Electric Polarization and Homogeneous Electric Fields in Periodic Systems

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Outline

1. Computational Framework

2. Homogeneous electric fields
Density functional theory

Minimize

\[ E_{\text{el}} \{ \psi \} = \sum_{\alpha}^{\text{occ}} \langle \psi_\alpha | T + v_{\text{ext}} | \psi_\alpha \rangle + E_{\text{Hxc}}[n] - \sum_{\alpha\beta}^{\text{occ}} \epsilon_{\beta\alpha} (\langle \psi_\alpha | \psi_\beta \rangle - \delta_{\alpha\beta}) \]

where

\[ n(r) = \sum_{\alpha}^{\text{occ}} \psi^*_\alpha(r) \psi_\beta(r) \]

and gradient is \( \delta E / \delta \langle \psi_\alpha \rangle \)
Planewaves and pseudopotentials

Periodicity of the solid leads to Bloch theorem:

\[ \psi_{nk}(r) \propto e^{i\mathbf{k} \cdot \mathbf{r}} u_{nk}(\mathbf{r}) \]

and the cell periodic part is expanded in planewaves:

\[ u_{nk}(\mathbf{r}) = \sum_{\mathbf{G}} u_{nk}(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}} \]

This is efficient if the core electrons are replaced by pseudopotentials.
The PAW method (Blöchl) projects from pseudofunctions back to all-electron valence space functions.

\[
|\psi\rangle = T|\tilde{\psi}\rangle
\]

\[
T = 1 + \sum_{i,R} \left( |\phi_{iR}\rangle - |\tilde{\phi}_{iR}\rangle \right) \langle \tilde{\phi}_{iR} | \langle \psi | A | \psi \rangle = \langle \tilde{\psi} | A | \tilde{\psi} \rangle + \sum_{ij,R} \langle \tilde{\psi} | \tilde{p}_{iR} \rangle \langle \tilde{p}_{jR} | \tilde{\psi} \rangle \times
\]

\[
\left( \langle \phi_{iR} | A | \phi_{jR} \rangle - \langle \tilde{\phi}_{iR} | A | \tilde{\phi}_{jR} \rangle \right)
\]
Polarization

Polarization refers to electric dipole moment per volume. Simple in finite systems, not simple to compute in extended systems (thermodynamic limit).
Homogeneous electric field

\[ V(R + r) = V(r) \]

\[ V(r) + eE \cdot r \]

- “Obvious” coupling between external electric field \( E \) and electric charge leads to energy term \( eE \cdot r \)
- This term is OK for finite systems but not for infinite systems!
- Appear to have lost all bound states!
This approach begins with work of Resta:

\[ P(\lambda) = \frac{1}{V} \int d\mathbf{r} \rho(\lambda)(\mathbf{r}) \mathbf{r} \]
\[ = \frac{e}{V} \sum_i f_i \langle \phi_i | \mathbf{r} | \phi_i \rangle \]
\[ P'(\lambda) = \frac{e}{V} \sum_i f_i \langle \phi'_i | \mathbf{r} | \phi_i \rangle + \langle \phi_i | \mathbf{r} | \phi'_i \rangle \]

Shift of emphasis to derivative of \( P \) is crucial step.\(^1\)

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\(^1\)Resta, *Ferroelectrics* 136, 51 (1992)
To first order:

\[ P'(\lambda) = \frac{-ie}{m_e V} \sum_i f_i \sum_{j \neq i} \left[ \frac{\langle \phi_i | p | \phi_j \rangle \langle \phi_j | V' | \phi_i \rangle}{(E_i - E_j)^2} + \text{c.c} \right] \]

where \( V' \) is the perturbed KS potential and \( E_i \) are the KS eigenenergies.

Working in the parallel transport gauge where \( \langle \phi'_i | \phi_j \rangle = 0 \) for all occupied states \( j \), can write\(^2\)

\[ P'(\lambda) = \frac{-ief}{m_e N \Omega} \sum_{k} \sum_{\text{occ}} \sum_{\text{unocc}} \left[ \frac{\langle \phi_{kn} | p | \phi_{km} \rangle \langle \phi_{km} | V' | \phi_{kn} \rangle}{(E_i - E_j)^2} + \text{c.c} \right] \]

\(^2\)Gonze PRA 52, 1096 (1995); King-Smith and Vanderbilt, PRB 47, 1651 (1993)
Further development:

By exploiting commutators such as \([\partial/\partial k, H_k]\) and parallel transport gauge, formula in k-space becomes

\[
P'_{\alpha}(\lambda) = \frac{-ief}{N\Omega} \sum_k \sum_n^{\text{occ}} \left[ \langle \partial u_{kn}/\partial k_{\alpha} | \partial u_{kn}/\partial \lambda \rangle + c.c. \right]
\]

Note that only ground state wavefunctions appear here!

Going from summation to integration, and integrating by parts, the key result is obtained:

\[
\Delta P = P_1 - P_0 \\
P_{\alpha} = \frac{ife}{8\pi^3} \sum_n^{\text{occ}} \int dk \langle u_{kn} | \partial/\partial k_{\alpha} | u_{kn} \rangle
\]
Finite difference formula for line integral

The integration along the loop in \( k \) space is done via discretization:\(^3\)

\[
\sum_n \int d\mathbf{k}_\alpha \langle u_{nk} | \nabla_{k_\alpha} | u_{nk} \rangle \rightarrow \text{Im} \ln \prod_j \det \langle u_{nk_j} | u_{mk_j+b} \rangle
\]

This form is invariant to phase differences between the states at different \( k \) points. In case of PAW:

\[
\langle u_{nk_j} | u_{mk_j+b} \rangle \rightarrow \langle \tilde{u}_{nk_j} T_{k_j} | T_{k_j+b} \tilde{u}_{mk_j+b} \rangle
\]

\(^3\)Resta, *PRL* 80, 1800 (1998)
The total electric polarization is the sum of the electronic part above and the ionic part:

\[ P = P_{\text{ion}} + P_{\text{elec}}, \]

with

\[ P_{\text{ion}} = \sum_i Z_i r_i \]

just the sum over the charges and positions of the ions in the unit cell, then folded into unit interval (-1,1).
Executing the calculation in **Abinit**

To compute the polarization, just do the following:

- Insulating system
- $n_{\text{band}}$ is number of valence bands, no empty bands
- normal ground state calculation
- $\text{berryopt} -1$
- $\text{rfdir} 1 1 1$
- PAW, $n_{\text{sppol}}, n_{\text{spinor}}$ 2 all ok
In output file for AlAs in zero field:

Summary of the results

Electronic Berry phase    7.682370411E-03
Ionic phase              -7.500000000E-01
Total phase              -7.423176296E-01
Remapping in [-1,1]     -7.423176296E-01

Polarization            -1.435570235E-02 (a.u. of charge)/bohr^2
Polarization            -8.213580860E-01 C/m^2

Polarization in cartesian coordinates (a.u.):
(the sum of the electronic and ionic Berry phase has been folded into [-1, 1])
Electronic berry phase:  0.257330072E-03  0.257330072E-03  0.257330072E-03
...includes PAW on-site term:  0.000000000E+00  0.000000000E+00  0.000000000E+00
Ionic:                   -0.251221359E-01 -0.251221359E-01 -0.251221359E-01
Total:                   -0.248648059E-01 -0.248648059E-01 -0.248648059E-01
Inclusion of a Finite Electric Field

Minimize $E = E_0 - \mathbf{P} \cdot \mathbf{E}$, \(^4\) where:

- $\mathbf{P}$ is computed as above
- Norm constraint is imposed: $\langle \psi_n | S | \psi_m \rangle = \delta_{nm}$ ($S$ is identity if NCPP)
- Form gradient:

$$\frac{\delta E}{\delta \langle u_{mk} \rangle} = \frac{\delta E_0}{\delta \langle u_{mk} \rangle} - \mathbf{E} \cdot \frac{\delta \mathbf{P}}{\delta \langle u_{mk} \rangle}$$

- Implemented in \textsc{Abinit}, including PAW,\(^5\) spin polarized systems, spinors, spin-orbit coupling

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Finite field in **ABINIT**

- `ndtset 4 (say)`
- `getwfk -1`
- `rfdir 1 1 1`
- `efield1 3*0.0`
- `berryopt1 -1` (Start with zero field, build up field slowly)
- `efield2 0.0001 0.0 0.0`
- `berryopt2 4`
- Look at polarization in output file
Forces and Stress in finite field

- In NCPP, no additional force terms arise (because additional polarization term does not involve ion positions so Hellman-Feynman force (derivative w.r.t position is zero)
- There is NCPP stress
- In PAW, due to ion position dependence of projectors, there are additional force and stress terms in finite field.
- In Abinit, NCPP includes force and stress but PAW is in development.

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6Souza, Íñiguez, Vanderbilt, PRL 89, 117602 (2002)
Forces for E-field with PAW

The problem is that in $\text{Im} \ln \prod \det M$, the $M$ matrix elements

$$M_{n,m} = \langle \tilde{u}_{nkj} \ T_{kj} | T_{kj+b} \tilde{u}_{mkj+b} \rangle$$

depend on ionic position through the projectors in $T$. They must be included in the Hellmann-Feynman force through $^7$

$$\frac{\partial}{\partial R_i} \text{Im} \ln \prod \det M = \text{Im} \sum \frac{\partial}{\partial R_i} \ln \det M$$

$$= \text{Im} \sum \text{Tr} \left[ M^{-1} \frac{\partial M}{\partial R_j} \right]$$

$^7$Nunes and Gonze *PRB* 63, 155107 (2001); Audouze, Jollet, Torrent, Gonze *PRB* 73, 235101 (2006)
Effect of PAW force

Forces included in jzwanzig/7.7.3-private. Example: AlAs with PAW and finite electric field.

![Graph showing the force error (F - F_{fd})/F_{fd} vs. kptrlen.](image)

- Ionic force
- Ionic+PAW force
Convergence of polarization with k-mesh for Si.

\[ \mathbf{P} = \chi \mathbf{E} \]

\[ \varepsilon^\infty = 1 + 4\pi\chi \]
Applications

Polarization is computed as a function of applied field and fit to the form (SI units for polarization and field):

\[ P_i = \varepsilon_0 \chi_{ij}^{(1)} E_j + 2\varepsilon_0 d_{ijk} E_j E_k, \]
Applications

- High and low frequency susceptibility: \( \chi_{\alpha\beta} = \frac{dP_\alpha}{dE_\beta} \)
- Second order susceptibility

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \epsilon^0 )</th>
<th>( \epsilon^\infty )</th>
<th>( d_{123} ) pm/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIP (LDA)</td>
<td>10.26</td>
<td>8.01</td>
<td>21.5</td>
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<tr>
<td>(PBE)</td>
<td>10.09</td>
<td>7.84</td>
<td>23.2</td>
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<tr>
<td>(expt)</td>
<td>9.8</td>
<td>7.5</td>
<td></td>
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<tr>
<td>AlAs (LDA)</td>
<td>11.05</td>
<td>8.75</td>
<td>32.7</td>
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<tr>
<td>(PBE)</td>
<td>10.89</td>
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<td>38.8</td>
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<tr>
<td>(expt)</td>
<td>10.16</td>
<td>8.16</td>
<td>32</td>
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<tr>
<td>AlSb (LDA)</td>
<td>12.54</td>
<td>11.17</td>
<td>98.3</td>
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<tr>
<td>(PBE)</td>
<td>12.83</td>
<td>11.45</td>
<td>103</td>
</tr>
<tr>
<td>(PBE + SO)</td>
<td></td>
<td>9.76</td>
<td></td>
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<tr>
<td>(expt)</td>
<td>11.68</td>
<td>9.88</td>
<td>98</td>
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</table>
Application: MgO Dielectric

<table>
<thead>
<tr>
<th>Method</th>
<th>$\epsilon^\infty$</th>
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<tbody>
<tr>
<td>PAW E-field, PBE</td>
<td>3.089</td>
</tr>
<tr>
<td>PAW DFPT, LDA</td>
<td>3.057</td>
</tr>
<tr>
<td>NCPP DFPT, LDA</td>
<td>3.063</td>
</tr>
<tr>
<td>Expt</td>
<td>3.014</td>
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</tbody>
</table>

N.B. in DFPT, $\frac{\partial^2 E}{\partial E_i \partial E_j} \bigg|_0$ is computed directly, without presence of a field.

MgO in Finite Electric Field

slope = $\chi = 0.1662$
$1 + 4\pi\chi = 3.089$
Inverse of dielectric tensor changed by stress or strain:

\[ \Delta B_{ij} = p_{ijkl} \epsilon_{kl} = \pi_{ijkl} \sigma_{kl} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\epsilon$</th>
<th>$p_{11}$</th>
<th>$p_{21}$</th>
<th>$p_{44}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (LDA)</td>
<td>12.4</td>
<td>-0.106</td>
<td>0.015</td>
<td>-0.052</td>
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<tr>
<td>(PBE)</td>
<td>12.2</td>
<td>-0.112</td>
<td>0.010</td>
<td>-0.061</td>
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<tr>
<td>(expt)</td>
<td>11.7</td>
<td>-0.094</td>
<td>0.017</td>
<td>-0.051</td>
</tr>
<tr>
<td>C (LDA)</td>
<td>5.71</td>
<td>-0.263</td>
<td>0.0673</td>
<td>-0.160</td>
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<tr>
<td>(PBE)</td>
<td>5.79</td>
<td>-0.268</td>
<td>0.0643</td>
<td>-0.171</td>
</tr>
<tr>
<td>(expt)</td>
<td>5.65–5.7</td>
<td>-0.244–-0.42</td>
<td>0.042–0.27</td>
<td>-0.172–-0.162</td>
</tr>
</tbody>
</table>
Photoelasticity in oxides

<table>
<thead>
<tr>
<th>Quantity</th>
<th>MgO</th>
<th>BaO</th>
<th>SnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>325.8</td>
<td>158.3</td>
<td>111.7</td>
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<tr>
<td>$C_{33}$</td>
<td></td>
<td>43.4</td>
<td></td>
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<tr>
<td>$C_{12}$</td>
<td>98.8</td>
<td>46.8</td>
<td>95.0</td>
</tr>
<tr>
<td>$C_{13}$</td>
<td></td>
<td>18.9</td>
<td></td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>162.5</td>
<td>35.7</td>
<td>30.4</td>
</tr>
<tr>
<td>$C_{66}$</td>
<td></td>
<td>85.2</td>
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<tr>
<td>$\pi_{11}$</td>
<td>-0.980</td>
<td>0.990</td>
<td>-1.70</td>
</tr>
<tr>
<td>$\pi_{33}$</td>
<td></td>
<td>0.91</td>
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</tr>
<tr>
<td>$\pi_{12}$</td>
<td>0.172</td>
<td>-0.176</td>
<td>2.19</td>
</tr>
<tr>
<td>$\pi_{13}$</td>
<td></td>
<td>6.20</td>
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</tr>
<tr>
<td>$\pi_{44}$</td>
<td>-0.446</td>
<td>-1.26</td>
<td>2.31</td>
</tr>
<tr>
<td>$\pi_{66}$</td>
<td></td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_{11}^\infty$</td>
<td>3.04</td>
<td>4.27</td>
<td>8.67</td>
</tr>
<tr>
<td>$\varepsilon_{33}^\infty$</td>
<td></td>
<td>7.04</td>
<td></td>
</tr>
</tbody>
</table>

![Graph showing stress-strain relationship](image)
Summary

- Modern theory of polarization and finite electric fields
- NCPP, PAW, spinors, spin polarized systems
- Applications to linear and nonlinear electric susceptibility
- MANY thanks to Xavier Gonze, Marc Torrent, Abinit development and theory community