ABINIT School

Non-linear responses to atomic displacements and static electric fields

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September, 2019
Prague

Outline:

1. Introduction
2. Computation of energy derivatives within DFPT
3. Non-linear optical susceptibilities
4. Raman susceptibilities
5. Electro-optic tensor

1. Introduction : 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)

General framework

- DFT : nowadays considered as a conventional and successful tool to study the properties of materials.

R. M. Martin, Electronic structure (Cambridge University Press 2004)

- Various functional properties related to derivatives of the energy with respect to external perturbations $\lambda = (R_\kappa, \eta, \mathcal{E})$:

$$F_{e+i}[\lambda] = F_{e+i}[\lambda] + \sum_i \frac{\partial F_{e+i}}{\partial \lambda_i}\,\lambda_i + \frac{1}{2}\sum_{ij} \underbrace{\frac{\partial^2 F_{e+i}}{\partial \lambda_i \partial \lambda_j}}_{\text{LR}}\,\lambda_i\lambda_j + \frac{1}{6}\sum_{ijk} \underbrace{\frac{\partial^3 F_{e+i}}{\partial \lambda_i \partial \lambda_j \partial \lambda_k}}_{\text{NLR}}\,\lambda_i\lambda_j\lambda_k + \ldots$$

- Linear-responses (LR): routinely computed within DFPT

S. Baroni et al. , Rev. Mod. Phys. 73, 515 (2001).

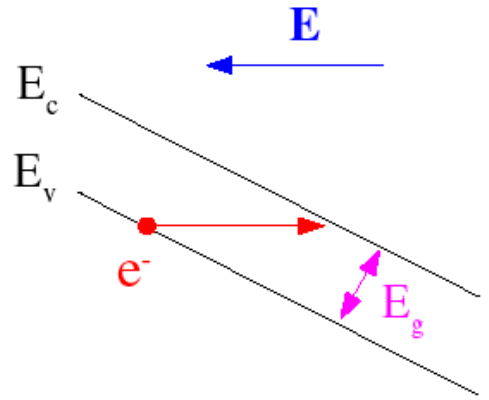
- Non-linear responses (NLR) to electric fields more marginally applied because of conceptual difficulties.

Electric field perturbation

-Difficulty : scalar potential "$\mathcal{E}$. **r**"

-breaks the periodicity of the crystal

-is unbound from below



- Electric field dependent energy functional :

$$F_{e+i}[\mathbf{R}_\kappa, E] = E_{e+i}[\mathbf{R}_\kappa] - \Omega_0 \; E \cdot P \qquad [-(\Omega_0/8\pi)\, E^2]$$

*Nunes and Vanderbilt, PRL **73,** 712 (1994); Nunes and Gonze, PRB **63,** 155107 (2001)*

- Modern theory of the polarization:

$$P = -\frac{2ie}{(2\pi)^3} \sum_n^{occ} \int_{BZ} d\mathbf{k} \left\langle u_{n\mathbf{k}} \middle| \nabla_k \middle| u_{n\mathbf{k}} \right\rangle$$

*King-Smith and Vanderbilt, PRB **47**, 1651 (1993); Resta, Rev. Mod. Phys. **66**, 899 (1994)*

Physical quantities:

$$F_{e+i}[\mathbf{R}_\kappa, E] = F_{e+i}[\mathbf{R}^0_\kappa, 0] - \Omega_0 \sum_\alpha P^s_\alpha E_\alpha - \sum_\alpha \sum_\kappa F^0_\alpha \tau_{\kappa\alpha}$$

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

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

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

Physical quantities:

- **Atomic forces :**

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

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

- **Electric polarization :**

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

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

To be discussed today:

- Non-linear optical susceptibilities :

$$\chi_{ijl}^{\infty(2)} = \frac{-1}{2\Omega_0} \frac{\partial^3 F_{e+i}}{\partial E_i \partial E_j \partial E_l}$$

- Raman coefficients :

$$\frac{\partial \chi_{ij}^{\infty(1)}}{\partial \tau_{\kappa\alpha}} = \frac{-1}{\Omega_0} \frac{\partial^3 F_{e+i}}{\partial E_i \partial E_j \partial \tau_{\kappa\alpha}}$$

- Electro-optic coefficients :

$$r_{ij\gamma} = \frac{-1}{n_i^2 n_j^2} \frac{d\varepsilon_{ij}^{\infty}}{dE_\gamma} = \frac{4\pi}{n_i^2 n_j^2 \Omega_0} \frac{\partial^3 F_{e+i}}{\partial E_i \partial E_j \partial E_\gamma}$$

Roman indices (i,j,l) : **optical** fields - **Greek** indice (γ) : (quasi-)**static** field

2. Computation of energy derivatives within DFPT:

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

"2n+1" theorem

Computation of $F_{e+i}^{(\lambda_1 \lambda_2 \lambda_3)}$ only requires knowledge of ground-state $\psi^{(0)}$ and first-order ψ^{λ_i} wave-functions

*Gonze PRA **52**, 1086 (1995); ibid. 1096 (1995)*

Two-step procedure :

- *Determination of first-order wave-functions $\psi^{\lambda i}$*

  → already done for second-order quantities.

  - minimization of a **variational** expression of $E_{e+i}^{(2)}$

    *X. Gonze, PRB **55**, 10337 (1997)*
  - Solving the corresponding Sternheimer equation

    *P. Giannozzi et al., PRB **43**, 7231 (1991)*

- *Evaluation of the appropriate expression of $F_{e+i}^{(3)}$*

Computation of 3rd derivatives

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

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

using standard DFPT formula

*Gonze PRA **52**, 1096 (1995)*

Additional term
- linear in $\mathcal{E}$ and
- independent of R_κ

Acts as an additional potential
to be added to the ionic potential v_{ext}

Contribution only in DFPT terms involving
first derivative of v_{ext} with respect to $\mathcal{E}$

*Veithen, Gonze and Ghosez, PRB **71**, 125107 (2005)*

PEAD and DAPE

- Modern theory of the polarization:

  - continuous form[1] : $$P = -\frac{2ie}{(2\pi)^3}\sum_n^{occ}\int_{BZ} d\mathbf{k}\left\langle u_{n\mathbf{k}}\left|\nabla_k\right|u_{n\mathbf{k}}\right\rangle$$

  - discretized form[2] : $$P = -\frac{2e}{N_k\Omega_0}\sum_{\mathbf{k}}\sum_b w_b\mathbf{b}\,\mathcal{I}m\ln\left(\det\left[S\left(\mathbf{k},\mathbf{k}+\mathbf{b}\right)\right]\right)$$
    (use regular grid instead of strings)

[1] *King-Smith and Vanderbilt, PRB **47**, 1651 (1993); Resta, Rev. Mod. Phys. **66**, 899 (1994)*
[2] *Marzari and Vanderbilt, PRB **56**, 12847 (1997)*

- **D**iscretization **A**fter **P**erturbation **E**xpansion (DAPE)
  continuous form → 2n+1 theorem → discretization

- **P**ertubation **E**xpansion **A**fter **D**iscretization (PEAD)
  continuous form → discretization → 2n+1 theorem

*Nunes and Gonze, PRB **63,** 155107 (2001)*

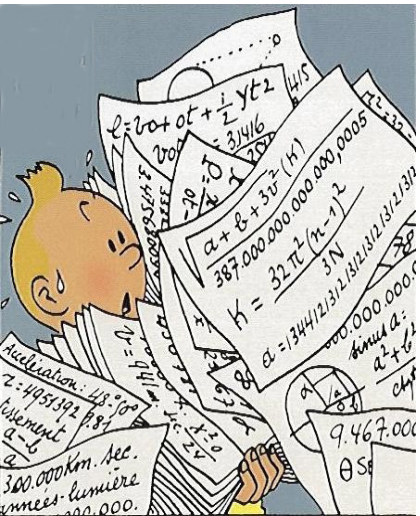
Computation of 3rd derivatives

- DFPT

$$E^{\lambda_1\lambda_2\lambda_3} = \frac{1}{6}(\tilde{E}^{\lambda_1\lambda_2\lambda_3} + \tilde{E}^{\lambda_1\lambda_3\lambda_2} + \tilde{E}^{\lambda_2\lambda_1\lambda_3} + \tilde{E}^{\lambda_2\lambda_3\lambda_1} + \tilde{E}^{\lambda_3\lambda_2\lambda_1} + \tilde{E}^{\lambda_3\lambda_1\lambda_2}), \tag{2}$$

with

$$\begin{aligned}\tilde{E}^{\lambda_1\lambda_2\lambda_3} = &\sum_{\alpha} [\langle\psi_\alpha^{\lambda_1}|(T+v_{ext})^{\lambda_2\lambda_3}|\psi_\alpha^{(0)}\rangle + \langle\psi_\alpha^{\lambda_1}|(T+v_{ext}+v_{Hxc})^{\lambda_2}|\psi_\alpha^{\lambda_3}\rangle + \langle\psi_\alpha^{(0)}|(T+v_{ext})^{\lambda_1\lambda_2\lambda_3}|\psi_\alpha^{(0)}\rangle + \langle\psi_\alpha^{(0)}|(T+v_{ext})^{\lambda_1\lambda_2}|\psi_\alpha^{\lambda_3}\rangle] \\ &- \sum_{\alpha,\beta}\Lambda_{\beta\alpha}^{\lambda_2}\langle\psi_\alpha^{\lambda_1}|\psi_\beta^{\lambda_3}\rangle + \frac{1}{6}\int d\mathbf{r}d\mathbf{r}'d\mathbf{r}''\frac{\delta^3 E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')\delta n(\mathbf{r}'')}n^{\lambda_1}(\mathbf{r})n^{\lambda_2}(\mathbf{r}')n^{\lambda_3}(\mathbf{r}'') \\ &+ \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\frac{d}{d\lambda_2}\left.\frac{\delta^2 E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{\lambda=0} n^{\lambda_1}(\mathbf{r})n^{\lambda_3}(\mathbf{r}') + \frac{1}{2}\int d\mathbf{r}\frac{d^2}{d\lambda_1 d\lambda_3}\left.\frac{\delta E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r})}\right|_{\lambda=0} n^{\lambda_2}(\mathbf{r}) + \frac{1}{6}\left.\frac{d^3 E_{Hxc}[n^{(0)}]}{d\lambda_1 d\lambda_2 d\lambda_3}\right|_{\lambda=0}.\end{aligned} \tag{3}$$



- DAPE

$$\tilde{E}_{pol}^{\lambda_1\varepsilon_i\lambda_3} = \frac{2ie}{N_k}\sum_{\mathbf{k}}\sum_{\mathbf{b}}\sum_{n,m}^{occ} w_{\mathbf{b}}(\mathbf{b}\cdot\mathbf{G}_i) \times \{\langle u_{n\mathbf{k}}^{\lambda_1}|u_{m\mathbf{k}+\mathbf{b}}^{\lambda_3}\rangle\langle u_{m\mathbf{k}+\mathbf{b}}^{(0)}|u_{n\mathbf{k}}^{(0)}\rangle - \langle u_{n\mathbf{k}}^{\lambda_1}|u_{m\mathbf{k}}^{\lambda_3}\rangle\delta_{n,m}\},$$

- PEAD

$$\begin{aligned}\tilde{E}_{pol}^{\lambda_1\varepsilon_i\lambda_3} = &\frac{-e}{N_k}\mathrm{Im}\sum_{\mathbf{k}}\sum_{\mathbf{b}} w_{\mathbf{b}}(\mathbf{b}\cdot\mathbf{G}_i) \\ &\times\Bigg[2\sum_{n,m}^{occ}\langle u_{n\mathbf{k}}^{\lambda_1}|u_{m\mathbf{k}+\mathbf{b}}^{\lambda_3}\rangle Q_{mn}(\mathbf{k},\mathbf{k}+\mathbf{b}) \\ &-\sum_{n,m,l,l'}^{occ} S_{mn}^{\lambda_1}(\mathbf{k},\mathbf{k}+\mathbf{b})Q_{nl}(\mathbf{k},\mathbf{k}+\mathbf{b}) \\ &\times S_{ll'}^{\lambda_3}(\mathbf{k},\mathbf{k}+\mathbf{b})Q_{l'm}(\mathbf{k},\mathbf{k}+\mathbf{b})\Bigg]\end{aligned}$$

Original ABINIT implementation

*Veithen, Gonze and Ghosez, PRB **71**, 125107 (2005)*

- Local density approximation (LDA) to density functional theory (DFT) only [no GGA nor LSDA yet].

- ABINIT code (www.abinit.org) within the planewave/ pseudopotential approach [now also in PAW].
  *X. Gonze et al., Comput. Mater. Sci. **25**, 478 (2002).*

- Variational approach to density functional perturbation theory (DFPT).
  *X. Gonze, PRB **55**, 10337 (1997)*

- PEAD formulation of 3rd derivatives

- Finite-field technique also available
  *Souza et al., PRL **89**, 117602 (2002)*

ABINIT input

```
#DATASET1 : scf calculation: GS WF in the BZ
#*********************************************
   prtden1    1
   kptopt1    1
   toldfe1  1.0d-10

#DATASET2 : non scf calculation: GS WF in the whole BZ
#*****************************************************
   getden2    1
   kptopt2    2
     iscf2   -2
   getwfk2    1
   tolwfr2    1.0d-18


#DATASET3 : ddk on the MP grid of k-points
#*****************************************
   getwfk3    2
    rfdir3    1 1 1
   rfelfd3    2
   tolwfr3    1.0d-18
   kptopt3    2
nstep3 60


#DATASET4 : ddE + phonons on the MP grid of k-points
#***************************************************
   prtden4    1
   getwfk4    2
   getddk4    3
    rfdir4    1 1 1
   toldfe4    1.0d-10
   rfelfd4    3
   rfphon4    1
  rfatpol4    1 6
   kptopt4    2
  prepanl4    1
```

```
#DATASET5 : 3DTE calculation
#***************************
   getden5    1
  get1den5    4
   getwfk5    2
   get1wf5    4
   kptopt5    2
optdriver5    5

  rf1elfd5    1
  rf1phon5    1
 rf1atpol5    1 6
   rf1dir5    1 1 1

  rf2elfd5    1
   rf2dir5    1 1 1

  rf3elfd5    1
   rf3dir5    1 1 1

nbdbuf 0
```

nband = number valence bands

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*

$$P_i[\mathbf{R}^0_\kappa, E] = P^s_i + \sum_j \chi^{\infty(1)}_{ij} E_j + \sum_{jl} \chi^{\infty(2)}_{ijl} E_j E_l + \ldots$$

Non-linear optical susceptibility tensor :

$$\chi^{\infty(2)}_{ijl} = \frac{-1}{2\Omega_0} \frac{\partial^3 F_{e+i}}{\partial E_i \partial E_j \partial E_l}$$

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

Note : (2n+1) theorem applied to static DFT → we neglect the dispersion
Frequency dependence would require to consider TD-DFT *(Dal Corso et al., PRB 53, 15638 (1996))* or SoS techniques *(Levine and Allan, PRL 66, 41 (1991))*.

Non-linear optical susceptibilities:

Earlier studies :

- Sums over states

Levine and Allan, PRL 66, 41 (1991)

-Density functional perturbation theory

Dal Corso et al., PRB 53, 15638 (1996)

-Finite electric fields

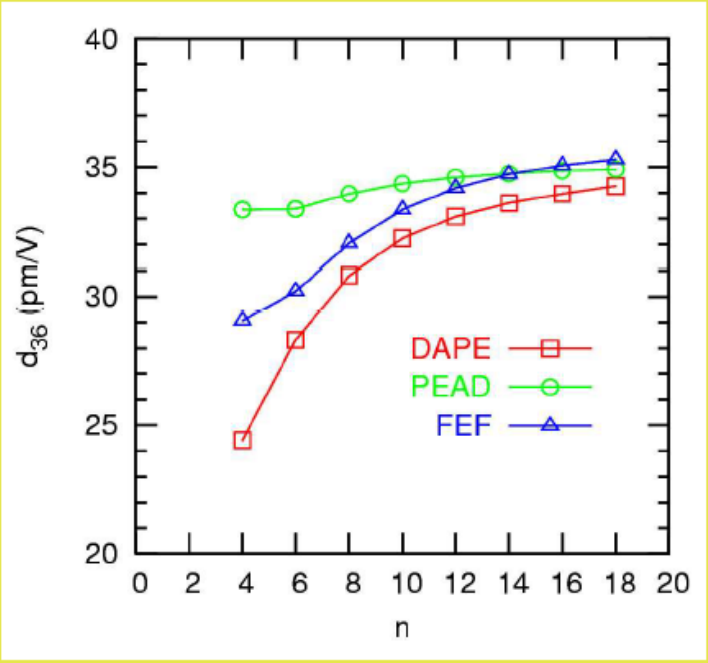
Souza et al., PRL 89, 117602 (2002)

Method	AlAs	AlP
2n + 1 theorem	35	21
2n + 1 theorem [1]	32	19
Finite electric fields [2]	32	19
Sum over states [3]	34	21
2N + 1 theorem + SCI	21	13
Sum over states + SCI [3]	21	13

[1] A. Dal Corso *et al.*, PRB 53, 15638 (1996)
[2] I. Souza *et al.*, PRL 89, 117602 (2002)
[3] Z. H. Levine and D. C. Allan, PRB 44, 12781 (1991)

- PEAD formula converges faster
- LDA (GGA) inaccurate → SCI

Non-linear optical susceptibility of AlAs
n × n × n grid of k-points



DAPE < FEF < PEAD

Non-linear optical susceptibilities:

Example 1 : ABO_3 compounds

	$BaTiO_3$			$PbTiO_3$	
	Rhombohedral	Tetragonal		Tetragonal	
	Present	Present	Exp.	Present	Exp.
d_{15}	10.97	-11.09	-17.0	-27.69	-37.9
d_{31}	10.97	-11.09	-15.7	-27.69	-42.8
d_{33}	24.69	-18.31	-6.8	-5.69	+8.5
d_{22}	-0.98				
ϵ_{11}^{∞}	6.15	6.48	5.19	7.30	6.64
ϵ_{33}^{∞}	5.73	5.84	5.05	6.79	6.63

$LiNbO_3$ – R3c

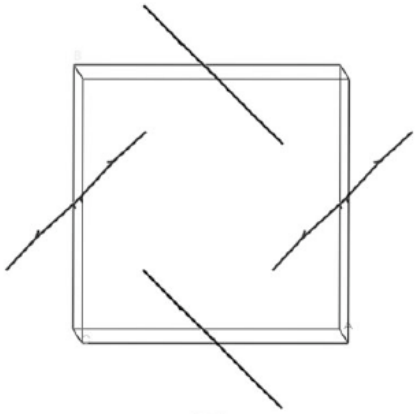
	d_{31}	d_{22}	d_{33}
Present	−8.01	−1.23	−30.21
Exp. [26]	−4.64	+2.46	−41.7
Exp. [19]	−6.75	+3.6	−37.5

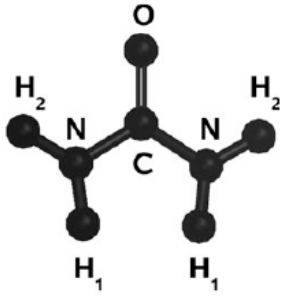
- Qualitative agreement only
- Sometimes a sign problem

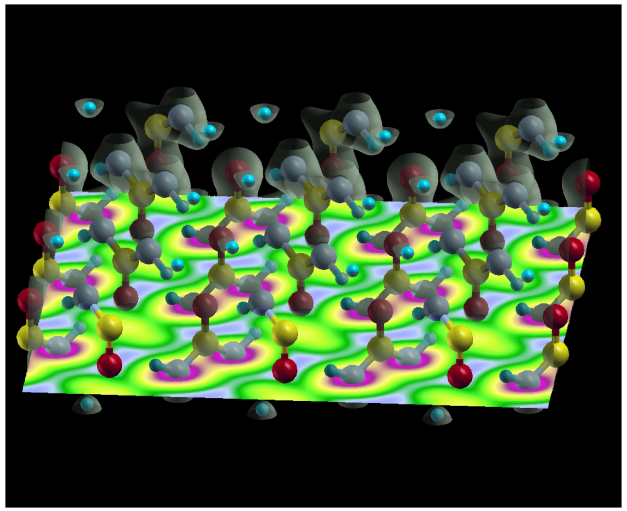
P. Hermet, M. Veithen and Ph. Ghosez, J. Phys.: Condens. Matter 21, 215901 (2009); ibid., J. Phys. : Condens. Matter 19, 456202 (2007)

Non-linear optical susceptibilities:

Example 2 : Urea







	Theory				Experiment	
	Present	[13]^a	[13]^b	[2]	[1] ([11])	[12]
d_{14} (pm/V)	1.09	2.1	1.10	1.04	1.2± 0.1	1.3± 0.3
ϵ^{∞}_{xx}	2.29	2.27	2.03		(2.17)	2.17
ϵ^{∞}_{zz}	2.67	2.47	2.14		(2.49)	

without/with
Local fields

- Surprizingly accurate in LDA
- Comparable to previous studies

P. Hermet and Ph. Ghosez, Phys. Chem. Chem. Phys. 12, 835 (2010)

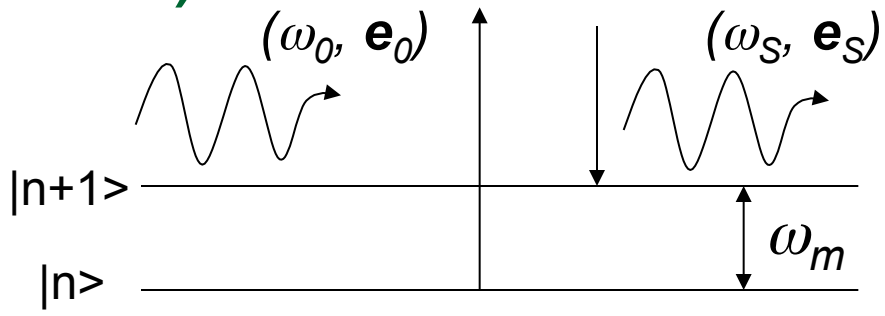
4. Raman efficiencies

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)

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

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

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

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

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

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 :

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

Results

Earlier studies :

- Finite difference of χ

[129] Baroni and Resta, PRB 33, 5969 (1986)

Umari et al., PRL 90, 027401 (2003)

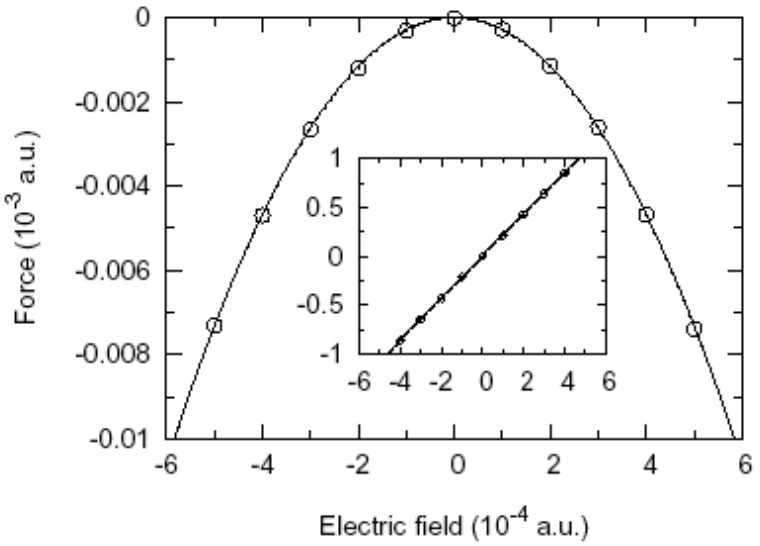
-Derivative of density matrix

Lazzeri and Mauri, PRL 90, 036401 (2003)

- 2n+1 theorem (DAPE)

[60] Deinzer and Strauch, PRB 66, 100301 (2002)

AlAs (finite field)



	LDA			
Method	Si	AlAs	AlP	GaP
PEAD (present)	21.53	8.66	4.79	10.70
FEF (present)	20.24	8.23	4.55	10.19
FP (present)	21.81	8.69	4.79	10.79
DAPE [60]	23.56	7.39	5.13	11.38
FP [60]	20.44	5.64	4.44	9.48
FP [129]	26.16			
Exp. [148,149]	23 ± 4			19,16,23

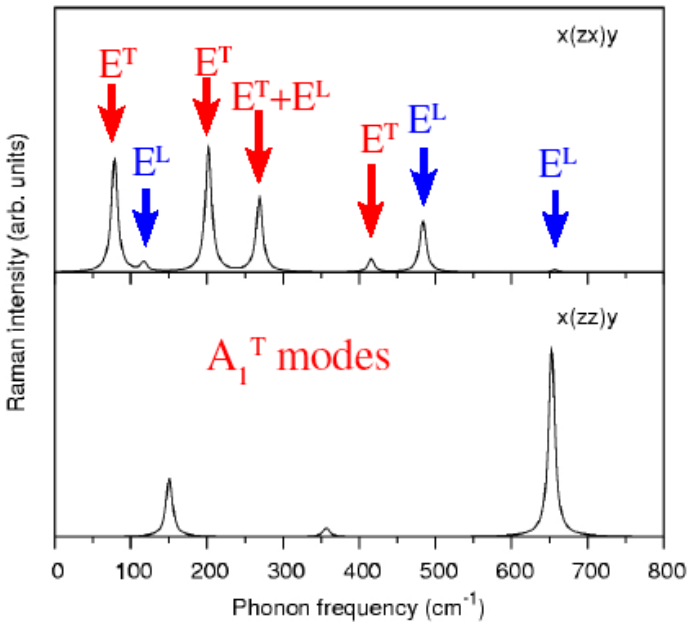
Present approach :

- PEAD formulation
- allows for non-linear core correction

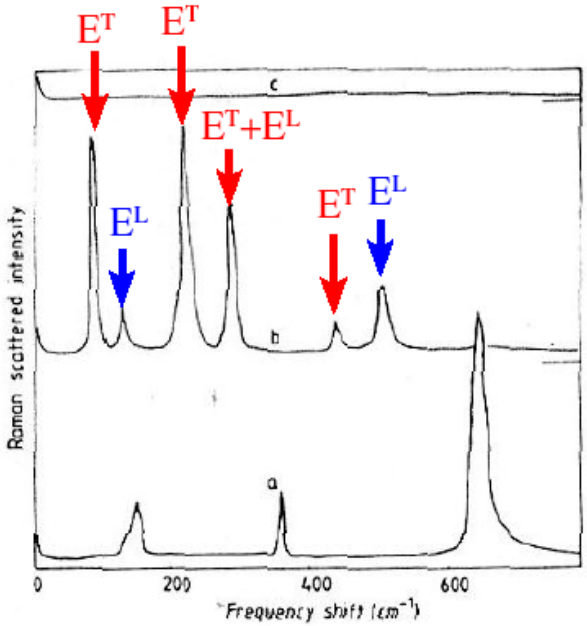
*Veithen, Gonze and Ghosez, PRB **71**, 125107 (2005)*

Raman spectrum of $PbTiO_3$

Theoretical spectrum



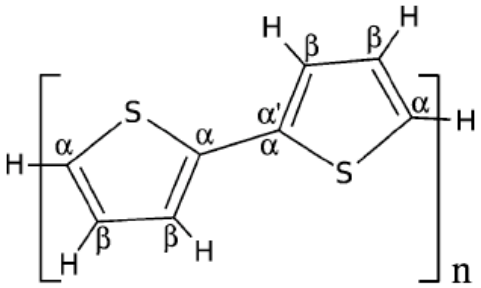
Experimental spectrum



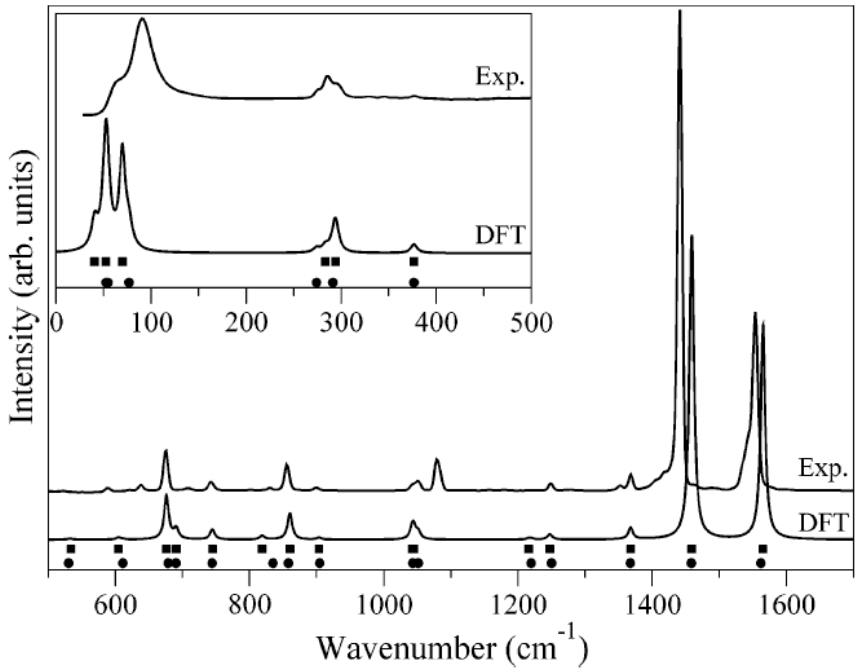
M. D. Fontana et al.,
J. Phys. C **3**, *8695 (1991)*

Veithen, PhD thesis, ULG (2005); P. Hermet, M. Veithen and Ph. Ghosez, J. Phys.: Condens. Matter 21, 215901 (2009)

Raman spectrum of α-bithiophene



bi-(n=2), quarter-(n=4) and sexi (n=6) thiophene
monoclinic structure, 2 molecules per unit cell



P. Hermet, N. Izard, A. Rahmani and Ph. Ghosez, J. Chem. Phys. B 110, 24869 (2006).

Transferability of parameters

Bond polarizability model

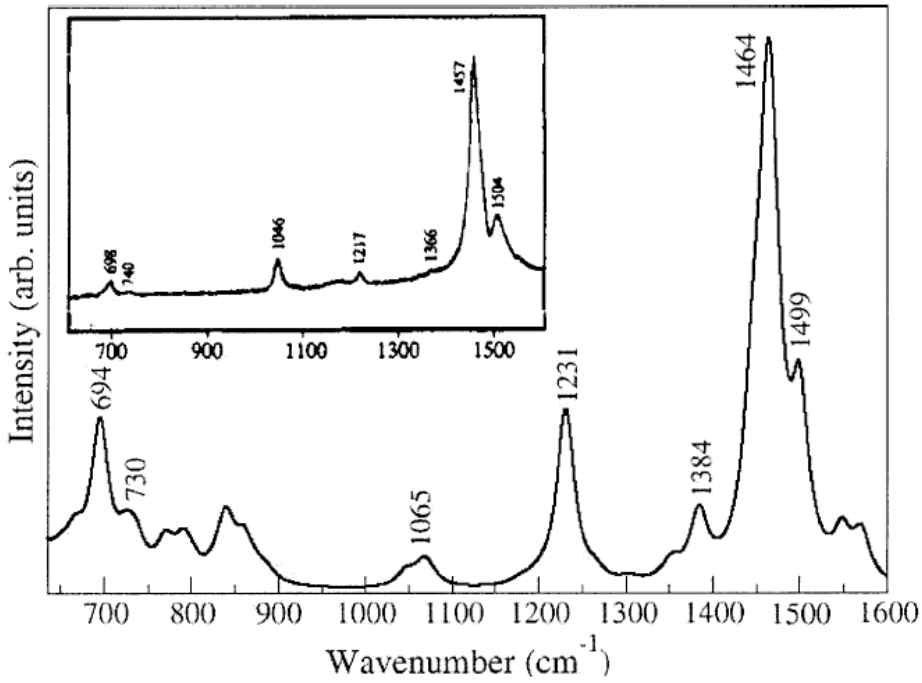
$$\chi_{ij}^{\infty} = \frac{1}{\Omega_0}\sum_b \alpha_{ij}^b$$

$$\alpha_{ij}^b = \frac{1}{3}(\alpha_l + 2\alpha_p)\delta_{ij} + (\alpha_l - \alpha_p)\left(\hat{r}_i\hat{r}_j - \frac{1}{3}\delta_{ij}\right)$$

$$\pi_{ij,\gamma}^{\kappa} = \frac{1}{\Omega_0}\sum_b \frac{\partial \alpha_{ij}^b}{\partial \tau_{\kappa\gamma}}$$

$$\frac{\partial \alpha_{ij}^{\upsilon}}{\partial \tau_{\kappa\gamma}} = \frac{1}{3}(2\alpha'_p + \alpha'_l)\delta_{ij}\hat{r}_\gamma + (\alpha'_l - \alpha'_p)\left(\hat{r}_i\hat{r}_j - \frac{1}{3}\delta_{ij}\right)\hat{r}_\gamma + \frac{\alpha_l - \alpha_p}{r}(\delta_{i\gamma}\hat{r}_j + \delta_{j\gamma}\hat{r}_i - 2\hat{r}_i\hat{r}_j\hat{r}_\gamma)$$

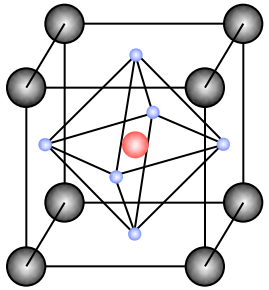
	BP/$\tilde{\pi}$ model			BP/spectrum model		
	$\bar{\alpha}$	$\bar{\beta}$	$\bar{\gamma}$	$\bar{\alpha}$	$\bar{\beta}$	$\bar{\gamma}$
$C_\alpha - C_\alpha$	−113.7	−183.4	−11.3	−113.6	8.9	17.1
$C_\alpha = C_\beta$	110.2	−15.9	9.5	310.0	88.8	75.5
$C_\beta - C_\beta$	−11.2	−82.7	−10.5	−60.4	−10.2	−7.4
$C_\alpha - S$	78.8	28.8	18.1	153.7	77.8	−63.2
$C_\alpha - H$	48.2	4.3	−3.0	59.6	5.1	−6.1
$C_\beta - H$	31.5	18.7	0.8	59.9	4.6	4.6



- Better to fit on DFT
- Transferability from α-2T to α-6T

P. Hermet, N. Izard, A. Rahmani and Ph. Ghosez, J. Chem. Phys. B 110, 24869 (2006).

Transferability of parameters



$$\pi^{\kappa}_{ij,\alpha} = \frac{\partial \chi^{\infty(1)}_{ij}}{\partial \tau_{\kappa\alpha}}$$

κ		$BaTiO_3$	$PbTiO_3$
Ba/Pb	a,b	-0.0038	-0.0265
	c,d	-0.0065	-0.0826
	e	0.0218	-0.0485
Ti	a,b	-0.0873	-0.1405
	c,d	-0.1289	-0.1561
	e	-0.3093	-0.1276
O_1	a,b	0.0335	0.0620
	c,d	0.1206	0.1924
	e	0.2462	0.1783
O_2	a	-0.0029	-0.0240
	b	0.0606	0.1289
	c	-0.0063	-0.0362
	d	0.0210	0.0825
	e	0.0207	-0.0011

Can we transfer $\pi^{\kappa}_{ij,\alpha}$ from one perovskite compound to another ?
(like atomic polarizabilities)

- No, $\pi^{\kappa}_{ij,\alpha}$ can takes very different values for the same atom in different compounds.
- Atoms with largest Z* also exhibit the largest $\pi^{\kappa}_{ij,\alpha}$.

P. Hermet, M. Veithen and Ph. Ghosez, J. Phys.: Condens. Matter 21, 215901 (2009

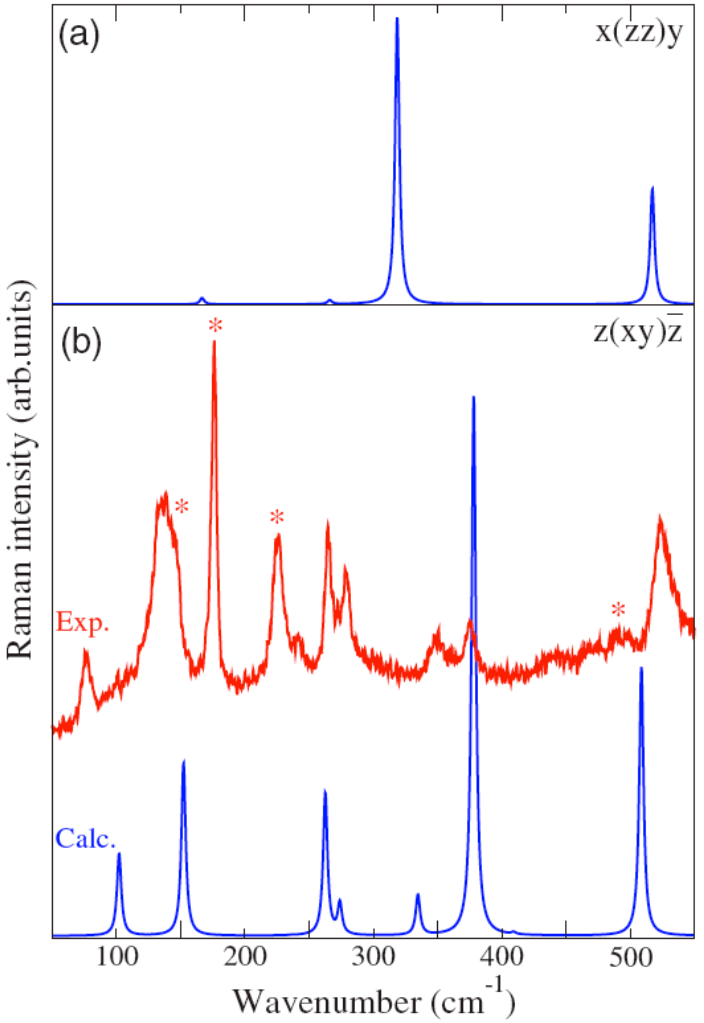
Raman spectra of magnetic compound

$BiFeO_3$

- Ferroelectric
- G-type AFM

Raman spectrum

- Not directly accessible in present ABINIT DFPT implementation.
- To be computed from finite differences of $d\chi/d\tau$.
- Only for TO modes (no access to $\chi^{(2)}$)



P. Hermet, M. Goffinet, J. Kreisel and Ph. Ghosez, PRB 75, 220102(R) (2007)

Raman spectrum of powder

Often, Raman spectra are made on powder with unpolarized laser.

➔Need to sum-up on all crystal orientations and laser polarizations

$$G_0 = \frac{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2}{3},$$

$$G_1 = \frac{(\alpha_{xy} - \alpha_{yz})^2 + (\alpha_{yz} - \alpha_{zx})^2 + (\alpha_{zx} - \alpha_{xy})^2}{2},$$

$$G_2 = \frac{(\alpha_{xy} + \alpha_{yz})^2 + (\alpha_{yz} + \alpha_{zx})^2 + (\alpha_{zx} + \alpha_{xy})^2}{2} + \frac{(\alpha_{xy} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2}{3}.$$

$$I_{\parallel}^{powder} = C(10G_0 + 4G_2),$$

$$I_{\perp}^{powder} = C(5G_1 + 3G_2),$$

$$I_{total}^{powder} = I_{\parallel}^{powder} + I_{\perp}^{powder}.$$

[Prosandeev et al., PRB 71, 214307 (2005) from G. Placzek, in Handbuch der Radiologie Vol 6, 1934]

Raman spectrum of powder

More examples

http://www.wurm.info

A database of the physical properties
of various minerals

(R. Caracas)

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

$$\Delta\varepsilon_{ij}^{\infty} = \sum_{\gamma} \frac{d\varepsilon_{ij}^{\infty}}{dE_{\gamma}} E_{\gamma}$$

- Electro-optic coefficients

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

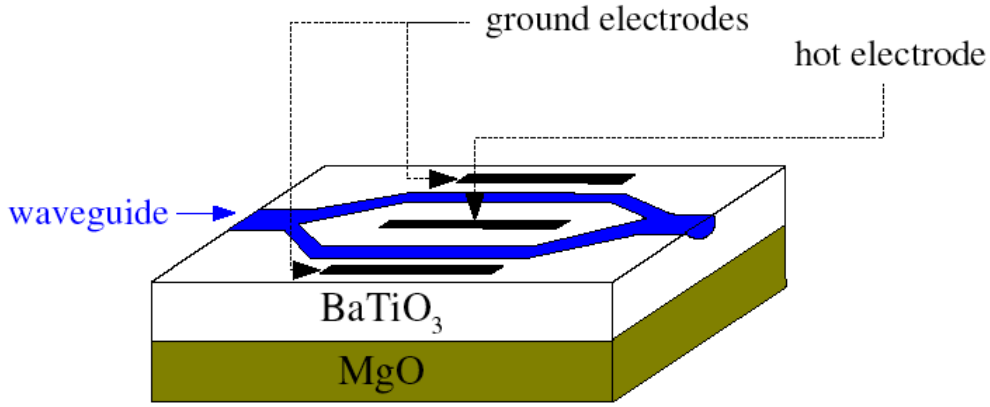
Using $\Delta\left(\varepsilon^{\infty-1}\right)_{ij} = -\sum_{mn} \varepsilon_{im}^{\infty-1} \Delta\varepsilon_{mn}^{\infty} \varepsilon_{nj}^{\infty-1}$, we get when expressed in the principal axes (in zero field)

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

Motivation

Applications: EO modulators

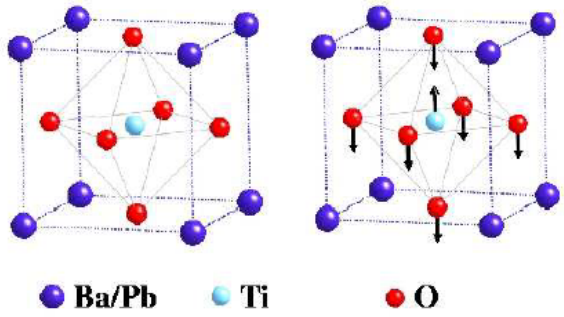
Epitaxial films of $BaTiO_3$ on an MgO substrate



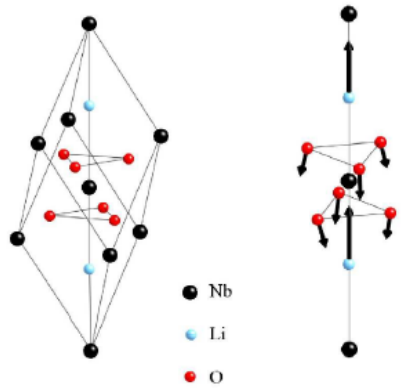
A. Petraru *et al.*, Appl. Phys. Lett. **81**, 1375 (2002)

Materials of interest: ferroelectric oxides

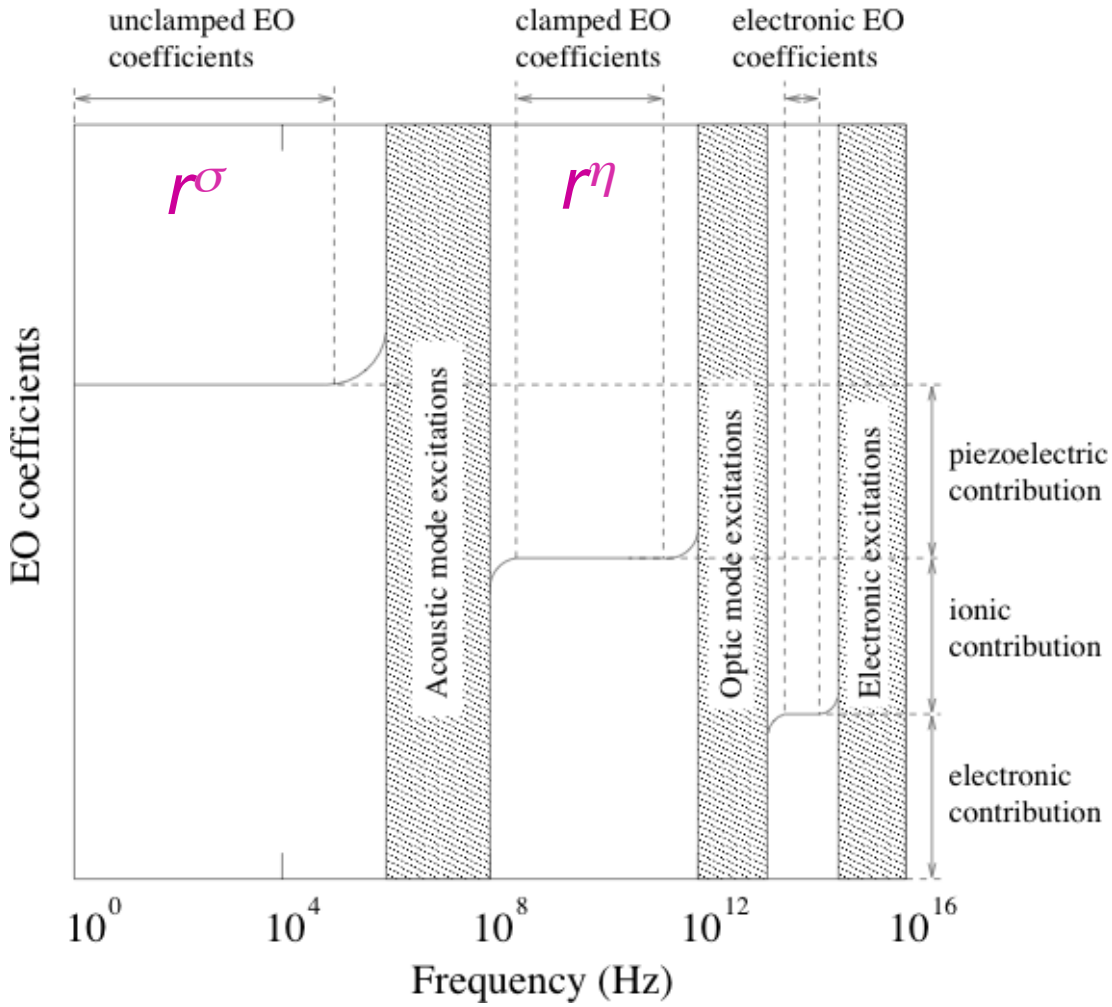
Perovskite structure ($BaTiO_3$, $PbTiO_3$)



Trigonal structure ($LiNbO_3$)



Clamped and unclamped electro-optic coefficients:



Depends on the frequency range of ε_γ

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

Clamped electro-optic response:

Electronic + ionic response

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

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

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

$$\tau_{\kappa\alpha}^{E_\gamma} = \frac{\partial \tau_{\kappa\alpha}}{\partial E_\gamma} = \sum_m \tau_m^{E_\gamma}\ \eta_m(\kappa\alpha)$$

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

Atomic relaxation:

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

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

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

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

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

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

Clamped electro-optic response:

Electronic + ionic response

$$\frac{d\varepsilon_{ij}^{\infty}}{dE_{\gamma}} = \left.\frac{\partial\varepsilon_{ij}^{\infty}}{\partial E_{\gamma}}\right|_{\mathbf{R}_{\kappa 0}} + 4\pi\sum_{m}\left.\frac{\partial\varepsilon_{ij}^{\infty}}{\partial\tau_{m}}\right|_{E=0}\frac{\partial\tau_{m}}{\partial E_{\gamma}}$$

$$= 8\pi\,\chi_{ij\gamma}^{\infty(2)} + 4\pi\sum_{m}\frac{1}{\omega_{m}^{2}}\underbrace{\sum_{\kappa'\beta}Z_{\kappa',\beta\gamma}^{*}\eta_{m}(\kappa'\beta)}_{p_{m,\gamma}}\underbrace{\sum_{\kappa\alpha}\frac{\partial\chi_{ij}^{\infty(1)}}{\partial\tau_{\kappa\alpha}}\eta_{m}(\kappa\alpha)}_{\alpha_{ij}^{m}/\sqrt{\Omega_{0}}}$$

$$= 8\pi\,\chi_{ij\gamma}^{\infty(2)} + \frac{4\pi}{\sqrt{\Omega_{0}}}\sum_{m}\frac{p_{m,\gamma}.\alpha_{ij}^{m}}{\omega_{m}^{2}}$$

$$\Rightarrow \quad r_{ij\gamma}^{\eta} = \frac{-8\pi}{n_{i}^{2}n_{j}^{2}}\,\chi_{ij\gamma}^{\infty(2)} - \frac{4\pi}{n_{i}^{2}n_{j}^{2}\sqrt{\Omega_{0}}}\sum_{m}\frac{p_{m,\gamma}.\alpha_{ij}^{m}}{\omega_{m}^{2}}$$

Electronic response

Ionic contribution (mode by mode)

Unclamped electro-optic response:

Electronic + ionic + **piezoelectric** responses

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

Elasto-optic coefficients

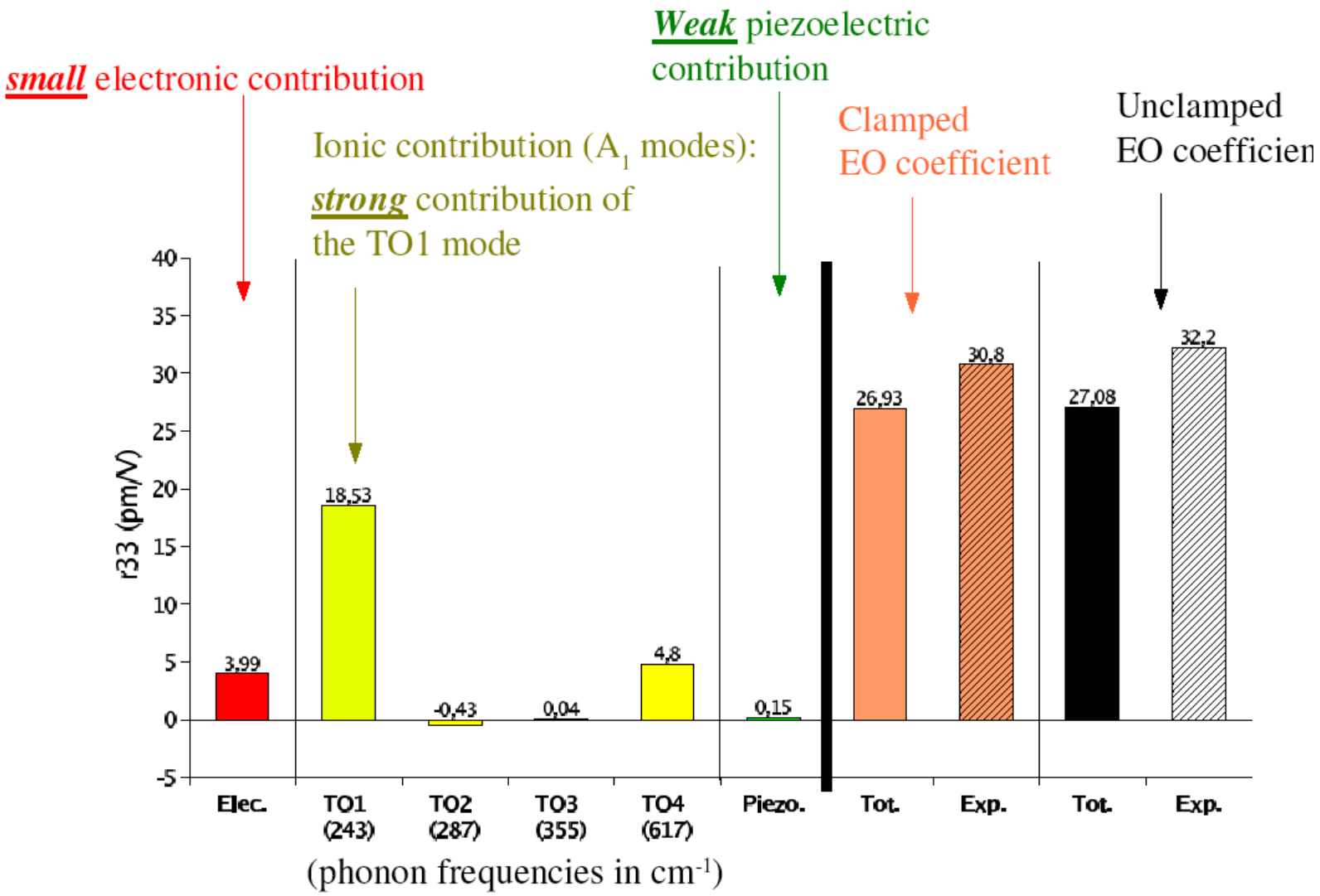
Change of the dielectric constant versus strain

Piezoelectric strain coefficients

Change of the strain versus electric field

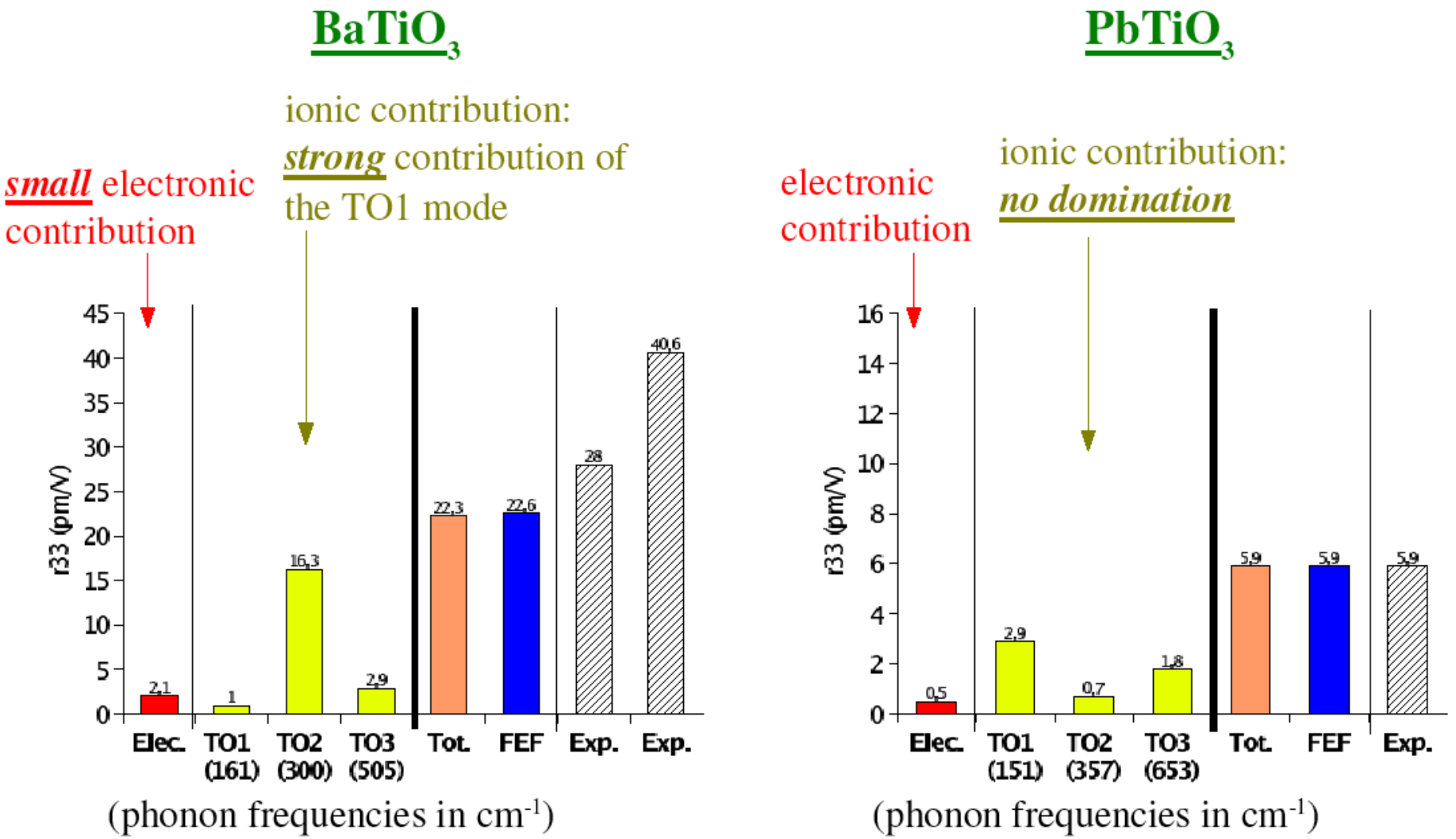
Computed here by finite differences …

EO coefficient r_{33} in $LiNbO_3$



*Veithen, Gonze and Ghosez, PRL **93**, 187401 (2004)*

EO coefficient r_{33} in $BaTiO_3$ and $PbTiO_3$



*Veithen, Gonze and Ghosez, PRL **93**, 187401 (2004)*

Analysis of the ionic contribution to r_{33}

Contribution of TO modes:

Raman susceptibility

$$\frac{\alpha_m \cdot p_m}{\omega_m^2}$$

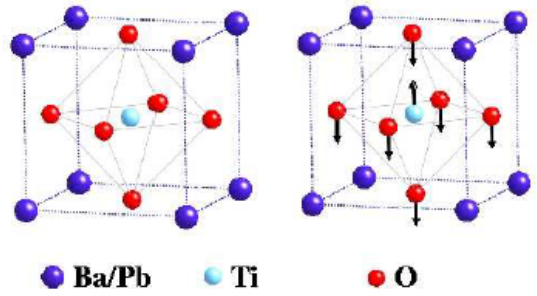
Polarity

Frequency

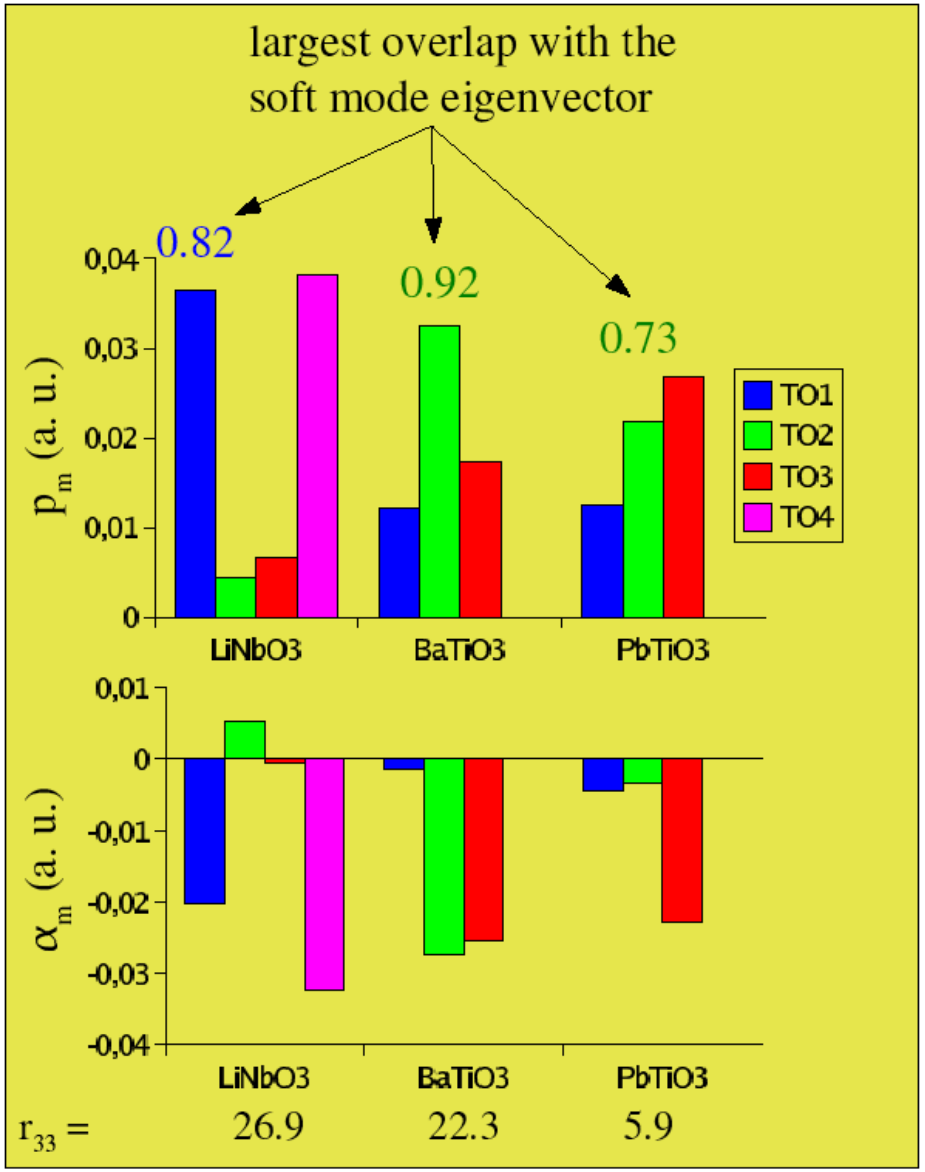
Ferroelectric crystals

(ex: perovskite structure)

$T > T_c$	$T < T_c$
paraelectric phase	ferroelectric phase



Phase transition driven by a highly polar soft mode



Conclusions

- Computation and easy analysis of non-linear optical susceptibilities, Raman susceptibilities and electrooptics coefficients within DFT-LDA **freely** accessible within the ABINIT software package (see http://www.abinit.org)

- A fastly converging PEAD formulation has been implemented and allows computation on relatively complex systems. Now also a new implementation in PAW and for magnetic systems.

- Easy to compute when first-order wavefunctions are known.

- $\chi^{(2)}$ electronic response poorly reproduced within LDA while ionic and piezoelectric responses to EO coefficients more accurately estimated.