Computation of quantum resonances in solids and molecules

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Context

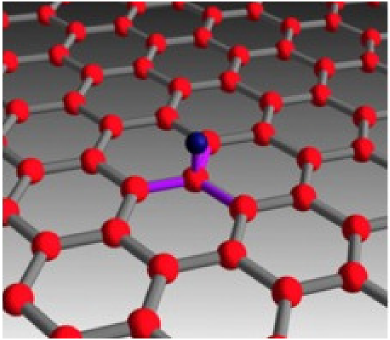

Figure: Adatom on a graphene lattice

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Hamiltonian and Green function

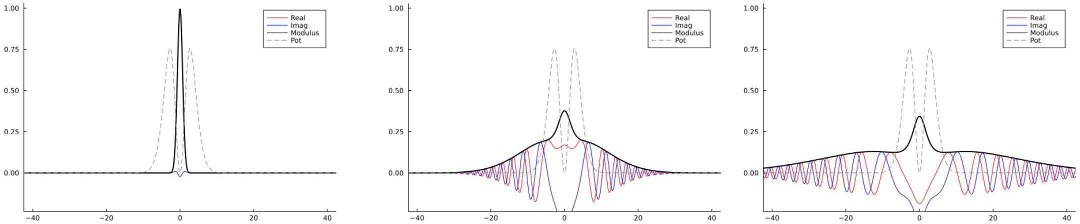
- One-body Schrödinger equation: $i\partial_t \psi = H\psi = (-\Delta + V)\psi$ on $L^2(\mathbb{R}^d)$
- $V \in L^\infty_{\mathrm{comp}}$
- The Hamiltonian is self-adjoint.

Figure: Spectrum of the Hamiltonian

- The Green function is defined for $z \in \mathbb{C} \setminus \sigma(H)$ as the inverse of $z - H$ on $L^2(\mathbb{R}^d)$ or the Fourier-Laplace transform of the propagator $U(t) = -i\theta(t)e^{-iHt}$.
- A resonance is a pole of the continuation of the Green function from the upper complex plane to the lower complex plane.

Example: wavepacket in a potential well

Take a gaussian wavepacket localized in a potential well V at $t = 0$; $H = -\Delta + V$ the Hamiltonian.



(a) T=0 (b) T=14 (c) T=31

Figure: Wavepacket at different moments.

The state oscillates at frequency ω and has a lifetime $\frac{1}{\Gamma} = 66$. It is associated to a resonance located at $\omega - i\Gamma$, $\Gamma = 0.015$.

Extension of the Green function

Theorem (Meromorphic continuation of the resolvent, *Dyatlov, Zworski 2019*)

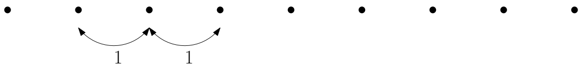
Let $V \in L^\infty_{\mathrm{comp}}(\mathbb{R}^d)$, $H = -\Delta + V$. Let $\psi, \varphi \in L^2_{\mathrm{comp}}(\mathbb{R}^d)$ and let $f(z) = \langle \psi | \frac{1}{z-H} | \varphi \rangle$. Let U an open domain which does not contain 0, simply connected in $\mathbb{C}$, and containing z_0 such that $\mathrm{Im}(z_0) > 0$.
Then f extends meromorphically to U.

The poles in the lower complex planes are the resonances.
Our work applies to more sophisticated Hamiltonians:

$$H = -\Delta + V_{per} + V_{def}$$
$$H = H_0 + V_{def}$$

We will introduce it in a discrete context, with $H = H_0 + V$, H_0 periodic, V localized.

Monoatomic chain in 1D



$$H_0 = \begin{pmatrix} & \ddots & & & & & & \\ \ddots & \ddots & 1 & & & & & \\ & 1 & 0 & 1 & & & & \\ & & 1 & 0 & 1 & & & \\ & & & 1 & 0 & 1 & & \\ & & & & 1 & 0 & 1 & \\ & & & & & 1 & \ddots & \ddots \\ & & & & & & \ddots & \end{pmatrix}$$

$$H_0 \left(e^{i\mathbf{k}n}\right)_n = 2\cos(\mathbf{k}) \left(e^{i\mathbf{k}n}\right)_n$$

$\varepsilon_{\mathbf{k}=2\cos(\mathbf{k})}$

Monoatomic chain in 1D

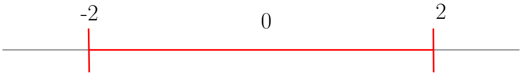
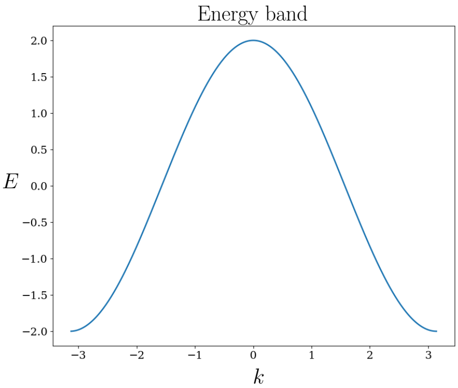


Figure: Spectrum of the Hamiltonian

$$\varepsilon_{\mathbf{k}} = 2\cos(\mathbf{k})$$



Plan

Bloch theorem

Theorem (Bloch Theorem)

Let $H_0 : l^2(\mathbb{Z}^d, \mathbb{C}^S) \to l^2(\mathbb{Z}^d, \mathbb{C}^S)$ *periodic and self-adjoint. Suppose* H_0 *is finite-range i.e.* $\mathbf{R} \mapsto H_0(0, \mathbf{R})$ *is compactly supported. Denote by* $\mathcal{B}$ *the Brillouin zone* $[-\pi, \pi[^d$.

$$\text{Let } U : \begin{cases} l^2(\mathbb{Z}^d) & \to L^2([-\pi, \pi[^d, \mathbb{C}^S) \\ Uu(\mathbf{k}) & = f(\mathbf{k}) = \frac{1}{\sqrt{2\pi}^d} \sum_{\mathbf{R}' \in \mathbb{Z}^d} e^{i\mathbf{k}\cdot\mathbf{R}'} u(\mathbf{R}') \end{cases} \quad \text{the Fourier Transform}$$

For $\mathbf{k} \in \mathcal{B}$, *let* $H_{\mathbf{k}} = \sum_{\mathbf{R}' \in \mathbb{Z}^d} H_0(0, \mathbf{R}') e^{i\mathbf{k}\cdot\mathbf{R}'}$. *Then*

$$\left(UH_0U^{-1}f\right)(\mathbf{k}) = H_{\mathbf{k}} f(\mathbf{k})$$

Inverse of a periodic Hamiltonian

It allows to write, for $z \in \mathbb{C}, \mathrm{Im(z)} > 0$:

$$R_0(\mathbf{R}, \mathbf{R}'; z) = \int_{\mathbf{k} \in \mathcal{B}} \frac{e^{i\mathbf{k}(\mathbf{R}-\mathbf{R}')}}{z - H_{\mathbf{k}}} d\mathbf{k}$$

Take any $H_{\mathbf{k}}$ periodic with eigenvalues $\varepsilon_{\mathbf{k}}$, and do the integration for z in the strict upper complex plane.

Integrand for a z in the upper complex plane (for one band)

Take $z = E_0 + i\eta$, $\eta > 0$.
Zoom on $E_0 = \varepsilon_{k_{01}} \in \sigma(H)$. At k_{01}, with $\nabla\varepsilon_k \neq 0$, ε_k is locally invertible.

$$E_0 + i\eta = \varepsilon_{k_1} \Rightarrow k_1 = k_{01} + \frac{i\eta}{\nabla\varepsilon_{k_{01}}} + \mathcal{O}(\eta^2)$$

For a z in the upper complex plane, the k for which $z - \varepsilon_k = 0$ is shifted in the direction of the gradient.

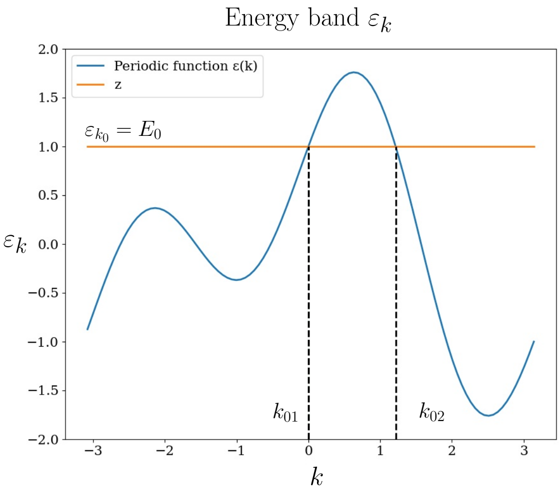
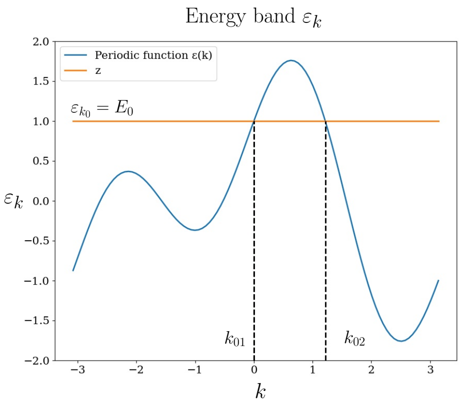
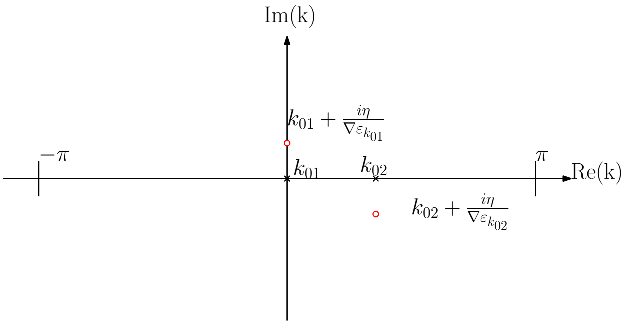


Figure: One periodic energy band ε_k for some H_k.

Problematic points



(a) One periodic energy band ε_k for some H_k.



(b) Points k for which the integrand $z - \varepsilon_k$ vanishes for a $z = E_0 + i\eta$ in the upper complex plane.

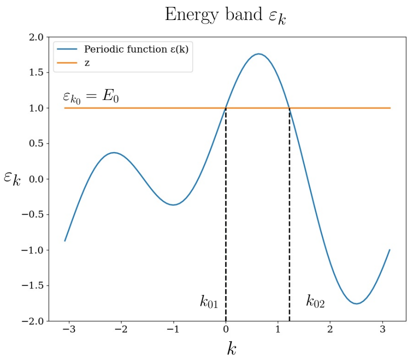
Generalization of the contour deformation

Theorem (Closed integral deformation)

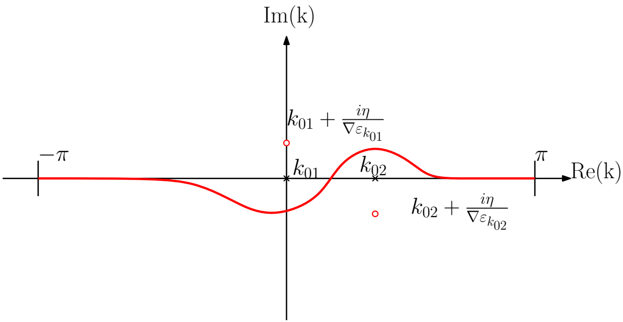
Let $A(\mathbf{k})$ *be a* $(2\pi)^d -$ *periodic function, analytic in an open set* $U = \mathbb{R}^d + i[-\eta, \eta]^d$. *Then, for all periodic and smooth functions* $\mathbf{k}_i(\mathbf{k}) : \mathbb{R}^d \to [-\eta, \eta]^d$, *we have*

$$\int_{[-\pi,\pi]^d} A(\mathbf{k}) d\mathbf{k} = \int_{[-\pi,\pi]^d} A(\mathbf{k} + i\mathbf{k}_i(\mathbf{k})) \det(1 + i\mathbf{k}_i'(\mathbf{k})) d\mathbf{k}$$

Contour deformation



(a) One periodic energy band ε_k for some H_k.



(b) Contour deformation for a $z = E_0 + i\eta$ in the upper complex plane.

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Form of $\mathbf{k}_i$

$$\varepsilon_{\mathbf{k}+i\mathbf{k}_i} = \varepsilon_{\mathbf{k}} + i\mathbf{k}_i \nabla \varepsilon_{\mathbf{k}} + \mathcal{O}(k_i^2)$$

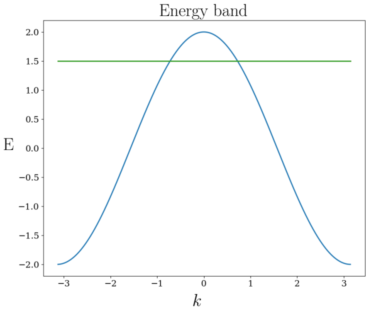
$$\mathbf{k}_i(\mathbf{k}, z) = -E_1 \frac{\nabla \varepsilon_{\mathbf{k}}}{(|\nabla \varepsilon_{\mathbf{k}}|^2 + \alpha^2)} \chi\left(\frac{\varepsilon_{\mathbf{k}} - \mathrm{Re}(z)}{E_2}\right)$$

$$\chi(x) = e^{-x^2}$$

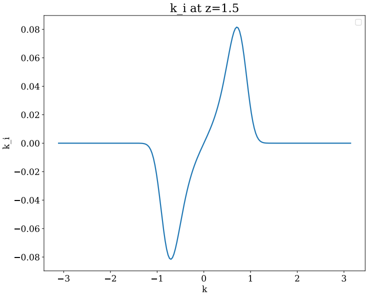
Form of $\mathbf{k}_i$

$$\varepsilon_{\mathbf{k}+i\mathbf{k}_i} = \varepsilon_{\mathbf{k}} + i\mathbf{k}_i \nabla\varepsilon_{\mathbf{k}} + \mathcal{O}(k_i^2) \qquad \mathbf{k}_i(\mathbf{k}, z) = -E_1 \frac{\nabla\varepsilon_{\mathbf{k}}}{(|\nabla\varepsilon_{\mathbf{k}}|^2 + \alpha^2)} \chi\left(\frac{\varepsilon_{\mathbf{k}} - \mathrm{Re(z)}}{E_2}\right)$$

$$\chi(x) = e^{-x^2}$$



(a) Energy band of the Hamiltonian.



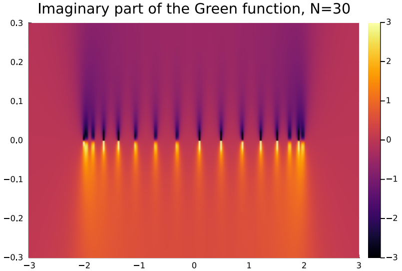
(b) $\mathbf{k}_i(z)$ for this expression.

Green function for H_0

$$R_0(\mathbf{R},\mathbf{R}';z) = \int_{\mathbf{k}\in\mathcal{B}} \frac{e^{i\mathbf{k}(\mathbf{R}-\mathbf{R}')}}{z-\varepsilon_{\mathbf{k}}} d\mathbf{k} = \lim_{N\to\infty} \frac{2\pi}{N} \sum_{\mathbf{n}\in\{1,\dots N\}^d} \frac{e^{i\frac{2\mathbf{n}\pi}{N}(\mathbf{R}-\mathbf{R}')}}{z-\varepsilon_{\frac{2\mathbf{n}\pi}{N}}}$$

Green function for H_0

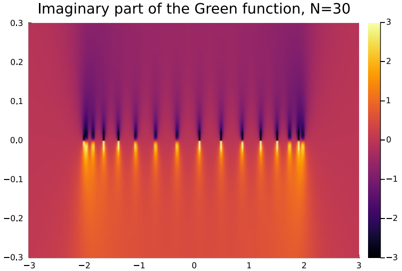
$$R_0(\mathbf{R},\mathbf{R}';z) = \int_{\mathbf{k}\in\mathcal{B}} \frac{e^{i\mathbf{k}(\mathbf{R}-\mathbf{R}')}}{z-\varepsilon_{\mathbf{k}}} d\mathbf{k} = \lim_{N\to\infty} \frac{2\pi}{N} \sum_{\mathbf{n}\in\{1,\dots N\}^d} \frac{e^{i\frac{2\mathbf{n}\pi}{N}(\mathbf{R}-\mathbf{R}')}}{z-\varepsilon_{\frac{2\mathbf{n}\pi}{N}}}$$



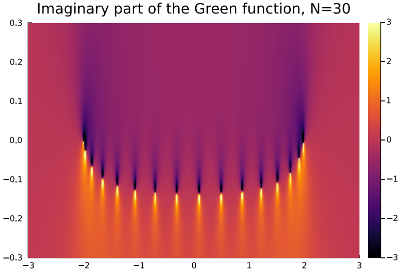
(a) Coefficient [0,0] of the Green function in the complex plane.

Green function for H_0

$$R_0(\mathbf{R},\mathbf{R}';z) = \int_{\mathbf{k}\in\mathcal{B}} \frac{e^{i\mathbf{k}(\mathbf{R}-\mathbf{R}')}}{z-\varepsilon_{\mathbf{k}}}d\mathbf{k} = \lim_{N\to\infty}\frac{2\pi}{N}\sum_{\mathbf{n}\in\{1,\dots N\}^d}\frac{e^{i\frac{2\mathbf{n}\pi}{N}(\mathbf{R}-\mathbf{R}')}}{z-\varepsilon_{\frac{2\mathbf{n}\pi}{N}}}$$



(a) Coefficient [0,0] of the Green function in the complex plane.



(b) Coefficient [0,0] of the Green function continuation with contour deformation in a neighbourhood of the spectrum.

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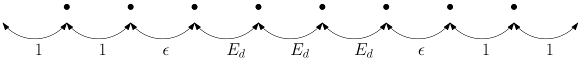
Monoatomic chain in 1D



$$H = \begin{pmatrix}
\ddots & \ddots & & & & & & & & \\
\ddots & & 1 & & & & & & & \\
& 1 & \ddots & \epsilon & & & & & & \\
& & \epsilon & 0 & E_d & & & & & \\
& & & E_d & 0 & E_d & & & & \\
& & & & E_d & 0 & E_d & & & \\
& & & & & E_d & 0 & \epsilon & & \\
& & & & & & \epsilon & \ddots & 1 & \\
& & & & & & & 1 & & \ddots \\
& & & & & & & & \ddots & \ddots
\end{pmatrix}$$

Dyson formula

Theorem (Dyson equation)

Let V compactly supported on $l^2(\mathbb{Z}^d)$, H_0 self-adjoint on $l^2(\mathbb{Z}^d)$, $z \in \mathbb{C}, \mathrm{Im(z)} > 0$.
Then $R(z) = (z - (H_0 + V))^{-1}$ is defined and

$$R(z) = R_0(z)(1 - VR_0(z))^{-1} \tag{1}$$

For our defect V localized on four sites, provided $R_0(z)$ is known, $(1 - VR_0(z))^{-1}$ is easy to compute.

Position of the resonances

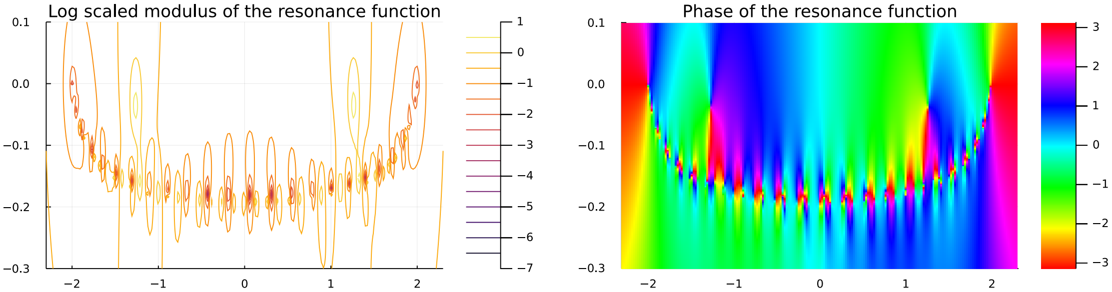
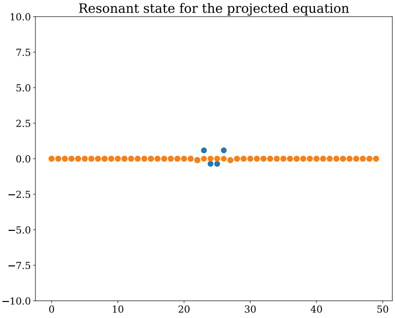


Figure: Determinant of the resonance matrix $(1 - VR_0(z))^{-1}$

Resonant states

We take z at which $(1 - VR_0(z))$ is not invertible. We display the eigenvector ϕ associated to the eigenvalue 0 in this equation. We also display $\psi = R_0\phi$, which is the resonant state for the whole system.



(a) ϕ

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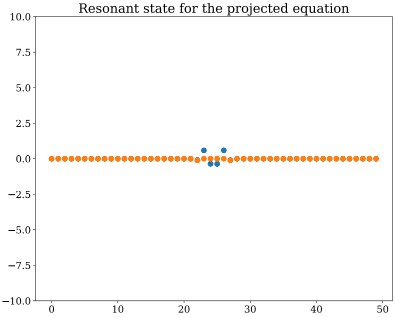
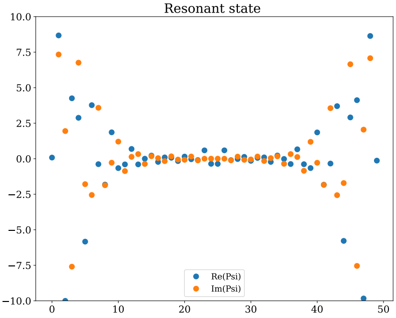


(a) ϕ



(b) ψ

Unperturbed Green function for the diatomic chain

$$H_0 = \begin{pmatrix} \ddots & \ddots & \ddots & & & & & \\ & 1 & 1 & 1 & & & & \\ & & 1 & 0 & 1 & & & \\ & & & 1 & 1 & 1 & & \\ & & & & 1 & 0 & 1 & \\ & & & & & \ddots & \ddots & \ddots \end{pmatrix}$$

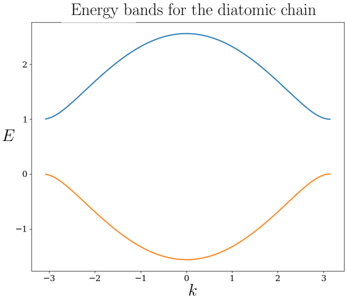


Figure: Energy bands for the diatomic chain

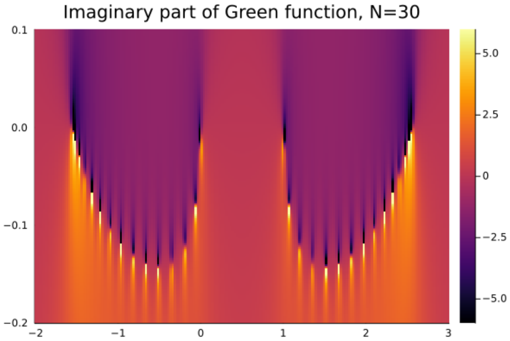


Figure: Coefficient [0,0] of the Green function in the complex plane for this Hamiltonian.

Resonances for the diatomic chain

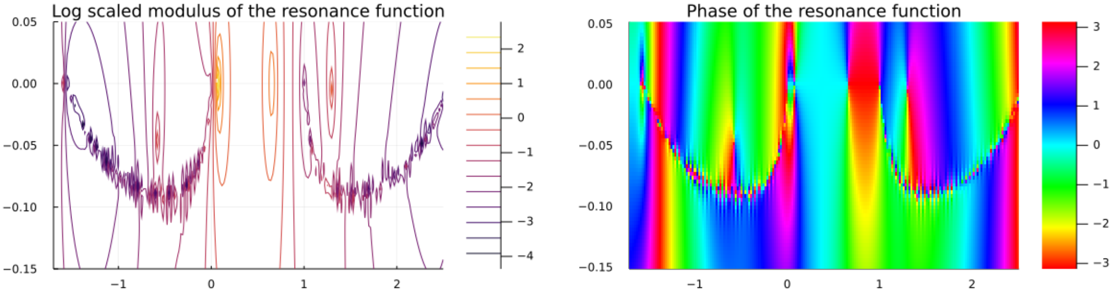


Figure: Two poles appearing in the resonance function for the diatomic chain when we add the defect.

Convergence of the method

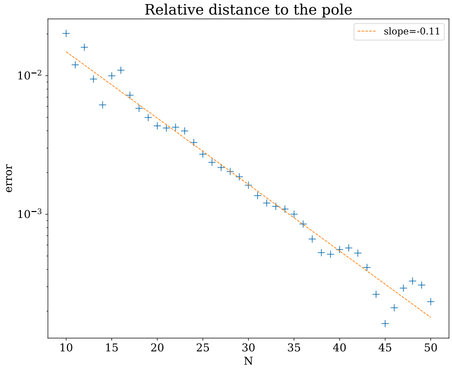


Figure: Relative error on the position of one of the the poles.

Plan

Conclusion

- Model for periodic Hamiltonians in infinite domains without finite-size box
- Flexibility on the potential
- To be integrated in DFT?

Thank you for your attention!