Spectra of graphene nanoribbons with armchair and zigzag boundary conditions

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Graphene

- 2D material, one layer sheet of carbon atoms

- many interesting physical properties
  - both metallic and semiconducting properties
  - anomalous quantum Hall effect, nonlinear Kerr effect, spintronics, Casimir effect, . . . \(^a\)

- nanoribbons: strips of graphene\(^b\)

- models: tight-binding (solid state physics), further approximations for low energies and long wavelengths

⇒ Dirac operator + boundary conditions\(^c,d\)


Domain $\Omega \subset \mathbb{R}^2$ and space

- finite rectangle (strip)
- arbitrary sufficiently regular
- infinite strip (waveguide)
- Hilbert space $L^2(\Omega, \mathbb{C}^4)$

Operator

$$H := \begin{pmatrix} 0 & \tau^* & 0 & 0 \\ \tau & 0 & 0 & 0 \\ 0 & 0 & 0 & -\tau \\ 0 & 0 & -\tau^* & 0 \end{pmatrix}, \quad \tau := -i\partial_1 + \partial_2, \quad \tau^* := -i\partial_1 - \partial_2$$

Boundary conditions

Zig-zag BC

$$\Psi_1(x_1, -b) = 0,$$
$$\Psi_2(x_1, b) = 0,$$
$$\Psi_3(x_1, -b) = 0,$$
$$\Psi_4(x_1, b) = 0.$$  

Armchair BC

$$\Psi_1(-a, x_2) = \Psi_3(-a, x_2),$$
$$\Psi_2(-a, x_2) = \Psi_4(-a, x_2),$$
$$\Psi_1(a, x_2) = e^{i\Theta} \Psi_3(a, x_2),$$
$$\Psi_2(a, x_2) = e^{i\Theta} \Psi_4(a, x_2), \quad \Theta \in \mathbb{R}.$$
Operator and BC

$$H = \begin{pmatrix} 0 & \tau^* & 0 & 0 \\ \tau & 0 & 0 & 0 \\ 0 & 0 & 0 & -\tau \\ 0 & 0 & -\tau^* & 0 \end{pmatrix}, \quad \tau = -i\partial_1 + \partial_2$$

$$\tau^* = -i\partial_1 - \partial_2$$

Dom \( (H) \) : \( \Psi \in C^1(\Omega, \mathbb{C}^4) + \text{BC} \)

Armchair : \( \Psi_1(-a, x_2) = \Psi_3(-a, x_2), \quad \Psi_2(-a, x_2) = \Psi_4(-a, x_2), \)

\( \Psi_1(a, x_2) = e^{i\Theta} \Psi_3(a, x_2), \quad \Psi_2(a, x_2) = e^{i\Theta} \Psi_4(a, x_2), \quad \Theta \in \mathbb{R}, \)

Periodic : \( \Psi_i(x_1, -b) = \Psi_i(x_1, b). \)

Spectral problem for \( H^2 \)

$$H^2 = \begin{pmatrix} -\Delta & 0 & 0 & 0 \\ 0 & -\Delta & 0 & 0 \\ 0 & 0 & -\Delta & 0 \\ 0 & 0 & 0 & -\Delta \end{pmatrix}$$
Eigenvalues and eigenfunctions

- separation of variables: simple ODE problems
- eigenvalues:
  \[ \lambda_{m,n} = \sigma_m^2 + \zeta_n^2, \]
  \[ \sigma_m = m\pi/b, \quad \zeta_n = n\pi/(2a) - \Theta/(4a). \]
- eigenfunctions:
  \[ \Psi_{m,n} = e^{i\sigma_m x_2} \begin{pmatrix} A e^{-i\zeta_n x_1} \\ B e^{-i\zeta_n x_1} \\ A(-1)^n e^{-i\frac{\Theta}{2}} e^{i\zeta_n x_1} \\ B(-1)^n e^{-i\frac{\Theta}{2}} e^{i\zeta_n x_1} \end{pmatrix}. \]
- spectrum is discrete, \( 0 \in \sigma(H^2) \) for particular \( \Theta \)
- eigenfunctions form orthonormal basis in \( L^2(\Omega, \mathbb{C}^4) \), \( H^2 \) is ess. self-adjoint
- spectrum of \( H \) : \( \pm \sqrt{\lambda_{m,n}} \)
- \( \text{Dom}(H) = W^{1,2}(\Omega, \mathbb{C}^4) + \text{BC}, \) graph norm \( \|H\Psi\|^2 + \|\Psi\|^2 = \|\Psi\|_{W^{1,2}}^2 \)


\(^b\text{J. Wurm et al. New J. Phys. 11 (2009), p. 095022.}\)
Zigzag Example

Operator and BC

\[ H = \begin{pmatrix} 0 & \tau^* & 0 & 0 \\ \tau & 0 & 0 & 0 \\ 0 & 0 & 0 & -\tau \\ 0 & 0 & -\tau^* & 0 \end{pmatrix}, \quad \tau = -i\partial_1 + \partial_2, \quad \tau^* = -i\partial_1 - \partial_2 \]

\[ \text{Dom} \,(H) : \Psi \in C^1(\Omega, \mathbb{C}^4) + \text{BC} \]

Zig – zag : \( \Psi_1(x_1, -b) = 0, \Psi_2(x_1, b) = 0 \),

Periodic : \( \Psi_i(-a, x_2) = \Psi_i(a, x_2) \).

Reduction

\[ H = \begin{pmatrix} 0 & \tau^* \\ \tau & 0 \end{pmatrix} \]

Zig – zag : \( \Psi_1(x_1, -b) = 0, \Psi_2(x_1, b) = 0 \),

Periodic : \( \Psi_i(-a, x_2) = \Psi_i(a, x_2) \).
Spectrum of $H^2$

$$H^2 = \begin{pmatrix} -\Delta & 0 \\ 0 & -\Delta \end{pmatrix}$$

Zigzag:

$$\Psi_1(x_1, -b) = 0, \quad \Psi_2(x_1, b) = 0,$$

$$(i \partial_1 - \partial_2)\Psi_1(x_1, b) = 0, \quad (i \partial_1 + \partial_2)\Psi_2(x_1, -b) = 0,$$

Periodic:

$$\Psi_i(-a, x_2) = \Psi_i(a, x_2),$$

$$\partial_1 \Psi_i(-a, x_2) = \partial_1 \Psi_i(a, x_2).$$

Reduction II

$$H^2 = -\Delta$$

Zigzag:

$$\psi(x_1, -b) = 0, \quad (i \partial_1 - \partial_2)\psi(x_1, b) = 0,$$

Periodic:

$$\psi(-a, x_2) = \psi(a, x_2), \quad \partial_1 \psi(-a, x_2) = \partial_1 \psi(a, x_2).$$
Spectrum of $H^2$

- separation of variables:
  \[ \psi(x_1, x_2) = e^{-i\sigma x_1} \xi(x_2) \]
- periodic BC: \( \sigma_m = m\pi / a \)
- “Cauchy-Riemann” BC:
  \[
  \begin{cases}
  -\xi''' = \omega^2 \xi & \text{in } (-b, b), \\
  \xi = 0 & \text{at } -b, \\
  \xi' - \sigma_m \xi = 0, & \text{at } b,
  \end{cases}
  \]
- \( \lambda_{m,n} = \sigma_m^2 + \omega_{m,n}^2 \).
- \( \lambda_{m,1} \to 0 \) as \( m \to +\infty \), more precisely
  \[ \lambda_{m,1} = 4\sigma_m^2 e^{-4\sigma_m b} + O(\sigma_m^4 e^{-8\sigma_m b}). \]
  
- \( 0 \in \sigma_{\text{ess}}(H^2) \)
- \( \{\psi_{m,n}\} \) form orthonormal basis, \( \sigma(H) : \pm \sqrt{\lambda_{m,n}} \)

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Eigenfunctions

- “usual” states: \( \psi_{m,n} = e^{-i \sigma_m x_1} \sin(\omega_{m,n} (x_2 + b)) \)

- “edge” states: \( \psi_{m,n} = e^{-i \sigma_m x_1} \sinh(\omega_{m,1} (x_2 + b)) \)
General situation

Goals

- understand spectra of Dirac operator with zigzag BC
- essential spectrum, explain and describe the edge states
- domains of definition
- perturbations by (diagonal) potential

Available mathematical literature

- 1995 K. M. Schmidt\textsuperscript{a}
  - special case in 2D,
  - domains of definition, supersymmetry
- 1970 W. D. Evans\textsuperscript{b,c}
  - 3D problems (ball and $\mathbb{R}^3$) with potentials
  - proofs based also on spherical symmetry
  - perturbations, Glazman’s decomposition method\textsuperscript{d}

Lemma (Self-adjointness):
Let $T$ be closed, densely defined operator. Then
\[
H = \begin{pmatrix} 0 & T^* \\ T & 0 \end{pmatrix}
\]
is self-adjoint.

- we search for closed realization of $\tau = -i\partial_1 + \partial_2$ and its adjoint $\tau^*$

Proposition (SUSY):
Let $T$ be densely defined and closed. $T^*T$, $TT^*$ are associated with the closed symmetric quadratic forms $t_{T^*T}[\psi] := \|T\psi\|^2$, $t_{TT^*}[\psi] := \|T^*\psi\|^2$ defined on $\text{Dom}(T)$, $\text{Dom}(T^*)$, respectively. Moreover, $\sigma(TT^*) \cup \{0\} = \sigma(T^*T) \cup \{0\}$.

- $T^*T$ corresponds to Laplacian with “Cauchy-Riemann” BC
- proofs in 1993 Thaller\textsuperscript{a}

\textsuperscript{a}B. Thaller. Springer, 1993.
Schmidt’s case

- arbitrary (sufficiently regular) domain $\Omega$
- $H = \begin{pmatrix} 0 & \tau^* \\ \tau & 0 \end{pmatrix}$
- different BC (not precisely zig-zag): $\psi_1 \mid \partial \Omega = 0$

Theorem [Schmidt’95]

Let $\tau_0 := -i\partial_1 + \partial_2$ be defined on $\text{Dom}(\tau_0) := C_0^\infty(\Omega)$. Then

$$\tau := -i\partial_1 + \partial_2,$$

$$\text{Dom}(\tau) := W^{1,2}_0(\Omega),$$

is the closure of $\tau_0$ and the adjoint reads

$$\tau^* := -i\partial_1 - \partial_2,$$

$$\text{Dom}(\tau^*) := \{ \psi \in L^2(\Omega) \cap W^{1,2}_{\text{loc}}(\Omega) : \tau^* \psi \in L^2(\Omega) \}.$$ 

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Corollaries [Schmidt’95]

- $H = \begin{pmatrix} 0 & \tau^* \\ \tau & 0 \end{pmatrix}$ is self-adjoint.

- $H^2 = \begin{pmatrix} \tau^* \tau & 0 \\ 0 & \tau \tau^* \end{pmatrix}$

- $\tau^* \tau = -\Delta_D$, i.e. $\text{Dom}(\tau^* \tau) = W_0^{1,2}(\Omega) \cap W^{2,2}(\Omega)$.

- $\sigma(\tau^* \tau) = \sigma(-\Delta_D)$, i.e. discrete spectrum

- $\text{Dom}(\tau^*)$ is larger than $W^{1,2}(\Omega)$

- $0 \in \sigma_{\text{ess}}(\tau \tau^*)$, 0 is eigenvalue of infinite multiplicity

- $\{(x_1 + ix_2)^n\} \subset \text{Ker}(\tau \tau^*)$

- $\sigma(\tau \tau^*) = \sigma(\tau^* \tau) \cup \{0\}$
More general situation

Complementary (A) and interchanging (B) BC

- in both cases:
  \[ \psi_1 \mid \partial \Omega_1 = 0, \quad \psi_2 \mid \partial \Omega_2 = 0. \]
- we search for closed realization of \( \tau \) and its adjoint
- description of domains of definition
- analysis of spectra
Proposition (A)

Let Ω be sufficiently regular and let ∂Ω have two components. Then $A\psi = \tau\psi$ defined on the domain

$$\text{Dom}(A) = \{\psi \in L^2(\Omega) \cap W^{1,2}_{\text{loc}}(\Omega \cup \partial\Omega_1) : \psi \upharpoonright \partial\Omega_1 = 0, \ \tau\psi \in L^2(\Omega)\},$$

is closed and $A^*$ acts as $A^*\phi = \tau^*\phi$ on the domain

$$\text{Dom}(A^*) = \{\phi \in L^2(\Omega) \cap W^{1,2}_{\text{loc}}(\Omega \cup \partial\Omega_2) : \phi \upharpoonright \partial\Omega_2 = 0, \ \tau^*\phi \in L^2(\Omega)\}.$$

($W^{1,2}_{\text{loc}}(\Omega \cup \partial\Omega_1)$ are functions from $W^{1,2}(\Omega')$ for any $\Omega' \subset \Omega$, $\overline{\Omega'} \subset \Omega \cup \partial\Omega_1$)

Remarks

- proof is a modification of Schmidt’s case\(^a\)
- $A$ is a closure of $\tau$ defined on smooth functions satisfying BC

Proposition
Zero is not an eigenvalue of either $T^*T$ or $TT^*$, for $T = A, B$.

Remarks

- Schmidt’s case: $\ker(TT^*) \supset \{(x_1 + ix_2)^n\}_{n \in \mathbb{N}}$
- “new” part of boundary $\partial \Omega_2$ with Dirichlet BC
Zero is in the essential spectrum

Proposition

Zero is in the essential spectrum of both $T^* T$ and $TT^*$, $T = A, B$.

Proof and remarks

• Dirichlet bracketing argument

• SUSY and description of domains of definition

• particular singular sequence from “zig-zag – periodic” example

• 0 is not an eigenvalue
Local compactness of resolvent

- 0 is in the essential spectrum \(\Rightarrow\) the resolvent of \(H^2\) and \(H\) is not compact
- \(\chi_K(H - z)^{-1}\) might be compact for compact \(K \subset \Omega\)
- local compactness of resolvent: typical for Schrödinger operators in \(L^2(\mathbb{R}^n)\)
  - essential spectrum \(\Leftrightarrow\) "behaviour at infinity"
  - singular sequences corresponding to \(\lambda \in \sigma_{\text{ess}}\) must vanish in limit in every compact subset of \(\mathbb{R}^n\)
- for Dirac operators in \(L^2(\mathbb{R}^n)\) valid as well

\(^a\)P. D. Hislop and I. M. Sigal. Springer Verlag, 1996.

Proposition

Let \(\varphi_{1,2} \in C_0^\infty(\mathbb{R}^2)\) such that \(\text{supp} \varphi_1 \cap \partial \Omega_2 = \emptyset\) and \(\text{supp} \varphi_2 \cap \partial \Omega_1 = \emptyset\). Then

\[
\begin{pmatrix}
\varphi_1 & 0 \\
0 & \varphi_2
\end{pmatrix}
\begin{pmatrix}
-z & A^* \\
A & -z
\end{pmatrix}^{-1}
\]

is a compact for any \(z \in \mathbb{C} \setminus \mathbb{R}\).

Corollaries

0 is the only point of essential spectrum of \(H\) in case \((A)\).
Let \(V \in C(\overline{\Omega})\) be a real potential. \(\sigma_{\text{ess}}(H + V) \subset [\min_{\partial \Omega} V, \max_{\partial \Omega} V]\).
Edge states

- \( \lambda_{m,1} = \frac{-4m(1-m)}{r_2^2} \left( \frac{r_1}{r_2} \right)^{-2m} + \mathcal{O} \left( m^4 \left( \frac{r_1}{r_2} \right)^{-4m} \right) \), as \( m \to -\infty \)
Motivation and literature

- straight planar strips: \( \sigma_{\text{ess}}(H) = [E_0^2, +\infty) \)
  - \( E_0 \) depends on BC: \( E_0^{(D)} = 2\pi/d, E_0^{(N)} = 0 \)
- what happens if the waveguide is bent?
  - bound states below essential spectrum\(^{a,b}\)
  - similar effects for strips on manifolds\(^c\)
  - in 3D also twisting: opposite effect (Hardy inequality)\(^d\)
- graphene waveguides?

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Proposition

\[ \sigma(H_{ac}) = \sigma_{\text{ess}}(H_{ac}) = (-\infty, -E_0] \cup [E_0, +\infty), \] where \( E_0 := \min_{n \in \mathbb{Z}} |\zeta_n| \) with \( \zeta_n = n\pi/(2a) - \Theta/(4a). \)

Proof

- standard approach: separation of variables
- \( E_0 \) determined by the transverse 1D problem
- gap around 0 depends on \( \Theta \)
Proposition

Let \( \Omega \) be asymptotically straight, \( i.e. \quad \gamma(s) \to 0 \) as \( s \to \pm \infty \), then \( \sigma_{\text{ess}}(H_{zz}) = \mathbb{R} \).

Proof

- construction of singular sequences for straight waveguide
- \( \sigma_{\text{ess}}(H_{zz}) = \mathbb{R} \) due to edge states
- singular sequences can be modified for bent waveguide
Remarks

- difficulties with definition of operator $H$: essentially self-adjoint or more extensions?
- for $H^2$ definition via quadratic forms (Friedrichs extension)
- for $H^2$: $\sigma_{\text{ess}}(H^2) \supset \{0\} \cup [E_0^2, +\infty)$
- variational techniques in the gap (if any) of essential spectrum
Summary

- spectra of graphene nanoribbons
- armchair and zigzag boundary conditions
- 0 in essential spectrum
- edge states and their properties
- potential perturbations

Further directions

- physical restrictions for appearance of edge states (necessary high-frequencies)
- non-trivial geometry (manifolds), lattice defects, magnetic fields (off-diagonal perturbations)
- non-self-adjoint perturbations (gains/losses)