Finite-size effects in response functions of molecular systems

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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 space domain. This is necessarily a singular approximation because of the discreteness of the spectrum of the truncated Hamiltonian, and in practice a suitable regularization 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.

Keywords: linear response, limiting absorption principle, finite-size effects.

1 Setting and assumptions

The dynamics of N electrons in a molecule, formally modeled by the many-body Schrödinger equation, can be approximated by time-dependent density functional theory, which results in a coupled set of 3-dimensional nonlinear partial differential equations for a set of L^2-orthogonal functions $(\psi_1, \dots, \psi_N)$. In the regime of weak external fields, a linear response approximation yields response functions that describe the reaction of the electrons to an applied field at a particular frequency ω.

In this study, we simplify the problem by considering a single electron. The evolution of $\psi \in L^\infty_t(\mathbb{R}, L^2(\mathbb{R}^d))$ $(d = 1, 2, 3)$ is then given by the time-dependent Schrödinger equation

$$\left\{ \begin{array}{l} i\partial_t \psi = (-\Delta + V)\psi + \varepsilon f(t) V_{\mathcal{P}} \psi, \\ \psi(0) = \psi_0. \end{array} \right. \tag{1}$$

ψ_0 is the ground-state of $H = -\Delta + V$ where V is a multiplicative potential.

$V_{\mathcal{P}}$ is a perturbation potential, typically an electric field in a direction $e \in \mathbb{R}^d$ $V_{\mathcal{P}}(x) = x \cdot e$. The function $f \in L^\infty(\mathbb{R})$ is bounded. All the results in this work are established under the following assumptions

1. the ground-state ψ_0 is nondegenerate;
2. V is smooth and bounded ;
3. V decays as $1/|x|^{2+\varepsilon}$, $\varepsilon > 0$;
4. the observable $V_{\mathcal{O}}$ and the perturbation $V_{\mathcal{P}}$ are smooth and their derivatives are bounded.

2 Linear response theory

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

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

Under the above assumptions, the response function K is defined by the Kubo formula

$$K(\tau) = -i\theta(\tau) \big\langle V_{\mathcal{O}} \psi_0, e^{-i(H-E_0)\tau} V_{\mathcal{P}} \psi_0 \big\rangle + \text{c.c.}, \tag{3}$$

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 response function has a Fourier transform at least defined in distribution

$$\begin{aligned} \widehat{K}(\omega) = \lim_{\eta \to 0^+} \big\langle V_{\mathcal{O}} \psi_0, (\omega + i\eta - (H - E_0))^{-1} V_{\mathcal{P}} \psi_0 \big\rangle \\ - \big\langle V_{\mathcal{P}} \psi_0, (\omega + i\eta + (H - E_0))^{-1} V_{\mathcal{O}} \psi_0 \big\rangle. \end{aligned} \tag{4}$$

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 can study the boundary value of the resolvent $(z - H)^{-1}$ as the divergence merely indicates a loss of locality of the associated Green's function. This is known as a limiting absorption principle [1] which has a long history in mathematical physics.

Under our assumptions, it is standard to show that $\widehat{K}$ is a continuously differentiable function for $|\omega| > -E_0$ so

$$|\widehat{K}(\omega + i\eta) - \widehat{K}(\omega)| \leq C\eta. \tag{5}$$

3 Space truncation and main result

We now truncate our problem (4) by diagonalizing the operator $-\Delta + V$ 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 which is a singular approximation of K as the spectrum of the operator H_L is only discrete.

Theorem 1 ([2]) *K_L converges towards K in the sense of tempered distributions. Furthermore, for all $\omega \in \mathbb{R}$ there is $\alpha > 0$ such that for all $0 < \eta < 1$, $L > 0$,*

$$|\widehat{K}_L(\omega + i\eta) - \widehat{K}(\omega)| \lesssim \frac{e^{-\alpha\eta L}}{\eta^2} + \eta. \tag{6}$$

There is a balance of error to set between the size of the domain L and the regularization η as can be seen in Figure 1 and Figure 2.

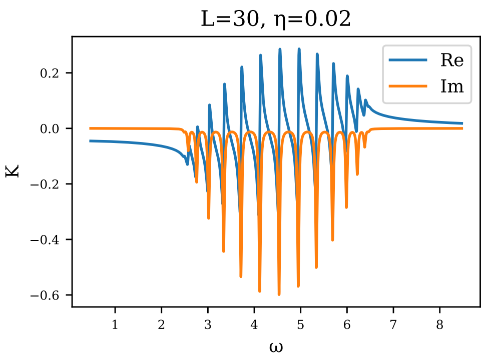

Figure 1: $\eta \ll \frac{1}{L}$

The proof of Theorem 1 relies on a limiting absorption principle that is derived along the lines of the seminal paper by Agmon [1], and on Combes-Thomas estimates to relate the resolvent of the full operator $(z - H)^{-1}$ and of the truncated one $(z - H_L)^{-1}$. We also use the fact that the ground-state is exponentially localized to be able to handle possibly unbounded perturbations and observables.

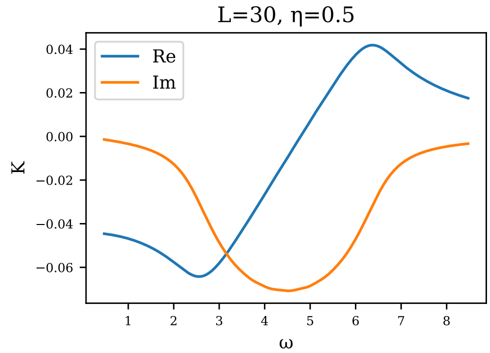

Figure 2: $\eta \gg \frac{1}{L}$

4 Conclusion and perspectives

In this work, we have established the convergence rate of the truncated linear response function $\widehat{K}_L$ and the exact one. The homogeneous Dirichlet boundary condition is a simple but crude approximation which can be improved by imposing frequency dependent boundary conditions (absorbing boundary conditions, perfectly matching layers) that better reproduce the continuous spectrum. Another limitation of our work is the linearity of the model that does not reflect what is used in practice. We would need to prove a limiting absorption principle in that case.

References

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