Summer School on First-principles calculations for Condensed Matter and Nanoscience
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I. Linear responses to atomic displacements and static electric fields

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Outline:

1. Energy derivatives and physical properties
2. Computation of energy derivatives within DFPT
3. Dynamical charges
4. Zone-center phonons
5. Dielectric tensor
6. In practice

1. Energy derivatives and physical properties:

X Gonze and Ch. Lee, Phys. Rev. B 55, 10355 (1997)
R. W. Nunes and X. Gonze, Phys. Rev. B ***63*** *, 155107 (2001)*

Energy functionals :

The energy functional minimized in terms of the electronic degrees of freedom within ABINIT is

- In zero field:

The Born-Oppenheimer energy :

$$E_{e+i}[\mathbf{R}_\kappa] = \min_{\psi_{n\mathbf{k}}} \left(E_{e+i}[\mathbf{R}_\kappa, \psi_{n\mathbf{k}}] \right)$$

with

$$E_{e+i}[\mathbf{R}_\kappa, \psi_{n\mathbf{k}}] = \underbrace{\left(T_e[\psi_{n\mathbf{k}}] + E_H[\psi_{n\mathbf{k}}] + E_{xc}[\psi_{n\mathbf{k}}] + E_{ei}[\mathbf{R}_\kappa, \psi_{n\mathbf{k}}] \right)}_{E_{el}[\mathbf{R}_\kappa, \psi_{n\mathbf{k}}]} + U_{ii}[\mathbf{R}_\kappa]$$

Energy functionals:

- In non-zero field:

The related functional *

$$\mathcal{F}_{e+i}[\mathbf{R}_\kappa, \mathcal{E}] = \min_{\psi_{n\mathbf{k}}} \left(E_{e+i}[\mathbf{R}_\kappa, \psi_{n\mathbf{k}}] - \Omega_0 \ \mathcal{E} \cdot \mathcal{P}[\psi_{n\mathbf{k}}] \right)$$

or the electric enthalpy

$$\mathscr{F}_{e+i}[\mathbf{R}_\kappa, \mathcal{E}] = \min_{\psi_{n\mathbf{k}}} \left(E_{e+i}[\mathbf{R}_\kappa, \psi_{n\mathbf{k}}] - \Omega_0 \ \mathcal{E} \cdot \mathcal{P}[\psi_{n\mathbf{k}}] \right) - \frac{\Omega_0}{8\pi} \mathcal{E}^2$$

** R. W. Nunes and X. Gonze , Phys. Rev. B **63**, 155107 (2001)*
I. Souza, J. Iniguez and D. Vanderbilt, Phys. Rev. Lett. 89, 117602 (2002)

Energy expansion:

Various physical quantities are related to successive derivatives of E_{e+i} or $\mathscr{F}_{e+i}$ in terms of $\mathcal{E}$ and $\tau_\kappa = \mathbf{R}_\kappa - \mathbf{R}_\kappa^0$

$$\mathscr{F}_{e+i}[\mathbf{R}_\kappa, \mathcal{E}] = \mathscr{F}_{e+i}[\mathbf{R}_\kappa^0, 0]$$
$$+ \sum_\alpha \frac{\partial \mathscr{F}_{e+i}}{\partial \mathcal{E}_\alpha} \mathcal{E}_\alpha + \sum_\alpha \sum_\kappa \frac{\partial \mathscr{F}_{e+i}}{\partial \tau_{\kappa\alpha}} \tau_{\kappa\alpha}$$
$$+ \frac{1}{2} \sum_{\alpha\beta} \frac{\partial \mathscr{F}_{e+i}}{\partial \mathcal{E}_\alpha \partial \mathcal{E}_\beta} \mathcal{E}_\alpha \mathcal{E}_\beta + \sum_{\alpha\beta} \sum_\kappa \frac{\partial \mathscr{F}_{e+i}}{\partial \tau_{\kappa\alpha} \partial \mathcal{E}_\beta} \tau_{\kappa\alpha} \mathcal{E}_\beta$$
$$+ \frac{1}{2} \sum_{\alpha\beta} \sum_{\kappa\kappa'} \frac{\partial \mathscr{F}_{e+i}}{\partial \tau_{\kappa\alpha} \partial \tau_{\kappa'\beta}} \tau_{\kappa\alpha} \tau_{\kappa'\beta} + \ldots$$

Note : can be generalized to include strains $\rightarrow \mathscr{F}_{e+i}[\mathbf{R}_\kappa, \mathcal{E}, \eta]$

Physical quantities:

$$\mathscr{F}_{e+i}[\mathbf{R}_\kappa, \mathcal{E}] = \mathscr{F}_{e+i}[\mathbf{R}^0_\kappa, 0]$$
$$- \Omega_0 \sum_\alpha \mathcal{P}^s_\alpha \mathcal{E}_\alpha - \sum_\alpha \sum_\kappa F^0_\alpha \tau_{\kappa\alpha}$$
$$- \frac{\Omega_0}{8\pi} \sum_{\alpha\beta} \varepsilon^\infty_{\alpha\beta} \mathcal{E}_\alpha \mathcal{E}_\beta - \sum_{\alpha\beta} \sum_\kappa Z^*_{\kappa,\alpha\beta} \tau_{\kappa\alpha} \mathcal{E}_\beta$$
$$+ \frac{1}{2} \sum_{\alpha\beta} \sum_{\kappa\kappa'} C_{\alpha\beta}(\kappa,\kappa') \tau_{\kappa\alpha} \tau_{\kappa'\beta}$$

Physical quantities:

- Atomic forces :

$$F_{\kappa\alpha}[\mathbf{R}_\kappa,\mathcal{E}] = -\frac{d\mathcal{F}_{e+i}[\mathbf{R}_\kappa,\mathcal{E}]}{d\tau_{\kappa\alpha}}$$

$$= \underbrace{F^0_{\kappa\alpha}}_{=0} + \sum_\beta Z^*_{\kappa,\alpha\beta}\ \mathcal{E}_\beta - \sum_\beta \sum_{\kappa'} C_{\alpha\beta}(\kappa,\kappa')\tau_{\kappa'\beta}$$

- Electric displacement field :

$$\mathcal{D}_\beta[\mathbf{R}_\kappa,\mathcal{E}] = -\frac{4\pi}{\Omega_0}\ \frac{d\mathcal{F}_{e+i}[\mathbf{R}^0_\kappa,0]}{d\mathcal{E}_\beta}$$

$$= 4\pi\left(\underbrace{\mathcal{P}^s_\beta}_{=0} + \frac{1}{\Omega_0}\sum_\alpha\sum_\kappa Z^*_{\kappa,\alpha\beta}\ \tau_{\kappa\alpha}\right) + \sum_\alpha \varepsilon^\infty_{\alpha\beta}\,\mathcal{E}_\alpha$$

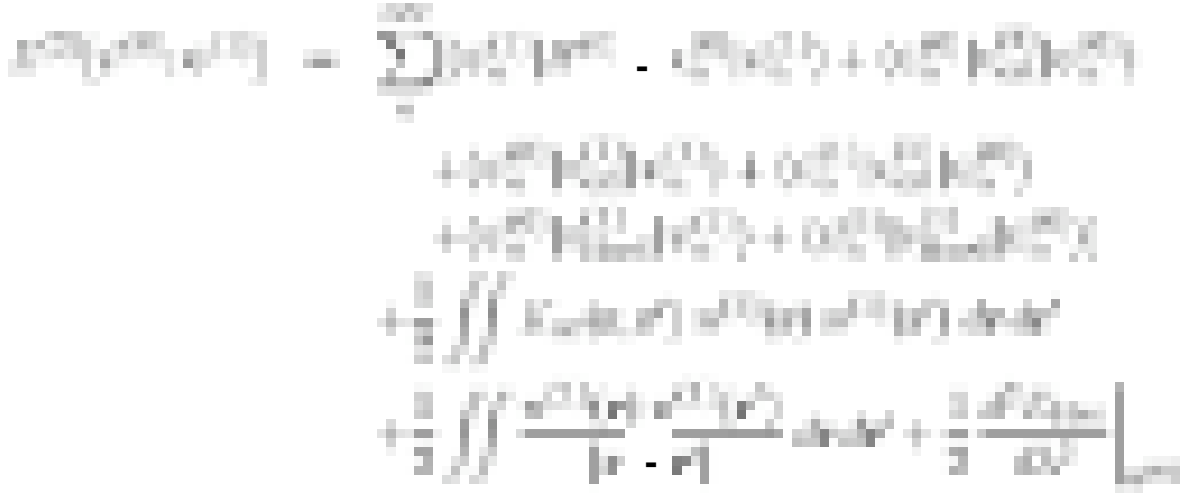
2. Computation of energy derivatives within DFPT:

X. Gonze, Phys. Rev. B ***55*** *, 10337 (1997)*
X Gonze and Ch. Lee, Phys. Rev. B 55, 10355 (1997)

Energy derivatives:

Computed through a **two-steps** procedure

1. Determination of **first-order wave-functions** from the minimization of a **variational** expression:

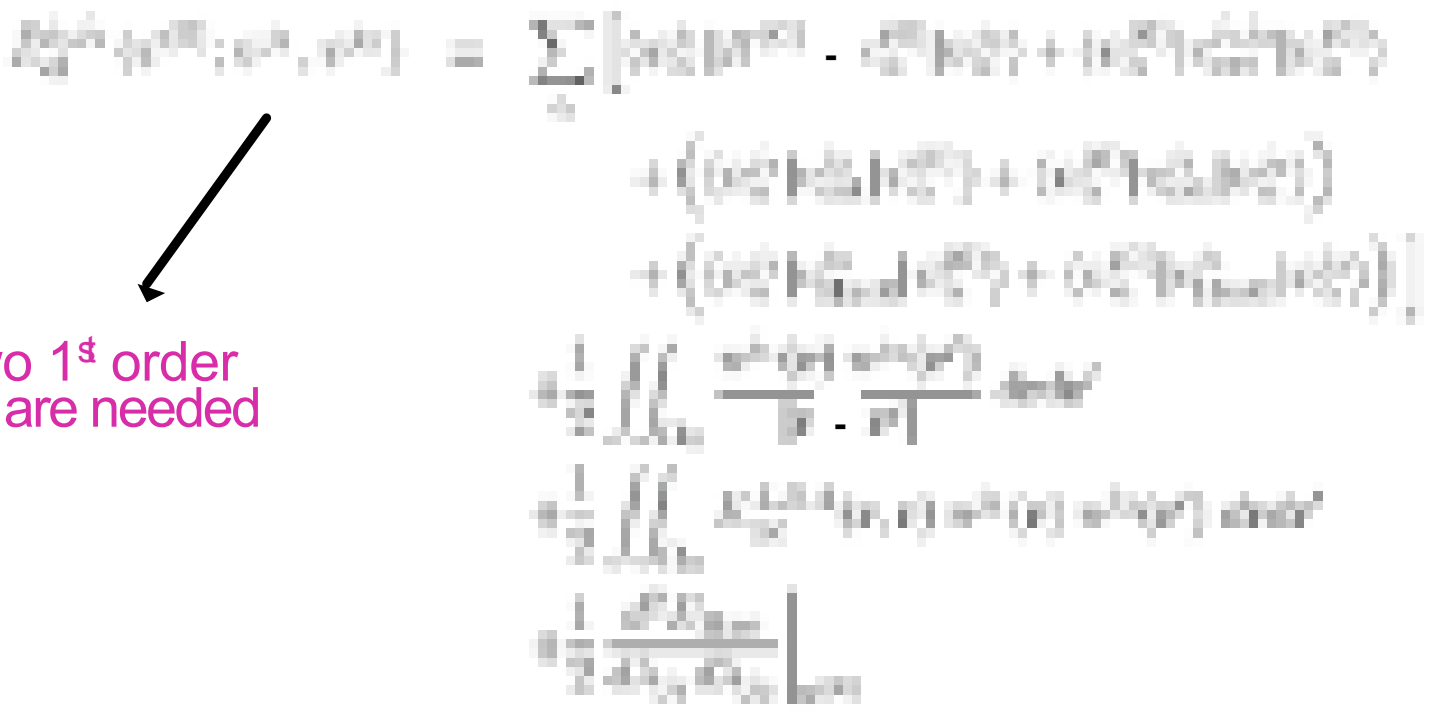


under the constraint that

Energy derivatives:

2. Evaluation of the appropriate energy derivative using :

   a. stationary expression



Two 1st order wfs are needed

Energy derivatives:

2. Evaluation of the appropriate

b. non-stationary expression

$$E_{\mathrm{el}}^{j_1 j_2} = \sum_{\alpha}^{\mathrm{occ}} \langle \psi_\alpha^{j_2} | v_{\mathrm{ext}}^{j_1} + v_{\mathrm{Hxc}}^{j_1} | \psi_\alpha^{(0)} \rangle + E_{\mathrm{non\_var}}^{j_1 j_2}$$

with

$$E_{\mathrm{non\_var}}^{j_1 j_2} = \sum_{\alpha}^{\mathrm{occ}} \langle \psi_\alpha^{(0)} | v_{\mathrm{ext}}^{j_1 j_2} | \psi_\alpha^{(0)} \rangle + \frac{1}{2} \frac{d^2 E_{\mathrm{Hxc}}}{d\lambda_{j_1} d\lambda_{j_2}} \bigg|_{n^{(0)}}$$

Only **one** 1$ order wf is needed

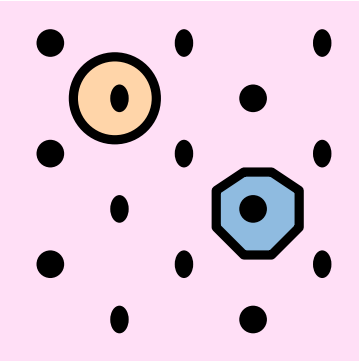
3. Dynamical charges

X Gonze and Ch. Lee, Phys. Rev. B 55, 10355 (1997)
Ph. Ghosez, J.-P. Michenaud and X. Gonze , Phys. Rev. B ***58****, 6224 (1998)*
Ph. Ghosez and X. Gonze, J. Phys. : Condens . Matter ***12****, 9179 (2000)*

Born effective charges:

- Related to a **mixed second derivative** of the Born-Oppenheimer energy.
- **Dynamical concept** distinct from conventional static ionic charges.
- Monitor various properties of ionic crystals (such as the LO-TO splitting).

Static ionic charges:



- **Popular but ill-defined concept :**

  Dependent of the theoretical model ***arbitrarily*** chosen to affect a given electron to a particular atom.

- **Numerous definitions** :

  - from wave-functions : Mulliken pop. analysis, natural atomic orbitals
  - from integrated density : sphere, **Hirshfeld** , **Bader** topological analysis
  - from the electrostatic potential : fitting by point charges (Lee)
  - from empirical models: bond-orbital model, shell-model...

- **No quantitative but *qualitative* informations :**

  - underlined by a **unique** physical factor (similar trends)
  - useful to identify **changes** (from one phase to another)
  - hybridizations **reduce** the static charges

Dynamical ionic charges:

… whenever an ambiguity arises about the definition of a concept such as the atomic charge, it can be removed by discussing only quantities that can be experimentally determined at least in principles. **W. A. Harrison**

- **Molecule :** **(atomic polar tensor)**

$$Z^*_{\kappa,\alpha\beta} = \frac{dp_\beta}{d\tau_{\kappa,\alpha}}$$

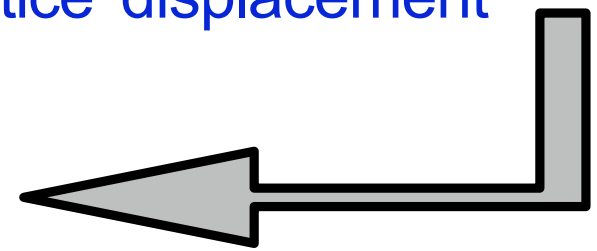
change of dipole moment under atomic displacement

- **Periodic solids :**

$$Z^*_{\kappa,\alpha\beta} = \Omega_0 \frac{d\mathcal{P}_\beta}{d\tau^{\mathbf{q}=0}_{\kappa,\alpha}}$$

change of polarization under sublattice displacement

Depends on the condition on the macroscopic electric field



Dynamical ionic charges:

$$Z^*_{\kappa,\alpha\beta} = \Omega_0 \frac{d\mathcal{P}_\beta}{d\tau_{\kappa,\alpha}}$$

$$= \Omega_0 \left.\frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}}\right|_{\mathcal{E}=0} + \Omega_0 \sum_j \left.\frac{\partial \mathcal{P}_\beta}{\partial \mathcal{E}_j}\right|_{\tau=0} \frac{\partial \mathcal{E}_j}{\partial \tau_{\kappa,\alpha}}$$

$$= Z^{*(T)}_{\kappa,\alpha\beta} + \Omega_0 \sum_j \left.\frac{(\varepsilon^\infty_{\beta j} - 1)}{4\pi}\right|_{\tau=0} \frac{\partial \mathcal{E}_j}{\partial \tau_{\kappa,\alpha}}$$

Using :

$$\mathcal{D}_\alpha = \mathcal{E}_\alpha + 4\pi\, \mathcal{P}_\alpha = \sum_j \varepsilon^\infty_{\alpha,j}\, \mathcal{E}_j$$

Born effective charge:

(*alias* **transverse** charge)

$$Z^{*(T)}_{\kappa,\alpha\beta} = \Omega_0 \left.\frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}}\right|_{\mathcal{E}=0} = -\left.\frac{\partial^2 E_{e+i}}{\partial \tau_{\kappa,\alpha}\partial \mathcal{E}_\beta}\right|_{\tau_{\kappa,\alpha}=0,\mathcal{E}=0} = \left.\frac{\partial F_{\kappa\alpha}}{\partial \mathcal{E}_\beta}\right|_{\tau_{\kappa,\alpha}=0}$$

Can be computed from different techniques:

- **linear response** : $Z^{*(T)}_{\kappa,\alpha\beta} = Z^{ion}_{\kappa}\,\delta_{\alpha\beta} + \Delta Z^{*el}_{\kappa,\alpha\beta}$

  3 different formulations

- **difference of polarization** under finite atomic displacement

- **difference of force** under finite electric field

Born effective charge:

stationary formulation

Born effective charge:

non-stationary formulations

$$\Delta Z_{\kappa,\alpha\beta} = 2\frac{\Omega_0}{(2\pi)^3}\int_{BZ}\sum_{m}^{occ} s\,\langle u^{\tau_{\kappa\alpha}}_{m\mathbf{k},\mathbf{q}=\mathbf{0}}| \; - i\frac{d}{dk_\beta}|u^{(0)}_{m\mathbf{k}}\rangle d\mathbf{k}$$

$$\Delta Z_{\kappa,\alpha\beta} = 2\left[\frac{\Omega_0}{(2\pi)^3}\int_{BZ}\sum_{m}^{occ} s\,\langle u^{(0)}_{m\mathbf{k}}|v^{/\tau_{\kappa\alpha}}_{\mathrm{ext},\mathbf{k},\mathbf{k}}|u^{\varepsilon_\beta}_{m\mathbf{k}}\rangle d\mathbf{k} + \frac{1}{2}\int_{\Omega_0}[v^{\tau_{\kappa\alpha}}_{\mathrm{xc}0,\mathbf{q}=\mathbf{0}}(\mathbf{r})][\bar{n}^{\varepsilon_\beta}(\mathbf{r})]^* d\mathbf{r}\right]$$

Callen effective charge:

(*alias* **longitudinal** charge)

$$Z^{*(L)}_{\kappa,\alpha\beta} = \Omega_0 \left.\frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}}\right|_{\mathcal{D}=0 \text{ or } \mathcal{E}=-4\pi\mathcal{P}}$$

- With $D = \mathcal{E} + 4\pi\mathcal{P} = 0$:

$$Z^{*(L)}_{\kappa,\alpha\beta} = Z^{*(T)}_{\kappa,\alpha\beta} + \Omega_0 \sum_j \left.\frac{(\varepsilon^{\infty}_{\beta j} - 1)}{4\pi}\right|_{\tau=0} \underbrace{\left.\frac{\partial \mathcal{E}_j}{\partial \tau_{\kappa,\alpha}}\right|_{\mathcal{E}=-4\pi\mathcal{P}}}_{-\frac{4\pi}{\Omega_0} Z^{*(L)}_{\kappa,\alpha j}}$$

- *Born* and *Callen* charges are related through:

$$Z^{*(T)}_{\kappa,\alpha\beta} = \sum_j \varepsilon^{\infty}_{\beta j} \, Z^{*(L)}_{\kappa,\alpha j}$$

Szigeti effective charge:

$$Z^{*(s)}_{\kappa,\alpha\beta} = \Omega_0 \left.\frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}}\right|_{\mathcal{E}_{\text{loc}}=0}$$

- With $\mathcal{E}_{\text{loc}} = \mathcal{E} + \frac{4\pi}{3}\mathcal{P}$ for an **isotropic** material :

$$Z^{*(s)}_{\kappa} = Z^{*(T)}_{\kappa} + \Omega_0 \left.\frac{(\varepsilon^{\infty}-1)}{4\pi}\right|_{\tau=0} \underbrace{\left.\frac{\partial \mathcal{E}}{\partial \tau_{\kappa}}\right|_{\mathcal{E}_{\text{loc}}=0}}_{-\frac{4\pi}{3\Omega_0} Z^{*(s)}_{\kappa}}$$

- *Born* and *Szigeti* charges are related through:

$$\boxed{Z^{*(T)}_{\kappa} = \frac{(\varepsilon^{\infty}+2)}{3} Z^{*(s)}_{\kappa}}$$

Effective charge in an ellipsoid:

$$Z^{*(E)}_{\kappa,\alpha\beta} = \Omega_0 \left. \frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}_i = -4\pi n_i \mathcal{P}_i}$$

- With $\mathcal{E}_i = -4\pi n_i \mathcal{P}_i$ with n_i the depolarizing factors ($\Sigma n_i = 1$) :

$$Z^{*(E)}_{\kappa,\alpha\beta} = Z^{*(T)}_{\kappa,\alpha\beta} + \Omega_0 \sum_j \left. \frac{(\varepsilon^{\infty}_{\beta j} - 1)}{4\pi} \right|_{\tau=0} \underbrace{\left. \frac{\partial \mathcal{E}_j}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}_i = -4\pi n_i \mathcal{P}_i}}_{-4\pi n_j Z^{*(E)}_{\kappa,\alpha j}}$$

- *Born* and *ellipsoid* charges are related through:

$$Z^{*(T)}_{\kappa,\alpha\beta} = \sum_j \left[(\varepsilon^{\infty}_{\beta j} - \delta_{\beta j}) n_j + \delta_{\beta j} \right] Z^{*(E)}_{\kappa,\alpha j}$$

Z* in slabs,wires and spherical clusters:

- **Spherical clusters:**

$n_x = n_y = n_z = 1/3 \quad \rightarrow \quad Z^{*(E)}_{\kappa,\alpha\beta} = Z^{*(S)}_{\kappa,\alpha\beta}$

- **Slabs:**

$n_x = n_y = 0 \quad n_z = 1 \quad \rightarrow \quad Z^{*(E)}_{\kappa,zz} = \frac{Z^{*(T)}_{\kappa,zz}}{\varepsilon_{zz}} = Z^{*(L)}_{\kappa,zz}$

- **Wires:**

$n_x = n_y = 1/2 \;\; n_z = 0 \quad \rightarrow \quad \ldots$

Computation Z^*_{zz} in slabs:

- **Periodic boundary conditions** correspond to **artificial** conditions on the electric field in the direction $\perp$ to the surface (*i.e.* dependent of the vacuum thickness : $\mathcal{E}$=0 over the **whole** supercell).

- Computed Z* and ε^{∞} in the direction $\perp$ to the surface (from anaddb) are **dependent** of the supercell !

- The meaningful quantity to be considered is the **longitudinal charge** :

$$Z^{*(L)}_{\kappa,zz} = \frac{Z^{*(T)}_{\kappa,zz}}{\varepsilon_{zz}}$$

Charge neutrality sum rule

The crystal is neutral.

- This imposes a constraint on the dynamical charges known as the **charge neutrality sum rule** (ASR) :

$$\sum_{\kappa} Z^{*}_{\kappa,\alpha\beta} = 0$$

- This relation is slightly broken within DFPT. The sum rule is restored using for instance :

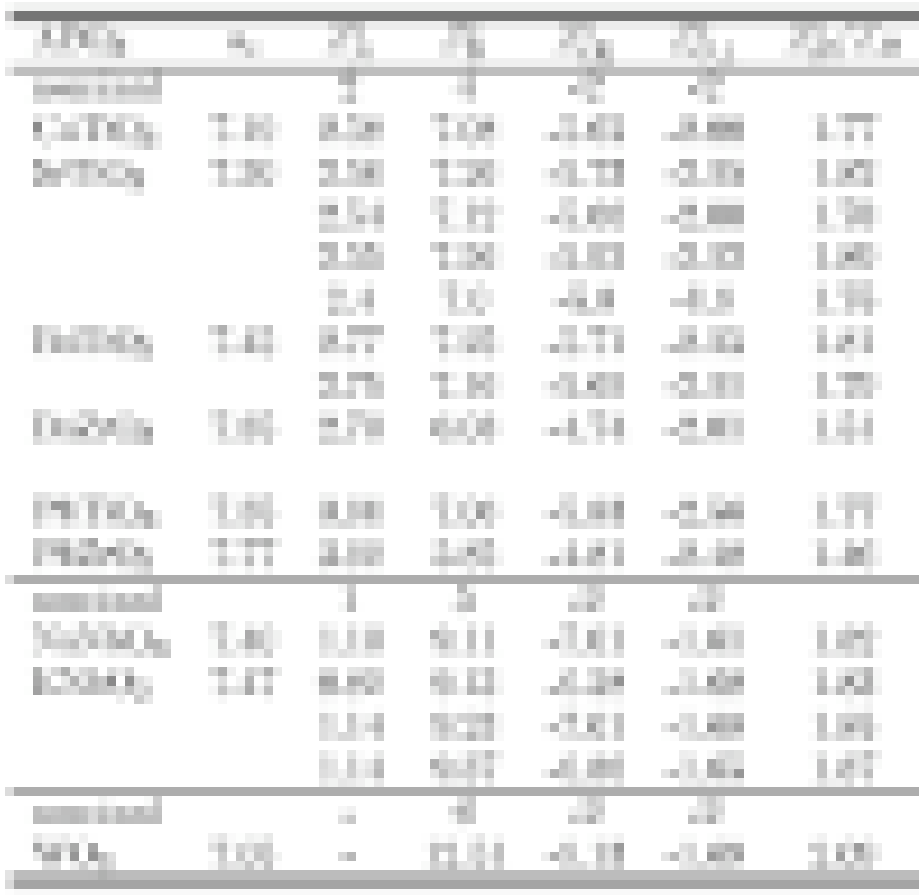
$$Z^{*}_{\kappa,\alpha\beta} \rightarrow Z^{*}_{\kappa,\alpha\beta} - \frac{1}{N_{at}} \sum_{\kappa} Z^{*}_{\kappa,\alpha\beta}$$

- Note : another sum rule at surfaces and interfaces

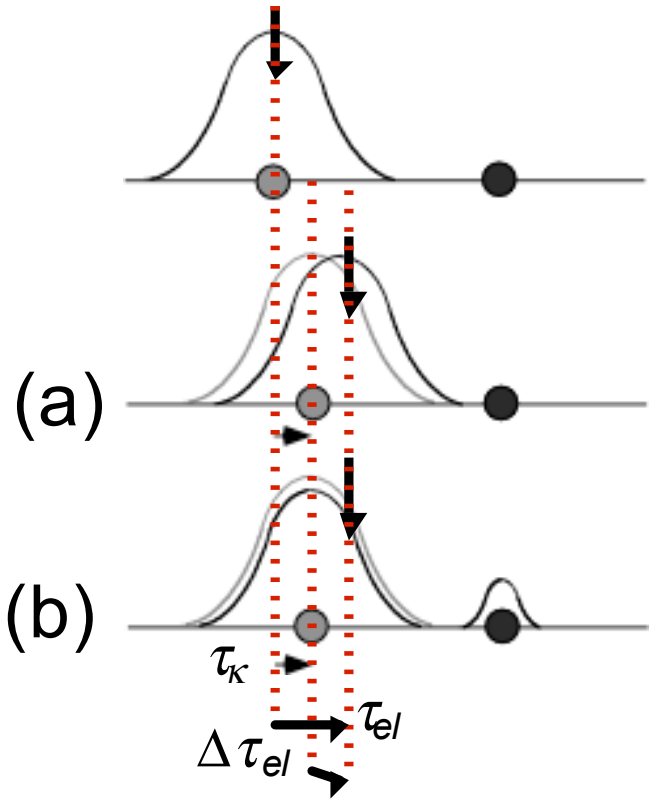
Typical results

Dynamical charges can be significantly larger than static formal charges and take **anomalous** values

The case of perovskite ABO_3 compounds



Origin of anomalous charges



For the purpose of understanding the polarization electrons can be considered as classical point charges located at the center of gravity of the Wannier functions

$$\begin{aligned}
\Omega_0 \mathcal{P} &= Z_\kappa^{ion}\tau_\kappa + Z_\kappa^{el}\tau_{el} \\
&= Z_\kappa^{ion}\tau_\kappa + Z_\kappa^{el}\left(\tau_\kappa + \Delta\tau_{el}\right) \\
&= (Z_\kappa^{ion} + Z_\kappa^{el})\tau_\kappa + Z_\kappa^{el}\Delta\tau_{el} \\
&= Z_\kappa^{nom}\tau_\kappa + Z_\kappa^{el}\Delta\tau_{el} \\
&= \underbrace{\left(Z_\kappa^{nom} + Z_\kappa^{el}\frac{\Delta\tau_{el}}{\tau_\kappa}\right)}_{Z_\kappa^{*(T)}}\tau_\kappa
\end{aligned}$$

Anomalous charge originates in the off-centering of the electronic charge due to either *local polarizability* (a) or *charge transfers* (b).

4. Phonon frequencies

X. Gonze, Phys. Rev. B ***55*** *, 10337 (1997)*
X Gonze and Ch. Lee, Phys. Rev. B 55, 10355 (1997)

Zone-center phonons
(TO modes : $\mathcal{E} = 0$):

- Harmonic energy :

$$\mathscr{F}_{e+i}[\mathbf{R}_\kappa, \mathcal{E}] = \mathscr{F}_{e+i}[\mathbf{R}^0_\kappa, 0] + \frac{1}{2}\sum_{a\kappa\alpha}\sum_{b\kappa'\beta} C^{ab}_{\alpha\beta}(\kappa,\kappa')\,\tau^a_{\kappa\alpha}\tau^b_{\kappa'\beta}$$

- Equation of motion

$$M_\kappa \frac{\partial^2 \tau^a_{\kappa\alpha}}{\partial t^2} = F^a_{\kappa\alpha} = -\sum_{b\kappa'\beta} C^{ab}_{\alpha\beta}(\kappa,\kappa')\,\tau^b_{\kappa'\beta}$$

- Solution

$$\tau^a_{\kappa\alpha}(t) = \eta_{m\mathbf{q}}(\kappa\alpha)\; e^{i\,\mathbf{q}\cdot\mathbf{R}^a}\; e^{-i\omega_{m\mathbf{q}}t}$$

Dynamical equation

$$-M_\kappa \omega_{m\mathbf{q}}^2 \eta_{m\mathbf{q}}(\kappa\alpha) = -\sum_{\kappa'\beta} \underbrace{\left(\sum_b C_{\alpha\beta}^{ab}(\kappa,\kappa') e^{i\mathbf{q}\cdot(\mathbf{R}^b-\mathbf{R}^a)}\right)}_{\tilde{C}_{\alpha\beta}^{\mathbf{q}}(\kappa,\kappa')=\frac{1}{N}\sum_{ab} C_{\alpha\beta}^{ab}(\kappa,\kappa') e^{i\mathbf{q}\cdot(\mathbf{R}^b-\mathbf{R}^a)}} \eta_{m\mathbf{q}}(\kappa'\beta)$$

$$M_\kappa \omega_{m\mathbf{q}}^2 \underbrace{\eta_{m\mathbf{q}}(\kappa\alpha)}_{\gamma_{m\mathbf{q}}(\kappa\alpha)/\sqrt{M_\kappa}} = \sum_{\kappa'\beta} \underbrace{\tilde{C}_{\alpha\beta}^{\mathbf{q}}(\kappa,\kappa')}_{\tilde{D}_{\alpha\beta}^{\mathbf{q}}(\kappa,\kappa')\sqrt{M_\kappa M_{\kappa'}}} \underbrace{\eta_{m\mathbf{q}}(\kappa'\beta)}_{\gamma_{m\mathbf{q}}(\kappa'\beta)/\sqrt{M_{\kappa'}}}$$

$$\omega_{m\mathbf{q}}^2 \gamma_{m\mathbf{q}}(\kappa\alpha) = \sum_{\kappa'\beta} \tilde{D}_{\alpha\beta}^{\mathbf{q}}(\kappa,\kappa')\, \gamma_{m\mathbf{q}}(\kappa'\beta)$$

Phonon frequency

Dynamical matrix

Phonon eigenvector

Notations

- Force constant matrix → $\tilde{C}^{\mathbf{q}}_{\alpha\beta}(\kappa,\kappa') = \dfrac{\partial^2 E_{e+i}}{\partial\tau^{\mathbf{q}}_{\kappa\alpha}\partial\tau^{\mathbf{q}}_{\kappa'\beta}}$
- Dynamical matrix → $\tilde{D}^{\mathbf{q}}_{\alpha\beta}(\kappa,\kappa') = \dfrac{\tilde{C}^{\mathbf{q}}_{\alpha\beta}(\kappa,\kappa')}{\sqrt{M_\kappa M_{\kappa'}}}$
- Phonon eigenvector → $\gamma_{m\mathbf{q}}(\kappa\alpha)$

  with $\langle\gamma|\gamma\rangle = 1$
- Phonon eigendisplacements → $\eta_{m\mathbf{q}}(\kappa\alpha) = \dfrac{\gamma_{m\mathbf{q}}(\kappa\alpha)}{\sqrt{M_\kappa}}$

  with $\langle\eta|M|\eta\rangle = 1$
- Phonon frequency → $\omega_{m\mathbf{q}}$

Zone-center phonons ($\mathbf{q} \to 0$)

(LO modes : $\mathcal{D} = 0$):

- Force :

$$F_{\kappa\alpha} = -\sum_{b\kappa'\beta} C^{0b}_{\alpha\beta}(\kappa,\kappa')\,\tau^{b}_{\kappa'\beta} + \sum_{\beta'} Z^{*}_{\kappa,\alpha\beta'}\ \hat{q}_{\beta'}\,|\mathcal{E}|$$

- Displacement field

$$\mathcal{D}_{\alpha} = \frac{4\pi}{\Omega_0}\sum_{\alpha}\sum_{\kappa} Z^{*}_{\kappa',\alpha\beta}\ \tau^{b}_{\kappa'\beta} + \sum_{\beta}\varepsilon^{\infty}_{\alpha\beta}\,\hat{q}_{\beta}\ \ |\mathcal{E}|$$

Along $\mathbf{q}$, $\mathcal{D}$ must be preserved : $q_{\alpha}.\mathcal{D}_{\alpha}=0$

$$|\mathcal{E}| = -\frac{4\pi}{\Omega_0}\frac{\sum_{b\kappa'}\sum_{\alpha'\beta} Z^{*}_{\kappa',\alpha'\beta}\ \tau^{b}_{\kappa'\beta}\,\hat{q}_{\alpha'}}{\sum_{\alpha'\beta'}\hat{q}_{\alpha'}\ \varepsilon^{\infty}_{\alpha'\beta'}\ \hat{q}_{\beta'}}$$

LO-TO correction at Γ

$$F_{\kappa\alpha} = -\sum_{b\kappa'\beta} C^{0b}_{\alpha\beta}(\kappa,\kappa')\,\tau^{b}_{\kappa'\beta} + \sum_{\beta'} Z^{*}_{\kappa,\alpha\beta'}\;\hat{q}_{\beta'}\left(-\frac{4\pi}{\Omega_0}\frac{\sum_{b\kappa'}\sum_{\alpha'\beta} Z^{*}_{\kappa',\alpha'\beta}\;\tau^{b}_{\kappa'\beta}\,\hat{q}_{\alpha'}}{\sum_{\alpha'\beta'}\hat{q}_{\alpha'}\;\varepsilon^{\infty}_{\alpha'\beta'}\;\hat{q}_{\beta'}}\right)$$

$$= -\sum_{b\kappa'\beta}\tau^{b}_{\kappa'\beta}\left(C^{0b}_{\alpha\beta}(\kappa,\kappa') + \frac{4\pi}{\Omega_0}\frac{\sum_{\beta'}\left(Z^{*}_{\kappa,\alpha\beta'}\hat{q}_{\beta'}\right)\sum_{\alpha'}\left(Z^{*}_{\kappa',\alpha'\beta}\,\hat{q}_{\alpha'}\right)}{\sum_{\alpha'\beta'}\hat{q}_{\alpha'}\;\varepsilon^{\infty}_{\alpha'\beta'}\;\hat{q}_{\beta'}}\right)$$

Non-analytical term to be added to $C_{\alpha\beta}(\kappa, \kappa')$ to compute the LO-TO splitting in the limit of $\mathbf{q} \to \mathbf{0}$

Acoustic sum rule

The crystal energy must be invariant under global translation of the whole crystal.

- This imposes a constraint on the force constant matrix known as the **acoustic sum rule** (ASR) :

$$\sum_{\kappa'} \tilde{C}^{\mathbf{q}=0}_{\alpha\beta}(\kappa,\kappa') = 0$$

- This relation is slightly broken due to the use of a real space grid to evaluate the exchange-correlation energy. The ASR is restored using :

$$\sum_{\kappa'} \tilde{C}^{\mathbf{q}=0}_{\alpha\beta}(\kappa,\kappa') \rightarrow \sum_{\kappa'} \tilde{C}^{\mathbf{q}=0}_{\alpha\beta}(\kappa,\kappa') - \delta_{\kappa\kappa'} \sum_{\kappa''} \tilde{C}^{\mathbf{q}=0}_{\alpha\beta}(\kappa,\kappa'')$$

- Note : same "q=0 correction" used at all q

5. Dielectric tensor

X. Gonze, Phys. Rev. B ***55*** *, 10337 (1997)*
X Gonze and Ch. Lee, Phys. Rev. B 55, 10355 (1997)

Optical dielectric tensor:

Electronic response only ($\tau_{\kappa\alpha}=0$)

$$\mathcal{D}_\beta[\mathbf{R}_\kappa,\mathcal{E}] = -\frac{4\pi}{\Omega_0}\,\frac{d\mathcal{F}_{e+i}[\mathbf{R}^0_\kappa,0]}{d\mathcal{E}_\beta} = \frac{4\pi}{\Omega_0}\sum_\alpha\sum_\kappa Z^*_{\kappa,\alpha\beta}\,\tau_{\kappa\alpha} + \sum_\alpha \varepsilon^\infty_{\alpha\beta}\,\mathcal{E}_\alpha$$

$$\begin{aligned}\varepsilon^\infty_{\alpha\beta} &= \frac{\partial\mathcal{D}_\beta[\mathbf{R}_\kappa,\mathcal{E}]}{\partial\mathcal{E}_\alpha}\\ &= -\frac{4\pi}{\Omega_0}\,\frac{\partial^2\mathcal{F}_{e+i}[\mathbf{R}^0_\kappa,0]}{\partial\mathcal{E}_\beta\partial\mathcal{E}_\alpha}\\ &= \delta_{\alpha\beta} - \frac{4\pi}{\Omega_0}\,\frac{\partial^2 E_{e+i}[\mathbf{R}^0_\kappa,0]}{\partial\mathcal{E}_\beta\partial\mathcal{E}_\alpha}\end{aligned}$$

Optical dielectric tensor:

DPFT expression

- Stationary

$$\bar{E}^{\mathcal{E}_\alpha^* \mathcal{E}_\beta}_{\text{ell}}\{u^{(0)}; u^{\mathcal{E}_\alpha}, u^{\mathcal{E}_\beta}\} = \frac{\Omega_0}{(2\pi)^3}\int_{\text{BZ}}\sum_m^{\text{occ}} s\Big(\langle u^{\mathcal{E}_\alpha}_{m\mathbf{k}}|H^{(0)}_{\mathbf{k},\mathbf{k}} \perp \epsilon^{(0)}_{m\mathbf{k}}|u^{\mathcal{E}_\beta}_{m\mathbf{k}}\rangle + \langle u^{\mathcal{E}_\alpha}_{m\mathbf{k}}|iu^{k_\beta}_{m\mathbf{k}}\rangle + \langle iu^{k_\alpha}_{m\mathbf{k}}|u^{\mathcal{E}_\beta}_{m\mathbf{k}}\rangle\Big) d\mathbf{k}$$

$$+\frac{1}{2}\int_{\Omega_0} K^{LDA}_{\text{xc}}(\mathbf{r},\mathbf{r})\,[n^{\mathcal{E}_\alpha}(\mathbf{r})]^* n^{\mathcal{E}_\beta}(\mathbf{r})\, d\mathbf{r}$$

$$+2\pi\Omega_0 \sum_{\mathbf{G}\neq\mathbf{0}} \frac{[n^{\mathcal{E}_\alpha}(\mathbf{G})]^* n^{\mathcal{E}_\beta}(\mathbf{G})}{|\mathbf{G}|^2}.$$

- Non-stationary

$$\bar{E}^{\mathcal{E}_\alpha^* \mathcal{E}_\beta}_{\text{ell}}\{u^{(0)}; u^{\mathcal{E}_\alpha}\} = \frac{\Omega_0}{(2\pi)^3}\int_{\text{BZ}}\sum_m^{\text{occ}} s\langle u^{\mathcal{E}_\alpha}_{m\mathbf{k}}|iu^{k_\beta}_{m\mathbf{k}}\rangle d\mathbf{k}$$

Requires $\left|u^{\mathcal{E}_\alpha}_{m\mathbf{k}}\right\rangle$ and $r\left|u^{0}_{m\mathbf{k}}\right\rangle \rightarrow -i\frac{\partial}{\partial k}\left|u^{0}_{m\mathbf{k}}\right\rangle = -i\left|u^{k_\beta}_{m\mathbf{k}}\right\rangle$

Optical dielectric tensor:

Scissors correction

• LDA (and other local functionals) typically **overestimates** the optical dielectric tensor (sometimes up to 25%)

• This can sometimes be empirically corrected using a so-called **scissors correction** (*i.e.* an artificial rigid shift of the conduction bands that adjusts the LDA bandgap - typically too small- to its experimental value) :

$$\Delta_{SCI} = E_g^{EXP} - E_g^{LDA}$$

Ph. Ghosez, X. Gonze and R. W. Godby, Phys. Rev. B ***56*** *, 12811 (1997).*

Static dielectric tensor:

Including also the **ionic** response

$$\mathcal{P}_\beta[\mathbf{R}_\kappa,\mathcal{E}] = \frac{4\pi}{\Omega_0}\sum_{\gamma\kappa} Z^*_{\kappa,\gamma\beta}\ \underbrace{\tau_{\kappa\gamma}}_{\sum_\alpha \frac{\partial \tau_{\kappa\gamma}}{\partial \mathcal{E}_\alpha}\mathcal{E}_\alpha} + \sum_\alpha \varepsilon^\infty_{\alpha\beta}\,\mathcal{E}_\alpha$$

$$\varepsilon^0_{\alpha\beta} = \frac{d\mathcal{P}_\beta[\mathbf{R}_\kappa,\mathcal{E}]}{d\mathcal{E}_\alpha}$$

$$= \varepsilon^\infty_{\alpha\beta} + \frac{4\pi}{\Omega_0}\sum_{\kappa\gamma} Z^*_{\kappa,\gamma\beta}\ \tau^{\mathcal{E}_\alpha}_{\kappa\gamma}$$

$$\tau^{\mathcal{E}_\alpha}_{\kappa\gamma} = \frac{\partial \tau_{\kappa\gamma}}{\partial \mathcal{E}_\alpha} = \sum_m \tau^{\mathcal{E}_\alpha}_m\ \eta_m(\kappa\gamma)$$

Atomic relaxation:

$$F_{\kappa\alpha}[\mathbf{R}_\kappa,\mathcal{E}] = \sum_\beta Z^*_{\kappa,\alpha\beta}\ \mathcal{E}_\beta - \sum_{\alpha'\kappa'} C_{\alpha\alpha'}(\kappa,\kappa')\left(\sum_\beta \tau^{\mathcal{E}_\beta}_{\kappa'\alpha'}\ \mathcal{E}_\beta\right) = 0$$

$$Z^*_{\kappa,\alpha\beta} - \sum_{\alpha'\kappa'} C_{\alpha\alpha'}(\kappa,\kappa')\,\tau^{\mathcal{E}_\beta}_{\kappa'\alpha'} = 0$$

$$\Rightarrow \sum_{\alpha'\kappa'} C_{\alpha\alpha'}(\kappa,\kappa')\,\tau^{\mathcal{E}_\beta}_m\ \eta_m(\kappa'\alpha') = Z^*_{\kappa,\alpha\beta}$$

$$\Rightarrow \tau^{\mathcal{E}_\beta}_m\ \omega_m^2 M_\kappa\ \eta_m(\kappa\alpha) = Z^*_{\kappa,\alpha\beta}$$

$$\Rightarrow \tau^{\mathcal{E}_\beta}_m\ \omega_m^2 \underbrace{\sum_{\kappa\alpha} \eta_m(\kappa\alpha) M_\kappa\ \eta_m(\kappa\alpha)}_{1} = \sum_{\kappa\alpha} Z^*_{\kappa,\alpha\beta}\eta_m(\kappa\alpha)$$

$$\Rightarrow \tau^{\mathcal{E}_\beta}_m = \frac{1}{\omega_m^2}\sum_{\kappa\alpha} Z^*_{\kappa,\alpha\beta}\eta_m(\kappa\alpha)$$

Static dielectric tensor:

$$\varepsilon^0_{\alpha\beta} = \frac{d\mathcal{D}_\beta[\mathbf{R}_\kappa, \mathcal{E}]}{d\mathcal{E}_\alpha}$$

$$= \varepsilon^\infty_{\alpha\beta} + \frac{4\pi}{\Omega_0} \sum_m \tau_m^{\mathcal{E}_\alpha} \left(\sum_{\kappa'\gamma} Z^*_{\kappa',\gamma\beta}\ \eta_m(\kappa'\gamma) \right)$$

$$= \varepsilon^\infty_{\alpha\beta} + \frac{4\pi}{\Omega_0} \sum_m \frac{\left(\sum_{\kappa\gamma} Z^*_{\kappa,\gamma\alpha} \eta_m(\kappa\gamma) \right) \left(\sum_{\kappa'\gamma} Z^*_{\kappa',\gamma\beta}\ \eta_m(\kappa'\gamma) \right)}{\omega_m^2}$$

$$= \varepsilon^\infty_{\alpha\beta} + \frac{4\pi}{\Omega_0} \sum_m \frac{p_{m,\alpha} \cdot p_{m,\beta}}{\omega_m^2}$$

Mode polarity

$$\Rightarrow \varepsilon^0_{\alpha\beta} = \varepsilon^\infty_{\alpha\beta} + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\beta}}{\omega_m^2}$$

Oscillator strength

6. In practice

DFPT calculations

- Perform a GS calculation to get the GS wave-functions
- Electric field perturbation
  - Perform ddk perturbation to get -i d/ dk |u>
  - Perform electric field perturbation
  - **ANADDB: provides full optical dielectric tensor and the full set of effective charges.**
- Atomic displacement perturbation
  - Perform individual atomic displacement perturbations at a given q-point to get the dynamical matrix
  - **ANADDB : provides phonon frequencies and eigenvectors (TO and LO modes) as well as infra-red oscillator strengths and infra-red dielectric tensor.**

Finite difference versus DFPT

- All previous quantities can be alternatively accessed using finite difference techniques (finite atomic displacements and finite electric fields).
- Finite difference techniques are directly accessible with "minor" implementation effort (Berry phase and finite electric field approachesd) but requires a lot of human work to access individual coefficients in appropriate units and coordinates.
- DFPT requires a huge implementation effort but directly provides full tensors in appropriate units taking advantage of symmetry and build a coherent database without any additional human effort.

DFPT not mandatory but
highly preferred when available!