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Mathematical contributions to static and time-dependent density functional theory

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Abstract

In this dissertation, we analyze some mathematical models with applications in quantum chemistry and material science.

First, we study the exchange energy of the free electron gas in the thermodynamic limit. The free electron gas consists of a collection of non-interacting electrons trapped in a bounded region of space. The thermodynamic limit then corresponds to the limit where the number of electrons and the volume of the region goes to infinity with their ratio kept constant. In this limit, we derive a two-term asymptotic expansion with explicit coefficients for the exchange energy of the free electron gas. In addition, we derive a similar asymptotic expansion for semi-local density functionals when applied to the ground state density of the free electron gas. By matching the coefficients of these asymptotic expansions, we obtain a novel integral constraint on exchange density functionals, such as the celebrated generalized gradient approximations (GGA), that might be of interest to density functional theory (DFT).

The second part of the dissertation deals with the Dyson equation for the density-density response function that appears in the linear response formulation of time-dependent density functional theory (LR-TDDFT). This Dyson equation provides an efficient framework for computing the electronic excitation energies of large quantum systems. Here we study the well-posedness of the Dyson equation for some widely used adiabatic approximations of the exchange-correlation kernel of time-dependent density functional theory (TDDFT). Moreover, we present a rigorous analysis of the pole structure (in the frequency domain) of the solution of the Dyson equation within the random phase approximation (RPA). As a by-product of this analysis, we conclude that the excitation energies of the Kohn-Sham system always underestimate the excitation energies computed in the RPA. Finally, we show that the eigenvalues of the Casida matrix converge to the actual poles of the solution of the Dyson equation in the infinite basis limit, i.e., the limit where the number of virtual Kohn-Sham orbitals used to construct the Casida matrix goes to infinity.

Zusammenfassung

In dieser Dissertation analysieren wir einige mathematische Modelle mit Anwendungen in der Quantenchemie und den Materialwissenschaften.

Zuerst untersuchen wir die Austauschenergie des freien Elektronengases im thermodynamischen Limes. Das freie Elektronengas besteht aus einer Ansammlung einer nur durch das Pauli'sche Exklusionsprinzip aber nicht durch ein Potential wechselwirkenden Elektronen, die sich in einem endlichen Volumen bewegen. Der thermodynamische Limes entspricht dann dem Grenzwert, bei dem sowohl die Anzahl der Elektronen als auch das Volumen bei konstant gehaltenem Verhältnis gegen Unendlich gehen. In diesem Limes leiten wir eine Zwei-Term asymptotische Entwicklung mit expliziten Koeffizienten für die Austauschenergie des freien Elektronengases ab. Darüber hinaus leiten wir eine analoge asymptotische Entwicklung für semilokale Dichtefunktionale ab, angewendet auf die Grundzustandsdichte des freien Elektronengases. Indem wir die Koeffizienten dieser asymptotischen Entwicklungen abgleichen, erhalten wir eine neuartige Integralbedingung für Austauschdichtefunktionale wie beispielsweise die berühmte Verallgemeinerte Gradientennäherung (engl. GGA). Diese Bedingung könnte für die Entwicklung zukünftiger Dichtefunktionale von Interesse sein.

Der zweite Teil der Dissertation befasst sich mit der Dyson-Gleichung für die Dichte-Dichte-Antwortfunktion (engl. density-density response function) aus der Linear-Response-Formulierung der zeitabhängigen Dichtefunktionaltheorie (LR-TDDFT). Diese Dyson-Gleichung bietet eine effiziente Herangehensweise für die Berechnung der Anregungsenergien großer Elektronensysteme. Hier beweisen wir, dass die Dyson-Gleichung für einige weit verbreitete adiabatische Näherungen des Austauschkorrelationskerns der zeitabhängigen Dichtefunktionaltheorie (TDDFT) wohldefinierte und eindeutige L" osungen besitzt. Darüber hinaus präsentieren wir eine rigorose Analyse der Polstruktur (im Frequenzbereich) der Lösung der Dyson-Gleichung innerhalb der Zufälligen-Phasen-Approximation (RPA). Als Nebenprodukt dieser Analyse erhalten wir, dass die in der RPA berechneten Anregungsenergien in Bezug auf die Anregungsenergien des Kohn-Sham-Systems immer nach oben korrigiert sind. Schließlich zeigen wir, dass die Eigenwerte der Casida-Matrix gegen die wahren Pole der Lösung der Dyson-Gleichung konvergieren, wenn die Anzahl der virtuellen Kohn-Sham-Orbitale (die zum Konstruieren der Casida-Matrix verwendet werden) gegen Unendlich geht.

Contents

Chapter 1

Introduction and overview

The Schrödinger equation (SE)[106] is ubiquitous to quantum chemistry, where one is interested in understanding and accurately predicting many properties of atoms and molecules from first principles. In the situations where it can be solved explicitly, the Schrödinger equation yields remarkable results; the classic example is the Hydrogen atom, where the SE explains its stability and predicts the quantization of the absorption/emission spectrum in good agreement with experiments.

Unfortunately, the SE can not be solved analytically for most molecules, and one has to turn to numerical methods. The success of standard (wave function) methods, however, is very limited as the number of particles in the system grows. The reasons are in fact well-understood; in the words of Nobel prize winner Walter Kohn [64], these methods encounter an exponential wall when the number of particles exceeds $N \approx 10$. In other words, the SE suffers from the curse of dimension, which means that the computational cost for solving these equations (or, in fact, just storing the solutions) grows exponentially with the number of particles involved. Therefore, much effort from the scientific community has been invested into proposing and developing approximate (or effective) theories that can make quantitative predictions on specific properties of atoms and molecules. (See, for instance, [84] for a few of them.)

Among such theories, the density functional theory (DFT) of Kohn and Sham [65] stood out [13, 84, 90]; it has become the method of choice in most ab initio electronic structure calculations as can be seen from the impressive number of publications on the topic in the past years [12]. DFT is a formally exact theory for computing the electronic ground state energy and ground state density of molecules. Moreover, its time-dependent version (TDDFT) [19, 96, 103, 120] provides an efficient framework for computing the excitation energies. As opposed to the exponentially scaling cost for solving the SE, the computational cost of standard DFT and TDDFT calculations scales cubically, or sometimes even linearly [27, 80, 97], with the number of particles. In particular, DFT and TDDFT calculations on molecules with thousands of particles can now be performed [27, 98].

Despite this success, the DFT and TDDFT approaches ultimately rely on semi-empirical approximations of unknown functionals: the exchange-correlation (xc) func-

tional in the case of DFT and the exchange-correlation (xc) kernel in the case of (linear response) TDDFT. Consequently, the many different approximations developed so far (see [82] for an overview) can not be reliably applied to general atoms and molecules; a suitable approximation has to be chosen on a case-by-case basis, which undermines the role of DFT and TDDFT as predictive theories. Moreover, in the TDDFT case, the foundations of the theory are not yet justified in physically relevant cases [36], and a consistent mathematical framework is still missing.

In this thesis, we shall address two related problems. In the first part, we shall study exchange effects for the free electron gas. More precisely, we derive asymptotic expansion for the exact exchange energy and the exchange energy of general semi-local density functionals when applied to the free electron gas in the thermodynamic limit. By matching the coefficients of these asymptotic expansions, we obtain a novel exact constraint for semi-local functionals such as the celebrated generalized gradient approximations (GGA) [6, 92, 93]. As such functionals are usually designed by fitting a (relatively) simple ansatz to a mixture of exact constraints and empirical data, the constraint derived here might be useful for designing more accurate density functionals.

In the second part of this thesis, we study the Dyson equation that appears in the linear response formulation of time-dependent density functional theory (LR-TDDFT). The Dyson equation formally connects the density-density response function of an interacting system of interest to the density-density response function of an equivalent non-interacting system, the Kohn-Sham system. In this way, the Dyson equation provides an efficient framework for computing the excitation spectra of large systems. Here we present a functional analytic setting for the well-posedness of the Dyson equation that applies to general non-relativistic quantum mechanical systems and widely used adiabatic approximations of the exchange-correlation kernel. Furthermore, we analyze the poles of the solution of the Dyson equation, which in applications, correspond to the approximations of the excitation spectra of the interacting system of interest. These results set the linear response formulation of time-dependent density functional theory in the infinite-dimensional (or continuum) setting in a rigorous mathematical framework.

Let us now outline the content of this thesis. In the rest of this chapter, we present a short (and rather informal) introduction to DFT and TDDFT and then give an overview of the main results of this thesis. In Chapter 2 we study the exchange energy of the free electron gas on a cubic box. Using different methods, we then improve and generalize these results in Chapter 3. In Chapter 4, we study the Dyson equation from LR-TDDFT. All chapters are self-contained so that they can be read in any order.

1.1 Introduction to DFT and LR-TDDFT

In this section we present the basics of the (Kohn-Sham) density functional theory (KS-DFT) and of the linear response formulation of time-dependent density functional theory (LR-TDDFT). For more detailed introductions to these topics, we refer the reader to [90, 30, 79, 80, 84, 85] for DFT and to [30, 79, 83, 120] for TDDFT.

The plan for this section is the following. We start by introducing the ground and excited state problems in quantum mechanics and describing the standard variational approach for solving them. We then present the DFT approach for the ground state problem as initiated by Hohenberg-Kohn [57] and Kohn-Sham [65]. In the sequel, we describe the connection between linear response theory and the excitation energies of a given system. We then give a short introduction to TDDFT and present the linear response approach for computing the excitation energies within the framework of TDDFT.

1.1.1 The quantum ground state probem

In quantum mechanics, the state of an isolated system with N electrons is described by a (wave) function $\Psi : (\mathbb{R}^3)^N \to \mathbb{C}$ satisfying the following constraints:

- (Normalization) $\|\Psi\|^2_{L^2(\mathbb{R}^{3N})} = \int_{\mathbb{R}^{3N}} |\Psi(r_1, ..., r_N)|^2 \mathrm{d}r_1 ... \mathrm{d}r_N = 1$.
- (Anti-symmetry) $\Psi(r_{\sigma(1)}, ..., r_{\sigma(N)}) = \mathrm{sgn}(\sigma)\Psi(r_1, ..., r_N)$, for any permutation of N-variables $\sigma : \{1, ..., N\} \to \{1, ..., N\}$ and every points $r_1, ..., r_N \in \mathbb{R}^3$.

(For simplicity, we do not consider spin here.) The normalization constraint comes from the fact that $|\Psi(r_1, ..., r_N)|^2$ represents the probability density of finding electrons at the positions $(r_1, ..., r_N)$. The anti-symmetry accounts for the fact that all electrons are identical particles and that identical particles are not allowed to occupy the same quantum state. This is called the Pauli exclusion principle for fermions (e.g., electrons) and is one of the postulates of quantum mechanics. Hence, the set of admissible states of the system is the set of normalized functions in the anti-symmetric N-fold tensor product of $L^2(\mathbb{R}^3)$,

$$\mathcal{H}_N = \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3) = \{\Psi : \mathbb{R}^{3N} \to \mathbb{C} : \ \Psi \text{ anti-symmetric and } \|\Psi\|^2_{L^2(\mathbb{R}^{3N})} < \infty\},$$

which is a Hilbert space with respect to the standard $L^2(\mathbb{R}^{3N})$ inner-product

$$\langle \Psi, \Phi \rangle = \int_{\mathbb{R}^{3N}} \overline{\Psi(r_1, ..., r_N)} \Phi(r_1, ..., r_N) \mathrm{d}r_1 ... \mathrm{d}r_N.$$

As is often the case in physics, one is mostly (at least in a first analysis) interested in the states of the system that minimize some energy functional. For a system with N electrons, the energy functional usually has the form

$$\mathcal{E}[\Psi] = \int_{\mathbb{R}^{3N}} \frac{1}{2} |\nabla \Psi(r_1, ..., r_N)|^2 + \left(\sum_{1 \leqslant i < j \leqslant N} w(r_i - r_j) + \sum_{i=1}^{N} v(r_i) \right) |\Psi(r_1, ..., r_N)|^2 \mathrm{d}r_1 ... \mathrm{d}r_N,$$

where $\nabla \Psi$ is the (weak) gradient of Ψ and w and v are real-valued functions describing the electron-electron interaction and the interaction between the electrons and some external source, respectively. Here we use the convenient atomic units $m_e = e = 4\pi\epsilon_0 = \hbar = 1$, where m_e and e are respectively the mass and the charge of the electron, ϵ_0 is the vacuum

permittivity, and $\hbar$ is the reduced Planck's constant. Within the Born-Oppenheimer approximation for a molecule with M nuclei, the electron-electron interaction and the external potential are given by the Coulomb potential,

$$w(r) = \frac{1}{|r|} \quad \text{and} \quad v(r) = \sum_{m=1}^{M} \frac{Z_m}{|R_m - r|},$$

where Z_m and R_m are respectively the atomic number and position of the m^{th}-nucleus, and $|r| = \sum_{j=1}^{3} r_j^2$ is the standard norm in $\mathbb{R}^3$. Here we shall keep the discussion general and simply assume that v and w are regular enough real-valued functions.

The ground state problem then consists in finding the minimum value and the minimizer of the energy functional $\mathcal{E}$ over the set of admissible states:

$$\mathcal{E}_0 = \inf\left\{ \frac{\mathcal{E}[\Psi]}{\|\Psi\|^2} : \Psi \in \mathcal{H}_N \backslash \{0\}, \quad \|\nabla \Psi\|_{L^2(\mathbb{R}^{3N})} < \infty \right\} = \frac{\mathcal{E}[\Psi_0]}{\|\Psi_0\|^2}. \tag{1.1.1}$$

The value $\mathcal{E}_0$ and the minimizer Ψ_0 are called, respectively, the ground state energy and the ground state wave function (or simply ground state). Note that in general, the infimum may not be finite ($\mathcal{E}_0 = -\infty$) or not be attained. While conditions on v, w, and N for the minimum to be finite are fairly general, the existence (and uniqueness) of a minimizer is a subtle question [88, 100, 117]. Here we shall simply assume that the ground state energy is finite and a minimizer Ψ_0 exists.

Next, by formally computing the Euler-Lagrange equation of the above functional, we obtain the stationary Schrödinger equation (SSE)

$$\underbrace{\left(-\frac{1}{2}\Delta + \sum_{1 \leqslant i < j \leqslant N} w(r_i - r_j) + \sum_{1 \leqslant i \leqslant N} v(r_i) \right)}_{:= H_N(v,w)} \Psi_0 = \mathcal{E}_0 \Psi_0, \tag{1.1.2}$$

where Δ is the Euclidean Laplacian in $\mathbb{R}^{3N}$. The operator $H_N(v, w)$ is called the (N-body or N-particles) Hamiltonian of the system and, under suitable assumptions on v and w, defines a self-adjoint operator whose quadratic form domain is given by

$$\mathcal{Q}_N := Q\big(H_N(v,w)\big) = \mathcal{H}_N \cap H^1(\mathbb{R}^{3N}) = \{\Psi \in \mathcal{H}_N : \|\nabla \Psi\|_{L^2(\mathbb{R}^{3N})} < \infty\}.$$

(For the relation between self-adjointness and quadratic forms and the precise assumptions on v and w, we refer the reader to [63, 108].) Consequently, one can rigorously show that minimizing $\mathcal{E}$ is equivalent to finding a solution of the SSE (in $\mathcal{H}_N$) with $\mathcal{E}_0$ being the lowest value in the spectrum of $H_N(v, w)$.

Ideally, one would like to go beyond the ground state and compute all excited-state energies and wave functions of the system. These correspond to the pairs $(\mathcal{E}_j, \Psi_j) \in \mathbb{R} \times \mathcal{H}_N$ satisfying the SSE,

$$H_N(v,w)\Psi_j = \mathcal{E}_j \Psi_j,$$

where $\mathcal{E}_0 \leqslant \mathcal{E}_1 \leqslant \mathcal{E}_2 \leqslant ...$ are values in the discrete spectrum[1] of $H_N(v, w)$. It turns out that these states can also be computed by a variational principle known as the (Courant-Fischer) min-max principle:

$$\mathcal{E}_j = \frac{\mathcal{E}[\Psi_j]}{|\Psi_j|^2} = \min\left\{ \frac{\mathcal{E}[\Psi]}{\|\Psi\|^2} : \Psi \in \mathcal{Q}_N \cap \mathrm{span}\{\Psi_0, ..., \Psi_{j-1}\}^\perp \right\}, \tag{1.1.3}$$

where $\mathrm{span}\{\Psi_0, ..., \Psi_{j-1}\}^\perp$ denotes the orthogonal complement of the spaced spanned by the first $j-1$ excited states $\Psi_0, ..., \Psi_{j-1}$.

In summary, all solutions of the SSE and the associated energies (below the essential spectrum of $H_N(v, w)$) can be computed by solving the chain of variational problems described in (1.1.3). Unfortunately, standard numerical approaches for solving this problem scale exponentially with the number of electrons, which makes any calculation for systems with more than $N \approx 10$ electrons unfeasible. One possible way to bypass this problem is to completely abdicate of computing the ground state wave function and settle for reduced quantities such as the single-particle electronic density. This is the underlying idea of the density functional approach that we describe next.

Density functional theory: the Kohn-Sham scheme

In density functional theory, we shift the focus from the high-dimensional wave function to the low-dimensional single-particle electronic density (or simply density henceforth). For a system in a state $\Psi \in \mathcal{H}_N$, the corresponding density ρ_Ψ is defined as

$$\rho_\Psi(r) = N \int_{\mathbb{R}^{3N-3}} |\Psi(r, r_2, ..., r_N)|^2 \mathrm{d}r_2 ... \mathrm{d}r_N. \tag{1.1.4}$$

Note that, whilst the state of a system of N electrons is described by a function in $\mathbb{R}^{3N}$, its density ρ_Ψ is always a positive function in $\mathbb{R}^3$. Therefore, we would like to reformulate the ground state problem as a minimization over the space of densities.

The typical starting point of DFT is the foundational theorem of Hohenberg and Kohn [57]. The Hohenberg-Kohn (HK) theorem states that, for a fixed interaction potential w, there exists a one-to-one mapping between potentials v (up to an additive constant) and ground state single-particle densities of Hamiltonians of the form $H_N(v, w)$. Conceptually, this is an important step because it justifies the idea that any property of the system can be computed via its ground state density. In practice, however, the proof of the HK theorem does not lead to any practical insights into the precise form of the mapping between densities and potentials. We shall therefore skip any precise statement of the HK theorem[2] and directly present the approximated Kohn-Sham scheme [65] for computing the ground state density.

[1] The discrete spectrum of a self-adjoint operator is defined as the set of isolated eigenvalues of finite multiplicity [99, 117].

[2] For the precise statement of the HK Theorem, we refer the reader to [57, 90]. For a rigorous proof, we refer to [42, 43].

To this end, we first recall (see [76]) that the set of N-representable densities, defined as the image of the map $\Psi \mapsto \rho_\Psi$ (i.e. the map defined via (1.1.4)) with normalized $\Psi \in \mathcal{Q}_N = \mathcal{H}_N \cap H^1(\mathbb{R}^{3N})$, can be characterized as

$$\mathcal{R}_N = \left\{ \rho \in L^1(\mathbb{R}^3; [0,\infty)) : \sqrt{\rho} \in H^1(\mathbb{R}^3) \quad \text{and} \int_{\mathbb{R}^3} \rho(r)\mathrm{d}r = N \right\}. \tag{1.1.5}$$

Thus the minimization problem in (1.1.1) can be reformulated as

$$\mathcal{E}_0 = \inf_{\rho \in \mathcal{R}_N} \left\{ \int_{\mathbb{R}^3} \rho(r) v(r) \mathrm{d}r + \underbrace{\inf_{\substack{\Psi \in \mathcal{Q}_N \\ \rho_\Psi = \rho}} \left\{ \int_{\mathbb{R}^{3N}} \frac{1}{2} |\nabla \Psi(\tilde{r})|^2 + \sum_{1 \leqslant i < j \leqslant N} w(r_i - r_j) |\Psi(\tilde{r})|^2 \mathrm{d}\tilde{r} \right\}}_{:= F_{\mathrm{LL}}(\rho)} \right\}, \tag{1.1.6}$$

where F_{LL} is called the Levy-Lieb constrained search functional [70, 71, 76]. We now have a variational problem in terms of the density only; of course, nothing has been achieved so far as any evaluation of F_{LL} requires a minimization over the space of wave functions again.

Remark (The HK functional and v-representability)**.** *In the physics/chemistry literature, F_{LL} is sometimes called the Hohenberg-Kohn functional [57] and denoted by F_{HK}. However, strictly speaking, the HK functional is the restriction of F_{LL} to the set of w-interacting $\mathcal{V}$-representable densities*

$$\mathcal{R}_N(w) = \{\rho = \rho_{\Psi_0} : \Psi_0 \text{ is a ground state of } H_N(v,w) \text{ for some } v \in \mathcal{V}\} \subset \mathcal{R}_N, \tag{1.1.7}$$

where $\mathcal{V} \subset \{v : \mathbb{R}^3 \to \mathbb{R}\}$ is a suitable class of measurable potentials. For a mathematically rigorous account of the functionals F_{HK}, F_{LL}, and yet another functional defined as the Legendre transform of the energy, we refer to the work by Lieb [76].

The ingenious idea of Kohn and Sham [65] was then to approximate the functional F_{LL} in a way that is reasonably accurate and can be efficiently computed. Precisely, they proposed the following scheme. First, let us denote the space of anti-symmetric product states (or Slater determinants) by $\mathcal{S}_N$, i.e., $\Psi \in \mathcal{S}_N$ if and only if

$$\Psi(r_1, ..., r_N) = \det \begin{pmatrix} \phi_1(r_1) & ... & \phi_N(r_1) \\ \vdots & & \vdots \\ \phi_1(r_N) & \dots & \phi_N(r_N) \end{pmatrix} = \big(\phi_1 \wedge ... \wedge \phi_N\big)(r_1, ..., r_N)$$

for some functions $\{\phi_i\}_{i=1}^N \subset H^1(\mathbb{R}^3)$ which are orthonormal with respect to the $L^2(\mathbb{R}^3)$-inner-product. The functions ϕ_j are usually called the (occupied) orbital functions. Next, let us recall that any density in $\mathcal{R}_N$ is N-representable by a Slater determinant [45, 52, 76]. Stated differently, the image of the set of normalized Slater determinants under the map

$\Psi \mapsto \rho_\Psi$ is also equal to the set of N-representable densities $\mathcal{R}_N$. This allows us to define the Kohn-Sham (KS) kinetic energy of any density $\rho \in \mathcal{R}_N$ as

$$T_{\mathrm{KS}}[\rho] = \inf_{\substack{\Psi \in \mathcal{S}_N \\ \Psi \mapsto \rho}} \frac{1}{2} \|\nabla \Psi\|^2_{L^2(\mathbb{R}^{3N})}.$$

Using T_{KS} as an approximation for the kinetic energy, Kohn and Sham then proposed the following decomposition of the functional F_{LL}:

$$F_{\mathrm{LL}}[\rho] = T_{\mathrm{KS}}[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho],$$

where J is the Hartree (or direct) term,

$$J[\rho] = \frac{1}{2} \int_{\mathbb{R}^6} w(r - r')\rho(r)\rho(r')\mathrm{d}r\mathrm{d}r',$$

and E_{xc} is called the exchange-correlation (xc-)functional. The xc-functional then contains all unknown contributions to the energy and must be efficiently approximated. The advantage of this approach, instead of directly approximating F_{LL}, is that E_{xc} is often small compared to the other two terms; hence only a small part of the energy has to be approximated.

In their seminal paper, Kohn and Sham further proposed to approximate the xc-functional by a functional that depends locally on the pointwise values of the density,

$$E_{\mathrm{xc}}[\rho] \approx E^{\mathrm{LDA}}_{\mathrm{xc}}[\rho] = \int_{\mathbb{R}^3} f(\rho(r))\mathrm{d}r, \tag{1.1.8}$$

for some function $f : \mathbb{R} \to \mathbb{R}$. This is called the local density approximation (LDA). With this ansatz for the exchange-correlation, we can now re-state (the approximation of) problem (1.1.6) as a minimization over the manifold of N-tuples of orbital functions

$$\mathcal{M}_N = \{\Phi = (\phi_1, ..., \phi_N) \in (H^1(\mathbb{R}^3))^N : \langle \phi_i, \phi_j \rangle_{L^2(\mathbb{R}^3)} = \delta_{ij}\} \tag{1.1.9}$$

in the following way:

$$\begin{aligned}
\mathcal{E}^{\mathrm{LDA}}_0 &= \inf_{\rho \in \mathcal{R}_N} \Bigg\{ \underbrace{\inf_{\substack{\Phi \in \mathcal{M}_N \\ \rho_\Phi = \rho}} \int_{\mathbb{R}^3} \frac{1}{2} \sum_{j=1}^N |\nabla \phi_j(r)|^2 \mathrm{d}r}_{T_{\mathrm{KS}}[\rho]} + J[\rho] + E^{\mathrm{LDA}}_{\mathrm{xc}}[\rho] + \int_{\mathbb{R}^3} v(r)\rho(r)\mathrm{d}r \Bigg\} \\
&= \inf_{\Phi \in \mathcal{M}_N} \Bigg\{ \underbrace{\sum_{j=1}^N \frac{1}{2} \|\nabla \phi_j\|^2_{L^2(\mathbb{R}^3)} + J[\rho_\Phi] + E^{\mathrm{LDA}}_{\mathrm{xc}}[\rho_\Phi] + \int_{\mathbb{R}^3} v(r)\rho_\Phi(r)\mathrm{d}r}_{:= \mathcal{E}^{\mathrm{LDA}}[\Phi]} \Bigg\},
\end{aligned}$$

where

$$\rho_\Phi(r) = \sum_{j=1}^N |\phi_j(r)|^2 \tag{1.1.10}$$

is the single-particle density of the Slater determinant generated by the orbitals $\Phi = (\phi_1, ..., \phi_N)$. So by computing the Euler-Lagrange equations of the above functional and using the (gauge) invariance of $\mathcal{E}^{\mathrm{LDA}}$ under unitary transformations of $\mathbb{C}^N$, i.e., $\mathcal{E}^{\mathrm{LDA}}[U\Phi] = \mathcal{E}^{\mathrm{LDA}}[\Phi]$ for any unitary linear transformation $U : \mathbb{C}^N \to \mathbb{C}^N$, we arrive at the celebrated single-particle Kohn-Sham equations (within the LDA)

$$-\frac{1}{2}\Delta\phi_j + \Big(\underbrace{v(r) + v_{\mathrm{xc}}^{\mathrm{LDA}}[\rho_\Phi](r) + \big(\rho_\Phi * w\big)(r)}_{:= v_{\mathrm{KS}}^{\mathrm{LDA}}[\rho_\Phi](r)}\Big)\phi_j = \lambda_j\phi_j, \quad \text{for } 1 \leqslant j \leqslant N, \tag{1.1.11}$$

where ρ_Φ is defined by (1.1.10), the mean-field potential is given by the convolution

$$\rho_\Phi * w(r) = \int_{\mathbb{R}^3} w(r - r')\rho_\Phi(r')\mathrm{d}r',$$

and the exchange-correlation potential is given by

$$v_{\mathrm{xc}}^{\mathrm{LDA}}[\rho_\Phi](r) = \frac{\delta E_{\mathrm{xc}}^{\mathrm{LDA}}}{\delta\rho}[\rho_\Phi](r) = \frac{d}{d\rho} f\big(\rho_\Phi(r)\big). \tag{1.1.12}$$

Note that the solutions $(\lambda_j, \phi_j) \in \mathbb{R} \times H^1(\mathbb{R}^3)$ of (1.1.11) are eigenpairs of the single-particle Schrödinger operator

$$h_{\mathrm{KS}}^{\mathrm{LDA}}[\rho_\Phi] := -\frac{1}{2}\Delta + v_{\mathrm{KS}}^{\mathrm{LDA}}[\rho_\Phi](r) \quad \text{acting on } L^2(\mathbb{R}^3).$$

If in addition $\{\lambda_j\}_{j\leqslant N}$ are the N lowest eigenvalues of the Kohn-Sham Hamiltonian $h_{\mathrm{KS}}^{\mathrm{LDA}}$, then the (Kohn-Sham) Slater determinant

$$\Psi_{\mathrm{KS}} = \phi_1 \wedge ... \wedge \phi_N$$

is the ground state of the N-particles *non-interacting* Hamiltonian

$$H_N^{\mathrm{LDA}}[\rho_\Phi] = H_N(v_{\mathrm{KS}}^{\mathrm{LDA}}[\rho_\Phi], 0).$$

In this case, the resulting density $\rho_{\Psi_{\mathrm{KS}}} = \rho_\Phi$ is expected to be a minimizer[3] of $\mathcal{E}^{\mathrm{LDA}}$ and provides an approximation to the ground state density of the interacting Hamiltonian $H_N(v, w)$. Similarly, the energy $\mathcal{E}_0^{\mathrm{LDA}} = \mathcal{E}(\rho_{\Psi_{\mathrm{KS}}})$ is an approximation of the ground state energy of $H_N(v, w)$.

Remark (xc-functional derivative)**.** *The middle term in* (1.1.12) *is the Schwartz kernel of the functional derivative of the xc-functional. For the LDA xc-functional (with regular f), this kernel is indeed a function in $\mathbb{R}^3$. For more general approximations, the functional derivative is no longer given by integration against a local potential, and the approximated xc-potential is only defined in a weak sense (see, e.g., [84, Section 8.6]).*

[3]For rigorous results on the existence of minimizers for the LDA model we refer the reader to [4] and references therein.

In summary, the Kohn-Sham scheme for computing the ground state density and ground state energy of some system consists of the following steps.

(1) One chooses an approximation for the xc-functional $E_{\mathrm{xc}}^{\mathrm{app}}$ and an initial guess, say ρ_1, for the ground state density of the system.

(2) The effective Kohn-Sham potential $v_{\mathrm{KS}}^{\mathrm{app}}[\rho_1]$ is constructed by summing the external potential (given, e.g., by the position and the atomic number of the nuclei), the mean-field potential $\rho_1 * w$, and the xc-potential obtained from formula (1.1.12) with ρ_Φ and $E_{\mathrm{xc}}^{\mathrm{LDA}}$ replaced respectively by ρ_1 and the chosen xc-approximation $E_{\mathrm{xc}}^{\mathrm{app}}$.

(3) The first N eigenpairs of the single-particle Kohn-Sham Hamiltonian $h_{\mathrm{KS}}^{\mathrm{app}}[\rho_1] = -\frac{1}{2}\Delta + v_{\mathrm{KS}}^{\mathrm{app}}[\rho_1]$ are numerically evaluated. These eigenpairs are then used to construct a new approximation for the ground state density, say ρ_2, via formula (1.1.10).

(4) This new density ρ_2 is then compared with the previous one for consistency. If $\rho_1 - \rho_2$ is small (to some pre-determined accuracy), then the computation is done, and the density ρ_1 is taken as the approximation to the ground state density. If the two densities do not agree, one updates the guess for the ground state density by interpolating between ρ_1 and ρ_2 and re-starts the procedure from step (2) with the updated density. These steps are then repeated until convergence.

This is called the self-consistent field (SCF) method and can be efficiently implemented for reasonable approximations of the xc-functional [80, 90, 30].

Remark (Exact xc-potential)**.** *For a density ρ that is both w-interacting and non-interacting $\mathcal{V}$-representable, i.e. $\rho \in R_N(0) \cap R_N(w)$ (see (1.1.7)), the existence of an external potential $v[\rho]$ and an exact Kohn-Sham potential $v_{\mathrm{KS}}[\rho]$ such that the ground state densities of the Hamiltonians $H_N(v[\rho], w)$ and $H_N(v_{\mathrm{KS}}[\rho], 0)$ are equal to ρ is guaranteed. Since $v[\rho]$ and $v_{\mathrm{KS}}[\rho]$ are unique (up to an additive constant) by the HK theorem, the exact xc-potential is*

$$v_{\mathrm{xc}}^{\mathrm{static}}[\rho] = v_{\mathrm{KS}}[\rho] - v[\rho] - \rho * w. \tag{1.1.13}$$

(Here, we use the superscript static to differentiate it from the exact time-dependent xc-potential introduced later.) Unfortunately, very little is known about the sets $\mathcal{R}_N(0)$ and $\mathcal{R}_N(w)$ (see, e.g., [71, 76] for a proof that they are not the same). Nevertheless, the approximated Kohn-Sham scheme can be justified by the argument that non-interacting $\mathcal{V}$-representable densities can reasonably approximate the w-interacting ones [122].

Approximations to the xc-functional

The crucial step in the Kohn-Sham scheme is the choice of the approximated xc-functional. Over the past decades, hundreds of distinct approximations were proposed by the electronic structure community [82]. In most cases, such approximations are designed to (i)

have a simple expression that can be efficiently computed, (ii) satisfy some known constraints on the exact functional F_{LL}, and (iii) fit some empirical data from benchmark experiments [6, 95, 92, 93]. Moreover, asymptotic results for quantum systems on different regimes play a fundamental role in choosing and designing such approximations. (For instance, the energy density f from the original LDA [65] is the thermodynamic limit of the exchange-correlation energy of the electron gas with constant density, the uniform electron gas (UEG)[4] [72].) In this regard, several interesting mathematical developments appeared in the last few years; let us briefly mention a few of them and refer the reader to the references therein for further information.

- (The LDA in the small gradient regime) Based on Lieb-Thiring inequalities with gradient corrections [87], the LDA functional has been rigorously justified in [73] for densities with small fluctuations.
- (Correlation energy in the high-density limit) The correlation energy formula for the electron gas in the high-density limit derived in the physics literature [11, 44] has been rigorously justified for certain mean-field scaling limits of the electron gas (with interactions less singular then Coulomb) in [7, 8, 23]. This is an important development for DFT because many approximations to the correlation part of the xc-functional are based on this formula [85].
- (Strictly correlated or low-density limit) A different regime from the ones mentioned above (and from the one studied in this thesis) is the strictly correlated electrons (SCE) limit (or low-density limit) where the interaction energy dominates. From the recently revealed connection of this limit with optimal transportation theory [14, 26], several asymptotic results for F_{LL} have emerged. For a comprehensive review, we refer to [41].

The xc-functional approximations are commonly divided into distinct categories represented by the rungs of a ladder, the Jacob's ladder of DFT [94]. Each rung then incorporates the ingredients of lower rungs and is, typically, more accurate and more computationally demanding than the previous ones [94]. The first and second rungs of the Jacob's Ladder correspond respectively to the local density approximation (LDA) described above and the generalized gradient approximations (GGA). Although the LDA is typically more accurate than the Hartree-Fock approximation, they are usually too crude and of little use to practitioners. On the other hand, the development of the GGAs was a milestone in elevating DFT from a conceptually appealing theory to a practical tool for calculations. These are by far the most used xc-approximations due to their balance between accuracy and low computational cost. The GGAs are semi-local density functionals of the form

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[\rho] = \int_{\mathbb{R}^3} f\big(\rho(r), |\nabla\rho(r)|\big)\mathrm{d}r,$$

[4]The UEG is often identified with the Jellium, which corresponds to the thermodynamic limit of an electron gas moving on a positively charged background [48]. Whether this identification is correct or not is still up to debate; see [72] and references therein for a rigorous account of the UEG

where $f : \mathbb{R}^2 \to \mathbb{R}$ is now a function of the density and the density gradient[5]. The LDA and GGA functionals for the exchange energy will be studied in more detail in Chapters 2 and 3. The subsequent rungs of the Jacob's Ladder include more complex functionals such as the meta-GGAs, briefly mentioned in Section 3.7, the exact exchange, studied in detail in Chapter 2 and 3, and the random phase approximations (RPA) for the correlation energy. For a detailed discussion of each rung's components, advantages and limitations, and numerical implementations, we refer the reader to the previously mentioned textbooks and the vast literature referenced therein.

1.1.2 Excitation energies

We have now summarized the DFT scheme for computing the ground state energy and density of a system of interacting electrons. In applications, one would like to go beyond the ground state and also compute the excited state properties of the system. In this section, we shall present an approach for computing the (optical) excitation energies.

The optical excitation energies are defined as the difference

$$\omega_k := \mathcal{E}_k - \mathcal{E}_0, \tag{1.1.14}$$

where $\mathcal{E}_0$ and $\mathcal{E}_k$ are respectively the ground state and the j^{th} excited-state energies of a given system of interest. These energy differences are important in many applications (e.g., to understand a given molecule's absorption/emission spectrum). Although the variational problem for the excited states (cf. (1.1.3)) can be easily stated in the N-body wave function space, a similar reformulation of this problem in terms of the density is not known. For instance, one could repeat the constrained search approach from the previous section to obtain

$$\mathcal{E}_1 = \inf_{\rho \in \mathcal{R}_N} \{\mathcal{E}[\rho] = V[\rho] + F_{\mathrm{LL}}^{\Psi_0^\perp}[\rho]\},$$

where

$$V[\rho] = \int_{\mathbb{R}^3} \rho(r) v(r) \mathrm{d}r \quad \text{and} \quad F_{\mathrm{LL}}^{\Psi_0^\perp}[\rho] = \inf_{\substack{\Psi \mapsto \rho \\ \Psi \perp \Psi_0}} \langle \Psi, \big(-\frac{1}{2}\Delta + \sum_{1 \leqslant j < k \leqslant N} w(r_j - r_k) \big) \Psi \rangle.$$

The difficulty now is that $F_{\mathrm{LL}}^{\Psi_0^\perp}$ implicitly depends on the ground state wave function Ψ_0, which can not be computed in practice for large systems. Moreover, as Ψ_0 depends on the potential v, the above splitting of $\mathcal{E}[\rho]$ does not decouple its dependence on v and w. In other words, the functional $F_{\mathrm{LL}}^{\Psi_0^\perp}$ is not universal with respect to v.

We shall therefore abandon the variational formulation (1.1.3) and present an indirect approach for computing the excitation energies instead. This approach combines linear response theory (LRT) with time-dependent density functional theory (TDDFT).

[5] The common approach in the physics literature is to define the GGAs as the local density approximation of the exchange-correlation energy density of the homogeneous electron gas times an enhancement factor depending on the reduced gradient $|\nabla\rho|/\rho^{\frac{4}{3}}$ (see Chapter 2).

Excitation energies via linear response

Let us start by describing how the linear response of a system of electrons at equilibrium relates to the excitation energies of the Hamiltonian of the system.

In typical applications of linear response theory, one is interested in the response of an observable after the system is driven out of equilibrium by some perturbation. In our case, the system of interest is a collection of N electrons whose energy is described by some self-adjoint operator H acting on the N-body wave function space $\mathcal{H}_N$. (Here, we do *not* assume any specific form for the operator H.) Moreover, we assume that the system is initially in the ground state of H, which corresponds to the equilibrium at zero temperature. In this setting, the response of the system to a perturbation in the Hamiltonian of the form

$$H_1(t) = \epsilon f(t) B,$$

where the perturbing operator $B : \mathcal{H}_N \to \mathcal{H}_N$ is bounded and symmetric, the *time profile* $f : \mathbb{R} \to \mathbb{R}$ is bounded and causal (i.e., $f(t) = 0$ for $t \leqslant 0$), and ϵ is a parameter representing the strength of the perturbation, is given by the strong solution of the time-dependent Schrödinger equation

$$\begin{cases} i\partial_t \Psi(t) = \big(H + H_1(t)\big)\Psi(t) & \text{for } t > 0, \\ \Psi(0) = \Psi_0, \end{cases} \tag{1.1.15}$$

where Ψ_0 is the ground state wave function of H and $\partial_t \Psi(t)$ denotes the time-derivative of the $\mathcal{H}_N$-valued function of time $t \mapsto \Psi(t)$. Consequently, one can show (see Section 4.3) that the variation in the expectation value of any (bounded) observable $A : \mathcal{H}_N \to \mathcal{H}_N$[6] has the expansion

$$\langle \Psi(t), A\Psi(t) \rangle_{L^2(\mathbb{R}^{3N})} = \langle \Psi_0, A\Psi_0 \rangle_{L^2(\mathbb{R}^{3N})} + \epsilon \int_0^t f(s) \chi_{AB}(t-s) \mathrm{d}s + \mathcal{O}_t(\epsilon^2), \tag{1.1.16}$$

where $\chi_{AB}(t-s)$ is the linear response function defined as

$$\chi_{AB}(t) = 2\theta(t) \mathrm{Im} \langle \Psi_0, A e^{-it(H_0 - \mathcal{E}_0)} B \Psi_0 \rangle_{L^2(\mathbb{R}^{3N})}. \tag{1.1.17}$$

Here $\theta(t)$ is the Heaviside step function, and $\mathrm{Im}(z)$ denotes the imaginary part of some complex number $z \in \mathbb{C}$. Eq. (1.1.16) is sometimes called the Kubo formula for the linear dynamical response of the system [66, 67].

The connection between the excitation energies of H and the linear response function can now be understood by looking at the Fourier transform of χ_{AB}. More precisely, the Fourier transform of χ_{AB} is given by the formula[7]

$$\widehat{\chi_{AB}}(\omega) = \lim_{\eta \to 0^+} \langle \Psi_0, BR(-\omega - i\eta) A \Psi_0 \rangle + \langle \Psi_0, AR(\omega + i\eta) B \Psi_0 \rangle, \tag{1.1.18}$$

[6] In quantum mechanics, the observables are self-adjoint operators acting on the Hilbert space of states $\mathcal{H}$. For a system at state $\Psi \in \mathcal{H}$, the expectation value of some observable $A : \mathcal{H} \to \mathcal{H}$ is then given by the inner-product $\langle A \rangle_\Psi = \langle \Psi, A\Psi \rangle_{\mathcal{H}}$.

[7] Here we adopt the physicist's convention for the Fourier transform in time, $\widehat{\chi_{AB}}(\omega) = \int_{\mathbb{R}} \chi_{AB}(t) e^{i\omega t} \mathrm{d}t$.

where $R(z) = P_{\Psi_0^\perp}(z + \mathcal{E}_0 - H)^{-1} P_{\Psi_0^\perp}$ is the reduced resolvent of $H - \mathcal{E}_0$ on the subspace $\{\Psi_0\}^\perp$ and the one-sided limit $\eta \to 0^+$ is taken in the distributional sense. In particular, the function $\omega \mapsto \widehat{\chi_{AB}}(\omega)$ is well-defined and analytic around any point in the open set $\{\omega \in \mathbb{R} : |\omega| \notin \sigma(H - \mathcal{E}_0)\}$. On the other hand, the regularity (or singularity) of $\widehat{\chi_{AB}}(\omega)$ at the points $|\omega| \in \sigma(H - \mathcal{E}_0)$ depends[8] on the spectral properties of $H - \mathcal{E}_0$ at $|\omega|$. Nevertheless, let us consider the holomorphic extension of $\widehat{\chi_{AB}}(z)$ to the complex upper half-plane (which exists since $\chi_{AB}(t)$ is causal). It is not hard to see that this extension has simple poles at the discrete excitation energies $|\omega| \in \sigma_d(H - \mathcal{E}_0)$. The physical consequence of this fact is that the system's response blows up when the Fourier transform of the time profile of the perturbation becomes localized around the excitation energies of the system. In practice, this implies that the excitation energies can be measured by probing the system to different perturbations.

For us, the essential point is that the excitation energies of a given Hamiltonian are accessible through the poles of the Fourier transform of the linear response function. Therefore, if it is possible to efficiently compute (approximations of) $\chi_{AB}(t)$ for various operators A and B, then we have a way to compute the excitation energies of H. Note, however, that constructing $\chi_{AB}(t)$ via formula (1.1.17) (or (1.1.18)) is by no means easier than solving the variational problem (1.1.3); it requires not only knowledge on the ground state wave function Ψ_0 but also on the Schrödinger propagator (or resolvent) of H. Fortunately, a major simplification is achieved by employing the TDDFT framework described below.

Time-dependent density functional theory

TDDFT aims to reproduce (or approximate) the time-dependent density of a system of electrons, whose evolution is governed by a time-dependent interacting Hamiltonian, via the time-dependent density of a system of non-interacting electrons. More precisely, one would like to compute the density $\rho_{\Psi(t)}$ of the solution $\Psi(t)$ of the time-dependent Schrödinger equation (TDSE)

$$\begin{cases} i\partial_t \Psi(t) = H_N(v(t), w)\Psi(t) & \text{for } t > 0, \\ \Psi(0) = \Psi_0, \end{cases} \tag{1.1.19}$$

where the time-dependent external potential $v(t, \cdot) : \mathbb{R}^3 \to \mathbb{R}$ is given a priori by the physics of the problem at hand (e.g., $v(t)$ can represent the interaction of the electrons with classically moving nuclei, or with the external field of a laser beam [83]). To this end, one postulates the existence of a time-dependent exchange-correlation (xc-)potential $v_{\mathrm{xc}}^{\mathrm{TD}}[\rho_\Psi; \Psi_0; \Phi_0] : \mathbb{R}_+ \times \mathbb{R}^3 \to \mathbb{R}$ such that the solution $\Phi(t)$ of

$$\begin{cases} i\partial_t \Phi(t) = H_N(v_{\mathrm{eff}}(t), 0)\Phi(t) & \text{for } t > 0, \\ \Phi(0) = \Phi_0, \end{cases} \tag{1.1.20}$$

[8] This dependence is particularly subtle for points in the essential spectrum of $H - \mathcal{E}_0$ where it is related to the celebrated limiting absorption principle (LAP) [3]

where the effective potential is given by

$$v_{\text{eff}}(t,r) = v_{\text{xc}}^{\text{TD}}[\rho_\Psi;\Psi_0;\Phi_0](t,r) + v(t,r) + \rho_{\Psi(t)} * \frac{1}{|\cdot|}(r),$$

satisfies

$$\rho_{\Psi(t)} = \rho_{\Phi(t)} \quad \text{for all } t \geqslant 0.$$

The initial state Φ_0 can be chosen arbitrarily as long as it reproduces the density and the divergence of the current density of Ψ_0 (see [83, Chapter 4]). Note, however, that the xc-potential $v_{\text{xc}}^{\text{TD}}$ depends on this choice.

Remark (The time-dependent xc-potential)**.** *A few remarks on the xc-potential are now in place.*

(i) (Dependence on the density) *The potential $v_{\text{xc}}^{\text{TD}}[\rho_\Psi;\Psi_0;\Phi_0](t)$ at a given time $t \geqslant 0$ depends on all the past values of the time-dependent density $\{\rho_{\Psi(s)}\}_{s\leqslant t}$.*

(ii) (v-representability) *Proving the existence of the potential $v_{\text{xc}}^{\text{TD}}$ is known as the (time-dependent) $\mathcal{V}$-representability problem. More precisely, the $\mathcal{V}$-representability problem consists in characterizing the set of w-interacting and non-interacting $\mathcal{V}$-representable time-dependent densities. These sets are defined respectively as*

$$\mathcal{R}_N^{TD}(w) = \{\rho(t) = \rho_{\Psi(t)} \text{ for } t \geqslant 0 : \Psi \text{ solves (1.1.19) for some } (v,\Psi_0) \in \mathcal{V}^{\text{TD}} \times \mathcal{I}_N.\},$$
$$\mathcal{R}_N^{TD}(0) = \{\rho(t) = \rho_{\Phi(t)} \text{ for } t \geqslant 0 : \Phi \text{ solves (1.1.20) for some } (v_s,\Phi_0) \in \mathcal{V}^{\text{TD}} \times \mathcal{I}_N.\},$$

where $\mathcal{V}^{\text{TD}} \subset \{v : \mathbb{R}^3 \times [0,\infty) \to \mathbb{R} \text{ measurable}\}$ and $\mathcal{I}_N \subset \{\Psi_0 \in \mathcal{H}_N : \|\Psi_0\| = 1\}$ are suitable classes of time-dependent potentials and initial states. As in the ground state case, an effective potential $v_{\text{eff}} \in \mathcal{V}^{\text{TD}}$ that exactly reproduces the density ρ_Ψ exists if and only if $\rho_\Psi \in \mathcal{R}_N^{\text{TD}}(0)$. For more detailed discussions on the time-dependent $\mathcal{V}$-representability problem, we refer to [121, 102].

(iii) (Runge-Gross theorem) *The Runge-Gross theorem is the analog of the HK theorem to the time-dependent case; it states that, for a fixed interaction w and an initial state Ψ_0, the time-dependent external potential is uniquely determined (up to a time-dependent constant) by the time-dependent density. In particular, the xc-potential $v_{\text{xc}}^{\text{TD}}$ (when existing) is unique. However, the original proof of Runge and Gross using Taylor expansions (see [103]) was recently shown to be essentially incompatible with the physically relevant case of Hamiltonians with singular interactions (e.g. Coulomb)[36].*

By choosing the initial compatible state Φ_0 to be the Slater determinant of some orbital functions $\{\phi_1,...,\phi_N\} \in \mathcal{M}_N$ and using the identification $\rho_\Psi = \rho_\Phi$, eq. (1.1.20) reduces to

a system of N single-particle Schrödinger equations known as the time-dependent Kohn-Sham equations:

$$\begin{cases} i\partial_t \phi_j(t,r) = \Big(-\frac{1}{2}\Delta + v_{\text{eff}}[\rho_\Phi; \Psi_0; \Phi_0](t,r) \Big) \phi_j(t,r) \quad \text{for } j \in \{1,...,N\} \\ \phi_j(0,r) = \phi_j(r), \end{cases} \tag{1.1.21}$$

where $\rho_{\Phi(t)}(r) = \sum_{j=1}^N |\phi_j(t,r)|^2$ is the density of the Slater determinant $\Phi(t) = \phi_1(t) \wedge ... \wedge \phi_N(t)$. Due to the dependence of the effective potential on ρ_Φ, the time-dependent Kohn-Sham equations are a set of N coupled *non-linear* partial differential equations in $\mathbb{R}^3$. Nevertheless, if the map $\rho \mapsto v_{\text{eff}}[\rho; \Psi_0; \Phi_0]$ is explicitly known, then a self-consistent scheme similar to the one described in Section 1.1.1 would (with some luck) allow us to compute the exact time-dependent density $\rho_{\Psi(t)}$ of the interacting system. The philosophy behind this approach is the same behind ground state DFT: solving the N-particles TDSE for a non-interacting Hamiltonian, even self-consistently, is more treatable than solving the N-particles TDSE for an interacting one.

Formal derivation of the TDDFT Dyson equation

We can now present a formal derivation of the Dyson equation from TDDFT. For this, let us go back to the linear response setting and denote by $\Psi^\epsilon(t)$ the solution to the perturbed Schrödinger equation

$$\begin{cases} i\partial_t \Psi^\epsilon(t) = \Big(H_N(v,w) + \epsilon f(t) B \Big) \Psi^\epsilon(t), \\ \Psi^\epsilon(0) = \Psi_0, \end{cases} \tag{1.1.22}$$

where Ψ_0 is the ground state of some interacting Hamiltonian $H_N(v,w)$ of interest.

The key observation which allows bringing to bear TDDFT is now the following: by reducing the set of observables and perturbations to one-body multiplicative potentials, the linear response function $\chi_{AB}(t)$ (defined via (1.1.17) with $H = H_N(v,w)$) depends only on the variation of the time-dependent density

$$\rho^\epsilon(t,r) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi^\epsilon(t,r,r_2,...,r_N)|^2 \mathrm{d}r_2 ... \mathrm{d}r_N.$$

More precisely, we consider only operators A and B of the form

$$A\Psi(r_1,...,r_N) = \sum_{j=1}^N a(r_j)\Psi(r_1,...,r_N) \quad \text{and} \quad B\Psi(r_1,...,r_N) = \sum_{j=1}^N b(r_j)\Psi(r_1,...,r_N),$$

where $a, b \in L^\infty(\mathbb{R}^3)$ are real-valued functions and observe that the linear response function $\chi_{AB}(t)$ is $\mathbb{R}$-bilinear in a and b. Consequently, we can view $\chi(t)$ as a family of time-dependent bilinear forms on $L^\infty(\mathbb{R}^3; \mathbb{R})$. In fact, one can show (see Section 4.2) that

$$\chi_{AB}(t) = \langle a, \chi(t)b \rangle_{L^2(\mathbb{R}^3)} = \int_{\mathbb{R}^3} a(r) \big(\chi(t)b\big)(r) \mathrm{d}r$$

for a strongly continuous operator-valued function $t \mapsto \chi(t) \in \mathcal{B}\big(L^\infty(\mathbb{R}^3;\mathbb{R}), L^1(\mathbb{R}^3;\mathbb{R})\big)$. This operator-valued function is called the *density-density response function*[9] of $H(v,w)$. Note that $\chi(t)$ only depends on the static Hamiltonian $H_N(v,w)$. Moreover, it gives the linear variation (in ϵ) of the density of Ψ^ϵ via the formula

$$\rho^\epsilon(t) = \rho_{\Psi_0} + \epsilon \int_0^t f(s)\big(\chi(t-s)b\big)(r)\mathrm{d}s + \mathcal{O}_t(\epsilon^2). \tag{1.1.23}$$

Remark. *Let us remark that the poles of the Fourier transform of the density-density response function correspond to a proper subset of the excitation energies (see Section 4.2). For instance, in the case of a non-interacting Hamiltonian $H_N(v,0)$, the poles of $\widehat{\chi}$ are precisely the single particle-hole excitation energies, i.e., the energies necessary for moving one electron from an occupied orbital to an unoccupied one. This implies that not all the excitation energies may be accessible through the density-density response function.*

The goal of the Dyson equation is then to approximate the exact density-density response function of the interacting Hamiltonian $H_N(v,w)$ via the density-density response function of the equivalent non-interacting Kohn-Sham system. To present a formal derivation of this equation, let us now make the following assumptions:

(i) The ground state density ρ_{Ψ_0} is non-interacting $\mathcal{V}$-representable and can be exactly reproduced by a Kohn-Sham Slater determinant Φ_0.

(ii) The time-dependent densities $\{\rho^\epsilon\}_{\epsilon\leqslant\epsilon_0}$ are non-interacting $\mathcal{V}$-representable and the compatible initial state can be chosen as the Kohn-Sham Slater determinant Φ_0.

(iii) The exact time-dependent xc-potential $v_{\mathrm{xc}}^{\mathrm{TD}}[\rho^\epsilon;\Psi_0;\Phi_0]$ (whose existence is guaranteed by the second assumption) is differentiable with respect to ρ^ϵ at ρ^0. We call its derivative the xc-operator[10] and denote it by

$$F_{\mathrm{xc}} = \frac{\delta v_{\mathrm{xc}}^{\mathrm{TD}}[\rho;\Psi_0;\Phi_0]}{\delta\rho}\Big|_{\rho=\rho^0}.$$

Note that F_{xc} is an operator from (the tangent space of) time-dependent densities to (the tangent space of) time-dependent potentials.

Using these assumptions, we now proceed as follows. First, from assumption (ii), we know that the solution $\Phi^\epsilon(t)$ of the non-interacting Schrödinger equation

$$\begin{cases} i\partial_t\Phi^\epsilon(t) = \left(H_{\mathrm{eff}}(t) + \epsilon\sum_{j=1}^N f(t)b(r_j)\right)\Phi^\epsilon(t), \\ \Phi^\epsilon(0) = \Phi_0, \end{cases}$$

[9] In the physics literature, the name density-density response function (or linear density response function) is commonly used to refer to the Schwartz kernel of the operator $\chi(t)$, which is then denoted by $\chi(t,r,r')$. This notation can be misleading as such a kernel is not necessarily an integral kernel (hence not a function of r and r').

[10] The common approach in the physics/chemistry literature is to approximate the Schwartz kernel of F_{xc}, which is then called the exchange-correlation kernel.

where the effective Hamiltonian is given by

$$H_{\text{eff}}(t) = H_N\big(v + \rho^\epsilon(t) * w + v_{\text{xc}}^{\text{TD}}[\rho^\epsilon; \Psi_0; \Phi_0](t), 0\big), \tag{1.1.24}$$

satisfies

$$\rho_{\Phi^\epsilon(t)} = \rho^\epsilon(t) \quad \text{for any } t \geqslant 0. \tag{1.1.25}$$

Moreover, since Ψ_0 and Φ_0 are respectively the ground states of the interacting Hamiltonian $H_N(v, w)$ and of the non-interacting Kohn-Sham Hamiltonian

$$H_0 := H_N(v + \rho_{\Phi_0} * w + v_{\text{xc}}^{\text{static}}[\rho_{\Phi_0}], 0), \tag{1.1.26}$$

assumption (i) implies that, for $\epsilon = 0$, the time-dependent xc-potential reduces to the exact static xc-potential from ground state DFT (see (1.1.13)). This observation, together with assumption (iii) and eq. (1.1.23), implies that

$$v_{\text{xc}}^{\text{TD}}[\rho^\epsilon; \Psi_0; \Phi_0](t, r) = v_{\text{xc}}^{\text{static}}[\rho_{\Phi_0}] + \epsilon F_{\text{xc}}\big(\chi \star (f \otimes b)\big)(t, r) + \mathcal{O}(\epsilon^2), \tag{1.1.27}$$

where the time-dependent function $\chi \star (f \otimes b)$ is defined as

$$\big(\chi \star (f \otimes b)\big)(t, r) = \int_0^t f(s)\big(\chi(t - s)b\big)(r)\mathrm{d}s.$$

Similarly, the mean field potential $\frac{1}{|\cdot|} * \rho^\epsilon(t)$ can be expanded in powers of ϵ. Using this expansion and eq. (1.1.27), the effective Hamiltonian of (1.1.24) becomes

$$H_{\text{eff}}(t) = H_0 + \epsilon \sum_{j=1}^{N} \Big(f(t)b(r_j) + \big(F_H + F_{\text{xc}}\big)\big(\chi \star (fb)\big)(t, r) \Big) + \mathcal{O}(\epsilon^2),$$

where F_H is the Hartree operator given by instantaneous convolution against the Coulomb potential,

$$\big(F_H(f \otimes b)\big)(t, r) = f(t)\big(\frac{1}{|\cdot|} * g\big)(r).$$

In particular, the ϵ correction above can be viewed as a one-body multiplicative perturbation of the Kohn-Sham Hamiltonian H_0. Consequently, by using the equivalence of the densities in (1.1.25) and the expansion of the density in (1.1.23) (for both the interacting and non-interacting systems), we obtain

$$\begin{aligned} \chi \star (f \otimes b) &= \lim_{\epsilon \downarrow 0} \frac{\rho_{\Psi^\epsilon} - \rho_{\Psi_0}}{\epsilon} = \lim_{\epsilon \downarrow 0} \frac{\rho_{\Phi^\epsilon} - \rho_{\Phi_0}}{\epsilon} \\ &= \chi_0 \star (f \otimes b) + \chi_0 \star \big(F_H + F_{\text{xc}}\big)\big(\chi \star (f \otimes b)\big), \end{aligned}$$

where χ and χ_0 are respectively the density-density response functions of $H_N(v, w)$ and H_0. Assuming that the above equation holds for any (reasonable) f and b, we finally arrive at the celebrated TDDFT Dyson equation

$$\chi = \chi_0 + \chi_0 \star \big(F_H + F_{\text{xc}}\big)\chi. \tag{1.1.28}$$

Approximations to the xc-operator

Formally, the Dyson equation yields the exact density-density response of the Hamiltonian $H_N(v, w)$, thus allowing access to the excitation spectrum of $H_N(v, w)$. In practice, neither the exact static xc-potential used to construct the Kohn-Sham Hamiltonian H_0 nor the exact xc-operator are known. As in ground state DFT, one then relies on approximations of these two objects. For the static xc-potential, a few approximations (defined as the derivative of approximations to the xc-functional) were already discussed in Section 1.1.1. For the xc-operator, let us mention just the two most common ones. These are:

- **The random phase approximation (RPA):** in this approximation, only the mean-field potential (being the most significant part of electron-electron interaction) is dynamically updated. In particular, the time-dependent xc-potential reduces to the static approximation, and the xc-operator vanishes. The RPA Dyson equation then reads

$$\chi(t) = \chi_0(t) + \int_0^t \chi_0(t-s) F_H \chi(t) \mathrm{d}s.$$

- **The adiabatic local density approximation (ALDA):** in the ALDA, the time-dependent xc-potential is given by the local density approximation

$$v_{\mathrm{xc}}^{\mathrm{TD}}[\rho_\Psi; \Psi_0; \Phi_0](t) = \frac{d}{d\rho} e_{xc}^{\mathrm{HEG}}\big|_{\rho=\rho_{\Psi(t)}},$$

  where $e_{xc}^{\mathrm{HEG}}(\rho)$ is the exchange-correlation energy density of the homogeneous electron gas[11]. In particular, the approximated xc-operator in the ALDA is given by the multiplication operator

$$\big(F_{\mathrm{xc}}^{\mathrm{ALDA}}[\rho_{\Phi_0}]v\big)(t,r) = \frac{d^2}{d\rho^2} e_{\mathrm{xc}}^{\mathrm{HEG}}\big(\rho_{\Phi_0}(r)\big) v(t,r)$$

  for any (regular) $v : \mathbb{R}_+ \times \mathbb{R}^3 \to \mathbb{R}$.

Both the RPA and ALDA are examples of adiabatic approximations. In these approximations, the time-dependent xc-potential depends only instantaneously on the time-dependent density. To emphasize this fact, we use the notation

$$v_{\mathrm{xc}}^{\mathrm{TD}}[\rho; \Psi_0; \Phi_0](t,r) \approx v_{\mathrm{xc}}^{\mathrm{adia}}[\rho(t); \Psi_0; \Phi_0](r).$$

For adiabatic approximations, the approximated Hartree plus xc-operator $F_{Hxc}^{\mathrm{approx}} = F_H + F_{\mathrm{xc}}^{\mathrm{approx}}$ acts instantaneously in time. Consequently, they can be viewed as operators between suitable function spaces in $\mathbb{R}^3$. This is the viewpoint adopted throughout Chapter 4, where general adiabatic approximations are studied. For examples of more refined (frequency-dependent) approximations, we suggest looking at the references mentioned at the beginning of this introduction.

[11] and should not be confused with the homogeneous exchange-correlation energy per particle of the electron gas $\varepsilon_{xc}^{\mathrm{HEG}}(\rho) = e_{xc}^{\mathrm{HEG}}(\rho)/\rho$.

Remark (Random Phase Approximations)**.** *The term RPA has different meanings in the physics literature. Within DFT, there is an important distinction between the ground-state RPA and the time-dependent one. In the ground-state case, the RPA (and its variants) are approximations to the correlation energy based on the high-density limit of the electron gas [11, 44], which we briefly mentioned in Section 1.1.1. In the time-dependent case, the RPA is a synonym to the time-dependent Hartree model, i.e., the time-dependent Kohn-Sham equations (1.1.21) with the time-dependent xc-potential set to zero. In the mathematical literature, the time-dependent Hartree model (or equations) were studied in a variety of settings (e.g., for trace-class operators [5], for crystals [16], and for extended systems [74], to name a few).*

1.2 Summary of results

We now describe the main results of this thesis in more detail. All proofs and rigorous statements are delegated to Chapters 2 to 4.

1.2.1 Exchange effects on the free electron gas

In the first part of this thesis, we consider a collection of N non-interacting electrons freely moving inside some bounded domain $\Omega \subset \mathbb{R}^3$. For such a collection of electrons, the ground state is described by a wave function $\Psi : (\Omega \times \mathbb{Z}_2)^N \to \mathbb{C}$ minimizing the kinetic energy functional

$$T[\Psi] = \frac{1}{2} \sum_{s_1,...,s_N \in \mathbb{Z}_2} \int_{\Omega^N} |\nabla \Psi(r_1, s_1, ..., r_N, s_N)|^2 \mathrm{d}r_1 ... \mathrm{d}r_N$$

and subject to the following constraints: (i) normalization, (ii) anti-symmetry, and (iii) boundary conditions. The Hamiltonian associated with this system is the Laplacian on Ω^N (with suitable boundary conditions), which can be seen as the sum of the 3-dimensional Laplacians acting on each coordinate $r_j \in \Omega$ separately. Consequently, the ground state wave function[12] is given by the anti-symmetric tensor product (Slater determinant) of N orbital functions $\{\phi_j\}_{j \leqslant N} \subset L^2(\Omega^3 \times \mathbb{Z}_2)$. Such wave functions are called uncorrelated; their exchange energy is defined as

$$E_x[\Psi] := \sum_{s_1,...,s_N \in \mathbb{Z}_2} \int_{\Omega^N} \sum_{1 \leqslant j < k \leqslant N} \frac{|\Psi(r_1, s_1, .., r_N, s_N)|^2}{|r_j - r_k|} \mathrm{d}r_1 ... \mathrm{d}r_N - \frac{1}{2} \int_{\Omega^2} \frac{\rho_\Psi(r) \rho_\Psi(r')}{|r - r'|} \mathrm{d}r \mathrm{d}r',$$

where $\rho_\Psi : \mathbb{R}^3 \to \mathbb{R}$ is the single-particle density of the state Ψ,

$$\rho_\Psi(r) = N \sum_{s_1,...,s_N \in \mathbb{Z}_2} \int_{\mathbb{R}^3} |\Psi(r, s_1, r_2, s_2, ..., r_N, s_N)|^2 \mathrm{d}r_1 ... \mathrm{d}r_N.$$

[12] For general values of N, ground state wave functions which are *not* Slater determinants are possible due to degeneracies. However, for the values of N satisfying the closed-shell condition (see Chapter 2), the ground state is indeed unique and given by a single Slater determinant.

Remark. *At first sight, evaluating the exchange energy for the ground state of a non-interacting system may seem contradictory. As briefly mentioned, however, for weakly interacting systems (i.e., in the high-density limit [81]), the ground state is close to the ground state of the non-interacting system (see [47, 23]) and the interaction energy can be viewed as a first-order correction at the level of perturbation theory.*

In Chapter 2, we study the asymptotic behaviour of $E_x[\Psi_{N,L}]$, where $\Psi_{N,L}$ is the ground state of the free electron gas with N particles in the rescaled box $\Omega_L = [0, L]^3$, in the limit where $N, L \to \infty$ with the average density $\bar{\rho} = N/|\Omega_L|$ kept constant. This is called the thermodynamic limit. In this limit, we derive a two-term asymptotic formula of the form

$$E_x[\Psi_{N,L}] = -c_x \bar{\rho}^{\frac{4}{3}} L^3 + c_2^{BC} \bar{\rho} L^2 + o(L^2),$$

where the first coefficient is the well-known Dirac exchange constant, $c_x = 3/4(3/\pi)^{\frac{1}{3}}$, and was rigorously obtained in [40]. The second coefficient depends on the boundary conditions chosen for the Laplacian and is hitherto unknown. Here we pay special attention to the Dirichlet case, where the gradient of the ground state single-particle density has variations of order one close to the boundary.

Moreover, we compare the asymptotics of the exact exchange energy with the asymptotics of semi-local density functionals. More precisely, we consider the functional

$$F[\rho] = \int_{\mathbb{R}^3} f(\rho(r), |\nabla \rho(r)|) \mathrm{d}r,$$

under reasonable assumptions on the function $f : \mathbb{R}^2 \to \mathbb{R}$, and study the thermodynamic limit of the free electron gas, i.e., the thermodynamic limit of $F[\rho_{N,L}]$, where $\rho_{N,L} = \rho_{\Psi_{N,L}}$ is the single-particle density of the ground state of the free N-electron gas in Ω_L. In this case, we also derive two-term asymptotic expansions of the form

$$F[\rho_{N,L}] = c_1(f, \bar{\rho}) L^3 + c_2^{BC}(f, \bar{\rho}) L^2 + o(L^2),$$

where the coefficients $c_1(f, \bar{\rho})$ and $c_2^{BC}(f, \bar{\rho})$ now depend on the function f and the fixed average density $\bar{\rho}$, and $c_2^{BC}(f, \bar{\rho})$ depends additionally on the boundary conditions. Matching the first coefficients $c_1^{BL}(f, \bar{\rho}) = -c_x \bar{\rho}^{\frac{4}{3}}$ of the above expansions, for all positive values of $\bar{\rho}$, yields the well-known local density approximation for the exchange energy,

$$f(\rho, 0) = -c_x \rho^{\frac{4}{3}},$$

which is implicitly used in most exchange DFT functionals. The dependence of f on the gradient only appears in the second coefficient $c_2^{BL}(f, \bar{\rho})$. Thus by matching this coefficient with the second coefficient in the asymptotic expansion of the exact exchange energy, we obtain a novel integral constraint on f (see the next chapter for the precise constraint).

Besides the exchange energy, we also consider the asymptotics of the kinetic energy. In this case, analogous two-term asymptotic expansions are derived. These expansions are

well-known in the literature [37, 38, 60] and directly related to the asymptotic distributions of eigenvalues of the Laplacian. Moreover, the first asymptotic coefficient of the kinetic energy is also related to the Thomas-Fermi theory [35, 118, 77, 75, 90], which is known to be asymptotically correct for neutral atoms in a large nuclear charge limit [77]. In particular, matching the coefficients of the asymptotic expansion of semi-local density functionals with the corresponding ones for the kinetic energy may provide a useful exact constraint for semi-local kinetic energy density functionals [89, 91, 69, 24], which play a central role in orbital-free density functional theory [125, 78].

We conclude Chapter 2 with some numerical experiments. Specifically, we evaluate the exact exchange energy and the exchange energy predicted by some generalized gradient approximations [6, 92, 93] for the free N-electron gas in a box with up to $N = 30000$ electrons. These numerical results illustrate to which extent some widely used GGAs satisfy the proposed constraint.

In Chapter 3, we considerably generalize the results of Chapter 2 by using different methods. Specifically, we extend the results in the following directions: (i) we include a broader class of domains, called here strictly tessellating polytopes; (ii) we consider Riesz interactions between the electrons; and (iii) we generalize the results to arbitrary space dimensions $n \geqslant 2$. In addition, we significantly improve the remainders for the two-term expansion of the exchange energy obtained in Chapter 2.

1.2.2 Adiabatic approximations in LR-TDDFT

In the second part of this thesis, we study the solution χ_F to the Dyson equation

$$\chi_F(t) = \chi_H(t) + \int_0^t \chi_H(t-s) F \chi_F(s) \mathrm{d}s, \tag{1.2.1}$$

where χ_H is the density-density response function of a general Hamiltonian H and F is an approximation of the Hartree plus xc-operator of TDDFT.

The first result of this part is the description of a general functional analytic setting for the well-posedness of the Dyson equation. More precisely, we first characterize the density-density response function of a general Hamiltonian as a strongly continuous family of operators between weighted L^2-spaces depending on the ground state density of H. Then, we show that the Dyson equation is well-posed in this space under a compatible boundedness assumption on the operator F. This functional analytic setting is then applied to prove the existence and uniqueness of the solutions of the Dyson equation for widely used adiabatic approximations of the xc-kernel, such as the random phase approximation (RPA) [83, 103, 120], the Petersilka, Grossman, Gross (PGG) approximation [96], and the adiabatic local density approximations (ALDA) [127, 19], under the sole condition that the Hamiltonian H admits a bounded (in $L^\infty(\mathbb{R}^3)$) ground state density. (In fact, for RPA and PGG we only need the ground state density of H to be in $L^1(\mathbb{R}^3) \cap L^{\frac{3}{2}}(\mathbb{R}^3)$.)

In the second part of Chapter 4, we study some relevant properties of the solution χ_F under the assumption that the operator F is positive in a suitable sense. The prototypical

example for this assumption is the RPA, where F is given by convolution against the Coulomb potential:

$$F^{\mathrm{RPA}} f(r) = F_H f(r) = \int_{\mathbb{R}^3} \frac{f(r')}{|r - r'|} \mathrm{d}r'.$$

The positivity of F greatly simplifies the analysis of the Dyson equation in the frequency domain, which allows for a detailed analysis of its pole structure. Among the main results of this part, we show that the Fourier transform of the solution χ_F, denoted here by $\widehat{\chi_F}$, defines a family of meromorphic operators in a suitable open subset of $\mathbb{C}$. We then show that all poles of this meromorphic extension are simple, have finite rank, and can be characterized by the existence of non-trivial solutions f to the eigenvalue equation

$$\widehat{\chi_H}(\omega) F f = f. \tag{1.2.2}$$

Despite the lack of previous proofs, this characterization is tacitly assumed in the physics literature. In the finite-dimensional case (i.e., after discretization), it can be justified by a mixture of complex analytic and compactness arguments. However, for the current setting where $\widehat{\chi_H}(\omega)$ is a meromorphic function with values on the space of bounded operators between infinite dimensional Banach space, such a characterization is not trivial. Furthermore, we show that in the situations where some poles of $\widehat{\chi_H}$ and $\widehat{\chi_F}$ coincide (which may happen), the poles ω can be characterized via a similar eigenvalue problem but in a reduced space.

Another interesting consequence of the positivity of F that is observed in practical implementations of LR-TDDFT is the forward shift of the poles of the solution $\widehat{\chi_F}$ with respect to the poles of the reference density-density response function $\widehat{\chi_H}$ (see [123]). In Chapter 4, we give a rigorous proof of this fact. Precisely, we show that the positive poles of $\widehat{\chi_F}$ ordered in non-decreasing order and counted with rank are always shifted to the right of the positive poles of $\widehat{\chi_H}$ ordered in the same manner. (There is no need to discuss the negative poles since they are reflections of the positive poles over the imaginary axis.) In practice, this implies that the excitation energies computed in the RPA approximation are always greater than the Kohn-Sham excitations.

As a last result in Chapter 4, we analyze the convergence of the Casida formalism in the continuum (or infinite basis/energy) limit. Roughly speaking, the Casida formalism consists in a truncation of $\widehat{\chi_H}$ at some energy level μ of H followed by an ingenious – but in general not one-to-one – re-parametrization of the finite-dimensional function space spanned by the overlapping functions

$$\rho_{0,j}(r) = N \int_{\mathbb{R}^{3N-1}} \overline{\Psi_0(r, r_2, ..., r_N)} \Psi_j(r, r_2, ..., r_N) \mathrm{d}r_2 ... \mathrm{d}r_N,$$

where Ψ_0 is the ground state wave function of H and Ψ_j are the excited states with energy up to μ. This re-parametrization allows us to obtain all solutions (ω, f) satisfying equation (1.2.2) for a truncated version of the density-density response function by computing the eigenvalues and eigenvectors of a non-symmetric but ω-independent matrix, the Casida

matrix. Here we show that, under the assumption that H has a purely discrete spectrum (e.g. $H = -\Delta + v$ for a trapping potential), the eigenvalues of the Casida matrix converge in an ordered manner to the poles of $\widehat{\chi_F}$ as the energy level μ (which in practice is related to the number of virtual Kohn-Sham orbitals used) goes to infinity. The caveat here is that the lack of injectivity of the mentioned re-parametrization has to be accounted for by excluding some spurious eigenvalues of the Casida matrix.

Part I

The Free Electron Gas in the Thermodynamic Limit

Chapter 2

Exchange Phenomena on the Box

In this chapter, we derive the next order correction to the Dirac exchange energy for the free electron gas in a box with zero boundary conditions in the thermodynamic limit. Like Dirac exchange, the correction is of significant interest for density functional theory (DFT). In particular, it yields a novel exact constraint on generalized gradient approximations (GGAs). The work presented here was done in collaboration with Gero Friesecke.

2.1 Main results

The dominating part of the exchange-correlation energy for real molecular and solid-state systems consists of the exchange energy, on which we focus in this chapter. The local density approximation (LDA) of the exchange energy is the celebrated Dirac exchange; it consists in applying the local exchange energy density of the uniform electron gas (UEG), whose density is homogeneous, to the inhomogeneous density of the system (see (2.1.8)). To some extent, this fails to account for the fluctuations of the density over its average value, which is of order 1 (in atomic units) for real systems. More successful approximations to the exchange energy, such as the generalized gradient approximations (GGA), attempt to overcome this problem by multiplying the LDA exchange energy density by an enhancement factor that depends not only on the pointwise values of the density but also on its gradient (see (2.1.9) and (2.1.10)). However, the precise form of this enhancement factor is not sacrosanct; distinct GGAs use different semi-empirical ansatzes, whose parameters are adjusted to fit empirical data and/or known exact constraints [6, 92].

In this chapter, we analyze the exchange energy of the free electron gas (FEG) that underlies the Dirac exchange, but with an important difference: instead of periodic boundary conditions, we impose *zero boundary conditions*. While the former yield a uniform density, the latter yield density gradients of order 1 near the boundary (see Figure 2.1). This makes the Dirichlet FEG a natural reference system for gaining insight into exchange GGAs. Therefore, we study its asymptotic behavior in the thermodynamic limit where the number of electrons N and the sidelength L of the box tend to infinity with the number of electrons per unit volume, $N/L^3 = \bar{\rho}$, remaining constant.

By careful asymptotic analysis, we are able to determine not just the bulk contribution

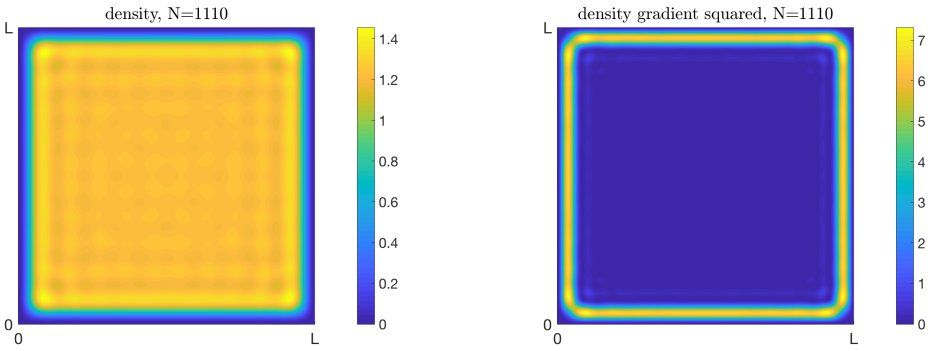

Figure 2.1: Density (left) and density gradient squared (right) of the free electron gas with 1110 electrons in a three-dimensional box with zero boundary conditions. The picture shows a two-dimensional cross-section through the center of the box, and the number of electrons per unit volume was normalized to 1. The density gradients of order 1 near the boundary persist in the thermodynamic limit.

to the exchange energy, which is just the familiar Dirac exchange regardless of the imposed boundary conditions (as has been shown previously [40]), but also the next-order (surface) contribution to the exchange energy, see Theorem 2.1.1 below. The next-order term is to our knowledge new and captures the inhomogeneous boundary layer depicted in Figure 2.1. It also captures two additional effects: a boundary-condition-induced small shift of Fermi momentum and bulk density, and a long-range electrostatic finite-size correction which would also be present for periodic boundary conditions (i.e. unform density). Our asymptotic methods also yield the next-order (surface) contribution to the exchange energy for GGA exchange functionals with general f. Requiring these contributions to match yields a novel exact constraint on GGAs (see eq. (2.1.12) below).

Main result in more detail. The free electron gas in a box consists of N electrons moving freely in a three-dimensional box $Q_L = [0, L]^3$ of sidelength L and volume $V = L^3$ in the thermodynamic limit $N \to \infty$, $V \to \infty$, with the number of electrons per unit volume, $\bar{\rho} = N/V$, remaining constant. Mathematically, ground states of the finite system are defined as minimizers of kinetic energy

$$T[\Psi] = \sum_{s_1,...,s_N \in \mathbb{Z}_2} \int_{Q_L^N} \frac{1}{2} \sum_{i=1}^{N} |\nabla_{r_i} \Psi(r_1, s_1, ..., r_N, s_N)|^2 dr_1 ... dr_N \tag{2.1.1}$$

over square-integrable N-electron wave functions Ψ with finite kinetic energy (i.e., functions in the Sobolev space $H^1((Q_L \times \mathbb{Z}_2)^N; \mathbb{C})$) subject to the following constraints: normalization, $||\Psi||_{L^2} = 1$; antisymmetry, $\Psi(..., r_i, s_i, ..., r_j, s_j, ...) = -\Psi(.., r_j, s_j, ..., r_i, s_i, ...)$ for $i \neq j$ (where $(r_i, s_i) \in Q_L \times \mathbb{Z}_2$ are space-spin coordinates for the ith electron); and one

of the boundary conditions

$$\Psi(r_1,s_1,...,r_N,s_N)=\Psi(r_1',s_1,...,r_N',s_N) \text{ if } r'-r\in L\mathbb{Z}^{3N} \quad \text{(periodic case)} \tag{2.1.2}$$

$$\Psi(r_1,s_1,...,r_N,s_N)=0 \text{ if any } r_i\in\partial[0,L]^3 \quad \text{(Dirichlet case)} \tag{2.1.3}$$

$$\nabla_{r_i}\Psi(r_1,s_1,...,r_N,s_N)\cdot\nu(r_i)=0 \text{ if any } r_i\in\partial[0,L]^3 \quad \text{(Neumann case).} \tag{2.1.4}$$

Here $\nu(r_i)$ denotes the outward unit normal to $\partial[0,L]^3$ at r_i. (Of course, in the Neumann case no boundary conditions are imposed on the admissible functions; instead, minimizers then automatically satisfy Neumann conditions.)

For ground states of non-interacting systems, such as the one above, the exchange energy is defined as the *difference between the quantum-mechanical electron-electron interaction energy and the mean-field energy*,

$$E_x[\Psi]=V_{ee}[\Psi]-\frac{1}{2}\int_{Q_L^2}\frac{\rho(r)\rho(r')}{|r-r'|}dr\,dr' \tag{2.1.5}$$

with

$$V_{ee}[\Psi]=\sum_{s_1,...,s_N\in\mathbb{Z}^2}\int_{Q_L^N}\sum_{1\leqslant i<j\leqslant N}\frac{1}{|r_i-r_j|}|\Psi(r_1,s_1,...,r_N,s_N)|^2dr_1...dr_N \tag{2.1.6}$$

(interaction energy) and

$$\rho(r)=N\sum_{s_1,...,s_N\in\mathbb{Z}^2}\int_{Q_L^{N-1}}|\Psi(r,s_1,r_2,s_2,...,r_N,s_N)|^2dr_2...dr_N \tag{2.1.7}$$

(single-particle density of the system). For explicit expressions of the exchange energy in terms of the single-particle orbitals (Laplace eigenfunctions in the box) see Section 2.2.

We are not just interested in the exact exchange energy functional (2.1.5), but also want to compare it to two important types of simpler functionals defined only in terms of the single-particle density:

- The Local Density Approximation (LDA) [65]:

$$E_x^{\mathrm{LDA}}[\rho]=\int_{\mathbb{R}^3}e_x^{\mathrm{LDA}}(\rho(r))\mathrm{d}r \tag{2.1.8}$$

  where the exchange energy density per unit volume is given by the Dirac-Bloch formula [10, 29] $e_x^{\mathrm{LDA}}(\rho)=-c_x\rho^{4/3}$ with $c_x=\frac{3}{4}(\frac{3}{\pi})^{\frac{1}{3}}$.

- The GGA functionals [6, 92, 93]:

$$E_x^{\mathrm{GGA}}[\rho]=E_x^{\mathrm{LDA}}[\rho]+\underbrace{\int_{\mathbb{R}^3}g^{\mathrm{GGA}}(\rho(r),|\nabla\rho(r)|)\mathrm{d}r}_{:=\Delta E_x^{\mathrm{GGA}}[\rho]} \tag{2.1.9}$$

  with the assumptions that $g^{\mathrm{GGA}}\in C^0([0,\infty)^2)\cap C^1((0,\infty)\times[0,\infty))$ and $g^{\mathrm{GGA}}(\bar\rho,0)=0$, for all $\bar\rho\geqslant 0$ (i.e. the functional reduces to the LDA for the homogeneous density).

In the physics literature [6, 92, 93], GGAs are commonly expressed in terms of the density and the dimensionless gradient $s = |\nabla\rho|/\rho^{4/3}$. This has the advantage that, by a scaling argument, one arrives at the simpler ansatz

$$g^{\mathrm{GGA}}(\rho, |\nabla\rho|) = e_x^{\mathrm{LDA}}(\rho)G(s), \tag{2.1.10}$$

with different GGAs differing only by the choice of G.[1] The reason we prefer to work with the density and the density gradient instead is because $s(r) \to \infty$ as r approaches the boundary (for Dirichlet boundary conditions) while $\nabla\rho(r)$ remains bounded, making the mathematical analysis simpler. Our assumptions on g^{GGA} required in Theorem 2.1.1 below are satisfied for typical GGAs of form (2.1.10) such as those in [6, 92, 93]. (See Section 2.8 for a proof.)

With the functionals (2.1.5), (2.1.8), (2.1.9) in mind, the main result of this chapter can be stated as follows.

Theorem 2.1.1 (Asymptotic expansion of exchange functionals)**.** *Let $N, L > 0$, and let $\Omega \subset \mathbb{R}^3$ be a rectangular box. Let $\Psi_{N,L}$ be any determinantal ground state wave function of the free N-electron gas in $\Omega_L = \{x \in \mathbb{R}^3 : x/L \in \Omega\}$ under either Dirichlet, Neumann, or periodic boundary conditions, and let $\rho_{N,L}$ denote the associated single-particle density. Moreover, assume that the GGA functional (2.1.9) satisfies $g^{\mathrm{GGA}} \in C^0([0,\infty)^2) \cap C^1((0,\infty)\times[0,\infty))$ with $g^{\mathrm{GGA}}(\bar\rho, 0) = 0$ for all $\bar\rho$. Then in the thermodynamic limit, i.e., for $N, L \to \infty$ and $\bar\rho = N/(|\Omega|L^3) =$ constant, one has:*

- *Under periodic boundary conditions:*

$$\begin{aligned} E_x[\Psi^{\mathrm{Per}}_{N,L}] &= -c_x\bar\rho^{4/3}|\Omega|L^3 + c^{\mathrm{Per}}_{x,2}\bar\rho|\partial\Omega|L^2 + \mathcal{O}(L^{\frac{45}{23}+\epsilon}) \\ E_x^{\mathrm{LDA}}[\rho^{\mathrm{Per}}_{N,L}] &= -c_x\bar\rho^{4/3}|\Omega|L^3 + \mathcal{O}(L^{\frac{34}{23}+\epsilon}) \\ \Delta E_x^{\mathrm{GGA}}[\rho^{\mathrm{Per}}_{N,L}] &= \mathcal{O}(L^{\frac{34}{23}+\epsilon}) \end{aligned}$$

- *Under Dirichlet boundary condtions:*

$$\begin{aligned} E_x[\Psi^{\mathrm{Dir}}_{N,L}] &= -c_x\bar\rho^{\frac{4}{3}}|\Omega|L^3 - c^{\mathrm{Dir}}_{x,2}\bar\rho|\partial\Omega|L^2 + \mathcal{O}(L^{\frac{45}{23}+\epsilon}) \\ E_x^{\mathrm{LDA}}[\rho^{\mathrm{Dir}}_{N,L}] &= -c_x\bar\rho^{\frac{4}{3}}|\Omega|L^3 - c^{\mathrm{Dir}}_{LDA}\bar\rho|\partial\Omega|L^2 + o(L^2) \\ \Delta E_x^{\mathrm{GGA}}[\rho^{\mathrm{Dir}}_{N,L}] &= c^{\mathrm{Dir}}_{GGA}(\bar\rho)|\partial\Omega|L^2 + o(L^2) \end{aligned}$$

[1] I.e., by the "gradient enhancement factor" $F = 1 + G$ of the overall integrand $f(\rho, |\nabla\rho|) = e_x(\rho) + g^{\mathrm{GGA}}(\rho, |\nabla\rho|) = e_x(\rho)F(s)$

- *Under Neumann boundary conditions:*

$$\begin{aligned} E_x[\Psi_{N,L}^{\mathrm{Neu}}] &= -c_x\bar{\rho}^{\frac{4}{3}}|\Omega|L^3 - c_{x,2}^{\mathrm{Neu}}\bar{\rho}|\partial\Omega|L^2 + \mathcal{O}(L^{\frac{45}{23}+\epsilon}) \\ E_x^{\mathrm{LDA}}[\rho_{N,L}^{\mathrm{Neu}}] &= -c_x\bar{\rho}^{\frac{4}{3}}|\Omega|L^3 - c_{LDA}^{\mathrm{Neu}}\bar{\rho}|\partial\Omega|L^2 + o(L^2) \\ \Delta E_x^{\mathrm{GGA}}[\rho_{N,L}^{\mathrm{Neu}}] &= c_{GGA}^{\mathrm{Neu}}(\bar{\rho})|\partial\Omega|L^2 + o(L^2) \end{aligned}$$

where $|\Omega|$ and $|\partial\Omega|$ denotes the volume and surface area of the domain Ω, h is the explicit function $h(t) = 3(\sin t - t\cos t)/t^3$, $p_F = (3\pi^2\bar{\rho})^{1/3}$ (Fermi momentum), and the constants are given by

$$c_{x,2}^{\mathrm{Per}} = \frac{1}{8}, \quad c_{x,2}^{\mathrm{Dir}} = \frac{1-\log 2}{4} \approx 0.0767, \quad c_{LDA}^{\mathrm{Dir}} = \frac{3}{8\pi}\int_0^\infty (1-h(t))^{\frac{4}{3}} - 1\mathrm{d}t + \frac{3}{8} \approx 0.0673,$$

$$c_{x,2}^{\mathrm{Neu}} = \frac{3\log 2 - 2}{4} \approx 0.0199, \quad c_{LDA}^{\mathrm{Neu}} = \frac{3}{8\pi}\int_0^\infty (1+h(t))^{\frac{4}{3}} - 1\mathrm{d}t - \frac{3}{8} \approx 0.0430,$$

$$c_{GGA}^{\mathrm{Dir}}(\bar{\rho}) = \frac{1}{2p_F}\int_0^\infty g^{\mathrm{GGA}}\Big(\bar{\rho}(1-h(t)), 2\bar{\rho}p_F|\dot{h}(t)|\Big)\mathrm{d}t,$$

$$c_{GGA}^{\mathrm{Neu}}(\bar{\rho}) = \frac{1}{2p_F}\int_0^\infty g^{\mathrm{GGA}}\Big(\bar{\rho}(1+h(t)), 2\bar{\rho}p_F|\dot{h}(t)|\Big)\mathrm{d}t.$$

This result extends that of a previous work by Friesecke [40] as we determine not just the leading but also the next-order terms (of order L^2) and include the GGA functionals. Also, to further illustrate the role of the boundary conditions, we have included the Neumann case.

An immediate corollary of Theorem 2.1.1 is the following simple exact constraint on GGAs. The next-order correction to Dirac exchange for the free electron gas with zero boundary conditions is captured exactly, i.e.

$$\frac{E_x[\Psi_{N,L}] - E_x^{\mathrm{GGA}}[\rho_{N,L}]}{L^2} \to 0 \quad \text{as } N, L \to \infty \text{ with } \bar{\rho} = \frac{N}{L^3} = \textit{constant} \tag{2.1.11}$$

for all values of the average density $\bar{\rho}$, if and only if the gradient enhancement factor $F(s) = 1 + G(s)$ defined by (2.1.10) satisfies

$$\frac{3}{8\pi}\int_0^\infty (1-h(t))^{\frac{4}{3}} G\left(2(3\pi^2)^{\frac{1}{3}}\frac{|\dot{h}(t)|}{(1-h(t))^{\frac{4}{3}}}\right)\mathrm{d}t = c_{x,2}^{\mathrm{Dir}} - c_{LDA}^{\mathrm{Dir}} \tag{2.1.12}$$

where the constants and the function h are those from Theorem 2.1.1. In contrast with previous exact conditions on G which refer to small-s asymptotics [92] (for the weakly inhomogeneous electron gas) respectively large-s asymptotics [6] (for atomic densities), the above condition is an *integral constraint* which sees the whole profile of G. Note that as t varies from 0 to ∞, the argument s of G (which corresponds to the reduced density gradient of the Dirichlet free electron gas along a ray moving from the boundary in perpendicular direction into the interior, see below) traces out all possible s values from

∞ to 0. The extent to which current GGAs fail to satisfy (2.1.12) is discussed in Section 2.7.

Strategy of the proof. We follow the overall strategy introduced in [40] of deriving an accurate continuum approximation to the ground state density matrix (see Theorem 2.4.2 below, or Theorems 4.1 and 4.2 in [40]) and analyzing the ensuing interior and boundary contributions to the exchange energy. While the continuum approximation is the same already introduced in [40], the main advance, and most involved part of our work, is an improved error estimate (see Theorem 2.4.2) which shows that it is accurate enough to infer the next-order contributions to the exchange functionals which are of the order of the surface area of the box. This is achieved by leveraging, on top of Fourier analysis techniques [111] as already used in [40], the theory of exponential sums [49, 54]. The main step is the proof of the following technical lemma.

Lemma 2.1.1. *Let $\alpha \in \mathbb{N}_0^3$ and $D \in \mathbb{R}^{3\times 3}$ be a positive diagonal matrix. Then there exists $c = c(\alpha, D) > 0$ such that*

$$\left| \sum_{k\in\mathbb{Z}^3\cap B_R^D} (ik)^\alpha e^{ik\cdot z} - \int_{B_R^D} (ik)^\alpha e^{ik\cdot z} \mathrm{d}k \right| \leqslant c(1 + R^{|\alpha|+\frac{34}{23}+\epsilon}), \tag{2.1.13}$$

for all z with $|z|_{max} := \max_{j\leqslant 3}\{|z_j|\} \leqslant \pi$, where $\mathbb{N}_0 = \mathbb{N} \cup \{0\}$ and $B_R^D := \{k \in \mathbb{R}^3 : |D^{-1}k| \leqslant R\}$.

The exponent $\frac{34}{23}$ may seem peculiar at first, and we do not claim it to be optimal, but the main point is that it improves over the $\frac{3}{2}$ exponent obtained in [40]. This improvement is necessary for rigorous derivation of the asymptotic terms of the order of magnitude of the surface area of the box. This can be quickly seen by integrating the square of an error proportional to $L^{-\frac{3}{2}}$ (like in Theorem 4.1 and 4.2 of [40]) against the Coulomb potential in the double box $[0, L]^6$, which yields an error proportional to L^2 and is therefore not enough for our purpose.

Estimates of this kind were originally motivated by analytic number theory. In particular, by setting $z = 0$ and $\alpha = 0$ one recognizes the famous lattice point counting problem in $\mathbb{R}^3$ (also known as the sphere problem) [124, 22, 21, 53]. The remarkable difference here is that the estimate holds uniformly in z, even though the integrand oscillates, for typical $k \in B_R^D$, on the length scale of the lattice. The key step in the proof of Lemma 2.1.1 is to estimate some three dimensional weighted exponential sums that appear naturally when applying the Poisson summation formula to the Fourier transform of (an smoothed version of) the characteristic function of the unit ball in $\mathbb{R}^3$ (see Lemma 2.4.1). While the weights of such sums are dealt with partial summation, the cancellation of the oscillatory terms is achieved by estimating higher order derivatives of the phase function and applying a recent improvement on the k^{th}-order derivative estimate of van der Corput due to Heath-Brown [54].

The continuum approximation of the density matrix which we justify with the help of the above lemma (see Theorem 2.4.2) entails, in particular, the following accurate

approximation to the boundary layer for zero boundary conditions and the box $[0, L]^3$:

$$\rho_{N,L}(r_0 + r') = \bar{\rho}\Big(\frac{p_{N,L}}{p_F}\Big)^3 \big(1 - h(2p_{N,L}|r'|)\big) + O(L^{-\frac{35}{23}+\varepsilon}) \tag{2.1.14}$$

whenever r_0 belongs to the boundary of the box, its distance from the edges is of order L, and r' points in normal direction to $\partial[0, L]^3$ into the interior. Here $p_{N,L}$ is the Fermi momentum of the finite system, which is found (see Lemma 2.3.2) to differ from its thermodynamic limit $p_F = (3\pi^2\bar{\rho})^{1/3}$ by an order L^{-1} shift,

$$p_{N,L} = p_F + \frac{3\pi}{4}L^{-1} + O(L^{\frac{35}{23}+\epsilon}). \tag{2.1.15}$$

This shift produces meaningful contributions to the surface corrections for both the exact exchange and the semi-local approximations (see c_{FM} in Theorems 2.5.1 and 2.5.2).

For the semi-local approximations, the proof of Theorem 2.1.1 then consists in using the continuum approximation (2.1.14) for evaluating the semi-local functional and considering Taylor expansions of the semi-local energy density (i.e. the function $f(a, b) = e_x^{\mathrm{LDA}}(a) + g^{\mathrm{GGA}}(a, b)$) with respect to the density and its gradient. A crucial step here is that the continuum approximation is not only justified for the density but also for its gradient (and higher-order derivatives). This is the main reason for including the factor (ik^α) in Lemma 2.1.1. For the exact exchange, no gradient estimates are necessary as the integrand is quadratic on the density matrix. In this case, the decay of the function h plays an important role in justifying the use of the continuum approximation and in the overall analysis of the bulk and boundary terms.

Structure of the chapter. We start with a small subsection to introduce the notation used throughout the chapter. In Section 2.2 we begin by recalling some basic facts about the ground state of the free electron gas in the box under different boundary conditions. In Section 2.3 we discuss the control of open shell effects and the Fermi momentum asymptotics in the thermodynamic limit. Section 2.4 contains the proof of Lemma 2.1.1 and the derivation of the continuum approximation of the density matrix. In Section 2.5 we present the proof of Theorem 2.1.1 by first dealing with the semi-local functionals (Theorem 2.5.1) and then the exact exchange (Theorem 2.5.2). Section 2.6 briefly discusses the asymptotics of the kinetic energy, which can easily be extracted with our methods. Section 2.7 compares the asymptotic behaviour of different exchange functionals (exact exchange, LDA, B88, PBE, PBEsol) when applied to the free electron gas in a box with zero boundary conditions and up to 30 000 electrons. We find good agreement between asymptotics and numerics. Physics-minded readers may want to skip Sections 2.2–2.6 and move forward directly to Section 2.7.

Notation

The following notation will be used throughout the text.

- We use the standard big-O and small-o notation: for functions $f : (0,\infty) \to \mathbb{R}$ and $g : \mathbb{R} \to (0,\infty)$, we say that $f = \mathcal{O}(g)$ respectively $f = o(g)$ if

$$\limsup_{L\to\infty} \frac{|f(L)|}{g(L)} < \infty \quad \text{respectively} \quad \limsup_{L\to\infty} \frac{|f(L)|}{g(L)} = 0.$$

  Moreover, for functions $f, g : \mathbb{R} \to \mathbb{R}$, we say that $f(L) \lesssim g(L)$ or $f(L) \sim g(L)$ to indicate, respectively, the existence of a constant $C > 0$ which does not depend on L such that

$$|f(L)| \leqslant C|g(L)| \quad \text{or} \quad C^{-1}|f(L)| \leqslant |g(L)| \leqslant C|f(L)|$$

  for all sufficiently large values of L. Sometimes we will also use the notation $\lesssim_\epsilon$ to indicate dependence of the implicit constant on an additional parameter (ϵ in this case).

- Throughout the text, $D \in \mathbb{R}^{3\times 3}_+$ will always denote a diagonal matrix with entries $d_1, d_2, d_3 > 0$, and $|D| := \det D$ stands for its determinant. The balls of radius R and D-radius R are denoted by

$$B_R := \{r \in \mathbb{R}^3 : |r| \leqslant R\} \quad \text{and} \quad B^D_R := \{r \in \mathbb{R}^3 : |D^{-1}r| \leqslant R\}.$$

  The cubic box, the D-rectangular box, and their re-scaled versions are denoted by

$$Q := [0,1]^3, \quad Q^D := [0,d_1] \times [0,d_2] \times [0,d_3],$$
$$Q_L := [0,L]^3, \quad Q^D_L := \{r \in \mathbb{R}^3 : \frac{r}{L} \in Q^D\}.$$

- For the Fourier transform of a function $f : \mathbb{R}^n \to \mathbb{C}$, we use the normalization convention

$$\widehat{f}(k) = \int_{\mathbb{R}^n} f(r) e^{-ik\cdot r} \mathrm{d}r \tag{2.1.16}$$

  where $k \cdot r := \sum_{j=1}^n k_j r_j$ is the standard Euclidean scalar product. We also denote by $\check{f}$ the inverse Fourier transform of f.

- For a set $\Omega \subset \mathbb{R}^n$, we use χ_Ω for its characteristic function. In particular, with the above convention for the Fourier transform, in $\mathbb{R}^3$ one has that $\widehat{\chi}_{B_1} = \frac{4\pi}{3} h(|k|)$, where the function $h : \mathbb{R} \mapsto \mathbb{R}$ will appear many times in the sequel and is given by

$$h(t) = 3\frac{\sin(t) - t\cos(t)}{t^3}. \tag{2.1.17}$$

  For an elementary derivation of this formula see e.g. [40, Lemma 6.1].

- The group generated by reflections at coordinates hyperplanes of $\mathbb{R}^3$ is denoted by G and its elements by σ, i.e.,

$$G = \{\sigma \in \mathbb{R}^{3\times 3} : \sigma \text{ diagonal and } \sigma_{jj} = \pm 1 \text{ for any } j = 1,2,3\}. \tag{2.1.18}$$

- The projection on the i^{th} coordinate hyperplane is denoted by $\pi_i : \mathbb{R}^3 \to \mathbb{R}^2$, e.g. $\pi_1(r_1, r_2, r_3) = (r_2, r_3)$. Moreover, for any $z \in \mathbb{R}^3$, we define $|z|_{\max} := \max_{j\leqslant 3} |z_j|$.
- We use respectively $\mathbb{R}_+ = (0, \infty)$, $\mathbb{N}_0 = \mathbb{N} \cup \{0\}$ and $\mathbb{Z}_2 = \{0, 1\}$ for the positive reals, non-negative integers and the additive group of order 2.
- For any set in $\mathbb{R}^3$, we use $|\cdot|$ for either its volume, surface area or cardinality depending on whether the set has dimension 3, 2, or 0, e.g, $|B_1| = \frac{4\pi}{3}$, $|\partial B_1| = 4\pi$, and $|B_1 \cap \mathbb{Z}^3|$ is the number of elements in $\mathbb{Z}^3$ with Euclidean norm smaller than 1.

2.2 Ground state of the free electron gas: closed shell formulas

We now recall some basic facts and formulas for the ground state of the free N-electron gas in the box subject to Dirichlet, Periodic or Neumann boundary conditions. (A rigorous account for the free electron gas in a box can be found in [99, 100] .)

It is well known that the Laplacian in Q_L^D under any of the discussed boundary conditions (BCs) is diagonalizable in the sense that there exists an orthonormal basis (in $L^2(Q_L^D)$) of eigenvectors. Furthermore, the eigenvectors and eigenvalues can be labelled by

- vectors $k \in \mathbb{Z}^3$ for periodic boundary conditions:

$$\phi_k^L(r) = \frac{1}{\sqrt{|D|L^3}} e^{i\frac{2\pi}{L}D^{-1}k\cdot r}, \quad \lambda_k = \frac{4\pi^2|D^{-1}k|^2}{L^2}. \tag{2.2.1}$$

- vectors $k \in \mathbb{N}^3$ for Dirichlet boundary condition:

$$\phi_k^L(r) = \frac{1}{\sqrt{|D|L^3}} \prod_{i=1}^{3} \sqrt{2}\sin\left(k_i \frac{\pi}{d_i L} r_i\right), \quad \lambda_k = \frac{\pi^2|D^{-1}k|^2}{L^2}. \tag{2.2.2}$$

- vectors $k \in \mathbb{N}_0^3$ for Neumann boundary conditions:

$$\phi_k^L(r) = \frac{1}{\sqrt{|D|L^3}} \prod_{\substack{i=1 \\ k_i\neq 0}}^{3} \sqrt{2}\cos\left(k_i \frac{\pi}{d_i L} r_i\right), \quad \lambda_k = \frac{\pi^2|D^{-1}k|^2}{L^2}. \tag{2.2.3}$$

As a consequence, one possible ground state for the N-electron gas (i.e. a normalized anti-symmetric minimizer of (2.1.1) under one of the BCs (2.1.2)–(2.1.4)) is given by the determinantal wave function (or Slater determinant)

$$\Psi_{N,L}(x_1, ..., x_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_1(x_1) & \dots & \psi_1(x_N) \\ \vdots & & \vdots \\ \psi_N(x_1) & \dots & \psi_N(x_N) \end{pmatrix}, \tag{2.2.4}$$

where $x_\ell = (r_\ell, s_\ell) \in Q_L^D \times \mathbb{Z}_2$ are the space-spin variables and ψ_i are the space-spin orbitals given by

$$\psi_{2i-1}(x) = \phi_{k_i}^L(r)\chi_1(s), \qquad \psi_{2i}(x) = \phi_{k_i}^L(r)\chi_0(s) \quad \text{for } i \in \left\{1, ..., \frac{N}{2}\right\}, \tag{2.2.5}$$

where $\phi_{k_i}^L$ are the eigenfunctions defined in (2.2.1)–(2.2.3), and $\{k_i\}_{i\leqslant N/2}$ is any subset of distinct vectors in $\mathbb{N}^3$ (in the Dirichlet case) such that $B_{\max_i |k_i|-\epsilon} \cap \mathbb{N}^3 \subset \{k_i\}_{i\leqslant N/2}$, for all $\epsilon > 0$. In fact, the collection of all such Slater determinants forms a basis for the ground state eigenspace of the free N-electron gas in Q_L^D.

Let us also introduce the Fermi radius[2]

$$R_N := \begin{cases} \min\{R > 0 : \frac{N}{2} \leqslant |B_R^D \cap \mathbb{Z}^3|\}, & \text{for periodic BCs,} \\ \min\{R > 0 : \frac{N}{2} \leqslant |B_R^D \cap \mathbb{N}^3|\}, & \text{for Dirichlet BCs,} \\ \min\{R > 0 : \frac{N}{2} \leqslant |B_R^D \cap \mathbb{N}_0^3|\}, & \text{for Neumann BCs.} \end{cases} \tag{2.2.6}$$

Then the ground state of the free electron gas is unique for any N satisfying the closed shell condition

$$N = \begin{cases} 2|B_{R_N^{\mathrm{Per}}}^D \cap \mathbb{Z}^3|, & \text{for periodic BCs,} \\ 2|B_{R_N^{\mathrm{Dir}}}^D \cap \mathbb{N}^3|, & \text{for Dirichlet BCs,} \\ 2|B_{R_N^{\mathrm{Neu}}}^D \cap \mathbb{N}_0^3|, & \text{for Neumann BCs,} \end{cases} \tag{2.2.7}$$

where here and thereafter the superscripts Per, Dir and Neu denote periodic, Dirichlet and Neumann boundary conditions respectively. In particular, by recalling that the spinless one-particle density matrix of a state Ψ is defined by

$$\gamma_\Psi(r, \tilde{r}) := N \sum_{s_1,...,s_N \in \mathbb{Z}^2} \int_{(\mathbb{R}^3)^{N-1}} \Psi(r, s_1, r_2, s_2, ...r_N, s_N)\overline{\Psi(\tilde{r}, s_1, r_2, s_2, ..., r_N, s_N)}\mathrm{d}r_2...\mathrm{d}r_N, \tag{2.2.8}$$

then for any N satisfying the closed shell condition (2.2.7), the spinless density matrix of the (unique) aforementioned ground state is given by

$$\gamma_{N,L}(r, \tilde{r}) = \begin{cases} \frac{2}{|D|L^3} \sum_{k \in \mathbb{Z}^3 \cap B_{R_N^{\mathrm{Per}}}^D} e^{i\frac{2\pi}{L}D^{-1}k\cdot(r-\tilde{r})}, & \text{for periodic BCs,} \\ \frac{1}{4|D|L^3} \sum_{\sigma\in G} \det\sigma \sum_{k \in \mathbb{Z}^3 \cap B_{R_N^{\mathrm{Dir}}}^D} e^{i\frac{\pi}{L}D^{-1}k\cdot(r-\sigma\tilde{r})}, & \text{for Dirichlet BCs,} \\ \frac{1}{4|D|L^3} \sum_{\sigma\in G} \sum_{k \in \mathbb{Z}^3 \cap B_{R_N^{\mathrm{Neu}}}^D} e^{i\frac{\pi}{L}D^{-1}k\cdot(r-\sigma\tilde{r})}, & \text{for Neumann BCs,} \end{cases} \tag{2.2.9}$$

[2]Note that the Fermi radius also depends on D. However, as D will be fixed and N, L will vary, we will not exhibit this dependence in our notation.

where G is the reflection group defined in (2.1.18). Therefore, the one-body (spin-less) density can be written as

$$\rho_{N,L}(r) = \begin{cases} \gamma^{\mathrm{Per}}_{N,L}(r,r) = \dfrac{N}{|D|L^3}, & \text{for periodic BCs,} \\ \gamma^{\mathrm{Dir}}_{N,L}(r,r) = \dfrac{1}{4|D|L^3} \displaystyle\sum_{\sigma\in G} \det\sigma \sum_{k\in\mathbb{Z}^3\cap B^D_{R_N^{\mathrm{Dir}}}} e^{i\frac{\pi}{L}D^{-1}k\cdot(r-\sigma r)}, & \text{for Dirichlet BCs,} \\ \gamma^{\mathrm{Neu}}_{N,L}(r,r) = \dfrac{1}{4|D|L^3} \displaystyle\sum_{\sigma\in G} \sum_{k\in\mathbb{Z}^3\cap B^D_{R_N^{\mathrm{Neu}}}} e^{i\frac{\pi}{L}D^{-1}k\cdot(r-\sigma r)}, & \text{for Neumann BCs,} \end{cases} \tag{2.2.10}$$

and the exact exchange energy can be rewritten[3] as

$$E_x[\Psi_{N,L}] = -\frac{1}{4}\int_{Q_L^D\times Q_L^D} \frac{|\gamma_{N,L}(r,\tilde{r})|^2}{|r-\tilde{r}|}\mathrm{d}r\mathrm{d}\tilde{r}, \tag{2.2.11}$$

with $\gamma_{N,L}$ from equation (2.2.9).

Remark. *The derivation of formula (2.2.9) from the Slater determinant of the orbitals in (2.2.1) and (2.2.2) can be found in [40]. (For the Neumann case one can proceed similarly.)*

The above expressions have a few simple but important symmetries that we state as a lemma for further reference. (The proof is a straightforward verification.)

Lemma 2.2.1 (Symmetries of $\rho_{N,L}$)**.** *Let $\rho_{N,L}$ be defined by equation (2.2.10), then $|\nabla\rho_{N,L}|$ and $\rho_{N,L}$ are unchanged under the following reflections:*

$$r_i \mapsto d_i L - r_i.$$

2.3 Open shell effects and Fermi momentum asymptotics in the thermodynamic limit

In this section we consider two important aspects of the FEG in the thermodynamic limit: (i) we justify the use of formulas (2.2.9) for determinantal ground states with a general number of particles $N \in \mathbb{N}$ (Lemma 2.3.1), and (ii) we derive a two-term asymptotic formula for the finite-size Fermi momentum (Lemma 2.3.2).

[3] The equivalence of (2.1.5) and (2.2.11) with γ_Ψ defined by (2.2.8) is in fact valid for any Slater determinant Ψ of doubly-occupied spatial orbitals. It follows from (2.2.4)-(2.2.5) by straightforward calculation.

2.3.1 Open shell effects

Our goal now is to show that, in the thermodynamic limit, the single-particle density matrix (and its derivatives) for any determinantal ground state is pointwise close to the unique closed shell formulas in (2.2.9).

To this end, let us introduce the previous and the current shells for some $N \in \mathbb{N}$ as

$$N_- := \max\{n \in \mathbb{N} : n < N \text{ and } n/2 = |B_R^D \cap \mathbb{N}^3| \text{ for some } R > 0\} = \max_{\epsilon>0} |B_{R_N-\epsilon}^D \cap \mathbb{N}^3|,$$
$$N_+ := \min\{n \in \mathbb{N} : n \geqslant N \text{ and } n/2 = |B_R^D \cap \mathbb{N}^3| \text{ for some } R > 0\} = |B_{R_N}^D \cap \mathbb{N}^3|,$$

where again $\mathbb{N}$ is replaced by $\mathbb{N}_0$ or $\mathbb{Z}$ for Neumann or periodic boundary conditions, respectively. Then according to [40, Section 3], one can work with the unique (closed shell) ground state density matrix $\gamma_{N_-,L}$ up to a pointwise error proportional to $N^{-1/2}$ (or $L^{-\frac{3}{2}}$). However, as previously remarked, these estimates are not enough to justify the use of the exact closed shell formulas on the analysis of the next-to-leading order term in the asymptotic expansion for the exact exchange. To improve on this error estimate and include the more general rectangular box case, we use our own estimate in Lemma 2.1.1. More precisely, setting $\alpha = 0$ and $z = 0$ in Lemma 2.1.1, we obtain[4]

$$|\mathbb{Z}^3 \cap B_R^D| - \frac{4\pi}{3}|D|R^3 = \mathcal{O}(R^{\frac{34}{23}+\epsilon}). \tag{2.3.1}$$

As a consequence, by adapting the arguments in [40] we can prove the following lemma.

Lemma 2.3.1 (Open shell control)**.** *Let $\alpha, \beta \in \mathbb{N}_0^3$ and $\epsilon > 0$. Then, there exists a constant $c = c(\alpha, \beta, \epsilon) > 0$ independent of N and L such that for any determinantal ground state of the free N-electron gas in Q_L^D (under either Dirichlet, Neumann or periodic boundary conditions) we have*

$$|\partial_r^\alpha \partial_{\tilde{r}}^\beta \gamma_{N,L}(r,\tilde{r}) - \partial_r^\alpha \partial_{\tilde{r}}^\beta \gamma_{N_-,L}(r,\tilde{r})| \leqslant c\frac{N^{\frac{|\alpha|+|\beta|}{3}+\frac{34}{69}+\epsilon}}{L^{3+|\alpha|+|\beta|}}. \tag{2.3.2}$$

In particular, if $\bar{\rho} = \frac{N}{|Q^D|L^3}$ is constant, one has

$$\partial_r^\alpha \partial_{\tilde{r}}^\beta \gamma_{N,L}(r,\tilde{r}) = \partial_r^\alpha \partial_{\tilde{r}}^\beta \gamma_{N_-,L}(r,\tilde{r}) + \mathcal{O}(L^{-\frac{35}{23}+\epsilon}).$$

Proof. For simplicity we disregard spin here. First, we note that by eq. (2.3.1), the degeneracy of the open shell can be controlled by

$$d(N) = N_+ - N_- \lesssim R_N^{\frac{34}{23}+\epsilon} \lesssim N^{\frac{34}{69}+\epsilon}, \tag{2.3.3}$$

[4]Note that for the case of the cubic box, finding the optimal (algebraic) coefficient on the remainder goes under the name of sphere problem and has been studied by many authors [124, 22, 21, 53]. In particular, better estimates (with smaller exponent) than (2.3.1) are available in this case.

where the ϵ in the second inequality is different from the first by a factor of 1/3. Next, if Ψ is a determinantal ground state of the free N-electron gas in Q_L^D, then we know (see Section 2.2) that, up to a phase factor,

$$\Psi = \underbrace{\left(\bigwedge_{k \in B_{R_{N_-}}} \phi_k^L \right)}_{=\Psi_{N_-,L}} \wedge \widetilde{\phi}_1 \wedge \ldots \wedge \widetilde{\phi}_{N-N_-},$$

where $\wedge$ is the anti-symmetric tensor product (see (2.2.4)) and $\{\tilde{\phi}_i\}_{i \leqslant N-N_-}$ is a set of orthonormal functions given by linear combinations of the orbitals in the open shell, i.e.

$$\widetilde{\phi}_i(r) = \sum_{\substack{k \in \mathbb{N}^3 \\ |k|=R_N}} c_{ik} \phi_k^L(r), \text{ for a.e. } r \in Q_L^D,$$

for some $c_{ik} \in \mathbb{C}$. Since $C^* = \{\overline{c_{ki}}\}$ defines an isometric transformation from $\mathbb{C}^{N-N_-}$ to $\mathbb{C}^{d(N)}$ (as $\sum_k c_{ik}\bar{c}_{jk} = \langle \widetilde{\phi}_i, \widetilde{\phi}_j \rangle = \delta_{ij}$), one can show that

$$\left| \sum_{i,j,k} c_{ij} \overline{c_{ik}} a_j b_k \right| \leqslant \left(\sum_j |a_j|^2 \right)^{\frac{1}{2}} \left(\sum_k |b_k| \right)^{\frac{1}{2}}, \tag{2.3.4}$$

for any $(a_1, ..a_{d(N)}), (b_1, ..., b_{d(N)}) \in \mathbb{C}^{d(N)}$. Finally, we can use the formula

$$\gamma_\Psi(r, \tilde{r}) = \underbrace{\sum_{k \in B_{R_{N_-}} \cap \mathbb{N}^3} \phi_k^L(r) \overline{\phi_k^L}(\tilde{r})}_{=\gamma_{N_-,L}(r,\tilde{r})} + \sum_{i=1}^{N-N_-} \widetilde{\phi}_i(r) \overline{\widetilde{\phi}_i}(\tilde{r}),$$

and the estimates (2.3.4),(2.3.3)), and $|\partial^\alpha \phi_k^L(r)| \leqslant c_\alpha (R/L)^{|\alpha|} L^{-\frac{3}{2}} \leqslant c_\alpha N^{\frac{|\alpha|}{3}} L^{-\frac{3}{2}-|\alpha|}$ (see (2.2.1)–(2.2.3)) to conclude that

$$\begin{aligned} |\partial_r^\alpha \partial_{\tilde{r}}^\beta \gamma_\Psi(r, \tilde{r}) - \partial_r^\alpha \partial_{\tilde{r}}^\beta \gamma_{N_-,L}(r, \tilde{r})| &= \left| \sum_{i=1}^{N-N_-} \partial^\alpha \widetilde{\phi}_i(r) \partial^\beta \overline{\widetilde{\phi}_i}(\tilde{r}) \right| = \left| \sum_{i,j,k} c_{ij} \bar{c}_{ik} \partial^\alpha \phi_j^L(r) \overline{\partial^\beta \phi_k^L}(\tilde{r}) \right| \\ &\leqslant \left(\sum_{|j|=R_N} |\partial^\alpha \phi_j^L(r)|^2 \right)^{\frac{1}{2}} \left(\sum_{|k|=R_N} |\overline{\partial^\beta \phi_k^L}(\tilde{r})|^2 \right)^{\frac{1}{2}} \\ &\lesssim \frac{N^{\frac{|\alpha|+|\beta|}{3} + \frac{34}{69} + \epsilon}}{L^{3+|\alpha|+|\beta|}}. \end{aligned}$$

□

Remark. *One could equally well consider the density matrix of the current closed shell $\gamma_{N_+,L}$ in Lemma 2.3.1.*

2.3.2 Fermi momentum asymptotics

Here we derive the asymptotics of the finite-size Fermi momentum appearing in (2.1.15).

For the non-interacting electron gas model, the finite-size Fermi momentum is defined as the momentum of the highest occupied orbital of the ground state wave function. For the free N-electron gas in Q_L^D, it is simply given (in atomic units) by

$$p_{N,L} := \begin{cases} \dfrac{2\pi R_N^{\mathrm{Per}}}{L}, & \text{for periodic BCs,} \\ \dfrac{\pi R_N^{\mathrm{Dir}}}{L}, & \text{for Dirichlet BCs,} \\ \dfrac{\pi R_N^{\mathrm{Neu}}}{L}, & \text{for Neumann BCs,} \end{cases} \tag{2.3.5}$$

where R_N is the Fermi radius. It is well known that in the thermodynamic limit, the finite-size Fermi momentum converges to the (continuum) Fermi momentum, defined as

$$p_F = (3\pi^2\bar{\rho})^{\frac{1}{3}}.$$

The next lemma presents the next-order correction of the finite-size Fermi momentum, which is crucial for deriving the next-order corrections from Theorem 2.1.1.

Lemma 2.3.2 (Fermi momentum asymptotics)**.** *Let $\bar{\rho} = \frac{N}{|Q^D|L^3}$ be constant, p_F be the Fermi momentum and $p_{N,L}$ be the finite-size Fermi momentum. Then*

$$p_{N,L} = \begin{cases} p_F + \mathcal{O}(L^{-\frac{35}{23}+\epsilon}), & \textit{for periodic BCs,} \\ p_F + \dfrac{\pi|\partial Q^D|}{8|Q^D|}L^{-1} + \mathcal{O}(L^{-\frac{35}{23}+\epsilon}), & \textit{for Dirichlet BCs,} \\ p_F - \dfrac{\pi|\partial Q^D|}{8|Q^D|}L^{-1} + \mathcal{O}(L^{-\frac{35}{23}+\epsilon}), & \textit{for Neumann BCs.} \end{cases} \tag{2.3.6}$$

Proof. We present the proof only for Dirichlet case and denote R_N^{Dir} simply by R_N. First, from the previous section we already know that $R_N \lesssim N^{\frac{1}{3}}$ and $0 \leqslant N_+ - N \leqslant d(N) \lesssim N^{\frac{34}{69}+\epsilon}$. Since $|Q^D| = |D|$, one has

$$\begin{aligned} \frac{\bar{\rho}L^3}{2} = \frac{N}{2|D|} &= \frac{|\mathbb{N}^3 \cap B_{R_N}^D|}{|D|} + \mathcal{O}(N^{\frac{34}{69}+\epsilon}) \\ &= \frac{1}{8|D|}(|\mathbb{Z}^3 \cap B_{R_N}^D| - \sum_{j=1}^{3} |\mathbb{Z}^2 \cap \pi_j(B_{R_N}^D)|) + \mathcal{O}(N^{\frac{34}{69}+\epsilon}) \\ &= \frac{\pi}{6}R_N^3 - \frac{\pi|\partial Q^D|}{16|D|}R_N^2 + \mathcal{O}(N^{\frac{34}{69}+\epsilon}), \end{aligned}$$

which implies that

$$p_F^3 = p_{N,L}^3 - \frac{3\pi|\partial Q^D|}{8|D|}\frac{1}{L}p_{N,L}^2 + \frac{\mathcal{O}(N^{\frac{34}{69}+\epsilon})}{L^3}. \tag{2.3.7}$$

Then, with $\bar{\rho} = \frac{N}{|Q^D|L^3}$ fixed, it is clear that $p^3_{N,L} \to p^3_F$. The correction proportional to $1/L$ now follows from equation (2.3.7) by taking the cubic root and using a mean value inequality argument. □

Remark. *Note that the above lemma is simply a restatement of the famous two term Weyl's law [60] on the asymptotic behaviour of eigenvalues of the Laplacian (with an improved remainder). We shall comment more on this fact in the next chapter.*

2.4 Discrete to continuum approximation

In this section we present the proof of Lemma 2.1.1 and use it to derive the continuum approximation for the density matrix with explicit estimates. To avoid a cumbersome notation and to make the proofs more efficient, we will focus on the case of the cube Q and simply comment on the modifications necessary for the general case (on Q^D) at the end of each proof.

2.4.1 Estimate on exponential sums

Here we want to derive non-trivial[5] estimates for some weighted exponential sums that appear naturally in the proof of Lemma 2.1.1. More precisely, let $\alpha \in \mathbb{N}_0^3$, $M, R > 0$ and Q_M^h be the cubic holed box defined by

$$Q_M^h := \{r \in \mathbb{R}^3 : M < |r|_{max} \leqslant \frac{4}{3}M\}, \tag{2.4.1}$$

then our goal is to find a better than trivial estimate for the sum

$$S_M^\alpha(R, z) := \sum_{k \in Q_M^h \cap (2\pi\mathbb{Z})^3} \frac{(k+z)^\alpha}{|k+z|^{|\alpha|+2}} e^{iR|k+z|}, \tag{2.4.2}$$

when M is large and $R \sim M^2$. Using the above notation the main estimate can be stated as follows.

Lemma 2.4.1. *Let $\epsilon > 0$, $\alpha \in \mathbb{N}_0^3$ and $z \in \mathbb{R}^3$ with $|z|_{\max} \leqslant \pi$. Then*

$$S_M^\alpha(R, z) \lesssim M^\epsilon (R^{\frac{1}{12}} M^{\frac{3}{4}} + M^{\frac{11}{12}} + R^{-\frac{1}{24}} M^{\frac{23}{24}}),$$

where the implicit constant depends on ϵ and α, but is independent of M, R and z.

Before proving this result, we recall a recent improvement of the standard Van der Corput k^{th}-derivative estimate [49] on exponential sums due to Heath-Brown [54].

[5] In the theory of exponential sums, the elementary estimate $\sum_{k \in \mathbb{Z}^n \cap S} e^{if(k)} \leqslant |\mathbb{Z}^n \cap S|$, which holds for any subset $S \subset \mathbb{R}^n$ and any real-valued function $f(k)$, is called trivial. The goal of the theory is then to improve over such estimates.

Theorem 2.4.1 (Heath-Brown [54]). *Let $k \geqslant 3$ be an integer and $f \in C^k([0,M],\mathbb{R})$. Suppose that*

$$0 < \lambda_k \leqslant f^{(k)}(s) \leqslant A\lambda_k, \quad s \in (0,M),$$

for some $A > 0$. Then

$$\sum_{n\leqslant M} e^{if(n)} \lesssim_{k,A,\epsilon} M^{1+\epsilon}\Big(\lambda_k^{\frac{1}{k(k-1)}} + M^{-\frac{1}{k(k-1)}} + M^{-\frac{2}{k(k-1)}}\lambda_k^{-\frac{2}{k^2(k-1)}}\Big).$$

Remark. *Note that for any $c < 1$, the estimate above still holds for the sum in the interval $cM \leqslant n \leqslant M$ (with two times the implicit constant above). Indeed, one can simply consider the sum in this interval as the sum until M minus the sum until cM, where both can be controlled by the same factor.*

We also recall an elementary partial summation lemma (see e.g. [49, 59] for the proof) that is used to deal with the weight function in $S^\alpha_M(R,z)$.

Lemma 2.4.2 (Partial summation [59]). *Let $g \in C^1([a,b])$ and denote the total variation $\int_a^b |g'|$ of g by $V_g[a,b]$. Then for any sequence a_n, one has*

$$\Big|\sum_{n\geqslant a}^{b} g(n)a_n\Big| \leqslant (V_g[a,b] + |g(a)|)\max_{\gamma\leqslant b}\Big|\sum_{\gamma}^{b} a_n\Big|.$$

Proof of Lemma 2.4.1. First note that if M is small (compared to R), then the estimate is trivial. Therefore, we need to consider only the case where M is big. Next, defining

$$f(k) := R|k+z| \quad \text{and} \quad g(k) := \frac{(k+z)^\alpha}{|k+z|^{2+|\alpha|}}, \tag{2.4.3}$$

the idea is to see f and g as functions of one coordinate, estimate the inner sum by Theorem 2.4.1 and Lemma 2.4.2, and then use the trivial estimate for the outer sums. To verify the assumptions of Theorem 2.4.1, let us consider the sets

$$U^j_M := \{k \in \mathbb{R}^3 : |k_j| \geqslant M \text{ and } \max_{\ell\neq j}\{|k_\ell|\} \geqslant M/10\} \cap Q^h_M, \tag{2.4.4}$$

$$L^j_M := \{k \in \mathbb{R}^3 : |k_j| \geqslant M \text{ and } \max_{\ell\neq j}\{|k_\ell|\} < M/10\} \cap Q^h_M, \tag{2.4.5}$$

and observe that a straightforward calculation yields

$$\partial^4_{k_j} f(k) = -3R\frac{|\pi_j(k+z)|^2(|\pi_j(k+z)|^2 - 4(k_j+z_j)^2)}{|k+z|^7}. \tag{2.4.6}$$

Now the reason for our choice of $\frac{4}{3}$ in the definition of Q^h_M (any number between 1 and $\sqrt{2}$ would be enough) is that, since $|z|_{max} \leqslant \pi$ is small compared to M, inside of U^j_M we have

$$4(k_j+z_j)^2 - |\pi_j(k+z)|^2 \sim M^2, \qquad |k+z| \sim M, \quad \text{and} \quad |\pi_j(k+z)|^2 \sim M^2$$

(with implicit constants independent of M and R). In particular, from (2.4.6), we find that

$$|\partial_{k_j}^4 f(k)| \sim \frac{R}{M^3} \tag{2.4.7}$$

inside U_M^j. Moreover, note that $|g(k)| \lesssim \frac{1}{|k|^2}$ and $|\partial_{k_j} g(k)| \lesssim \frac{1}{|k|^3}$. Hence, as $|k| \geqslant M$ for any $k \in Q_M^h$, if we consider g as a function of only one coordinate, say k_3, for any $\{k_1\} \times \{k_2\} \times I \subset Q_M^h$, we have

$$V_{g(k_1,k_2,\cdot)}[I] + |g(k)| \lesssim M^{-2}, \tag{2.4.8}$$

with constant independent of k_1, k_2, I, M and R. Therefore, we can apply Lemma 2.4.2 and Theorem 2.4.1 (see (2.4.7),(2.4.8)) to conclude that, for any $I_1 \times I_2 \times I_3 \subset U_M^j$,

$$\begin{aligned}\sum_{\substack{k \in I_1 \times I_2 \times I_3 \\ k \in (2\pi\mathbb{Z})^3}} g(k) e^{if(k)} &\lesssim_\epsilon \sum_{\substack{k_\ell \in 2\pi\mathbb{Z} \cap I_\ell \\ \ell \neq j}} M^{-2} M^{1+\epsilon} (R^{\frac{1}{12}} M^{-\frac{1}{4}} + M^{-\frac{1}{12}} + R^{-\frac{1}{24}} M^{-\frac{1}{24}}) \\ &\lesssim M^{\epsilon} (R^{\frac{1}{12}} M^{\frac{3}{4}} + M^{\frac{11}{12}} + R^{-\frac{1}{24}} M^{\frac{23}{24}}). \end{aligned} \tag{2.4.9}$$

On the other hand, if $I_1 \times I_2 \times I_3 \subset L_M^j$, then from equation (2.4.6) and the definition of L_M^j (see (2.4.5)), one can show that $\partial_{k_\ell}^4 f(k) \sim \frac{R}{M^3}$ for $\ell \neq j$. In particular, by summing over I_ℓ first and using the same arguments as before, we conclude that as long as $I_1 \times I_2 \times I_3 \subset L_M^j$, the sum over $I_1 \times I_2 \times I_3$ is again bounded by the right hand side of (2.4.9).

Finally, note that we can split the summation over Q_M^h as

$$\sum_{k \in Q_M^h \cap (2\pi\mathbb{Z})^3} g(k) e^{if(k)} = \sum_{p=1}^{P} \Bigg(\sum_{\substack{k \in I_p^1 \times I_p^2 \times I_p^3 \\ k \in (2\pi\mathbb{Z})^3}} g(k) e^{if(k)} \Bigg),$$

where I_p^j are intervals such that the product $I_p^1 \times I_p^2 \times I_p^3$ is contained in one of the U_M^j or L_M^j, and the number P is independent of M. Therefore, the result follows from estimating each sum on p independently by (2.4.9) and summing them up (since P is independent of M). □

Remark. *Here are some remarks concerning the proof above.*

- *The classical Van der Corput 4^{th}-derivative estimate (see [49]) would actually be enough for our purposes. However, Theorem 2.4.1 gives a slightly better estimate on the error term.*

- *If we assume that $z \in \mathbb{Q}^3$, then one can show that the same estimate from [21, Lemma 3.1] holds, which would then lead to the Vinogradov, Chen [124, 22] exponent of 4/3 in (2.1.13). Unfortunately, in this case the implicit constant depends on the least common multiple of the denominators of z_1, z_2, z_3, and therefore, we lose the uniform control that is essential for our purposes in the next section.*

Remark (Generalization to Q^D)**.** *For general Q^D we need an analog of Lemma 2.4.1 with f and g from equation (2.4.3) replaced by $f(k) = R|D(k+z)|$ and $g(k) = \frac{(D(k+z))^\alpha}{|D(k+z)|^{|\alpha|+2}}$. In particular, the only significant modifications are that equation (2.4.6) has to change accordingly, and the sets U_M^j and L_M^j defined in (2.4.4) and (2.4.5) have to be replaced by their pre-images under D (as a map in $\mathbb{R}^3$).*

2.4.2 Proof of Lemma 2.1.1

To complete the proof of Lemma 2.1.1, we shall use two classical results. The first one is the celebrated Poisson summation formula (see e.g. [111]), which we write in a slightly different form to fit our goal.

Lemma 2.4.3 (Poisson summation formula)**.** *Let $u \in C_c^\infty(\mathbb{R}^n)$, then (see the Fourier transform convention adopted (2.1.16)) the Poisson summation formula states that*

$$\sum_{k\in\mathbb{Z}^n} \frac{1}{(2\pi)^n}\widehat{u}(k)e^{ik\cdot z} - u(z) = \sum_{\substack{k\in(2\pi\mathbb{Z})^n \\ k\neq 0}} u(z+k). \tag{2.4.10}$$

The second one is an (optimal) estimate on the decay of the Fourier transform of the characteristic function of the ball and its derivatives. The proof is a straightforward calculation (at least in $\mathbb{R}^3$).

Lemma 2.4.4 (Fourier transform of the ball)**.** *Let χ_{B_1} be the characteristic function of the unit ball in $\mathbb{R}^3$. Then*

$$\widehat{\chi_{B_1}}(k) = \frac{4\pi}{3}h(|k|),$$

where $h(s) = 3(\sin s - s\cos s)/s^3$. Moreover, for any $\alpha \in \mathbb{N}_0^3$, there exists $c_\alpha > 0$ such that

$$|\partial^\alpha \widehat{\chi_{B_1}}(k)| \leqslant \frac{c_\alpha}{(1+|k|)^2}, \quad \forall k \in \mathbb{R}^3. \tag{2.4.11}$$

Proof of Lemma 2.1.1. Let $R > 0$, then our goal is to bound the error term

$$\mathcal{E}^\alpha(R,z) := \sum_{k\in B_R\cap\mathbb{Z}^3} (ik)^\alpha e^{ik\cdot z} - \int_{B_R} (ik)^\alpha e^{ik\cdot z}dk.$$

For this, the main idea is to apply the Poisson summation formula to a smooth version of the characteristic function of the ball of radius R, use Lemma 2.4.1 to control the error on the Fourier side and then estimate the difference between our smoothed error and the error $\mathcal{E}^\alpha$ defined above. So first, let $H > 0$ be a small parameter to be chosen later, pick any non-positive function $\phi \in C_c^\infty(0,1)$ with $\int\phi(s)ds = -1$, and define

$$f_{R,H}(r) = \begin{cases} 1, & \text{if} \quad |r| \leqslant R, \\ 1 + \displaystyle\int_0^{|r|-R} \phi^H(s)\mathrm{d}s, & \text{otherwise}, \end{cases} \tag{2.4.12}$$

where $\phi^H(s) := \frac{1}{H}\phi\big(\frac{s}{H}\big)$. Then, one can check that $f_{R,H}$ is smooth, it assumes only values between 0 and 1, and it vanishes outside B_{R+H}. Moreover, observing that $\check{f}_{R,H}(k) = \frac{1}{(2\pi)^3}\widehat{f}_{R,H}(k)$ (as $f_{R,H}$ is symmetric) and applying the Poisson summation formula to $\widehat{u} = f_{R,H}$ we obtain

$$\underbrace{\sum_{k\in\mathbb{Z}^3} f_{R,H}(k)e^{ik\cdot z} - \widehat{f}_{R,H}(z)}_{:=\mathcal{E}_H(R,z)} = \underbrace{\sum_{\substack{k\in(2\pi\mathbb{Z})^3\\ k\neq 0}} \widehat{f}_{R,H}(z+k)}_{:=\widehat{\mathcal{E}}_H(R,z)}.$$

The next step is to use Lemma 2.4.1 to estimate the right hand side of the above. For this, we first use spherical coordinates to obtain

$$\begin{aligned}
\widehat{f}_{R,H}(z+k) &= \int_{\mathbb{R}^3} f_{R,H}(r)e^{-ir\cdot(z+k)}\mathrm{d}r \\
&= 4\pi\int_0^R \frac{\tau\sin(|k+z|\tau)}{|k+z|}\mathrm{d}\tau + 4\pi\int_R^{R+H}\frac{\tau\sin(|k+z|\tau)}{|k+z|}\bigg(1+\int_0^{\tau-R}\phi^H(s)ds\bigg)\mathrm{d}\tau \\
&= -4\pi\int_R^{R+H}\frac{\sin(|k+z|\tau)-(|k+z|\tau)\cos(|k+z|\tau)}{|k+z|^3}\phi^H(\tau-R)\mathrm{d}\tau.
\end{aligned}$$

In particular, by partial integration and re-scaling we have

$$\begin{aligned}
\widehat{\mathcal{E}}_H(R,z) &= -4\pi\int_R^{R+H}\Big(3\dot{\phi}^H(\tau-R)+\tau\ddot{\phi}^H(\tau-R)\Big)\sum_{\substack{k\in(2\pi\mathbb{Z})^3\\ k\neq 0}}\frac{\cos(|k+z|\tau)}{|k+z|^4}\mathrm{d}\tau \\
&= -4\pi\int_0^1\Bigg(\overbrace{\frac{3}{H}\dot{\phi}(\tau)+\frac{\tau}{H}\ddot{\phi}(\tau)}^{=\mathcal{O}(\frac{1}{H})}+\frac{R}{H^2}\ddot{\phi}(\tau)\Bigg)\sum_{\substack{k\in(2\pi\mathbb{Z})^3\\ k\neq 0}}\frac{\cos\big((R+H\tau)|k+z|\big)}{|k+z|^4}\mathrm{d}\tau \\
&= \mathcal{O}\bigg(\frac{1}{H}\bigg) - \frac{4\pi R}{H^2}\int_0^1\ddot{\phi}(\tau)\sum_{\substack{k\in(2\pi\mathbb{Z})^3\\ k\neq 0}}\frac{\cos\big((R+H\tau)|k+z|\big)}{|k+z|^4}\mathrm{d}\tau,
\end{aligned} \tag{2.4.13}$$

where we used that $\sum_{k\in(2\pi\mathbb{Z})^3\setminus\{0\}}|k+z|^{-4}\leqslant c$ (since $|z|_{\max}\leqslant\pi$). Here we slightly abused the big-O notation to denote $\mathcal{O}(H^{-1})$ as something bounded in absolute value by a constant times H^{-1}. Now let $M>0$, then by partial integrating n times, throwing out the terms outside the box $Q_M\setminus Q_1 = [-M,M]^3\setminus[-1,1]^3$ and partial integrating back (recall that $\phi\in C_c^\infty(0,1)$), we find that

$$\begin{aligned}
\widehat{\mathcal{E}}_H(R,z) = 4\pi R\int_0^1\phi(\tau)\sum_{k\in(2\pi\mathbb{Z})^3\cap Q_M\setminus Q_1}\frac{\cos\big((R+H\tau)|(k+z)|\big)}{|k+z|^2}\mathrm{d}\tau \\
+\mathcal{O}\bigg(\frac{1}{H}+\frac{R}{H^{n+1}M^n}\bigg).
\end{aligned}$$

Next, after possibly replacing the implicit constant above by a factor independent of M, H and R, we can assume that $M = (\frac{4}{3})^q$ for some $q \in \mathbb{N}$. Thus by using the decomposition $Q_M \backslash Q_1 = \bigcup_{k=1}^{q-1} Q^h_{(\frac{4}{3})^k}$, the facts that $H < 1$ and $|z|_{max} \leqslant \pi$ (by periodicity, and Lemma 2.4.1, we find that

$$\begin{aligned}\widehat{\mathcal{E}}_H(R,z) &\lesssim_{\epsilon,n} \frac{1}{H} + \frac{R}{H^{n+1}M^n} + \sum_{k=1}^{q-1} R\left(\frac{4}{3}\right)^{k\epsilon}\left(R^{\frac{1}{12}}\left(\frac{4}{3}\right)^{\frac{3k}{4}} + \left(\frac{4}{3}\right)^{\frac{11k}{12}} + R^{-\frac{1}{24}}\left(\frac{4}{3}\right)^{\frac{23k}{24}}\right) \\ &\lesssim_{\epsilon,n} \frac{1}{H} + \frac{R}{H^{n+1}M^n} + \log M\left(R^{\frac{13}{12}}M^{\frac{3}{4}+\epsilon} + RM^{\frac{11}{12}+\epsilon} + R^{\frac{23}{24}}M^{\frac{23}{24}+\epsilon}\right), \qquad (2.4.14)\end{aligned}$$

where the $\log M$ can be absorbed in M^ϵ. Moreover, we can estimate the error coming from the smoothing procedure as

$$|\mathcal{E}^0(R,z) - \mathcal{E}_H(R,z)| \leqslant \sum_{\substack{k\in\mathbb{Z}^3\cap B_{R+H}\\ k\notin B_R}} |f_{R,H}(k)| + |\widehat{f}_{R,H}(z) - \widehat{\chi_{B_R}}(z)| \lesssim R^2 H. \qquad (2.4.15)$$

Hence by summing estimates (2.4.14) and (2.4.15), setting $M = R^m, H = R^{-h}$, and minimizing the exponents, one concludes that

$$\mathcal{E}^0(R,z) \lesssim_{\epsilon,n} R^{2-h(n)+\epsilon m(n)} \log R, \quad \forall n \in \mathbb{N},$$

where $h(n) := \frac{12n+11}{23n+22}$ and $m(n) := \frac{12n+12}{23n+22}$. Thus, since $h \uparrow \frac{12}{23}$ for $n \to \infty$, by choosing n big enough, the result for $\alpha = 0$ follows.

For the estimates with $\alpha \neq 0$, we repeat the same arguments by taking $f^\alpha_{R,H}(r) = (ir)^\alpha f_{R,H}(r)$. In this case, note that by the Leibniz rule and using that $\partial^\alpha(|r|^{-4}) \lesssim |r|^{-4-|\alpha|}$ away of the origin, we have

$$\begin{aligned}\partial_k^\alpha\left(\frac{\cos((R+H\tau)|k+z|)}{|k+z|^4}\right) - \frac{\big(iR(k+z)\big)^\alpha}{2|k+z|^{|\alpha|+4}}\left(e^{i(R+H\tau)|k+z|} + (-1)^{|\alpha|}e^{-i(R+H\tau)|k+z|}\right) \\ \lesssim \frac{R^{|\alpha|-1}}{|k+z|^4}. \qquad (2.4.16)\end{aligned}$$

We also have from the Poisson summation (and symmetry of $f^\alpha_{R,H}$) that

$$\underbrace{\sum_{k\in\mathbb{Z}^3} f^\alpha_{R,H}(k)e^{ik\cdot z} - \widehat{f}^\alpha_{R,H}(z)}_{:=\mathcal{E}^\alpha_H(R,z)} = \underbrace{\sum_{\substack{k\in(2\pi\mathbb{Z})^3\\ k\neq 0}} \widehat{f}^\alpha_{R,H}(z+k)}_{:=\widehat{\mathcal{E}}^\alpha_H(R,z)}.$$

Hence using the identity $\widehat{(i\cdot)^\alpha f} = \partial^\alpha \check{f}$ together with estimate (2.4.16), and repeating the

same steps from before (see (2.4.13)), we conclude that

$$\begin{aligned}\mathcal{E}^{\alpha}_{H}(R,z) &= -4\pi\int_0^1\left(\frac{3}{H}\dot{\phi}(\tau)+\frac{R+H\tau}{H^2}\ddot{\phi}(\tau)\right)\sum_{\substack{k\in(2\pi\mathbb{Z})^3\\ k\neq 0}}\partial^{\alpha}\left(\frac{\cos((R+H\tau)|k+z|)}{|k+z|^4}\right)\\ &= -\frac{4\pi R}{H^2}\int_0^1\ddot{\phi}(\tau)\sum_{\substack{k\in(2\pi\mathbb{Z})^3\\ k\neq 0}}\frac{\big(iR(k+z)\big)^{\alpha}}{2|k+z|^{|\alpha|+4}}\left(e^{i(R+H\tau)|k+z|}+(-1)^{|\alpha|}e^{-i(R+H\tau)|k+z|}\right)\mathrm{d}\tau\\ &\quad+\mathcal{O}\left(\frac{R^{|\alpha|}}{H^2}\right).\end{aligned}$$

Thus we can again integrate n times, throw out all terms for $|k|\notin Q_M\backslash Q_1$ and use Lemma 2.4.1 to show that

$$\mathcal{E}^{\alpha}_{H}(R,z)\lesssim_{\epsilon} R^{|\alpha|}\left(\frac{1}{H^2}+\frac{R}{H^{n+1}M^n}+R^{\frac{13}{12}}M^{\frac{3}{4}+\epsilon}+RM^{\frac{11}{12}+\epsilon}+R^{\frac{23}{24}}M^{\frac{23}{24}+\epsilon}\right). \tag{2.4.17}$$

Finally, by summing (2.4.17) to the following estimate for the smoothing error

$$|\mathcal{E}^{\alpha}(R,z)-\mathcal{E}^{\alpha}_{H}(R,z)|\lesssim R^{2+|\alpha|}H,$$

and optimizing the exponent , the result follows from the same limit $n\to\infty$ argument. □

Remark (Generalization to Q^D)**.** *To deal with the general case, one has to replace $f_{R,H}$ by $f^D_{R,H}(r):=f_{R,H}(D^{-1}r)$ and observe that $\widehat{f^D_{R,H}}(k)=|D|\widehat{f}_{R,H}(Dk)$. The rest of the proof follows from the same steps by using the generalization of Lemma 2.4.1 discussed in the previous remark.*

2.4.3 Continuum version of density matrices

We are now in position to present the continuum formulas for the density matrices and prove that they provide good approximations to the exact ground state density matrices.

Looking back at formula (2.2.9) and replacing sum by integral, we can define the continuum version of the density matrix as

$$\gamma^{\mathrm{ctm}}_{N,L}(r,\tilde{r})=\begin{cases}\bar{\rho}\dfrac{p^3_{N,L}}{p^3_F}h(p_{N,L}|r-\tilde{r}|_{D,L}), & \text{for periodic BCs,}\\ \bar{\rho}\dfrac{p^3_{N,L}}{p^3_F}\displaystyle\sum_{\sigma\in G}\det\sigma h(p_{N,L}|r-\sigma\tilde{r}|_{D,2L}), & \text{for Dirichlet BCs,}\\ \bar{\rho}\dfrac{p^3_{N,L}}{p^3_F}\displaystyle\sum_{\sigma\in G}h(p_{N,L}|r-\sigma\tilde{r}|_{D,2L}), & \text{for Neumann BCs ,}\end{cases} \tag{2.4.18}$$

where $p_{N,L}$ and p_F are the finite-size and continuum Fermi momentum (see (2.3.5)), the function h is defined in (2.1.17), and $|r|_{D,2L}=|r \mod D(2L\mathbb{Z})^3|$ (the torus distance). Then, the following estimate is a direct consequence of Lemma 2.1.1.

Theorem 2.4.2 (Continuum approximation estimates). *Let $\bar{\rho} = \frac{N}{|Q^D|L^3}$ be fixed. Let $\Psi_{N,L}$ be any determinantal ground state of the free N-electron gas on Q_L^D, denote its single-particle density matrix by $\gamma_{N,L}$. Then for any $\epsilon > 0$ we have*

$$|\gamma_{N,L}(r,\tilde{r}) - \gamma_{N,L}^{\mathrm{ctm}}(r,\tilde{r})| \lesssim_\epsilon \bar{\rho} N^{-\frac{35}{69}+\epsilon} \lesssim_\epsilon \bar{\rho}^{\frac{34}{69}+\epsilon} L^{-\frac{35}{23}+3\epsilon}. \tag{2.4.19}$$

More generally, for any $\alpha, \beta \in \mathbb{N}_0^3$,

$$|\partial_r^\alpha \partial_{\tilde{r}}^\beta \gamma_{N,L}(r,\tilde{r}) - \partial_r^\alpha \partial_{\tilde{r}}^\beta \gamma_{N,L}^{\mathrm{ctm}}(r,\tilde{r})| \lesssim_{\epsilon,\alpha,\beta} \bar{\rho}^{1+\frac{|\alpha|+|\beta|}{3}} N^{-\frac{35}{69}+\epsilon} \lesssim_{\epsilon,\alpha,\beta} \bar{\rho}^{\frac{34}{69}+\frac{|\alpha|+|\beta|}{3}+\epsilon} L^{-\frac{35}{23}+3\epsilon}. \tag{2.4.20}$$

Moreover, one has

$$|\gamma_{N,L}^{\mathrm{Dir/Neu}}(r,\tilde{r})| \lesssim_\epsilon \bar{\rho}\left(N^{-\frac{35}{69}+\epsilon} + (1+|r-\tilde{r}|_{D,2L})^{-2} \right), \tag{2.4.21}$$

$$|\gamma_{N,L}^{\mathrm{Per}}(r,\tilde{r})| \lesssim_\epsilon \bar{\rho}\left(N^{-\frac{35}{69}+\epsilon} + (1+|r-\tilde{r}|_{D,L})^{-2} \right). \tag{2.4.22}$$

Proof. According to Lemma 2.3.1, up to an error $\lesssim \bar{\rho}^{\frac{34}{69}+\epsilon} L^{-\frac{35}{69}+3\epsilon}$, we can use the closed shell formulas for any determinantal ground state.

Next, we know that (i) $R \sim L$, (ii) $\widehat{\chi}_{B_R^D}(z) = |D|R^3 \widehat{\chi}_{B_1}(RDz)$, (iii) $\widehat{\chi}_{B_1}(z) = \frac{4\pi}{3} h(|z|)$, and (iv) the sums $\sum_{k\in\mathbb{Z}^3\cap B_R} e^{i\frac{\pi}{L}k\cdot D^{-1}w}$ and $\sum_{k\in\mathbb{Z}^3\cap B_R} e^{i\frac{2\pi}{L}k\cdot D^{-1}w}$ are periodic (in w) with respect to $D((2L\mathbb{Z})^3)$ and $D((L\mathbb{Z})^3)$ respectively. Hence, estimate (2.4.19) follows directly from the closed shell formulas (2.2.9) by applying Lemma 2.1.1 with $z = \frac{\pi}{L}D^{-1}(r-\sigma\tilde{r})$ mod $(2\pi\mathbb{Z})^3$ and $z = \frac{2\pi}{L}D^{-1}(r-\tilde{r})$ mod $(2\pi\mathbb{Z})^3$ for Dirichlet/Neumann and periodic case, respectively.

For the derivative estimates in (2.4.20), one can simply use Lemma 2.1.1 together with the identity $\widehat{(-i\cdot)^\alpha f} = \partial^\alpha \widehat{f}$. Note that each derivation gives an additional factor of $1/L$ which compensates for the $R^{|\alpha|}$ gained in (2.1.13) and accounts for the factor $\bar{\rho}^{\frac{|\alpha|}{3}}$ in (2.4.20). The decay estimates (2.4.21) and (2.4.22) follow from estimate (2.4.19) and the decay of h (see Lemma 2.4.4). □

2.5 Proof of Theorem 2.1.1

In this section we make the following simplification to the current notation: as we are dealing with the thermodynamic limit ($N, L \to \infty$ with $\bar{\rho} = \frac{N}{|Q^D|L^3}$ fixed), all functions and constants depending on both N and L will simply be indexed by L (e.g., $\rho_L = \rho_{N,L}$).

2.5.1 Semi-local functionals

Our goal now is to prove the following two-term asymptotic expansion for general semi-local functionals of the density and its gradient.

Theorem 2.5.1 (General semi-local functional asymptotics). *Let* $\frac{N}{|Q^D|L^3} = \bar{\rho} = constant$, Ψ_L *be any determinantal ground state of the free* N*-electron gas in* Q_L^D*, and* ρ_L *be the associated single-particle density. Suppose that* $f(a,b) \in C^0([0,\infty)^2) \cap C^1((0,\infty)\times[0,\infty))$ *and let* $F[\rho_L] := \int_{Q_L^D} f(\rho_L(r), |\nabla\rho_L(r)|)\mathrm{d}r$*. Then for any* $\epsilon > 0$ *we have*

$$F[\rho_L] = \begin{cases} f(\bar{\rho},0)|Q^D|L^3 + \mathcal{O}(L^{-\frac{34}{23}+\epsilon}), & \text{for periodic BCs,} \\ f(\bar{\rho},0)|Q^D|L^3 + \Big(c_{BL}^{\mathrm{Dir}}(\bar{\rho}) + c_{FM}(\bar{\rho})\Big)|\partial Q^D|L^2 + o(L^2), & \text{for Dirichlet BCs,} \\ f(\bar{\rho},0)|Q^D|L^3 + \Big(c_{BL}^{\mathrm{Neu}}(\bar{\rho}) - c_{FM}(\bar{\rho})\Big)|\partial Q^D|L^2 + o(L^2), & \text{for Neumann BCs,} \end{cases}$$

where the boundary layer and Fermi momentum corrections are given by

$$c_{BL}(\bar{\rho}) = \begin{cases} \dfrac{1}{2p_F}\displaystyle\int_0^\infty f\big(\bar{\rho}(1-h(s)), 2\bar{\rho}p_F|\dot{h}(s)|\big) - f(\bar{\rho},0)\mathrm{d}s, & \text{for Dirichlet BCs,} \\ \dfrac{1}{2p_F}\displaystyle\int_0^\infty f\big(\bar{\rho}(1+h(s)), 2\bar{\rho}p_F|\dot{h}(s)|\big) - f(\bar{\rho},0)\mathrm{d}s, & \text{for Neumann BCs,} \end{cases}$$

$$c_{FM}(\bar{\rho}) := \frac{3\pi\bar{\rho}}{8p_F}\partial_a f(\bar{\rho},0).$$

Proof. In the periodic case, since f is differentiable close to $(\bar{\rho},0)$ for any $\bar{\rho} > 0$, the result follows from Theorem 2.4.2 and a simple Lipschitz estimate.

As the Neumann and Dirichlet case are analogous, we give the details only for the Dirichlet case. First note that, since $f(\rho, |\nabla\rho|)$ depends only on ρ and on the norm of $|\nabla\rho|$, by the symmetries pointed out in Lemma 2.2.1 we can reduce the integration domain to

$$F[\rho_L] = 8\int_{Q_{\frac{L}{2}}^D} f(\rho_L, |\nabla\rho_L|)\mathrm{d}r.$$

Thus the continuum approximation from Theorem 2.4.2 reads

$$\rho_L^{\mathrm{ctm}}(r) = \gamma_L^{\mathrm{ctm}}(r,r) = \bar{\rho}\frac{p_L^3}{p_F^3}\sum_{\sigma\in G}\det\sigma\, h(p_L\|r-\sigma r\|) \tag{2.5.1}$$

(since $\|r-\sigma r\|_{D,2L} = \|r-\sigma r\|$ for any $r \in Q_{\frac{L}{2}}^D$ and $\sigma \in G$). The idea now is to use the continuum approximation to show that ρ_L is only small close to the faces and edges of the box. For this, first note that $h(r) = 1$ if and only if $r = 0$. Therefore, for any $\delta > 0$ there exist $c(\delta) > 0$ such that $1 - h(2p_L|r_i|) \geqslant c(\delta)$ as long as $|r_i| > \delta$ and L is big enough. Moreover, from (2.5.1) and the fact that h decays at infinity, we see that we can choose $R(\delta) > 0$ such that

$$C \geqslant \rho_L^{\mathrm{ctm}}(r) \geqslant \frac{c(\delta)}{2} \quad \text{for any } r \in Q_{L,\delta} \text{ and some } C > 0, \tag{2.5.2}$$

where $Q_{L,\delta}$ is the region defined by

$$Q_{L,\delta} := \{r \in Q^D_{\frac{L}{2}} : \min_{j\leqslant 3} |r_j| > \delta \quad \text{and} \quad \min_{j\leqslant 3} |\pi_j r| > R(\delta)\}.$$

Next, note that by the continuum approximation estimate (see equation (2.4.20)) and estimate (2.5.2), we find that

$$2C \geqslant \rho_L(r) \geqslant \frac{c(\delta)}{4} \quad \text{for any } r \in Q_{L,\delta} \text{ and } L \text{ big enough.}$$

In particular, by the assumptions on f (C^1 away from $a = 0$ and C^0 up to $a = 0$), there exists a Lipschitz constant $C(\delta) > 0$ and a uniform (with respect to δ and L) constant $C_0 > 0$ such that

$$\begin{aligned} |F[\rho_L] - F[\rho_L^{\mathrm{ctm}}]| &\lesssim \int_{Q^D_{\frac{L}{2}}\setminus Q_{L,\delta}} C_0 + C(\delta) \int_{Q_{L,\delta}} |\rho_L - \rho_L^{\mathrm{ctm}}| + |\nabla\rho_L - \nabla\rho_L^{\mathrm{ctm}}| \\ &\lesssim \delta L^2 + R(\delta)^2 L + C(\delta) L^{\frac{34}{23}+\epsilon}. \end{aligned}$$

Therefore, by dividing the above by L^2, taking the limit as $L \to \infty$, and then the limit $\delta \to 0$, one has

$$F[\rho_L] = F[\rho_L^{\mathrm{ctm}}] + o(L^2). \tag{2.5.3}$$

The next step is to work with the continuum versions on $Q_{L,\delta}$ and use a Taylor expansion of f together with the decay of h to determine the asymptotic coefficients. To shorten the notation, let us define

$$f_k^L(r,t) := \partial_k f\big(\bar\rho(1-t) + t\rho_L^{\mathrm{ctm}}(r), t|\nabla\rho_L^{\mathrm{ctm}}(r)|\big), \qquad k \in \{a,b\}.$$

Then, note that by estimate (2.5.2) and the assumptions on f, we have

$$|f_k^L(r,t)| \leqslant C(\delta), \tag{2.5.4}$$

for any $(r,t) \in Q_{L,\delta} \times [0,1]$, for any $k \in \{a,b\}$, and for some $C(\delta) > 0$. In addition, by the

fundamental theorem of calculus we find

$$
\begin{aligned}
F[\rho_L^{\mathrm{ctm}}] &= \underbrace{8\int_{Q^D_{\frac{L}{2}}\setminus Q_{L,\delta}} f(\rho_L^{\mathrm{ctm}}, |\nabla\rho_L^{\mathrm{ctm}}|)\mathrm{d}r}_{\lesssim \delta L^2 + R(\delta)^2 L} + 8\int_{Q_{L,\delta}}\Bigg(f(\bar\rho,0) + \int_0^1 f_a^L(r,t)(\rho_L^{\mathrm{ctm}}(r)-\bar\rho)\mathrm{d}t \\
&\quad + \int_0^1 \frac{f_b^L(r,t)}{|\nabla\rho_L^{\mathrm{ctm}}(r)|}\Bigg(\sum_{j=1}^3 \partial_{r_j}\rho_L^{\mathrm{ctm}}(r)\Bigg)^2\mathrm{d}t\Bigg)\mathrm{d}r \\
&= \mathcal{O}(\delta L^2 + R(\delta)^2 L) + f(\bar\rho,0)|Q^D|L^3 + \underbrace{8\bar\rho\int_0^1\int_{Q_{L,\delta}} f_a^L(r,t)\Bigg(\frac{p_L^3}{p_F^3}-1\Bigg)\mathrm{d}r\mathrm{d}t}_{:=I(\delta)} \\
&\quad + \sum_{\sigma\neq id}\underbrace{\frac{8\bar\rho p_L^3}{p_F^3}\int_0^1\int_{Q_{L,\delta}} f_a^L(r,t)\det\sigma h(p_L\|r-\sigma r\|)\mathrm{d}r\mathrm{d}t}_{:=J_\sigma(\delta)} \\
&\quad + \sum_{j=1}^3\underbrace{\frac{8\bar\rho^2 p_L^6}{p_F^6}\int_0^1\int_{Q_{L,\delta}}\frac{f_b^L(r,t)}{|\nabla\rho_L^{\mathrm{ctm}}(r)|}\Bigg(\sum_{\sigma_{jj}=-1}\det\sigma p_L\dot h(p_L\|r-\sigma r\|)\frac{4r_j}{\|r-\sigma r\|}\Bigg)^2\mathrm{d}r\mathrm{d}t}_{:=K_j(\delta)}.
\end{aligned}
\tag{2.5.5}
$$

Therefore, to complete the proof we need to study the (L dependent) terms $I(\delta)$, $J_\sigma(\delta)$ and $K(\delta)$. Let us start with $I(\delta)$. In this case, we first note that

$$
\frac{p_L^3}{p_F^3} - 1 = \frac{3\pi|\partial Q^D|}{8p_F|Q^D|}\frac{1}{L} + \mathcal{O}(L^{-\frac{35}{23}+\epsilon})
$$

by Lemma 2.3.2. Hence by scaling out the L in $I(\delta)$ and making the following observations: (i) $f_a^L(r,t)$ is bounded in $Q_{\delta,L}$ by a constant depending on δ, but independent of L (see (2.5.4)) , (ii) $\lim_{L\to\infty} f_a^L(Lr,t) = \partial_a f(\bar\rho,0)$ for a.e. $(r,t)\in Q^D_{\frac{1}{2}}\times[0,1]$, and (iii) $\lim_{L\to\infty}\chi_{Q_{L,\delta}}(Lr) = \chi_{Q^D_{\frac{1}{2}}}(r)$ in $L^1(\mathbb{R}^3)$, we conclude that

$$
I(\delta) = \frac{3\pi\bar\rho|\partial Q^D|}{8p_F}\partial_a f(\bar\rho,0)L^2 + o(L^2) = c_{FM}(\bar\rho)|\partial Q^D|L^2 + o(L^2), \tag{2.5.6}
$$

We consider next the terms J_σ with $trace(\sigma)\leqslant -1$. In this case, note that by the decay of h (see Lemma 2.4.4), there exists some $j\in\{1,2,3\}$, such that $|h(p_L\|r-\sigma r\|)|\lesssim (1+\pi_j r)^{-2}$.(Recall that $\pi_j:\mathbb{R}^3\to\mathbb{R}^2$ is the projection given by removing the coordinate r_j.) Hence by estimate (2.5.4) we find that $J_\sigma\lesssim_\delta L\log L$, and therefore, we just need to worry about the terms K_j and J_σ with $trace(\sigma)=1$. For simplicity let us label the reflection σ with $trace(\sigma)=1$ and $\sigma_{jj}=-1$ by σ_j. Now note that, by the decay of h and estimate (2.5.4), we have

$$
|f_a^L(r,t)h(2p_L r_j) + f_b^L(r,t)\frac{|\partial_{r_j}\rho^{\mathrm{ctm}}(r)|^2}{|\nabla\rho^{\mathrm{ctm}}(r)|}| \lesssim \frac{C(\delta)}{(1+r_j)^2}.
$$

As a consequence, up to an error bounded by $C(\delta)L$, one can change the domain of integration of $K_j(\delta) + J_{\sigma_j}(\delta)$ from $Q_{L,\delta}$ to

$$Q^j_{L,\delta} := \{r : r_j \in (0,\infty), \pi_j r \in \pi_j Q^D_{\frac{L}{2}}, \quad \min_{j\leqslant 3} |r_j| \geqslant \delta, \text{ and } \min_{j\leqslant 3} |\pi_j r| > R(\delta)\}.$$

In summary, we have

$$K_j(\delta) + J_{\sigma_j}(\delta) = \frac{8\bar\rho p_L^3}{p_F^3}\int_0^1\int_{\mathbb{R}^3} \chi_{Q^j_{L,\delta}}(r)\Bigg(\frac{\bar\rho p_L^3}{p_F^3}\frac{f_b^L(r,t)}{|\nabla\rho_L^{\mathrm{ctm}}(r)|}\Bigg(\sum_{\sigma_{jj}=-1}\frac{p_L \det\sigma \dot h(p_L\|r-\sigma r\|)4r_j}{\|(1-\sigma)(r_j, L\pi_j r)\|}\Bigg)^2 + f_a^L(r,t)(-h(2p_L r_j))\Bigg)\mathrm{d}r\mathrm{d}t + \mathcal{O}(C(\delta)L). \tag{2.5.7}$$

Now note that by the decay of h, for a.e. $(r_j, \pi_j r) \in [0,\infty)\times\pi_j(Q^D_{\frac12})$, the following holds:

$$\begin{aligned}
&\lim_{L\to\infty}\rho_L^{\mathrm{ctm}}(r_j, L\pi_j r) - \bar\rho = -\bar\rho h(2p_F r_j),\\
&\lim_{L\to\infty}|\nabla\rho_L^{\mathrm{ctm}}(r_j, L\pi_j r)| = 2\bar\rho p_F|\dot h(2p_F r_j)|,\\
&\lim_{L\to\infty}\sum_{\sigma_{jj}=-1}\det\sigma\bar\rho p_L\dot h\big(p_L\|(1-\sigma)(r_j, L\pi_j r)\|\big)\frac{4r_j}{\|(1-\sigma_j)(r_j, L\pi_j r_j)\|} = -2\bar\rho p_F\dot h(2p_F r_j),\\
&\lim_{L\to\infty}\chi_{Q^j_{L,\delta}}(r_j, L\pi_j r) = \chi_{(\delta,\infty)}(r_j)\chi_{\pi_j(Q^D_{\frac12})}(\pi_j r).
\end{aligned}$$

Therefore, by scaling out the L in the variables $\pi_j r$ in $K_j(\delta)$ and noting that the integrand in equation (2.5.7) is bounded by $C(\delta)\chi_{Q_{L,\delta}}(r)(1+|r_j|)^{-2}$ (by the decay of h), we conclude from dominated convergence and the continuity of ∇f that

$$\begin{aligned}
K_j(\delta) + J_{\sigma_j}(\delta) &= 2\Bigg(\prod_{\ell\neq j} d_\ell\Bigg)L^2\int_\delta^\infty\int_0^1\Big(\partial_b f\big(\bar\rho(1-th(2p_F r_j)), t2\bar\rho p_F|\dot h(2p_F r_j)|\big)2\bar\rho p_F|\dot h(2p_F r_j)|\\
&\quad - \partial_a f\big(\bar\rho(1-th(2p_F r_j)), t2\bar\rho p_F|\dot h(2p_F r_j)|\big)\bar\rho h(2p_F r_j)\Big)\mathrm{d}t\mathrm{d}r_j + \mathcal{O}(\delta L^2) + \varpi_\delta(L^2)\\
&= \frac{\prod_{\ell\neq j} d_\ell}{p_F}L^2\int_{2p_F\delta}^\infty f\big(\bar\rho(1-h(r_j), 2\bar\rho p_F|\dot h(r_j)|\big) - f(\bar\rho,0)\mathrm{d}r_j + \mathcal{O}(\delta L^2) + \varpi_\delta(L^2),
\end{aligned} \tag{2.5.8}$$

where ϖ_δ emphasizes that the bounds may depend on δ. As a consequence, the proof follows from equations (2.5.3),(2.5.5),(2.5.6), and (2.5.8) by first taking the limit $L\to\infty$ and then $\delta\to 0$. □

Remark. *Here are some remarks about Theorem 2.5.1.*

- *Note that $c_{FM}(\bar\rho)$ above depends on $\bar\rho$ which is in contrast with the constant c_{FM} defined in Theorem 2.5.2 below. The reason is that for the "physically" relevant cases (see the discussion before Theorem 2.1.1), we have $c_{FM}(\bar\rho) = -c_{FM}\bar\rho$, where $c_{FM} = \frac38$ is precisely the value defined there (see Corollary 2.5.1 below).*

- *The same arguments can be used for semi-local functionals of higher order derivatives by considering generalized variables like* $(\rho, \nabla\rho, ..., \partial^\alpha\rho)$ *and applying estimate* (2.1.13). *As we are only interested in LDA and GGAs for the moment, we leave the asymptotics of functionals for higher order derivatives for future works*
- *If* f *is more regular and one knows the ratio at which the derivatives diverge when* $(a, b) \to 0$, *one can further use the decay of* h *to improve the remainder term from* $o(L^2)$ *(for Dirichlet and Neumann cases) to, possibly,* $\mathcal{O}(L^{\frac{34}{23}+\epsilon})$.

As straightforward corollaries of Theorem 2.5.1, we obtain the two term asymptotic expansion for LDA and GGAs from Theorem 2.1.1.

Corollary 2.5.1 (Asymptotic of LDA). *Let* ρ_L *be the single-particle density of any determinantal ground state of the free* N*-electron gas in* Q_L^D *(under our usual boundary conditions). Then in the thermodynamic limit we have*

$$E_x^{\mathrm{LDA}}[\rho_L] = \begin{cases} -c_x\bar{\rho}^{4/3}|Q^D|L^3 + \mathcal{O}(L^{\frac{34}{23}+\epsilon}), & \text{for periodic BCs,} \\ -c_x\bar{\rho}^{4/3}|Q^D|L^3 - c_{LDA}^{\mathrm{Dir}}\bar{\rho}|\partial Q^D|L^2 + o(L^2), & \text{for Dirichlet BCs,} \\ -c_x\bar{\rho}^{4/3}|Q^D|L^3 - c_{LDA}^{\mathrm{Neu}}\bar{\rho}|\partial Q^D|L^2 + o(L^2), & \text{for Neumann BCs,} \end{cases}$$

where the constants are

$$c_{LDA} = \begin{cases} c_{FM} + \dfrac{3}{8\pi}\displaystyle\int_0^\infty (1-h(s))^{\frac{4}{3}} - 1\mathrm{d}s, & \text{for Dirichlet BCs,} \\ -c_{FM} + \dfrac{3}{8\pi}\displaystyle\int_0^\infty (1+h(s))^{\frac{4}{3}} - 1\mathrm{d}s, & \text{for Neumann BCs,} \end{cases}$$

with $c_{FM} = \frac{3}{8}$. *(Compare with the constant in Theorem 2.5.2.)*

Corollary 2.5.2 (Asymptotics for GGA). *Let* $g^{\mathrm{GGA}}(a, b) \in C^0([0,\infty)^2) \cap C^1((0,\infty) \times [0,\infty))$ *such that* $g^{\mathrm{GGA}}(a, 0) = 0$, *for all* $a \geqslant 0$. *Moreover, let* ρ_L *be the single-particle density of any determinantal ground state of the free* N*-electron gas in* Q_L^D *(under our usual boundary conditions). Then, for* $\Delta E_x^{\mathrm{GGA}}[\rho_L] = \int_{Q_L^D} g^{\mathrm{GGA}}(\rho_L, |\nabla\rho_L|)$, *in the thermodynamic limit we have*

$$\Delta E_x^{\mathrm{GGA}}[\rho_L] = \begin{cases} \mathcal{O}(L^{-\frac{34}{23}+\epsilon}) & \text{for periodic BCs,} \\ c_{GGA}^{\mathrm{Dir}}(\bar{\rho})|\partial Q^D|L^2 + o(L^2), & \text{for Dirichlet BCs,} \\ c_{GGA}^{\mathrm{Neu}}(\bar{\rho})|\partial Q^D|L^2 + o(L^2), & \text{for Neumann BCs,} \end{cases}$$

where the constants are given by

$$c_{GGA}(\bar{\rho}) = \begin{cases} \dfrac{1}{2p_F}\displaystyle\int_0^\infty g^{\mathrm{GGA}}\Big(\bar{\rho}(1-h(s)), 2\bar{\rho}p_F|\dot{h}(s)|\Big)\mathrm{d}s, & \text{for Dirichlet BCs,} \\ \dfrac{1}{2p_F}\displaystyle\int_0^\infty g^{\mathrm{GGA}}\Big(\bar{\rho}(1+h(s)), 2\bar{\rho}p_F|\dot{h}(s)|\Big)\mathrm{d}s, & \text{for Neumann BCs.} \end{cases}$$

Proof of Corollary 2.5.1 and 2.5.2. In the first corollary, just apply Theorem 2.5.1 to $f(\rho) = c_x\rho^{4/3}$. For the second one, set $f(\rho, |\nabla\rho|) = g^{\mathrm{GGA}}(\rho, |\nabla\rho|)$ and note that $f(a, 0) = 0$ for all $a \geqslant 0$ implies that $\partial_a f(a, 0) = 0$ for all $a > 0$. □

2.5.2 Exact exchange

Now we turn to the asymptotic expansion of the exact exchange.

Theorem 2.5.2 (Asymptotics of exact exchange)**.** *Let $\bar{\rho} = \frac{N}{|Q^D|L^3} = constant$, Ψ_L be a determinantal ground state of the free N-electron gas in Q_L^D. Then, we have*

$$E_x[\Psi_L] = \begin{cases} -c_x\bar{\rho}^{\frac{4}{3}}|Q^D|L^3 + c_{FS}\bar{\rho}|\partial Q^D|L^2 + \mathcal{O}(L^{\frac{45}{23}+\epsilon}), & \text{for periodic BCs,} \\ -c_x\bar{\rho}^{\frac{4}{3}}|Q^D|L^3 - (c_{BL}^{\mathrm{Dir}} + c_{FM} - c_{FS})\bar{\rho}|\partial Q^D|L^2 + \mathcal{O}(L^{\frac{45}{23}+\epsilon}), & \text{for Dirichlet BCs,} \\ -c_x\bar{\rho}^{\frac{4}{3}}|Q^D|L^3 - (c_{BL}^{\mathrm{Neu}} - c_{FM} - c_{FS})\bar{\rho}|\partial Q^D|L^2 + \mathcal{O}(L^{\frac{45}{23}+\epsilon}), & \text{for Neumann BCs,} \end{cases}$$

where the finite-size, Fermi momentum and boundary layer corrections are

$$c_{FS} = \frac{1}{8}, \quad c_{FM} = \frac{3}{8}, \quad c_{BL}^{\mathrm{Dir}} = -\frac{\log 2}{4}, \text{ and } \quad c_{BL}^{\mathrm{Neu}} = \frac{3\log 2}{4}.$$

Proof. As before, we prove the Dirichlet case in detail and outline the proof for the other two boundary conditions at the end.

The first step is again to justify the use of the continuum density matrices (2.4.20). For this, we use the identity

$$|\gamma_L(r,\tilde{r})|^2 - |\gamma_L^{\mathrm{ctm}}(r,\tilde{r})|^2 = Re\{\overline{(\gamma_L(r,\tilde{r}) - \gamma_L^{\mathrm{ctm}}(r,\tilde{r}))}(\gamma_N(r,\tilde{r}) + \gamma_N^{\mathrm{ctm}}(r,\tilde{r}))\}$$

together with estimates (2.4.19) and (2.4.21) from Theorem 2.4.2 to obtain

$$\begin{aligned} \left|\int_{Q_L^D\times Q_L^D} \frac{|\gamma_L(r,\tilde{r})|^2 - |\gamma_L^{\mathrm{ctm}}(r,\tilde{r})|^2}{|r-\tilde{r}|}\right| \mathrm{d}r\mathrm{d}\tilde{r} &\lesssim L^{-\frac{70}{23}+\epsilon}\int_{Q_L^D\times Q_L^D}|r-\tilde{r}|^{-1}\mathrm{d}r\mathrm{d}\tilde{r} \\ &\quad + L^{-\frac{35}{23}+\epsilon}\int_{Q_L^D\times Q_L^D}\frac{(1+|r-\tilde{r}|_{D,2L})^{-2}}{|r-\tilde{r}|}\mathrm{d}r\mathrm{d}\tilde{r} \\ &\lesssim L^{\frac{45}{23}+\epsilon} + L^{\frac{34}{23}+\epsilon}\log L. \end{aligned}$$

Therefore, by the continuum formulas we have

$$E_x[\rho_L] \approx -\sum_{\tau,\sigma\in G}\det(\sigma\tau)\frac{\bar{\rho}^2 p_L^6}{4p_F^6}\underbrace{\int_{Q_L^D\times Q_L^D}\frac{h(p_L|r-\sigma\tilde{r}|_{D,2L})h(p_L|r-\tau\tilde{r}|_{D,2L})}{|r-\tilde{r}|}\mathrm{d}r\mathrm{d}\tilde{r}}_{:=J_{\sigma,\tau}(L)}, \quad (2.5.9)$$

where $\approx$ will be used throughout this proof to denote equality up to errors included in the remainder of Theorem 2.5.2. Now, to estimate the terms $J_{\sigma,\tau}$ we start with the following lemma.

Lemma 2.5.1. *If $trace(\sigma) \leqslant -1$ or $trace(\tau) \leqslant -1$, then $J_{\sigma,\tau}(L) \lesssim L(\log L)^2$. Furthermore, if $trace(\sigma) = 1 = trace(\tau)$ and $\sigma \neq \tau$, we also have $J_{\sigma,\tau}(L) \lesssim L(\log L)^4$.*

Proof. First observe that since $r_j, \tilde{r}_j \in [0, d_j L]$, one has

$$|r_j + \tilde{r}_j \mod 2d_jL| = \min\{r_j + \tilde{r}_j, 2d_jL - r_j - \tilde{r}_j\} \geqslant |r_j - \tilde{r}_j|.$$

In particular, by the decay of h, we see that

$$|h(p_L|r - \sigma\tilde{r}|_{D,2L})| \lesssim \frac{1}{(1 + |r - \sigma\tilde{r}|_{D,2L})^2} \lesssim \frac{1}{(1 + |r - \tilde{r}|)^2}, \tag{2.5.10}$$

for any $\sigma \in G$. On the other hand, if $trace(\sigma) \leqslant -1$, there exists $j \in \{1, 2, 3\}$ such that

$$|r - \sigma\tilde{r}| \geqslant \min_{\substack{p \in \pi_j(D(2L\mathbb{Z})^3) \\ p \in \pi_j(Q_{2L}^D)}} |\pi_j(r + \tilde{r}) - p|,$$

and therefore,

$$|h(p_L|r - \sigma\tilde{r}|_{D,2L})| \lesssim \sum_{\substack{p \in \pi_j(D(2L\mathbb{Z})^3) \\ p \in \pi_j(Q_{2L}^D)}} \frac{1}{(1 + |\pi_j(r + \tilde{r}) - p|)^2}. \tag{2.5.11}$$

As a result, assuming that $trace(\sigma) \leqslant -1$, we can see from (2.5.10) and (2.5.11) that

$$J_{\sigma,\tau}(L) \lesssim \int_{Q_L^D \times Q_L^D} \sum_{\substack{p \in \pi_j(D(2L\mathbb{Z})^3) \\ p \in \pi_j(Q_{2L}^D)}} \frac{1}{(1 + |\pi_j(r + \tilde{r}) - p|)^2} \frac{1}{(1 + |r - \tilde{r}|)^2} \frac{1}{|r - \tilde{r}|} \mathrm{d}r\mathrm{d}\tilde{r} \lesssim L(\log L)^2.$$

For the terms $J_{\sigma,\tau}$ with $trace(\sigma) = 1 = trace(\tau)$ and $\sigma \neq \tau$, note that there exists $j \neq \ell \in \{1, 2, 3\}$ such that

$$|h(p_L|r - \sigma\tilde{r}|)| \lesssim \sum_{p_j \in \{0, 2d_jL\}} \frac{1}{(1 + |r_j + \tilde{r}_j - p_j|)(1 + |\pi_j(r - \tilde{r}|)},$$
$$|h(p_L|r - \tau\tilde{r}|)| \lesssim \sum_{p_\ell \in \{0, 2d_\ell L\}} \frac{1}{(1 + |r_\ell + \tilde{r}_\ell - p_\ell|)(1 + |\pi_\ell(r - \tilde{r})|)}.$$

The lemma thus follows by integrating the product of the estimates above against the coulomb potential in the box $Q_L^D \times Q_L^D$. □

From the lemma above, it is enough to study $J_{\mathrm{id},\mathrm{id}}(L)$, $J_{\sigma,\mathrm{id}}(L)$ and $J_{\sigma,\sigma}(L)$ where $trace(\sigma) = 1$.

We start with $J_{\mathrm{id},\mathrm{id}}(L)$. In this case, we first note that $|r - \tilde{r}|_{D,2L} = |r - \tilde{r}|$ for any $r, \tilde{r} \in Q_L^D$. In particular, by the change of variables $(w(r, \tilde{r}), \tilde{w}(r, \tilde{r})) = (r - \tilde{r}, \tilde{r})$, we obtain

$$J_{\mathrm{id},\mathrm{id}}(L) = |Q^D|L^3 \int_{Q_L^D - Q_L^D} \frac{h(p_L|w|)^2}{|w|} \mathrm{d}w - L^2 \sum_{j=1}^{3} \Big(\prod_{\ell \neq j} d_\ell \Big) \int_{Q_L^D - Q_L^D} \frac{h(p_L|w|)^2 |w_j|}{|w|} \mathrm{d}w$$
$$+ \int_{Q_L^D - Q_L^D} \frac{h(p_L|w|)^2}{|w|} \Big(L \sum_{j=1}^{3} d_j \prod_{\ell \neq j} |w_\ell| - \prod_{j=1}^{3} |w_j| \Big) \mathrm{d}w.$$

Now, note that by the decay of h and a simple estimate, up to an error $\lesssim L\log L$, the integral on the first two terms can be taken over the whole $\mathbb{R}^3$, and the third integral can be neglected. In addition, by scaling out p_L, using spherical coordinates, and recalling that $|\partial Q^D| = 2(d_1d_2 + d_1d_3 + d_2d_3)$, we have

$$J_{\mathrm{id},\mathrm{id}}(L) \approx \frac{4\pi|Q^D|L^3}{p_L^2}\underbrace{\int_0^\infty h(r)^2 r\mathrm{d}r}_{:=I_0} - \frac{\pi|\partial Q^D|L^2}{p_L^3}\underbrace{\int_0^\infty h(r)^2r^2\mathrm{d}r}_{:=I_1}. \tag{2.5.12}$$

Next for the term $J_{\sigma,\sigma}$ we assume without loss of generality that $\sigma_{11} = -1$. Then, by invariance of the integrand over the reflections $r_i - \tilde{r}_i \mapsto \tilde{r}_i - r_i$, the change of variables $(w(r,\tilde{r}), \tilde{w}(r,\tilde{r})) = (r-\tilde{r}, r_1+\tilde{r}_1, \tilde{r}_2, \tilde{r}_3)$ (notice $\frac{\mathrm{d}w\mathrm{d}\tilde{w}}{2} = \mathrm{d}r\mathrm{d}\tilde{r}$), and the decay of h, we have

$$\begin{aligned}
J_{\sigma,\sigma}(L) &= \int_{Q_L^D - Q_L^D}\int_{|w_1|}^{2d_1L-|w_1|} \frac{h(p_L|(\tilde{w}_1 \mod 2d_1L, \pi_1 w)|)^2\prod_{\ell\neq 1}(d_\ell L - |w_\ell|)}{|w|}\frac{\mathrm{d}\tilde{w}_1\mathrm{d}w}{2}\\
&= 8d_2d_3L^2\int_{Q_L^D}\int_{w_1}^{d_1L}\frac{h(p_L|(\tilde{w}_1,\pi_1w)|)^2}{|w|}\mathrm{d}\tilde{w}_1\mathrm{d}w + \mathcal{O}(L\log L)\\
&= 8d_2d_3L^2\int_{Q_L^D} h(p_L|(\tilde{w}_1,\pi_1w)|)^2\left(\int_0^{\tilde{w}_1}\frac{1}{|w|}\mathrm{d}w_1\right)\mathrm{d}\tilde{w}_1\mathrm{d}\pi_1 w + \mathcal{O}(L\log L)
\end{aligned}$$

(where we inverted the order of integration between $\tilde{w}_1$ and w_1 in the last step). In addition, since $\int_0^{|\tilde{w}_1}\frac{1}{|w|}\mathrm{d}w_1 = \frac{1}{2}\log\left(\frac{\tilde{w}_1+|(\tilde{w}_1,\pi_1w)|}{|(\tilde{w}_1,\pi_1w)|-\tilde{w}_1}\right) \lesssim \frac{|\tilde{w}_1|}{|\pi_1 w|}$, by the decay of h one can see that, up to an error $\lesssim L$, we can replace the integration over Q_L^D by $\mathbb{R}^3_+$. Hence, by scaling out p_L, changing to spherical coordinates, and recalling the definition of I_1 in (2.5.12), we find that

$$J_{\sigma,\sigma}(L) \approx \frac{2\pi d_2d_3}{p_L^3}L^2\int_0^\infty h(r)^2r^2\mathrm{d}r\underbrace{\int_0^{\frac{\pi}{2}}\log\left(\frac{1+\cos\theta}{1-\cos\theta}\right)\sin\theta\mathrm{d}\theta}_{=(\cos\theta-1)\log(1-\cos\theta)-(1+\cos\theta)\log(1+\cos\theta)} = \frac{4\pi\log(2)}{p_L^3}d_2d_3I_1L^2. \tag{2.5.13}$$

At last, for $J_{\mathrm{id},\sigma}$ (again assuming that $\sigma_{11} = -1$ without loss of generality), by the change of variables $(w(r,\tilde{r}), \tilde{w}(r,\tilde{r})) = (r-\tilde{r}, r_1+\tilde{r}_1, \tilde{r}_2, \tilde{r}_3)$ and the same arguments from before, we conclude that

$$\begin{aligned}
J_{\mathrm{id},\sigma} &= \int_{Q_L^D - Q_L^D}\int_{|w_1|}^{d_1L}\frac{h(p_L|(\tilde{w}_1,\pi_1w)|)h(p_L|w|)\prod_{\ell\neq 1}(d_\ell L - |w_\ell|)}{|w|}\mathrm{d}\tilde{w}_1\mathrm{d}w\\
&= 8d_2d_3L^2\int_{\mathbb{R}^3_+}\int_{|w_1|}^\infty\frac{h(p_L|(\tilde{w}_1,\pi_1w)|)h(p_L|w|)}{|w|}\mathrm{d}\tilde{w}_1\mathrm{d}w + \mathcal{O}(L\log L).
\end{aligned}$$

Hence, scaling the p_L out and using spherical coordinates on w, we have

$$J_{\mathrm{id},\sigma}(L) \approx \frac{4\pi d_2d_3}{p_L^3}L^2\underbrace{\int_0^\infty\int_0^{\frac{\pi}{2}}\int_{r\cos\theta}^\infty h(\sqrt{(r\sin\theta)^2+\tilde{w}_1^2})h(r)r\sin\theta\mathrm{d}\tilde{w}_1\mathrm{d}\theta\mathrm{d}r}_{:=I_2}. \tag{2.5.14}$$

Thus by plugging (2.5.12),(2.5.13) and (2.5.14) into (2.5.9), we have

$$E_x[\rho_L] \approx -\frac{\bar{\rho}^2 p_L^6}{4p_F^6}\Big(J_{\mathrm{id},\mathrm{id}}(L) + \sum_{j=1}^{3} J_{\sigma_j,\sigma_j}(L) - \sum_{j=1}^{3}\big(J_{\mathrm{id},\sigma_j}(L) + J_{\sigma_j,\mathrm{id}}(L)\big)\Big)$$
$$\approx -\frac{\pi\bar{\rho}^2 p_L^4}{p_F^6} I_0 |Q^D|L^3 - \Big(-\frac{\pi\bar{\rho}^2 p_L^3}{4p_F^6} I_1 + \frac{\pi\log 2\bar{\rho}^2 p_L^3}{2p_F^6} I_1 - \frac{\pi\bar{\rho}^2 p_L^3}{p_F^6} I_2\Big)|\partial Q^D|L^2.$$

As a result, using Lemma 2.3.2 to replace p_L by p_F plus correction, we conclude that

$$E_x[\rho_L] \approx -\underbrace{\frac{\pi}{(3\pi^2)^{\frac{2}{3}}} I_0}_{c_x} \bar{\rho}^{\frac{4}{3}} |Q^D|L^3 - \Big(\underbrace{\frac{1}{6} I_0}_{c_{FM}} - \underbrace{\frac{1}{12\pi} I_1}_{c_{FS}} + \underbrace{\frac{\log 2}{6\pi} I_1 - \frac{1}{3\pi} I_2}_{c_{BL}}\Big)\bar{\rho}|\partial Q^D|L^2.$$

The proof is then completed by using the values of the integrals computed in the next lemma.

Lemma 2.5.2. *$I_0 = \frac{9}{4}$, $I_1 = \frac{3\pi}{2}$ and $I_2 = \frac{3\pi\log 2}{2}$.*

Proof. For I_0, we can use the identity $\int \frac{(\sin s - s\cos s)^2}{s^5}\mathrm{d}s = \frac{-2s^2+2s\sin(2s)+\cos(2s)-1}{s^4}$ (see e.g., [40, Lemma 6.1] for an elegant evaluation) to obtain

$$I_1 = \int_0^\infty 9\frac{(\sin s - s\cos s)^2}{s^5}\mathrm{d}s = -9\lim_{s\to 0}\frac{-2s^2+2s\sin(2s)+\cos(2s)-1}{s^4} = \frac{9}{4},$$

where the limit can be done by L'Hôpital's rule. Next, note that for any $a > 0$, by Plancherel's theorem, we have

$$\begin{aligned}\int_0^\infty h(r)h(ar)\mathrm{d}r &= \frac{1}{4\pi|B_1|^2}\int_{\mathbb{R}^3}\widehat{\chi}_{B_1}(k)\widehat{\chi}_{B_1}(ak)\mathrm{d}k \\ &= \frac{(2\pi)^3}{4\pi|B_1|^2 a^3}\int_{\mathbb{R}^3}\chi_{B_1}(k)\chi_{B_1}\Big(\frac{k}{a}\Big)\mathrm{d}k \\ &= \frac{3\pi}{2\max\{a,1\}^3}. \end{aligned} \tag{2.5.15}$$

In particular, the value of I_1 follows by setting $a = 1$. For I_2, first note that by using the inverse of polar coordinates $(r,\theta) = (\sqrt{x^2+y^2}, \arctan(y/x))$, one has

$$I_2 = \int_{\mathbb{R}^2_+}\int_x^\infty h\big(\sqrt{y^2+\tilde{w}_1^2}\big)h\big(\sqrt{x^2+y^2}\big)\frac{y}{\sqrt{x^2+y^2}}\mathrm{d}\tilde{w}_1\mathrm{d}x\mathrm{d}y.$$

Next, set $\mathcal{R} := \{(x,y,\tilde{w}_1) \in \mathbb{R}^3 : x > 0, y > 0, \tilde{w}_1 > x\}$ and consider the change of coordinates

$$T : \Big\{(s,\phi,v) \in \mathbb{R}^3 : s > 0, 0 < \phi < \frac{\pi}{2}, 0 < v < \log\Big(\frac{\sin\phi+1}{\cos\phi}\Big)\Big\} \to \mathcal{R}$$

$$(s,\phi,v) \mapsto (x,y,\tilde{w}_1) = T(s,\phi,v) = (s\cos\phi\sinh v, s\sqrt{\sin^2\phi - \cos^2\phi\sinh^2 v}, s\cos\phi\cosh v),$$

for which

$$\det \nabla T(s,\phi,v) = s^2 \frac{\sin(\phi)\cos(\phi)}{\sqrt{\sin^2\phi - \cos^2\phi \sinh^2 v}} = s^2 \cos\phi \frac{\sqrt{x^2+y^2}}{y}.$$

Then, by (2.5.15) and the substituion $\tau = \sin\phi$, we conclude that

$$\begin{aligned} I_2 &= \int_0^{\frac{\pi}{2}} \cos(\phi) \log\left(\frac{\sin\phi + 1}{\cos\phi}\right) \underbrace{\int_0^\infty h(s)h(s\sin\phi)s^2 \mathrm{d}s}_{=\frac{3\pi}{2}} \mathrm{d}\phi \\ &= \frac{3\pi}{2} \int_0^1 \log\left(\frac{\sqrt{1+\tau}}{\sqrt{1-\tau}}\right) \mathrm{d}\tau = \frac{3\pi \log 2}{2}, \end{aligned}$$

which completes the proof of Theorem 2.5.2 for the Dirichlet case. □

For the periodic case, we first note that by the decay of h,

$$|h(p_L|r-r'|_{L,D}|)^2 - \sum_{\substack{p\in DL\mathbb{Z}^3 \\ |D^{-1}p|_{\max}\leqslant L}} h(p_L|r-r'-p|)^2 \lesssim L^{-2}(1-|r-r'|_{L,D})^{-2}.$$

Moreover, one can show that

$$\int_{Q_L^D \times Q_L^D} \frac{h(p_L|r-\tilde{r}-p|)^2}{|r-\tilde{r}|} \mathrm{d}r\mathrm{d}\tilde{r} \lesssim L\log L \quad \text{for any } p \in DL\mathbb{Z}^3\backslash\{0\},$$

and therefore, $E_x[\Psi_L] \approx -\frac{\bar{\rho}^2 p_L^6}{4p_F^6} J_{id,id}(L)$. The result now follows from Lemma 2.3.2, estimate (2.5.12) and Lemma 2.5.2). □

2.6 Kinetic energy

In this section we use Lemma 2.1.1 to compute the asymptotic expansion of the kinetic energy.

Theorem 2.6.1 (Asymptotics of kinetic energy)**.** *Let D fixed, $\bar{\rho} = \frac{N}{|Q^D|L^3}$ = constant and $\Psi_{N,L}$ be any ground state of the free N-electron gas in the box Q_L^D under our usual boundary conditions. Let T be the kinetic energy functional defined in (2.1.1). Then, we have*

$$T[\Psi_{N,L}] = \begin{cases} c_{TF}\bar{\rho}^{5/3}|Q^D|L^3 + \mathcal{O}(L^{\frac{34}{23}+\epsilon}), & \text{for periodic BCs,} \\ c_{TF}\bar{\rho}^{5/3}|Q^D|L^3 + c_K\bar{\rho}^{4/3}|\partial Q^D|L^2 + \mathcal{O}(L^{\frac{34}{23}+\epsilon}), & \text{for Dirichlet BCs,} \\ c_{TF}\bar{\rho}^{5/3}|Q^D|L^3 - c_K\bar{\rho}^{4/3}|\partial Q^D|L^2 + \mathcal{O}(L^{\frac{34}{23}+\epsilon}), & \text{for Neumann BCs,} \end{cases}$$

where $c_{TF} = \frac{3}{10}(3\pi^2)^{2/3}$ is the Thomas-Fermi constant and $c_K = \frac{3\pi}{32}(3\pi^2)^{1/3}$.

Proof. For the Dirichlet case, just note that

$$T[\Psi_{N,L}] = \langle \Psi_{N,L}, -\frac{\Delta}{2}\Psi_{N,L}\rangle = \sum_{k\in\mathbb{N}^3\cap B^D_{R_N}} \frac{\pi^2|D^{-1}k|^2}{L^2} - (N_+ - N)\frac{\pi^2 R_N^2}{L^2}$$
$$= \frac{\pi^2}{L^2}\frac{1}{8}\Bigg(\sum_{k\in\mathbb{Z}^3\cap B^D_{R_N}} |D^{-1}k|^2 - \sum_{j=1}^{3}\sum_{\substack{k\in\mathbb{Z}^3\cap B^D_{R_N}\\ k_j=0}} |D^{-1}k|^2\Bigg) + \mathcal{O}(L^{\frac{34}{23}+\epsilon}).$$

Moreover, by a simple estimate[6] we find that

$$\sum_{\substack{k\in B^D_{R_N}\cap\mathbb{Z}^3\\ k_j=0}} |D^{-1}k|^2 = \int_{\mathbb{R}^2} \chi_{\pi_j(B^D_{R_N})}(k)\sum_{\ell\neq j}(d_\ell^{-1}k_\ell)^2 \mathrm{d}k + \mathcal{O}(R_N^3) = \frac{\pi}{4}R_N^4\prod_{\ell\neq j} d_\ell + \mathcal{O}(R_N^3) \tag{2.6.1}$$

Thus using estimate (2.6.1) and Lemma 2.1.1, we conclude that

$$T[\Psi_{N,L}] = \frac{1}{10\pi^2}p_{N,L}^5|Q^D|L^3 - \frac{1}{32\pi}p_{N,L}^4|\partial Q^D|L^3 + \mathcal{O}(L^{\frac{34}{23}+\epsilon}).$$

The result now follows from the asymptotic of p_L in Lemma 2.3.2. The Neumann and periodic case are entirely analogous. □

Remark. *Note that we do not assume $\Psi_{N,L}$ to be a determinantal ground states as the kinetic energy is simply the ground state energy of the Laplacian and therefore unique (even if the ground state is not).*

2.7 Numerical results

We now compare our asymptotic results to numerical values of different exchange functionals for the free electron gas with zero boundary conditions, for up to 30 000 electrons. Our numerical computations were carried out in Matlab. All energy functionals other than exact exchange were evaluated by direct numerical integration of the exact formulas given in section 2. For exact exchange, accurate direct numerical evaluation of the expression (2.2.11), (2.2.9) is impossible, because of the high-dimensionality of the domain of integration (6D) and the $1/|r-r'|$ singularity of the integrand. We tackled these obstructions by reducing the problem to the numerical computation of a small ($O(N^{1/3})$) number of one-dimensional integrals of smooth functions (see Section 2.7.1 for a detailed description). Moreover, we focus here on the case of a cubic box $[0,L]^3$ and $\bar{\rho} = 1$.

To begin with, in Figure 2.2 we have plotted the exact exchange energy per unit volume, together with the theoretical one-term (just c_x) and two-term asymptotics ($c_x + c_{x,2}\cdot 6L^{-1}$) from Theorem 2.1.1. For comparison we have also included the LDA exchange

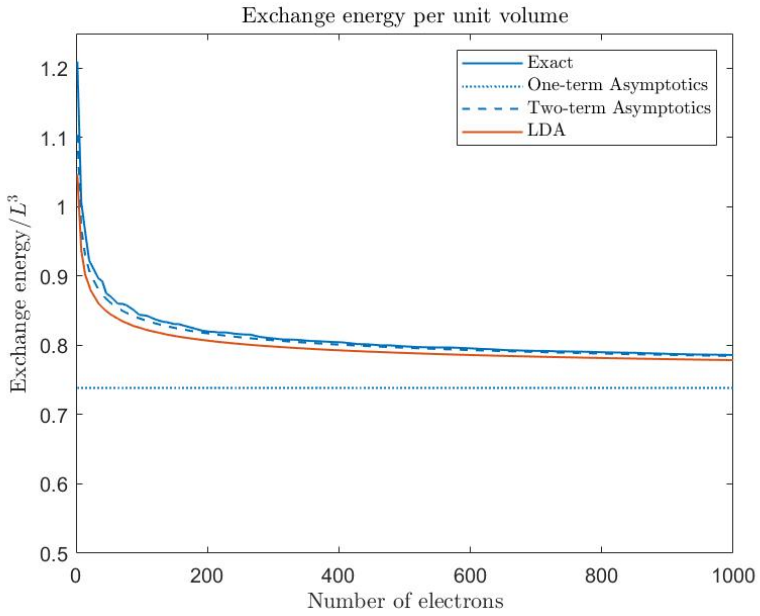

Figure 2.2: Exact exchange energy per unit volume of the free electron gas in a box with zero boundary conditions, compared with the LDA, one-term asymptotics (Dirac exchange constant) and two-term asymptotics (present work, Theorem 2.1.1).

energy per unit volume. Note that even for small N, the two-term asymptotics is a much better approximation than the one-term asymptotics, and also a better one than the more complicated LDA. Note that the latter requires integration of an inhomogeneous N-electron exchange energy density of the system.

Let us now look in more detail at the next-order contribution. Besides exact exchange and the LDA, we consider the widely used GGAs introduced by Becke in 1988 (B88) [6] and Perdew, Burke and Ernzerhof in 1996 (PBE) [92], and the modified version of PBE introduced by Perdew et al. in 2008 (PBEsol)[93]. For convenience of the reader, we recall the expressions for these functionals here:

$$g^{B88}(\rho, |\nabla\rho|) = \frac{2^{\frac{1}{3}}\beta\big(|\nabla\rho|/\rho^{\frac{4}{3}}\big)^2}{1 + 6\beta 2^{\frac{1}{3}}\big(|\nabla\rho|/\rho^{\frac{4}{3}}\big)\sinh^{-1}\big(2^{\frac{1}{3}}|\nabla\rho|/\rho^{\frac{4}{3}}\big)}\rho^{\frac{4}{3}} \tag{2.7.1}$$

$$g^{PBE}(\rho, |\nabla\rho|) = c_x\frac{\mu\big(|\nabla\rho|/\rho^{\frac{4}{3}}\big)^2}{4(3\pi^2)^{\frac{2}{3}} + \frac{\mu}{\kappa}\big(|\nabla\rho|/\rho^{\frac{4}{3}}\big)^2}\rho^{\frac{4}{3}} \tag{2.7.2}$$

where $\sinh^{-1}$ is the inverse hyperbolic sine and the constants are $\beta = 0.0042$, $\kappa = 0.804$, and $\mu = 0.2195$. For PBEsol, one has the same expression as for PBE in (2.7.2), but with $\mu = 0.1235$.

[6] In fact, by adapting the proof of [40], one can get a remainder of order $\mathcal{O}(R^{2+\frac{2}{3}})$ in estimate (2.6.1).

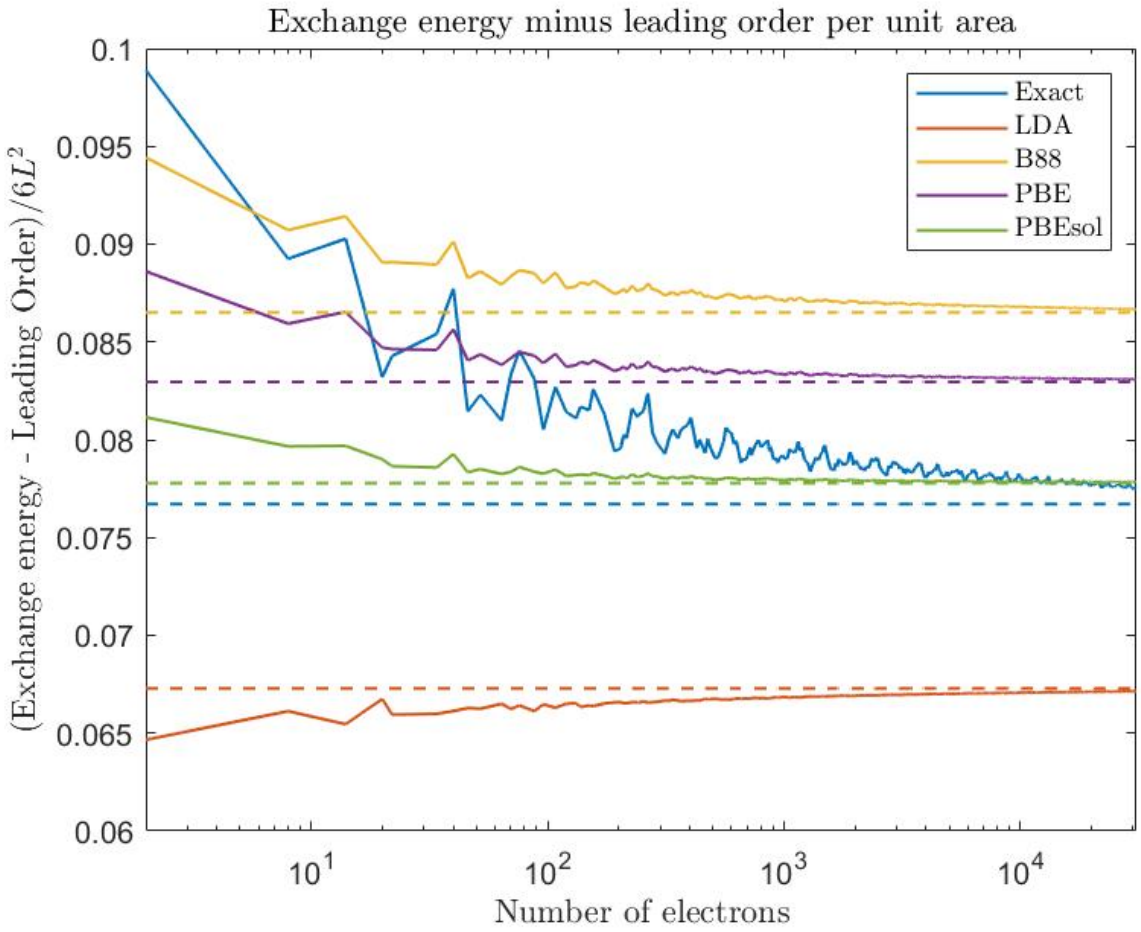

Figure 2.3: Exchange energy of the free electron gas in a box with zero boundary conditions minus leading order term, per unit boundary area, for various functionals. The number of electrons per unit volume was normalized to 1. Solid lines: Numerical values. Dashed lines: asymptotic values (second order coefficients from Theorem 2.1.1, present work).

Numerical evaluation of the exact one-dimensional integral expression for the GGA constant in Theorem 2.1.1 gives the following values:

$$c^{\mathrm{Dir}}_{PBE} \approx 0.0157, \quad c^{\mathrm{Dir}}_{B88} \approx 0.0192, \quad c^{\mathrm{Dir}}_{PBEsol} \approx 0.0105. \tag{2.7.3}$$

To numerically verify the next-order asymptotics, we plotted in Figure 2.3 the graph of the energy functionals minus the leading order term divided by the boundary area $|\partial[0,L]^3| = 6L^2$, together with the asymptotic values predicted by Theorem 2.1.1 and (2.7.3). Precisely, since $\bar{\rho} = 1$, the values for the dashed lines in Figure 2.3 are, respectively, $c^{\mathrm{Dir}}_{x,2}$, c^{Dir}_{LDA}, $c^{\mathrm{Dir}}_{LDA} + c^{\mathrm{Dir}}_{B88}$, $c^{\mathrm{Dir}}_{LDA} + c^{\mathrm{Dir}}_{PBE}$, and $c^{\mathrm{Dir}}_{LDA} + c^{\mathrm{Dir}}_{PBEsol}$.

Overall, there is a good match between numerics and asymptotics as N gets large. More detailed observations are the following.

- Asymptotically, the LDA underestimates the surface term by 12%, whereas B88 and PBE overestimate it by 13% respectively 8%.
- Asymptotically, only PBEsol is much more accurate than the LDA, exhibiting an error of just 1.4%. This should not come as a surprise to experts, as certain surface data (although not the ones considered here) entered into the choice of the parameters. Thus one may say that the present work provides an alternative theoretical justification of the PBEsol parameters. The price to pay is that PBEsol is the least accurate of the GGAs for very small N.
- B88 is the most accurate GGA for very small N. This is not unexpected given the fact that the parameter β was fitted to data for the first few noble gas atoms. The price to pay is that B88 does not improve on the LDA beyond a few hundred electrons.
- In the regime of 20 to 100 electrons, which is certainly relevant in applications, particularly in chemistry, PBE fares best.
- The slowest convergence to the asymptotic value, and the largest fluctuations, occur for exact exchange. Neither asymptotics up to second order nor any of the GGA functionals correctly reproduce these significant finite-N fluctuations. Note that they would be captured exactly by the universal Hohenberg-Kohn functional.

In the context of our model system, the free electron gas in a box with zero boundary conditions, our rigorous asymptotic results and the above observations illustrate both the advances that have been made in the physics and chemistry literature in designing computationally simple exchange-correlation functionals, and the immense difficulties in improving on the current state of the art. For the latter, we hope that the new exact constraint on GGAs presented here (eq. (2.1.12)) will in the future turn out to be useful.

2.7.1 Numerical scheme for exact exchange

Here we detail our scheme for accurate and efficient evaluation of exact exchange for the free electron gas in a box. As already explained, the closed-form expression (2.2.11), (2.2.9) cannot be evaluated directly by numerical integration, because of the high-dimensionality of the domain of integration (6D) and the Coulomb singularity of the integrand.

Recall that the eigenfunctions of the Laplacian with zero boundary conditions on $Q = [0,1]^3$ are given by the following expression:

$$\phi_k(x) = \prod_{i=1}^{3} \sqrt{2}\sin(\pi k_i x_i) \quad (k \in \mathbb{N}^3). \tag{2.7.4}$$

Hence for closed shell N, the ground state $\Psi_{N,L}$ of the free N-electron gas in $Q_L = [0,L]^3$ with $\bar{\rho} = N/L^3 = 1$ is unique and the exact exchange energy is, by rescaling to the fixed

domain Q,

$$E_x[\psi_{N,L}] = -\frac{1}{L}\int_{Q\times Q} \frac{\left|\sum_{k\in\mathbb{N}^3,\,|k|\leqslant R_N} \phi_k(x)\overline{\phi_k(y)}\right|^2}{|x-y|}dx\,dy$$
$$= -\frac{1}{L}\sum_{\substack{k,\ell\in\mathbb{N}^3\\ |k|,|\ell|\leqslant R_N}} \underbrace{\int_{Q\times Q} \frac{\prod_{i=1}^3 4\sin(\pi k_i x_i)\sin(\pi \ell_i x_i)\sin(\pi k_i y_i)\sin(\pi \ell_i y_i)}{|x-y|}dx\,dy}_{=:I_{k,\ell}} \tag{2.7.5}$$

where R_N is the Dirichlet Fermi radius defined in (2.2.6).

The starting point of our numerical scheme is a simple calculation which reduces the above six-dimensional integral to the three-dimensional integral of a separable function times the Coulomb potential over a finite region. For periodic boundary conditions such a reduction is trivial because the system is translation invariant, which implies that the exchange integrand depends only on the relative coordinate $z = x - y$; but the zero boundary condition breaks the translation invariance. Nevertheless the following holds:

Lemma 2.7.1. *For k, $\ell \in \mathbb{N}^3$, and $I_{k,\ell}$ as defined above,*

$$I_{k,\ell} = 8\int_{[0,1]^3} \frac{\prod_{i=1}^3 f_{k_i,\ell_i}(z_i)}{|z|}dz \tag{2.7.6}$$

where for $a, b \in \mathbb{N}$, $f_{a,b}$ is defined as

$$f_{a,b}(\tau) = \frac{1-\tau}{2}\Big(\cos(\pi(a+b)\tau) + \cos(\pi(a-b)\tau)\Big) + \left(\frac{1}{a}+\frac{1}{b}-\frac{1}{(a+b)}\right)\frac{\sin(\pi(a+b)\tau)}{2\pi}$$
$$+ \begin{cases} \left(\frac{1}{a}-\frac{1}{b}-\frac{1}{a-b}\right)\frac{\sin(\pi(a-b)\tau)}{2\pi} & \text{if } a \neq b,\\ \frac{1-\tau}{2} & \text{otherwise.}\end{cases} \tag{2.7.7}$$

We remark that there is a well known alternative reduction of any 6D Coulomb integral of the form $\int u(x)\frac{1}{|x-y|}v(y)\,dx\,dy$ to a 3D integral over reciprocal space, by using the convolution theorem for the Fourier transform. But this leads to an integral over an unbounded domain, a stronger ($\sim 1/|k|^2$) singularity, and – in our case – a slow decay of the integrand, making the expression (2.7.6) numerically much more favourable.

Proof. Using the identity $2\sin(A)\sin(B) = \cos(A-B) - \cos(A+B)$ and the change of variables $w = x + y$, $z = x - y$, and noting that the volume element becomes $\mathrm{d}x_i\mathrm{d}y_i = \frac{1}{2}\mathrm{d}w_i\mathrm{d}z_i$,

$$I_{k,\ell} = \int_{[-1,1]^3} \frac{1}{|z|}\prod_{i=1}^3 \underbrace{\left\{\frac{1}{2}\int_{|z_i|}^{2-|z_i|} \big(\cos\pi k_i z_i - \cos\pi k_i w_i\big)\big(\cos\pi \ell_i z_i - \cos\pi \ell_i w_i\big)dw_i\right\}}_{=:f_{k_i,\ell_i}(z_i)} dz.$$

The integral in the definition of $f_{a,b}(z_i)$ is elementary to evaluate by using the identity $2\cos A\cos B = cos(A+B) + \cos(A-B)$ for the term $\cos\pi a w_i \cos\pi b w_i$, yielding

$$f_{a,b}(z_i) = (1-|z_i|)\cos(\pi a z_i)\cos(\pi b z_i) + \cos(\pi a z_i)\frac{\sin(\pi b|z_i|)}{\pi b} + \cos(\pi b z_i)\frac{\sin(\pi a|z_i|)}{\pi a}$$
$$- \frac{\sin(\pi(a+b)|z_i|)}{2\pi(a+b)} \quad \begin{cases} -\frac{\sin(\pi(a-b)|z_i|)}{2\pi(a-b)} & \text{if } a \neq b, \\ +\frac{1-|z_i|}{2} & \text{otherwise.} \end{cases}$$

Next, we note that since $f_{a,b}(-z_i) = f_{a,b}(z_i)$ and the Coulomb potential $1/|z|$ is invariant under the transformations $z_i \mapsto -z_i$, we can replace $[-1,1]^3$ by $[0,1]^3$ by adding a factor of 8 in front of the integral. The final expression for $f_{a,b}$ given in the lemma now follows from the trigonometric identities $2\cos A\cos B = \cos(A+B)+\cos(A-B)$ and $\alpha\sin A\cos B + \beta\cos A\sin B = \frac{\alpha+\beta}{2}\sin(A+B) + \frac{\alpha-\beta}{2}\sin(A-B)$. □

Since the integrand in (2.7.6) is a separable function except for the Coulomb potential, the idea now is to also approximate the latter by separable functions, therefore reducing the problem to the computation of one dimensional integrals. Such an approximation is provided by recent advances in low-rank tensor approximation; more specifically, we use results of Hackbusch ([51, Section 9.8.2]). The Coulomb potential can be very accurately approximated by a sum of weighted Gaussians,

$$\frac{1}{r} \approx \sum_{j=1}^{M} \omega_j e^{-\alpha_j r^2}. \tag{2.7.8}$$

Plugging this approximation into equation (2.7.6) and factorizing $e^{-\alpha_j|z|^2} = \prod_{i=1}^{3} e^{-\alpha_j z_j^2}$, one obtains

$$I_{k,\ell} \approx 8\sum_{j=1}^{M}\omega_j \prod_{i=1}^{3} I_{k_i,\ell_i,j} \quad \text{with} \quad I_{a,b,j} = \int_0^1 f_{a,b}(t)e^{-\alpha_j t^2}dt, \tag{2.7.9}$$

which reduces the 3D integral in (2.7.6) to one-dimensional integrals of analytic functions.[7]

To reduce the overall number of 1D integrals that must be computed, let us introduce, for $p \in \{0,1,...,2\lfloor R_N^{\mathrm{Dir}}\rfloor\}$ and $j \in \{1,...,M\}$ (where $\lfloor\ \rfloor$ denotes the integer part), the auxiliary integrals

$$C_{p,j} := \int_0^1 \frac{1-t}{2}\cos(\pi p\, t)e^{-\alpha_j t^2}\mathrm{d}t \quad \text{and} \quad S_{p,j} := \int_0^1 \frac{\sin(\pi p\, t)}{2\pi}e^{-\alpha_j t^2}\mathrm{d}t. \tag{2.7.10}$$

It follows from the explicit expression for $f_{a,b}$ in (2.7.7) that

$$I_{a,b,j} = C_{a+b,j} + C_{|a-b|,j} + \left(\tfrac{1}{a}+\tfrac{1}{b}-\tfrac{1}{a+b}\right)S_{a+b,j}$$
$$+ \begin{cases} \left(\tfrac{1}{a}-\tfrac{1}{b}-\tfrac{1}{a-b}\right)\mathrm{sign}(a-b)S_{|a-b|,j} & \text{if } a \neq b \\ C_{0,j} & \text{if } a = b. \end{cases} \tag{2.7.11}$$

[7] In fact, one could represent these integrals exactly in terms of the error function $\mathtt{erf}$ and the imaginary error function $\mathtt{erfi}$, but we do not use this fact on our scheme.

Thus in total

$$E_x[\Psi_{N,L}] \approx -\frac{8}{L} \sum_{\substack{k,\ell\in\mathbb{N}^3 \\ |k|,|\ell|\leqslant R_N}} \sum_{j=1}^{M} \omega_j \prod_{i=1}^{3} I_{k_i,\ell_i,j} \tag{2.7.12}$$

with $I_{a,b,j}$ given by (2.7.10)–(2.7.11). In particular, as $R_N^{\mathrm{Dir}} \sim N^{1/3}$, calculating the exchange energy of the free N-electron gas reduces to the problem of evaluating $\mathcal{O}(N^{1/3}M)$ one-dimensional integrals of analytic functions on the interval $[0,1]$, and multiplying and summing them according to equation (2.7.12).

Next, let us discuss the choice of weights and exponents, and the error, in (2.7.8). We used the values $\{\omega_j^H, \alpha_j^H\}_{j=1}^{51}$ given on Hackbusch's webpage [50] for the (approximately) best approximation of the Coulomb potential as the sum of $M = 51$ Gaussians, which satisfy $\|1/r - v^H(r)\|_{L^\infty([1,10^9])} \leqslant 10^{-9}$ where $v^H(r) = \sum_{j=1}^{51} \omega_j^H e^{-\alpha_j^H r^2}$. Moreover since we are interested in a good approximation of $1/r$ on the unit cube, we rescaled Hackbusch's parameters by setting

$$\omega_j = \frac{\omega_j^H}{r_0} \quad \text{and} \quad \alpha_j = \frac{\alpha_j^H}{r_0^2},$$

which yields a pointwise error of

$$\|v(r) - 1/r\|_{L^\infty([r_0,10^9 r_0])} \leqslant r_0^{-1} \times 10^{-9} \tag{2.7.13}$$

where $v(r) = \sum_{j=1}^{51} \omega_j e^{-\alpha_j r^2}$. In our numerical results we chose $r_0 = 10^{-4}$, to achieve good accuracy in (2.7.6) both in the region $|z| < r_0$ (note that the integral of $1/|z|$ over this region is $\sim r_0^2$) and outside it.

Finally, let us discuss evaluation of the 1D integrals (2.7.10), which requires a moment's thought as one needs to resolve both the oscillatory trigonometric factor and the Gaussian factor. The wavevector πp is $\leqslant \pi \cdot 2R_N^{\mathrm{Dir}}$ and hence $\lesssim 200$ for up to $N = 30\,000$ electrons (in which case $R_N^{\mathrm{Dir}} \approx 31$), so the trigonometric oscillations can be accurately resolved by any standard quadrature method. The Gaussian factor, however, turns out to be more delicate, as the maximum value of α_j is $\approx 8 \times 10^8$. For $\alpha_j > 1$ we therefore used the following alternative expressions obtained by re-scaling:

$$C_{a,j} = \frac{1}{\sqrt{\alpha_j}} \int_0^{\sqrt{\alpha_j}} \left(\frac{1}{2} - \frac{t}{2\sqrt{\alpha_j}}\right) \cos(\pi a \frac{t}{\sqrt{\alpha_j}}) e^{-t^2} \mathrm{d}t, \tag{2.7.14}$$

$$S_{a,j} = \frac{1}{\sqrt{\alpha_j}} \int_0^{\sqrt{\alpha_j}} \frac{1}{2\pi} \sin(\pi a \frac{t}{\sqrt{\alpha_j}}) e^{-t^2} \mathrm{d}t. \tag{2.7.15}$$

Note that even though the integration interval may be big, for practical purposes one can truncate at $\min\{\sqrt{\alpha_j}, 10\}$ (as $\int_{10}^{\infty} e^{-t^2} \mathrm{d}t \approx 10^{-45}$).

2.8 Assumptions on GGAs

We now show that the expressions for the PBE and B88 functionals (see equations (2.7.2) and (2.7.1)) satisfy the assumptions of Theorem 2.1.1.

The C^1 regularity in $(0,\infty)\times\mathbb{R}$ is straightforward, so we just need to worry about the continuity when a goes to zero and b remains bounded. For this, let us rewrite equations (2.7.1) and (2.7.2) as

$$g^{PBE}(a,b) = c_x \frac{\mu s^2}{4(3\pi^2)^{\frac{2}{3}} + \frac{\mu}{\kappa}s^2} a^{\frac{4}{3}}$$
$$g^{B88}(a,b) = \frac{2^{\frac{1}{3}}s^2}{1+6\beta 2^{\frac{1}{3}} s \sinh^{-1}(2^{\frac{1}{3}}s)} a^{\frac{4}{3}} = \frac{2^{\frac{1}{3}}s}{1+6\beta 2^{\frac{1}{3}} s \sinh^{-1}(2^{\frac{1}{3}}s)} b$$

where $s = b/a^{\frac{4}{3}}$. Thus for the PBE, since the (enhancement) factor in front of $a^{\frac{4}{3}}$ is bounded, we see that $g^{PBE}(a,b) \to 0$ as $a \to 0$ regardless of b. For the B88, we make two observations: first, if $s \to \infty$ and b stays bounded, then $g^{B88}(a,b)$ goes to zero because of the superlinear growth of the denominator in the enhancement factor; and second, if s is bounded and $b \to 0$, then $g^{B88}(a,b)$ also goes to zero. In particular, as taking the limit $a \to 0$ with b bounded falls into one of these two cases, the assumption holds.

Chapter 3

Exchange Phenomena on Strictly Tessellating Polytopes

In this chapter, we extend the results from the previous chapter in three directions: (i) we extend the two-term asymptotics for the exchange energy and for semi-local density functionals to strictly tesselating polytopes and fundamental domains of lattices, (ii) we deal with general Riesz-type of interactions, and (iii) we work on arbitrary dimension $\mathbb{R}^n$ with $n \geqslant 2$. The methods used in this chapter also lead to a significant improvement on the remainder of Theorem 2.1.1. In addition, we prove a two-term generalized version of Weyl's law that includes boundary corrections.

3.1 Main results

We start with some notation and then present the main results of this chapter. Although the setting is quite similar to the previous chapter, we shall approach the problem from the spectral asymptotics point of view. Therefore, we will follow the notation from [110] and speak of eigenfunctions and spectral functions as opposed to the orbital functions and density matrix terminology from the previous chapter. The connection between the two viewpoints will be clarified later on.

Let $\Omega \subset \mathbb{R}^n$ denote an open, bounded, and connected subset with regular boundary. Then under either Dirichlet or Neumann boundary conditions (BCs), there exists a sequence $0 \leqslant \lambda_1 \leqslant \lambda_2 \leqslant ... \to \infty$ and an orthonormal basis (in $L^2(\Omega)$) of smooth functions $\{e_j\}_{j\in\mathbb{N}} \subset C^\infty(\Omega)$ such that

$$-\Delta e_j = \lambda_j^2 e_j,$$

where Δ is the Euclidean Laplacian (see [116]). One can thus define the spectral function and its scaled diagonal up to λ as

$$S_\lambda(r,\tilde{r}) := \sum_{\lambda_j \leqslant \lambda} e_j(r)\overline{e_j}(\tilde{r}) \quad \text{and} \quad S_{s,\lambda}(r) = \frac{1}{\lambda^n} S_\lambda\left(\frac{r}{\lambda}, \frac{r}{\lambda}\right). \tag{3.1.1}$$

Our goal for this chapter is to derive two-term asymptotic expansions for the exchange energy with Riesz interaction,

$$E_x(\lambda) = \int_{\Omega\times\Omega} \frac{|S_\lambda(r,\tilde{r})|^2}{|r-\tilde{r}|^s} \mathrm{d}r\mathrm{d}\tilde{r} \quad \text{with } 0 < s < n, \tag{3.1.2}$$

and for semi-local functionals

$$F(\lambda) = \int_{\Omega_\lambda} f\big(2S_{s,\lambda}(r), 2\nabla S_{s,\lambda}(r)\big)\mathrm{d}r, \tag{3.1.3}$$

in the limit as $\lambda \to \infty$. (The factor of 2 inside f comes from the spin of the electrons, see (3.1.10).) Note that the class of semi-local functionals includes the important example of the counting function

$$N(\lambda) := \#\{j : \lambda_j \leqslant \lambda\} = \int_{\Omega_\lambda} S_{s,\lambda}(r)\mathrm{d}r. \tag{3.1.4}$$

From this example and the extensive literature on it (see [62, 60, 61, 110, 104] and references therein), one sees that two-term asymptotics of this kind are often subtle and influenced by the regularity of the boundary and geometry of the domain. Even in the simple case of a connected domain with smooth boundary in $\mathbb{R}^n$, it is not known[1] whether the following two-term asymptotic formula holds:

$$N(\lambda) = \begin{cases} \frac{\omega_n}{(2\pi)^n}\lambda^n|\Omega| - \frac{\omega_{n-1}}{4(2\pi)^{n-1}}\lambda^{n-1}|\partial\Omega| + o(\lambda^{n-1}), & \text{for Dirichlet BCs,} \\ \frac{\omega_n}{(2\pi)^n}\lambda^n|\Omega| + \frac{\omega_{n-1}}{4(2\pi)^{n-1}}\lambda^{n-1}|\partial\Omega| + o(\lambda^{n-1}), & \text{for Neumann BCs,} \end{cases} \tag{3.1.5}$$

where ω_n is the volume of the unit ball on $\mathbb{R}^n$. Therefore, we restrict ourselves in this chapter to two types of domains where such asymptotics can be obtained: (i) the set of strictly tesselating polytopes $\Omega \subset \mathbb{R}^n$ (see Definition 3.2.1), and (ii) fundamental domains of lattices $\Gamma \subset \mathbb{R}^n$ with the periodic Laplacian.

On such domains, the main theorems of this chapter can be stated as follows.

Theorem 3.1.1 (Asymptotics of exchange energy)**.** *Let $\Omega \subset \mathbb{R}^n$ be a strictly tessellating polytope (see Definition 3.2.1) or the fundamental domain of a lattice. Let $E_x(\lambda)$ be the exchange energy defined in (3.1.2) and suppose that $n \geqslant 2$ and $\frac{n-1}{2} - \frac{n-1}{n+1} < s < n$. Then, for any $\epsilon > 0$ we have*

$$E_x(\lambda) = c_{x,1}(n,s)\lambda^{n+s}|\Omega| + \big(c_{FS}(n,s) + c_{BL}(n,s)\big)\lambda^{n-1+s}|\partial\Omega| + \mathcal{O}(\lambda^{r(n,s)+\epsilon}), \tag{3.1.6}$$

[1] Formula (3.1.5) is known to hold under some non-periodicity assumptions on the geodesic flow [62, 86]. Such assumptions are conjectured to hold for general smooth domains but only proved (to the knowledge of the author) for special cases such as convex domains (see [104])

where

$$r(n,s) = \begin{cases} \max\{s, 7/6, 1+s/6\} & \text{for } n=2, \\ \max\{n-2+s, (3n-2)/2-(n-1)/(n+1)\} & \text{otherwise,} \end{cases}$$

The leading exchange constant, the finite size, and the boundary layer corrections are given, respectively, by

$$c_{x,1}(n,s) = \frac{\omega_n^2}{(2\pi)^{2n}} \int_{\mathbb{R}^n} \frac{h_n(|z|)^2}{|z|^s} \mathrm{d}z, \qquad c_{FS}(n,s) = -\frac{\omega_n^2}{(2\pi)^{2n}} \int_{\mathbb{R}^n} \frac{h_n(|z|)^2 |z_n|}{2|z|^s} \mathrm{d}z,$$
$$c_{BL}^{\mathrm{Per}}(n,s) = 0,$$
$$c_{BL}^{\mathrm{Dir}}(n,s) = \frac{\omega_n^2}{(2\pi)^{2n}} \int_{\mathbb{R}^n} \int_{|z_n|}^{\infty} h_n(|(\pi_n z, w_n)|) \frac{h_n(|(\pi_n z, w_n)|) - 2h_n(|z|)}{2|z|^s} \mathrm{d}w_n \mathrm{d}z,$$
$$c_{BL}^{\mathrm{Neu}}(n,s) = \frac{\omega_n^2}{(2\pi)^{2n}} \int_{\mathbb{R}^n} \int_{|z_n|}^{\infty} h_n(|(\pi_n z, w_n)|) \frac{h_n(|(\pi_n z, w_n)|) + 2h_n(|z|)}{2|z|^s} \mathrm{d}w_n \mathrm{d}z,$$

where $\omega_n = |B_1|$ is the volume of the unit ball in $\mathbb{R}^n$, $h_n(|r|) = \widehat{\chi_{B_1}}(r)/\omega_n$ is the normalized Fourier transform of the characteristic function of B_1, π_n is the projection $\pi_n(r) = (r_1, ..., r_{n-1})$, and the superscript Per, Dir, and Neu indicate periodic, Dirichlet, and Neumann boundary conditions.

Theorem 3.1.2 (Asymptotics of semi-local functionals)**.** *Let $\Omega \subset \mathbb{R}^n$ be either a strictly tessellating polytope or a fundamental domain of a lattice. Suppose $f \in C^1\big((0,\infty) \times \mathbb{R}^n\big) \cap L^\infty_{\mathrm{loc}}([0,\infty) \times \mathbb{R}^n)$. Then, for $F(\lambda)$ defined in (3.1.3) we have*

$$F(\lambda) = f(\nu_0)\lambda^n |\Omega| + c(f,\Omega)\lambda^{n-1} + o(\lambda^{n-1}), \tag{3.1.7}$$

where

$$c(f,\Omega) = \begin{cases} \displaystyle\int_{\partial\Omega} \left(\int_0^\infty f(\nu_0 - \nu_1(\tau, r')) - f(\nu_0) \mathrm{d}\tau \right) \mathrm{d}\mathcal{H}^{n-1}(r'), & \text{for Dirichlet BCs,} \\ \displaystyle\int_{\partial\Omega} \left(\int_0^\infty f(\nu_0 + \nu_1(\tau, r')) - f(\nu_0) \mathrm{d}\tau \right) \mathrm{d}\mathcal{H}^{n-1}(r'), & \text{for Neumann BCs,} \end{cases}$$

and

$$\nu_0 := \frac{2\omega_n}{(2\pi)^n}(1,0) \in \mathbb{R} \times \mathbb{R}^n, \quad \nu_1(\tau, r') := \frac{2\omega_n}{(2\pi)^n}\big(h_n(2\tau), 2\dot{h_n}(2\tau) n(r')\big),$$

where $n(r')$ is the inwards pointing unit normal to $\partial\Omega$ at r', $\mathcal{H}^{n-1}$ is the $(n-1)$-dimensional Hausdorff measure, and ω_n and h_n are the same from Theorem 3.1.1.

Remark. *A few remarks are in place:*

(i) Due to radial symmetry of the interaction $1/|r|^s$, the coefficients $c_{x,1}(n,s)$, $c_{FS}(n,s)$ and $c_{BL}(n,s)$ can be computed by numerically evaluating a 1D, 2D, and 3D integral respectively. In fact, Theorem 3.1.1 can be directly extended to non-radial interactions w satisfying $c/|r|^s \leqslant w(r) \leqslant C/|r|^s$ for some positive constants $c, C > 0$ (e.g. positively homogeneous interactions).

(ii) For the Coulomb interaction in 3D, the constants can be analytically computed (see Lemma 2.5.2 in Chapter 2) and are given by

$$c_{x,1}(3,1) = \frac{1}{4\pi^3}, \quad c_{FS}(3,1) = -\frac{1}{24\pi^2}, \quad \text{and} \quad c_{BL}^{Dir}(3,1) = -\frac{\log 2}{12\pi^2}.$$

(iii) By $f \in L_{\mathrm{loc}}([0,\infty) \times \mathbb{R}^3)$ we mean that f is bounded on $[0,T] \times K$ for any $T > 0$ and $K \subset \mathbb{R}^n$ compact.

(iv) The asymptotics of semi-local functionals for the periodic case is trivial and has no boundary corrections because $S_{s,\lambda}(r) = \frac{N(\lambda)}{\lambda^n} = \frac{\omega_n}{(2\pi)^n} + \mathcal{O}(\lambda^{-1-\frac{n-1}{n+1}})$ in this case. The seemingly unphysical boundary corrections for the exchange energy come from the fact that the interaction considered is not periodic (as in Chapter 2).

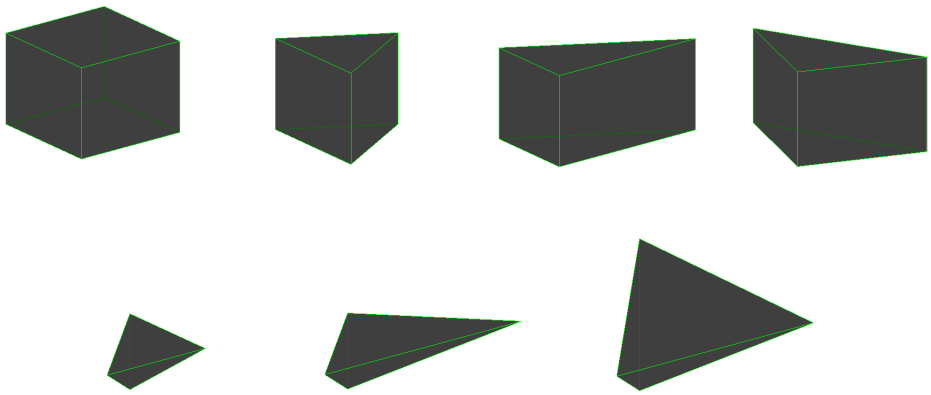

Figure 3.1: Kaleidoscopic polytopes in $\mathbb{R}^3$. From left upper corner: rectangular parallelepiped, equilateral prism, 30-60-90 prism, isosceles (45-45-90) prism, quadrirectangular tetrahedron, trirectangular tetrahedron, and tetragonal disphenoid.

The thermodynamic limit of the free electron gas. Let us now briefly describe how the quantities $E_x(\lambda)$ and $F(\lambda)$ in the limit $\lambda \to \infty$ are related to the thermodynamic limit for the free electron gas (FEG). First, recall that the FEG is a collection of non-interacting electrons confined to a region $\Omega \subset \mathbb{R}^3$. For N particles, the ground state of the system is described by a N-body wave function $\Psi : (\Omega \times \mathcal{S})^N \to \mathbb{C}$ minimizing the kinetic energy

$$T[\Psi] = \frac{1}{2} \int_{(\Omega \times \mathcal{S})^N} |\nabla \Psi(x_1, ..., x_N)|^2 \mathrm{d}x_1 ... \mathrm{d}x_N$$

and subject to the following constraints: (i) normalization in $L^2((\Omega \times \mathcal{S})^N)$, (ii) anti symmetry with respect to the permutation of the space-spin variables $x_\ell = (r_\ell, s_\ell)$[2], and (iii) suitable boundary conditions (e.g. Dirichlet or Neumann). Here, $\mathcal{S} \coloneqq \{0, 1\}$ denotes the spin states. Therefore, any ground state wave function of the FEG is a linear combination of antisymmetric N-fold tensor products (or Slater determinants) of the (orbital) functions $\phi_\ell \in L^2(\Omega \times \mathcal{S})$ given by

$$\phi_\ell(r, s) = e_{\lfloor \ell/2 \rfloor}(r)\chi_{\ell - 2\lfloor \ell/2 \rfloor}(s) \tag{3.1.8}$$

where $\lfloor \ell/2 \rfloor$ is the greatest integer smaller than or equal to $\ell/2$ (the floor function) and $\chi_j(s) = 1$ for $s = j$ and zero otherwise. In particular, if N satisfies the closed shell condition

$$N = 2N(\lambda) \quad \text{for some } \lambda > 0, \tag{3.1.9}$$

where $N(\lambda)$ is the counting function (see (3.1.4)), then the ground state Ψ_N is unique, and the associated (spinless) single-particle reduced density matrix is related to the spectral function by the formula

$$\gamma_{\Psi_N}(r, r') = N \sum_{s \in \mathcal{S}} \int_{(\Omega \times \mathcal{S})^{N-1}} \Psi(r, s, x_2.., x_N)\overline{\Psi}(r', s, x_2, ..., x_N)\mathrm{d}x_2...\mathrm{d}x_N = 2S_\lambda(r, r'). \tag{3.1.10}$$

Moreover, if we assume the interactions between electrons to be of Coulomb type, the exchange energy of a Slater determinant Ψ is defined as the difference

$$E_x[\Psi] = \underbrace{\langle \Psi, \sum_{1 \leqslant i < j \leqslant N} \frac{1}{|r_i - r_j|} \Psi \rangle}_{V_{ee}[\Psi]} - \underbrace{\frac{1}{2} \int_{\Omega \times \Omega} \frac{\rho_\Psi(r)\rho_\Psi(r')}{|r - r'|} dr\, dr'}_{J[\rho_\psi]}, \tag{3.1.11}$$

where V_{ee} is the electron-electron interaction energy and $J[\rho_\Psi]$ is the classical electrostatic energy of a charged cloud with distribution given by the single-particle density

$$\rho_\Psi(r) = N \sum_{s \in \mathcal{S}} \int_{(\Omega \times \mathcal{S})^{N-1}} |\Psi(r, s, x_2, ..., x_N)|^2 \mathrm{d}x_2...\mathrm{d}x_N. \tag{3.1.12}$$

Therefore, the exchange energy of the ground state Ψ_N of the FEG with $2N(\lambda)$ particles in Ω can be written as[3]

$$E_x[\Psi_N] = -\frac{1}{4} \int_{\Omega \times \Omega} \frac{|\gamma_{\Psi_N}(r, r')|^2}{|r - r'|} \mathrm{d}r\mathrm{d}r' = -\int_{\Omega \times \Omega} \frac{|S_\lambda(r, r')|^2}{|r - r'|} \mathrm{d}r\mathrm{d}r' = -E_x(\lambda), \tag{3.1.13}$$

[2]In this section we will always use x for space-spin variables and r for space only. We also use the notation $\int_{\Omega \times \mathcal{S}} f(x)\mathrm{d}x = \sum_{s \in \mathcal{S}} \int_\Omega f(r, s)dr$

[3]This follows from straightforward computation by taking the Slater determinant of the orbitals in (3.1.8) and plugging into (3.1.11).

where $E_x(\lambda)$ is the function defined in (3.1.2). Similarly, we can relate the function $F(\lambda)$ defined in (3.1.3) with generalized gradient approximations (GGA) for the exchange energy. In the physics literature [6, 92], exchange GGAs are commonly expressed as

$$E_x^{\mathrm{GGA}}[\rho] = -\int_\Omega c_x \rho(r)^{\frac{4}{3}} F_x\big(s(r)\big)\mathrm{d}r, \tag{3.1.14}$$

where $c_x = (3/\pi)^{\frac{1}{3}}3/4$ is the Dirac constant, $s(r) = |\nabla\rho(r)|/\rho(r)^{\frac{4}{3}}$ is the dimensionless reduced gradient and the function $F_x : [0,\infty) \to \mathbb{R}$ is called the enhancement factor and satisfy $F_x(0) = 1$. So if we apply E_x^{GGA} to the ground state density ρ_λ (defined via (3.1.12)) of the FEG with $2N(\lambda)$ particles in Ω, then (after a scaling argument) we arrive at the formula

$$E_x^{\mathrm{GGA}}[\rho_\lambda] = \lambda F(\lambda), \tag{3.1.15}$$

where F is defined by (3.1.3) with $f(2\rho, 2\nabla\rho) = -c_x\rho^{\frac{4}{3}}F_x(|\nabla\rho|/\rho^{\frac{4}{3}})$. Therefore, Theorems 3.1.1 and 3.1.2 yield the following corollary.

Corollary 3.1.1 (Exchange functionals for the FEG in the thermodynamic limit)**.** *Let Ω be a strictly tessellating polyhedron or a fundamental domain of a lattice and define $\Omega_\lambda = \{r \in \mathbb{R}^3 : r/\lambda \in \Omega\}$. Let ρ_λ be the single-particle density associated to the unique ground state Ψ_λ of the free electron gas in Ω_λ with $2N(\lambda)$ particles under either Dirichlet, Neumann, or periodic boundary conditions. Suppose also that $(a,b) \mapsto a^{\frac{4}{3}}F_x(b/a^{\frac{4}{3}}) \in C^1((0,\infty)\times[0,\infty)) \cap L^\infty_{\mathrm{loc}}([0,\infty)\times[0,\infty))$. Then we have*

$$E_x[\Psi_\lambda] = -c_x\bar{\rho}^{\frac{4}{3}}|\Omega|\lambda^3 + c_{x,2}\bar{\rho}|\partial\Omega|\lambda^2 + \mathcal{O}(\lambda^{\frac{3}{2}}\log\lambda), \tag{3.1.16}$$

$$E_x^{\mathrm{GGA}}[\rho_\lambda] = -c_x\bar{\rho}^{\frac{4}{3}}|\Omega|\lambda^3 + c_{x,2}^{\mathrm{GGA}}\bar{\rho}|\partial\Omega|\lambda^2 + o(\lambda^2) \tag{3.1.17}$$

where $c_x = (3/4)(3/\pi)^{\frac{1}{3}}$ is the Dirac constant, $\bar{\rho} = \lim_{\lambda\to\infty}\frac{2N(\lambda)}{|\Omega_\lambda|} = \frac{1}{3\pi^2}$ is the average density in the thermodynamic limit, and the second coefficients are given by

$$c_{x,2} = \begin{cases} 1/8 & \text{for periodic BCs,} \\ (1+2\log 2)/8 & \text{for Dirichlet BCs,} \\ (1-6\log 2)/8 & \text{for Neumann BCs,} \end{cases} \tag{3.1.18}$$

and

$$c_{x,2}^{\mathrm{GGA}} = \begin{cases} \dfrac{c_x}{(3\pi^2)^{\frac{1}{3}}}\displaystyle\int_0^\infty \left[1-\big(1-h_3(2\tau)\big)^{\frac{4}{3}}F_x\left(\frac{2(3\pi^2)^{\frac{1}{3}}|\dot{h_3}(2\tau)|}{\big(1-h_3(2\tau)\big)^{\frac{4}{3}}}\right)\right]\mathrm{d}\tau & \text{for Dirichlet BCs,} \\ \dfrac{c_x}{(3\pi^2)^{\frac{1}{3}}}\displaystyle\int_0^\infty \left[1-\big(1+h_3(2\tau)\big)^{\frac{4}{3}}F_x\left(\frac{2(3\pi^2)^{\frac{1}{3}}|\dot{h_3}(2\tau)|}{\big(1+h_3(2\tau)\big)^{\frac{4}{3}}}\right)\right]\mathrm{d}\tau & \text{for Neumann BCs,} \end{cases} \tag{3.1.19}$$

where $h_3(\tau) = 3(\sin\tau - \tau\cos\tau)/\tau^3$.

We, therefore, conclude that exchange GGAs can capture the surface corrections to the exchange energy of the Dirichlet FEG in the thermodynamic limit exactly, as long as the enhancement factor F_x satisfies the following constraint:

$$\frac{1}{2(3\pi^2)^{\frac{1}{3}}}\int_0^\infty \left[1-\big(1-h_3(\tau)\big)^{\frac{4}{3}} F_x\left(2(3\pi^2)^{\frac{1}{3}}\frac{|\dot{h}_3(\tau)|}{(1-h_3(\tau))^{\frac{4}{3}}}\right)\right]\mathrm{d}\tau = \frac{c_{x,2}}{c_x}. \tag{3.1.20}$$

with $c_{x,2}$ and c_x defined in Corollary 3.1.1.

Connection to the previous chapter. Let us briefly comment on how the results presented above are connected to the results from the previous chapter. First, observe that the thermodynamic limit considered here differs slightly from the one in Chapter 2. While in Chapter 2 we considered the limit $N \to \infty$ with a fixed average density of particles $\bar{\rho}$, in this chapter the average density is

$$\bar{\rho} = 2N(\lambda)/|\Omega_\lambda| = (3\pi^2)^{-\frac{1}{3}} + c\lambda^{-1} + \mathcal{O}(\lambda^{-\frac{3}{2}}),$$

which is only approximately constant. On the other hand, the finite-size Fermi momentum here is constant (equals to 1 for every λ) as opposed to Chapter 2, where it has an asymptotic expansion with a correction of order $1/L$ (see Lemma 2.3.2). In particular, the asymptotic expansions stated here are more natural from the mathematical perspective. (Compare the coefficients in Theorem 2.1.1 and Corollary 3.1.1.) Nonetheless, we remark that the proposed constraint for the GGAs in (3.1.20) and in (2.1.12) are *the same* and, therefore, independent of the precise specifics of the thermodynamic limit.

Proof strategy. The underlying strategy in the proofs of Theorems 3.1.1 and 3.1.2 is the same and consists of two main steps: (i) we obtain precise asymptotics for the spectral function, including the behavior close to the boundary, and (ii) we perform a careful analysis of the interior and boundary terms.

The first step is done via the wave equation (or kernel) method (see the next section). To construct the exact wave kernel for all times, we use the symmetries of the domain Ω. At this step, the reflection (respectively, translation) symmetry of the strictly tessellating polytopes (respectively, fundamental domains of lattices) plays a central role and is the main reason for our restriction to such domains. With the exact wave kernel at hand, we follow the approach in [110, Chapter 3] to obtain the continuum limit of the spectral function with explicit uniform estimates. Such estimates include derivatives and are not restricted to the diagonal; they can be stated as follows.

Theorem 3.1.3 (Asymptotics of the spectral function)**.** *Let $\Omega \subset \mathbb{R}^n$ be a strictly tessellating polytope or a fundamental domain of a lattice. Then for any $\alpha, \beta \in \mathbb{N}_0^n$, there exists a constant $C = C(\Omega, \alpha, \beta) > 0$ such that*

$$\left|\partial_r^\alpha \partial_{r'}^\beta S_\lambda(r,r') - \partial_r^\alpha \partial_{r'}^\beta S_\lambda^{\mathrm{ctm}}(r,r')\right| \leqslant C\left(1+\lambda^{n-1-\frac{n-1}{n+1}+|\alpha|+|\beta|}\right), \tag{3.1.21}$$

where

$$S_\lambda^{\mathrm{ctm}}(r,r') = \begin{cases} \dfrac{\omega_n}{(2\pi)^n}\lambda^n \displaystyle\sum_{v\in\mathcal{T}_\Omega^{nb}} h_n(\lambda|r-r'+v|) & \text{for periodic BCS,} \\ \dfrac{\omega_n}{(2\pi)^n}\lambda^n \displaystyle\sum_{\sigma\in\mathcal{R}_\Omega^{nb}} \det\sigma h_n(\lambda|r-\sigma r'|) & \text{for Dirichlet BCs,} \\ \dfrac{\omega_n}{(2\pi)^n}\lambda^n \displaystyle\sum_{\sigma\in\mathcal{R}_\Omega^{nb}} h_n(\lambda|r-\sigma r'|)\big) & \text{for Neumann BCs,} \end{cases} \tag{3.1.22}$$

where ω_n and h_n are the same from Theorem 3.1.1, $\mathcal{T}_\Omega^{nb}$ and $\mathcal{R}_\Omega^{nb}$ are respectively the sets of neighbouring translations and reflections of Ω, and $\det\sigma$ is the determinant of the linear part of σ. (See (3.2.7) and the preceding discussion for the proper definitions.)

Remark. *Let us remark that upon completion of this work, we found an old paper by Berard [9] containing similar formulas as the ones proved in Theorem 3.1.3 and Corollary 3.2.1. The method of proof also seems to be similar. Unfortunately, we could not find an English version of [9] to compare them properly.*

As a corollary of the above estimates, we obtain a generalized version of the two-term Weyl law with improved remainders (see Theorem 3.3.1). Estimates (3.1.21) are also enough to justify using the continuum spectral function for the asymptotics of $F(\lambda)$. This follows by using the Lipschitz regularity of the function f in the integrand of $F(\lambda)$, and a cut-off away from the boundary to avoid the points where $\rho = 0$ and f is no longer Lipschitz (see Section 3.4).

On the other hand, the above estimates are not enough to justify using the continuum approximation S_λ^{ctm} for the exchange energy. Roughly speaking, this is because the exchange energy is given by integration against the square of the spectral function. Therefore, the error estimate in (3.1.21) yields an error proportional to $(\lambda^{\frac{3}{2}})^2 = \lambda^3$ (in the 3D Coulomb case) between the exchange energy of the spectral function and its continuum version, which is precisely of the order of the second term in Theorem 3.1.1. In Chapter 2, we overcame this problem by using the theory of exponential sums to improve the remainder in (3.1.21) from $\lambda^{\frac{3}{2}}$ to $\lambda^{\frac{3}{2}-\frac{1}{46}+\epsilon}$. This was possible because explicit eigenfunction formulae are available in the rectangular box. In this chapter, however, our goal is to derive such asymptotics without any explicit expressions for the eigenfunctions. Inspired by the work of Schmidt [105], where the bulk asymptotics of the spectral function as well as the leading order exchange constant were justified for general domains, we realized that interpolating the L^∞ estimates from Theorem 3.1.3 with L^2 estimates is a much more efficient approach for two reasons: first, the L^2 estimates can be obtained by slightly modifying the proof of the L^∞ estimates; and second, they lead to a significant improvement in the remainder of the asymptotic expansion of the exchange energy. Our main estimate in the L^2 setting is the following.

Theorem 3.1.4 (L^2 estimate of spectral function)**.** *Let $\Omega \subset \mathbb{R}^n$ be a strictly tessellating polytope or a fundamental domain of a lattice. Then, there exists $C = C(n,\Omega) > 0$ such*

that

$$\|S_\lambda - S_\lambda^{\mathrm{ctm}}\|_{L^2(\Omega\times\Omega)} \leqslant C(1+\lambda^{\frac{n-1}{2}}), \tag{3.1.23}$$

where S_λ^{ctm} *is the same from Theorem 3.1.3.*

By combining Theorems 3.1.3 and 3.1.4, we can justify the use of the continuum spectral function in the calculation of the exchange energy. The asymptotic expansion for $E_x(\lambda)$ then follows from geometric considerations and a careful analysis of the boundary and interior terms (see Section 3.4).

Structure of the chapter. In Section 3.2, we construct the exact wave kernel and derive a generalized Poisson summation formula on strictly tessellating polytopes. We then use this Poisson summation formula to prove Theorems 3.1.3 and 3.1.4 in Section 3.3. The proof of the main theorems of this chapter is given in Section 3.4. In Section 3.5, we show that the definition of strictly tessellating polytopes presented here is equivalent to [101, Definition 2]. We postpone the proof of the generalized Weyl law (Theorem 3.3.1) to Section 3.6. Finally, in Section 3.7 we comment on possible extensions and applications of the results presented here.

Notation

In this chapter $\Omega \subset \mathbb{R}^n$ will always denote a bounded, connected, and open subset of $\mathbb{R}^n$, where $n \geqslant 2$. Moreover, we denote the characteristic function of a set $\Omega \subset \mathbb{R}^n$ by χ_Ω and its re-scaled version by a factor $c > 0$ by $\Omega_c = \{r \in \mathbb{R}^n : r/c \in \Omega\}$. The unit ball in $\mathbb{R}^n$ is denoted by B_1. For the Fourier transform of a function $f : \mathbb{R}^n \to \mathbb{C}$ we use the convention

$$\widehat{f}(k) = \int_{\mathbb{R}^n} f(r)e^{-ik\cdot r}\mathrm{d}r,$$

where $k\cdot r = \sum_{j=1}^n k_j r_j$ is the standard scalar product in $\mathbb{R}^n$. The inverse Fourier transform is denoted by $\widehat{f}$. The Schwartz space of smooth fast decaying functions in $\mathbb{R}^n$ and its dual, the space of tempered distribution, are denoted respectively by $S(\mathbb{R}^n)$ and $S'(\mathbb{R}^n)$. Here we use the standard big-O and small-O notation. More precisely, for functions $f : [0,\infty) \to \mathbb{R}$ and $g : [0,\infty) \to \mathbb{R}$ we say that $f = \mathcal{O}(g)$ respectively $f = o(g)$ provided that

$$\limsup_{\lambda\to\infty} \frac{|f(\lambda)|}{|g(\lambda)|} < \infty \quad \text{respectively} \quad \limsup_{\lambda\to\infty} \frac{|f(\lambda)|}{|g(\lambda)|} = 0.$$

We also use the notation $f \lesssim g$ to indicate the existence of an unimportant constant $C > 0$ such that $|f(\lambda)| \leqslant C|g(\lambda)|$ for all values of λ large enough. In addition, if f or g depends on additional parameters (e.g. ϵ), we indicate the dependence of the constant C on this parameter by using the notation $f \lesssim_\epsilon g$.

3.2 The wave kernel and Poisson summation

In this section, we recall some basic facts about the homogeneous wave equation (see for instance [110, 104] for more detailed discussions). We then use these classical results to construct the exact wave kernel on strictly tessellating polytopes and fundamental domains of lattices, which leads to a generalized Poisson summation formula for radial functions. This summation formula is the key ingredient in the proofs of Theorems 3.1.3 and 3.1.4.

We start by recalling some classical existence, uniqueness and regularity results for the solutions of the wave equation on bounded domains. In what follows, we assume $\Omega \subset \mathbb{R}^n$ to be an open, bounded, and connected domain with Lipschitz boundary. Then, let us consider the initial value problem (IVP) for the wave equation in Ω,

$$\begin{cases} \partial_{tt} u - \Delta u = 0 & \text{in } \Omega \times \mathbb{R}, \\ \partial_t u(r,0) = 0, & \\ u(r,0) = g(r) & \text{for some } g \in C_c^\infty(\Omega), \end{cases} \tag{3.2.1}$$

with the boundary conditions (BCs)

$$\begin{cases} u(r,t) = 0 & \text{on } \partial\Omega \times \mathbb{R} \text{ (Dirichlet BCs), or} \\ \nabla_r u(r,t) \cdot n(r) = 0 & \text{on } \partial\Omega \times \mathbb{R} \text{ (Neumann BCs),} \end{cases} \tag{3.2.2}$$

where $n(r)$ is the unit normal vector to $\partial\Omega$ at r. Then, for an initial condition $g \in C_c^\infty(\Omega)$, the unique solution to (3.2.1)(3.2.2) in $C^\infty(\Omega \times \mathbb{R})$ is given by

$$u(r,t) = \big(\cos(t\sqrt{-\Delta_\Omega})g\big)(r),$$

where Δ_Ω is the self-adjoint extension of the Laplacian in Ω defined by the boundary conditions, and $\cos(t\sqrt{-\Delta_\Omega})$ is defined via the spectral calculus. (We refer the reader to [116, Chapter 6] for a proof.) In particular, if u is the solution of (3.2.1) for some $g \in C_c^\infty(\Omega)$, then from the spectral theorem we have

$$\int_{\mathbb{R}} f(t)u(r,t)\mathrm{d}t = \big(\widehat{f}(\sqrt{-\Delta_\Omega})g\big)(r) \tag{3.2.3}$$

for any $f \in S(\mathbb{R})$ even (i.e. $f(s) = f(-s)$ for any $s \in \mathbb{R}$). The identity above lies at the heart of the wave equation method in spectral asymptotics because it allows us to obtain information on the kernel of $\widehat{f}(\sqrt{-\Delta_\Omega})$ through (approximate) solutions of (3.2.1).

Remark. *If Ω is the fundamental domain of a lattice, then periodic boundary conditions can be imposed and the same results described above hold.*

To construct the wave kernel on bounded domains, we will need an explicit representation of the wave kernel in $\mathbb{R}^n$ and its finite speed of propagation property. For later use, we state it as a lemma here.

Lemma 3.2.1 (Wave kernel on $\mathbb{R}^n$ [110]). *Let $E_0(t)$ be the distribution defined by*

$$\langle E_0(t), g\rangle_{\mathcal{D}'(\mathbb{R}^n),\mathcal{D}(\mathbb{R}^n)} = \frac{1}{(2\pi)^n}\int_{\mathbb{R}^n} \cos(t|k|)\widehat{g}(k)\mathrm{d}k, \quad \text{for } g \in C_c^\infty(\mathbb{R}^n). \tag{3.2.4}$$

Then, $E_0(t) \in \mathcal{E}'(\mathbb{R}^n)$ (where $\mathcal{E}'$ is the set of distributions with compact support) and $\mathrm{supp}(E_0(t)) = \{r \in \mathbb{R}^n : |r| \leqslant |t|\}$. *Moreover, for any $g \in C^\infty(\mathbb{R}^n)$, the function defined by*

$$u(r,t) := \big(E_0(t) * g\big)(r) = \frac{1}{(2\pi)^n}\int_{\mathbb{R}^n} \cos(t|k|)\widehat{g}(k)e^{ik\cdot r}\mathrm{d}k$$

is smooth and satisfies the wave equation in $\mathbb{R}^n \times \mathbb{R}$ with initial condition $u(r,0) = g$ and $\partial_t u(r,0) = 0$.

3.2.1 Wave kernel on symmetric polytopes

Now we turn to the construction of the wave kernel on strictly tessellating polytopes and fundamental domains of lattices. The key idea is to exploit the symmetries of the reflection/translation group associated to such polytopes. Let us start by introducing some notation and the proper definitions.

Let Ω be a polytope in $\mathbb{R}^n$. We denote by $\{F_1, ..., F_m\}$ the set of boundary faces of Ω, and by $\{\sigma_1, ..., \sigma_m\}$ the corresponding set of reflections over the faces of Ω. The group of reflections, $\mathcal{R}_\Omega$, is then defined as the group generated by the reflections $\{\sigma_\ell\}_{1\leqslant\ell\leqslant m}$ through composition, i.e.,

$$\mathcal{R}_\Omega = \{\tau : \mathbb{R}^n \to \mathbb{R}^n : \tau = \sigma_{j_1} \circ ... \circ \sigma_{j_M}, \text{ where } j_k \in \{1, ..., m\}\}. \tag{3.2.5}$$

For any $\sigma \in \mathcal{R}_\Omega$, we denote the determinant of the linear part of σ by $\det\sigma$. Note that $\det\sigma \in \{1, -1\}$ for any $\sigma \in \mathcal{R}_\Omega$. The set of strictly tessellating polytopes can then be defined as follows.

Definition 3.2.1 (Strictly tesselating polytopes). *We say that an open polytope $\Omega \subset \mathbb{R}^n$ strictly tessellates $\mathbb{R}^n$ if for any $\sigma, \tau \in \mathcal{R}_\Omega$ with $\sigma \neq \tau$, the reflected polytopes $\sigma(\Omega)$ and $\tau(\Omega)$ do not intersect. In mathematical terms, Ω is strictly tessellating if and only if the following holds:*

$$\sigma(\Omega) \cap \tau(\Omega) \neq \varnothing \iff \tau = \sigma. \tag{3.2.6}$$

(See Figure 3.2.)

Remark. *The term strictly tessellates is adopted from [101]. Note, however, that the definition given here is different from the one in [101, Definition 2]. The reason for this difference is that the property stated above is precisely the one needed for the construction of the wave kernel in Lemma 3.2.2 below. That both definitions are equivalent is shown in Section 3.5*

Similarly, we can define the fundamental domain of a lattice Γ as follows.

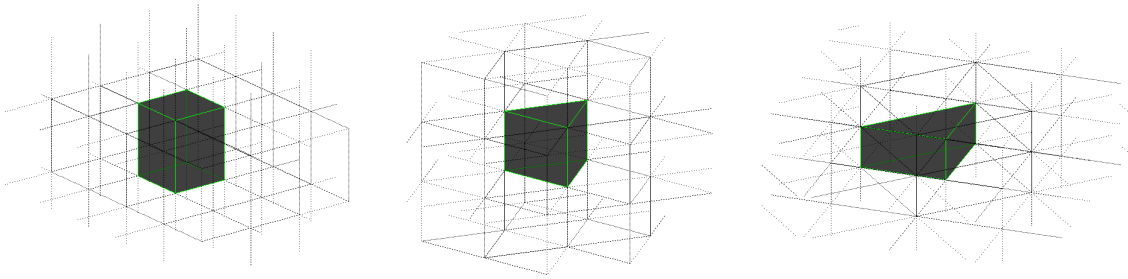

Figure 3.2: Example of strict tessellations of the space by some solids of Figure 3.1.

Definition 3.2.2 (Fundamental domains)**.** *We say that an open polytope $\Omega \subset \mathbb{R}^n$ is the fundamental domain of a lattice $\Gamma = \operatorname{span}_{\mathbb{Z}}\{v_1, ..., v_n\}$[4] if and only if (after a translation)*

$$\Omega = \Big\{ \sum_{j=1}^{n} t_j v_j : 0 < t_j < 1 \quad \textit{for any } 1 \leqslant j \leqslant n. \Big\}.$$

Let us also define the set of neighbouring reflections/translations of Ω as the set of reflections/translations for which the distance between the reflected/translated polytope and the original one is zero, i.e.,

$$\mathcal{R}_\Omega^{nb} = \{\sigma \in \mathcal{R}_\Omega : \overline{\sigma(\Omega)} \cap \overline{\Omega} \neq \varnothing\}, \quad \mathcal{T}_\Omega^{nb} = \{v \in \Gamma : \overline{\Omega + v} \cap \overline{\Omega} \neq \varnothing\}. \tag{3.2.7}$$

We can now construct the wave kernel in Ω explicitly. For this, it is helpful to introduce the reflection and translation of a function g, respectively, as

$$\sigma^{\#}(g)(r) = g(\sigma r) \quad \text{for } \sigma \in \mathcal{R}_\Omega \quad \text{and} \quad \tau_v g(r) = g(r - v) \quad \text{for } v \in \Gamma.$$

Lemma 3.2.2 (Wave kernel on symmetric polytopes)**.** *Let $\Omega \subset \mathbb{R}^n$ be a strictly tessellating polytope or a fundamental domain of a lattice $\Gamma \subset \mathbb{R}^n$. Then, for any $g \in C_c^\infty(\Omega)$, the unique solution in $C^\infty(\overline{\Omega})$ to the initial value problem*

$$\partial_{tt} u = \Delta_\Omega u, \text{ in } \Omega \times (0, \infty) \quad \textit{with initial conditions} \begin{cases} \partial_t u(r, 0) = 0 \\ u(r, 0) = g(r) \end{cases} \tag{3.2.8}$$

where Δ_Ω is either the Dirichlet, Neumann, or periodic Laplacian, is given by

$$u(r,t) = \begin{cases} \displaystyle\sum_{\sigma \in \mathcal{R}_\Omega} \det \sigma \big(E_0(t) * (\sigma^{\#} g)\big)(r) & \textit{for Dirichet BCs,} \\ \displaystyle\sum_{\sigma \in \mathcal{R}_\Omega} \big(E_0(t) * (\sigma^{\#} g)\big)(r) & \textit{for Neumann BCs,} \\ \displaystyle\sum_{v \in \Gamma} \big(E_0(t) * (\tau_v g)\big)(r) & \textit{for periodic BCs,} \end{cases} \tag{3.2.9}$$

where E_0 is defined in (3.2.4).

[4]Here we assume that the lattice Γ has dimension n, i.e. $\{v_1, ..., v_n\}$ is a set of linearly independent vectors in $\mathbb{R}^n$.

Proof. For simplicity, we prove only the Dirichlet case. (The other two are entirely analogous.) First, note that since $\operatorname{supp}(g) \subset \Omega$, by the strictly tessellating property (3.2.6),

$$\operatorname{supp}(\sigma^{\#} g) \cap \operatorname{supp}(\tau^{\#} g) = \varnothing,$$

for any $\sigma \neq \tau \in \mathcal{R}_\Omega$. In particular, $\sum_{\sigma\in\mathcal{R}_\Omega} \det\sigma\, \sigma^{\#} g$ is a sum of smooth functions with disjoint support and therefore smooth. Thus by Lemma 3.2.1, the function $u(r,t)$ defined in (3.2.9) is smooth and solves the wave equation in $\mathbb{R}^n$ with initial condition $u(r,0) = \sum_{\sigma\in\mathcal{R}_\Omega} \det\sigma\, \sigma^{\#} g$ and $\partial_t u(r,0) = 0$. Since uniqueness follows from the previous discussion, we just need to check that the boundary condition is satisfied. To this end, note that

$$\sum_{\sigma\in\mathcal{R}_\Omega} \det\sigma\, \sigma^{\#}(\sigma_\ell^{\#} g) = \sum_{\sigma\in\mathcal{R}_\Omega} \det\sigma(\sigma_\ell \circ \sigma)^{\#} g = -\sum_{\sigma\in\mathcal{R}_\Omega} \det\sigma\, \sigma^{\#} g,$$

where we used that σ_ℓ is invertible and $\det(\sigma\circ\sigma_\ell) = -\det\sigma$. Thus

$$u(\sigma_\ell r, t) = \sum_{\sigma\in\mathcal{R}_\Omega} \det\sigma\, \sigma_\ell^{\#}\big(E_0 * (\sigma^{\#} g)\big)(r) = \sum_{\sigma\in\mathcal{R}_\Omega} \det\sigma E_0(t) * \Big((\sigma_\ell\circ\sigma)^{\#} g\Big)(r) = -u(r,t).$$

To conclude, we note that $\sigma_\ell(r) = r$ for any $r \in F_\ell$ and $\partial\Omega = \bigcup_\ell F_\ell$, which implies that $u(r,t) = 0$ on $\partial\Omega$. □

An useful corollary of the lemma above is the following generalized Poisson summation formula for radial functions.

Corollary 3.2.1 (Generalized Poisson summation formula)**.** *Let $\Omega \subset \mathbb{R}^n$ be a strictly tessellating polytope or a fundamental domain of a lattice Γ. Let Δ_Ω be either the Dirichlet, Neumann, or periodic Laplacian in Ω. Then, for any $f \in S(\mathbb{R})$ even (i.e. $f(s) = f(-s)$ for any $s \in \mathbb{R}$), we have*

$$\sum_{\lambda_j} f(\lambda_j) e_j(r) e_j(\tilde r) = \begin{cases} \dfrac{1}{(2\pi)^n} \displaystyle\sum_{\sigma\in\mathcal{R}} \det\sigma\, \widehat{f(|\cdot|)}(r - \sigma\tilde r) & \text{for Dirichlet BCs,} \\ \dfrac{1}{(2\pi)^n} \displaystyle\sum_{\sigma\in\mathcal{R}} \widehat{f(|\cdot|)}(r - \sigma\tilde r) & \text{for Neumann BCs,} \\ \dfrac{1}{(2\pi)^n} \displaystyle\sum_{v\in\Gamma} \widehat{f(|\cdot|)}(r - \tilde r - v) & \text{for periodic BCs,} \end{cases} \tag{3.2.10}$$

where $\widehat{f(|\cdot|)}$ is the Fourier transform of the radial function $r \in \mathbb{R}^n \mapsto f(|r|)$.

Proof. First, observe that by the standard elliptic regularity estimate, for any $V \subset\subset U$, there exists some constant $C = C(V) > 0$ such that

$$\|e_j\|_{W^{m,2}(V)} \leqslant C(1+\lambda_j)^{2m},$$

for any $m \in \mathbb{N}$ and λ_j. Moreover, by the leading order Weyl law (see (3.1.5)), which can be shown to hold by the Dirichlet-Neumann bracketing technique [100, Section XIII.15], one can control the degeneracy of any eigenvalue by

$$d(\lambda_j) := \dim \ker(-\Delta_\Omega - \lambda_j^2) \lesssim \lambda^n.$$

Thus from the classical Sobolev embedding we conclude that

$$\sum_{\lambda_j \leqslant \lambda} |e_j(r)|^2 \lesssim (1+\lambda)^M,$$

for some $M \in \mathbb{N}$ and uniformly for $r \in V$. As a consequence, the left hand side of (3.2.10) is summable and the convergence is locally uniform in $\Omega \times \Omega$ as long as f decays fast enough. Similarly, the right hand side of (3.2.10) is also an absolutely convergent sum, since $\widehat{f(|\cdot|)} \in S(\mathbb{R}^n)$ (as f is even) and the set $\{\sigma r\}_{\sigma \in \mathcal{R}_\Omega}$ is uniformly discrete for any $r \in \Omega$. Finally, to obtain (3.2.10) we can integrate the right hand side of (3.2.10) against some test function $g \in C_c^\infty(\Omega)$ and use the identity (3.2.3) with u given by Theorem 3.2.2. Then, we find

$$\begin{aligned}
\sum_j f(\lambda_j) e_j(r) \langle e_j, g\rangle_{L^2(\Omega)} &= \frac{1}{2\pi} \int_{\mathbb{R}} \widehat{f}(t) \sum_{\sigma \in \mathcal{R}_\Omega} \det \sigma \frac{1}{(2\pi)^n} \int_{\mathbb{R}^n} \cos(t|k|) e^{ik\cdot r} \widehat{\sigma^\# g}(k) \mathrm{d}k \mathrm{d}t \\
&= \sum_{\sigma \in \mathcal{R}_\Omega} \frac{\det \sigma}{(2\pi)^n} \int_{\mathbb{R}^n} f(|k|) e^{ik\cdot r} \widehat{\sigma^\# g}(k) \mathrm{d}k \\
&= \sum_{\sigma \in \mathcal{R}_\Omega} \frac{\det \sigma}{(2\pi)^n} \int_{\mathbb{R}^n} \widehat{f(|\cdot|)}(r - \sigma\tilde{r}) g(\tilde{r}) \mathrm{d}\tilde{r}
\end{aligned}$$

(where the change in the order of integration/summation can again be justified by the fast decay of f and g). As the above identity holds for any test function $g \in C_c^\infty(\Omega)$, the result follows. □

3.3 Asymptotics of the spectral function

The goal of this section is to prove Theorems 3.1.3 and 3.1.4. Throughout these proofs, we will often use some decaying properties of the Fourier transfoms of the n-dimensional ball and $(n-1)$-dimensional sphere. For later reference, we state these properties in the lemma below. (The reader can consult [55] or [111, Section 1.2] for a proof.)

Lemma 3.3.1 (Fourier transform of the ball and sphere). *Let $h_n(|k|) = \widehat{\chi_{B_1}}(k)/\omega_n$ be the normalized Fourier transform of the characteristic function of the unit ball in $\mathbb{R}^n$, and $\mu_n = \mathcal{H}^{n-1} \llcorner S^{n-1}$ be the $n-1$ Hausdorff measure restricted to the sphere $S^{n-1} = \{r \in \mathbb{R}^n : |r| = 1\}$. Then we have*

$$|\partial^\alpha \widehat{\mu_n}(k)| \lesssim_{\alpha,n} \frac{1}{(1+|k|)^{\frac{n-1}{2}}} \quad \text{and} \quad |\partial^\alpha \big(h_n(|k|)\big)| \lesssim_{\alpha,n} \frac{1}{(1+|k|)^{\frac{n+1}{2}}},$$

where the implicit constant depends on $\alpha \in \mathbb{N}_0^n$ and $n \in \mathbb{N}$, but not on $k \in \mathbb{R}^n$.

3.3.1 Uniform estimates

We now present the proof of Theorem 3.1.3. This proof is an adaptation of the arguments in [110, Chapter 3], where the diagonal version of Theorem 3.1.3 is proved for the periodic case.

The first step in the proof is a uniform control on the growth of the sum of eigenfunctions (and its derivatives) in a small interval around λ.

Lemma 3.3.2 (Sup-norm of Spectral ϵ-Band)**.** *Let Ω be a strictly tessellating polytope or a fundamental domain of a lattice and e_j be the eigenfunctions of the Laplacian under our usual BCs. Then, for any $\alpha \in \mathbb{N}_0^3$ and $1 \leqslant \epsilon^{-1} \leqslant \lambda$, there exists a constant $C = C(\alpha) > 0$ (independent of λ and ϵ) such that*

$$\sum_{|\lambda_j - \lambda| \leqslant \epsilon} |\partial^\alpha e_j(r)|^2 \leqslant C\big(1 + \lambda^{\frac{n-1}{2}+2|\alpha|}(\epsilon\lambda^{\frac{n-1}{2}} + \epsilon^{-\frac{n-1}{2}})\big) \quad \textit{for any } r \in \Omega \tag{3.3.1}$$

Proof. The idea here is to estimate the sum in (3.3.1) by studying the kernel of $\eta_\lambda^\epsilon(\sqrt{-\Delta_\Omega})$ for some fast decaying non-negative function η_λ^ϵ that is positive in the interval $[\lambda-\epsilon, \lambda+\epsilon]$. For this, let $\mu_n = \mathcal{H}^{n-1} \llcorner S^{n-1}$, and let $\eta \in S(\mathbb{R})$ be a non-negative even function such that $\eta(s) > 1$ for $|s| \leqslant 1$, and $\operatorname{supp}(\widehat{\eta}) \subset [-1, 1]$. Then, we define its even rescaled version by

$$\eta_\lambda^\epsilon(\tau) := \eta\left(\frac{\tau - \lambda}{\epsilon}\right) + \eta\left(\frac{\tau + \lambda}{\epsilon}\right),$$

and note that $\operatorname{supp}(\widehat{\eta_\lambda^\epsilon}) \subset [-\frac{1}{\epsilon}, \frac{1}{\epsilon}]$. Thus from Lemma 3.3.1,

$$\begin{aligned}
\partial^\alpha \widehat{\eta_\lambda^\epsilon(|\cdot|)}(z) &= \int_0^\infty \eta_\lambda^\epsilon(\tau)\partial^\alpha\big(\widehat{\mu_n}(\tau z)\big)\tau^{n-1}\mathrm{d}\tau \\
&= \epsilon \int_0^\infty \big(\eta(\tau - \lambda/\epsilon) + \eta(\tau + \lambda/\epsilon)\big)\partial^\alpha \widehat{\mu_n}\big(\epsilon\tau z\big)(\epsilon\tau)^{n-1+|\alpha|}\mathrm{d}\tau \\
&\lesssim_\eta \epsilon\lambda^{\frac{n-1}{2}+|\alpha|} \min\left\{\lambda^{\frac{n-1}{2}}, \frac{1}{|z|^{\frac{n-1}{2}}}\right\}.
\end{aligned} \tag{3.3.2}$$

Now, let us consider the set of reflections in $\mathcal{R}_\Omega$ for which the reflected polytope $\sigma(\Omega)$ lies at most a distance of $\frac{1}{\epsilon}$ away of the original polytope Ω, i.e.,

$$\mathcal{R}_\epsilon := \{\sigma \in \mathcal{R}_\Omega : dist(\sigma(\Omega), \Omega) \leqslant \epsilon^{-1}\}. \tag{3.3.3}$$

Then, due to the strictly tessellating property, one can see that $\#\mathcal{R}_\epsilon \lesssim \frac{1}{\epsilon^n}$. Moreover, we claim that

$$\big(\partial^\alpha \widehat{\eta_\lambda^\epsilon(|\cdot|)}\big)(r - \sigma\tilde{r}) = 0 \quad \text{for any } \sigma \notin \mathcal{R}_\epsilon, r, \tilde{r} \in \Omega \text{ and } \alpha \in \mathbb{N}_0^n. \tag{3.3.4}$$

To show (3.3.4), just note that since $\operatorname{supp}(E_0(t)) \subset \{|r| \leqslant |t|\}$, we have

$$\begin{aligned}\int_{\mathbb{R}^n} \widehat{\eta_\lambda^\epsilon(|\cdot|)}(\tilde{r}-r)g(r)\mathrm{d}r &= \int_{\mathbb{R}^n}\left(\int_{\mathbb{R}^n}\left(\frac{1}{\pi}\int_0^{\frac{1}{\epsilon}} \widehat{\eta}_\lambda^\epsilon(t)\cos(t|k|)\mathrm{d}t\right)e^{-ik\cdot(r-\tilde{r})}\mathrm{d}k\right)g(r)\mathrm{d}r \\ &= \frac{(2\pi)^n}{\pi}\int_0^{\frac{1}{\epsilon}} \widehat{\eta}_\lambda^\epsilon(t)(E_0(t)*g)(\tilde{r})\mathrm{d}t = 0,\end{aligned}$$

for any $g \in C_c^\infty(\mathbb{R}^n)$ with $dist(\operatorname{supp}(g), \tilde{r}) \geqslant \frac{1}{\epsilon}$. As g was arbitrary, we conclude that $\widehat{\eta}_\lambda^\epsilon(r) = 0$ for any $|r| \geqslant \frac{1}{\epsilon}$ and (3.3.4) holds. Hence, from Leibniz rule we have

$$\partial_r^\alpha \partial_{\tilde{r}}^\alpha \widehat{\eta_\lambda^\epsilon(|\cdot|)}(r-\sigma\tilde{r}) = \sum_{|\gamma|=|\alpha|} c_{\gamma,\sigma}\big(\partial^{\alpha+\gamma}\widehat{\eta}_\lambda^\epsilon(|\cdot|)\big)(r-\sigma\tilde{r}), \tag{3.3.5}$$

where all $c_{\gamma,\sigma}$ are bounded by a constant independent of ϵ, λ and σ (since all entries in the linear part of σ are bounded by 1). Therefore, by (3.3.4), Corollary 3.2.1, and estimate (3.3.2) (and recalling that $\eta_\lambda^\epsilon \geqslant 1$ on $[\lambda-\epsilon, \lambda+\epsilon]$), we conclude that

$$\begin{aligned}\sum_{|\lambda_j-\lambda|\leqslant\epsilon} |\partial^\alpha e_j(r)|^2 &\leqslant \sum_{\lambda_j}\eta_\lambda^\epsilon(\lambda_j)|\partial^\alpha e_j(r)|^2 = \sum_{\sigma\in\mathcal{R}_\epsilon}\det\sigma\sum_{|\gamma|=|\alpha|} c_{\gamma,\sigma}\big(\partial^{\alpha+\gamma}\widehat{\eta_\lambda^\epsilon(|\cdot|)}\big)(r-\sigma r) \\ &\lesssim \epsilon\lambda^{n-1+|\alpha|} + \epsilon\lambda^{\frac{n-1}{2}+|\alpha|}\sum_{1\leqslant dist(\sigma(\Omega),\Omega)\leqslant\frac{1}{\epsilon}}\frac{1}{|r-\sigma r|^{\frac{n-1}{2}}} \\ &\lesssim \lambda^{\frac{n-1}{2}+|\alpha|}\big(\epsilon\lambda^{\frac{n-1}{2}} + \epsilon^{-\frac{n-1}{2}}\big).\end{aligned}$$

□

We can now complete the proof of Theorem 3.1.3.

Proof of Theorem 3.1.3. The idea here is similar to the previous proof; we choose a smooth version of the characteristic function of the interval $[-\lambda, \lambda]$ and use Lemma 3.3.2 and the generalized Poisson summation to get the continuum version with error estimates controlled by powers of ϵ and λ. We can then estimate the error from smoothing the characteristic function and optimize ϵ to complete the proof.

Let $\chi_\lambda(s)$ be the characteristic function on the interval $[-\lambda, \lambda]$, and let $\eta \in S(\mathbb{R})$ be an even nonnegative function with $\widehat{\eta}(0) = 1$ and $\operatorname{supp}(\widehat{\eta}) \subset [-1, 1]$. In addition, let χ_λ^ϵ be the mollification of χ_λ on the scale ϵ, i.e., $\chi_\lambda^\epsilon(s) = \chi_\lambda * \big(\epsilon^{-1}\eta(\epsilon^{-1}\cdot)\big)(s)$, and $r_\lambda^\epsilon = \chi_\lambda - \chi_\lambda^\epsilon$ be the mollification error function. As η decays fast, it is not hard to see that

$$|r_\lambda^\epsilon(s)| \lesssim_N \frac{1}{(1+\epsilon^{-1}|\lambda-s|)^N} + \frac{1}{(1+\epsilon^{-1}|\lambda+s|)^N} \lesssim_N \frac{1}{(1+\epsilon^{-1}|\lambda-s|)^N} \tag{3.3.6}$$

for any $s \geqslant 0$. Thus denoting the mollified version of the spectral function by

$$S_\lambda^\epsilon(r, \tilde{r}) = \sum_{\lambda_j}\chi_\lambda^\epsilon(\lambda_j)e_j(r)e_j(\tilde{r}),$$

we can use (3.3.1), Cauchy-Schwarz and (3.3.6) to bound the error with respect to S_λ by

$$\begin{aligned}
|\partial_r^\alpha \partial_{\tilde{r}}^\beta S_\lambda - \partial_r^\alpha \partial_{\tilde{r}}^\beta S_\lambda^\epsilon| &\leqslant \sum_{\ell=1}^{\infty} \sum_{|\lambda_j - \ell\epsilon| \leqslant \epsilon} |r_\lambda^\epsilon(\lambda_j) \partial^\alpha e_j(r) \partial^\beta e_j(\tilde{r})| \\
&\lesssim_N \sum_\ell \frac{1}{(1+|\epsilon^{-1}\lambda - \ell|)^N} \Big(\sum_{|\lambda_j - \ell\epsilon| \leqslant \epsilon} |\partial^\alpha e_j(r)|^2 \Big)^{\frac{1}{2}} \Big(\sum_{|\lambda_j - \ell\epsilon| \leqslant \epsilon} |\partial^\beta e_j(\tilde{r})|^2 \Big)^{\frac{1}{2}} \\
&\lesssim \sum_\ell \frac{1 + \ell^{n-1+|\alpha|+|\beta|} \epsilon^{n+|\alpha|+|\beta|} + \ell^{\frac{n-1}{2}+|\alpha|+|\beta|} \epsilon^{|\alpha|+|\beta|}}{(1+|\epsilon^{-1}\lambda - \ell||)^N} \\
&\lesssim \lambda^{\frac{n-1}{2}+|\alpha|+|\beta|} \big(\epsilon \lambda^{\frac{n-1}{2}} + \epsilon^{-\frac{n-1}{2}} \big). \quad \text{(for } \lambda \text{ big).}
\end{aligned} \tag{3.3.7}$$

On the other hand, by applying Corollary 3.2.1 to S_λ^ϵ and recalling from the last proof that $\widehat{\chi_\lambda^\epsilon(|\cdot|)}(k) = 0$ for $|k| \geqslant \frac{1}{\epsilon}$ (since $\operatorname{supp}(\widehat{\eta^\epsilon}) \subset [-1/\epsilon, 1/\epsilon]$), we find that

$$\begin{aligned}
\partial_r^\alpha \partial_{\tilde{r}}^\beta S_\lambda^\epsilon(r, \tilde{r}) &= \sum_{\sigma \in \mathcal{R}_\epsilon} \det \sigma \frac{1}{(2\pi)^n} \int_{\mathbb{R}^n} \big(\chi_\lambda(|k|) + r_\lambda^\epsilon(|k|) \big) \partial_r^\alpha \partial_{\tilde{r}}^\beta \big(e^{ik\cdot(r - \sigma\tilde{r})} \big) \mathrm{d}k \\
&= \sum_{\sigma \in \mathcal{R}_\epsilon} \frac{\det \sigma}{(2\pi)^n} \bigg(\omega_n \lambda^n \partial_r^\alpha \partial_{\tilde{r}}^\beta h_n(\lambda |r - \sigma\tilde{r}|) + \int_0^\infty r_\lambda^\epsilon(\tau) \tau^{n-1} \partial_r^\alpha \partial_{\tilde{r}}^\beta \widehat{\mu_n}\big(\tau(r - \sigma\tilde{r})\big) \mathrm{d}\tau \bigg).
\end{aligned} \tag{3.3.8}$$

Moreover, from (3.3.6) and Lemma 3.3.1 we have

$$r_\lambda^\epsilon(\tau) \tau^{n-1} \partial_r^\alpha \partial_{\tilde{r}}^\beta \widehat{\mu_n}\big(\tau(r - \sigma\tilde{r})\big) \lesssim \frac{\tau^{\frac{n-1}{2}+|\alpha|+|\beta|}}{(1+\epsilon^{-1}|\lambda - \tau|)^N} \min\{\tau^{\frac{n-1}{2}}, |r - \sigma\tilde{r}|^{-\frac{n-1}{2}}\}.$$

By integrating the estimate above over $(0, \infty)$ and summing over $\sigma \in \mathcal{R}_\epsilon$, we can see that the last term in (3.3.8) yields (at most) an error of order $\mathcal{O}\big(\lambda^{\frac{n-1}{2}+|\alpha|+|\beta|}(\epsilon\lambda^{\frac{n-1}{2}} + \epsilon^{-\frac{n-1}{2}})\big)$. Therefore, we conclude from (3.3.7), (3.3.8), and the decay of h_n that

$$\begin{aligned}
\partial_r^\alpha \partial_{\tilde{r}}^\beta S_\lambda(r, \tilde{r}) &= \partial_r^\alpha \partial_{\tilde{r}}^\beta S_\lambda^{\mathrm{ctm}}(r, \tilde{r}) + \sum_{\sigma \in \mathcal{R}_\epsilon \setminus \mathcal{R}_1} \det \sigma \frac{\omega_n}{(2\pi)^n} \underbrace{\lambda^n \partial_r^\alpha \partial_{\tilde{r}}^\beta h_n(\lambda |r - \lambda\tilde{r}|)}_{\lesssim \lambda^{\frac{n-1}{2}+|\alpha|+|\beta|} |r - \sigma\tilde{r}|^{-\frac{n+1}{2}}} \\
&\quad + \mathcal{O}\big(\lambda^{\frac{n-1}{2}+|\alpha|+|\beta|}(\epsilon\lambda^{\frac{n-1}{2}} + \epsilon^{-\frac{n-1}{2}})\big) \\
&= \partial_r^\alpha \partial_{\tilde{r}}^\beta S_\lambda^{\mathrm{ctm}}(r, \tilde{r}) + \mathcal{O}\big(\lambda^{\frac{n-1}{2}+|\alpha|+|\beta|}(\epsilon\lambda^{\frac{n-1}{2}} + \epsilon^{-\frac{n-1}{2}})\big).
\end{aligned} \tag{3.3.9}$$

The result now follows by setting $\epsilon = \lambda^{-\frac{n-1}{n+1}}$. The proof for the periodic and Neumann cases is a straightforward adaptation of the arguments presented above. □

An interesting consequence of Theorem 3.1.3 is the following generalized Weyl law, which gives the next term of the Cesàro means considered in the work by Schmidt [105, Theorem 1.1]. (For the proof, see Section 3.6.)

Theorem 3.3.1 (Two-term generalized Weyl law)**.** *Let $\Omega \subset \mathbb{R}^n$ be a strictly tessellating polytope or a fundamental domain of a lattice. Let e_j the eigenfunctions of the Dirichlet, Neumann or periodic Laplacian. Let $a \in C^\infty\big(\mathbb{R}^n; S(\mathbb{R}^n)\big)$, then we have*

$$\sum_{\lambda_j \leqslant \lambda} \langle e_j, a^w(r, \lambda^{-1}D)e_j\rangle = c_L(a)\lambda^n + \big(c_{FS}(a) + c_{BC}(a)\big)\lambda^{n-1} + \mathcal{O}(\lambda^{n-1-\frac{n-1}{n+1}}), \tag{3.3.10}$$

where $a^w(r, \lambda^{-1}D)$ is the Weyl quantization of $a(r,\xi)$ at scale $h = \lambda^{-1}$ (see [130, Section 4.1]), and the leading, finite-size, and boundary correction constants are given by

$$c_L(a) = \frac{1}{(2\pi)^n}\int_{\Omega\times B_1} a(r,\xi)\mathrm{d}r\mathrm{d}\xi \tag{3.3.11}$$

$$c_{FS}(a) = \frac{1}{(2\pi)^{n+1}}\int_{\partial\Omega\times B_1}\left[\text{p.v.}\left(\frac{1}{\tau}\right)\right]\big(\nabla_\xi a\big(r,\xi-\tau n(r)\big)\cdot n(r)\big)\mathrm{d}\xi\mathrm{d}\mathcal{H}^{n-1}(r) \tag{3.3.12}$$

$$c_{BC}(a) = \frac{m_{BC}}{(2\pi)^{n+1}}\int_{B_1^*}\int_{\mathbb{R}} a\left(r,\xi' + (1-|\xi'|^2)^{\frac{1}{2}}\tau n(r)\right)\frac{\log(\frac{|1+\tau|}{|1-\tau|})}{\tau}\mathrm{d}\tau\mathrm{d}\mathcal{H}^{n-1}(\xi')d\mathcal{H}^{n-1}(r), \tag{3.3.13}$$

where $n(r)$ is the outward-pointing normal vector at $r \in \partial\Omega$, $B_1^* = \{(r,\xi) \in \partial\Omega \times B_1 : r \in \partial\Omega$ and $\xi\cdot n(r) = 0\}$ is the unit ball bundle in the (co)tangent bundle of $\partial\Omega$, $\text{p.v.}[1/\tau]$ is the Cauchy principal value distribution (see (3.6.1)), and $m_{BC} = -1, 1$ and 0 for Dirichlet, Neumann, and periodic BCs, respectively.

Remark. *The assumption on $a(r,\xi)$ are chosen mostly to simplify the proof. For instance, Theorem 3.3.1 still holds (with essentially the same proof) under the assumption that the Fourier transform of the function $\xi \mapsto a(r,\xi)$ (and its derivatives with respect to r) are tempered distribution of order 0 with compact singular support and decay fast enough. In particular, for $a(r,\xi) = 1$ we recover the classical two-term Weyl law (3.4.3) with improved remainder.*

3.3.2 L^2 estimate

We now turn to the L^2 estimates for the spectral function. This result can be seen as a quantified version of the L^2 convergence of the density in the work by Schmidt [105, Theorem 1.2]. However, unlike the more classical (and more general) methods used in [105], our proof is again based on the wave kernel constructed before.

Proof of Theorem 3.1.4. As in the proof of Theorem 3.1.3, we let χ_λ be the characteristic function on the interval $[-\lambda,\lambda]$ and $\eta \in S(\mathbb{R})$ be an nonnegative even function with $\widehat{\eta} = 1$ on a neighbourhood of 0. Then, we define the mollified version of χ_λ, the mollifying error function, and the smoothed spectral function as $\chi_\lambda^1 := \chi_\lambda * \eta$, $r_\lambda := \chi_\lambda^1 - \chi_\lambda$, and

$S^1_\lambda = \sum_j \chi^1_\lambda(\lambda_j) e_j(r)\overline{e_j}(\tilde{r})$, respectively. Hence, by the orthogonality of e_j, we have

$$\begin{aligned}\|S_\lambda - S^1_\lambda\|^2_{L^2(\Omega\times\Omega)} &= \sum_{j,k} r_\lambda(\lambda_j)\overline{r}_\lambda(\lambda_k)\int_{\Omega\times\Omega}(e_j\overline{e_k})(r)(\overline{e_j}e_k)(\tilde{r})\mathrm{d}r\mathrm{d}\tilde{r}\\ &\lesssim \sum_j |r_\lambda(j)|^2(N(j+1)-N(j)) \lesssim \sum_{j=1}(1+(\lambda-j))^{-N}j^{n-1} \lesssim \lambda^{n-1}.\end{aligned}$$

So up to an error $\lesssim \lambda^{\frac{n-1}{2}}$, we can work with the smoothed spectral function S^1_λ. Now, since we do not vary the support of $\widehat{\eta}$ in this proof (no scaling with ϵ), we see that $\widehat{\chi^1_\lambda} = \widehat{\chi}_\lambda\widehat{\eta}$ has support on a fixed neighbourhood of 0. In particular, if we choose the support of $\widehat{\eta}$ small enough and apply the generalized Poisson summation in Corollary 3.2.1 to χ^1_λ, we conclude (see (3.3.4) in the previous proof) that all terms with $\sigma \in \mathcal{R}_\Omega\backslash\mathcal{R}^{nb}_\Omega$ vanish. Therefore, the result follows if we show that for any $\sigma \in \mathcal{R}_\Omega$ the following estimate holds:

$$\|\widehat{\chi^1_\lambda(|\cdot|)}(r-\sigma\tilde{r}) - \widehat{\chi_\lambda(|\cdot|)}(r-\sigma\tilde{r})\|_{L^2(\Omega\times\Omega)} = \|\widehat{r_\lambda(|\cdot|)}(r-\sigma\tilde{r})\|_{L^2(\Omega\times\Omega)} \lesssim \lambda^{\frac{n-1}{2}},$$

where $\widehat{g(|\cdot|)}$ is the Fourier transform in $\mathbb{R}^n$ of the function $r \mapsto g(|r|)$. This estimate is a direct consequence of Plancherel's theorem and the estimate $r_\lambda(|r|) \leqslant (1+|\lambda-|r||)^{-N}$. □

Remark. *Note that we only used the wave kernel for times of order* 1 *here*[5] *. In particular, the same estimate is expected to hold on more general domains (e.g. smooth ones).*

We can now interpolate between the L^2 and L^∞ estimate to obtain

Corollary 3.3.1 (L^p estimates)**.** *Let Ω be a strictly tessellating polytope or a fundamental domain of a lattice, and let S_λ be the spectral function of the periodic, Dirichlet or Neumann Laplacian in Ω. Then,*

$$\|S_\lambda - S^{\mathrm{ctm}}_\lambda\|_{L^p(\Omega\times\Omega)} \lesssim \lambda^{(n-1)\left(1-\frac{1}{p}\right)-\frac{n-1}{n+1}\left(1-\frac{2}{p}\right)}, \tag{3.3.14}$$

where S^{ctm}_λ is the continuum spectral function defined in Theorem 3.1.3.

3.4 Asymptotics of exchange functionals

In this section we present the proof of the main results of this chapter. For these proofs, we shall use two geometric lemmas.

The first lemma is a lower bound on the distance between points in the original polytope and points in the reflected one. To state this lemma, let us introduce some more notation. First recall that, since Ω is an open convex polytope with faces $\{F_j\}_{j\leqslant m}$, there exists $\{\alpha_j\}_{j\leqslant m} \subset \mathbb{R}$ such that

$$\Omega = \{r \in \mathbb{R}^n : r\cdot n_j < \alpha_j \text{ for any } 1 \leqslant j \leqslant m\}, \tag{3.4.1}$$

[5] Unlike in the L^∞ case, we could not use the large times wave kernel to improve the remainders in the L^2 case.

where n_j is the unit outward-pointing normal vector to the face F_j. Moreover, for any $\sigma \in \mathcal{R}_\Omega^{nb}$ there exists $\{j_1, ..., j_p\} \subset \{1, ..., m\}$ such that $\overline{\Omega} \cap \overline{\sigma(\Omega)} = \bigcap_{k=1}^p F_{j_k}$ and the interior

$$\operatorname{int} \bigcap_{k=1}^{p} F_{j_k} := \left\{ r \in \mathbb{R}^n : r \cdot n_j \begin{cases} = \alpha_j & \text{if } j \in \{j_k\}_{k \leqslant p}, \\ < \alpha_j & \text{otherwise} \end{cases} \right\} \tag{3.4.2}$$

is non-empty (see Lemma 3.5.1 below). We then denote the metric projection along the affine space extending this intersection by π_σ, i.e.,

$$\pi_\sigma r = \operatorname{argmin}\{|r - r'| : r' \in \mathbb{R}^n \quad \text{and} \quad n_{j_k} \cdot r' = \alpha_{j_k} \quad \text{for all } 1 \leqslant k \leqslant p\}. \tag{3.4.3}$$

We also define the complementary projection as $\pi_\sigma^\perp r := r - \pi_\sigma r$.

Lemma 3.4.1 (Lower bound on reflected distances)**.** *Let $\sigma \in \mathcal{R}_\Omega^{nb}$, then*

$$|r - \sigma r'| \gtrsim |\pi_\sigma r - \pi_\sigma r'| + |\pi_\sigma^\perp r + \pi_\sigma^\perp r'| \quad \text{and} \quad |r - \sigma r'| \gtrsim |r - r'|$$

for any $r, r' \in \Omega$. (With the convention that $\pi_\sigma(r) = r$ if σ is the identity.)

Proof. After relabelling the faces and translating our reference frame, we can assume that $0 \in \bigcap_{j=1}^p F_j = \overline{\Omega} \cap \overline{\sigma(\Omega)}$. In this case, σ is a linear transformation given by some composition of the (linear) reflections $\{\sigma_j\}_{j \leqslant p}$ (see Lemma 3.5.1 below) and π_σ becomes the orthogonal projections along the subspace

$$V_\sigma = \{r \in \mathbb{R}^n : r \cdot n_j = 0 \quad \text{for all } j \leqslant p\}. \tag{3.4.4}$$

In particular, $\sigma r = r$ for any $r \in V_\sigma$ and $\sigma r \in V_\sigma^\perp$ for any $r \in V_\sigma^\perp$. If we now define the closed conic sets $C_\Omega = \{r \in V_\sigma^\perp : r \cdot n_j \leqslant 0 \text{ for } 1 \leqslant j \leqslant p\}$ and $\sigma(C_\Omega) = \{\sigma r \in V_\sigma^\perp : r \in C_\Omega\}$, then we have

$$\overline{\Omega} \subset V_\sigma \oplus C_\Omega \quad \text{and} \quad \overline{\sigma(\Omega)} \subset V_\sigma \oplus \sigma(C_\Omega). \tag{3.4.5}$$

Moreover, one can show that $C_\Omega \cap \sigma(C_\Omega) = \{0\}$. Indeed, if $r, \tilde{r} \in C_\Omega$ with $r = \sigma\tilde{r}$, then for any $p \in \operatorname{int} \bigcup_{k=1}^p F_k$ (see (3.4.2)) we have $\delta r + p = \sigma(\delta\tilde{r} + p) \in \overline{\Omega} \cap \overline{\sigma(\Omega)} \subset V_\sigma$ for $\delta > 0$ small enough, which implies that $r = \tilde{r} = 0$. Thus C_Ω and $\sigma(C_\Omega)$ are closed conic subsets that intersect only at zero. Consequently,

$$|r - \sigma r'| \gtrsim |r| + |\sigma r'| \quad \text{for any } r, r' \in C_\Omega,$$

where the implicit constant is independent of r and r'. From this inequality, the inclusions in (3.4.5), and the fact that V_σ is invariant under σ, we conclude that

$$\begin{aligned} |r - \sigma r'|^2 &= |\pi_\sigma(r - r')|^2 + |\pi_\sigma^\perp(r - \sigma r')|^2 = |\pi_\sigma(r - r')|^2 + |\pi_\sigma^\perp r - \sigma\pi_\sigma^\perp r'|^2 \\ &\gtrsim |\pi_\sigma(r - r')|^2 + (|\pi_\sigma^\perp r| + |\pi_\sigma^\perp \sigma r'|)^2 \quad \text{for any } r, r' \in \Omega. \end{aligned} \tag{3.4.6}$$

Lemma 3.4.1 now follows from (3.4.6), the triangle inequality, and the fact that σ is an isometry. □

The second geometric lemma we need is a first-order Taylor expansion of the function $w \mapsto |(\Omega - w) \cap \Omega|$ at $w = 0$.

Lemma 3.4.2 (Distributional derivative of $\Omega \cap (\Omega - w)$)**.** *Let $\Omega \subset \mathbb{R}^n$ be a polytope. Then, for any $a \in C_c^\infty(\mathbb{R}^n)$, there exists a constant $C = C(|\Omega|, |\partial\Omega|, \|a\|_{L^\infty}, \|\nabla a\|_{L^\infty}) > 0$ such that*

$$\left| \int_{\Omega\cap(\Omega-w)} a(r)\mathrm{d}r - \int_\Omega a(r)\mathrm{d}r + \int_{\partial\Omega} a(r)(n(r)\cdot w)_+ \mathrm{d}\mathcal{H}^{n-1}(r) \right| \leqslant C|w|^2, \quad \forall w \in \mathbb{R}^n, \tag{3.4.7}$$

where $n(r)$ is the outward-pointing unit normal and $f(r)_+ := \max\{f(r), 0\}$. In particular, we have

$$\begin{aligned} \int_{(\Omega-w_1)\cap(\Omega+w_2)} a(r)\mathrm{d}r = \int_\Omega a(r)\mathrm{d}r - \int_{\partial\Omega} a(r)\frac{|n(r)\cdot(w_1+w_2)| + n(r)\cdot(w_1-w_2)}{2}\mathrm{d}\mathcal{H}^{n-1}(r) \\ + \mathcal{O}(|w_1|^2 + |w_2|^2). \end{aligned} \tag{3.4.8}$$

Proof. Since Ω is bounded, it is clear that $F(z) = \int_{\Omega\cap(\Omega-z)} a(r)\mathrm{d}r$ is continuous and compactly supported. Therefore, it is enough to show that (3.4.7) holds on a neighbourhood of 0. For this, let us define the sets

$$F_k(z) := \{r \in \Omega : \alpha_k - (n_k \cdot z)_+ \leqslant n_k \cdot r \leqslant \alpha_k\},$$

where α_k and n_k are the same from (3.4.1). Then we find that $\Omega\backslash(\Omega - z) = \bigcup_{k=1}^m F_k(z)$ and $|F_k(z) \cap F_j(z)| = \mathcal{O}(|z|^2)$ for $j \neq k$. Thus,

$$\int_{(\Omega-z)\cap\Omega} a(r)\mathrm{d}r - \int_\Omega a(r)\mathrm{d}r + \sum_{k=1}^m \int_{F_k(z)} a(r)\mathrm{d}r + \mathcal{O}(\|a\|_{L^\infty}|z|^2) \tag{3.4.9}$$

Next, note that since Ω is a convex polytope, up to an error $\lesssim \|a\|_{L^\infty}|z|^2$, we can replace the integration over the set $F_k(z)$ by integration over the set $\{r - \tau n_j : r \in F_k, 0 \leqslant \tau \leqslant (n(r)\cdot z)_+\} \cong F_k \times [0, (n_k \cdot z)_+]$. Therefore, we find that

$$\begin{aligned} \int_{F_k(z)} a(r)\mathrm{d}r &= \int_{F_k} \mathrm{d}\mathcal{H}^{n-1}(r) \int_0^{(n(r)\cdot z)_+} a\big(r - \tau n(r)\big)\mathrm{d}\tau + \mathcal{O}(\|a\|_{L^\infty}|z|^2) \\ &= \int_{F_k} a(r)(n(r)\cdot z)_+ \mathrm{d}\mathcal{H}^{n-1}(r) + \mathcal{O}\big(\||a|\|_{L^\infty}|z|^2 + \|\nabla a\|_{L^\infty}|z|^2\big), \end{aligned}$$

which together with (3.4.9) completes the proof. □

Remark. *Note that Lemma 3.4.2 also holds for smooth domains by taking a partition of the unity along the boundary.*

3.4.1 Proof of Theorem 3.1.2

Throughout this section, we use ν_λ for the combined function

$$\nu_\lambda(r) = 2(S_{s,\lambda}(r), \nabla S_{s,\lambda}(r)) \in \mathbb{R}^{1+n}, \tag{3.4.10}$$

where $S_{s,\lambda}$ and $\nabla S_{s,\lambda}$ are the re-scaled spectral function and its gradient. Similarly, the continuum version $\nu_\lambda^{\mathrm{ctm}}(r)$ is defined by using the continuum spectral function

$$S_{s,\lambda}^{\mathrm{ctm}}(r) = \frac{2\omega_n}{(2\pi)^n}\left(1 - \sum_{\sigma\in\mathcal{R}_{\Omega_\lambda}^{nb}\setminus\{id\}} \det\sigma h_n(|r-\sigma r|)\right). \tag{3.4.11}$$

We start with the asymptotic expansion of

$$F^{\mathrm{ctm}}(\lambda) = \int_{\Omega_\lambda} f\big(\nu_\lambda^{\mathrm{ctm}}(r)\big)\mathrm{d}r. \tag{3.4.12}$$

Lemma 3.4.3 (Continuum semi-local asymptotics)**.** *Let $f \in C^1((0,\infty)\times\mathbb{R}^n)\cap L^\infty_{\mathrm{loc}}([0,\infty)\times\mathbb{R}^n)$. Then we have*

$$F^{\mathrm{ctm}}(\lambda) = \int_{\Omega_\lambda} f(\nu_\lambda^{\mathrm{ctm}}(r))\mathrm{d}r = f(\nu_0)|\Omega|\lambda^n + c(f,\Omega)\lambda^{n-1} + o(\lambda^{n-1}),$$

where ν_0 and the coefficient $c(f,\Omega)$ are defined in Theorem 3.1.2.

Proof. First, we want to use the C^1 regularity of f to estimate the difference $F^{\mathrm{ctm}}(\lambda) - f(\nu_0)|\Omega_\lambda|$. Since $f(a,b)$ is only C^1 at the points $a > 0$, we start by showing that $S_{s,\lambda}^{\mathrm{ctm}}$ only vanishes close to the edges and faces of Ω. For this, first note that $h_n(\tau) = 1$ if and only if $\tau = 0$ and that $h_n(\tau) \to 0$ as $\tau \to \infty$. Therefore, for any $\delta > 0$ we can find $C_0, C(\delta), c(\delta) > 0$ such that

$$S_{s,\lambda}^{\mathrm{ctm}}(r) > c(\delta) \quad \text{and} \quad |\nabla\nu_\lambda^{\mathrm{ctm}}(r)| \leqslant C_0, \tag{3.4.13}$$

for any r in the set

$$\Omega_\lambda^\delta := \{r\in\Omega_\lambda : \min_{1\leqslant\ell\leqslant m}\{|r-\sigma_\ell(r)|\} \geqslant \delta \text{ and } \min_{\sigma\in\mathcal{R}_{\Omega_\lambda}^{nb}\setminus\{\sigma_\ell\}_{0\leqslant\ell\leqslant m}}\{|r-\sigma r|\} \geqslant C(\delta)\}, \tag{3.4.14}$$

where σ_ℓ is the reflection over the re-scaled face λF_ℓ of the re-scaled polytope Ω_λ and σ_0 is the identity on $\mathbb{R}^n$. In other words, Ω_λ^δ is the set of points of Ω_λ which are at least a distance δ of the faces and a distance of order $C(\delta)$ of the edges of Ω_λ (see Lemmas 3.4.1 and 3.5.1). So from (3.4.13), the assumptions on f, and the simple estimate

$$|\Omega_\lambda\setminus\Omega_\lambda^\delta| \lesssim C(\delta)^2\lambda^{n-2} + \delta\lambda^{n-1},$$

we find that

$$\begin{aligned} F(\lambda) - f(\nu_0)|\Omega_\lambda| = &\int_{\Omega_\lambda^\delta}\int_0^1 \nabla f\big(\nu_0 + t(\nu_\lambda^{\mathrm{ctm}}(r)-\nu_0)\big)\cdot(\nu_\lambda^{\mathrm{ctm}}(r)-\nu_0)\mathrm{d}t\mathrm{d}r \\ &+ \mathcal{O}(C(\delta)^2\lambda^{n-2} + \delta\lambda^{n-1}). \end{aligned} \tag{3.4.15}$$

The next step is to expand the difference $\nu_\lambda^{\mathrm{ctm}} - \nu_0$ that appears outside ∇f in a sum of terms over $\mathcal{R}_\Omega^{nb}\backslash\{\sigma_0\}$, and then get rid of the terms that only give lower order contributions. To this end, let us define

$$\rho_\sigma(r) := \frac{2\omega_n}{(2\pi)^n} h_n(|r - \sigma r|) \quad \text{and} \quad \nu_\sigma := (\rho_\sigma, \nabla\rho_\sigma).$$

Then since $\mathrm{range}(\pi_\sigma)$ is an affine subspace of dimension at most $n-2$ for any $\sigma \in \mathcal{R}_{\Omega_\lambda}\backslash\{\sigma_\ell\}_{0\leqslant\ell\leqslant m}$, we can use Lemma 3.4.1, the decay of h_n, and the local boundedness of the gradient of f to show that

$$\int_{\Omega_\lambda^\delta}\int_0^1 \nabla f\big(\nu_0 + t(\nu_\lambda^{\mathrm{ctm}} - \nu_0)\big)\cdot\nu_\sigma(r)\mathrm{d}r \lesssim_\delta \int_{\Omega_\lambda^\delta}(1+|\pi_\sigma^\perp r|)^{-\frac{n+1}{2}}\mathrm{d}r \lesssim_\delta \lambda^{n-\min\{\frac{n+1}{2},2\}} \tag{3.4.16}$$

for any $\sigma \in \mathcal{R}_{\Omega_\lambda}^{nb}\backslash\{\sigma_\ell\}_{0\leqslant\ell\leqslant m}$. As a consequence, we are left with the terms

$$K_\ell(\lambda,\delta) := \int_{\Omega_\lambda^\delta}\int_0^1 \nabla f\big(\nu_0 + t(\nu_\lambda^{\mathrm{ctm}}(r) - \nu_0)\big)\cdot\big(-\nu_{\sigma_\ell}(r)\big)\mathrm{d}t\mathrm{d}r \quad \text{for } 1\leqslant\ell\leqslant m.$$

To obtain the asymptotics of K_ℓ, we can assume (without loss of generality) that the face F_ℓ lies on the plane $\{r\in\mathbb{R}^n : r_n = 0\}$ and the inward-pointing normal is $n_\ell = (0,....,1)$. Under this assumption, $\rho_\ell(r) = 2\omega_n/(2\pi)^n h_n(2r_n)$ and

$$\nu_{\sigma_\ell}(r) = \frac{2\omega_n}{(2\pi)^n}\big(h_n(2r_n), 2n_\ell\dot{h}_n(2r_n)\big).$$

Moreover, one can check that

$$\lim_{\lambda\to\infty}\chi_{\Omega_\lambda^\delta}(\lambda r_1,...,\lambda r_{n-1}, r_n) = \chi_{F_\ell}(r_1,...,r_{n-1},0)\chi_{(\delta,\infty)}(r_n) \quad \text{and} \tag{3.4.17}$$

$$\lim_{\lambda\to\infty}\nu_\lambda^{\mathrm{ctm}}(\lambda r_1,...,\lambda r_{n-1}, r_n) - \nu_0 = -\nu_{\sigma_\ell}(r_n) \tag{3.4.18}$$

for almost every $r\in\mathbb{R}^{n-1}\times(0,\infty)$, where χ_A stands for the characteristic function of the set A. Thus since $\nu_{\sigma_\ell}(r)\lesssim(1+|r_n|)^{-\frac{n+1}{2}}\in L^1(\mathbb{R})$, we can now re-scale the variables $r_1,...,r_{n-1}$ by λ and apply the dominated convergence theorem to conclude that

$$\begin{aligned}\frac{K_\ell(\lambda,\delta)}{\lambda^{n-1}} &\to \int_{\mathbb{R}^{n-1}}\int_\delta^\infty \chi_{F_\ell}(r_1,..,r_{n-1},0)\int_0^1 \nabla f\big(\nu_0 - t\nu_{\sigma_\ell}(r_n)\big)\cdot\big(-\nu_{\sigma_\ell}(r_n)\big)\mathrm{d}t\mathrm{d}r_n\mathrm{d}r_1...\mathrm{d}r_{n-1}\\ &= \int_{F_\ell}\int_0^\infty f\big(\nu_0 - t\nu_1(r_n,r')\big) - f(\nu_0)\mathrm{d}r_n\mathrm{d}\mathcal{H}^{n-1}(r') + \mathcal{O}(\delta),\end{aligned} \tag{3.4.19}$$

where $\nu_1(r_n,r') = \frac{2\omega_n}{(2\pi)^n}\big(h(2r_n), 2n(r')\dot{h}(2r_n)\big)$. The proof now follows by plugging (3.4.16) and (3.4.19) in (3.4.15) and taking the limit $\lambda\to 0$ and then $\delta\to 0$. □

To complete the proof of Theorem 3.1.2, it is enough to show that

$$F^{\mathrm{ctm}}(\lambda) - F(\lambda) = o(\lambda^{n-1}). \tag{3.4.20}$$

So fix again some $\delta > 0$ and let Ω_λ^δ be defined as in (3.4.14). Then from (3.4.13) and Theorem 3.1.3 we find that

$$S_{s,\lambda}(r) \geqslant c(\delta)/2 \text{ in } \Omega_\lambda^\delta \quad \text{and} \quad |\nabla \nu_\lambda(r)| \leqslant 2C_0 \text{ in } \Omega_\lambda \tag{3.4.21}$$

for λ big enough. It thus follows from the assumptions on f and Theorem 3.1.3 that

$$\begin{aligned}\int_{\Omega_\lambda} f(\nu_\lambda) - f(\nu_\lambda^{\mathrm{ctm}})\mathrm{d}r &\lesssim |\Omega_\lambda \backslash \Omega_\lambda^\delta| + \|\nabla f\|_{L^\infty\left((\frac{c(\delta)}{2}, 2C_0)\times(-2C_0,2C_0)^3\right)} \int_{\Omega_\lambda^\delta} |\nu^{\mathrm{ctm}}(r)_\lambda - \nu_\lambda(r)|\mathrm{d}r \\ &\lesssim C(\delta)^2\lambda^{n-2} + \delta\lambda^{n-1} + D(\delta)\lambda^{n-1-\frac{n-1}{n+1}} \quad \text{for some } D(\delta) > 0.\end{aligned}$$

Therefore, we can divide the estimate above by λ^{n-1}, send $\lambda \to \infty$ and then $\delta \to 0$ to obtain (3.4.20).

3.4.2 Proof of Theorem 3.1.1

As in the previous section, we only work out the Dirichlet case in detail. We comment on the modifications necessary for the Neumann and periodic cases at the end of the proof. We start again by computing the asymptotics of the exchange energy for the continuum spectral function

$$E_x^{\mathrm{ctm}}(\lambda) = \int_{\Omega^2} \frac{|S_\lambda^{\mathrm{ctm}}|^2}{|r-r'|}\mathrm{d}r\mathrm{d}r' = \frac{\omega_n^2\lambda^s}{(2\pi)^{2n}} \sum_{\sigma,\tau\in\mathcal{R}_{\Omega_\lambda}^{nb}} \det\sigma\tau \underbrace{\int_{\Omega_\lambda^2} \frac{h_n(|r-\sigma r'|)h_n(|r-\tau r'|)}{|r-r'|^s}\mathrm{d}r\mathrm{d}r'}_{:=E_{\sigma,\tau}(\lambda)}. \tag{3.4.22}$$

The first step here is to get rid of the terms $E_{\sigma,\tau}(\lambda)$ that only gives lower order contributions; to this end, we use the following Lemma.

Lemma 3.4.4 (Lower order contribution)**.** *Suppose that either $\sigma \notin \{\sigma_\ell\}_{0\leqslant\ell\leqslant m}$ or $(\sigma,\tau) = (\sigma_j,\sigma_k)$ where $1 \leqslant j \neq k \leqslant m$. Then we have*

$$\lambda^s E_{\sigma,\tau}(\lambda) = \mathcal{O}(\lambda^{\max\{n-2+s, n-1, \frac{n-1}{2}+s\}+\epsilon}), \tag{3.4.23}$$

for any $\epsilon > 0$.

Proof. The key idea is to split the decay of h_n over linear combinations of the components of r and r' in order to compensate for the integration in $\Omega_\lambda \times \Omega_\lambda$ in as many directions as possible. So first, from Lemma 3.4.1 we have

$$E_{\sigma,\tau}(\lambda) \lesssim \int_{\Omega_\lambda^2} (1+|\pi_\sigma r - \pi_\sigma r'|)^{-\frac{n+1}{2}+x}(1+|\pi_\sigma^\perp r + \pi_\sigma^\perp r'|)^{-x}(1+|r-r'|)^{-\frac{n+1}{2}}|r-r'|^{-s}\mathrm{d}r\mathrm{d}r',$$

for any $0 \leqslant x \leqslant (n+1)/2$. Hence, identifying the spaces $\mathrm{range}(\pi_\sigma) \approx \mathbb{R}^d$ and $\mathrm{range}(\pi_\sigma^\perp) \approx \mathbb{R}^{n-d}$, we can make the change of variables $(z, z', w, w') = (\pi_\sigma r - \pi_\sigma r', \pi_\sigma^\perp r - \pi_\sigma^\perp r', \pi_\sigma^\perp r + \pi_\sigma^\perp r', \pi_\sigma r + \pi_\sigma r') \in \mathbb{R}^d \times \mathbb{R}^{n-d} \times \mathbb{R}^{n-d} \times \mathbb{R}^d$ to find that

$$\begin{aligned}\lambda^s E_{\sigma,\tau}(\lambda) &\lesssim \lambda^s \int_{\substack{|z|+|z'|\lesssim\lambda \\ |w|+|w'|\lesssim\lambda}} (1+|z|)^{-\frac{n+1}{2}+x}(1+|w|)^{-x}(|z|+|z'|)^{-\frac{n+1}{2}-s}\mathrm{d}z'\mathrm{d}z\mathrm{d}w'\mathrm{d}w \\ &\lesssim \lambda^{s+d+\max\{n-d-x,0\}+\max\{x-s-1,0\}+\epsilon} \leqslant \lambda^{\max\{d+s,n-1,\frac{n-1}{2}+s\}+\epsilon},\end{aligned}$$

where the last inequality follows from minimizing the function $x \mapsto \max\{n-x, d\} + \max\{x-1, s\}$ in the interval $0 \leqslant x \leqslant \frac{n+1}{2}$. Thus since $d \leqslant n-2$ for any $\sigma \notin \{\sigma_\ell\}_{0\leqslant\ell\leqslant m}$, estimate (3.4.23) follows in this case.

For the second case, we first assume that $F_k \cap F_j = \varnothing$. Under this assumption, the faces F_j and F_k of the re-scaled polytope Ω_λ are a distance $\sim \lambda$ away of each other. So close to F_j, respectively F_k, we have $h_n(|r-\sigma_k r|) \lesssim \lambda^{-\frac{n+1}{2}}$, respectively $h_n(r-\sigma_j r|) \lesssim \lambda^{-\frac{n+1}{2}}$. Thus again from Lemma 3.4.1,

$$\lambda^s E_{\sigma_j,\sigma_k}(\lambda) \lesssim \lambda^s \int_{\Omega_\lambda^2} \lambda^{-\frac{n+1}{2}}(1+|r-r'|)^{-\frac{n+1}{2}}|r-r'|^{-s}\mathrm{d}r\mathrm{d}r' \lesssim \lambda^{\max\{n-1,\frac{n-1}{2}+s\}+\epsilon}.$$

Finally, if $F_j \cap F_k \neq \varnothing$, then the normal vectors n_j, n_k are not parallel. Consequently, the variables $w_j = \pi_{\sigma_j}^\perp r + \pi_{\sigma_j}^\perp r' \in \mathbb{R}$, $w_k = \pi_{\sigma_k}^\perp r + \pi_{\sigma_k}^\perp r' \in \mathbb{R}$ and $r - r' \in \mathbb{R}^n$ are independent. Therefore, we can split the decay of h_n and use Lemma 3.4.1 to compensate for the integration in the directions w_j, w_k and $r-r'$. This yields the estimate

$$\begin{aligned}\lambda^s E_{\sigma_k,\sigma_j}(\lambda) &\lesssim \lambda^s \int_{\substack{|r-r'|\lesssim\lambda \\ |w_j|+|w_k|\lesssim\lambda}} \frac{(1+|w_j|)^{-1}(1+|\pi_{\sigma_j}(r-r')|)^{-\frac{n-1}{2}}}{(1+|w_k|)(1+|\pi_{\sigma_k}(r-r')|)^{\frac{n-1}{2}}}|r-r'|^{-s}\mathrm{d}r\mathrm{d}r' \\ &\lesssim \lambda^{\max\{n-2+s+,n-1\}+\epsilon},\end{aligned}$$

which completes the proof of the lemma. □

From Lemma 3.4.4 and the symmetric relation $E_{\sigma,\tau}(\lambda) = E_{\tau,\sigma}(\lambda)$, we see that only the terms $E_{\sigma_\ell,\sigma_\ell}(\lambda)$ and $E_{\sigma_0,\sigma_\ell}(\lambda)$ (where σ_0 is the identity in $\mathbb{R}^n$) gives significant contributions. We thus need to compute their asymptotics. Let us start with the term $E_{\sigma_0,\sigma_0}(\lambda)$. In this case, from Lemma 3.4.2, the decay of h_n, and the change of variables $z = r - r'$, we find that

$$\begin{aligned}E_{\sigma_0,\sigma_0}(\lambda) &= \int_{\Omega_\lambda-\Omega_\lambda} \frac{|h_n(|z|)|^2}{|z|^s}\int_{(\Omega_\lambda-z)\cap\Omega_\lambda)}\mathrm{d}r'\mathrm{d}z \\ &= \int_{\Omega_\lambda-\Omega_\lambda}\frac{h_n(|z|)^2}{|z|^s}\left(\lambda^n|\Omega| - \lambda^{n-1}\int_{\partial\Omega}(z\cdot n(r'))_+\mathrm{d}\mathcal{H}^{n-1}(r') + \lambda^{n-2}\mathcal{O}(|z|^2)\right)\mathrm{d}z \\ &= \lambda^n|\Omega|\int_{\mathbb{R}^n}\frac{h_n(|z|)^2}{|z|^s}\mathrm{d}z - \lambda^{n-1}|\partial\Omega|\int_{\mathbb{R}^{n-1}\times[0,\infty)}\frac{h_n(|z|)^2 z_n}{|z|^s}\mathrm{d}z + \mathcal{O}(\lambda^{n-2+\max\{1-s,0\}}).\end{aligned} \tag{3.4.24}$$

Next, let us look to the terms E_{σ_j,σ_j} with $j \geqslant 1$. For simplicity, let us assume without loss of generality that $F_j \subset \mathbb{R}^{n-1} \times \{0\}$ and $n_j = (0, ..., 0, 1)$. Let us also denote the height of Ω by $H = \max\{r_n : \mathbb{R}^{n-1} \times \{r_n\} \cap \Omega \neq \varnothing\}$, the cross-section of Ω at height h by $\Omega(h) = \{r \in \mathbb{R}^{n-1} : (r, h) \in \Omega\}$, and the projection sending $(r_1, ..., r_n) \in \mathbb{R}^n$ to $(r_1, ..., r_{n-1}) \in \mathbb{R}^{n-1}$ by π_n. Since Ω is a convex polytope, we can bound the area of the symmetric difference of the cross-sections at different heights by $|\Omega(h) \triangle \Omega(h')| \lesssim |h - h'|$. In particular, a scaling argument yields

$$\big|\big(\Omega_{2\lambda}(h + z_n) - \pi_n z\big) \cap \big(\Omega_{2\lambda}(h - z_n) + \pi_n z\big)\big| - |\Omega_{2\lambda}(0)| \lesssim \lambda^{n-2}(|h| + |z|), \tag{3.4.25}$$

for any $z \in \Omega_\lambda$. We can now use the above estimate with the change of variables $z = r - r', w = r + r'$ and the decay of h_n to obtain

$$\begin{aligned} E_{\sigma_j,\sigma_j}(\lambda) &= \int_{\Omega_\lambda - \Omega_\lambda} \int_{(\Omega_{2\lambda} - z) \cap (\Omega_{2\lambda} + z)} \frac{h_n(|(\pi_n z, w_n)|)^2}{|z|^s} \frac{\mathrm{d}z\mathrm{d}w}{2^n} \\ &= \int_{\Omega_\lambda - \Omega_\lambda} \int_{|z_n|}^{2\lambda H - |z_n|} \frac{h_n(|(\pi_n z, w_n)|)^2}{|z|^s} |\Omega_{2\lambda}(0)| \frac{\mathrm{d}w_n \mathrm{d}z}{2^n} + \mathcal{O}(\lambda^{\max\{n-1-s, n-2\}+\epsilon}) \\ &= \frac{\lambda^{n-1}|F_j|}{2} \int_{\mathbb{R}^n} \int_{|z_n|}^{\infty} \frac{h_n(|(\pi_n z, w_n)|)^2}{|z|^s} \mathrm{d}w_n \mathrm{d}z + \mathcal{O}(\lambda^{\max\{n-1-s, n-2\}+\epsilon}), \end{aligned} \tag{3.4.26}$$

where we used that $\mathrm{d}z\mathrm{d}w = 2^n \mathrm{d}r\mathrm{d}r'$, $|\Omega_{2\lambda}(0)| = 2^{n-1}\lambda^{n-1}|F_j|$, and that

$$\begin{aligned} &\lambda^{n-2} \int_{|z| \lesssim \lambda} \int_{|z_n|}^{2H\lambda} (1 + |(\pi_n z, w_n)|)^{-n-1} |z|^{-s} (|w_n| + |z|) \mathrm{d}w_n \mathrm{d}z \lesssim \lambda^{\max\{n-1-s, n-2\}+\epsilon}, \\ &\lambda^{n-1} \int_{|z| \lesssim \lambda} \int_{2H\lambda - |z_n|}^{\infty} (1 + |(\pi_n z, w_n)|)^{-n-1} |z|^{-s} \mathrm{d}w_n \mathrm{d}z \lesssim \lambda^{\max\{n-2, n-1-s\}+\epsilon}, \quad \text{and} \\ &\lambda^{n-1} \int_{|z| \gtrsim \lambda} \int_{|z_n|}^{\infty} (1 + |(\pi_n z, w_n)|)^{-n-1} |z|^{-s} \mathrm{d}w_n \mathrm{d}z \lesssim \lambda^{n-1-s+\epsilon} \end{aligned}$$

for any $\epsilon > 0$. For the last terms, $E_{\sigma_0,\sigma_j}(\lambda)$ with $1 \leqslant j \leqslant m$, one can use the same change of coordinates together with (3.4.25) to find that

$$E_{\sigma_0,\sigma_j}(\lambda) = \frac{\lambda^{n-1}|F_j|}{2} \int_{\mathbb{R}^n} \int_{|z_n|}^{\infty} \frac{h_n(|(\pi_n z, w_n)|) h_n(|z|)}{|z|^s} \mathrm{d}w_n \mathrm{d}z + \mathcal{O}(\lambda^{\max\{n-1-s, n-2\}+\epsilon}). \tag{3.4.27}$$

Hence by summing (3.4.24),(3.4.26), and (3.4.27) with the estimates in Lemma 3.4.4 we conclude that

$$E_x^{\mathrm{ctm}}(\lambda) = c_{x,1}(n, s)\lambda^{n+s} + \big(c_{FS}(n, s) + c_{BL}(n, s)\big)\lambda^{n-1+s} + \mathcal{O}(\lambda^{\max\{n-1, n-2+s, \frac{n-1}{2}+s\}+\epsilon}), \tag{3.4.28}$$

with the constants $c_{x,1}, c_{FS}$ and c_{BL} defined according to Theorem 3.1.1.

Finally, to complete the proof we just need to bound the difference $E_x^{\mathrm{ctm}}(\lambda) - E_x(\lambda)$. For this, we use Corollary 3.3.1, Theorem 3.1.3, and the decay of h (Lemma 3.3.1) to obtain the estimate

$$\begin{aligned}\int_{\Omega\times\Omega} \frac{|S_\lambda|^2 - |S_\lambda^{\mathrm{ctm}}|^2}{|r-r'|^s}\mathrm{d}x\mathrm{d}y &\leqslant \int_{\Omega\times\Omega} \frac{|S_\lambda - S_\lambda^{\mathrm{ctm}}|^2}{|r-r'|^s} + \frac{2|S_\lambda - S_\lambda^{\mathrm{ctm}}||S_\lambda^{\mathrm{ctm}}|}{|r-r'|^s}\mathrm{d}r\mathrm{d}r' \\ &\lesssim \|S_\lambda - S_\lambda^{\mathrm{ctm}}\|_{L^p}^2 \||r-r'|^{-s}\|_{L^q(\Omega^2)} + \|S_\lambda - S_\lambda^{\mathrm{ctm}}\|_{L^\infty}\int \frac{|S_\lambda^{\mathrm{ctm}}|}{|r-r'|^s} \\ &\lesssim \lambda^{2n-2-\frac{n-1}{n+1}\left(2+\frac{2(n-1)}{p}\right)} \||r|^{-s}\|_{L^q(\Omega_2)} + \lambda^{(n-1)\frac{n}{n+1}+\max\{\frac{n-1}{2},s\}}\log\lambda\end{aligned} \tag{3.4.29}$$

where $\frac{2}{p}+\frac{1}{q}=1$ and the $\log\lambda$ term is just needed for the case $\frac{n-1}{2}=s$ (e.g. Coulomb in 3D). Now given $\epsilon>0$ we can choose $q<n/s$ such that $2/p = 1-s/n-\epsilon$. For such q, the function $|r|^{-s}$ belongs to $L^q_{\mathrm{loc}}(\mathbb{R}^n)$ and the first term in (3.4.29) is of order $\lambda^{n-1+s(n-1)^2/(n^2+1)+\epsilon}$. Therefore,

$$E_x(\lambda) = E_x^{\mathrm{ctm}}(\lambda) + \mathcal{O}\left(\lambda^{n-1+s\frac{(n-1)^2}{n^2+n}+\epsilon} + \lambda^{(n-1)\left(\frac{3}{2}-\frac{1}{n+1}\right)}\log\lambda\right), \tag{3.4.30}$$

which together with (3.4.28) completes the proof of Theorem 3.1.1 for the Dirichlet case. For the Neumann case, one just need to change the sign before the terms $E_{\sigma_\ell,\sigma_0}(\lambda)$. For the periodic case, one replaces $E_{\sigma,\tau}(\lambda)$ by

$$E_{v,w}(\lambda) = \int_{\Omega_\lambda^2} \frac{h_n(|r-r'+\lambda v|)h_n(|r-r'+\lambda w|)}{|r-r'|^s}\mathrm{d}r\mathrm{d}r',$$

where $v,w\in\mathcal{R}_\Omega^{nb}$. By using arguments similar to the ones presented above, one can show that all the terms $E_{v,w}(\lambda)$ with $v\neq 0$ or $w\neq 0$ give lower order contributions. The proof then reduces to computing the asymptotic expansion of $E_{0,0}(\lambda) = E_{\sigma_0,\sigma_0}(\lambda)$, which we already did (see (3.4.24)).

3.5 Strictly tessellating polytopes

We now show that our definition of a strictly tessellating polytope is equivalent to [101, Definition 2].

Proposition 3.5.1. *Let $\Omega\subset\mathbb{R}^n$ be an open polytope. Then Ω is strictly tessellating in the sense of Definition 3.2.1 if and only if $\mathbb{R}^n = \bigcup_{j\in\mathbb{N}}\overline{\Omega_j}$, where each Ω_j is obtained by reflecting Ω across its boundary faces and the hyperplanes extending the boundary faces of each Ω_j have empty intersection with (the interior of) Ω_k for any $j,k\in\mathbb{N}$.*

Proof. First, let us assume that Ω is strictly tessellating in the sense of [101, Definition 2] and then show that Ω satisfies Definition 3.2.1. For this, first observe that by [101, Corollary 1], all eigenfunctions of the Dirichlet Laplacian $-\Delta_\Omega$ are trigonometric, thus

real analytic in $\mathbb{R}^n$. Lamé's fundamental theorem (see [101, Theorem 4]) then implies that any eigenfunction e_j is anti-symmetric with respect to reflection over the faces of Ω, and therefore, $e_j(r) = \det\sigma e_j(\sigma r)$ for any $\sigma \in \mathcal{R}_\Omega$. Now suppose that $\sigma(\Omega) = \tau(\Omega)$ for some $\sigma, \tau \in \mathcal{R}_\Omega$. Then we have $(\tau^{-1}\sigma)(\Omega) = \Omega$ and $\det(\tau^{-1}\circ\sigma)e_j(\tau^{-1}\sigma r) = e_j(r)$ for any eigenfunction $j \in \mathbb{N}$. But since $\{e_j\}_{j\in\mathbb{N}}$ is an orthonormal basis of $L^2(\Omega)$, the push-back map $f \mapsto \det(\sigma\circ\tau)\big(\sigma^\# \circ (\tau^{-1})^\#\big)f$ is the identity in $L^2(\Omega)$, which shows that $\tau = \sigma$ and Ω satisfies Definition 3.2.1.

For the converse implication, just note that Ω clearly tessellates $\mathbb{R}^n$ with reflected copies of itself, hence, it is enough to show that the hyperplanes extending the boundary faces of any reflected polytope do not intersect the interior of Ω. So let $\sigma \in \mathcal{R}_\Omega$ and H_ℓ be the hyperplane extending the face $\sigma(F_\ell)$ of $\sigma(\Omega)$. Then the reflection over H_ℓ is given by the composition $\tau_\ell = \sigma\circ\sigma_\ell\circ\sigma^{-1} \in \mathcal{R}_\Omega$ where σ_ℓ is the reflection over the face F_ℓ of Ω. As a consequence, if we suppose that $H_\ell \cap \Omega \neq \varnothing$, then we have $\tau_\ell(\Omega)\cap\Omega \neq \varnothing$ because H_ℓ is invariant under the reflection τ_ℓ. But from our definition of strictly tessellating polytopes, this implies that τ_ℓ is the identity, which contradicts the fact that τ_ℓ is a reflection over the hyperplane H_ℓ. We thus conclude that $H_\ell \cap \Omega = \varnothing$, which completes the proof. □

Next, we prove the characterization of the intersection $\overline{\Omega}\cap\overline{\sigma(\Omega)}$ that was used in the proof of Lemma 3.4.1.

Lemma 3.5.1 (Intersection characterization)**.** *Let $\Omega = \{r \in \mathbb{R}^n : r\cdot n_j < \alpha_j, 1 \leqslant j \leqslant m\}$ be a strictly tessellating polytope with faces $F_\ell = \{r \in \overline{\Omega} : r\cdot n_\ell = \alpha_\ell\}$. Suppose that $I_\sigma = \overline{\Omega}\cap\overline{\sigma(\Omega)} \neq \varnothing$ for some $\sigma \in \mathcal{R}_\Omega^{nb}\backslash\{\sigma_0\}$. Then there exists $j_1, ..., j_p$ such that $I_\sigma = \bigcap_{k=1}^p F_{j_k}$, $\sigma \in \langle\sigma_{j_1}, ..., \sigma_{j_p}\rangle$, and the interior*

$$\operatorname{int}\bigcap_{k=1}^{p} F_{j_k} = \left\{ r\in\mathbb{R}^n : r\cdot n_j \begin{cases} = \alpha_j & \text{if } j = j_k \text{ for some } 1\leqslant k\leqslant p. \\ < \alpha_j & \text{otherwise.} \end{cases} \right\} \tag{3.5.1}$$

is non-empty. Here (and in the proof below) $\langle\sigma_{j_1}, ..., \sigma_{j_p}\rangle$ denotes the group generated by $\sigma_{j_1}, ..., \sigma_{j_p}$.

Proof. The result follows if we show the following claim:

$$\textbf{Claim: } \operatorname{int}\textstyle\bigcap_{k=1}^p F_{j_k} \text{ is contained in the interior of } \bigcup_{\sigma\in\langle\sigma_{j_1},...,\sigma_{j_k}\rangle}\overline{\sigma(\Omega)}. \tag{3.5.2}$$

Indeed, if this holds, then we can argue as follows. Since $\partial\Omega$ is the union of the interior of all possible face intersections, for any $\tau \in \mathcal{R}_\Omega^{nb}$ we can find $q \in \operatorname{int}\bigcap_{k=1}^p F_{j_k} \cap \partial\overline{\tau(\Omega)}$ for some faces $\{F_{j_k}\}_{k\leqslant p}$. By the claim, the non-empty open set $B_\delta(q)\cap\tau(\Omega)$ is contained in $\bigcup_{\sigma\in\langle\sigma_{j_1},...\sigma_{j_p}\rangle}\overline{\sigma(\Omega)}$ (for δ small) and must intersect some $\sigma(\Omega)$ (because $\bigcup_{\sigma\in\langle\sigma_{j_1},...,\sigma_{j_k}\rangle}\partial\sigma(\Omega)$ is a countable union of sets with Hausdorff dimension $n-1$). By the strictly tessellating property, we have $\tau = \sigma \in \langle\sigma_{j_1}, ..., \sigma_{j_p}\rangle$, hence $\bigcap_{k=1}^p F_{j_k} \subset \partial\tau(\Omega)$. Moreover, if $j_1, ..., j_p$ is minimal in the sense that $\operatorname{int}\bigcap_{\ell=1}^{p-1} F_{j_{k_\ell}} \cap \partial\tau(\Omega) = \varnothing$ for all possible choice $\{j_{k_\ell}\}_{\ell=1}^{p-1} \subset \{j_k\}_{k=1}^p$, then $\overline{\tau(\Omega)}\cap\overline{\Omega} = \bigcap_{k=1}^p F_{j_k}$ (by a convexity argument), which proves the lemma.

To prove the claim we use induction and argue by contradiction. First, it is clear that $\mathrm{int}F_k$ is contained in the interior of $\overline{\Omega} \cap \overline{\sigma_k(\Omega)}$. Now suppose that the claim holds for intersections of $n-1$ faces and there exists some $q \in \mathrm{int} \bigcap_{k=1}^n F_{j_k}$ for which

$$B_\delta(q) \nsubseteq C_n := \bigcup_{\sigma \in \langle \sigma_{j_1}, \dots, \sigma_{j_n} \rangle} \overline{\sigma(\Omega)} \quad \text{for any } \delta > 0 \text{ small.}$$

Since $B_\delta(q) \backslash \bigcap_{k=1}^n F_{j_k}$ is open and connected (as $n \geqslant 2$) and C_n is closed and has non empty interior inside $B_\delta(q)$, there exists some point $q_2 \in B_\delta(q) \cap \partial C_n \backslash \bigcap_{k=1}^n F_{j_k}$. In particular, $q_2 \in \partial\sigma(\Omega)$ for some $\sigma \in \langle \sigma_{j_1}, \dots \sigma_{j_n} \rangle$. Moreover, since σ is an isometry that leaves the intersection $\bigcap_{k=1}^n F_{j_k}$ invariant, we have $\sigma^{-1}(q_2) \in B_\delta(q) \cap \partial\Omega \backslash \bigcap_{k=1}^n F_{j_k}$. Therefore, if $\delta > 0$ is small enough, $\sigma^{-1}(q_2)$ must be contained in the interior of the intersection of at most $n-1$ of the faces $\{F_{j_k}\}_{k \leqslant n}$. By assumption, this implies that $\sigma^{-1}(q_2)$ is in the interior of C_n. But since σ is an isometry (hence open) and C_n is invariant under σ, we conclude that q_2 belongs to the interior of C_n, contradicting the fact that $q_2 \in \partial C_n$.

□

3.6 Generalized Weyl law with boundary corrections

Here we give a proof of Theorem 3.3.1. We start with the following identities.

Lemma 3.6.1. *Let $\omega_n h_n(|k|) = \widehat{\chi_{B_1}}(k)$ be the Fourier transform of the unit ball in $\mathbb{R}^n$, $b \in S(\mathbb{R}^n)$, and $\pi_n : \mathbb{R}^n \to \mathbb{R}^{n-1}$ be the projection on the first $n-1$ coordinates, then*

$$\int_{\mathbb{R}^n} \check{b}(w) h_n(|w|) |z \cdot w| \mathrm{d}z = \frac{1}{\pi\omega_n} \int_{|\xi| \leqslant 1} \left[p.v. \frac{1}{\tau} \right] \big(\nabla_\xi b(\xi - \tau z) \cdot z \big) \mathrm{d}\xi \quad \textit{for any } z \in \mathbb{R}^n,$$

$$\int_{\mathbb{R}^n} \int_{|w_n|}^\infty \check{b}(w) h_n(|(\pi_n w, s)|) \mathrm{d}s \mathrm{d}w = \frac{1}{\pi\omega_n} \int_{|\xi'| \leqslant 1} b\big(\xi', (1 - |\xi'|^2)^{\frac{1}{2}} \tau\big) \frac{\log(\frac{|1+\tau|}{|1-\tau|})}{\tau} \mathrm{d}\tau \mathrm{d}\xi',$$

where $\xi' \in \mathbb{R}^{n-1}$, $p.v.\frac{1}{\tau}$ is the principal value distribution

$$\left[p.v. \frac{1}{\tau} \right] (f(\tau)) = \lim_{\epsilon \to 0^+} \int_{|\tau| > \epsilon} \frac{f(\tau)}{\tau} \mathrm{d}\tau, \tag{3.6.1}$$

and $\check{b}$ is the inverse Fourier transform of b.

Proof. The first identity follows from Parseval's formula, the convolution property of the Fourier transform and the identities $w\check{b}(w) = i\widecheck{\nabla b}$ and $\frac{i}{2}\widehat{\mathrm{sgn}(\cdot)}(\tau) = p.v.\frac{1}{\tau}$, where $\mathrm{sgn}(\tau)$ is the signum function.

For the second identity from the lemma, we use Fubini's theorem, the identities $\widetilde{\chi_{[-s,s]}}(\tau) = \frac{\sin(\tau s)}{\pi\tau}$ and $h_n(|\pi_n w, s|) = \frac{2}{\omega_n} \int_{|\xi'| \leqslant 1} e^{-i\xi' \cdot \pi_n w} \frac{\sin((1-|\xi'|^2)^{\frac{1}{2}} s)}{s} \mathrm{d}\xi'$ and Parseval's for-

mula to obtain

$$\begin{aligned}\int_{\mathbb{R}^n}\int_{|w_n|}^{\infty}\check{b}(w)h_n(|\pi_n w,s|)\mathrm{d}s\mathrm{d}w &= \lim_{R\to\infty}\int_0^R\int_{-s}^{s}\int_{\mathbb{R}^{n-1}} h_n(|\pi_n w,s|)\check{b}(w)\mathrm{d}\pi_n w\mathrm{d}w_n\mathrm{d}s\\ &= \lim_{R\to\infty}\frac{2}{\omega_n}\int_0^R\int_{-s}^{s}\int_{\mathbb{R}^{n-1}}\int_{|\xi'|\leqslant 1}\frac{\sin((1-|\xi'|^2)^{\frac{1}{2}}s)}{s}\check{b}(w)e^{-i\xi'\cdot\pi_n w}\mathrm{d}\xi'\mathrm{d}\pi_n w\mathrm{d}w_n\mathrm{d}s\\ &= \lim_{R\to\infty}\frac{2}{\pi\omega_n}\int_{|\xi'|\leqslant 1}\int_{\mathbb{R}} b(\xi',\tau)\int_0^R\frac{\sin((1-|\xi'|^2)^{\frac{1}{2}}s)}{s}\frac{\sin(\tau s)}{\tau}\mathrm{d}s\mathrm{d}\tau\mathrm{d}\xi'.\end{aligned}$$

To complete the proof we can now use the identity

$$\begin{aligned}2\int_0^R\frac{\sin(as)\sin(\tau s)}{s}\mathrm{d}s &= \int_0^R\frac{\cos(|\tau-a|s)-\cos(|\tau+a|s)}{s}\mathrm{d}s\\ &= \int_0^R\frac{1-\cos(|\tau+a|s)}{s}\mathrm{d}s-\int_0^R\frac{1-\cos(|\tau-a|s)}{s}\mathrm{d}s\\ &= \log\left(\frac{|\tau+a|}{|\tau-a|}\right)-\int_{R|\tau-a|}^{R|\tau+a|}\frac{\cos(s)}{s}\mathrm{d}s.\end{aligned}$$

Indeed, from this identity we find that $\lim_{R\to\infty}2\int_0^R\frac{\sin(as)\sin(\tau s)}{\tau s}\mathrm{d}s=\frac{1}{\tau}\log(\frac{|\tau+a|}{|\tau-a|})$ and $2\int_0^R\frac{\sin(\tau s)\sin(\tau s)}{\tau s}\mathrm{d}s\lesssim 2|\frac{1}{\tau}\log(\frac{|a+b|}{|a-b|})|$ for $\tau\neq\pm a$, and therefore, the result follows from dominated convergence, since $\int_{\mathbb{R}}|\frac{1}{\tau}\log(\frac{|\tau+a|}{|\tau-a|})\mathrm{d}\tau=\int_{\mathbb{R}}|\frac{1}{\tau}\log(\frac{|\tau+1|}{|\tau-1|})\mathrm{d}\tau|\leqslant C$ for any a. □

Proof of Theorem 3.3.1. From the definition of $a^w(r,hD)$ with $h=\lambda^{-1}$ (see [130, Section 4.1]),

$$\underbrace{\sum_{k\leqslant N(\lambda)}\langle e_k,a^w(r,hD)e_k\rangle}_{:=A(\lambda)}=\frac{\lambda^n}{(2\pi)^n}\int_{\Omega\times\Omega\times\mathbb{R}^n}a\big(r/2+r'/2,\xi\big)e^{i\lambda(r-r')\cdot\xi}S_\lambda(r,r')\mathrm{d}\xi\mathrm{d}r\mathrm{d}r'$$

Hence, by the change of variables $z=(r+r')/2$, $w=\lambda(r-r')$ we have

$$A(\lambda)=\int_{\mathbb{R}^{2n}}\chi_\Omega\left(z+\frac{w}{2\lambda}\right)\chi_\Omega\left(z-\frac{w}{2\lambda}\right)\widetilde{a}(z,w)S_\lambda\big(z+\frac{w}{2\lambda},z-\frac{w}{2\lambda}\big)\mathrm{d}w\mathrm{d}z,$$

where $\widetilde{a}(z,w)=\widecheck{a(z,\cdot)}(w)$ is the inverse Fourier transform of the function $w\mapsto a(z,w)$. Then from Theorem 3.1.3 and the bound $\widetilde{a}(z,w)\lesssim_N(1+|w|)^{-N}$ we find that

$$A(\lambda)=\frac{\omega_n\lambda^n}{(2\pi)^n}\sum_{\sigma\in\mathcal{R}_\Omega}\det\sigma A_\sigma(\lambda)+\mathcal{O}(\lambda^{n-1-\frac{n-1}{n+1}}),\tag{3.6.2}$$

where

$$A_\sigma(\lambda)=\int_{\Omega_\lambda-\Omega_\lambda}\int_{(\Omega-\frac{w}{2\lambda})\cap(\Omega+\frac{w}{2\lambda})}\widetilde{a}(z,w)h_n\big(|\lambda\underbrace{(1-\sigma)z}_{:=z_\sigma}+\underbrace{(1+\sigma)w/2}_{:=w_\sigma}|\big)\mathrm{d}w\mathrm{d}z.$$

For $\sigma = \sigma_0$, we have $z_{\sigma_0} = 0$ and $w_{\sigma_0} = w$. We can then use Lemma 3.4.2, the bounds $|\nabla_z \widetilde{a}(z,w)| + |\widetilde{a}(z,w)| \lesssim_N (1+|w|)^{-N}$ and the first identity in Lemma 3.6.1 to obtain

$$\begin{aligned} A_{\sigma_0}(\lambda) &= \int_{\Omega_\lambda - \Omega_\lambda} \int_{(\Omega - \frac{w}{2\lambda}) \cap (\Omega + \frac{w}{2\lambda})} \widetilde{a}(z,w) h_n(|w|) \mathrm{d}z \mathrm{d}w \\ &\approx \underbrace{\int_{\Omega \times \mathbb{R}^n} \widetilde{a}(z,w) h_n(|w|) \mathrm{d}z \mathrm{d}w}_{= \frac{(2\pi)^n}{\omega_n} c_L(a)} - \frac{1}{\lambda} \underbrace{\int_{\partial\Omega \times \mathbb{R}^n} \widetilde{a}(z,w) h_n(|w|) \frac{|n(z) \cdot w|}{2} \mathrm{d}\mathcal{H}^{n-1}(z) \mathrm{d}w}_{= \frac{(2\pi)^n}{\omega_n} c_{FS}(a)}, \end{aligned}$$

where we use $\approx$ to indicate equality up to $\mathcal{O}(\lambda^{-1-\frac{n-1}{n+1}})$. This yields the first two constants from Theorem 3.3.1.

For the boundary layer correction, we need to analyze the terms $A_\sigma(\lambda)$ with $\sigma \in \mathcal{R}_\Omega^{nb} \backslash \{\sigma_0\}$. So first, note that if $\sigma \in \mathcal{R}_\Omega \backslash \{\sigma_\ell\}_{\ell=0}^m$, then the range of $\pi_\sigma^\perp$ is at least 2 dimensional. Thus by Lemma 3.4.1 and the decay of h_n, one can show that $A_\sigma(\lambda) \lesssim \lambda^{\max\{-2, -\frac{n+1}{2}\}}$ for any $\sigma \in \mathcal{R}_\Omega^{nb} \backslash \{\sigma_\ell\}_{\ell=0}^m$. We are thus left with the terms $A_{\sigma_\ell}(\lambda)$ where $\{\sigma_\ell\}_{1 \leqslant \ell \leqslant m}$ are the reflections across the boundary faces of Ω. For theses terms, we proceed as we did in the proof of Theorem 3.1.1. More precisely, we can now assume that the face F_ℓ lies on the hyperplane $\{r_n = 0\}$ with outward normal vector $n_\ell = (0, ..., 0, -1)$, denote the height of Ω by $H = \sup\{h : \mathbb{R}^{n-1} \times \{h\} \cap \Omega\} \neq \varnothing$, and denote the cross-section of Ω at height h by $\Omega(h) = \{r \in \mathbb{R}^{n-1}, (r,h) \in \Omega\}$. Then, by re-scaling the variable z_n by $(2\lambda)^{-1}$, using the decay of $\widetilde{a}$ and h_n, applying Lemma 3.4.2, and using the estimate

$$\left| \left(\Omega\left(\frac{z_n + w_n}{2\lambda} \right) - \frac{\pi_n w}{2\lambda} \right) \cap \left(\Omega\left(\frac{z_n - w_n}{2\lambda} \right) + \frac{\pi_n w}{2\lambda} \right) \triangle \Omega(0) \right| \lesssim \frac{|z| + |w|}{\lambda}$$

we find that

$$\begin{aligned} A_{\sigma_\ell}(\lambda) &\approx \frac{1}{2\lambda} \int_{\Omega_\lambda - \Omega_\lambda} \int_{|\omega_n|}^{2\lambda H - |\omega_n|} h_n(|\pi_n w, z_n|) \int_{\Omega(0)} \widetilde{a}(\pi_n z, z_n/(2\lambda), w) \mathrm{d}\pi_n z \mathrm{d}z_n \mathrm{d}w \\ &\approx \frac{1}{2\lambda} \int_{F_\ell \times \mathbb{R}^n} \widetilde{a}(z,w) \int_{|w_n|}^\infty h_n(|(\pi_n w, s)|) \mathrm{d}s \mathrm{d}w \mathrm{d}\mathcal{H}^{n-1}(z). \end{aligned}$$

Finally, we obtain $c_{BL}(a)$ from the equation above after summing the terms A_{σ_ℓ} for $1 \leqslant \ell \leqslant m$ and using the second identity from Lemma 3.6.1. □

3.7 Concluding remarks

We have now proved two-term asymptotic expansions for the exchange energy and for semi-local density functionals for the free electron gas on a broad class of domains $\Omega \subset \mathbb{R}^n$, and for any dimension $n \geqslant 2$. By matching the coefficients of such expansions in the case of the Coulomb potential in 3D, we obtained a novel exact constraint for generalized gradient approximations of the exchange energy. To conclude this chapter, we now mention some possible extensions and further applications of these results.

Extensions. The asymptotics of $F(\lambda)$ can be extended to smooth domains for which the two-term Weyl law (3.1.5) holds, under the stronger condition that $f \in L^\infty_{\text{loc}}([0,\infty) \times \mathbb{R}^3) \cap C^2((0,\infty) \times \mathbb{R}^3)$. This can be done by using the gradient estimates in [107] to extend Theorem 17.5.10 in [58, Chapter XVII, pp.52] to first-order derivatives. With the extended version of Hörmander's theorem, one can justify the use of the continuum version of the spectral function from [58] inside the integration in $F(\lambda)$ by using a second-order Taylor expansion of f. The rest of the proof follows the same steps from the proof of Theorem 3.1.2.

Unfortunately, we can not extend the asymptotics of $E_x(\lambda)$ to smooth domains because our approach requires an error in the pointwise Weyl law (3.1.21) that is uniform over $\Omega \times \Omega$ and of order $o(\lambda^2/\log\lambda)$. (This can be seen from estimate (3.4.29) in Section 3.4.) An error of this order, however, represents an improvement over the sharp pointwise Weyl law [104, 60, 39], which usually requires strong assumptions on the geodesic flow [31, 17, 18] (see also [104, Chapter 1]. Another possibility is to improve the L^2 version of the Weyl law from Theorem 3.1.4. Such improvements would likely require the use of more refined tools from microlocal analysis such as pseudo-differential operators and Fourier integral operators [115, 32, 111]. Nevertheless, the extension of these results to smooth domains and to general Schrödinger operators seems like an interesting topic for further research.

Further applications. As briefly mentioned in the introduction, the asymptotic formulas derived here can also be used to obtain exact constraint on semi-local density functionals for the kinetic energy. More precisely, we can match the coefficients of Theorem 3.1.2 with the coefficients of the asymptotic expansion for the kinetic energy of the free $2N(\lambda)$-electron gas in Ω_λ,

$$T[\Psi_{2N(\lambda),\lambda}] = \sum_{\lambda_j \leqslant \lambda} \frac{\lambda_j^2}{\lambda^2} = \underbrace{\frac{n\omega_n}{(n+2)(2\pi)^n}}_{:=c_{T,1}(n)} |\Omega|\lambda^n - \underbrace{\frac{1}{4}\frac{(n-1)\omega_{n-1}}{(n+1)(2\pi)^{n-1}}}_{:=c_{T,2}(n)} |\partial\Omega|\lambda^{n-1} + o(\lambda^{n-1})$$

(see [37, 38] or Section 2.6)[6], to obtain the constraints

$$f\left(\frac{2\omega_n\mu^n}{(2\pi)^n}, 0\right) = \mu^{n+2} c_{T,1}(n) \quad \text{and} \tag{3.7.1}$$

$$\int_{\partial\Omega}\int_0^\infty f\left(\frac{\mu^n 2\omega_n}{(2\pi)^n}\big(1 - h_n(2\tau)\big), -\frac{\mu^{n+1}2\omega_n}{(2\pi)^n} 2\dot{h}_n(2\tau) n(r')\right) d\tau d\mathcal{H}^{n-1}(r') = \mu^{n+2} c_{T,2}(n)|\partial\Omega|$$

for any $\mu > 0$. Here h_n and ω_n are defined in Theorem 3.1.1 and $\mu > 0$ is a scale parameter coming from replacing the length scale $L = \lambda$ by $L = \mu\lambda$. For the case $n = 3$,

[6] Note that, from the kinetic energy density stated in (3.7.2), one can also use the results from this chapter (namely Theorem 3.1.3) to derive the asymptotic of $T[\Psi_{2N(\lambda),\lambda}]$ with the improved remainder $\mathcal{O}(\lambda^{n-1-\frac{n-1}{n+1}})$.

constraint (3.7.1) singles out the Thomas-Fermi functional for the local part of f,

$$f(\rho, 0) = f_{TF}(\rho) = c_{TF}\rho^{\frac{5}{3}} \quad \text{with} \quad c_{TF} = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}.$$

The second constraint on the other hand is new and might be of interest for the design of semi-local density functionals for the kinetic energy, which play an important role in orbital-free density functional theory [89, 91, 69, 125, 78, 24].

To conclude, let us mention that the results from this chapter can be used to obtain a similar integral constraint for the meta generalized gradient approximations (meta-GGAs) [114, 129, 112]. These are semi-local functionals depending not only on the density and its gradient but also on the kinetic energy density of the Kohn-Sham system and/or on higher derivatives of the single-particle density. More precisely, they have the form

$$F^{mGGA}[\rho] = \int_\Omega f\big(\rho(r), |\nabla\rho(r)|, \tau(r), \Delta\rho(r)\big)\mathrm{d}r$$

for some $f : \mathbb{R}^4 \to \mathbb{R}$, where $\Delta\rho$ is the Laplacian of the density, and the kinetic energy density is defined as

$$\tau(r) = \frac{1}{2}\sum_{j=1}^{N} |\nabla\phi_j(r)|^2 = \frac{1}{2}\sum_{j=1}^{n} \partial_{r_j}\partial_{r'_j}\gamma(r, r')\big|_{r'=r}, \tag{3.7.2}$$

where $\gamma(r, r')$ is the single-particle density matrix of the Kohn Sham system. For the free electron gas, the single-particle density matrix is related to the spectral function via (3.1.10). So by noticing that Theorem 3.1.3 also holds for derivatives of the spectral function of any order, we can repeat the analysis of Section 3.4 to obtain two-term asymptotic expansions for meta-GGAs.

Part II

Linear Response Formalism in Time-Dependent Density Functional Theory

Chapter 4

Positive Adiabatic Approximations

In this chapter, we study the solution χ_F of the Dyson equation

$$\chi_F(t) = \chi_0(t) + \int_0^t \chi_0(t-s) F \chi_F(s) \mathrm{d}s, \tag{4.0.1}$$

where χ_0 is the density-density response function of a general Hamiltonian and F is an operator whose Schwartz kernel corresponds to an adiabatic approximation of the Hartree plus exchange-correlation kernel of time-dependent density functional theory. More precisely, we shall study (i) the well-posedness of the above equation in an appropriate setting and (ii) the pole structure of the Fourier transform of the solution χ_F and their relation with the poles of the Fourier transform of χ_0. The results presented here set the linear response time-dependent density functional theory (LR-TDDFT) approach for computing the (electronic) optical excitation energies [19, 79, 120] on a rigorous mathematical footing. These results are extensions and improvements of the results obtained in collaboration with Gero Friesecke and Mi-Song Dupuy [25].

4.1 Main results and applications

We now present and discuss the main results of this chapter in detail. For this, let us first introduce our main assumptions and some notation. Throughout this chapter, H is a self-adjoint operator acting on the anti-symmetric N-fold tensor product of $L^2(\mathbb{R}^3)$,

$$\mathcal{H}_N = \bigwedge_{j=1}^{N} L^2(\mathbb{R}^3). \tag{4.1.1}$$

(For the sake of simplicity, we neglect any internal degrees of freedom.) Moreover, we assume that H satisfies the following assumptions.

Assumption 4.1.1. *(i) (Real Hamiltonian) H commutes with complex conjugation.*

(ii) (Spectral Gap) The ground state energy $\mathcal{E}_0 = \inf \sigma(H) > -\infty$ is in the discrete spectrum of H.

(iii) (Non-degeneracy) $\mathcal{E}_0$ is a simple eigenvalue.

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

$$\rho_0(r) := N \int_{\mathbb{R}^{3N-3}} |\Psi_0(r, r_2, ..., r_N)|^2 \mathrm{d}r_2 ... \mathrm{d}_{r_N},$$

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

$$\|f\|_{\rho_0} = \Big(\int_{\mathbb{R}^3} |f(r)|^2 \rho_0(r) \mathrm{d}r \Big)^{\frac{1}{2}} \quad \text{and} \quad \|f\|_{1/\rho_0} = \Big(\int_{\mathbb{R}^3} |f(r)|^2 \rho_0(r)^{-1} \mathrm{d}r \Big)^{\frac{1}{2}},$$

and define the respective weighted L^2 spaces as

$$\begin{aligned} L^2_{\rho_0} &= \{f : \mathrm{supp}(\rho_0) \to \mathbb{C} \text{ (Lebesgue) measurable } : \|f\|_{L^2_{\rho_0}} < \infty\}, \\ L^2_{1/\rho_0} &= \{f : \mathrm{supp}(\rho_0) \to \mathbb{C} \text{ measurable } : \|f\|_{1/\rho_0} = \|f \rho_0^{-\frac{1}{2}}\|_{L^2} < \infty\}. \end{aligned} \tag{4.1.2}$$

As usual, $\mathrm{d}r$ is the Lebesgue measure in $\mathbb{R}^3$, and we identify all measurable functions that coincide Lebesgue almost everywhere. The density-density response function (DDRF) of H can be rigorously defined as

$$\begin{aligned} \chi_H : \mathbb{R} &\to \mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0}) \\ t &\mapsto \chi_H(t) = 2\theta(t) S \sin\big((\mathcal{E}_0 - H)t\big) S^*, \end{aligned} \tag{4.1.3}$$

where $\theta(t)$ is the Heaviside step function, $\mathcal{E}_0$ is the ground state energy of H, and the operators $S = S_{\Psi_0} : \mathcal{H}_N \to L^2_{1/\rho_0}$ and $S^* = S^*_{\Psi_0} : L^2_{\rho_0} \to \mathcal{H}_N$ are defined as follows:

$$\big(S\Phi\big)(r) = N \int_{\mathbb{R}^{3N-3}} \overline{\Psi_0(r, r_2, ..., r_N)} \Phi(r, r_2, ..., r_N) \mathrm{d}r_2 ... \mathrm{d}r_N, \tag{4.1.4}$$

$$\big(S^* f\big)(r_1, ..., r_N) = \sum_{j=1}^{N} f(r_j) \Psi_0(r_1, ..., r_N). \tag{4.1.5}$$

The connection of this definition with the linear response of the system will be clarified in Section 4.2. For now, we want to briefly discuss how the Fourier transform of χ_H is related to the excitation energies of H.

Remark. *In the physics literature [83, 120], the name density-density response function usually refers to the Schwartz kernel of $\chi_H(t)$. Here we see no advantage in such a kernel representation and refer to the operator-valued function $t \mapsto \chi_H(t)$ as the density-density response function. Let us also remark that χ_H is sometimes called the (linear) susceptibility, or the reducible (or irreducible) polarizability operator [79].*

The Fourier transform of χ_H (see Proposition 4.2.4) is given by the formula

$$\widehat{\chi_H}(\omega) = \lim_{\eta \to 0^+} \int_{\mathcal{E}_0+\omega_1} \frac{2(\lambda - \mathcal{E}_0)}{(\omega + i\eta)^2 - (\lambda - \mathcal{E}_0)^2} \mathrm{d}SE_\lambda S^*,$$

where $\omega_1 = \inf \sigma(H) \backslash \{\mathcal{E}_0\} - \mathcal{E}_0$ is the first optical excitation (if H has more than one eigenvalue), E_λ is the spectral projection-valued measure of H, and the limit is taken in the distributional sense. Consequently, $\widehat{\chi_H}$ admits a (unique) meromorphic extension to the set

$$\mathcal{D}_\Omega = \{z \in \mathbb{C} : \mathrm{Im}(z) \neq 0 \text{ or } |\mathrm{Re}(z)| < \Omega\}, \tag{4.1.6}$$

where $\Omega = \inf \sigma_{\mathrm{ess}}(H) - \mathcal{E}_0 > 0$ is the *ionization threshold* of H (see Section 4.2). The positive poles of this meromorphic extension are all simple and lie in the set

$$\mathcal{P}(\widehat{\chi_H}) \coloneqq \{0 < \omega < \Omega : \mathcal{E}_0 + \omega \in \sigma(H) \text{ with } \operatorname{ran} SP^H_{\mathcal{E}_0+\omega} \neq \varnothing\}, \tag{4.1.7}$$

where $P^H_{\mathcal{E}_0+\omega}$ is the orthogonal projection on $\ker \mathcal{E}_0 + \omega - H \subset \mathcal{H}_N$. $\mathcal{P}(\widehat{\chi_H})$ is a subset of the excitation energies of H, which we call the *one-body* excitations[1]. Hence the one-body excitations of H correspond to the poles of $\widehat{\chi_H}$, and the degeneracy of the associated excited energies can be estimated by the formula

$$\mathrm{rank}_\omega(\widehat{\chi_H}) \leqslant \operatorname{rank} P^H_{\mathcal{E}_0+\omega} = \dim \ker \mathcal{E}_0 + \omega - H,$$

where $\mathrm{rank}_\omega(\widehat{\chi_H})$ denotes the rank of the pole $\omega \in \mathcal{P}(\widehat{\chi_H})$. (See Section 4.2 for the definition of the rank of a pole.)

For the Hamiltonian of a system with many interacting electrons, computing χ_H directly from H becomes unfeasible due to the high-dimensionality of the N-body space $\mathcal{H}_N$. Therefore, finding accurate approximations of χ_H that can be efficiently computed is paramount for understanding the response of large molecules to external perturbations. The solution of the Dyson equation for some specific choice of χ_0 and F are believed to provide such approximations (see Section 1.1.2). This belief is to some extent (e.g., for computing the low-lying excitation spectra of H) supported by the agreement of numerical calculations with experimental data [19, 68, 96, 120, 123]. Understanding precisely to which extent this approach is justified goes beyond the scope of the current chapter. Instead, our goal here is two-fold. First, we want to prove the well-posedness of the Dyson equation in a setting that is general enough to include many situations of interest in LR-TDDFT. Second, we want to investigate the relationship between the poles of $\widehat{\chi_F}$ and the poles of $\widehat{\chi_0}$ under the assumption that F is positive.

Let us start with the well-posedness theory. The first step for studying the existence and uniqueness of solutions to any equation is to agree on the underlying solution space.

[1]For non-interacting (or independent-particle) Hamiltonians H, these excitations are called the single particle-hole excitations as they correspond to the excitation energies necessary for moving a single electron from an occupied orbital to an unoccupied one. This terminology, however, seems misleading for interacting Hamiltonians, where this orbital picture does not hold.

In LR-TDDFT, the goal of the Dyson equation is to approximate the density-density response function of an interacting system of interest by starting with the density-density response function of an equivalent non-interacting system (the Kohn-Sham system). The equivalence here is in the sense that the Hamiltonians of both the interacting and non-interacting systems have the same ground state density ρ_0. Thus, in virtue of the definition of χ_H in (4.1.3), one natural choice for the solution space is given by the space of strongly continuous time-dependent families of operators on $\mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})$, denoted here by

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

This choice is not unique but rather useful for our purposes. It is also, in some sense, maximal (see Proposition 4.2.3). In this space, the following theorem holds.

Theorem 4.1.1 (Well-posedness of the Dyson equation)**.** *Let $F \in \mathcal{B}(L^2_{1/\rho_0}, L^2_{\rho_0})$ and $\chi_0 \in C_s\big(\mathbb{R}_+; \mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})\big)$. Then, there exists a unique solution χ_F of the Dyson equation (4.0.1) in the space $C_s\big(\mathbb{R}_+; \mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})\big)$. Moreover, the solution map*

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

is bijective.

The proof of the above theorem is a standard application of Banach's fixed point theorem. For the convenience of the reader, we sketch it in Section 4.3. Although the proof is rather simple, we shall see later on that the above theorem guarantees the existence and uniqueness of the solution of the Dyson equation with widely used adiabatic approximations whenever χ_0 is the density-density response function of a general Hamiltonian. In addition, the bijectivity of the solution map shows that any density-density response function can be obtained by solving the Dyson equation for some reference χ_0. Of course, this does not guarantee that $\chi_0 = \chi_{H_0}$ for some non-interacting Hamiltonian H_0, a standard premise of LR-TDDFT.

Next, we want to discuss the poles of the Fourier transform of the solution χ_F when χ_0 is the density-density response of a Hamiltonian – interacting or not – satisfying Assumption 4.1.1. To illustrate the kind of results we aim for and the difficulties entailed, let us consider the following simplified situation. Suppose that $F = f > 0$ is a real number and $\widehat{\chi_0}$ is the complex-valued meromorphic function given by

$$\widehat{\chi_0}(z) = \sum_{\omega \in \mathcal{P}(\widehat{\chi_0})} \frac{2\omega}{z^2 - \omega^2} b(\omega),$$

where all $b(\omega) > 0$ are also real numbers. This simplification is achieved if $\chi_0 = \chi_H$ for some Hamiltonian with purely discrete spectrum and one considers 1D approximations of

the spaces $L^2_{\rho_0}$ and L^2_{1/ρ_0}. Then, by formally applying the Fourier transform to (4.0.1), we obtain

$$\widehat{\chi_F}(z) = \widehat{\chi_0}(z) + \widehat{\chi_0}(z)F\widehat{\chi_F}(z), \tag{4.1.8}$$

which is the frequency version of the Dyson equation. This leads to the explicit formula

$$\widehat{\chi_F}(z) = (1 - \widehat{\chi_0}(z)F)^{-1}\widehat{\chi_0}(z) = \frac{\sum_{\omega\in\mathcal{P}(\widehat{\chi_0})} \frac{2\omega}{z^2-\omega^2} b(\omega)}{1 - \sum_{\omega\in\mathcal{P}(\widehat{\chi_0})} \frac{2\omega}{z^2-\omega^2} b(\omega) f}.$$

From this formula, we can directly read some properties of $\widehat{\chi_F}$. First, $\widehat{\chi_F}$ is meromorphic on $\mathcal{D}_\Omega$ (which is the whole complex plane in this example) and

$$\lim_{z\to\omega} \widehat{\chi_F}(z) = -f^{-1} \quad \text{for any } \omega \in \mathcal{P}(\widehat{\chi_0}). \tag{4.1.9}$$

In particular, $\widehat{\chi_0}$ and $\widehat{\chi_F}$ have no mutual poles. Second, a point $z \in \mathbb{C}$ is a pole of $\widehat{\chi_F}$ if and only if it satisfy the equation

$$1 = \widehat{\chi_0}(z)f = \sum_{\omega\in\mathcal{P}(\widehat{\chi_0})} \frac{2z}{z^2-\omega^2} b(\omega) f. \tag{4.1.10}$$

This implies that any pole of $\widehat{\chi_F}$ must lie in the real axis. Moreover, by noticing that

(i) $\widehat{\chi_0}(\alpha)f < 0$ for any $\alpha \in \mathbb{R}$ with $|\alpha| < \min \mathcal{P}(\widehat{\chi_0})$,

(ii) $\widehat{\chi_0}(\alpha)f$ is continuous and decreasing along any interval on $\mathbb{R}\backslash\mathcal{P}(\widehat{\chi_0})$, and

(iii) $\lim_{\alpha\downarrow\omega} \widehat{\chi_0}(\alpha)f = \infty = -\lim_{\alpha\uparrow\omega} \widehat{\chi_0}(\alpha)f$, for any $\omega \in \mathcal{P}(\widehat{\chi_0})$,

we can deduce that

$$0 < \omega_1 < \omega_1^F < \omega_2 < \omega_2^F < \omega_3 < \omega_3^F < ..., \tag{4.1.11}$$

where $0 < \omega_1 < \omega_2 < ...$ and $0 < \omega_1^F < \omega_2^F < ...$ are respectively the positive poles of $\widehat{\chi_0}$ and $\widehat{\chi_F}$. (Note that the negative poles are the reflections of the positive poles over the imaginary axis.)

These results, in special eq. (4.1.11), are precisely the results we would like to transfer to the infinite-dimensional setting. In this setting, however, the following difficulties arise. First, since we are dealing with operators between infinite-dimensional spaces, the inverse $(1-\widehat{\chi_0}(z)F)^{-1}$ is not necessarily meromorphic and could be ill-defined everywhere. Second, the product of positive operators such as $b(\omega)f$ in our example is not necessarily positive if the space is no longer one-dimensional. Third, the operators in question act on different Hilbert spaces, which raises the question of what a positive operator should mean.

So let us start by precisely defining what a positive F means. The key observation here is that F maps a Banach space to its dual, which allows for the following natural definition of a positive operator.

Definition 4.1.1 (Positive operator)**.** *We say that* $F \in \mathcal{B}(L^2_{1/\rho_0}, L^2_{\rho_0})$ *is positive if*

$$\langle f, Ff\rangle_{L^2(\mathbb{R}^3)} = \int_{\mathbb{R}^3} \overline{f(r)}(Ff)(r)\mathrm{d}r > 0 \quad \textit{for any } 0 \neq f \in L^2_{1/\rho_0}. \tag{4.1.12}$$

This property has various useful implications for the analysis of the Dyson equation; we now mention a few that are necessary for stating our main results. For starters, we see that for positive F, the sesquilinear form

$$\langle f, g\rangle_F = \langle f, Fg\rangle_{L^2(\mathbb{R}^3)}$$

defines a continuous inner-product on the space L^2_{1/ρ_0}. Indeed, continuity follows since $F \in \mathcal{B}(L^2_{1/\rho_0}, L^2_{\rho_0})$ and symmetry follows from the polarization identity. Consequently, for any finite-dimensional subspace $V \subset L^2_{1/\rho_0}$, there exists an *F-orthogonal* decomposition

$$L^2_{1/\rho_0} = V \oplus V^\perp \tag{4.1.13}$$

with associated projections P_V, $P_{V^\perp} = 1 - P_V \in \mathcal{B}(L^2_{1/\rho_0})$. Here $V^\perp$ is the orthogonal complement with respect to the inner-product $\langle\cdot,\cdot\rangle_F$ and should not be confused with the orthogonal complement with respect to the natural inner-product in L^2_{1/ρ_0}. (The latter will play no role in our analysis.) In particular, for any density-density response function χ_H, the F-orthogonal projections $P_{V_\omega^\perp}$ on the finite-dimensional subspaces

$$V_\omega := \operatorname{ran} SP^H_{\mathcal{E}_0+\omega}, \quad \text{where } \omega \in \mathcal{P}(\widehat{\chi_H}), \tag{4.1.14}$$

are well-defined. To simplify the next statements, it is also useful to define $V_z := \{0\}$ for any $z \notin \mathcal{P}(\widehat{\chi_H})$. Observe that the operator-valued function $z \mapsto P_{V_{z_0}^\perp}\widehat{\chi_H}(z)F$ is holomorphic around $z = z_0$ for any $z_0 \in \mathcal{D}_\Omega$.

Meromorphic function and pole equation. We are now in position to present our first main result; it states that $\widehat{\chi_F}$ is a meromorphic function with poles of finite rank and gives a criterion for identifying the rank of each pole. For this and the subsequent results, we implicitly assume that $F \in \mathcal{B}(L^2_{1/\rho_0}, L^2_{\rho_0})$ is positive and $\chi_0 = \chi_H$ for some H satisfying Assumption 4.1.1.

Theorem 4.1.2 (Fourier transform of χ_F)**.** *The solution* χ_F *is a tempered distribution, and its Fourier transform satisfies the following:*

(i) $\widehat{\chi_F}(z)$ *has a (unique) meromorphic extension from* $\mathcal{D}_\Omega$ *(see (4.1.6)) to* $\mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})$.

(ii) The poles of $\widehat{\chi_F}$ *are all simple and lie inside the interval* $(-\Omega, \Omega)$.

(iii) The rank of each pole $\omega \in \mathcal{P}(\widehat{\chi_F})$ *is finite and can be computed via the formula*

$$\operatorname{rank}_\omega(\widehat{\chi_F}) = \dim \underbrace{\ker 1 - P_{V_\omega^\perp}\widehat{\chi_H}(\omega)F}_{:=Z_\omega} < \infty, \tag{4.1.15}$$

where $P_{V_\omega^\perp} = 1 - P_{V_\omega}$ is the F-orthogonal projection defined above.

This theorem shows that many aspects of our simple 1D example persist in the infinite-dimensional case. Precisely, $\widehat{\chi_F}$ is still a meromorphic function whose poles are all simple, have finite rank, and lie in the real axis. Note also that eq. (4.1.15) is the equivalent of (4.1.10). In addition, one can find explicit formulae for $\widehat{\chi_F}$ in terms of $\widehat{\chi_H}$ and F. To state these formulae, we define the projection P_{FV_ω} as the projection associated with the decomposition

$$L^2_{\rho_0} = \underbrace{\operatorname{ran} FSP^H_{\mathcal{E}_0+|\omega|}}_{=FV_\omega} \oplus \ker SP^H_{\mathcal{E}_0+|\omega|}S^*.$$

(That this decomposition is possible is another consequence of the positivity of F.)

Theorem 4.1.3 (Formula for $\widehat{\chi_F}$)**.** *Let $\omega \in \mathcal{D}_\Omega$ and $\mathcal{P}(\widehat{\chi_F})$ denote the set of positive poles of $\widehat{\chi_F}$. Let P_{Z_ω} be the F-orthogonal projection on Z_ω (defined in (4.1.15)). Then, the following holds:*

(i) If $z \notin \mathcal{P}(\widehat{\chi_F})$, then the operator $P^\perp_{V_z}(1 - \widehat{\chi_H}(z)F)|_{V_z^\perp}$ is invertible in $\mathcal{B}(V_z^\perp)$ and

$$\widehat{\chi_F}(z) = (P_{V_z^\perp}(1 - \widehat{\chi_H}(z)F)\big|_{V_z^\perp})^{-1}P_{V_z^\perp}\widehat{\chi_H}(z)(1 - P_{FV_z}) - F^{-1}P_{FV_z}. \quad (4.1.16)$$

(ii) If $\omega \in \mathcal{P}(\widehat{\chi_F})$, then the operator $T_\omega = P_{V_\omega}SP^H_{\mathcal{E}_0+\omega}S^*\big|_{FV_\omega}$ is invertible in $\mathcal{B}(FV_\omega, V_\omega)$, the operator

$$K_\omega = P_{Z_\omega}\left(\widehat{\chi_H}(\omega)P_{FV_\omega}T_\omega^{-1}P_{V_\omega}\widehat{\chi_H}(\omega)F - \dot{\widehat{\chi_H}}(\omega)F\right)P_{Z_\omega} \quad (4.1.17)$$

is invertible in $\mathcal{B}(Z_\omega)$, and we have

$$\widehat{\chi_F}(z) = \frac{K_\omega^{-1}P_{Z_\omega}\widehat{\chi_H}(\omega)(1 - P_{FV_\omega})}{z - \omega} + \mathcal{O}(1) \quad (4.1.18)$$

for z close to ω.

Remark. *Some remarks are now in place.*

- *First, note that the operator K_ω defined in (4.1.17) is bounded. Indeed, this follows from the identities $P_{V_\omega^\perp}SP^H_{\mathcal{E}_0+\omega}S^* = 0 = SP^H_{\mathcal{E}_0+\omega}S^*FP_{V_\omega^\perp}$ (see Proposition 4.5.4) and the fact that $Z_\omega \subset V_\omega^\perp$. Moreover, we see that (4.1.16) reduces to the familiar formula $\widehat{\chi_F}(z) = (1 - \widehat{\chi_H}(z)F)^{-1}\widehat{\chi_H}(z)$ for any $z \notin \mathcal{P}(\widehat{\chi_H})$. Similarly, the operator K_ω reduces to $K_\omega = -P_{Z_\omega}\dot{\widehat{\chi_H}}(\omega)FP_{Z_\omega}$ for any $\omega \notin \mathcal{P}(\widehat{\chi_H})$.*
- *Second, observe that the functions $\widehat{\chi_F}(z)$ and $\widehat{\chi_H}(z)$ may have mutual poles. That this is not the case in our 1D example is a consequence of the lack of dimension. Nonetheless, note that (4.1.16) generalizes (4.1.9).*

- *Third, note that (4.1.18) only describes the leading order coefficient of $\widehat{\chi_F}(z)$ as z approaches one of its poles. Explicit formulae for the coefficients of a full asymptotic expansion of the form $\widehat{\chi_F}(z) = \sum_{k=1}^{\infty}(z-\omega)^{k-2}K_k$ could also be computed by using the results of Section 4.4. As these formulas become increasingly cumbersome to state (and compute), we have chosen to omit them here.*

Pole shifting. We have now given an explicit way to compute $\widehat{\chi_F}$ together with a criteria for verifying whether some $\omega \in (-\Omega, \Omega)$ is a pole of $\widehat{\chi_F}$. However, neither of these results provides an insight into the distribution of the poles of $\widehat{\chi_F}$ along the interval $(-\Omega, \Omega)$. Such an insight, as the alternating behavior in eq. (4.1.11), might be useful for designing efficient algorithms for finding the poles of $\widehat{\chi_F}$. Therefore, our next theorem might be particularly interesting for applications; roughly speaking, it gives a variational procedure for estimating the number of poles of $\widehat{\chi_F}$ in a given interval $I \subset (-\Omega, \Omega)$. To state this theorem precisely, let us define the F-max-min values of $\widehat{\chi_H}F$ as

$$\mu^k(\omega) := \sup_{\substack{V \subset V_\omega^\perp \\ \dim V = k}} \inf_{\substack{f \in V \\ \langle f, Ff\rangle = 1}} \langle Ff, \widehat{\chi_H}(\omega) Ff\rangle, \tag{4.1.19}$$

and the F-min-max values as

$$\mu_k(\omega) := \inf_{\substack{V \subset V_\omega^\perp \\ \dim V = k}} \sup_{\substack{f \in V \\ \langle f, Ff\rangle = 1}} \langle Ff, \widehat{\chi_H}(\omega) Ff\rangle. \tag{4.1.20}$$

Note that because we restrict the search to subspaces of the F-orthogonal complement $V_\omega^\perp$, the above values are well-defined real numbers for any $\omega \in (-\Omega, \Omega)$ and $k \in \mathbb{N}$.

Theorem 4.1.4 (Variational approach)**.** *For any $\omega \in (-\Omega, \Omega)$ we have*

$$\operatorname{rank}_\omega(\widehat{\chi_F}) = \#\{k : \mu^k(\omega) = 1\} \tag{4.1.21}$$

(with the convention that ω is not a pole if the right-hand side is zero). Moreover, the functions $\mu^k, \mu_k : [0, \Omega) \to \mathbb{R}$ are non-increasing on any interval $J \subset [0, \Omega) \backslash \mathcal{P}(\widehat{\chi_H})$, and they satisfy

(i) $\mu^1(s) \leqslant 0$ *for any* $|s| \leqslant \min \mathcal{P}(\widehat{\chi_H})$,

(ii) $\lim_{s \downarrow \omega} \mu^k(s) = \infty = -\lim_{s \uparrow \omega} \mu_k(s)$ *for any* $k \leqslant \dim V_\omega$ *and* $\omega \in \mathcal{P}(\widehat{\chi_H})$,

(iii) $\lim_{s \uparrow \omega} \mu^k(s) = \mu^k(\omega) = \lim_{s \downarrow \omega} \mu^{k+\dim V_\omega}(s)$ *for any* $k \in \mathbb{N}$, *and*

(iv) $\lim_{s \uparrow \omega} \mu_{k+\dim V_\omega}(s) = \mu_k(\omega) = \lim_{s \downarrow \omega} \mu_k(s)$ *for any* $k \in \mathbb{N}$,

where the subspaces V_ω are defined according to (4.1.14) (again with the convention that $V_\omega = \{0\}$ for $\omega \notin \mathcal{P}(\widehat{\chi_H})$).

Let us now briefly clarify the content of Theorem 4.1.4 and explain how it yields the analogous of eq. (4.1.11). First, we see from (4.1.21) and (i) that the function $\widehat{\chi_F}$ has no poles inside the interval $[0, \min \mathcal{P}(\widehat{\chi_H})]$. Moreover, since μ^k is non-increasing and continuous on any interval $(a, b] \subset [0, \Omega) \backslash \mathcal{P}(\widehat{\chi_H})$, the sum of the rank of all poles inside this interval is

$$\sum_{\omega \in (a,b]} \mathrm{rank}_\omega(\widehat{\chi_F}) = \max\{k : \mu^k(a) > 1\} - \max\{k : \mu^k(b) > 1\}.$$

In addition, Theorem 4.1.4 also tells us how to compute the total rank of the poles inside an interval containing some of the one-body excitations of H. Indeed, it follows from statements (ii) and (iii) that

$$\sum_{\omega \in (a,b]} \mathrm{rank}_\omega(\widehat{\chi_F}) = \max\{k : \mu^k(a) > 1\} - \max\{k : \mu^k(b) > 1\} + \sum_{\omega \in [a,b) \cap \mathcal{P}(\widehat{\chi_H})} \dim V_\omega$$

for any $(a, b] \subset [0, \Omega)$. If we now combine this statement with the fact that

$$\mathrm{rank}_\omega(\widehat{\chi_H}) = \dim V_\omega \quad \text{for any } \omega \in \mathcal{P}(\widehat{\chi_H}),$$

we then conclude that the poles of $\widehat{\chi_F}$, when counted with rank, are forward shifted with respect to the poles of $\mathcal{P}(\widehat{\chi_H})$. In mathematical notation, we have just proved

Corollary 4.1.1 (Forward shift of poles)**.** *The poles of $\widehat{\chi_F}$ are forward shifted with respect to the poles of $\widehat{\chi_H}$ in the sense that*

$$\sum_{0<\omega<b} \mathrm{rank}_\omega(\widehat{\chi_F}) \leqslant \sum_{0<\omega<b} \mathrm{rank}_\omega(\widehat{\chi_H}),$$

for any $0 < b < \Omega$.

The Casida formalism. In practice, neither χ_H nor the solution χ_F can be computed analytically. To solve the equation $\widehat{\chi_H}(\omega)Ff = f$, and hence find the poles of $\widehat{\chi_F}$, one has to appeal to numerical methods. Such methods require some discretization procedure that reduces the problem to a finite-dimensional approximation, which some numerical scheme can then tackle. As a final result for this chapter, we prove the convergence of one such discretization procedure, namely the Casida formalism [19, 79], in the continuum (or infinite basis) limit. More specifically, we show that, under the additional assumption that the Hamiltonian H has a purely discrete spectrum, the poles obtained via the Casida equations converge in an ordered manner to the true poles of $\widehat{\chi_F}$ in the continuum limit. To state this result precisely, let us briefly describe the Casida formalism.

Assuming that H has a purely discrete spectrum, we can choose an orthonormal basis of eigenfunctions $\{\Psi_j\}_{j\geqslant 1}$ with corresponding eigenvalues $\{\mathcal{E}_0 + \omega_j\}_{j\geqslant 1}$ and spanning the space $\{\Psi_0\}^\perp$. After possibly relabelling and excluding some of the eigenfunctions, we can further assume that the diagonal of the mixed single-particle density matrices do not vanish, i.e.,

$$S_{\Psi_0}\Psi_j = N \int_{\mathbb{R}^3} \overline{\Psi_0}(\cdot, r_2, ..., r_N)\Psi_j(\cdot, r_2, ..., r_N)\mathrm{d}r_2...\mathrm{d}r_N \in L^2_{1/\rho_0} \tag{4.1.22}$$

is not identically zero for any $j \in \mathbb{N}$. Hence the set $\{\omega_j\}_{j\geqslant 1}$ is precisely the set of one-body excitations of H. However, note that we do *not* assume the excitations to be in increasing order, and we allow for degeneracies in the sense that $\omega_j = \omega_k$ for some $j \neq k$ is possible. Moreover, note that for degenerated excitations $\omega \in \{\omega_j\}_{j=1}^{\infty}$, it may happen that

$$d(\omega) := \#\{j : \omega_j = \omega\} - \dim \operatorname{span}\{S\Psi_j : \omega_j = \omega\} > 0 \tag{4.1.23}$$

because there may be linear combinations of Ψ_j that belong to the kernel of S. The Casida formalism then consists in truncating the set of excitations at some $m \in \mathbb{N}$, computing the eigenvalues of the m^{th} Casida matrix[2]

$$C^m \in \mathbb{C}^{m\times m}, \quad C^m_{i,j} := 2\omega_i \langle S\Psi_i, FS\Psi_j\rangle + \omega_i^2 \delta_{ij}, \quad \text{where} \quad \delta_{ij} = \begin{cases} 1 & \text{if } i = j, \\ 0 & \text{otherwise,} \end{cases}$$

and using their square roots as approximations for the poles of $\widehat{\chi_F}$. The next theorem shows that, after excluding spurious eigenvalues coming from the mismatch in (4.1.23), this approach is justified for large m.

Theorem 4.1.5 (Casida formalism)**.** *Let $\chi_0 = \chi_H$ be the DDRF of a Hamiltonian satisfying Assumption 4.1.1 and with purely discrete spectrum. Then C^m is diagonalizable, all its eigenvalues are positive, and for any $\lambda > 0$ we have*

$$\dim\ker \lambda - C^m \geqslant \underbrace{\#\{j : j \leqslant m, \omega_j = \sqrt{\lambda}\} - \dim \operatorname{span}\{S\Psi_j : j \leqslant m, \omega_j = \sqrt{\lambda}\}}_{:= d_m(\sqrt{\lambda})}.$$

Let $0 < \lambda_1 \leqslant \lambda_2 ... \leqslant \lambda_{m-\sum_{\omega>0} d_m(\omega)}$ be the eigenvalues of C^m counted in a way that

$$\#\{k : \lambda_k = \lambda\} = \dim\ker(\lambda - C^m) - d_m(\sqrt{\lambda}),$$

then we have monotone convergence of $\sqrt{\lambda_k}$ to the ordered poles of $\widehat{\chi_F}$ in the following sense:

(i) $\sqrt{\lambda_k^m} \geqslant \sqrt{\lambda_k^{m+1}} \geqslant \omega_k^F$ *for any $\omega_k^F \leqslant \omega_m \in \mathbb{N}$ and $m \in \mathbb{N}$, and*

(ii) $\lim_{m\to\infty} \sqrt{\lambda_k^m} = \omega_k^F$ *for any $k \in \mathbb{N}$,*

where $0 < \omega_1^F \leqslant \omega_2^F \leqslant ... \to \infty$ are the ordered poles of $\widehat{\chi_F}$ counted with rank.

Remark. *In typical applications of the Casida formalism, the Hamiltonian H is a sum of one-body Hamiltonians h acting on each coordinate separately. In this case, the ground*

[2]The usual definition of the Casida matrix [19, 83, 120] is slightly different from the one above. Nevertheless, as shown in Section 4.7.2 below, the above definition of the Casida matrix is essentially equivalent to the original one under the assumptions of real Hamiltonian and real-valued (or constant phase) ground state wave function. Such assumptions are usually satisfied in applications.

state wave function is the Slater determinant of the first N eigenfunctions of h (the occupied orbitals). Moreover, the excited states satisfying (4.1.22) are (usually chosen as) the Slater determinants of $N-1$ occupied orbitals with 1 unoccupied (or virtual) orbital. In this situation, $m = Nk$ where k is the number of virtual orbitals used to construct the Casida matrix (see Section 4.7.2).

Applications. Let us now describe how the functional analytic setting described so far is applicable in the context of LR-TDDFT. For this, the key observation is that most Hamiltonians appearing in non-relativistic quantum mechanics share the common property that their ground state density ρ_0 (when it exists) is bounded. For instance, this is the case for any Schrödinger operators of the form

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

where V is some real-valued potential whose positive and negative part lies respectively in the local and global Kato class of $\mathbb{R}^{3N}$ [109]. (In fact, the ground state densities of such operators decay exponentially fast, see [1, 28, 56, 109] and references therein). For bounded ρ_0 we have the following criteria for adiabatic approximations. (The proof is a straightforward application of Hölder's inequality.)

Proposition 4.1.1 (Sufficient criteria 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*

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

Then $F \in \mathcal{B}(L^2_{1/\rho_0}, L^2_{\rho_0})$.

The above criteria can be easily verified for the following adiabatic approximations:

- The random phase approximation (RPA). In the RPA, F is the Hartree operator

$$\big(F^{\mathrm{RPA}} g\big)(r) = \big(F_H g\big)(r) = \int_{\mathbb{R}^3} \frac{g(r')}{|r-r'|} \mathrm{d}r'.$$

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

- The Petersilka, Gossmann, and Gross approximation (PGG) [96]. In the PGG approximation, the operator F is given by

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

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

- The adiabatic local density approximation (ALDA) [127, 120]. This is not a single approximation but rather a class of approximations. In the ALDA, the operator F is given by

$$\big(F_{\rho_0}^{\mathrm{ALDA}} g\big)(r) = \big(F_H g\big)(r) + \underbrace{\frac{d^2}{d\rho^2}\big(\rho\varepsilon_{\mathrm{xc}}^{\mathrm{HEG}}(\rho)\big)\big|_{\rho=\rho_0(r)}}_{=f_{\mathrm{xc}}^{\mathrm{HEG}}\left(\rho_0(t)\right)} g(r),$$

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

$$\varepsilon_{\mathrm{x}}^{\mathrm{HEG}}(\rho) = -C\rho^{\frac{1}{3}}, \tag{4.1.24}$$

  the correlation part has to be approximated, which leads to different operators $F_{\rho_0}^{\mathrm{ALDA}}$. To see why these operators also belong to $\mathcal{B}(L^2_{1/\rho_0}, L^2_{\rho_0})$, let us take the parametrization of $\varepsilon_c^{\mathrm{HEG}}$ introduced by Perdew and Wang [95]. This correlation approximation can be written as

$$\varepsilon_{\mathrm{c}}^{\mathrm{PW92}}(\rho) = -2A(1+\alpha_1\rho^{-\frac{1}{3}})\log\left(1 + \frac{1}{\beta_1\rho^{-\frac{1}{6}} + \beta_2\rho^{-\frac{1}{3}} + \beta_3\rho^{-\frac{1}{2}} + \beta_4\rho^{-\frac{1+P}{3}}}\right), \tag{4.1.25}$$

  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 $\varepsilon_{\mathrm{c}}^{\mathrm{HEG}}$ in the low and high-density limits, and to fit data from quantum Monte Carlo simulations [20] for intermediate densities. Thus from (4.1.24) and (4.1.25) (and some tedious calculations), one can check that

$$|f_{\mathrm{xc}}^{\mathrm{PW92}}\big(\rho_0(r)\big)| = \left|\frac{d^2}{d\rho^2}(\rho\varepsilon_x^{\mathrm{HEG}}(\rho) + \rho\varepsilon_c^{\mathrm{PW92}}(\rho))\big|_{\rho=\rho_0(r)}\right| \lesssim_{\|\rho_0\|_{L^\infty}} \rho_0(r)^{-1}.$$

  Therefore, $F_{\rho_0}^{\mathrm{ALDA}} \in \mathcal{B}(L^2_{1/\rho_0}, L^2_{\rho_0})$ for any bounded ρ_0. Other approximations to $\varepsilon_c^{\mathrm{HEG}}(\rho)$ can also be shown to satisfy the above inequality as long as they reproduce (up to second derivatives) the asymptotic expansion of $\varepsilon_c^{\mathrm{HEG}}(\rho)$ in the low-density limit.

In summary, Theorem 4.1.1 and Proposition 4.1.1 guarantees the well-posedness of the Dyson equation with widely used adiabatic approximations of the xc-operator (see Section 1.1.2) under the sole condition that $\chi_0 = \chi_H$ for some Hamiltonian with bounded ground state density.

Regarding the applicability range of Theorems 4.1.2 to 4.1.5, the positive assumption is a big drawback. Indeed, among the approximations mentioned above, only the RPA is positive; this can be seen from the Fourier space representation

$$\langle g, F_H g\rangle_{L^2(\mathbb{R}^3)} = 4\pi\int_{\mathbb{R}^3}\frac{|\widehat{g}(\xi)|^2}{|\xi|^2}\mathrm{d}\xi > 0 \quad \text{for any } g \in L^1(\mathbb{R}^3)\cap L^2(\mathbb{R}^3).$$

Nevertheless, we can conclude that the excitation energies obtained from the RPA approximation are always greater than the excitation energies of the non-interacting Kohn-Sham system (see Appendix 1.1). Moreover, the results from Theorem 4.1.2–4.1.5 also apply to the RPA approximation with other interaction potentials such as the Riesz interactions (see Chapter 3) or the Yukawa potential [126]. Finally, let us remark that we do *not* use the assumption that the underlying physical space is $\mathbb{R}^3$ in the proof of the main results of this chapter. All assumptions and proofs are, in fact, of an operator-theoretical nature. In particular, the same results can be straightforwardly applied to systems on bounded domains $\Omega \subset \mathbb{R}^n$ with general dimensions $n \geqslant 2$, or to spin systems where the single-particle state is given by $\ell^2(\mathbb{N})$ or variants thereof.

Outline of the chapter. We start by introducing some notation in the next paragraph. In Section 4.2, we give a rigorous definition for the density-density response function, compute its Fourier transform, and discuss the mentioned maximality of $\mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})$. In Section 4.3 we prove Theorem 4.1.1. In Section 4.4, we derive some results about the spectrum and the inverse of operator-valued functions around one of its poles. These results are then applied to the operator $1 - \chi_H F$ in Section 4.5. In this section, we give a detailed description of the operator-valued function $(1 - \widehat{\chi_H} F)^{-1}$, which corresponds to the main step in the proof of Theorems 4.1.2 to 4.1.4. We then complete their proofs in Section 4.6. In Section 4.7 we study the convergence of the Casida eigenvalues under the assumption of pure discrete spectrum for H. In Section 4.8, we comment on possible extensions of the results presented here and related open questions.

Notation

The set $\mathbb{R}_+ = [0, \infty)$ denotes the set of non-negative real numbers. For A and B scalar quantities, $A \lesssim B$ means that there is an irrelevant positive constant C such that $A \leqslant CB$. Let F, G be Banach spaces. We will denote their respective norms by $\|\cdot\|_F$ and $\|\cdot\|_G$. Moreover, we denote the set of continuous linear operators from F to G by $\mathcal{B}(F, G)$, and their operator norm by

$$\|T\|_{F,G} = \sup_{\substack{f \in F \\ \|f\|_F = 1}} \|Tf\|_G.$$

For an operator $T \in \mathcal{B}(F, G)$, we denote its kernel and range 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. For $1 \leqslant p \leqslant \infty$, $L^p(\mathbb{R}^3)$ (or just L^p) denotes the standard L^p spaces with respect to Lebesgue measure. 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 measurable (with respect to the Lebesgue measure) functions with the respective norms

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

Moreover, for a continuous function $A(\mu)$ with values in a Banach space F and defined on the neighborhood of some smooth closed curve $\gamma \subset \mathbb{C}$,

$$\frac{1}{2\pi i} \oint_{\gamma} A(\mu) \mathrm{d}\mu \in F$$

denotes the standard contour integral along the path γ oriented counter-clockwise. For time-dependent functions with values in a Banach space F, we define the Fourier transform as

$$\widehat{f}(\omega) = \int_{\mathbb{R}} f(t) e^{it\omega} \mathrm{d}t. \tag{4.1.26}$$

(Note that this is different from the convention for the spatial Fourier transform used in Chapters 2 and 3.)

4.2 The density-density response function

In this section we give a rigorous definition for the density-density response function (DDRF) and relate it to the Kubo formula from linear response theory. We then give an alternative definition that relies on our assumptions on the Hamiltonian H, and give a representation formula for its Fourier transform in terms of the resolvent of H.

4.2.1 Definition and Kubo formula

The density-density response function can be defined as follows.

Definition 4.2.1 (Density-density response function)**.** *Let H be a Hamiltonian with ground state Ψ_0, then, for any $\tau \in \mathbb{R}$ we define the density-density response function of H as the unique operator $\chi_H(\tau) : L^\infty(\mathbb{R}^3;\mathbb{R}) \to L^1(\mathbb{R}^3;\mathbb{R})$ satisfying*

$$\langle v_{\mathcal{O}}, \chi_H(\tau) v_{\mathcal{P}} \rangle_{L^2(\mathbb{R}^3)} = i\theta(\tau) \left\langle \Psi_0, \left[\sum_{k=1}^N v_{\mathcal{P}}(r_k), \Big(\sum_{k=1}^N v_{\mathcal{O}}(r_k) \Big)_I(\tau) \right] \Psi_0 \right\rangle, \tag{4.2.1}$$

for all $v_{\mathcal{P}}, v_{\mathcal{O}} \in L^\infty(\mathbb{R}^3;\mathbb{R})$. In the above, $[A,B] = AB - BA$ denotes the commutator, θ is the Heaviside function

$$\theta(t) = \begin{cases} 0, & \text{if } t < 0, \\ 1, & \text{otherwise,} \end{cases}$$

and $(A)_I(t) = e^{itH} A e^{-itH}$ is the time evolution of the operator A in the Heisenberg picture.

To motivate the above definition, let us relate χ_H to the Kubo formula for the linear response of the density of the system at the ground state Ψ_0. The starting point for the Kubo formula is to consider a time-dependent perturbation of H,

$$H(t) = H + \varepsilon f(t) V_{\mathcal{P}}, \tag{4.2.2}$$

where the perturbing operator $V_{\mathcal{P}} : \mathcal{H}_N \to \mathcal{H}_N$ is bounded and symmetric, the *time profile* $f \in L^\infty(\mathbb{R};\mathbb{R})$ is causal (i.e. $f(t) = 0$ for $t \leqslant 0$), and $\varepsilon \in \mathbb{R}$ is the strength of the perturbation. Then for an observable of interest, $V_{\mathcal{O}} : \mathcal{H}_N \to \mathcal{H}_N$, we would like to compute the variation in the expectation value $\langle V_{\mathcal{O}} \rangle_t := \langle \Psi(t), V_{\mathcal{O}} \Psi(t) \rangle$, where $\Psi(t)$ is the solution of the time-dependent Schrödinger equation

$$\begin{cases} i\partial_t \Psi(t) = H(t)\Psi(t), & t > 0, \\ \Psi(0) = \Psi_0 \end{cases} \tag{4.2.3}$$

with Ψ_0 being the ground state wave function of H. For this, one can iterate the Duhamel representation formula for the solutions of (4.2.3),

$$\psi(t) = e^{-itH}\Psi_0 - i \int_0^t e^{-i(t-s)H} \epsilon f(s) V_{\mathcal{P}} \psi(s) \mathrm{d}s,$$

to show that the following holds.

Proposition 4.2.1. *Let $H(t)$ be the family of self-adjoint operators defined in (4.2.2). Let $\Psi(t)$ be the solution of (4.2.3) and $V_{\mathcal{O}} : \mathcal{H}_N \to \mathcal{H}_N$ be a bounded operator. Then $\langle V_{\mathcal{O}} \rangle_t = \langle \Psi(t), V_{\mathcal{O}} \Psi(t) \rangle$ has the following expansion:*

$$\langle V_{\mathcal{O}} \rangle_t = \langle V_{\mathcal{O}} \rangle_0 + i\varepsilon \int_{-\infty}^{\infty} \theta(t-t') f(t') \langle \Psi_0, \left[V_{\mathcal{P}}, (V_{\mathcal{O}})_I(t-t') \right] \Psi_0 \rangle \mathrm{d}t' + \mathcal{O}(\varepsilon^2), \tag{4.2.4}$$

where the remainder is locally uniform with respect to t.

Therefore, if we now assume that the perturbation $V_{\mathcal{P}}$ as well as the observable $V_{\mathcal{O}}$ are given by one-body potentials

$$V_{\mathcal{P}} = \sum_{k=1}^{N} v_{\mathcal{P}}(r_k), \quad V_{\mathcal{O}} = \sum_{k=1}^{N} v_{\mathcal{O}}(r_k),$$

with $v_{\mathcal{O}}$ and $v_{\mathcal{P}}$ real-valued bounded functions, we arrive at the Kubo formula for the first order (with respect to ϵ) variation of $\langle V_{\mathcal{O}} \rangle_t$ due to the perturbation $\epsilon f(t) V_{\mathcal{P}}$.

Corollary 4.2.1 (Kubo formula)**.** *Let χ_H be defined in (4.2.1), then*

$$\langle V_{\mathcal{O}} \rangle_t - \langle V_{\mathcal{O}} \rangle_0 = \varepsilon \int_{-\infty}^{\infty} \langle v_{\mathcal{O}}, \chi_H(t-t') v_{\mathcal{P}} \rangle f(t') \, \mathrm{d}t' + \mathcal{O}(\varepsilon^2).$$

4.2.2 Regularity of the density-density response function

We now present an alternative representation for the DDRF of H and discuss the mentioned optimality of the space $\mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})$.

First, recall that the operators S and S^* are defined by

$$(S\Phi)(r) = N\int_{(\mathbb{R}^3)^{N-1}} \overline{\Psi_0(r, r_2, ..., r_N)}\Phi(r, r_2, \dots, r_N)\mathrm{d}r_2...\mathrm{d}r_N, \tag{4.2.5}$$

$$(S^*v)(r_1, .., r_N) = \sum_{i=1}^{N} v(r_i)\Psi_0(r_1, ..., r_N). \tag{4.2.6}$$

Thus from Definition 4.2.1, the fact that $e^{itH}\Psi_0 = e^{it\mathcal{E}_0}\Psi_0$, and the (anti-)symmetry of $\mathcal{H}_N$, we see that

$$\chi_H(t)g(r) = 2\theta(t)\mathrm{Im}\big\{Se^{it(\mathcal{E}_0-H)}S^*g(r)\big\}.$$

This expression is similar but not equivalent to (4.1.3) in general. However, under the assumption that the Hamiltonian is real (i.e. commutes with complex conjugation) and Ψ_0 is real-valued (or has constant phase), we recover the formula from the introduction:

$$\chi_H(t) = 2\theta(t)S\sin\big(t(\mathcal{E}_0 - H)\big)S^*.$$

Remark ($\mathbb{C}$-linear extension)**.** *We remark that χ_H is in fact a $\mathbb{R}$-linear operator acting on $\mathbb{R}$-valued functions. However, it is useful to extend it to a $\mathbb{C}$-linear operator acting on $\mathbb{C}$-valued functions in the obvious way,*

$$\chi_H(f + ig) = \chi_H f + i\chi_H g, \quad \textit{for real-valued } f \textit{ and } g. \tag{4.2.7}$$

Since this is the unique way to extend it, there is no harm in doing so. Also, note that if F is another $\mathbb{R}$-linear operator, then first composing the $\mathbb{C}$-extensions of $\chi_H(t)$ and F and later restricting to $\mathbb{R}$ yields the composition of the original $\mathbb{R}$-linear operators. Thus solving the Dyson equation for the $\mathbb{C}$-extensions and restricting to $\mathbb{R}$ afterwards yields the unique solution in the space of $\mathbb{R}$-linear operator-valued functions.

Next, we show that χ_H has more regularity than simply mapping L^∞ to L^1.

Proposition 4.2.2 (Regularity of χ_H)**.** *The operators $S : \mathcal{H}_N \to L^2_{1/\rho_0}$ and $S^* : L^2_{\rho_0} \to \mathcal{H}_N$ are bounded. In particular, $\{\chi_H(t)\}_{t\in\mathbb{R}}$ is a strongly continuous and uniformly bounded family of operators in $\mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})$.*

Proof. Let $\phi \in \mathcal{H}_N$, then using that $\rho_0(r) = N\int_{\mathbb{R}^{3N-1}} |\Psi_0(r, r_2, .., r_N)|^2\mathrm{d}r_2...\mathrm{d}r_N$,

$$\rho_0(r)^{-1}|S\phi(r)|^2 = \rho_0(r)^{-1}\left|N\int_{\mathbb{R}^{3N-3}} \overline{\Psi_0}(r, r_2, ..., r_N)\Phi(r, r_2, ..., r_N)\mathrm{d}r_2...\mathrm{d}r_N\right|^2 \leqslant \rho_\Psi(r).$$

As $\rho_\Psi(r) \in L^1(\mathbb{R}^3)$, we have $S \in \mathcal{B}(\mathcal{H}_N, L^2_{1/\rho_0})$. Similarly, by the (anti-)symmetry of Ψ_0 and Cauchy-Schwarz,

$$\|S^* f\|^2_{\mathcal{H}_N} = \int_{\mathbb{R}^{3N}} \left| \sum_{i=1}^N f(r_i) \right|^2 |\Psi_0(r_1, ..., r_N)|^2 \mathrm{d}r_1 ... \mathrm{d}r_N \leqslant N \int \sum_{i=1}^N |f(r_i)|^2 |\Psi_0|^2 = N \|f\|^2_{L^2_{\rho_0}}.$$

The strong continuity and uniform boundedness follow from the fact that $\theta(t) \sin(t(\mathcal{E}_0 - H))$ is strongly continuous and uniformly bounded in $\mathcal{B}(\mathcal{H}_N)$. □

We have now shown that $\chi_H(t) \in \mathcal{B}(E^*, E)$ for the spaces $E = L^2_{1/\rho_0}$ and $E = L^1(\mathbb{R}^3)$. Moreover, for bounded ρ_0 we could also take $E = L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$[3]. In this case we have (from Hölder's inequality) the inclusions

$$L^2_{1/\rho_0} \subset L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3) \subset L^1(\mathbb{R}^3).$$

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

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 $\chi_H(t) \in \mathcal{B}(E, E^*)$ as long as we can show that $S : \mathcal{H}_N \to E$ is bounded. Thus a reasonable approach is to look for a minimal subspace E for which $S : \mathcal{H}_N \to E$ is bounded. As we show next, $E = L^2_{1/\rho_0}$ is in fact minimal among a general class of function spaces .

Proposition 4.2.3 (Minimality of L^2_{1/ρ_0})**.** *Let E be a Banach space of (Lebesgue) measurable functions such that, for any $0 \leqslant g \leqslant f$ with $f \in E$, we have $g \in E$ and $\|g\|_E \leqslant \|f\|_E$. Then if $S : \mathcal{H}_N \to E$ is bounded and $E \subset L^2_{1/\rho_0}$, we have $E = L^2_{1/\rho_0}$.*

Proof. First, observe that by the assumptions on E we have $g \in E$ for any $|g| \in E$. Second, note that by duality, $L^2_{\rho_0} \subset E^*$ and $SS^* : E^* \to E$ is bounded. Thus for any $g \in L^2_{1/\rho_0}$, we have $|g|/\rho_0 \in L^2_{\rho_0}$ and

$$SS^*|g|/\rho_0 = |g(r)| + N(N-1) \int_{\mathbb{R}^3} |g(r_2)| \frac{|\Psi_0(r, r_2, ..., r_N)|^2}{\rho_0(r)} \mathrm{d}r_2 ... \mathrm{d}r_N \geqslant |g(r)|$$

But since $SS^*|g|/\rho_0 \in E$, from the assumption on E we conclude that $g \in E$. □

In particular, the space L^2_{1/ρ_0} is minimal among the class of sums, intersections, and interpolations of weighted spaces of the form $L^p(|w(r)|\mathrm{d}r)$ for any p and measurable weight function w.

Remark (Reduced weighted spaces)**.** *Note that $\chi_H(t)1 = 0$ for the constant function $1 \in L^2_{\rho_0}$. Consequently, the operators S and S^* can be replaced by the operators $B = P_{\Psi_0^\perp} S$ and $B^* = S^* P_{\Psi_0^\perp}$, and the spaces $L^2_{\rho_0}$ and L^2_{1/ρ_0} can be reduced to the quotient spaces*

[3] $E = L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$ is in fact the setting used in [25].

of functions up to an additive constant and the annihilator of the constant function 1*, respectively. In other words, we can replace* $S, S^*, L^2_{\rho_0}$ *and* L^2_{1/ρ_0} *respectively by*

$$B\Phi(r) = S\Phi(r) - \langle \Psi_0, \Phi\rangle \rho_0(r), \quad B^* f(r_1, ..., r_N) = S^* f(r_1, ..., r_N) - \langle \rho_0, f\rangle \Psi_0(r_1, ..., r_N),$$

$$L^2_{\rho_0}/1 = \{[f] : f \sim g \text{ if } f(r) - g(r) = c\}, \quad \text{and} \quad \{1\}^\perp = \left\{ f \in L^2_{1/\rho_0} : \int_{\mathbb{R}^3} f(r)\mathrm{d}r = 0 \right\}.$$

This leads to a more precise description of the spaces of multiplicative potential perturbations and density variations. For simplicity, we keep working with $S, S^*, L^2_{\rho_0}$ *and* L^2_{1/ρ_0}*.*

4.2.3 Fourier transform and poles

We now turn to the representation of $\widehat{\chi_H}$ in terms of the resolvent of H. This representation is called the Lehmann representation in the physics literature[4] . In the sequel, we present the definition of a meromorphic operator-valued function and show that the poles of $\widehat{\chi_H}$ are located at the one-body excitations of H. We start with the Fourier transform.

Proposition 4.2.4 (Fourier transform of χ_H)**.** *Let* χ_H *be the DDRF of some* H *satisfying Assumption 4.1.1. Then, the Fourier transform of* χ_H *is given by*

$$\widehat{\chi_H}(z) = S(1 - P^H_{\mathcal{E}_0})\big((\mathcal{E}_0 - z - H)^{-1} + (\mathcal{E}_0 + z - H)^{-1}\big)(1 - P^H_{\mathcal{E}_0})S^*, \quad \text{for } \mathrm{Im}(z) > 0,$$

where the operators S *and* S^* *are defined in (4.2.5),(4.2.6),* $\mathcal{E}_0$ *is the ground state energy of* H*, and* $P^H_{\mathcal{E}_0}$ *is the orthogonal projection onto the space spanned by* Ψ_0*. In particular, the Fourier transform of* χ_H *along the real line is the tempered distribution given by*

$$\widehat{\chi_H}(\omega) = \lim_{\eta \to 0^+} S(1 - P^H_{\mathcal{E}_0})\big((\mathcal{E}_0 - \omega - i\eta - H)^{-1} + (\mathcal{E}_0 + \omega + i\eta - H)^{-1}\big)(1 - P^H_{\mathcal{E}_0})S^*,$$

where the limit is taken in the distributional sense.

Proof. Since H is self-adjoint, we can apply the spectral theorem to find

$$\begin{aligned}
\int_0^\infty \chi_H(t) e^{i(\omega + i\eta)t}\mathrm{d}t &= S\int_0^\infty \int_{\mathcal{E}_0}^\infty 2\sin\big(t(\mathcal{E}_0 - \lambda)\big) e^{i(\omega+i\eta)t}\mathrm{d}E_\lambda \mathrm{d}t S^* \\
&= S\int_{\mathcal{E}_0}^\infty \frac{1}{\mathcal{E}_0 - \omega - i\eta - \lambda} + \frac{1}{\mathcal{E}_0 + \omega + i\eta - \lambda}\mathrm{d}E_\lambda S^* \\
&= S(1 - P^H_{\mathcal{E}_0})\big((\mathcal{E}_0 - z - H)^{-1} + (\mathcal{E}_0 + z - H)^{-1}\big)(1 - P^H_{\mathcal{E}_0})S^*,
\end{aligned}$$

where $z = \omega + i\eta$, E_λ is the spectral projection-valued measure of H, and we have used that $(\mathcal{E}_0 + \omega + i\eta - H)^{-1}\Psi_0 + (\mathcal{E}_0 - \omega - i\eta - H)^{-1}\Psi_0 = 0$. That the limit $\eta \to 0^+$ is a tempered distribution follows from the fact that $\chi_H(t)$ is causal and uniformly bounded in time. □

[4] The classical Lehmann representation assumes that H admits an orthonormal basis of eigenfunctions. On the other hand, the formula presented below accounts for the essential spectrum of H, which is not empty in many physically relevant situations.

Remark. *Explicit expressions for the distributional limit defined above can be obtained in terms of operator-valued versions of the principal value and delta distributions (see [15] for a rigorous account). As they will play no role in our analysis, we refrain from stating them here.*

We can now characterize the poles of $\widehat{\chi_H}$ according to the following definition of a meromorphic operator-valued function.

Definition 4.2.2 (Meromorphic operator-valued function)**.** *Let $\mathcal{D} \subset \mathbb{C}$ be open and E, F be Banach spaces. Then we say that $K : \mathcal{D} \to \mathcal{B}(E, F)$ is a meromorphic function if for any $z_0 \in \mathcal{D}$, there exist finitely many operators $\{K_{-j}\}_{j \leqslant k} \subset \mathcal{B}(E, F)$ such that*

$$K(z) = K_0(z) + \sum_{j=1}^{k} (z - z_0)^{-j} K_{-j},$$

where $K_0(z)$ is holomorphic near z_0. If $K_{-j} \neq 0$ for some $j \geqslant 1$, then we say that z_0 is a pole of K. If in addition $K_{-j} = 0$ for all $j \geqslant 2$, we say that z_0 is a simple pole and define its rank as

$$\operatorname{rank}_{z_0}(K) = \operatorname{rank} K_{-1}.$$

Proposition 4.2.5 (Poles of $\widehat{\chi_H}$)**.** *Let χ_H be the DDRF of some Hamiltonian H satisfying Assumption 4.1.1 and*

$$\mathcal{D}_\Omega := \{z \in \mathbb{C} : \operatorname{Im}(z) \neq 0 \text{ or } |\operatorname{Re}(z)| < \Omega\} \subset \mathbb{C}. \tag{4.2.8}$$

Then $\widehat{\chi_H}$ extends to a meromorphic family of operators on $\mathcal{D}_\Omega$ with simple poles only. Moreover, the set of non-negative poles of $\widehat{\chi_H}$ is

$$\mathcal{P}(\widehat{\chi_H}) = \{\omega \in (0, \infty) : \mathcal{E}_0 + \omega \in \sigma_d(H) \text{ and } SP^H_{\mathcal{E}_0+\omega} \neq 0\}, \tag{4.2.9}$$

and the rank of any pole $\omega \in \mathcal{P}(\widehat{\chi_H})$ is given by

$$\operatorname{rank}_\omega(\widehat{\chi_H}) = \operatorname{rank} SP^H_{\mathcal{E}_0+|\omega|}, \tag{4.2.10}$$

where $P^H_{\mathcal{E}_0+\omega}$ is the orthogonal projection on the eigenspace $\ker(H - \mathcal{E}_0 - \omega)$. (Note that the set of negative poles is given by $-\mathcal{P}(\widehat{\chi_H})$ since $\widehat{\chi_H}(-z) = \widehat{\chi_H}(z)$.)

Proof. For $\operatorname{Im}(z) > 0$, from Proposition 4.2.4 and the spectral decomposition of H, we have

$$\begin{aligned}\widehat{\chi_H}(z) = \sum_{\lambda \in \sigma_d(H - \mathcal{E}_0) \setminus \{0\}} SP^H_{\mathcal{E}_0+\lambda} \Big(\frac{1}{-\lambda - z} + \frac{1}{z - \lambda} \Big) P^H_{\mathcal{E}_0+\lambda} S^* \\ + S \int_{\sigma_{\mathrm{ess}}(H)} \frac{1}{\mathcal{E}_0 - z - \lambda} + \frac{1}{\mathcal{E}_0 + z - \lambda} \, \mathrm{d}E_\lambda S^*,\end{aligned} \tag{4.2.11}$$

where $\sigma_d(H)$ denotes the discrete spectrum of H. So by the spectral gap assumption on H, we can extend $\widehat{\chi_H}(z)$ analytically to $\mathcal{D}_\Omega$. Moreover, from the spectral decomposition above we directly see that the set of poles in $\mathcal{D}_\Omega$ is contained in $\mathcal{P}(\widehat{\chi_H})$.

For the statement on the rank of the poles, note that

$$\langle f, SP^H_{\mathcal{E}_0+\omega}S^*f\rangle_{L^2(\mathbb{R}^3)} = \langle P^H_{\mathcal{E}_0+\omega}S^*f, P^H_{\mathcal{E}_0+\omega}S^*f\rangle_{L^2(\mathbb{R}^{3N})} = \|P^H_{\mathcal{E}_0+\omega}S^*f\|^2_{\mathcal{H}_N},$$

for any $f \in L^2_{1/\rho_0}$, and

$$\langle \Psi, P^H_{\mathcal{E}_0+\omega}S^*SP^H_{\mathcal{E}_0+\omega}\Psi\rangle_{\mathcal{H}_N} = \|SP^H_{\mathcal{E}_0+\omega}\Psi\|^2_{L^2(\mathbb{R}^3)},$$

for any $\Psi \in \mathcal{H}_N$. Thus $\mathrm{rank}_\omega(\widehat{\chi_H}) = \mathrm{rank}(SP^H_{\mathcal{E}_0+\omega}S^*) = \mathrm{rank}(SP^H_{\mathcal{E}_0+\omega})$. □

Remark (Regularity of $\widehat{\chi_H}$ past the ionization threshold)**.** *If H has compact resolvent (for instance, a Schrödinger operator with a trapping potential), then $\mathcal{D}_\Omega = \mathbb{C}$ and $\mathcal{P}(\widehat{\chi_H})$ is the whole set of singular points of (the meromorphic extension of) $\widehat{\chi_H}$. However, for typical Hamiltonians in electronic structure theory (such as the atomic or molecular Hamiltonians), the spectrum is divided in a discrete and a continuous part [100]. In some special cases, the regularity of $\widehat{\chi_H}$ along the continuous spectrum can be studied (see [33] for a related question) via the celebrated limiting absorption principle [2, 3, 34, 113].*

4.3 Well-posedness of the Dyson equation

We now turn to the proof of Theorem 4.1.1. To shorten the notation, for any $T > 0$ and $\chi \in C_s\big([0,T]; \mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})\big)$, we define

$$\|\chi\|_T := \operatorname*{ess\,sup}_{t\in[0,T]} \|\chi(t)\|_{L^2_{\rho_0}, L^2_{1/\rho_0}}. \tag{4.3.1}$$

Proof of Theorem 4.1.1. We start with the existence and uniqueness and then prove the bijection property. First, we define the convolution map

$$\mathcal{C}(\chi_0, \chi)(t) = \int_0^t \chi_0(t-s)F\chi(s)\mathrm{d}s.$$

Since $F \in \mathcal{B}(L^2_{1/\rho_0}, L^2_{\rho_0})$ we can use dominated convergence to show that $t \mapsto \mathcal{C}(\chi_0,\chi)(t)$ is strongly continuous. Moreover, we find

$$\|\mathcal{C}(\chi_0,\chi)\|_T \lesssim T\|\chi_0\|_T\|\chi\|_T. \tag{4.3.2}$$

Thus for T small enough, the map $\mathcal{C}(\cdot,\chi_0) : C_s\big([0,T]; \mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})\big) \to C_s\big([0,T]; \mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})\big)$ is a contraction. Therefore, the map $\cdot \to \chi_0 + \mathcal{C}(\chi_0,\cdot)$ has an unique fixed point $\chi = \chi_0 + \mathcal{C}(\chi_0,\chi)$ by the Banach fixed-point theorem. The solution χ defined for $t \leqslant T$ can now be uniquely extended to any interval $[0,K]$, and consequently to $\mathbb{R}_+$, by a classical

continuity and extension argument. To complete the proof, we need to show that the solution map

$$\begin{aligned}\mathcal{S}_F : C_s\big(\mathbb{R}_+; \mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})\big) &\to C_s\big(\mathbb{R}_+; \mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})\big)\\ \chi_0 &\mapsto \chi_F \in \ker\{\chi_0 + \mathcal{C}(\chi_0, \cdot) - \cdot\}.\end{aligned}$$

is bijective in $C_s\big([0,\infty]; \mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})\big)$. For this, we can exchange the roles of χ and χ_0 and repeat the same arguments to show the existence and uniqueness of the solution χ_0 to the equation $\chi_0 = \chi - \mathcal{C}(\chi_0, \chi)$ for fixed χ. In particular, $\chi = \mathcal{S}_F(\chi_0)$ is the unique solution of the Dyson equation, which implies that $\mathcal{S}_F$ is surjective. Similarly, the uniqueness of the solution χ_0 implies that $\mathcal{S}_F$ is injective, which completes the proof. □

4.4 The spectrum of operator-valued functions around poles

In this section, we derive asymptotic formulas for the inverse of an operator-valued function, $z \mapsto D(z)$, as z approaches one of its poles. We then use this asymptotic formula to study the spectrum of $D(z)$ close to its poles. The theory developed here in a general setting will be applied to the operator-valued function $\widehat{\chi_H} F$ in Section 4.5.

For the discussion to follow, it is convenient to introduce the concept of invertibility with respect to a projection.

Definition 4.4.1 (Inverse with respect to a projection)**.** *Let $P \in \mathcal{B}(\mathcal{H})$ be a projection on a Hilbert space $\mathcal{H}$, i.e., $P^2 = P$. Then we say that an operator $B \in \mathcal{B}(\mathcal{H})$ is invertible with respect to P if $PBP = B$ and there exists an operator $B^{-1} \in \mathcal{B}(\mathcal{H})$ such that*

$$PB^{-1}P = B^{-1} \quad \text{and} \quad BB^{-1} = B^{-1}B = P.$$

Moreover, for a closed subspace $V \subset \mathcal{H}$, we say that $B \in \mathcal{B}(\mathcal{H})$ is invertible on V provided that B is invertible with respect to the orthogonal projection on V, denoted henceforth by P_V.

Remark. *In block notation on $\mathcal{H} = \operatorname{ran} P \oplus \ker P$, the definition above is equivalent to saying that*

$$B = \begin{pmatrix} \tilde{B} & 0 \\ 0 & 0 \end{pmatrix} \quad \text{and } B^{-1} = \begin{pmatrix} \tilde{B}^{-1} & 0 \\ 0 & 0 \end{pmatrix},$$

where $\tilde{B} \in \mathcal{B}(\operatorname{ran} P)$ is invertible.

4.4.1 Spectral theory of bounded operators

We start by recalling two well-known results on the spectral theory of bounded operators. For convenience of the reader, we briefly sketch the proof of these results here. Detailed versions of the proofs below can be found in [46, Chapter 1].

The first classical result we recall is the continuity of the spectra with respect to the operator norm.

Proposition 4.4.1 (Continuity of spectra)**.** *Let $A \in \mathcal{B}(E)$ where E is a Banach space and $\mu \in \rho(A)$ (where $\rho(A)$ denotes the resolvent set of A). Then for any B with $\|B\| < \|(\mu - A)^{-1}\|^{-1}$ we have $\mu \in \rho(A + B)$. In particular, if $A : B_\delta(0) \subset \mathbb{C} \to \mathcal{B}(E)$ is continuous and $W \subset \rho\big(A(0)\big)$ is compact, then $W \subset \rho\big(A(z)\big)$ for any z close enough to 0.*

Proof. For $\mu \in \rho(A)$, we have

$$(\mu - A)^{-1}(\mu - A - B) = I - (\mu - A)^{-1}B \quad \text{and} \quad (\mu - A - B)(\mu - A)^{-1} = I - B(\mu - A)^{-1}$$

So for $\|B\| < \|(\mu - A)^{-1}\|^{-1}$, the operators above are of the form $I - K$ with $\|K\| < 1$. The inverse is then given by the Neumann series, $(I - K)^{-1} = \sum_{k \geqslant 0} K^n$. The second statement now follows from a continuity plus compactness argument. □

The second classical result we need is the decomposition of isolated parts of the spectra via the Riesz projections and a countour formula for the resolvent with respect to these projections.

Proposition 4.4.2 (Riesz projection and separation of spectra)**.** *Let $\gamma \subset \rho(A) \subset \mathbb{C}$ be a closed smooth curve separating the spectrum of A. Then, the operator*

$$P = \frac{1}{2\pi i} \oint_\gamma (\mu - A)^{-1} d\mu$$

is a projection commuting with A. Moreover, for $\mu_0 \notin \gamma$, the operator

$$S(\mu_0) = \frac{1}{2\pi i} \oint_\gamma \frac{1}{\mu - \mu_0} (\mu - A)^{-1} \mathrm{d}\mu. \tag{4.4.1}$$

satisfies

$$S(\mu_0) = \begin{cases} \big((1 - P)(\mu_0 - A)(1 - P)\big)^{-1} & \text{for } \mu_0 \text{ inside } \gamma, \\ -\big(P(\mu_0 - A)P\big)^{-1} & \text{for } \mu_0 \text{ outside } \gamma, \end{cases} \tag{4.4.2}$$

where the inverses are with respect to the projections $1 - P$ and P. In particular, the spectrum of $A\big|_{\mathrm{ran}\, P} \in \mathcal{B}(\mathrm{ran}\, P)$ and $A\big|_{\ker P} \in \mathcal{B}(\ker P)$ is given by the spectrum of A inside and outside of γ, respectively.

Proof. That the operator P is well-defined and bounded is clear since $\gamma \subset \rho(A)$ and $\mu \mapsto (\mu - A)^{-1}$ is continuous in μ. To see that P is a projection, note that one can choose a curve γ_1 inside γ such that all points lying between γ_1 and γ are in the resolvent of A. Thus from a standard argument of holomorphic function theory,

$$P = \frac{1}{2\pi i} \oint_{\gamma_1} (\lambda - A)^{-1} \mathrm{d}\lambda.$$

Hence multiplying the above integral by P (defined as a contour integral on γ), using the resolvent identity $(\mu - A)^{-1}(\lambda - A)^{-1} = (\mu - \lambda)^{-1}\big((\lambda - A)^{-1} - (\mu - A)^{-1}$, and using the Cauchy integral formula for holomorphic functions, one can show that $P^2 = P$.

Next, since $S(\mu_0)$ commutes with A, formula (4.4.2) follows from the identities

$$(\mu_0 - A)S(\mu_0) = \frac{1}{2\pi i}\oint_\gamma \frac{1}{\mu - \mu_0} - \frac{1}{2\pi i}\oint_\gamma (\mu - A)^{-1}\mathrm{d}\mu = \begin{cases} 1 - P, & \text{for } \mu_0 \text{ inside } \gamma, \\ -P, & \text{for } \mu_0 \text{ outside } \gamma, \end{cases}$$

and

$$S(\mu_0)P = \frac{1}{2\pi i}\oint_\gamma \oint_{\gamma_1} \frac{(\mu - A)^{-1} - (\lambda - A)^{-1}}{(\mu - \mu_0)(\lambda - \mu)}\mathrm{d}\lambda\mathrm{d}\mu = \begin{cases} 0, & \text{for } \mu_0 \text{ inside } \gamma, \\ S(\mu_0), & \text{for } \mu_0 \text{ outside } \gamma. \end{cases}$$

Finally, the last statement follows from two observations. First, the existence of the inverses in (4.4.2) implies that $\sigma(A\big|_{\mathrm{ran}\, P})$ lies inside γ and $\sigma(A\big|_{\ker P})$ lies outside γ. Second, from the decomposition

$$A = \begin{pmatrix} A\big|_{\mathrm{ran}\, P} & 0 \\ 0 & A\big|_{\ker P} \end{pmatrix}$$

with respect to $\mathcal{H} = \mathrm{ran}\, P \oplus \ker P$, we have $\sigma(A) = \sigma(A\big|_{\ker P}) \cup \sigma(A\big|_{\mathrm{ran}\, P})$. □

4.4.2 Inverse around a pole

We now consider operator-valued functions of the form $D(z) = A + z^{-1}B + C(z)$, for $z \in \mathbb{C}$ close to 0. To study the spectra of $D(z)$ as z goes to 0, our main tool is the following lemma.

Lemma 4.4.1 (Inverse of operator-valued function around a pole)**.** *Let $A, B, C, P \in \mathcal{B}(\mathcal{H})$ be such that (i) P is a projection, (ii) B is invertible with respect to P, (iii) A is invertible with respect to $P^\perp$, and (iv) $P^\perp C P^\perp = 0$. Then, for z small enough, the operator $D(z) = A + C + z^{-1}B$ is invertible and*

$$D(z)^{-1} = A^{-1} + z(1 - A^{-1}C)B^{-1}\sum_{k=0}^{\infty} z^n\big(C(A^{-1}C - 1)B^{-1}\big)^n(1 - CA^{-1}) \tag{4.4.3}$$

where A^{-1} is the inverse with respect to $P^\perp$.

Proof. The proof is based on the Schur complement [128] for the block representation of D on $\mathcal{H} = \ker P \oplus \mathrm{ran}\, P$. Precisely, let

$$D(z) = \begin{pmatrix} \mathcal{A} & \mathcal{B} \\ \mathcal{C} & \mathcal{D} \end{pmatrix} = \begin{pmatrix} A & (1 - P)CP \\ PC(1 - P) & z^{-1}B + PCP \end{pmatrix},$$

then the Schur complement of the block $\mathcal{A}$ is

$$\Delta := \mathcal{D} - \mathcal{C}\mathcal{A}^{-1}\mathcal{B} = z^{-1}B + PCP - PCA^{-1}CP.$$

Thus for small z, the inverse of Δ is given by the Neumann series

$$\Delta^{-1} = zB^{-1}\sum_{n=0}^{\infty} z^n\big(C(A^{-1}C-1)B^{-1}\big)^n.$$

But since $\mathcal{A} = A$ is invertible on $\mathcal{B}(\ker P)$, the result follows from the formula

$$D(z)^{-1} = \begin{pmatrix} \mathcal{A}^{-1} + \mathcal{A}^{-1}\mathcal{B}\Delta^{-1}\mathcal{C}\mathcal{A}^{-1} & -\mathcal{A}^{-1}\mathcal{B}\Delta^{-1} \\ -\Delta^{-1}\mathcal{C}\mathcal{A}^{-1} & \Delta^{-1} \end{pmatrix} = \mathcal{A}^{-1} + (1-\mathcal{A}^{-1}\mathcal{B})\Delta^{-1}(1-\mathcal{C}\mathcal{A}^{-1}).$$

□

As an immediate corollary of the lemma above, we find an asymptotic expansion for the resolvent of $D(z)$ in terms of C, B^{-1}, and the resolvent of A.

Corollary 4.4.1 (Resolvent expansion)**.** *Let $A, B, C, P \in \mathcal{B}(\mathcal{H})$ be such that (i) P is a projection, (ii) B is invertible with respect to P, (iii) $P^\perp A P^\perp = A$, and (iv) $P^\perp C P^\perp = 0$. Then for any compact set $W \subset \rho(A)$, we have $W \subset \rho\big(D(z) = A + z^{-1}B + C\big)$ for z small. Moreover, the resolvent $R_{D(z)}(\mu) = (\mu - D(z))^{-1}$ satisfies*

$$R_{D(z)}(\mu) = R_A(\mu) - z(1+R_A(\mu)C)B^{-1}\sum_{n=0}^{\infty} z^n\big(\mu B^{-1} - C(1+R_A(\mu)C)B^{-1}\big)^n(1+CR_A(\mu))$$

where $R_A(\mu) = \big(P^\perp(\mu - A)P^\perp\big)^{-1}$ is the resolvent with respect to $P^\perp$.

Proof. Just apply Lemma 4.4.1 to the operator $\mu - D(z) = (\mu P^\perp - A) + z^{-1}(-B) + (\mu P - C)$. □

With the above expansion of the resolvent of $C(z)$, one can compute functions of $C(z)$ in terms of B^{-1} and functions of A. For the applications in the next section however, the operator A will not be fixed but vary holomorphic with z. So in the next lemma, we compute the asymptotic expansion of $f(A(z) + z^{-1}B + C(z))$ when $A(z)$ and $C(z)$ are holomorphic around 0 and f is holomorphic around some isolated point μ_0 in the spectrum of $A(0)$. For simplicity, we state the formula only to second order, which is enough for our applications.

Lemma 4.4.2 (Convergence of spectra)**.** *Let P, A, B, C satisfy the assumption of Corollary 4.4.1. Suppose in addition that $\mu_0 \in \sigma(A)$ is an isolated point in the spectrum of A and $A(z)$ and $C(z)$ are holomorphic functions satisfying $A(0) = A$, $P^\perp A(z) P^\perp = A(z)$, and $C(0) = C$. Then, for any f holomorphic around μ_0 and z small, there exists $\delta > 0$ such that $\partial B_\delta(\mu_0)$ is in the resolvent set of $D(z) = A(z) + z^{-1}B + C(z)$ and*

$$f\big(D(z)\big) = \frac{1}{2\pi i}\oint_{\partial_\delta B_\delta(\mu_0)} f(\mu)\big(\mu - D(z)\big)^{-1}\mathrm{d}\mu = f(A) + \mathcal{O}(|z|), \tag{4.4.4}$$

where $f(A) = (2\pi i)^{-1} \oint_{\partial B_\delta(\mu_0)} f(\mu)(\mu P^\perp - A)^{-1} \mathrm{d}\mu$ *and* $(\mu P^\perp - A)^{-1}$ *is the inverse with respect to* $P^\perp$*. Furthermore, if the Riesz projection* $Q = 1(A)$ *satisfies* $AQ = \mu_0 Q$*, then*

$$f\big(D(z)\big) = f(\mu_0)Q + zf(\mu_0)\Big(Q\big(\dot{A}(0) - CB^{-1}C\big)R + R\big(\dot{A}(0) - CB^{-1}C\big)Q - QCB^{-1} - B^{-1}CQ\Big) + z\dot{f}(\mu_0)Q\big(\dot{A}(0) - CB^{-1}C\big)Q + \mathcal{O}(|z|^2), \tag{4.4.5}$$

where $R := \big((\mu - A)(1-Q)\big)^{-1}$ *is the inverse with respect to* $1 - Q$*.*

Proof. By Corollary 4.4.1, we can find $\delta > 0$ small such that

$$R_{D(z)}(\mu) = R_{A(z)}(\mu) - z\big(1 + R_{A(z)}(\mu)C(z)\big)B^{-1}\big(1 + C(z)R_{A(z)}(\mu)\big) + \mathcal{O}(|z|^2),$$

for any $\mu \in \partial B_\delta(\mu_0)$ and z small. We can now use the formula

$$\partial_z R_{A(z)}(\mu) = R_{A(z)}(\mu)\dot{A}(z)R_{A(z)}(\mu)$$

to obtain

$$R_{D(z)}(\mu) = R_A(\mu) + zR_A(\mu)\dot{A}(0)R_A(\mu) - z\big(1 + R_A(\mu)C\big)B^{-1}\big(1 + CR_A(\mu)\big) + \mathcal{O}(|z|^2). \tag{4.4.6}$$

The leading order of the above expansion yields (4.4.4). For the next formula, note that since $AQ = \mu_0 Q$, we have the expansion

$$R_A(\mu) = (\mu - \mu_0)^{-1}Q + \sum_{k=0}^{n-1}(\mu - \mu_0)^k R^{k+1} + \mathcal{O}\big((\mu - \mu_0)^n\big), \tag{4.4.7}$$

where $R = \big((\mu_0 P^\perp - A)(P^\perp - Q)\big)^{-1}$ is the inverse with respect to $P^\perp - Q$ (which is a projection since $\operatorname{ran} Q \subset \ker P$), and the remainder is holomorphic for μ close to μ_0. The result now follows by plugging (4.4.7) into (4.4.6), integrating on $\oint_{\partial B_\delta(\mu_0)}$, and using Cauchy's integral formula. □

4.5 The operator $\widehat{\chi_H}F$

In this section we want to understand how the positive spectra of $\widehat{\chi_H}(\omega)F$ behaves as ω moves along the interval $(-\Omega, \Omega)$, and to construct the inverse $(1 - \widehat{\chi_H}F)^{-1}$ around the poles of $\widehat{\chi_H}$. To achieve this, the key idea here is to define an abstract auxiliary Hilbert space, $\mathcal{H}_F$, on which the operator $\widehat{\chi_H}(z)F$ becomes self-adjoint for real values of z. This allow us to study the spectral properties of $\widehat{\chi_H}F$ on L^2_{1/ρ_0} via the spectral theory of self-adjoint operators on Hilbert spaces.

The plan for this section is the following. First, we introduce the Hilbert space $\mathcal{H}_F$ and prove a few useful lemmas regarding the composition BF for general $B \in \mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})$.

Then, we use the representation of $\widehat{\chi_H}$ from Proposition 4.2.4 and the positivity assumption on F to prove a series of lemmas concerning the positive spectra of $\widehat{\chi_H}(\omega)F$ for $\omega \in (-\Omega, \Omega)$. Once the behaviour of the positive spectra of $\widehat{\chi_H}F$ is well-understood, we turn to some asymptotic formulas for the inverse $(1-\widehat{\chi_H}(z)F)^{-1}$ when z approaches either a pole of $\widehat{\chi_H}$ or a zero of $1-\widehat{\chi_H}F$. The latter set will be shown to be the poles of $\widehat{\chi_F}$ in Section 4.6.

4.5.1 The Hilbert space $\mathcal{H}_F$.

Let $F \in \mathcal{B}(L^2_{1/\rho_0}, L^2_{\rho_0})$ be an operator satisfying the positivity assumption

$$\langle f, f\rangle_F = \langle f, Ff\rangle_{L^2} > 0, \qquad \text{for any } f \in L^2_{\frac{1}{\rho_0}}. \tag{4.5.1}$$

Then, F is symmetric (by the polarization identity) and $\langle \cdot, \cdot \rangle_F$ defines an inner-product on L^2_{1/ρ_0}. Therefore, we can define the Hilbert space $\mathcal{H}_F$ as the completion of L^2_{1/ρ_0} with respect to this inner-product, i.e.,

$$\mathcal{H}_F = \overline{L^2_{1/\rho_0}(\mathbb{R}^3)}^{\|\cdot\|_F}, \quad \text{where} \quad \|f\|_F^2 = \langle f, Ff\rangle, \qquad \text{for any } f \in L^2_{1/\rho_0}. \tag{4.5.2}$$

Even though $\mathcal{H}_F$ is an abstract space and not necessarily a function space, we will canonically identify L^2_{1/ρ_0} with a dense subspace of $\mathcal{H}_F$.

The first result we shall need is that the operator F can be uniquely extended to an operator in $\mathcal{B}(\mathcal{H}_F, L^2_{\rho_0})$.

Proposition 4.5.1 (Extension of F to $\mathcal{H}_F$)**.** *There exists a unique extension of F to $\mathcal{B}(\mathcal{H}_F, L^2_{\rho_0})$ and it satisfies*

$$\|F\|_{\mathcal{H}_F, L^2_{\rho_0}} \leqslant \sqrt{\|F\|_{L^2_{1/\rho_0}, L^2_{\rho_0}}} \tag{4.5.3}$$

Proof. Since $\|f\|_{L^2_{\rho_0}} = \sup_{\substack{g \in L^2_{1/\rho_0} \\ \|g\|_{L^2_{1/\rho_0}}=1}} \langle f, g\rangle_{L^2(\mathbb{R}^3)}$, we find that

$$\begin{aligned}\|Ff\|_{L^2_{\rho_0}} &= \sup_{\substack{g \in L^2_{1/\rho_0} \\ \|g\|_{L^2_{1/\rho_0}}=1}} \langle f, Fg\rangle = \sup_{\substack{g \in L^2_{1/\rho_0} \\ \|g\|_{L^2_{1/\rho_0}}=1}} \langle f, g\rangle_F \leqslant \sup_{\substack{g \in L^2_{1/\rho_0} \\ \|g\|_{L^2_{1/\rho_0}}=1}} \sqrt{\langle f, Ff\rangle\langle g, Fg\rangle} \\ &\leqslant \|f\|_F \sqrt{\|F\|_{L^2_{\rho_0}, L^2_{1/\rho_0}}}.\end{aligned}$$

The result then follows since L^2_{1/ρ_0} is dense in $\mathcal{H}_F$. □

The next result justifies the definition of $\mathcal{H}_F$. It will be used to show that $\widehat{\chi_H}(z)F$ is a meromorphic family of operators on $\mathcal{H}_F$ whose restriction to $\mathbb{R}$ is self-adjoint.

Proposition 4.5.2 (Adjoint on $\mathcal{H}_F$)**.** *Let $B \in \mathcal{B}(L^2_{1/\rho_0}, L^2_{\rho_0})$. Then BF has a unique extension to an operator in $\mathcal{B}(\mathcal{H}_F)$ and its adjoint on $\mathcal{H}_F$ is given by*

$$(BF)^{*_F} = B^*F,$$

where $B^* \in \mathcal{B}(L^2_{1/\rho_0}, L^2_{\rho_0})$ is the adjoint with respect to the L^2-inner-product.

Proof. Note that

$$\langle f, BFf\rangle_F = \langle f, FBFf\rangle = \langle B^*Ff, Ff\rangle = \langle B^*Ff, f\rangle_F,$$

for any $f \in L^2_{1/\rho_0}$. Hence, by the continuity of F and the density of L^2_{1/ρ_0} on $\mathcal{H}_F$, the result follows. □

As a last result here, we show that for any $B \in \mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})$, the spectrum of the composition BF on $\mathcal{H}_F$ is related to the spectrum on L^2_{1/ρ_0}.

Proposition 4.5.3 (Inverse of $\lambda - BF$)**.** *Let $B \in \mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})$ and $BF \in \mathcal{B}(\mathcal{H}_F)$ be the unique extension to $\mathcal{H}_F$. Then, for any $0 \neq \lambda \in \mathbb{C}$, we have*

$$\ker \lambda - BF \subset L^2_{1/\rho_0}.$$

Moreover, if $\lambda - BF$ is invertible in $\mathcal{H}_F$, then $\lambda - BF$ is invertible in L^2_{1/ρ_0} and the restriction of the inverse $(\lambda - BF)^{-1}$ is given by the inverse of the restriction.

Proof. As the unique extension BF is given by the composition of B with the unique extension $F \in \mathcal{B}(\mathcal{H}_F, L^2_{\rho_0})$ from Proposition 4.5.1, we have $BFg \in L^2_{1/\rho_0}$ for any $g \in \mathcal{H}_F$. Hence, if $\lambda \neq 0$ and $f \in \ker \lambda - BF$ we have

$$f = \frac{1}{\lambda}\lambda f = \frac{BFf}{\lambda} \in L^2_{1/\rho_0},$$

which shows that $\ker \lambda - BF \subset L^2_{1/\rho_0}$.

For the second statement, note that if $\lambda - BF$ is injective on $\mathcal{H}_F$, then $\lambda - BF$ is injective on L^2_{1/ρ_0}. Similarly, if $\lambda - BF$ is surjective on $\mathcal{H}_F$, then for any $g \in L^2_{1/\rho_0}$ there exists $f \in \mathcal{H}_F$ such that $(\lambda - BF)f = g$. But since $BFf \in L^2_{1/\rho_0}$ for any such f, we see that $\lambda f = g + BFf \in L^2_{1/\rho_0}$. Therefore, $\lambda - BF \in \mathcal{B}(L^2_{1/\rho_0})$ is bijective provided that $\lambda - BF \in \mathcal{B}(\mathcal{H}_F)$ is also bijective. The result now follows from the closed graph theorem. □

4.5.2 Positive spectra

Let us now combine the results about $\mathcal{H}_F$, the results from Section 4.4, and the formula for $\widehat{\chi_H}$ to prove a series of lemma concerning the positive spectra of $\widehat{\chi_H}(z)F$. These lemmas will provide us a fairly complete qualitative description of the positive spectra of $\widehat{\chi_H}(z)F$ as z moves along the real axis. This description is the main step in the proof of Theorem 4.1.4.

To simplify the next statements and proofs, let us introduce (and recall) some notation. First, recall that the set of poles of $\widehat{\chi_H}$ is given by

$$\mathcal{P}(\widehat{\chi_H}) = \{0 < \omega < \Omega : SP^H_{\mathcal{E}_0+\omega} \neq 0\}, \tag{4.5.4}$$

where $P^H_{\mathcal{E}_0+\omega}$ is the orthogonal projection on the eigenspace $\ker H - \mathcal{E}_0 - \omega$, S is our usual operator defined in (4.1.4), and $\Omega = \inf \sigma_{\mathrm{ess}}(H) - \mathcal{E}_0 > 0$ is the ionization threshold of H. We also recall the definition of the finite-dimensional subspaces V_ω and their F-orthogonal complement:

$$V_z := \operatorname{ran} SP^H_{\mathcal{E}_0+z} \subset L^2_{1/\rho_0} \subset \mathcal{H}_F, \quad V_z^\perp := \{f \in \mathcal{H}_F : \langle f, g\rangle_F = 0, \quad \forall g \in V_z\}. \tag{4.5.5}$$

The associated F-orthogonal projections (in $\mathcal{B}(\mathcal{H}_F)$) are denoted by P_{V_z} and $P_{V_z^\perp} = 1 - P_{V_z}$. We then introduce the operators B_ω and the operator-valued function $B_{\mathrm{ess}}(z)$ via the spectral decomposition

$$\widehat{\chi_H}(z)F = \sum_{\omega \in \mathcal{P}(\widehat{\chi_H})} \frac{2\omega}{z^2-\omega^2} \underbrace{SP^H_{\mathcal{E}_0+\omega}S^*F}_{:=B_\omega} + \underbrace{S\left(\int_\Omega \frac{2\lambda}{z^2-\lambda^2} \mathrm{d}P^H_{\mathcal{E}_0+\lambda}\right)S^*F}_{:=B_{\mathrm{ess}}(z)}. \tag{4.5.6}$$

Then, the starting point of our analysis is the observation that the family of operators $\widehat{\chi_H}(z)F$ is self-adjoint for real values of z.

Lemma 4.5.1 (Self-adjointness of $\widehat{\chi_H}(z)F$)**.** *The operator $\widehat{\chi_H}(z)F$ satisfies*

$$(\widehat{\chi_H}(\overline{z})F)^{*_F} = \widehat{\chi_H}(z)F = \widehat{\chi_H}(-z)F, \quad \text{for any } z \in \mathcal{D}_\Omega. \tag{4.5.7}$$

In particular, $\widehat{\chi_H}(z)F$ is self-adjoint for $z \in (-\Omega, \Omega)\backslash \pm \mathcal{P}(\widehat{\chi_H})$.

Proof. From the formula in Proposition 4.2.4, we have

$$\widehat{\chi_H}(\overline{z})^* = \widehat{\chi_H}(z) = \widehat{\chi_H}(-z).$$

Hence the symmetries in (4.5.7) follows from the ones above and Proposition 4.5.2. □

Next, we want to study the positive spectra of $\widehat{\chi_H}(\omega)F$ along the interval $\omega \in [0, \Omega)$. For this, we first observe that the operators B_ω defined in (4.5.6) can be seen as positive operators acting on the finite-dimensional subspaces V_ω.

Proposition 4.5.4 (B_ω as positive operators on V_ω)**.** *The operator B_ω defined on (4.5.6) is symmetric and bounded on $\mathcal{H}_F$ and satisfy*

$$P_{V_\omega}B_\omega P_{V_\omega} = B_\omega \quad \text{and} \quad \langle f, B_\omega f\rangle_F > 0, \quad \text{for any } f \in V_\omega. \tag{4.5.8}$$

In particular, B_ω is invertible with respect to the (F-)orthogonal projection P_{V_ω}.

Proof. That B_ω is symmetric follows from Proposition 4.5.2 since $(SP^H_{\mathcal{E}_0+\omega}S^*)^* = SP^H_{\mathcal{E}_0+\omega}S^*$. That B_ω is non-negative follows from the identity

$$\langle f, B_\omega f\rangle_F = \langle Ff, SP^H_{\mathcal{E}_0+\omega}S^*Ff\rangle = \|P^H_{\mathcal{E}_0+\omega}S^*Ff\|^2_{L^2(\mathbb{R}^3)} \geqslant 0. \tag{4.5.9}$$

Since $\operatorname{ran} B_\omega \subset V_\omega$ and B_ω is symmetric, we see that $B_\omega = P_{V_\omega}B_\omega P_{V_\omega}$. Finally, to see that B_ω is positive on V_ω, note that for any $0 \neq f \in V_\omega$ there exists $\Phi \in \mathcal{H}_N$ such that $f = SP^H_{\mathcal{E}_0+\omega}\Phi$. Therefore,

$$\langle \Phi, P^H_{\mathcal{E}_0+\omega}S^*Ff\rangle = \langle FSP^H_{\mathcal{E}_0+\omega}\Phi, f\rangle = \langle Ff, f\rangle > 0.$$

As a consequence, $P^H_{\mathcal{E}_0+\omega}S^*Ff \neq 0$ and the result follows from (4.5.9). □

We now use the positivity of B_ω to show that the positive spectra of $\widehat{\chi_H}(z)F$ is discrete for real z.

Lemma 4.5.2 (Positive spectra is discrete)**.** *For any $s \in [0,\Omega)\backslash\mathcal{P}(\widehat{\chi_H})$, we have*

$$\sigma_{\mathrm{ess}}\big(\widehat{\chi_H}(s)F\big) \subset (-\infty, 0]. \tag{4.5.10}$$

Proof. As $2\frac{\lambda}{s^2-\lambda^2} < 0$ for any $0 < |s| \leqslant \lambda$ and the operators B_ω are non-negative, we have

$$\langle f, \frac{2\omega}{s^2-\omega^2}B_\omega f\rangle_F \leqslant 0, \quad \text{for any } |s| < \omega, \text{ and} \tag{4.5.11}$$

$$\langle f, B_{\mathrm{ess}}(s)f\rangle_F \leqslant 0, \quad \text{for any } s < \Omega. \tag{4.5.12}$$

In addition, from Weyl's criteria and the fact that all B_ω have finite rank, we have

$$\sigma_{\mathrm{ess}}(\widehat{\chi_H}(s)F) = \sigma_{\mathrm{ess}}\left(\sum_{\omega\in\mathcal{P}(\widehat{\chi_H})\backslash\mathcal{F}} \frac{2\omega}{s^2-\omega^2}B_\omega + B_{\mathrm{ess}}(s)\right) \quad \text{for any finite set } \mathcal{F}\,. \tag{4.5.13}$$

Thus for $\Omega > |s| \notin \mathcal{P}(\widehat{\chi_H})$, the result follows from (4.5.11), (4.5.12), (4.5.13), and the Rayleigh-Ritz principle (max-min principle). □

Next, we want to understand the behaviour of the eigenvalues of $\widehat{\chi_H}(s)F$ as s approaches the excitations $\omega \in \mathcal{P}(\widehat{\chi_H})$. The idea is to use the operator $P^\perp_{V_\omega}\widehat{\chi_H}(z)FP^\perp_{V_\omega}$ as a reference. Precisely, we can apply Lemma 4.4.2 to prove the following lemma.

Lemma 4.5.3 (Positive spectra close to excitations)**.** *Let $\mu_0 > 0$. Then for any $\delta > 0$ small enough, there exists some neighborhood U_δ of ω on which the projection*

$$Q(z) = \frac{1}{2\pi i}\oint_{\partial B_\delta(\mu_0)} (\mu - \widehat{\chi_H}(z)F)^{-1}\mathrm{d}\mu \tag{4.5.14}$$

is well-defined, holomorphic, and satisfies

$$Q(z) = Q(\omega) + \mathcal{O}(|z-\omega_j|),$$

where $Q(\omega)$ is the orthogonal projection on $\ker\mu_0 - P^\perp_{V_\omega}\widehat{\chi_H}(\omega)F$. If $Q(\omega) = 0$, then $B_\delta(\mu_0)$ is on the resolvent of $\widehat{\chi_H}(z)F$ and $Q(z) = 0$ on U_δ.

Proof. Note that $A(z) := P_{V_\omega}^\perp \widehat{\chi_H}(z) F P_{V_\omega}^\perp$ is holomorphic and bounded for z close to ω. Moreover $\mu_0 > 0$ must be either on the discrete spectrum or on the resolvent set of $A(z)$ (see Lemma 4.5.2). Either way, we can apply Lemma 4.4.2 to the operator

$$\underbrace{\widehat{\chi_H}(z)F}_{:=D(z)} = A(z) + (z-\omega)^{-1}\underbrace{B_\omega}_{:=B} + \underbrace{P_{V_\omega}^\perp \widehat{\chi_H}(z) F P_{V_\omega} + P_{V_\omega}\widehat{\chi_H}(z)FP_{V_\omega}^\perp - (z+\omega)^{-1}B_\omega}_{:=C(z)},$$

with $f(\mu) = 1$ to prove the Lemma. (Note that $\ker \mu_0 - P_{V_\omega}^\perp \widehat{\chi_H}(\omega)F = \ker \mu_0 - P_{V_\omega}^\perp \widehat{\chi_H}(\omega) F P_{V_\omega}^\perp$ for any $\mu_0 \neq 0$.) □

We are now in position to complete the description of the qualitative behaviour of the positive eigenvalues of $\widehat{\chi_H}(z)F$ as z moves along the interval $(-\Omega, \Omega)$. To state this last lemma, let us denote the max-min and the min-max values of $\widehat{\chi_H}F$ over $V_\omega^\perp \subset \mathcal{H}_F$ as

$$\mu^k(\omega) := \sup_{\substack{W \subset V_\omega^\perp \\ \dim W = k}} \inf_{\substack{f \in W \\ \|f\|_F = 1}} \langle f, \widehat{\chi_H}(\omega) F f\rangle_F \quad \text{and} \quad \mu_k(\omega) := \inf_{\substack{W \subset V_\omega^\perp \\ \dim W = k}} \sup_{\substack{f \in W \\ \|f\|_F = 1}} \langle f, \widehat{\chi_H}(\omega) F f\rangle_F.$$

Lemma 4.5.4 (Max-min and min-max values)**.** *The functions μ^k and μ_k are non-increasing along any excitation-free interval $J \subset [0,\Omega)\backslash\mathcal{P}(\widehat{\chi_H})$. Moreover, they satisfy*

(i) $\mu^1(s) \leqslant 0$, *for* $|s| < \min \mathcal{P}(\widehat{\chi_H})$,

(ii) $\lim_{s\to\omega^+} \mu^k(s) = \infty = -\lim_{s\to\omega^-} \mu_k(s)$, *for any* $1 \leqslant k \leqslant \dim V_\omega$,

(iii) $\lim_{s\to\omega^-} \mu^k(s) = \mu^k(\omega) = \lim_{s\to\omega^+} \mu^{k+\dim V_\omega}(\omega)$, *for any* $\omega \in \mathcal{P}(\widehat{\chi_H})$, *and*

(iv) $\lim_{s\to\omega^-} \mu_{k+\dim V_\omega}(\omega) = \mu_k(\omega) = \lim_{s\to\omega^+} \mu_k(\omega)$, *for any* $\omega \in \mathcal{P}(\widehat{\chi_H})$.

Proof. From the proof of Lemma 4.5.2, we see that $\widehat{\chi_H}(\omega)F \leqslant 0$ for $|\omega| < \min \mathcal{P}(\widehat{\chi_F})$, which proves item (i). Next, note that for $\omega \in [0,\Omega)\backslash\mathcal{P}(\widehat{\chi_H})$, items $(ii), (iii)$ and (iv) are equivalent to the continuity of μ_k and μ^k (since $V_\omega = \{0\}$ at these points), which follows from the continuity of $\widehat{\chi_H}(\omega)F$ around these points. To see why μ^k and μ_k are non-increasing along any interval $J \subset [0,\Omega)\backslash\mathcal{P}(\widehat{\chi_H})$, just note that

$$\begin{aligned}\langle f, \widehat{\chi_H}(s) F f\rangle_F &= \int_{\omega_1}^\infty \frac{\lambda}{s^2-\lambda^2} \mathrm{d}\|E^H_{\lambda+\mathcal{E}_0} S^* F f\|^2 \geqslant \int_{\omega_1}^\infty \frac{\lambda}{\tilde{s}^2-\lambda^2} \mathrm{d}\|E^H_{\lambda+\mathcal{E}_0} S^* F f\|^2 \\ &\geqslant \langle f, \widehat{\chi_H}(\tilde{s}) F f\rangle_F, \quad \text{for any } \tilde{s} > s > 0 \text{ in } J. \end{aligned} \tag{4.5.15}$$

In particular, the limits $\lim_{s\to\omega^+} \mu^k(s) \in \mathbb{R} \cup \{+\infty\}$ exists for any $k \in \mathbb{N}$ and $\omega \in [0,\Omega)$. To show that this limit goes to infinity for $k \leqslant \dim V_\omega$, we note that

$$\lim_{s\to\omega^+} \langle f, \widehat{\chi_H}(s) F f\rangle = \lim_{s\to\omega^+} \frac{2\omega}{s^2-\omega^2} \langle f, B_\omega f\rangle + \mathcal{O}(1) = \infty, \quad \text{for any } 0 \neq f \in V_\omega,$$

by the positivity of B_ω. On the other hand, we can use that $P_{V_\omega^\perp}\widehat{\chi_H}(s)FP_{V_\omega^\perp}$ is bounded for s close to ω to show that the limit is finite for $k > \dim V_\omega$. A similar argument implies that $\lim_{s\to\omega^-} \mu_k(s) \to -\infty$ if and only if $k \leqslant \dim V_\omega$.

Finally, the last two items follow from Lemma 4.5.3. Indeed, since $\widehat{\chi_H}(s)F$ is self-adjoint, we have $\mu^k(s) \in \sigma(\widehat{\chi_H}(s)F)$ for any $k \in \mathbb{N}$ and $s \notin \mathcal{P}(\widehat{\chi_H})$. Lemma 4.5.3 then implies that $\lim_{s\to\omega^\pm} \mu^k(s)$ belongs to the spectrum of $P_{V_\omega^\perp}\widehat{\chi_H}(\omega)FP_{V_\omega^\perp}$ (on $\mathcal{B}(V_\omega^\perp)$) as long as it is finite. Moreover, Lemma 4.5.3 also implies that any point $\mu_0 \in \sigma(P_{V_\omega^\perp}\widehat{\chi_H}(\omega)FP_{V_\omega^\perp})$ that lies above the essential spectrum must be the limit of exactly $\dim\ker \mu_0 - P_{V_\omega^\perp}\widehat{\chi_H}(\omega)FP_{V_\omega^\perp}$ eigenvalues of $\widehat{\chi_H}(\omega)F$. Item (ii) and an ordering argument then completes the proof of (iii). Item (iv) follows from similar arguments. □

4.5.3 The inverse of $1 - \widehat{\chi_H}(z)F$

We now combine the results from the previous sections to show that the inverse of $1-\widehat{\chi_H}F$ is meromorphic and to obtain asymptotic formulas for $(1-\widehat{\chi_H}(z)F)^{-1}$ when z approaches the set of poles of $\widehat{\chi_H}$ or the set of zeros of $1 - \widehat{\chi_H}F$. These formulas will be used in the next section to prove Theorem 4.1.3.

We start by showing that $1 - \widehat{\chi_H}(z)F$ is invertible for z away of the real axis, or before the first excitation $\omega_1 \coloneqq \min \mathcal{P}(\widehat{\chi_H})$. In addition, we obtain an upper bound on the growth of $\|(1 - \widehat{\chi_H}(\omega + i\eta)F)^{-1}\|$ as $\eta \to 0$. This bound will be used to show that the poles of $\widehat{\chi_F}$ are all simple.

Lemma 4.5.5 (Inverse away of the real axis and before ω_1)**.** *Let $\mu_0 > 0$. Then, the operator $\mu_0 - \widehat{\chi_H}(z)F$ is invertible for any $z \in \{\omega + i\eta \in \mathbb{C} : \eta \neq 0 \text{ or } |\omega| \leqslant \omega_1\}$, where $\omega_1 \coloneqq \min \mathcal{P}(\widehat{\chi_H})$. Moreover, we have*

$$\|(\mu_0 - \widehat{\chi_H}(\omega + i\eta)F)^{-1}\| \lesssim \mu_0^{-1}|z||\eta|^{-1}, \tag{4.5.16}$$

for any $z \in \mathbb{C}\backslash\mathbb{R}$.

Proof. The first step is to prove the following estimate on the ratio between the real and imaginary part of $\widehat{\chi_H}(z)F$:

$$\mathrm{Re}\big(\langle f, \widehat{\chi_H}(z)Ff\rangle_F\big) \leqslant \max\left\{0, \frac{\omega^2 - \eta^2 - \omega_1^2}{|\omega\eta|}\right\}\big|\mathrm{Im}\big(\langle f, \widehat{\chi_H}(z)Ff\rangle_F\big)\big|. \tag{4.5.17}$$

For this, let $z = \omega + i\eta$ and suppose that $\omega^2 - \eta^2 \leqslant \omega_1^2$. Then from the spectral theorem and the representation of $\widehat{\chi_H}(z)$ in Proposition 4.2.4, we find that

$$\mathrm{Re}\langle f, \widehat{\chi_H}(z)Ff\rangle_F = 2\int_{\omega_1}^{\infty} \frac{\overbrace{\lambda(\omega^2 - \eta^2 - \lambda^2)}^{\leqslant 0}}{|\lambda^2 + z^2|^2}\mathrm{d}\|P^H_{\mathcal{E}_0+\lambda}S^*Ff\|^2 \leqslant 0,$$

which gives estimate (4.5.17) in this case. Now suppose that $\omega^2 - \eta^2 > \omega_1^2$. Then since

$\frac{\overbrace{\lambda(\omega^2-\eta^2-\lambda^2)}^{\leqslant 0}}{|\lambda^2+z^2|^2}$ is negative for $\lambda \geqslant \sqrt{\omega^2-\eta^2}$, we find that

$$\begin{aligned}
\mathrm{Re}\langle f, \widehat{\chi_H}(z)Ff\rangle &\leqslant 2\int_{\omega_1}^{\sqrt{\omega^2-\eta^2}} \frac{\lambda(\omega^2-\eta^2-\lambda^2)}{|\lambda^2-z^2|^2}\mathrm{d}\|E^H_{\mathcal{E}_0+\lambda}S^*Ff\|^2 \\
&\leqslant 2\int_{\omega_1}^{\sqrt{\omega^2-\eta^2}} \frac{\lambda|\omega\eta|}{|\lambda^2-z^2|^2}\left(\frac{\omega^2-\eta^2-\lambda^2}{|\omega\eta|}\right)\mathrm{d}\|E^H_{\mathcal{E}_0+\lambda}S^*Ff\|^2 \\
&\leqslant \frac{\omega^2-\eta^2-\omega_1^2}{|\omega\eta|}\left|2\int_{\omega_1}^{\sqrt{\omega^2-\eta^2}} \frac{\lambda\omega\eta}{|\lambda^2-z^2|^2}\mathrm{d}\|E^H_{\mathcal{E}_0+\lambda}S^*Ff\|^2\right| \\
&\leqslant \frac{\omega^2-\eta^2-\omega_1^2}{|\omega\eta|}|\mathrm{Im}\langle f, \widehat{\chi_H}(z)Ff\rangle_F|,
\end{aligned}$$

which proves (4.5.17). Next, let $g : \mathbb{C}\backslash\{\omega_1, -\omega_1\} \to [0,\infty]$ be the function

$$g(\omega+i\eta) = \max\left\{0, \frac{\omega^2-\eta^2-\omega_1^2}{|\omega\eta|}\right\}. \tag{4.5.18}$$

Then by estimate (4.5.17),

$$\begin{aligned}
\|(\mu_0 - \widehat{\chi_H}(z)F)f\|_F^2 &\geqslant \left(\mathrm{Re}\langle f, \mu_0 - \widehat{\chi_H}(z)Ff\rangle_F\right)^2 + |\mathrm{Im}\langle f, \widehat{\chi_H}(z)Ff\rangle_F|^2 \\
&\geqslant (\mathrm{Re}\langle f, \widehat{\chi_H}(z)Ff\rangle_F)^2(1+g(z)^{-2}) - 2\mu_0\mathrm{Re}\langle f, \widehat{\chi_H}(z)Ff\rangle_F + \mu_0^2,
\end{aligned}$$

for any $f \in \mathcal{H}_F$ with $\|f\|_F = 1$. Hence by minimizing the function $\tau \mapsto \tau^2(1+g(z)^{-2}) - 2\mu_0\tau + \mu_0^2$, we find that

$$\|(\mu_0 - \widehat{\chi_H}(z)F)f\|_F \geqslant \frac{\mu_0}{\sqrt{1+g(z)^2}}\|f\|_F. \tag{4.5.19}$$

Moreover, because $g(z) = g(\overline{z})$, the same lower bound holds for the F-adjoint $(\widehat{\chi_H}(z)F)^{*_F} = \widehat{\chi_H}(\overline{z})F$. Therefore, $\mu_0 - \widehat{\chi_H}(z)F$ is invertible whenever $g(z) < \infty$, which is precisely the set $\{\omega+i\eta : \eta \neq 0 \text{ or } |\omega| < \omega_1\}$. Estimate (4.5.16) now follows from (4.5.19) and the estimate $g(z) = \max\{0, (\omega^2-\eta^2-\omega_1^2)/|\omega\eta|\} \leqslant |\omega|/|\eta|$. □

Now we can use the estimate just proved and the results of Section 4.4 to show that $(1-\widehat{\chi_H}F)^{-1}$ is meromorphic.

Lemma 4.5.6 (Inverse of $1-\widehat{\chi_H}F$)**.** *The function $(1-\widehat{\chi_H}F)^{-1} : \mathcal{D}_\Omega \to \mathcal{B}(\mathcal{H}_F)$ is meromorphic and its positive poles are precisely the set of zeros of $1-\widehat{\chi_H}F$, i.e.,*

$$\mathcal{P}(\widehat{\chi_F}) = \left\{0 < \omega < \Omega : Z_\omega := \ker 1 - P_{V_\omega^\perp}\widehat{\chi_H}(\omega)F \neq \{0\}\right\}.$$

Furthermore, we have the following expansions of $(1-\widehat{\chi_H}F)^{-1}$ near the $\omega \in \mathcal{P}(\widehat{\chi_H}) \cup \mathcal{P}(\widehat{\chi_F})$:

(i) For $\omega \in \mathcal{P}(\widehat{\chi_H})\backslash\mathcal{P}(\widehat{\chi_F})$, we have

$$(1-\widehat{\chi_H}(\omega+z)F)^{-1} = R_\omega - z(1+R_\omega\widehat{\chi_H}(\omega)F)B_\omega^{-1}(1+\widehat{\chi_H}(\omega)FR_\omega) + \mathcal{O}(|z|^2), \tag{4.5.20}$$

where $R_\omega := \big(P_{V_\omega^\perp}(1-\widehat{\chi_H}(\omega)F)P_{V_\omega^\perp}\big)^{-1}$ is the inverse with respect to $P_{V_\omega^\perp}$.

(ii) For $\omega \in \mathcal{P}(\widehat{\chi_F})$, the operator

$$K_\omega = P_{Z_\omega}\big(\widehat{\chi_H}(\omega)FB_\omega^{-1}\widehat{\chi_H}(\omega)F - \dot{\widehat{\chi_H}}(\omega)F\big)P_{Z_\omega}$$

is invertible with respect to the orthogonal projection P_{Z_ω} and we have

$$(1-\widehat{\chi_H}(\omega+z)F)^{-1} = z^{-1}K_\omega^{-1} + \mathcal{O}(1), \tag{4.5.21}$$
$$(1-\widehat{\chi_H}(\omega+z)F)^{-1}P_{V_\omega} = -K_\omega^{-1}\widehat{\chi_H}(\omega)FB_\omega^{-1} + \mathcal{O}(|z|). \tag{4.5.22}$$

Proof. Since $1-\widehat{\chi_H}F$ is holomorphic on $\mathcal{D}_\Omega\backslash \pm\mathcal{P}(\widehat{\chi_H})$, the inverse $(1-\widehat{\chi_H}F)^{-1}$ is also holomorphic on this set whenever it exists. Thus by Lemmas 4.5.2 and 4.5.5, the inverse $(1-\widehat{\chi_H}F)^{-1}$ is holomorphic on $\mathcal{D}_\Omega\backslash\big(\pm\mathcal{P}(\widehat{\chi_H})\cup\pm\mathcal{P}(\widehat{\chi_F})\big)$.

For $\omega \in \mathcal{P}(\widehat{\chi_H})$, we want to apply the results of Section 4.4 to the operator $\widehat{\chi_H}(\omega+z)F = A(z) + z^{-1}B + C(z)$ where

$$A(z) := P_{V_\omega^\perp}\widehat{\chi_H}(\omega+z)FP_{V_\omega^\perp}, \quad B := B_\omega, \quad \text{and}$$
$$C(z) = P_{V_\omega}\widehat{\chi_H}(\omega+z)FP_{V_\omega^\perp} + P_{V_\omega^\perp}\widehat{\chi_H}(\omega+z)FP_{V_\omega} + P_{V_\omega}\left(\widehat{\chi_H}(\omega+z)F - \frac{B_\omega}{z}\right)P_{V_\omega} \tag{4.5.23}$$

In the case $Z_\omega = \{0\}$, the operator $A(0)$ is invertible with respect to $P_{V_\omega^\perp}$ (as its positive spectra is discrete). Hence formula (4.5.20) follows directly from Corollary 4.4.1. For the case $Z_\omega \neq \{0\}$, we start by showing that K_ω is invertible on Z_ω. For this, note that the Riesz projection of $\widehat{\chi_H}(z)F$ around 1 is well-defined by Lemma 4.5.3, and it satisfies

$$Q(z) := (2\pi i)^{-1}\oint_{\partial B_\delta(1)}(\mu - \widehat{\chi_H}(\omega+z)F)^{-1}\mathrm{d}\mu = P_{Z_\omega} + \mathcal{O}(|z|) \tag{4.5.24}$$

for z close to 0 and $\delta > 0$ small. Moreover, by applying Lemma 4.4.2 to $\widehat{\chi_H}(\omega+z)F = A(z) + z^{-1}B + C(z)$ with $f(\mu) = 1-\mu$ we find that

$$Q(z)(1-\widehat{\chi_H}(z)F) = (2\pi i)^{-1}\oint_{\partial B_\delta(1)}(1-\mu)(\mu-\widehat{\chi_H}(z)F)^{-1}\mathrm{d}\mu = zK_\omega + \mathcal{O}(|z|^2).$$

Thus from the blow-up estimate (4.5.16) we obtain

$$(1-\widehat{\chi_H}(\omega+i\eta)F)Q(i\eta)f = \eta K_\omega Q(i\eta)f + \mathcal{O}(|\eta|^2) \gtrsim \eta\|f\|, \quad \text{for any } f \in \operatorname{ran}Q(i\eta).$$

But since $\operatorname{rank} Q(i\eta) = \dim Z_\omega < \infty$ for η small, the above estimate implies that K_ω is invertible on Z_ω.

The next step is to compute the expansion of $(1 - \widehat{\chi_H} F)^{-1}$. For this, let us rewrite $1 - \widehat{\chi_H}(z)F$ in block notation on $V_\omega^\perp \oplus V_\omega$:

$$1 - \widehat{\chi_H}(\omega + z)F = \begin{pmatrix} P_{V_\omega^\perp}(1 - \widehat{\chi_H}(\omega + z)F)P_{V_\omega^\perp} & -P_{V_\omega^\perp}\widehat{\chi_H}(\omega + z)FP_{V_\omega} \\ -P_{V_\omega}\widehat{\chi_H}(\omega + z)FP_{V_\omega^\perp} & P_{V_\omega}(1 - \widehat{\chi_H}(\omega + z)F)P_{V_\omega}, \end{pmatrix} = \begin{pmatrix} \mathcal{A} & \mathcal{B} \\ \mathcal{C} & \mathcal{D} \end{pmatrix}.$$

Thus since B_ω is invertible on V_ω, we have

$$\mathcal{D}^{-1} = \Bigg(P_{V_\omega}(1 \underbrace{-\widehat{\chi_H}(z + \omega)F + z^{-1}B_\omega}_{=\mathcal{O}(1)})P_{V_\omega} - z^{-1}B_\omega \Bigg)^{-1} = -zB_\omega^{-1} + \mathcal{O}(|z|^2) \tag{4.5.25}$$

From this equation and the identities $P_{Z_\omega}P_{V_\omega^\perp}(1-\widehat{\chi_H}(\omega)F)P_{V_\omega^\perp} = 0 = P_{V_\omega^\perp}(1-\widehat{\chi_H}(\omega)F)P_{V_\omega^\perp}P_{Z_\omega}$, the Schur complement of the block $\mathcal{D}$ is given by

$$\begin{aligned} \Delta \coloneqq \mathcal{A} - \mathcal{B}\mathcal{D}^{-1}\mathcal{C} &= P_{V_\omega^\perp}\Big(1 - \widehat{\chi_H}(z)F + z\widehat{\chi_H}(z)FB_\omega^{-1}\widehat{\chi_H}(z)F\Big)P_{V_\omega^\perp} + \mathcal{O}(|z|^2) \\ &= P_{V_\omega^\perp}\Big((1 - \widehat{\chi_H}(\omega)F) - z\dot{\widehat{\chi_H}}(\omega)F + z\widehat{\chi_H}(\omega)FB_\omega^{-1}\widehat{\chi_H}(\omega)F\Big)P_{V_\omega^\perp} + \mathcal{O}(|z|^2) \\ &= \underbrace{P_{Z_\omega^\perp}P_{V_\omega^\perp}(1 - \widehat{\chi_H}(\omega)F)P_{V_\omega^\perp}P_{Z_\omega^\perp}}_{\coloneqq\tilde{B}} + z\underbrace{K_\omega}_{\coloneqq\tilde{A}} + z\widetilde{C}(z)\Big), \end{aligned}$$

where $\widetilde{C}(z)$ satisfies $P_{Z_\omega}\widetilde{C}(z)P_{Z_\omega} = \mathcal{O}(|z|)$. An application of Lemma 4.4.1 to $\Delta = z(\tilde{A} + z^{-1}\tilde{B} + \tilde{C}(z)) \in \mathcal{B}(Z_\omega^\perp \cap V_\omega^\perp)$ then yields $\Delta^{-1} = z^{-1}K_\omega^{-1} + \mathcal{O}(1)$, which together with (4.5.25) and the Schur complement inverse formula

$$(1 - \widehat{\chi_H}(z)F)^{-1} = \mathcal{D}^{-1} + (1 - \mathcal{D}^{-1}\mathcal{C})\Delta^{-1}(1 - \mathcal{B}\mathcal{D}^{-1})$$

completes the proof of (4.5.22). The case $\omega \in \mathcal{P}(\widehat{\chi_F})\backslash\mathcal{P}(\widehat{\chi_H})$ follows from similar calculations. □

4.6 The Fourier transform of χ_F

We are now ready to prove the main theorems of this chapter. We start by showing that χ_F is a tempered distribution and then compute the asymptotic expansion of $\widehat{\chi_F}$ around its poles. This will be enough to prove Theorems 4.1.2 and 4.1.3. Theorem 4.1.4 is an immediate consequence of Lemma 4.5.4 and Theorem 4.1.2.

4.6.1 $\widehat{\chi_F}$ as a tempered distribution

To show that χ_F is a tempered distribution, we combine Lemma 4.5.5 with the following lemma from [119].

Lemma 4.6.1 (Tempered distribution as boundary value of holomorphic functions)**.** *Let E be a Banach space and $F : \{z \in \mathbb{C} : 0 < \mathrm{Im}(z) < 2\} \to E$ be a holomorphic function such that*

$$\|F(\omega + i\eta)\|_E \lesssim \frac{(1+|\omega|)^M}{\eta^K}, \tag{4.6.1}$$

for any $0 < \eta < 1$ and for some $M \in \mathbb{R}$ and $K \in \mathbb{N}$. Then, for any $f \in S(\mathbb{R})$, the limit $\lim_{\eta\to 0^+} \int_{\mathbb{R}} F(\omega + i\eta) f(\omega) \mathrm{d}\omega$ exists in E and satisfies

$$\left\| \lim_{\eta\to 0} \int_{\mathbb{R}} F(\omega + i\eta) f(y) \mathrm{d}\omega \right\|_E \lesssim \|f^{(K+1)}(\omega)(1+|\omega|)^{M+K}\|_{L^1(\mathbb{R})}.$$

In particular, $\lim_{\eta\downarrow 0} F(\omega + i\eta)$ defines a E-valued tempered distribution.

Proof of Lemma 4.6.1. The proof is a simple iteration of an integration by parts argument with Morrera's theorem. For $n \in \mathbb{N}$, let us define

$$F^{(-n)}(\omega + i\eta) = \int_1^\eta F^{-n+1}(i\eta')\mathrm{d}\eta' + \int_0^\omega F^{(-n+1)}(\omega' + i\eta)\mathrm{d}\omega',$$

where $F^{(0)} = F$. Then, since the line integral of a holomorphic function on a simply connected domain along a closed rectifiable curve is zero, from estimate (4.6.1) we find that

$$\|F^{(-1)}(\omega + i\eta_0) - F^{(-1)}(\omega + i\eta_1)\|_E = \left\| \int_{\eta_1}^{\eta_0} F(\omega + i\eta')\mathrm{d}\eta' \right\|_E \lesssim \frac{(1+|\omega|)^M}{\eta_0^{K-1}}$$

for any $0 < \eta_0 < \eta_1 < 2$. In particular, we have

$$\|F^{(-1)}(\omega + i\eta_0)\|_E \lesssim \frac{(1+|\omega|)^M}{\eta^{K-1}} + \|F^{(-1)}(\omega + i)\|_E \lesssim \frac{(1+|\omega|)^{M+1}}{\eta^{K-1}}.$$

Next, by induction we can show that

$$\|F^{(-K)}(\omega + i\eta)\|_E \lesssim (1+|\omega|)^{M+K}(1 + \log \eta_0^{-1}),$$

for $0 < \eta_0 < \eta_1 < 2$, which implies that

$$\|F^{(-K-1)}(\omega + i\eta_0) - F^{(-K-1)}(\omega + i\eta_1)\|_E \lesssim (1+|\omega|)^{M+K}\eta_1(1 + \log \eta_1^{-1}), \tag{4.6.2}$$

for $0 < \eta_0 < \eta_1 < 1$. Therefore, integrating by parts we have

$$\begin{aligned}
&\int_{\mathbb{R}} \big(F(\omega + i\eta_0) - F(\omega + i\eta_1)\big) f(\omega)\mathrm{d}\omega \\
&\qquad = \int_{\mathbb{R}} \big(F^{(-K-1)}(\omega + i\eta_0) - F^{(-K-1)}(\omega + i\eta_1)\big) f^{(K+1)}(\omega)\mathrm{d}\omega \\
&\qquad\qquad \lesssim \eta_1(1 + \log \eta_1^{-1}) \|f^{(K+1)}(1+|\omega|)^{M+K}\|_{L^1(\mathbb{R})},
\end{aligned}$$

for any $0 < \eta_0 \leqslant \eta_1 < 1$, where the bound is in the E-norm. The result then follows since $\eta_1(1 + \log \eta_1^{-1}) \to 0$ as $\eta_1 \to 0$ and E is a Banach space. □

Theorem 4.6.1 (χ_F as a tempered distribution)**.** *Let χ_H be the DDRF of a Hamiltonian satisfying Assumption 4.1.1 and $F \in \mathcal{B}(L^2_{1/\rho_0}, L^2_{\rho_0})$ be positive. Then the unique solution χ_F of the Dyson equation (4.0.1) is a tempered distribution.*

Proof. Since $C = \sup_{t\in\mathbb{R}_+} \|\chi_H(t)\| < \infty$, the Fourier transform $\widehat{\chi_F}(z)$ is holomorphic and well-defined for $\mathrm{Im}(z) > C$. Hence applying the Fourier transform to (4.0.1) and using the convolution property,

$$\widehat{\chi_F}(z) = \widehat{\chi_H}(z) + \widehat{\chi_H}(z)F\widehat{\chi_F}(z), \tag{4.6.3}$$

for $\mathrm{Im}(z) > C$. But since the operator-valued function $z \mapsto (1 - \widehat{\chi_0}(z)F)^{-1} \in \mathcal{B}(\mathcal{H}_F)$ is holomorphic on the upper half-plane (by Lemma 4.5.5), we see that

$$\widehat{\chi_F}(z) = (1 - \widehat{\chi_H}(z)F)^{-1}\widehat{\chi_H}(z)$$

is the analytic extension of $\widehat{\chi_F} \in \mathcal{B}(L^2_{\rho_0}, \mathcal{H}_F)$ to the upper half plane. Moreover, we have the bound $\|(\omega + i\eta - H)^{-1}\|_{\mathcal{H}_N,\mathcal{H}_N} \leqslant |\eta|^{-1}$ because H is self-adjoint. So from the formula for $\widehat{\chi_H}(z)$ in terms of the resolvent of H (see Proposition 4.2.4), we obtain

$$\|\widehat{\chi_H}(\omega + i\eta)\|_{L^2_{\rho_0},L^2_{1/\rho_0}} \lesssim |\eta|^{-1}. \tag{4.6.4}$$

Therefore, by using this estimate and the blow-estimate (4.5.16) in (4.6.3), we have

$$\|\widehat{\chi_F}(\omega + i\eta)\|_{L^2_{\rho_0},\mathcal{H}_F} \lesssim \eta^{-2}(1 + |\omega|), \tag{4.6.5}$$

for any $1 > \eta > 0$ and $\omega \in \mathbb{R}$. Note however that the bound here is on the operator norm in $\mathcal{B}(L^2_{\rho_0}, \mathcal{H}_F)$ and not in $\mathcal{B}(L^2_{\rho_0}, L^2_{1/\rho_0})$ as we would like. To obtain the bound on the right norm, we now use (4.6.3) again. Indeed, since $F \in \mathcal{B}(\mathcal{H}_F, L^2_{\rho_0})$ (by Proposition 4.5.1), from estimates (4.6.4) and (4.6.5) and the identity (4.6.3) we obtain

$$\begin{aligned}\|\widehat{\chi_F}(\omega + i\eta)\|_{L^2_{\rho_0},L^2_{1/\rho_0}} &\leqslant \|\widehat{\chi_H}(\omega + i\eta)\|_{L^2_{\rho_0},L^2_{1/\rho_0}} \big(1 + \|F\|_{\mathcal{H}_F,L^2_{\rho_0}} \|\widehat{\chi_F}(\omega + i\eta)\|_{L^2_{\rho_0},\mathcal{H}_F}\big) \\ &\lesssim \eta^{-3}(1 + |\omega|).\end{aligned}$$

The result now follows from Lemma 4.6.1.

□

4.6.2 The poles of $\widehat{\chi_F}$

Let us now prove Theorems 4.1.2 and 4.1.3.

Proof of Theorems 4.1.2 and 4.1.3. We have already shown in the proof of Theorem 4.6.1 that

$$\widehat{\chi_F}(z) = (1 - \widehat{\chi_H}(z)F)^{-1}\widehat{\chi_H}(z)$$

is the (unique) analytic extension of $\widehat{\chi_F}(\omega)$ to the upper half-plane. Since the composition of meromorphic functions is also meromorphic, from Lemma 4.5.6 and Proposition 4.2.5 we see that $\widehat{\chi_F}$ is also meromorphic on $\mathcal{D}_\Omega$. Moreover, its poles can only lie on the set $\mathcal{P}(\widehat{\chi_H}) \cup \mathcal{P}(\widehat{\chi_F})$ as both $\widehat{\chi_H}(z)$ and $(1 - \widehat{\chi_H}(z))^{-1}$ are holomorphic outside this set.

Next, let us consider the points $\omega \in \mathcal{P}(\widehat{\chi_H}) \cup \mathcal{P}(\widehat{\chi_F})$ and fist show that

$$L^2_{\rho_0} = FV_\omega \oplus \ker SP^H_{\mathcal{E}_0+\omega}S^*$$

is a decomposition of $L^2_{\rho_0}$ into closed complementary subspaces. That they are closed subspaces of $L^2_{\rho_0}$ is clear because $SP^H_{\mathcal{E}_0+\omega}S^*$ is bounded and $\dim V_\omega < \infty$. To see that they are complementary, note that $B_\omega = SP^H_{\mathcal{E}_0+\omega}S^*F$ is injective on V_ω. Hence $FV_\omega \cap \ker SP^H_{\mathcal{E}_0+\omega}S^* = \{0\}$ and $\operatorname{codim} \ker SP^H_{\mathcal{E}_0+\omega}S^* = \dim V_\omega = \dim FV_\omega < \infty$. Therefore, the above decomposition holds and the associated projection $P_{FV_\omega} \in \mathcal{B}(L^2_{\rho_0})$ is well-defined. Moreover, we see that the restriction $SP^H_{\mathcal{E}_0+\omega}S^*\big|_{FV_\omega} \in \mathcal{B}(FV_\omega, V_\omega)$ is invertible and

$$B_\omega^{-1} = F^{-1}(SP^H_{\mathcal{E}_0+\omega}S^*\big|_{FV_\omega})^{-1}P_{V_\omega} \quad \text{and} \quad B_\omega^{-1}SP^H_{\mathcal{E}_0+\omega}S = F^{-1}P_{FV_\omega}. \tag{4.6.6}$$

Using this formula, the expansions in (4.1.16) and (4.1.18) follows directly from the identity $\widehat{\chi_F}(z) = (1 - \widehat{\chi_H}(z)F)^{-1}\widehat{\chi_H}(z)$ and the expansion on (4.5.20) and (4.5.22).

Finally, to see that (4.1.15) holds, it is enough to show that

$$\operatorname{rank}_\omega(\widehat{\chi_F}) = \operatorname{rank}_\omega((1 - \widehat{\chi_F})^{-1}), \quad \text{for any } \omega \in \mathcal{P}(\widehat{\chi_F}).$$

The inequality $\operatorname{rank}_\omega(\widehat{\chi_F}) \leqslant \operatorname{rank}_\omega((1 - \widehat{\chi_H}F)^{-1}$ follows from the explicit formulas in Theorem 4.1.3 and the characterization of $(1 - \widehat{\chi_H}F)^{-1}$ in Lemma 4.5.6. The opposite inequality follows from the identity

$$\widehat{\chi_F}F = (1 - \widehat{\chi_H}F)^{-1}\widehat{\chi_H}F = (1 - \widehat{\chi_H}F)^{-1} - 1.$$

□

4.7 Casida formalism

The goal of this section is to prove Theorem 4.1.5 and briefly discuss how the general Casida formalism presented here reduces to the original one in the non-interacting case.

4.7.1 Proof of Theorem 4.1.5

Throughout this section we assume that H is a Hamiltonian with purely discrete spectrum and satisfying Assumption 4.1.1. Since H is an operator on an infinite dimensional space, we can choose an orthonormal family

$$\{\Psi_j\}_{j=1}^\infty \subset \mathcal{H}_N \quad \text{such that} \quad H\Psi_j = (\mathcal{E}_0 + \omega_j)\Psi_j \quad \text{and} \quad \lim_{j\to\infty} \omega_j = +\infty.$$

As mentioned in the introduction, we can further assume that $\{\omega_j\}_{j=1}^{\infty} = \mathcal{P}(\widehat{\chi_H})$ after possibly reducing and relabelling the set $\{\Psi_j\}_{j=1}^{\infty}$. As in the introduction, we do *not* assume that $\omega_j \leqslant \omega_{j+1}$, and $\omega_j = \omega_k$ for some $k \neq j$ is allowed. The m^{th} Casida matrix is then defined as

$$C^m_{jk} = 2\omega_j \langle S\Psi_j, FS\Psi_k\rangle_{L^2(\mathbb{R}^3)} + \omega_j^2\delta_{jk}, \quad \text{where} \quad \delta_{jk} = \begin{cases} 1, & \text{if } j = k, \\ 0, & \text{otherwise.} \end{cases} \tag{4.7.1}$$

Let us also define the m^{th} truncation of the finite-dimensional subspaces $\{V_\omega\}_{\omega>0}$ and their direct sum as

$$V^m_\omega = \operatorname{span}\{S\Psi_j : j \leqslant m \text{ and } \omega_j = \omega\} \quad \text{and} \quad \mathcal{H}^m := \oplus_{\omega>0} V^m_\omega, \tag{4.7.2}$$

where we use again the convention that $V^m_\omega = \{0\}$ if $\omega \notin \{\omega_j\}_{j=1}^m$. In addition, we define the degeneracy of ω with respect to the truncated space V^m_ω as

$$d_m(\omega) = \#\{k \leqslant m : \omega_k = \omega\} - \dim V^m_\omega. \tag{4.7.3}$$

Then, we start by showing that the eigenvalues of C^m are related to the truncated density-density response function

$$\widehat{\chi^m_H}(z) = \sum_{j=1}^{m} \frac{2\omega_j}{z^2 - \omega_j^2} SP_{\Psi_j}S^*,$$

where P_{Ψ_j} is the projection on the space spanned by Ψ_j.

Proposition 4.7.1 (Casida matrix and truncated response function)**.** *Let $\widehat{\chi^m_H}(z)$ be defined as above, then for any $\omega > 0$ we have*

$$\dim\ker\omega^2 - C^m = \dim\ker 1 - P^{\perp}_{V^m_\omega}\widehat{\chi^m_H}(\omega) + d_m(\omega),$$

where $P^{\perp}_{V^m_\omega}$ is the F-orthogonal projection on the F-orthogonal complement of the space V^m_ω defined in (4.7.2).

Proof. Let $0 \neq f \in L^2_{1/\rho_0}$ satisfy $P^{\perp}_{V^m_\omega}\widehat{\chi^m_H}(\omega)Ff = f$, and define

$$\alpha_j := (\omega^2 - \omega_j^2)^{-1} 2\omega_j \langle S\Psi_j, Ff\rangle \quad \text{for any } j \leqslant m \text{ with } \omega_j \neq \omega. \tag{4.7.4}$$

For j with $\omega_j = \omega$, we can choose the rest of the coefficients $\{\alpha_j\}$ in a way that

$$\sum_{\substack{j\leqslant m \\ \omega_j=\omega}} \alpha_j S\Psi_j := -P_{V^m_\omega} \sum_{\substack{j\leqslant m \\ \omega_j\neq\omega}} \alpha_j S\Psi_j. \tag{4.7.5}$$

This is possible because $V^m_\omega = \operatorname{span}\{S\Psi_j : j \leqslant m, \omega_j = \omega\}$. So by the definition of C^m (see (4.7.1)) and the assumption $P^{\perp}_{V^m_\omega}\widehat{\chi^m_H}(\omega)Ff = f$, one can easily check that

$$f = \sum_{j=1}^{m} \alpha_j S\Psi_j \quad \text{and} \quad (C^m\alpha)_j = 2\omega_j\langle S\Psi_j, Ff\rangle + \omega_j^2\alpha_j \quad \text{for any } j \leqslant m. \tag{4.7.6}$$

Since $f \in (V_\omega^m)^\perp$ implies that $\langle S\Psi_j, Ff\rangle = 0$ for any $\omega_j = \omega$, we conclude from (4.7.4) and (4.7.6) that $\alpha \in \ker \omega^2 - C^m$. Moreover, there are exactly $d_m(\omega)+1$ ways of choosing the α_j's satisfying (4.7.5), by the definition of $d_m(\omega)$. Hence $\dim\ker\omega^2 - C^m \geqslant d_m(\omega) + \dim\ker 1 - P^\perp_{V_\omega^m}\widehat{\chi^m_H}(\omega)F$.

For the opposite inequality we let $\alpha \in \ker\omega^2 - C^m$ and construct $f \in L^2_{1/\rho_0}$ via the first equation in (4.7.6). The second equation in (4.7.6) then shows that $f = 0$ if and only if $\alpha_j = 0$, for any $j \leqslant m$ with $\omega_j \neq \omega$, and $\sum_{j:\omega_j=\omega}^m \alpha_j S\Psi_j = 0$. Then on one hand, we have at most $d_m(\omega)$ linearly independent solutions $\alpha \in \ker\omega^2 - C^m$ with $\sum_j \alpha_j S\Psi_j = 0$. On the other hand, we can use both equations in (4.7.6) to show that $P^\perp_{V_\omega^m}\widehat{\chi^m_H}(\omega)Ff = f$. These two statements then imply that $\dim\ker\omega^2 - C^m \leqslant d_m(\omega) + \dim\ker 1 - P^\perp_{V_\omega^m}\widehat{\chi^m_H}(\omega)F$, which concludes the proof. □

Note that $\widehat{\chi^m_H}(z)$ has the same form as the Fourier transform of the density-density response function of some Hamiltonian. As a consequence, one can show that the min-max/max-min results from Lemma 4.5.4 also holds for $\widehat{\chi^m_H}(\omega)F$. This fact together with Proposition 4.7.1 can be used to show the following corollary.

Corollary 4.7.1 (Eigenvalues of Casida matrix)**.** *The Casida matrix C^m is diagonalizable and all its eigenvalues are positive.*

Proof. By Proposition 4.7.1 and the identity $m = \sum_{\omega>0} d_m(\omega) + \dim V_\omega^m$, it is enough to show that

$$\sum_{\omega>0} \dim\ker Z_\omega^m = \sum_{\omega>0}^m \dim V_\omega^m, \qquad \text{where} \qquad Z_\omega^m = \ker 1 - P^\perp_{V_\omega^m}\widehat{\chi^m_H}(\omega)F. \tag{4.7.7}$$

To this end, we first note that since $(\oplus_{\omega>0}^m V_\omega^m)^\perp = \bigcap_{\omega>0}(V_\omega^m)^\perp \subset \ker\widehat{\chi^m_H}(\omega)F$ and $\widehat{\chi^m_H}(\omega)$ is symmetric, it is enough to deal with the restriction $\widehat{\chi^m_H}(\omega)F$ to the finite dimensional space $\mathcal{H}^m$. In particular, the eigenvalues of $\widehat{\chi^m_H}(\omega)F$ on $\mathcal{H}^m$ are given by the F-max-min values,

$$\mu^{k,m} = \sup_{\substack{V\subset\mathcal{H}^m\cap(V_\omega^m)^\perp \\ \dim V = k}} \inf_{\substack{f\in V \\ \|f\|_F=1}} \langle Ff, \widehat{\chi^m_H}(\omega)Ff\rangle \quad \text{for } k \leqslant \dim\mathcal{H}^m.$$

Moreover, the F-min-max values over $\mathcal{H}^m$, denoted here by $\{\mu_{k,m}\}_{k\leqslant\dim\mathcal{H}^m}$, also correspond to eigenvalues and the following relation holds:

$$\mu^{k,m}(\omega) = \mu_{\dim\mathcal{H}^m-k+1,m}(\omega), \quad \text{for any } 1 \leqslant k \leqslant \dim\mathcal{H}^m. \tag{4.7.8}$$

Next, let us compactify the extended real line by identifying the points $\{\pm\infty\}$ with $\pm\pi$ on the circle $S^1 \cong [-\pi,\pi]/\sim$ via the stereographic projection $s \mapsto s/(\pi^2 - s^2)$. The eigenvalues of $\widehat{\chi^m_H}(\omega)F$ can then be seen as functions $\mu^{k,m} : [0,\infty)\backslash\{\omega_j\}_{j=1}^m \to S^1$. Moreover, if we define

$$\mu_k^m(s) := \mu^{k-1+\sum_{\omega<s}\dim V_\omega^m \mod \dim\mathcal{H}^m+1,m}, \quad \text{for any } s \in [0,\infty)\backslash\{\omega_j\}_{j=1}^m,$$

then we see from Theorem 4.1.4 and the relation in (4.7.8) that the functions μ_k^m can be continuously extended to the whole interval $[0,\infty)$, and they move in the clockwise direction as ω grows. Furthermore, we have

$$\dim Z_\omega^m = \#\{k : \mu_k^m(\omega) = 1/(\pi^2-1)\}. \tag{4.7.9}$$

To conclude we now make two observations. First, since $\lim_{\omega\to\infty}\|\widehat{\chi_H^m}(\omega)\| = 0$, we have

$$\lim_{\omega\to\infty} \mu_k^m(\omega) = 0 \quad \text{for any } 1 \leqslant k \leqslant \dim \mathcal{H}^m.$$

Second, Theorem 4.1.4 (ii) implies that the eigenvalues functions $\mu_1^m, ..., \mu_{\dim\mathcal{H}^m}^m$ cross the point $\{\pm\pi\} \cong \{\pm\infty\}$ exactly $\sum_{\omega>0}\dim V_\omega^m$ times. Consequently, the eigenvalue functions $\mu_1^m, ..., \mu_{\dim\mathcal{H}^m}^m$ must cross the point $1/(\pi^2-1)$ in the circle exactly $\sum_{\omega>0}\dim V_\omega^m$ times as ω moves from 0 to ∞, which completes the proof of (4.7.7). □

To complete the proof of Theorem 4.1.5, we need to show that the poles of $\widehat{\chi_F^m}$ converge to the poles of $\widehat{\chi_F}$. This is now a consequence of the convergence of $\widehat{\chi_H^m}$ to $\widehat{\chi_H}$ and the ordered monotone behaviour of the F-max-min values depicted in Theorem 4.1.4.

Proof of Theorem 4.1.5. We start by showing that the F-max-min values of the truncated LRF converge monotonically locally uniformly to the F-min-max values of $\widehat{\chi_H}$. For this, let us define

$$\omega_{\min}^m = \min\{\omega_j\}_{j>m} > 0.$$

Then, we have

$$0 \leqslant \underbrace{\sum_{j>m} \frac{2\omega_j}{\omega^2-\omega_j^2}\langle S^*Ff, \Psi_j\rangle\langle\Psi_j, S^*Ff\rangle}_{=\langle f, \left(\widehat{\chi_H^m}(\omega)-\widehat{\chi_H}(\omega)\right)Ff\rangle_F} \leqslant N\|F\|_{L^2_{1/\rho_0},L^2_{\rho_0}} \frac{2\omega_{\min}^m}{(\omega_{\min}^m)^2-\omega^2}, \tag{4.7.10}$$

for any $0 \leqslant \omega < \omega_{\min}^m$ with $\omega \notin \{\omega_j\}_{j\geqslant 1}$ and $f \in L^2_{1/\rho_0}$ with $\|f\|_F = 1$. Here we used the estimates $\|S^*\|_{L^2_{\rho_0},\mathcal{H}_N} \leqslant \sqrt{N}$ and $\|F\|_{\mathcal{H}_F,L^2_{\rho_0}} = \sqrt{\|F\|_{L^2_{1/\rho_0},L^2_{\rho_0}}}$. Moreover, since $V_\omega^m = V_\omega$ for any $\omega < \omega_{\min}^m$, (4.7.10) yields the estimate

$$0 \leqslant \mu^{k,m}(\omega) - \mu^k(\omega) \lesssim \frac{2\omega_{\min}^m}{(\omega_{\min}^m)^2-\omega^2} \quad \text{for any } \omega < \omega_{\min}^m, \tag{4.7.11}$$

for the difference between the F-max-min values of $\widehat{\chi_H^m}F$ and $\widehat{\chi_H}F$. But since $\omega_{\min}^m \to 0$ as $m\to\infty$, we conclude that the max-min functions of $\widehat{\chi_H^m}$ converge locally uniformly and monotonically from above to the F-max-min values of $\widehat{\chi_H}$.

Now let $\omega_1^F \leqslant \omega_2^F \leqslant ...$ be the poles of $\widehat{\chi_F}$ counted with rank and $\lambda_1^m \leqslant \lambda_2^m ... \leqslant \lambda^m_{\sum_{\omega>0}\dim V_\omega^m}$ be the eigenvalues of C^m counted in a way that $\#\{k : \lambda_k = \lambda\} + d_m(\sqrt{\lambda}) = \dim\ker\lambda - C^m$ for any $\lambda > 0$. Suppose that m is so big that $\omega_1^F < \omega_{\min}^m$. The monotone

convergence of the max-min values together with Lemma 4.5.4 (which holds for both $\widehat{\chi_H^m}$ and $\widehat{\chi_H}$) then shows that all F-max-min values of $\widehat{\chi_H^m}F(\omega)$ in the interval $\omega \in [0, \omega_1^F]$ must lie either above 1 or below 0. From Proposition 4.7.1, we thus conclude that $\sqrt{\lambda_1^m} \geqslant \omega_1^F$. An induction argument then shows that

$$\omega_k^F \leqslant \sqrt{\lambda_k^m}, \quad \text{for any } \omega_k^F < \omega_{\min}^m.$$

The convergence $\sqrt{\lambda_k^m} \downarrow \omega_k^F$ now follows from the convergence of the max-min values, Proposition 4.7.1, and a continuity argument. □

Remark (Convergence error estimates)**.** *Note that estimate* (4.7.11) *can be used to estimate the difference between the eigenvalues of the Casida matrix and the true poles of* $\widehat{\chi_F}$ *by plotting the max-min values of the truncated density-density response function* $\widehat{\chi_H}(\omega)$ *over the interval* $(0, \omega_m)$*.*

4.7.2 The original Casida matrix: non-interacting case

Let us now comment on the relation between the Casida formalism described in the previous section and the situation often encountered in practice.

In practice [19, 96, 83, 120], the Hamiltonian H acting on the N-body electronic space $\mathcal{H}_N$ is given by the sum

$$H = \sum_{j=1}^{N} 1 \otimes ... \otimes \underbrace{h}_{j^{th} \text{ position}} \otimes ... \otimes 1,$$

where h is a self-adjoint operator acting on the single-electron space $L^2(\mathbb{R}^3)$. In this case, and under the assumption that the spectrum of h is purely discrete, the set of anti-symmetric tensor products of N distinct eigenfunctions of h, i.e. the set of functions

$$\Psi_I(r_1, ..., r_N) = \det \begin{pmatrix} \phi_{i_1}(r_1) & ... & \phi_{i_1}(r_N) \\ \vdots & \ddots & \vdots \\ \phi_{i_N}(r_1) & ... & \phi_{i_N}(r_N) \end{pmatrix}, \quad I = (i_1, ..., i_N) \in \mathbb{N}^N,$$

where $1 \leqslant i_1 < i_2 ... < i_N$ and $\{\phi_j\}_{j \in \mathbb{N}}$ is the orthonormal basis of eigenfunctions of h, form an orthonormal basis (for $\mathcal{H}_N$) of eigenfunctions of H. If we denote the eigenvalues associated to ϕ_i by ε_i, then the ground state wave function and ground state energy of H are given respectively by

$$\Psi_0 = \Psi_{\{1,2,...,N\}} = \phi_1 \wedge ... \phi_N \quad \text{and} \quad \mathcal{E}_0 = \sum_{j=1}^{N} \varepsilon_j.$$

A simple calculation then shows that $S\Psi_I = 0$ for any I with $\#I \cap \{1, ..., N\} \leqslant N - 2$, where S is our usual operator defined in (4.2.5). Consequently, the one-body excitations are given by the following subset of the excitation energies of h:

$$\mathcal{P}(\widehat{\chi_H}) = \{\omega_{\ell,j} = \varepsilon_\ell - \varepsilon_j : \ell > N, \quad j \leqslant N\}.$$

Moreover, the Schwartz kernel of the Fourier transform of χ_H in the upper complex plane can be written as the sum

$$\widehat{\chi_H}(z,r,r') = \sum_{k=N+1}^{\infty}\sum_{j=1}^{N} \frac{\overline{\phi_k}(r)\phi_j(r)\phi_k(r')\overline{\phi_j}(r')}{z-\omega_{k,j}} - \frac{\phi_k(r)\overline{\phi_j}(r)\overline{\phi_k}(r')\phi_j(r')}{z+\omega_{k,j}} \tag{4.7.12}$$

where the limit of the series $k \to \infty$ is understood in the distributional sense[5].

Remark. *Eq. (4.7.12) is the standard representation for the density-density response function appearing in the DFT literature. In said literature, the Hamiltonian h is called the single-particle Kohn-Sham Hamiltonian, χ_H is the density-density response function of the Kohn-Sham system, and the orbital functions ϕ_j and ϕ_k are respectively the Kohn-Sham occupied and virtual orbital functions.*

In the original formulation [19], the Casida matrix is defined as

$$C^{N(m-N)}_{\text{original}} = \begin{pmatrix} A & -B \\ B' & -A' \end{pmatrix} \in \mathbb{C}^{2N(m-N)\times 2N(m-N)},$$

where $A, B, A', B' \in \mathbb{C}^{N(m-N)\times N(m-N)}$ are given by

$$\begin{aligned} A_{I(j,k),I(p,q)} &= \langle \phi_j\overline{\phi_k}, F\phi_p\overline{\phi_q}\rangle_{L^2(\mathbb{R}^3)} + \omega_{j,k}\delta_{j,p}\delta_{k,q}, \quad & B_{I(j,k),I(p,q)} &= \langle \phi_j\overline{\phi_k}, F\overline{\phi_p}\phi_q\rangle_{L^2(\mathbb{R}^3)}, \\ A'_{I(j,k),I(p,q)} &= \langle \overline{\phi_j}\phi_k, F\overline{\phi_p}\phi_q\rangle_{L^2(\mathbb{R}^3)} + \omega_{j,k}\delta_{j,p}\delta_{k,q}, \quad & B'_{I(j,k),I(p,q))} &= \langle \overline{\phi_j}\phi_k, F\phi_p\overline{\phi_q}\rangle_{L^2(\mathbb{R}^3)}, \end{aligned}$$

where $p, j \leqslant N < k, q \leqslant m$ and the indexing map is given by $I(j,k) = N(k-N-1)+j$. Under the assumption that h is a real Hamiltonian (and Ψ_0 has constant phase), all the orbital functions ϕ_j can be taken real-valued. So if we further assume that F is real (i.e., Ff is real-valued for f real-valued), then the Casida matrix reduces to

$$C^{N(m-N)}_{\text{original}} = \begin{pmatrix} B+W & -B \\ B & -B-W \end{pmatrix} \quad \text{where} \quad W_{I(j,k),I(p,q)} = \omega_{j,k}\delta_{j,p}\delta_{k,q}.$$

We can now show that the eigenvalues of $C^{N(m-N)}_{\text{original}}$ appear in pairs of negative and positive values and that their squares are the eigenvalues of the previously defined Casida matrix

$$C^{N(m-N)}_{I(j,k),I(p,q)} = 2\omega_{j,k}\langle \phi_j\phi_k, F\phi_p\phi_q\rangle_{L^2(\mathbb{R}^3)} + \omega^2_{j,k}\delta_{j,p}\delta_{k,q}. \tag{4.7.13}$$

Proposition 4.7.2 (Original Casida matrix)**.** *Let $C^{N(m-N)}_{\text{original}}$ and $C^{N(m-N)}$ be defined as above, then $C^{N(m-N)}_{\text{original}}$ is diagonalizable and we have*

$$\dim\ker C^{N(m-N)}_{\text{original}} \pm \lambda = \dim C^{N(m-N)} - \lambda^2, \tag{4.7.14}$$

for any $\lambda \in \mathbb{R}$.

[5]For Schrödinger operators with Kato class potentials, one can show that the above distributional kernel is an integral kernel for any $\pm z \notin \sigma(H-\mathcal{E}_0)$ by the results of [109].

Proof. The proof follows from straightforward algebraic manipulations. Precisely, for

$$0 \neq \begin{pmatrix} \beta_1 \\ \beta_2 \end{pmatrix} = \beta \in \ker C_{\text{original}}^{N(m-N)} \pm \lambda \in \mathbb{C}^{2(m-N)N},$$

one can check that $\alpha := \beta_1 - \beta_2 \in C^{(m-N)N}$ is non trivial and satisfies $C^{N(m-N)}\alpha = \lambda^2\alpha$. On the other hand, for $\alpha \in \ker C^{N(m-N)} - \lambda^2$, one can check that

$$\beta = \begin{pmatrix} (\pm\lambda W^{-1} + 1)\alpha \\ (\pm\lambda W^{-1} - 1)\alpha \end{pmatrix} \neq 0$$

and satisfy $C_{\text{original}}^{N(m-N)}\beta = \pm\lambda\beta$. (The matrix W is invertible because it is diagonal with only positive entries). That $C_{\text{original}}^{N(m-N)}$ is diagonalizable follows from (4.7.14) and the fact that $C^{N(m-N)}$ is diagonalizable by Corollary 4.7.1. □

4.8 Concluding remarks

We have now presented a mathematical framework for the analysis of the Dyson equation from LR-TDDFT. More precisely, we (i) presented a functional analytic setting for the well-posedness of the Dyson equation that is applicable to various adiabatic approximations of the xc-operator and to general Hamiltonians of interest in electronic structure theory, (ii) provided a careful and rigorous analysis of the poles of the solution of the Dyson equation within the random phase approximation (RPA), and (iii) proved the convergence of the poles computed via the Casida formalism in the continuum (or infinite orbital basis) limit. To conclude this chapter, let us now briefly comment on some possible extensions of these results and further related questions.

Non-positive adiabatic approximations. The proof of all results on the pole structure of $\widehat{\chi_F}$ rely on the positivity assumption on the adiabatic approximation F. With the exception of the simplest adiabatic approximation, the RPA, this assumption is not satisfied as the exchange-correlation kernel is usually negative. So a natural question is whether the results presented here can be extended to the case where the operator F is given by the difference of two positive operators (in the sense discussed here). In this case, we do not expect all poles of the solution $\widehat{\chi_F}$ to be forward shifted with respect to the poles of the $\widehat{\chi_H}$. Nonetheless, we expect that a rigorous characterization of the poles of $\widehat{\chi_F}$ via an eigenvalue equation as in Theorem 4.1.2 can be achieved by methods from analytic Fredholm theory [34, Appendix]. If this is the case, it would also be interesting to understand whether standard approaches for computing the poles of $\widehat{\chi_H}$, such as the Casida equations described in Section 4.7, converge in the continuum limit.

Casida formalism with essential spectrum. To prove the convergence of the poles computed via the Casida formalism, we have explicitly assumed that the Hamiltonian H has purely discrete spectrum. Although this assumption holds in some physically relevant situations, such as Schrödinger operators with trapping potentials, this is no longer true for the molecular Hamiltonian that plays a central role in quantum chemistry. In this case, the

Casida formalism is usually applied to a truncation of the Hamiltonian to some bounded domain with appropriate boundary conditions. Therefore, an interesting problem is to understand the relation between the poles computed via the Casida equations for the truncated Hamiltonian and the true poles of the infinite-dimensional solution of the Dyson equation, in the limit where both the size of the domain and the number of virtual orbitals goes to infinity.

Frequency-dependent exchange-correlation kernel. Here we have only considered adiabatic approximations to the exchange-correlation kernel. Hence, another natural question is whether the results presented here can be extended to frequency-dependent approximations of the exchange-correlation kernels. Such kernels typically yield better approximations to the excitation energies at a higher computational cost. Hence a mathematical understanding of the solution $\widehat{\chi_F}$ for such approximations is not only relevant from a theoretical perspective, but may also provide insight on how to design more efficient numerical schemes. We expect that the functional analytic setting presented here for the well-posedness can be adapted to this case. However, for a rigorous analysis of the poles of $\widehat{\chi_F}$ in such situations, one would also need to bypass the positivity assumption on F, which requires different methods.

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