Dynamical response properties of molecules and solids

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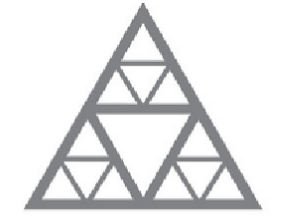
First part joint with M-S. Dupuy (SMAI JCM)

Second part joint with I. Duchemin, L. Genovese, É. Letournel, S. Ruget (arxiv)



Summary

Electronic structure

Linear response

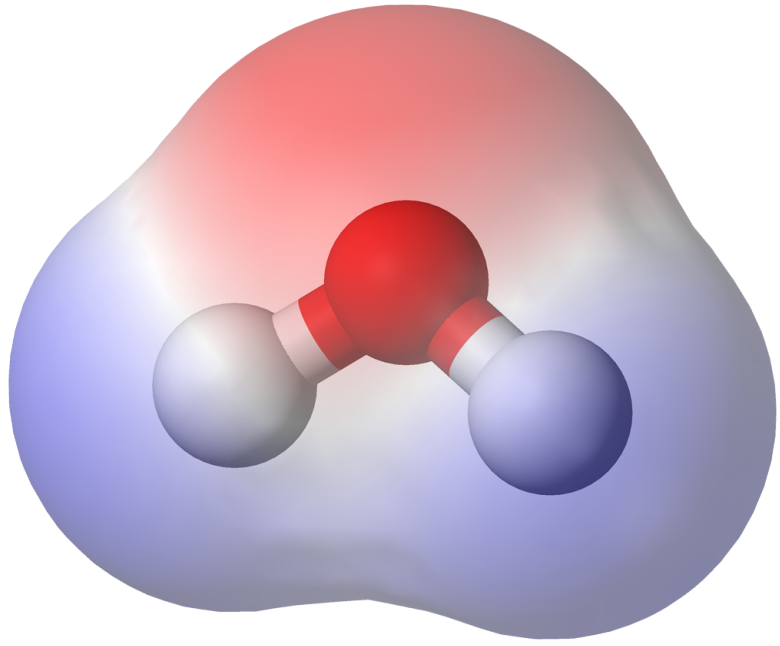
The limiting absorption principle

Space truncation

Resonances in solids

Electronic structure theory

- The behavior of "ordinary" matter is driven by the behavior of nuclei and electrons
- Nuclei can be considered point particles, but electrons must be modeled with quantum mechanics



Water is a good solvent because its electron distribution gives it a dipole moment

The Schrödinger equation (1926)

In atomic units (no spin):

$$i\partial_t \psi = H\psi$$

$$H = \sum_{n=1}^{N} \left(\underbrace{-\frac{1}{2}\Delta_{x_n}}_{\text{Kinetic}} + \underbrace{V_{\text{ext}}(x_n)}_{\text{El-nucl Coulomb}} \right) + \sum_{n=1}^{N} \sum_{m \neq n} \underbrace{\frac{1}{|x_n - x_m|}}_{\text{El-el Coulomb}}$$

- $|\psi(t, x_1, \ldots, x_N)|^2$: probability of finding electrons at positions $x_1, \ldots, x_N$
- Electrons are fermions: ψ changes sign under coordinate permutation
- Stationary states $H\psi = E\psi$. Lowest E is the **ground state**
- Entanglement because of el-el interaction: the state of an electron depends parametrically on the state of all other electrons!
- Complexity explosion
  - Conceptual: the wave function is too rich to be directly useful
  - Computational: solve a PDE in dimension $3N$

Need for approximations

$$i\partial_t \psi = H\psi$$
$$\psi(t) \in L^2(\mathbb{R}^{3N})$$

Dirac 1929:

- "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known...
- ...and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.
- It therefore becomes desirable that **approximate** practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."

An approximation: KSDFT (1965)

Kohn-Sham density functional theory for the ground state of N electrons

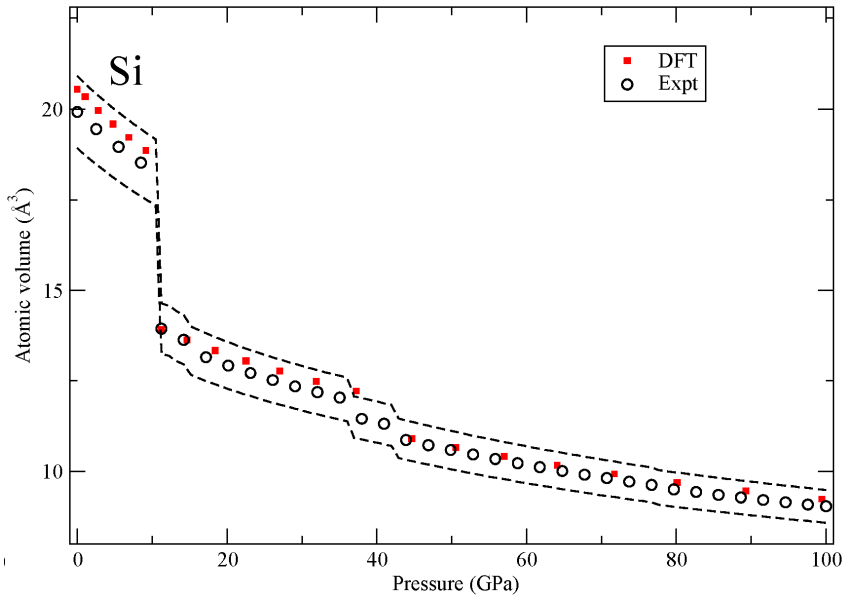
$$\begin{cases} -\frac{1}{2}\Delta\phi_n + V_{\text{ext}}\phi_n + V_{\text{HXC}}[\rho]\phi_n = \lambda_n\phi_n, \quad \langle\phi_n, \phi_m\rangle_{L^2(\mathbb{R}^3)} = \delta_{mn} \\ \rho(x) = \sum_{n=1}^{N} |\phi_n(x)|^2 \\ V_{\text{HXC}}[\rho] = \frac{1}{|x|} * \rho + V_{\text{XC}}[\rho] \end{cases}$$

- V_{XC} is an approximation of the true exchange-correlation potential; e.g. LDA: $(V_{\text{XC}}[\rho])(x) = v_{\text{xc}}(\rho(x))$
- N nonlinear coupled PDEs in dimension 3
- Generalizes to dynamics (TDDFT)

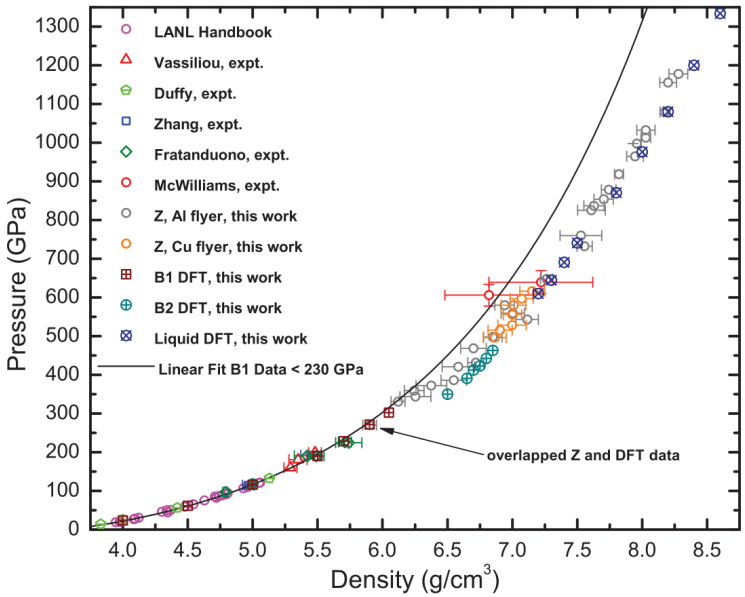
$$i\partial_t\phi_n = -\frac{1}{2}\Delta\phi_n + V_{\text{ext}}\phi_n + V_{\text{HXC}}[\rho, t]\phi_n$$

DFT in practice

- Methodological developments since the '90s (pseudopotentials, numerical methods, HPC...): routinely solved for hundreds of atoms
- Workhorse of condensed matter physics and quantum chemistry



Equation of state of Si, Söderlind, Per, and David A. Young, Computation 6.1 (2018).



Equation of state of MgO, Root, Seth, et al., Physical Review Letters 115.19 (2015).

... despite severe deficiencies (excited states, strongly correlated materials)

Electronic structure for mathematicians

- Complex equations
- Need for reliable, automatic, accurate and fast methods
- Involves many branches of mathematics

Analysis	Computing	"Pure" math
PDEs	Linear algebra	Probability
Spectral theory	Optimization	Group theory
Complex analysis	Numerical analysis	Topology
Nonlinear analysis	HPC	Differential geometry

- Underexplored mathematically

Keyword	Web of Science	MathSciNet	Ratio
Maxwell equations	19,459	2,055	10%
Boltzmann equation	24,519	2,268	10%
Navier Stokes	47,341	9,436	20%
Density Functional Theory	142,374	171	0.1%

- Topics for applied mathematics: rigorous results on structure, asymptotics, numerical methods
- This talk: numerical analysis of computational methods for response properties, $N = 1$ electron

Summary

Static response

Physical systems are characterized by their **response properties**

Mathematically: **perturbation theory** for $F(X, \varepsilon)$ around equilibrium

$$F(X_*, 0) = 0$$

Equilibrium perturbation:

$$F(X(\varepsilon), \varepsilon) = 0.$$

Implicit function theorem:

$$X(\varepsilon) = X_* - \varepsilon(\partial_X F)^{-1}\partial_\varepsilon F + O(\varepsilon^2)$$

derivatives evaluated at $(X_*, 0)$
Expansion of observables to first order provide response coefficients (mechanical, electrical, thermal, magnetic, optical...)

$\partial_X F$ also determines the mathematical structure (error control, sensitivity, convergence of numerical methods...)

Dynamical response

Time-dependent:

$$\dot{X} = F(X, \varepsilon f(t)), \quad X(0) = X_*$$
$$\dot{X} \approx \partial_X F (X - X_*) + \varepsilon f(t) \partial_\varepsilon F$$

Duhamel formula: (Dyson/variation of constant/interaction picture/perturbation theory/...)

$$X(\varepsilon, t) = X_* + \varepsilon \int_0^t \underbrace{e^{\partial_X F (t-t')} (\partial_\varepsilon F)}_{K(t-t')} f(t') dt' + O_t(\varepsilon^2)$$
$$= X_* + \varepsilon (K * f)(t) + O_t(\varepsilon^2)$$

by extending K and f to zero for negative times (causal functions).

- For physically stable systems (eg damped oscillator), $e^{\partial_X F t} \to 0$
  - Validity of linear response clear (O independent on time)
  - $\widehat{K}(\omega)$ well-defined (AC response)
- Quantum mechanics is purely oscillatory: $e^{\partial_X F t}$ unitary
  - Validity of linear response much more subtle (model as open system)
  - K does not decay: $\widehat{K}(\omega)$?

Response functions and the "η trick"

Consider a classical undamped oscillator

$$\ddot{x} + \omega_0^2 x = f(t), \quad x(0) = \dot{x}(0) = 0$$

$$x(t) = \int_0^t f(t')K(t-t')dt', K \text{ oscillatory}$$

What is the AC response? "$\widehat{K}(\omega) = \int_0^{+\infty} K(t)e^{i\omega t}dt$?" is divergent!

Various ways to give a meaning to this

1. Adiabatic switching: $f(t) = e^{\eta t}e^{-i\omega t}, t \leq 0$
2. Physical dissipation: $\ddot{x} + \eta\dot{x} + \omega_0^2 x = f(t)$
3. Artificial dissipation: $K(t) \Rightarrow e^{-\eta t}K(t)$
4. Time windowing: $K(t) = 0$ for $t > 1/\eta$
5. Cesaro averaging of divergent integral
6. Distributional definition of $\widehat{K}$

$$\text{"}\int \overline{\widehat{K}(\omega)}\widehat{\phi}(\omega)d\omega\text{"} := 2\pi \int \overline{K(t)}\phi(t)dt \quad \forall \phi \in S(\mathbb{R})$$

All equivalent! (http://antoine.levitt.fr/response_oscillatory.pdf)

$$\boxed{\widehat{K}(\omega) := \lim_{\eta \to 0^+} \widehat{K}(\omega + i\eta) \text{ in the sense of distributions}}$$

Dynamical polarizability

Consider a **single electron** in a localized potential (e.g. hydrogen atom)

$$H = -\tfrac{1}{2}\Delta + V$$
$$\sigma(H) = \{E_0, E_1, \ldots\} \cup \mathbb{R}^+$$

Start in ground state:

$$\psi(0) = \psi_0, \quad H\psi_0 = E_0\psi_0$$

turn on a small dynamical electric field

$$\boxed{i\partial_t\psi = H\psi + \varepsilon f(t) V_{\mathcal{P}}}$$

and observe the result

$$\boxed{\langle V_{\mathcal{O}}\rangle(t) = \langle \psi(t), V_{\mathcal{O}}\psi(t)\rangle.}$$

Eg dynamical polarizability / light absorption cross-section:

$$V_{\mathcal{O}} = x_\alpha, \quad V_{\mathcal{P}} = x_\beta$$

$\widehat{K}(\omega)$ has a rich physical meaning

Linear response theory

Duhamel:

$$i\partial_t \psi = H\psi + \varepsilon f(t) V_{\mathcal{P}} \psi$$

$$\psi(t) = e^{-iHt}\psi_0 - \varepsilon i \int_0^t U(t,t') f(t') V_{\mathcal{P}} e^{-iHt'} \psi_0 dt'$$

and therefore linear response: (Kubo, Green-Kubo, fluctuation-dissipation)

$$\langle V_{\mathcal{O}} \rangle(t) = \langle \psi_0, V_{\mathcal{O}} \psi_0 \rangle + \varepsilon \int_0^t K(t-t') f(t') dt' + O_t(\varepsilon^2)$$

$$\boxed{K(\tau) = -i\theta(\tau) \left\langle V_{\mathcal{O}} \psi_0, e^{-i(H-E_0)\tau} V_{\mathcal{P}} \psi_0 \right\rangle + \text{c.c.},}$$

θ the Heaviside function

$K(\tau)$ and $\widehat{K}(\omega)$

$$K(\tau) = -i\theta(\tau)\left\langle V_{\mathcal{O}}\psi_0, e^{-i(H-E_0)\tau}V_{\mathcal{P}}\psi_0\right\rangle + \text{c.c.},$$

K does not decay, but Fourier transform defined in the distributional sense

$K(\tau) = 0$ for $\tau < 0$: K is **causal**, Fourier transform can be computed as a limit:

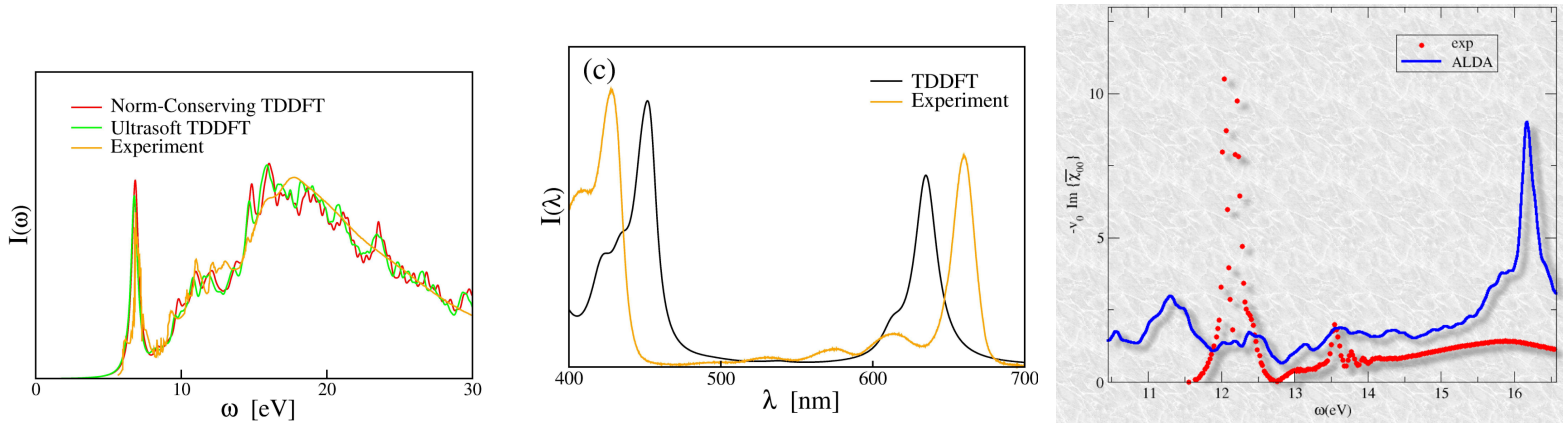
$$\begin{aligned}\widehat{K}(\omega) &= \lim_{\eta\to 0^+}\int_0^\infty e^{i(\omega+i\eta)\tau}K(\tau)d\tau \\ &= \lim_{\eta\to 0^+}\left\langle \psi_0, V_{\mathcal{O}}\Big(\omega+i\eta-(H-E_0)\Big)^{-1}V_{\mathcal{P}}\psi_0\right\rangle \\ &\qquad -\left\langle \psi_0, V_{\mathcal{P}}\Big(\omega+i\eta+(H-E_0)\Big)^{-1}V_{\mathcal{O}}\psi_0\right\rangle,\end{aligned}$$

in the sense of distributions.

(unusual sign of Fourier transform, to match Schrödinger's e^{-iEt})

Context

- Formalism can be extended to TDDFT
- Allows direct comparison with experiment: predictions, understanding, optimization



Absorption spectrum of benzene (C_6H_6)and chlorophyll ($C_{55}H_{72}O_5N_4Mg$), D. Rocca '07; Solid Argon, F. Sottile et al (2007)

Computationally, needs to be discretized (eg finite differences, plane waves, localized basis sets...)

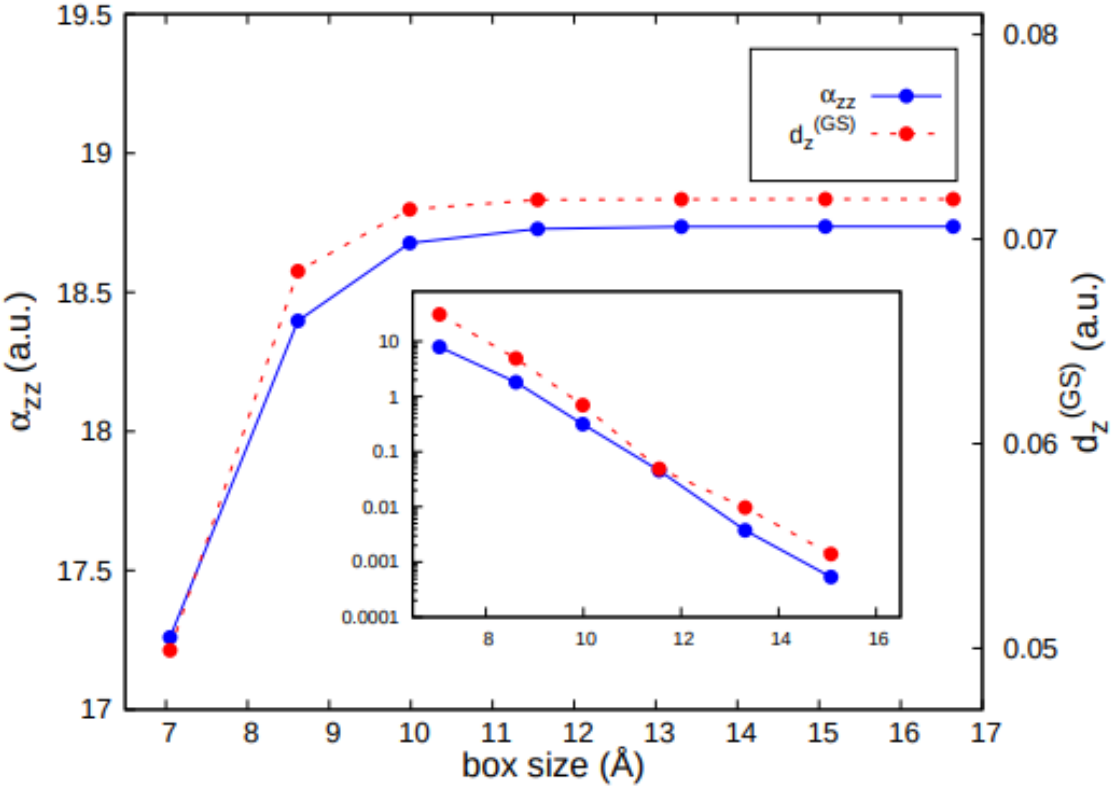
- Conceptually, two numerical parameters: size of box L, and mesh size h
- Convergence with respect to h "standard" (similar to ground state)
- Convergence with respect to L?

Convergence with L: ground state and static response

$$V_{\mathcal{P}} = V_{\mathcal{O}} = x_3$$

$$d_z = \langle \psi_0, V_{\mathcal{O}} \psi_0 \rangle$$

$$\alpha_{zz} = \widehat{K}(0)$$

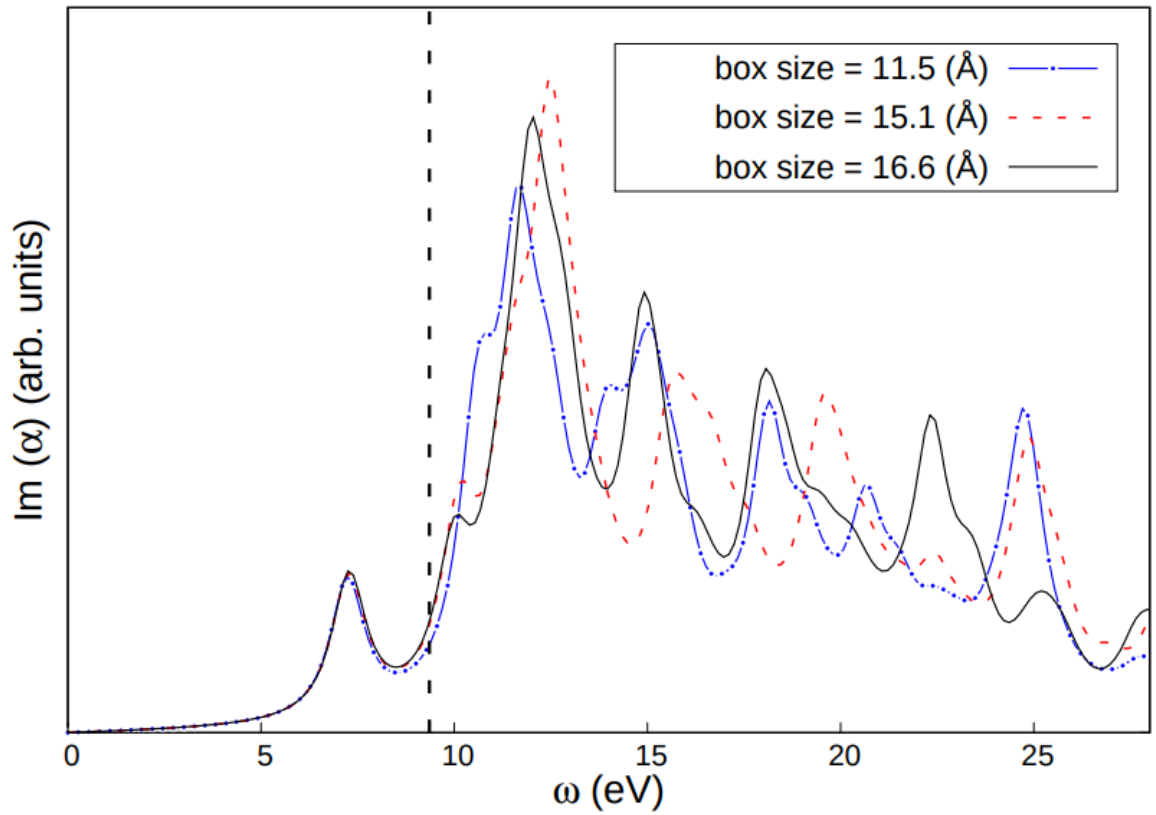


CO molecule, adiabatic LDA. M. D'Alessandro, L. Genovese, Phys. Rev. Mat. 2019

Exponential locality for both ground state and static response

Convergence with L: dynamical response

$$\alpha_{zz}(\omega) = \widehat{K}(\omega)$$



CO molecule, adiabatic LDA. M. D'Alessandro, L. Genovese, Phys. Rev. Mat. 2019

??????

Assumptions

We work in d space dimensions. Japanese brackets $\langle x \rangle = \sqrt{1 + |x|^2}$

H1: V

V is smooth, $|V(x)| \leq C\langle x \rangle^{-(2+\varepsilon)}$ for some $\varepsilon > 0, C > 0$

H2: Ground state

There is a simple ground state (E_0, ψ_0) of $H = -\Delta + V$, $E_0 < 0$.

H3: $V_{\mathcal{P}}$, $V_{\mathcal{O}}$

$V_{\mathcal{P}}$ and $V_{\mathcal{O}}$ are smooth and sublinear (x OK)

Smoothness and sublinearity are just there to prove existence as in [Fujiwara '79], could be relaxed for the analysis of K itself

$1/|x|^{2+\varepsilon}$ decay is for C^1 limiting absorption principle

Lemma: $e^{\alpha_0 \langle x \rangle} \psi_0 \in H^2(\mathbb{R}^d)$ for some $\alpha_0 > 0$.

Proof: classical (Combes-Thomas estimates)

The Kubo formula

Theorem (Kubo formula)

For all continuous and causal functions $f : \mathbb{R} \to \mathbb{R}$ *uniformly bounded by* 1, *for all* $0 < \varepsilon < 1$, *the Schrödinger equation with Hamiltonian* $H + \varepsilon f(t) V_{\mathcal{P}}$ *and initial condition* ψ_0 *has a unique strong solution* $\psi(t)$, *and*

$$\langle \psi(t), V_{\mathcal{O}} \psi(t) \rangle = \langle \psi_0, V_{\mathcal{O}} \psi_0 \rangle + \varepsilon (K * f)(t) + O(\varepsilon^2 (1 + |t|^8)) \qquad (1)$$

with

$$K(\tau) = -i\theta(\tau) \left\langle V_{\mathcal{O}} \psi_0, e^{-i(H-E_0)\tau} V_{\mathcal{P}} \psi_0 \right\rangle + \text{c.c.}$$

Proof: Duhamel, as previously. Bound needs control on $\|\langle x \rangle^2 \psi(t)\|$; use "commutator method"

$$A\psi(t) = U(t,s) A \psi(s) - i \int_s^t U(t,t') [A, H(t')] U(t',s) dt'.$$

Summary

$\widehat{K}(\omega)$

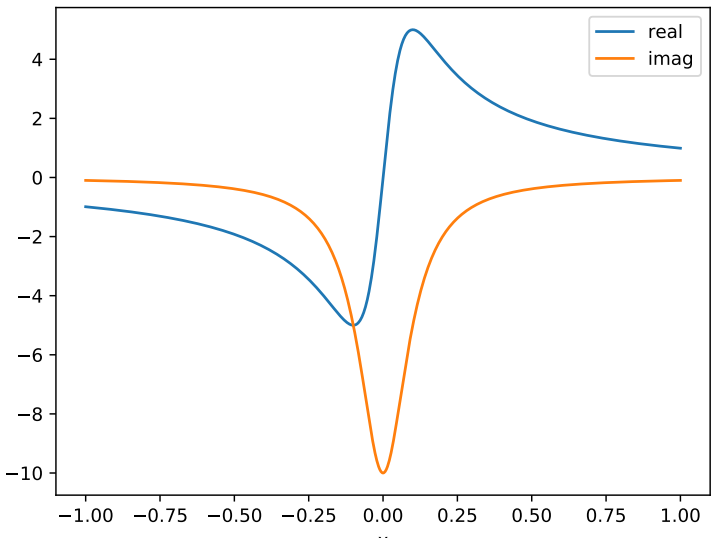
Insert a resolution of the identity $H = \int_{\mathbb{R}} \lambda dP_\lambda$

$$\widehat{K}(\omega) = \lim_{\eta \to 0^+} \int_{\mathbb{R}} \frac{\langle \psi_0, V_{\mathcal{O}} dP_\lambda V_{\mathcal{P}} \psi_0 \rangle}{\omega - (\lambda - E_0) + i\eta} - \frac{\langle \psi_0, V_{\mathcal{P}} dP_\lambda V_{\mathcal{O}} \psi_0 \rangle}{\omega + (\lambda - E_0) + i\eta},$$

$\widehat{K}(\omega)$ is a priori a regular function for the non-resonant frequencies $|\omega| \notin \sigma(H) - E_0$, and a distribution otherwise

However, Plemelj-Sokhotski formula

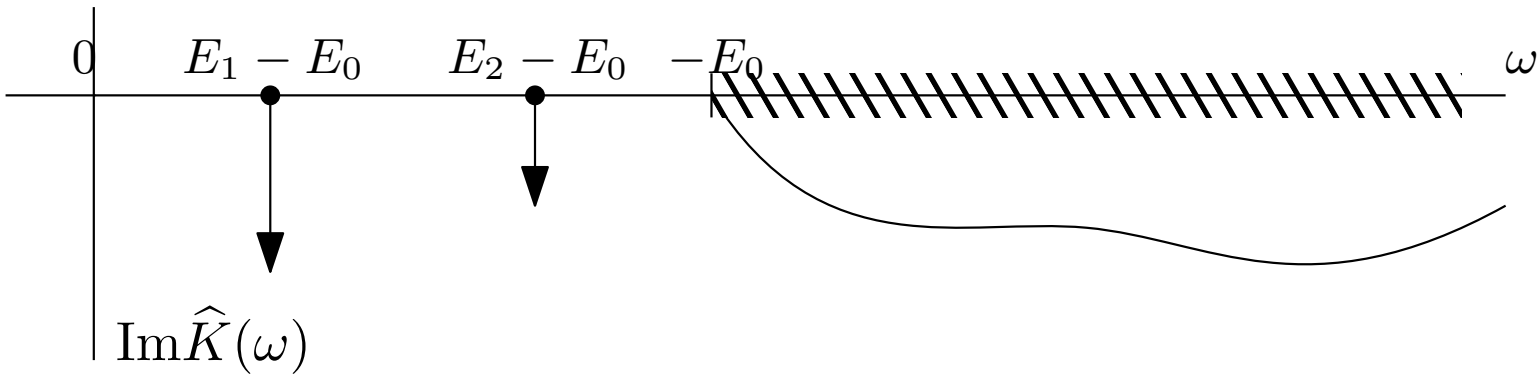
$$\lim_{\eta \to 0^+} \frac{1}{x + i\eta} = \lim_{\eta \to 0^+} \frac{x}{x^2 + \eta^2} - i \frac{\eta}{x^2 + \eta^2} = \text{p.v.} \frac{1}{x} - i\pi\delta_0$$



$\widehat{K}(\omega)$

Eg when $V_{\mathcal{O}} = V_{\mathcal{P}}$, $\omega > 0$,

$$\mathrm{Im}\widehat{K}(\omega) = -\pi \langle \psi_0, V_{\mathcal{O}} dP_{\omega+E_0} V_{\mathcal{O}} \psi_0 \rangle$$



Probes transitions between energy levels (Planck relation $\hbar\omega = \Delta E$)

Theorem

The function $\widehat{K}(\omega)$, holomorphic on the open upper-half plane, extends to a C^1 function on $(-E_0, +\infty] + i[0, \infty)$

(Limiting absorption principle)

Recall

$$\widehat{K}(\omega) = \lim_{\eta \to 0^+} \left\langle \psi_0, V_{\mathcal{O}} \Big(\omega + i\eta - (H - E_0) \Big)^{-1} V_{\mathcal{P}} \psi_0 \right\rangle - \left\langle \psi_0, V_{\mathcal{P}} \Big(\omega + i\eta + (H - E_0) \Big)^{-1} V_{\mathcal{O}} \psi_0 \right\rangle,$$

Regularity of $\widehat{K}$ consequence of

Theorem (Limiting absorption principle)

If $V(x) \leq C|x|^{-(1+k+\varepsilon)}$, then the resolvent

$$G(z) = (z - H)^{-1},$$

holomorphic on the upper half complex plane, extends to a C^k function on $(0, +\infty) + i[0, +\infty)$, in the topology of bounded operators from $L^2(\langle x \rangle^s)$ to $H^2(\langle x \rangle^{-s})$, for all $s > \frac{1}{2} + k$

Proof using classical tools [Agmon '75]

(Limiting absorption principle: proof for $k = 0$)

In the case $V = 0$,

$$\begin{aligned}\langle \phi, G_{V=0}(E + i\eta)\psi \rangle &= \int_{\mathbb{R}^d} \frac{\mathcal{F}\phi(q)^* \mathcal{F}\psi(q)}{E + i\eta - |q|^2} dq \\ &= \int_0^\infty \frac{D_{\phi\psi}(\lambda)}{E + i\eta - \lambda} d\lambda \\ &\to \text{p.v.} \int_0^\infty \frac{D_{\phi\psi}(\lambda)}{E - \lambda} d\lambda - i\pi D_{\phi\psi}(E)\end{aligned}$$

with the projected density of states

$$D_{\phi\psi}(\lambda) \propto \frac{1}{2\sqrt{\lambda}} \int_{S(\sqrt{\lambda})} \mathcal{F}\phi(q)^* \mathcal{F}\psi(q) dq.$$

Non-zero V:

$$G(z) = (1 - G_{V=0}(z)V)^{-1} G_{V=0}(z),$$

Fredholm theory and absence of embedded eigenvalues.

Summary

Truncation

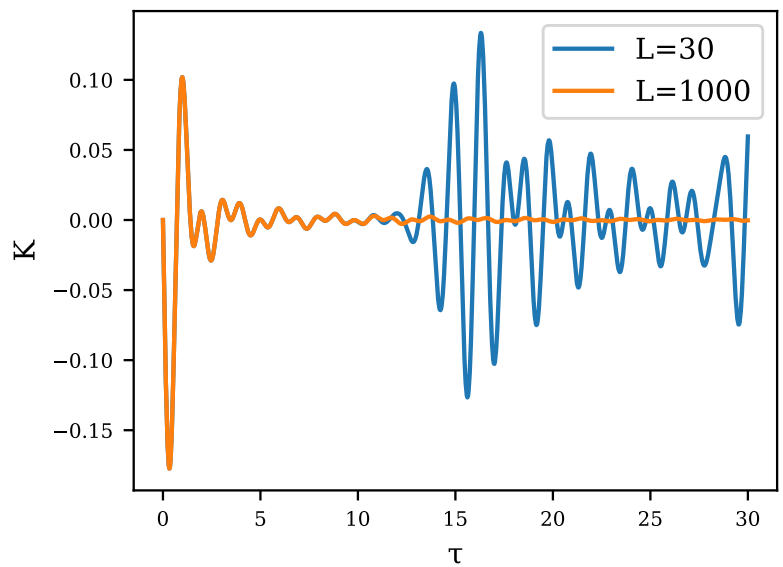
Truncate to a finite box $\Omega_L = [-L, L]^d$ using Dirichlet boundary conditions

Needs further discretization with a finite-sized grid (more standard error analysis, not treated here)

Define H_L, $E_{0,L}, \psi_{0,L}$, and

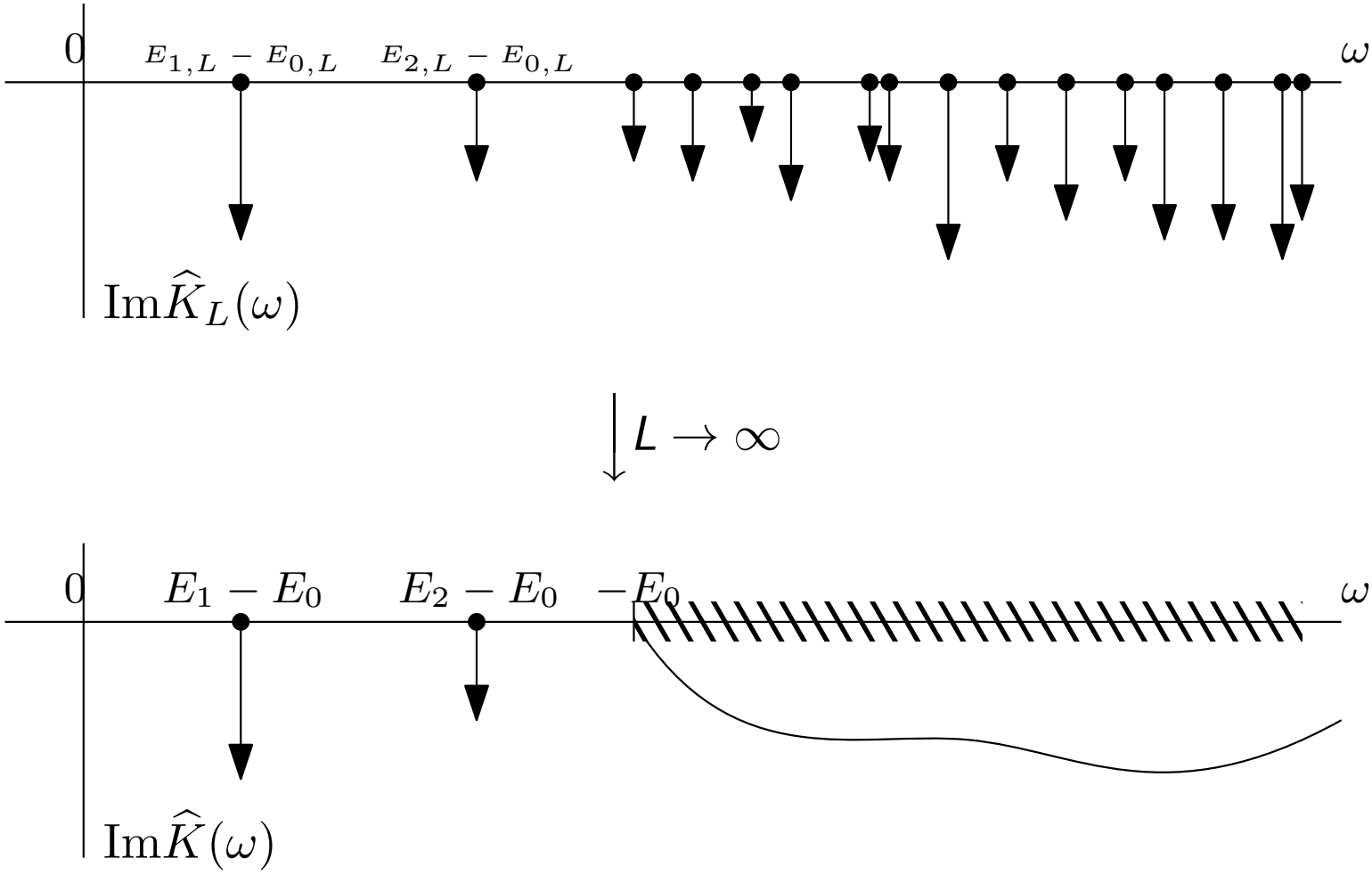
$$K_L(\tau) = -i\theta(\tau) \left\langle V_{\mathcal{O}} \psi_{0,L}, e^{-i(H_L - E_{0,L})\tau} V_{\mathcal{P}} \psi_{0,L} \right\rangle + \text{c.c.},$$

Problem: spurious boundary reflections



H_L has compact resolvent: discrete spectrum, K_L is purely oscillatory and $\widehat{K}_L$ purely singular

$\widehat{K}_L(\omega)$



Theorem

$K_L \to K$ in the sense of tempered distributions

(Error estimates)

In practice, need to compute with regularization

Theorem

For all $\omega \in \mathbb{R}$,

$$\left|\widehat{K}_L(\omega + i\eta) - \widehat{K}(\omega + i\eta)\right| \leq C\frac{e^{-\alpha\eta L}}{\eta^2}$$

for some $C, \alpha > 0$ *depending on* ω *but not on* η.

Therefore for $|\omega| > -E_0$:

$$|\widehat{K}_L(\omega + i\eta) - \widehat{K}(\omega)| \leq C\left(\frac{e^{-\alpha\eta L}}{\eta^2} + \eta\right)$$

Minimize error at fixed L: $\eta_{\text{opt}} \approx 1/L$ (up to logarithmic factors)

In practice:

- Better regularization kernels? ($\widehat{K}_L(\omega + i\eta) \Leftrightarrow$ Lorentzian, bad!)
- Adaptive $\eta(\omega, L)$?
- Absorbing boundary conditions?

(Ideas of proof)

Need control on difference of propagators

$$U(t) = e^{-iHt}, \quad U_L(t) = e^{-iH_L t}$$

and resolvents

$$G(z) = (z - H)^{-1}, \quad G_L(t) = (z - H_L)^{-1}.$$

Usually done using the Duhamel/Dyson comparison formulas

$$U(t) - U_L(t) = \int_0^t U_L(t - t')(H - H_L)U(t')dt'$$
$$G(z) - G_L(z) = G_L(z)(H - H_L)G(z)$$

(dual through Laplace transform)

Problem: H and H_L are not "close": they have the same action $-\Delta + V$ but different domains

$$D(H) = H^2(\mathbb{R}^d)$$
$$D(H_L) = \left\{\psi \in L^2(\mathbb{R}^d), \psi|_{\Omega_L} \in H^2(\Omega_L), \psi|_{\partial\Omega_L} = 0\right\}$$

(Ideas of proof)

$$G(z) - G_L(z) = G_L(z)(H - H_L)G(z)$$

- H and H_L agree on functions living inside Ω_L
- $V_{\mathcal{P}}\psi_0$ and $V_{\mathcal{O}}\psi_0$ are exponentially localized
- G preserves locality:

Lemma (Combes-Thomas)

There is $c > 0$ such that, for all $z \notin \sigma(H)$, there is $C_z > 0$

$$\|G(z)\psi\|_{H^2(e^{\alpha\langle x\rangle})} \leq C_z \|\psi\|_{L^2(e^{\alpha\langle x\rangle})}$$

for all $\alpha < c\, d(z, \sigma(H))$

Proof:

$$e^{\alpha\langle x\rangle}(-\Delta + V)e^{-\alpha\langle x\rangle} = -\Delta + V + O(\alpha) \qquad \square$$

Extensions

- Several independent electrons (easy)
- Interacting electrons: TDDFT (WIP)
- Defects in periodic media: $-\frac{1}{2}\Delta \to -\frac{1}{2}\Delta + V_{\mathrm{per}}$
- Better numerical schemes!

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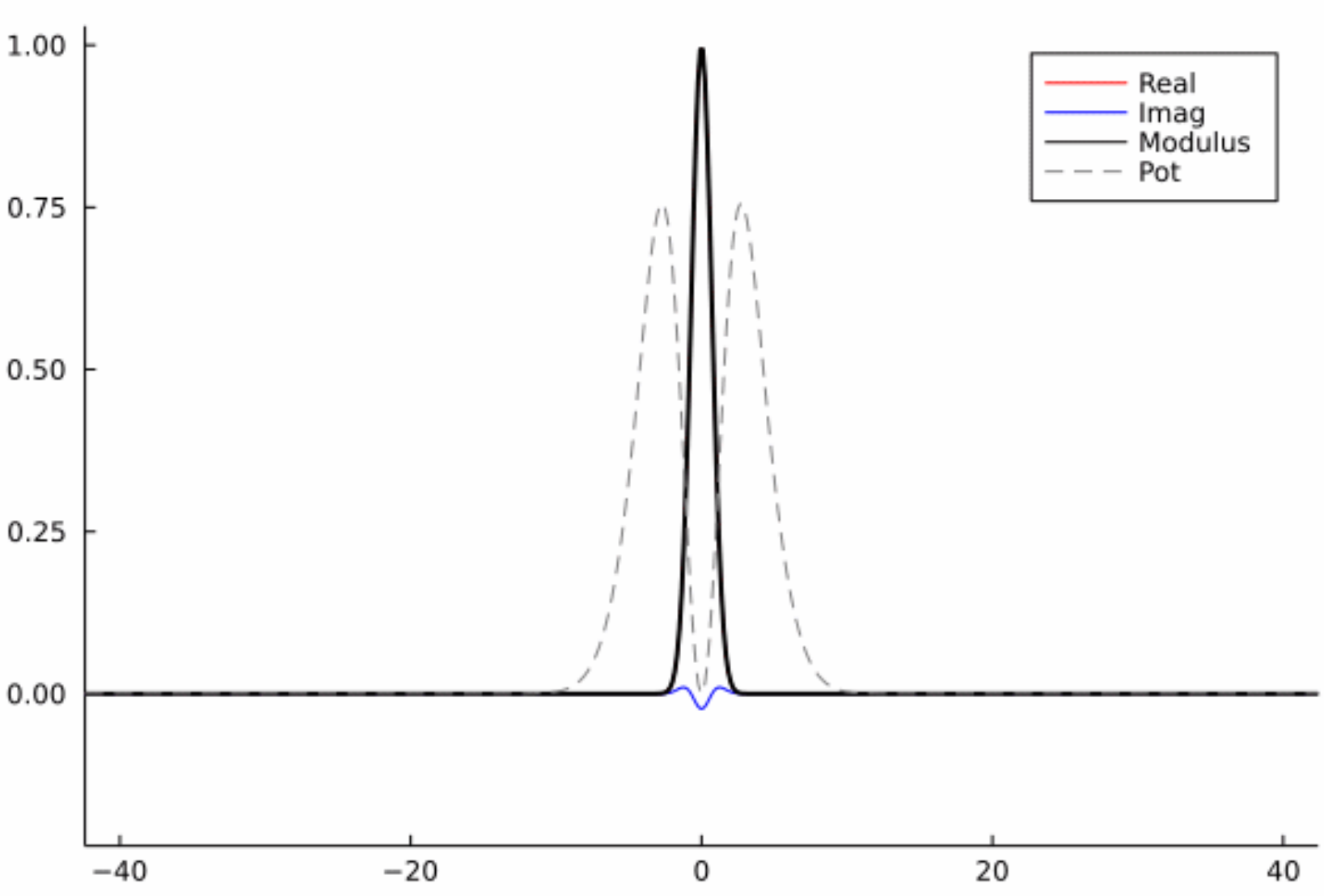
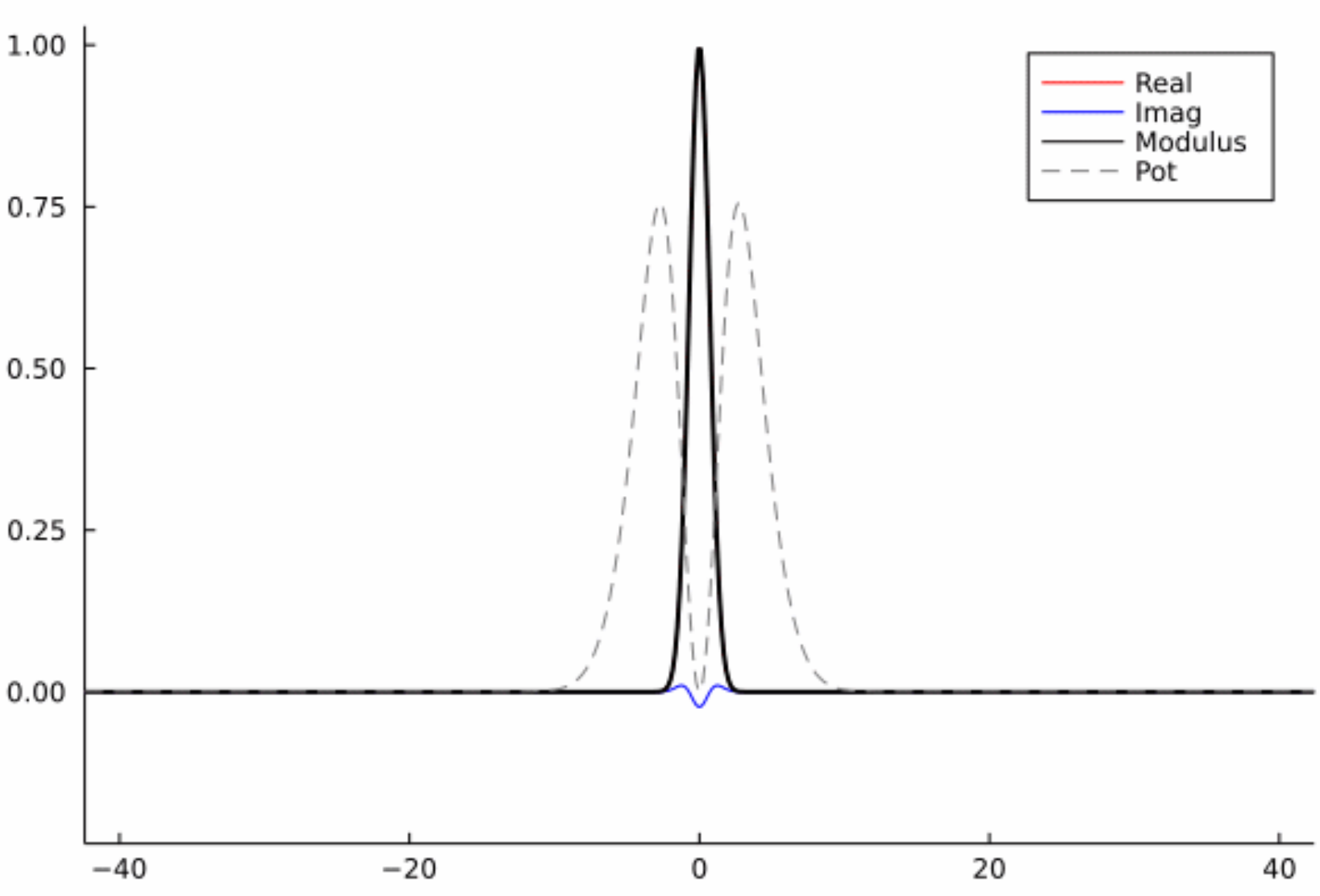
Resonances in solids

Resonances: example ("shape resonance")



Resonances: example ("shape resonance")



Mathematical meaning?

Resonances: definition

Definition (Simon '71)

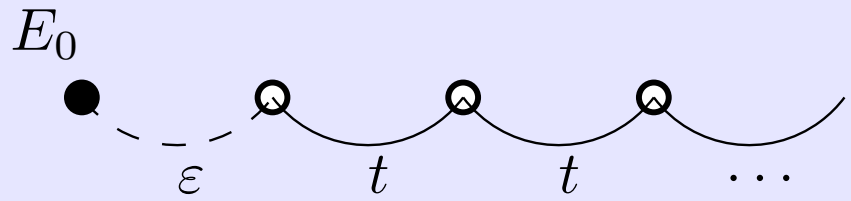
A resonance of (H, ψ) is a pole of the analytic continuation from the upper complex plane to the lower of the Green function element

$$\langle \psi, (z - H)^{-1} \psi \rangle$$

Resonance at $E - i\Gamma \Leftrightarrow \mathrm{Im}\langle \psi, (\lambda + i0^+ - H)^{-1} \psi \rangle$ has a bump at $\lambda = E$

$$\Leftrightarrow \langle \psi, e^{-iHt} \psi \rangle \approx \alpha e^{-iEt} e^{-\Gamma t}$$

Elementary example ("Feshbach resonance")



$$E_0 \notin [-2t, 2t] \Rightarrow \text{ bound state } \approx E_0 + \varepsilon^2 \Delta E$$

$$E_0 \in [-2t, 2t] \Rightarrow \text{ resonance } \approx E_0 + \varepsilon^2 \Delta E - i\varepsilon^2 \Gamma$$

Mathematical theory of resonances

Resonances generalize bound states: they are exponentially growing in space, exponentially decaying in time, and correspond to finite-width bumps in frequency

Classical topic in mathematical physics [Dyatlov-Zworski '19]

Theorem (example)

Let $V \in L^\infty_{\mathrm{comp}}(\mathbb{R}^d)$, $\psi, \varphi \in L^2_{\mathrm{comp}}(\mathbb{R}^d)$ *and for* $\mathrm{Im}(z) > 0$

$$f(z) = \left\langle \psi, (z - (-\tfrac{1}{2}\Delta + V))^{-1} \varphi \right\rangle .$$

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.

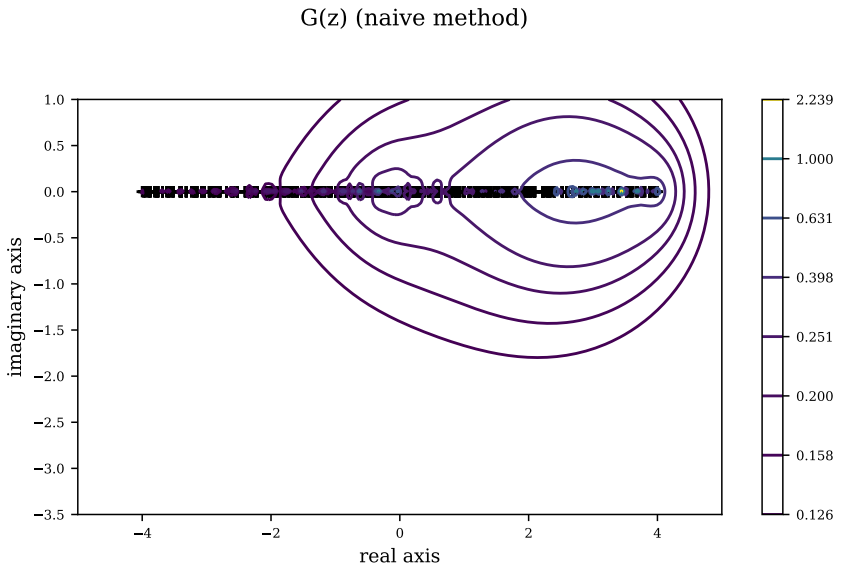
- 0 special point ($\varepsilon(k) = \frac{k^2}{2}$ has zero group velocity at 0)
- In the periodic case ($-\frac{1}{2}\Delta + V_{\mathrm{per}} + V$), analytic structure more complicated because of band thresholds and van Hove singularities [Gérard '90]
- Numerical methods?

Space truncation and resonances

Naive space truncation destroys the analytic structure:

$$\frac{1}{z - H_{\text{truncated}}} = \sum_{n=1}^{N} \frac{1}{z - \lambda_n} |v_n\rangle\langle v_n|$$

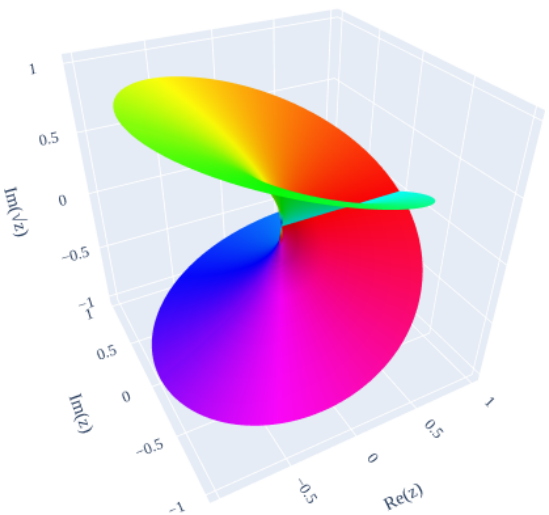
analytic on $\mathbb{C} \setminus \sigma(H_{\text{truncated}})$.



Riemann surface Im(√z)),
colored according to the argument values on each branch

If $H_0 = -\frac{1}{2}\Delta$ and $\mathrm{Im}(z) > 0$,

$$G_0(r, r'; z) = \frac{1}{z - H_0}(r, r') = -\frac{e^{i\sqrt{2z}|r-r'|}}{2\pi|r - r'|}$$

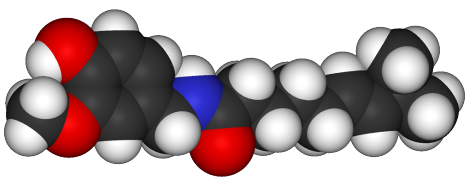
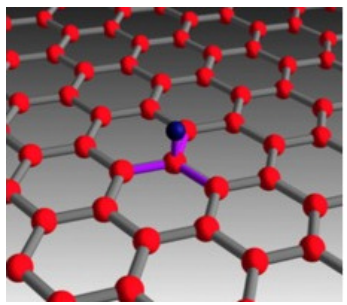
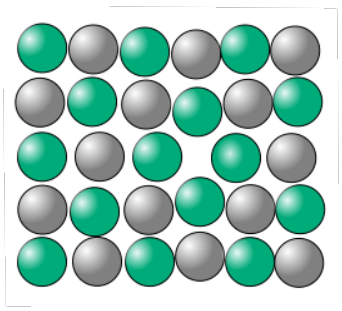


Truncation always "picks" the localized branch (discontinuous on $\mathbb{R}^+$)

Numerical methods

- Solution 0: numerical analytical continuation, unstable
- Solution 1: exact boundary conditions / Green function / scattering matrix methods, limited applicability
  - 1D/2D/3D free Laplacian in a sphere (used in atomic scattering)
  - 1D periodic systems (used in transport)
- Solution 2: complex scaling / perfectly matched layers
  - Only applicable for free Laplacian and special geometries
- Solution 3: complex absorbing potentials $V(x) + i\eta V_{\mathrm{CAP}}(x)$
  - Slow convergence, somewhat of a black art

How to compute resonances in complex environments?

General strategy

Assume

$$H = H_0 + V$$

where H_0 is "simple", and V decays quickly

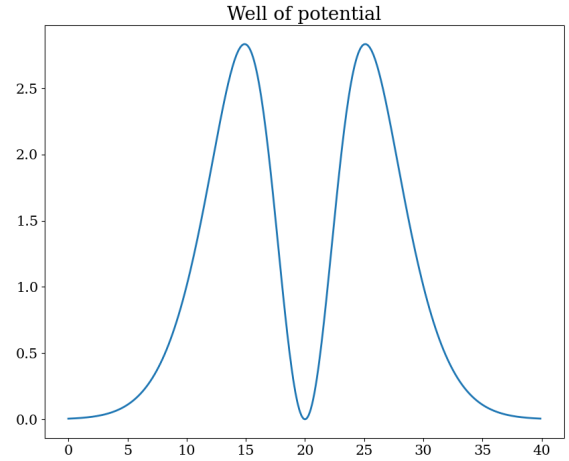
With G (resp. G_0) the resolvent of H (resp. H_0),

$$G(z) = G_0(z)(1 - VG_0(z))^{-1}$$

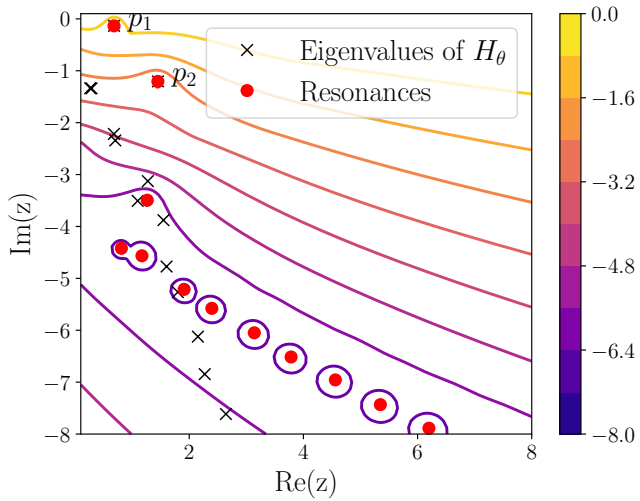
- Additive splitting, not geometric (Schur-like) splitting
- Must only be able to compute G_0: does not rely on geometry at all (more flexible)
- Resonances: solutions of $\phi = VG_0(z)\phi$ (nice Fredholm equation with decaying solutions $\Rightarrow$ good for numerics)
- Can also be used to compute $G(E + i0^+) \Rightarrow$ response properties

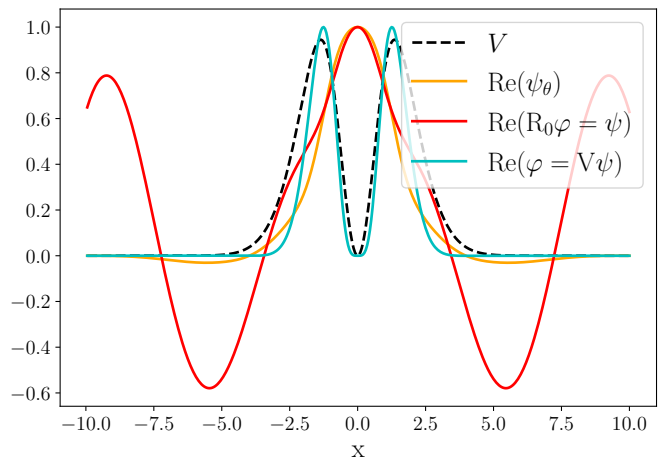
Example: 1D potential

$$H = -\frac{1}{2}\Delta + V$$



- Simple example, can also be done with exact boundary conditions or complex scaling
- Green function of $-\frac{1}{2}\Delta$ known explicitly, simple discretization of resulting integral equation $\phi = VG_0(z)\phi$





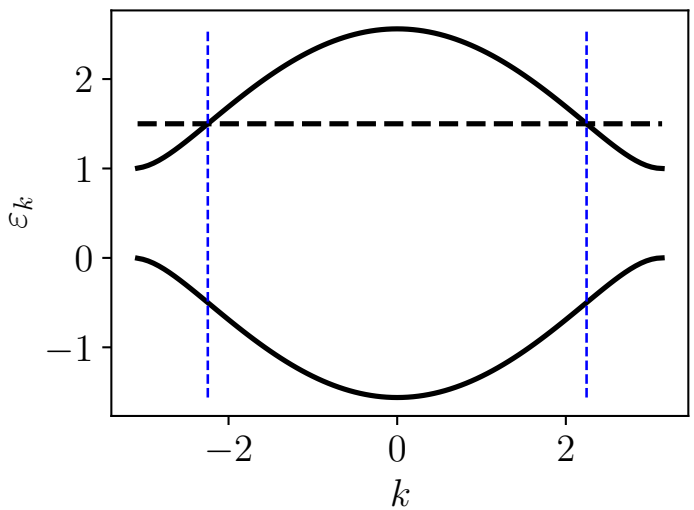
Periodic systems

Assume H_0 is $\mathbb{Z}^d$ periodic (e.g. $-\frac{1}{2}\Delta + V_{\mathrm{per}}$, or tight-binding model).
Bloch theory:

$$H_0 e^{ikr} u_{nk}(r) = \varepsilon_{nk} e^{ikr} u_{nk}(r),$$
$$u_{nk} \text{ periodic, } k \in \mathrm{BZ} \simeq [-\pi, \pi]^d$$

Need to compute analytic continuation of

$$G_0(r, r'; z) = \int_{\mathrm{BZ}} \sum_{n=1}^{\infty} \frac{e^{ik(r-r')} u_{nk}(r) \overline{u_{nk}(r')}}{z - \varepsilon_{nk}} dk \text{ when } \mathrm{Im} z > 0$$



Trouble when z crosses $\sigma(H_0) = \{\varepsilon_{nk}, n \in \mathbb{N}, k \in \mathrm{BZ}\}$

A simpler problem: contour deformation to the rescue

Compute the analytic continuation of

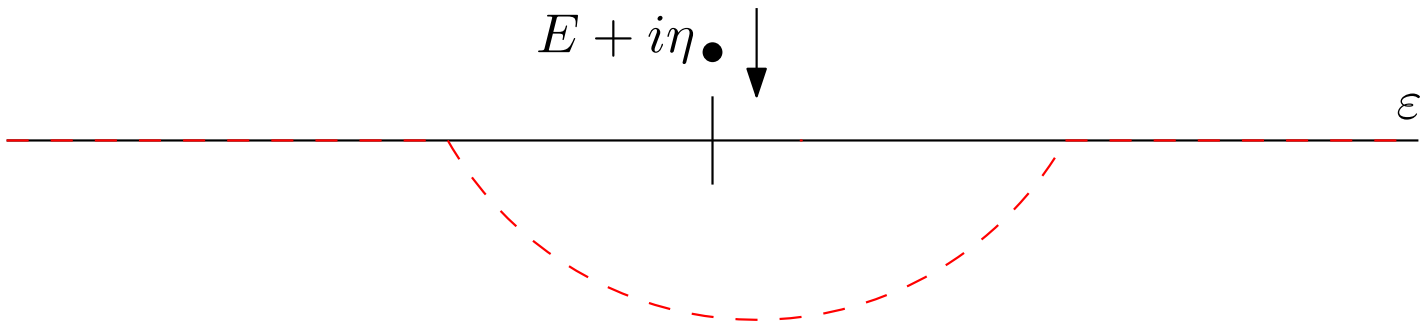
$$I_1(z) = \int_{\mathbb{R}} \frac{\phi(\varepsilon)}{z-\varepsilon} d\varepsilon \qquad \text{from } \mathrm{Im(z)} > 0 \text{ to } \mathrm{Im(z)} < 0$$

- When $z = E + i\eta$, $\eta > 0$,

$$\frac{\phi(\varepsilon)}{z-\varepsilon} = \phi(\varepsilon)\frac{E-\varepsilon+i\eta}{(E-\varepsilon)^2+\eta^2}$$

  Bump of height $1/\eta$, width η around $\varepsilon = E$
- Numerical integration needs $N \gg \frac{1}{\eta}$ quadrature points
- Continuation past $\eta = 0$ impossible once discretized

Solution: contour deformation

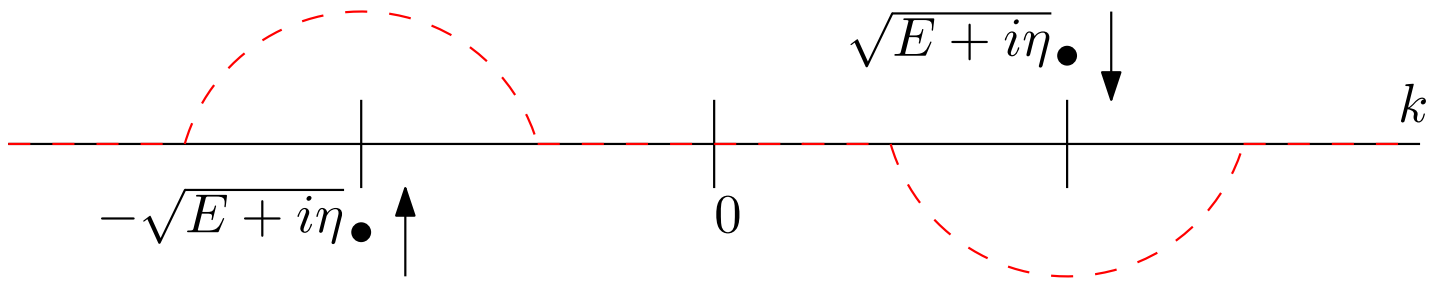


A more complicated problem

Compute the analytic continuation of

$$I_2(z) = \int_{\mathbb{R}} \frac{\phi(k)}{z - \varepsilon(k)} dk \qquad \text{from } \mathrm{Im(z)} > 0 \text{ to } \mathrm{Im(z)} < 0$$

Eg if $\varepsilon(k) = k^2$, singularities near the Fermi surface $k = \pm\sqrt{E}$



- More generally, at $z = E + i\eta$, if k_0 is a point of the Fermi surface $\varepsilon(k_0) = E$, singularity at

$$k = k_0 + \frac{i\eta}{\varepsilon'(k_0)} + O(\eta^2)$$

- Need $\varepsilon' \neq 0$, no continuation possible otherwise (van Hove singularity)

One band, multiple dimensions: Brillouin zone deformation

Lemma

Let $A(k)$ 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 $k_i(k) : \mathbb{R}^d \to [-\eta, \eta]^d$, we have

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

Proof:

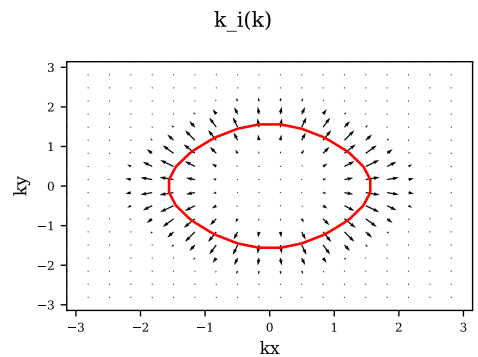
$$I(\alpha) = \int_{[0,2\pi]^d} A(k + \alpha k_i(k)) \det(1 + \alpha k_i'(k))dk,$$

is analytic and constant in $\alpha \in [-1, 1] \Rightarrow I(i) = I(0)$. □

Take k_i such that $k + ik_i(k)$ avoids the Fermi surface:

$$\boxed{k_i = -\alpha \nabla \varepsilon(k) \chi(\varepsilon(k) - E)}$$

where χ is a cutoff function and E the energy of interest.



The full problem

$$G_0(r, r'; z) = \int_{\mathrm{BZ}} \sum_{n=1}^{\infty} \frac{e^{ik(r-r')} u_{nk}(r) \overline{u_{nk}(r')}}{z - \varepsilon_{nk}} dk$$

deformed with $k \to k + ik_i(k)$ with

$$k_i(k) = -\alpha \sum_n \chi(\varepsilon_{nk} - E) \nabla \varepsilon_{nk}$$

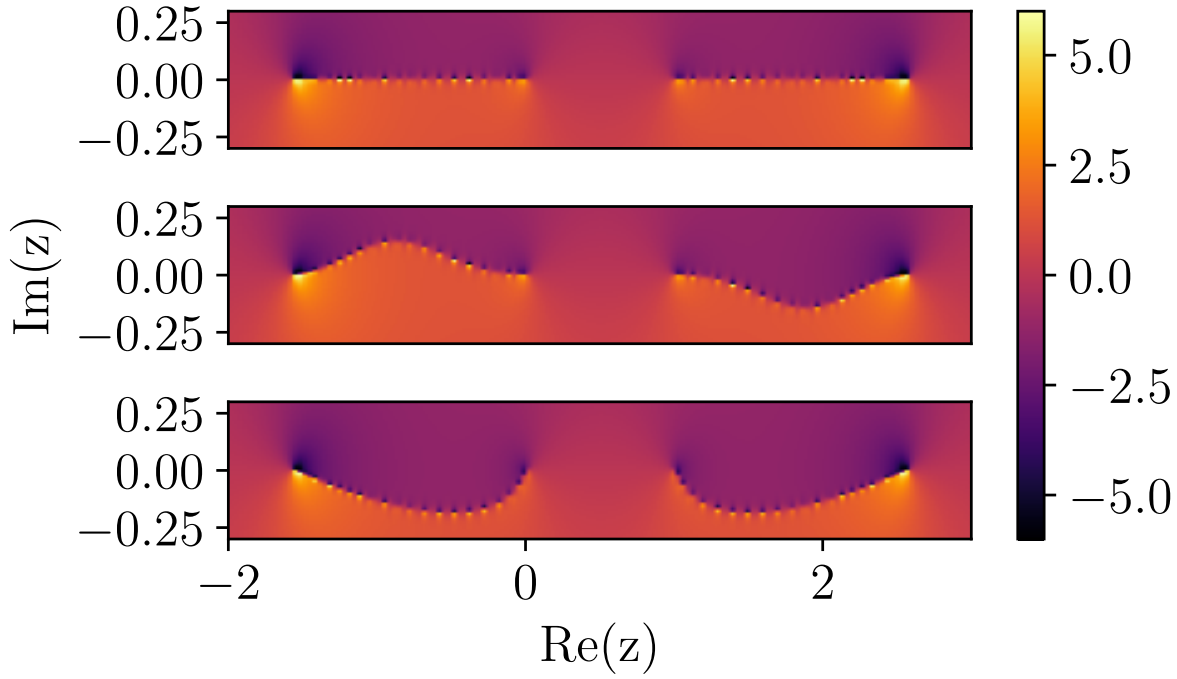
where χ is a cutoff function and E the energy of interest.

Can continue numerically near E if there are no van Hove singularities (crossing or bands with zero gradient at the "Fermi surface" $\{k, \varepsilon_{nk} = E\}$)

- **Only requires unit cell computations**
- Exponential convergence wrt Brillouin zone sampling
- Natural generalization of complex scaling to periodic systems: when $H_0 = -\frac{1}{2}\Delta$, $\nabla\varepsilon(k) = k$, compare with complex scaling $k \to e^{-i\alpha}k$ Main difference: we only transform H_0 (because V might be complicated)

Example: 1D diatomic chain

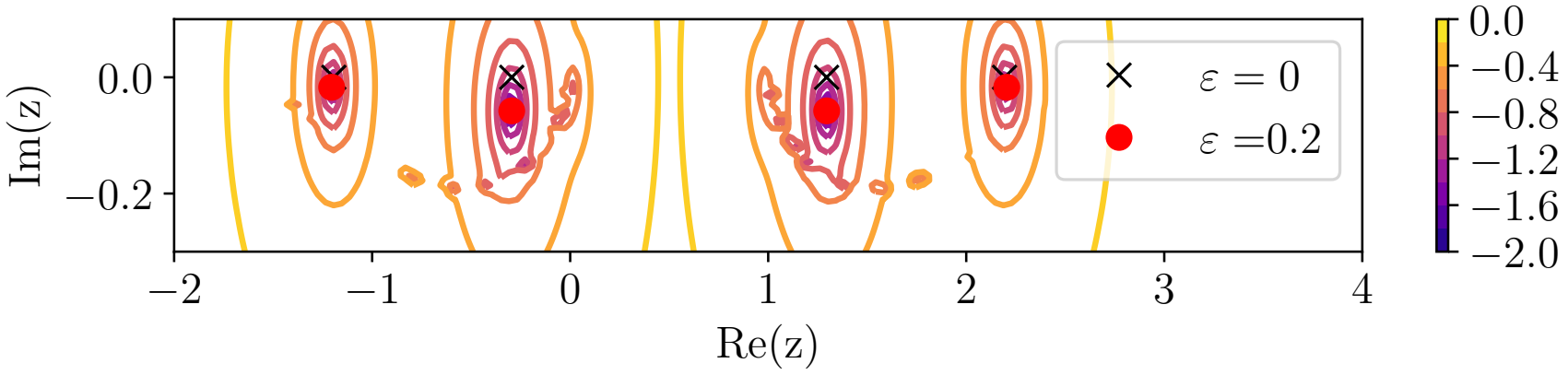
$$H_0 = \begin{pmatrix} \ddots & \ddots & \ddots & & & & & \\ & 1 & E_a & 1 & & & & \\ & & 1 & E_b & 1 & & & \\ & & & 1 & E_a & 1 & & \\ & & & & 1 & E_b & 1 & \\ & & & & & \ddots & \ddots & \ddots \end{pmatrix}$$

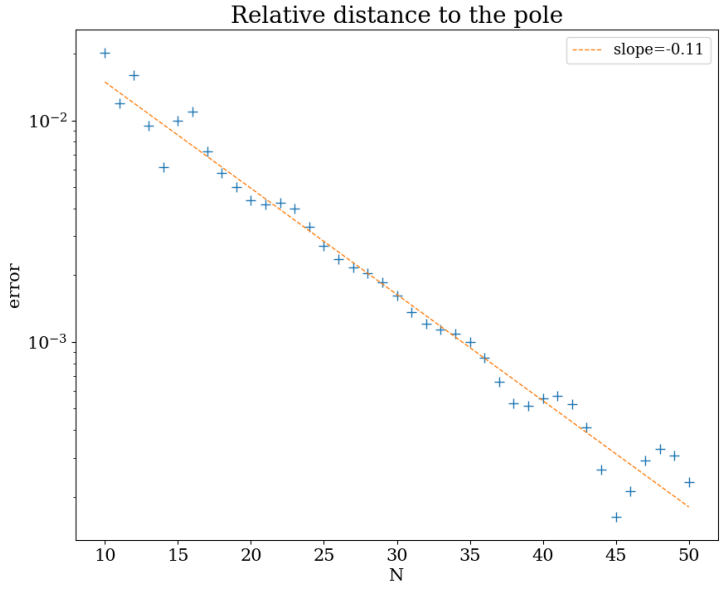


Top to bottom: periodic Green functions with (a) no deformation, (b) deformation at fixed $E = 2$, (c) deformation at $E = \mathrm{Re}(z)$.

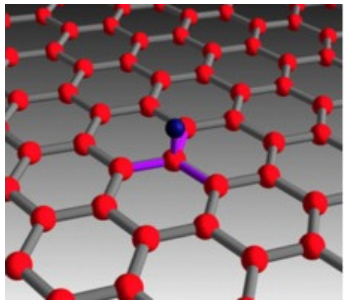
Example: 1D diatomic chain

Now take $H = H_0 + V$, V localized

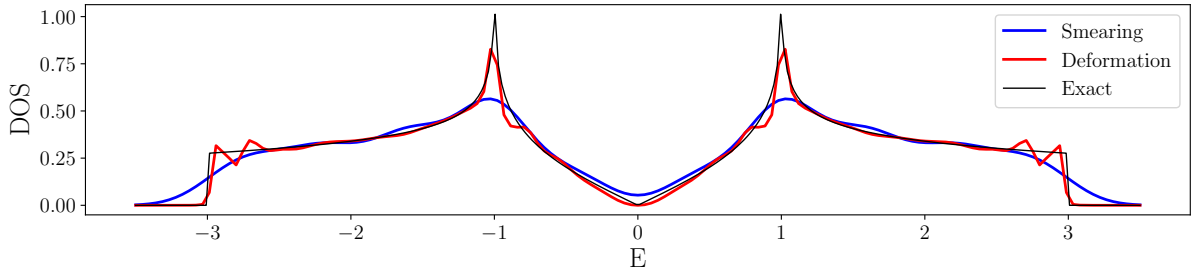


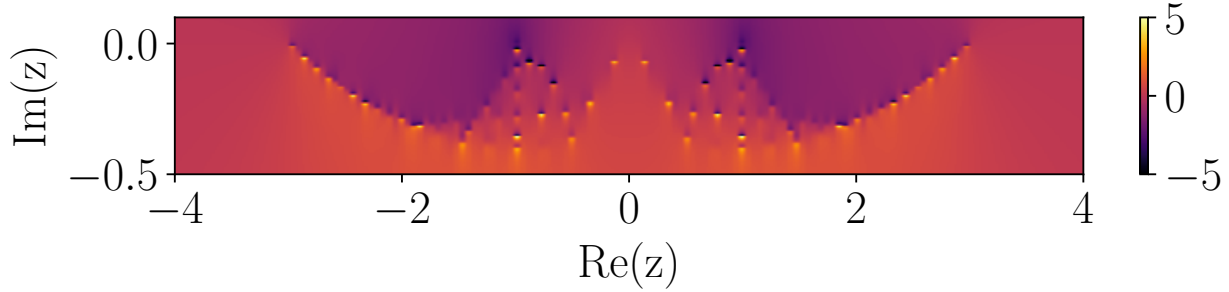


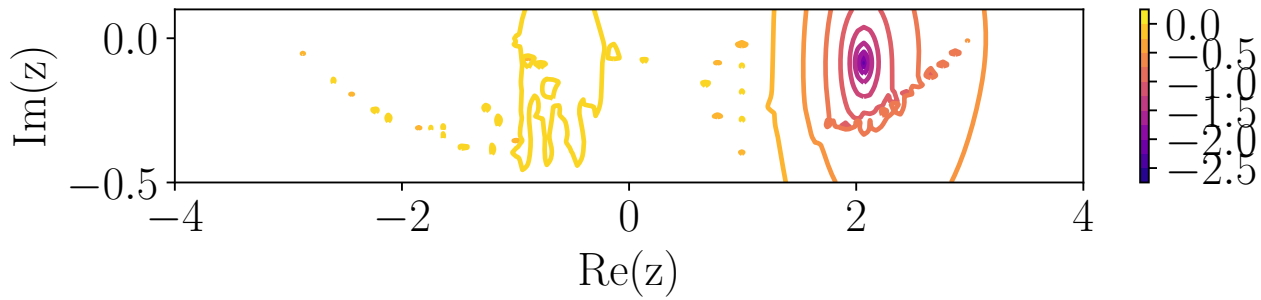
Example: adatom on 2D surface



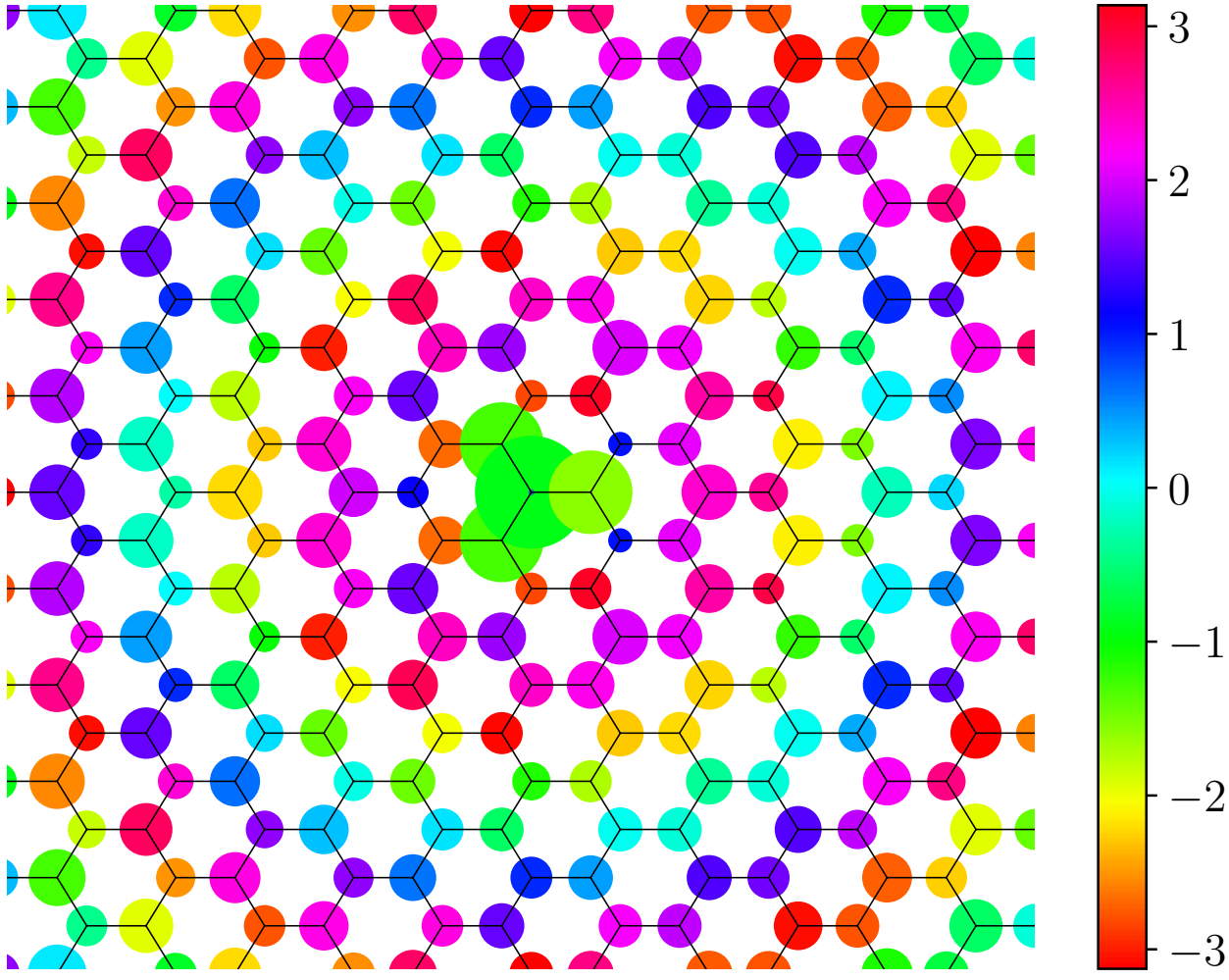
H_0: graphene sheet + isolated adatom. V: graphene-adatom coupling







Example: adatom on 2D surface



Perspectives

Methodology

- Sufficiently accurate quadrature (Wannier functions?)
- Avoid expensive sums over eigenstates (Sternheimer formalism $\Rightarrow$ only iterative preconditioned eigen/linear problems)
- Find poles efficiently (nonlinear eigenvalue problem)
- Extend to TDDFT
- Implement in DFT codes

Applications

- Include resonant states in basis set expansions?
- Materials science: conductivity?
- General scattering problems?