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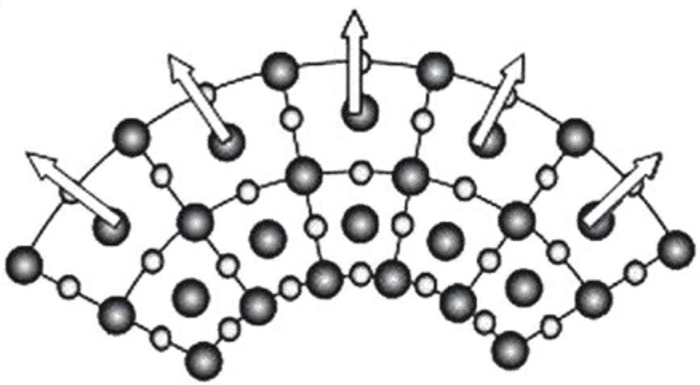
SPATIAL DISPERSION PROPERTIES FROM DFPT: DYNAMICAL QUADRUPOLES AND FLEXOELECTRIC TENSOR

9th ABINIT Developers Workshop

Louvain-la-Neuve, May 2019

CONTENTS

Flexoelectricity



$$P_\alpha = \mu_{\alpha\beta,\gamma\delta} \frac{\partial \varepsilon_{\beta\delta}}{\partial r_\gamma}$$

Polarization response to a *strain gradient*

3 Contributions to $\mu_{\alpha\beta,\gamma\delta}$:

- Electronic (clamped-ion)
- Lattice
- Mixed

Clamped-Ion Flexoelectric tensor

Spatial dispersion of CI piezoelectric tensor

$$e_{\alpha\beta\delta} \propto \left.\frac{d^2 E}{d\varepsilon_\alpha \, d\eta_{\beta\delta}}\right|_{\boldsymbol{q}=0} = E^{\varepsilon_\alpha \eta_{\beta\delta}}$$

$$\mu_{\alpha\beta,\gamma\delta} \propto \left.\frac{d^3 E}{d\varepsilon_\alpha \, d\eta_{\beta\delta} dq_\gamma}\right|_{\boldsymbol{q}=0} = E_\gamma^{\varepsilon_\alpha \eta_{\beta\delta}}$$

✗ Electric field and strain perturbations formulated at **q**=0

$$\varepsilon_\alpha^{\boldsymbol{q}} \leftarrow \frac{dA_\alpha^{\boldsymbol{q}}}{dt}$$ ← Vector potential

$$\eta_{\beta\delta}^{\boldsymbol{q}} \leftarrow \frac{d(\beta)^{\boldsymbol{q}}}{dq_\delta}$$ ← Metric wave

Long-wave DFPT formulation of CI FxE tensor

$$\mu_{\alpha\beta,\gamma\delta} = \frac{1}{\Omega} E^{\mathcal{E}^*_\alpha (\beta)}_{\gamma\delta}$$

METRIC WAVE - HOMOGENEOUS STRAIN

$$\hat{H}^{(\beta)}_{\mathbf{k},\delta} = i\hat{H}^{\eta_{\beta\delta}}_{\mathbf{k}}$$

$$|u^{(\beta)}_{m\mathbf{k},\delta}\rangle = i|u^{\eta_{\beta\delta}}_{m\mathbf{k}}\rangle$$

NEW OBJECTS

$$\widetilde{E}^{\mathcal{E}^*_\alpha (\beta)}_{\gamma\delta} = s\int_{\rm BZ}[d^3k]\sum_m \widetilde{E}^{\mathcal{E}^*_\alpha (\beta)}_{m\mathbf{k},\gamma\delta} + \frac{i}{2}\int_\Omega\int K_\gamma(\mathbf{r},\mathbf{r}') n^{\mathcal{E}_\alpha}(\mathbf{r}) n^{\eta_{\beta\delta}}(\mathbf{r}') d^3r d^3r'$$

$$\widetilde{E}^{\mathcal{E}^*_\alpha (\beta)}_{m\mathbf{k},\gamma\delta} = i\langle u^{\mathcal{E}_\alpha}_{m\mathbf{k}}|\partial_\gamma \hat{H}^{(0)}_{\mathbf{k}}|u^{\eta_{\beta\delta}}_{m\mathbf{k}}\rangle + i\langle u^{\mathcal{E}_\alpha}_{m\mathbf{k}}|\partial_\gamma \hat{Q}_{\mathbf{k}}\mathcal{H}^{\eta_{\beta\delta}}_{\mathbf{k}}|u^{(0)}_{m\mathbf{k}}\rangle + i\langle u^{(0)}_{m\mathbf{k}}|\hat{V}^{\mathcal{E}_\alpha}\partial_\gamma \hat{Q}_{\mathbf{k}}|u^{\eta_{\beta\delta}}_{m\mathbf{k}}\rangle$$

$$+\frac{1}{2}\langle u^{\mathcal{E}_\alpha}_{m\mathbf{k}}|\hat{H}^{(\beta)}_{\mathbf{k},\gamma\delta}|u^{(0)}_{m\mathbf{k}}\rangle + i\langle i\, u^{A_\alpha}_{m\mathbf{k},\gamma}|u^{\eta_{\beta\delta}}_{m\mathbf{k}}\rangle$$

M. Royo and M. Stengel, PRX (accepted)

Dynamical quadrupoles

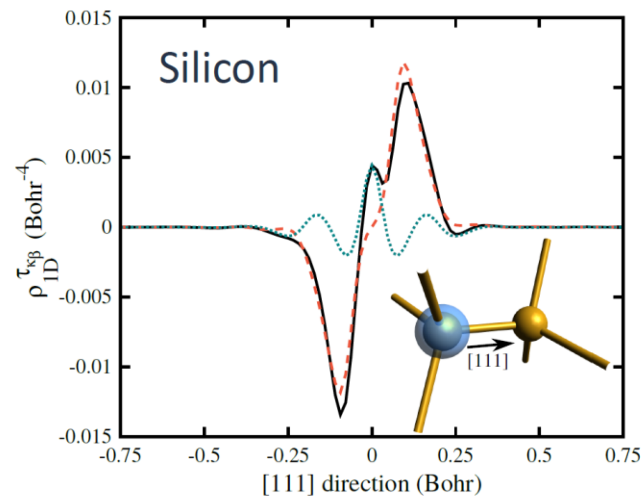
Second moment of the charge response to an atomic displacement

$$Q^{\mathbf{q}}_{\kappa\beta} = \int_{\Omega} \rho^{\tau_{\kappa\beta}}_{\mathbf{q}}(\mathbf{r}) d^3 r = -i q_\beta Z_\kappa + 2 \underbrace{E^{\varphi^* \tau_{\kappa\beta}}_{\mathbf{q}}}_{\frac{d^2 E}{d\varphi_{-\mathbf{q}} \, d\tau_{\kappa\beta,\mathbf{q}}}}$$

$$Q^{\mathbf{q}}_{\kappa\beta} = -i q_\gamma \underbrace{Q^{(1,\gamma)}_{\kappa\beta}}_{\text{Born effective charge}} - \frac{q_\gamma q_\delta}{2} \underbrace{Q^{(2,\gamma\delta)}_{\kappa\beta}}_{\text{Quadrupole}} + \cdots$$

Born effective charge: $\delta_{\beta\gamma} Z_\kappa + 2E^{\varphi^* \tau_{\kappa\beta}}_{\gamma}$

Quadrupole: $2E^{\varphi^* \tau_{\kappa\beta}}_{\gamma\delta}$



ONLY AT NON CENTROSYMMETRIC ATOMIC POSITIONS

Long-wave DFPT formulation of dynamic quadrupoles

$$Q_{\kappa\beta}^{(2,\gamma\delta)} = -2E_{\gamma\delta}^{\varphi^* \tau_{\kappa\beta}}$$

SCALAR POTENTIAL - ELECTRIC FIELD

$$|u_{m\mathbf{k}}^{\mathcal{E}_\delta}\rangle = |i u_{m\mathbf{k},\delta}^{\varphi}\rangle$$

$$E_{\gamma\delta}^{\varphi^* \tau_{\kappa\beta}} = -iE_{\gamma}^{\mathcal{E}_\delta^* \tau_{\kappa\beta}} - iE_{\delta}^{\mathcal{E}_\gamma^* \tau_{\kappa\beta}}$$

New Objects

$$E_{\gamma}^{\mathcal{E}_\delta^* \tau_{\kappa\beta}} = s\int_{\mathrm{BZ}}[d^3k]\sum_m E_{m\mathbf{k},\gamma}^{\mathcal{E}_\delta^* \tau_{\kappa\beta}} + \frac{1}{2}\int_\Omega\int K_\gamma(\mathbf{r},\mathbf{r}')n^{\mathcal{E}_\delta}(\mathbf{r})n^{\tau_{\kappa\beta}}(\mathbf{r}')d^3r d^3r'$$

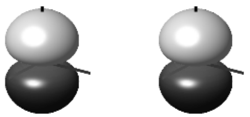
$$E_{m\mathbf{k},\gamma}^{\mathcal{E}_\delta^* \tau_{\kappa\beta}} = \langle u_{m\mathbf{k}}^{\mathcal{E}_\delta}|\partial_\gamma \hat{H}_{\mathbf{k}}^{(0)}|u_{m\mathbf{k}}^{\tau_{\kappa\beta}}\rangle + \langle u_{m\mathbf{k}}^{\mathcal{E}_\delta}|\partial_\gamma \hat{Q}_{\mathbf{k}}\hat{\mathcal{H}}_{\mathbf{k}}^{\tau_{\kappa\beta}}|u_{m\mathbf{k}}^{(0)}\rangle + \langle u_{m\mathbf{k}}^{(0)}|V^{\mathcal{E}_\delta}\partial_\gamma \hat{Q}_{\mathbf{k}}|u_{m\mathbf{k}}^{\tau_{\kappa\beta}}\rangle +$$
$$\langle u_{m\mathbf{k}}^{\mathcal{E}_\delta}|\hat{H}_{\mathbf{k},\gamma}^{\tau_{\kappa\beta}}|u_{m\mathbf{k}}^{(0)}\rangle + \langle i\, u_{m\mathbf{k},\gamma}^{A_\delta}|u_{m\mathbf{k}}^{\tau_{\kappa\beta}}\rangle$$

M. Royo and M. Stengel, PRX (accepted)

Why to care about dynamic quadrupoles?

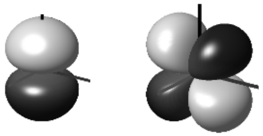
Long-range interatomic forces

$$\Phi^{\mathbf{q},\mathrm{DD}}_{\kappa\alpha,\kappa'\beta} = \frac{4\pi}{\Omega}\frac{(\mathbf{q}\cdot\mathbf{Z}^*_\kappa)_\alpha(\mathbf{q}\cdot\mathbf{Z}^*_{\kappa'})_\beta}{\mathbf{q}\cdot\boldsymbol{\epsilon}\cdot\mathbf{q}},$$



$\approx d^{-3}$

$$\Phi^{\mathbf{q},\mathrm{DQ}}_{\kappa\alpha,\kappa'\beta} = -i\frac{4\pi}{2\Omega}\frac{(\mathbf{q}\cdot\mathbf{Z}^*_\kappa)_\alpha(\mathbf{q}\,\mathbf{q}\cdot\mathbf{Q}^*_{\kappa'})_\beta}{\mathbf{q}\cdot\boldsymbol{\epsilon}\cdot\mathbf{q}} +i\frac{4\pi}{2\Omega}\frac{(\mathbf{q}\,\mathbf{q}\cdot\mathbf{Q}^*_\kappa)_\alpha(\mathbf{q}\cdot\mathbf{Z}^*_{\kappa'})_\beta}{\mathbf{q}\cdot\boldsymbol{\epsilon}\cdot\mathbf{q}},$$



$\approx d^{-4}$

Frozen-ion piezoelectric tensor (Martin's theory, 1972)

$$\bar{e}_{\alpha\beta\gamma} = \frac{\partial P_\alpha}{\partial \varepsilon_{\beta\gamma}}\Big|_{\mathrm{FI}}$$

$$\bar{e}_{\alpha\beta\gamma} + \bar{e}_{\gamma\beta\alpha} = \frac{1}{\Omega}\sum_\kappa Q^{(2,\alpha\gamma)}_{\kappa\beta}$$

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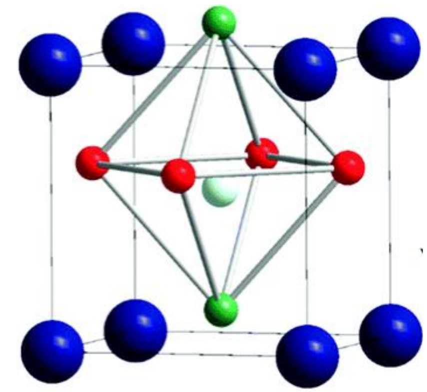
Quadrupoles testcase: Tetragonal $PbTiO_3$

All calculations are performed using the LDA and norm conserving PSPs

Ecut=70 Ha and 8x8x8 MP k-points

	$\kappa=$Pb	$\kappa=$Ti	$\kappa=O_1$	$\kappa=O_2$	$\kappa=O_3$
$Q_{\kappa 3}^{(2,11)}$	2.264	−3.545	2.884	−4.186	0.406
$Q_{\kappa 3}^{(2,22)}$	2.264	−3.545	−4.186	2.884	0.406
$Q_{\kappa 1}^{(2,31)}$	−0.062	−3.799	3.123	−1.115	−1.784
$Q_{\kappa 2}^{(2,32)}$	−0.062	−3.799	−1.115	3.123	−1.784
$Q_{\kappa 3}^{(2,33)}$	1.240	−0.195	2.027	2.027	6.653

TABLE I. Quadrupole moments in e·Bohr of $PbTiO_3$.



Recall: Martin's 1972 formula

$$e^{P}_{\alpha\beta\gamma} = v_0^{-1} \sum_K \Big[\sum_\delta e^{*}_{K\alpha\delta}\ \Gamma_{K\delta\beta\gamma} - \tfrac{1}{2}\left(Q_{K\alpha\beta\gamma} - Q_{K\gamma\alpha\beta} + Q_{K\beta\gamma\alpha} \right) \Big].$$

Clamped-ion Piezoelectric Tensor

	$e_{113}=e_{223}$	$e_{311}=e_{322}$	e_{333}
Strain	0.1547	0.3617	−0.8345
Quadrupoles	0.1548	0.3614	−0.8347

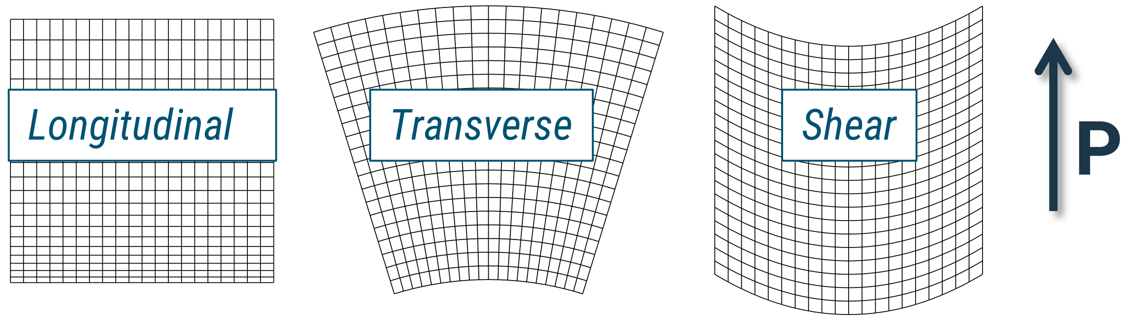
TABLE II. Clamped-ion piezoelectric coefficients (in C/m^2) of $PbTiO_3$

Flexoelectric tensor: Cubic materials

Cubic symmetry

↓

3 independent components



Testcase 1: Isolated noble gas atoms

	μ_L	μ_T	μ_S ($\times 10^{-4}$)
He	-0.479 (-0.479^a)	-0.479 (-0.479^a)	-0.08 (-0.08^a)
Ar	-4.821 (-4.813^a)	-4.823 (-4.820^a)	-1 (-10^a)
Kr	-6.471 (-6.474^a)	-6.477 (-6.476^a)	-4 (-20^a)

TABLE III. Flexoelectric coefficients (pC/m) of noble-gas atom systems. [a] Ref. [3]

( ) values obtained via numerical derivation in ***q***

A. Schiaffino et al. PRB 99, 085107 (2019)

Testcase 2: Real materials

A.Schiaffino et al. PRB 99, 085107 (2019) → Ref. 3

Stengel PRB 90, 201112(R) (2014) → Ref. 6

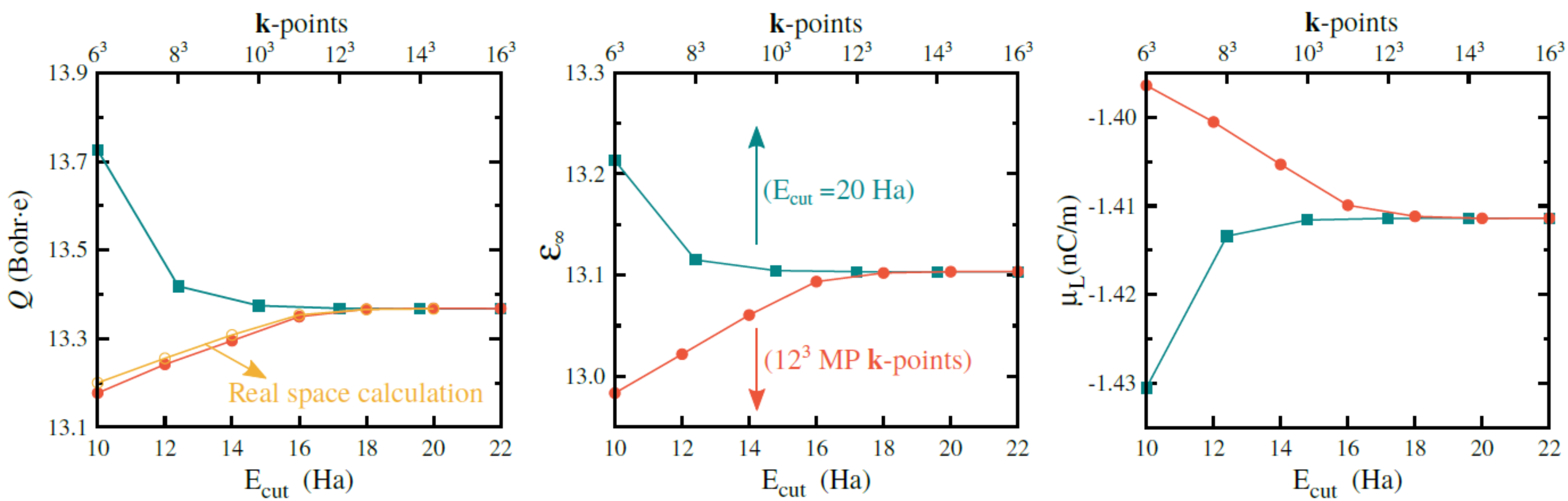
	μ_L	μ_T	μ_S
Si (this work)	-1.4114	-1.0491	-0.1895
Ref. 3	-1.4110	-1.0493	-0.1894
$SrTiO_3$ (this work)	-0.8848	-0.8262	-0.0823
Ref. 3	-0.8851	-0.8260	-0.0823
Ref. 6	-0.883	-0.825	-0.082

TABLE V. Flexoelectric coefficients (nC/m) of Si and $SrTiO_3$.

Convergence study

SYSTEM: Silicon

All calculations are performed using the LDA and norm conserving PSPs



THE SPATIAL-DISPERSION TENSORS CALCULATION REQUIRES A COMPUTATIONAL EFFORT COMPARABLE TO THE CALCULATION OF OTHER STANDARD LINEAR-RESPONSE QUANTITIES

CONTENTS

New objects to implement

$$K_\gamma(\mathbf{G},\mathbf{G}') = -8\pi G_\gamma \frac{\delta_{\mathbf{G}\mathbf{G}'}}{G^4}$$

hartredq (54_spacepar/m_spacepar.F90)

$$\hat{H}^{\tau_{\kappa\beta}}_{\mathbf{k},\gamma} = V^{\text{loc},\tau_{\kappa\beta}}_{\gamma} + V^{\text{sep},\tau_{\kappa\beta}}_{\mathbf{k},\gamma}$$

dfpt_vlocaldq (67_common/m_mklocl.F90)

nonlop (choice=22) (66_nonlocal/m_nonlop.F90)

$$\hat{H}^{(\beta)}_{\mathbf{k},\gamma\delta} = \hat{T}^{(\beta)}_{\mathbf{k},\gamma\delta} + V^{\text{loc},\,(\beta)}_{\gamma\delta} + V^{\text{sep},(\beta)}_{\mathbf{k},\gamma\delta} + \hat{V}^{\text{H0},(\beta)}_{\delta\gamma}$$

mkkin_metdqdq (56_recipspace/m_kg.F90)

dfpt_vlocaldqdq (67_common/m_mklocl.F90)

nonlop (choice=33) (66_nonlocal/m_nonlop.F90)

$$\langle i\, u^{A_\alpha}_{m\mathbf{k},\gamma} | u^{\eta_{\beta\delta}}_{m\mathbf{k}} \rangle \rightarrow -\frac{i}{2} \langle \underbrace{\tilde{\partial}_{\alpha\gamma} u^{(0)}_{m\mathbf{k}}}_{u^{k_\alpha k_\gamma}_{m\mathbf{k}}} | u^{\eta_{\beta\delta}}_{m\mathbf{k}} \rangle - \frac{i}{2} \langle \underbrace{u^{CG}_{m\mathbf{k},\alpha\gamma}}_{\text{Response to an orbital } \mathbf{B}\text{-field}} | u^{\eta_{\beta\delta}}_{m\mathbf{k}} \rangle$$

NOT IMPLEMENTED

Example of input file

```
# Crystalline silicon: computation of the Quadrupole
# and CI FxE Tensors

ndtset                    5

#Set 1: Ground state self-consistency

getwfk1        0
kptopt1        1
nqpt1          0
tolvrs1        1.0d-18

#Set 2: Response function calculation of d/dk

iscf2          -3
kptopt2        2
rfelfd2        2
tolwfr2        1.0d-22
rfdir2         1 1 1

#Set 3: Response function calculation of d2/dkdk

getddk3        2
iscf3          -3
kptopt3        2
rf2_dkdk3      1
tolwfr3        1.0d-22

#Set 4 : Response function calculation of Q=0 phonons,
# electric field and strain perturbations

getddk4        2
kptopt4        2
rfelfd4        3
rfphon4        1
rfatpol4       1 2
rfdir4         1 1 1
tolvrs4        1.0d-10
prepalw4       1    # Deactivates symmetries for the lw routines

#Set 5: Long-wave magnitudes calculation

optdriver5     10   # Activates long-wave driver
kptopt5        2
get1wf5        4
get1den5       4
getddk5        2
getdkdk5       3
lw_qdrpl5      1    # Calculate Quadrupoles
lw_flexo5      2    # Calculate CI flexoelectric tensor

#Common input variables
getwfk         1
useylm         1
nqpt           1
qpt            0.0E+00  0.0E+00  0.0E+00
…
…
```

Example of output files

abi_out

```
Quadrupole tensor, in cartesian coordinates,
atom   atddir   efidir   qgrdir        real part           imaginary part
   1       1        1        1       -0.0000000044       0.0000000000
   2       1        1        1        0.0000000044       0.0000000000
   1       2        1        1        0.0000000000       0.0000000000
  ...
  ...
   1       2        2        1       -0.0000000021       0.0000000000
   2       2        2        1        0.0000000022       0.0000000000
   1       3        2        1        13.3682664286      0.0000000000
   2       3        2        1       -13.3682664284      0.0000000000
   1       1        3        1       -0.0000000023       0.0000000000
  ...
```

```
Electronic flexoelectric tensor, in cartesian coordinates,
efidir  qgrdir  strdir1  strdir2       real part         imaginary part
   1       1       1        1        -0.4661642508       0.0000000000
   2       1       1        1        -0.0000000000       0.0000000000
   3       1       1        1        -0.0000000000       0.0000000000
   1       2       1        1        -0.0000000000       0.0000000000
   2       2       1        1        -0.3465045498       0.0000000000
   3       2       1        1         0.0000000000       0.0000000000
   1       3       1        1        -0.0000000000       0.0000000000
   2       3       1        1         0.0000000000       0.0000000000
   3       3       1        1        -0.3465045498       0.0000000000
  ...
```

_O_DS5_DDB

```
**** Database of total energy derivatives ****
 Number of data blocks=    1

 3rd derivatives              - # elements :     216
 qpt  0.00000000E+00  0.00000000E+00  0.00000000E+00   1.0
      0.00000000E+00  0.00000000E+00  0.00000000E+00   1.0
      0.00000000E+00  0.00000000E+00  0.00000000E+00   1.0
   1   1   1   1   1  10  0.00000000000000D+00  0.22644265123610D-14
   2   1   1   1   1  10  0.00000000000000D+00  0.24355993235786D+00
   3   1   1   1   1  10  0.00000000000000D+00  0.17956332706089D+00
   1   2   1   1   1  10  0.00000000000000D+00  0.45460672058968D+01
   2   2   1   1   1  10  0.00000000000000D+00  0.24655503777839D+03
   3   2   1   1   1  10  0.00000000000000D+00  0.24726956950978D+03
   1   4   1   1   1  10  0.00000000000000D+00  0.58234827336192D+02
   2   4   1   1   1  10  0.00000000000000D+00 -0.29456056346091D+02
   3   4   1   1   1  10  0.00000000000000D+00 -0.29063615520488D+02
   1   1   2   1   1  10  0.00000000000000D+00 -0.24355993235786D+00
   2   1   2   1   1  10  0.00000000000000D+00 -0.10841168799945D-14
   3   1   2   1   1  10  0.00000000000000D+00  0.26583336681518D+00
   1   2   2   1   1  10  0.00000000000000D+00  0.24656233568811D+03
   2   2   2   1   1  10  0.00000000000000D+00  0.24376369487631D+03
   3   2   2   1   1  10  0.00000000000000D+00  0.24643072491876D+03
   1   4   2   1   1  10  0.00000000000000D+00  0.35339045543433D+00
 ....
```

ddq   ipert=natom+8

State of the implementation

NOT YET MERGED WITH THE TRUNK

Current limitations:

- Perturbations symmetries deactivated
- LDA exclusive
- Not adapted for non-linear core corrections
- kptopt ≠ 1
- useylm = 1

TO DO

CONTENTS

Conclusions and Outlook

- CI FxE and quadrupole tensor from a multi-dataset ABINIT run
- No *new* ddq response functions required
- Little computational cost
- Developing of full FxE tensor (lattice and mixed contribs.)
- Other spatial dispersion properties (natural optical/acoustical activity)

THANK YOU!

M. Royo and M. Stengel, Phys. Rev. X (accepted), arXiv:1812.05935