Quantum network model of zigzag carbon nanotube

Korotayev E. L. Lobanov I. S.

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First graph models of aromatic molecules

- L. Pauling. The Diamagnetic Anisotropy of Aromatic Molecules. *Journal of Chemical Physics* **4** (1936) 673-677.
- K. Ruedenberg, C. W. Scherr. Free-Electron Network Model for Conjugated Systems. I. Theory *Journal of Chemical Physics* **21** (1953) 1565-1581.

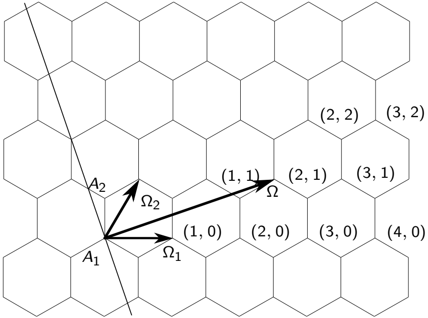

Figure: The graphene lattice. The unit cell is spanned by the vectors Ω_1 and Ω_2.

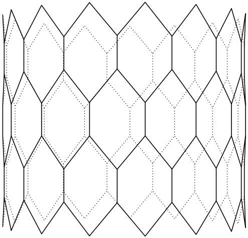

Figure: Zigzag graph

We investigate only the motion of π electrons under assumption that the σ-electrons form bonds which maintaind the molecule structure and that the π electrons move in the potential of this frame.

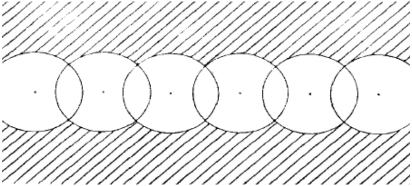

Figure: [K. Ruedenberg, C. W. Scherr *J. Chem. Phys.* **4** (1953) 673]

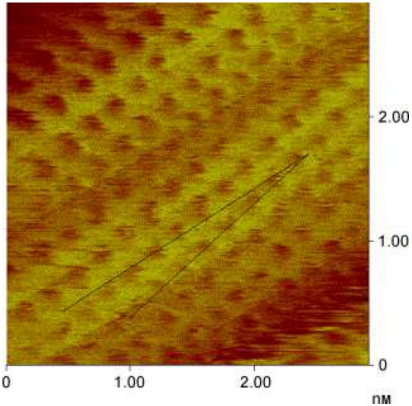

Figure: Atomic resolution STM image. Dark areas are the centres of carbon hexagons. [A. Hassanien, M. Tokumoto, T. Shimizum, H. Tokumoto. **Thin Solid Films** 464-465 (2004) 338-341]

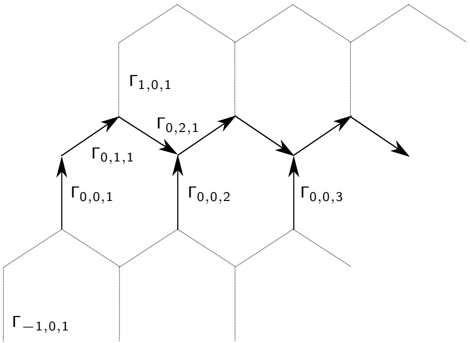

Figure: Zigzag graph

Let f_ω denote the restriction of a function $f \in W^{2,2}(\Gamma^N)$ to an edge $\omega \in \mathbb{Z} \times \mathbb{J} \times \mathbb{Z}_N$, $\mathbb{J} = \{0, 1, 2\}$. Our Schrödinger operator $\mathcal{H}_B$ defined in a subset of $W^{2,2}(\Gamma^N)$ containing functions satisfying the **magnetic Kirchhoff boundary conditions**:

1. f is continuous on Γ^N;
2. $$-\partial_{(n,0,k)} f_{(n,0,k)}(1) + \partial_{(n,1,k)} f_{(n,1,k)}(0) - \partial_{(n,2,k-1)} f_{(n,2,k-1)}(1) = 0,$$
$$\partial_{(n+1,0,k)} f_{(n+1,0,k)}(0) - \partial_{(n,1,k)} f_{(n,1,k)}(1) + \partial_{(n,2,k)} f_{(n,2,k)}(0) = 0.$$

where $\partial_\omega = \frac{d}{dt} - ia_\omega$.

The action of $\mathcal{H}_B$ is given by

$$(\mathcal{H}_B f)_\omega = -\partial_\omega^2 f_\omega(t) + q(t) f_\omega(t), \tag{1}$$

where $q \in L^2(0,1)$, $a_\omega(t) = \langle \mathcal{A}(\mathbf{r}_\omega + t\mathbf{e}_\omega) | \mathbf{e}_\omega \rangle$, and $\mathbf{r}_\omega$, $\mathbf{r}_\omega + \mathbf{e}_\omega$ are ends of the edge ω. For uniform magnetic field parallel to the axis of the nanotube

$$a_{n,0,k} = 0, \qquad a = a_{n,1,k} = a_{n,2,k} = \frac{3B}{16} \cot \frac{\pi}{2N},$$

where B is the magnetic flux density.

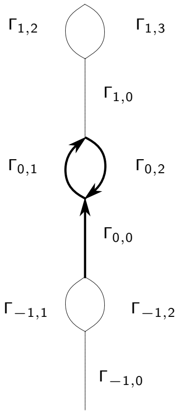

Figure: (1,0)-zigzag graph.

The operator $\mathcal{H}_B$ is unitarily equivalent to $H^a = \oplus_1^N H_k^a$, where the operator H_k^a is defined on functions f from $W^{2,2}(\Gamma^1)$ satisfying **modified Kirchhoff conditions**

$$f_{n,0}(1) = f_{n,1}(0) = e^{ia} s^k f_{n,2}(1), \quad f_{n+1,0}(0) = e^{ia} f_{n,1}(1) = f_{n,2}(0),$$

$$-f'_{n,0}(1) + f'_{n,1}(0) - e^{ia} s^k f'_{n,2}(1) = 0, \quad f'_{n+1,0}(0) - e^{ia} f'_{n,1}(1) + f'_{n,2}(0) = 0,$$

$$s = e^{i\frac{2\pi}{N}},$$

and is given by $(H_k^a f)_\omega = -f''_\omega + q f_\omega$.

Let $(k, a) \in \mathbb{Z}_N \times \mathbb{R}$ be fixed. If $c_k = \cos(a + \frac{\pi k}{N}) \neq 0$, then for every $\lambda \in \mathbb{C} \setminus \sigma_D$ there exist unique fundamental solutions Θ_k, Φ_k for the spectral problem $H_k^a f = \lambda f$ satisfying $\Phi_k(0,\lambda) = \Theta_k'(0,\lambda) = 0$, $\Phi_k'(0,\lambda) = \Theta_k(0,\lambda) = 1$. For all $x \in \Gamma^1$, the functions $\Theta_k(x,\cdot)$, $\Phi_k(x,\cdot)$, are meromorphic in $\lambda \in \mathbb{C} \setminus \sigma_D$, where σ_D is the Dirichlet spectrum of the problem $-f'' + qf = \lambda f$ on $[0,1]$. The monodromy matrix is given by

$$\mathcal{M}_k = \begin{pmatrix} \Theta_k & \Phi_k \\ \Theta_k' & \Phi_k' \end{pmatrix} = \mathcal{R}^{-1}\mathcal{T}_k\mathcal{R}\mathcal{M},$$

$$\mathcal{T}_k = \frac{s^{-\frac{k}{2}}}{2c_k}\begin{pmatrix} 2\Delta & 1 \\ 4\Delta^2 - 4c_k^2 & 2\Delta \end{pmatrix}, \quad \mathcal{R} = \begin{pmatrix} 1 & 0 \\ 0 & \varphi(1,\cdot) \end{pmatrix},$$

where $c_k = \cos(a + \frac{\pi k}{N})$, $\Delta = \frac{1}{2}(\varphi'(1,\lambda) + \vartheta(1,\lambda))$, $\varphi(x,\lambda)$ and $\vartheta(x,\lambda)$ are fundamentail solutions of $-f''(x) + q(x)f(x) = \lambda f(x)$ satisfying $\varphi(0,\lambda) = \vartheta'(0,\lambda) = 0$, $\varphi'(0,\lambda) = \vartheta(0,\lambda) = 1$.

In contrast to the Schrödinger operator with periodic matrix potential on the real line, the monodromy matrix $\mathcal{M}_k$ has poles at the points $\lambda \in \sigma_D$, which are eigenvalues of H_k.
However, the monodromy matrix $\mathcal{M}_k$ is similar to $\mathcal{R}\mathcal{M}_k\mathcal{R}^{-1}$ which is an entire matrix-valued function.

Every eigenvalue of H_k^a has infinite multiplicity. Moreover, the point spectrum of H_a^k can be decomposed to the following two parts:
1) $\lambda \in \sigma_D$. The correspoding eigenfunctions vanish at all vertexes of Γ^1. The supports of these eigenfunctions depend on $\eta = 1 - e^{2ia} s^k \varphi'(1, \lambda)^2$.

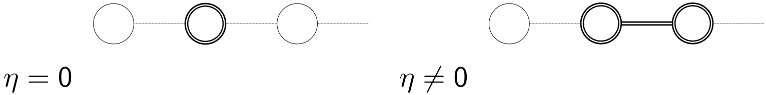

Figure: The support of the eigenfunction $\psi^{(0)}$.

Denoting the function $\psi^{(0)}$ shifted to n periods along the nanotube axes by $\psi^{(n)}$, every eigenfunction f can be decomposed as follows

$$f = \sum_{n\in\mathbb{Z}} \widehat{f}_n \psi^{(n)}, \qquad \widehat{f}_n = \begin{cases} \eta^{-1} f'_{n,0}(0) & \textit{if } \eta \neq 0 \\ f'_{n,1}(0) & \textit{if } \eta = 0 \end{cases}, (\widehat{f}_n)_{n\in\mathbb{Z}} \in \ell^2.$$

Moreover, the mapping $f \to (\widehat{f}_n)_{n\in\mathbb{Z}}$ is a linear isomorphism between the eigensubspace and ℓ^2.

2) Assume that the magnetic field is *singular*, i.e. a equals $\widetilde{a}_{k,m} = \frac{\pi}{2} - \frac{\pi k}{N} + \pi m$, for some $(k, m) \in Z_N \times \mathbb{Z}$. Then every $\lambda \in \mathbb{R} \setminus \sigma_D$ such that $F(\lambda) := 2\Delta^2 + \frac{\varphi(1,\cdot)\vartheta'(1,\cdot)}{4} - 1 = -1$ is an eigenvalue of H_k^a.

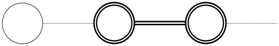

Figure: The supports of the corresponding eigenfunctions $\psi^{(k)}$.

Every eigenfunction f has the form

$$f = \sum_{n\in\mathbb{Z}} \widehat{f}_n \psi^{(n)}, \qquad \widehat{f}_n = f_{n,1}(0), \qquad (\widehat{f}_n)_{n\in\mathbb{Z}} \in \ell^2.$$

Moreover, the mapping $f \to (\widehat{f}_n)_{n\in\mathbb{Z}}$ is a linear isomorphism between the eigensubspace and ℓ^2.

Lyapunov function

The monodromy matrix is not symplectic, $\det \mathcal{M}_k = s^{-k}$, $s = e^{i\frac{2\pi}{N}}$. Nevertheless, the Lyapunov function $F_k^{\pm}$ can be defined by $F_k^{\pm} = \frac{1}{2}(\tau_k^{\pm} + \frac{1}{\tau_k^{\mp}})$ where $\tau^{\pm}$ are eigenvalues of the monodromy matrix $\mathcal{M}_k$.

$\lambda \in \sigma_{ac}(H_k^a)$ *if and only if* $-1 \leqslant F_k^{\pm}(\lambda) \leqslant 1$.

Explicite form: $F_k^{\pm} = c_{0k}\xi_k \pm \sqrt{\rho_k}$, where $\xi_k = \frac{F+s_k^2}{c_k}$, $\rho_k = s_{0k}^2(1-\xi_k^2)$, $F_0^{\pm} = \xi_0$, $s_{0,k} = \sin\frac{\pi k}{N}$, $c_{0,k} = \cos\frac{\pi k}{N}$, $c_k = \cos(a + \frac{\pi k}{N})$, $s_k = \sin(a + \frac{\pi k}{N})$.

There are two types of spectral gaps:

1. Stable gaps: $F_k^+(\lambda) \in \mathbb{R}$ and $|F_k^+(\lambda)| > 1$. The ends λ' of stable gaps are periodic and antiperiodic eigenvalues, i.e. the corresponding generalized eigenfunction satisfies $f_{n+1,k} = \pm f_{n,j}$.
2. Resonance gaps: $F_k^+(\lambda) \notin \mathbb{R}$. The ends of resonance gaps are resonances, which are zeros of ρ_k.

Due to the symmetry of the zigzag graph

$$\sigma_{ac}(H_k^a) = \sigma_{ac}(H_0^{a_k}), \quad a_k = a + \frac{\pi k}{N}.$$

Direct calculations prove that for $k \neq 0$.

$$\sigma_{ac}(H_k^a) = \{\lambda \in \mathbb{R} : \xi_k(\lambda) \in [-1, 1]\} = \{\lambda \in \mathbb{R} : \rho_k(\lambda) \geqslant 0\}.$$

It is sufficient to know the Lyapunov function F_0 to calculate F_k^+, ρ_k, $k \neq 0$.

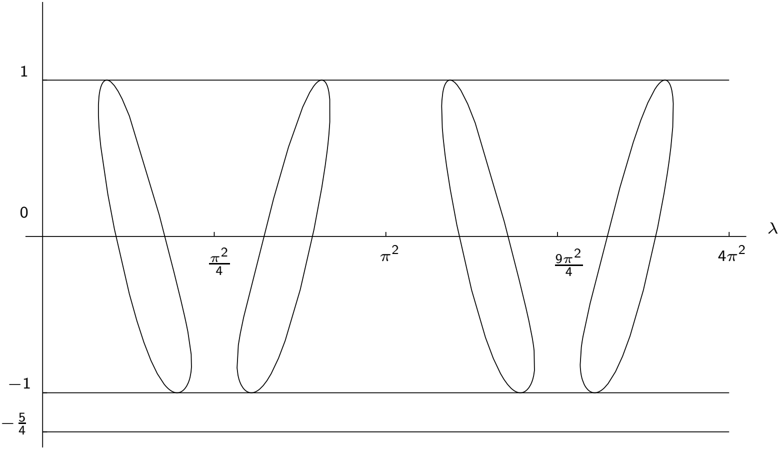

Figure: The function $F_{1,\pm}(\lambda, a)$ for $a = 0$.

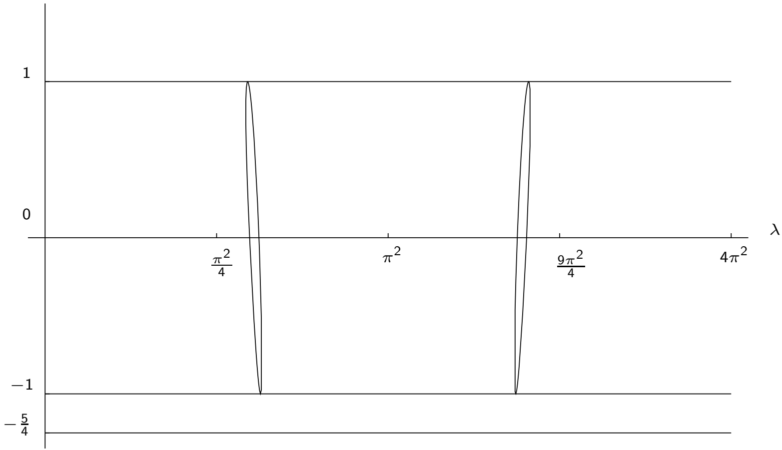

Figure: The function $F_{1,\pm}(\lambda, a)$ for $a = \frac{\pi}{3}$.

For zigzag graph resonances are allways real. However, in general (e.g. for armchair graph) the resonances can be complex.

All spectral gaps for H_k^a are resonance.

All spectral gaps for H_0^a are stable.

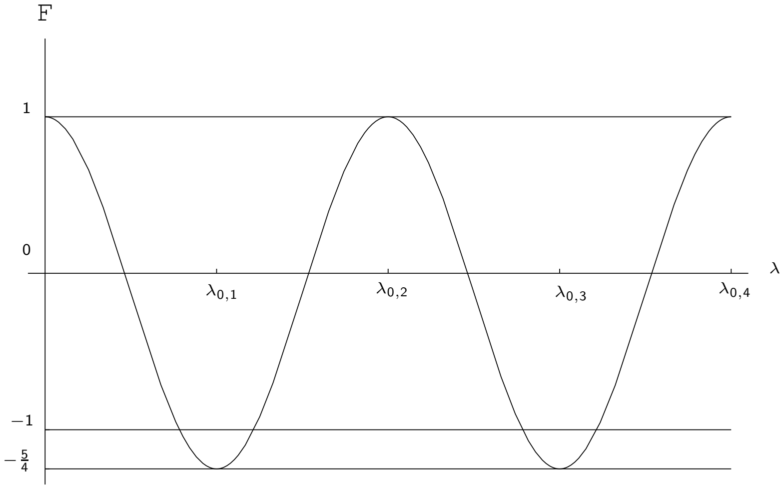

Figure: The function $F_0(\lambda, a)$ for $a = \frac{\pi}{6}$.

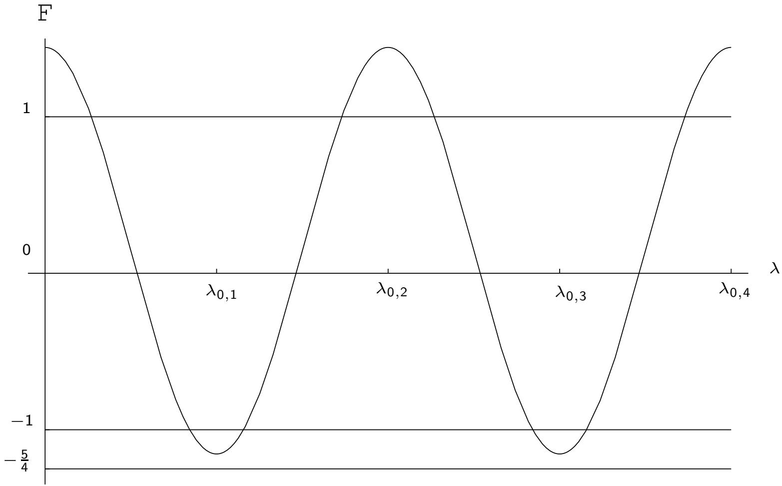

Figure: The function $F_0(\lambda, a)$ for $a = \frac{\pi}{6}$.

Absolute continuous spectrum of H^a

$\sigma_{\rm ac}(H^a) = \bigcup_{n\geqslant 1} S_n^a$, $S_n^a = [E_{n-1}^{a+}, E_n^{a-}]$, where $E_0^{a+} < E_1^{a-} \leqslant E_1^{a+} < \ldots$.

Let $a \in [0, \frac{\pi}{N}]$ **and** $n \geqslant 0$ **be even.** Then $E_n^{a\pm}$ are solutions of $F(E_n^{a\pm}) = c_*^2 + c_* - 1$, where $F = 2\Delta^2 + \frac{\varphi(1,\cdot)\vartheta'(1,\cdot)}{4} - 1$, $c_* = \cos\min\{a, \frac{\pi}{N}\}$. If $a \neq 0$, every gap $G_n^a = (E_n^{a-}, E_n^{a+})$ is not trivial, and $|G_n^a| \to \infty$ as $n \to \infty$.

$$E_n^{a\pm} = \left(\frac{\pi}{2} \pm \phi_0\right)^2 + q_0 + \frac{o(1)}{n}, \quad n \to \infty,$$

$$\phi_0 = \frac{1}{2}\arccos\frac{1 + 8(c_*^2 + c_* - 1)}{9} \in [0, \frac{\pi}{2}], \quad q_0 = \int_0^1 q(t)dt.$$

Let $a \in [0, \frac{\pi}{N}]$ **and** $n \geqslant 0$ **be odd.** If N is a multiple of 3, then $|G_n^a| \to 0$ as $n \to \infty$, otherwise all gaps are not trivial, and $|G_n^a| \to \infty$ as $n \to \infty$.

Assume that $\mathbf{a=0}$. Then the operator H^0 has only a finite number of non-degenerate gaps if and only if

1. N is a multiple of 3;
2. q is a finite gap potential for the operator $-f'' + qy$ on $\mathbb{R}$.

The spectral gaps of H^a tends to the solutions of $2\Delta^2 + \frac{\varphi(1,\cdot)\vartheta'(1,\cdot)}{4} = 0$ as the magnetic filed tends to singular one. Therefore we have a localization.

Assume $a = 0$. Then every Dirichlet eigenvalue λ for problem $-f'' + qf = \lambda f$ is an eigenvalue of H^0. Moreover, λ belongs to the gap G^0_{2n} or is one of the ends E^{0-}_{2n}, E^{0+}_{2n} of spectral bands. In particular, if q is even, the Dirichlet eigenvalue λ belongs to an end of the spectral band.

Inverse problem

Assume $a = 0$. Then the eigenvalues E_n of H^0 satysfies $E_n = \pi^2 n^2 + q_0 + \xi_n$, $n \geqslant 1$, $(\xi_n) \in \ell_2$. Moreover, the corresponding eigenfunctions satisfy $f'_{n,\omega}(1)^2 = f'_{n,\omega}(0)^2 e^{2h_n}$ for some constants h_n.
Let $\mathcal{K} = \left\{(\varkappa_n)_1^\infty \in \ell^2 : \pi^2 + \varkappa_1 < (2\pi)^2 + \varkappa_2 < \dots \right\} \subset \ell^2$.

The mapping $\Phi\colon q \mapsto \left(q_0, (\xi_n)_1^\infty; (h_n)_1^\infty\right)$ is a real-analytic isomorphism between $L^2(0,1)$ and $\mathbb{R} \times \mathcal{K} \times \ell_1^2$ where $\ell_p^2 = \{f = (f_n)_1^\infty\colon \sum_{n\geqslant 1} n^{2p} f_n^2 < \infty\}$.

The mapping $\Phi_e : q \mapsto \left(q_0, (\xi_n)_1^\infty \right)$ is a real-analytic isomorphism between all even square integrable potentials and $\mathbb{R} \times \mathcal{K}$.