Homogeneous Electric and Magnetic Fields in Periodic Systems

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Acknowledgments

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Computational Framework

Homogeneous electric fields

Homogeneous finite magnetic fields

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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 $\delta E/\delta\langle\psi_\alpha|$

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:

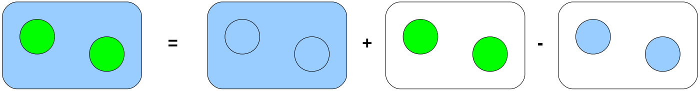
$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} u_{n\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

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

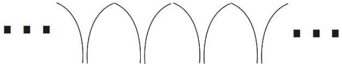
Projector Augmented Wave Method

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

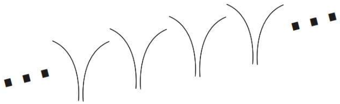
$$
\begin{aligned}
|\psi\rangle &= T|\tilde{\psi}\rangle \\
T &= 1 + \sum_{i,\mathbf{R}} \left[|\phi_{i\mathbf{R}}\rangle - |\tilde{\phi}_{i\mathbf{R}}\rangle \right] \langle \tilde{p}_{i\mathbf{R}}| \\
\langle\psi|A|\psi\rangle &= \langle\tilde{\psi}|A|\tilde{\psi}\rangle + \sum_{ij,\mathbf{R}} \langle\tilde{\psi}|\tilde{p}_{i\mathbf{R}}\rangle\langle\tilde{p}_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



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

- King-Smith and Vanderbilt showed that polarization does not suffer from unboundedness:

$$\mathbf{P} = -\frac{ie}{(2\pi)^3}\sum_n \int_{\mathrm{BZ}} d\mathbf{k}\langle u_{n\mathbf{k}}|\nabla_{\mathbf{k}}|u_{n\mathbf{k}}\rangle$$

- Nunes and Gonze showed how polarization enters into a well-posed minimization scheme with finite electric field:

$$E[\psi,\mathbf{E}] = E[\psi] - \Omega\mathbf{E}\cdot\mathbf{P}(\psi)$$

Inclusion of a Finite Electric Field

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Computational Framework

Homogeneous electric fields

Homogeneous finite magnetic fields

Minimize $E = E_0 - \mathbf{P} \cdot \mathbf{E}$, where:

- $\mathbf{P}$ is computed via PAW transform and discretization[1]
- Generalized norm constraint is imposed: $\langle \psi_n | S | \psi_m \rangle = \delta_{nm}$
- On-site dipole contribution from T is included:

$$\langle \tilde{u}_{n\mathbf{k}} | T^\dagger_{\mathbf{k}} i \nabla_{\mathbf{k}} T_{\mathbf{k}} | \tilde{u}_{n\mathbf{k}} \rangle,$$

$$|\varphi^{I}_{q,\mathbf{R},\mathbf{k}}\rangle = e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})} |\varphi^{I}_{q,\mathbf{k}}\rangle$$

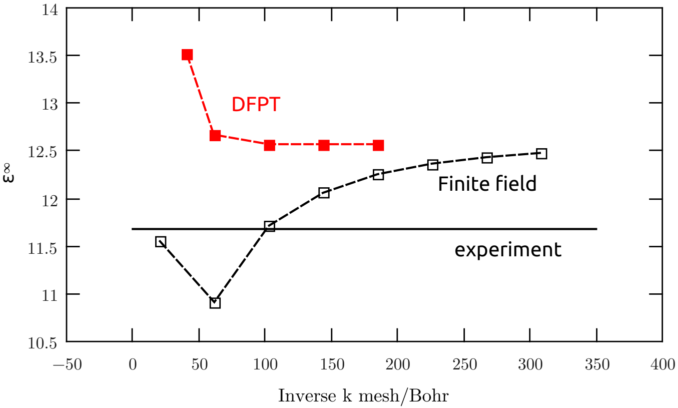
- Form gradient:

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

- Implemented in ABINIT, including spin polarized systems, spinors, spin-orbit coupling

[1] King-Smith and Vanderbilt, *cond-matt*; Zwanziger *et al.*, *Comp. Mater. Sci.* **58**, 113 (2012)

Convergence with k-mesh

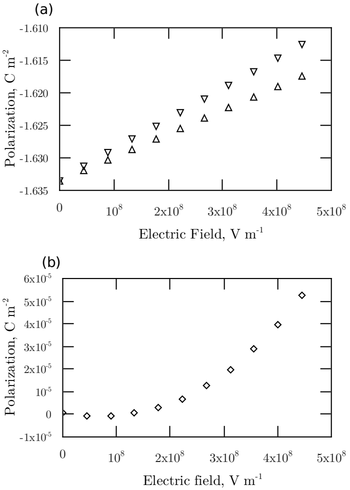


Convergence with mesh size for Si

Applications

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

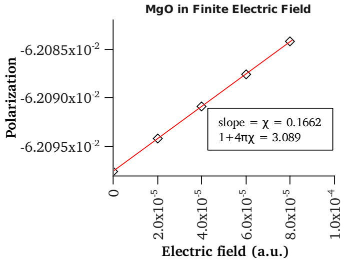
- High and low frequency susceptibility: $\chi_{\alpha\beta} = dP_\alpha / dE_\beta$
- Second order susceptibilities

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

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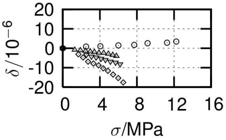
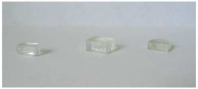
Quantity	MgO	BaO	SnO
C_{11}	325.8	158.3	111.7
C_{33}			43.4
C_{12}	98.8	46.8	95.0
C_{13}			18.9
C_{44}	162.5	35.7	30.4
C_{66}			85.2
π_{11}	-0.980	0.990	-1.70
π_{33}			0.91
π_{12}	0.172	-0.176	2.19
π_{13}		6 6.20	
π_{44}	-0.446	-1.26	2.31
π_{66}			0.97
ϵ_{11}^{∞}	3.04	4.27	8.67
ϵ_{33}^{∞}			7.04



- $(SnO)_{55}(P_2O_5)_{45}$: $C = 0.3$ B
- $(SnO)_{60}(P_2O_5)_{40}$: $C = -0.6$ B
- $(SnO)_{66}(P_2O_5)_{34}$: $C = -1.3$ B
- $(SnO)_{75}(P_2O_5)_{25}$: $C = -2.3$ B



Homogeneous magnetic fields in insulators

- One approach to magnetic fields in periodic insulators is the long wavelength approach of Louie and co-workers: $B \to B\cos(\mathbf{q}\cdot\mathbf{r})$ with $\mathbf{q} \to 0$.
- Problematic: cannot always find $|\partial_\mathbf{k} u\rangle$ such that $\langle \partial_\mathbf{k} u | u^0_\mathbf{k}\rangle = 0$ AND $|u^0_{\mathbf{k}+\mathbf{G}}\rangle = e^{i\mathbf{G}\cdot\mathbf{r}}|u^0_\mathbf{k}\rangle$.
- In 2005 and 2006, Ceresoli, Thonhauser, Resta, and Vanderbilt established:

$$\mathbf{M} = \frac{1}{2c(2\pi)^3}\mathrm{Im}\sum_{nn'}\int_{BZ} d\mathbf{k}\langle \partial_\mathbf{k} u_{n'\mathbf{k}}|\times(H_\mathbf{k}\delta_{nn'}+E_{nn'\mathbf{k}})|\partial_\mathbf{k} u_{n\mathbf{k}}\rangle$$

$$\mathbf{C} = \frac{i}{2\pi}\sum_{n}\int_{BZ} d\mathbf{k}\langle \partial_\mathbf{k} u_{n\mathbf{k}}| \times |\partial_\mathbf{k} u_{n\mathbf{k}}\rangle$$

Magnetic Translation Symmetry

- Recall gauge-dependent Hamiltonian:

$$H = \frac{1}{2}(\mathbf{p} + \frac{1}{c}\mathbf{A})^2 + V$$

- In 2010, Essin *et al.*[2] (see also Brown, Zak) discussed magnetic translation symmetry:

$$O_{\mathbf{r_1},\mathbf{r_2}} = \bar{O}_{\mathbf{r_1},\mathbf{r_2}} e^{-i\mathbf{B}\cdot\mathbf{r_1}\times\mathbf{r_2}/2c}$$

  where $\bar{O}$ has lattice symmetry.

[2] PRB **81** 205104 (2010)

Density operator perturbation theory

- Rather than perturbing the wave function, can work with the density operator:[3]:

$$\rho = \rho\rho \rightarrow \rho^1 = \rho^1\rho^0 + \rho^0\rho^1 + \mathcal{O}(2)$$

- Using magnetic translation symmetry operation, all field dependence has been transferred FROM the Hamiltonian TO the density operator and we must perturb

$$\rho_{\mathbf{r_1},\mathbf{r_2}} = \bar{\rho}_{\mathbf{r_1},\mathbf{r_2}} e^{-i\mathbf{B}\cdot\mathbf{r_1}\times\mathbf{r_2}/2c}$$

[3] Lazzeri and Mauri, PRB **68** 161101(R) (2003)

A New Theory of Orbital Magnetic Susceptibility

Based on the the previous ideas Xavier Gonze and I have developed a complete treatment of magnetic field response in a periodic insulator. Key new ingredient:[4]

$$
\begin{aligned}
\tilde{T}_{\mathbf{k}} &= \tilde{V}_{\mathbf{k}}\tilde{W}_{\mathbf{k}} \\
&+ \sum_{m=1}^{\infty}\frac{1}{m!}\left(\frac{i}{2c}\right)^{m}\left(\prod_{n=1}^{m}\varepsilon_{\alpha_n\beta_n\gamma_n}B_{\alpha_n}\right) \\
&\quad \times(\partial_{\beta_1}\cdots\partial_{\beta_m}\tilde{V}_{\mathbf{k}})(\partial_{\gamma_1}\cdots\partial_{\gamma_m}\tilde{W}_{\mathbf{k}}),
\end{aligned}
$$

$$
E^{(n)} = \int_{\mathrm{BZ}}\frac{d\mathbf{k}}{(2\pi)^3}\mathrm{Tr}[(\tilde{\rho}^{(n)}_{\mathbf{k}VV} + \tilde{\rho}^{(n)}_{\mathbf{k}CC})\bar{H}_{\mathbf{k}}].
$$

[4] X. Gonze and J. W. Zwanziger, PRB 84, 64445 (2011)

Development of ρ

Density operator perturbation theory is used:[5]

$$\begin{aligned}
\tilde{\rho}^{(1)}_{\mathbf{k}D} &= \frac{i}{2c}\varepsilon_{\alpha\beta\gamma}B_\alpha(\partial_\beta\tilde{\rho}^{(0)}_{\mathbf{k}})(\partial_\gamma\tilde{\rho}^{(0)}_{\mathbf{k}}), \\
\tilde{\rho}^{(2)}_{\mathbf{k}D} &= \tilde{\rho}^{(1)}_{\mathbf{k}}\tilde{\rho}^{(1)}_{\mathbf{k}} \quad \mathrm{q}\mathit{uadratic} \\
&+\frac{i}{2c}\varepsilon_{\alpha\beta\gamma}B_\alpha[(\partial_\beta\tilde{\rho}^{(0)}_{\mathbf{k}})(\partial_\gamma\tilde{\rho}^{(1)}_{\mathbf{k}}) + (\partial_\beta\tilde{\rho}^{(1)}_{\mathbf{k}})(\partial_\gamma\tilde{\rho}^{(0)}_{\mathbf{k}})] \quad \mathrm{l}\mathit{inear} \\
&-\frac{1}{8c^2}\left(\prod_{n=1}^{2}\varepsilon_{\alpha_n\beta_n\gamma_n}B_{\alpha_n}\right)\partial_{\beta_1}\partial_{\beta_2}\tilde{\rho}^{(0)}_{\mathbf{k}}.\partial_{\gamma_1}\partial_{\gamma_2}\tilde{\rho}^{(0)}_{\mathbf{k}} \quad \mathrm{f}\mathit{rozen}
\end{aligned}$$

Full $\rho^{(n)}$, including *CV* and *VC* parts, may be subsequently recovered if needed.

[5] McWeeny *Phys Rev* **126**, 1028 (1962); Lazzeri and Mauri, *PRB* **68** 161101(R) (2003)

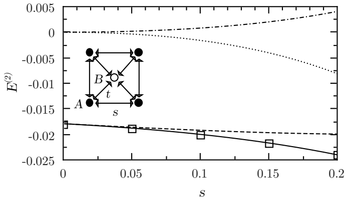
Checking the Theory

- The theory recovers the result for magnetization of Essin *et al.*, essentially $E^{(1)}$
- Second order, $E^{(2)}$, is a new, rigorous result for orbital susceptibility
- We then checked it with a tight binding model: analytical versus numerical

Checking the theory

- A sites at corners, initially occupied
- B sites at centers, initially empty
- on-site energies: $E_A < E_B$
- $A - A$ couplings s; $A - B$ couplings t
- B field applied perpendicular to plane:

$$H_{\mathbf{r}_1,\mathbf{r}_2} = \bar{H}_{\mathbf{r}_1,\mathbf{r}_2} e^{-i\mathbf{B}\cdot\mathbf{r}_1\times\mathbf{r}_2}$$



Example with $t = 2.0$. $E^{(2)}$ computed from theory, and by direct diagonalization

Mixed Perturbations

- In addition to the results for $\rho^{(n)}$ and $E^{(n)}$ due to magnetic fields, we have also established the response to mixed magnetic and other perturbations μ:

$$\frac{\partial^2 E}{\partial\mu\partial B} = \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^3} \mathrm{Tr}\left[\tilde{\rho}^{(1)} \frac{\partial H_{\mathbf{k}}}{\partial\mu}\right]$$

Summary

- Modern theory of polarization and finite electric fields in PAW formalism
- Applications to linear and nonlinear electric susceptibility
- Works with spin-orbit, spin-polarized, etc.
- New theory of orbital magnetic susceptibility, extension to mixed perturbations
- Implementation in ABINIT underway
- MANY thanks to Xavier Gonze, Marc Torrent, ABINIT development and theory community