Université de Liège

Computation of non-linear optical properties from density functional perturbation theory

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2nd- and 3th-order energy derivatives

- Taylor expansion of a thermodynamic potential $F(\tau,\eta,E)$

$$F(\lambda)=F(0)+\sum_i \frac{\partial F}{\partial \lambda_i}\lambda_i+\frac{1}{2}\sum_{i,j}\frac{\partial^2 F}{\partial \lambda_i \partial \lambda_j}\lambda_i\lambda_j+\frac{1}{6}\sum_{i,j,k}\frac{\partial^3 F}{\partial \lambda_i \partial \lambda_j \partial \lambda_k}\lambda_i\lambda_j\lambda_k+\ldots$$

- Perturbations λ_i
  - **E** : electric field
  - τ : atomic displacement
  - η : strain
- First-order derivatives
  - Forces : $f=-\frac{\partial F}{\partial \tau}$
  - Stress tensor : $\sigma=\frac{1}{\Omega}\frac{\partial F}{\partial \eta}$

  → Hellmann-Feynman theorem:
  - GS wavefunctions
  - 1st-order change of the external potential
  - Polarization : $P=-\frac{1}{\Omega}\frac{\partial F}{\partial E}$ → Berry phase formalism

2nd- and 3th-order energy derivatives

- Second-order derivatives (linear response approach)
  - Pure derivatives
    - Interatomic force constants : $K = \frac{\partial^2 F}{\partial \tau^2}$
    - Electronic dielectric tensor : $\varepsilon = 1 - \frac{4\pi}{\Omega}\frac{\partial^2 F}{\partial E^2}$
    - Rigid-atom elastic constants : $C = \frac{1}{\Omega}\frac{\partial^2 F}{\partial \eta^2}$
  - Mixed derivatives
    - Born effective charges : $Z^* = -\frac{\partial^2 F}{\partial E \partial \tau}$
    - Clamped-ion piezoelectric tensor : $e = -\frac{1}{\Omega}\frac{\partial^2 F}{\partial E \partial \eta}$
    - Internal strain coupling parameters : $\gamma = \frac{\partial F^2}{\partial \tau \partial \eta}$

2nd- and 3th-order energy derivatives

- Third-order derivatives
  - Non-linear optical susceptibilities : $\chi^{(2)} = \frac{-1}{2\Omega}\frac{\partial^3 F}{\partial E^3}$
  - 1st-order derivatives of $\chi^{(1)}$: $\frac{\partial \chi^{(1)}}{\partial \tau} = -\frac{1}{\Omega}\frac{\partial^3 F}{\partial \tau \partial E^2}$

  } Actually implemented in ABINIT

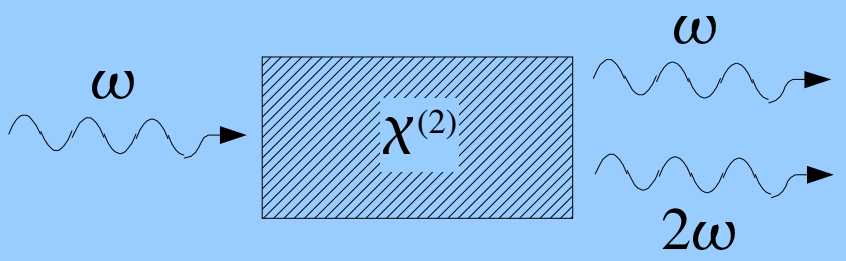
  - Rigid-atom elasto-optic coefficients : $\frac{\partial^3 F}{\partial \eta \partial E^2}$
  - Anharmonic force constants : $\frac{\partial^3 F}{\partial \tau^3}$
  - Non-linear dipole coefficients : $\frac{\partial^3 F}{\partial \tau^2 \partial E}$
  - ...

Non-linear optical properties

- Non-linear optical susceptibilities

$$P = P^s + \chi^{(1)} E + \chi^{(2)} E^2 + \ldots$$

Second harmonic generation



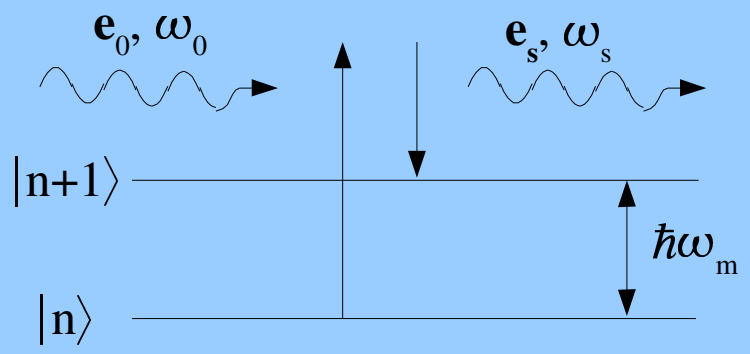
- Non-resonant Raman scattering (Stokes effect)

Scattering efficiency

$$\frac{dS}{d\Omega} = \frac{(\omega_0 - \omega_m)^4}{c^4} \left| \boldsymbol{e}_s \cdot \alpha^m \cdot \boldsymbol{e}_0 \right|^2 \frac{\hbar}{2\omega_m} (n_m + 1)$$

Raman susceptibility

$$\alpha_{ij}^m = \sqrt{\Omega} \sum_{\kappa\alpha} \frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{\kappa\alpha}} u_m(\kappa\alpha)$$



Non-linear optical properties

- Computation of $\frac{\partial \chi^{(1)}_{ij}}{\partial \tau_{\kappa\alpha}}$
  - Transverse optical (TO) phonon modes

$$\left.\frac{\partial \chi^{(1)}_{ij}}{\partial \tau_{\kappa\alpha}}\right|_{E=0} = \frac{-1}{\Omega}\left.\frac{\partial^3 F}{\partial \tau_{\kappa\alpha}\partial E_i \partial E_j}\right|_{E=0}$$

  - Longitudinal optical (LO) phonon modes ($\mathbf{q} \rightarrow 0$)

    → Macroscopic electric field generated by a polar LO mode

    → Additional change of $\chi^{(1)}$ related to the NLO susceptibilities $\chi^{(2)}$

$$\frac{\partial \chi^{(1)}_{ij}}{\partial \tau_{\kappa\alpha}} = \left.\frac{\partial \chi^{(1)}_{ij}}{\partial \tau_{\kappa\alpha}}\right|_{E=0} - \frac{8\pi}{\Omega}\frac{\sum_l Z^*_{\kappa\alpha l} q_l}{\sum_{l,l'} q_l \varepsilon_{ll'} q_{l'}} \sum_l \chi^{(2)}_{ijl} q_l$$

  - Sum rule

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

Non-linear optical properties

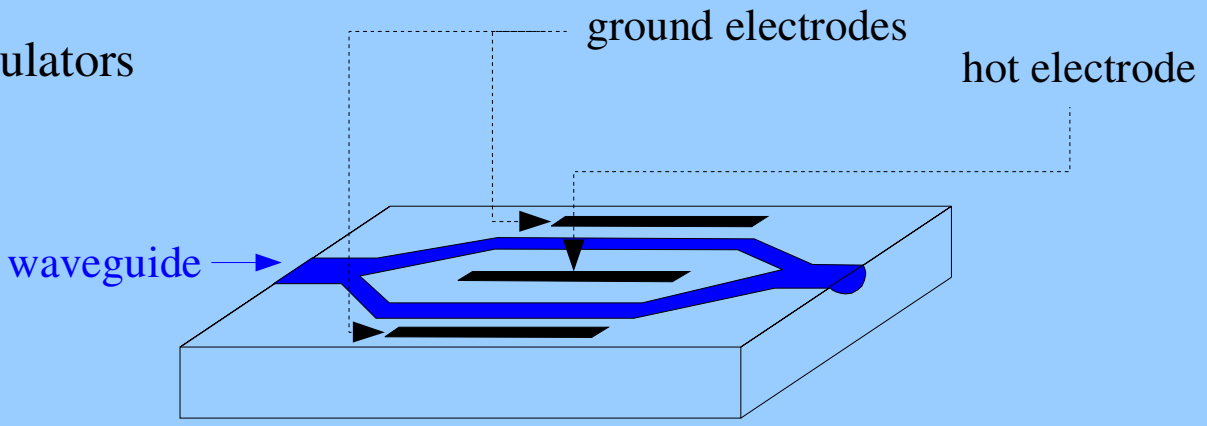
- Electrooptic effect

Modification of the index of refraction of a compound induced by a static (or low frequency) electric field

$$\Delta\left(\varepsilon^{-1}\right)_{ij} = \sum_{\gamma=1}^{3} r_{ij\gamma} E_{\gamma}$$

Applications:

- Electrooptic modulators



- Holographic applications (photorefractive effect)

Non-linear optical properties

- Computation of the clamped EO coefficients

$$\frac{d\,\varepsilon_{ij}}{d\,E_\gamma} = \frac{\partial\,\varepsilon_{ij}}{\partial\,E_\gamma}\Big|_{\tau=0} + \sum_{\kappa\,\alpha} \frac{\partial\,\varepsilon_{ij}}{\partial\,\tau_{\kappa\,\alpha}}\Big|_{E=0} \frac{\partial\,\tau_{\kappa\,\alpha}}{\partial\,E_\gamma}$$

bare electronic part

ionic contribution

  - Electronic contribution:
    - Interaction of the electric field with the valence electrons
    - Clamped atomic positions

$$r^{el}_{ij\,\gamma} = \frac{-8\,\pi}{n_i^2\,n_j^2}\,\chi^{(2)}_{ijk}\Big|_{k=\gamma}$$

  - Ionic contribution:
    - Electric field induced atomic displacements $\propto \frac{p_{m,\alpha}}{\omega_m^2}$

$$r^{ion}_{ij\,\gamma} = \frac{-4\,\pi}{\sqrt{\Omega}\,n_i^2\,n_j^2} \sum_m \frac{\alpha^m_{ij}\,p_{m,\gamma}}{\omega_m^2} \qquad p_{m,\alpha} = \sum_{\kappa\,\beta} Z^*_{\kappa\,\alpha\,\beta}\,u_m(\kappa\,\beta)$$

Computation of third-order energy derivatives

- Non-linear response functions: $\chi^{(2)}_{ijl}$ and $\frac{\partial \chi^{(1)}_{ij}}{\partial \tau_{\kappa\alpha}}$
- 2n + 1 theorem

$$F^{(3)} = \sum_{\alpha} \left\langle \psi^{(1)}_{\alpha} \middle| H^{(1)} \middle| \psi^{(1)}_{\alpha} \right\rangle - \sum_{\alpha\beta} \Lambda_{\beta\alpha} \left\langle \psi^{(1)}_{\alpha} \middle| \psi^{(1)}_{\beta} \right\rangle + \frac{1}{6} \int d\boldsymbol{r}\, d\boldsymbol{r}'\, d\boldsymbol{r}'' \frac{\delta^3 F_{xc}\left[n^{(0)}\right]}{\delta n(\boldsymbol{r}) \delta n(\boldsymbol{r}') \delta n(\boldsymbol{r}'')} n^{(1)}(\boldsymbol{r}) n^{(1)}(\boldsymbol{r}') n^{(1)}(\boldsymbol{r}'')$$

- Electric field dependent energy functional

$$F[\psi, E] = F^{(0)}[\psi] - \Omega \boldsymbol{P} \cdot \boldsymbol{E}$$

- Berry phase polarization

Continuous form: $\boldsymbol{P} = \frac{-2ie}{(2\pi)^3} \sum_n \int d\boldsymbol{k} \langle u_{n,k} | \nabla_k | u_{n,k} \rangle$

Discretized form: $\boldsymbol{P} = \frac{2e}{N_k \Omega} \sum_k \sum_b \omega_b \boldsymbol{b}\, \Im \ln[det\, S(\boldsymbol{k}, \boldsymbol{k}+\boldsymbol{b})]$

$$S_{mn}(\boldsymbol{k}, \boldsymbol{k}+\boldsymbol{b}) = \langle u_{m,k} | u_{n,k+b} \rangle$$

*R. W. Nunes and X. Gonze, PRB **63**, 155107 (2001)*

Computation of third-order energy derivatives

- Discretization After Perturbation Expansion (DAPE)
  - Perturbation expansion

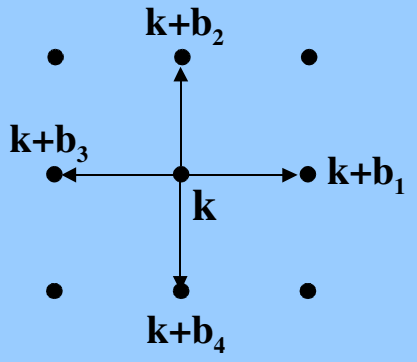
$$F^{(3)}_{pol} = \frac{2ie}{(2\pi)^3} \int d\,\boldsymbol{k} \sum_n \langle u^{(1)}_{nk} | \frac{\partial}{\partial k} \left(\sum_m | u^{(1)}_{mk} \rangle \langle u^{(0)}_{mk} | \right) | u^{(0)}_{nk} \rangle$$

Expression derived first by *A. Dal Corso and F. Mauri, PRB* ***50****, 5756 (1994).*

  - Discretization (finite difference formula of Marzari and Vanderbilt)

$$\nabla f(\boldsymbol{k}) = \sum_b \boldsymbol{b}\, \omega_b [f(\boldsymbol{k}+\boldsymbol{b}) - f(\boldsymbol{k})]$$

$$\sum_b \omega_b b_\alpha b_\beta = \frac{g_{\alpha\beta}}{(2\pi)^2}$$



N. Marzari and D. Vanderbilt, PRB ***56,*** *12847 (1997)*

Computation of third-order energy derivatives

- Perturbation Expansion After Discretization (PEAD)

$$F^{(3)}_{pol} = \frac{-e}{N_k} \sum_{\boldsymbol{k}} \sum_{\boldsymbol{b}} \omega_b \boldsymbol{b} \left\{ 2 \sum_{m,n} S^{(2)}_{nm} Q_{mn} - \sum_{m,n,l,l'} S^{(1)}_{mn} Q_{nl} S^{(1)}_{ll'} Q_{l'm} \right\}$$

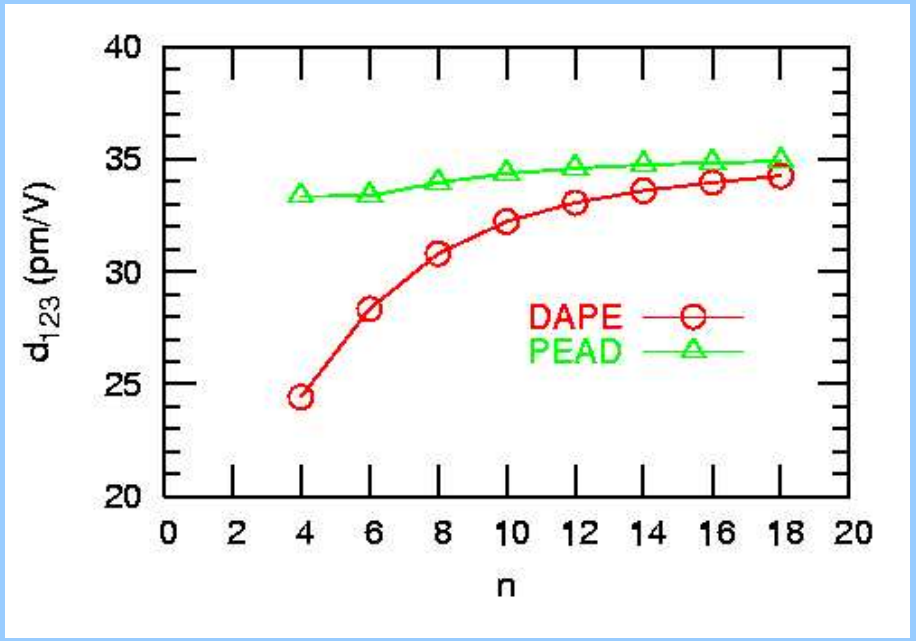
$$S_{mn}(\boldsymbol{k}, \boldsymbol{k}+\boldsymbol{b}) = \left\langle u_{m,k} \middle| u_{n,k+b} \right\rangle \qquad S^{(1)}_{mn}(\boldsymbol{k}, \boldsymbol{k}+\boldsymbol{b}) = \left\langle u^{(1)}_{m,k} \middle| u_{n,k+b} \right\rangle + \left\langle u_{m,k} \middle| u^{(1)}_{n,k+b} \right\rangle$$

$$Q(\boldsymbol{k}, \boldsymbol{k}+\boldsymbol{b}) = S^{-1}(\boldsymbol{k}, \boldsymbol{k}+\boldsymbol{b}) \qquad S^{(2)}_{mn}(\boldsymbol{k}, \boldsymbol{k}+\boldsymbol{b}) = \left\langle u^{(1)}_{m,k} \middle| u^{(1)}_{n,k+b} \right\rangle$$

- Convergence (k-point sampling)

Non-linear optical susceptibility of AlAs computed on a $n \times n \times n$ grid of special k-points

Better convergence of the PEAD formulation



Implementation in ABINIT: general structure

2n + 1 theorem: basic ingredients to compute 3th- order energy derivatives

- Ground-state density & wavefunctions
- 1st- order wavefunctions & densities

→ *no SCF cycles*

driver.f

→ **nonlinear.f** main routine to compute 3th- order energy derivatives
read GS density & wavefunction

→ **loop_3dte.f** loop over perturbations
read 1st-order wavefunctions & densities

→ **mv_3dte.f** perturbation expansion of the polarization
PEAD expression

→ **resp3dte.f** contributions to $F^{(3)}$ that do not require
a differentiation with respect to k

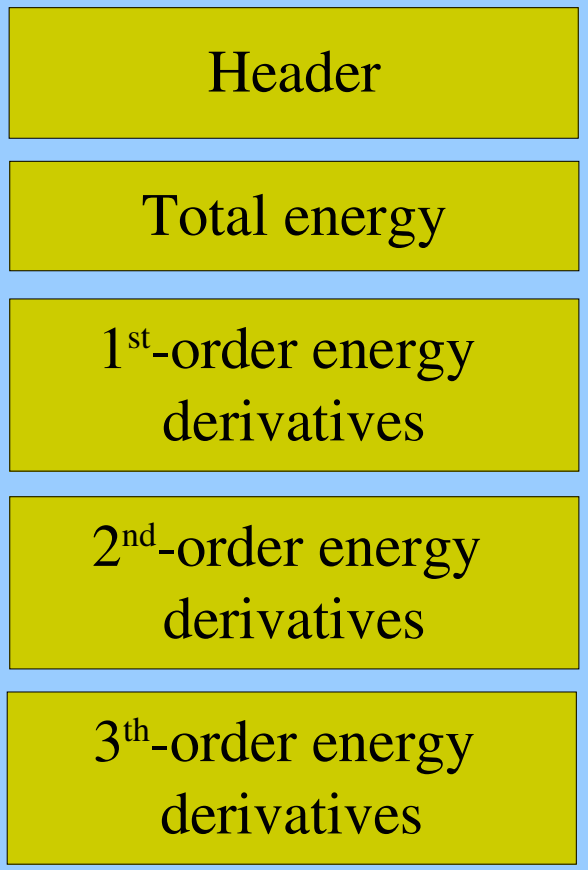
Implementation in ABINIT

- Use of symmetries
  - k-point sampling
    - use time-reversal symmetry to sample ½ BZ (kptopt = 2)
    - no spatial symmetry operations (reflections/rotations) are used to decrease further the number of k-points
    - similar to the linear response calculation of the electric field perturbation
  - Irreductible perturbations
    - Electric field : $\frac{d\,u_{nk}}{d\,E_{\alpha}}$ $\alpha = 1, 2, 3$
    - Phonons : $\frac{d\,u_{nk}}{d\,\tau_{\kappa\,\alpha}}$ irreductible perturbations only
    - When computing the $E^{(3)}$, exclude those elements that are zero by symmetry

Implementation in ABINIT

- Output of 3th-order energy derivative to a DDB

Structure of the DDB



Analysis with ANADDB

- Non-linear optical susceptibilities
- Reimpose Raman sum rule

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

- Raman susceptibilities of TO & LO modes
- EO tensor & decomposition on TO modes

Implementation in ABINIT: general structure

2n + 1 theorem: basic ingredients to compute 3th- order energy derivatives

- Ground-state density & wavefunctions
- 1st- order wafefunctions & densities

→ *no SCF cycles*

driver.f

→ **nonlinear.f**

main routine to compute 3th- order energy derivatives
read GS density & wavefunction

use symmetries to determine
- independent elements of $F^{(3)}$
- elements that are zero

→ **loop_3dte.f**

loop over perturbations
read 1st-order wavefunctions & densities

→ **mv_3dte.f**

perturbation expansion of the polarization
PEAD expression

→ **resp3dte.f**

contributions to $F^{(3)}$ that do not require
a differentiation with respect to k

use symmetries to complete missing elements of $F^{(3)}$
write 3th- order energy derivatives to DDB & output file

In practice: how to use the non-linear response part

- **First step:** GS calculation of the wavefunctions and the density
  - *kptopt* = 2
- **Second step:** linear response calculation of the 1WF and 1DEN
  - *prtden* = 1: write 1DEN to disk file
  - *prepanl* = 1
    - compute electric fiel perturbation along 3 directions
    - phonon perturbations: do not use symmetries to decrease the number of k-points
- **Third step:** non-linear response calculation
  - *optdriver* = 5
  - *getden, get1den, getwfk* & *get1wf*: read WF and DEN
  - *rf1elfd, rf1phon, rf1atpol, rf1dir*
    rf2elfd, rf2phon, rf2atpol, rf2dir
    rf3elfd, rf3phon, rf3atpol, rf3dir

    } define the 3th-order energy derivatives

In practice: how to use the non-linear response part

- **Fourth step:** use MRGDDB to merge the DDB's of the linear and non-linear response calculations
- **Fifth step:** use ANADDB to analyse the results
  - *nlflag*: non-linear properties flag
  - *ramansr*: reimpose Raman sum rule
  - *prtmbm*: print mode-by-mode decomposition of the EO tensor
  - *alphon*: align phonon-mode eigendisplacements of degenerate modes along the cartesian directions (ATTENTION: the cartesian axes must correspond to the principal axes of the crystal)

In practice: how to use the non-linear response part

- **Caution:**
  - The computation of 3th-order energy derivatives requires large k-point grids
  - The smaller the bandgap, the larger the number of k-points required to obtain converged results
  - *mkmem* = 0 is not yet available
  - Insulators only: *nband* = number of (doubly occupied) valence bands
  - No spin polarization/spinor wavefunctions (*nsppol* = 1 & *nspinor* = 1)
  - LDA only: actually *ixc* = 3 & *ixc* = 7 are available
  - Until v4.3: sequential execution only
  - k-point parallelization will probably be available in v4.4

Application to semiconductors

Non-linear optical susceptibilities

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 Corse *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)

Raman polarizabilities (Å^2)

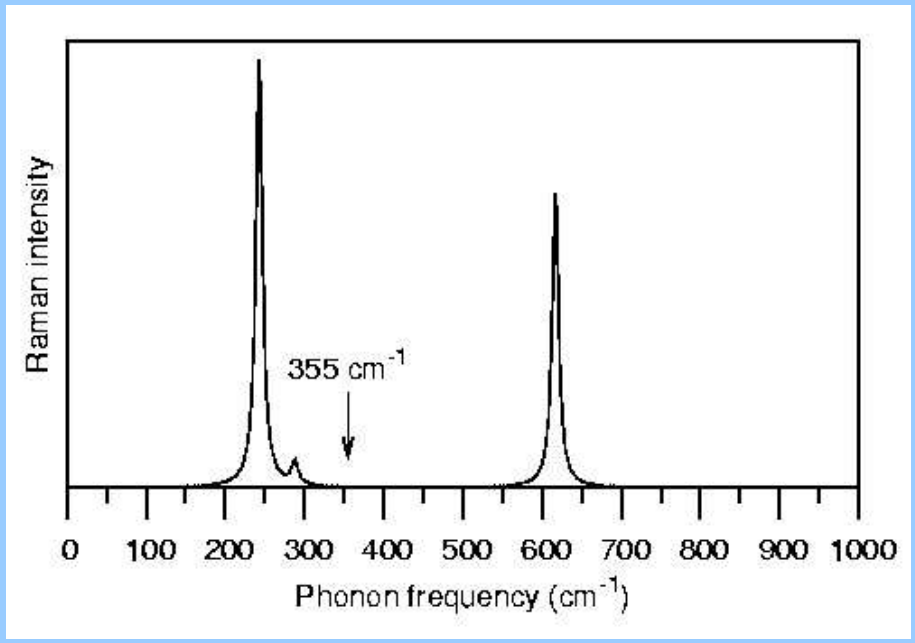
	Si	AlAs	AlP
2n + 1 theorem			
Present	20.02	8.48	4.3
DS [1]	23.56	7.39	5.13
Finite differences			
Present	20.17	8.59	4.25
DS [1]	20.44	5.64	4.44
BR [2]	26.16		
Experiment [3]	23 ± 4		

[1] G.Deinzer and D. Strauch, PRB **66**, 100301 (2002)
[2] S. Baroni and R. Resta, PRB **33**, 5969 (1986)
[3] J. Wagner and M. Cardona, Solid State Communications **48**, 301 (1983)

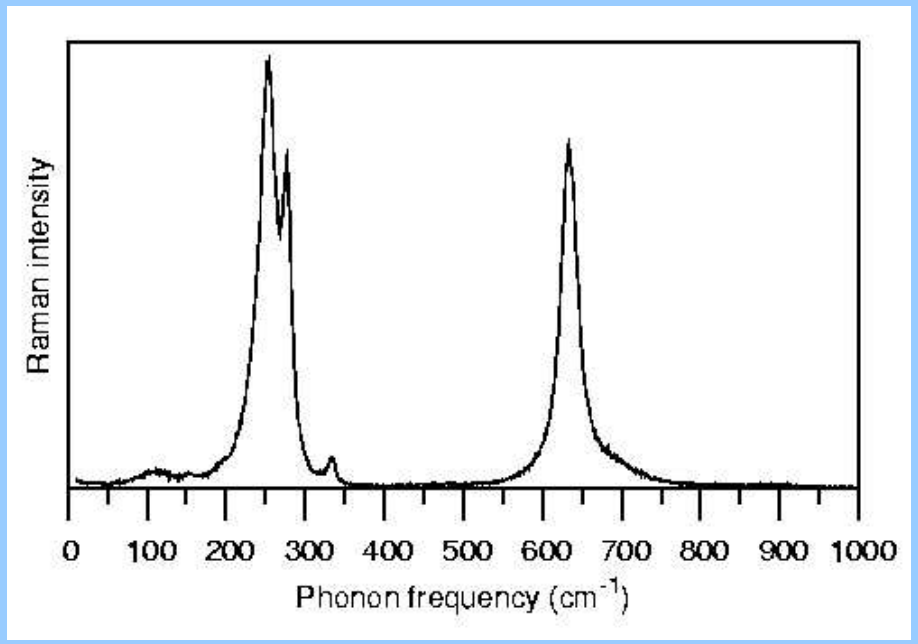
Raman intensities of ferroelectrics

- Raman spectrum of $LiNbO_3$ (A_1^T modes)

Theoretical spectrum



Experimental spectrum

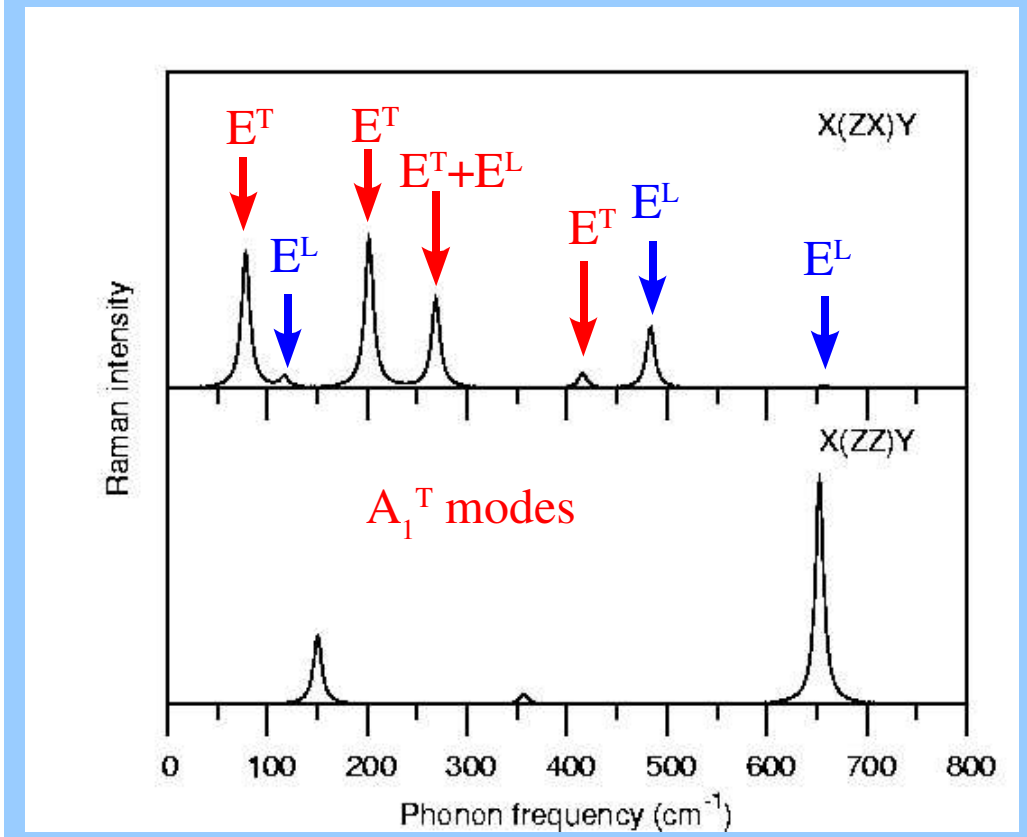


*Ridah et al., PRB **56**, 5967 (1997)*

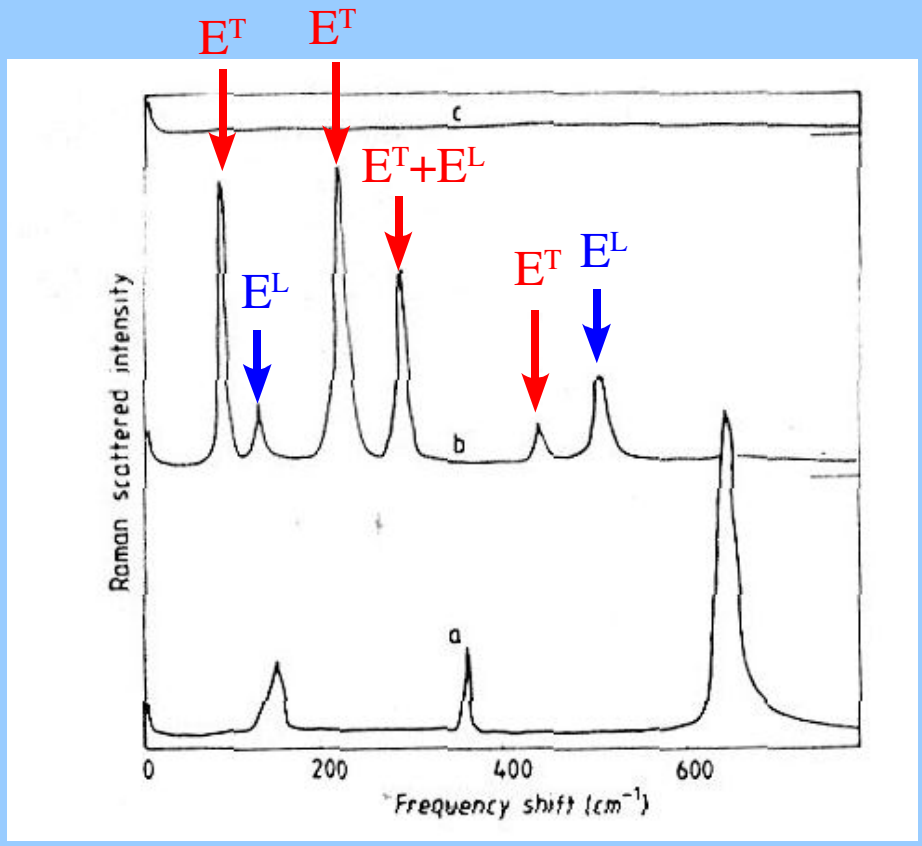
Raman intensities of ferroelectrics

- Raman spectrum of tetragonal $PbTiO_3$

Theoretical spectrum



Experimental spectrum



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

Clamped EO tensor in $LiNbO_3$

Zone-center TO phonons: $4\ A_1 + 5\ A_2 + 9\ E$

r_{13} & r_{33} $\qquad$ r_{22} & r_{51}

$$\underline{r} = \begin{pmatrix} \cdot & -r_{22} & r_{13} \\ \cdot & r_{22} & r_{13} \\ \cdot & \cdot & r_{33} \\ \cdot & r_{51} & \cdot \\ r_{51} & \cdot & \cdot \\ -r_{22} & \cdot & \cdot \end{pmatrix}$$

	A_1 modes			E modes		
	ω (cm^{-1})	r_{13} (pm/V)	r_{33} (pm/V)	ω (cm^{-1})	r_{22} (pm/V)	r_{51} (pm/V)
Elec.		1.02	3.99		0.16	1.04
TO1	243	6.20	18.53	155	3.02	7.46
TO2	287	-0.23	-0.43	218	0.36	1.46
TO3	355	-0.14	0.04	264	0.58	1.3
TO4	617	2.82	4.8	330	-0.26	1.24
TO5				372	-0.19	0.41
TO6				384	-0.09	-0.21
TO7				428	0.2	0.2
TO8				585	0.73	2.05
TO9				677	0.04	-0.02
Tot.		9.68	26.93		4.56	14.94
Exp. [1]		8.6	30.8		3.4	28
IR + Raman [2]		12	39		6	19
BC [3]			25.9			20.5

[1] H. Nishihara *et al.*, "Optical Integrated Circuits" (McGRAW-Hill,1985)

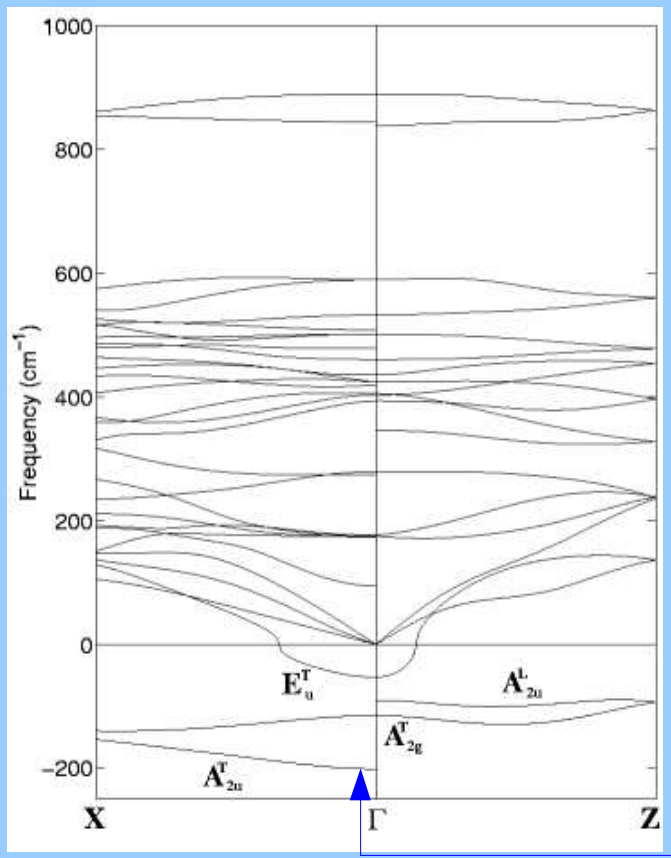
[2] W. D. Johnston Jr., PRB **1**, 3494 (1970)

[3] C.-C. Shih and A. Yariv, J. Phys. C **15**, 825 (1982)

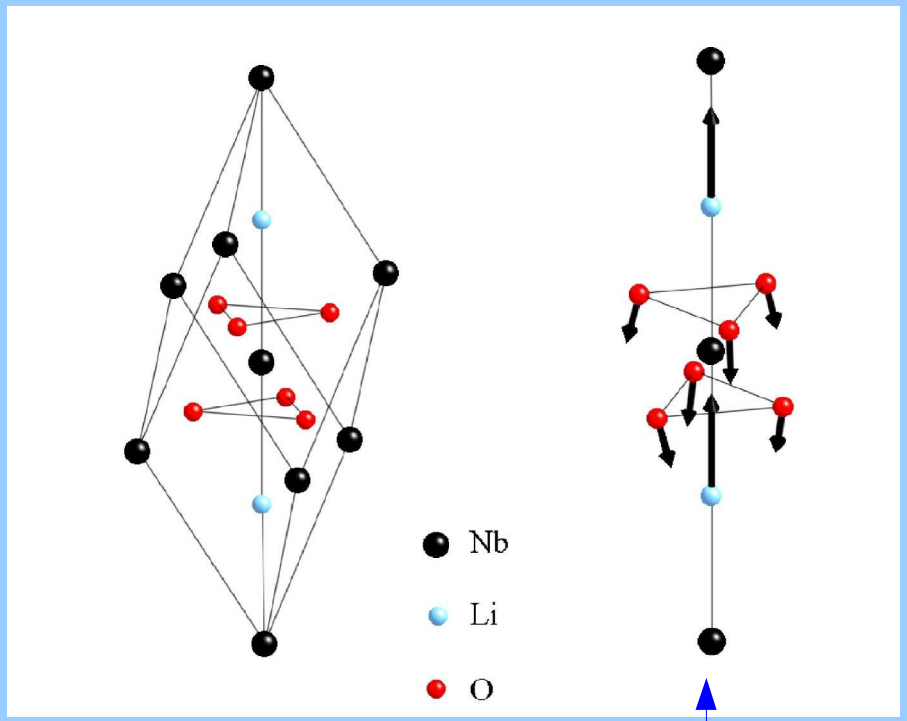
Phase transition in $LiNbO_3$

- Paraelectric phase stable above 1480 K
- One single transition to a ferroelectric ground state
- Phase transition driven by a soft $A_{2u}{}^{T}$ mode

Phonons in the paraelectric phase



Rhombohedral unit cell



Conclusions

Implementation of non-linear response functions in ABINIT

- 3th-order energy derivatives actually implemented

$$\left.\begin{array}{l} \dfrac{\partial^3 F}{\partial E^3} \\ \dfrac{\partial^3 F}{\partial \tau \partial E^2} \end{array}\right\} \longrightarrow$$

Non-linear optical susceptibilities
Raman intensities of TO & LO modes
EO coefficients

- PEAD expression for the perturbation expansion of the polarization
- Use of symmetry operations & DDB output

  ➔ easy and efficient compuation of 3th-order energy derivatives