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FINITE-SIZE EFFECTS IN RESPONSE FUNCTIONS OF MOLECULAR SYSTEMS

MI-SONG DUPUY*, ANTOINE LEVITT†

Abstract. We consider an electron in a localized potential submitted to a weak external, time-dependent field. In the linear response regime, the response function can be computed using Kubo's formula. In this paper, we consider the numerical approximation of the response function by means of a truncation to a finite region of space. This is necessarily a singular approximation because of the discreteness of the spectrum of the truncated Hamiltonian, and in practice a regularization (smoothing) has to be used. Our results provide error estimates for the response function past the ionization threshold with respect to both the smoothing parameter and the size of the computational domain.

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1. Introduction

Consider a molecule in its electronic ground state, to which an external time-dependent electric field is applied. The resulting change in the electronic density can be computed using linear response theory, resulting in a quantity $\widehat{K}(\omega)$ describing the response at frequency ω. To compute it in practice, the domain of computation has to be truncated to a region of size L, yielding an approximate response function $\widehat{K}_L(\omega)$. Since the dynamics on the full space and on a finite region of space are qualitatively different, $\widehat{K}_L$ is qualitatively different from $\widehat{K}$: in particular, even when $\widehat{K}$ is a regular function, $\widehat{K}_L$ is always a singular distribution, reflecting the discreteness of the spectrum of the Hamiltonian. Numerical computations of spectra in quantum chemistry are often regularized, more or less explicitly, with convergence to the true $\widehat{K}$ not always clear [18]. This paper aims to answer on a simple model the following question: in which sense does $\widehat{K}_L$ converge to $\widehat{K}$, and with what convergence rate?

Practical numerical computations for real molecules use approximations to the intractable non-relativistic full many-body problem. One of the most popular such approximation is the time-dependent density functional theory in the adiabatic local density approximation. Considering a d-dimensional system of N electrons in a potential V created by nuclei and an external forcing potential $\varepsilon f(t)V_{\mathcal{P}}$, this takes the form (using a system of units where all the constant prefactors are set to 1, and ignoring spin)

$$i\partial_t\gamma = [-\Delta + V + V_{\mathrm{HXC}}(\gamma), \gamma] + \varepsilon f(t)[V_{\mathcal{P}}, \gamma],$$

where ε is a small parameter, $f(t)$ is a continuous causal function (*i.e.* $f(t) = 0$ for $t < 0$), $V_{\mathcal{P}}$ is a perturbing potential, and the initial state $\gamma(0)$ is a solution of the stationary Kohn-Sham equations

$$[-\Delta + V + V_{\mathrm{HXC}}(\gamma(0)), \gamma(0)] = 0.$$

The density matrix γ is an orthogonal projector of rank N on $L^2(\mathbb{R}^3)$. The Hartree-exchange-correlation potential is given by

$$V_{\mathrm{HXC}}(\gamma)(x) = \int_{\mathbb{R}^3} \frac{\rho_\gamma(y)}{|x-y|}\,\mathrm{d}y + v_{\mathrm{LDA}}(\rho_\gamma(x))$$

where $\rho_\gamma(x) = \gamma(x,x)$ is the density associated with the density matrix γ, and $v_{\mathrm{LDA}}(\rho)$ is an explicit function (calibrated on the uniform electron gas). Mathematically, this is a complicated nonlinear integro-differential equation. Although existence, uniqueness and various properties of this and related equations has been studied mathematically in various regimes [10, 33, 15, 30], the linear response theory and its numerical approximation has not, to the best of our knowledge.

The above model is complicated, and for the purposes of mathematical analysis we will consider in this paper the drastic over-simplification $V_{\mathrm{HXC}} = 0$. We will also take $N = 1$ for notational simplicity, although this is not essential and the results of this paper also apply to the case $N > 1$ (see Section 3.4.3). Then the non-perturbed system is described by the Hamiltonian

$$H = -\Delta + V, \tag{1}$$

with V decaying at infinity in a sense to be made precise. The Hamiltonian H is self-adjoint on $L^2(\mathbb{R}^d)$, with possible negative eigenvalues and continuous spectrum $[0,\infty)$. Assume that there is a simple lowest eigenvalue $E_0 < 0$, with associated eigenfunction ψ_0. The evolution of ψ is given by the time-dependent Schrödinger equation

$$i\partial_t\psi = H\psi + \varepsilon f(t) V_{\mathcal{P}}\psi, \quad \psi(0) = \psi_0 \tag{2}$$

If $V_{\mathcal{O}}$ is a potential representing an observable, to first order in ε, we have for all $t \in \mathbb{R}$ the first order expansion

$$\langle \psi(t), V_{\mathcal{O}}\psi(t)\rangle = \langle \psi_0, V_{\mathcal{O}}\psi_0\rangle + \varepsilon(K * f)(t) + O(\varepsilon^2), \tag{3}$$

proven in our setting in Proposition 3.1. The function

$$K(\tau) = -i\theta(\tau)\left\langle V_{\mathcal{O}}\psi_0, e^{-i(H-E_0)\tau}V_{\mathcal{P}}\psi_0\right\rangle + \text{c.c.}, \tag{4}$$

is the response function. For instance, when $V_{\mathcal{P}} = -x_\beta$ and $V_{\mathcal{O}} = x_\alpha$, then $K(t)$ is the polarizability impulse response: the dipole response at time t in the direction α of the system to an impulse uniform field at time 0 in the direction β.

Mathematically, K is a continuous causal function of at most polynomial growth, and has a distributional Fourier transform

$$\widehat{K}(\omega) = \lim_{\eta\to 0^+}\left\langle \psi_0, V_{\mathcal{O}}\Big(\omega + i\eta - (H-E_0)\Big)^{-1}V_{\mathcal{P}}\psi_0\right\rangle - \left\langle \psi_0, V_{\mathcal{P}}\Big(\omega + i\eta + (H-E_0)\Big)^{-1}V_{\mathcal{O}}\psi_0\right\rangle, \tag{5}$$

where the limit is taken in the sense of distributions, and $\eta \to 0^+$ means the one-sided limit as η converges to zero by positive values. Using a spectral resolution of $H = \int_{\mathbb{R}} \lambda\,\mathrm{d}P(\lambda)$, where $\mathrm{d}P(\lambda)$ is a projection-valued measure, one can formally rewrite it as

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

The distributional limit (Plemelj-Sokhotski formula)

$$\lim_{\eta\to 0^+}\frac{1}{x+i\eta} = \lim_{\eta\to 0^+}\frac{x}{x^2+\eta^2} - i\frac{\eta}{x^2+\eta^2} = \text{p.v.}\frac{1}{x} - i\pi\delta_0, \tag{6}$$

where p.v. stands for the Cauchy principal value, shows that $\widehat{K}$ is a singular distribution at the excitation energies $\omega = \pm(E_n - E_0)$, where E_n are the eigenvalues of H other than E_0. Past $\lambda > 0$ however, the spectrum of H is continuous, and therefore for $|\omega| > -E_0$, the nature of $\widehat{K}$ depends on that of $\langle V_{\mathcal{O}}\psi_0, \mathrm{d}P(|\omega| - E_0)V_{\mathcal{P}}\psi_0\rangle$. Under certain conditions, one can prove that this quantity is regular: this is one avatar of a limiting absorption principle. Such principles have a long history in mathematical physics, and are a first step towards scattering theory [1, 31]. Physically, this corresponds to ionization: the electron, under the action of the forcing field, dissolves into the continuum and goes away to infinity.

The structure of the response at higher orders might be very complex; see for instance [17] for a case study of ionization in the non-perturbative regime in a simple model.

The formula (4) and its generalizations (to several particles as well as various thermodynamical ensembles) is extensively used in quantum chemistry and solid-state physics, where it is variously known as the Kubo formula [24], or simply as linear response theory [28]. It can be extended to mean-field theories such as time-dependent density functional theory, using the Casida or Sternheimer formalism [13, 36]. In the context of molecules, the response function $\widehat{K}$ contains valuable physical information and can be used to compute macroscopic properties such as photo-absorption spectra (and therefore, for instance, the color of chemical compounds), which can be directly compared to experiment. Physically relatively crude approximations like adiabatic time-dependent density functional theory generally give good results for photo-absorption spectra of small molecules [6]. Such approximations fail to reproduce more involved properties or more complex molecules or solids, although these can be corrected in certain cases using more complicated theories such as the Bethe-Salpeter equation. Computationally, linear response adiabatic time-dependent density functional theory is non-trivial but tractable for molecules of small to moderate size, and such computations are routinely performed in quantum chemistry [28]. Practical implementations involve several layers of approximations, with the problem of convergence of the response past the ionization threshold with respect to the computational domain known to be particularly difficult [18].

Consider a box $[-L, L]^d$ with Dirichlet boundary conditions, giving rise to a (semi-)discretized operator H_L. In practice, this box is further discretized onto a grid for instance; however the convergence as a function of the grid size is a different, more standard problem, which we do not consider in this paper. From H_L we can define a response function K_L and its Fourier transform $\widehat{K}_L$, similarly to the definition of K and $\widehat{K}$ in (5). Note that H_L has compact resolvent and a discrete set of eigenvalues, tending to infinity. Therefore $\widehat{K}_L$ is a singular distribution, reflecting the fact that complete ionization is not possible in a finite system. A smooth function can be obtained by computing $\widehat{K}_L(\omega + i\eta)$ at finite nonzero η, which blurs the discrete energy levels into a continuum, and physically corresponds to adding an artificial dissipation. This however results in a distortion of the true response function. In physically relevant three-dimensional computations, for instance using time-dependent density functional theory, obtaining converged spectra requires a manual selection of an appropriate η parameter. Furthermore, only moderate values of L can realistically be taken, and convergence is often slow and unpredictable [18]. The main contribution of our paper is to clarify in which sense $\widehat{K}_L$ converges to $\widehat{K}$, and to quantify sources of error due to finite η and L.

The mathematical and numerical analysis of ground state properties of molecular systems is by now relatively well established. At finite volume the convergence of a number of numerical methods for various mean-field models has been established [8]. Finite-size effects have been studied mathematically in periodic systems [21, 22, 7]. However, although a number of authors have focused on establishing the validity of linear response theory [5, 4, 35, 12], and studying its properties [11, 29], work on the numerical analysis of response quantities remains scarce. In particular, we believe our work to be the first to address rigorously the important question of ionization in this context.

The Kubo formula, the limiting absorption principle and the locality estimates we use are all established mathematically; the main contribution of this paper is to use these tools in the numerical approximation of response functions on unbounded domains, which has never been addressed rigorously before. When possible, we present explicit and self-contained proofs in the hope of making this paper accessible to numerical practitioners. We mostly follow the classical paper of Agmon [1] to show the required limiting absorption principle.

The outline of this paper is as follows. We introduce our notations and assumptions in Section 2 before stating our main results in Section 3, and illustrating them numerically in Section 4. We then show the Kubo formula (3) in Section 5, study the limiting absorption principle and the properties of $\widehat{K}$ in Section 6, and its numerical approximation in Section 7. The appendices contain standard trace and resolvent estimates.

2. Notations and assumptions

We work in d space dimensions. Following conventions usual in quantum mechanics, we use

$$\widehat{f}(\omega) = \int_{\mathbb{R}} e^{i\omega t} f(t)dt, \quad (\mathcal{F}f)(q) = \int_{\mathbb{R}^d} e^{-iq\cdot x} f(x)dx$$

for the Fourier transforms in time and space respectively. The unusual sign in the time Fourier transform is done so that the elementary solution e^{-iEt} to the Schrödinger equation has a Fourier transform localized on $\{E\}$.

For $k \in \mathbb{N}, 0 \leq \alpha \leq 1$, $C^{k,\alpha}$ denotes the space of k times continuously differentiable functions with a Hölder α continuous k-th derivative. We denote by $L^2(\mathbb{R}^d)$ the Lebesgue space, by $H^k(\mathbb{R}^d)$ the Sobolev space, by $\mathcal{S}(\mathbb{R}^d)$ the space of Schwartz functions and by $\mathcal{S}'(\mathbb{R}^d)$ the space of tempered distributions. When left unspecified, $\|\cdot\|$ refers to the $L^2(\mathbb{R}^d)$ norm. For a weight function $w : \mathbb{R}^d \to (0, \infty)$, we denote by

$$L^2(w) = \{\psi,\, \psi w \in L^2(\mathbb{R}^d)\}$$
$$H^k(w) = \{\psi,\, \psi w \in H^k(\mathbb{R}^d)\}$$

the weighted spaces, with naturally associated Hilbert space structure. We use the Japanese bracket convention $\langle x \rangle = \sqrt{1 + |x|^2}$ for the regularized norm. Spaces of particular interest are $L^2(\langle x \rangle^n)$, the space of polynomially decaying functions of exponent n, and $L^2(e^{\alpha\langle x \rangle})$ and exponentially decaying functions with rate α. We will use in proofs only the notation $a \lesssim b$ to mean that there exists $C > 0$ such that $a \leq Cb$, where the dependence of C on other quantities is made clear in the statement to be proved.

We first assume a strong regularity on V.

Assumption 2.1 (Smoothness of V)**.** *The potential $V : \mathbb{R}^d \to \mathbb{R}$ is smooth (infinitely differentiable) with bounded derivatives of any order.*

This strong assumption is only required to establish the existence of a propagator in Proposition 3.1, using the results of [19], and of the linear response function $\widehat{K}$ given by the Kubo formula (Equation (9)). It could significantly be relaxed for the other results in this paper, as our focus is on the properties of $\widehat{K}$, which are related to the behavior at infinity of the potential.

More important are the decay properties of V.

Assumption 2.2 (Decay of V)**.** *There is $\varepsilon > 0$ such that $|x|^{2+\varepsilon}V(x)$ is bounded.*

This assumption is to establish the differentiability of the resolvent on the boundary; see remarks after our main result for possible extensions to potentials decaying less quickly.

Under these two assumptions, as is standard, H has domain $H^2(\mathbb{R}^d)$, and continuous spectrum $[0, \infty)$; in particular, there are no embedded eigenvalues in $[0, \infty)$ [32, Theorem XIII.58].

Assumption 2.3 (Non-degenerate ground state)**.** *There is at least one negative eigenvalue. The lowest eigenvalue E_0 is simple. We denote by ψ_0 the unique (up to sign) associated normalized eigenfunction.*

We establish our results for the ground state for concreteness, but this is not crucial: the same results would be valid for any simple eigenvalue.

Assumption 2.4 (Observable and perturbation)**.** *The observable $V_{\mathcal{O}} : \mathbb{R}^d \to \mathbb{R}$ and perturbation $V_{\mathcal{P}} : \mathbb{R}^d \to \mathbb{R}$ are infinitely differentiable and sub-linear: for all $|\alpha| \geq 1$, $\partial^\alpha V_{\mathcal{O}}$ and $\partial^\alpha V_{\mathcal{P}}$ are bounded.*

In particular this allows the potentials x_i, in which case the response functions are the dynamical polarizabilities. Again this is to establish the existence of a propagator in Proposition 3.1. Our results from then on only require potentials growing at most polynomially, and could also be extended to accomodate more general operators (such as the current operator).

3. Main results

3.1. Kubo's formula.

We first give Kubo's formula in our context and define the response function K.

Proposition 3.1 (Kubo)**.** *For all causal functions $f \in L^\infty(\mathbb{R})$ (i.e. $f(t) = 0$ for all $t \leq 0$), for all $0 < \varepsilon < 1$, the Schrödinger equation*

$$i\partial_t \psi = H\psi + \varepsilon f(t) V_{\mathcal{P}} \psi, \quad \psi(0) = \psi_0$$

has a unique strong solution for all times. Furthermore,

$$\langle \psi(t), V_{\mathcal{O}} \psi(t) \rangle = \langle \psi_0, V_{\mathcal{O}} \psi_0 \rangle + \varepsilon (K * f)(t) + R_\varepsilon(t) \tag{7}$$

with

$$|R_\varepsilon(t)| \leq C\varepsilon^2 \|f\|_\infty^2 (1 + |t|^8)$$

for some $C > 0$ independent of t, ε. The response function K is defined by

$$K(\tau) = -i\theta(\tau) \left\langle V_{\mathcal{O}}\psi_0, e^{-i(H-E_0)\tau} V_{\mathcal{P}}\psi_0 \right\rangle + \text{c.c.}, \tag{8}$$

where $z + \text{c.c.}$ is a notation for $z + \overline{z}$, and θ is the Heaviside function. It is continuous, of at most polynomial growth, and causal.

The proof of this proposition is given in Section 5. The expression for K results from a Dyson expansion, and the bound on $R_\varepsilon(t)$ from a control of the growth of moments of $\psi(t)$ using the commutator method.

Since K is causal and of at most polynomial growth, one can define its Fourier transform in two different senses: as a tempered distribution $\widehat{K}(\omega)$ on the real line (defined by duality against Schwartz functions), and as a holomorphic function $\widehat{K}(z)$ on the open upper-half complex plane (defined by the convergent integral $\int_0^{+\infty} K(\tau)e^{iz}\mathrm{d}\tau$). Since $K(\tau)e^{-\eta\tau}$ converges towards K at $\eta \to 0$ by positive values, in the sense of tempered distributions, both these definitions agree in the sense that

$$\widehat{K}(\omega) = \lim_{\eta \to 0^+} \widehat{K}(\omega + i\eta)$$

in the sense of tempered distributions.

Using for $\eta > 0$

$$\int_0^{+\infty} e^{i(\omega+i\eta-\lambda)\tau}\mathrm{d}\tau = \frac{i}{\omega + i\eta - \lambda}$$

and functional calculus, it follows that

$$\widehat{K}(\omega) = \lim_{\eta \to 0^+} \left\langle V_{\mathcal{O}}\psi_0, \Big(\omega + i\eta - (H - E_0)\Big)^{-1} V_{\mathcal{P}}\psi_0 \right\rangle - \left\langle V_{\mathcal{P}}\psi_0, \Big(\omega + i\eta + (H - E_0)\Big)^{-1} V_{\mathcal{O}}\psi_0 \right\rangle \tag{9}$$

in the sense of tempered distributions.

3.2. **The limiting absorption principle.** When $|\omega| \notin \sigma(H) - E_0$, $\widehat{K}$ defines an analytic function in a neighborhood of ω. When $|\omega| = E_n - E_0$ for E_n an eigenvalue of H, $\lim_{\eta\to 0^+} \widehat{K}(\omega + i\eta)$ diverges, and the distribution $\widehat{K}$ is singular at ω. When $|\omega| > -E_0$, *i.e.* above the ionization threshold, we have the following result.

Theorem 3.2. *The tempered distribution $\widehat{K}$ is a continuously differentiable function for $|\omega| > -E_0$. Furthermore, for all such ω there is $C > 0$ such that for all $0 < \eta < 1$,*

$$|\widehat{K}(\omega + i\eta) - \widehat{K}(\omega)| \leq C\eta. \tag{10}$$

The proof of Theorem 3.2, in Section 6, involves the study of the boundary values of the resolvent $(z - H)^{-1}$ as z approaches the real axis in the upper half complex plane. This resolvent diverges as an operator on $L^2(\mathbb{R}^d)$ as z approaches the spectrum of H. When z approaches an eigenvalue of H, this is a real divergence and the resolvent can not be defined in any meaningful sense. However, when z approaches the continuous spectrum from the upper half plane, the divergence merely indicates a loss of locality in the associated Green's function and, under appropriate decay assumptions on V, the limit exists as an operator on weighted spaces. This fact is known as a limiting absorption principle, with a long history in mathematical physics; the proof we use follows that of [1].

3.3. **Discretization.** We now discretize our problem on a domain $[-L, L]^d$ with Dirichlet boundary conditions. The corresponding approximations $H_L, \psi_{0,L}$ and $E_{0,L}$ give rise to an approximate response function K_L (see exact definitions in Section 7). Our main result is then:

Theorem 3.3. *K_L converges towards K in the sense of tempered distributions. Furthermore, for all $\omega \in \mathbb{R}$ there are $\alpha > 0$, $C > 0$ such that for all $0 < \eta < 1$, $L > 0$,*

$$|\widehat{K}_L(\omega + i\eta) - \widehat{K}(\omega + i\eta)| \leq C\frac{e^{-\alpha\eta L}}{\eta^2} \tag{11}$$

The proof of this theorem is given in Section 7. When $|\omega| < -E_0$ is not equal to a difference of eigenvalues, the function $\widehat{K}$ is analytic, and our scheme of proof combined with the estimates in Lemma 7.1 imply that there exist $C, \alpha > 0$ such that $|\widehat{K}_L(\omega + i\eta) - \widehat{K}(\omega + i\eta)| \leq Ce^{-\alpha L}$ for all η small enough.

The convergence of K_L towards K in the sense of distributions (i.e. when integrated against a quickly decaying function of time) can be heuristically understood in as follows: since the initial condition ψ_0 is

localized close to the origin, for moderate times (compared to some power of L) finite size effects are not relevant; only for longer times (damped by the test function) will the reflections against the boundary affect the value of K_L. To obtain (11), we note that at a fixed $\eta > 0$, the resolvent $(\lambda + i\eta - H)^{-1}$ is a well-defined operator, and its kernel $G(x, y)$ decays exponentially for large $||x| - |y||$, with a decay rate proportional to η. Since ψ_0 is exponentially localized, the quantity $\widehat{K}(\omega + i\eta)$ only involves quantities localized on a region of space of size of order $1/\eta$, and can therefore be computed accurately when $L \gg 1/\eta$, leading to our result.

It follows from the two results above that one can approximate $\widehat{K}(\omega)$ for $|\omega| > -E_0$ by taking the limit $L \to \infty$ (at finite η) then $\eta \to 0$, but not the reverse. At a fixed box size L, the optimal η is the one that minimizes the total error $\frac{e^{-\alpha\eta L}}{\eta^2} + \eta$. This results in a total error of order arbitrarily close to one: for instance, by taking $\eta = \frac{1}{L^{1-\varepsilon}}$ for $\varepsilon > 0$, we obtain a total error of order $\frac{1}{L^{1-\varepsilon}}$.

3.4. **Remarks.**

3.4.1. *Decay of the potential and regularity of $\widehat{K}$.* Our assumption that $|x|^{2+\varepsilon}V(x)$ is bounded guarantees that $|\widehat{K}(\omega + i\eta) - \widehat{K}(\omega)|$ is of order η. We actually show in our proof the stronger result that, if $|x|^{1+k+\alpha+\varepsilon}V(x)$ is bounded for some $k \in \mathbb{N}, \alpha \in [0, 1], \varepsilon > 0$, then

$$\widehat{K} \in C^{k,\alpha}\Big(((-\infty, E_0) \cup (-E_0, +\infty)) + i[0, +\infty]\Big),$$

For instance this shows that if $|x|^{1+\alpha+\varepsilon}V(x)$ is bounded for some $\alpha \in [0, 1], \varepsilon > 0$, then Theorem 3.2 holds with the error bound $C\eta^\alpha$. However, long-range potentials (decaying like $1/|x|$) are not covered by the results in this paper. This originates from a limitation in Agmon's argument that we follow closely (see Section 6). Total potentials originating from semilocal density functional theory in molecules decay like $|x|^{-2}$ and are therefore covered by the results in this paper.

Limiting absorption principles can also be obtained using Mourre theory [26] which relies on the local positivity of the commutator $i[H, A]$ where $A = x \cdot p + p \cdot x$ is the generator of the dilations. With this approach, it is possible to deal with potentials with slower decay - *e.g.* $V \in L^2(\mathbb{R}^d) + L^\infty_\varepsilon(\mathbb{R}^d)$ suffices- provided that additional conditions on the derivatives of V are known, *i.e.* $x \cdot \nabla V \in L^2(\mathbb{R}^d) + L^\infty_\varepsilon(\mathbb{R}^d)$ would be sufficient and $(x \cdot \nabla)^2 V$ is a bounded operator from $H^2(\mathbb{R}^d)$ to $H^{-2}(\mathbb{R}^d)$. Local regularity of the boundary value operator can also be proved [23], assuming that higher derivatives of V have a fast enough decay. For instance, differentiability of the boundary value operator is ensured if $(x \cdot \nabla)^2 V$ is a bounded operator from $H^2(\mathbb{R}^d)$ to $L^2(\mathbb{R}^d)$ and $(x \cdot \nabla)^3 V$ is a bounded operator from $H^2(\mathbb{R}^d)$ to $H^{-2}(\mathbb{R}^d)$. Compared to Agmon's approach which is detailed in Section 6, the same result is achieved by assuming a fast enough decay of the potential itself and not of its derivatives. The interested reader may refer to the monograph [2] for a thorough exposition of the commutator estimates and Mourre theory.

The reason we use the "classical" theory rather than Mourre's method is that the clasical theory is simpler, allowing fully self-contained proofs and being easier to extend to other contexts. Furthermore, it defines the boundary value of the resolvent through an explicit Fredholm integral equation, a useful starting point to design numerical methods.

3.4.2. *Higher order approximations.* In the common case where $V_{\mathcal{O}} = V_{\mathcal{P}}$, it follows from the Plemelj-Sokhotski formula (6) that the imaginary part of $\widehat{K}(\cdot + i\eta)$ is the convolution of the imaginary part of $\widehat{K}$ with a Lorentzian profile of width η and height $1/\eta$, an approximation of the Dirac distribution. In general, if ϕ is a Schwartz function of integral 1, $\phi_\eta(x) = \phi(x/\eta)/\eta$ and if f is of class C^{p+1} near ω, then

$$(f * \phi_\eta)(\omega) = f(\omega) + O(\eta^{p+1}),$$

where the order p of ϕ is the smallest integer such that $\int x^{p'}\phi(x)dx = 0$ for all $0 < p' \leq p$ (see for instance [7, Section 5.1]). Since the Lorentzian kernel is even, we would naively expect an error proportional to η^2; however, the Lorentzian kernel has heavy tails (decaying like $1/x^2$) and therefore the error is only of order η in general.

When V decays sufficiently rapidly, the above analysis suggests the possibility of using different kernels, such as a Gaussian kernel, or even a higher-order one. We refer for instance to [16] in the general context of the computation of spectral measures of generic self-adjoint operators.

3.4.3. *Several electrons.* We have here considered a one-electron model. Our results can straightforwardly be extended to the case of several non-interacting electrons. Under the assumption that $E_{N-1} < E_N$, we can consider the equation

$$i\partial_t \gamma = [-\Delta + V, \gamma] + \varepsilon f(t)[V_{\mathcal{P}}, \gamma],$$

with $\gamma(0)$ the projector onto the first N eigenstates $E_0, \dots, E_{N-1}$ of $-\Delta + V$. Then it holds that

$$\mathrm{Tr}(V_{\mathcal{O}}\gamma(t)) = \mathrm{Tr}(V_{\mathcal{O}}\gamma(0)) + \varepsilon(K * f)(t) + O(\varepsilon^2)$$

with

$$K(\tau) = -i\theta(\tau) \sum_{n=0}^{N-1} \left\langle V_{\mathcal{O}}\psi_n, e^{-i(H-E_n)\tau} V_{\mathcal{P}}\psi_n \right\rangle + \text{c.c.},$$

Then K is simply a sum of terms of the type we consider in our statements, and the results generalize easily. The case of interacting electrons (for instance using time-dependent density functional theory with an adiabatic exchange-correlation potential) requires more care, and would be an interesting topic for further research.

3.4.4. *Periodic background Hamiltonians.* We have here considered a Hamiltonian $-\Delta + V$, with the aim to model a molecule. We could also consider models of the type $H = H_0 + V$ with more general H_0. For instance, one can think of periodic operators $H_0 = -\Delta + V_{\text{per}}$, or lattice models acting on $\ell^2(\mathbb{Z}^d)$, both of which can be used to model crystals, and are analyzed using the Bloch transform. Extending our results needs two ingredients. The first is the error analysis of the effect of truncation on eigenvectors, which is complicated by the possibility of spectral pollution (see [9]) but holds for states lying below the continuous spectrum. The second is a limiting absorption principle for H_0. This can be established following the method of Section 6. The crucial point to establish a limiting absorption principle is to show regularity of the projected density of states (see the proof of Proposition 6.1), which now involves an integral on isosurfaces of the dispersion relations (Fermi surfaces). This can be done at frequencies for which bands do not cross or have a zero gradient, so that the Fermi surface is a smooth manifold. We refer to [20, 7] for details.

3.4.5. *Boundary conditions.* We here use Dirichlet boundary conditions; this is done for conceptual simplicity, and because Dirichlet boundary conditions yield a conforming scheme (in the sense that the eigenfunctions obtained at finite L are valid trial functions for the whole-space problem). Using Neumann or periodic boundary conditions would presumably yield a similar result, but the mathematical analysis is slightly more involved.

More interesting is the use of "active", frequency-dependent boundary conditions, designed to better reproduce the continuous spectrum. Such boundary conditions are widely used in scattering problems (absorbing boundary conditions, perfectly matched layers [3]) and in the study of resonances in quantum chemistry (complex scaling [14, 34]). They are however often less flexible than the approach presented here of an imaginary shift (and the closely related complex absorbing potential [27]), which is simpler and does not require any specific structure on the problem, generalizing trivially to time-dependent density functional theory. We have focused in this paper on the simplest method; the use of active boundary conditions or other techniques to lessen boundary effects in realistic computational models is an important topic for future research.

4. Numerical illustration

We illustrate our results with a simple model: a discrete tight-binding model, set on $\ell^2(\mathbb{Z})$, with the Hamiltonian H given by the matrix elements

$$H_{mn} = \delta_{m,n+1} + \delta_{m,n-1} + V\delta_{m,n}\delta_{n,0}. \tag{12}$$

The first two terms ("hopping terms") are analogous to a kinetic energy and describe the motion of a particle to neighboring sites. The third term is an impurity potential on site 0. The free Hamiltonian (corresponding to the first two terms of (12)) is unitarily equivalent through the Fourier transform to a multiplication operator on $L^2([-\pi, \pi])$ with multiplier $\lambda(k) = 2\cos k$. Since the third term is a compact perturbation of the free Hamiltonian, H has continuous spectrum $[-2, 2]$. We choose $V = -4$, which leads to a single negative eigenvalue $E_0 \approx -4.47$. We choose both for the perturbing potential $V_{\mathcal{P}}$ and for the observable $V_{\mathcal{O}}$ the operator with coefficients $\delta_{nm}\delta_{n0}$, localized on site 0.

This model is shown for illustrative purposes only and is not strictly covered by our results above. It was chosen only for numerical simplicity (since, unlike continuous models, it only involves a truncation in

space, not a further discretization), and as the simplest model in which the phenomenon discussed in this paper occurs. The ionization region, which was $|\omega| \geq -E_0$ in the continuous case (since the continuous spectrum in that case was $[0, +\infty)$), becomes $|\omega| \in [-2 - E_0, 2 - E_0]$ (since the continuous spectrum is $[-2, 2]$). The extension of our methods of proof in the discrete setting is possible (see Section 3.4.4 above), and shows that $\widehat{K}$ is smooth everywhere except at the band edges $\pm(-2 - E_0)$ and $\pm(2 - E_0)$, at which points the Fermi surfaces become degenerate.

To compute K_L, we truncate the Hamiltonian to a finite set of $2L+1$ sites $\{-L, \ldots, L\}$, with Dirichlet boundary conditions and diagonalize the resulting Hamiltonian H_L to obtain the eigenpairs $(\psi_{n,L}, E_{n,L})$ for $n = 0, \ldots, 2L$, with $\psi_{n,L}$ orthonormal, ordered by increasing eigenvalue. The expression for K_L and $\widehat{K}_L$ can be expanded in this basis, turning into "sum-over-states" formulas

$$K_L(\tau) = -i\theta(\tau) \sum_{n=0}^{2L} e^{-i(E_{n,L} - E_{0,L})\tau} \langle V_{\mathcal{O}} \psi_{0,L}, \psi_{n,L} \rangle \langle \psi_{n,L}, V_{\mathcal{P}} \psi_{0,L} \rangle + \text{c.c.},$$

and a similar expression for $\widehat{K}_L(\omega)$.

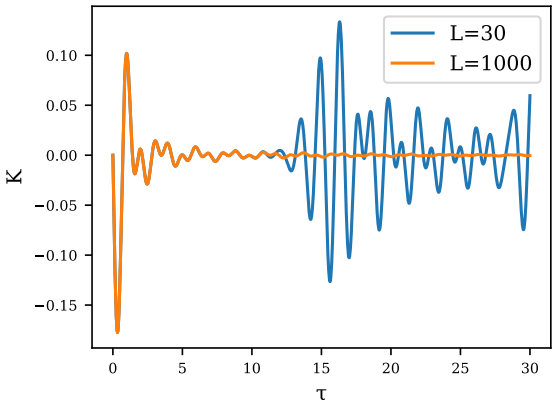

FIGURE 1. Time response function $K_L(\tau)$.

We plot in Figure 1 the response function $K_L(\tau)$ for different values of L. The exact response function $K(\tau)$ decays to zero, as the initial disturbance propagates to infinity. However when observed on a finite-sized box for long times, spurious reflections at the boundary introduce non-decaying oscillations.

This same phenomenon can be seen in frequency space in Figure 2, where we plot the frequency response function $\widehat{K}_L(\omega + i\eta)$ for different values of η and L. We plot the region $\omega \in [0, 9]$, which contains the region $[-2, 2] - E_0$ corresponding to ionization; not represented is the other ionization region $E_0 - [-2, 2]$. When η is small and $L \ll 1/\eta$, the discrete nature of the spectrum is evident, and the response function is composed of individual peaks. When $L \gg 1/\eta$, these peaks are blurred into a continuous function. Higher η result in more accurate functions at moderate L, at the price of over-smoothing.

5. The Kubo formula

We begin by studying the eigenfunction ψ_0 associated to the eigenvalue E_0.

Lemma 5.1. *There is $\alpha_0 > 0$ such that $\psi_0 \in H^2(e^{\alpha_0 \langle x \rangle})$.*

Proof. Since V decays at infinity, for all $\varepsilon > 0$, we can write $V = V_c + V_\varepsilon$ with V_c compactly supported and $\|V_\varepsilon\|_{L^\infty(\mathbb{R}^d)} \leq \varepsilon$. Then, for $\varepsilon \leq -E_0/2$ we can write

$$\psi_0 = -(-\Delta + V_\varepsilon - E_0)^{-1} V_c \psi_0.$$

Since V_c is compactly supported, $V_c \psi_0$ is in $L^2(e^{\alpha \langle x \rangle})$ for all $\alpha > 0$, and so by Lemma 9.2, ψ_0 belongs to $H^2(e^{\alpha_0 \langle x \rangle})$ for some $\alpha_0 > 0$ small enough. □

Note that this estimate is not sharp since the actual decay rate of ψ_0 is $\sqrt{-E_0}$ (which can be obtained by sharper Combes-Thomas estimates), but this will be sufficient for our purposes.

We now prove Kubo's formula.

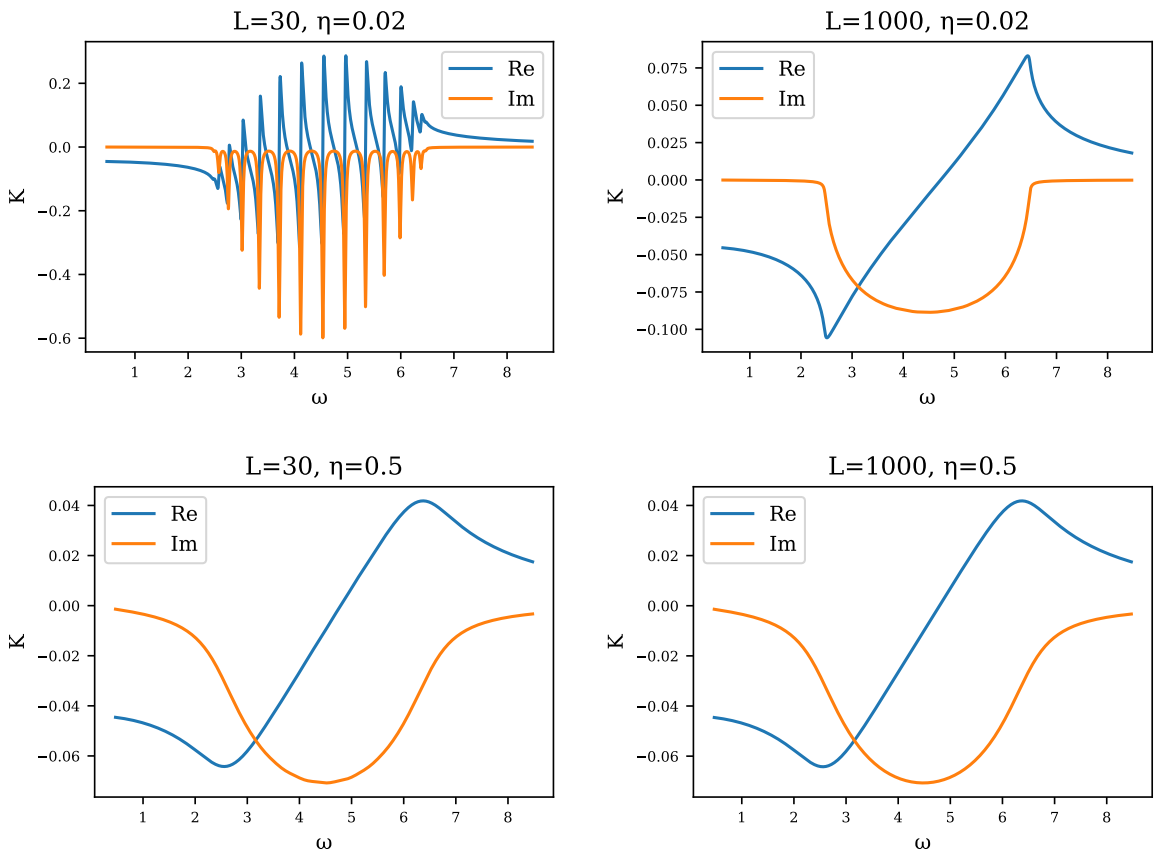

FIGURE 2. Frequency response function $\widehat{K}_L(\omega + i\eta)$.

Proof of Proposition 3.1. Let $U_0(t,s) = e^{-iH(t-s)}$ be the unitary propagator of the unperturbed Hamiltonian $H = -\Delta + V$, and $U_\varepsilon(t,s)$ that of the perturbed Hamiltonian $H_\varepsilon(t) = -\Delta + V + \varepsilon f(t) V_{\mathcal{P}}$, whose existence is guaranteed by Lemma 9.1. By the Duhamel/variation of constant formula,

$$\psi(t) = \underbrace{e^{-iE_0 t}\psi_0}_{\psi^{0,0}(t)} \underbrace{-i\varepsilon \int_0^t U_0(t,t') f(t') V_{\mathcal{P}} U_\varepsilon(t',0)\psi_0 dt'}_{\varepsilon\psi^{1,\varepsilon}(t)} .$$

Iterating this formula, we obtain the first-order Dyson expansion

$$\psi^{1,\varepsilon}(t) = \underbrace{-i\int_0^t f(t') U_0(t,t') V_{\mathcal{P}} U_0(t',0)\psi_0 dt'}_{\psi^{1,0}(t)} \underbrace{-\varepsilon \int_0^t \int_0^{t'} U_0(t,t') f(t') V_{\mathcal{P}} U_0(t',t'') f(t'') V_{\mathcal{P}} U_\varepsilon(t'',0)\psi_0 dt' dt''}_{\varepsilon\psi^{2,\varepsilon}(t)} .$$

From $\psi(t) = \psi^{0,0}(t) + \varepsilon\psi^{1,0}(t) + \varepsilon^2\psi^{2,\varepsilon}(t)$ it follows that

$$\begin{aligned}\langle \psi(t), V_{\mathcal{O}}\psi(t)\rangle &= \langle \psi_0, V_{\mathcal{O}}\psi_0\rangle + \varepsilon\Big(\langle \psi^{1,0}(t), V_{\mathcal{O}}\psi^{0,0}(t)\rangle + \langle \psi^{0,0}(t), V_{\mathcal{O}}\psi^{1,0}(t)\rangle\Big) \\ &\quad \underbrace{+ \varepsilon^2\Big(\langle \psi^{2,\varepsilon}(t), V_{\mathcal{O}}\psi^{0,0}(t)\rangle + \langle \psi^{0,0}(t), V_{\mathcal{O}}\psi^{2,\varepsilon}\rangle + 2\langle \psi^{1,0}(t), V_{\mathcal{O}}\psi^{1,0}(t)\rangle\Big)}_{R_\varepsilon(t)}\end{aligned}$$

The first-order term can be computed as

$$\begin{aligned}\langle \psi^{0,0}(t), V_{\mathcal{O}}\psi^{1,0}(t)\rangle + \text{c.c.} &= \left\langle e^{iE_0 t} V_{\mathcal{O}}\psi_0, -i\int_0^t f(t') e^{-iH(t-t')} V_{\mathcal{P}} e^{-iE_0 t'}\psi_0 dt'\right\rangle + \text{c.c.} \\ &= -i\int_0^t f(t')\langle V_{\mathcal{O}}\psi_0, e^{-i(H-E_0)(t-t')} V_{\mathcal{P}}\psi_0\rangle dt' + \text{c.c.}. \\ &= (K * f)(t).\end{aligned}$$

Since $|V_{\mathcal{O}}(x)| \lesssim 1+|x|$ and $\psi_0 \in L^2(e^{\alpha_0\langle x\rangle})$,

$$|R_\varepsilon(t)| \lesssim \|\psi^{2,\varepsilon}(t)\| + \|(1+|x|)\psi^{1,0}(t)\|.$$

Using $|V_{\mathcal{P}}(x)| \lesssim 1+|x|$ and Lemma 9.1, we get

$$\begin{aligned}
\|\psi^{2,\varepsilon}(t)\| &\lesssim (1+|t|^2) \sup_{t'\in[0,t],t''\in[0,t]} \|U_0(t,t')V_{\mathcal{P}}U_0(t',t'')V_{\mathcal{P}}U_\varepsilon(t'',0)\psi_0\| \\
&\lesssim (1+|t|^2) \sup_{t'\in[0,t],t''\in[0,t]} \|(1+|x|)U_0(t',t'')V_{\mathcal{P}}U_\varepsilon(t'',0)\psi_0\| \\
&\lesssim (1+|t|^4) \sup_{t''\in[0,t]} \Big(\|(1+|x|)V_{\mathcal{P}}U_\varepsilon(t'',0)\psi_0\| + \|\nabla(V_{\mathcal{P}}U_\varepsilon(t'',0)\psi_0)\|\Big) \\
&\lesssim (1+|t|^4) \sup_{t''\in[0,t]} \Big(\||x|^2U_\varepsilon(t'',0)\psi_0\| + \|\nabla U_\varepsilon(t'',0)\psi_0\| + \|\psi_0\|\Big) \\
&\lesssim (1+|t|^8)\left(\||x|^2\psi_0\| + \|\Delta\psi_0\| + \|x\otimes\nabla\psi_0\| + \|\psi_0\|\right)
\end{aligned}$$

The bound on $R_\varepsilon(t)$ then follows by establishing a bound on $\|(1+|x|)\psi^{1,0}(t)\|$ by the same method. □

6. Properties of the response function K

Theorem 3.2 is a consequence of a limiting absorption principle for the Hamiltonian $H = -\Delta + V$ stated in Proposition 6.2. Our proof is a simplification of the one in Agmon [1], with a careful tracking of the regularity with respect to the spectral parameter.

The general idea in Agmon's proof of the limiting absorption principle is to use the explicit formula of the resolvent of the free Laplacian $(z+\Delta)^{-1}$, for z in the open upper half space and show that it admits a boundary value $(\lambda+\Delta+i0^+)^{-1}$ from $L^2(\langle x\rangle^s)$ to $H^2(\langle x\rangle^{-s})$ for $s>\frac{1}{2}$. This can be extended to nonzero potentials V using a resolvent identity. In doing so, we need at first the invertibility of $1-(z+\Delta)^{-1}V$ in $L^2(\langle x\rangle^{-s})$, which translates into a decay condition on V, *i.e.* V decays faster than $\frac{1}{|x|}$.

We begin the proof of the limiting absorption principle by studying the free Laplacian.

Proposition 6.1 (Limiting absorption principle for the free Laplacian)**.** *Let $s=\frac{1}{2}+k+\alpha$ for $k\in\mathbb{N}$ and $\alpha\in[0,1]$. The resolvent $(z+\Delta)^{-1}$ defined for $\operatorname{Im} z>0$ extends to an operator of class $C^{k,\alpha}$ on the semi-open set $(0,+\infty)+i[0,+\infty)$, in the topology of bounded operators from $L^2(\langle x\rangle^s)$ to $H^2(\langle x\rangle^{-s})$.*

Proof. Let $\lambda_0>0$. Let χ be a smooth cutoff function, equal to 1 in $[\lambda_0/2, 2\lambda_0]$ and to zero outside of $[\lambda_0/3, 3\lambda_0]$. Let $\psi\in L^2(\langle x\rangle^s)$, and ϕ belong to the L^2-dual of $H^2(\langle x\rangle^{-s})$.

Let M_χ be the multiplication operator in Fourier space defined by $\mathcal{F}(M_\chi\psi)(q) = \chi(|q|^2)\mathcal{F}(q)$. Then by spectral calculus, $(z+\Delta)^{-1}(1-M_\chi)$ extends to a $C^{k,\alpha}$ operator on a set $[\lambda_0-\varepsilon,\lambda_0+\varepsilon]+i[0,+\infty)$ for ε small enough, in the topology of operators $L^2(\mathbb{R}^d)$ to $H^2(\mathbb{R}^d)$. Therefore, it is enough to consider the term

$$\begin{aligned}
\langle\phi,(z+\Delta)^{-1}M_\chi\psi\rangle &= \frac{1}{(2\pi)^d}\int_{\mathbb{R}^d}\frac{\chi\left(|q|^2\right)\mathcal{F}\phi(q)^*\mathcal{F}\psi(q)}{z-|q|^2}\mathrm{d}q \\
&= \int_{\mathbb{R}}\frac{D_{\phi\psi}(\lambda)}{z-\lambda}\mathrm{d}\lambda, \qquad (13)
\end{aligned}$$

with the projected density of states

$$D_{\phi\psi}(\lambda) = \frac{1}{(2\pi)^d}\lambda^{(d-2)/2}\chi(\lambda)\int_{S^{d-1}}\mathcal{F}\phi(\sqrt{\lambda}\hat{q})^*\mathcal{F}\psi(\sqrt{\lambda}\hat{q})\mathrm{d}\hat{q}.$$

Since $\mathcal{F}(M_{\sqrt{\chi}}\phi)$ and $\mathcal{F}(M_{\sqrt{\chi}}\psi)$ are in $H^s(\mathbb{R}^d)$, by Lemma 8.1 $D_{\phi\psi}$ is in $H^s(\mathbb{R})$.

We can compute by contour integration the inverse Fourier transform of the function $\frac{1}{z-\cdot}$ for $\operatorname{Im} z>0$:

$$\frac{1}{2\pi}\int\frac{1}{z-\lambda}e^{-i\lambda\tau}\mathrm{d}\lambda = i\theta(-\tau)e^{-iz\tau}$$

Therefore, by the Parseval formula,

$$\langle\phi,(z+\Delta)^{-1}M_\chi\psi\rangle = 2\pi i\int_{\mathbb{R}^+}e^{iz\tau}\check{D}_{\phi\psi}(\tau)\mathrm{d}\tau.$$

Letting $g_\tau(z)=e^{iz\tau}$, it follows from

$$|g_\tau^{(k)}(z_1)-g_\tau^{(k)}(z_2)| \lesssim |z_1-z_2|^\alpha|\tau|^{k+\alpha}$$

and the Cauchy-Schwarz inequality that $\langle\phi,(z-\Delta)^{-1}M_\chi\psi\rangle$ is $C^{k,\alpha}$ on $(0,+\infty)+i[0,+\infty)$. □

For $\lambda > 0$, we denote by

$$(\lambda + i0^+ + \Delta)^{-1} = \lim_{\eta \to 0^+} (\lambda + i\eta + \Delta)^{-1}$$

the boundary value of the free resolvent. Its action can be explicitly computed using the spectral representation (13) and the Plemelj-Sokhotski formula (6). Note in particular that it differs from $(\lambda + i0^- + \Delta)^{-1}$ by the sign of its anti-hermitian part.

Proposition 6.2 (Limiting absorption principle for $H = -\Delta + V$)**.** *Let $s = \frac{1}{2} + k + \alpha$ for $k \in \mathbb{N}$ and $\alpha \in [0, 1]$. Let $V : \mathbb{R}^d \to \mathbb{R}$ be a continuous potential such that $\langle x \rangle^{2s+\epsilon} V$ is bounded, for some $\varepsilon > 0$. The resolvent $(z - H)^{-1}$ defined for $\mathrm{Im} z > 0$ extends to an operator of class $C^{k,\alpha}$ on the semi-open set $(0, +\infty) + i[0, +\infty)$, in the topology of bounded operators from $L^2(\langle x \rangle^s)$ to $H^2(\langle x \rangle^{-s})$.*

Proof. We use the following resolvent inequality:

$$(z - H)^{-1} = B(z)^{-1}(z + \Delta)^{-1} \tag{14}$$

with

$$B(z) = 1 - (z + \Delta)^{-1} V,$$

valid for $z \in \mathbb{C}$ with $\mathrm{Im} z > 0$. Since V is bounded from $H^2(\langle x \rangle^{-s})$ to $L^2(\langle x \rangle^s)$, it follows from Proposition 6.1 that $B(z)$ extends to an operator of class $C^{k,\alpha}$ on the semi-open set $(0, +\infty) + i[0, +\infty)$, in the topology of bounded operators on $H^2(\langle x \rangle^{-s})$.

We will show that for all $\lambda > 0$, $B(\lambda + i0^+)$ is invertible on $H^2(\langle x \rangle^{-s})$. This shows that $B(z)^{-1}$ is $C^{k,\alpha}$ on the semi-open set in the topology of bounded operators on $H^2(\langle x \rangle^{-s})$, which implies our result by (14) and Proposition 6.1.

Let $\lambda > 0$. Since $\langle x \rangle^{2s+\varepsilon} V$ is bounded, the multiplication operator V is compact from $H^2(\langle x \rangle^{-s})$ to $L^2(\langle x \rangle^s)$. It follows that $(\lambda + i0^+ + \Delta)^{-1} V$ is compact on $H^2(\langle x \rangle^{-s})$. By the Fredholm alternative, it is then enough to show that there are no non-zero solutions of

$$u = (\lambda + i0^+ + \Delta)^{-1} V u \tag{15}$$

in $H^2(\langle x \rangle^{-s})$. Let $u \in H^2(\langle x \rangle^{-s})$ be such a non-zero solution. We will show that $u \in H^2\left(\langle x \rangle^{s-1}\right)$, which by a bootstrap argument on s will imply that $u \in H^2(\mathbb{R}^d)$.

Testing the equality (15) against Vu and taking imaginary parts, we obtain from the Plemelj-Sokhotski formula (6) that

$$0 = \mathrm{Im}(\langle Vu, u \rangle) = \mathrm{Im}\langle Vu, (\lambda + i0^+ + \Delta)^{-1} Vu \rangle = -\frac{\pi}{2\sqrt{\lambda}} \int_{|q| = \sqrt{\lambda}} |\mathcal{F}(Vu)(q)|^2 \, \mathrm{d}q.$$

By assumption on V, $Vu \in L^2(\langle x \rangle^s)$ thus $\mathcal{F}(Vu) \in H^s(\mathbb{R}^d)$ and with zero trace on the sphere $|q| = \sqrt{\lambda}$ by the equation above. By Lemma 8.2, this means that $\frac{\mathcal{F}(Vu)}{\lambda - |q|^2} \in H^{s-1}(\mathbb{R}^d)$. We then have

$$\langle q \rangle^2 (\mathcal{F}u)(q) = \lim_{\eta \to 0^+} \langle q \rangle^2 \frac{\mathcal{F}(Vu)(q)}{\lambda + i\eta - |q|^2} = \langle q \rangle^2 \frac{\mathcal{F}(Vu)(q)}{\lambda - |q|^2}$$

in the sense of distributions. This shows that $\mathcal{F}u$ belongs to $H^{s-1}(\langle q \rangle^2)$, and therefore that $u \in H^2(\langle x \rangle^{s-1})$. More generally, the argument above shows that if $u \in H^2(\langle x \rangle^{s'})$ with $s' \geq -s$, then $u \in H^2(\langle x \rangle^{s'+2s-1})$. By a bootstrap argument, since $s > \frac{1}{2}$, it follows that $u \in H^2(\mathbb{R}^d)$, and therefore that λ is a positive embedded eigenvalue, which is impossible. □

Proof of Theorem 3.2. By Theorem 3.1, the response function is given by

$$\widehat{K}(\omega) = \lim_{\eta \to 0^+} \left\langle \psi_0, V_{\mathcal{O}} \Big(\omega + i\eta - (H - E_0) \Big)^{-1} V_{\mathcal{P}} \psi_0 \right\rangle - \left\langle \psi_0, V_{\mathcal{P}} \Big(\omega + i\eta + (H - E_0) \Big)^{-1} V_{\mathcal{O}} \psi_0 \right\rangle. \tag{16}$$

By the exponential localization of the ground state wave function ψ_0, and the assumptions on the potentials $V_{\mathcal{O}}$ and $V_{\mathcal{P}}$, $V_{\mathcal{O}}\psi_0$ and $V_{\mathcal{P}}\psi_0$ belong to every $L^2(\langle x \rangle^s)$ for $s \in \mathbb{R}$. Since by Assumption 2.2 the function $\langle x \rangle^{2+\epsilon} V$ is bounded, the result follows by Proposition 6.2 in the case $k = 0, \alpha = 1$. □

7. Truncation in space

Consider the domain $\Omega_L = [-L, L]^d$ with Dirichlet boundary conditions. We define $\widetilde{H}_L$ the operator $-\Delta + V$ with domain $D(\widetilde{H}_L) = \{\widetilde{\psi} \in H^2(\Omega_L), \widetilde{\psi}|_{\partial\Omega_L} = 0\}$, self-adjoint on $L^2(\Omega_L)$. This operator is bounded from below and has compact resolvent.

We now define the operator H_L on $L^2(\mathbb{R}^d)$ in the following way: if $\psi \in L^2(\mathbb{R}^d)$ and $\psi|_{\Omega_L} \in D(\widetilde{H}_L)$, then

$$(H_L\psi)|_{\Omega_L} = \widetilde{H}_L\psi|_{\Omega_L},$$

and $(H_L\psi)|_{\mathbb{R}^d\setminus\Omega_L} = 0$. This defines an operator on $L^2(\mathbb{R}^d)$, self-adjoint with domain $D(H_L) = L^2(\mathbb{R}^d \setminus \Omega_L) \oplus D(\widetilde{H}_L)$, and with spectrum $\sigma(\widetilde{H}_L) \cup \{0\}$. Let $\psi_{0,L}$ be an L^2-normalized eigenvector associated to the lowest eigenvalue of H_L.

Note that by adapting the proof in Lemma 9.1, the estimates shown there for e^{-itH} on $L^2(\mathbb{R}^d)$ are also valid for $e^{-it\widetilde{H}_L}$ on $L^2(\Omega_L)$, with constants independent of L. Similarly, the estimates of Lemma 9.2 for $(z - H)^{-1}$ on $L^2(\mathbb{R}^d)$ and $L^2(e^{\alpha\langle x\rangle})$ are also valid for $(z - \widetilde{H}_L)^{-1}$ on $L^2(\Omega_L)$ and $L^2(e^{\alpha\langle x\rangle}; \Omega_L) = \{\psi, e^{\alpha\langle x\rangle}\psi \in L^2(\Omega_L)\}$ with natural norms, still with constants independent of L.

We can now define K_L analogously to K:

$$K_L(\tau) = -i\theta(\tau)\left\langle V_{\mathcal{O}}\psi_{0,L}, e^{-i(H_L - E_{0,L})\tau}V_{\mathcal{P}}\psi_{0,L}\right\rangle + \text{c.c.}, \tag{17}$$

and

$$\begin{aligned}\widehat{K}_L(\omega) = \lim_{\eta\to 0^+} &\left\langle \psi_{0,L}, V_{\mathcal{O}}\Big(\omega + i\eta - (H_L - E_{0,L})\Big)^{-1} V_{\mathcal{P}}\psi_{0,L}\right\rangle \\ &- \left\langle \psi_{0,L}, V_{\mathcal{P}}\Big(\omega + i\eta + (H_L - E_{0,L})\Big)^{-1} V_{\mathcal{O}}\psi_{0,L}\right\rangle.\end{aligned} \tag{18}$$

The operator H and H_L have the same action, but H has domain $D(H) = H^2(\mathbb{R}^d)$, whereas H_L has domain $D(H_L) = \{\psi \in L^2(\mathbb{R}^d), \psi|_{\Omega_L} \in H^2(\Omega_L), \psi|_{\partial\Omega_L} = 0\}$. These different domains do not even share a common core, making the direct comparison of K_L and K difficult. However, we will prove and use the fact that, when evaluated on localized quantities, their resolvents

$$R(z) = (z - H)^{-1}, \quad R_L(z) = (z - H_L)^{-1} \tag{19}$$

and propagators e^{-iHt} and e^{-iH_Lt}, both defined on $L^2(\mathbb{R}^d)$, are close. To that end, we let $\chi : \mathbb{R}^d \to \mathbb{R}$ be a smooth truncation function equal to 1 for $|x|_\infty \leq 1/4$ and to 0 for $|x|_\infty \geq 3/4$, and

$$\chi_L(x) = \chi(x/L).$$

Note that, as a multiplication operator, χ_L maps $D(H) \cup D(H_L)$ to $D(H) \cap D(H_L)$.

Furthermore, this truncation is exponentially accurate on exponentially localized functions: by direct computation, for all $k \in \mathbb{N}$ there is $C_k > 0$ such that, for all $0 \leq \alpha_1 \leq \alpha_2 \leq 1$, for all $\psi \in H^k(e^{\alpha_2\langle x\rangle})$

$$\|(1 - \chi_L)\psi\|_{H^k(e^{\alpha_1\langle x\rangle})} = \|e^{(\alpha_1-\alpha_2)\langle x\rangle}(1 - \chi_L)e^{\alpha_2\langle x\rangle}\psi\|_{H^k(\mathbb{R}^d)} \leq C_k e^{-(\alpha_2-\alpha_1)L}\|\psi\|_{H^k(e^{\alpha_2\langle x\rangle})}.$$

Lemma 7.1. *There are $c > 0, C > 0$ such that, for all $z \in \mathbb{C}$ and $L > 0$ such that $d(z, \sigma(H)) \geq g$ and $\liminf d(K, \sigma(H_L)) \geq g$ with $g > 0$, for all $0 \leq \alpha \leq \alpha' \leq cg$,*

$$\|R_L(z) - R(z)\|_{L^2(e^{\alpha'\langle x\rangle})\to L^2(e^{\alpha\langle x\rangle})} \leq C\left(1 + \frac{1}{g}\right)^2 (1 + |z|)^3 e^{-(\alpha'-\alpha)L}.$$

Proof. Because of the aforementioned domain issues, we cannot directly use the resolvent formula $R(z) - R_L(z) = R_L(z)(H - H_L)R(z)$. However, we can approximate any $\psi \in L^2(\mathbb{R}^d)$ by $R(z)^{-1}\chi_L R(z)\psi$, for which

$$(R(z) - R_L(z))\, R(z)^{-1}\chi_L R(z)\psi = R_L(z)(H - H_L)\chi_L R(z)\psi = 0,$$

where we have used that $H\phi = H_L\phi$ for all $\phi \in D(H_L)\cap D(H)$. Therefore, using the estimates of Lemma 9.2 for both H and H_L,

$$\begin{aligned}
\|(R(z)-R_L(z))\psi\|_{L^2(e^{\alpha\langle x\rangle})} &= \|(R(z)-R_L(z))(R(z)^{-1}(1-\chi_L)R(z)\psi)\|_{L^2(e^{\alpha\langle x\rangle})} \\
&\lesssim \left(1+\frac{1}{d(z,\sigma(H))}+\frac{1}{d(z,\sigma(H_L))}\right)(1+|z|)\|R(z)^{-1}(1-\chi_L)R(z)\psi\|_{L^2(e^{\alpha\langle x\rangle})} \\
&\lesssim \left(1+\frac{1}{d(z,\sigma(H))}+\frac{1}{d(z,\sigma(H_L))}\right)(1+|z|)^2\|(1-\chi_L)R(z)\psi\|_{H^2(e^{\alpha\langle x\rangle})} \\
&\lesssim \left(1+\frac{1}{d(z,\sigma(H))}+\frac{1}{d(z,\sigma(H_L))}\right)^2(1+|z|)^3 e^{-(\alpha'-\alpha)L}\|\psi\|_{L^2(e^{\alpha'\langle x\rangle})}.
\end{aligned}$$

□

Using this we can compare the eigenpairs of H_L and H.

Lemma 7.2. *There are $C,\alpha_1,\alpha_2>0$ such that, for all L large enough,*

$$|E_{0,L}-E_0| \le Ce^{-\alpha_0 L} \tag{20}$$

$$\|\psi_{0,L}-\psi_0\|_{L^2(e^{\alpha_1\langle x\rangle})} \le Ce^{-\alpha_2 L} \tag{21}$$

where the sign of $\psi_{0,L}$ is chosen such that $\langle\psi_{0,L},\psi_0\rangle \ge 0$, and where α_0 is the constant in Lemma 5.1.

Proof. Since by Lemma 5.1 $\psi_0 \in H^2(e^{\alpha_0\langle x\rangle})$,

$$\|(1-\chi_L)\psi_0\|_{H^2(\mathbb{R}^d)} \lesssim e^{-\alpha_0 L}.$$

and (20) follows from the variational principle

$$E_0 \le E_{0,L} \le \frac{\langle \chi_L\psi_0, H\chi_L\psi_0\rangle_{L^2(\mathbb{R}^d)}}{\langle \chi_L\psi_0,\chi_L\psi_0\rangle_{L^2(\mathbb{R}^d)}} \le E_0 + Ce^{-\alpha_0 L}.$$

for some $C>0$.

Let $E_{1,L}$ and E_1 be the second-lowest eigenvalue (or zero if there are no second eigenvalue) of H_L and H respectively. From the min-max principle, $E_{1,L}\ge E_1$ and therefore for L large enough there is a gap $g>0$ in $\sigma(H_L)$ above $E_{0,L}$. Let C be the circle with center E_0 and radius $g/2$ in the complex plane, oriented trigonometrically. Then, by Lemma 7.1 there is $\alpha_2>0$ such that

$$\begin{aligned}
1-\langle\psi_0,\psi_{0,L}\rangle^2 &= \Big\langle \psi_0, \Big(|\psi_0\rangle\langle\psi_0| - |\psi_{0,L}\rangle\langle\psi_{0,L}|\Big)\psi_0\Big\rangle \\
&= \frac{1}{2\pi i}\oint_{\mathcal{C}} \langle\psi_0,(R(z)-R_L(z))\psi_0\rangle\, dz \\
|1-\langle\psi_0,\psi_{0,L}\rangle^2| &\lesssim e^{-\alpha_2 L}
\end{aligned}$$

Then

$$\frac{1}{2}\|\psi_0-\psi_{0,L}\|^2_{L^2(\mathbb{R}^d)} = 1-\langle\psi_0,\psi_{0,L}\rangle = 1-\sqrt{\langle\psi_0,\psi_{0,L}\rangle^2} \lesssim e^{-\alpha_2 L}.$$

Now, as in Lemma 5.1, let $V = V_\varepsilon + V_c$ with V_c compactly supported and $\|V_\varepsilon\|_{L^\infty(\mathbb{R}^d)} \le -E_0/2$. Let $H_{L,\varepsilon} = -\Delta + V_\varepsilon$ on Ω_L, extended as before to act on $L^2(\Omega)$. For L large enough so that the support of V_c is contained in Ω_L, we have

$$\psi_{0,L} = (E_{0,L}-H_{L,\varepsilon})^{-1}V_c\psi_{0,L}.$$

Arguing as in Lemma 7.1, there are $\alpha_1,\alpha'>0$ such that $(E_{0,L}-H_{L,\varepsilon})^{-1}$ converges exponentially quickly to $(E_0-H)^{-1}$ as an operator from $L^2(e^{\alpha'\langle x\rangle})$ to $L^2(e^{\alpha_1\langle x\rangle})$. Furthermore, because V_c is compactly supported, we have

$$\|V_c\psi_{0,L}-V_c\psi_0\|_{L^2(e^{\alpha'\langle x\rangle})} \lesssim \|\psi_{0,L}-\psi_0\|_{L^2(\mathbb{R}^d)} \lesssim e^{-\alpha_2 L}$$

and the result follows. □

With this we can now prove the convergence of $K_L(\omega+i\eta)$ for positive η.

Theorem 7.3. *There are $\alpha_3>0, C>0$ such that for all $0<\eta<1$, $\omega\in\mathbb{R}$,*

$$|\widehat{K}_L(\omega+i\eta)-\widehat{K}(\omega+i\eta)| \le \frac{C(1+\omega)^3}{\eta^2}e^{-\alpha_3\eta L}$$

Proof. Since $\psi_{0,L}$ converges exponentially towards ψ_0 in $L^2(e^{\alpha\langle x\rangle})$ for some $\alpha > 0$, and $V_{\mathcal{O}}$ and $V_{\mathcal{P}}$ have at most polynomial growth, $V_{\mathcal{O}}\psi_{0,L}$ and $V_{\mathcal{P}}\psi_{0,L}$ converge exponentially quickly in $L^2(\mathbb{R}^d)$ towards $V_{\mathcal{O}}\psi_0$ and $V_{\mathcal{P}}\psi_0$ respectively. $E_{0,L}$ converges exponentially towards E_0 and $\Big(\omega + i\eta - (H_L - E_{0,L})\Big)^{-1}$ is uniformly bounded by $1/\eta$ as an operator on $L^2(\mathbb{R}^d)$. It therefore follows that we can reduce to terms of the form

$$\Big\langle \psi_l, \Big(R_L(\omega - E_0 + i\eta) - R(\omega - E_0 + i\eta)\Big)\psi_r \Big\rangle$$

with $\psi_{l/r} \in L^2(e^{\alpha\langle x\rangle})$ for some $\alpha > 0$ independent on ω, η. We can then conclude using Lemma 7.1. □

Finally, we conclude the proof of Theorem 3.3.

Theorem 7.4. *K_L converges as a tempered distribution towards K.*

Proof. We will prove that, for all $f \in \mathcal{S}(\mathbb{R})$,

$$\int_0^\infty \Big\langle V_{\mathcal{O}}\psi_{0,L}, e^{-i(H_L - E_{0,L})t} V_{\mathcal{P}}\psi_{0,L} \Big\rangle f(t)dt \to \int_0^\infty \Big\langle V_{\mathcal{O}}\psi_0, e^{-i(H - E_0)t} V_{\mathcal{P}}\psi_0 \Big\rangle f(t)dt.$$

Since $\psi_{0,L} \to \psi_0$ in $H^2(e^{\alpha_1\langle x\rangle})$,

$$\|V_{\mathcal{O}}\psi_{0,L} - \chi_L V_{\mathcal{O}}\psi_0\| \to 0$$

and similarly for $V_{\mathcal{P}}$. It is therefore sufficient to prove that

$$\|\chi_L(e^{-iHt} - e^{-iH_L t})\chi_L V_{\mathcal{P}}\psi_0\| \leq \frac{P(t)}{L}$$

for some polynomial P. Let

$$\phi(t) = e^{-iHt}\chi_L V_{\mathcal{P}}\psi_0, \quad \phi_L(t) = e^{-iH_L t}\chi_L V_{\mathcal{P}}\psi_0$$

To estimate $\chi_L(\phi(t) - \phi_L(t))$ we compute

$$\begin{aligned} i\partial_t \chi_L(\phi - \phi_L) &= H\chi_L\phi - H_L\chi_L\phi_L + [\chi_L, H]\phi - [\chi_L, H_L]\phi_L \\ &= H\chi_L(\phi - \phi_L) + [\chi_L, H]\phi - [\chi_L, H_L]\phi_L \end{aligned}$$

and therefore by the Duhamel formula

$$\begin{aligned} \chi_L(\phi(t) - \phi_L(t)) &= -i\int_0^t e^{-iH(t-t')}\left([\chi_L, H]\phi(t') - [\chi_L, H_L]\phi_L(t')\right)dt' \\ \|\chi_L(\phi(t) - \phi_L(t))\| &\leq t \sup_{t'\in[0,t]} \|[\chi_L, H]\phi(t') - [\chi_L, H_L]\phi_L(t')\|. \end{aligned}$$

Since $[\chi_L, H]\phi = 2\nabla\chi_L \cdot \nabla\phi + \Delta\chi_L\phi$ is zero for $|x|_\infty < L/4$, by Lemma 9.1 we have

$$\begin{aligned} \|[\chi_L, H]\phi(t')\| &\lesssim \frac{1}{L}\|(1 + |x|)[\chi_L, H]\phi(t')\| \\ &\lesssim \frac{1}{L}\left(\|x \otimes \nabla\phi(t')\| + \|\nabla\phi(t')\| + \|(1 + |x|)\phi(t')\|\right) \\ &\lesssim \frac{1 + |t|^4}{L} \end{aligned}$$

and similarly with $[\chi_L, H_L]\phi_L(t')$. The result follows. □

8. Appendix: trace theory in Sobolev spaces

We will need the following lemma on the regularity of traces on surfaces with respect to variations of the surface.

Lemma 8.1. *Let $\chi : \mathbb{R} \to \mathbb{R}$ be a smooth function with support $[R_1, R_2]$, with $R_1 > 0$, and s_1, s_2, s nonnegative real numbers such that $s_1 + s_2 = s$. Then for all $u \in H^s(\mathbb{R}^d)$, the function*

$$r \mapsto (\hat{x} \mapsto \chi(r)u(r\hat{x}))$$

is in $H^{s_1}(\mathbb{R}, H^{s_2}(S^{d-1}))$.

Proof. We first treat the case of the restriction to a hyperplane: if $u \in H^s(\mathbb{R}^d)$, then

$$v_u : x_1 \mapsto (x' \mapsto u(x_1, x'))$$

is in $H^{s_1}(\mathbb{R}, H^{s_2}(\mathbb{R}^{d-1}))$. Indeed, denoting for clarity by $\mathcal{F}_1$ the one-dimensional Fourier transform, we have by the Parseval formula on $L^2(\mathbb{R}^{d-1})$ that for all $q_1 \in \mathbb{R}$,

$$\|\mathcal{F}_1 v_u(q_1)\|^2_{H^{s_2}(\mathbb{R}^{d-1})} = \frac{1}{(2\pi)^{d-1}} \int_{\mathbb{R}^{d-1}} \langle q' \rangle^{2s_2} |\mathcal{F}u(q_1, q')|^2 \mathrm{d}q'$$

and therefore

$$\|v_u\|^2_{H^{s_1}(\mathbb{R}, H^{s_2}(\mathbb{R}^{d-1}))} = \frac{1}{2\pi} \int_{\mathbb{R}} \langle q_1 \rangle^{2s_1} \|\mathcal{F}_1 v_u(q_1)\|^2_{H^{s_2}(\mathbb{R}^{d-1})} \mathrm{d}q_1 \leq \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \langle q \rangle^{2s} |\mathcal{F}u(q)|^2 \mathrm{d}q = \|u\|^2_{H^s(\mathbb{R}^d)}.$$

To lift this property to the sphere $S^{d-1}(R)$ of radius R, we use a classical "flattening" argument. Using spherical coordinates, we can construct a cover of the annulus of inner radius R_1 and outer radius R_2 by open sets $\{X_i\}_{i=1,\dots,N}$ not touching zero with the property that, for every $i \in \{1, \dots, N\}$, there is a smooth diffeomorphism Φ_i from a an open set $\mathcal{R}_i \times \mathcal{T}_i \subset \mathbb{R} \times \mathbb{R}^{d-1}$ to X_i such that, for all $(r, \theta) \in \mathcal{R}_i \times \mathcal{T}_i$,

$$\Phi_i(r, \theta) = r\, \Theta_i(\theta)$$

with Θ_i having values on the sphere S^{d-1}. One can then construct a partition of the unity $\zeta_i : \mathbb{R}^d \to \mathbb{R}$ where, for each $i \in \{1, \dots, N\}$, ζ_i is supported inside X_i, and $\sum_{i=1}^N \zeta_i = 1$ on the annulus. Then, for all $u \in H^s(\mathbb{R}^d)$, $|x| \in [R_1, R_2]$,

$$\chi(|x|)u(x) = \sum_{i=1}^N \chi(|x|)\, \zeta_i(x)\, u(x) = \sum_{i,\, x \in X_i} w_i(\Phi_i^{-1}(x))$$

where

$$w_i(r, \theta) = \chi(r)\, \zeta_i(r\Theta_i(\theta))\, u(r\Theta_i(\theta)),$$

defined on $\mathcal{R}_i \times \mathcal{T}_i$, extends on the whole $\mathbb{R}^d$ to a $H^s(\mathbb{R}^d)$ function. It follows from the hyperplane case that

$$\chi(r)u(r\hat{x}) = \sum_{i,\, x \in X_i} w_i\left(r, \Theta_i^{-1}(\hat{x})\right)$$

is in $H^{s_1}(\mathbb{R}, H^{s_2}(S^{d-1}))$. □

Note that from the fact that $H^{\frac{1}{2}+\varepsilon}(\mathbb{R})$, $\varepsilon > 0$, functions are continuous, we recover the classical trace theorem that traces of $H^{s+\frac{1}{2}+\varepsilon}(\mathbb{R}^d)$ functions are H^s on surfaces.

The proof of the limiting absorption principle for the nonzero potential case requires the following Hardy-type inequality.

Lemma 8.2. *Let $s > 0$, and $u \in H^s(\mathbb{R}^d)$ such that u is zero on the sphere of radius a (in the sense of traces). Then the function $v(x) = \frac{u(x)}{|x|^2 - a^2}$ is $H^{s-1}(\mathbb{R}^d)$.*

Proof. Using as before a smooth cutoff function and a partition of unity of a neighborhood of the sphere of radius a, it is enough to show that for $u \in H^s(\mathbb{R}^d)$ with $u(0, x') = 0$ for all $x' \in \mathbb{R}^{d-1}$, then $v(x) = \frac{u(x)}{x_1}$ is $H^{s-1}(\mathbb{R}^{d-1})$.

Proceeding by density, we can assume that $\mathcal{F}u \in C_c^\infty(\mathbb{R}^d)$.

Using the fact that $\int \mathcal{F}u(q_1, q')\mathrm{d}q_1 = 0$ for all $q' \in \mathbb{R}^{d-1}$, we have that $\mathcal{F}v \in C_c^\infty(\mathbb{R}^d)$, and $\mathcal{F}u(q) = -i\frac{\partial \mathcal{F}v}{\partial q_1}(q)$. By integration by parts and the Cauchy-Schwarz inequality, we have the following Hardy inequality, for $q = (q_1, q')$ and $\alpha \in \mathbb{R}$:

$$\int_{\mathbb{R}} |\mathcal{F}v(q)|^2 \langle q_1 \rangle^{2(\alpha-1)}\, \mathrm{d}q_1 \lesssim \int_{\mathbb{R}} |\mathcal{F}v(q)||\mathcal{F}u(q)| \langle q_1 \rangle^{(\alpha-1)+\alpha}\, \mathrm{d}q_1 \lesssim \int_{\mathbb{R}} |\mathcal{F}u(q)|^2 \langle q_1 \rangle^{2\alpha}\, \mathrm{d}q_1.$$

In the case $s \geq 1$, we have $\langle q \rangle^{2(s-1)} \lesssim \langle q_1 \rangle^{2(s-1)} + \langle q' \rangle^{2(s-1)}$ and so

$$\|v\|^2_{H^{s-1}} \lesssim \int_{\mathbb{R}^{d-1}} \int_{\mathbb{R}} |\mathcal{F}v(q)|^2 \left(\langle q_1 \rangle^{2(s-1)} + \langle q' \rangle^{2(s-1)} \right) \mathrm{d}q_1 \mathrm{d}q'.$$

By using the Hardy inequality with $\alpha = s$ for the first term and $\alpha = 1$ for the second, we get

$$\begin{aligned}\|v\|_{H^{s-1}}^2 &\lesssim \int_{\mathbb{R}^d} |\mathcal{F}u(q)|^2 \langle q_1\rangle^{2s}\,\mathrm{d}q + \int_{\mathbb{R}^d} |\mathcal{F}u(q)|^2 \langle q_1\rangle^2 \langle q'\rangle^{2(s-1)}\,\mathrm{d}q \\ &\lesssim \int_{\mathbb{R}^d} |\mathcal{F}u(q)|^2 \langle q\rangle^{2s}\,\mathrm{d}q \lesssim \|u\|_{H^s}^2.\end{aligned}$$

In the case $0 < s < 1$, we have $\langle q\rangle^{2(s-1)} \leq \langle q_1\rangle^{2(s-1)}$ and we can repeat the above argument. □

9. Appendix: locality estimates on resolvents and propagators

We prove in this appendix results on the locality of the resolvents and propagators of Schrödinger operators. This appendix is independent from the rest of the paper.

Lemma 9.1 (Properties of the propagator)**.** *Let $W : \mathbb{R}\times\mathbb{R}^d \to \mathbb{R}$ be a measurable real-valued potential such that, for all $t \in \mathbb{R}$, $W(t,\cdot)$ is C^∞ and, for all multi-indices α with $|\alpha| \geq 2$, the function*

$$M_\alpha(t) = \sup_{x\in\mathbb{R}^d} |W^{(\alpha)}(t,x)| + \sup_{|x|\leq 1} |W(t,x)|$$

is bounded on compact intervals.

Then there exists a unitary propagator $U(t,s)$ such that if $\psi_s \in \mathcal{S}(\mathbb{R}^d)$, $U(t,s)\psi_s \in \mathcal{S}(\mathbb{R}^d)$ satisfies the Schrödinger equation

$$i\partial_t U(t,s)\psi_s = (-\Delta + W(t))U(t,s)\psi_s.$$

Furthermore, there is $C_0 > 0$ not depending on W such that, for all $t, s \in \mathbb{R}, \psi_s \in L^2(\mathbb{R}^d)$,

$$\|xU(t,s)\psi_s\| + \|\nabla U(t,s)\psi_s\| \leq C_1(t,s)\left(\|x\psi_s\| + \|\nabla\psi_s\| + \|\psi_s\|\right) \tag{22}$$

$$\||x|^2U(t,s)\psi_s\| + \|\Delta U(t,s)\psi_s\| \leq C_2(t,s)\left(\||x|^2\psi_s\| + \|\Delta\psi_s\| + \|x\otimes\nabla\psi_s\| + \|\psi_s\|\right) \tag{23}$$

where

$$C_1(t,s) = C_0(1+|t-s|)^2\left(1 + \sup_{t'\in[t,s]} |\nabla W(t')|\right)$$

$$C_2(t,s) = C_0(1+|t-s|)^4\left(1 + \sup_{t'\in[t,s]} |\nabla W(t')|^2 + \sup_{t'\in[t,s]} |\nabla^2 W(t')|\right)$$

Note that these estimates are natural in the case $W = 0$. In this case, $(\mathcal{F}\psi)(t,q) = (\mathcal{F}\psi)(s,q)e^{-i(t-s)|q|^2}$, and so $\partial_q(\mathcal{F}\psi)(t,q) = \partial_q(\mathcal{F}\psi)(s,q)e^{-i|q|^2(t-s)} - 2iq(t-s)(\mathcal{F}\psi)(s,q)e^{-i|q|^2(t-s)}$, which is in $L^2(\mathbb{R}^d)$ if $\psi_s \in L^2(\langle x\rangle)\cap H^1(\mathbb{R}^d)$.

Proof. The existence of the propagator is obtained using the results of [19], and our hypotheses are the same as in that paper.

We will obtain these inequalities by the following standard commutator method. Let A be an operator, and $\psi_s \in L^2(\mathbb{R}^d)$. Then, if $\psi(t) = U(t,s)\psi_s$, we have

$$i\partial_t(A\psi)(t') = AH(t')\psi(t') = H(t')A\psi(t') + [A, H(t')]\psi(t')$$

and therefore by Duhamel's formula,

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

We compute the following commutators

$$[\nabla, H(t)] = \nabla W(t)$$
$$[x, H(t)] = 2\nabla$$

Since ∇W is a bounded operator, we obtain

$$\|\nabla U(t,s)\psi_s\| \leq \|\nabla\psi_s\| + |t-s|\sup_{t'\in[s,t]} |\nabla W(t')|\|\psi_s\|$$

$$\begin{aligned}\|xU(t,s)\psi_s\| &\leq \|x\psi_s\| + 2|t-s|\sup_{t'\in[s,t]} \|\nabla U(t',s)\psi_s\| \\ &\leq \|x\psi_s\| + 2|t-s|\left(\|\nabla\psi_s\| + |t-s|\sup_{t'\in[s,t]} |\nabla W(t')|\|\psi_s\|\right)\end{aligned}$$

and (22) follows. Similarly, from the commutators

$$[\nabla^2, H(t)] = \nabla^2 W + 2(\nabla W(t)) \otimes \nabla$$
$$[x \otimes \nabla, H(t)] = -2\nabla^2 + x \otimes \nabla W(t)$$
$$[x \otimes x, H(t)] = 2x \otimes \nabla + 2I$$

we obtain (23). □

Lemma 9.2 (Properties of the resolvent)**.** *Let $W : \mathbb{R}^d \to \mathbb{R}$ be a bounded function, and $R(z) = (z - (-\Delta + W))^{-1}$. Then there are $c > 0, C > 0$ such that, for all $z \notin \sigma(H)$,*

$$\|R(z)\|_{L^2(\mathbb{R}^d)\to H^2(\mathbb{R}^d)} \leq C(1+|z|)\left(1 + \frac{1}{d(z,\sigma(H))}\right)$$
$$\|R(z)\|_{L^2(e^{\alpha\langle x\rangle})\to H^2(e^{\alpha\langle x\rangle})} \leq C(1+|z|)\left(1 + \frac{1}{d(z,\sigma(H))}\right) \quad \forall \alpha \leq \alpha_z := cd(z,\sigma(H))$$

Proof. The first inequality is classical (see for instance [25] Lemma 3.6).

The second is a (non-sharp) Combes-Thomas estimate, which we prove for completeness here. Denote by

$$H_\alpha := e^{\alpha\langle x\rangle}(-\Delta + W)e^{-\alpha\langle x\rangle} = (-\Delta + W) + \underbrace{-2\alpha\nabla\langle x\rangle \cdot \nabla + \alpha^2\Delta(\langle x\rangle)}_{\alpha B_\alpha}. \tag{24}$$

Let $R(z) = (z - (-\Delta + W))^{-1}$. We have that

$$B_\alpha R(z) = (-2\nabla\langle x\rangle \cdot \nabla + \alpha\Delta(\langle x\rangle))(1-\Delta)^{-1}(1-\Delta)R(z)$$

is bounded as an operator on $L^2(\mathbb{R}^d)$ by $C/d(z,\sigma(H))$, for all $\alpha \leq 1$, for some $C > 0$. It follows that, for $\alpha \leq d(z,\sigma(H))/(2C)$

$$(z - H_\alpha)^{-1} = R(z)(1 + \alpha B_\alpha R(z))^{-1}$$

is bounded from $L^2(\mathbb{R}^d)$ to $H^2(\mathbb{R}^d)$ with norm smaller than $\frac{C'}{d(z,\sigma(H))}$ for some $C' > 0$. Then, for all $\psi \in L^2(e^{\alpha\langle x\rangle})$,

$$\|R(z)\psi\|_{H^2(e^{\alpha\langle x\rangle})} = \|(z - H_\alpha)^{-1}e^{\alpha\langle x\rangle}\psi\|_{H^2(\mathbb{R}^d)} \leq \frac{C'}{d(z,\sigma(H))}\|\psi\|_{L^2(e^{\alpha\langle x\rangle})}$$

□

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