# Spatial dispersion effects via long-wave DFPT

ICREA

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CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS
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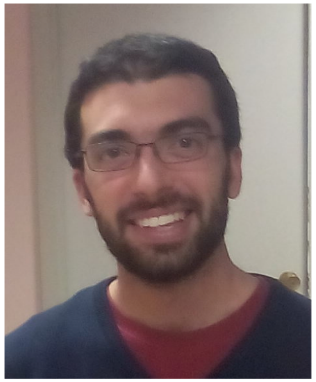

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Cyrus Dreyer

David Vanderbilt

# Spatial dispersion

Real space: Response to a gradient of the applied field
Reciprocal space: **q**-dependence of the response function

## OPTICAL RESPONSE

$$\sigma_{ab}(\mathbf{q},\omega) = \sigma^{(0)}_{ab}(\omega) + \sigma_{abc}(\omega) q_c + \cdots$$

*Magneto-electric (ME)*
*Natural optical activity*

R. M. Hornreich and S. Shtrikman, Phys. Rev. **171**, 1065 (1968)
A. Malashevich and I. Souza, Phys. Rev. B **82**, 245118 (2010)

## ELASTICITY

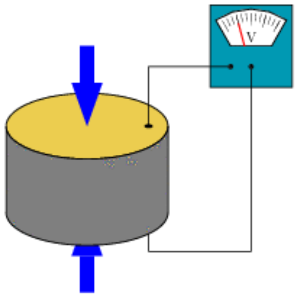
$$c_{ij}(\omega,\mathbf{k}) = c_{ij}(\omega) + i d_{ij,l}(\omega) k_l + e_{ij,lm}(\omega) k_l k_m + \cdots$$

*Acoustical activity*

D. Portigal and E. Burstein, Phys. Rev. **170**, 673 (1968)

# Electromechanical response

## PIEZOELECTRICITY



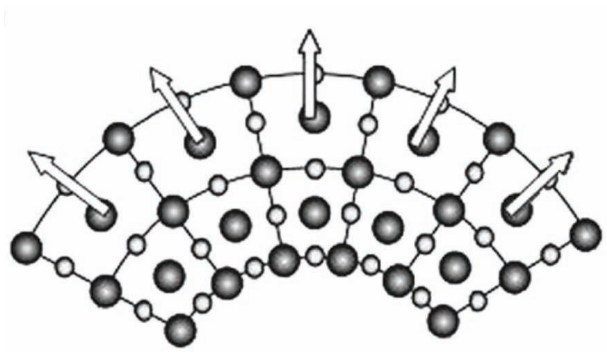
$$P_\alpha = e_{\alpha\beta\gamma}\varepsilon_{\beta\gamma}$$

**P** response to uniform strain

Few materials display this effect

Size-independent property

## FLEXOELECTRICITY



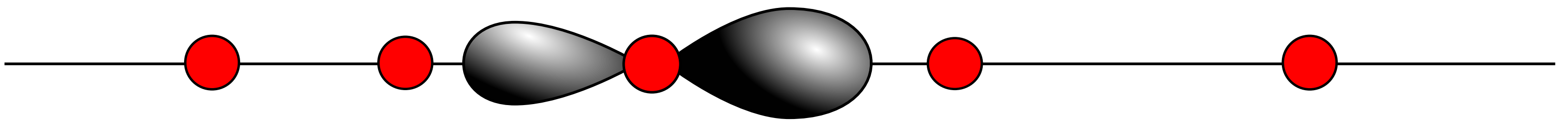
$$P_\alpha = \mu_{\alpha\lambda\beta\gamma}\frac{\partial \varepsilon_{\beta\gamma}}{\partial r_\lambda}$$

**P** response to **strain gradient**

**Universal** property of all materials

Scales as the inverse of the sample size

# How to calculate **μ** from first principles?



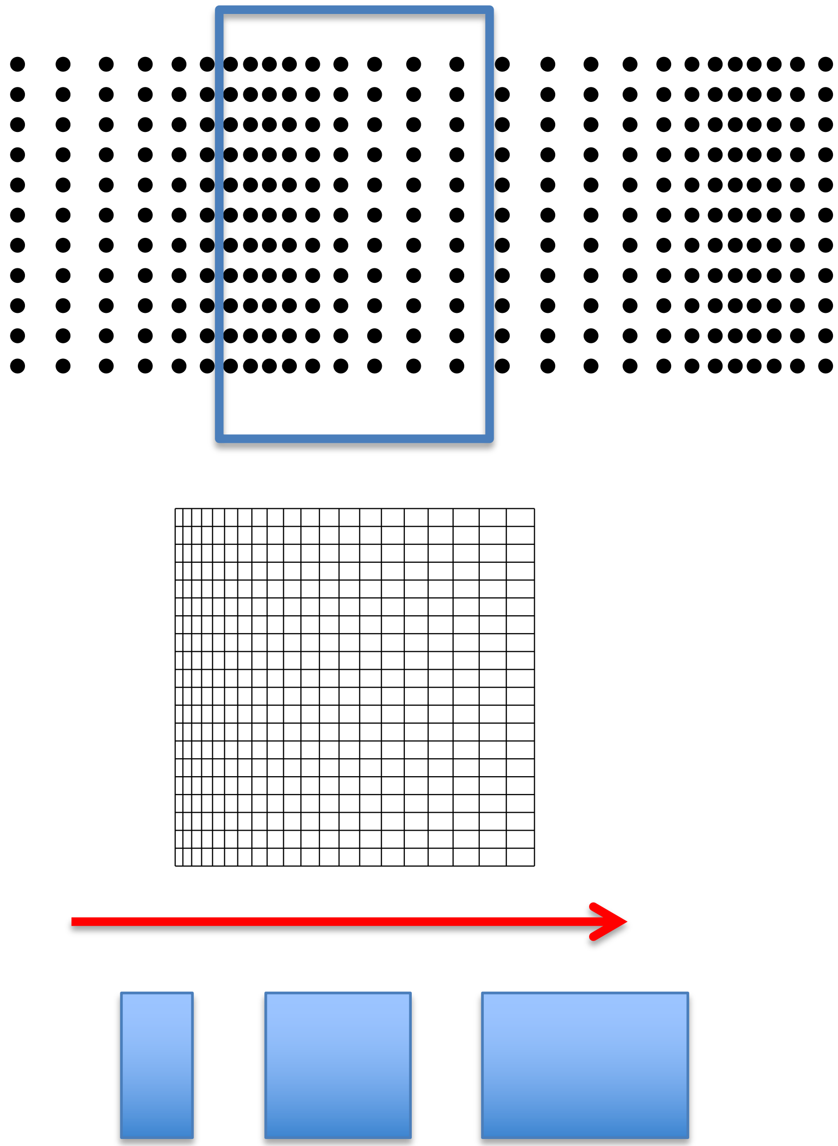
PROBLEM: Translational symmetry is broken!

Cannot use periodic boundary conditions, Bloch theorem, plane waves, etc.

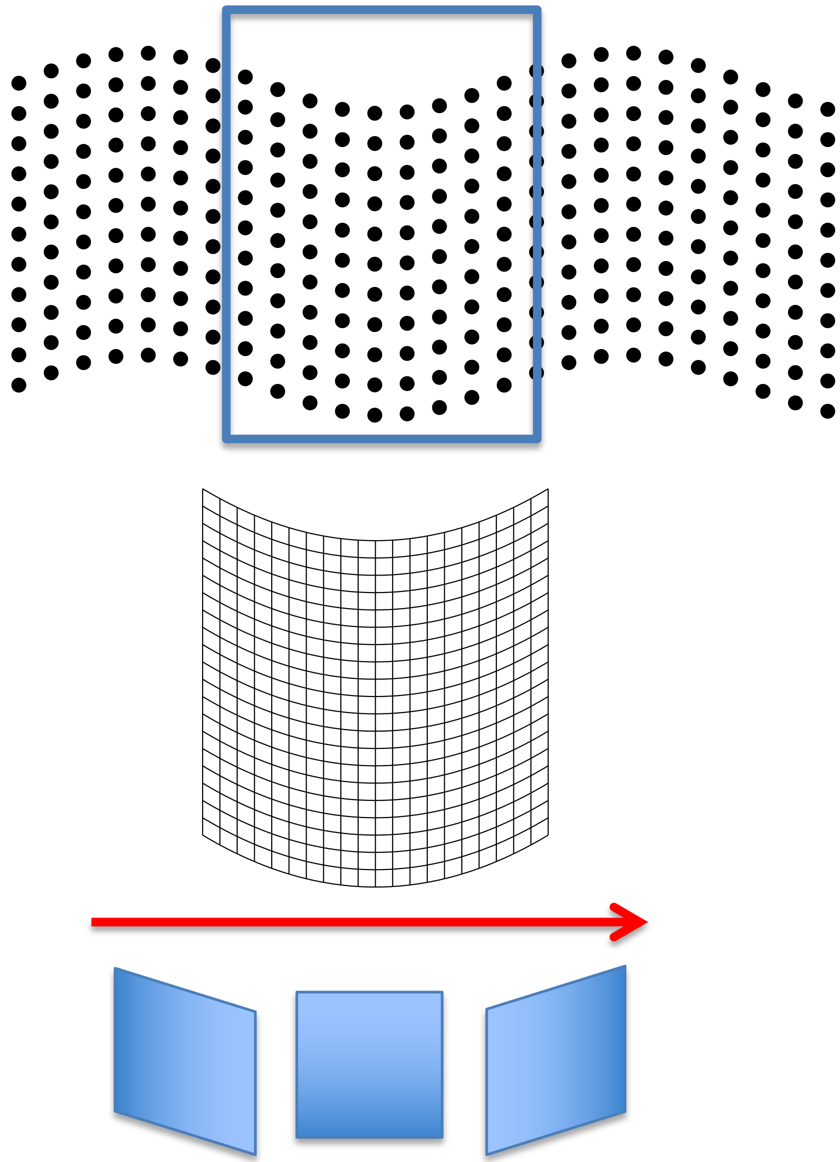
…or is there a way around??

# Solution: acoustic phonons

Longitudinal strain gradient



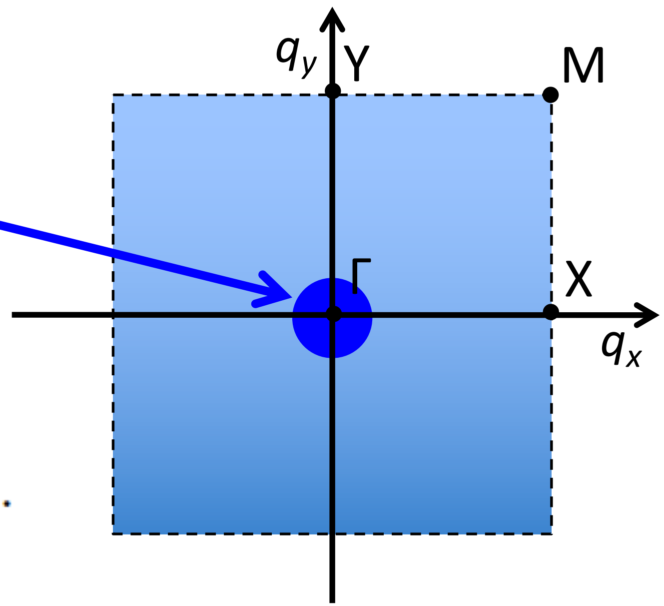
Shear strain gradient



# Long-wave linear-response approach

1. Use density-functional perturbation theory (DFPT) to calculate the **P**-response at small wavevectors **q** (both electronic & lattice-mediated)

2. Taylor expansion around the Γ point (long-wave limit):




$$\overline{P}_\alpha(\mathbf{q}) = \boxed{\phantom{xx}} + iq_\gamma e_{\alpha\beta\gamma} - q_\gamma q_\lambda \mu_{\alpha\beta,\gamma\lambda} + \dots$$

*O(q⁰)*: translation (vanishes)

*O(q¹)*: strain (PIEZO)

***O(q²)*: strain gradient (FLEXO)**

# Density-functional perturbation theory

$$\hat{V}_{\text{ext}}(\lambda) = \hat{V}_{\text{ext}}^{(0)} + \lambda \hat{V}_{\text{ext}}^{(1)} + \lambda^2 \hat{V}_{\text{ext}}^{(2)} + \cdots$$

$$E(\lambda) = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots$$

$$\psi_i(\lambda) = \psi_i^{(0)} + \lambda \psi_i^{(1)} + \cdots$$

$$E^{(1)} = \sum_i \langle \psi_i^{(0)} | \hat{V}_{\text{ext}}^{(1)} | \psi_i^{(0)} \rangle.$$

atomic forces (Hellmann-Feynman)

$$E^{(2)} = \sum_i \left[ \langle \psi_i^{(0)} | \hat{V}_{\text{ext}}^{(1)} | \psi_i^{(1)} \rangle + \langle \psi_i^{(0)} | \hat{V}_{\text{ext}}^{(2)} | \psi_i^{(0)} \rangle \right].$$

second-order energy

$$\left( \hat{\mathcal{H}}^{(0)} + a\hat{P} - \epsilon_m^{(0)} \right) | \psi_m^{(1)} \rangle = -\hat{Q} \hat{\mathcal{H}}^{(1)} | \psi_m^{(0)} \rangle,$$

Sternheimer equation

$$\hat{P} = \sum_{i=1}^{N} |\psi_i\rangle\langle\psi_i|, \quad \hat{Q} = 1 - \hat{P}.$$

(band projectors)

# Variational principle: "2n+1" theorem

$$E^{(2)} = \sum_m \langle \psi_m^{(1)} | \left( H^{(0)} - \epsilon^{(0)} \right) | \psi_m^{(1)} \rangle$$
$$+ \sum_m \left( \langle \psi_m^{(1)} | H^{(1)} | \psi_m^{(0)} \rangle + \langle \psi_m^{(0)} | H^{(1)} | \psi_m^{(1)} \rangle \right)$$
$$+ \frac{1}{2} \int_\Omega \int K_{\rm Hxc}(\mathbf{r}, \mathbf{r}') n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}') d^3r d^3r'$$
$$+ \frac{1}{2} \frac{\partial^2 E}{\partial \lambda^2},$$

$$\langle \psi_j^{(1)} | \psi_l^{(0)} \rangle = 0, \qquad j, l \in \mathcal{V}.$$ constraint (parallel transport gauge)

$$\hat{Q} \left( H^{(0)} - \epsilon^{(0)} \right) \hat{Q} | \psi_m^{(1)} \rangle = -\hat{Q} \hat{\mathcal{H}}^{(1)} | \psi_m^{(0)} \rangle$$ stationary condition (Sternheimer equation)

# Unconstrained variational formulation

$$E^{(2)} = \sum_m \langle \psi_m^{(1)} | \left( \hat{H}^{(0)} + a\hat{P} - \epsilon_m^{(0)} \right) | \psi_m^{(1)} \rangle$$
$$+ \sum_m \langle \psi_m^{(1)} | \hat{Q}\, \hat{H}^{(1)} | \psi_m^{(0)} \rangle + c.c.$$
$$+ \frac{1}{2} \int_\Omega \int K_{\mathrm{Hxc}}(\mathbf{r}, \mathbf{r}') n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}') d^3r d^3r'$$
$$+ \frac{1}{2} \frac{\partial^2 E}{\partial \lambda^2},$$

$$n^{(1)}(\mathbf{r}) = \sum_m \langle \psi_m^{(1)} | \hat{Q} | \mathbf{r} \rangle \langle \mathbf{r} | \psi_m^{(0)} \rangle + c.c.$$

$$\hat{P} = \sum_{i=1}^{N} |\psi_i\rangle\langle\psi_i|, \quad \hat{Q} = 1 - \hat{P}.$$

(band projectors)

$$\langle \psi_v^{(0)} | (\hat{H}^{(0)} + a\hat{P} - \epsilon_n) | \psi_v^{(0)} \rangle = \epsilon_v + a - \epsilon_n,$$
$$\langle \psi_c^{(0)} | (\hat{H}^{(0)} + a\hat{P} - \epsilon_n) | \psi_c^{(0)} \rangle = \epsilon_c - \epsilon_n.$$

*Automatically enforces orthogonality to the valence subspace if a is larger than the valence bandwidth!*

# Monochromatic perturbations

$$E_{\mathbf{q}}^{\lambda_1^*\lambda_2} = s\int_{\mathrm{BZ}}[d^3k]\sum_m E_{m\mathbf{k},\mathbf{q}}^{\lambda_1^*\lambda_2}$$
$$+\frac{1}{2}\int_\Omega\int K_{\mathbf{q}}(\mathbf{r},\mathbf{r}')n_{\mathbf{q}}^{\lambda_1*}(\mathbf{r})n_{\mathbf{q}}^{\lambda_2}(\mathbf{r}')d^3rd^3r'$$
$$+\frac{1}{2}\frac{\partial^2 E}{\partial\lambda_1^*\partial\lambda_2},$$

$$E_{m\mathbf{k},\mathbf{q}}^{\lambda_1^*\lambda_2} = \langle u_{m\mathbf{k},\mathbf{q}}^{\lambda_1}|\left(\hat{H}_{\mathbf{k}+\mathbf{q}}^{(0)} + a\hat{P}_{\mathbf{k}+\mathbf{q}} - \epsilon_{m\mathbf{k}}\right)|u_{m\mathbf{k},\mathbf{q}}^{\lambda_2}\rangle$$
$$+\langle u_{m\mathbf{k},\mathbf{q}}^{\lambda_1}|\hat{Q}_{\mathbf{k}+\mathbf{q}}\hat{H}_{\mathbf{k},\mathbf{q}}^{\lambda_2}|u_{m\mathbf{k}}^{(0)}\rangle$$
$$+\langle u_{m\mathbf{k}}^{(0)}|\left(\hat{H}_{\mathbf{k},\mathbf{q}}^{\lambda_1}\right)^\dagger\hat{Q}_{\mathbf{k}+\mathbf{q}}|u_{m\mathbf{k},\mathbf{q}}^{\lambda_2}\rangle,$$

$$n_{\mathbf{q}}^{\lambda}(\mathbf{r}) = 2s\int_{\mathrm{BZ}}[d^3k]\sum_m\langle u_{m\mathbf{k}}^{(0)}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{Q}_{\mathbf{k}+\mathbf{q}}|u_{m\mathbf{k},\mathbf{q}}^{\lambda}\rangle.$$

Parametric **q**-dependence only via "gauge-invariant" objects (operators, Coulomb kernel, etc.)

Can perform a perturbative **q**-expansion by using the "2n+1" theorem

Need to derive
Variational
Density
No **q** dependence

# Long-wave DFPT

$$E_\gamma^{\lambda_1^* \lambda_2} = \frac{dE_{\mathbf{q}}^{\lambda_1^* \lambda_2}}{dq_\gamma}\Big|_{\mathbf{q}=0} = \frac{\partial E_{\mathbf{q}}^{\lambda_1^* \lambda_2}}{\partial q_\gamma}\Big|_{\mathbf{q}=0}$$

$$E_\gamma^{\lambda_1^* \lambda_2} = s \int_{\mathrm{BZ}} [d^3k] \sum_m E_{m\mathbf{k},\gamma}^{\lambda_1^* \lambda_2} + \frac{1}{2} \int_\Omega \int K_\gamma(\mathbf{r},\mathbf{r}') n^{\lambda_1 *}(\mathbf{r}) n^{\lambda_2}(\mathbf{r}') d^3r d^3r' + \frac{1}{2} \frac{\partial}{\partial q_\gamma} \left( \frac{\partial^2 E}{\partial \lambda_1^* \partial \lambda_2} \right) \Big|_{\mathbf{q}=0},$$

**q**-gradient of the Coulomb kernel

velocity operator

$$E_{m\mathbf{k},\gamma}^{\lambda_1^* \lambda_2} = \langle u_{m\mathbf{k}}^{\lambda_1} | \partial_\gamma \hat{H}_{\mathbf{k}}^{(0)} | u_{m\mathbf{k}}^{\lambda_2} \rangle + \langle u_{m\mathbf{k}}^{\lambda_1} | \partial_\gamma \hat{Q}_{\mathbf{k}} \hat{\mathcal{H}}_{\mathbf{k}}^{\lambda_2} | u_{m\mathbf{k}}^{(0)} \rangle + \langle u_{m\mathbf{k}}^{(0)} | \left( \hat{\mathcal{H}}_{\mathbf{k}}^{\lambda_1} \right)^\dagger \partial_\gamma \hat{Q}_{\mathbf{k}} | u_{m\mathbf{k}}^{\lambda_2} \rangle + \langle u_{m\mathbf{k}}^{\lambda_1} | \hat{H}_{\mathbf{k},\gamma}^{\lambda_2} | u_{m\mathbf{k}}^{(0)} \rangle + \langle u_{m\mathbf{k}}^{(0)} | \left( \hat{H}_{\mathbf{k},\gamma}^{\lambda_1} \right)^\dagger | u_{m\mathbf{k}}^{\lambda_2} \rangle.$$

**k**-gradient of the band projector ("*d/dk*")

*Only **q**=0 response needs to be calculated!!*

# Is this useful to our scopes?

**FLEXOELECTRIC TENSOR**

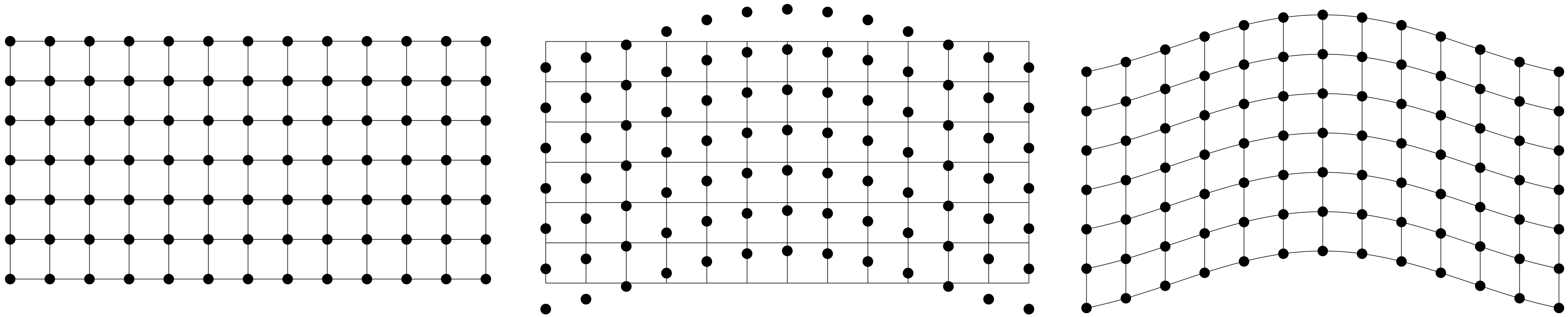
$$\mu_{\alpha\beta,\gamma\delta} = \frac{1}{2} \frac{d^2 P_{\alpha,\beta}(\mathbf{q})}{dq_\gamma dq_\delta}\Big|_{\mathbf{q}=\mathbf{0}}. \qquad P_{\alpha,\beta}(\mathbf{q}) = \frac{dP_\alpha^{\mathbf{q}}}{d\lambda_\beta^{\mathbf{q}}} = -\frac{d^2 E}{d\mathcal{E}_\alpha^{-\mathbf{q}} d\lambda_\beta^{\mathbf{q}}}.$$

electric field

acoustic phonon

- ✗ Standard electric field not applicable (only defined at **q**=0)
- ✗ Acoustic phonon perturbation needs to be specified first (some subtleties here)
- ✗ I know how to calculate first derivatives, but the flexoelectric tensor is 2nd order in **q**

# Metric and electric fields @ finite **q**



Acoustic phonon described via a "metric wave" perturbation

- Translation @ **q**=0, vanishes in the curvilinear frame
- Uniform strain @ $O(q^1)$, recovers Hamann's theory

Andrea Schiaffino, Cyrus E. Dreyer, David Vanderbilt, and Massimiliano Stengel, Phys. Rev. B 99, 085107 (2018)

Electric field from vector potential:

$$\mathcal{E} = -\frac{d\mathbf{A}}{dt}$$

- **q**=0: *d/dk* perturbation
- $O(q^1)$: $d^2/dk^2$ + orbital **B**-field

"Microscopic polarization response" ➔ next talk by C. Dreyer

# $2^{nd}$ order formula

✓ "2n+1" theorem again: To calculate second order, knowledge of the gradient response to one of the perturbations is enough!

✓ If the response vanishes at **q**=0, the formula is essentially the same as at *O(q¹)*!

electric field

$$\widetilde{E}^{\mathcal{E}^*_\alpha(\beta)}_{m\mathbf{k},\gamma\delta} = i\langle u^{\mathcal{E}_\alpha}_{m\mathbf{k}}|\partial_\gamma \hat{H}^{(0)}_{\mathbf{k}}|u^{\eta_{\beta\delta}}_{m\mathbf{k}}\rangle + i\langle u^{\mathcal{E}_\alpha}_{m\mathbf{k}}|\partial_\gamma \hat{Q}_{\mathbf{k}}\hat{\mathcal{H}}^{\eta_{\beta\delta}}_{\mathbf{k}}|u^{(0)}_{m\mathbf{k}}\rangle + i\langle u^{(0)}_{m\mathbf{k}}|\hat{V}^{\mathcal{E}_\alpha}\partial_\gamma\hat{Q}_{\mathbf{k}}|u^{\eta_{\beta\delta}}_{m\mathbf{k}}\rangle$$

$$+ \frac{1}{2}\langle u^{\mathcal{E}_\alpha}_{m\mathbf{k}}|\hat{H}^{(\beta)}_{\mathbf{k},\gamma\delta}|u^{(0)}_{m\mathbf{k}}\rangle + i\langle i\,u^{A_\alpha}_{m\mathbf{k},\gamma}|u^{\eta_{\beta\delta}}_{m\mathbf{k}}\rangle$$

uniform strain

symmetric $\alpha \leftrightarrow \gamma$: $d^2/dk^2$ wavefunctions (OK)

antisymm. $\alpha \leftrightarrow \gamma$: orbital magnetic field (??)

# Summary

- Unconstrained variational formulation of DFPT
- Long-wave expansion of the second-order energy via *2n+1*
- Can calculate dispersion properties without ever treating a gradient explicitly
- Finite-**q** generalization of electric field and strain perturbations ➔ flexo
- Dynamical quadrupoles (replace strain with phonon) ➔ talk by M. Royo

## Ongoing work:

- Full flexoelectric tensor (w/ lattice contrib.)
- Other dispersion properties: Natural gyrotropy, etc.
- Frequency (ω) expansion: Nonadiabatic lattice dynamics, optical response, etc.
- **ANADDB**: How should we treat spatial dispersion tensors?

M. Royo and M. Stengel, Phys. Rev. X, in press (**arXiv:1812.05935**)