Towards multiscale modeling of incommensurate 2D van der Waals heterostructures

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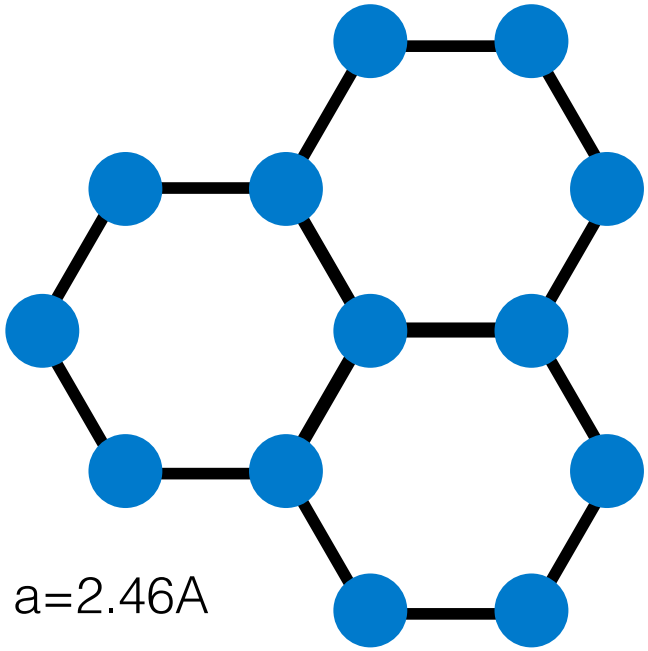
Cornocupia of 2D materials

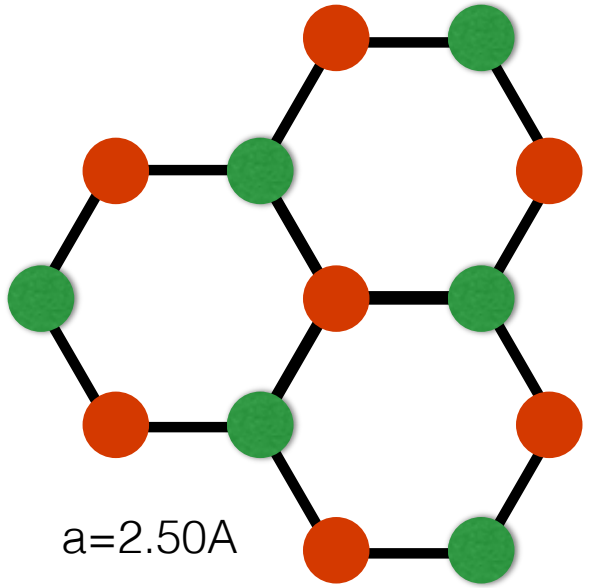
Graphene



Semimetal

- Dirac cone: linear dispersion
- Inversion symmetry
- Extraordinary properties (mechanical strength, etc.)

Hexagonal Boron Nitride (hBN)

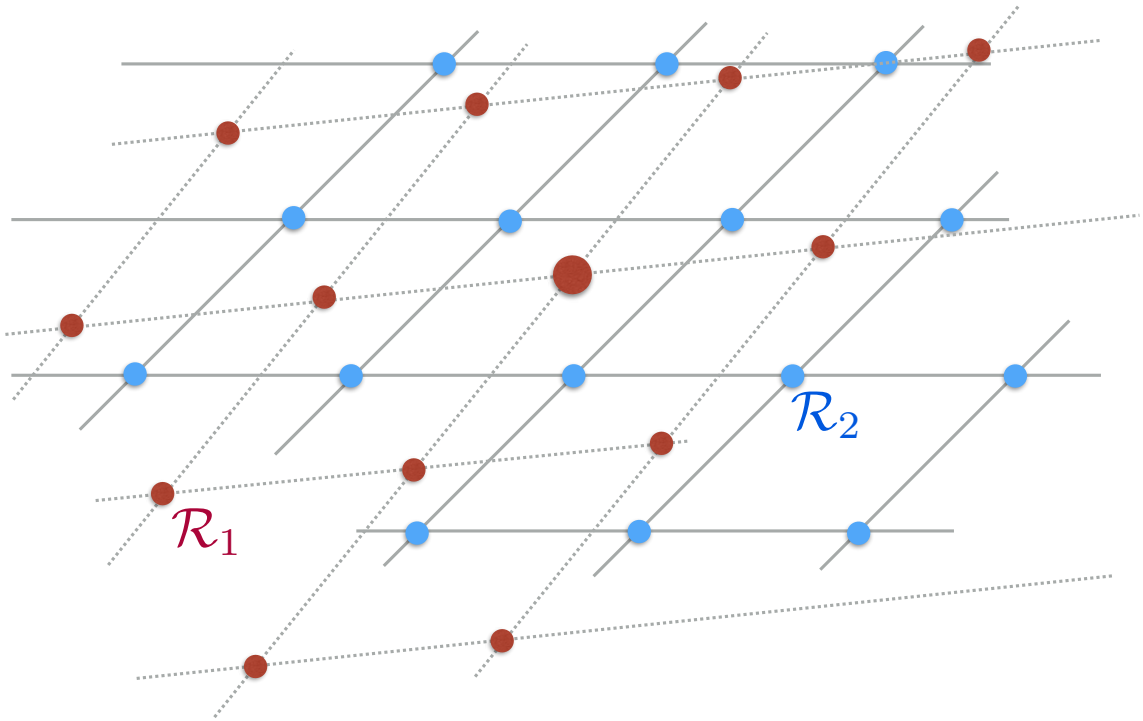


Insulator

- Broken inversion symmetry
- Large band gap, 5eV
- Stability
- Used to encapsulate graphene

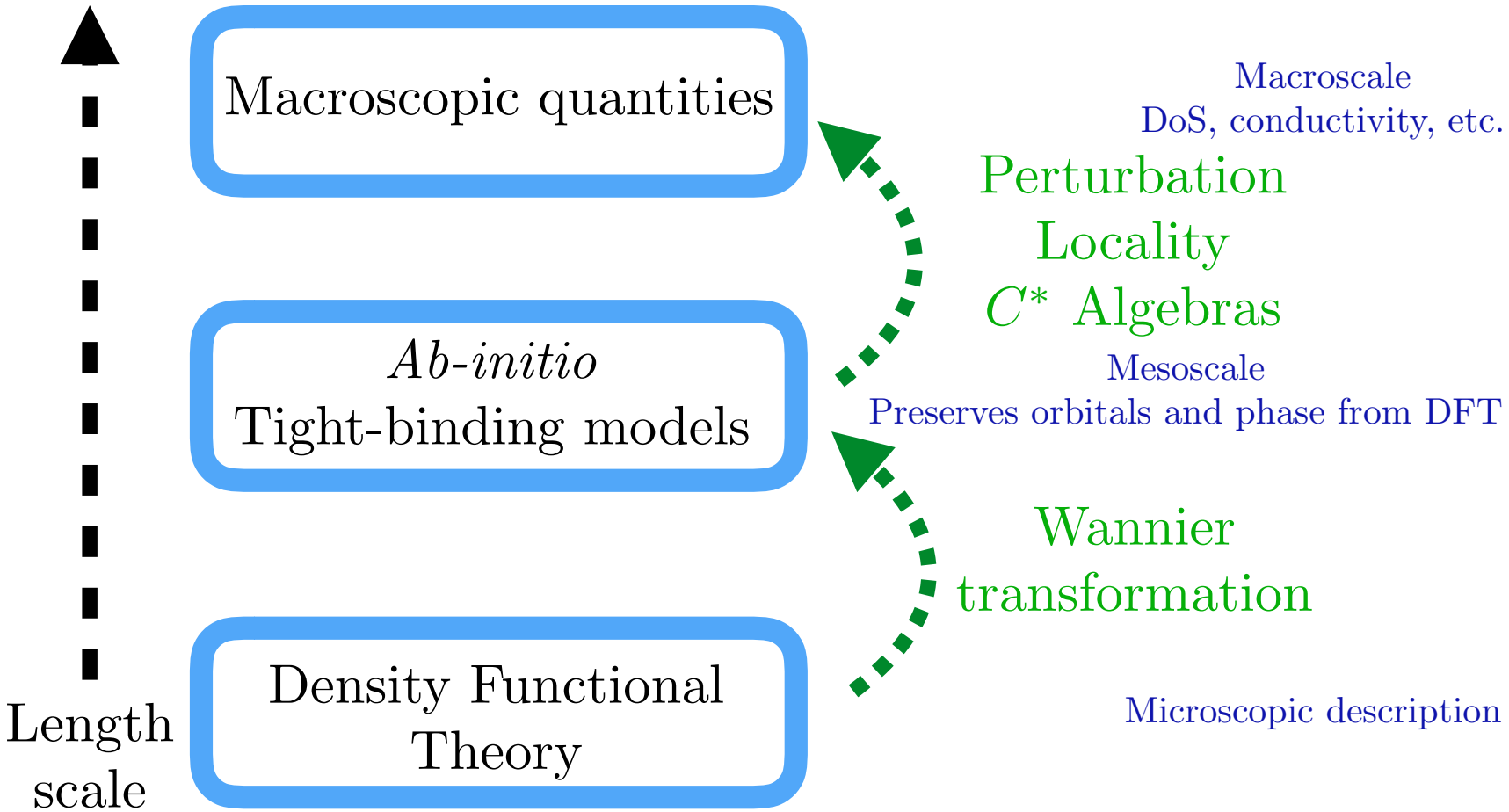
And also: transition metal dichalcogenides MX_2, phosphorene, etc.

Heterostructures and incommensurability



- In general, the crystal lattices of the layers do not match.
- No more Bloch theorem!
- Traditionally, construction of supercells:
  - Possible for some *magic* angles for twisted bilayers;
  - Size increases quickly, very expensive calculations.

Multiscale hierarchy of models



Overview

1. Perturbation approach.

2. Incommensurate systems and noncommutative algebras.

3. 1D Toy Model

Perturbation approach

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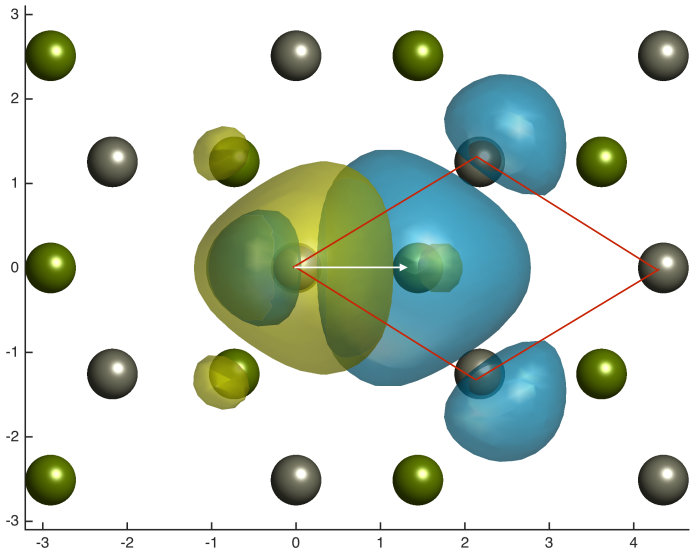
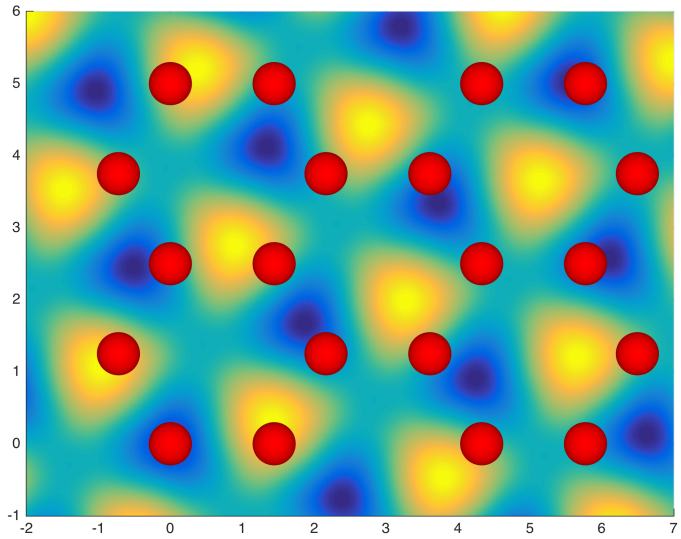
Perturbation calculation for the density matrix

- Practical example: h-BN monolayer perturbed by the the potential of another h-BN monolayer.
- Two ingredients:



$\rightsquigarrow$ 5-bands Wannier orbital model



- 3D electric potential V computed from monolayer DFT calculations,

$\rightsquigarrow$ Calculated by S. Shirodkar using the GPAW DFT code.

General tight-binding framework and notations

- **Orthonormal basis of localized Wannier orbitals** on a crystal lattice $\mathcal{R}$:

$$(\chi_{\mu,R})_{\substack{1\leqslant\mu\leqslant N_b \\ R\in\mathcal{R}}} \qquad \text{where} \qquad \chi_{\mu,R}(x) = \chi_\mu(x-R).$$

  - $R \in \mathcal{R}$ indexes the lattice cell, μ the basis element within each cell.
  - N_b basis elements per cell.

- **Unperturbed hamiltonian H_0**:
  - $\rightsquigarrow$ Represented by a matrix h, provided by the TB model:

$$\left[h^{R,R'}_{\mu,\mu'}\right] = \langle\chi_{\mu,R}|H_0|\chi_{\mu',R'}\rangle\,.$$

  - $\rightsquigarrow$ Invariant by lattice translations:

$$\left[h^{R,R'}_{\mu,\mu'}\right] = \mathfrak{h}_{\mu,\mu'}(R-R').$$

- **Perturbing potential V:**
  - $\rightsquigarrow$ represented by an operator v in the TB model:

$$\left[v^{R,R'}_{\mu,\mu'}\right] = \langle\chi_{\mu,R}|V|\chi_{\mu',R'}\rangle\,.$$

Density matrix perturbation

$\rightsquigarrow$ We investigate the perturbation of the **electronic density matrix**:

$$\begin{cases} \gamma_0 = 1_{(-\infty,\varepsilon_F]}(H_0), \\ \gamma_V = 1_{(-\infty,\varepsilon_F]}(H_0 + V) \end{cases}$$

- H_0: Hamiltonian of the unperturbed layer, $\mathcal{R}$–periodic, ε_F: Fermi level,
- V: perturbing potential, $\widetilde{\mathcal{R}}$–periodic.
  Weak Van der Waals forces between the layers $\Longrightarrow$ use a perturbation approach.
- In the Wannier basis, the density matrix coefficients write:

$$[D(V)]^{R,R'}_{\mu,\mu'} = \langle \chi_{\mu,R} | \gamma_V | \chi_{\mu',R'} \rangle .$$

$\rightsquigarrow$ We seek a **perturbative expansion in the potential V:**

$$D(V) \approx D_0 + D_1 + \mathcal{O}(\|V\|^2).$$

Note that the periodic lattices $\mathcal{R}$ and $\widetilde{\mathcal{R}}$ can be incommensurate!

Discrete Floquet-Bloch transform

The discrete Bloch transform writes for $u \in \ell^2(\mathcal{R}, \mathbb{C}^m)$:

$$\text{For } q \in \Gamma^*, \qquad \breve{u}(q) = \sum_{R \in \mathcal{R}} u(R) e^{-iq \cdot R}.$$

- Γ^* is the Brillouin zone.
- Bloch theorem $\Longrightarrow$ the Hamiltonian and the (unperturbed) density matrix are **diagonalized by the Bloch transform:**

$$\widetilde{(hu)}(q) = \left(\sum_{n=1}^{N_b} \varepsilon_{n,q} C_{n,q} C_{n,q}^* \right) \breve{u}(q), \quad \widetilde{(D_0 u)}(q) = \left(\sum_{n=1}^{N_f} C_{n,q} C_{n,q}^* \right) \breve{u}(q),$$

- $\rightsquigarrow$ N_b is the number of orbitals per cell,
- $\rightsquigarrow$ N_f the number of occupied orbitals per cell,
- $\rightsquigarrow$ $\varepsilon_{n,q}$ and $C_{n,q}$ are the Bloch eigenvalues and eigenvectors of the Hamiltonian matrix.

Main formula

The first-order perturbation of the density matrix is given by:

$$(D_1)_{R,R'} = -\sum_{\tilde{K}\in\tilde{R}^*} \fint_{\Gamma^*} \mathrm{d}q \left(\widetilde{D_1}\right)_{\tilde{K}}(q) e^{iq\cdot R - i(q-\tilde{K})\cdot R'} + \text{h.c.}$$

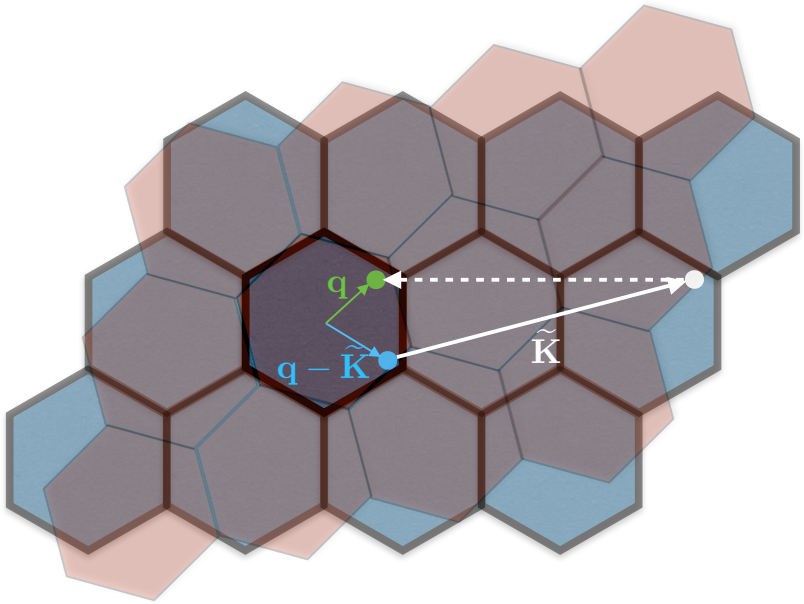
where Γ^* is the Brillouin zone and $\widetilde{\mathcal{R}^*}$ the reciprocal lattice of $\widetilde{\mathcal{R}}$,

$$\begin{cases} \left(\widetilde{D_1}\right)_{\tilde{K}}(q) = \displaystyle\sum_{n\leqslant N<n'} \left(\frac{C^*_{n,q}\widetilde{W}_{\tilde{K}}(q)C_{n',q-\tilde{K}}}{\varepsilon_{n',q-\tilde{K}} - \varepsilon_{n,q}}\right) C_{n,q}C^*_{n',q-\tilde{K}}, \\ \widetilde{W}_{\tilde{K}}(q) = \displaystyle\sum_{R\in\mathcal{R}} W_{\tilde{K}}(R)e^{-iq\cdot R}, \qquad \text{and} \\ (W_{\tilde{K}})_{\mu,\mu'}(R) = \dfrac{1}{|\widetilde{\Gamma}^*|^{1/2}} \displaystyle\int_{\mathbb{R}^3} \chi^*_\mu(r-R)\chi_{\mu'}(r)\widehat{V}_{\tilde{K}}(z)e^{i\tilde{K}\cdot r}\mathrm{d}r. \end{cases}$$

- **Main assumption:** unperturbed layer is an insulator (**band gap**).
- **Rapid decay** of $W_{\tilde{K}}(R)$ due to basis localization $\rightsquigarrow$ few terms.

Physical understanding

- Each (x, y) Fourier mode $\widehat{V}_{\tilde{K}}(z)$ of the potential leads to scattering of the Bloch modes:

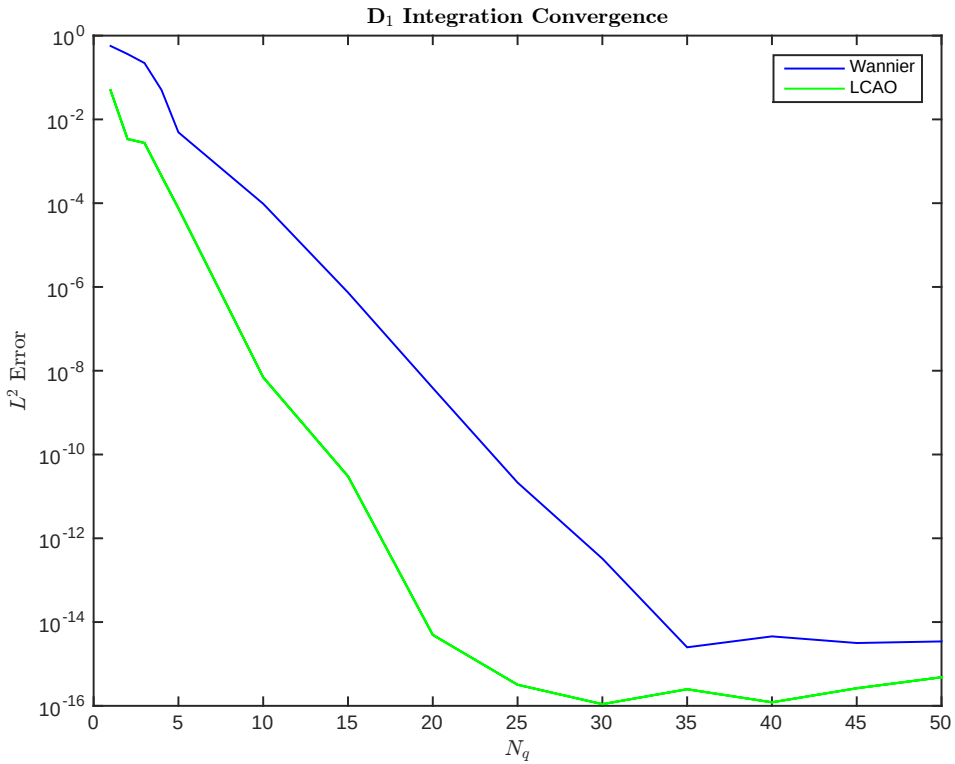


$\rightsquigarrow$ Commensurate case: finite scattering (folding of the Brillouin zone),

$\rightsquigarrow$ Incommensurate case: each point of the Brillouin zone is scattered to an infinite number of other modes.

Numerical validation: k-sampling and convergence

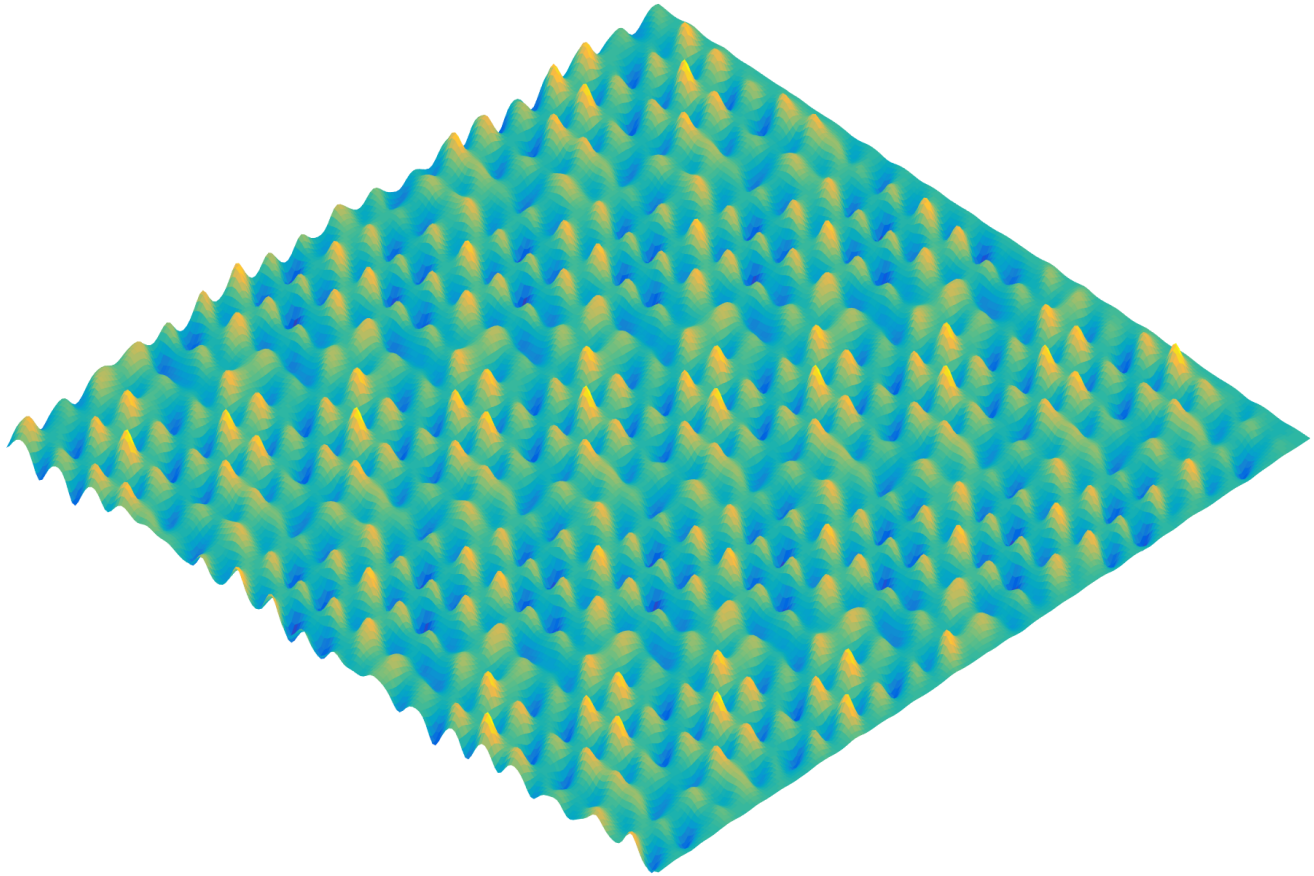
- Uniform Monkhorst–Pack grid used for numerical integration over the Brillouin zone.
- Exponentially fast convergence due to smoothness of the Wannier functions.



Comparison between the convergence for the Wannier function basis (in blue) and for a Gaussian LCAO basis using analytic integrals (in green).

Calculations in the incommensurate case

- The perturbation formula allows us to visualize the electronic density perturbation for arbitrary angles.
- Example: h-BN layer perturbed by h-BN potential with a 8° twist:



$\rightsquigarrow$ Modulations of the electron density perturbation induced by a Moire pattern.

Incommensurate systems and noncommutative algebras. Towards electronic transport

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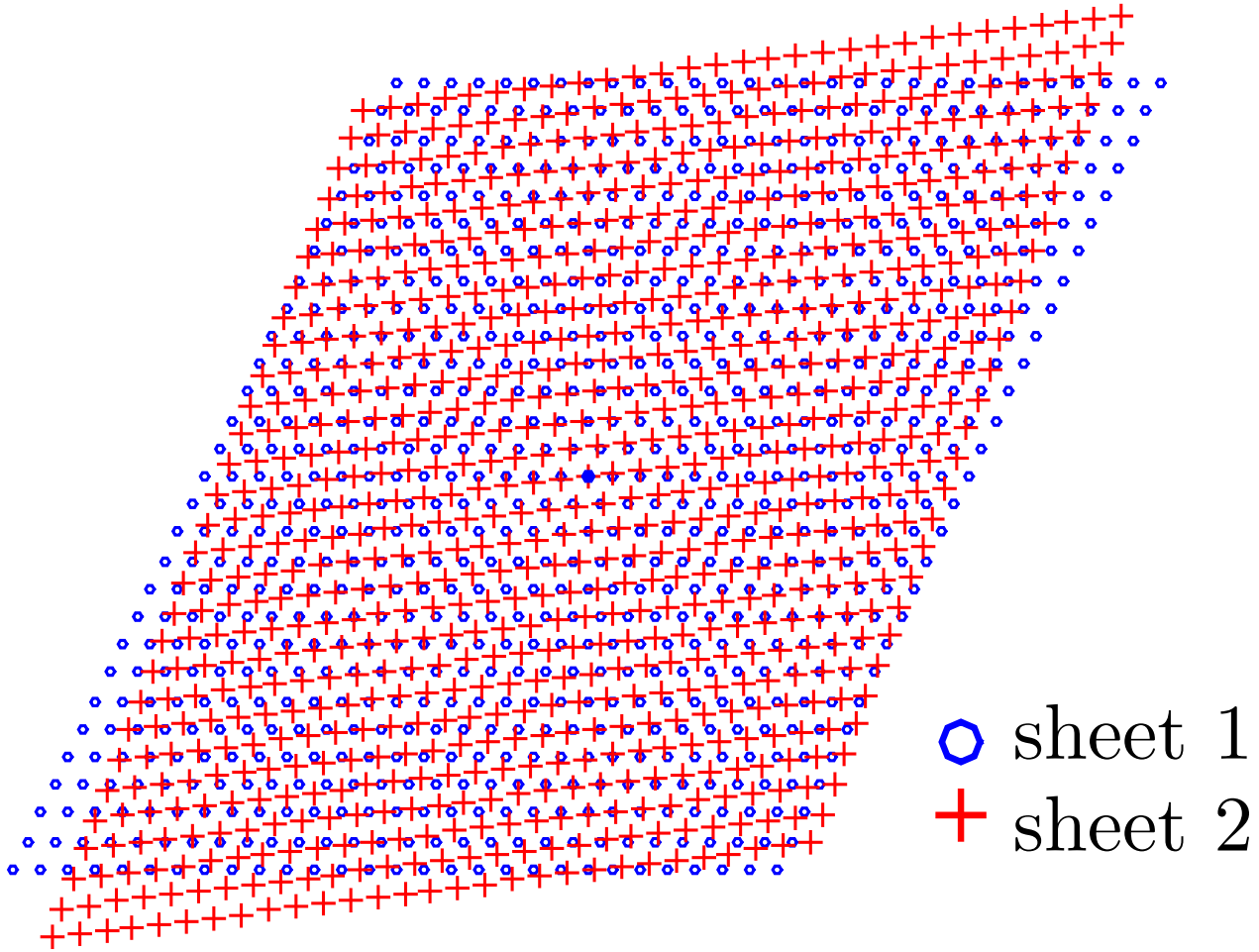
Incommensurate bilayer systems

- Two layers: incommensurate lattices $\mathcal{L}_1$, $\mathcal{L}_2$.



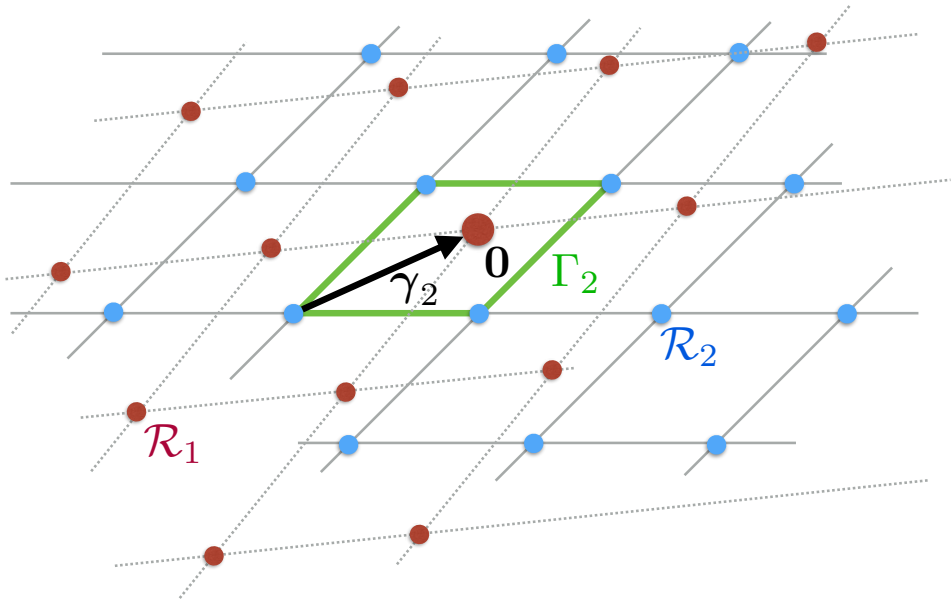
Incommensurate rotated hexagonal bilayer, $\theta = 6^{\circ}$.

Space of configurations

1. **Sites of $\mathcal{R}_1$**:

   - Other sites of layer $\mathcal{R}_1$ are known,
   - Other sites of layer $\mathcal{R}_2$ are given by

   $$\gamma_2 \in \Gamma_2 = \mathbb{R}^2/\mathcal{R}_2.$$



2. **Sites of $\mathcal{R}_2$**: local configuration parameterized by

   $$\gamma_1 \in \Gamma_1 = \mathbb{R}^2/\mathcal{R}_1.$$

- Each possible configuration corresponds to a point of the disjoint union

  $$X \equiv \Gamma_2 \sqcup \Gamma_1.$$

- For each possible configuration, discrete set of hopping vectors towards $\mathbf{0}$:

  $$\Gamma(X).$$

Parameterization of bilayer systems

- **Natural** C-* algebra formulation [Belissard, Shulz-Baldes, Prodan,...]
- One can write a block decomposition of functions $f \in C^*(\Gamma(X), B)$ as:

$$f = \begin{bmatrix} f_{11} & f_{12} \\ f_{21} & f_{22}. \end{bmatrix}$$

- Each block corresponds to a set of possible hoppings:

$$\begin{aligned} f_{11}: &\quad \vec{\Gamma}_{11} = \Gamma_2 \times \mathcal{R}_1 \to \mathbb{C}, \\ f_{12}: &\quad \vec{\Gamma}_{12} = \mathbf{R}^2 \to \mathbb{C}, \\ f_{21}: &\quad \vec{\Gamma}_{21} = \mathbf{R}^2 \to \mathbb{C}, \\ f_{22}: &\quad \vec{\Gamma}_{22} = \Gamma_1 \times \mathcal{R}_2 \to \mathbb{C}. \end{aligned}$$

- Sum, product rules including magnetic fields.
- Operator representation.

Ergodicity and trace

Suppose now that the lattices are **incommensurate**:

$$\mathcal{R}_1 \cap \mathcal{R}_2 = \mathbf{0}.$$

$\Longrightarrow$ **Equidistribution theorem** for shifts under groupoid translations.

Proposition

Let $\mathbb{P}$ be the probability measure on X with uniform density $(|\Gamma_1| + |\Gamma_2|)^{-1}\mathrm{d}\boldsymbol{\gamma}$ on both Γ_1 and Γ_2. Then

- *$\mathbb{P}$ is invariant and ergodic under the action of the groupoid $\Gamma(X)$,*
- *$\mathcal{T} := \mathcal{T}_{\mathbb{P}}$ is uniquely defined as a trace per unit volume in the sense that*

$$\mathcal{T}(f) = \lim_{R\to\infty} \frac{1}{\#\left(B_R \cap \mathcal{L}^\omega\right)} \mathrm{Tr}\left(\pi_\omega(f)|_{B_R}\right),$$

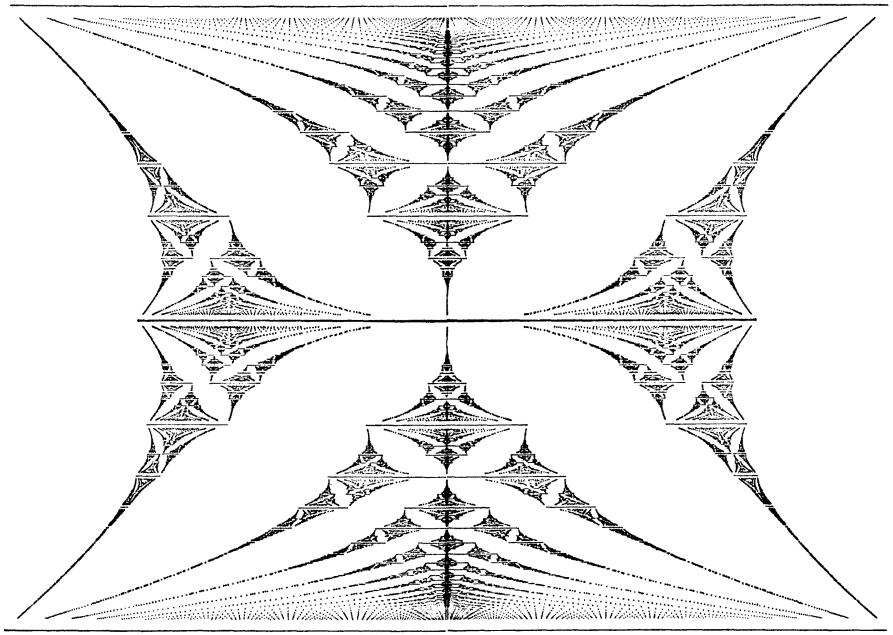
  where B_R is the ball of radius R centered at $\mathbf{0}$.

- *The trace is computed by the formula:*

$$\mathcal{T}(f) = \frac{1}{|\Gamma_1| + |\Gamma_2|}\left(\int_{\Gamma_2} f_{11}(\boldsymbol{\gamma}_2, \mathbf{0}) d\boldsymbol{\gamma}_2 + \int_{\Gamma_1} f_{22}(\boldsymbol{\gamma}_1, \mathbf{0}) d\boldsymbol{\gamma}_1\right).$$

A reference example: the Hofstadter butterfly

- Square lattice,
- Harper tight-binding model,
- Single band,
- Peierls substitution.

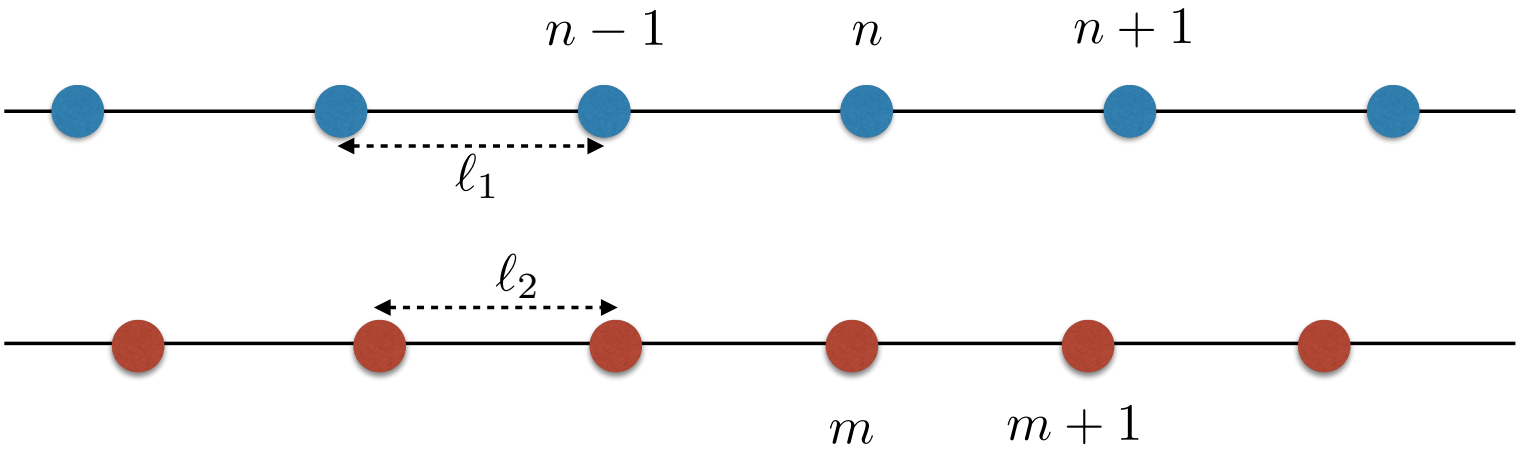


[Hofstadter 1976, *Energy levels and wave functions of Bloch electrons in rational and irrational magnetic fields*]

Incommensurability between magnetic flux and lattice constant.

A one-dimensional bilayer toy model

- Idea: two atomic chains with different lattice constants.



- Geometric normalization:

$$\ell_1 \ell_2 = 1.$$

Model Hamiltonian:

- Intra-chain interactions: nearest neighbor hopping with parameter 1,
- Distance-dependent inter-chains interactions:

$$t_{mn} = We^{-\frac{1}{2}\left(\frac{x_m - x_n}{\sigma}\right)^2}.$$

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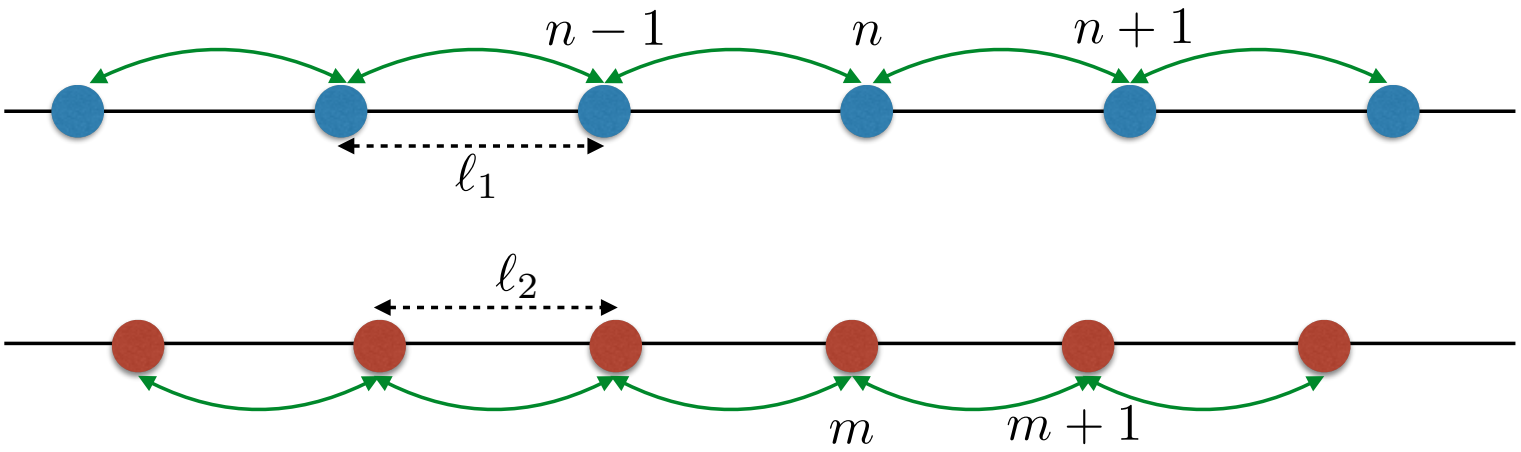

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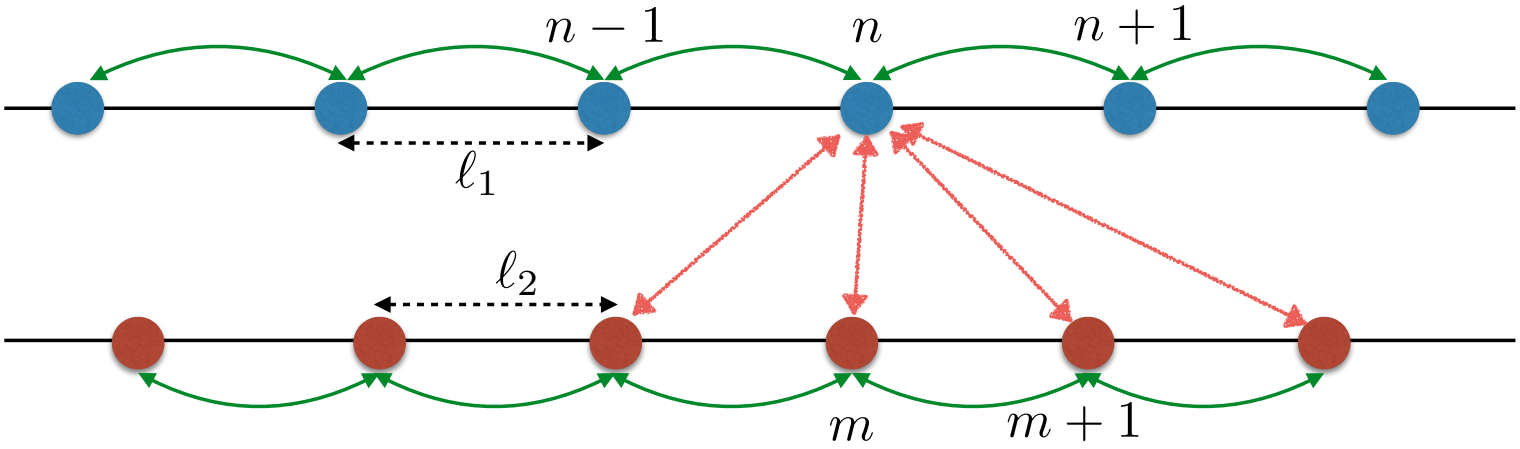

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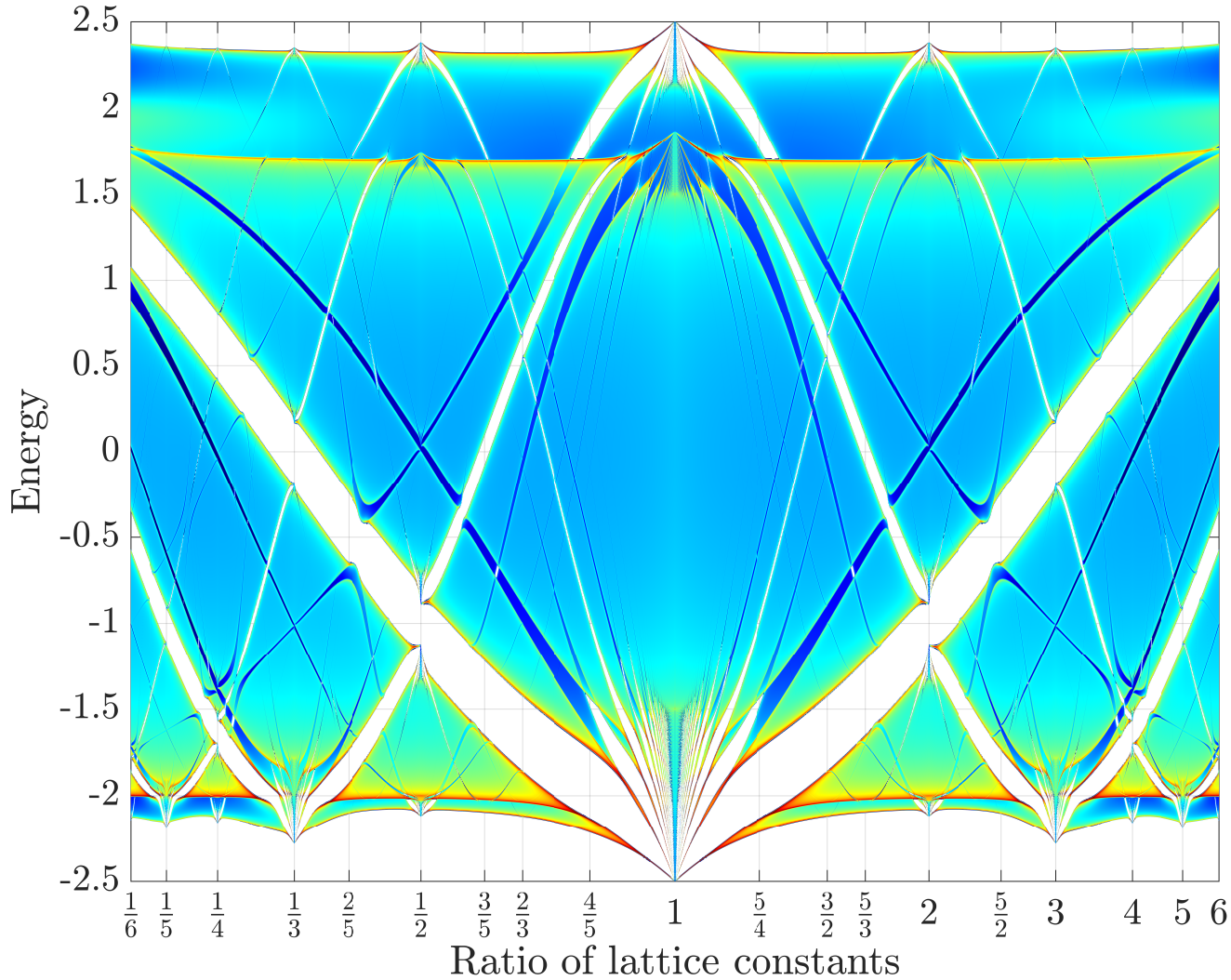
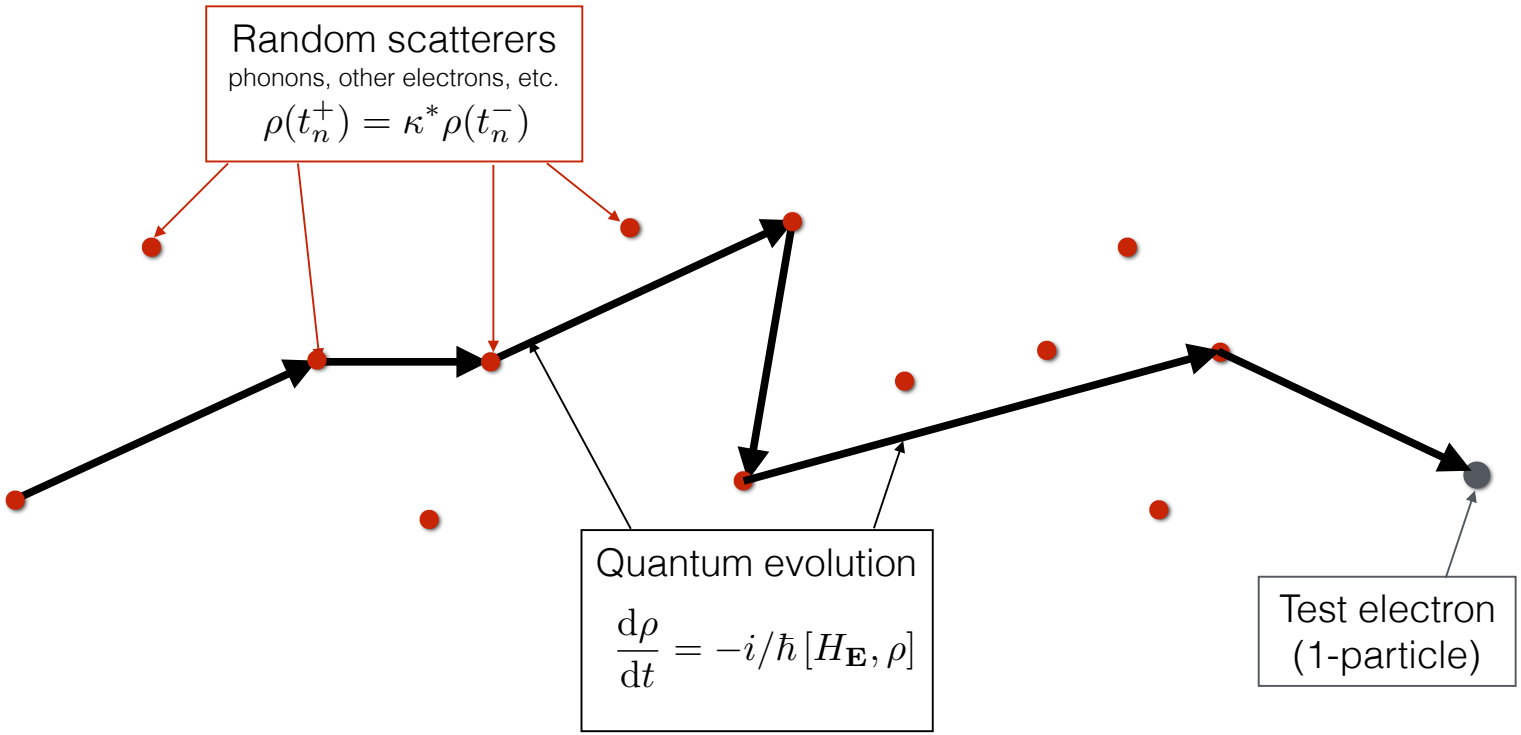
Density of States



Density of states for our 1D model, with $\sigma = .25$ and $W = .5$.

Technique: Periodic approximants and Kernel Polynomial Method.

Electronic transport: a phenomenological model



- Effective quantum Boltzman equation [Schulz-Baldes and Belissard, 1994]:

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} + \mathcal{L}_{H_{\mathbf{E}}}(\rho) = -\frac{1-\kappa^*}{\tau}(\rho), \quad \mathcal{L}_H(\cdot) = i/\hbar[H, \cdot].$$

- **Noncommutative Kubo formula** (Relaxation Time Approximation):

$$\sigma_{kl} = \left(\frac{e}{\hbar}\right)^2 \mathcal{T}\left(i[X_k, H] * (1/\tau_{rel} + \mathcal{L}_H)^{-1} i[X_l, f_{\beta,\mu}(H)]\right).$$

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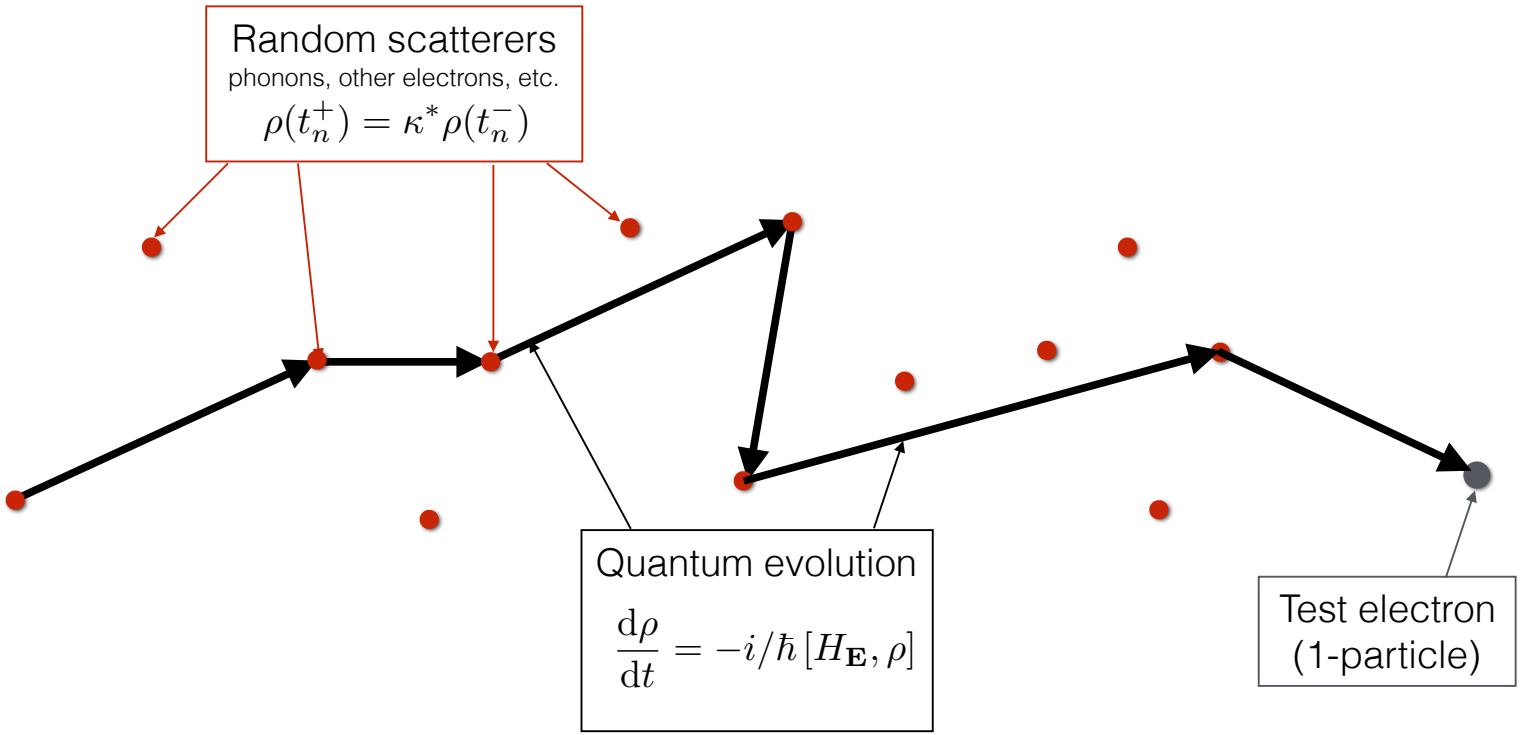

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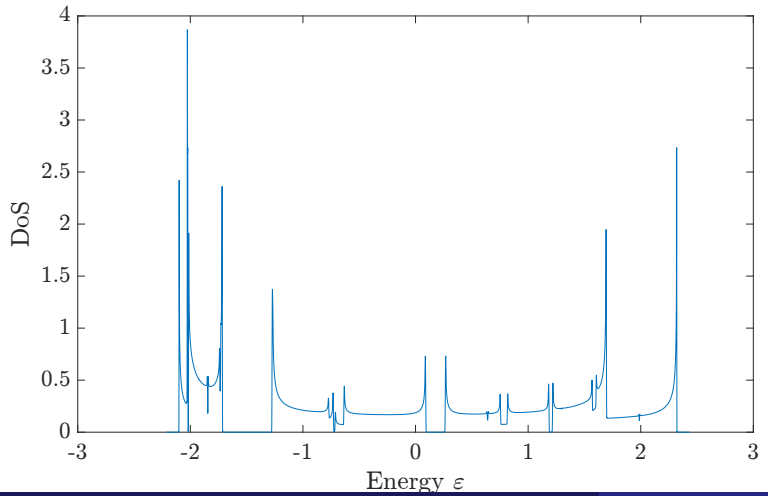
Current-current correlation function

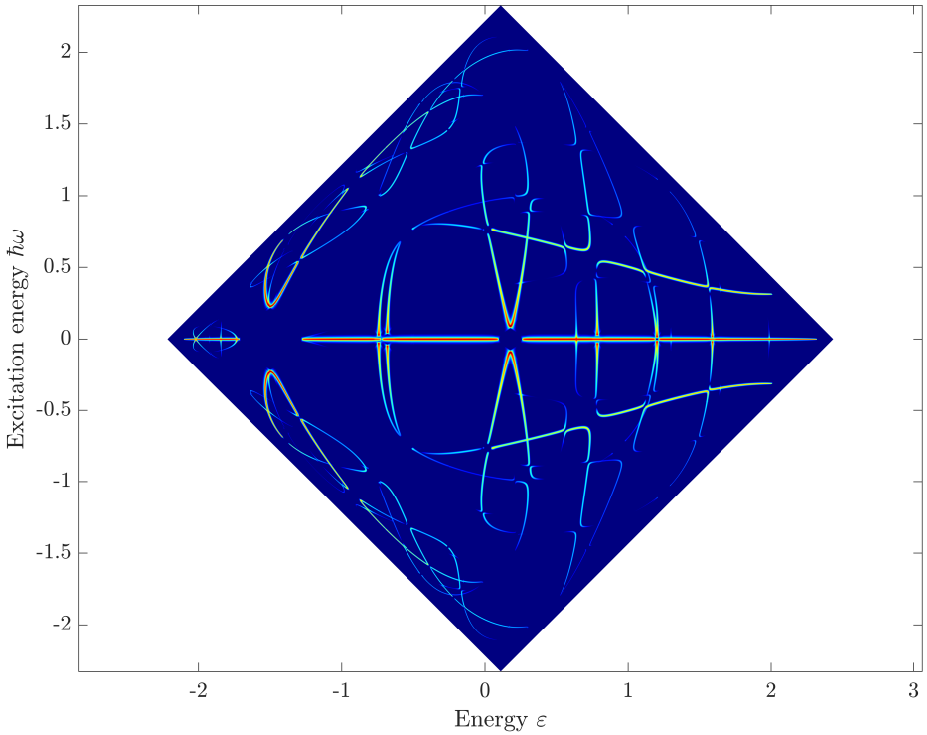
$$\int\int_{\mathbf{R}^2} f(E)g(E')\mathrm{d}m_{kl}(E,E') = \mathcal{T}\left(f(E)i[X_i,H]g(E)i[X_j,H]\right).$$

$\rightsquigarrow$ Computation of the conductivity for any (β,μ,τ_{rel}):

$$\sigma_{kl} = \left(\frac{e}{\hbar}\right)^2 \int\int_{\mathbf{R}^2} \frac{f_{\beta,\mu}(E') - f_{\beta,\mu}(E)}{E-E'} \frac{\mathrm{d}m_{kl}(E,E')}{1/\tau_{rel} - i/\hbar(E-E')}.$$

- 2D Kernel Polynomial Method.
- Example:
  $\dfrac{\ell_1}{\ell_2} = \phi = (1+\sqrt{5})/2.$





Conclusion and perspectives

Perturbation methods:

- An appropriate first-order approach for heterostructures.
- Need for higher order perturbation to compute the linear response.

C^*-algebras:

- A mathematical tool appropriate for describing observables in disordered / incommensurate materials.
- A lot of work to do to implement correctly the existing formulas, e.g.
  - Contour integrals,
  - Chebyshev polynomials,
  - Lanczos recursion chains.

Atomic relaxation and conduction

$\rightsquigarrow$ how accurate are the tight-binding coefficients in this case?

Thank you for your attention!