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A mathematical analysis of the adiabatic Dyson equation from time-dependent density functional theory

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Abstract

In this article, we analyse the Dyson equation for the density–density response function (DDRF) that plays a central role in linear response time-dependent density functional theory (LR-TDDFT). First, we present a functional analytic setting that allows for a unified treatment of the Dyson equation with general adiabatic approximations for discrete (finite and infinite) and continuum systems. In this setting, we derive a representation formula for the solution of the Dyson equation in terms of an operator version of the Casida matrix. While the Casida matrix is well-known in the physics literature, its general formulation as an (unbounded) operator in the N-body wavefunction space appears to be new. Moreover, we derive several consequences of the solution formula obtained here; in particular, we discuss the stability of the solution and characterise the maximal meromorphic extension of its Fourier transform. We then show that for adiabatic approximations satisfying a suitable compactness condition, the maximal domains of meromorphic continuation of the initial DDRF and the solution of the Dyson equation are the same. The results derived here apply to widely used adiabatic approximations such as (but not limited to) the random phase approximation and the adiabatic local density approximation. In particular, these results show that neither of these approximations can shift the ionisation threshold of the Kohn–Sham system.

Keywords: time-dependent density functional theory, Dyson equation, adiabatic approximation, density–density response function

Contents

1. Introduction

Time-dependent density functional theory (TDDFT) is a formally exact theory to study the time evolution of a system of electrons; it has many applications in quantum chemistry, condensed-matter physics, and material science [7, 12, 36, 37]. Most of these applications lie within the perturbative regime, where linear response theory applies (LR-TDDFT). In this regime, one is no longer interested in the whole nonlinear evolution of the single-particle density of the system but instead in the linear dynamical response of the density to a variation of the external potential. Stated differently, one is interested in the *density–density response function* (DDRF) of the system.

The fundamental equation of LR-TDDFT is the celebrated Dyson equation that formally connects the DDRF of a given system of interest to the DDRF of an equivalent system of non-interacting electrons, the Kohn–Sham system. The equivalence is in the sense that both systems have the same ground state density. In shorthand notation, the Dyson equation reads[2]

$$\chi(t) = \chi_0(t) + \int_0^t \chi_0(t-s) \int_0^s F_{\mathrm{Hxc}}(s-\tau)\chi(\tau)\,\mathrm{d}\tau,$$

where χ is the DDRF of the system of interest, χ_0 is the DDRF of the Kohn–Sham system of non-interacting electrons, and F_{Hxc} is the linear operator whose Schwartz kernel is the Hartree plus exchange–correlation (Hxc-)kernel of TDDFT. In principle, the *Hxc-operator* depends on the ground state density of the system or, equivalently, on the Kohn–Sham ground state density. In practice, this density dependence is highly non-trivial, and the exact Hxc-operator is unknown; one then relies on approximations of this operator.

While several classes of approximations for the Hxc-operator were suggested in the physics literature (see [22, 36] for an overview), the overwhelming majority of calculations are performed with *adiabatic approximations*. In the adiabatic approximation, the Hxc-operator acts instantaneously and can be formally represented as

$$F_{\mathrm{Hxc}}^{\mathrm{adiabatic}}(t) = \delta_0(t)F,$$

where δ_0 is a Dirac delta distribution at $t = 0$ and F is a linear operator acting from the (tangent) space of densities to the (tangent) space of spatial potentials. Within the adiabatic approximation, the Dyson equation becomes

$$\chi_F(t) = \chi_0(t) + \int_0^t \chi_0(t-s)F\chi_F(s)\,\mathrm{d}s, \tag{1.1}$$

where χ_0 is again the DDRF of the non-interacting Kohn–Sham system, and χ_F is now an approximation of the true DDRF of the system of interest. For suitable choices of F, such approximations are observed to reproduce many response properties of large quantum systems accurately (see, e.g. [37]).

In the non-perturbative regime, TDDFT models were considered in various settings (see, e.g. [9, 10, 14, 19, 27, 34]). By contrast, the mathematical literature on the linear response regime is scarce. Some works [4–6, 32] have focused on the numerical aspects of extracting relevant properties (e.g. excitation energies, oscillator strengths, and absorption spectrum cross-section) of the solution χ_F in the finite-dimensional case, i.e. by properly discretising the underlying function space. Moreover, a first step towards a rigorous understanding of the Dyson equation (1.1) in the infinite-dimensional (continuum) setting has been taken recently by the author and collaborators in [15]. There, we presented a mathematical framework for studying the Dyson equation within the random phase approximation (RPA), thereby rigorously proving that the RPA excitation frequencies are always larger than the Kohn–Sham excitations. Unfortunately, the approach presented in [15] heavily relies on the positivity of the adiabatic approximation F, which is only applicable to the RPA with Coulomb potential (or positive definite interaction potentials).

[2] For a formal derivation of the Dyson equation, we refer to [15, appendix].

In the current paper, we not only extend the framework presented in [15] to deal with more general adiabatic approximations but also derive an explicit solution formula for χ_F. More precisely, the main contributions of this article can be summarised as follows:

(1) We generalise the functional analytic setting presented in [15] to allow for a unified treatment of the Dyson equation with general adiabatic approximations for both discrete (finite and infinite) and continuum systems. Notably, this new setting allows us to study the celebrated adiabatic local density approximation (ALDA).
(2) We derive an explicit representation formula for the solution χ_F in the case where χ_0 is the DDRF of a self-adjoint Hamiltonian. For this, the key result is a representation formula for the Fourier transform $\widehat{\chi_F}$ in terms of an operator version of the Casida matrix.
(3) We derive and discuss several consequences of this representation formula. In particular, we characterise the maximal meromorphic extension[3] of $\widehat{\chi_F}$ and show that, for widely used adiabatic approximations such as the RPA and ALDA, the maximal domain of meromorphic continuation of $\widehat{\chi_F}$ and $\widehat{\chi_0}$ are the same. Physically, this means that these approximations are not able to shift the ionisation threshold of the Kohn–Sham system.

Remark (response theory terminology). In the physics literature, the name DDRF usually refers to the Schwartz kernel of $\chi(t)$. Here we refer instead to the operator-valued function $t \mapsto \chi(t)$ as the DDRF. We also remark that χ is sometimes called the (linear) susceptibility [7] or the reducible (or irreducible in the case of χ_0) polarisability operator [21].

2. Main results

We now introduce some notation and discuss our main results. Throughout this article, H is a self-adjoint operator acting on the anti-symmetric N-fold tensor product of $L^2(\Omega, \mathrm{d}\mu)$,

$$\mathcal{H}_N := \bigwedge_{j=1}^{N} L^2(\Omega, \mathrm{d}\mu), \tag{2.1}$$

where (Ω, μ) is a σ-finite measure space and $L^2(\Omega, \mathrm{d}\mu)$ denotes the space of (equivalent classes of) $\mathbb{C}$-valued measurable functions that are square integrable with respect to μ. The specific measure space is not relevant to our results; in particular, μ can be the counting measure on some countable set $\Omega \subset \mathbb{R}^n$ (discrete systems), the Lebesgue measure on some open set $\Omega \subset \mathbb{R}^n$ (continuum systems), or a combination of both (continuum systems with internal spin). Moreover, we assume the following.

Assumption 1. The self-adjoint operator $H : D(H) \subset \mathcal{H}_N \to \mathcal{H}_N$ satisfies the following:

(i) (Spectral gap) The ground state energy $\mathcal{E}_0 := \inf \sigma(H) > -\infty$ is a simple isolated eigenvalue.
(ii) (Real Hamiltonian) H commutes with complex conjugation.

Remark (complex Hamiltonians). The assumption that H is a real Hamiltonian is not explicitly used in any part of the paper and the proofs do not depend on it. The reason for including

[3] Here we consider meromorphic extensions with respect to the operator norm topology (see definition 2.10) and not on weaker topologies, which is typically the case when studying resonances [17].

this assumption here is that the formula for the DDRF of real Hamiltonians simplifies to equation (2.7) below (see [15, proposition 2.3]).

Since the ground state of H is non-degenerate, we can unambiguously define its ground state single-particle density (or simply density) as

$$\rho_0(r) := N\int_{\Omega^{N-1}} |\Psi_0(r, r_2, \ldots, r_N)|^2 \mathrm{d}\mu(r_2)\ldots\mathrm{d}\mu(r_N), \tag{2.2}$$

where Ψ_0 is the unique (up to phase) normalised ground state wave function of H. We then introduce the norms

$$\|f\|_{\rho_0} = \left(\int_\Omega |f(r)|^2 \rho_0(r)\,\mathrm{d}\mu(r)\right)^{\frac{1}{2}} \quad \text{and} \quad \|f\|_{\frac{1}{\rho_0}} = \left(\int_\Omega |f(r)|^2 \rho_0(r)^{-1}\,\mathrm{d}\mu(r)\right)^{\frac{1}{2}}, \tag{2.3}$$

and define the respective weighted L^2 spaces as

$$L^2_{\rho_0} = \{f : \mathrm{supp}(\rho_0) \to \mathbb{C}\,\mu\text{-measurable} : \|f\|_{\rho_0} < \infty\}, \tag{2.4}$$

$$L^2_{\frac{1}{\rho_0}} = \left\{f : \mathrm{supp}(\rho_0) \to \mathbb{C}\,\mu\text{-measurable} : \|f\|_{\frac{1}{\rho_0}} < \infty\right\}, \tag{2.5}$$

where $\mathrm{supp}(\rho_0)$ denotes the support of ρ_0. As usual, we identify the functions that coincide μ-almost everywhere. Let us also introduce the reduced Hamiltonian

$$H_\# := P_{\Psi_0^\perp}(H - \mathcal{E}_0)P_{\Psi_0^\perp}, \tag{2.6}$$

where $P_{\Psi_0^\perp}$ is the orthogonal projection on $\{\Psi_0\}^\perp$. Note that $H_\#$ is a positive operator acting on $\{\Psi_0\}^\perp$ with domain $D(H_\#) = D(H) \cap \{\Psi_0\}^\perp$.

2.1. The DDRF

The DDRF of H is the operator-valued function

$$t \in \mathbb{R} \mapsto \chi_H(t) = -2\theta(t)B\sin(tH_\#)B^*, \tag{2.7}$$

where $\theta(t)$ is the Heaviside step function, $\mathcal{E}_0$ is the ground state energy of H, and the operator $B = B_{\Psi_0} : \mathcal{H}_N \to L^2_{\frac{1}{\rho_0}}$ [4] and its adjoint $B^* = B^*_{\Psi_0} : L^2_{\rho_0} \to \mathcal{H}_N$ are defined as follows:

$$(B\Phi)(r) = N\int_{\Omega^{N-1}} \overline{\Psi_0(r, r_2, \ldots, r_N)}\Phi(r, r_2, \ldots, r_N)\,\mathrm{d}\mu(r_2)\ldots\mathrm{d}\mu(r_N) - \langle\Psi_0, \Phi\rangle_{\mathcal{H}_N}\rho_0(r), \tag{2.8}$$

$$(B^*f)(r_1, \ldots, r_N) = \left(\sum_{j=1}^N f(r_j) - \langle\rho_0, f\rangle_{L^2(\Omega, d\mu)}\right)\Psi_0(r_1, \ldots, r_N). \tag{2.9}$$

[4] Here we use the operator B introduced in [8] instead of the operator $S\Phi(r) = N\int_{\Omega^{N-1}} \overline{\Psi_0}(r, \ldots)\Phi(r, \ldots)$ introduced in [15]. This choice conveniently reduces the notation because $B = SP_{\Psi_0^\perp}$ and we mostly work in the space $\{\Psi_0\}^\perp$. Note that B is the linearised version (derivative at Ψ_0) of the map sending a N-body wavefunctions to its density (see equation (2.2)).

The motivation for this definition comes from the fact that χ_H is related to the density response of the system to a perturbation of the external potential. More precisely, if we consider the solution of the Schrödinger equation

$$\begin{cases} i\partial\Psi_\epsilon(t) = H\Psi_\epsilon(t) + \epsilon V(t)\Psi_\epsilon(t), & t > 0, \\ \Psi_\epsilon(0) = \Psi_0, \end{cases}$$

where Ψ_0 is the ground state of H and $V(t)$ is the multiplication operator

$$\Psi \in \mathcal{H}_N \mapsto (V(t)\Psi)(r_1,\ldots,r_N) = \sum_{j=1}^{N} v(t,r_j)\Psi(r_1,\ldots,r_N), \quad t \in \mathbb{R}_+, (r_1,\ldots,r_N) \in \Omega^N,$$

for some real-valued potential $v : \mathbb{R}_+ \times \Omega \to \mathbb{R}$, then the associated density $\rho_{\Psi_\epsilon(t)}$ satisfies[5]

$$\rho_{\Psi_\epsilon(t)} = \rho_0 + \epsilon\int_0^t \chi_H(t-s)\, v(s)\,\mathrm{d}s + \mathcal{O}\left(\epsilon^2\right).$$

This formula establishes the connection between χ_H and the linear response of the system.

In the sequel, we focus on describing the main properties of χ_H and present a characterisation of the maximal meromorphic extension of its Fourier transform. Let us start by recalling some results from [15]. In [15], it is shown that the DDRF of typical Schrödinger operators on $\mathbb{R}^{3N}$ is a uniformly bounded and strongly continuous function with values in the set of bounded operators between suitable L^p spaces. By adapting the proof in [15, section 2] to the current setting, we can show that χ_H is, in fact, uniformly bounded and strongly continuous on the space of bounded linear operators from $L^2_{\rho_0}$ to $L^2_{\frac{1}{\rho_0}}$, denoted here by $\mathcal{B}(L^2_{\rho_0}, L^2_{\frac{1}{\rho_0}})$. Consequently, the Fourier transform of χ_H, given by

$$\widehat{\chi_H}(\omega) = \lim_{\eta\to 0^+}\int_{\mathbb{R}} \chi_H(t)\, e^{i\omega t} e^{-\eta t}\mathrm{d}t = \lim_{\eta\to 0^+} B\frac{2H_\#}{(\omega + i\eta)^2 - H_\#^2}B^*, \tag{2.10}$$

where the limit is taken in the distributional sense, is a tempered distribution with values on $\mathcal{B}(L^2_{\rho_0}, L^2_{\frac{1}{\rho_0}})$. (See, e.g. [15, proposition 2.8] for a derivation of (2.10).) In particular, $\widehat{\chi_H}$ has an analytic extension to the upper half-plane. With some abuse of notation, we denote this extension also by $\widehat{\chi_H}$.

An immediate consequence of the spectral gap assumption on H is that $\widehat{\chi_H}$ can be analytically extended to the larger set $\mathbb{C}\setminus\big(\sigma(H_\#)\cup\sigma(-H_\#)\big)$. In fact, it is shown in [15] that $\widehat{\chi_H}$ can be meromorphically extended to the domain

$$\mathcal{D}_\Gamma := \{z \in \mathbb{C} : |\mathrm{Re}(z)| < \Gamma \quad \text{or} \quad \mathrm{Im}(z) \neq 0\}, \tag{2.11}$$

where $\Gamma := \inf\sigma^{\mathrm{ess}}(H_\#)$ is the *ionisation threshold* of H. However, this extension is not maximal in general. For instance, some cancellations can occur due to the product of the resolvent of $H_\#$ with the operators B and B^*. To precisely characterise the maximal meromorphic extension of $\widehat{\chi_H}$, let us define the *single-particle excitation spectrum* of H as

$$\sigma_1(H_\#) := \left\{\lambda \in \sigma(H_\#) : BP^{H_\#}(B_\epsilon(\lambda)) \neq 0, \quad \text{for any } \epsilon > 0\right\}, \tag{2.12}$$

[5] See, e.g. [15, section 2] for the details.

where $B_\epsilon(\lambda)\subset\mathbb{C}$ denotes the ball centred at λ with radius ϵ and $P^{H_\#}(U)$ denotes the spectral projection of $H_\#$ on some Borel subset $U\subset\mathbb{C}$. We also define the discrete and essential parts of $\sigma_1(H_\#)$ as

$$\sigma_1^{\mathrm{disc}}(H_\#) := \left\{\lambda\in\sigma_1(H_\#) : \lambda \text{ isolated and } \operatorname{rank}\ BP^{H_\#}(\{\lambda\})<\infty\right\},$$
$$\sigma_1^{\mathrm{ess}}(H_\#) := \sigma_1(H_\#)\setminus\sigma_1^{\mathrm{disc}}(H_\#).$$

The first result of this paper is then the following.

Theorem 2.1 (maximal meromorphic extension). *Let H be a Hamiltonian satisfying assumption 1. Then the maximal meromorphic (see definition 2.10) extension of the Fourier transform of χ_H is given by*

$$\begin{aligned}\widehat{\chi_H} :&\mathcal{D}\to\mathcal{B}\left(L^2_{\rho_0},L^2_{\frac{1}{\rho_0}}\right)\\ &z\mapsto\widehat{\chi_H}(z)=\sum_{\lambda\in\sigma_1^{\mathrm{disc}}(H_\#)}\frac{2\lambda}{z^2-\lambda^2}BP^{H_\#}(\{\lambda\})B^*+B\int_{\sigma_1^{\mathrm{ess}}(H_\#)}\frac{2\lambda}{z^2-\lambda^2}\mathrm{d}P^{H_\#}_\lambda B^*.\end{aligned}$$

where

$$\mathcal{D}:=\{z\in\mathbb{C}:\pm z\notin\sigma_1^{\mathrm{ess}}(H_\#)\}. \tag{2.13}$$

In particular, the set of poles of $\widehat{\chi_H}$ is given by $\sigma_1^{\mathrm{disc}}(H_\#)\cup\sigma_1^{\mathrm{disc}}(-H_\#)$. Moreover, these poles are all simple, and their rank is given by

$$\textit{rank}_\lambda(\widehat{\chi_H}) = \textit{rank}\ BP^{H_\#}(\{\lambda\}).$$

Remark (poles with infinite rank). In fact, any isolated point in $\sigma^{\mathrm{ess}}(H_\#)$ can also be seen as a pole of infinite rank of $\widehat{\chi_H}$. The reason for excluding such poles from the discrete spectrum is that compact perturbations of the operator $H_\#$ may turn these poles into an accumulation point of poles, thereby making these singularities no longer isolated.

Remark (single-particle excitations). The term single-particle excitation is inspired by the observation that, for one-body Hamiltonians

$$H=\sum_{j=1}^N 1\otimes\dots\overbrace{h}^{jth\text{ position}}\dots\otimes 1\quad\text{for a self-adjoint operator } h \text{ on } L^2(\Omega,d\mu), \tag{2.14}$$

the set $\sigma_1(H_\#)$ corresponds to a subset of the excitation spectrum of the single-particle operator h. More precisely, we have the relation[6]

$$\sigma_1(H_\#)\subset\{\lambda-\lambda_j\in\sigma(h)-\lambda_j:\lambda\geqslant\lambda_{N+1}\quad\text{and}\quad j\leqslant N\}, \tag{2.15}$$

where λ_j denotes the j^{th} lowest eigenvalue of h.

[6] For physically relevant operators h (e.g. Schrödinger operators) one expects that the product of two eigenfunctions of h do not vanish (by the unique continuation property), which implies equality in (2.15) instead of inclusion (see equation (B.2) in appendix B). However, under the sole condition that h is self-adjoint, one can artificially construct examples for which the product between distinct eigenfunctions of h vanishes almost everywhere, and therefore, only the strict inclusion in (2.15) holds.

Remark (dark excitations). The complementary spectrum $\sigma(H_\#)\setminus\sigma_1(H_\#)$ corresponds to the dark excitations of H, i.e. the part of the spectrum that cannot be obtained by shining light on the system and measuring the absorption cross-section. For instance, in the case of (non-interacting) Hamiltonians as in equation (2.14), the set of dark excitations contain all double (and higher order) excitations.

2.2. Well-posedness of the Dyson equation

Let us now turn to the solution of the adiabatic Dyson equation (1.1). The first step is to agree on the underlying solution space. In LR-TDDFT, the goal of the Dyson equation is to approximate the DDRF of a system of interacting electrons via the DDRF of the equivalent non-interacting Kohn–Sham system. The equivalence is in the sense that the Hamiltonians of both the interacting and non-interacting systems have the same ground state density ρ_0. In particular, the DDRF of both systems should lie on the space of strongly continuous maps from $\mathbb{R}_+$ to $\mathcal{B}(L^2_{\rho_0}, L^2_{\frac{1}{\rho_0}})$, denoted here by

$$C_s\left(\mathbb{R}_+;\mathcal{B}\left(L^2_{\rho_0}, L^2_{\frac{1}{\rho_0}}\right)\right).$$

Therefore, it seems natural to study the well-posedness of the Dyson equation within this space. This choice is not unique, and we shall further motivate it later. Nevertheless, the Dyson equation is well-posed in this space under a compatible boundedness assumption on the adiabatic approximation of the Hxc-operator.

Theorem 2.2 (well-posedness of the Dyson equation). *Let $F\in\mathcal{B}(L^2_{\frac{1}{\rho_0}}, L^2_{\rho_0})$ and $\chi_0\in C_s\big(\mathbb{R}_+;\mathcal{B}(L^2_{\rho_0}, L^2_{\frac{1}{\rho_0}})\big)$. Then, there exists a unique solution χ_F of the Dyson equation*

$$\chi_F(t)=\chi_0(t)+\int_0^t \chi_0(t-s)F\chi_F(s)\,\mathrm{d}s$$

in the space $C_s\big(\mathbb{R}_+;\mathcal{B}(L^2_{\rho_0}, L^2_{\frac{1}{\rho_0}})\big)$. Moreover, the solution map

$$\begin{aligned}\mathcal{S}_F: C_s\left(\mathbb{R}_+;\mathcal{B}\left(L^2_{\rho_0}, L^2_{\frac{1}{\rho_0}}\right)\right) &\to C_s\left(\mathbb{R}_+;\mathcal{B}\left(L^2_{\rho_0}, L^2_{\frac{1}{\rho_0}}\right)\right),\\ \chi_0 &\mapsto \chi_F\end{aligned}$$

is bijective.

The proof of theorem 2.2 is a standard application of Banach's fixed point theorem. For the details, we refer the reader to [15, section 3], where the same theorem in a different function space is proved. Although the proof is rather simple, we show that theorem 2.2 guarantees the well-posedness of the Dyson equation for widely used adiabatic approximations of the Hxc-operator under general conditions on the ground state density ρ_0. In addition, the bijectivity of the solution map implies that, for any $F\in\mathcal{B}(L^2_{\frac{1}{\rho_0}}, L^2_{\rho_0})$, the DDRF of a Hamiltonian with ground state density ρ_0 can be obtained by solving the Dyson equation for a unique reference χ_0. Of course, this does not guarantee that χ_0 is the DDRF of a non-interacting Hamiltonian, a common premise of LR-TDDFT.

2.3. The Dyson DDRF

Throughout this section, we assume that H is a Hamiltonian satisfying assumption 1 and let F be a linear operator in $\mathcal{B}(L^2_{\frac{1}{\rho_0}}, L^2_{\rho_0})$, where ρ_0 is the ground state density of H. Our goal is then to characterise the solution χ_F of the Dyson equation

$$\chi_F(t) = \chi_H(t) + \int_0^t \chi_H(t-s) F \chi_F(s)\,\mathrm{d}s,$$

where χ_H is the DDRF of H, and establish some of its fundamental properties. For this, the key ingredient is a representation formula for $\widehat{\chi_F}$ based on an operator version of the Casida matrix.

More precisely, let us formally define the *Casida* operator as

$$\mathcal{C} := H_{\#}^2 + 2H_{\#}^{\frac{1}{2}} B^* F B H_{\#}^{\frac{1}{2}}.$$

Then under the assumption that F is symmetric (which is satisfied for physically relevant adiabatic approximations), we can apply the KLMN theorem (see section 3) to properly define $\mathcal{C}$ as a semi-bounded self-adjoint operator on $\{\Psi_0\}^{\perp}$. Moreover, one can show (see lemma 4.3) that

$$H_{\#}^{\frac{1}{2}} \left(z^2 - \mathcal{C}\right)^{-1} H_{\#}^{\frac{1}{2}}, \quad \text{for } z^2 \notin \sigma(\mathcal{C}),$$

defines a bounded operator on $\{\Psi_0\}^{\perp}$. The key result of this paper is that the Fourier transform of χ_F is given by the conjugation of B with the operator above. Precisely, we have

Theorem 2.3 (solution in the frequency domain). *Let $F \in \mathcal{B}(L^2_{\frac{1}{\rho_0}}, L^2_{\rho_0})$ be symmetric, then the Fourier transform of $\widehat{\chi_F}$ is well-defined for $|\mathrm{Im}(z)| > \|B^*FB\|$ and satisfies*

$$\widehat{\chi_F}(z) = 2BH_{\#}^{\frac{1}{2}} \left(z^2 - \mathcal{C}\right)^{-1} H_{\#}^{\frac{1}{2}} B^*. \tag{2.16}$$

Remark (the Casida equations). For one-body Hamiltonians with purely discrete spectrum, the Casida operator can be written in the basis of products of occupied and virtual orbitals of the single-particle operator, which leads to the usual Casida equations appearing in the physics literature [11] (see appendix B for more details). The construction presented here, however, is completely general and does not require any spectral or structural assumptions on the operator H.

We can now derive several properties of the solution χ_F. For starters, we can take the inverse Fourier transform of equation (2.16) to obtain the following representation formula for χ_F in the time domain.

Corollary 2.4 (solution in the time domain). *The solution χ_F is given by the formula*

$$\chi_F(t) = -2\theta(t)\, tBH_{\#}^{\frac{1}{2}} f_t(\mathcal{C}) H_{\#}^{\frac{1}{2}} B^*, \tag{2.17}$$

where $f_t(\lambda) = \mathrm{sinc}(t\sqrt{\lambda})$ and $\mathrm{sinc}(s) = \sin(s)/s$ is the analytic sinc function.

Remark. As the sinc function has a power series with only quadratic terms, the function $\mathrm{sinc}(\sqrt{s})$ defines an entire function. Moreover, this function is bounded on any half-line $[\alpha,\infty)$. In particular, $\mathrm{sinc}(t\sqrt{\mathcal{C}})$ uniquely defines a bounded operator for any self-adjoint operator bounded from below. The fact that $H_{\#}^{\frac{1}{2}}\mathrm{sinc}(t\sqrt{\mathcal{C}})H_{\#}^{\frac{1}{2}}$ is also bounded in $\{\Psi_0\}^{\perp}$ will be shown in section 4.

The above representation formula highlights some important features of the solution χ_F. For instance, note that we can decompose

$$\sqrt{\mathcal{C}} = \sqrt{\mathcal{C}_+} + i\sqrt{\mathcal{C}_-}$$

where $\mathcal{C}_+$ and $\mathcal{C}_-$ are the non-negative self-adjoint operators corresponding respectively to the positive part (on $(0,\infty)$) and the non-positive part (on $(-\infty,0]$) of the spectrum of $\mathcal{C}$. As these are mutually orthogonal operators, we have the decomposition

$$\chi_F(t) = \underbrace{-2\theta(t)\,tBH_{\#}^{\frac{1}{2}}\mathrm{sinc}\left(t\sqrt{\mathcal{C}_+}\right)H_{\#}^{\frac{1}{2}}B^*}_{=:\chi_F^+(t)} + \underbrace{-2\theta(t)\,tBH_{\#}^{\frac{1}{2}}\mathrm{sinc}\left(it\sqrt{\mathcal{C}_-}\right)H_{\#}^{\frac{1}{2}}B^*}_{=:\chi_F^-(t)}.$$

Consequently, if $0\notin\sigma(\mathcal{C})$, then the positive part χ_F^+ is stable in the sense that it is uniformly bounded in time, as expected from a DDRF of an isolated quantum system. The negative part, on the other hand, grows exponentially fast with time. Nevertheless, note that, since the operator $\mathcal{C}$ is bounded from below, the exponential growth of χ_F^- is bounded by

$$\|\chi_F^-(t)\| \lesssim e^{t\sqrt{-\inf\sigma(\mathcal{C})}}.$$

When $0\in\sigma(\mathcal{C})$, the solution may contain a linearly growing part, corresponding to the spectral projection of $\mathcal{C}$ on 0. In particular, if we gradually increase the strength of the adiabatic approximation by setting $F(\epsilon)=\epsilon F$, the point ϵ_0 where the spectrum of the Casida operator reaches 0 corresponds to a phase transition of the system.

The next corollary shows that the stability condition $\mathcal{C}>\delta$ can be re-stated in terms of the simpler operator

$$\mathcal{M} := H_{\#} + 2B^*FB. \quad \text{(with domain } D(H_{\#})). \tag{2.18}$$

Corollary 2.5 (stability condition). *Let $\mathcal{M}$ be the operator defined in (2.18), then we have*

$$0\in\sigma(\mathcal{M}) \iff 0\in\sigma(\mathcal{C}) \quad \text{and} \quad \sigma(\mathcal{M})\cap(-\infty,0)\neq\emptyset \iff \sigma(\mathcal{C})\cap(-\infty,0)\neq\emptyset.$$

In particular, the solution χ_F is stable (in the sense described above) if and only if

$$\mathcal{M}\geqslant\delta \tag{2.19}$$

for some $\delta>0$. Moreover, χ_F is a tempered distribution and $\widehat{\chi_F}$ admits an analytic extension to the upper half-plane if and only if

$$\mathcal{M}\geqslant 0. \tag{2.20}$$

Since χ_F is supposed to approximate the DDRF of another Hamiltonian (which is causal and bounded), the stability condition is expected to hold for physically relevant F. For the RPA, condition (2.19) follows from the positivity of F^{RPA} (see equation (2.25)) and the fact that $\inf\sigma(H_{\#})>0$. For the ALDA, however, we are not aware of a general argument to prove that (2.19) or (2.20) holds.

Remark (quantitative stability). One can show the following quantitative version of corollary 2.5 (see the remark after the proof of corollary 2.5)

$$\mathcal{M} \geqslant \delta > 0 \quad \text{implies} \quad \mathcal{C} \geqslant \delta\omega_1, \text{and} \tag{2.21}$$

$$\mathcal{C} \geqslant \delta > 0 \quad \text{implies} \quad \mathcal{M} \geqslant \sqrt{\|B^*FB\|^2 + \delta} - \|B^*FB\|, \tag{2.22}$$

where $\omega_1 := \inf \sigma(H_\#) > 0$.

Remark (stability condition in the finite-dimensional case). A finite-dimensional analogue of $\mathcal{M}$, and the associated stability condition, also appear in previous works where linear-response eigenvalue problems in finite dimensions are considered [4–6, 23, 35]. More precisely, $\mathcal{M}$ is an operator version of the matrix $M = A + B$ defined in the basis of occupied and virtual orbital products in [6].

Theorem 2.3 also allows us to characterise the maximal meromorphic extension of $\widehat{\chi_F}$. This characterisation requires a spectral gap assumption on $\mathcal{C}$ and resembles the characterisation of $\widehat{\chi_H}$ given in theorem 2.1. To state it precisely, let us define the single-particle spectrum of $\mathcal{C}$ as

$$\sigma_1(\mathcal{C}) := \left\{ \lambda \in \mathbb{C} : BH_\#^{\frac{1}{2}} P^{\mathcal{C}}(B_\epsilon(\lambda)) \neq 0 \quad \text{for any } \epsilon > 0 \text{ small} \right\},$$

where $P^{\mathcal{C}}$ is the spectral projection of $\mathcal{C}$. As before, we define the discrete part of $\sigma_1(\mathcal{C})$ as the set of isolated points with $\operatorname{rank} BH_\#^{\frac{1}{2}} P^{\mathcal{C}}(\{\lambda\}) < \infty$, and the essential part as the complement of the discrete part. Then, we have the following characterisation.

Corollary 2.6 (maximal meromorphic extension of $\widehat{\chi_F}$). *Suppose that $\sigma_1(\mathcal{C})$ has a spectral gap on the non-negative part of the spectrum, i.e. $[0,\infty) \not\subset \sigma_1(\mathcal{C})$. Then the maximal meromorphic extension of $\widehat{\chi_F}$ is given by*

$$\begin{aligned} \widehat{\chi_F} :& \mathcal{D}_F \to \mathcal{B}\left(L^2_{\rho_0}, L^2_{\frac{1}{\rho_0}}\right) \\ & z \mapsto \widehat{\chi_F}(z) = \sum_{\lambda \in \sigma_1^{\mathrm{disc}}(\mathcal{C})} \frac{2}{z^2 - \lambda} BH_\#^{\frac{1}{2}} P^{\mathcal{C}}(\{\lambda\}) H_\#^{\frac{1}{2}} B^* + BH_\#^{\frac{1}{2}} \int_{\sigma_1^{\mathrm{ess}}(\mathcal{C})} \frac{2}{z^2 - \lambda} \mathrm{d}P_\lambda^{\mathcal{C}} H_\#^{\frac{1}{2}} B^*, \end{aligned}$$

where

$$\mathcal{D}_F := \left\{ z \in \mathbb{C} : z^2 \notin \sigma_1^{\mathrm{ess}}(\mathcal{C}) \right\}. \tag{2.23}$$

In particular, the set of poles of $\widehat{\chi_F}$ is given by $\{z \in \mathbb{C} : z^2 \in \sigma_1^{\mathrm{disc}}(\mathcal{C})\}$.

Remark (poles rank and order). The non-zero poles of $\widehat{\chi_F}$ are all simple and satisfy

$$\operatorname{rank}_\lambda(\widehat{\chi_F}) = \operatorname{rank} BH_\#^{\frac{1}{2}} P^{\mathcal{C}}(\{\lambda\}).$$

On the other hand if $0 \in \sigma_1^{\mathrm{disc}}(\mathcal{C})$, then $\widehat{\chi_F}$ has a pole of second order at the origin.

As a last consequence of theorem 2.3, we show that under a compactness condition on F, the domain of maximal meromorphic continuation of $\widehat{\chi_F}$ agrees with the domain of maximal meromorphic continuation of $\widehat{\chi_H}$. As the proof of this result is more involved than the proof of the previous corollaries, we promote it to a theorem.

Theorem 2.7 (invariance of maximal domain). *Suppose that* $F \in \mathcal{B}(L^2_{\frac{1}{\rho_0}}, L^2_{\rho_0})$ *satisfies*

$$B^* F B \in \mathcal{B}_\infty \left(D(H_\#), \{\Psi_0\}^\perp \right), \tag{2.24}$$

where $\mathcal{B}_\infty(D(H_\#), \{\Psi_0\}^\perp)$ *denotes the set of compact operators from* $D(H_\#)$ *(endowed with the graph norm) to* $\{\Psi_0\}^\perp$*, then*

$$\mathcal{D}_F = \mathcal{D},$$

where $\mathcal{D}$ *and* $\mathcal{D}_F$ *are the maximal domains defined in (2.13) and (2.23), respectively.*

The relevance of the above theorem is that for typical Schrödinger operators, the maximal domain of meromorphic continuation of $\widehat{\chi_H}$ is related to its ionisation threshold via equation (2.11). Since the compactness condition (2.24) holds for standard adiabatic approximations (see proposition 2.9 below), the above corollary implies that such approximations are not able to shift the ionisation threshold of H (which is the Kohn–Sham Hamiltonian in applications).

2.4. Applications

We now discuss some applications of the previous results in the context of LR-TDDFT. Throughout this section, we work within the quantum chemistry set-up where $\Omega = \mathbb{R}^3$ and the underlying single-particle space is the classical Lebesgue space $L^2(\mathbb{R}^3)$.

In this setting, the typical Hamiltonians of interest (e.g. the molecular Hamiltonian) are Schrödinger operators

$$H = -\Delta + V(r_1, \ldots, r_N),$$

where Δ is the Laplacian on $\mathbb{R}^{3N}$ and V is some real-valued function that acts by multiplication. Under general assumptions on V (e.g. V is in the Kato class of $\mathbb{R}^{3N}$ [33]), the ground state density of H is bounded whenever it exists. In particular, the following criterion applies to many situations encountered in practice. (The proof is a straightforward application of Hölder's inequality.)

Proposition 2.8 (sufficient criterion for adiabatic approximations). *Let* $\rho_0 \in L^1(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$*, and* $F = F_1 + F_2$ *satisfy*

$$\|F_1 f\|_{L^2(\mathbb{R}^3)+L^\infty(\mathbb{R}^3)} \lesssim \|f\|_{L^1(\mathbb{R}^3)\cap L^2(\mathbb{R}^3)} \quad \textit{and} \quad |(F_2 f)(r)| \lesssim \rho_0(r)^\delta |f(r)|,$$

for some $\delta \geqslant -1$*. Then* $F \in \mathcal{B}(L^2_{\frac{1}{\rho_0}}, L^2_{\rho_0})$*.*

The above criterion is easily verified for the following adiabatic approximations:

- The random phase approximation (RPA). In the RPA, F is given by

$$\left(F^{\mathrm{RPA}} g\right)(r) = \int_{\mathbb{R}^3} \frac{g(r')}{|r - r'|} \mathrm{d}r'. \tag{2.25}$$

  Thus from the Hardy–Littlewood–Sobolev (HLS) inequality, we conclude that $F^{\mathrm{RPA}} \in \mathcal{B}(L^2_{\frac{1}{\rho_0}}, L^2_{\rho_0})$. (In fact, we just need $\rho_0 \in L^{\frac{3}{2}}(\mathbb{R}^3)$ here.)

- The Petersilka, Gossmann, and Gross approximation (PGG) [25]. In the PGG approximation, the operator F is given by

$$\left(F^{\mathrm{PGG}}g\right)(r) = \left(F^{\mathrm{RPA}}g\right)(r) - \frac{1}{2}\int_{\mathbb{R}^3} \frac{|\gamma_H(r,r')|^2}{\rho_0(r)\rho_0(r')} \frac{g(r')}{|r-r'|}\mathrm{d}r',$$

where $\gamma_H(r,r')$ is the ground state single-particle density matrix of the Hamiltonian associated to χ_H. Hence, from the simple inequality $|\gamma_H(r,r')|^2 \leqslant \rho_0(r)\rho_0(r')$ and the HLS inequality, we also have $F^{\mathrm{PGG}} \in \mathcal{B}(L^2_{\frac{1}{\rho_0}}, L^2_{\rho_0})$ for any $\rho_0 \in L^{\frac{3}{2}}(\mathbb{R}^3)$.

- The adiabatic local density approximation (ALDA) [22, 36, 38]. The ALDA is not a single approximation but rather a class of approximations. In the ALDA, the operator F is given by

$$\left(F^{\mathrm{ALDA}}_{\rho_0}g\right)(r) = \left(F^{\mathrm{RPA}}g\right)(r) + \underbrace{\frac{\mathrm{d}^2\left(\rho\varepsilon^{\mathrm{HEG}}_{\mathrm{xc}}(\rho)\right)}{\mathrm{d}\rho^2}\bigg|_{\rho=\rho_0(r)}}_{:=f^{\mathrm{HEG}}_{\mathrm{xc}}(\rho_0(r))} g(r),$$

where $\varepsilon^{\mathrm{HEG}}_{\mathrm{xc}}(\rho) = \varepsilon^{\mathrm{HEG}}_{\mathrm{x}}(\rho) + \varepsilon^{\mathrm{HEG}}_{\mathrm{c}}(\rho)$ is the exchange–correlation energy per particle of the homogeneous electron gas. While the exchange part is known and given by

$$\varepsilon^{\mathrm{HEG}}_{\mathrm{x}}(\rho) = -C\rho^{\frac{1}{3}}, \tag{2.26}$$

the correlation can only be approximated, which leads to different approximations of $F^{\mathrm{ALDA}}_{\rho_0}$. To see why such approximations also belong to $\mathcal{B}(L^2_{\frac{1}{\rho_0}}, L^2_{\rho_0})$, let us take the parametrisation of $\varepsilon^{\mathrm{HEG}}_{c}$ introduced by Perdew and Wang [24] as an example. The PW correlation approximation is

$$\varepsilon^{\mathrm{PW92}}_{\mathrm{c}}(\rho) = -2A\left(1+\alpha_1\rho^{-\frac{1}{3}}\right)\log\left(1+\frac{1}{\beta_1\rho^{-\frac{1}{6}}+\beta_2\rho^{-\frac{1}{3}}+\beta_3\rho^{-\frac{1}{2}}+\beta_4\rho^{-\frac{1+P}{3}}}\right), \tag{2.27}$$

where $P = 1$ or $\frac{3}{4}$, and $A, \alpha_1, \beta_1, \beta_2, \beta_3, \beta_4 > 0$ are parameters chosen to reproduce the asymptotics expansions of $\varepsilon^{\mathrm{HEG}}_{\mathrm{c}}$ in the low and high-density limits, and to fit data from quantum Monte Carlo simulations [13] in the intermediate regime. Thus from (2.26) and (2.27), one can check (see appendix C) that

$$|f^{\mathrm{HEG}}_{\mathrm{xc}}(\rho_0(r))| \lesssim_{\|\rho_0\|_{L^\infty}} \rho_0(r)^{\max\left\{\frac{1}{2},\frac{1+P}{3}\right\}-\frac{4}{3}} \lesssim_{\|\rho_0\|_{L^\infty}} \rho_0(r)^{-\frac{5}{6}}, \tag{2.28}$$

where the implicit constants depend on $\|\rho_0\|_{L^\infty}$ but not on $r \in \Omega$. Therefore, $F^{\mathrm{ALDA}}_{\rho_0} \in \mathcal{B}(L^2_{\frac{1}{\rho_0}}, L^2_{\rho_0})$ for any bounded ρ_0. Other parametrisations of $\varepsilon^{\mathrm{HEG}}_{c}(\rho)$ also satisfy the above inequality as long as they reproduce (up to second derivatives) the asymptotic expansion of $\varepsilon^{\mathrm{HEG}}_{\mathrm{c}}$ in the low-density limit.

The above list contains the most common adiabatic approximations used in practice and is not exhaustive. Note also that all adiabatic approximations mentioned above are symmetric (as they correspond to the Hessian of approximated exchange–correlation energy functionals). In particular, proposition 2.8 guarantees that the solution formulas derived here apply to the Dyson equation with these approximations under the sole condition that the ground state density of the Kohn–Sham system is bounded.

Remark (generalised gradient approximations). Unfortunately, the results presented here do not apply to generalised gradient approximations (GGA) of the exchange–correlation operator, as these involve not only the pointwise values of the ground state density but also of its gradient. At the moment, we do not know how to adapt the framework introduced here to the GGA case, but we plan to address this question in the future.

Remark (absorption spectrum). It turns out that the ground state density of typical quantum systems is not only bounded but also decays exponentially fast at infinity [1, 2, 33]. In this case, the weighted density space $L^2_{\rho_0}$ contains functions that can grow exponentially fast at infinity. In particular, the polarisability tensor

$$A_{jk}(\omega) = -\mathrm{Im}\langle r_j, \widehat{\chi_H}(\omega)\, r_k\rangle$$

is a well-defined tempered distribution. Similarly, if the stability condition (2.20) holds, the polarisability tensor of the solution χ_F also defines a tempered distribution.

As a final result, we present a simple sufficient criterion for the compactness property (2.24) that applies to the aforementioned adiabatic approximations. As a consequence, theorem 2.7 shows that none of these adiabatic approximations are able to shift the ionisation threshold of the Kohn–Sham system.

Proposition 2.9 (compactness criterion). *Suppose that $\rho_0 \in L^1(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$ and that the domain of H is continuously embedded in the classical Sobolev space $\mathcal{H}^1(\Delta) = \{\Psi \in L^2(\mathbb{R}^{3N}) : \int_{\mathbb{R}^{3N}} |\nabla\Psi|^2 \mathrm{d}r < \infty\}$. Then for any $F = F^{\mathrm{RPA}} + F_{\rho_0}$ with F_{ρ_0} satisfying*

$$|F_{\rho_0} g(r)| \lesssim \rho_0(r)^\delta\, |g(r)| \quad \textit{for all } g \in L^2_{\frac{1}{\rho_0}} \textit{ and some } \delta > -1, \tag{2.29}$$

we have $B^* F B \in \mathcal{B}_\infty(D(H_\#), \{\Psi_0\}^\perp)$.

Remark (optimality of (2.29)). The condition $\delta > -1$ in proposition 2.9 is optimal, as the following example shows. Let $N = 1$ and define the adiabatic approximation F_{ρ_0} as

$$(F_{\rho_0} f)(r) = c\rho_0(r)^{-1} f(r),$$

for some $c \in \mathbb{R}$. Since $N = 1$, the ground state density is simply $\rho_0(r) = |\Psi_0(r)|^2$ and the operators B and B^* reduce to

$$B\Phi(r) = \overline{\Psi_0}(r)\,\Phi(r) - \langle\Psi_0, \Phi\rangle \rho_0(r) \quad \text{and} \quad (B^* f)(r) = f(r)\,\Psi_0(r) - \langle\rho_0, f\rangle \Psi_0(r).$$

Thus we have $\mathcal{C} = H_\#^2 + 2cH_\#$, which implies that

$$(\mathbb{C} \setminus \mathcal{D}_F)^2 = \sigma_1^{\mathrm{ess}}(\mathcal{C}) = \left\{\lambda^2 + 2c\lambda : \lambda \in \sigma_1^{\mathrm{ess}}(H_\#)\right\} \neq \left\{\lambda^2 : \lambda \in \sigma_1^{\mathrm{ess}}(H_\#)\right\} = (\mathbb{C} \setminus \mathcal{D})^2,$$

provided that $c \neq 0$ and $\sigma_1^{\mathrm{ess}}(H_\#)$ is non-empty.

Outline of the paper. We introduce some notation in the next paragraph. In the following section, we recall some well-known results about self-adjoint operators, their quadratic forms, and the associated Sobolev scale of spaces. These results are then used in section 4 to prove the main results of this paper. In the appendices, we briefly discuss the optimality of weighted density spaces as the domain and co-domain of the DDRF (appendix A), clarify the connection between the Casida operator $\mathcal{C}$ and the usual formulation of the Casida equations from LR-TDDFT (appendix B), and give a proof of estimate (2.28) (appendix C).

2.4.1. Notation. We denote the set of non-negative real numbers by $\mathbb{R}_+$. For A and B scalar quantities, $A \lesssim B$ means that there is an irrelevant positive constant C such that $|A| \leqslant C|B|$. Occasionally, we also use $A \lesssim_\epsilon B$ to indicate the dependence of the implicit constant on the additional parameter ϵ.

Let F be a Banach space, then we denote its norm by $\|\cdot\|_F$, or simply by $\|\cdot\|$ if the space is clear from the context. The set of linear continuous operators from F to another Banach space G is denoted by $\mathcal{B}(F,G)$; the set of compact operators is denoted by $\mathcal{B}_\infty(F,G)$. The operator norm is denoted by $\|T\|_{F,G}$ or simply by $\|T\|$ if the Banach spaces are clear from the context. The kernel and the range of T are denoted, respectively, by $\ker T \subset F$ and $\operatorname{ran} T \subset G$. We also use $\operatorname{rank} T = \dim \operatorname{ran} T$ for the rank of T. The anti-dual of a Banach space F, i.e. the space of antilinear continuous functions from F to $\mathbb{C}$ endowed with the operator norm is denoted by $F^\star$. For the Fourier transform of a function $f : \mathbb{R} \to F$, we use the physics convention

$$\widehat{f}(\omega) = \int_{\mathbb{R}} f(t)\, e^{it\omega} \mathrm{d}t. \tag{2.30}$$

For any Hilbert space $\mathcal{H}$, we adopt the convention that the inner-product $\langle \cdot, \cdot \rangle_{\mathcal{H}}$ is antilinear in the first variable and linear in the second.

For $1 \leqslant p \leqslant \infty$, $L^p(\mathbb{R}^n) = L^p(\mathbb{R}^n;\mathbb{C})$ denotes the standard L^p spaces of $\mathbb{C}$-valued measurable functions with respect to the Lebesgue measure on $\mathbb{R}^n$. We also use $L^p(\mathbb{R}^n) + L^q(\mathbb{R}^n)$ and $L^p(\mathbb{R}^n) \cap L^q(\mathbb{R}^n)$ for the Banach spaces of Lebesgue-measurable functions with the norms

$$\|f\|_{L^p+L^q} := \inf_{f=f_p+f_q} \{\|f_p\|_{L^p} + \|f_q\|_{L^q}\} \quad \text{and} \quad \|f\|_{L^p\cap L^q} := \max\{\|f\|_{L^p}, \|f\|_{L^q}\}.$$

Lastly, we recall the definition of an operator-valued meromorphic function [17, appendix C].

Definition 2.10 (meromorphic operator-valued function). Let $\mathcal{D} \subset \mathbb{C}$ be open, then we say that $K : \mathcal{D} \to \mathcal{B}(F,G)$ is a meromorphic operator-valued function if for any $z_0 \in \mathcal{D}$ there exists (i) a neighbourhood $U_{z_0} \subset \mathcal{D}$ of z_0, (ii) finitely many finite rank operators $\{K_j\}_{j\leqslant M} \subset \mathcal{B}(F,G)$, and (iii) a holomorphic function $K_0 : U_{z_0} \to \mathcal{B}(F,G)$ such that

$$K(z) = K_0(z) + \sum_{j=1}^{M} (z - z_0)^{-j} K_j \quad \text{for } z \in U_{z_0}.$$

If $K_j \neq 0$ for some $j \geqslant 1$, we say that z_0 is a pole of K. In addition, if $K_j = 0$ for $j \geqslant 2$, then we say that z_0 is a simple pole of K and define its rank as

$$\operatorname{rank}_{z_0}(K) = \operatorname{rank} K_1.$$

Moreover, we say that $\mathcal{D}$ is the maximal domain of K if there exists no meromorphic extension of K to a strictly larger connected domain.

3. Mathematical background

In this section we briefly recall some well-known facts about the scale of Sobolev spaces associated to self-adjoint operators and their quadratic forms. We also use this short recap to set-up some additional notation that will be used during the proofs from section 4. The material presented here can be found in standard references such as [28–30].

3.1. Sobolev scale of spaces

Throughout this section, we let $A : D(A) \subset \mathcal{H} \to \mathcal{H}$ be some self-adjoint operator on a Hilbert space $\mathcal{H}$ satisfying the inequality

$$\langle \Psi, A\psi \rangle \geqslant \|\Psi\|^2 \quad \text{for any } \Psi \in D(A).$$

(In the case $A \geqslant 1 - c$ for some $c > 0$, we replace A by $A + c$ everywhere in the discussion below.) Then by the spectral theorem, there exists a measure space (X, ν), a unitary map $U : \mathcal{H} \to L^2(X, \mathrm{d}\nu)$, and a real-valued ν-measurable function $a : X \to [1, \infty)$ such that

$$U(D(A)) = L^2\left(X, a^2 \mathrm{d}\nu\right) = \left\{ f \in L^2(X, \mathrm{d}\nu) : \int_X |f(x)|^2 a(x)^2 \mathrm{d}\nu(x) < \infty \right\},$$

and A acts on $L^2(X, \mathrm{d}\nu)$ by multiplication by a, i.e.

$$(UAU^* f)(x) = a(x) f(x).$$

We then define the Sobolev spaces induced by A as follows.

Definition (Sobolev spaces). For $s \geqslant 0$, the Sobolev space of order s is the set

$$\mathcal{H}^s(A) := \left\{ \Psi \in \mathcal{H} : U\Psi \in L^2(X, a^s \mathrm{d}\nu) \right\}$$

endowed with the norm

$$\|\Psi\|^2_{\mathcal{H}^s(A)} := \int_X |U\Psi(x)|^2 a(x)^s \mathrm{d}\nu(x) = \|A^{\frac{s}{2}} \Psi\|^2. \tag{3.1}$$

Moreover, the negative Sobolev space of order $-s$ is defined as the anti-dual space of $\mathcal{H}^s(A)$, i.e. the set

$$\mathcal{H}^{-s}(A) := \mathcal{H}^s(A)^\star = \{ T : \mathcal{H}^s(A) \to \mathbb{C} \quad \text{antilinear and continuous} \}$$

endowed with the operator norm.

By the Riesz representation theorem, we can isometrically identify $\mathcal{H}$ with its anti-dual $\mathcal{H}^\star$ via the Riesz map

$$\mathcal{R} : \mathcal{H} \to \mathcal{H}^\star \quad \Psi \mapsto \mathcal{R}\Psi = \langle \cdot, \Psi \rangle_{\mathcal{H}}.$$

In this way, we have a natural chain of dense inclusions

$$\ldots \subset \mathcal{H}^s(A) \ldots \subset \mathcal{H}^m(A) \ldots \subset \mathcal{H} \overset{\mathcal{R}}{\cong} \mathcal{H}^\star \ldots \subset \mathcal{H}^{-m}(A) \ldots \subset \mathcal{H}^{-s}(A) \ldots \quad (s \geqslant m \geqslant 0). \tag{3.2}$$

From (3.1), the operator A^s restricted to $\mathcal{H}^m(A)$ defines an isometric isomorphism between $\mathcal{H}^m(A)$ and $\mathcal{H}^{m-s}(A)$ for any $0 \leqslant s \leqslant m$. Consequently, the adjoint map induces an isometric isomorphism from $\mathcal{H}^{s-m}(A)$ to $\mathcal{H}^{-m}(A)$. In particular, by the chain of inclusions in (3.2) and using the commutation relations

$$A^s A^m = A^{s+m} = A^m A^s,$$

the operator A^s can be uniquely extended to a continuous[7] operator on the whole Sobolev scale of spaces

$$A^s : \mathcal{H}^{-\infty}(A) := \bigcup_{m\in\mathbb{R}} \mathcal{H}^m(A) \to \mathcal{H}^{-\infty}(A) \quad (\text{for any } s \in \mathbb{R}).$$

Furthermore, the chain of inclusions in (3.2) also allow us to naturally define the operator

$$\mu - A : \mathcal{H}^s(A) \to \mathcal{H}^{s-2}(A)$$

for any $s \in \mathbb{R}$ and $\mu \in \mathbb{C}$. A useful consequence of the spectral theorem is that the spectrum of A is independent of the Sobolev scale used. More precisely, we have

Lemma 3.1 (inverse on Sobolev scale). *Let $\mu \in \mathbb{C}$, then the operator $\mu - A$ is invertible in $\mathcal{B}(\mathcal{H}^s(A), \mathcal{H}^{s-2}(A))$ for some $s \in \mathbb{R}$ if and only if it is invertible for every $s \in \mathbb{R}$.*

Proof. First, we can use the Riesz representation theorem on $L^2(X, \mathrm{d}\nu)$ to extend the unitary map (given by the spectral theorem) $U : \mathcal{H} \to L^2(X, d\nu)$ to $U : \mathcal{H}^{-s}(A) \to L^2(X, a^{-s}d\nu)$ for any $s \geqslant 0$. More precisely, $UT \in L^2(X, a^{-s}\mathrm{d}\nu)$ is the unique operator satisfying

$$T(U^* g) = \int_X \overline{g}(x)(UT)(x)\,\mathrm{d}\nu(x) \quad \text{for any } g \in L^2(X, a^s \mathrm{d}\nu).$$

Hence, the operator $U(\mu - A)U^*$ acts on $L(X, a^{-s}\mathrm{d}\nu)$ as pointwise multiplication by $\mu - a(x)$ for any $s \in \mathbb{R}$. One can now check that this operator is invertible if and only if $|\mu - a(x)| > \delta$ μ-a.e. for some $\delta > 0$, which is equivalent to $\mu - A$ being invertible on $\mathcal{H}$. ☐

Let us conclude this section with a distributional version of Stone's formula (see [28, theorem VII.13]) that will be useful to establish the maximality of the meromorphic extensions from theorem 2.1 and corollary 2.6.

Lemma 3.2 (Stone's formula). *Let A be a semi-bounded self-adjoint operator and $R_A(z) = (z - A)^{-1}$ denote the resolvent of A. Then for any $f \in C_c^\infty(\mathbb{R})$ we have*

$$\lim_{\eta\to 0^+} \int_{\mathbb{R}} f(\mu)\left(R_A(\mu - i\eta) - R_A(\mu + i\eta)\right)\mathrm{d}\mu = 2\pi i \int_{\mathbb{R}} f(\lambda)\,\mathrm{d}P_\lambda^A,$$

where P_λ^A is the spectral projection-valued measure of A and the convergence is in the operator norm on $\mathcal{B}(\mathcal{H}^s(A), \mathcal{H}^{s+2}(A))$ for any $s \in \mathbb{R}$.

Proof. Since $(\mu \pm i\eta - \lambda)^{-1}$ is uniformly bounded in $\lambda \in \mathbb{R}$ for $\eta > 0$ fixed, from Fubini's theorem we have

$$\int_{\mathbb{R}} f(\mu)\left(R_A(\mu - i\eta) - R_A(\mu + i\eta)\right)\mathrm{d}\mu = 2i \int_{\mathbb{R}} (f * p_\eta)(\lambda)\,\mathrm{d}P_\lambda^A = 2i\,(f * p_\eta)(A)$$

where $p_\eta(\mu) = \frac{\eta}{\mu^2 + \eta^2}$ is the Poisson kernel. As $g(A)$ commutes with A for any continuous function g, it is enough to show that

$$\lim_{\eta\to 0^+} \|A(f * p_\eta(A) - \pi f(A))\|_{\mathcal{B}(\mathcal{H})} = 0.$$

[7] with respect to the inductive limit topology on $\mathcal{H}^{-\infty}(A)$.

This now follows from the continuity of the spectral calculus and the estimate

$$|\lambda|\big|(f*p_\eta)(\lambda)-\pi f(\lambda)\big|\lesssim\eta\int_{\mathbb{R}}|\omega|\big(|\widehat{f}(\omega)|+|\partial_\omega\widehat{f}(\omega)|\big)\mathrm{d}\omega\quad(\text{for any }\lambda\in\mathbb{R}),$$

which can be shown by using the Fourier transform of the Poisson kernel $\widehat{p_\eta}(\omega)=\pi\,e^{-\eta|\omega|}$. □

3.2. *Quadratic forms*

Let us now introduce the quadratic form associated to a semi-bounded operator A and present the KLMN theorem [29, theorem X.17]. For a proof, consult [29].

Definition (quadratic form). For a semi-bounded self-adjoint operator A satisfying $A\geqslant 1-c$ for some $c\in\mathbb{R}$, the associated quadratic form is the sesquilinear map $q_A:\mathcal{H}^1(A)\times\mathcal{H}^1(A)\to\mathbb{C}$ defined as

$$q_A(\Psi,\Phi)=\langle(A+c)^{\frac{1}{2}}\Psi,(A+c)^{\frac{1}{2}}\Phi\rangle-c\langle\Psi,\Phi\rangle.$$

The Sobolev space of order 1 is also called the form domain of A.

Note that, by definition,

$$\Psi\mapsto q_A(\cdot,\Psi)=(A+c)^{\frac{1}{2}}(A+c)^{\frac{1}{2}}\Psi-c\Psi=A\Psi\in\mathcal{H}^{-1}(A).$$

Next, let $\beta:\mathcal{H}^1(A)\times\mathcal{H}^1(A)\to\mathbb{C}$ be another symmetric sesquilinear form. Then we say that β is relatively bounded with respect to q_A if there exists some $0<a<1$ and $b>0$ such that

$$|\beta(\Phi,\Phi)|\leqslant aq_A(\Phi,\Phi)+b\|\Phi\|^2\quad\text{for any }\Phi\in\mathcal{H}^1(A).\tag{3.3}$$

With this definition, we can now state the KLMN theorem, which is essentially a quadratic form version of the celebrated Kato–Rellich theorem.

Lemma 3.3 (KLMN theorem [29]). *Let A be a self-adjoint operator satisfying $A\geqslant 1-c$ and β be a symmetric sesquilinear form on $\mathcal{H}^1(A)$ satisfying (3.3). Then, there exists a unique self-adjoint operator B with the same form domain as A and satisfying*

$$q_B=q_A+\beta.\tag{3.4}$$

Moreover, $B\geqslant(1-a)(1-c)-b$.

The proof of the KLMN theorem consists in using inequality (3.3) to show that there exists $\alpha\in\mathbb{R}$ such that the norms $q_B+\alpha\langle\cdot,\cdot\rangle$ and $\|(A+c)^{\frac{1}{2}}\cdot\|$ are equivalent and exploit the one-to-one relation between semi-bounded closed quadratic forms and semi-bounded self-adjoint operators. In particular, using interpolation theory one can show that

$$\mathcal{H}^s(A)=\mathcal{H}^s(B)\quad\text{and}\quad\|(B+\alpha)^{\frac{s}{2}}\Phi\|\sim\|(A+c)^{\frac{s}{2}}\Phi\|\quad\text{for any }\Phi\in\mathcal{H}^s(A),\tag{3.5}$$

provided that $-1\leqslant s\leqslant 1$. (The identity above means that these are the same subsets of $\mathcal{H}$ for $s\geqslant 0$, and not simply isometric.)

3.3. Reducing subspaces and block decomposition

We now recall the definition of reducing subspaces for unbounded self-adjoint operators and the associated block decomposition. For the proofs of the results presented next, we refer to [31, section 1.4]. As before, we assume that $A : D(A) \subset \mathcal{H} \to \mathcal{H}$ is self-adjoint.

Definition (invariant and reducing subspaces). We say that some closed subspace $V \subset \mathcal{H}$ is an invariant subspace of A if A maps the intersection $D(A) \cap V$ to V. Moreover, we say that V is a reducing subspace for A if both V and $V^{\perp}$ are invariant and the decomposition

$$D(A) = (D(A) \cap V) \oplus \left(D(A) \cap V^{\perp}\right)$$

holds.

The main motivation for introducing the notion of reducing spaces is the following well-known block decomposition.

Theorem 3.4 (block decomposition [31]). *Suppose that V is a reducing subspace for A, then*

$$A|_V : D(A) \cap V \to V \quad \text{and} \quad A|_{V^{\perp}} : D(A) \cap V^{\perp} \to V^{\perp}$$

are self-adjoint operators in V and $V^{\perp}$, respectively, and we have $A = A|_V \oplus A|_{V^{\perp}}$. In particular, we have the spectral decomposition

$$\sigma(A) = \sigma(A|_V) \cup \sigma(A|_{V^{\perp}}),$$

where $\sigma(A|_V)$ and $\sigma(A|_{V^{\perp}})$ are the spectra on V and $V^{\perp}$, respectively.

While every invariant subspace is also reducing for bounded self-adjoint operators, this is no longer true for unbounded self-adjoint operators. For the latter, we shall use the following criterion for reducing subspaces.

Lemma 3.5 (criterion for reducing subspaces [31]). *Let $V \subset \mathcal{H}$ be a closed subspace. Then V is reducing for A if and only if V and $V^{\perp}$ are invariant for A and the orthogonal projection on V maps D(A) to itself.*

4. Proofs

In this section, we present the proofs of the main results of this paper.

4.1. Proof of theorem 2.1

The first step in the proof of theorem 2.1 is to show that the operators $B : \mathcal{H}_N \to L^2_{\frac{1}{\rho_0}}$ and $B^* : L^2_{\rho_0} \to \mathcal{H}_N$ are bounded. For the boundedness of B, we can use the estimate

$$B\Phi(r) = N \int_{\Omega^{N-1}} \overline{\Psi_0(r, r_2, \ldots, r_N)} \Phi(r, r_2, \ldots, r_N) \, \mathrm{d}\mu(r_2) \ldots \mathrm{d}\mu(r_N) \leqslant \sqrt{\rho_0(r)} \sqrt{\rho_\Phi(r)} \quad (4.1)$$

for any $\Phi \in \{\Psi_0\}^{\perp}$, and the fact that $B\Psi_0 = 0$. Moreover, by identifying $L^2_{\rho_0} \cong (L^2_{\frac{1}{\rho_0}})^{\star}$ via the Riesz map on $L^2(\Omega, \mathrm{d}\mu)$ and using the identity

$$\langle B\Phi, g\rangle_{L^2(\Omega,\mathrm{d}\mu)} = \langle \Phi, B^* g\rangle_{\mathcal{H}_N},$$

we conclude that $B^* \in \mathcal{B}(L^2_{\rho_0}, \mathcal{H}_N)$ by duality. Hence, recalling that $\int \rho_\Phi(r)\mathrm{d}\mu(r) = N$ for any normalised Φ, we have just proved the following proposition.

Proposition 4.1 (boundedness on weighted density spaces). *The operators B and B^* satisfy*

$$\|B\|_{\mathcal{B}\left(\mathcal{H}_N, L^2_{1/\rho_0}\right)} = \|B^*\|_{\mathcal{B}\left(L^2_{\rho_0}, \mathcal{H}_N\right)} \leqslant N.$$

In particular, $\chi_H : \mathbb{R} \to \mathcal{B}(L^2_{\rho_0}, L^2_{\frac{1}{\rho_0}})$ is bounded and strongly continuous.

We can now complete the proof of theorem 2.1

Proof of theorem 2.1. Since χ_H is bounded and strongly continuous, its Fourier transform is well-defined as a tempered distribution. Moreover, since χ_H is causal (i.e. $\chi_H(t) = 0$ for $t \leqslant 0$), the Fourier transform is analytic on the upper half-plane $\{z \in \mathbb{C} : \mathrm{Im}(z) > 0\}$. From the spectral Theorem and straightforward computations (see [15, section 2]), this analytic continuation is given by

$$\widehat{\chi_H}(z) = B\left((z - H_\#)^{-1} - (z + H_\#)^{-1}\right)B^*.$$

Now note that, since the single-particle excitation spectrum $\sigma_1(H_\#)$ is closed (thus Borel measurable), we can decompose the resolvent of $H_\#$ in two terms:

$$(z - H_\#)^{-1} = P^{H_\#}(\sigma_1(H_\#))(z - H_\#)^{-1} + P^{H_\#}(\mathbb{R} \setminus \sigma_1(H_\#))(z - H_\#)^{-1}.$$

From the definition of $\sigma_1(H_\#)$, the second term vanishes when multiplied by B on the left. In particular, the spectral theorem yields

$$\widehat{\chi_H}(z) = B \int_{\sigma_1(H_\#)} \frac{2\lambda}{z^2 - \lambda^2} \mathrm{d}P^{H_\#}_\lambda B^*. \tag{4.2}$$

Next, observe that the spectral gap assumption on H implies that the set $\{z \in \mathbb{C} : \pm z \notin \sigma_1(H_\#)\}$ is open and connected. Thus the right-hand side of (4.2) defines the unique analytic extension of $\widehat{\chi_H}$ to this set. Moreover, for any isolated point $\lambda_0 \in \sigma_1(H_\#)$, we have

$$\widehat{\chi_H}(z) = \frac{2\lambda_0}{z^2 - \lambda_0^2} BP^{H_\#}(\{\lambda_0\})B^* + B\int_{\sigma_1(H_\#)\setminus\{\lambda_0\}} \frac{2\lambda}{z^2 - \lambda^2}\mathrm{d}P^{H_\#}_\lambda B^*,$$

where the second term is analytic around λ_0. In particular, $\widehat{\chi_H}$ is meromorphic on

$$\mathcal{D} := \{z \in \mathbb{C} : \pm z \notin \sigma_1^{\mathrm{ess}}(H_\#)\}. \tag{4.3}$$

From the identity $\operatorname{rank} S = \operatorname{rank} SS^*$, we also obtain the rank equality

$$\operatorname{rank}_{\lambda_0}(\widehat{\chi_H}) = \operatorname{rank} BP^{H_\#}(\{\lambda_0\})B^* = \operatorname{rank} BP^{H_\#}(\{\lambda_0\}) \quad \text{for any } \lambda_0 \in \sigma_1^{\mathrm{disc}}(H_\#).$$

To conclude the proof, we need to show that $\mathcal{D}$ is the maximal domain of meromorphic continuation of $\widehat{\chi_H}$. So suppose that $\widehat{\chi_H}$ is analytic around some $\lambda_0 \in \mathbb{R}$, then it is enough to show that $\lambda_0 \notin \sigma_1(H_\#)$. Moreover, since $\widehat{\chi_H}(z) = \widehat{\chi_H}(-z)$, we can assume (without loss of generality) that $\lambda_0 \in \mathbb{R}_+$. Then, define

$$T(z) := \widehat{\chi_H}(z) - B(z+H_\#)^{-1}B^*.$$

As the right-hand side is continuous close to λ_0, Stone's formula (see lemma 3.2) yields

$$0 = \lim_{\eta\to 0^+}\int_{\mathbb{R}} f(\lambda)\,(T(\lambda - i\eta) - T(\lambda + i\eta))\,\mathrm{d}\lambda = 2\pi i B\int_{\mathbb{R}} f(\lambda)\,\mathrm{d}P_\lambda^{H_\#}B^*$$

for any $f \in C_c^\infty(\mathbb{R})$ with support in $B_\epsilon(\lambda_0)$ for $\epsilon > 0$ small enough. Choosing a sequence f_n converging monotonically to the indicator function on $B_\epsilon(\lambda_0)\cap\mathbb{R}$ and using the strong convergence property of the spectral calculus (see [28, theorem VIII.5.(d)]), we find that $BP^{H_\#}(B_\epsilon(\lambda_0))B^* = 0$. Therefore, $\lambda_0 \notin \sigma_1(H_\#)$, which completes the proof. □

Remark (regularity of $\widehat{\chi_H}$ along the continuous spectrum). If H has compact resolvent (e.g. a Schrödinger operator with a trapping potential), then the maximal domain of meromorphic continuation is the whole complex plane. However, for typical Hamiltonians in electronic structure theory (e.g. the atomic and molecular Hamiltonians), the spectrum is divided into discrete and continuous parts [30]. In some special cases, and for suitable f and g, the regularity of the map $\omega \mapsto \langle g, \widehat{\chi_H}(\omega) f\rangle$ along the continuous spectrum can be rigorously studied (see [16]) via the celebrated limiting absorption principle [3, 17].

4.2. *Proof of theorem 2.3*

We split the proof of theorem 2.3 into two parts. In the first part, we properly define the Casida operator and relate its resolvent to the inverse of the operator

$$\mathcal{C}_\#(z) = z^2 H_\#^{-1} - H_\# - 2B^*FB.$$

In the second part, we show that $\widehat{\chi_H}$ is given by the conjugation of B with $\mathcal{C}_\#(z)^{-1}$ via the convolution property of the Fourier transform and a well-known resolvent identity.

4.2.1. The Casida operator. To properly define the Casida operator, we consider the quadratic form $\beta : D(H_\#)\times D(H_\#) \to \mathbb{C}$ defined as

$$(\Psi,\Phi) \mapsto \beta(\Psi,\Phi) = \langle H_\#^{\frac{1}{2}}\Psi, 2B^*FBH_\#^{\frac{1}{2}}\Phi\rangle.$$

Recall that we assumed $F \in \mathcal{B}(L^2_{\frac{1}{\rho_0}}, L^2_{\rho_0})$ to be symmetric, and

$$H_\# = H - \mathcal{E}_0\big|_{\{\Psi_0\}^\perp} : D(H_\#) = D(H)\cap\{\Psi_0\}^\perp \to \{\Psi_0\}^\perp,$$

where Ψ_0 and $\mathcal{E}_0$ are the ground state and ground state energy of H. Therefore, we can use the KLMN theorem to prove the following proposition.

Proposition 4.2 (the Casida operator). *There exists a unique self-adjoint operator* $\mathcal{C} : D(\mathcal{C}) \subset \{\Psi_0\}^\perp \to \{\Psi_0\}^\perp$ *such that* $\mathcal{H}^1(\mathcal{C}) = D(H_\#)$ *and*

$$q_{\mathcal{C}}(\Psi,\Phi) = \langle H_\#\Psi, H_\#\Phi\rangle + \beta(\Psi,\Phi) \quad \text{for any } \Psi,\Phi \in D(H_\#).$$

Moreover, we have

$$\mathcal{C} \geqslant \begin{cases} \omega_1(\omega_1 - 2\|B^*FB\|) & \text{if } \omega_1 \geqslant \|B^*FB\|, \\ -\|B^*FB\|^2 & \text{otherwise,} \end{cases} \tag{4.4}$$

where $\omega_1 = \inf\sigma(H_\#) > 0$.

Proof. Note that $q_{H_\#^2} = \langle H\cdot, H\cdot\rangle$ is the quadratic form of the positive operator

$$H_\#^2 : \mathcal{H}^4(H_\#) \subset \{\Psi_0\}^\perp \to \{\Psi_0\}^\perp.$$

Consequently, to apply the KLMN theorem, we just need to check that β is relatively bounded with respect to $q_{H_\#^2}$. For this, we can use Cauchy–Schwarz and Young's inequality to obtain

$$\begin{aligned} |\langle H_\#^{\frac{1}{2}}\Psi, 2B^*FBH_\#^{\frac{1}{2}}\Psi\rangle| &\leqslant 2\|H^{\frac{1}{2}}\Psi\|^2\|B^*FB\| \leqslant 2\|H_\#\Psi\|\|\Psi\|\|B^*FB\| \\ &\leqslant a\|H_\#\Psi\|^2 + a^{-1}\|B^*FB\|^2\|\Psi\|^2 \\ &= aq_{H_\#^2}(\Psi,\Psi) + a^{-1}\|B^*FB\|^2\|\Psi\|^2 \end{aligned} \tag{4.5}$$

for any $a > 0$. To prove equation (4.4) we note that by equation (4.5),

$$q_{\mathcal{C}}(\Psi,\Psi) = \|H_\#\Psi\|^2 + \beta(\Psi,\Psi) \geqslant \|H_\#\Psi\|^2 - 2\|H_\#\Psi\|\|B^*FB\|$$

for any $\Psi \in D(H_\#)$ with $\|\Psi\| = 1$. Thus by minimising the above expression over $\|H_\#\Psi\| \geqslant \omega_1$, we obtain equation (4.5). ☐

The next step is to relate the Casida operator to the operator

$$\mathcal{C}_\#(z) = z^2 H_\#^{-1} - H_\# - 2B^*FB \quad \text{with domain} \quad D(\mathcal{C}_\#(z)) = D(H_\#). \tag{4.6}$$

Since $H_\#$ is self-adjoint and the operators $H_\#^{-1}$ and B^*FB are both bounded and symmetric, the operator $\mathcal{C}_\#(z)$ is closed and normal. Formally, the operator $\mathcal{C}$ is given by

$$H_\#^2 + 2H_\#^{\frac{1}{2}}B^*FBH_\#^{\frac{1}{2}}.$$

We thus expect that

$$z^2 - \mathcal{C} = H_\#^{\frac{1}{2}}\mathcal{C}_\#(z)H_\#^{\frac{1}{2}}$$

in an appropriate sense. Rigorously clarifying this statement is the goal of the next lemma.

Lemma 4.3 (the resolvent of $\mathcal{C}$). *Let* $\mathcal{C}$ *be the Casida operator defined according to proposition 4.2 and* $\mathcal{C}_\#(z)$ *be the operator defined above. Then* $z^2 - \mathcal{C}$ *is invertible if and only if* $\mathcal{C}_\#(z)$ *is invertible. In this case, the operator* $(z^2-\mathcal{C})^{-1}$ *maps* $\mathcal{H}^{-1}(H_\#)$ *onto* $\mathcal{H}^3(H_\#)$ *and we have*

$$\mathcal{C}_\#(z)^{-1} = H_\#^{\frac{1}{2}}\left(z^2-\mathcal{C}\right)^{-1}H_\#^{\frac{1}{2}} \in \mathcal{B}\left(\{\Psi_0\}^\perp, \mathcal{H}^2(H_\#)\right) \tag{4.7}$$

Proof. Let $\mathcal{H}^1(\mathcal{C})$ be the first Sobolev space associated with $\mathcal{C}$. Then by lemma 3.1, a point z^2 is in the resolvent set of $\mathcal{C}$ if and only if the extension $z^2-\mathcal{C}:\mathcal{H}^1(\mathcal{C})\to\mathcal{H}^{-1}(\mathcal{C})$ is invertible. Since $\mathcal{H}^1(\mathcal{C})=D(H_\#)=\mathcal{H}^2(H_\#)$ (by proposition 4.2), this is equivalent to the map

$$\begin{aligned} z^2-\mathcal{C}:&\mathcal{H}^2(H_\#)\to\mathcal{H}^{-2}(H_\#)\\ &\Phi\mapsto z^2\langle\cdot,\Phi\rangle-q_{\mathcal{C}}(\cdot,\Phi)=z^2\langle\cdot,\Phi\rangle-\langle H_\#\cdot,H_\#\Phi\rangle-\langle H_\#^{\frac12}\cdot,B^*FBH_\#^{\frac12}\Phi\rangle\end{aligned}$$

being bijective (by the closed graph theorem). However, the right-hand side of the above is equal to

$$q_{\mathcal{C}_\#(z)}\left(H_\#^{\frac12}\cdot,H_\#^{\frac12}\Phi\right)=H_\#^{\frac12}\mathcal{C}_\#(z)H_\#^{\frac12}\Phi,$$

where $\mathcal{C}_\#(z)$ is the unique extension of $\mathcal{C}_\#(z)$ in $\mathcal{B}(\mathcal{H}^1(H_\#),\mathcal{H}^{-1}(H_\#))$. In particular, we have

$$z^2-\mathcal{C}=H_\#^{\frac12}\mathcal{C}_\#(z)H_\#^{\frac12}\quad\text{as a map from }\mathcal{H}^2(H_\#)\text{ to }\mathcal{H}^{-2}(H_\#).\tag{4.8}$$

Thus since $H_\#^{\frac12}:\mathcal{H}^s(H_\#)\to\mathcal{H}^{s-1}(H_\#)$ is an isomorphism for every $s\in\mathbb{R}$, we conclude that $z^2-\mathcal{C}$ is invertible on $\mathcal{B}(\mathcal{H}^2(H_\#),\mathcal{H}^{-2}(H_\#))$ if and only if $\mathcal{C}_\#(z)$ is invertible on $\mathcal{B}(\mathcal{H}^1(H_\#),\mathcal{H}^{-1}(H_\#))$.

To show (4.7), we note that if either $\mathcal{C}_\#(z)$ or $z^2-\mathcal{C}$ is invertible, then from (4.8) we obtain

$$\left(z^2-\mathcal{C}\right)^{-1}=H_\#^{-\frac12}\mathcal{C}_\#(z)^{-1}H_\#^{-\frac12}\quad\text{in }\mathcal{B}\left(\mathcal{H}^{-2}(H_\#),\mathcal{H}^2(H_\#)\right).\tag{4.9}$$

Since $H_\#^{-\frac12}\mathcal{C}_\#(z)^{-1}$ maps $\{\Psi_0\}^\perp$ bijectively to $\mathcal{H}^3(H_\#)$, equation (4.9) implies that

$$\left(z^2-\mathcal{C}\right)\Phi\in\mathcal{H}^3(H_\#)\quad\text{for any }\Phi\in\mathcal{H}^{-1}(H_\#).$$

Equation (4.7) now follows by multiplying equation (4.9) by $H_\#^{\frac12}$ on the left and on the right. □

4.2.2. Proof of theorem 2.3. We are now in position to prove theorem 2.3. For this, we shall use the following well-known resolvent identity.

Lemma 4.4 (first resolvent identity). *Let $\mathcal{C}_\#(z)$ be the operator defined in (4.6). Then, if the operators $\mathcal{C}_\#(z)$ and $(z^2H_\#^{-1}-H_\#):D(H_\#)\to\{\Psi_0\}^\perp$ are both invertible, we have*

$$\begin{aligned}\mathcal{C}_\#(z)^{-1}-\left(z^2H_\#^{-1}-H_\#\right)^{-1}&=2\mathcal{C}_\#(z)^{-1}B^*FB\left(z^2H_\#^{-1}-H_\#\right)^{-1}&(4.10)\\&=2\left(z^2H_\#^{-1}-H_\#\right)^{-1}B^*FB\mathcal{C}_\#(z)^{-1}.&(4.11)\end{aligned}$$

Proof of theorem 2.3. First, note that from the Dyson equation (1.1), the simple estimate $\sup_{t\in\mathbb{R}}\|\chi_H(t)\|\leqslant\|B\|\|B^*\|=\|B\|^2$, and Gronwall's inequality we have

$$\|\chi_F(t)\|\leqslant\|B\|^2e^{\|B\|^2\|F\|t}\quad\text{for}t\geqslant0.$$

In particular, the Fourier transform is well-defined and analytic for $\mathrm{Im}(z) > \|B\|^2\|F\|$. In this case, by the convolution property of the Fourier transform, we have

$$\widehat{\chi_F}(z) = \widehat{\chi_H}(z) + \widehat{\chi_H}(z)F\widehat{\chi_F}(z), \tag{4.12}$$

which is the frequency version of the Dyson equation.

The idea now is to find a representation formula for the inverse of the dielectric operator

$$\varepsilon(z) := 1 - \widehat{\chi_H}(z)F = 1 - 2B\left(z^2H_\#^{-1} - H_\#\right)^{-1}B^*F,$$

where the second equality comes from the expression

$$\widehat{\chi_H}(z) = B\left((z-H_\#)^{-1} - (z+H_\#)^{-1}\right)B^* = 2B\left(z^2H_\#^{-1} - H_\#\right)^{-1}B^*.$$

For this, we can now use the resolvent identities from lemma 4.4. Precisely, let $\mathcal{C}_\#(z)$ be defined as in equation (4.6). Thus since $\mathcal{C}$ is self-adjoint and bounded from below by $-\|B^*FB\|^2$, lemma 4.3 guarantees that $\mathcal{C}_\#(z)$ is invertible for any z with $|\mathrm{Im}(z)| \geqslant \|B^*FB\|$. Similarly, the operator

$$z^2H_\#^{-1} - H_\# = H_\#^{-\frac{1}{2}}\left(z^2 - H_\#^2\right)H_\#^{-\frac{1}{2}}$$

is invertible for any z with $z^2 \notin (0,\infty)$. We now claim that

$$\varepsilon(z)^{-1} = 1 + 2B\mathcal{C}_\#(z)^{-1}B^*F \quad \text{for any } z \text{ with } \mathrm{Im}(z) \text{ large.}$$

Indeed, from (4.10) we have

$$\begin{aligned}&\left(1 + 2B\mathcal{C}_\#(z)^{-1}B^*F\right)\varepsilon(z)\\ &\quad = 1 + 2B\underbrace{\left(\mathcal{C}_\#(z)^{-1} - \left(z^2H_\#^{-1} - H_\#\right)^{-1} - 2\mathcal{C}_\#(z)^{-1}B^*FB\left(z^2H_\#^{-1} - H_\#\right)^{-1}\right)}_{=0}B^*F = 1.\end{aligned} \tag{4.13}$$

On the other hand, equation (4.11) implies that $\varepsilon(z)(1 + 2B\mathcal{C}_\#(z)^{-1}B^*) = 1$ as well, which proves our claim. To conclude, we note that from the (frequency) Dyson equation (4.12) we have

$$\begin{aligned}\widehat{\chi_F}(z) &= \varepsilon(z)^{-1}\widehat{\chi_H}(z) = \left(1 + 2B\mathcal{C}_\#(z)^{-1}B^*F\right)2B\left(z^2H_\#^{-1} - H_\#\right)^{-1}B^*\\ &= 2B\left(\left(z^2H_\#^{-1} - H_\#\right)^{-1} + 2\mathcal{C}_\#(z)^{-1}B^*FB\left(z^2H_\#^{-1} + H_\#\right)^{-1}\right)B^* \overset{(4.10)}{=} 2B\mathcal{C}_\#(z)^{-1}B^*.\end{aligned}$$

Thus theorem 2.3 follows from the equation above and lemma 4.3. □

4.3. Proof of corollaries 2.4–2.6

We now present the proofs of the corollaries from theorem 2.3. We start with the proof of corollary 2.4.

Proof of corollary 2.4. First, note that the power series of the sinc function is composed only of even terms. Thus the function

$$\lambda \in \mathbb{C} \mapsto f(\lambda) := \operatorname{sinc}\left(\sqrt{\lambda}\right)$$

defines an analytic function in the whole complex plane. Moreover, this function is bounded on any half-line $\{\lambda \in \mathbb{R} : \lambda \geqslant -c\}$ for $c > 0$. In particular, the operator $f(t^2\mathcal{C})$ defined via the spectral theorem belongs to $\mathcal{B}(\{\Psi_0\}^{\perp})$ for any $t \in \mathbb{R}$. In fact, by taking any function $g : \mathbb{R} \to [1, \infty)$ satisfying $g(\lambda) \sim \sqrt{\lambda}$ for λ big we can re-write

$$f\left(t^2\mathcal{C}\right) = g\left(\mathcal{C}\right)^{-\frac{1}{2}} h\left(t, \mathcal{C}\right) g\left(\mathcal{C}\right)^{-\frac{1}{2}}, \tag{4.14}$$

where $h(t, \lambda) = g(\lambda) f(t^2\lambda)$ is bounded on $\sigma(\mathcal{C})$. So by recalling that $\mathcal{H}^s(\mathcal{C}) = \mathcal{H}^{2s}(H_\#)$ for any $-1 \leqslant s \leqslant 1$ (because $\mathcal{H}^1(\mathcal{C}) = D(H_\#)$ with equivalence of norms), equation (4.14) implies that

$$f\left(t^2\mathcal{C}\right) \in \mathcal{B}\left(\mathcal{H}^{-1}\left(H_\#\right), \mathcal{H}^1\left(H_\#\right)\right).$$

Therefore, the operator-valued map

$$t \in \mathbb{R} \mapsto \widetilde{\chi}\left(t\right) := -2\theta\left(t\right) t B^* H_\#^{\frac{1}{2}} f\left(t^2\mathcal{C}\right) H_\#^{\frac{1}{2}} B \tag{4.15}$$

defines a strongly continuous family of operators in $\mathcal{B}(L^2_{\rho_0}, L^2_{\frac{1}{\rho_0}})$. To conclude the proof, we can use the identity

$$\int_0^\infty \frac{\sin(\lambda t)}{\lambda} e^{i(\omega + i\eta)t} \mathrm{d}t = \frac{-1}{(\omega + i\eta)^2 - \lambda^2} \quad \text{(valid for any } \eta > |\mathrm{Im}(\lambda)|\text{)}$$

to show that the Fourier transform of $\chi_F(t) e^{-\eta t}$ and $\widetilde{\chi}(t) e^{-i\eta t}$ coincide for η large enough, and therefore, $\widetilde{\chi}(t) = \chi_F(t)$ for every $t \in \mathbb{R}$. (Note that equality holds everywhere because both functions are strongly continuous.) □

Next, let us turn to the proof of the stability criterion.

Proof of corollary 2.5. First, note that

$$\mathcal{M} = H_\# + 2B^* F B = -\mathcal{C}\left(0\right),$$

where $\mathcal{C}_\#(z)$ is the operator defined in (4.6). In particular, by lemma 4.3 we have $0 \in \sigma(\mathcal{C})$ if and only if $0 \in \sigma(\mathcal{M})$. Moreover, from the proof of lemma 4.3 we know that

$$q_{\mathcal{C}}\left(\Psi, \Psi\right) = q_{\mathcal{M}}\left(H_\#^{\frac{1}{2}}\Psi, H_\#^{\frac{1}{2}}\Psi\right) \quad \text{for any } \Psi \in D\left(H_\#\right). \tag{4.16}$$

Since a self-adjoint operator is non-negative if and only if its quadratic form is non-negative, the above identity (and the fact that $H_\#^{\frac{1}{2}} : D(H_\#) \to \mathcal{H}^1(H_\#)$ is bijective) implies that $\mathcal{C} \geqslant 0$ if and only if $\mathcal{M} \geqslant 0$, which completes the proof. □

Remark (quantitative stability). To prove estimate (2.21), one can directly use (4.16). To prove estimate (2.22), we let $\mathcal{C} \geqslant \delta$ and note that from (4.16) and the definition of $\mathcal{M}$ we have

$$q_{\mathcal{M}}(\Psi,\Psi) \geqslant \max\left\{\delta \|H_{\#}^{-\frac{1}{2}}\Psi\|^2, \|H_{\#}^{\frac{1}{2}}\Psi\|^2 - 2\|B^*FB\|\|\Psi\|^2\right\}.$$

Combining this estimate with the inequality

$$\|H_{\#}^{\frac{1}{2}}\Psi\| \geqslant \left(\|H_{\#}^{-\frac{1}{2}}\Psi\|\right)^{-1}\langle H_{\#}^{\frac{1}{2}}\Psi, H_{\#}^{-\frac{1}{2}}\Psi\rangle = \|H_{\#}^{-\frac{1}{2}}\Psi\|\|\Psi\|^2$$

and minimising over $\|H_{\#}^{-\frac{1}{2}}\Psi\| \in \mathbb{R}_+$ for normalised $\|\Psi\| = 1$ yields (2.22).

Lastly, we present the proof of corollary 2.6.

Proof of corollary 2.6. Let us define

$$\widetilde{\chi}(z) := BH_{\#}^{\frac{1}{2}} \int_{\sigma_1(\mathcal{C})} \frac{2}{z^2-\lambda} \mathrm{d}P_{\lambda}^{\mathcal{C}} H_{\#}^{\frac{1}{2}} B^*.$$

Then by multiplying and dividing by $g(\mathcal{C})^{\frac{1}{2}}$ as we did in equation (4.14), we see that $\widetilde{\chi}(z)$ is bounded on $\mathcal{B}(L^2_{\rho_0}, L^2_{\frac{1}{\rho_0}})$ for any $z^2 \notin \sigma_1(\mathcal{C})$. Moreover, $\widetilde{\chi}(z)$ is meromorphic on

$$\mathcal{D}_F = \left\{z \in \mathbb{C} : z^2 \notin \sigma_1^{\mathrm{ess}}(\mathcal{C})\right\}, \tag{4.17}$$

and its poles are located at $\{z \in \mathbb{C} : z^2 \in \sigma_1^{\mathrm{disc}}(\mathcal{C})\}$. From the spectral gap assumption on $\sigma_1(\mathcal{C})$, the open set $\mathcal{D}_F$ is connected. Thus since $\widehat{\chi_F}(z) = \widetilde{\chi}(z)$ for $\mathrm{Im}(z)$ big enough, the function $\widetilde{\chi}$ is the unique meromorphic extension of $\widehat{\chi_F}$ to $\mathcal{D}_F$.

To show that this extension is maximal, we can now use Stone's formula as we did in the proof of theorem 2.1. Precisely, let $\mu_0 \in \mathbb{C}$ with $\mu_0^2 \in \mathbb{R}$ and suppose that $\widehat{\chi_F}$ can be analytically extended to a neighbourhood U of μ_0. Then it suffices to show that $\mu_0^2 \notin \sigma_1(\mathcal{C})$. In the case $\mu_0^2 > 0$, we can assume that $\overline{U}$ does not intersect the imaginary axis and define

$$\alpha^{\pm}(\mu,\eta) = -\mu + \sqrt{\mu^2 \pm i\eta}, \tag{4.18}$$

where we choose the branch of the square root such that $\lim_{\eta\to 0}\alpha^{\pm}(\eta,\mu) = 0$. Note that $\alpha^{\pm}$ is continuous in a neighbourhood of $\eta = 0$ and $\mu \in U$. Thus from the continuity of $\widehat{\chi_F}$ on U and Stone's formula in lemma 3.2 we have

$$\begin{aligned}
0 &= \lim_{\eta\to 0^+} \int_{\mathbb{R}_+} 2\mu f(\mu^2)\left(\widehat{\chi_F}(\mu+\alpha^+(\mu,\eta)) - \widehat{\chi_F}(\mu+\alpha^-(\mu,\eta))\right)\mathrm{d}\mu \\
&= \lim_{\eta\to 0^+} BH_{\#}^{\frac{1}{2}} \int_{\mathbb{R}_+} 2\mu f(\mu^2)\left(\left(\mu^2+i\eta-\mathcal{C}\right)^{-1} - \left(\mu^2-i\eta-\mathcal{C}\right)^{-1}\right)\mathrm{d}\mu H_{\#}^{\frac{1}{2}}B^* \\
&= BH_{\#}^{\frac{1}{2}} \int_{\mathbb{R}} f(\mu)\,\mathrm{dP}_{\mu}^{\mathcal{C}} H_{\#}^{\frac{1}{2}} B^*
\end{aligned}$$

for any $f \in C_c^{\infty}(\mathbb{R})$ with support on $\{\lambda^2 \in U \cap \mathbb{R}\}$. As in the proof of theorem 2.1, we can now use the strong-convergence property of the functional spectral calculus to conclude that $\mu_0^2 \notin \sigma_1(\mathcal{C})$.

In the case $\mu_0^2 < 0$, we can choose the neighbourhood U so that $\overline{U}$ does not intersect the real axis. By defining $\alpha^{\pm}(\mu,\eta)$ via (4.18) with the opposite branch of the square root, and using similar arguments, one can prove that $\mu_0^2 \notin \sigma_1(\mathcal{C})$. Finally, if $\mu_0 = 0$, then μ_0 is at most an isolated point in $\sigma_1(\mathcal{C})$ by the preceding arguments. In this case, however, μ_0 would be a pole of $\widehat{\chi_F}$, which is not possible because we assumed that $\widehat{\chi_F}$ is bounded around μ_0. Therefore, $\mu_0^2 \notin \sigma_1(\mathcal{C})$, which concludes the proof. □

4.4. Proof of theorem 2.7

For the proof of theorem 2.7, it is more convenient to work with the single-particle excitation spectrum of $H_\#^2$ than of $H_\#$, where the former is defined as

$$\sigma_1\left(H_\#^2\right) := \left\{\lambda \in \mathbb{R} : BP^{H_\#^2}\left(B_\epsilon(\lambda)\right) \neq 0 \quad \text{for any } \epsilon > 0 \text{ small}\right\}.$$

More precisely, note that from the definitions of $\mathcal{D}$ and $\mathcal{D}_F$ (see (2.13) and (2.23)), the proof of theorem 2.7 is done if we show that

$$\sigma_1^{\mathrm{ess}}(\mathcal{C}) = \sigma_1^{\mathrm{ess}}\left(H_\#^2\right), \tag{4.19}$$

where the essential part of $\sigma_1(H_\#^2)$ is defined in the same way as for $H_\#$. For this, the first step is the following lemma.

Lemma 4.5 (reducing subspaces of $H_\#^2$ and $\mathcal{C}$). *Let*

$$V_H := P^{H_\#^2}\left(\sigma_1\left(H_\#^2\right)\right) \quad \text{and} \quad V_{\mathcal{C}} := P^{\mathcal{C}}\left(\sigma_1(\mathcal{C})\right). \tag{4.20}$$

Then V_H and $V_{\mathcal{C}}$ are reducing subspaces for both $H_\#^2$ and $\mathcal{C}$ and we have

$$\sigma_1(\mathcal{C}) \subset \sigma\left(\mathcal{C}|_{V_H}\right) \quad \text{and} \quad \sigma_1\left(H_\#^2\right) \subset \sigma\left(H_\#^2|_{V_{\mathcal{C}}}\right). \tag{4.21}$$

Proof. From the spectral theorem, V_H and $V_{\mathcal{C}}$ are clearly reducing subspaces for $H_\#^2$ and $\mathcal{C}$, respectively. Let us then show that V_H is reducing for $\mathcal{C}$. First, we claim that

$$D\left(H_\#^2\right) \cap V_H^\perp = D(\mathcal{C}) \cap V_H^\perp \quad \text{and} \quad H_\#^2|_{D\left(H_\#^2\right)\cap V_H^\perp} = \mathcal{C}|_{D\left(H_\#^2\right)\cap V_H^\perp}. \tag{4.22}$$

To prove this claim, first note that there exists a sequence $\{(\lambda_j,\epsilon_j)\}_{j\in\mathbb{N}} \subset \mathbb{R}\times(0,1]$ such that

$$BP^{H_\#^2}\left(B_{\epsilon_j}(\lambda_j)\right) = 0 \quad \text{for any } j \text{ and } \lim_{m\to\infty}\sum_{j=1}^m P^{H_\#^2}\left(B_{\epsilon_j}(\lambda_j)\right) = P^{H_\#^2}\left(\mathbb{R}\setminus\sigma_1\left(H_\#^2\right)\right) =: P_{V_H^\perp}$$

in the strong sense. As a consequence,

$$BP_{V_H^\perp} = 0 \quad \text{and} \quad P_{V_H^\perp}B^* = 0. \tag{4.23}$$

Next, recall that

$$q_{\mathcal{C}}(\cdot,\cdot) = q_{H_\#^2}(\cdot,\cdot) + 2\langle H_\#^{\frac12}\cdot, B^*FBH_\#^{\frac12}\cdot\rangle.$$

Thus since $P_{V_H^\perp} = P^{H_\#^2}(\mathbb{R}\setminus\sigma_1(H_\#^2))$ commutes with $H_\#^{\frac{1}{2}}$, equation (4.23) implies that

$$q_{\mathcal{C}}\left(\Psi, P_{V_H^\perp}\Phi\right) = q_{H_\#^2}\left(\Psi, P_{V_H^\perp}\Phi\right) = q_{H_\#^2}\left(P_{V_H^\perp}\Psi, \Phi\right) = q_{\mathcal{C}}\left(P_{V_H^\perp}\Psi, \Phi\right) \tag{4.24}$$

for any $\Psi, \Phi \in D(H_\#)$. From the first identity in (4.24), we see that (4.22) holds. From the last identity in (4.24), we find that $P_{V_H^\perp}$ maps $D(\mathcal{C})$ to itself and V_H and $V_H^\perp$ are invariant subspaces for $\mathcal{C}$. We thus conclude from lemma 3.5 that V_H is a reducing subspace for $\mathcal{C}$.

To prove the first identity in (4.21), we now let $\lambda \notin \sigma(\mathcal{C}|_{V_H})$ and show that $\lambda \notin \sigma_1(\mathcal{C})$. So first, as $\sigma(\mathcal{C}|_{V_H})$ is closed, we can find $\epsilon > 0$ such that $B_\epsilon(\lambda)\cap\sigma(\mathcal{C}|_{V_H}) = \emptyset$. Thus from the block decomposition in theorem 3.4, we must have ran $P^{\mathcal{C}}(B_\epsilon(\lambda)) \subset V_H^\perp$. But since $P_{V_H^\perp}$ commutes with $H_\#$, we find that

$$BH_\#^{\frac{1}{2}}P^{\mathcal{C}}(B_\epsilon(\lambda)) = BH_\#^{\frac{1}{2}}P_{V_H^\perp}P^{\mathcal{C}}(B_\epsilon(\lambda)) = BP_{V_H^\perp}H_\#^{\frac{1}{2}}P^{\mathcal{C}}(B_\epsilon(\lambda)) \overset{(4.23)}{=} 0,$$

which implies that $\lambda \notin \sigma_1(\mathcal{C})$ by definition.

Finally, to prove that $V_{\mathcal{C}}$ is reducing for $H_\#^2$ and that the second inclusion in (4.21) holds, we can reverse the roles of $\mathcal{C}$ and $H_\#^2$. More precisely, we let $\alpha > 0$ be big enough (e.g. $\alpha > \|B^*FB\|^2 + 1$ will do) and note that

$$\begin{aligned} &q_{H_\#^2}(\cdot,\cdot) = q_{\mathcal{C}}(\cdot,\cdot) - \langle(\mathcal{C}+\alpha)^{\frac{1}{4}}\cdot, \widetilde{B}^*F\widetilde{B}(\mathcal{C}+\alpha)^{\frac{1}{4}}\cdot\rangle, \\ &\sigma_1\left(H_\#^2\right) = \left\{\lambda\in\mathbb{R} : \widetilde{B}(\mathcal{C}+\alpha)^{\frac{1}{4}}P^{H_\#^2}(B_\epsilon(\lambda)) \neq 0 \quad \text{for small } \epsilon > 0\right\}, \quad \text{and} \\ &\sigma_1(\mathcal{C}) = \left\{\lambda\in\mathbb{R} : \widetilde{B}P^{\mathcal{C}}(B_\epsilon(\lambda)) \neq 0 \quad \text{for small } \epsilon > 0\right\}, \end{aligned}$$

where

$$\widetilde{B} := BH_\#^{\frac{1}{2}}(\mathcal{C}+\alpha)^{-\frac{1}{4}} \tag{4.25}$$

is bounded on $\{\Psi_0\}^\perp$ because $\mathcal{H}^{\frac{1}{2}}(\mathcal{C}) = \mathcal{H}^1(H_\#)$. So repeating the same steps from before with the roles of $\mathcal{C}$ and $H_\#^2$ exchanged, the result follows. $\square$

Next, we use the compactness assumption from theorem 2.7 to show that the essential spectrum of $\mathcal{C}|_{V_H}$,respectively, $\mathcal{C}|_{V_{\mathcal{C}}}$ is equal to the essential spectrum of $H_\#^2|_{V_H}$, respectively, $H_\#^2|_{V_{\mathcal{C}}}$.

Lemma 4.6 (invariance of essential spectrum). *Suppose that $B^*FB \in \mathcal{B}_\infty(D(H_\#), \{\Psi_0\}^\perp)$, then*

$$\sigma^{\mathrm{ess}}(\mathcal{C}|_{V_H}) = \sigma^{\mathrm{ess}}\left(H_\#^2|_{V_H}\right) \quad \textit{and} \quad \sigma^{\mathrm{ess}}\left(H_\#^2|_{V_{\mathcal{C}}}\right) = \sigma^{\mathrm{ess}}(\mathcal{C}|_{V_{\mathcal{C}}}). \tag{4.26}$$

Proof. First, note that from lemma 4.3 and the resolvent identity in lemma 4.4 we have

$$(\mu+\mathcal{C})^{-1} = \left(\mu+H_\#^2\right)^{-1} + (\mu+\mathcal{C})^{-1}H_\#^{\frac{1}{2}}B^*FBH_\#^{\frac{1}{2}}\left(\mu+H_\#^2\right)^{-1} \tag{4.27}$$

as a bounded operator from $\mathcal{H}^{-1}(H_\#)$ to $\mathcal{H}^3(H_\#)$ for any $\mu > 0$ big enough. In particular, by recalling the chain of inclusions in equation (3.2), identity (4.27) holds in $\mathcal{B}(\{\Psi_0\}^\perp)$. Furthermore, from lemma 4.5 we have the block decomposition

$$(\mu+\mathcal{C})^{-1} = \begin{pmatrix} \left(\mu+H_\#^2\right)^{-1}|_{V_H^\perp} & 0 \\ 0 & \left(\mu+H_\#^2\right)^{-1}|_{V_H} + (\mu+\mathcal{C})^{-1}H_\#^{\frac{1}{2}}B^*FBH_\#^{\frac{1}{2}}\left(\mu+H_\#^2\right)^{-1}|_{V_H} \end{pmatrix}.$$

Since $B^*FB \in \mathcal{B}_\infty(D(H_\#), \{\Psi_0\}^\perp)$, the second term in (4.27) is compact in $\mathcal{B}(\{\Psi_0\}^\perp)$. Therefore, from Weyl's criterion, we conclude that

$$\sigma^{\mathrm{ess}}\left((\mu+\mathcal{C})^{-1}|_{V_H}\right) = \sigma^{\mathrm{ess}}\left(\left(\mu+H_\#^2\right)^{-1}|_{V_H}\right).$$

Moreover, a similar argument shows that

$$\sigma^{\mathrm{ess}}\left((\mu+\mathcal{C})^{-1}|_{V_\mathcal{C}}\right) = \sigma^{\mathrm{ess}}\left(\left(\mu+H_\#^2\right)^{-1}|_{V_\mathcal{C}}\right).$$

Equation (4.26) now follows from the relations $\sigma(f(A)) = f(\sigma(A))$ and $\ker f(\lambda) - f(A) = \ker \lambda - A$ (for injective f), which is a well-known corollary of the spectral theorem. □

Remark (weaker compactness assumption). From lemma 4.3 and the proof above, the weaker assumption $B^*FB \in \mathcal{B}_\infty\left(\mathcal{H}^3(H_\#), \mathcal{H}^{-2}(H_\#)\right)$ is actually enough to prove theorem 2.7.

We can now complete the proof of theorem 2.7.

Proof of theorem 2.7. Since σ_1 is closed, from the spectral theorem and the definitions of $V_\mathcal{C}$ and V_H we have

$$\sigma_1(\mathcal{C}) = \sigma(\mathcal{C}|_{V_\mathcal{C}}) \quad \text{and} \quad \sigma_1\left(H_\#^2\right) = \sigma\left(H_\#^2|_{V_H}\right).$$

In particular, we have

$$\sigma_1^{\mathrm{ess}}(\mathcal{C}) = \sigma^{\mathrm{ess}}(\mathcal{C}|_{V_\mathcal{C}}) \overset{(4.26)}{=} \sigma^{\mathrm{ess}}\left(H_\#^2|_{V_\mathcal{C}}\right) \quad \text{and} \quad \sigma_1^{\mathrm{ess}}\left(H_\#^2\right) = \sigma^{\mathrm{ess}}\left(H_\#^2|_{V_H}\right) \overset{(4.26)}{=} \sigma^{\mathrm{ess}}(\mathcal{C}|_{V_H}).$$

Hence to conclude the proof, it is enough to show that

$$\sigma_1^{\mathrm{ess}}(\mathcal{C}) \subset \sigma^{\mathrm{ess}}(\mathcal{C}|_{V_H}) \quad \text{and} \quad \sigma_1^{\mathrm{ess}}\left(H_\#^2\right) \subset \sigma^{\mathrm{ess}}\left(H_\#^2|_{V_\mathcal{C}}\right). \tag{4.28}$$

So suppose that $\lambda \notin \sigma^{\mathrm{ess}}(\mathcal{C}|_{V_H})$. Then λ can be, at most, an isolated point in the spectrum of $\mathcal{C}|_{V_H}$, which implies that

$$P^\mathcal{C}(B_\epsilon(\lambda)) = P^{\mathcal{C}|_{V_H}}(\{\lambda\}) + P^{\mathcal{C}|_{V_H^\perp}}(B_\epsilon(\lambda)) \quad (\text{ for } \epsilon > 0 \text{ small}).$$

From the fact that $P_{V_H^\perp}$ commutes with $H_\#$ and $BP_{V_H^\perp} = 0$ (see equation (4.23)), we find that

$$\text{rank } BH_\#^{\frac{1}{2}}P^\mathcal{C}(B_\epsilon(\lambda)) = \text{ rank } BH_\#^{\frac{1}{2}}P^{\mathcal{C}|_{V_H}}(\{\lambda\}) \leqslant \text{ rank } P^{\mathcal{C}|_{V_H}}(\{\lambda\}) < \infty,$$

which shows that $\lambda \notin \sigma_1^{\mathrm{ess}}(\mathcal{C})$. The second inclusion in (4.28) follows from the same arguments with the roles of $H_\#^2$ and $\mathcal{C}$ interchanged. □

4.5. Proof of proposition 2.9

For the proof of proposition 2.9, we shall use the following version of the Rellich–Kondrachov (aka compact Sobolev embedding) theorem.

Lemma 4.7 (Rellich–Kondrachov theorem). *Let $\{\Psi_j\}_{j\in\mathbb{N}} \subset \mathcal{H}^1(\Delta) = \{\Psi : \mathbb{R}^n \to \mathbb{C} : \|\Psi\|_{L^2(\mathbb{R}^n)} + \|\nabla\Psi\|_{L^2(\mathbb{R}^n)} < \infty\}$ be a bounded sequence. Then we can extract a subsequence such that for any $\Omega \subset \mathbb{R}^n$ with finite (Lebesgue) measure, we have*

$$\int_\Omega |\Phi_j(r) - \Phi_k(r)|^2 \mathrm{d}r \to 0 \quad \textit{as} \ \min\{j,k\} \to \infty. \tag{4.29}$$

Proof. By the standard compact Sobolev embedding (see [18, theorem 1, section 5.7]) and a standard diagonal argument, we can extract a subsequence such that (4.29) holds for $\Omega = B_M$ for any radius $M > 0$. Thus from Hölder's inequality,

$$\int_\Omega |\Phi_j - \Phi_k|^2 \mathrm{d}r \lesssim \int_{\Omega\cap B_M} |\Phi_j - \Phi_k|^2 \mathrm{d}r + |\Omega \setminus B_M|^{1-\frac{2}{p}} \|\Phi_j - \Phi_k\|_{L^p}^{\frac{2}{p}} \quad \text{for } p \in [2,\infty).$$

From the classical Sobolev embedding, the norms $\|\Phi_j - \Phi_k\|_{L^p}$ are uniformly bounded (in j,k) for any $2 < p \leqslant \frac{2n}{n-2}$. So choosing $M > 0$ arbitrarily large, the second term can be made arbitrarily small, which completes the proof. □

Proof of proposition 2.9. For the RPA, we have $B^* F^{\mathrm{RPA}} B = P_{\Psi_0^\perp} T$, where T is an integral operator with integral kernel given by

$$T(r_1,..,r_N,r_1',\dots,r_N') = N \sum_{j=1}^N \frac{\overline{\Psi_0(r_1,\dots,r_N)}\Psi_0(r_1',\dots,r_N')}{|r_j - r_1'|}.$$

Then from Cauchy–Schwarz,

$$\|T\|_{L^2(\mathbb{R}^{3N}\times\mathbb{R}^{3N})}^2 \lesssim \int_{\mathbb{R}^6} \frac{\rho_0(r)\rho_0(r')}{|r-r'|^2} \mathrm{d}r\mathrm{d}r' \lesssim \|\rho_0\|_{L^1\cap L^\infty}^2 \||\cdot|^{-2}\|_{L^1+L^\infty} < \infty,$$

which implies that T is Hilbert–Schmidt, and therefore compact (even in $\mathcal{B}_\infty(\{\Psi_0\}^\perp)$.

For the operator F_{ρ_0}, we first note that $B^* F_{\rho_0} B = B^* F_{\rho_0} S P_{\Psi_0^\perp}$ where

$$S\Phi(r) = N \int_{\mathbb{R}^{3N-3}} \overline{\Psi_0(r,r_2,\dots,r_N)} \Phi(r,r_2,\dots,r_N) \mathrm{d}r_2 \dots \mathrm{d}r_N.$$

In particular, from the assumption that $D(H_\#)$ is continuously embedded in $\mathcal{H}^1(\Delta)$, it is enough to show that for any bounded sequence $\{\Phi_j\}_{j\in\mathbb{N}}$ in $\mathcal{H}^1(\Delta)$, there exists a subsequence that satisfies (after re-labelling the indices)

$$\|F_{\rho_0} S(\Phi_j - \Phi_k)\|_{L^2_{\rho_0}}^2 \to 0 \quad \text{as } \min\{j,k\} \to \infty. \tag{4.30}$$

To find such a subsequence, we apply the Rellich–Kondrachov theorem (lemma 4.7). Precisely, let $\{\Phi_j\}$ be a subsequence satisfying (4.29) and define

$$I_\epsilon := \left\{ r \in \mathbb{R}^3 : \rho_0(r) > \epsilon \right\}.$$

Then by the Cauchy–Schwarz inequality (as in (4.1)) and assumption (2.29) we obtain

$$\begin{aligned}\|F_{\rho_0}S\left(\Phi_j-\Phi_j\right)\|_{L^2_{\rho_0}}^2 &\lesssim \int_{\mathbb{R}^3}\rho_0\left(r\right)^{2\delta+1}\left|\int_{\mathbb{R}^{3N-3}}\overline{\Psi_0\left(r,\tilde{r}\right)}\left(\Phi_j\left(r,\tilde{r}\right)-\Phi_k\left(r,\tilde{r}\right)\right)\mathrm{d}\tilde{r}\right|^2\mathrm{d}r\\ &\lesssim \int_{\mathbb{R}^3\setminus I_\epsilon}\rho_0\left(r\right)^{2\delta+2}\rho_{\Phi_j-\Phi_k}\left(r\right)\mathrm{d}r+\|\rho_0\|_{L^\infty}^{2\delta+2}\int_{I_\epsilon\times B_M}\left|\Phi_j\left(r,\tilde{r}\right)-\Phi_k\left(r,\tilde{r}\right)\right|^2\mathrm{d}r\mathrm{d}\tilde{r}\\ &+\int_{I_\epsilon}\rho_0\left(r\right)^{2\delta+1}\left|\int_{\mathbb{R}^{3N-3}\setminus B_M}\Psi_0\left(r,\tilde{r}\right)\left(\Phi_j-\Phi_k\right)\left(r,\tilde{r}\right)\mathrm{d}\tilde{r}\right|^2\mathrm{d}r,\end{aligned}$$

where $B_M\subset\mathbb{R}^{3N-3}$ is the ball of radius M centred at the origin. From the definition of I_ϵ, the first term is bounded by $\lesssim\epsilon^{2\delta+2}$. Moreover, the $\mathbb{R}^3$-measure of I_ϵ is finite (because $\rho_0\in L^1$) and the second term vanishes as $\min\{j,k\}\to\infty$ by (4.29). Lastly, we can bound the third term by

$$\begin{aligned}&\int_{I_\epsilon}\rho_0\left(r\right)^{2\delta+1}\left(\int_{\mathbb{R}^{3N-3}\setminus B_M}\Psi_0\left(r,\tilde{r}\right)\left(\Phi_j-\Phi_k\right)\left(r,\tilde{r}\right)\mathrm{d}\tilde{r}\right)^2\mathrm{d}r\\ &\quad\leqslant\max\left\{\epsilon^{-2\delta-1},\|\rho_0\|_{L^\infty}^{2\delta+1}\right\}\int_{I_\epsilon}\rho_{0,M}\left(r\right)\rho_{\Phi_j-\Phi_k}\left(r\right)\mathrm{d}r\leqslant C\left(\epsilon,\rho_0\right)\|\rho_{0,M}\|_{L^p}\|\rho_{\Phi_j-\Phi_k}\|_{L^q}\end{aligned}$$

for any $p^{-1}+q^{-1}=1$, where

$$\rho_{0,M}\left(r\right)=\int_{\mathbb{R}^{3N-3}\setminus B_M}|\Psi_0\left(r,\tilde{r}\right)|^2\mathrm{d}\tilde{r}.$$

Therefore, from the inequality

$$\|\nabla\sqrt{\rho_\Phi}\|_{L^2(\mathbb{R}^3)}\lesssim\|\nabla\Phi\|_{L^2(\mathbb{R}^{3N})}\quad\text{(see [20] for a proof)}$$

and the classical Sobolev embedding in $\mathbb{R}^3$, the norms $\|\rho_{\Phi_j-\Phi_k}\|_{L^q(\mathbb{R}^3)}$ are uniformly bounded for any $1\leqslant q\leqslant 3$. Consequently, by dominated convergence (recall that $\rho\in L^1\cap L^\infty$), the last term can be made arbitrarily small by choosing M large. □

Data availability statement

No new data were created or analysed in this study.

Appendix A. Optimality of weighted density spaces

We have shown that $\chi_H(t)\in\mathcal{B}(E^\star,E)$ for the spaces $E=L^2_{\frac{1}{\rho_0}}$ and $E=L^1(\Omega,\mathrm{d}\mu)$ (see equation (4.1)). In addition, if $\rho_0\in L^1\cap L^\infty$, then we can also choose $E=L^1(\Omega,\mathrm{d}\mu)\cap L^2(\Omega,\mathrm{d}\mu)$ by Hölder's inequality. Moreover, in this case we have the inclusions

$$L^2_{\frac{1}{\rho_0}}\subset L^1\left(\Omega,\mathrm{d}\mu\right)\cap L^2\left(\Omega,\mathrm{d}\mu\right)\subset L^1\left(\Omega,\mathrm{d}\mu\right).$$

Hence a natural question is whether $E=L^2_{\frac{1}{\rho_0}}$ is a minimal space for which $\chi_H\in C_s\left(\mathbb{R},\mathcal{B}(E^\star,E)\right)$. This question is not only natural but also relevant because a minimal E yields a maximal space of allowed adiabatic approximations $\mathcal{B}(E,E^\star)$.

We now give a partial answer to this question. The idea is the following. Looking back at the definition of χ_H, we see from a duality argument that $\chi_H(t) \in \mathcal{B}(E^\star, E)$ as long as we can show that $B : \{\Psi_0\}^\perp \to E$ is bounded. Thus a reasonable approach is to look for a minimal subspace E for which $B : \{\Psi_0\}^\perp \to E$ is bounded. It turns out that $E = L^2_{\frac{1}{\rho_0}}$ is minimal among a general class of function spaces.

Proposition A.1 (minimality of $L^2_{\frac{1}{\rho_0}}$). *Let E be a Banach space of μ-measurable functions such that*

(i) $\rho_0 \in E$ and
(ii) E has the lattice property , i.e. for any measurable g with $|g| \leqslant |f|$ a.e. for some $f \in E$, we have $g \in E$ and $\|g\|_E \leqslant \|f\|_E$.

Then if $B : \{\Psi_0\}^\perp \to E$ is bounded and $E \subset L^2_{\frac{1}{\rho_0}}$, we have $E = L^2_{\frac{1}{\rho_0}}$.

Proof. Let $f \in L^2_{\frac{1}{\rho_0}}$ and define $\Phi_f := B^* |f| \in \{\Psi_0\}^\perp$. Then the function

$$B\Phi_f = |f(r)| + N(N-1) \int_{\Omega^{N-1}} |f(r_2)| \frac{|\Psi_0(r, r_2, \ldots, r_N)|^2}{\rho_0(r)} \mathrm{d}\mu(r_2) \ldots \mathrm{d}\mu(r_N) - N^2 \langle 1, f \rangle \rho_0(r)$$

belongs to E by assumption. But since $\rho_0 \in E$, we have $|f| \leqslant B\Phi_f + N^2 \langle 1, f \rangle \rho_0 \in E$, which implies that $f \in E$ by the lattice property. □

In particular, we see that the space $L^2_{\frac{1}{\rho_0}}$ is minimal over the large class of Banach function spaces [26, chapter 6].

Remark (reduced weighted density spaces). The weighted density space $L^2_{\frac{1}{\rho_0}}$ is in fact the range of the operator B when extended to the whole tensor product space $\otimes_{j=1}^N L^2(\Omega, d\mu)$ via equation (2.8). When restricting this extension to the orthogonal complement $\{\Psi_0\}^\perp$ on $\otimes_{j=1}^N L^2(\Omega, d\mu)$, the range of B is given by the annihilator of $1 \in L^2_{\rho_0}$, i.e.

$$1^\perp := \left\{ f \in L^2_{\frac{1}{\rho_0}} : \int_\Omega f(r) \, \mathrm{d}\mu(r) = 0 \right\}.$$

In particular, we could replace the spaces $L^2_{\frac{1}{\rho_0}}$ and $L^2_{\rho_0}$, respectively, by $1^\perp$ and the quotient space

$$\left(1^\perp\right)^\star = L^2_{\rho_0}/1 = \{[f] : f \sim g \quad \text{if and only if} \quad f(r) - g(r) = \text{constant } \mu \text{ -a.e.}\}$$

with the induced norm. This choice of spaces incorporates the fact that possible variations of the density have zero average, thus preserving the number of particles in the system, and the fact that potentials differing by a constant give the same variation of the density. The main reason for working with the spaces $L^2_{\frac{1}{\rho_0}}$ and $L^2_{\rho_0}$ instead is that they simplify the presentation.

Appendix B. The Casida equations

In this section, we clarify how the Casida operator

$$\mathcal{C} = H_{\#}^2 + 2H_{\#}^{\frac{1}{2}} B^* F B H_{\#}^{\frac{1}{2}}$$

is related to the usual Casida matrix equations appearing in the physics literature [11].

For this, let us assume that the Hamiltonian H can be written as

$$H = \sum_{j=1}^{N} 1 \otimes \ldots \overbrace{h}^{jth \text{ position}} \ldots \otimes 1,$$

where 1 is the identity operator in the single-particle space $L^2(\Omega, \mathrm{d}\mu)$ and h is a self-adjoint operator in $L^2(\Omega, \mathrm{d}\mu)$. Let us also assume that h admits an orthonormal basis of eigenfunctions $\{\phi_j\}_{j\in\mathbb{N}}$ with eigenvalues $\{\lambda_j\}_{j\in\mathbb{N}}$. Under these assumptions, the set of Slater determinants

$$\{\Phi_I = \phi_{i_1} \wedge \ldots \wedge \phi_{i_N}\}_{I\in\mathcal{I}}, \quad \text{where} \quad \mathcal{I} := \left\{(i_1, \ldots, i_N) \in \mathbb{N}^N \quad \text{such that} \quad i_1 < i_2 \ldots < i_N\right\}$$

and $\phi_{i_1} \wedge \ldots \phi_{i_N}$ denotes the normalised antisymmetric tensor product of $\{\phi_i\}_{i\in I}$, is an orthonormal basis on the N-body wavefunction space $\mathcal{H}_N$ satisfying

$$H\Phi_I = \underbrace{\sum_{j=1}^{N} \lambda_{i_j}}_{=:\mathcal{E}_I} \Phi_I. \tag{B.1}$$

As a consequence, the spectral gap assumption on H implies that $\lambda_{N+1} > \lambda_N$ and the unique (up to phase) normalised ground state of H is given by the Slater determinant

$$\Psi_0 = \Phi_{I_0}, \quad \text{where} \quad I_0 = (1, \ldots, N).$$

We now want to write down the Casida operator $\mathcal{C}$ in the basis of Slater determinants $\{\Phi_I\}_{I\in\mathcal{I}}$. To this end, we first note that any Slater determinant containing at least two eigenfunctions with eigenvalue greater than λ_N (i.e. two excited orbitals) is on the kernel of the operator B (see (2.8)). More precisely, if we define

$$\mathcal{I}_2 := \{I = (i_1, \ldots, i_N) \in \mathcal{I} : i_{N-1} > N\}$$

then we have $B\Phi_I = 0$ for any $I \in \mathcal{I}_2$. In particular,

$$\langle \Phi_I, \mathcal{C}\Phi_J \rangle = \langle \Phi_I, H_{\#}^2 \Phi_I \rangle + \langle B\Phi_I, FB\Phi_J \rangle = \omega_I \omega_J \delta_{I,J}, \quad \text{if either } I \in \mathcal{I}_2 \text{ or } J \in \mathcal{J}_2,$$

where $\delta_{I,J} = 1$ if $I = J$ and 0 otherwise, and $\omega_I = \sum_{j=1}^{N} \lambda_{i_j} - \lambda_j = \mathcal{E}_I - \mathcal{E}_0 > 0$ is the excitation energy of the state Φ_I.

On the other hand, for Slater determinants with a single excited orbital, i.e.

$$\Phi_{j,k} = \phi_1 \wedge ..\phi_{j-1} \wedge \phi_{j+1} \ldots \wedge \phi_N \wedge \phi_k \quad \text{for some } j \leqslant N \text{ and } k > N,$$

we have

$$B\Phi_{j,k} = \overline{\phi_j}\phi_k. \tag{B.2}$$

Therefore, from equations (B.1) and (B.2) we conclude that

$$\begin{aligned}\langle \Phi_{j,k}, \mathcal{C}\Phi_{i,\ell}\rangle &= \langle \Phi_{j,k}, H_{\#}^2 \Phi_{i,\ell}\rangle + \langle B\Phi_{j,k}, FB\Phi_{i,\ell}\rangle \\ &= \overbrace{\omega_{j,k}\omega_{i,\ell}\delta_{j,i}\delta_{k,\ell} + 2\sqrt{\omega_{j,k}}\sqrt{\omega_{i,\ell}}\,\underbrace{\langle \overline{\phi_j}\phi_k, F\overline{\phi_i}\phi_\ell\rangle}_{=:\mathcal{K}_{jk,i\ell}}}^{=:\Omega_{jk,i\ell}},\end{aligned} \tag{B.3}$$

where $\omega_{j,k} = \lambda_k - \lambda_j > 0$ is the (single-particle) excitation energy of the state $\Phi_{j,k}$.

The matrices $\mathcal{K}_{jk,i\ell}$ and $\Omega_{jk,i\ell}$ are respectively the adiabatic (frequency-independent) versions of the coupling matrix [11, section 4.1] and of the $\Omega(\omega)$ matrix [11, equations (4.33) and (4.35)] appearing in Casida's original work[8]. This establishes the connection between the Casida operator $\mathcal{C}$ and the celebrated Casida equations used to compute approximations to the excitation energies and oscillator strengths of interacting quantum systems.

Appendix C. Local density approximation of exchange–correlation

In this section, we show that estimate (2.28) holds for the adiabatic local density approximation of the exchange–correlation operator with PW92 correlation.

For the (Dirac) exchange energy density, it is immediate to see that

$$\left.\frac{\mathrm{d}^2\left(\rho\varepsilon_{\mathrm{x}}^{\mathrm{HEG}}(\rho)\right)}{\mathrm{d}\rho^2}\right|_{\rho=\rho_0(r)} = -\frac{4C}{9}\rho_0(r)^{-\frac{2}{3}} \lesssim \|\rho_0\|_{L^\infty}^{\frac{1}{6}}\rho_0(r)^{-\frac{5}{6}},$$

which establishes estimate (2.28) for the exchange part.

For the (PW92) correlation part, we re-write the correlation energy density as

$$\rho\varepsilon_{\mathrm{c}}^{\mathrm{PW92}}(\rho) = \alpha(\rho)\log(1+\beta(\rho)), \tag{C.1}$$

where

$$\alpha(\rho) = -2A\left(\rho + \alpha_1\rho^{\frac{2}{3}}\right), \qquad \beta(\rho) = \frac{1}{\beta_1\rho^{-\frac{1}{6}} + \beta_2\rho^{-\frac{1}{3}} + \beta_3\rho^{-\frac{1}{2}} + \beta_4\rho^{-\frac{1+P}{3}}},$$

and we recall that all constants are positive. Hence, by taking derivatives we find that

$$\alpha(\rho) \lesssim \rho + \rho^{\frac{2}{3}}, \quad \dot{\alpha}(\rho) \lesssim 1 + \rho^{-\frac{1}{3}}, \quad \ddot{\alpha}(\rho) \lesssim \rho^{-\frac{4}{3}}, \tag{C.2}$$

and

$$0 \leqslant \beta(\rho) \lesssim \rho^{\max\left\{\frac{1}{2},\frac{1+P}{3}\right\}}, \quad \dot{\beta}(\rho) \lesssim \rho^{\max\left\{\frac{1}{2},\frac{1+P}{3}\right\}-1}, \quad \ddot{\beta}(\rho) \lesssim \rho^{\max\left\{\frac{1}{2},\frac{1+P}{3}\right\}-2}. \tag{C.3}$$

From the upper and lower bound on $\beta(\rho)$, we then have

$$0 \leqslant \log(1+\beta(\rho)) \lesssim \rho^{\max\left\{\frac{1}{2},\frac{1+P}{3}\right\}} \quad \text{and} \quad \frac{1}{1+\beta(\rho)} \lesssim 1. \tag{C.4}$$

[8] See also [22, equation (4.74)], where the different factor of 4 comes from the closed shell assumption and the spin degrees of freedom.

We can now take two derivatives in (C.1), and use estimates (C.2)–(C.4) to conclude that

$$\begin{aligned}\left.\frac{\mathrm{d}^2\left(\rho\varepsilon_{\mathrm{xc}}^{\mathrm{HEG}}(\rho)\right)}{\mathrm{d}\rho^2}\right|_{\rho=\rho_0(r)} =& \underbrace{\ddot{\alpha}(\rho_0(t))\log(1+\beta(\rho_0(r)))}_{\lesssim\rho_0(r)^{\max\left\{\frac{1}{2},\frac{1+P}{3}\right\}-\frac{4}{3}}} + \underbrace{2\frac{\dot{\alpha}(\rho_0(r))\dot{\beta}(\rho_0(t))}{1+\beta(\rho_0(r))}}_{\lesssim\left(1+\rho_0(r)^{\frac{1}{3}}\right)\rho_0(r)^{\max\left\{\frac{1}{2},\frac{1+P}{3}\right\}-\frac{4}{3}}} \\ &+ \underbrace{\frac{\alpha(\rho_0(t))\ddot{\beta}(\rho_0(r))}{1+\beta(\rho_0(t))}}_{\lesssim(1+\rho_0(r)^{\frac{1}{3}})\rho_0(r)^{\max\left\{\frac{1}{2},\frac{1+P}{3}\right\}-\frac{4}{3}}} - \underbrace{\frac{\alpha\left(\rho_0(t)\right)\dot{\beta}\left(\rho_0(t)\right)^2}{\left(1+\beta\left(\rho_0(r)\right)\right)^2}}_{\lesssim(1+\rho_0(r)^{\frac{1}{3}})\rho_0(r)^{2\max\left\{\frac{1}{2},\frac{1+P}{3}\right\}-\frac{4}{3}}} \\ \lesssim& \left(1+\|\rho_0\|_{L^\infty}^{\frac{1}{3}}+\|\rho_0\|_{L^\infty}^{\max\left\{\frac{1}{2},\frac{1+P}{3}\right\}}+\|\rho_0\|_{L^\infty}^{\max\left\{\frac{1}{2},\frac{1+P}{3}\right\}+\frac{1}{3}}\right)\rho_0(r)^{\max\left\{\frac{1}{2},\frac{1+P}{3}\right\}-\frac{4}{3}},\end{aligned}$$

which proves (2.28).

References

[1] Agmon S 1975 Spectral properties of Schrödinger operators and scattering theory *Ann. Scuola Norm. Sup. Pisa Cl. Sci.* **2** 151–218

[2] Agmon S 1982 *Lectures on Exponential Decay of Solutions of Second-Order Elliptic Equations: Bounds on Eigenfunctions of N-Body Schrödinger Operators* (*Mathematical Notes* vol 29) (Princeton University Press) (https://doi.org/10.2307/j.ctt13x1d8z)

[3] Amrein W O, de Monvel A B and Georgescu V 1996 *C_0-Groups, Commutator Methods and Spectral Theory of N-Body Hamiltonians* (*Modern Birkhäuser Classics*) (Birkhäuser Verlag) (https://doi.org/10.1007/978-3-0348-0733-3)

[4] Bai Z and Li R-C 2012 Minimisation principles for the linear response eigenvalue problem I: theory *SIAM J. Matrix Anal. Appl.* **33** 1075–100

[5] Bai Z and Li R-C 2013 Minimization principles for the linear response eigenvalue problem II: computation *SIAM J. Matrix Anal. Appl.* **34** 392–416

[6] Brabec J, Lin L, Shao M, Govind N, Yang C, Saad Y and Ng E G 2015 Efficient algorithms for estimating the absorption spectrum within linear response TDDFT *J. Chem. Theory Comput.* **11** 5197–208

[7] Burke K, Werschnik J and Gross E 2005 Time-dependent density functional theory: past, present and future *J. Chem. Phys.* **123** 62206

[8] Cancés E, Gontier D and Stoltz G 2016 A mathematical analysis of the GW^0 method for computing electronic excited energies of molecules *Rev. Math. Phys.* **28** 1650008

[9] Cancès E and Le Bris C 1999 On the time-dependent Hartree-Fock equations coupled with a classical nuclear dynamics *Math. Models Methods Appl. Sci.* **9** 963–90

[10] Cancès E and Stoltz G 2012 A mathematical formulation of the random phase approximation for crystals *Ann. Inst. H. Poincaré* C **29** 887–925

[11] Casida M E 1995 Time-dependent density functional response theory for molecules *Recent Advances in Density Functional Methods* (World Scientific) pp 155–92

[12] Casida M E 2009 Time-dependent density-functional theory for molecules and molecular solids *J. Mol. Struct.* **914** 3–18

[13] Ceperley D M and Alder B J 1980 Ground state of the electron gas by a stochastic method *Phys. Rev. Lett.* **45** 566–9

[14] Chadam J M and Glassey R T 1975 Global existence of solutions to the Cauchy problem for time-dependent Hartree equations *J. Math. Phys.* **16** 1122–30

[15] Corso T C, Dupuy M-S and Friesecke G 2023 The density-density response function in time-dependent density functional theory: mathematical foundations and pole shifting (arXiv:2301.13070)

[16] Dupuy M-S and Levitt A 2022 Finite-size effects in response functions of molecular systems *SMAI J. Comput. Math.* **8** 273–94

[17] Dyatlov S and Zworski M 2019 *Mathematical Theory of Scattering Resonances* (*Graduate Studies in Mathematics* vol 20) (American Mathematical Society) (https://doi.org/10.1090/gsm/200)

[18] Evans L C 2010 *Partial Differential Equations* 2nd edn (*Graduate Studies in Mathematics* vol 19) (American Mathematical Society) (https://doi.org/10.1090/gsm/019)
[19] Lewin M and Sabin J 2014 The Hartree equation for infinitely many particles, II: dispersion and scattering in 2D *Anal. PDE* **7** 1339–63
[20] Lieb E H 1983 Density functionals for Coulomb systems *Int. J. Quantum Chem.* **24** 243–77
[21] Lin L and Lu J 2019 *A Mathematical Introduction to Electronic Structure Theory* (Society for Industrial and Applied Mathematics) (https://doi.org/10.1137/1.9781611975802)
[22] Marques M A L, Maitra N T, Nogueira F M S, Gross E K U and Rubio A (eds) 2012 *Fundamentals of Time-Dependent Density Functional Theory* (*Lecture Notes in Physics* vol 837) (Springer) (https://doi.org/10.1007/978-3-642-23518-4)
[23] Olsen J, Jensen H J A and Jørgensen P 1988 Solution of the large matrix equations which occur in response theory *J. Comput. Phys.* **74** 265–82
[24] Perdew J P and Wang Y 1992 Accurate and simple analytic representation of the electron-gas correlation energy *Phys. Rev.* B **45** 13244–9
[25] Petersilka M, Gossmann U J and Gross E K U 1996 Excitation energies from time-dependent density-functional theory *Phys. Rev. Lett.* **76** 1212–5
[26] Pick L, Kufner A, John O and Fučík S 2013 *Function Spaces* 2nd edn (*De Gruyter Series in Nonlinear Analysis and Applications* vol 1) (De Gruyter) (https://doi.org/10.1515/9783110250428)
[27] Pusateri F and Sigal I M 2021 Long-time behaviour of time-dependent density functional theory *Arch. Ration. Mech. Anal.* **241** 447–73
[28] Reed M and Simon B 1972 *Methods of Modern Mathematical Physics. I. Functional Analysis* (Academic) (https://doi.org/10.1016/b978-0-12-585001-8.x5001-6)
[29] Reed M and Simon B 1975 *Methods of Modern Mathematical Physics. II. Fourier Analysis, Self-Adjointness* (Academic, Harcourt Brace Jovanovich, Publishers)
[30] Reed M and Simon B 1978 *Methods of Modern Mathematical Physics. IV. Analysis of Operators* (Academic, Harcourt Brace Jovanovich, Publishers)
[31] Schmüdgen K 2012 *Unbounded Self-Adjoint Operators on Hilbert Space* (*Graduate Texts in Mathematics* vol 265) (Springer) (https://doi.org/10.1007/978-94-007-4753-1)
[32] Schwinn K, Zapata F, Levitt A, Cancès E Luppi E and Toulouse J 2022 Photoionization and core resonances from range-separated density-functional theory: general formalism and example of the beryllium atom *J. Chem. Phys.* **156** 224106
[33] Simon B 1982 Schrödinger semigroups *Bull. Am. Math. Soc.* **7** 447–526
[34] Sprengel M, Ciaramella G and Borzì A 2017 A theoretical investigation of time-dependent Kohn-Sham equations *SIAM J. Math. Anal.* **49** 1681–704
[35] Thouless D J 1961 Vibrational states of nuclei in the random phase approximation *Nucl. Phys.* **22** 78–95
[36] Ullrich C 2012 *Time-Dependent Density-Functional Theory: Concepts and Applications* (*Oxford Graduate Texts*) (Oxford University Press) (https://doi.org/10.1093/acprof:oso/9780199563029.001.0001)
[37] Vasiliev I, Öğüt S and Chelikowsky J R 2002 First-principles density-functional calculations for optical spectra of clusters and nanocrystals *Phys. Rev.* B **65** 115416
[38] Zangwill A and Soven P 1980 Density-functional approach to local-field effects in finite systems: photoabsorption in the rare gases *Phys. Rev.* A **21** 1561–72