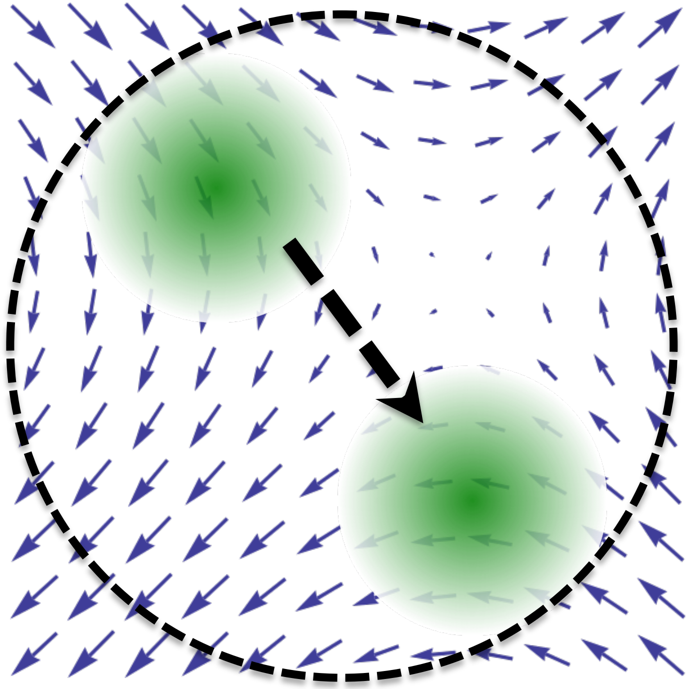
Current density at finite **q** for clamped-ion flexoelectricity



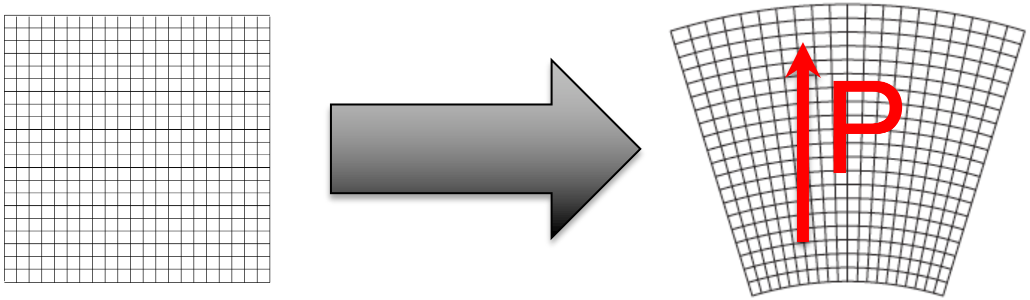
Cyrus E. Dreyer[1], Andrea Schiaffino[2], Massimiliano Stengel[2,3], David Vanderbilt[4]

1. FLATIRON INSTITUTE, Division of Simons Foundation; Stony Brook University
2. ICMAB, INSTITUT DE CIÈNCIA DE MATERIALS DE BARCELONA; EXCELENCIA SEVERO OCHOA; CSIC, CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS
3. ICREA
4. RUTGERS

Office of Naval Research, Science & Technology

arXiv **1802.06390, 1811.12893**

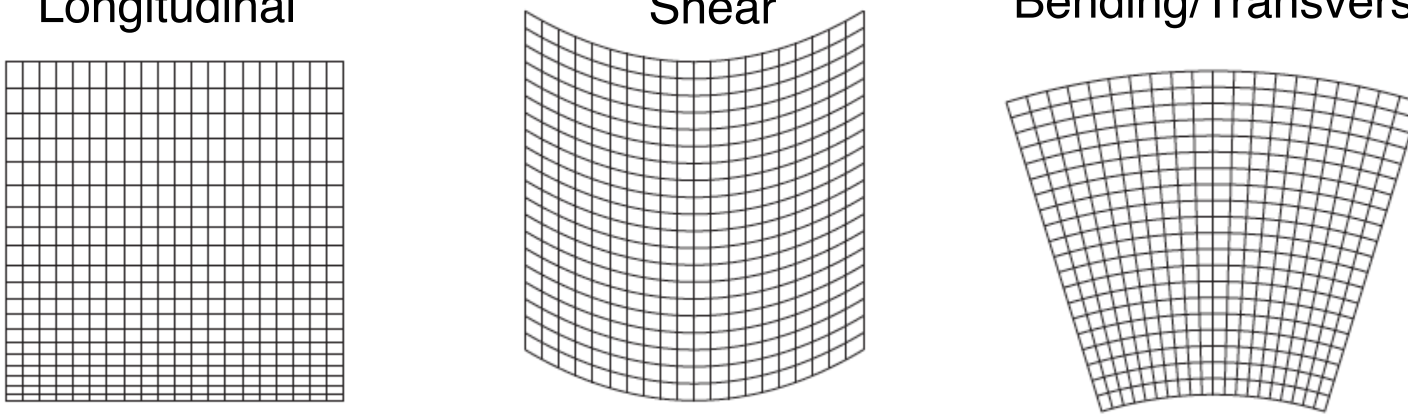
Flexoelectricity: Polarization induced by **strain gradient**



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

Types of strain gradients

Longitudinal | Shear | Bending/Transverse



$\eta_{1,11}$
$\varepsilon_{11,1}$

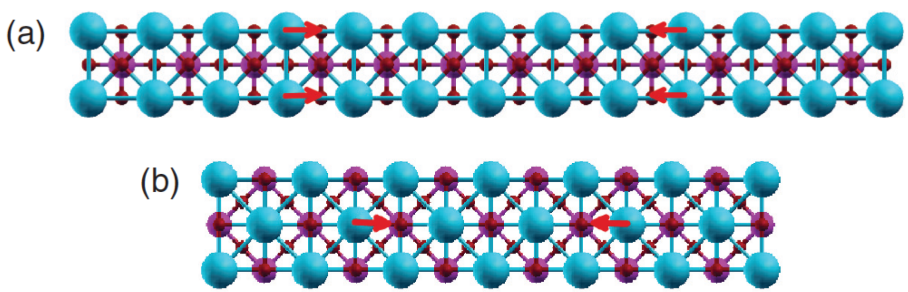
$\eta_{2,11}$
$\varepsilon_{12,1} = \varepsilon_{21,1}$

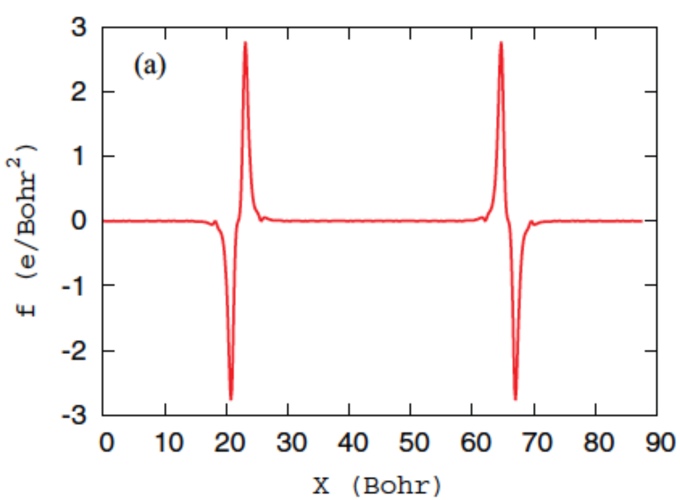
$\varepsilon_{11,2}$

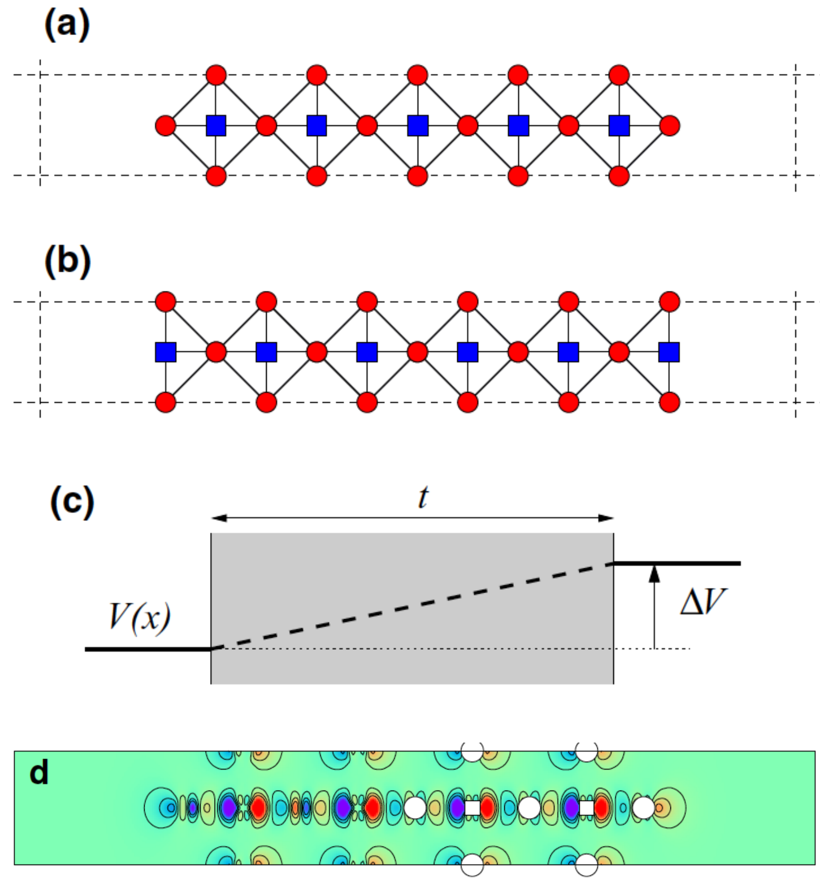
M. Stengel, Phys. Rev. B **88**, 174106 (2013).

Goal: Develop an *efficient* DFT implementation to calculate the full bulk flexoelectric response.

Previous implementations for calculating μ required supercells



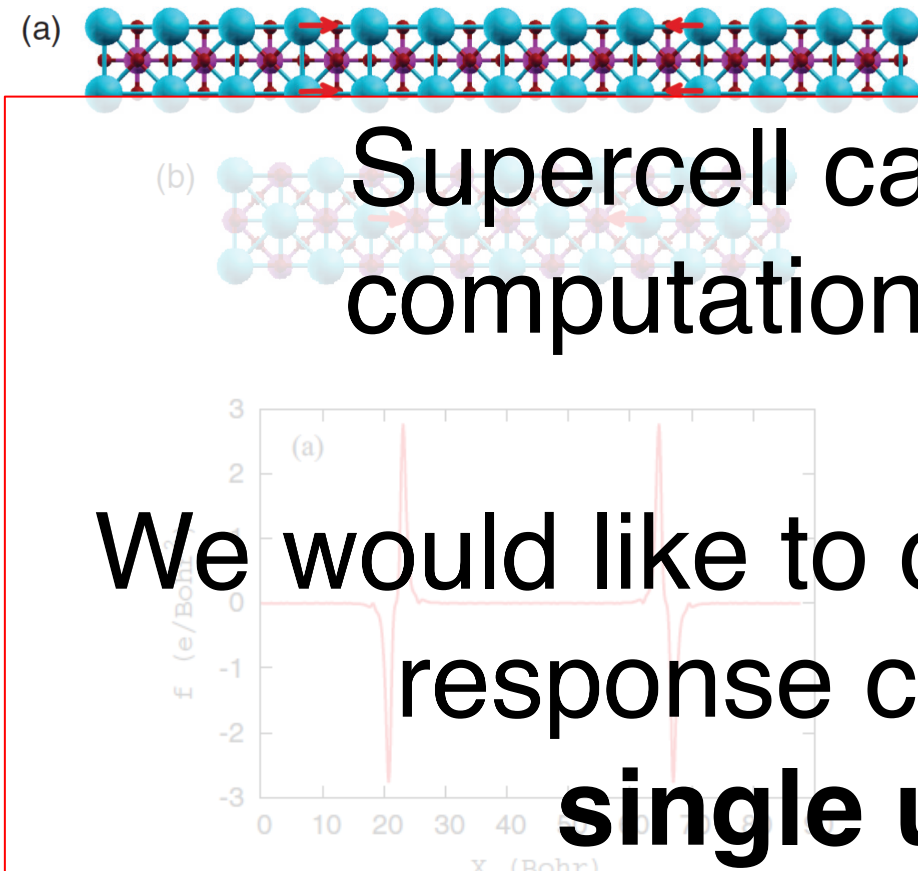


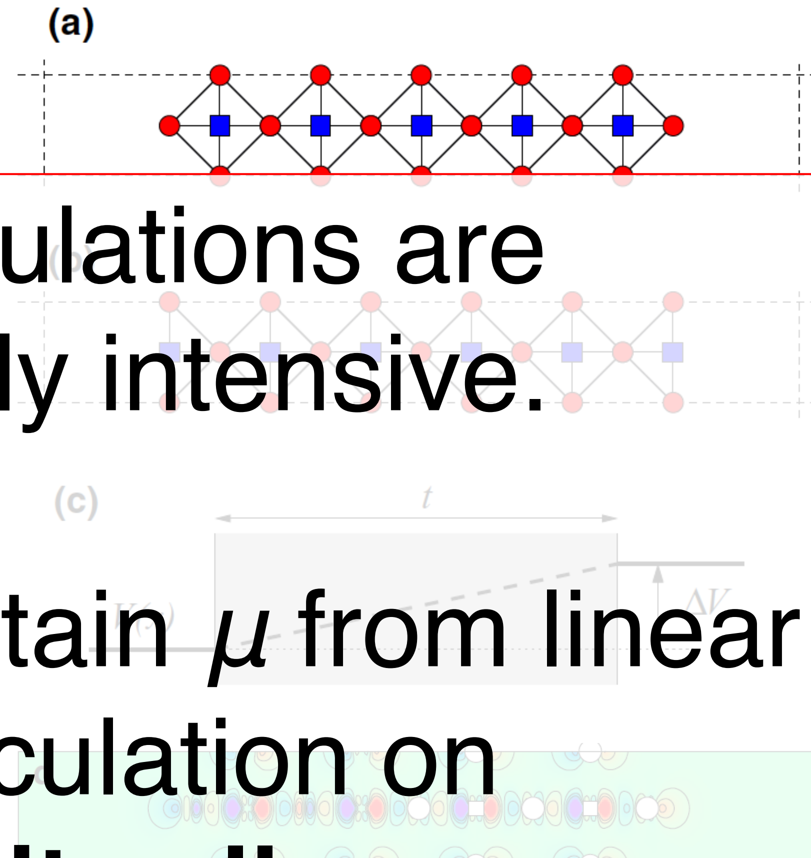


J. Hong and D. Vanderbilt,
Phys. Rev. B **88**, 174107 (2013).

M. Stengel,
Phys. Rev. B, **90**, 201112, (2014).

Previous implementations for calculating μ required supercells





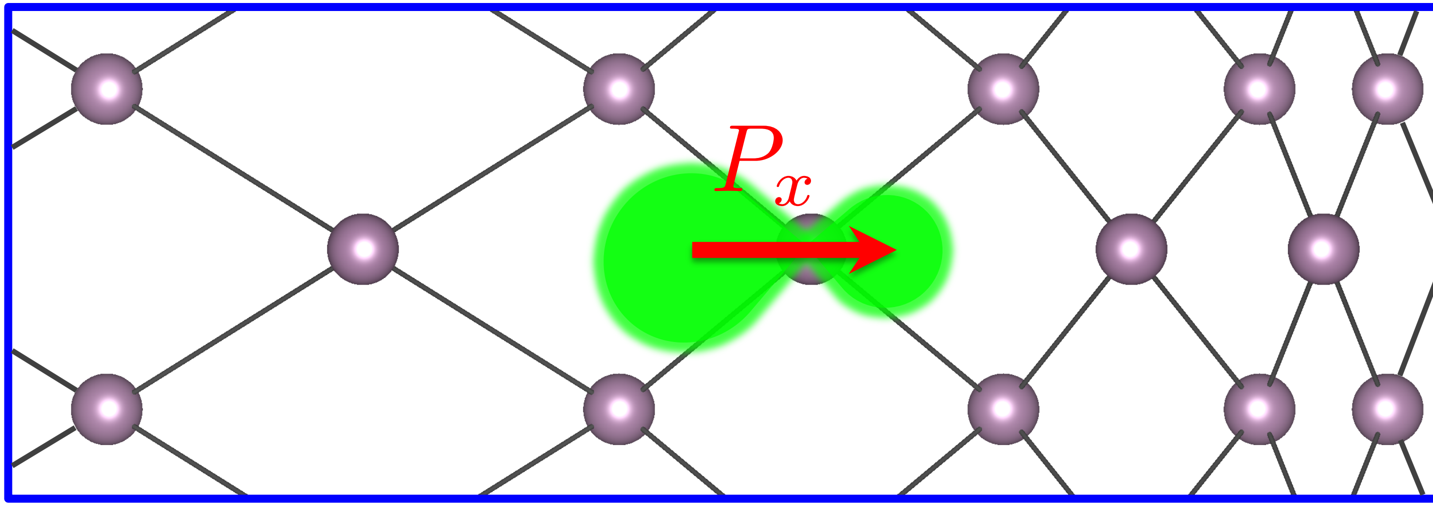
Supercell calculations are computationally intensive.

We would like to obtain μ from linear response calculation on **single unit cells**

J. Hong and D. Vanderbilt, Phys. Rev. B **88**, 174107 (2013).

M. Stengel, Phys. Rev. B, **90**, 201112, (2014).

Part of the polarization response can be determined from charge density

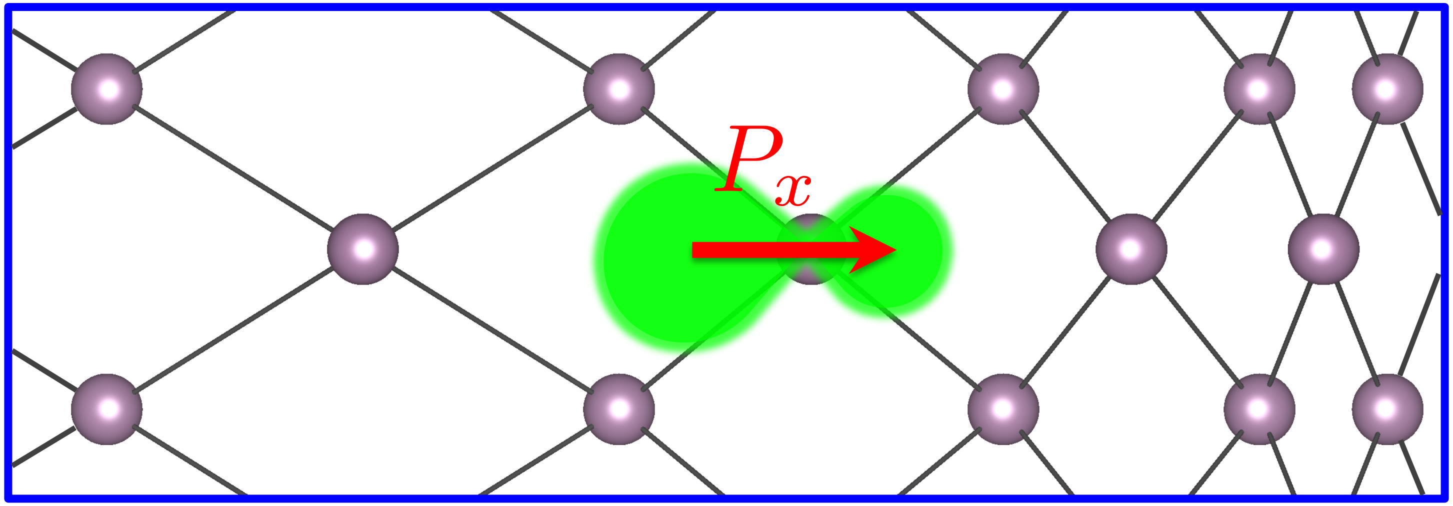


$$\nabla \cdot \mathbf{P}(\mathbf{r}) = -\rho(\mathbf{r})$$

- 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



$$\mathbf{J}(\mathbf{r},t) = \frac{\partial \mathbf{P}(\mathbf{r},t)}{\partial t}$$

- Calculation of the time-dependent **current** provides the **full** polarization response

Current density in DFT

- Magnetic susceptibility: **J** induced by **A**

  Mauri and Louie, PRL **76**, 4246 (1996)

- Dielectric susceptibility: **P** induced by **E**

  Umari, Dal Corso, and Resta, AIP Conf. Proc., **582**, 107 (2001).

- NMR chemical shifts: Local **J** induced by external **B**

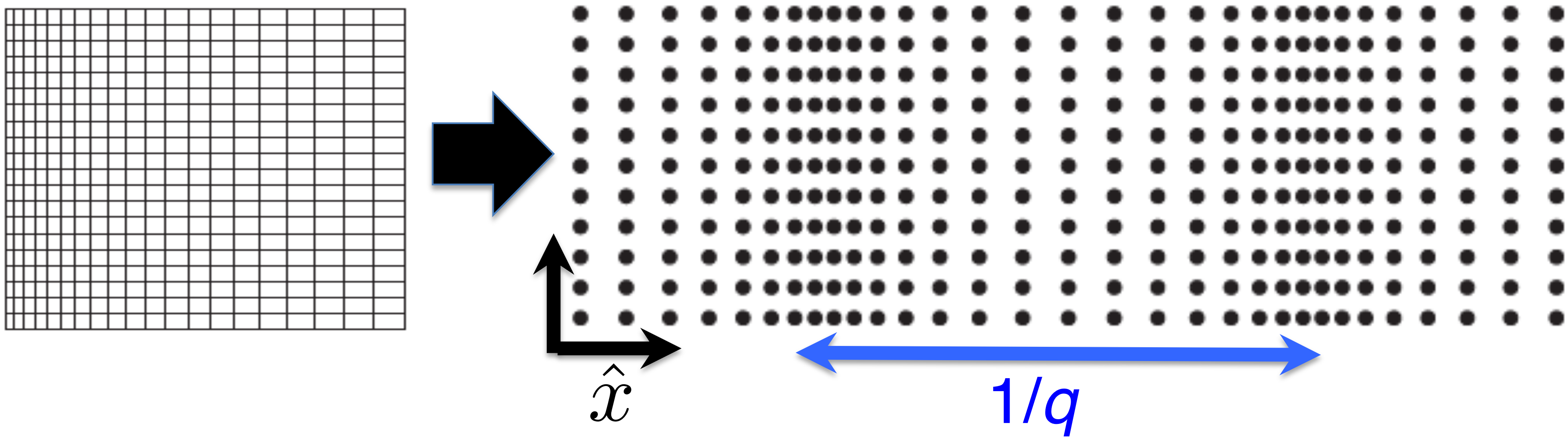
  Pickard and Mauri, PRB **63**, 245101 (2001)

- EPR *g* tensor (SO): Local spin **J** induced by external **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



$$P^{\mathbf{q}}_{x,x} = P^{(\mathbf{q}=0)}_{x,x} - i q_x \left. \frac{\partial P^{\mathbf{q}}_{x,x}}{\partial q_x} \right|_{\mathbf{q}=0} - \frac{q_x^2}{2} \left. \frac{\partial^2 P^{\mathbf{q}}_{x,x}}{\partial q_x^2} \right|_{\mathbf{q}=0} + \cdots$$

Born effective charge

CI Piezoelectric response

CI Flexoelectric response

M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford Univ. Press, Oxford, 1954)

R. M. Martin, Phys. Rev. B 5,1607 (1972)

M. Stengel, Phys. Rev. B 88, 174106 (2013

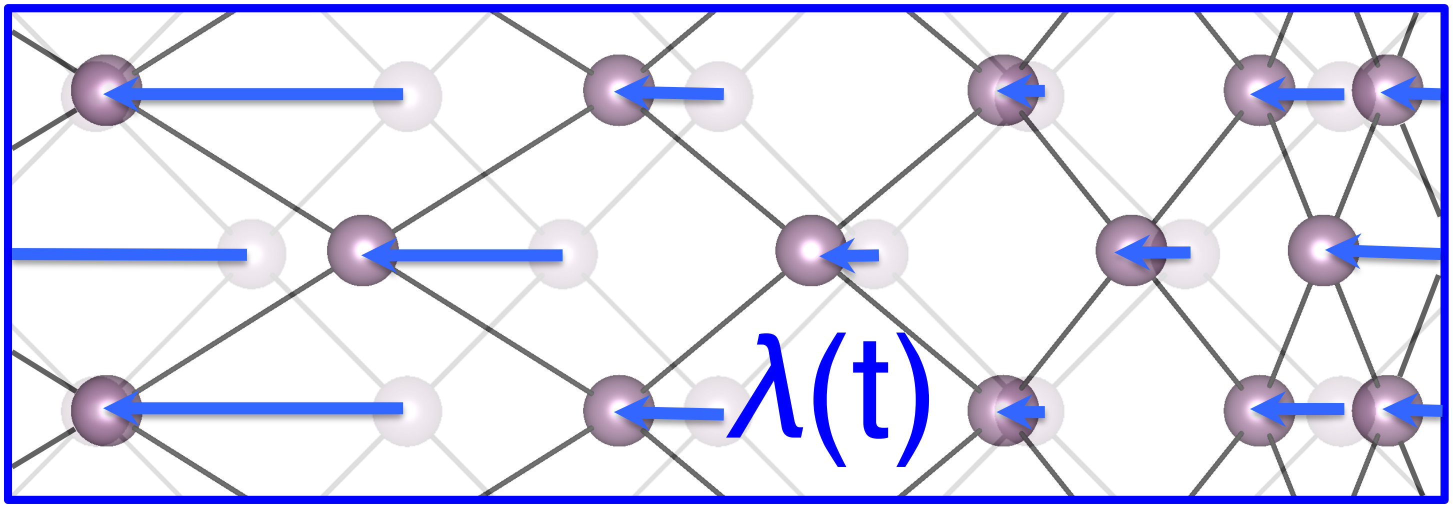
Time-dependent current density

Need to treat time-dependent perturbation

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

Need to define a current density operator

Time dependence: Adiabatic expansion of the wavefunction



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

Time-dependent atomic displacements

Static eigenfunction at λ

Adiabatic, first order wavefunction

Thouless, Phys. Rev. B **27**, 6083 (1983)

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

$$|\delta\psi_n\rangle = -i \sum_m^{\text{unocc}} \frac{|\psi_m\rangle\langle\psi_m|\Delta_\lambda \hat{H}|\psi_n\rangle}{(\epsilon_n - \epsilon_m)^2}$$

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

Thouless, Phys. Rev. B **27**, 6083 (1983)
P. Umari, *et al.*, AIP Conference Proceedings **582**, 107 (2001)

Time-dependent current density

- Adiabatic expansion of the time-dependent wavefunctions

$$\mathbf{P}^{\mathbf{q}} = \sum_n \langle \psi_n | \hat{\mathcal{J}}^{\mathbf{q}} | \delta\psi_{n\mathbf{q}} \rangle$$

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:

$$i\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = H\Psi(\mathbf{r},t)$$

$$\Downarrow$$

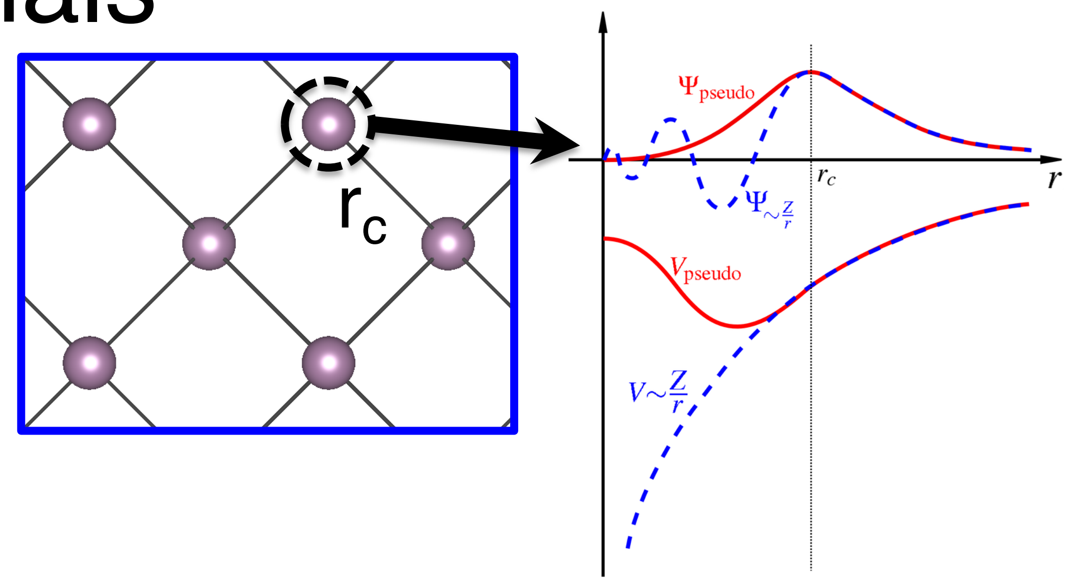
Quantum-mechanical microscopic current density:

$$\mathbf{J}(\mathbf{r},t) = -\frac{i}{2}\left[\Psi^*(\mathbf{r},t)\nabla\Psi(\mathbf{r},t) - \Psi(\mathbf{r},t)\nabla\Psi^*(\mathbf{r},t)\right]$$

Operator form:

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

Pseudopotentials involve **nonlocal** potentials



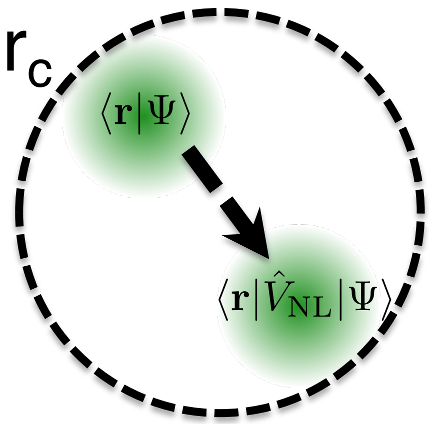
wikipedia

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

e.g., L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

Textbook current operator violates continuity condition for nonlocal *H*

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



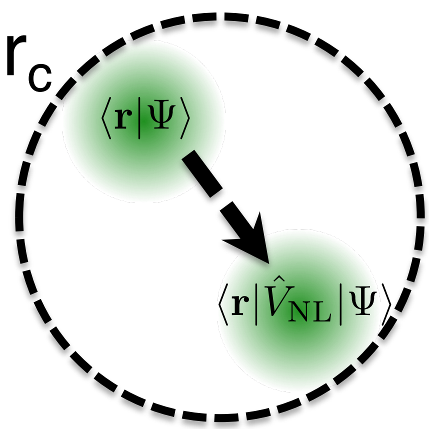
$$\nabla \cdot \mathbf{J}(\mathbf{r},t) = -\frac{\partial \rho(\mathbf{r})}{\partial t} \quad ?$$

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

C. Li, *et al.*, Nanotechnology **19,** 155401 (2008)

Textbook current operator violates continuity condition for nonlocal *H*

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



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

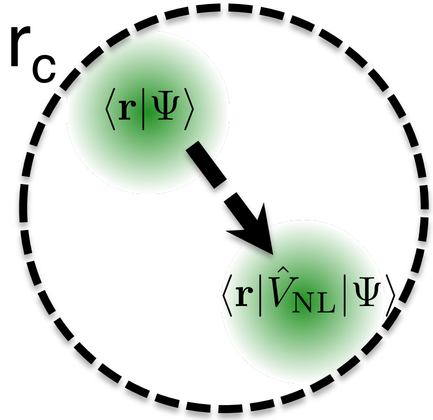
$$\mathcal{J}(\mathbf{r}) = -\frac{1}{2}\{|\mathbf{r}\rangle\langle\mathbf{r}|, \mathbf{p}\}$$

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

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



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

?

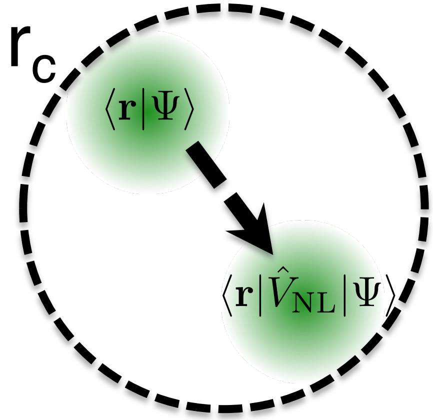
$$\hat{\mathcal{J}}(\mathbf{r}) = -\frac{1}{2}\left\{|\mathbf{r}\rangle\langle\mathbf{r}|, \hat{\mathbf{v}}\right\} \qquad \hat{\mathbf{v}} = -i\left[\hat{\mathbf{r}}, \hat{H}\right]$$

?

C. Li, *et al.*, Nanotechnology **19,** 155401 (2008)

Replacing **p** with **v** gives only gives correct *macroscopic* current

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



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

?

Correct **macroscopic** current, but we need **microscopic** current since we have a finite **q** (nonuniform) perturbation

C. Li, *et al.*, Nanotechnology **19,** 155401 (2008)

Alternative def. of current density from electrodynamics

- Energy stored in a magnetic field:

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

Alternative def. of current density from electrodynamics

- Energy stored in a magnetic field:

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

- We can define current operator:

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

Alternative def. of current density: Response to vector potential

$$\hat{\mathcal{J}}^{\mathbf{q}} = \frac{\partial \hat{H}^{\mathbf{A}}}{\partial \mathbf{A}^{\mathbf{q}}}$$

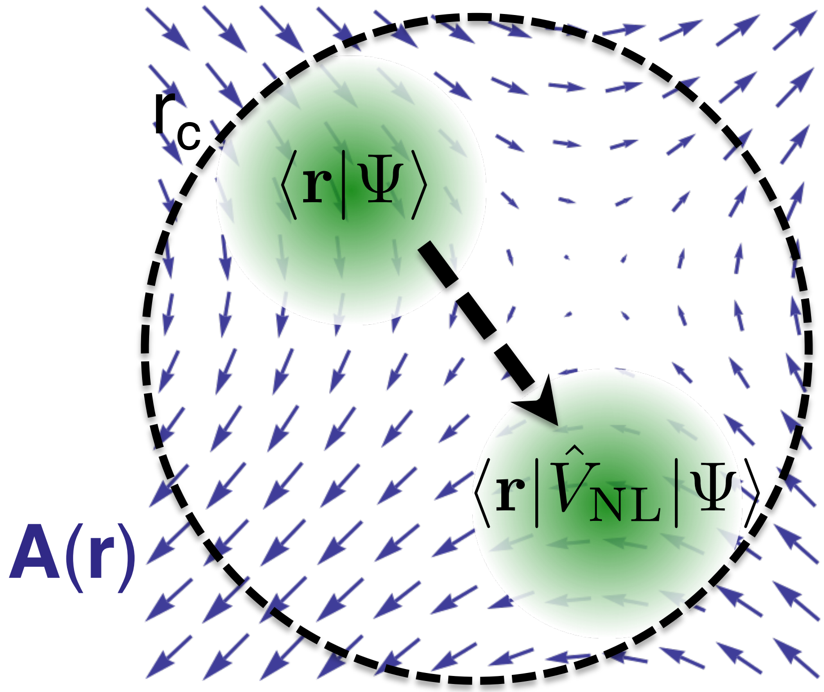
$$\Downarrow$$

$$\mathbf{P}^{\mathbf{q}} = \sum_n \langle \psi_n | \frac{\partial \hat{H}^{\mathbf{A}}}{\partial \mathbf{A}^{\mathbf{q}}} | \delta\psi_{n\mathbf{q}} \rangle$$

- How to couple **A** to *H* with nonlocal potentials?

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

Coupling **A** to nonlocal potentials

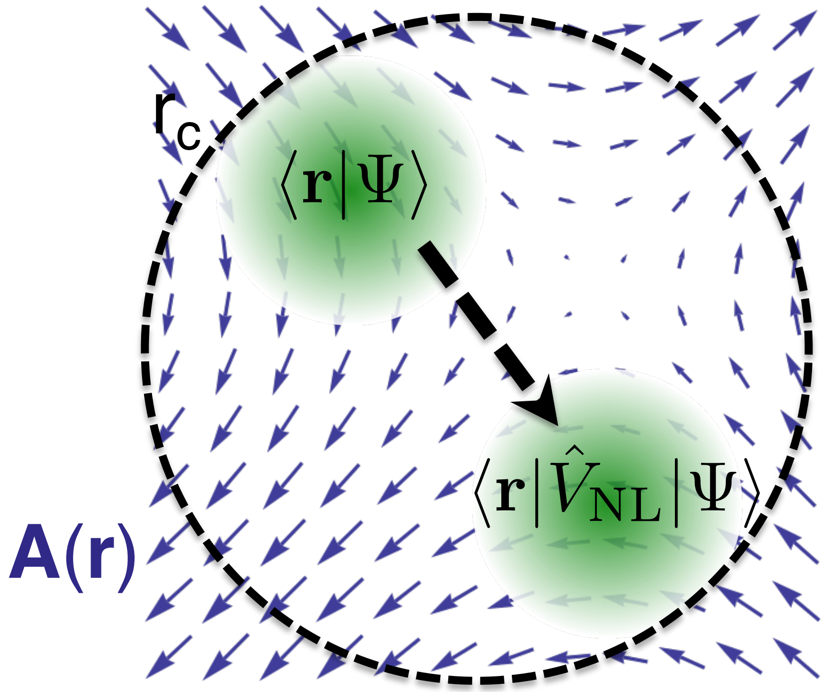


Path integral from **r** to **r’**

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

S. Ismail-Beigi, *et al.*, Phys. Rev. Lett. **87**, 087402 (2001)
C. Pickard and F. Mauri, Phys. Rev. Lett. **88**, 086403 (2002)
A. M. Essin, *et al.*, Phys. Rev. B **81,** 205104 (2010)

Coupling **A** to nonlocal potentials



$$H^{\mathbf{A}}(\mathbf{r},\mathbf{r}') = H(\mathbf{r},\mathbf{r}') - iH(\mathbf{r},\mathbf{r}') \int_{\mathbf{r}'}^{\mathbf{r}} \mathbf{A} \cdot d\ell + \cdots$$

Strategy: Use vector potential to probe response to phonon perturbation

- Vector potential:

$$A_\alpha(\mathbf{r}) = A^*_\alpha(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{r}}$$

- Hamiltonian:

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

- Current density operator:

$$\hat{\boldsymbol{\mathcal{J}}}(\mathbf{q}) = \frac{\partial \hat{H}^{\mathbf{A}}}{\partial \mathbf{A}(\mathbf{q})}$$

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

Strategy: Use vector potential to probe response to phonon perturbation

- Vector potential:

$$A_\alpha(\mathbf{r}) = A^*_\alpha(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{r}}$$

- Hamiltonian:

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

- Current density operator:

$$\langle \mathbf{r} | \hat{\boldsymbol{\mathcal{J}}}(\mathbf{q}) | \mathbf{r}' \rangle = -iH(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}') \frac{e^{-i\mathbf{q}\cdot\mathbf{r}} - e^{-i\mathbf{q}\cdot\mathbf{r}'}}{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}$$

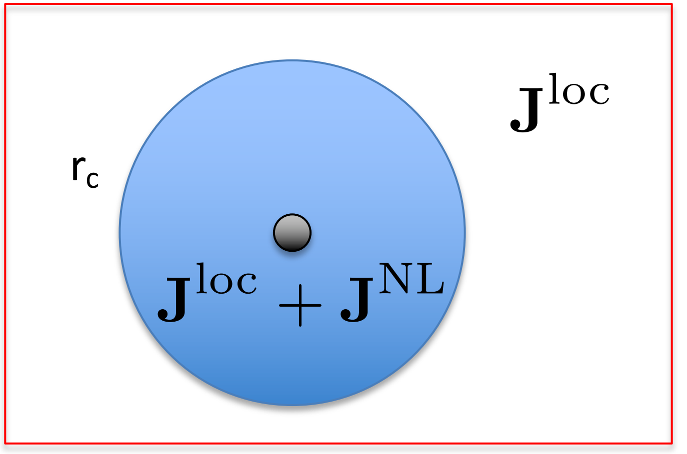
CED, M. Stengel, D. Vanderbilt, *arXiv* 1802.06390

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

$$\langle \mathbf{J} \rangle = -e \langle \mathbf{v} \rangle$$

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

Summary of current-density implementation

- Polarization response:

$$\mathbf{P}^{\mathbf{q}} = \sum_n \langle \psi_n | \hat{\boldsymbol{\mathcal{J}}}^{\mathbf{q}} | \delta\psi_{n\mathbf{q}} \rangle$$

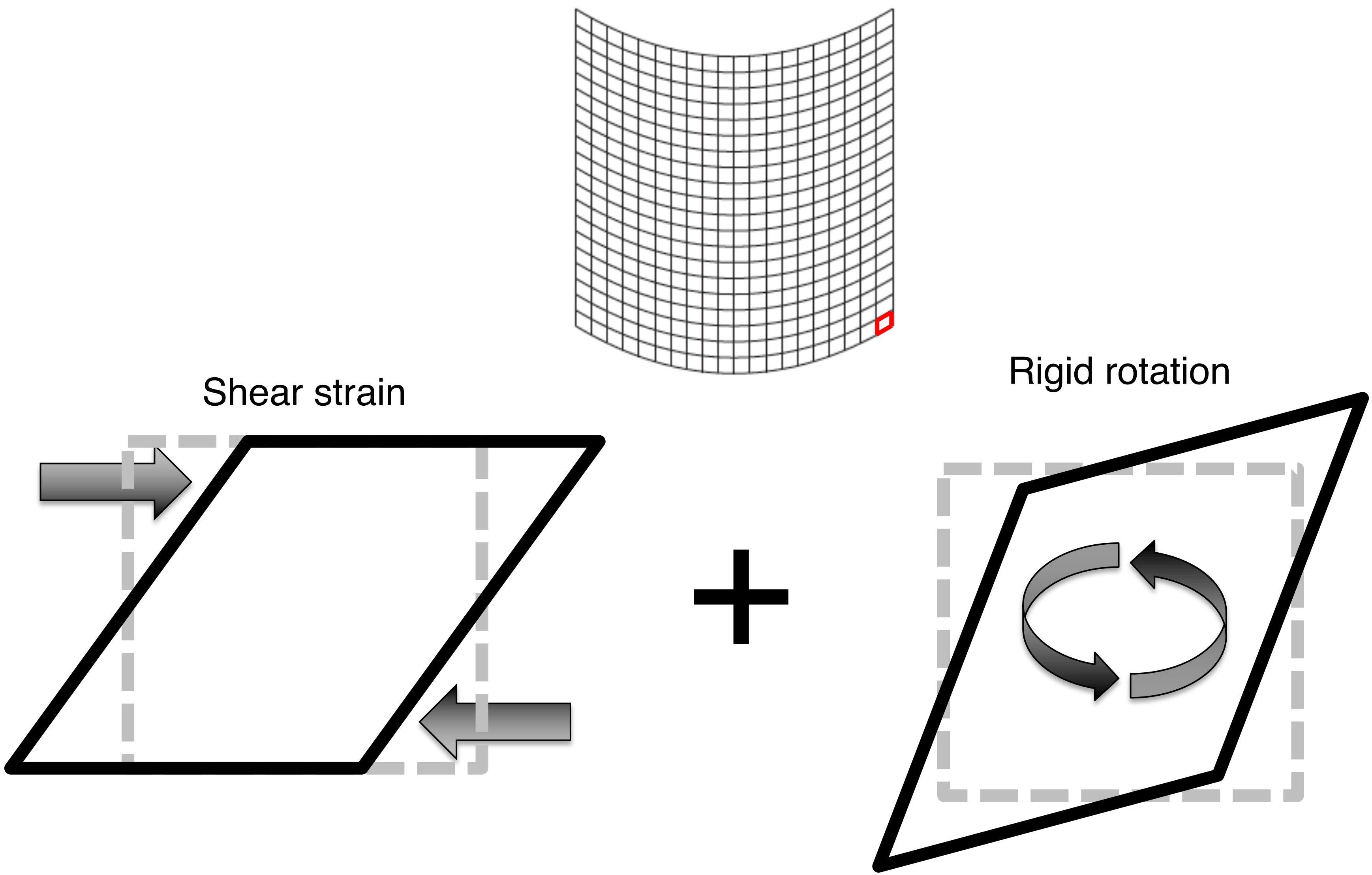
- To second order in **q**:

Local part d/d**k** derivatives

$$\overline{P}^{\mathbf{q}}_{\alpha,\kappa\beta} = -\frac{4}{N_k}\sum_{n\mathbf{k}}\Bigg[\langle u_{n\mathbf{k}}|\hat{p}^{\mathbf{k}}_{\alpha} + \frac{q_\alpha}{2}|\delta u^{\kappa\beta}_{n\mathbf{k},\mathbf{q}}\rangle + \langle u_{n\mathbf{k}}|\frac{\partial \hat{V}^{\mathbf{k},\mathrm{nl}}}{\partial k_\alpha}|\delta u^{\kappa\beta}_{n\mathbf{k},\mathbf{q}}\rangle$$
$$+\frac{1}{2}\sum_{\gamma=1}^{3} q_\gamma \langle u_{n\mathbf{k}}|\frac{\partial^2 \hat{V}^{\mathbf{k},\mathrm{nl}}}{\partial k_\alpha \partial k_\gamma}|\delta u^{\kappa\beta}_{n\mathbf{k},\mathbf{q}}\rangle + \frac{1}{6}\sum_{\gamma=1}^{3}\sum_{\xi=1}^{3} q_\gamma q_\xi \langle u_{n\mathbf{k}}|\frac{\partial^3 \hat{V}^{\mathbf{k},\mathrm{nl}}}{\partial k_\alpha \partial k_\gamma \partial k_\xi}|\delta u^{\kappa\beta}_{n\mathbf{k},\mathbf{q}}\rangle\Bigg]$$

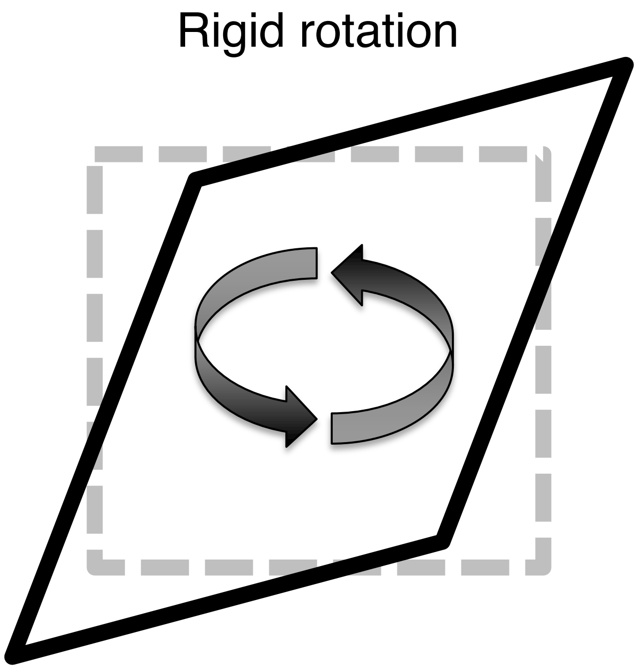
Phys. Rev. B **98**, 075153 (2018)

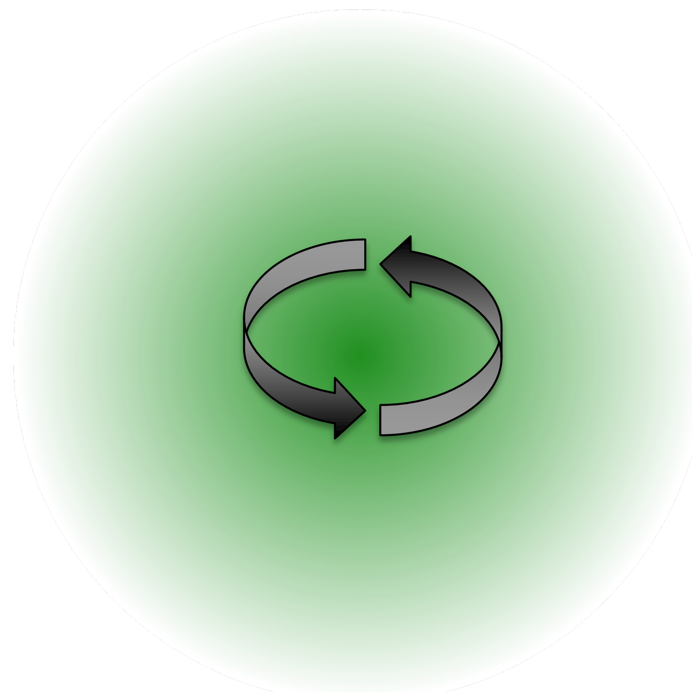
For μ_S (and μ_T), two contributions to the flexo coefficients:



M. Stengel and D. Vanderbilt, arXiv 1806.05587

Rotation of a rigid charge density: Diamagnetic current

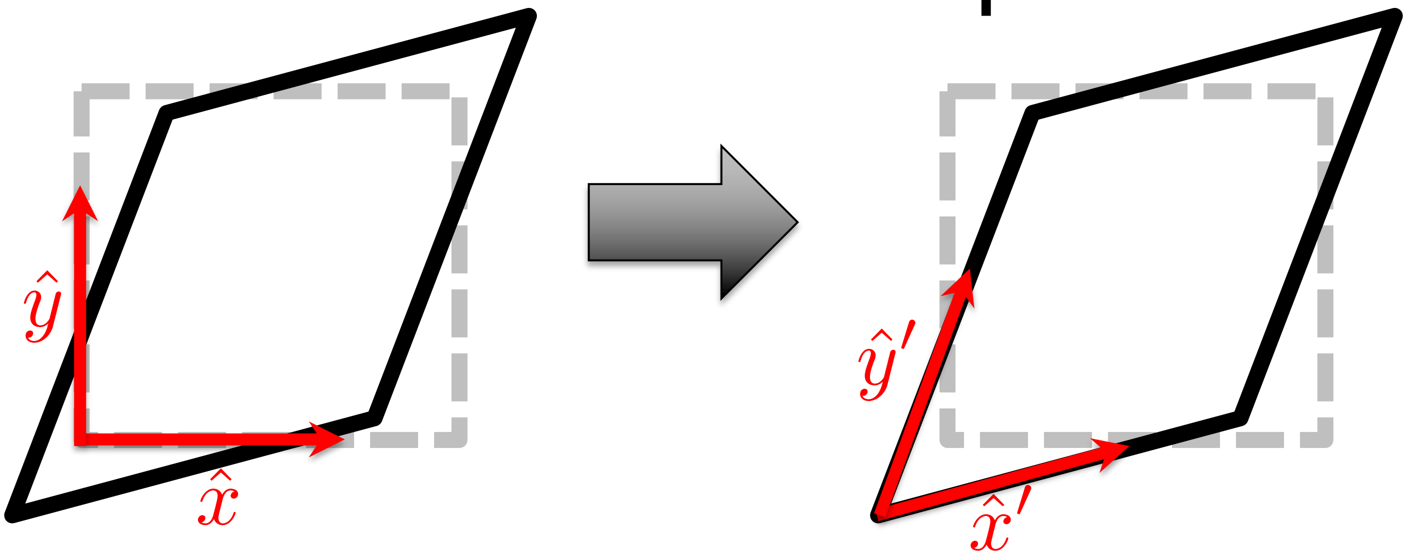


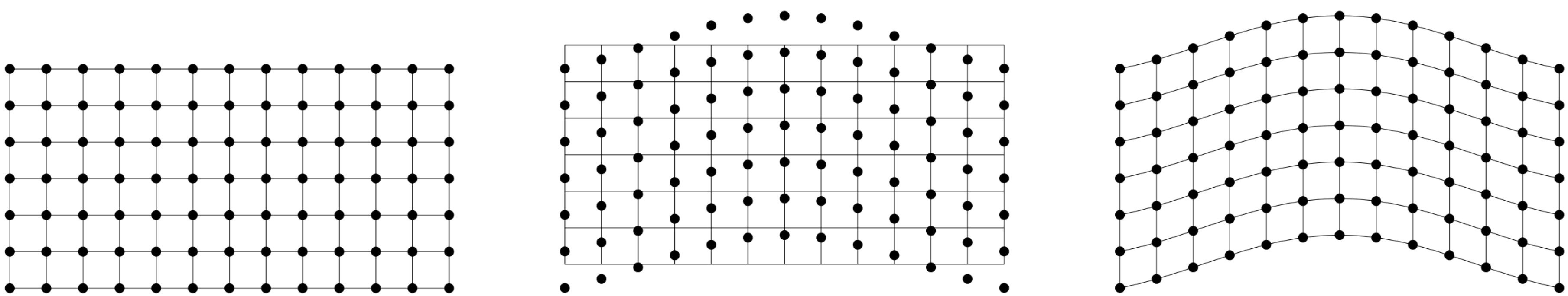


$$\mathbf{J} \propto \chi_{\rm mag}$$

M. Stengel and D. Vanderbilt, arXiv 1806.05587

Alternative to removing χ: "Metric" wave instead of phonon





(a) (b) (c)

CED, M. Stengel, D. Vanderbilt, *arXiv* 1802.06390
A. Schiaffino, **CED**, D. Vanderbilt, and M. Stengel, *arXiv:* 1811.12893

Computational details

- Density functional perturbation theory
- PBE generalized gradient functional

J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996)

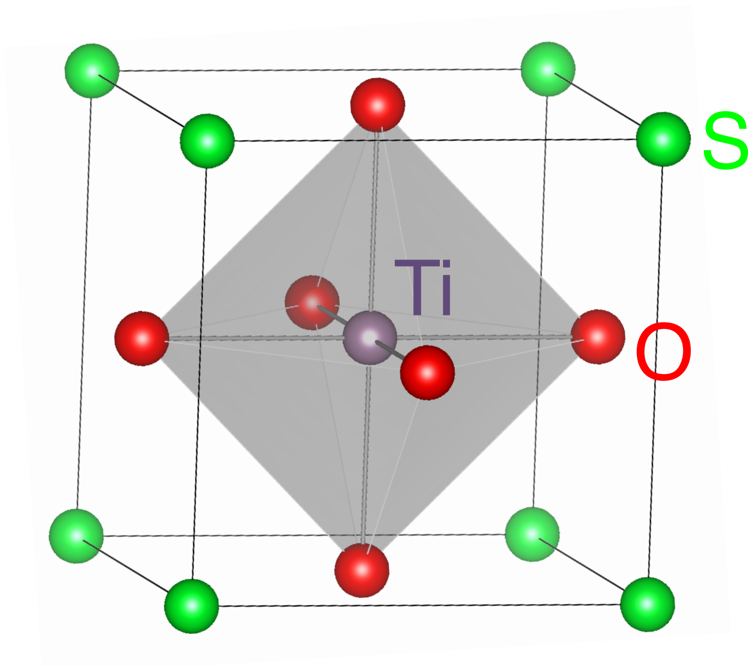
- Optimized norm-conserving Vanderbilt pseudopotentials

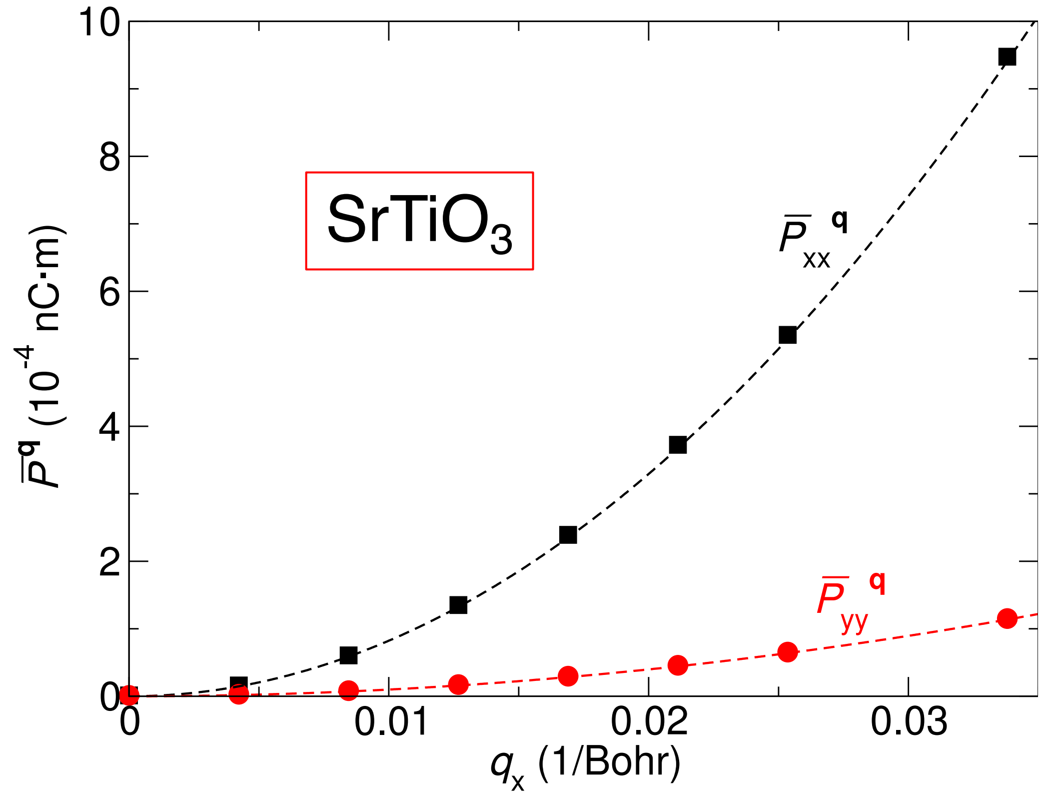
D. R. Hamann, Phys. Rev. B **88**, 085117 (2013)

- Abinit code

X. Gonze, *et al.,* Computer Physics Commun. **180**, 2582 (2009)

Excellent agreement with previous supercell calculations (nC/m)





$\mu_{xx,xx}$	$\mu_{xx,yy}$	$\mu_{xy,xy}$
-0.87 (-0.9^a, -0.88^b)	-0.84 (-0.83^b)	-0.08 (-0.08^b)

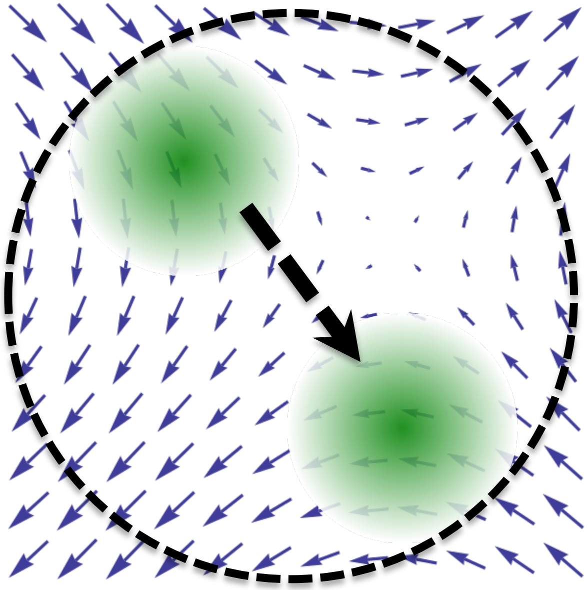
CED, M. Stengel, D. Vanderbilt, *arXiv* 1802.06390

Previous calculations:

(a) J. Hong and D. Vanderbilt, PRB **88**, 174107 (2013)

(b) M. Stengel, PRB, **90**, 201112, (2014)

Summary



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

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

- 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

arXiv **1802.06390, 1811.12893**