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SPATIAL DISPERSION PROPERTIES FROM DFPT: DYNAMICAL QUADRUPOLES AND FLEXOELECTRIC TENSOR

9th ABINIT Developers Workshop
Louvain-la-Neuve, May 2019
CONTENTS

I  LONG-WAVE DFPT APPROACH TO SPATIAL DISPERSION
   Flexoelectric Tensor
   Dynamical Quadrupole Tensor

II  NUMERICAL RESULTS
   Method validation
   Convergence study

III  IMPLEMENTATION DETAILS

IV  CONCLUSIONS AND OUTLOOK
**SPATIAL DISPERSION PROPERTIES**

**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

\[
\begin{align*}
    e_{\alpha\beta\delta} &\propto \frac{d^2 E}{d\varepsilon_\alpha \, d\eta_{\beta\delta}} \bigg|_{q=0} = E^{\varepsilon_{\alpha\eta_{\beta\delta}}}
    \\
    \mu_{\alpha\beta,\gamma\delta} &\propto \frac{d^3 E}{d\varepsilon_\alpha \, d\eta_{\beta\delta} \, dq_\gamma} \bigg|_{q=0} = E^{\varepsilon_{\alpha\eta_{\beta\delta}}}
\end{align*}
\]

**Electric field and strain perturbations formulated at \( q=0 \)**

\[ \varepsilon_\alpha^q \leftarrow \frac{dA_\alpha^q}{dt} \]  
Vector potential

\[ \eta_{\beta\delta}^q \leftarrow \frac{d(\beta)^q}{dq_\delta} \]  
Metric wave

Miquel Royo Valls
**SPATIAL DISPERSION PROPERTIES**

Long-wave DFPT formulation of CI FxE tensor

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

\[
\hat{H}^{(\beta)}_{k,\delta} = i\hat{H}^{\eta\beta\delta}_{k}
\]

\[
|u^{(\beta)}_{m,k,\delta}\rangle = i|u^{\eta\beta\delta}_{m,k}\rangle
\]

**NEW OBJECTS**

\[
\tilde{E}^{\mathcal{E}^*}_{\gamma\delta}(\beta) = \int_{BZ} [d^3k] \sum_m \tilde{E}^{\mathcal{E}^*}_{\alpha}(\beta) + \frac{i}{2} \int_{\Omega} \int K_{\gamma}(r, r') n^{\mathcal{E}^*}(r) n^{\eta\beta\delta}(r') d^3r d^3r'
\]

\[
\tilde{E}^{\mathcal{E}^*}_{m,k,\gamma\delta} = i\langle u^{\mathcal{E}^*}_{m,k} | \partial_{\gamma} \hat{H}^{(0)}_{k} | u^{\eta\beta\delta}_{m,k}\rangle + i\langle u^{\mathcal{E}^*}_{m,k} | \partial_{\gamma} \hat{Q}_{k} \hat{H}^{\eta\beta\delta}_{k} | u^{(0)}_{m,k}\rangle + i\langle u^{(0)}_{m,k} | \hat{V}^{\mathcal{E}^*} \partial_{\gamma} \hat{Q}_{k} | u^{\eta\beta\delta}_{m,k}\rangle
\]

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

M. Royo and M. Stengel, PRX (accepted)
**Dynamical quadrupoles**

**Second moment of the charge response to an atomic displacement**

\[
Q^q_{\kappa\beta} = \int_\Omega \rho^\tau_{\kappa\beta}(\mathbf{r}) d^3r = -i q_\beta Z_\kappa + 2 E_{\mathbf{q}}^{\phi^* \tau_{\kappa\beta}} \frac{d^2 E}{d\varphi_{-\mathbf{q}} d\tau_{\kappa\beta,\mathbf{q}}}
\]

\[
Q^q_{\kappa\beta} = -i q_\gamma Q^{(1,\gamma)}_{\kappa\beta} - \frac{q_\gamma q_\delta}{2} Q^{(2,\gamma\delta)}_{\kappa\beta} + \cdots
\]

Born effective charge

\[
\delta_\beta\gamma Z_\kappa + 2 E_\gamma^{\phi^* \tau_{\kappa\beta}}
\]

Quadrupole

\[
2 E_\gamma^{\phi^* \tau_{\kappa\beta}}
\]

**ONLY AT NON CENTROSYMMETRIC ATOMIC POSITIONS**

Miquel Royo Valls

Louvain-la-Neuve, May 2019
SPATIAL DISPERSION PROPERTIES

Long-wave DFPT formulation of dynamic quadrupoles

\[ Q^{(2, \gamma \delta)}_{\kappa \beta} = -2E^{\phi^* \tau_{\kappa \beta}}_{\gamma \delta} \]

SCALAR POTENTIAL - ELECTRIC FIELD

\[ |u_{m_k}^{\delta} \rangle = |i u_{m_k, \delta}^\phi \rangle \]

\[ E^{\phi^* \tau_{\kappa \beta}}_{\gamma \delta} = -i E^{E^* \tau_{\kappa \beta}}_{\gamma \delta} - i E^{E^* \tau_{\kappa \beta}}_{\delta} \]

New Objects

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

\[ E^{E^* \tau_{\kappa \beta}}_{m_k, \gamma} = \langle u_{m_k}^{E \delta} | \partial_{\gamma} \hat{H}^{(0)}_{k} | u_{m_k}^{\tau_{\kappa \beta}} \rangle \]

M. Royo and M. Stengel, PRX (accepted)
Why to care about dynamic quadrupoles?

Long-range interatomic forces

$$\Phi_{q,DD}^{\kappa\alpha,\kappa'\beta} = \frac{4\pi}{\Omega} \frac{(q \cdot Z^*_\kappa)_{\alpha}(q \cdot Z^*_{\kappa'})_{\beta}}{q \cdot \epsilon \cdot q} \approx d^{-3}$$

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

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

$$\bar{e}_{\alpha\beta\gamma} = \left. \frac{\partial P_{\alpha}}{\partial \varepsilon_{\beta\gamma}} \right|_{FI}$$

$$\bar{e}_{\alpha\beta\gamma} + \bar{e}_{\gamma\beta\alpha} = \frac{1}{\Omega} \sum_{\kappa} Q^{(2,\alpha\gamma)}_{\kappa\beta}$$
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LONG-WAVE DFPT: NUMERICAL RESULTS

Quadrupoles testcase: Tetragonal PbTiO$_3$

All calculations are performed using the LDA and norm conserving PSPs

Ecut=70 Ha and 8x8x8 MP k-points

<table>
<thead>
<tr>
<th>$Q_{\kappa^3}$</th>
<th>$\kappa =$Pb</th>
<th>$\kappa =$Ti</th>
<th>$\kappa =$O$_1$</th>
<th>$\kappa =$O$_2$</th>
<th>$\kappa =$O$_3$</th>
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</thead>
<tbody>
<tr>
<td>$Q_{\kappa^3}^{(2,11)}$</td>
<td>2.264</td>
<td>-3.545</td>
<td>2.884</td>
<td>-4.186</td>
<td>0.406</td>
</tr>
<tr>
<td>$Q_{\kappa^3}^{(2,22)}$</td>
<td>2.264</td>
<td>-3.545</td>
<td>-4.186</td>
<td>2.884</td>
<td>0.406</td>
</tr>
<tr>
<td>$Q_{\kappa^1}^{(2,31)}$</td>
<td>-0.062</td>
<td>-3.799</td>
<td>3.123</td>
<td>-1.115</td>
<td>-1.784</td>
</tr>
<tr>
<td>$Q_{\kappa^2}^{(2,32)}$</td>
<td>-0.062</td>
<td>-3.799</td>
<td>-1.115</td>
<td>3.123</td>
<td>-1.784</td>
</tr>
<tr>
<td>$Q_{\kappa^3}^{(2,33)}$</td>
<td>1.240</td>
<td>-0.195</td>
<td>2.027</td>
<td>2.027</td>
<td>6.653</td>
</tr>
</tbody>
</table>

*TABLE I. Quadrupole moments in e·Bohr of PbTiO$_3$."

Recall: Martin’s 1972 formula

$$e^{P}_{\alpha\beta\gamma} = v_0^{-1} \sum_K \left[ \sum_6 e^{*}_{K\alpha\delta} \Gamma_{K\delta\beta\gamma} \right] - \frac{1}{2} \left( Q_{K\alpha\beta\gamma} - Q_{K\gamma\alpha\beta} + Q_{K\beta\gamma\alpha} \right)$$

Clamped-ion Piezoelectric Tensor

<table>
<thead>
<tr>
<th>Strain</th>
<th>$e_{113} = e_{223}$</th>
<th>$e_{311} = e_{322}$</th>
<th>$e_{333}$</th>
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</thead>
<tbody>
<tr>
<td>0.1547</td>
<td>0.3617</td>
<td>-0.8345</td>
<td></td>
</tr>
</tbody>
</table>

*TABLE II. Clamped-ion piezoelectric coefficients (in C/m$^2$) of PbTiO$_3"*
LONG-WAVE DFPT: NUMERICAL RESULTS

Flexoelectric tensor: Cubic materials

Cubic symmetry

3 independent components

Testcase 1: Isolated noble gas atoms

<table>
<thead>
<tr>
<th></th>
<th>$\mu_L$</th>
<th>$\mu_T$</th>
<th>$\mu_S \times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>$-0.479 , (0.479^a)$</td>
<td>$-0.479 , (0.479^a)$</td>
<td>$-0.08 , (0.08^a)$</td>
</tr>
<tr>
<td>Ar</td>
<td>$-4.821 , (-4.813^a)$</td>
<td>$-4.823 , (-4.820^a)$</td>
<td>$-1 , (-10^a)$</td>
</tr>
<tr>
<td>Kr</td>
<td>$-6.471 , (-6.474^a)$</td>
<td>$-6.477 , (-6.476^a)$</td>
<td>$-4 , (-20^a)$</td>
</tr>
</tbody>
</table>

( ) 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)

Stengel
PRB 90, 201112(R) (2014)

<table>
<thead>
<tr>
<th></th>
<th>$\mu_L$</th>
<th>$\mu_T$</th>
<th>$\mu_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (this work)</td>
<td>$-1.4114$</td>
<td>$-1.0491$</td>
<td>$-0.1895$</td>
</tr>
<tr>
<td>Ref. 3</td>
<td>$-1.4110$</td>
<td>$-1.0493$</td>
<td>$-0.1894$</td>
</tr>
<tr>
<td>SrTiO$_3$ (this work)</td>
<td>$-0.8848$</td>
<td>$-0.8262$</td>
<td>$-0.0823$</td>
</tr>
<tr>
<td>Ref. 3</td>
<td>$-0.8851$</td>
<td>$-0.8260$</td>
<td>$-0.0823$</td>
</tr>
<tr>
<td>Ref. 6</td>
<td>$-0.883$</td>
<td>$-0.825$</td>
<td>$-0.082$</td>
</tr>
</tbody>
</table>

TABLE V. Flexoelectric coefficients (nC/m) of Si and SrTiO$_3$.  

"TABLE III. Flexoelectric coefficients (pC/m) of noble-gas atom systems.  $^a$Ref. [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**
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LONG-WAVE DFPT: IMPLEMENTATION DETAILS

New objects to implement

\[ K_\gamma(G, G') = -8\pi G_\gamma \frac{\delta_{GG'} \alpha\beta}{G^4} \]

\[ \hat{H}_{k,\gamma}^{\tau,\kappa,\beta} = V^{\text{loc},\tau,\kappa,\beta}_{\gamma} + V^{\text{sep},\tau,\kappa,\beta}_{k,\gamma} \]

\[ \hat{H}_{k,\gamma}^{\beta} = \hat{T}_{k,\gamma}^{\beta} + V^{\text{loc},\gamma}_{\delta} + V^{\text{sep},\gamma}_{k,\gamma} + \hat{V}^{H_0,\gamma}_{\delta} \]

\[ \left\langle i\, u^A_{\alpha m_k,\gamma} | u^\eta_{\beta m_k} \right\rangle \rightarrow -\frac{i}{2} \left\langle \tilde{\partial}_{\alpha\gamma} u_{m_k}^{(0)} | u^\eta_{\beta m_k} \right\rangle - \frac{i}{2} \left\langle u_{m_k,\alpha\gamma} | u^\eta_{\beta m_k} \right\rangle \]

Response to an orbital B-field

NOT IMPLEMENTED

- **hartredq** (54_spacepar/m_spacepar.F90)
- **dfpt_vlocaldq** (67_common/m_mklocl.F90)
- **nonlop (choice=22)** (66_nonlocal/m_nonlop.F90)
- **mkkin_metdqmdq** (56_recipspace/m_kg.F90)
- **dfpt_vlocaldqmdq** (67_common/m_mklocl.F90)
- **nonlop (choice=33)** (66_nonlocal/m_nonlop.F90)
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_dkd3  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
getdkd5  3
lw_qdrpl5  1  # Calculate Quadrupoles
lw_flexo5  2  # Calculate CI flexoelectric tensor

#Common input variables

getwfkg   1
useylm   1
nqpt   1
qpt   0.0E+00  0.0E+00  0.0E+00
...
...
### LONG-WAVE DFPT: IMPLEMENTATION DETAILS

#### Example of output files

**abi_out**

Quadripole tensor, in cartesian coordinates,

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<th>efdir</th>
<th>qgrdir</th>
<th>real part</th>
<th>imaginary part</th>
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...  

Electronic flexoelectric tensor, in cartesian coordinates,

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**_O_DS5_DDB**

**** Database of total energy derivatives ****

Number of data blocks= 1

3rd derivatives - # elements : 216

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ddq ipert=natom+8
LONG-WAVE DFPT: IMPLEMENTATION DETAILS

State of the implementation

**NOT YET MERGED WITH THE TRUNK**

Current limitations:

- Perturbations symmetries deactivated
- LDA exclusive
- Not adapted for non-linear core corrections
- \( \text{kptopt} \neq 1 \)
- \( \text{useylm} = 1 \)
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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!