Electric Polarization and Homogeneous Electric Fields in Periodic Systems

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Outline

Density functional theory

Minimize

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

where

$$n(\mathbf{r}) = \sum_{\alpha}^{\mathrm{occ}} \psi_\alpha^*(\mathbf{r})\psi_\beta(\mathbf{r})$$

and gradient is $\delta E/\delta\langle\psi_\alpha|$

Planewaves and pseudopotentials

Periodicity of the solid leads to Bloch theorem:

$$\psi_{n\mathbf{k}}(\mathbf{r}) \propto e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$$

and the cell periodic part is expanded in planewaves:

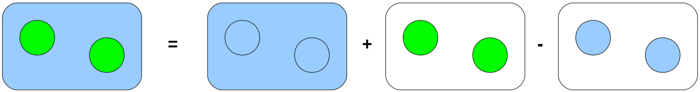
$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} u_{n\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

This is efficient *if* the core electrons are replaced by pseudopotentials.

Projector Augmented Wave Method

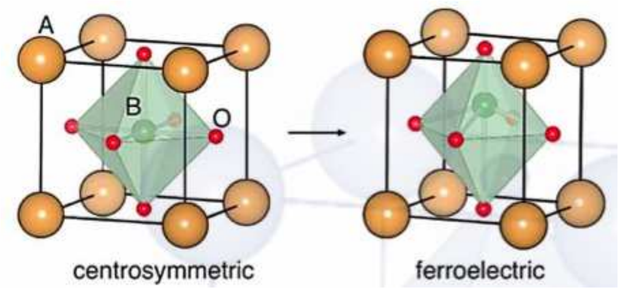
The PAW method (Blöchl) *projects* from pseudofunctions back to all-electron valence space functions.

$$
\begin{aligned}
|\psi\rangle &= T|\tilde{\psi}\rangle \\
T &= 1 + \sum_{i,\mathbf{R}} \left[|\phi_{i\mathbf{R}}\rangle - |\tilde{\phi}_{i\mathbf{R}}\rangle \right] \langle \tilde{p}_{i\mathbf{R}}| \\
\langle\psi|A|\psi\rangle &= \langle\tilde{\psi}|A|\tilde{\psi}\rangle + \sum_{ij,\mathbf{R}} \langle\tilde{\psi}|\tilde{p}_{i\mathbf{R}}\rangle\langle\tilde{p}_{j\mathbf{R}}|\tilde{\psi}\rangle \times \\
& \left(\langle\phi_{i\mathbf{R}}|A|\phi_{j\mathbf{R}}\rangle - \langle\tilde{\phi}_{i\mathbf{R}}|A|\tilde{\phi}_{j\mathbf{R}}\rangle \right)
\end{aligned}
$$

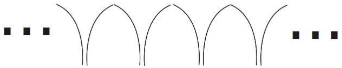


Polarization

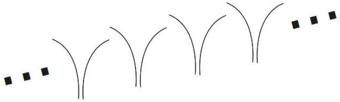
Polarization refers to electric dipole moment per volume. Simple in finite systems, not simple to compute in extended systems (thermodynamic limit).



Homogeneous electric field



$V(\mathbf{R}+\mathbf{r}) = V(\mathbf{r})$



$V(\mathbf{r}) + e\mathbf{E}\cdot\mathbf{r}$

- "Obvious" coupling between external electric field $\mathbf{E}$ and electric charge leads to energy term $e\mathbf{E}\cdot\mathbf{r}$
- This term is OK for finite systems but not for infinite systems!
- Appear to have lost all bound states!

Modern Theory of Polarization

This approach begins with work of Resta:

$$\begin{aligned}
\mathbf{P}(\lambda) &= \frac{1}{V}\int d\mathbf{r}\rho_\lambda(\mathbf{r})\mathbf{r} \\
&= \frac{e}{V}\sum_i f_i\langle\phi_i|\mathbf{r}|\phi_i\rangle \\
\mathbf{P}'(\lambda) &= \frac{e}{V}\sum_i f_i\langle\phi_i'|\mathbf{r}|\phi_i\rangle + \langle\phi_i|\mathbf{r}|\phi_i'\rangle
\end{aligned}$$

Shift of emphasis to derivative of **P** is crucial step.[1]

[1] Resta, *Ferroelectrics* **136**, 51 (1992)

To first order:

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

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]

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

[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

$$P'_\alpha(\lambda) = \frac{-ief}{N\Omega}\sum_{\mathbf{k}}\sum_{n}^{\mathrm{occ}}[\langle\partial u_{\mathbf{k}n}/\partial k_\alpha|\partial u_{\mathbf{k}n}/\partial\lambda\rangle + \mathrm{c.c}]$$

Note that *only* ground state wavefunctions appear here!
Going from summation to integration, and integrating by parts, the key result is obtained:

$$\begin{aligned}\Delta\mathbf{P} &= \mathbf{P}_1 - \mathbf{P}_0 \\ P_\alpha &= \frac{ife}{8\pi^3}\sum_{n}^{\mathrm{occ}}\oint d\mathbf{k}\langle u_{\mathbf{k}n}|\partial/\partial k_\alpha|u_{\mathbf{k}n}\rangle\end{aligned}$$

Finite difference formula for line integral

The integration along the loop in k space is done via discretization:[3]

$$\sum_n \int d\mathbf{k}_\alpha \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}_\alpha} | u_{n\mathbf{k}} \rangle \rightarrow \mathrm{Im} \ln \prod_j \det \langle u_{n\mathbf{k_j}} | u_{m\mathbf{k_j}+\mathbf{b}} \rangle$$

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

$$\langle u_{n\mathbf{k_j}} | u_{m\mathbf{k_j}+\mathbf{b}} \rangle \rightarrow \langle \tilde{u}_{n\mathbf{k_j}} T_{\mathbf{k_j}} | T_{\mathbf{k_j}+\mathbf{b}} \tilde{u}_{m\mathbf{k_j}+\mathbf{b}} \rangle$$

[3] Resta, *PRL* **80**, 1800 (1998)

Total polarization

The total electric polarization is the sum of the electronic part above and the ionic part:

$$\mathbf{P} = \mathbf{P}_{\mathrm{ion}} + \mathbf{P}_{\mathbf{elec}},$$

with

$$\mathbf{P}_{\mathrm{ion}} = \sum_i Z_i \mathbf{r}_i$$

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
- `nband` is number of valence bands, no empty bands
- normal ground state calculation
- `berryopt -1`
- `rfdir 1 1 1`
- PAW, `nsppol`, `nspinor 2` all ok

berryopt output

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:

$$\delta E / \delta \langle u_{m\mathbf{k}} | = \delta E_0 / \delta \langle u_{m\mathbf{k}} | - \mathbf{E} \cdot \delta \mathbf{P} / \delta \langle u_{m\mathbf{k}} |$$

- Implemented in ABINIT, including PAW,[5] spin polarized systems, spinors, spin-orbit coupling

[4] Nunes and Gonze *PRB* **63**, 155107 (2001); Stengel, Spaldin, Vanderbilt *Nature Physics* **5**, 304 (2009)

[5] Zwanziger *et al.*, *Comp. Mater. Sci.* **58**, 113 (2012)

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[6]
- 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.

[6] Souza, Íñiguez, Vanderbilt, *PRL* **89**, 117602 (2002)

Forces for E-field with PAW

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

$$M_{n,m} = \langle \tilde{u}_{n\mathbf{k_j}} T_{\mathbf{k_j}} | T_{\mathbf{k_j}+\mathbf{b}} \tilde{u}_{m\mathbf{k_j}+\mathbf{b}} \rangle$$

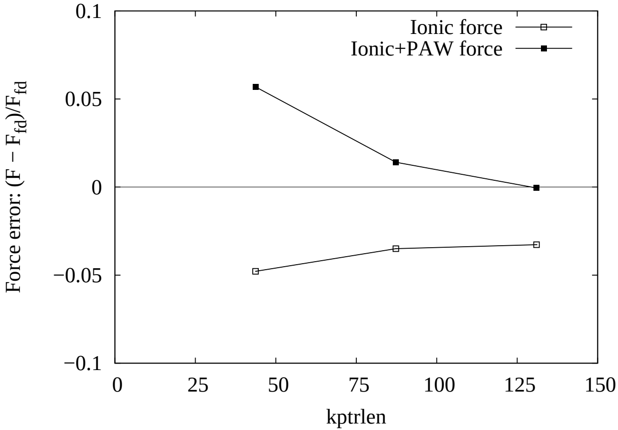
depend on ionic position through the projectors in T. They must be included in the Hellmann-Feynman force through[7]

$$\begin{aligned} \frac{\partial}{\partial R_i} \mathrm{Im}\ln\Pi\det M &= \mathrm{Im}\sum \frac{\partial}{\partial R_i}\ln\det M \\ &= \mathrm{Im}\sum \mathrm{Tr}\left[M^{-1}\frac{\partial M}{\partial R_j}\right] \end{aligned}$$

[7] Nunes and Gonze *PRB* **63**, 155107 (2001); Audouze, Jollet, Torrent, Gonz *PRB* **73**, 235101 (2006)

Effect of PAW force

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

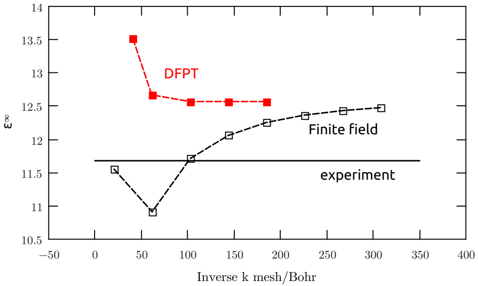


Convergence of polarization with k-mesh

Convergence with mesh size for Si.

$$\mathbf{P} = \chi \mathbf{E}$$

$$\epsilon^{\infty} = 1 + 4\pi\chi$$



Applications

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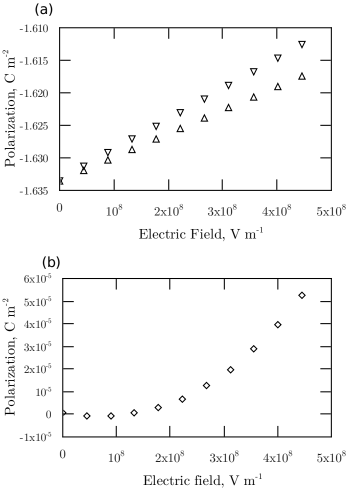
Computational Framework

Homogeneous electric fields

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

$$P_i = \epsilon_0 \chi_{ij}^{(1)} E_j + 2\epsilon_0 d_{ijk} E_j E_k,$$



Applications

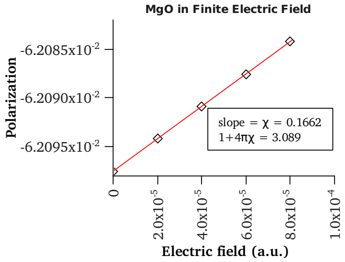
- High and low frequency susceptibility: $\chi_{\alpha\beta} = dP_\alpha/dE_\beta$
- Second order susceptibilities

Compound	ϵ^0	ϵ^∞	d_{123} pm/V
AlP (LDA)	10.26	8.01	21.5
(PBE)	10.09	7.84	23.2
(expt)	9.8	7.5	
AlAs (LDA)	11.05	8.75	32.7
(PBE)	10.89	8.80	38.8
(expt)	10.16	8.16	32
AlSb (LDA)	12.54	11.17	98.3
(PBE)	12.83	11.45	103
(PBE + SO)		9.76	
(expt)	11.68	9.88	98

Application: MgO Dielectric

Method	ϵ^{∞}
PAW E-field, PBE	3.089
PAW DFPT, LDA	3.057
NCPP DFPT, LDA	3.063
Expt	3.014

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



Photoelasticity

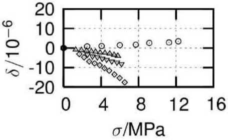
Inverse of dielectric tensor changed by stress or strain:

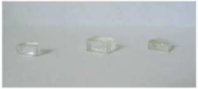
$$\Delta B_{ij} = p_{ijkl}\epsilon_{kl} = \pi_{ijkl}\sigma_{kl}$$

Compound	ϵ	p_{11}	p_{21}	p_{44}
Si (LDA)	12.4	-0.106	0.015	-0.052
(PBE)	12.2	-0.112	0.010	-0.061
(expt)	11.7	-0.094	0.017	-0.051
C (LDA)	5.71	-0.263	0.0673	-0.160
(PBE)	5.79	-0.268	0.0643	-0.171
(expt)	5.65–5.7	-0.244 – -0.42	0.042–0.27	-0.172 – -0.162

Photoelasticity in oxides

Quantity	MgO	BaO	SnO
C_{11}	325.8	158.3	111.7
C_{33}			43.4
C_{12}	98.8	46.8	95.0
C_{13}			18.9
C_{44}	162.5	35.7	30.4
C_{66}			85.2
π_{11}	-0.980	0.990	-1.70
π_{33}			0.91
π_{12}	0.172	-0.176	2.19
π_{13}			6.20
π_{44}	-0.446	-1.26	2.31
π_{66}			0.97
ϵ_{11}^{∞}	3.04	4.27	8.67
ϵ_{33}^{∞}			7.04





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