Finite Homogeneous Electric and Magnetic Fields

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April 2011

Outline

1 Introduction

2 Homogeneous Finite Electric Fields

3 Homogeneous Finite Magnetic Fields

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Acknowledgments

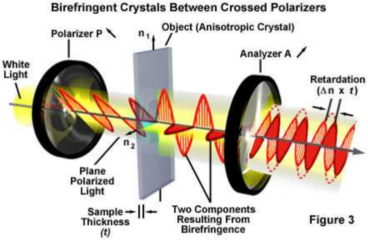
- Xavier Gonze
- Marc Torrent
- Matteo Giantomassi
- Justine Galbraith

Motivation

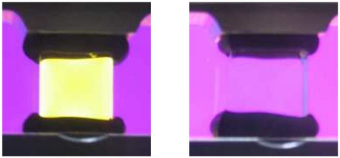
- Two primary projects in my experimental lab involve linear optical response and linear magnetic field response.
- Both can be addressed by computing response to finite, homogeneous fields.
- Plan of attack: minimize $E - \mathbf{P} \cdot \mathbf{E}$ or $E - \mathbf{M} \cdot \mathbf{B}$ subject to constraints.
- Outcome: **P** as a function of **E**, hence susceptibility, and wavefunctions in presence of magnetic field, hence orbital currents.

Electric Fields Motivation

A measurement we make in the lab:



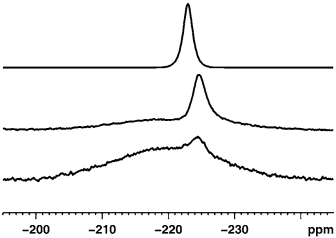
Introduction to the Photoelastic Response



20 mol-% PbO	40 mol-% PbO
$\sigma = 50$ bar	$\sigma = 50$ bar
$C = 2.65$ B	$C = 0.02$ B

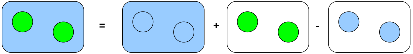
Magnetic Fields Motivation

Another measurement we make in the lab:



All implementation done in PAW

- Recall that Projector Augmented Wave method yields all-electron accuracy in valence space using modest planewave size
- For electric fields, this approach is efficient
- For magnetic fields, it is also easiest because it provides a simple way to include gauge dependence of vector potential properly



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What to Calculate

- "Obvious" coupling between external electric field **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:

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

Discretization

The continuum version of $\langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle$ leads to numerical problems, while a discretized version does not:

$$\mathcal{P}_{\mathrm{el}} \cdot \mathbf{b}_i = \frac{fe}{\Omega} \frac{1}{N_{\perp}^{i}} \sum^{N_{\perp}^{i}} \mathrm{Im} \ln \prod^{N_{\parallel}^{i}} \det M^{\mathbf{k}_i, \mathbf{k}_i + \Delta \mathbf{k}_i}$$

with

$$M_{mn}^{\mathbf{k}_i, \mathbf{k}_i + \Delta \mathbf{k}_i} = \langle u_{m\mathbf{k}_i} | u_{n\mathbf{k}_i + \Delta \mathbf{k}_i} \rangle.$$

PAW Transform

We must consider

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

Note that ∇ acts on both T and $|\tilde{u}\rangle$. T part gives an "on-site" dipole contribution, while $|\tilde{u}\rangle$ part is discretized:

$$M_{mn}^{\mathbf{k},\mathbf{k}+\Delta\mathbf{k}} = \langle \tilde{u}_{m\mathbf{k}} | \tilde{u}_{n\mathbf{k}+\Delta\mathbf{k}} \rangle + \sum_{q,r,I} \langle \tilde{u}_{m\mathbf{k}} | \tilde{p}_{q\mathbf{k}}^{I} \rangle Q_{qr}^{I}(\Delta\mathbf{k}) \langle \tilde{p}_{r\mathbf{k}+\Delta\mathbf{k}}^{I} | \tilde{u}_{n\mathbf{k}+\Delta\mathbf{k}} \rangle,$$

$$Q_{qr}^{I}(\Delta\mathbf{k}) = e^{-iI\cdot\Delta\mathbf{k}} \left[\langle \varphi_q^I | e^{-i\Delta\mathbf{k}\cdot(\mathbf{r}-I)} | \varphi_r^I \rangle - \langle \tilde{\varphi}_q^I | e^{-i\Delta\mathbf{k}\cdot(\mathbf{r}-I)} | \tilde{\varphi}_r^I \rangle \right].$$

Inclusion of a Finite Electric Field

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

- $\mathbf{P}$ is computed via PAW transform and discretization as above
- Generalized norm constraint is imposed: $\langle \psi_n | S | \psi_m \rangle = \delta_{nm}$
- On-site dipole contribution from T is included
- Form $\delta E / \delta \langle u_{m\mathbf{k}} |$ as gradient in conjugate gradient algorithm.

Code Additions

- Additional PAW terms added to `cgwf.F90` for conjugate gradient minimization
- Compute necessary $\langle \tilde{u}_{m\mathbf{k}} | \tilde{p}^{l}_{q\mathbf{k}} \rangle$ terms (“`cprj`”) by symmetry where possible:

$$\langle \tilde{p}^{l}_{j} | \Psi_{nR\mathbf{k}} \rangle = e^{i\mathbf{k}\cdot\mathbf{L}} \sum_{\alpha} D^{l_j}_{\alpha m_j}(R^{-1}) \langle \tilde{p}^{l'}_{n_j l_j \alpha} | \Psi_{n\mathbf{k}} \rangle,$$

  Currently works for `symmorphi 0` only
- Parallelized over k points

Applications

- Born effective charge: $Z^*_{j\alpha\beta} = dF_{j\alpha}/E_\beta$
- High frequency susceptibility: $\chi_{\alpha\beta} = dP_\alpha/dE_\beta$
- Low frequency susceptibility: same but with relaxation in field.

Compound	Z^*	ϵ^0	ϵ^∞
AlP (calc)	2.22	10.26	7.97
(expt)	2.28	9.8	7.5
AlAs (calc)	2.18	11.05	8.78
(expt)	2.20	10.16	8.16
AlSb (calc)	1.84	12.54	11.21
(expt)	1.93	11.68	9.88

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Problems and Advances

- Until 2005, best approach to magnetic fields in periodic insulators was the long wavelength approach of Louie and co-workers: $B \to B\cos(\mathbf{q}\cdot\mathbf{r})$ with $\mathbf{q} \to 0$.
- In 2005 and 2006, Ceresoli, Thonhauser, Resta, and Vanderbilt established:

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

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

Magnetic Translation Symmetry

- Recall gauge-dependent Hamiltonian:

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

- In 2010, Essin, Turner, Moore and Vanderbilt 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.

- They used this together with density operator perturbation theory to describe magneto-electric coupling.

$$\rho = \rho\rho \to \rho^1 = \rho^1\rho^0 + \rho^0\rho^1$$

A New Theory of Orbital Magnetic Susceptibility

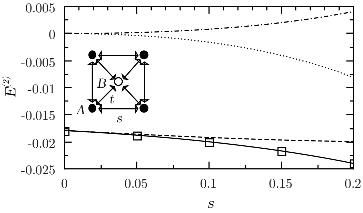
Based on the the previous ideas XG has developed a complete treatment of magnetic field response in a periodic insulator. Key new ingredient:

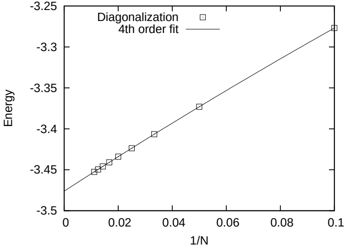
$$\begin{aligned}\tilde{T}_{\mathbf{k}} &= \tilde{V}_{\mathbf{k}}\tilde{W}_{\mathbf{k}} \\ &+ \sum_{m=1}^{\infty}\frac{1}{m!}\left(\frac{i}{2c}\right)^m\left(\prod_{n=1}^{m}\varepsilon_{\alpha_n\beta_n\gamma_n}B_{\alpha_n}\right) \\ &\quad\times(\partial_{\beta_1}\cdots\partial_{\beta_m}\tilde{V}_{\mathbf{k}})(\partial_{\gamma_1}\cdots\partial_{\gamma_m}\tilde{W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

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

Checking the Theory

Using the factorization formula in density operator perturbation theory, XG developed an expression for the energy to second order, hence orbital magnetic susceptibility.
We then checked it with a tight binding model: analytical versus numerical.





Implementing it all in ABINIT

Implementing the magnetization formula is fairly straightforward:

$$\langle \partial_{\mathbf{k}} u_{n'\mathbf{k}} | \times (H_{\mathbf{k}} \delta_{nn'} + E_{nn'\mathbf{k}}) | \partial_{\mathbf{k}} u_{n\mathbf{k}} \rangle$$

Derivatives are discretized, as in electric field case:

$$|\partial_{\mathbf{k}} u_{n\mathbf{k}}\rangle = \frac{1}{2}\left[|u_{n\mathbf{k}+\mathbf{b}}\rangle - |u_{n\mathbf{k}-\mathbf{b}}\rangle \right]$$

and

$$\langle u_{n\mathbf{k}_1} | H_{\mathbf{k}_2,\mathbf{k}_2} | u_{n\mathbf{k}_3} \rangle$$

which in the PAW case leads to computation of "phase-twisted" D_{ij} terms. Have completed kinetic energy, Hartree, and $\hat{D}$, v_{xc} is almost done.

Example Phase-twisted Term

See appendix of Torrent *et al.* Comp. Mater. Sci. **42**, 337 (2008):

$$\langle\phi_i|v_H[n^1]|\phi_j\rangle - \langle\tilde{\phi}_i|v_H[\tilde{n}^1]|\tilde{\phi}_j\rangle \rightarrow e^{i(\sigma_b\mathbf{k}_b-\sigma_k\mathbf{k}_k)\cdot\mathbf{I}}\langle\phi_i|e^{i(\sigma_b\mathbf{k}_b-\sigma_k\mathbf{k}_k)\cdot(\mathbf{r}-\mathbf{I})}v_H[n^1]|\phi_j\rangle - e^{i(\sigma_b\mathbf{k}_b-\sigma_k\mathbf{k}_k)\cdot\mathbf{I}}\langle\tilde{\phi}_i|e^{i(\sigma_b\mathbf{k}_b-\sigma_k\mathbf{k}_k)\cdot(\mathbf{r}-\mathbf{I})}v_H[\tilde{n}^1]|\tilde{\phi}_j\rangle \quad (1)$$

Finite magnetic field

- XG and I have also developed expressions for PAW energy in finite magnetic field and orbital current
- Will add to `cgwf.F90` and `outscfcv.F90` respectively
- Result will be current and hence NMR observables in insulators.

Summary

- Polarization and finite electric field in PAW are production-ready, parallelized over k points
- New theory of orbital magnetic susceptibility has been derived and fully checked
- PAW expressions for theory have been derived and mostly coded
- First stage outcome will be orbital currents and NMR shielding