Current density at finite $q$ for clamped-ion flexoelectricity

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arXiv 1802.06390, 1811.12893
Flexoelectricity: Polarization induced by strain gradient

\[ P_\alpha = \mu_{\alpha\beta\gamma\delta} \frac{\partial \varepsilon_{\beta\gamma}}{\partial r_\delta} \]

Types of strain gradients

- Longitudinal
- Shear
- Bending/Transverse

\( \eta_{1,11} \)
\( \varepsilon_{11,1} \)
\( \eta_{2,11} \)
\( \varepsilon_{12,1} = \varepsilon_{21,1} \)


Goal: Develop an efficient DFT implementation to calculate the full bulk flexoelectric response.
Previous implementations for calculating $\mu$ required supercells.


Previous implementations for calculating $\mu$ required supercells

Supercell calculations are computationally intensive.

We would like to obtain $\mu$ from linear response calculation on single unit cells

Part of the polarization response can be determined from charge density

\[ \nabla \cdot \mathbf{P}(\mathbf{r}) = -\rho(\mathbf{r}) \]

• Calculation of the charge density only provides the longitudinal response

For flexoelectric coefficients, implemented in:
M. Stengel, PRB, 90, 201112, (2014)
J. Hong and D. Vanderbilt, PRB 88, 174107 (2013)
Full polarization response can be determined from current

\[ J(r, t) = \frac{\partial P(r, t)}{\partial t} \]

- Calculation of the time-dependent current provides the full polarization response
Current density in DFT

• Magnetic susceptibility: $\mathbf{J}$ induced by $\mathbf{A}$
  Mauri and Louie, PRL 76, 4246 (1996)

• Dielectric susceptibility: $\mathbf{P}$ induced by $\mathbf{E}$

• NMR chemical shifts: Local $\mathbf{J}$ induced by external $\mathbf{B}$
  Pickard and Mauri, PRB 63, 245101 (2001)

• EPR $g$ tensor (SO): Local spin $\mathbf{J}$ induced by external $\mathbf{B}$
  Pickard and Mauri, PRL 88, 086403 (2002)

• Challenges for flexoelectric implementation:
  – Nonuniform perturbation (strain gradient)
  – Nonlocal pseudopotentials
Approach: Long-wavelength expansion of cell-periodic polarization

\[ P^{q}_{x,x} = P(x,x) - iq_{x} \left( \frac{\partial P^{q}_{x,x}}{\partial q_{x}} \right) + \frac{q_{x}^{2}}{2} \left( \frac{\partial^{2} P^{q}_{x,x}}{\partial q_{x}^{2}} \right) + \cdots \]

Born effective charge

CI Piezoelectric response

CI Flexoelectric response


Time-dependent current density

\[ \mathbf{J}(\mathbf{r}, t) = \sum_n \langle \Psi_n(t) | \hat{\mathbf{J}}(\mathbf{r}) | \Psi_n(t) \rangle \]

Need to define a current density operator

Need to treat time-dependent perturbation
Time dependence: Adiabatic expansion of the wavefunction

\[ \Psi(\lambda(t)) \propto \left( |\psi(\lambda)\rangle + \dot{\lambda} |\delta\psi\rangle \right) \]

First order adiabatic wavefunction from Density functional perturbation theory

\[
\Psi(\lambda(t)) \propto \left( |\psi(\lambda)\rangle + \dot{\lambda} |\delta \psi\rangle \right)
\]

First order Hamiltonian from phonon perturbation

\[
|\delta \psi_n\rangle = -i \sum_{m}^{\text{unocc}} \frac{|\psi_m\rangle \langle \psi_m | \Delta \lambda \hat{H} |\psi_n\rangle}{(\epsilon_n - \epsilon_m)^2}
\]

\[
(H - \epsilon_n) |\delta \psi_n\rangle = -i |\partial_\lambda \psi_n\rangle
\]

Time-dependent current density

• Adiabatic expansion of the time-dependent wavefunctions

\[ P^q = \sum_n \langle \psi_n | \hat{J}^q | \delta \psi_{nq} \rangle \]

Need to define cell-periodic current operator
Definition of microscopic current density via continuity condition

Continuity condition:
\[ \nabla \cdot \mathbf{J}(\mathbf{r}, t) = - \frac{\partial \rho(\mathbf{r})}{\partial t} \]

Schrödinger equation:
\[ i \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = H \Psi(\mathbf{r}, t) \]

\[ \downarrow \]

Quantum-mechanical microscopic current density:
\[ \mathbf{J}(\mathbf{r}, t) = - \frac{i}{2} [\Psi^*(\mathbf{r}, t) \nabla \Psi(\mathbf{r}, t) - \Psi(\mathbf{r}, t) \nabla \Psi^*(\mathbf{r}, t)] \]

Operator form:
\[ \hat{\mathbf{J}}(\mathbf{r}) = - \frac{1}{2} \{ |\mathbf{r}\rangle \langle \mathbf{r}|, \hat{\mathbf{p}} \} \]
Pseudopotentials involve nonlocal potentials

\[ \hat{V}_{\text{PSP}} = \hat{V}_{\text{local}} + \sum_{\zeta \ell m} |\phi_{\zeta \ell m}\rangle \langle \phi_{\zeta \ell m}| \]

Nonlocal potential operator

e.g., L. Kleinman and D.M. Bylander, Phys. Rev. Lett. 48, 1425 (1982).
Textbook current operator violates continuity condition for nonlocal $H$

$$\hat{V}_{PSP} = \hat{V}_{local} + \sum_{\zeta lm} |\phi_{\zeta lm}\rangle \langle \phi_{\zeta lm}|$$

$$\nabla \cdot \mathbf{J}(r, t) = -\frac{\partial \rho(r)}{\partial t}$$

$$\hat{J}(r) = -\frac{1}{2} \{ |r\rangle \langle r|, \hat{p} \}$$

C. Li, et al., Nanotechnology 19, 155401 (2008)
Textbook current operator violates continuity condition for nonlocal $H$

$$\hat{V}_{\text{PSP}} = \hat{V}_{\text{local}} + \sum_{\zeta l m} |\phi_{\zeta l m}\rangle \langle \phi_{\zeta l m}|$$

$$\nabla \cdot \mathbf{J}(\mathbf{r}, t) = -\frac{\partial \rho(\mathbf{r})}{\partial t}$$

Violates continuity condition in DFT with nonlocal pseudopotentials

C. Li, et al., Nanotechnology 19, 155401 (2008)
Replacing $p$ with $v$ gives only gives correct *macroscopic* current

$$\hat{V}_{PSP} = \hat{V}_{\text{local}} + \sum_{\zeta lm} |\phi_{\zeta lm}\rangle \langle \phi_{\zeta lm}|$$

$$\nabla \cdot \mathbf{J}(\mathbf{r}, t) = -\frac{\partial \rho(\mathbf{r})}{\partial t}$$

$$\hat{\mathcal{J}}(\mathbf{r}) = -\frac{1}{2} \{ |\mathbf{r}\rangle \langle \mathbf{r}|, \hat{\mathbf{v}} \} \quad \hat{\mathbf{v}} = -i \left[ \hat{\mathbf{r}}, \hat{H} \right]$$

Replacing $\mathbf{p}$ with $\mathbf{v}$ gives only gives correct macroscopic current

$$\hat{V}_{\text{PSP}} = \hat{V}_{\text{local}} + \sum_{\zeta l m} |\phi_{\zeta l m}\rangle \langle \phi_{\zeta l m}|$$

Correct macroscopic current, but we need microscopic current since we have a finite $\mathbf{q}$ (nonuniform) perturbation
Alternative def. of current density from electrodynamics

- Energy stored in a magnetic field:

\[ E = \frac{1}{2\mu_0} \int B^2 \, d^3r = \frac{1}{2} \int (\mathbf{A} \cdot \mathbf{J}) \, d^3r \]
Alternative def. of current density from electrodynamics

• Energy stored in a magnetic field:

\[
E = \frac{1}{2\mu_0} \int B^2 d^3 r = \frac{1}{2} \int (A \cdot J) d^3 r
\]

• We can define current operator:

\[
\mathbf{J}(r) = \frac{\partial E}{\partial A(r)} \Rightarrow \hat{\mathcal{J}}^q = \frac{\partial \hat{H}^A}{\partial A^q}
\]
Alternative def. of current density: Response to vector potential

\[ \mathbf{J}^q = \frac{\partial \hat{H}^A}{\partial A^q} \]

\[ \downarrow \]

\[ P^q = \sum_n \langle \psi_n | \frac{\partial \hat{H}^A}{\partial A^q} | \delta \psi_{nq} \rangle \]

• How to couple \( \mathbf{A} \) to \( \mathbf{H} \) with nonlocal potentials?

CED, M. Stengel, D. Vanderbilt, arXiv 1802.06390
Coupling \( A \) to nonlocal potentials

\[
H^A (r, r') = H (r, r') e^{-i \int_{r'}^r A \cdot d\ell}
\]

Coupling $A$ to nonlocal potentials

$$H^A(r, r') = H(r, r') - iH(r, r') \int_{r'}^{r} A \cdot d\ell + \cdots$$
Strategy: Use vector potential to probe response to phonon perturbation

- Vector potential:
  \[ A_\alpha(r) = A_\alpha^*(q)e^{-i\mathbf{q} \cdot \mathbf{r}} \]

- Hamiltonian:
  \[ H^A(r, r') = H(r, r')e^{-i \int_{r'}^{r} A \cdot dl} \]

- Current density operator:
  \[ \hat{J}(q) = \frac{\partial \hat{H}^A}{\partial A(q)} \]

CED, M. Stengel, D. Vanderbilt, arXiv 1802.06390
Strategy: Use vector potential to probe response to phonon perturbation

- Vector potential:
  \[ A_\alpha(r) = A^*_\alpha(q)e^{-iq \cdot r} \]

- Hamiltonian:
  \[ H^A(r, r') = H(r, r')e^{-i \int_{r'}^r A \cdot dl} \]

- Current density operator:
  \[ \langle r | \hat{J}(q) | r' \rangle = -iH(r, r')(r - r') \frac{e^{-iq \cdot r} - e^{-iq \cdot r'}}{iq \cdot (r - r')} \]

CED, M. Stengel, D. Vanderbilt, arXiv 1802.06390
What we need from our general microscopic current operator:

1. Satisfies the continuity equation

\[ \nabla \cdot \mathbf{J}(\mathbf{r}) = -\frac{\partial \rho(\mathbf{r})}{\partial t} \]

2. Reduces to the textbook expression outside of atomic spheres

3. Reproduces the known form of the macroscopic current

CED, M. Stengel, D. Vanderbilt,  arXiv 1802.06390
Summary of current-density implementation

• Polarization response:

\[
P_q = \sum_n \langle \psi_n | \hat{\mathcal{J}}_q^q | \delta \psi_{nq} \rangle
\]

• To second order in \( q \):

\[
\hat{P}_{q,\alpha,\kappa,\beta}^q = -\frac{4}{N_k} \sum_{nk} \left[ \langle u_{nk} \left| \hat{p}_\alpha \right| + \frac{q \alpha}{2} | \delta u_{nk,q}^{\kappa\beta} \rangle + \langle u_{nk} \left| \frac{\partial \hat{V}_{k,nl}}{\partial k_\alpha} \right| | \delta u_{nk,q}^{\kappa\beta} \rangle \right.
\]

\[
+ \frac{1}{2} \sum_{\gamma=1}^{3} q_{\gamma} \langle u_{nk} \left| \frac{\partial^2 \hat{V}_{k,nl}}{\partial k_\alpha \partial k_\gamma} \right| | \delta u_{nk,q}^{\kappa\beta} \rangle \right] + \frac{1}{6} \sum_{\gamma=1}^{3} \sum_{\xi=1}^{3} q_{\gamma} q_{\xi} \langle u_{nk} \left| \frac{\partial^3 \hat{V}_{k,nl}}{\partial k_\alpha \partial k_\gamma \partial k_\xi} \right| | \delta u_{nk,q}^{\kappa\beta} \rangle
\]

For $\mu_S$ (and $\mu_T$), two contributions to the flexo coefficients:

- Shear strain
- Rigid rotation

M. Stengel and D. Vanderbilt, arXiv 1806.05587
Rotation of a rigid charge density: Diamagnetic current

\[ J \propto \chi_{\text{mag}} \]

M. Stengel and D. Vanderbilt, arXiv 1806.05587
Alternative to removing $\chi$: “Metric” wave instead of phonon

CED, M. Stengel, D. Vanderbilt, *arXiv* 1802.06390
Computational details

- Density functional perturbation theory
- PBE generalized gradient functional
- Optimized norm-conserving Vanderbilt pseudopotentials
- Abinit code
Excellent agreement with previous supercell calculations (nC/m)

\[
\begin{align*}
\mu_{xx,xx} & = -0.87 \quad (-0.9^a, -0.88^b) \\
\mu_{xx,yy} & = -0.84 \quad (-0.83^b) \\
\mu_{xy,xy} & = -0.08 \quad (-0.08^b)
\end{align*}
\]

CED, M. Stengel, D. Vanderbilt, arXiv 1802.06390

Previous calculations:
(a) J. Hong and D. Vanderbilt, PRB 88, 174107 (2013)
(b) M. Stengel, PRB, 90, 201112, (2014)
Summary

- Implemented method to calculate current density at finite $q$
  - Couples nonlocal Hamiltonian to vector potential
  - Satisfies continuity condition for nonlocal pseudopotentials
  - Allows us to treat nonuniform perturbations

- Demonstrated the accuracy of the methodology by calculating flexoelectric coefficients

$$\mathbf{J}(\mathbf{r}) = \frac{\partial E}{\partial \mathbf{A}(\mathbf{r})} \Rightarrow \hat{\mathbf{J}}^q = \frac{\partial \hat{H}^A}{\partial \mathbf{A}^q}$$

$$\langle \mathbf{r} | \hat{\mathbf{J}}^q | \mathbf{r}' \rangle = -i \left[ \hat{\mathbf{r}}, \hat{H} \right]_{\mathbf{r}\mathbf{r}'} e^{-i \mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \frac{1}{i \mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')}$$