the first two rows and the last two columns, we get another expression that does not require to know the 2nd order wavefunctions :

$$\begin{aligned} \varepsilon_i^{(3)} & = \langle \psi_i^{(0)} | H^{(3)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(1)} | H^{(1)} - \varepsilon_i^{(1)} | \psi_i^{(1)} \rangle \\ & \quad + \langle \psi_i^{(0)} | H^{(2)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(1)} | H^{(2)} | \psi_i^{(0)} \rangle \end{aligned}$$

Summary

- There are 4 different methods to get the 1st order wavefunctions:
 - ★ solving the Sternheimer equation directly, complemented by a condition derived from the normalization requirement
 - ★ using the Green's function technique
 - ★ exploiting the sum over states expression
 - ★ minimizing the constrained functional for the 2nd order corrections to the energies
- With these 1st order wavefunctions, both the 2nd and 3rd order corrections to the energies can be obtained.
- More generally, the n^{th} order wavefunctions give access to the $(2n)^{\text{th}}$ and $(2n+1)^{\text{th}}$ order energy [**“2n+1” theorem**].

Outline

Perturbation Theory

Density Functional Perturbation Theory

**Atomic displacements and
homogeneous electric field**

Reference system

- In DFT, one needs to minimize the electronic energy functional:

$$E_{el}[\rho^{(0)}] = \sum_{i=1}^{N_e} \left\langle \psi_i^{(0)} \left| T + V_{ext}^{(0)} \right| \psi_i^{(0)} \right\rangle + E_{Hxc}^{(0)}[\rho^{(0)}]$$

in which the electronic density is given by:

$$\rho^{(0)}(\mathbf{r}) = \sum_{i=1}^{N_e} \left[\psi_i^{(0)}(\mathbf{r}) \right]^* \psi_i^{(0)}(\mathbf{r})$$

under the constraint that:

$$\left\langle \psi_i^{(0)} \left| \psi_j^{(0)} \right\rangle = \delta_{ij}$$

- Alternatively, one can solve the **reference Schrödinger equation**:

$$H^{(0)} \left| \psi_i^{(0)} \right\rangle = \left[-\frac{1}{2} \nabla^2 + V_{ext}^{(0)} + V_{Hxc}^{(0)} \right] \left| \psi_i^{(0)} \right\rangle = \varepsilon_i^{(0)} \left| \psi_i^{(0)} \right\rangle$$

where the Hartree and exchange correlation potential is:

$$V_{Hxc}^{(0)}(\mathbf{r}) = \frac{\delta E_{Hxc}^{(0)}[\rho^{(0)}]}{\delta \rho(\mathbf{r})}$$

Perturbed system

- The electronic energy functional to be minimized is:

$$E_{el}[\rho(\lambda)] = \sum_{i=1}^{N_e} \langle \psi_i(\lambda) | T + V_{ext}(\lambda) | \psi_i(\lambda) \rangle + E_{Hxc}[\rho(\lambda)]$$

in which the electronic density is given by:

$$\rho(\mathbf{r}; \lambda) = \sum_{i=1}^{N_e} \psi_i^*(\mathbf{r}; \lambda) \psi_i(\mathbf{r}; \lambda)$$

under the constraint that:

$$\langle \psi_i(\lambda) | \psi_j(\lambda) \rangle = \delta_{ij}$$

- Alternatively, the **Schrödinger equation** to be solved is:

$$H(\lambda) | \psi_i(\lambda) \rangle = \left[-\frac{1}{2} \nabla^2 + V_{ext}(\lambda) + V_{Hxc}(\lambda) \right] | \psi_i(\lambda) \rangle = \varepsilon_i(\lambda) | \psi_i(\lambda) \rangle$$

where the Hartree and exchange correlation potential is:

$$V_{Hxc}(\mathbf{r}; \lambda) = \frac{\delta E_{Hxc}[\rho(\lambda)]}{\delta \rho(\mathbf{r})}$$

1st order of perturbation theory in DFT

- For the energy, it can be shown that:

$$E_{el}^{(1)} = \sum_{i=1}^{N_e} \left\langle \psi_i^{(0)} \left| (T + V_{ext})^{(1)} \right| \psi_i^{(0)} \right\rangle + \frac{d}{d\lambda} E_{Hxc}[\rho^{(0)}] \Big|_{\lambda=0}$$

This is the equivalent of the Hellman-Feynman theorem for density-functional formalism.

- For the wavefunctions, the constraint leads to:

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

2nd order energy in DFPT

- For the energy, it can be shown that:

$$\begin{aligned}
 E_{el}^{(2)} = & \sum_{i=1}^{N_e} \left[\langle \psi_i^{(1)} | (T + V_{ext})^{(1)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(0)} | (T + V_{ext})^{(1)} | \psi_i^{(1)} \rangle \right] \\
 & + \sum_{i=1}^{N_e} \left[\langle \psi_i^{(0)} | (T + V_{ext})^{(2)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(1)} | (H - \epsilon_i)^{(0)} | \psi_i^{(1)} \rangle \right] \\
 & + \frac{1}{2} \int \int \frac{\delta^2 E_{Hxc}[\rho^{(0)}]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \rho^{(1)}(\mathbf{r}) \rho^{(1)}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\
 & + \int \frac{d}{d\lambda} \frac{E_{Hxc}[\rho^{(0)}]}{\delta \rho(\mathbf{r})} \Big|_{\lambda=0} \rho^{(1)}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \frac{d^2}{d\lambda^2} E_{Hxc}[\rho^{(0)}] \Big|_{\lambda=0}
 \end{aligned}$$

with

$$\rho^{(1)}(\mathbf{r}) = \sum_{i=1}^{N_e} \left([\psi_i^{(1)}(\mathbf{r})]^* \psi_i^{(0)}(\mathbf{r}) + [\psi_i^{(0)}(\mathbf{r})]^* \psi_i^{(1)}(\mathbf{r}) \right)$$

1st order wavefunctions in DFPT

- The 1st order wavefunctions can be obtained by minimizing:

$$E_{el}^{(2)} = E_{el}^{(2)} \left[\left\{ \psi_i^{(0)} \right\}, \left\{ \psi_i^{(1)} \right\} \right]$$

with respect to $\left\{ \psi_i^{(1)} \right\}$ under the constraint: $\left\langle \psi_i^{(0)} \mid \psi_j^{(1)} \right\rangle = 0$

- These can also be obtained by solving the Sternheimer equation:

$$\left(\hat{H}^{(0)} - \varepsilon_i^{(0)} \right) \mid \psi_i^{(1)} \rangle = - \left(\hat{H}^{(1)} - \varepsilon_i^{(1)} \right) \mid \psi_i^{(0)} \rangle$$

$$H^{(1)} = (T + V_{ext})^{(1)} + \int \frac{\delta^2 E_{Hxc}[\rho^{(0)}]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \rho^{(1)}(\mathbf{r}') d\mathbf{r}'$$

$$\varepsilon_i^{(1)} = \langle \psi_i^{(0)} \mid H^{(1)} \mid \psi_i^{(0)} \rangle$$

Higher orders in DFPT

- More generally, it is easy to show that since there is a **variational principle** for the 0th order energy:

$$E_{el}^{(0)} = E_{el}^{(0)} \left[\left\{ \psi_i^{(0)} \right\} \right]$$

non-variational expression can be obtained for higher orders:

$$E_{el}^{(1)} = E_{el}^{(1)} \left[\left\{ \psi_i^{(0)} \right\} \right]$$

$$E_{el}^{(2)} = E_{el}^{(2)} \left[\left\{ \psi_i^{(0)} \right\}, \left\{ \psi_i^{(1)} \right\} \right]$$

$$E_{el}^{(3)} = E_{el}^{(3)} \left[\left\{ \psi_i^{(0)} \right\}, \left\{ \psi_i^{(1)} \right\}, \left\{ \psi_i^{(2)} \right\} \right]$$

...

- But, this is not the best that can be done!

Higher orders in DFPT

- We assume that all wavefunctions are known up to $(n-1)^{\text{th}}$ order:

$$\bar{\psi}_i = \psi_i^{<n} + O(\lambda^n) = \psi_i^{(0)} + \lambda \psi_i^{(1)} + \dots + \lambda^{n-1} \psi_i^{(n-1)} + O(\lambda^n)$$

- The variational property of the energy functional implies that:

$$E_{el} [\{ \psi_{trial} + O(\eta) \}] = E_{el} [\{ \psi_{trial} \}] + O(\eta^2)$$

- Taking $\{ \psi_{trial} \} = \{ \psi_i^{<n} \}$ and $\eta = \lambda^n$, we see that:

- ★ if the wavefunctions are known up to $(n-1)^{\text{th}}$ order,
the energy is known up to $(2n-1)^{\text{th}}$ order;

- ★ if the wavefunctions are known up to n^{th} order,
the energy is known up to $(2n+1)^{\text{th}}$ order.

- This is the **“2n+1” theorem**.

Higher orders in DFPT

- Since the variational principle is also an **extremal principle** [the error is either $> 0 \rightarrow$ **minimal principle**, or $< 0 \rightarrow$ **maximal principle**], the leading missing term is also of definite sign (it is also an extremal principle):

$$E_{el}^{(0)} = E_{el}^{(0)} \left[\left\{ \psi_i^{(0)} \right\} \right] \quad \text{variational w.r.t. } \left\{ \psi_i^{(0)} \right\}$$

$$E_{el}^{(1)} = E_{el}^{(1)} \left[\left\{ \psi_i^{(0)} \right\} \right]$$

$$E_{el}^{(2)} = E_{el}^{(2)} \left[\left\{ \psi_i^{(0)} \right\}, \left\{ \psi_i^{(1)} \right\} \right] \quad \text{variational w.r.t. } \left\{ \psi_i^{(1)} \right\}$$

$$E_{el}^{(3)} = E_{el}^{(3)} \left[\left\{ \psi_i^{(0)} \right\}, \left\{ \psi_i^{(1)} \right\} \right]$$

$$E_{el}^{(4)} = E_{el}^{(4)} \left[\left\{ \psi_i^{(0)} \right\}, \left\{ \psi_i^{(1)} \right\}, \left\{ \psi_i^{(2)} \right\} \right] \quad \text{variational w.r.t. } \left\{ \psi_i^{(2)} \right\}$$

$$E_{el}^{(5)} = E_{el}^{(5)} \left[\left\{ \psi_i^{(0)} \right\}, \left\{ \psi_i^{(1)} \right\}, \left\{ \psi_i^{(2)} \right\} \right]$$

Mixed derivatives in DFPT

- Similar expressions exist for mixed derivatives (related to two different perturbations j_1 and j_2):

$$E_{el}^{j_1 j_2} = E_{el}^{j_1 j_2} \left\{ \psi_i^{(0)}; \psi_i^{j_1}; \psi_i^{j_2} \right\}$$

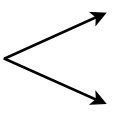
- The extremal principle is lost but the expression is stationary:
 - ★ the error is proportional to the product of errors made in the 1st order quantities for the first and second perturbations;
 - ★ if these errors are small, their product will be much smaller;
 - ★ however, the sign of the error is undetermined, unlike for the variational expressions.

Order of calculation in DFPT

1. Ground state calculation: $V_{ext}^{(0)} \rightarrow \psi_i^{(0)}$ and $\rho^{(0)}$

2. **FOR EACH** perturbation j_1 **DO**

use $\psi_i^{(0)}$ and $\rho^{(0)}$

$V_{ext}^{j_1} \rightarrow \psi_i^{j_1}$ and ρ^{j_1}  minimize 2nd order energy
solve Sternheimer equation

ENDDO

3. **FOR EACH** perturbation pair $\{j_1, j_2\}$ **DO**

determine $E^{j_1 j_2}$ using both $\psi_i^{j_1}$ and $\psi_i^{j_2}$ (stationary expression)

using just $\psi_i^{j_1}$

ENDDO

4. Post-processing to get the physical properties from $E^{j_1 j_2}$

Outline

Perturbation Theory

Density Functional Perturbation Theory

**Atomic displacements and
homogeneous electric field**

Perturbations of the periodic solid

- Let us consider the case where the reference system is periodic:

$$V_{ext}^{(0)}(\mathbf{r} + \mathbf{R}_a) = V_{ext}^{(0)}(\mathbf{r})$$

- It can be shown that if the perturbation is characterized by a wavevector \mathbf{q} such that:

$$V_{ext}^{(1)}(\mathbf{r} + \mathbf{R}_a) = e^{i\mathbf{q}\cdot\mathbf{R}_a} V_{ext}^{(1)}(\mathbf{r})$$

all the responses, at linear order, will also be characterized by \mathbf{q} :

$$\rho^{(1)}(\mathbf{r} + \mathbf{R}_a) = e^{i\mathbf{q}\cdot\mathbf{R}_a} \rho^{(1)}(\mathbf{r})$$

$$\psi_{i,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r} + \mathbf{R}_a) = e^{i\mathbf{q}\cdot\mathbf{R}_a} \psi_{i,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r})$$

...

Perturbations of the periodic solid

- We define related periodic quantities:

$$\bar{\rho}^{(1)}(\mathbf{r}) = e^{-i\mathbf{q}\cdot\mathbf{r}} \rho^{(1)}(\mathbf{r})$$

$$u_{i,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r}) = (N_e \Omega_0)^{1/2} e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{R}} \psi_{i,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r})$$

- In the equations of DFPT, only these periodic quantities appear: the phases $e^{-i\mathbf{q}\cdot\mathbf{r}}$ and $e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{R}}$ can be factorized.
- The treatment of perturbations incommensurate with the unperturbed system periodicity is mapped onto the original periodic system.
- This is interesting for atomic displacements but more importantly for electric fields.

Electronic dielectric permittivity tensor

- The **dielectric permittivity tensor** is the coefficient of proportionality between the macroscopic displacement field and the macroscopic electric field, in the linear regime:

$$\mathcal{D}_{\text{mac},\alpha} = \sum_{\alpha'} \epsilon_{\alpha\alpha'} \mathcal{E}_{\text{mac},\alpha'}$$

$$\epsilon_{\alpha\alpha'} = \frac{\partial \mathcal{D}_{\text{mac},\alpha}}{\partial \mathcal{E}_{\text{mac},\alpha'}} = \delta_{\alpha\alpha'} + 4\pi \frac{\partial \mathcal{P}_{\text{mac},\alpha}}{\partial \mathcal{E}_{\text{mac},\alpha'}}$$

- At high frequencies of the applied field, the dielectric permittivity tensor only includes a contribution from the electronic polarization:

$$\epsilon_{\alpha\alpha'}^{\infty} = \delta_{\alpha\alpha'} - \frac{4\pi}{\Omega_0} 2E_{el}^{\mathcal{E}_{\alpha}^* \mathcal{E}_{\alpha'}}$$

$$\sum_{\alpha\alpha'} \hat{q}_{\alpha} \epsilon_{\alpha\alpha'}^{\infty} \hat{q}'_{\alpha'} = \frac{1}{\epsilon_{\mathbf{G}=0, \mathbf{G}'=0}^{-1}(\mathbf{q} \rightarrow 0)}$$

unit vector

Treatment of homogeneous electric fields

- When the perturbation is an electric field, we have:

$$V_{ext}^{(1)}(\mathbf{r}) = \mathcal{E} \cdot \mathbf{r}$$

which breaks the periodic boundary conditions.

- To obtain the 2nd order derivative of the energy:

$$2E_{el}^{\mathcal{E}\alpha^* \mathcal{E}\alpha'} = \int \rho^{\mathcal{E}\alpha'}(\mathbf{r}) r_{\alpha} d\mathbf{r}$$

the following matrix elements need to be computed:

$$\left\langle u_{c,\mathbf{k}}^{(0)} \left| r_{\alpha'} \right| u_{v,\mathbf{k}}^{E\alpha} \right\rangle \text{ and } \left\langle u_{c,\mathbf{k}}^{E\alpha} \left| r_{\alpha'} \right| u_{v,\mathbf{k}}^{(0)} \right\rangle$$

↑ ↑
conduction valence

Treatment of homogeneous electric fields

- These matrix elements can be determined writing that:

$$\begin{aligned} \left(\varepsilon_{i,\mathbf{k}}^{(0)} - \varepsilon_{j,\mathbf{k}}^{(0)} \right) \left\langle u_{i,\mathbf{k}}^{(0)} \left| r_\alpha \right| u_{j,\mathbf{k}}^{(0)} \right\rangle &= \left\langle u_{i,\mathbf{k}}^{(0)} \left| H_{\mathbf{k}\mathbf{k}}^{(0)} r_\alpha - r_\alpha H_{\mathbf{k}\mathbf{k}}^{(0)} \right| u_{j,\mathbf{k}}^{(0)} \right\rangle \\ &= \left\langle u_{i,\mathbf{k}}^{(0)} \left| -i \frac{\partial H_{\mathbf{k}\mathbf{k}}^{(0)}}{\partial k_\alpha} \right| u_{j,\mathbf{k}}^{(0)} \right\rangle \end{aligned}$$

which leads to the Sternheimer equation:

$$P_c \left(H_{\mathbf{k}\mathbf{k}}^{(0)} - \varepsilon_{j,\mathbf{k}}^{(0)} \right) P_c r_\alpha \left| u_{j,\mathbf{k}}^{(0)} \right\rangle = -P_c i \frac{\partial H_{\mathbf{k}\mathbf{k}}^{(0)}}{\partial k_\alpha} \left| u_{j,\mathbf{k}}^{(0)} \right\rangle$$

$$P_{I\perp} \left(H^{(0)} - \varepsilon_i^{(0)} \right) P_{I\perp} \left| \psi_i^{(1)} \right\rangle = -P_{I\perp} H^{(1)} \left| \psi_i^{(0)} \right\rangle$$



DDK perturbation

Born effective charge tensor

- It is defined as the proportionality coefficient relating at linear order, the polarization per unit cell, created along the direction α , and the displacement along the direction α' of the atoms belonging to the sublattice κ :

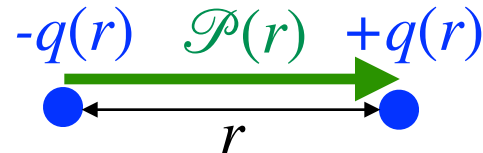
$$Z_{\kappa\alpha\alpha'}^* = \Omega_0 \left. \frac{\partial \mathcal{P}_{\text{mac},\alpha}}{\partial u_{\kappa\alpha'}} \right|_{\mathbf{q}=0} \Big|_{\mathcal{E}_\alpha=0} = \left. \frac{\partial F_{\kappa\alpha'}}{\partial \mathcal{E}_\alpha} \right|_{u_{\kappa\alpha'}=0}$$

- It also describes the linear relation between the force in the direction α' on an atom κ and the macroscopic electric field
- Both can be connected to the mixed 2nd order derivative of the energy with respect to $u_{\kappa\alpha'}$ and \mathbf{E}_α
- Sum rule: $\sum_{\kappa} Z_{\kappa\alpha\alpha'}^* = 0$

Born effective charge tensor

- Model system:

- ★ diatomic molecule:



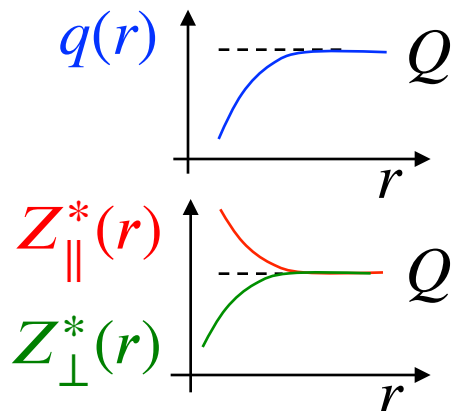
- ★ dipole moment related to static charge $q(r)$: $\mathcal{P}(r) = q(r) r$

- Atomic polar charge $Z^*(r)$ such that $\partial \mathcal{P}(r) = Z^*(r) \partial r$

- ★ purely covalent case: $q(r) = 0 = Z^*(r)$

- ★ purely ionic case: $q(r) = Q \neq 0 \Rightarrow Z^*(r) = Q$

- ★ mixed ionic-covalent: $\partial \mathcal{P}(r) = q(r) \partial r + \partial q(r) r$



$$Z^*(r) = q(r) + r \frac{\partial q(r)}{\partial r}$$

$$Z_{\alpha\beta}^*(r) = q(r) \delta_{\alpha\beta} + r_{\alpha} \frac{\partial q(r)}{\partial r_{\beta}}$$

Static dielectric permittivity tensor

- The **mode oscillator strength tensor** is defined as

$$S_{m,\alpha\alpha'} = \left(\sum_{\kappa\beta} Z_{\kappa\alpha\beta}^* U_{m\mathbf{q}=0}^*(\kappa\beta) \right) \left(\sum_{\kappa\beta'} Z_{\kappa\alpha'\beta'}^* U_{m\mathbf{q}=0}(\kappa\beta') \right)$$

- The macroscopic **static** (low-frequency) **dielectric permittivity tensor** is calculated by adding the ionic contribution to the electronic dielectric permittivity tensor:

$$\epsilon_{\alpha\alpha'}(\omega) = \epsilon_{\alpha\alpha'}^{\infty} + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\alpha'}}{\omega_m^2 - \omega^2}$$

$$\epsilon_{\alpha\alpha'}^0 = \epsilon_{\alpha\alpha'}^{\infty} + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\alpha'}}{\omega_m^2}$$

LO-TO splitting

- The macroscopic electric field that accompanies the collective atomic displacements at $\mathbf{q} \rightarrow 0$ can be treated separately:

$$\tilde{C}_{\kappa\alpha, \kappa'\alpha'}(\mathbf{q} \rightarrow 0) = \tilde{C}_{\kappa\alpha, \kappa'\alpha'}(\mathbf{q} = 0) + \tilde{C}_{\kappa\alpha, \kappa'\alpha'}^{\text{NA}}(\mathbf{q} \rightarrow 0)$$

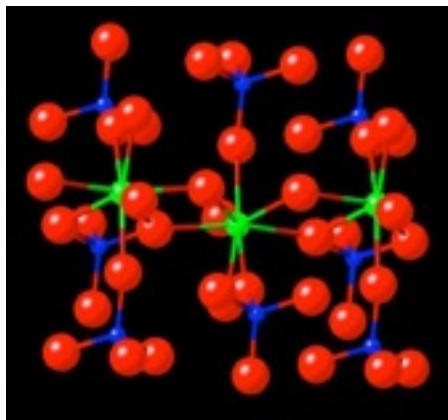
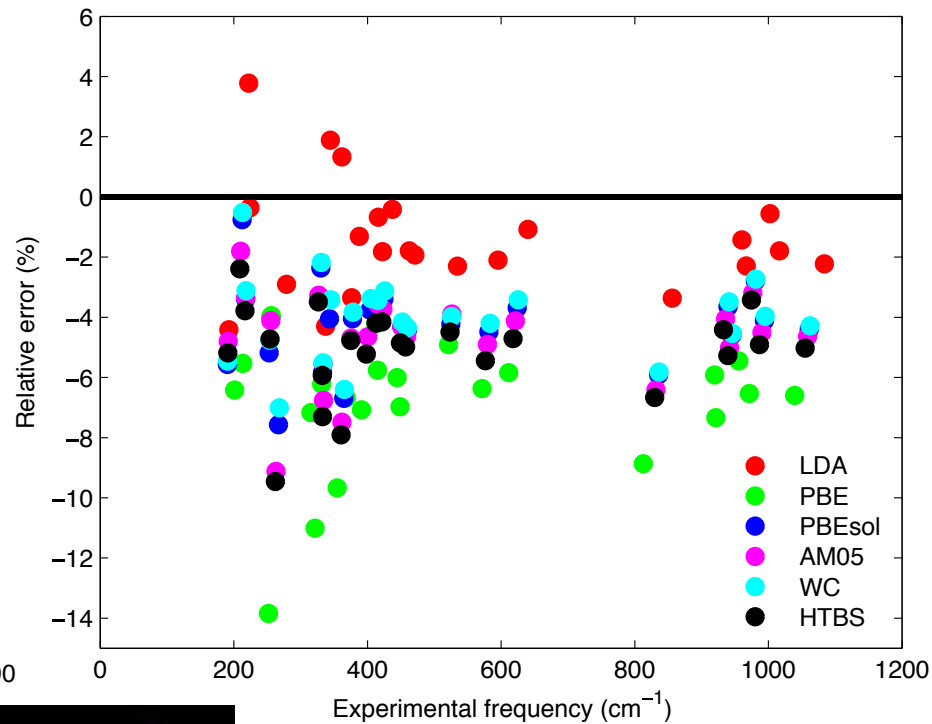
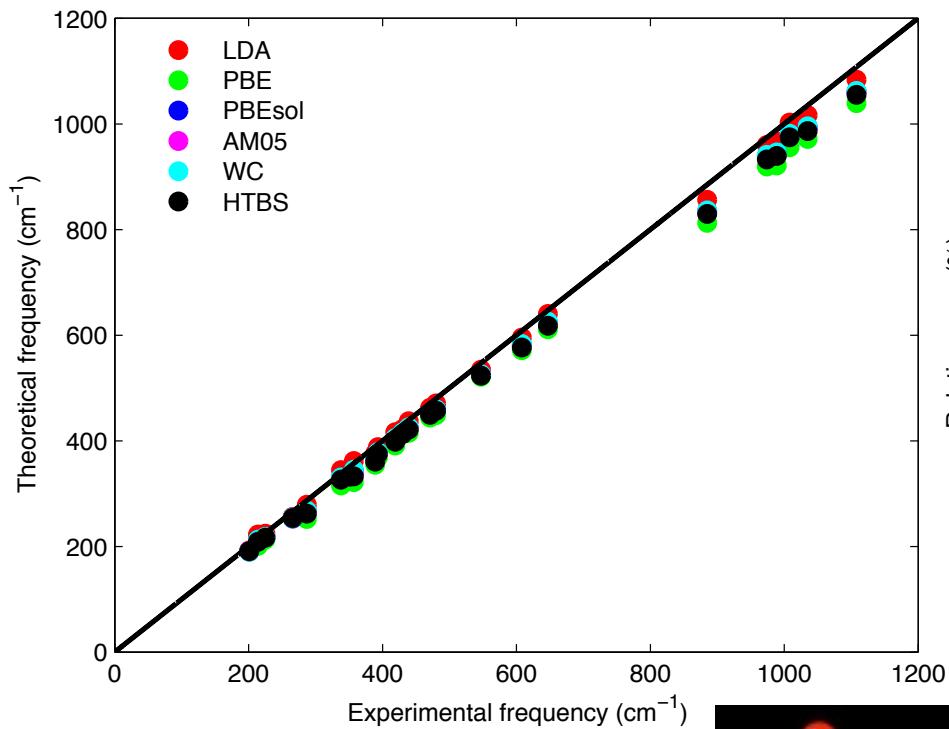
where the nonanalytical, direction-dependent term is:

$$\tilde{C}_{\kappa\alpha, \kappa'\alpha'}^{\text{NA}}(\mathbf{q} \rightarrow 0) = \frac{4\pi}{\Omega_0} \frac{\left(\sum_{\beta} q_{\gamma} Z_{\kappa\beta\alpha}^*\right) \left(\sum'_{\beta} q'_{\beta} Z_{\kappa'\beta'\alpha'}^*\right)}{\sum_{\beta\beta'} q_{\beta} \epsilon_{\beta\beta'}^{\infty} q'_{\beta}}$$

- The transverse modes are common to both \tilde{C} matrices but the longitudinal ones may be different, the frequencies are related by

$$\omega_m^2(\mathbf{q} \rightarrow 0) = \omega_m^2(\mathbf{q} = 0) + \frac{4\pi}{\Omega_0} \frac{\sum_{\alpha\alpha'} q_{\alpha} S_{m, \alpha\alpha'} q'_{\alpha}}{\sum_{\alpha\alpha'} q_{\alpha} \epsilon_{\alpha\alpha'}^{\infty} q'_{\alpha}}$$

Example 1: Zircon (phonons)



Example 1: Zircon (Born effective charges)

Atom	HfSiO ₄	ZrSiO ₄	
M	$\begin{pmatrix} +5.28 & +5.28 & +4.68 \\ +3.18 & +3.18 & +4.35 \\ -1.15 & 0 & 0 \\ 0 & -3.08 & -0.19 \\ 0 & -0.35 & -2.26 \\ [-1.15 & -3.16 & -2.18] \end{pmatrix}$	$\begin{pmatrix} +5.41 & +5.41 & +4.63 \\ +3.25 & +3.25 & +4.42 \\ -1.15 & 0 & 0 \\ 0 & -3.17 & -0.16 \\ 0 & -0.34 & -2.25 \\ [-1.15 & -3.23 & -2.19] \end{pmatrix}$	Nominal:
Si			M → +4
O			Si → +4
			O → -2

- M : **anomalously large** (esp. Z_{\perp}) → PbZrO₃, ZrO₂
- Si : smaller deviations (↗ and ↘) → SiO₂ (α-quartz or stishovite)
- O : **strong anisotropy** → SiO₂ stishovite or TiO₂ rutile
 - ↗ in the y-z plane (plane of the M-O bonds) (rem: ≠ from SiO₂ α-quartz)
 - ↘ in the x direction (where 2 ↘ components)

Interpretation:

- mixed ionic-covalent bonding
- closer to stishovite than α-quartz in agreement with naive bond counting for O atoms

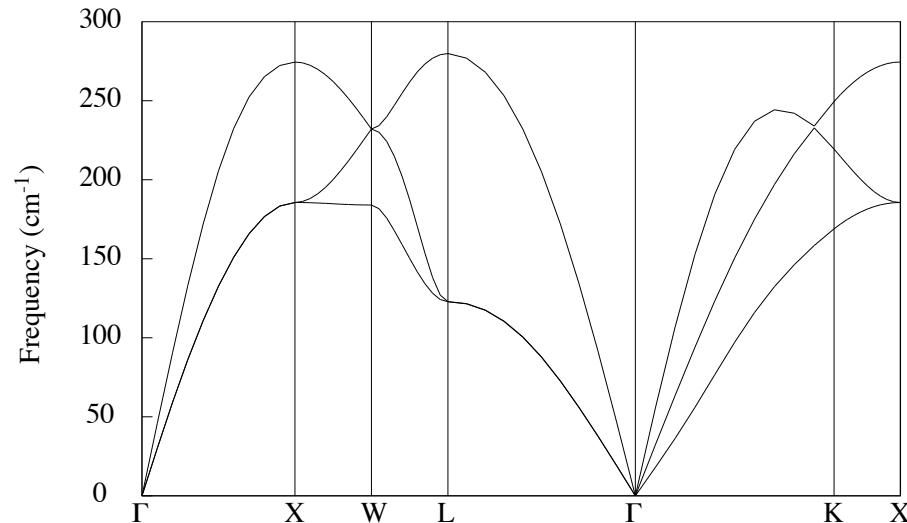
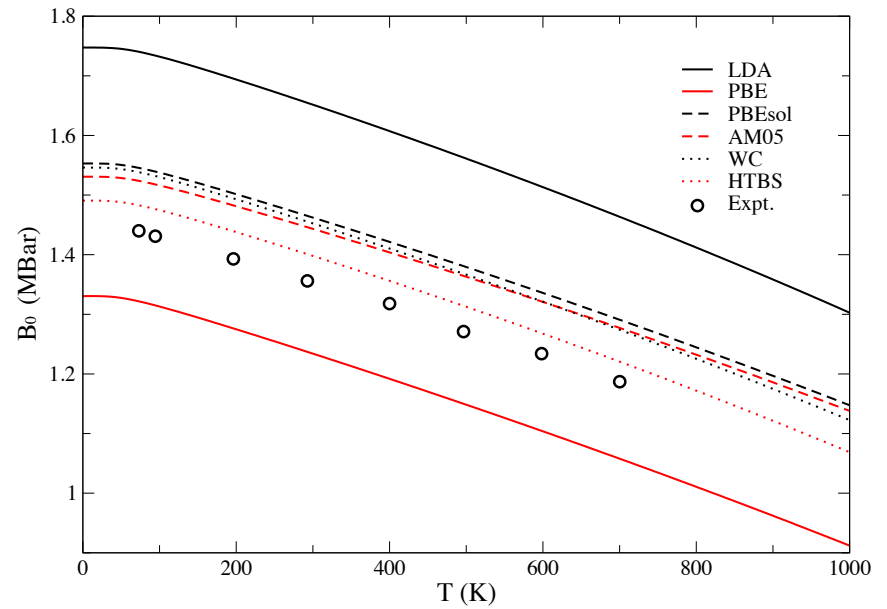
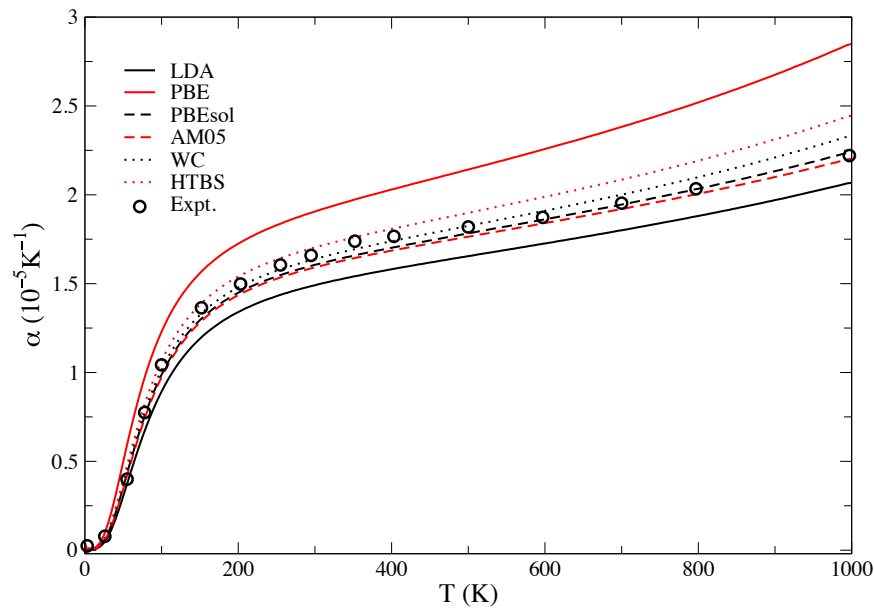
Example 1: Zircon (dielectric properties)

	HfSiO ₄		ZrSiO ₄	
		⊥		⊥
ϵ_∞	4.11	3.88	4.26	4.06
$\Delta\epsilon_1$	4.93	4.38	5.90	5.16
$\Delta\epsilon_2$	0.81	0.75	0.52	1.31
$\Delta\epsilon_3$	0.80	0.35	0.85	0.05
$\Delta\epsilon_4$		1.27		1.38
ϵ_0	10.65	10.63	11.53	11.96

	HfSiO ₄		ZrSiO ₄	
	Z_m^*	S_m	Z_m^*	S_m
A _{2u} (1)	6.85	7.39	7.68	10.06
A _{2u} (2)	3.78	4.24	2.76	2.64
A _{2u} (3)	6.60	11.22	6.71	11.50
E _u (1)	5.93	4.05	6.79	5.91
E _u (2)	2.94	1.70	3.51	2.71
E _u (3)	1.69	0.91	0.28	0.12
E _u (4)	7.21	14.02	7.37	14.69

- S_m and Z_m^* are the largest for the lowest and highest frequency modes
- due to the frequency factor, it is the lowest frequency mode that contributes the most to ϵ_0
- S_m and Z_m^* are smaller for HfSiO₄ ← mass difference and Born effective charges
- this effect can be compensated by a lower frequency for hafnon [e.g. A_{2u}(1)]

Example 2: Copper (thermodynamics)





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