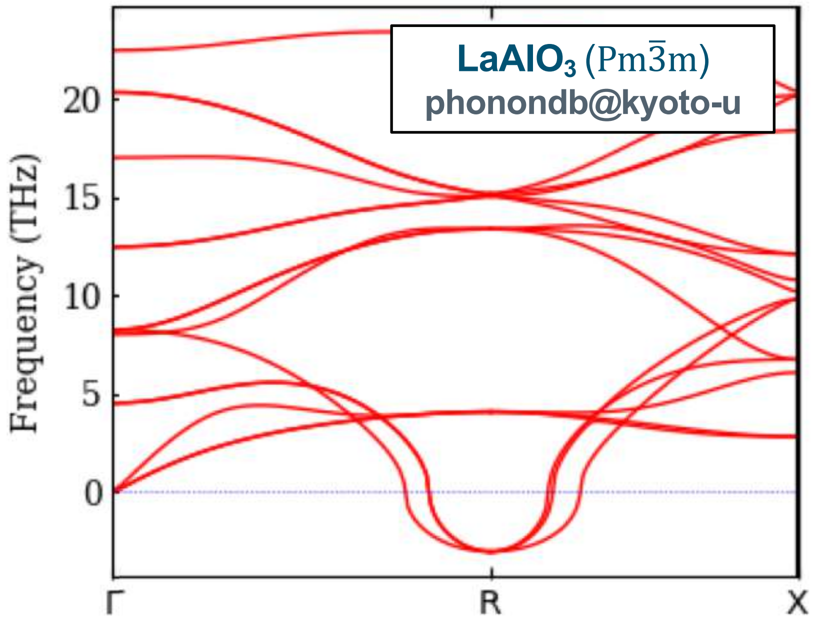
Long-range screening and interatomic forces: from 3D to 2D

Miquel Royo and Massimiliano Stengel

ABIDEV Workshop, June 3rd, 2021

Motivation: phonons



$$\hat{H}_{\text{ep}} = N_p^{-\frac{1}{2}} \sum_{\substack{\mathbf{k},\mathbf{q} \\ mn\nu}} g_{mn\nu}(\mathbf{k},\mathbf{q})\, \hat{c}^\dagger_{m\mathbf{k}+\mathbf{q}} \hat{c}_{n\mathbf{k}} (\hat{a}_{\mathbf{q}\nu} + \hat{a}^\dagger_{-\mathbf{q}\nu})$$

F. Giustino, Rev. Mod. Phys. **89**, 015003 (2016)

Phonon frequencies

- Structural characterization
- Lattice instabilities
- Thermal properties

Electron-phonon couplings

- Electron mobility
- Optical absorption
- Gap renormalization

G. Brunin *et al.*, Phys. Rev. Lett. **125**, 136601 (2020)

Ab initio lattice dynamics

Equations of motion

$$\sum_{\kappa'\beta} D^{\mathbf{q}}_{\kappa\alpha,\kappa'\beta} \cdot e^{\mathbf{q}}_{\kappa'\beta} = \underbrace{\omega^2(\mathbf{q})}_{\text{FREQUENCIES}} \cdot \underbrace{e^{\mathbf{q}}_{\kappa\alpha}}_{\text{EIGENVECTORS}}$$

Dynamical matrix

$$D^{\mathbf{q}}_{\kappa\alpha,\kappa'\beta} = \frac{1}{\sqrt{m_k m_{\kappa'}}} \Phi^{\mathbf{q}}_{\kappa\alpha,\kappa'\beta}$$

Force-constants matrix

$$\Phi^{\mathbf{q}}_{\kappa\alpha,\kappa'\beta} = \frac{\partial^2 E}{\partial\tau^{-\mathbf{q}}_{\kappa\alpha}\partial\tau^{\mathbf{q}}_{\kappa'\beta}}$$

- Accurate $\Phi^{\mathbf{q}}_{\kappa\alpha,\kappa'\beta}$ at any **q** point from *first principles* via DFPT

$\Phi^{\mathbf{q}}_{\kappa\alpha,\kappa'\beta}$ is not calculated but interpolated over the entire Brillouin Zone →

In polar insulators and semiconductors **short-range** and **long-range** force constants need to be separated

κ, κ': sublattice indices α, β: Cartesian directions τ: phonon perturbation

Dielectric matrix formalism

force-constants matrix

"bare" point dipoles produced by nuclear displacement

$$\Phi_{\kappa\alpha,\kappa'\beta} = \rho^{\text{ext}}_{\kappa\alpha} \cdot W \cdot \rho^{\text{ext}}_{\kappa'\beta}$$

screened Coulomb interaction

Long-range force constants stem from nonanalytic behavior of W at $\mathbf{q} = 0$

"Microscopic Theory of Force Constants in the Adiabatic Approximation"
Robert M. Pick, Morrel H. Cohen, and Richard M. Martin, Phys. Rev. B **1**, 910 (1970)

Screened Coulomb interaction

analytic

$$W = (\nu^{-1} - \chi_{\mathrm{ir}})^{-1}$$

screened potential produced by an external charge

$$\nu(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

"bare" Coulomb kernel

$$\chi_{\mathrm{ir}} = \chi_0 + \chi_0 f_{\mathrm{xc}} \chi_{\mathrm{ir}}$$

"irreducible polarizability"
(charge response to screened potential)

χ_0 : independent-particle polarizability

f_{xc} : exchange-correlation kernel

Range separation

$$v = v_{\mathrm{sr}} + v_{\mathrm{lr}} \quad \Longrightarrow \quad \Phi = \Phi^{\mathrm{sr}} + \Phi^{\mathrm{lr}}$$

short-range (local fields) → v_{sr}

nonanalytic → v_{lr}

$$\Phi^{\mathrm{lr}}_{\kappa\alpha,\kappa'\beta} = \rho^{\mathrm{sr}}_{\kappa\alpha} \cdot \underbrace{(v_{\mathrm{lr}}^{-1} - \chi_{\mathrm{sr}})^{-1}}_{W_{lr}} \cdot \rho^{\mathrm{sr}}_{\kappa'\beta}$$

- Only convenient if W_{lr} can be written in **separable** form:

"small space" representation → W_{ij}

$$W_{\mathrm{lr}}(\mathbf{r},\mathbf{r}') = \sum_{ij} \varphi_i(\mathbf{r})\, W_{ij}\, \varphi_j(\mathbf{r}')$$

macroscopic electrostatic potentials → φ_i, φ_j

	φ	$\boldsymbol{\tau}$
φ	χ_{sr}	ρ^{sr}
$\boldsymbol{\tau}$	ρ^{sr}	$\boldsymbol{\Phi}^{\mathrm{sr}}$

2nd order response to phonon (τ) and/or $\varphi_i(\mathbf{r})$; SCF @ $v_{\mathrm{sr}} + f_{\mathrm{xc}}$

Example: the 3D case

$$v(\mathbf{G}+\mathbf{q},\mathbf{G}'+\mathbf{q}) = \frac{4\pi}{|\mathbf{G}+\mathbf{q}|^2}\delta_{\mathbf{G}\mathbf{G}'}$$

$$\frac{4\pi}{K^2} = \underbrace{\frac{4\pi}{K^2}[1-f(K)]}_{v_{\rm sr}} + \underbrace{\frac{4\pi}{K^2}f(K)}_{v_{\rm lr}}$$

- Range separation function: $f(r) = \mathrm{erfc}\left(\frac{r}{\sigma}\right)$ in real space
- Filters out higher Fourier components ("local fields")
- $v_{\rm lr}$ and $W_{\rm lr}$ become **scalars** for small enough Λ
- Macroscopic potentials are **structureless** (uniform on the scale of the crystal cell)

$$f(K) = e^{-\frac{K^2}{\Lambda^2}}$$

$$W_{\rm lr}(\mathbf{q}) = \frac{4\pi f(q)}{q^2 - 4\pi f(q)\chi^{\rm sr}(\mathbf{q})}$$

charge response (cell avg.) to scalar potential SCF @ $v_{\rm sr} + f_{\rm xc}$

The 3D case: two possible strategies

1. Direct approach (exact)

- Need to implement modified “sr”electrostatic kernel & scalar potential perturbation
- Could be useful for accurate IFC’s and e-ph matrix elements in “difficult cases”…

2. Traditional Fourier-interpolation approach (approximate)

- Both $\rho_{\kappa\alpha}$ and χ^{sr} are **analytic** functions of **q**: can expand to lowest orders

$$\rho_{\kappa\alpha} = -i\mathbf{q}\cdot\boxed{\mathbf{Z}_{\kappa\alpha}} + \cdots$$

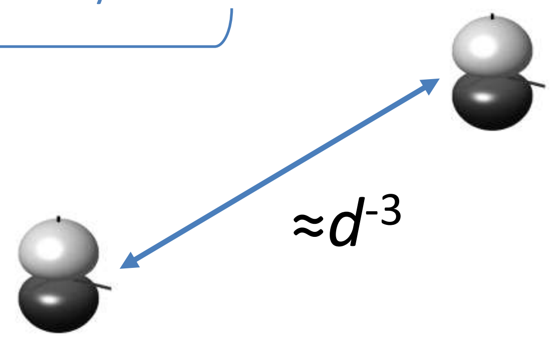
Born dynamical charges

$$\chi = -\mathbf{q}\cdot\boxed{\boldsymbol{\chi}^{\mathrm{mac}}}\cdot\mathbf{q} + \cdots$$

macroscopic dielectric susceptibility

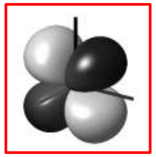
$$\Phi^{\mathbf{q},\mathrm{DD}}_{\kappa\alpha,\kappa'\beta} = \frac{4\pi}{\Omega}\frac{(\mathbf{q}\cdot\mathbf{Z}^*_{\kappa})_\alpha(\mathbf{q}\cdot\mathbf{Z}^*_{\kappa'})_\beta}{\mathbf{q}\cdot\boldsymbol{\epsilon}\cdot\mathbf{q}}$$

Cochran & Cowley, Proc. R. Soc. Ser. A **276**, 308 (1962)



Higher orders: dynamical quadrupoles

$$\rho_{\kappa\alpha} = -i\mathbf{q} \cdot \mathbf{Z}_{\kappa\alpha} - \frac{q_\beta q_\gamma}{2} Q_{\kappa\alpha}^{(\beta\gamma)} + \cdots$$



DQ interaction ≈d^{-4}

- Calculation of quadrupoles via long-wave DFPT, available in ABINIT v9.0
- Relationship to Martin's theory of piezoelectricity (PRB 1972)

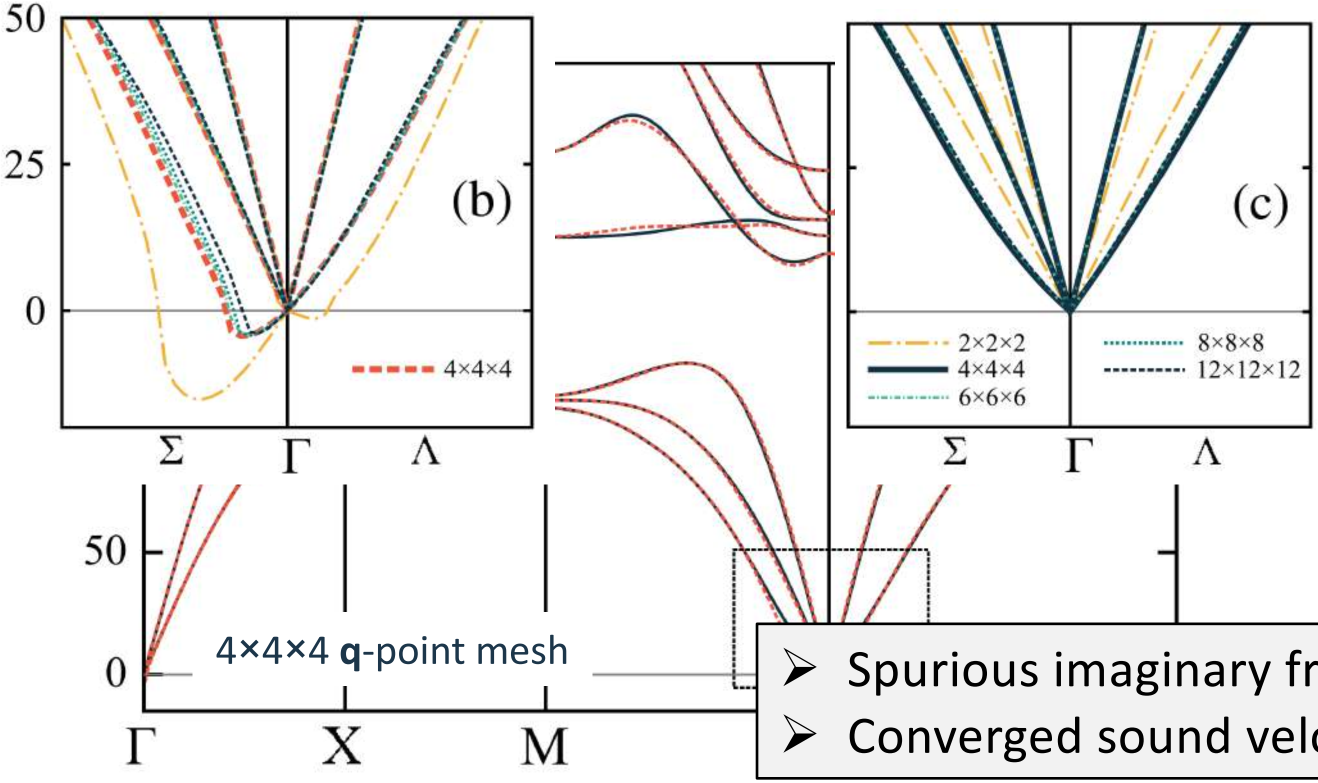
$$\underbrace{\bar{e}_{\alpha\beta\gamma} + \bar{e}_{\gamma\beta\alpha}}_{\text{clamped-ion piezo tensor}} = \frac{1}{\Omega} \sum_{\kappa} Q_{\kappa\beta}^{(\alpha\gamma)}$$

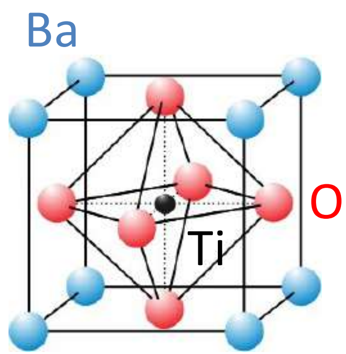
likely to be important for phonon interpolation in piezoelectrics…

M. Royo and M. Stengel, Phys. Rev. X **9**, 021050 (2019)

Numerical results: rhombohedral $BaTiO_3$

STANDARD DD APPROACH | **HIGHER-ORDER APPROACH**





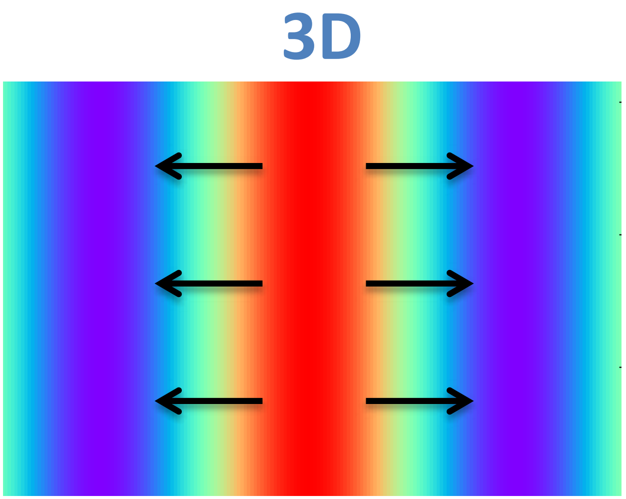
$R3m$ structure, $\mathbf{P} \parallel (111)$

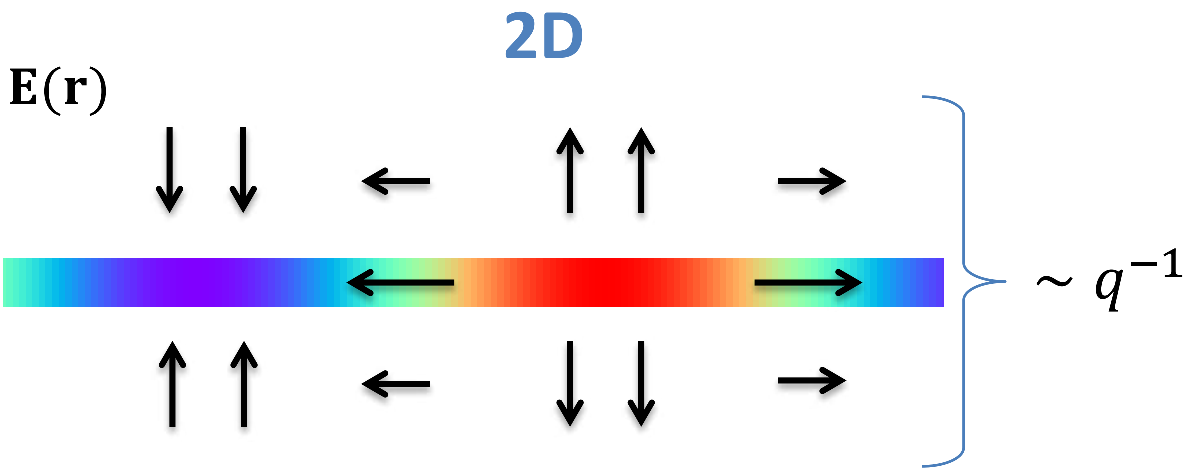
ferroelectric & piezoelectric

- Spurious imaginary frequencies disappear
- Converged sound velocities already at 4x4x4

Royo, Hahn and Stengel, *PRL* **125**, 217602 (2020)

Can we do the same in 2D?



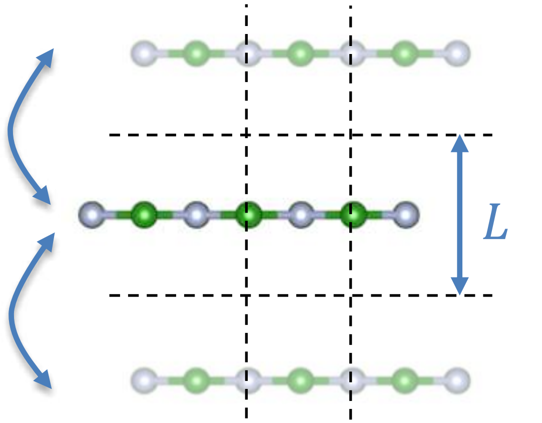


- Fields are only modulated along the longitudinal direction
- Phenomenological treatment:
  Cochran & Cowley, PRSS A **276**, 308 (1962)
- Fundamental theory:
  Pick, Cohen & Martin, PRB **1**, 910 (1970)

- Extreme anisotropy (extended in plane, microscopic out of plane), nonuniform fields
- First principles + 2D dielectric model:
  Sohier et al., *Nano Lett.* **17**, 3758 (2017)
- Fundamental theory still missing

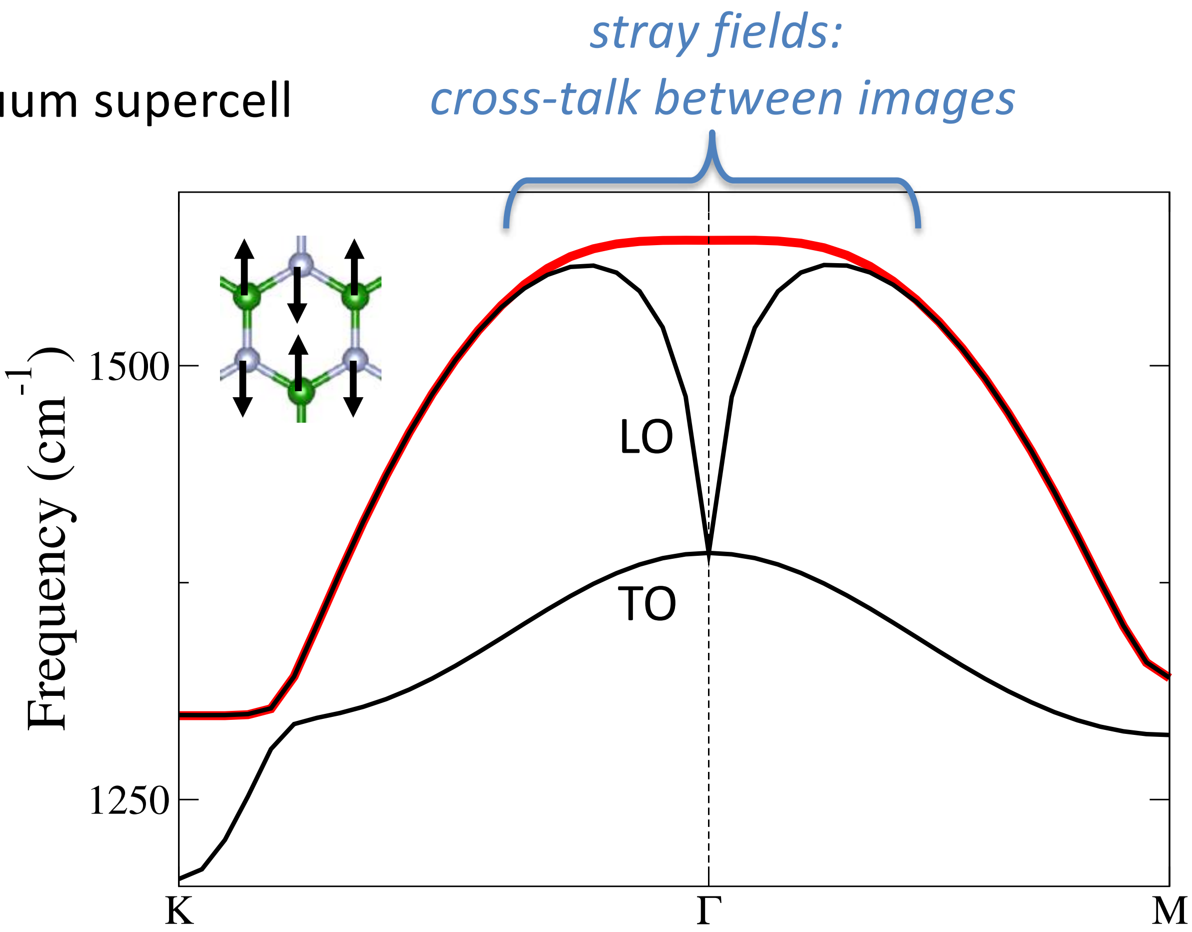
2D phonons in a 3D code

- Hexagonal BN, isolated layer + vacuum supercell



- Optical phonon $\mathbf{q} = (q_x, q_y, 0)$

Wrong LO dispersion for $q \to 0$



“Coulomb cutoff” method

$$v(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} \quad \text{for} \quad |z-z'| < \frac{L}{2}, \quad = 0 \text{ otherwise}$$

- Eliminates cross-talk between images
  S. Ismail-Beigi, PRB **73**, 233103 (2006); C. A. Rozzi *et al*., PRB **73**, 205119 (2006).
- Application to the phonon problem
  T. Sohier, M. Calandra, and F. Mauri, Phys. Rev. B **94**, 085415 (2016)
- Works nicely for the DFPT calculations, but how about the long-range forces?

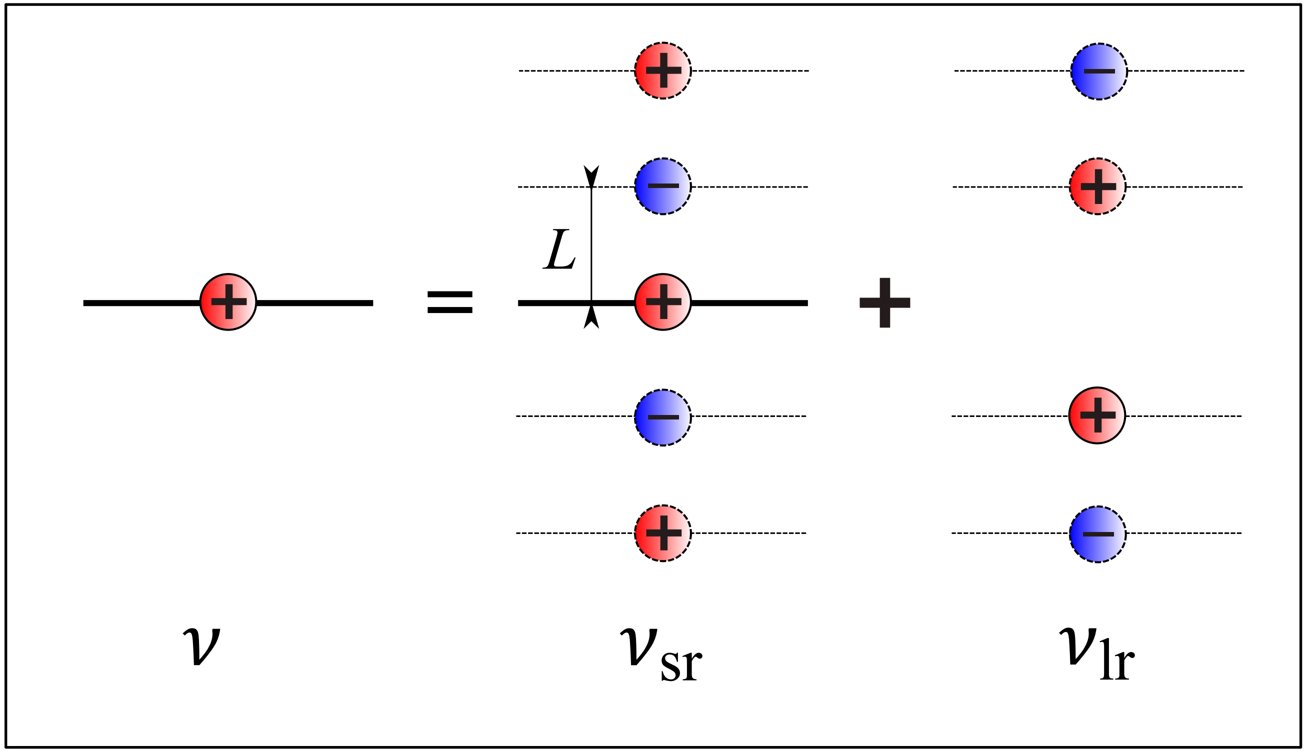
$$\nu(\mathbf{q}, G_n) = \frac{4\pi}{q^2 + G_n^2}[1 - (-1)^n e^{-qL}].$$

→ nonanalytic at any G_n

reciprocal-space representation (G_n= out-of-plane component)

Unclear how to split between “sr” and “lr”

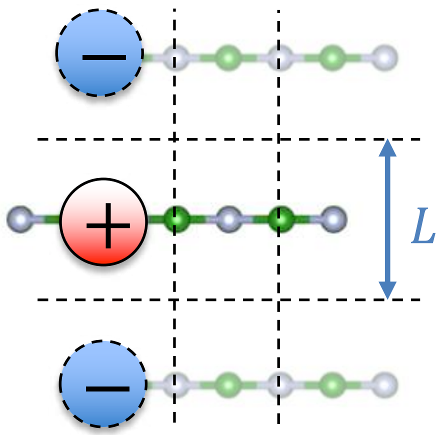
Range separation in 2D



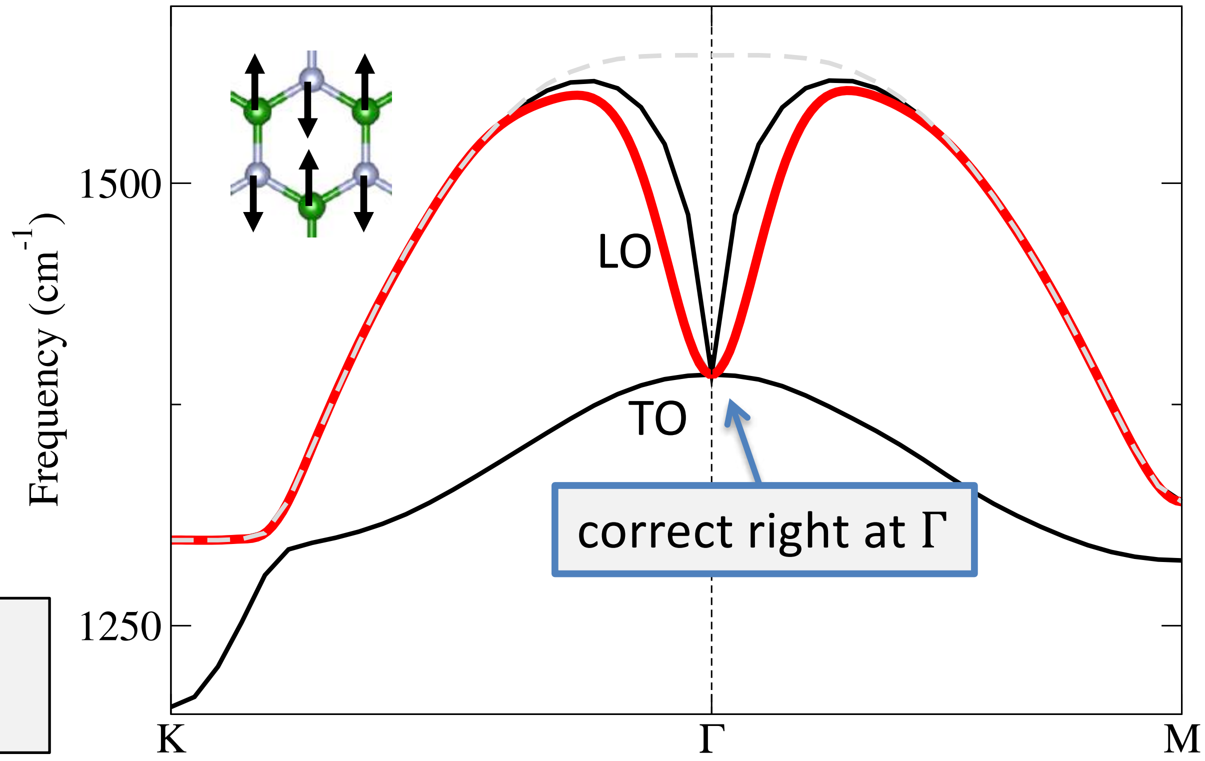
- Idea: replace the bare charge with a **vertical array of images**, taken with alternating signs
- Interaction between columns is **short-ranged**, we put the remainder into v_{lr}

Supercell representation of v_{sr}

- Optical phonon $\mathbf{q} = (q_x, q_y, \pi/L)$ (calculated at the zone boundary along z)



- 180° phase shift between images, reproduces the alternating sign!



Long-range Coulomb kernel in 2D

2D: $v_{lr}(q \to 0) \simeq \frac{2\pi}{q}$

$$\nu_{\mathrm{lr}}(\mathbf{q}, z - z') = \frac{2\pi f(q)}{q} \boldsymbol{\varphi}(z) \cdot \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \cdot \boldsymbol{\varphi}(z'),$$

$$\cosh(z)\cosh(z') - \sinh(z)\sinh(z') = \cosh(z - z')$$

(bisection formula)

$$f(q) = 1 - \tanh\left(\frac{qL}{2}\right)$$

range separation function, vanishes for $q \gg L^{-1}$
(L = "Ewald parameter")

$$\boldsymbol{\varphi}(z) = \begin{bmatrix} \cosh(qz) \\ \sinh(qz) \end{bmatrix}.$$

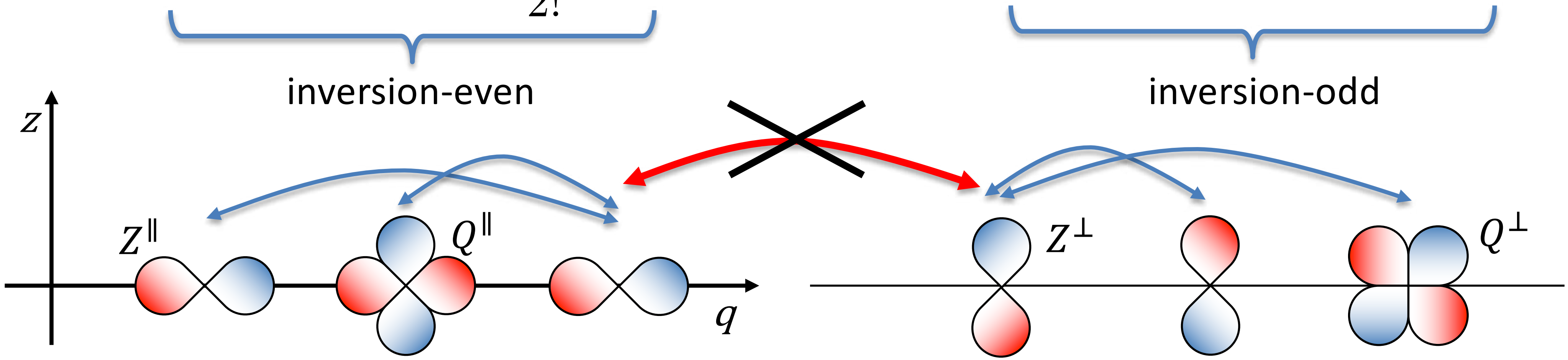
2D "scalar potential" perturbation, **nonuniform** along z

- LR electrostatics becomes a **2D problem**, involving 2×2 dielectric matrices

Why hyperbolic functions?

$\varphi^{\parallel}$: $\cosh(qz) = 1 + \frac{q^2 z^2}{2!} + \cdots$

$\varphi^{\perp}$: $\sinh(qz) = qz + \cdots$



sinh and cosh pick the two independent **traceless** components of the 2D charge multipoles (cylindrical harmonics)

Example (quadrupoles): $Q^{\parallel} = Q^{(xx)} - Q^{(zz)}$

Exact formula with mirror symmetry

$$\Phi^{\mathrm{lr}}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \frac{2\pi f(q)}{Sq}\left(\frac{(\mathbf{q}\cdot\boldsymbol{\mathcal{Z}})^{*}_{\kappa\alpha}\,(\mathbf{q}\cdot\boldsymbol{\mathcal{Z}})_{\kappa'\beta}}{\epsilon_{\parallel}(\mathbf{q})} - q^{2}\frac{\mathcal{Z}^{\perp *}_{\kappa\alpha}\,\mathcal{Z}^{\perp}_{\kappa'\beta}}{\epsilon_{\perp}(\mathbf{q})}\right) e^{-i\mathbf{q}\cdot(\boldsymbol{\tau}_{\kappa'}-\boldsymbol{\tau}_{\kappa})}$$

∥ : inversion-even ⊥ : inversion-odd

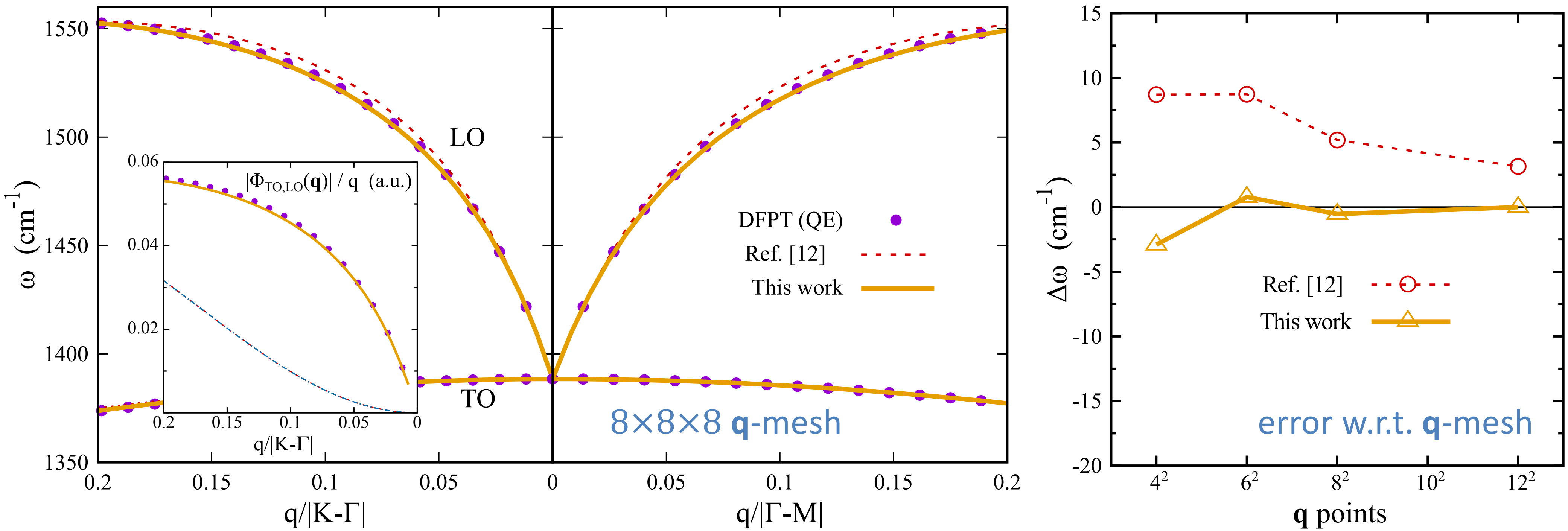
$Z(q) \simeq Z - iqQ + \cdots$

$\epsilon(q) \simeq 1 \pm 2\pi q\alpha + \cdots$

polarizability

- Inversion-even part consistent, at lowest order, with earlier 2D dielectric models (Sohier *et al.*, Nano Letters 2017)
- **Inversion-odd terms** are new; improved treatment of **screening**; inclusion of **dynamical quadrupoles**
- **Exact** up to arbitrary order in the multipolar expansion [present work: $O(q^2)$]

Application: interpolation of phonon bands (BN)

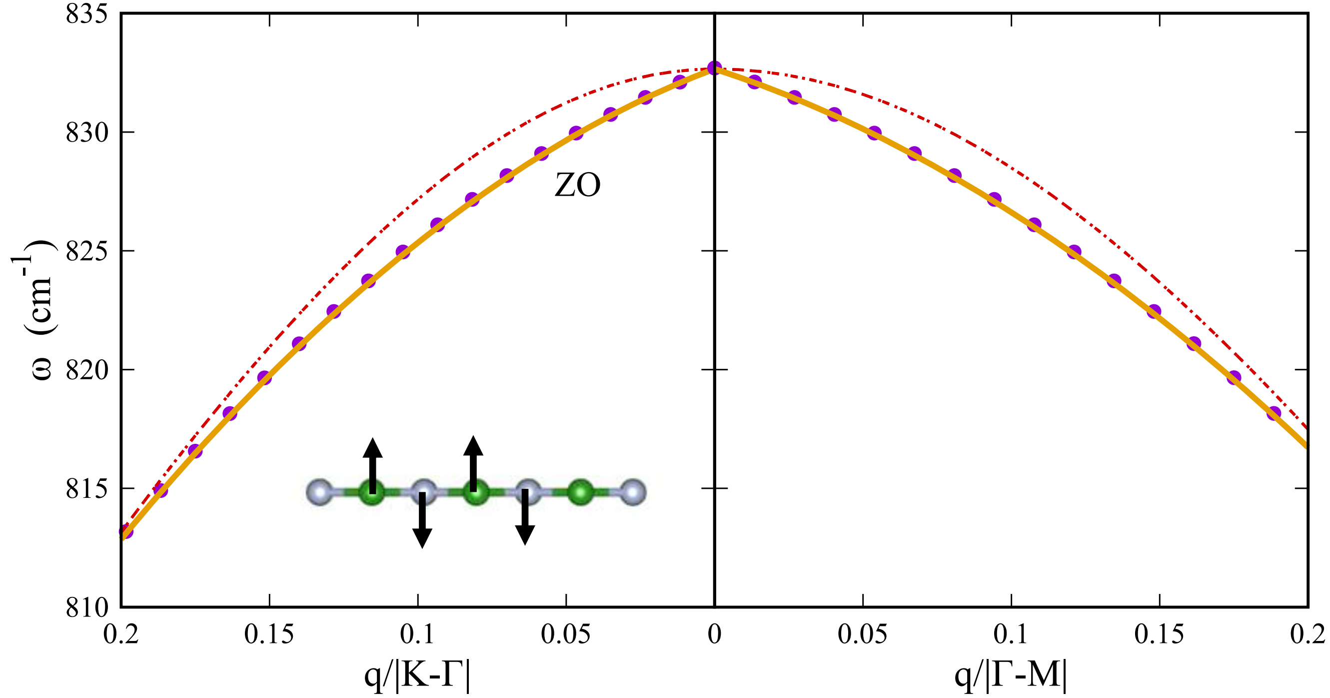


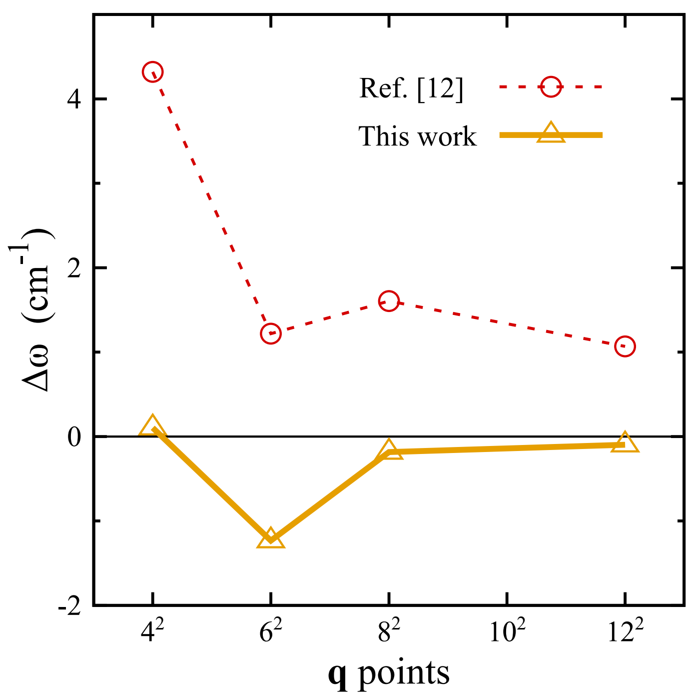
- LO band: More accurate interpolation due to better treatment of screening
- Quadrupoles important for the description of the off-diagonal elements

This work: https://arxiv.org/abs/2012.07961

[12]: Sohier et al., *Nano Lett.* **17**, 3758 (2017)

Application: interpolation of phonon bands (BN)





- ZO band: linear dispersion approaching Γ, but negative slope (inversion-odd part of the long-range electrostatics)

This work: https://arxiv.org/abs/2012.07961

[12]: Sohier et al., *Nano Lett.* **17**, 3758 (2017)

Summary

- Range separation of the bare Coulomb kernel in 2D: image-charge technique
- Long-range electrostatic interactions mediated by $\cosh(qz)$ and $\sinh(qz)$ potentials
- Exact formula for the long-range interatomic forces
- Multipolar expansion: Born charges, quadrupoles, etc.

- Inversion-odd part of the electrostatics (ZO branch in BN)
- Improved treatment of the dielectric function
- Implications for e-ph calculations (3D: see G. Brunin *et al.*, PRL 2020)

https://arxiv.org/abs/2012.07961