Summer School on First-principles calculations for Condensed Matter and Nanoscience
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II. Non-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. Non-linear susceptibilities
4. Raman intensities
5. Electrooptic tensor

1. Energy derivatives and physical properties:

*M. Veithen, X. Gonze and Ph. Ghosez, Phys. Rev. B **71**, 125107 (2005)*
*R. W. Nunes and X. Gonze, Phys. Rev. B **63**, 155107 (2001)*
*X Gonze, Phys. Rev. A **52**, 1086 (1995)*
*X Gonze, Phys. Rev. A **52**, 1096 (1995)*

Energy derivatives:

- Let us consider the functional

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

- Successive derivatives are connected to physical properties

$$\mathcal{F}_{e+i}[\lambda] = \mathcal{F}_{e+i}[\lambda] + \sum_i \frac{\partial \mathcal{F}_{e+i}}{\partial \lambda_i} \lambda_i + \frac{1}{2} \sum_{ij} \frac{\partial^2 \mathcal{F}_{e+i}}{\partial \lambda_i \partial \lambda_j} \lambda_i \lambda_j + \frac{1}{6} \sum_{ijk} \frac{\partial^3 \mathcal{F}_{e+i}}{\partial \lambda_i \partial \lambda_j \partial \lambda_k} \lambda_i \lambda_j \lambda_k + \ldots$$

Nowadays accessible within ABINIT

Non-linear susceptibilities : $\chi_{ijl}^{\infty(2)} = \frac{-1}{2\Omega_0} \frac{\partial^3 \mathcal{F}_{e+i}}{\partial \mathcal{E}_i \partial \mathcal{E}_j \partial \mathcal{E}_l}$

Raman coefficients : $\frac{\partial \chi_{ij}^{\infty(1)}}{\partial \tau_{\kappa\alpha}} = \frac{-1}{\Omega_0} \frac{\partial^3 \mathcal{F}_{e+i}}{\partial \mathcal{E}_i \partial \mathcal{E}_j \partial \tau_{\kappa\alpha}}$

Physical quantities:

$$\mathcal{F}_{e+i}[\mathbf{R}_\kappa,\mathcal{E}] = \mathcal{F}_{e+i}[\mathbf{R}^0_\kappa,0]$$

$$-\Omega_0 \sum_\alpha \mathcal{P}^s_\alpha \; \mathcal{E}_\alpha \; - \sum_\alpha \sum_\kappa F^0_\alpha \; \tau_{\kappa\alpha}$$

$$-\frac{\Omega_0}{2} \sum_{\alpha\beta} \chi^{\infty(1)}_{\alpha\beta} \; \mathcal{E}_\alpha \mathcal{E}_\beta \; - \sum_{\alpha\beta} \sum_\kappa Z^*_{\kappa,\alpha\beta} \; \tau_{\kappa\alpha} \; \mathcal{E}_\beta + \frac{1}{2} \sum_{\alpha\beta} \sum_{\kappa\kappa'} C_{\alpha\beta}(\kappa,\kappa')\tau_{\kappa\alpha}\tau_{\kappa'\beta}$$

$$-\frac{\Omega_0}{3} \sum_{\alpha\beta\gamma} \chi^{\infty(2)}_{\alpha\beta\gamma} \; \mathcal{E}_\alpha \mathcal{E}_\beta \mathcal{E}_\gamma \; - \frac{\Omega_0}{2} \sum_\kappa \sum_{\alpha\beta\gamma} \frac{\partial \chi^{\infty(1)}_{\alpha\beta}}{\partial \tau_{\kappa\gamma}} \mathcal{E}_\alpha \mathcal{E}_\beta \; \tau_{\kappa\gamma}$$

$$-\frac{1}{2} \sum_{\alpha\beta\gamma} \sum_{\kappa\kappa'} \frac{\partial Z^*_{\kappa,\alpha\beta}}{\partial \tau_{\kappa'\gamma}} \; \tau_{\kappa\alpha}\tau_{\kappa'\gamma}\mathcal{E}_\beta + \frac{1}{3} \sum_{\alpha\beta\gamma} \sum_{\kappa\kappa'\kappa''} \Xi_{\alpha\beta\gamma}(\kappa,\kappa',\kappa'')\tau_{\kappa\alpha}\tau_{\kappa'\beta}\tau_{\kappa''\gamma} + \ldots$$

Physical quantities:

- Atomic forces :

$$F_{\kappa\alpha}[\mathbf{R}_\kappa,\mathcal{E}] = -\frac{d\mathcal{F}_{e+i}[\mathbf{R}_\kappa,\mathcal{E}]}{d\tau_{\kappa\alpha}} = F^0_{\kappa\alpha} + \sum_\beta Z^*_{\kappa,\alpha\beta}\ \mathcal{E}_\beta - \sum_{\beta\kappa'} C_{\alpha\beta}(\kappa,\kappa')\,\tau_{\kappa'\beta}$$

$$+\frac{\Omega_0}{2}\sum_{\beta\gamma}\frac{\partial\chi^{\infty(1)}_{\alpha\beta\gamma}}{\partial\tau_{\kappa\alpha}}\mathcal{E}_\beta\mathcal{E}_\gamma + \sum_{\beta\gamma}\sum_{\kappa'}\frac{\partial Z^*_{\kappa',\gamma\beta}}{\partial\tau_{\kappa\alpha}}\ \tau_{\kappa'\gamma}\mathcal{E}_\beta - \sum_{\beta\gamma}\sum_{\kappa'\kappa''}\Xi_{\alpha\beta\gamma}(\kappa,\kappa',\kappa'')\,\tau_{\kappa'\beta}\tau_{\kappa''\gamma}$$

- Electric polarization :

$$\mathcal{P}_\alpha[\mathbf{R}_\kappa,\mathcal{E}] = -\frac{1}{\Omega_0}\ \frac{d\mathcal{F}_{e+i}[\mathbf{R}_\kappa,\mathcal{E}]}{d\mathcal{E}_\alpha} = \mathcal{P}^s_\alpha + \frac{1}{\Omega_0}\sum_\beta\sum_\kappa Z^*_{\kappa,\beta\alpha}\ \tau_{\kappa\beta} + \sum_\beta \chi^{\infty(1)}_{\alpha\beta}\mathcal{E}_\beta$$

$$+\sum_{\beta\gamma}\chi^{\infty(2)}_{\alpha\beta\gamma}\ \mathcal{E}_\beta\mathcal{E}_\gamma\ + \sum_\kappa\sum_{\beta\gamma}\frac{\partial\chi^{\infty(1)}_{\alpha\beta}}{\partial\tau_{\kappa\gamma}}\mathcal{E}_\beta\ \tau_{\kappa\gamma} + \frac{1}{2\Omega_0}\sum_{\alpha\beta\gamma}\sum_{\kappa\kappa'}\frac{\partial Z^*_{\kappa,\beta\alpha}}{\partial\tau_{\kappa'\gamma}}\ \tau_{\kappa\beta}\tau_{\kappa'\gamma}$$

2. Computation of energy derivatives within DFPT:

M. Veithen, X. Gonze and Ph. Ghosez , Phys. Rev. B ***71****, 125107 (2005)*

Energy derivatives:

Computed through a **two-steps** procedure

1. Determination of first-order wave-functions from the minimization of a **variational** expression of $E_{e+i}^{(2)}$
   $\rightarrow$ already done for second-order quantities.

2. Evaluation of the appropriate expression of $\mathcal{F}_{e+i}^{(3)}$

$$\mathcal{F}_{e+i}[\mathbf{R}_\kappa, \mathcal{E}] = E_{e+i}[\mathbf{R}_\kappa] - \Omega_0 \; \mathcal{E} \cdot \mathcal{P}$$

Computation of

$$E_{e+i}^{\lambda_1 \lambda_2 \lambda_3} = \frac{1}{6} \frac{\partial E_{e+i}}{\partial \lambda_1 \partial \lambda_2 \partial \lambda_3}$$

with standard DPFT formula

Derivatives of $(- \; \Omega_0 \, \mathcal{E} \, . \, \mathcal{P})$ computed using PEAD formulation

Only appear for pure electric field derivatives

Energy derivatives:

Typical expression!

$$
\begin{aligned}
E^{\zeta_1\zeta_2\zeta_3} = & \frac{-e}{N_k}\Omega \sum_{\mathbf{k}}\sum_{\mathbf{b}} w_{\mathbf{b}}(\mathbf{b}\cdot\mathbf{G}_i)\Bigg[2\sum_{n,m}^{occ}\langle u^{\zeta_1}_{n\mathbf{k}}|u^{\zeta_2}_{m\mathbf{k}+\mathbf{b}}\rangle Q_{mn}(\mathbf{k},\mathbf{k}+\mathbf{b}) \\
& - \sum_{n,m,n',m'}^{occ} S^{\zeta_1}_{mn}(\mathbf{k},\mathbf{k}+\mathbf{b})Q_{nn'}(\mathbf{k},\mathbf{k}+\mathbf{b})S^{\zeta_2}_{n'm'}(\mathbf{k},\mathbf{k}+\mathbf{b})Q_{m'm}(\mathbf{k},\mathbf{k}+\mathbf{b})\Bigg] \\
& + \frac{2}{N_k}\sum_{\mathbf{k}}\sum_{n,m}^{occ}\Bigg[\delta_{m,n}\langle u^{\zeta_1}_{n\mathbf{k}}|v^{\zeta_2}_{hxc}|u^{\zeta_3}_{m\mathbf{k}}\rangle - \langle u^{(0)}_{m\mathbf{k}}|v^{\zeta_1}_{hxc}|u^{(0)}_{n\mathbf{k}}\rangle\langle u^{\zeta_2}_{n\mathbf{k}}|u^{\zeta_3}_{m\mathbf{k}}\rangle\Bigg] \\
& + \frac{1}{6}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,\frac{\delta^3 E_{xc}[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')\delta n(\mathbf{r}'')}n^{\zeta_1}(\mathbf{r})n^{\zeta_2}(\mathbf{r}')n^{\zeta_3}(\mathbf{r}'').
\end{aligned}
$$

3. Non-linear optical susceptibilities

M. Veithen, X. Gonze and Ph. Ghosez , Phys. Rev. B ***71****, 125107 (2005)*

Non-linear optical susceptibilities:

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

Change of the refractive index induced by an ***optical*** *field*

$$\mathcal{P}_i[\mathbf{R}_\kappa^0, \mathcal{E}] = \mathcal{P}_i^s + \sum_j \chi_{ij}^{\infty(1)} \mathcal{E}_j + \sum_{jl} \chi_{ijl}^{\infty(2)} \mathcal{E}_j \mathcal{E}_l + \ldots$$

Non-linear optical susceptibility tensor :

$$\chi_{ijl}^{\infty(2)} = \frac{-1}{2\Omega_0} \frac{\partial^3 \mathcal{F}_{e+i}}{\partial \mathcal{E}_i \partial \mathcal{E}_j \partial \mathcal{E}_l}$$

$$d_{ijl} = \frac{1}{2} \chi_{ijl}^{\infty(2)}$$

Note : derivative respect to 3 **optical** electric fields

Non-linear optical susceptibility

Scissors correction

- LDA (and other local functionals) typically **overestimates** the non-linear optical susceptibility tensor.

- 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) :

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

- For cubic semiconductors: NO systematic improvement is observed using SCI correction …

Z. H. Levine and D. C. Allan, Phys. Rev. B, 44, 12781 (1991).
W. G. Aulbur , L. Jonsson and J. P. Wilkins, Phys. Rev. B 54, 8540 (1996)

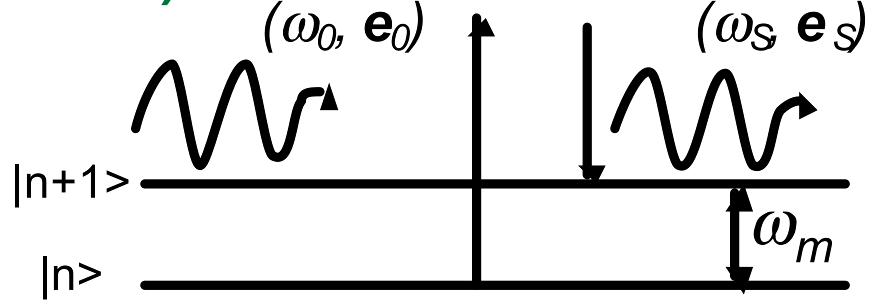
4. Raman efficiencies

*M. Veithen, X. Gonze and Ph. Ghosez , Phys. Rev. B **71**, 125107 (2005)*

Non-resonant Raman scattering

(Stokes effect)

Incoming photon (ω_0, $\mathbf{e}_0$) scattered to an outgoing photon (ω_S, $\mathbf{e}_S$) by creating a phonon ω_m



- Raman scattering efficiency (cgs):

$$\frac{dS}{dV} = \frac{\left(\omega_0 - \omega_m\right)^4}{c^4} \left| e_S \cdot \alpha_m \cdot e_0 \right|^2 \frac{\hbar}{2\omega_m}\left(n_m + 1\right)$$

Raman susceptibility :

$$\alpha_{ij}^m = \sqrt{\Omega_0} \sum_{\kappa\beta} \frac{\partial \chi_{ij}^{\infty(1)}}{\partial \tau_{\kappa\beta}} \eta_m(\kappa\beta)$$

Boson factor :

$$n_m = \frac{1}{e^{\hbar\omega_m / k_B T} - 1}$$

Raman susceptibility

$$\alpha_{ij}^{m} = \sqrt{\Omega_0}\sum_{\kappa\beta}\frac{\partial \chi_{ij}^{\infty(1)}}{\partial \tau_{\kappa\beta}}\,\eta_m(\kappa\beta)$$

- Transverse modes ($\mathcal{E}$ =0)

$$\left.\frac{\partial \chi_{ij}^{\infty(1)}}{\partial \tau_{\kappa\beta}}\right|_{\mathcal{E}=0} = -\frac{1}{\Omega_0}\frac{\partial \mathcal{F}_{e+i}}{\partial \tau_{\kappa\beta}\partial \mathcal{E}_i \partial \mathcal{E}_j} = -\frac{6}{\Omega_0}\mathcal{F}_{e+i}^{\tau_{\kappa\beta}\mathcal{E}_i\mathcal{E}_j}$$

- Longitudinal modes ($\mathcal{D}$ =0)

Non-zero electric field ($\mathcal{E}$ = - 4 π $\mathcal{P}$)

→ Modification of the optical susceptibility by $\chi^{(2)}$

$$\left.\frac{\partial \chi_{ij}^{\infty(1)}}{\partial \tau_{\kappa\beta}}\right|_{D=0} = \left.\frac{\partial \chi_{ij}^{\infty(1)}}{\partial \tau_{\kappa\beta}}\right|_{\mathcal{E}=0} - \frac{8\pi}{\Omega_0}\frac{\sum_l Z_{\kappa\beta l}^{*} q_l}{\sum_{ll'} q_l\,\varepsilon_{ll'}^{\infty}\,q_{l'}}\sum_l \chi_{ijl}^{\infty(2)} q_l$$

Acoustic sum rule

Dielectric susceptibility must be invariant under global translation of the whole crystal.

- This imposes a constraint :

$$\sum_{\kappa} \frac{\partial \chi_{ij}^{\infty(1)}}{\partial \tau_{\kappa\alpha}} = 0$$

- This relation is usually slightly broken. It can be restored using :

$$\frac{\partial \chi_{ij}^{\infty(1)}}{\partial \tau_{\kappa\alpha}} \rightarrow \frac{\partial \chi_{ij}^{\infty(1)}}{\partial \tau_{\kappa\alpha}} - \frac{1}{N_{at}} \sum_{\kappa} \frac{\partial \chi_{ij}^{\infty(1)}}{\partial \tau_{\kappa\alpha}}$$

5. Electrooptic coefficients

*M Veithen, X. Gonze and Ph. Ghosez, Phys. Rev. Lett. **93**, 187401 (2004)*
*M Veithen, X. Gonze and Ph. Ghosez, Phys. Rev. B **71**, 125107 (2005)*
*M. Veithen and Ph. Ghosez, Phys. Rev. B **71**, 132101 (2005)*

Electro-optic effect

(Pockels effect)

Change of refractive index induced by a (quasi-)static electric field

$$\Delta\varepsilon_{ij}^{\infty} = \sum_{\gamma} \frac{d\varepsilon_{ij}^{\infty}}{d\mathcal{E}_{\gamma}} \mathcal{E}_{\gamma}$$

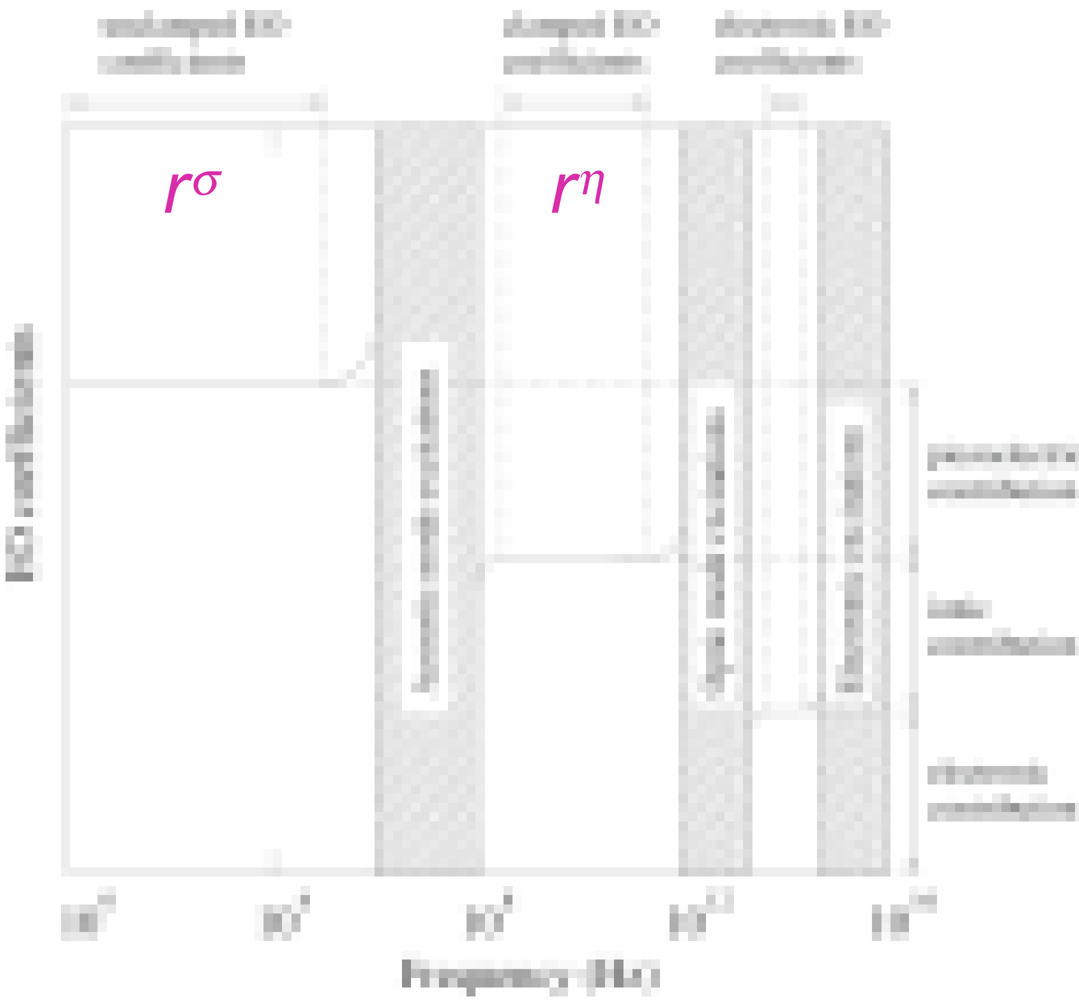
- Electro-optic coefficients

$$\Delta\left(\varepsilon^{\infty-1}\right)_{ij} = \sum_{\gamma} r_{ij\gamma} \mathcal{E}_{\gamma}$$

Using $\Delta\left(\varepsilon^{\infty-1}\right)_{ij} = -\sum_{mn} \varepsilon_{im}^{\infty-1} \Delta\varepsilon_{mn}^{\infty} \varepsilon_{nj}^{\infty-1}$, we get when expressed in the principal axes (in zero field)

$$r_{ij\gamma} = \frac{-1}{n_i^2 n_j^2} \frac{d\varepsilon_{ij}^{\infty}}{d\mathcal{E}_{\gamma}}$$

Clamped and unclamped electro-optic coefficients:



$$r_{ij\gamma} = \underbrace{\underbrace{r_{ij\gamma}^{el} + r_{ij\gamma}^{ion}}_{r_{ij\gamma}^{\eta}} + r_{ij\gamma}^{piezo}}_{r_{ij\gamma}^{\sigma}}$$

Clamped electro-optic response:

Electronic + ionic response

$$\varepsilon_{ij}^{\infty}[\mathbf{R}_\kappa,\mathcal{E}] = 1 - \frac{4\pi}{\Omega_0}\frac{\partial^2 \mathcal{F}_{e+i}[\mathbf{R}_\kappa,\mathcal{E}]}{\partial\mathcal{E}_i\partial\mathcal{E}_j}$$

$$= \underbrace{1 + 4\pi\,\chi_{ij}^{\infty(1)}}_{\varepsilon_{ij}^{\infty(1)}} + 8\pi\sum_{\gamma}\chi_{ij\gamma}^{\infty(2)}\,\mathcal{E}_\gamma \; + 4\pi\sum_{\alpha}\frac{\partial\chi_{ij}^{\infty(1)}}{\partial\tau_{\kappa\alpha}}\;\tau_{\kappa\alpha} + \ldots$$

$$\frac{d\varepsilon_{ij}^{\infty}}{d\mathcal{E}_\gamma} = 8\pi\,\chi_{ij\gamma}^{\infty(2)} + 4\pi\sum_{\kappa\alpha}\frac{\partial\chi_{ij}^{\infty(1)}}{\partial\tau_{\kappa\alpha}}\,.\tau_{\kappa\alpha}^{\mathcal{E}_\gamma}$$

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

$$= \sum_m \frac{1}{\omega_m^2}\sum_{\kappa'\beta} Z^*_{\kappa',\beta\gamma}\,\eta_m(\kappa'\beta)\,\eta_m(\kappa\alpha)$$

Clamped electro-optic response:

$$\frac{d\varepsilon_{ij}^{\infty}}{d\mathcal{E}_{\gamma}} = 8\pi\,\chi_{ij\gamma}^{\infty(2)} + 4\pi \sum_{m} \frac{1}{\omega_m^2} \underbrace{\sum_{\kappa'\beta} Z^{*}_{\kappa',\beta\gamma}\,\eta_m(\kappa'\beta)}_{p_{m,\gamma}} \underbrace{\sum_{\kappa\alpha} \frac{\partial \chi_{ij}^{\infty(1)}}{\partial \tau_{\kappa\alpha}}\,\eta_m(\kappa\alpha)}_{\alpha_{ij}^{m} / \sqrt{\Omega_0}}$$

$$= 8\pi\,\chi_{ij\gamma}^{\infty(2)} + \frac{4\pi}{\sqrt{\Omega_0}} \sum_{m} \frac{p_{m,\gamma}.\alpha_{ij}^{m}}{\omega_m^2}$$

$$\Rightarrow \quad r_{ij\gamma}^{\eta} = \frac{-8\pi}{n_i^2 n_j^2}\,\chi_{ij\gamma}^{\infty(2)} - \frac{4\pi}{n_i^2 n_j^2 \sqrt{\Omega_0}} \sum_{m} \frac{p_{m,\gamma}.\alpha_{ij}^{m}}{\omega_m^2}$$

Electronic response

Ionic contribution (mode by mode)

Unclamped electro-optic response:

Electronic + ionic + **piezoelectric** responses

$$r_{ij\gamma}^{\sigma} = r_{ij\gamma}^{\eta} + \sum_{\mu\nu} \pi_{ij\mu\nu} d_{\gamma\mu\nu}$$

Elasto-optic coefficients

Piezoelectric strain coefficients

Change of the dielectric constant versus strain

Change of the strain versus electric field

Not automatically accessible within ABINIT yet …

For more details…

Methodolgy

M Veithen, X. Gonze and Ph. Ghosez, Phys. Rev. B ***71****, 125107 (2005)*

Application to ABO_3 ferroelectric oxides

M Veithen, X. Gonze and Ph. Ghosez, Phys. Rev. Lett. ***93****, 187401 (2004)*

Finite temperature behavior

Using an effective Hamiltonian approach

M Veithen and Ph. Ghosez, Phys. Rev. B ***71****, 132101 (2005)*