Mathematical contributions to the calculations of electronic structures

David Gontier

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UNIVERSITÉ PARIS-EST

L'École Doctorale Mathématiques et Sciences et Technologies de l'Information et de la Communication (MSTIC)

Thèse de doctorat

Discipline : Mathématiques

présentée par

David Gontier

Contributions mathématiques aux calculs de structures électroniques

---

Thèse dirigée par Éric Cancès
préparée au CERMICS, Université Paris-Est (ENPC)

Soutenue le 28 septembre 2015 devant le Jury composé de :

Président du jury	M. Yvon Maday	Université Paris 6
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Directeur de Thèse	Éric Cancès	École des Ponts ParisTech

L'analyse numérique, c'est galère... kin
(William Minvielle)

Soit c'est décroissant, soit c'est des pains au chocolat
(Julia Wang)

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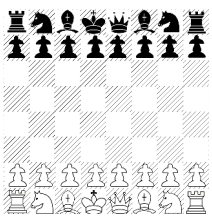
[1] Pour le citer : *Je t'en f**trai des «bien cordialement» !*

[2] Très peu au final, Claude Lebris nous ayant posé le problème suivant, qui nous a bien occupés :



[3] Dont la fameuse : *Est-ce que* ***mettre-ici-le-nom-d'un-espace-de-Banach*** *s'injecte dans BMO ?*

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Merci $\Big($ $\Big\{$ Julien, Silvain, Bastien, Vincent, Vincent, Pierre, Pierre, Irène, Daphné, Manon, Fathi, Max, Gabriel, Xavier, Arnaud, Jack, Ilia, Jean-François, Julien, Rémi, Guillaume, Martin, Jonathan et Nicolas[5] $\Big\}\Big)$.

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[4] *What else?*
[5] Que je remercie particulièrement pour son mail historique de contrepèteries et le gâteau qui a suivi.
[6] Surtout depuis qu'elle a dû relire et corriger ces remerciements...

Préambule

Cette thèse comprend trois sujets différents, tous en rapport à des problèmes de structures électroniques. Ces trois sujets sont présentés dans trois parties indépendantes.

Cette thèse commence par une introduction générale présentant les problématiques et les principaux résultats.

La première partie traite de la théorie de la fonctionnelle de la densité lorsqu'elle est appliquée aux modèles d'électrons avec spins polarisés. Cette partie est divisée en deux chapitres. Dans le premier de ces chapitres, nous introduisons la notion de N-représentabilité, et nous caractérisons les ensembles de matrices de densité de spin représentables. Dans le second chapitre, nous montrons comment traiter mathématiquement le terme de Zeeman qui apparaît dans les modèles comprenant une polarisation de spin. Le résultat d'existence qui est démontré dans [AC09] pour des systèmes de Kohn-Sham sans polarisation de spin est étendu au cas des systèmes avec polarisation de spin.

Dans la seconde partie, nous étudions l'approximation GW. Dans un premier temps, nous donnons une définition mathématique de la fonction de Green à un corps, et nous expliquons comment les énergies d'excitation des molécules peuvent être obtenues à partir de cette fonction de Green. La fonction de Green peut être numériquement approchée par la résolution des équations GW. Nous discutons du caractère bien posé de ces équations, et nous démontrons que les équations GW^0 sont bien posées dans un régime perturbatif. Ce travail a été effectué en collaboration avec Eric Cancès et Gabriel Stoltz.

Dans le troisième et dernière partie, nous analysons des méthodes numériques pour calculer les diagrammes de bandes de structures cristallines. Cette partie est divisée en deux chapitres. Dans le premier, nous nous intéressons à l'approximation de Hartree-Fock réduite (voir [CDL08]). Nous prouvons que si le cristal est un isolant ou un semi-conducteur, alors les calculs réalisés dans des supercellules convergent exponentiellement vite vers la solution exacte lorsque la taille de la supercellule tend vers l'infini. Ce travail a été réalisé en collaboration avec Salma Lahbabi. Dans le dernier chapitre, nous présentons une nouvelle méthode numérique pour le calcul des diagrammes de bandes de cristaux (qui peuvent être aussi bien isolants que conducteurs). Cette méthode utilise la technique des bases réduites, et accélère les méthodes traditionnelles. Ce travail a été fait en collaboration avec Eric Cancès, Virginie Ehrlacher et Damiano Lombardi.

Preamble

This thesis contains three different topics, all related to electronic structure problems. These three topics are presented in three independent parts.

This thesis begins with a general introduction presenting the problematics and main results.

The first part is concerned with Density Functional Theory (DFT), for spin-polarized models. This part is divided in two chapters. In the first of these chapters, the notion of N-representability is introduced and the characterizations of the N-representable sets of spin-density 2×2 matrices are given. In the second chapter, we show how to mathematically treat the Zeeman term in spin-polarized DFT models. The existence of minimizers that was proved in [AC09] for spin-unpolarized Kohn-Sham models within the local density approximation is extended to spin-polarized models.

The second part of this thesis focuses on the GW approximation. We first give a mathematical definition of the one-body Green's function, and explain why methods based on Green's functions can be used to calculate electronic-excited energies of molecules. One way to compute an approximation of the Green's function is through the self-consistent GW equations. The well-posedness of these equations is discussed, and proved in the GW^0 case in a perturbative regime. This is joint work with Eric Cancès and Gabriel Stoltz.

In the third and final part, numerical methods to compute band-diagrams of crystalline structure are analyzed. This part is divided in two chapters. In the first one, we consider a perfect crystal in the reduced Hartree-Fock approximation (see [CDL08]). We prove that, if the crystal is an insulator or a semi-conductor, then supercell calculations converge to the exact solution with an exponential rate of convergence with respect to the size of the supercell. This is joint work with Salma Lahbabi. In the last chapter, we provide a new numerical method to calculate the band diagram of a crystal (which can be either an insulator or a conductor). This method, based on reduced basis techniques, speeds up traditional calculations. This is joint work with Eric Cancès, Virginie Ehrlacher, and Damiano Lombardi.

List of publications

Here is a list of articles (accepted or submitted) that were written during this thesis:

- [Gon13] *N-Representability in noncollinear spin-polarized density-functional theory* (published in Phys. Rev. Lett. 111 (2013), p. 153001).
- [Gon15a] *Existence of minimizers for Kohn–Sham within the local spin density approximation* (published in Nonlinearity 28.1 (2015), pp. 57–76).
- [Gon15b] *Pure-state N-representability in current-spin-density-functional theory* (accepted in Commun. Math. Sci., (2015)).
- [CGS15] (with Eric Cancès and Gabriel Stoltz) *A mathematical analysis of the GW0 method for computing electronic excited energies of molecules* (arXiv 1506.01737).
- [GL15] (with Salma Lahbabi) *Convergence rates of supercell calculations in the reduced Hartree-Fock model* (accepted in M2AN (2015)).
- [CEG+15] (with Eric Cancès, Virginie Ehrlacher, Antoine Levitt and Damiano Lombardi) *Fast numerical methods for Brillouin-zone integration* (in preparation).

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CHAPTER 1

INTRODUCTION

1.1 Hamiltonians describing systems of electrons

This thesis focuses on electronic structure problems. We describe a molecule by the non-relativistic Schrödinger equation in the Born-Oppenheimer approximation. We are interested in the quantum configurations of the electrons for a given nuclear arrangement. The behavior of the electrons, from which one can deduce useful physical and chemical properties, is well-modeled by an electronic Hamiltonian.

1.1.1 The Hamiltonian for spinless systems

In atomic units, the Hamiltonian describing a spinless system of N electrons is of the form

$$H_N(V) := \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i \right) + \sum_{i=1}^{N} V(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{1.1}$$

where Δ_i denotes the Laplacian operator with respect to the i-th spatial component. The first term of (1.1) corresponds to the kinetic energy. The second term of (1.1) represents the external potential. For molecular systems, this potential is the classical Coulomb potential generated by the nuclei

$$V(\mathbf{r}) = \sum_{k=1}^{M} \frac{-z_k}{|\mathbf{r} - \mathbf{R}_k|}, \tag{1.2}$$

where $\mathbf{R}_k \in \mathbb{R}^3$ denotes the location of the k-th nucleus and $z_k \in \mathbb{N}^*$ its charge. We denote by $Z := \sum_{k=1}^{M} z_k$ the total nuclear charge of the system. The last term of (1.1) is the electron-electron Coulomb repulsion. The Hamiltonian $H_N(V)$ acts on the N-fermionic Hilbert space

$$\bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}) = \left\{ \Psi \in L^2(\mathbb{R}^{3N}, \mathbb{C}),\ \forall p \in S_N,\ \Psi(\mathbf{r}_{p(1)}, \ldots, \mathbf{r}_{p(N)}) = \epsilon(p)\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \right\}, \tag{1.3}$$

endowed with the natural $L^2(\mathbb{R}^{3N}, \mathbb{C})$ inner product. In (1.3), S_N denotes the set of permutations of $[\![1, \ldots, N]\!]$, and $\epsilon(p)$ the parity of the permutation p. The permutation condition appearing in (1.3) is referred to as the Pauli principle, and comes from the fact that electrons are fermions.

Theorem 1.1. *Suppose that V is of the form (1.2) with $N \leq Z$, and let*

$$D(H_N) := \left\{ \Psi \in \bigwedge^N L^2(\mathbb{R}^3),\ \Delta\Psi \in L^2(\mathbb{R}^{3N}) \right\},$$

where Δ denotes the Laplacian operator with respect to all $3N$ variables. Then the operator $H_N(V)$ with domain $D(H_N)$ is self-adjoint, and its spectrum is as follows:

- *the spectrum is bounded from below;*
- *there exists $\Sigma_N \in \mathbb{R}$ such that the essential spectrum of $H_N(V)$ is $\sigma_{\text{ess}}(H_N(V)) = [\Sigma_N, +\infty)$;*
- *there exist an infinity of eigenvalues below Σ_N, which accumulate only at Σ_N. All these eigenvalues are of finite multiplicities [Zhi60];*
- *if $N \geq 2$, then $\Sigma_N = E^0_{N-1}$ (HVZ Theorem [Hun66, vW64, Zhi60]).*

We denote by $E^0_N(V) \leq E^1_N(V) \leq E^2_N(V) \leq \cdots$ (or simply $E^0_N \leq E^1_N \leq E^2_N \leq \cdots$ when no confusion is possible) the eigenvalues of $H_N(V)$ below Σ_N, ranked in increasing order, counting multiplicities. With this notation, $E^0_N(V)$ is the *ground state energy* of $H_N(V)$ (and a corresponding eigenvector is called a *ground state wave-function*), and $E^k_N(V)$ is the k-th *excited state energy* of $H_N(V)$ (and a corresponding eigenvector is called an *excited state wave-function*). The spectrum of H_N is represented in Figure 1.1.

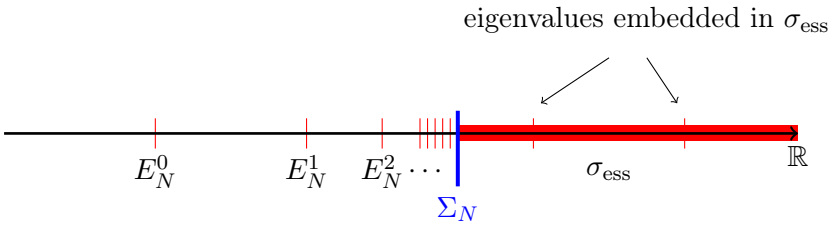

Figure 1.1 – The spectrum of $H_N(V)$.

The set of admissible wave-functions, also called the set of *pure-states*, is the set of normalized wave-functions with finite kinetic energy, namely

$$\mathcal{W}_N := \left\{ \Psi \in \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}),\ \|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1,\ \|\nabla\Psi\|_{L^2(\mathbb{R}^{3N})} < \infty \right\}, \tag{1.4}$$

where ∇ is the gradient with respect to all $3N$ variables. With this notation, $|\Psi|^2(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ represents the density of probability that the N (indistinguishable) electrons are located at $(\mathbf{r}_1, \ldots, \mathbf{r}_N)$.

The ground state energy $E^0_N(V)$ is also the solution of the minimization problem (we adopt Dirac's bra-ket notation)

$$E^0_N(V) := \inf \left\{ \langle \Psi | H_N(V) | \Psi \rangle,\ \Psi \in \mathcal{W}_N \right\}. \tag{1.5}$$

1.1.2 The Hamiltonian for spin-polarized systems

In this thesis, systems of electrons subjected to magnetic fields will also be studied. A good model to describe such systems is the Schrödinger-Pauli Hamiltonian, which reads, in atomic units,

$$H^{\text{full-SP}}_N(V, \mathbf{A}) := \left(\sum_{i=1}^N \left(\frac{1}{2} \left| -\mathrm{i}\nabla_i + \mathbf{A}(\mathbf{r}_i) \right|^2 + V(\mathbf{r}_i) \right) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \mathbb{I}_2 - \mu \sum_{i=1}^N \mathbf{B}(\mathbf{r}_i) \cdot \sigma_i, \tag{1.6}$$

where $\mathbb{I}_2$ is the 2×2 identity matrix, $\mathbf{A}$ is the external magnetic vector potential, and $\mathbf{B} := \mathbf{curl}\ \mathbf{A}$ is the external magnetic field. The constant μ is the Bohr magneton (whose value is $\mu = 1/2$ in atomic units). The $\mathbf{B} \cdot \sigma$ term in (1.6) is the Zeeman term, also called the Stern-Gerlach term, where σ_i contains the Pauli matrices acting on the i-th spin variable:

$$\sigma_i := (\sigma_{xi}, \sigma_{yi}, \sigma_{zi}) = \left(\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_i, \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}_i, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_i \right).$$

The Schrödinger-Pauli Hamiltonian $H_N^{\text{full-SP}}(V, \mathbf{A})$ acts on the N-fermionic Hilbert space

$$\begin{aligned} \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}^2) := \Big\{ & \Psi(\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N),\ \mathbf{r}_i \in \mathbb{R}^3, s_i \in \{\uparrow, \downarrow\}, \\ & \sum_{s_1, \cdots, s_N \in \{\uparrow,\downarrow\}^N} \int_{\mathbb{R}^{3N}} |\Psi(\mathbf{r}_1, s_1, \dots)|^2 \, \mathrm{d}\mathbf{r}_1 \dots \mathrm{d}\mathbf{r}_N < \infty, \\ & \forall p \in S_N, \quad \Psi(\mathbf{r}_{p(1)}, s_{p(1)}, \dots) = \epsilon(p) \Psi(\mathbf{r}_1, s_1, \dots) \Big\}. \end{aligned}$$

endowed with the inner product

$$\langle \Psi_1 | \Psi_2 \rangle = \sum_{(s_1, \cdots s_N) \in \{\uparrow,\downarrow\}^N} \int_{\mathbb{R}^{3N}} \overline{\Psi_1(\mathbf{r}_1, s_1, \dots)} \Psi_2(\mathbf{r}_1, s_1, \dots) \, \mathrm{d}\mathbf{r}_1 \cdots \mathrm{d}\mathbf{r}_N.$$

Here $\mathbf{r}_i \in \mathbb{R}^3$ denotes the position of the i-th electron, and $s_i \in \{\uparrow, \downarrow\}$ denotes its spin.

In this thesis, we focus on a simplified version of the Schrödinger-Pauli Hamiltonian that we describe now. Note that the external magnetic vector potential $\mathbf{A}$ in (1.6) acts on the spatial coordinates of the electrons, while the magnetic field $\mathbf{B}$ acts on the spin of the electrons. These two effects are of different nature, so that it is convenient to relax the constraint $\mathbf{B} = \mathbf{curl}\ \mathbf{A}$, and consider that the fields $\mathbf{A}$ and $\mathbf{B}$ are independent. Then, by setting $\mathbf{A} = \mathbf{0}$, which amounts to neglecting orbital magnetism effects, we find the simplified Schrödinger-Pauli Hamiltonian

$$H_N^{SP}(V, \mathbf{B}) := \sum_{i=1}^N \left(-\frac{1}{2}\Delta_i + V(\mathbf{r}_i) \right) \mathbb{I}_2 - \mu \sum_{i=1}^N \mathbf{B}(\mathbf{r}_i) \cdot \sigma_i + \sum_{1 \le i < j \le N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \mathbb{I}_2, \tag{1.7}$$

which acts on $\bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}^2)$. If the external potential V is of the form (1.2) and the magnetic field $\mathbf{B}$ is in $\left(L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)\right)^3$ and vanishes at infinity, results similar to the ones of Theorem 1.1 hold true [Gon15a]. We denote by $E_N^0(V, \mathbf{B}) \le E_N^1(V, \mathbf{B}) \le \dots$ the eigenvalues below the essential spectrum, ranked in increasing order and counting multiplicities. With this notation, $E_N^0(V, \mathbf{B})$ is the ground state energy of the system, and $E_N^k(V, \mathbf{B})$ is the k-th excited state energy. As in (1.5), it holds that

$$E_N^0(V, \mathbf{B}) := \inf \left\{ \left\langle \Psi \left| H_N^{\text{SP}}(V, \mathbf{B}) \right| \Psi \right\rangle,\ \Psi \in \mathcal{W}_N^{\text{spin}} \right\}, \tag{1.8}$$

where $\mathcal{W}_N^{\text{spin}}$ is the set of admissible spin-polarized wave-functions, defined by

$$\mathcal{W}_N^{\text{spin}} := \left\{ \Psi \in \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}^2),\ \|\Psi\|_{L^2((\mathbb{R}^3, \mathbb{C}^2)^N)} = 1,\ \|\nabla \Psi\|_{L^2((\mathbb{R}^3, \mathbb{C}^2)^N)} < \infty \right\}.$$

1.1.3 Problematics

As Dirac wrote in 1929 [Dir29],

> *The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.*

This problem is now known as the *curse of dimensionality*, and refers to the fact that the state space for problem (1.5) and (1.8) is of dimension $3N$, where N is the total number of electrons in the system into consideration. The state-space cannot be represented numerically whenever the number of electrons is "too large". Computing the solution of (1.5) for a small system like the water molecule H_2O ($N = 10$ electrons) is already unfeasible in practice. This makes the full problems (1.5) and (1.8) impossible to tackle numerically for most systems of interest.

The purpose of this thesis is to present some of the approximations that were proposed in the last decades in the physics and chemistry communities to simplify these problems, and to study the mathematical properties of the resulting models.

1.2 Density Functional Theory

1.2.1 Derivation of Density Functional Theory

We recall in this section how Density Functional Theory (DFT) is derived. Spin-unpolarized DFT was introduced in 1964 by Hohenberg and Kohn [HK64] and is a very popular tool in modern quantum chemistry. The goal of Density Functional Theory (DFT) is to calculate the ground state energy and the ground state density of an electronic system. It transforms the high-dimensional linear problems (1.5) or (1.8) into a nonlinear low-dimensional problem. While DFT has been extensively studied for spin-unpolarized or spinless Hamiltonians of the form (1.1), its counterpart for spin-polarized Hamiltonian of the form (1.7) (with the Zeeman term included) received much less attention. When spin is included, we use the name "Spin-DFT", or "SDFT". We present SDFT by following the constraint-search approach by Levy [Lev79], Valone [Val80] and Lieb [Lie83]. In this section we consider the Schrödinger-Pauli Hamiltonian $H_N^{\mathrm{SP}}(V, \mathbf{B})$ introduced in (1.7), and our goal is to solve (1.8).

The energy of an admissible normalized wave-function $\Psi \in \mathcal{W}_N^{\mathrm{spin}}$ is $\langle \Psi \left| H_N^{\mathrm{SP}}(V, \mathbf{B}) \right| \Psi \rangle$. By introducing the N-body density matrix $\Gamma_\Psi = |\Psi\rangle\langle\Psi|$, which is the orthogonal projector onto $\{\mathbb{C}\Psi\}$ in $\bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}^2)$, this quantity is also equal to $\mathrm{Tr}\left[H_N^{\mathrm{SP}}(V, \mathbf{B})\Gamma_\Psi\right]$. The set of *pure-state* N-body density matrices is

$$G_N^{\mathrm{pure}} := \left\{ \Gamma_\Psi,\ \Psi \in \mathcal{W}_N^{\mathrm{spin}} \right\},$$

and (1.8) can be recast into

$$E_N^0(V, \mathbf{B}) = \inf \left\{ \mathrm{Tr}\left[H_N^{\mathrm{SP}}(V, \mathbf{B})\Gamma\right],\ \Gamma \in G_N^{\mathrm{pure}} \right\}.$$

This is a minimization problem of a linear functional on a (bounded) set. It is therefore natural to introduce the set of *mixed-state* N-body density matrices G_N^{mixed}, defined as the convex hull of G_N^{pure}. Naturally, it holds that

$$E_N^0(V, \mathbf{B}) = \inf \left\{ \mathrm{Tr}\left[H_N^{\mathrm{SP}}(V, \mathbf{B})\Gamma\right],\ \Gamma \in G_N^{\mathrm{pure}} \right\} = \inf \left\{ \mathrm{Tr}\left[H_N^{\mathrm{SP}}(V, \mathbf{B})\Gamma\right],\ \Gamma \in G_N^{\mathrm{mixed}} \right\}. \tag{1.9}$$

For $\Gamma \in G_N^{\mathrm{mixed}}$ with Schwartz kernel $\Gamma(\mathbf{r}_1, s_1, \ldots, \mathbf{r}_N, s_N; \mathbf{r}'_1, s'_1, \ldots, \mathbf{r}'_N, s'_N)$, we introduce the spin-density 2×2 matrix

$$R_\Gamma(\mathbf{r}) := \begin{pmatrix} \rho_\Gamma^{\uparrow\uparrow} & \rho_\Gamma^{\uparrow\downarrow} \\ \rho_\Gamma^{\downarrow\uparrow} & \rho_\Gamma^{\downarrow\downarrow} \end{pmatrix}(\mathbf{r}),$$

where, for $\alpha, \beta \in \{\uparrow, \downarrow\}^2$, we set

$$\rho_\Gamma^{\alpha\beta}(\mathbf{r}) := N \sum_{\vec{s}\in\{\uparrow,\downarrow\}^{(N-1)}} \int_{\mathbb{R}^{3(N-1)}} \Gamma(\mathbf{r}, \alpha, \vec{\mathbf{z}}, \vec{s}; \mathbf{r}, \beta, \vec{\mathbf{z}}, \vec{s})\, \mathrm{d}\vec{\mathbf{z}}. \tag{1.10}$$

The key-point of SDFT is to notice that, for $\Gamma \in G_N^{\mathrm{mixed}}$, it holds that

$$\mathrm{Tr}\left[H_N^{\mathrm{SP}}(V, \mathbf{B})\Gamma\right] = \mathrm{Tr}\left[H_N^{\mathrm{SP}}(0, \mathbf{0})\Gamma\right] + \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}\left[\begin{pmatrix} V - \mu B_z & -\mu B_x + \mathrm{i}\mu B_y \\ -\mu B_x - \mathrm{i}\mu B_y & V + \mu B_z \end{pmatrix} R_\Gamma\right]. \tag{1.11}$$

Note that the first term of (1.11) no longer depends on the external potential and field. In the sequel, we denote by

$$U(V, \mathbf{B}) := \begin{pmatrix} V - \mu B_z & -\mu B_x + \mathrm{i}\mu B_y \\ -\mu B_x - \mathrm{i}\mu B_y & V + \mu B_z \end{pmatrix} \tag{1.12}$$

the matrix which contains all the external data. Let X represents either the word "pure" or the word "mixed". From (1.9) and (1.11), we get the so-called *constrained-search* equality

$$E_N^0(V, \mathbf{B}) = \inf_{\Gamma\in G_N^X} \left\{\mathrm{Tr}\left[H_N^{\mathrm{SP}}(V, \mathbf{B})\Gamma\right]\right\} = \inf_{R\in\mathcal{J}_N^X} \left\{\int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}\left[U(V, \mathbf{B})R\right] + F^X(R)\right\}, \tag{1.13}$$

where $\mathcal{J}_N^X$ is the set of (pure-state or mixed-state) spin-density 2×2 matrices, defined by

$$\mathcal{J}_N^X := \left\{R_\Gamma,\ \Gamma \in G_N^X\right\}, \tag{1.14}$$

and the function F^X is defined by the formula

$$F^X(R) := \inf\left\{\mathrm{Tr}\left[H_N^{\mathrm{SP}}(0, \mathbf{0})\Gamma\right],\ \Gamma \in G_N^X,\ R_\Gamma = R\right\}.$$

Let us compare (1.8) with (1.13). Problem (1.8) is linear, but suffers from the curse of dimensionality, while (1.13) is a minimization problem on a low-dimensional space, but is nonlinear. The name SDFT comes from the fact that (1.13) is the minimization of a functional which depends only on the spin-density 2×2 matrix R.

In order to solve (1.13), one needs a closed expression for both $\mathcal{J}_N^X$ and F^X. Characterizing the sets $\mathcal{J}_N^{\mathrm{pure}}$ and $\mathcal{J}_N^{\mathrm{mixed}}$ is the *N-representability problem*, and will be discussed in Section 1.2.2. As far as F^X is concerned, there is no convenient formula for it. Actually, it was proved that there exists potentials V such that the calculation of $E_N^0(V, \mathbf{0})$ at a polynomial accuracy is QMA[1]-hard [SV09]. This implies that the calculation of F^X at a polynomial accuracy is also QMA-hard. Fortunately, there exist very good computable approximations of F^X that give results in good agreement with physical experiments for most interesting physical systems. We will discuss one of these approximations in Section 1.2.3.

1.2.2 The N-representability problem

The N-representability problem is concerned with the characterization of the sets $\mathcal{J}_N^{\mathrm{pure}}$ and $\mathcal{J}_N^{\mathrm{mixed}}$ defined in (1.14). The first results on the N-representability problem were given by Gilbert [Gil75], Harriman [Har81] and Lieb [Lie83]. In these articles, the authors only considered the spin-unpolarized case, which amounts to setting $\mathbf{B} = \mathbf{0}$. In this case, it holds that

$$\mathrm{tr}_{\mathbb{C}^2}\left[U(V, \mathbf{0})R\right] = V\rho_R,$$

[1] QMA stands for Quantum Merlin-Arthur. QMA-hard is the quantum version of NP-hard.

where $\rho_R = \rho_R^{\uparrow\uparrow} + \rho_R^{\downarrow\downarrow}$ is the total electronic density. In the sequel, we denote by $\rho_\Gamma = \rho_{R_\Gamma} = \rho_R$ when no confusion is possible. The constrained-search method (1.13) in this case can be recast into

$$E_N^0(V, \mathbf{0}) = \inf_{\rho \in \mathcal{I}_N^X} \left\{ \int_{\mathbb{R}^3} V\rho + F_1^X(\rho) \right\},$$

with

$$\mathcal{I}_N^X = \left\{ \rho_\Gamma,\ \Gamma \in G_N^X \right\} \quad \text{and} \quad F_1^X(\rho) = \inf \left\{ \mathrm{Tr}\left[H_N(0,\mathbf{0})\Gamma \right],\ \Gamma \in G_N^X,\ \rho_\Gamma = \rho \right\}.$$

The N-representability problem in the spin-unpolarized case is therefore concerned with the characterization of $\mathcal{I}_N^{\mathrm{pure}}$ and of $\mathcal{I}_N^{\mathrm{mixed}}$.

Theorem 1.2 (Gilbert, Harriman, Lieb)**.** *For all $N \in \mathbb{N}^*$, it holds that*

$$\mathcal{I}_N^{\mathrm{pure}} = \mathcal{I}_N^{\mathrm{mixed}} = \mathcal{I}_N := \left\{ \rho \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3),\ \rho \geq 0,\ \int_{\mathbb{R}^3} \rho = N,\ \sqrt{\rho} \in H^1(\mathbb{R}^3) \right\}. \quad (1.15)$$

When the magnetic field is not null, we need to characterize the sets $\mathcal{J}_N^{\mathrm{pure}}$ and $\mathcal{J}_N^{\mathrm{mixed}}$ defined in (1.14). This problem was addressed, but left open, in the work by von Barth and Hedin [vBH72]. In the sequel, $\mathcal{M}_{2\times 2}(E)$ denotes the set of 2×2 matrices with coefficients in the Banach space E. We introduce

$$\mathcal{C}_N := \left\{ R \in \mathcal{M}_{2\times 2}(L^1(\mathbb{R}^3, \mathbb{C})), R^* = R, R \geq 0, \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}[R] = N, \sqrt{R} \in \mathcal{M}_{2\times 2}(H^1(\mathbb{R}^3, \mathbb{C})) \right\}, \quad (1.16)$$

and $\mathcal{C}_N^0 := \{R \in \mathcal{C}_N,\ \det R \equiv 0\}$. In Chapter 2, we following theorem is proved.

Theorem 1.3 (DG)**.**
Case *$N = 1$: It holds that*

$$\mathcal{J}_1^{\mathrm{pure}} = \mathcal{C}_1^0 \quad \textit{and} \quad \mathcal{J}_1^{\mathrm{mixed}} = \mathcal{C}_1.$$

Case *$N \geq 2$: For all $N \geq 2$, it holds that*

$$\mathcal{J}_N^{\mathrm{pure}} = \mathcal{J}_N^{\mathrm{mixed}} = \mathcal{C}_N.$$

Since G_N^X is convex and the map $\Gamma \mapsto R_\Gamma$ is linear, we deduce that the set $\mathcal{C}_N$ defined in (1.16) is convex (which is not obvious from its definition). Comparing (1.15) and (1.16), we see that Theorem 1.3 is a natural extension of Theorem 1.2.

Representability with paramagnetic-current.
The version of DFT dealing with both charge and current densities is called Current-(Spin)-DFT, or C(S)DFT [VR88]. For $\Gamma \in G_N^{\mathrm{mixed}}$, we introduce the paramagnetic current $\mathbf{j}_\Gamma = \mathbf{j}_\Gamma^\uparrow + \mathbf{j}_\Gamma^\downarrow$ where

$$\forall \alpha \in \{\uparrow, \downarrow\},\quad \mathbf{j}_\Gamma^\alpha = \mathrm{Im}\left(N \sum_{\vec{s} \in \{\uparrow,\downarrow\}^{N-1}} \int_{\mathbb{R}^{3(N-1)}} \nabla_{\mathbf{r}'} \Gamma(\mathbf{r}, \alpha, \vec{\mathbf{z}}, \vec{s}; \mathbf{r}', \alpha, \vec{\mathbf{z}}, \vec{s}) \Big|_{\mathbf{r}'=\mathbf{r}} \mathrm{d}\vec{\mathbf{z}} \right).$$

This current appears when performing the constrained-search method (see (1.13)) on the full Schrödinger-Pauli Hamiltonian $H_N^{\text{full-SP}}(V, \mathbf{A})$ defined in (1.6). More specifically, let us assume that $\mathbf{A}$ is smooth enough so that the domain of $H_N^{\text{full-SP}}(V, \mathbf{A})$ is exactly the one of $H_N^{\text{full-SP}}(V, \mathbf{0})$. The constrained-search method in this case leads to

$$E_N^0(V, \mathbf{A}) = \inf_{(R,\mathbf{j}) \in \mathcal{K}_N^X} \left\{ \int_{\mathbb{R}^3} \left(\mathrm{tr}_{\mathbb{C}^2}[U(R, \mathbf{B})R] + \frac{|\mathbf{A}|^2}{2}\rho + \mathbf{A} \cdot \mathbf{j} \right) + F_2^X(R, \mathbf{j}) \right\},$$

where $U(V, \mathbf{B})$ was defined in (1.12),

$$\mathcal{K}_N^X = \left\{(R_\Gamma, \mathbf{j}_\Gamma),\ \Gamma \in G_N^X\right\}$$

is the set we would like to characterize, and

$$F_2^X(R, \mathbf{j}) = \inf\left\{\mathrm{Tr}\left[H_N^{\text{full-SP}}(0, \mathbf{0})\Gamma\right],\ \Gamma \in G_N^X, (R_\Gamma, \mathbf{j}_\Gamma) = (R, \mathbf{j})\right\},$$

is an unknown functional. In C(S)DFT, the N-representability problem is concerned with the characterization of $\mathcal{K}_N^{\text{pure}}$ and $\mathcal{K}_N^{\text{mixed}}$. Giving an exact expression is known to be very difficult, but to give (mild) sufficient conditions for a pair $(R, \mathbf{j})$ to be representable is possible. In [LS13], Lieb and Schrader studied the spin-unpolarized case, and gave such conditions for the representability of a pair $(\rho, \mathbf{j})$, where ρ is the total electronic density. They proved the following result, valid for $N \geq 4$. Recall that $\mathcal{I}_N$ was defined in (1.15).

Theorem 1.4 (Lieb, Schrader)**.** *Suppose $N \geq 4$. A sufficient set of conditions for a pair $(\rho, \mathbf{j})$ to be pure-state N-representable is that, on the one hand,*

$$\rho \in \mathcal{I}_N, \quad \rho^{-1}|\mathbf{j}|^2 \in L^1(\mathbb{R}^3), \tag{1.17}$$

and that, on the other hand, there exists $\delta > 0$ such that

$$\sup_{\mathbf{r}\in\mathbb{R}^3} f(\mathbf{r})^{(1+\delta)/2}\big(|\mathbf{w}(\mathbf{r})| + |\nabla\mathbf{w}(\mathbf{r})|\big) < \infty, \tag{1.18}$$

where $\mathbf{w} := \boldsymbol{curl}\,(\rho^{-1}\mathbf{j})$ is the vorticity, and $f(\mathbf{r}) := (1 + (r_1)^2)(1 + (r_2)^2)(1 + (r_3)^2)$.

The conditions in (1.17) are necessary conditions, and the condition (1.18) is very mild. By adapting their proof to the spin-polarized case, we were able to prove a similar result, under the condition $N \geq 12$ (see Chapter 2). Recall that $\mathcal{C}_N$ was defined in (1.16).

Theorem 1.5 (DG)**.** *Suppose $N \geq 12$. A sufficient set of conditions for a pair $(R, \mathbf{j})$ to be pure-state N-representable is that, on the one hand,*

$$R \in \mathcal{C}_N, \quad \rho_R^{-1}|\mathbf{j}|^2 \in L^1(\mathbb{R}^3),$$

and that, on the other hand, there exists $\delta > 0$ such that

$$\sup_{\mathbf{r}\in\mathbb{R}^3} f(\mathbf{r})^{(1+\delta)/2}\big(|\mathbf{w}(\mathbf{r})| + |\nabla\mathbf{w}(\mathbf{r})|\big) < \infty.$$

1.2.3 The Local Spin-Density Approximation

We now turn to the question of how to approximate the functional $F^X(R)$ appearing in (1.13). In this thesis, we consider the approximation of $F^{\text{mixed}}(R)$. In spin-unpolarized models, the first successful approximation, called the *Local Density Approximation* (LDA) was introduced by Kohn and Sham [KS65], and is still broadly used nowadays. While in their article, the authors gave some clues on how to adapt their method to spin-polarized systems, the corresponding theory was pioneered by von Barth and Hedin [vBH72] and is known as the Local Spin-Density Approximation (LSDA).

For a mixed-state $\Gamma \in G_N^{\text{mixed}}$, we introduce the corresponding one-body spin-density matrix

$$\gamma_\Gamma := \begin{pmatrix} \gamma_\Gamma^{\uparrow\uparrow} & \gamma_\Gamma^{\uparrow\downarrow} \\ \gamma_\Gamma^{\downarrow\uparrow} & \gamma_\Gamma^{\downarrow\downarrow} \end{pmatrix},$$

where

$$\gamma_\Gamma^{\alpha\beta}(\mathbf{r},\mathbf{r}') := N \sum_{\vec{s}\in\{\uparrow,\downarrow\}^{N-1}} \int_{\mathbb{R}^{3(N-1)}} \Gamma(\mathbf{r},\alpha,\vec{\mathbf{z}},\vec{s};\mathbf{r}',\beta,\vec{\mathbf{z}},\vec{s})\,\mathrm{d}\vec{\mathbf{z}}. \tag{1.19}$$

Comparing (1.10) and (1.19), we see that $R_\Gamma(\mathbf{r}) = \gamma_\Gamma(\mathbf{r},\mathbf{r})$, so that R_Γ depends on Γ only through γ_Γ. We will write R_γ instead of R_Γ when no confusion is possible. Likewise, the total electronic density of a state $\Gamma \in G_N^{\text{mixed}}$ will be denoted by $\rho_\Gamma = \rho_R = \rho_\gamma$.

The set of mixed-state one-body spin-density 2×2 matrices is

$$\mathcal{P}_N := \{\gamma_\Gamma,\ \Gamma \in G_N^{\text{mixed}}\}.$$

Identifying the kernel $\gamma(\mathbf{r},\mathbf{r}')$ with the corresponding operator of $\mathcal{S}(L^2(\mathbb{R}^3,\mathbb{C}^2))$, where $\mathcal{S}(\mathcal{H})$ denotes the set of bounded self-adjoint operators acting on the Hilbert space $\mathcal{H}$, Coleman [Col63] proved that

$$\mathcal{P}_N = \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3,\mathbb{C}^2)),\ 0\le\gamma\le 1,\ \mathrm{Tr}(\gamma)=N,\ \mathrm{Tr}(-\Delta\gamma)<\infty\right\}.$$

Physically speaking, this is the set of one-body density matrices of systems with N-electrons ($\mathrm{Tr}(\gamma)=N$), satisfying the Pauli principle ($0\le\gamma\le 1$), and with finite kinetic energy ($\mathrm{Tr}(-\Delta\gamma)<\infty$). In a similar way, we can define, for $\lambda>0$,

$$\mathcal{P}_\lambda := \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3,\mathbb{C}^2)),\ 0\le\gamma\le 1,\ \mathrm{Tr}(\gamma)=\lambda,\ \mathrm{Tr}(-\Delta\gamma)<\infty\right\}. \tag{1.20}$$

We also define

$$\mathcal{J}_\lambda^{\text{mixed}} := \{R_\gamma,\ \gamma\in\mathcal{P}_\lambda\} \quad \text{and} \quad \mathcal{I}_\lambda^{\text{mixed}} := \{\rho_\gamma,\ \gamma\in\mathcal{P}_\lambda\}.$$

The sets $\mathcal{J}_\lambda^{\text{mixed}}$ and $\mathcal{I}_\lambda^{\text{mixed}}$ have expressions similar to $\mathcal{J}_N^{\text{mixed}}$ and $\mathcal{I}_N^{\text{mixed}}$ (see Theorem 1.5 and (1.15) respectively). The idea of Kohn and Sham [KS65], then adapted by von Barth and Hedin [vBH72] to the spin-unpolarized setting, is to split $F^{\text{mixed}}(R)$ into three contributions

$$F^{\text{mixed}}(R) = T_{\text{KS}}(R) + J(\rho_R) + E_{\text{xc}}(R). \tag{1.21}$$

The first term T_{KS} represents the kinetic energy of a non-interacting electronic system. It reads, in the one-body formalism,

$$\forall R\in\mathcal{J}_\lambda^{\text{mixed}},\quad T_{\text{KS}}(R) := \inf\left\{\frac{1}{2}\mathrm{Tr}\left(-\Delta\gamma\right),\ \gamma\in\mathcal{P}_\lambda,\ R_\gamma = R\right\}.$$

The second term of (1.21) is the Hartree term, defined by

$$\forall\rho\in\mathcal{I}_\lambda^{\text{mixed}},\quad J(\rho) := \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'.$$

Finally, the last term of (1.21) is the exchange-correlation functional defined by

$$E_{\text{xc}}(R) := F^{\text{mixed}}(R) - T_{\text{KS}}(R) - J(\rho_R).$$

Since F^{mixed} is a non-explicit functional, E_{xc} is also a non-explicit functional. It is however possible to construct explicit approximations of E_{xc} giving rise to accurate predictions for the ground state energies of most molecular systems [ED11]. In the Local Spin-Density Approximation derived by von Barth and Hedin [vBH72], it reads

$$E_{\text{xc}}(R) \approx E_{\text{xc}}^{\text{LSDA}}(\rho^+,\rho^-) := \frac{1}{2}\left[E_{\text{xc}}^{\text{LDA}}(2\rho^+) + E_{\text{xc}}^{\text{LDA}}(2\rho^-)\right], \tag{1.22}$$

where $\rho^{+/-}$ are the two eigenvalues of the spin-density 2×2 matrix R, and $E_{\mathrm{xc}}^{\mathrm{LDA}}$ is the standard LDA exchange-correlation functional in the spin-unpolarized case [KS65], of the form

$$E_{\mathrm{xc}}^{\mathrm{LDA}}(\rho) := \int_{\mathbb{R}^3} g(\rho(\mathbf{r}))\, \mathrm{d}\mathbf{r}. \tag{1.23}$$

For all $\overline{\rho} \in \mathbb{R}^+$, the real value $g(\overline{\rho})$ is an approximation of the exchange-correlation energy density of the uniform electron gas with density $\overline{\rho}$. Several functions g are available (VWS [VWN80], PZ81 [PZ81], CP [CP82], PW92 [PW92], ...), which all satisfy the same asymptotic conditions for low and high densities. The minimization problem (1.13) with the approximation (1.22)-(1.23) can be rewritten, using one-body density matrices, as a variational problem of the form

$$E_\lambda^0 := \inf \left\{ \mathcal{E}(\gamma),\ \gamma \in \mathcal{P}_\lambda \right\}, \tag{1.24}$$

where

$$\mathcal{E}(\gamma) = \frac{1}{2}\mathrm{Tr}\left(-\Delta\gamma^{\uparrow\uparrow}\right) + \frac{1}{2}\mathrm{Tr}\left(-\Delta\gamma^{\downarrow\downarrow}\right) + J(\rho_\gamma) + \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}\left[U R_\gamma\right] + E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_\gamma^+, \rho_\gamma^-).$$

We recall that the 2×2 matrix U contains all the external data, *i.e.* the electric potential V and the magnetic field $\mathbf{B}$ (see (1.12)). The physical situation corresponds to $\lambda = N \in \mathbb{N}$, but as usual in variational problems set on the whole space, it is useful to relax the constraint $\mathrm{Tr}(\gamma) \in \mathbb{N}$ to allow the particles to escape to infinity.

The spin-unpolarized model corresponds to the situation where we impose γ to satisfy $\gamma^{\uparrow\uparrow} = \gamma^{\downarrow\downarrow}$ and $\gamma^{\uparrow\downarrow} = \gamma^{\downarrow\uparrow} = 0$. The resulting model was studied mathematically by Anantharaman and Cancès [AC09].

In Chapter 3, we prove the following theorem.

Theorem 1.6 (DG). *Under the following assumptions*

1/ the function g in (1.23) is of class $C^1(\mathbb{R}^+)$ and satisfies:

$$\begin{cases} g(0) = 0 \\ g' \leq 0 \\ \exists\ 0 < \beta^- \leq \beta^+ < \dfrac{2}{3}, \quad \displaystyle\sup_{\rho \in \mathbb{R}^+} \frac{|g'(\rho)|}{\rho^{\beta^-} + \rho^{\beta^+}} < \infty \\ \exists\ 1 \leq \alpha < \dfrac{3}{2}, \quad \displaystyle\limsup_{\rho \to 0^+} \frac{g(\rho)}{\rho^\alpha} < 0, \end{cases} \tag{1.25}$$

2/ all entries of U are in $L^{\frac{3}{2}+\epsilon}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ and vanish at infinity, and $V := \mathrm{tr}_{\mathbb{C}^2}(U)$ has the form (1.2),

the problem E_λ^0 defined in (1.24) has a minimizer whenever $\lambda \leq Z$.

This theorem is a generalization of the spin-unpolarized result [AC09]. In particular, the conditions (1.25) are the ones found in [AC09]. These conditions are satisfied for the usual choices of g mentioned above.

1.3 The GW approximation

The fourth chapter of this thesis is concerned with the GW approximation.[2] This method was introduced by Hedin [Hed65, HL70] and is a very successful method to calculate *electronic-excitation energies* for finite systems, or band gaps for crystalline structures. Together with

[2] GW is not an acronym: G denotes the Green's function and W the screened Coulomb operator.

Eric Cancès and Gabriel Stoltz, we gave a rigorous definition of the operators involved in the GW formalism, we reformulated the so-called GW^0 equations, and proved the existence of a solution in a perturbative regime.

While the density functional theory introduced in the previous section works well to calculate ground state energies, it fails to predict excitation properties of molecules, such as the electronic-excitation energies. In order to calculate such quantities, several approaches have been considered in the last decades [ORR02]. Among them are the time-dependent DFT (TDDFT) [MMN+12, MUN+06], wave-function methods [HJO14] such as Coupled-Cluster or full-CI, and Green's function methods. The GW method is part of the last category.

From now on, we work with spinless systems for simplicity: our starting N-body Hamiltonian is the one in (1.1).

1.3.1 Electronic-excitation energies and Green's functions

Let us consider an N-electron system modeled by a Hamiltonian of the form (1.1). We perform the following experiment (called *angle-resolved photoelectron spectroscopy*, or ARPES):

- we start from the N-electron system in its ground state, with energy E_N^0;
- we give the system some energy (photons) in order to rip an electron off.

After this experiment, we expect the system to relax in either the ground state or an excited state of the corresponding $(N-1)$-electron system (see Figure 1.2).

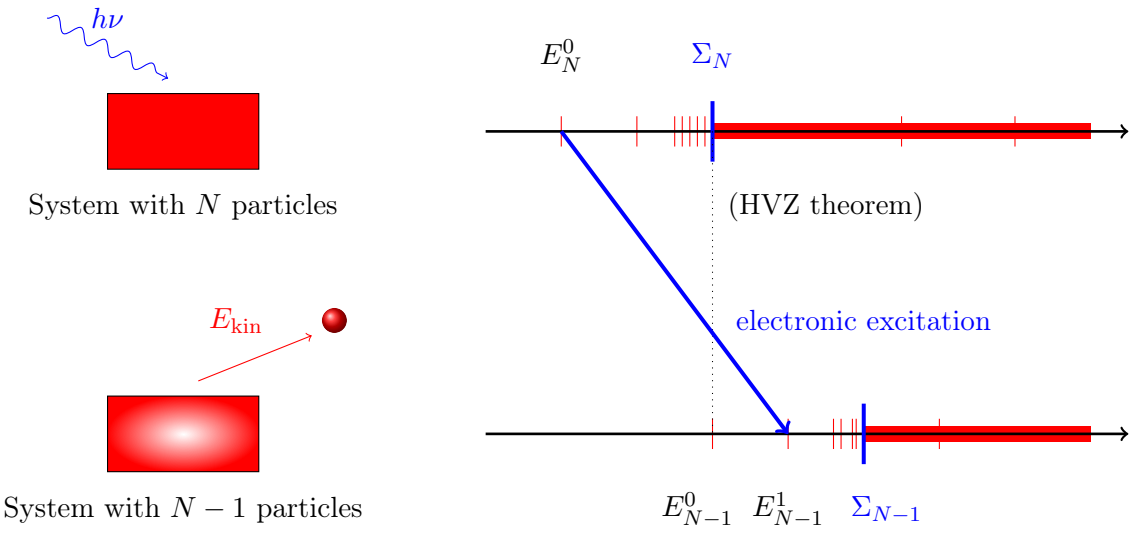

Figure 1.2 – Schematic view of an electronic excitation (here, loss of an electron). The system in the ground state of $H_N(V)$ goes to an excited state of $H_{N-1}(V)$.

One can also consider the experiment where the system absorbs an electron, and releases energy. With the notation introduced after Theorem 1.1, the quantities we would like to evaluate are

$$E_N^0 - E_{N+1}^k \quad \text{(gain of an electron)} \quad \text{and} \quad E_N^0 - E_{N-1}^k \quad \text{(loss of an electron)}, \tag{1.26}$$

called the *electronic-excitation energies* of the system. The electronic-excitation energies differ from the *optical-excitation energies*, which are quantities of the form $E_N^0 - E_N^k$ (same number of electrons). Note that we neglect the effects due to the relaxation of the nuclei: we impose the external potential V to be the same before and after the experiment.

We suppose in the sequel that V is of the form (1.2) with $N \geq 2$. We also make the following additional assumptions (we denote by $E_{N+1}^0 := \inf \sigma(H_{N+1})$):

- the ground state E_N^0 is a simple eigenvalue of H_N ;
- stability condition:[3] it holds $\boxed{2E_N^0 \leq E_{N+1}^0 + E_{N-1}^0.}$

The first assumption is a very standard one. The second assumption states that the *ionization energy* $E_{N-1}^0 - E_N^0 > 0$ is strictly greater than the *affinity energy* $E_N^0 - E_{N+1}^0 > 0$. It will be useful to "link" the problems with $N+1$, N and $N-1$ electrons. We denote by Ψ_N^0 the (real-valued) ground state of H_N.

In order to compute the electronic-excitation energies, we introduce the following natural sets

$$\begin{aligned} S_{\mathrm{p}} &:= \sigma(H_{N+1} - E_N^0) \quad \text{(particle electronic-excitation set)} \\ S_{\mathrm{h}} &:= \sigma(E_N^0 - H_{N-1}) \quad \text{(hole electronic-excitation set).} \end{aligned}$$

These sets are linked to the so-called particle and hole one-body Green's functions, that we define now. Since we are working with a variable number of electrons, it is natural to work in the Fock space

$$\mathbb{F} = \bigoplus_{N=0}^{\infty} \mathcal{H}_N, \quad \text{where} \quad \mathcal{H}_0 = \mathbb{C}, \quad \mathcal{H}_1 = L^2(\mathbb{R}^3, \mathbb{C}), \quad \mathcal{H}_N = \bigwedge^N \mathcal{H}_1.$$

The creation and annihilation operators $a^\dagger$ and a are bounded operators from $\mathcal{H}_1$ to $\mathcal{B}(\mathbb{F})$, where $\mathcal{B}(E)$ denotes the space of bounded operators from the Banach space E into itself. They satisfy

$$\forall \phi \in \mathcal{H}_1, \quad \forall N \in \mathbb{N}, \quad a^\dagger(\phi) : \mathcal{H}_N \to \mathcal{H}_{N+1}, \quad a(\phi) : \mathcal{H}_{N+1} \to \mathcal{H}_N, \quad a^\dagger(\phi) = (a(\phi))^*,$$

and the expression of a is given by

$$\forall \phi \in \mathcal{H}_1, \quad \forall \Psi_N \in \mathcal{H}_N, \quad \big(a(\phi)|\Psi_N\rangle\big)(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1}) = \sqrt{N} \int_{\mathbb{R}^3} \overline{\phi(\mathbf{r})} \Psi_N(\mathbf{r}, \mathbf{r}_1, \ldots, \mathbf{r}_{N-1}) \, \mathrm{d}\mathbf{r}.$$

When the creation and annihilation operators are evaluated on Ψ_N^0, we obtain the operators

$$\begin{array}{rccc} A_+^* : & \mathcal{H}_1 & \to & \mathcal{H}_{N+1} \\ & f & \mapsto & a^\dagger(f)|\Psi_N^0\rangle \end{array} \quad \text{and} \quad \begin{array}{rccc} A_- : & \mathcal{H}_1 & \to & \mathcal{H}_{N-1} \\ & f & \mapsto & a\left(\overline{f}\right)|\Psi_N^0\rangle \end{array}. \tag{1.27}$$

They satisfy $A_+^* \in \mathcal{B}(\mathcal{H}_1, \mathcal{H}_{N+1})$ and $A_- \in \mathcal{B}(\mathcal{H}_1, \mathcal{H}_{N-1})$. The adjoint of A_- is denoted by A_-^* and the one of A_+^* is denoted by $A_+ := \left(A_+^*\right)^*$. The one-body particle Green's function G_{p} and hole Green's function G_{h} are functions from the time domain $\mathbb{R}$ to $\mathcal{B}(\mathcal{H}_1)$, defined by

$$\forall \tau \in \mathbb{R}, \quad G_{\mathrm{p}}(\tau) := -\mathrm{i}\Theta(\tau) A_+ \mathrm{e}^{-\mathrm{i}\tau(H_{N+1} - E_N^0)} A_+^* \quad \text{(particle)}, \tag{1.28}$$

[3] The question "Is the stability condition always true for Coulomb systems?" is an open problem [BDS14, Part VII].

and

$$\forall \tau \in \mathbb{R}, \quad G_{\mathrm{h}}(\tau) := \mathrm{i}\Theta(-\tau) A_-^* \mathrm{e}^{\mathrm{i}\tau(H_{N-1}-E_N^0)} A_- \quad \text{(hole)}. \tag{1.29}$$

Here, Θ denotes the Heaviside function. Let us give a physical interpretation of the one-body particle Green's function G_{p}. From (1.27) and (1.28), we obtain

$$\forall f, g \in \mathcal{H}_1, \quad \langle g \,|G_{\mathrm{p}}(\tau)|\, f \rangle = -\mathrm{i}\Theta(\tau) \left\langle \Psi_N^0 \left| a(g) \mathrm{e}^{-\mathrm{i}\tau(H_{N+1}-E_N^0)} a^\dagger(f) \right| \Psi_N^0 \right\rangle,$$

which can be read as follows. We first start from the ground state with N electrons Ψ_N^0. We then add an electron in the "orbital" f, and let the system evolves with its $N+1$ electrons for some time $\tau > 0$. Finally, we remove the electron in the "orbital" g, and measure how close we are from the initial ground state Ψ_N^0. A similar interpretation can be given for the one-body hole Green's function.

The Green's functions are fundamental quantities in many-body perturbation theory. The hole Green's function contains a lot of useful information about the electronic system. For instance, by introducing the one-body density matrix $\gamma_N^0 \in \mathcal{B}(\mathcal{H}_1)$ with kernel

$$\gamma_N^0(\mathbf{r}, \mathbf{r}') := N \int_{\mathbb{R}^{3(N-1)}} \Psi_N^0(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)\, \Psi_N^0(\mathbf{r}', \mathbf{r}_2, \cdots, \mathbf{r}_N)\, \mathrm{d}\mathbf{r}_2 \cdots \mathrm{d}\mathbf{r}_N,$$

it can be checked that $\gamma_N^0 = -\mathrm{i}G_{\mathrm{h}}(0^-) = A_-^* A_-$. As a consequence, the electronic ground-state density

$$\rho_N^0(\mathbf{r}) := N \int_{\mathbb{R}^{3(N-1)}} \left|\Psi_N^0(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)\right|^2 \mathrm{d}\mathbf{r}_2 \cdots \mathrm{d}\mathbf{r}_N = \gamma_N^0(\mathbf{r}, \mathbf{r})$$

is a quantity encoded in the hole Green's function. The ground state energy E_N^0 can also be recovered from the hole Green's function via the Galiskii-Migdal formula [GM58]:

$$E_N^0 = \frac{1}{2} \mathrm{Tr}_{\mathcal{H}_1} \left[\left(\frac{d}{d\tau} - \mathrm{i} \left(-\frac{1}{2}\Delta + V \right) \right) G_{\mathrm{h}}(\tau) \Big|_{\tau=0^-} \right]. \tag{1.30}$$

Finally, it is possible to extract the particle and hole electronic-excitation sets from the Green's functions. To see this, we time-Fourier transform G_{p} and G_{h}. We use the following normalization for the time-Fourier transform:

$$\forall f \in L^1(\mathbb{R}, E), \quad E \text{ Banach space}, \quad [\mathcal{F}_T f](\omega) = \widehat{f}(\omega) = \int_{-\infty}^{+\infty} f(\tau)\, \mathrm{e}^{\mathrm{i}\omega\tau}\, \mathrm{d}\tau.$$

From the following equality, which holds in the negative Sobolev space $H^{-1}(\mathbb{R})$ for instance,

$$\widehat{\Theta}(\omega) = \pi\delta_0 + \mathrm{ip.v.}\left(\frac{1}{\omega}\right), \tag{1.31}$$

where p.v. is the Cauchy principal value and δ_0 is the Dirac distribution at the origin, we obtain

$$\widehat{G_{\mathrm{p}}} = A_+ \mathrm{p.v.}\left(\frac{1}{\cdot - (H_{N+1} - E_N^0)}\right) A_+^* - \mathrm{i}\left(\pi A_+ P^{H_{N+1}-E_N^0} A_+^*\right) \quad \text{in} \quad H^{-1}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)), \tag{1.32}$$

and

$$\widehat{G_{\mathrm{h}}} = A_-^* \mathrm{p.v.}\left(\frac{1}{\cdot - (E_N^0 - H_{N-1})}\right) A_- + \mathrm{i}\left(\pi A_-^* P^{E_N^0 - H_{N-1}} A_-\right) \quad \text{in} \quad H^{-1}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)), \tag{1.33}$$

where we denoted by $P_b^H := \mathbb{1}_b(H)$ the spectral projection on the Borelian $b \in \mathscr{B}(\mathbb{R})$ of the operator H (here $\mathscr{B}(\mathbb{R})$ denotes the Borel σ-algebra of $\mathbb{R}$). In the sequel, if A is a bounded operator on $\mathcal{H}_1$, we denote by $\operatorname{Re} A := \frac{1}{2}(A + A^*)$ its self-adjoint part (or real part), and by $\operatorname{Im} A := \frac{1}{2\mathrm{i}}(A - A^*)$ its skew-adjoint part (or imaginary part).

From (1.32) and (1.33), we see that the electronic-excitation sets S_h and S_p are linked to the imaginary part of the Green's functions (also called *spectral functions*, up to a multiplicative factor). More specifically, it holds that

$$S_\mathrm{p} \subset \operatorname{Supp}\left(\operatorname{Im}\widehat{G_\mathrm{p}}\right) \quad \text{and} \quad S_\mathrm{h} \subset \operatorname{Supp}\left(\operatorname{Im}\widehat{G_\mathrm{h}}\right).$$

From this we deduce two facts. First, we can indeed recover the electronic-excitation energies from the (time-Fourier transform of the) Green's functions. Then, we expect both $\widehat{G_\mathrm{p}}$ and $\widehat{G_\mathrm{h}}$ to be highly peaked (they are irregular distributions) which makes the mathematical analysis cumbersome and the numerical approximation of these operators quite difficult.

1.3.2 Analytic continuation and chemical potential

In order to work with more regular objects, we consider the analytical continuations of $\widehat{G_\mathrm{p}}$ and $\widehat{G_\mathrm{h}}$ in the complex plane. To give a flavor of the tools used to perform such an analytical continuation, we recall the Titchmarsh's theorem [Tit48] in its simplest form. In the sequel, we denote by $\mathbb{U} := \{z \in \mathbb{C},\ \operatorname{Im}(z) > 0\}$, and by $\mathbb{L} := \{z \in \mathbb{C},\ \operatorname{Im}(z) < 0\}$ the (strict) upper and lower half complex planes respectively. The Laplace transform of a function $f \in C_c^\infty(\mathbb{R})$ is[4]

$$\forall z \in \mathbb{C}, \quad \widetilde{f}(z) := \int_{\mathbb{R}} f(t)\mathrm{e}^{\mathrm{i}zt}\mathrm{d}t.$$

It can be extended in some distributional sense.

Theorem 1.7 (Titchmarsh's theorem in $L^2(\mathbb{R})$ [Tit48])**.** *Let $f \in L^2(\mathbb{R})$ and let $\widehat{f} \in L^2(\mathbb{R})$ be its time-Fourier transform. The following assertions are equivalent:*

(i) f is causal (i.e. $f(t) = 0$ for almost all $\tau < 0$) ;

(ii) there exists an analytic function F in the upper half-plane $\mathbb{U}$ satisfying

$$\sup_{\eta>0}\left(\int_{-\infty}^{+\infty} |F(\omega + \mathrm{i}\eta)|^2\,\mathrm{d}\omega\right) < \infty$$

and such that, $F(\cdot + \mathrm{i}\eta) \to \widehat{f}$ strongly in $L^2(\mathbb{R})$, as $\eta \to 0^+$;

If these assertions are satisfied, then the function F in (ii) is unique, and coincides with the Laplace transform $\widetilde{f}$ of f.

This theorem states that the function $\widehat{f}$ (which may be irregular) has a regular analytic continuation $\widetilde{f}$ in the strict upper half-plane $\mathbb{U}$, and that we can indeed recover $\widehat{f}$ from $\widetilde{f}$. A similar theorem holds true for anti-causal functions (*i.e.* $f(t) = 0$ for almost all $t < 0$) by changing $\mathbb{U}$ into $\mathbb{L}$.

[4] The Laplace transform is usually defined as

$$F(p) = \int_0^\infty f(\tau)\mathrm{e}^{-p\tau}\mathrm{d}\tau.$$

Our definition, which is better adapted to our setting, amounts to setting $z = \mathrm{i}p$.

In our case, the Laplace transforms of G_{p} and G_{h} are respectively given by

$$\forall z \in \mathbb{U},\ \widetilde{G_{\mathrm{p}}}(z) := A_+ \frac{1}{z - (H_{N+1} - E_N^0)} A_+^\dagger \quad \text{and} \quad \forall z \in \mathbb{L},\ \widetilde{G_{\mathrm{h}}}(z) := A_-^\dagger \frac{1}{z - (E_N^0 - H_{N-1})} A_-. \tag{1.34}$$

They are analytic functions on $\mathbb{U}$ and $\mathbb{L}$ respectively. However, from (1.34), we see that we can extend the domain of analyticity of $\widetilde{G_{\mathrm{p}}}$ and $\widetilde{G_{\mathrm{h}}}$ to $\mathbb{C} \setminus S_{\mathrm{p}}$ and $\mathbb{C} \setminus S_{\mathrm{h}}$ respectively (see Figures 1.3 and 1.4).

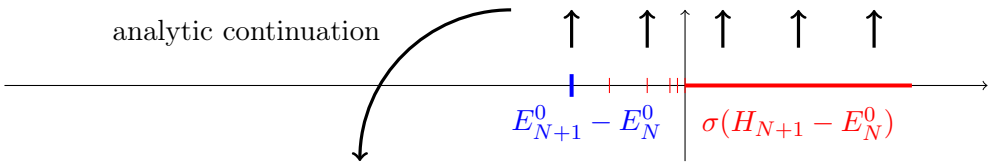

Figure 1.3 – The continuation of $\widetilde{G_{\mathrm{p}}}(z)$.

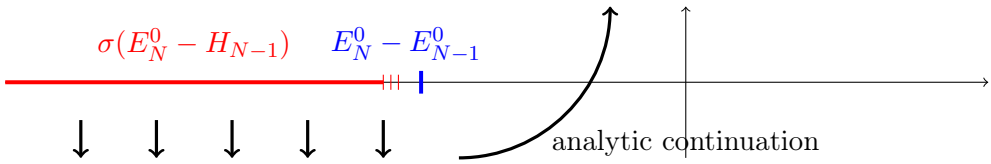

Figure 1.4 – The continuation of $\widetilde{G_{\mathrm{h}}}(z)$.

From the stability condition, it holds $E_N^0 - E_{N-1}^0 < E_{N+1}^0 - E_N^0$. We define the total Green's function $\widetilde{G}(z)$ by (see Figure 1.5)

$$\forall z \in \mathbb{U} \cup \mathbb{L} \cup (E_N^0 - E_{N-1}^0, E_{N+1}^0 - E_N^0), \quad \widetilde{G}(z) := \widetilde{G_{\mathrm{p}}}(z) + \widetilde{G_{\mathrm{h}}}(z). \tag{1.35}$$

We introduce the *chemical potential* μ, which is any real number satisfying

$$E_N^0 - E_{N-1}^0 < \mu < E_{N+1}^0 - E_N^0. \tag{1.36}$$

In the sequel, we will only work with the operator-valued *regular function* $\omega \mapsto \widetilde{G}(\mu + \mathrm{i}\omega)$. This function has very nice properties, both in term of regularity and integrability, and it contains the same information as G_{h} and G_{p} altogether. The goal of the GW method is to provide a computable approximation of this function.

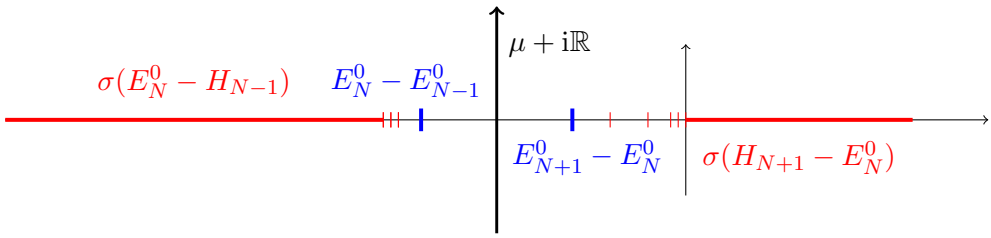

Figure 1.5 – The domain of analyticity of $\widetilde{G}(z)$.

Let us conclude this section by identifying the Green's function in the case of a non-interacting system. Let

$$h_1 = -\frac{1}{2}\Delta + V_1$$

be a one-body Hamiltonian, and consider the mean-field N-body non-interacting Hamiltonian

$$H_{0,N} := \sum_{i=1}^{N} h_{1,\mathbf{r}_i} = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_{\mathbf{r}_i} + V_1(\mathbf{r}_i) \right).$$

We assume that h_1 has at least N negative eigenvalues $\varepsilon_1 \leq \varepsilon_2 \leq \ldots \leq \varepsilon_N$, counting multiplicities, and that $\varepsilon_N < \varepsilon_{N+1}$, where ε_{N+1} is either the $(N+1)^{\text{st}}$ eigenvalue of h_1 if it exists, or the bottom of the essential spectrum of h_1 otherwise. This fact implies both that the ground state $E^0_{0,N}$ of $H_{0,N}$ is simple (with $E^0_{0,N} = \varepsilon_1 + \ldots + \varepsilon_N$), and that the stability condition is satisfied for the non-interacting system, since

$$E^0_{0,N} - E^0_{0,N-1} = \varepsilon_N < \varepsilon_{N+1} = E^0_{0,N+1} - E^0_{0,N}.$$

We denote by μ_0 the chemical potential of the non-interacting system, *i.e.* any real number satisfying

$$\varepsilon_N < \mu_0 < \varepsilon_{N+1}. \tag{1.37}$$

Finally, the $\mathcal{H}_1$-orthogonal projection on the occupied states is denoted by

$$\gamma^0_{0,N} := \mathbb{1}_{(-\infty,\mu_0)}(h_1) = \sum_{k=1}^{N} |\phi_k\rangle\langle\phi_k|, \tag{1.38}$$

where $\{\phi_k\}_{1\leq k\leq N}$ is an orthonormal family of (real-valued) eigenfunctions of h_1 corresponding to its lowest eigenvalues: $h_1\phi_k = \varepsilon_k\phi_k$. The one-body particle, hole and total Green's functions $G_{0,\mathrm{p}}$, $G_{0,\mathrm{h}}$ and G_0 of the non-interacting system have properties similar to the ones of the interacting system.

Lemma 1.8. *It holds*

$$\forall \tau \in \mathbb{R}, \quad G_{0,\mathrm{p}}(\tau) = -\mathrm{i}\Theta(\tau)\left(\gamma^0_{0,N}\right)^{\perp} \mathrm{e}^{-\mathrm{i}\tau h_1} \quad \textit{and} \quad G_{0,\mathrm{h}}(\tau) = \mathrm{i}\Theta(-\tau)\gamma^0_{0,N}\mathrm{e}^{-\mathrm{i}\tau h_1}. \tag{1.39}$$

The analytic continuations of their Laplace transforms, $\widetilde{G_{0,\mathrm{p}}}$ and $\widetilde{G_{0,\mathrm{h}}}$ are respectively

$$\forall z \in \mathbb{C}\setminus(\varepsilon_{N+1},\infty), \quad \widetilde{G_{0,\mathrm{p}}}(z) = \frac{\left(\gamma^0_{0,N}\right)^{\perp}}{z-h_1}, \quad \textit{and} \quad \forall z \in \mathbb{C}\setminus(-\infty,\varepsilon_N), \quad \widetilde{G_{0,\mathrm{h}}}(z) = \frac{\gamma^0_{0,N}}{z-h_1}.$$

The total Green's function of the non-interacting system is, in the complex frequency domain,

$$\forall z \in \mathbb{U}\cup\mathbb{L}\cup(\varepsilon_N,\varepsilon_{N+1}), \quad \widetilde{G_0}(z) = (z-h_1)^{-1}. \tag{1.40}$$

The Green's function for the non-interacting system is simply the resolvent of the corresponding one-body operator h_1.

1.3.3 The self-energy operator

By analogy to the non-interacting case (1.40), we define the *one-body dynamical Hamiltonian* $\widetilde{H}(z)$ as

$$\forall z \in \mathbb{U}\cup\mathbb{L}\cup(E^0_N - E^0_{N-1}, E^0_{N+1} - E^0_N), \quad \widetilde{H}(z) = z - \widetilde{G}(z)^{-1},$$

so that $\widetilde{G}(z) = \left(z - \widetilde{H}(z)\right)^{-1}$. The following lemma shows that this definition indeed makes sense.

Lemma 1.9. *For any $z \in \mathbb{U}\cup\mathbb{L}\cup((E^0_N - E^0_{N-1}), E^0_{N+1} - E^0_N)$, the operator $\widetilde{H}(z)$ is a well-defined closed operator on $\mathcal{H}_1$, with domain $\widetilde{D}(z)$, where $\widetilde{D}(z)$ is dense in $\mathcal{H}_1$ and $\widetilde{D}(z) \subset H^2(\mathbb{R}^3,\mathbb{C})$.*

For each complex frequency z, $\widetilde{H}(z)$ may have (complex) eigenvalues. Such an eigenvalue is called a *quasi-energy*, and a corresponding eigenvector is called a *quasi-particle*.

We finally link the one-body non-interacting Hamiltonian with the one-body dynamical Hamiltonian. To do so, we assume that the chemical potentials μ and μ_0 defined in (1.36) and (1.37) respectively can be chosen equal. In this case, we can define the self-energy Σ on the imaginary axis $\mu + \mathrm{i}\mathbb{R}$ by the Dyson equation

$$\forall \omega \in \mathbb{R}, \quad \widetilde{\Sigma}(\mu + \mathrm{i}\omega) := \widetilde{H}(\mu + \mathrm{i}\omega) - h_1 = \widetilde{G_0}(\mu + \mathrm{i}\omega)^{-1} - \widetilde{G}(\mu + \mathrm{i}\omega)^{-1} \quad \text{(Dyson equation)}. \tag{1.41}$$

The self-energy can be defined on a larger domain, but its definition on $\mu + \mathrm{i}\mathbb{R}$ will be enough for our purpose. Note that the Dyson equation defines the self-energy, and that the self-energy depends on the choice of h_1.

The road-map of the GW method is as follows:

- Construct a good one-body mean-field Hamiltonian h_1. In the original article by Hedin [Hed65], h_1 is the Hartree model, solution of the self-consistent equation

$$\begin{cases} h_1 = -\frac{1}{2}\Delta + V + \rho_{0,N}^0 * \dfrac{1}{|\cdot|}, \\ \rho_{0,N}^0 \quad \text{density of} \quad \gamma_{0,N}^0 := \mathbb{1}_{(-\infty,\mu_0)}(h_1). \end{cases} \tag{1.42}$$

  We refer to [Sol91] for a mathematical analysis of this model.

- Construct an approximation of the self-energy: $\widetilde{\Sigma^{\mathrm{GW}}}(\mu + \mathrm{i}\cdot) \approx \widetilde{\Sigma}(\mu + \mathrm{i}\cdot)$. To construct such an approximation is the topic on the next section.

- Define the approximation of the Green's function $\widetilde{G^{\mathrm{GW}}}(\mu + \mathrm{i}\cdot)$ via the Dyson equation (1.41).

1.3.4 The Hedin's equations, the GW equations and the GW^0 equations

The definition (1.34)-(1.35) of the Green's function $\widetilde{G}$ is not usable in practice, for it necessitates to compute quantities which suffer from the curse of dimensionality (for instance the resolvent of $H_{N+1} - E_N^0$). Fortunately, it turns out that $\widetilde{G}$ satisfies a set of self-consistent equations, called the Hedin's equations. These equations were introduced by Hedin in its pioneering article [Hed65]. They were derived from physical considerations, using many-body perturbation theory. The derivation of Hedin is beyond the scope of this thesis, and is not well-understood mathematically speaking.

We denote by $\mathbf{1} := (\mathbf{r}_1, t_1)$, $\mathbf{2} := (\mathbf{r}_2, t_2)$, etc. a space-time point. The space-time point $\mathbf{1}^+$ is $(\mathbf{r}_1, t_1^+)$, where t_1^+ is a time strictly after t_1, but infinitesimally close to t_1. The notation $\mathrm{d}\mathbf{1}$ stands for $\mathrm{d}\mathbf{r}_1\mathrm{d}t_1$. A space-time operator A has a kernel $A(\mathbf{12}) = A(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2)$, and all operators that we will consider satisfy the relation $A(\mathbf{12}) = A(\mathbf{r}_1, 0; \mathbf{r}_2, t_2 - t_1) := A(\mathbf{r}_1, \mathbf{r}_2; \tau)$ where $\tau = t_2 - t_1$. We denote by $A(\tau)$ the operator with kernel $A(\mathbf{r}_1, \mathbf{r}_2; \tau)$. The Hedin's

equations read as follows [Hed65]:

The Hedin's equations

$$G(\mathbf{12}) = G_0(\mathbf{12}) + \int \mathrm{d}(\mathbf{34}) G_0(\mathbf{13})\Sigma(\mathbf{34})G(\mathbf{42}) \qquad \text{(Dyson equation)}$$

$$\Sigma(\mathbf{12}) = \mathrm{i}\int \mathrm{d}(\mathbf{34}) G(\mathbf{13})W(\mathbf{41}^+)\Gamma(\mathbf{32};\mathbf{4}) \qquad \text{(Self-energy)}$$

$$W(\mathbf{12}) = v_\mathrm{c}(\mathbf{12}) + \int \mathrm{d}(\mathbf{34}) v_\mathrm{c}(\mathbf{13})P(\mathbf{34})W(\mathbf{42}) \qquad \text{(Screened interaction)}$$

$$P(\mathbf{12}) = -\mathrm{i}\int \mathrm{d}(\mathbf{34}) G(\mathbf{13})G(\mathbf{41}^+)\Gamma(\mathbf{34};\mathbf{2}) \qquad \text{(Irreducible polarization)}$$

$$\Gamma(\mathbf{12};\mathbf{3}) = \delta(\mathbf{12})\delta(\mathbf{13}) + \int \mathrm{d}(\mathbf{4567})\frac{\delta\Sigma(\mathbf{12})}{\delta G(\mathbf{45})}G(\mathbf{46})G(\mathbf{75})\Gamma(\mathbf{67};\mathbf{3}) \qquad \text{(Vertex function).}$$

Here, v_c represents the Coulomb operator, with kernel

$$v_c(\mathbf{12}) := v_c(\mathbf{r}_1,\mathbf{r}_2)\delta_0(\tau) := \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\delta_0(\tau). \tag{1.43}$$

As we can see, the Hedin's equations involve a lot of operator-valued functions. Some of them are well-defined, and some of them are not well-understood mathematically. In particular, it is unclear in what sense the partial derivative

$$\frac{\partial\Sigma(\mathbf{12})}{\partial G(\mathbf{45})} \tag{1.44}$$

is taken. In practice, it turns out that this term may be neglected for most interesting systems. To set it to 0 leads to the GW equations, also introduced by Hedin in the same article.

The GW equations Find G^{GW} solution to the system

$$G^{\mathrm{GW}}(\mathbf{12}) = G_0(\mathbf{12}) + \int \mathrm{d}(\mathbf{34}) G_0(\mathbf{13})\Sigma^{\mathrm{GW}}(\mathbf{34})G^{\mathrm{GW}}(\mathbf{42}) \tag{1.45a}$$

$$\Sigma^{\mathrm{GW}}(\mathbf{12}) = \mathrm{i}G^{\mathrm{GW}}(\mathbf{12})W^{\mathrm{GW}}(\mathbf{21}^+) \tag{1.45b}$$

$$W^{\mathrm{GW}}(\mathbf{12}) = v_\mathrm{c}(\mathbf{12}) + \int \mathrm{d}(\mathbf{34}) v_\mathrm{c}(\mathbf{13})P^{\mathrm{GW}}(\mathbf{34})W^{\mathrm{GW}}(\mathbf{42}) \tag{1.45c}$$

$$P^{\mathrm{GW}}(\mathbf{12}) = -\mathrm{i}G^{\mathrm{GW}}(\mathbf{12})G^{\mathrm{GW}}(\mathbf{21}^+) \tag{1.45d}$$

The name "GW" comes from (1.45b). These equations are usually solved self-consistently. In Chapter 4, we focus on the GW^0 equations, which adds an extra simplification. The GW^0 equations are obtained by setting $W^{\mathrm{GW}} \approx W^0$, where W^0 is the screened interaction in the *random phase approximation* (RPA).

The GW^0 equations Find G^{GW^0} solution to the system

$$G^{\mathrm{GW}^0}(\mathbf{12}) = G_0(\mathbf{12}) + \int \mathrm{d}(\mathbf{34}) G_0(\mathbf{13})\Sigma^{\mathrm{GW}^0}(\mathbf{34})G^{\mathrm{GW}^0}(\mathbf{42}) \tag{1.46a}$$

$$\Sigma^{\mathrm{GW}^0}(\mathbf{12}) = \mathrm{i}G^{\mathrm{GW}^0}(\mathbf{12})W^0(\mathbf{21}^+) \tag{1.46b}$$

In Chapter 4, we transform the GW^0 equations (1.46) into formally equivalent equations having better properties, and we study the resulting equations.

The kernel-product of operators

The GW^0 equation (1.46b) is of the form $C(\mathbf{12}) = A(\mathbf{12})B(\mathbf{21})$. The Schwartz kernels of the operators A and B are multiplied. It is unclear that such a definition makes sense, as the multiplication of two kernels is not, in general, the kernel of a well-defined operator. We need to clarify the meaning of such a multiplication.

We start with time-independent operators. Let $A \in \mathcal{B}(\mathcal{H}_1)$ and $B \in \mathcal{B}(\mathcal{H}_1)$ have kernels $A(\mathbf{r}, \mathbf{r}')$ and $B(\mathbf{r}, \mathbf{r}')$ respectively. We would like to define the operator C with kernel $C(\mathbf{r}, \mathbf{r}') := A(\mathbf{r}, \mathbf{r}')B(\mathbf{r}', \mathbf{r})$. *Formally*, it holds that, for $f, g \in \mathcal{H}_1$,

$$\begin{aligned}\langle f|C|g\rangle &= \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \overline{f}(\mathbf{r})C(\mathbf{r},\mathbf{r}')g(\mathbf{r}')\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \overline{f}(\mathbf{r})A(\mathbf{r},\mathbf{r}')g(\mathbf{r}')B(\mathbf{r}',\mathbf{r})\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' \\ &= \mathrm{Tr}_{\mathcal{H}_1}(AgB\overline{f}). \end{aligned} \tag{1.47}$$

This motivates the following definition.

Definition 1.10 (kernel-product)**.** *The kernel-product of $A \in \mathcal{H}_1$ and $B \in \mathcal{H}_1$ is the operator $C := A \odot B$, if it exists, defined by the sesquilinear form*

$$\forall f, g \in \mathcal{H}_1, \quad \langle f|C|g\rangle = \mathrm{Tr}_{\mathcal{H}_1}(AgB\overline{f}).$$

In practice, the well-posedness of the kernel-product $A \odot B$ is given by results similar to the following lemma. In the sequel, we denote by $\mathfrak{S}_k(\mathcal{H})$ the k-th Schatten class of the Hilbert space $\mathcal{H}$; $\mathfrak{S}_1(\mathcal{H})$ is the set of trace-class operators on $\mathcal{H}$, and $\mathfrak{S}_2(\mathcal{H})$ is the set of Hilbert-Schmidt operators on $\mathcal{H}$.

Lemma 1.11. *If $B \in \mathcal{B}(\mathcal{H}_1)$ is such that, for all $f, g \in \mathcal{H}_1$, the operator $gB\overline{f}$ is Hilbert-Schmidt (i.e. in the Schatten class $\mathfrak{S}_2(\mathcal{H}_1)$), with*

$$\exists K_B \in \mathbb{R}^+, \quad \forall f, g \in \mathcal{H}_1, \quad \left\|gB\overline{f}\right\|_{\mathfrak{S}_2(\mathcal{H}_1)} \leq K_B \|g\|_{\mathcal{H}_1}\|f\|_{\mathcal{H}_1},$$

then, for all $A \in \mathcal{B}(\mathcal{H}_1)$, the operator $A \odot B$ is a well-defined bounded operator on $\mathcal{H}_1$, and

$$\|A \odot B\|_{\mathcal{B}(\mathcal{H}_1)} \leq K_B \|A\|_{\mathcal{B}(\mathcal{H}_1)}.$$

Reformulation of the GW^0 equations

After some manipulations, that we do not describe in this introduction, we were able to show that the GW^0 equations (1.46) are formally equivalent to the following equations.

The -new- GW^0 equations

Find $\widetilde{G^{\mathrm{GW}^0}}(\mu_0 + \mathrm{i}\cdot) \in L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ solution to the system

$$(\mathrm{GW}^0) \quad \begin{cases} \widetilde{G^{\mathrm{GW}^0}}(\mu_0 + \mathrm{i}\omega) = \left[\mu_0 + \mathrm{i}\omega - \left(h_1 + \widetilde{\Sigma^{\mathrm{GW}^0}}(\mu_0 + \mathrm{i}\omega)\right)\right]^{-1}, \\ \widetilde{\Sigma^{\mathrm{GW}^0}}(\mu_0 + \mathrm{i}\omega) = K_x - \dfrac{1}{2\pi}\displaystyle\int_{-\infty}^{+\infty} \widetilde{G^{\mathrm{GW}^0}}\big(\mu_0 + \mathrm{i}(\omega + \omega')\big) \odot \widetilde{W_c^0}(\mathrm{i}\omega')\,\mathrm{d}\omega', \end{cases} \tag{1.48}$$

where h_1 is the one-body Hartree operator defined in (1.42), and K_x is the operator with kernel

$$K_x(\mathbf{r}, \mathbf{r}') = -\frac{\gamma_{0,N}^0(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{1.49}$$

The first equation of (1.48) is the Dyson equation (1.41). The right-hand side of the second equation of (1.48) contains two terms. The first one K_x is the Fock operator (the one that we find in Hartree-Fock models), and the second one involves the operator $\widetilde{W_c^0}$, which is the correlation part of the screened interaction (we do not define this operator in this introduction, and refer to Chapter 4, Section 4.4.2). Note that the convolution is performed on an imaginary axis. The fact that this convolution is equivalent to the time-multiplication (1.46b) comes from the so-called *contour deformation technique* introduced first by Rojas, Godby and Needs [RGN95] (see also [RSW+99]).

Seeing the RPA screened operator $\widetilde{W^0} = v_c + \widetilde{W_c^0}$ as a dynamical screened Coulomb operator, the GW approximation can be interpreted as a dynamical version of the Hartree-Fock model.

1.3.5 Well-posedness of the GW^0 equations in a perturbative regime

The main results of Chapter 4 is concerned with the study of the GW^0 equations (1.48). Together with Eric Cancès and Gabriel Stoltz, we first proved that the kernel-product of the first equation indeed makes sense.

Lemma 1.12. *For all $G^{\mathrm{app}}(\mu_0 + \mathrm{i}\cdot) \in L^2(\mathbb{R}, \mathcal{B}(\mathcal{H}_1))$ and all $\omega \in \mathbb{R}$, the operator*

$$\widetilde{\Sigma_c^{\mathrm{app}}}(\mu_0 + \mathrm{i}\omega) = -\frac{1}{2\pi}\int_{-\infty}^{+\infty} \widetilde{G^{\mathrm{app}}}\big(\mu_0 + \mathrm{i}(\omega+\omega')\big) \odot \widetilde{W_c^0}(\mathrm{i}\omega')\,\mathrm{d}\omega'$$

is a well-defined bounded operator on $\mathcal{H}_1$.

Unfortunately, we were not able to fully analyze (1.48): we did not find mathematical evidence that the operator $\mu_0 + \mathrm{i}\omega - \Big(h_1 + \widetilde{\Sigma^{\mathrm{app}}}(\mu_0 + \mathrm{i}\omega)\Big)$ should be invertible at each step of a self-consistent algorithm. We therefore studied the GW^0 equations in a perturbative regime. For $\lambda > 0$, we introduce

The GW_λ^0 equations

Find $\widetilde{G^{\mathrm{GW}_\lambda^0}} \in L^2(\mathbb{R}, \mathcal{B}(\mathcal{H}_1))$ solution to the system

$$(\mathrm{GW}_\lambda^0)\quad \begin{cases} \widetilde{G^{\mathrm{GW}_\lambda^0}}(\mu_0 + \mathrm{i}\omega) = \Big[\mu_0 + \mathrm{i}\omega - \Big(h_1 + \lambda\widetilde{\Sigma^{\mathrm{GW}_\lambda^0}}(\mu_0 + \mathrm{i}\omega)\Big)\Big]^{-1}, \\ \widetilde{\Sigma^{\mathrm{GW}_\lambda^0}}(\mu_0 + \mathrm{i}\omega) = K_x - \dfrac{1}{2\pi}\displaystyle\int_{-\infty}^{+\infty} \widetilde{G^{\mathrm{GW}_\lambda^0}}\big(\mu_0 + \mathrm{i}(\omega+\omega')\big) \odot \widetilde{W_c^0}(\mathrm{i}\omega')\,\mathrm{d}\omega', \end{cases} \tag{1.50}$$

The case $\lambda = 0$ corresponds to the non-interacting system: $\widetilde{G^{\mathrm{GW}_{\lambda=0}^0}}(\mu_0 + \mathrm{i}\cdot) = \widetilde{G_0}(\mu_0 + \mathrm{i}\cdot)$. The parameter λ can be seen as a coupling constant for the two-body interaction between electrons. We proved the following existence and unicity result.

Theorem 1.13 (Eric Cancès, DG, Gabriel Stoltz)**.** *There exists $\lambda_* > 0$ such that, for all $0 \le \lambda \le \lambda_*$, there exists a unique solution $\widetilde{G^{\mathrm{GW}_\lambda^0}}(\mu_0 + \mathrm{i}\cdot) \in L^2(\mathbb{R}, \mathcal{B}(\mathcal{H}_1))$ to (1.48) which is close to $\widetilde{G_0}(\mu_0 + \mathrm{i}\cdot)$ in $L^2(\mathbb{R}, \mathcal{B}(\mathcal{H}_1))$.*

1.4 Numerical simulation of crystalline structures

The last part of this thesis concerns the numerical simulation of perfect crystals. A perfect crystal is characterized by a lattice $\mathcal{R}$ of $\mathbb{R}^3$ and an $\mathcal{R}$-periodic function $\mu_{\rm per}$ representing the nuclear charge density. The electronic system is described by a mean-field one-body electronic Hamiltonian of the form

$$H_{\rm per} := -\frac{1}{2}\Delta + V_{\rm per}, \quad \text{acting on } L^2(\mathbb{R}^3, \mathbb{C}), \tag{1.51}$$

where $V_{\rm per}$ is an $\mathcal{R}$-periodic potential. In practice, $V_{\rm per}$ is the solution of a nonlinear self-consistent equation. Such type of equations are motivated by means of *thermodynamic limit* procedures [CLL98b]. In the sequel, we denote by Γ the unit cell of the lattice $\mathcal{R}$, and by $\Gamma_L := L\Gamma$, so that Γ_L contains L^3 times the unit cell Γ.

The thermodynamic limit

To perform a *thermodynamic limit*, one must first choose a model to calculate the ground state energy of a finite system. One can consider the full N-body Schrödinger model (1.5), or an approximation of it, like a Kohn-Sham model (see *e.g.* (1.24)), a GW model (1.30), and so on. We then consider, for $L \in \mathbb{N}^*$ the finite system with external (nuclear) potential

$$V_{{\rm nuc},L}(\mathbf{r}) := \int_{\mathbb{R}^3} \frac{\mu_{{\rm nuc},L}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}', \quad \text{with} \quad \mu_{{\rm nuc},L} := \mu_{\rm per}(\mathbf{r})\mathbb{1}\left(\mathbf{r} \in \Gamma_L\right).$$

In other words, we only consider the finite system consisting of the nuclei contained in a "box" of size L (see Figure 1.6). For $L \in N^*$, we calculate the corresponding ground state energy E_L. The questions then are

- **Existence:** Does the sequence of energies per unit volume $\left(|\Gamma_L|^{-1}E_L\right)_{L\in\mathbb{N}^*}$ converge to some $E_{\rm per}$ as L goes to infinity?
- **Characterization**: If it is the case, is $E_{\rm per}$ the solution to an explicit problem?

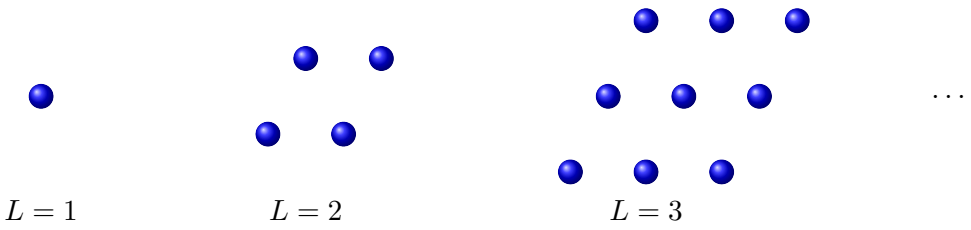

Figure 1.6 – The thermodynamic limit: $\mu_{{\rm per},L}$ for $L = 1$, $L = 2$ and $L = 3$.

These questions have a positive answer for the Thomas-Fermi (with or without the von Weizsäcker term) model [CLL96, CLL98b], the Hartree and restricted Hartree models [CLL98a, CLL02] and the Hartree-Fock and reduced Hartree-Fock models [CLL01]. In addition, some existence results (but no characterization) were proved for the full N-body Schrödinger model [Fef85, BLL03, HLS09a, HLS09b].

The supercell thermodynamic limit

Another natural thermodynamic limit one could think of is the *supercell thermodynamic limit*. This type of thermodynamic limit was considered in [CDL08] for the reduced Hartree-Fock model, and is closely linked to numerical simulations. In a supercell model, the system is

confined in a box $\Gamma_L := L\Gamma$ with periodic boundary conditions. We denote by $L^2_{\rm per}(\Gamma_L)$ the Hilbert space of locally square integrable functions that are $L\mathcal{R}$-periodic, and we would like to study one-body mean-field Hamiltonians of the form

$$H_L := -\frac{1}{2}\Delta_L + V_{{\rm per},L} \quad \text{acting on } L^2_{\rm per}(\Gamma_L). \tag{1.52}$$

Here, $-\Delta_L$ denotes the Laplacian operator acting on $L^2_{\rm per}(\Gamma_L)$, and $V_{{\rm per},L}$ is the sum of the periodic Coulomb potential generated by the nuclei (and a uniform background of negative charge)

$$V_{\rm nuc} := \int_\Gamma \mu_{\rm per}(\mathbf{r}')G_1(\mathbf{r}-\mathbf{r}')\,{\rm d}\mathbf{r}', \tag{1.53}$$

which is independent of L, and of a mean-field potential $V_{{\rm el},L}$ generated by the electrons (and a uniform background of positive charge), which may depend on L. The role of the uniform backgrounds is to neutralize the charge in the supercell so that the Poisson equation with periodic boundary conditions may be solved. In (1.53), G_1 denotes the $\mathcal{R}$-periodic Green kernel of the Poisson interaction [LS77], solution of

$$\begin{cases} -\Delta G_1 = 4\pi\left(\displaystyle\sum_{\mathbf{k}\in\mathcal{R}}\delta_{\mathbf{k}} - 1\right) \\ G_1 \text{ is } \mathcal{R}\text{-periodic and } \displaystyle\int_\Gamma G_1 = 0. \end{cases} \tag{1.54}$$

Once a model is chosen for the definition of $V_{{\rm el},L}$, one may ask oneself the same questions (existence and characterization of the energy per unit cell) as in the standard thermodynamic limit (see Figure 1.7).

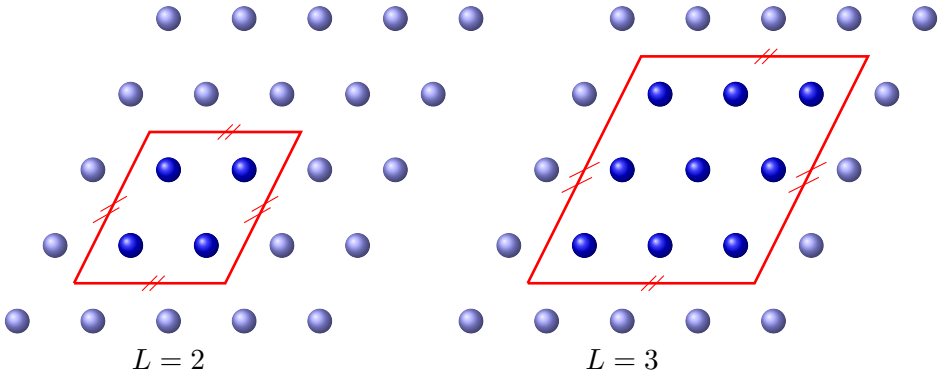

Figure 1.7 – The supercell thermodynamic limit: Γ_L for $L = 2$ and $L = 3$.

The supercell method for the linear model (where $V_{{\rm per},L}$ is an $\mathcal{R}$-periodic function independent of L) is equivalent to performing a regular sampling of the reciprocal Brillouin zone (see Section 1.4.3), and is the model usually considered in numerical codes [MP76]. The nonlinear reduced Hartree-Fock model was considered in [CDL08].

In this introduction, we will only present the results for the linear model, and briefly mention the results in the case of the reduced Hartree-Fock model.

1.4.1 The Bloch transformation

The Bloch transformation is a suitable tool to study periodic operators (see also [RS78, Chapter XIII] or [Del08]). Let $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ be a basis of $\mathbb{R}^3$ that generates the lattice $\mathcal{R}$, so

that

$$\mathcal{R} := \left\{ k_1\mathbf{a}_1 + k_2\mathbf{a}_2 + k_3\mathbf{a}_3,\ (k_1,k_2,k_3) \in \mathbb{Z}^3 \right\}.$$

We define the dual lattice

$$\mathcal{R}^* := \left\{ k_1\mathbf{a}_1^* + k_2\mathbf{a}_2^* + k_3\mathbf{a}_3^*,\ (k_1,k_2,k_3) \in \mathbb{Z}^3 \right\},$$

where the vectors $\mathbf{a}_i^*$ are such that $\mathbf{a}_i^* \cdot \mathbf{a}_j = 2\pi\delta_{ij}$. The unit cell and the reciprocal unit cell are respectively defined by

$$\Gamma := \left\{ \alpha_1\mathbf{a}_1 + \alpha_2\mathbf{a}_2 + \alpha_3\mathbf{a}_3,\ (\alpha_1,\alpha_2,\alpha_3) \in [-1/2,1/2)^3 \right\},$$

and

$$\Gamma^* := \left\{ \alpha_1\mathbf{a}_1^* + \alpha_2\mathbf{a}_2^* + \alpha_3\mathbf{a}_3^*,\ (\alpha_1,\alpha_2,\alpha_3) \in [-1/2,1/2)^3 \right\}.$$

For $w \in C_c^\infty(\mathbb{R}^3)$, we define the Bloch transform $\mathcal{Z}w$ of w by

$$\forall \mathbf{q} \in \mathbb{R}^3, \quad \forall \mathbf{r} \in \mathbb{R}^3, \quad (\mathcal{Z}w)(\mathbf{q},\mathbf{r}) := w_{\mathbf{q}}(\mathbf{r}) := \sum_{\mathbf{R}\in\mathcal{R}} \mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot(\mathbf{r}+\mathbf{R})} w(\mathbf{r}+\mathbf{R}). \tag{1.55}$$

Note that since w is compactly supported, the sum in the right-hand side of (1.55) is finite for all $\mathbf{r} \in \mathbb{R}^3$. For $\mathbf{R} \in \mathcal{R}$, we define the translation operator $\tau_{\mathbf{R}}$ on $L^2(\mathbb{R}^3)$ by $(\tau_{\mathbf{R}} f)(\mathbf{r}) = f(\mathbf{r}-\mathbf{R})$. From the definition (1.55), the function $w_{\mathbf{q}}$ is $\mathcal{R}$-periodic for any $\mathbf{q} \in \mathbb{R}^3$: $\tau_{\mathbf{R}} w_{\mathbf{q}} = w_{\mathbf{q}}$ for all $\mathbf{R} \in \mathcal{R}$. On the other hand, by introducing, for $\mathbf{m} \in \mathcal{R}^*$, the unitary operator $U_{\mathbf{m}}$ (on $L^2_{\mathrm{per}}(\Gamma)$) defined by

$$\forall \mathbf{m} \in \mathcal{R}^*, \quad \forall f \in L^2_{\mathrm{per}}(\Gamma), \quad (U_{\mathbf{m}} f)(\mathbf{r}) = \mathrm{e}^{-\mathrm{i}\mathbf{m}\cdot\mathbf{r}} f(\mathbf{r}), \tag{1.56}$$

we see that $w_{\mathbf{q}+\mathbf{m}} = U_{\mathbf{m}} w_{\mathbf{q}}$. Altogether,

$$\forall w \in C_c^\infty(\mathbb{R}^3), \quad \left\{ \begin{array}{l} \forall \mathbf{R} \in \mathcal{R}, \quad \forall \mathbf{q} \in \mathbb{R}^3, \quad \tau_{\mathbf{R}} w_{\mathbf{q}} = w_{\mathbf{q}} \\ \forall \mathbf{m} \in \mathcal{R}^*, \quad \forall \mathbf{q} \in \mathbb{R}^3, \quad w_{\mathbf{q}+\mathbf{m}} = U_{\mathbf{m}} w_{\mathbf{q}}. \end{array} \right. \tag{1.57}$$

In particular, the function $\mathcal{Z}w$ is completely characterized by its values for $\mathbf{q} \in \Gamma^*$ and $\mathbf{r} \in \Gamma$. We consider the Hilbert space $L^2(\Gamma^*, L^2_{\mathrm{per}}(\Gamma))$, endowed with the normalized inner product (we denote by $⨍_{\Gamma^*} = |\Gamma^*|^{-1} \int_{\Gamma^*}$)

$$\langle f(\mathbf{q},\mathbf{r}), g(\mathbf{q},\mathbf{r}) \rangle_{L^2(\Gamma^*, L^2_{\mathrm{per}}(\Gamma))} := ⨍_{\Gamma^*} \int_{\Gamma} \overline{f}(\mathbf{q},\mathbf{r}) g(\mathbf{q},\mathbf{r}) \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{q}.$$

A classical calculation shows that

$$\forall w \in C_c^\infty(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} |w(\mathbf{r})|^2 \, \mathrm{d}\mathbf{r} = ⨍_{\Gamma^*} \int_{\Gamma} |(\mathcal{Z}w)(\mathbf{q},\mathbf{r})|^2 \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{q} = \|\mathcal{Z}w\|^2_{L^2(\Gamma^*, L^2_{\mathrm{per}}(\Gamma))}.$$

We can therefore extend by continuity the Bloch transform $\mathcal{Z}$ to $L^2(\mathbb{R}^3)$. Its extension, still denoted by $\mathcal{Z}$, is an isometry from $L^2(\mathbb{R}^3)$ to $L^2(\Gamma^*, L^2_{\mathrm{per}}(\Gamma))$. Its inverse is given by

$$\begin{array}{rccl} \mathcal{Z}^{-1}: & L^2(\Gamma^*, L^2_{\mathrm{per}}(\Gamma)) & \to & L^2(\mathbb{R}^3) \\ & w_{\mathbf{q}}(\mathbf{r}) & \mapsto & (\mathcal{Z}^{-1}w)(\mathbf{r}) := ⨍_{\Gamma^*} \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} w_{\mathbf{q}}(\mathbf{x}) \, \mathrm{d}\mathbf{q}. \end{array}$$

Let A with domain $\mathcal{D}(A)$ be a possibly unbounded operator acting on $L^2_{\mathrm{per}}(\Gamma)$. We say that A commutes with $\mathcal{R}$-translations if $\tau_{\mathbf{R}} A = A \tau_{\mathbf{R}}$ for all $\mathbf{R} \in \mathcal{R}$. If A commutes with $\mathcal{R}$-translations, then $\mathcal{Z}A\mathcal{Z}^{-1}$ is block diagonal, which means that there exists a family of operators $(A_{\mathbf{q}})_{\mathbf{q}\in\mathbb{R}^3}$ acting on $L^2_{\mathrm{per}}(\Gamma)$, such that, if $f \in L^2(\mathbb{R}^3)$ and $g \in \mathcal{D}(A)$ are such that $f = Ag$, then, for almost any $\mathbf{q} \in \mathbb{R}^3$, $g_{\mathbf{q}} \in L^2_{\mathrm{per}}(\Gamma)$ is in the domain of $A_{\mathbf{q}}$, and

$$f_{\mathbf{q}} = A_{\mathbf{q}} g_{\mathbf{q}}.$$

From (1.57), we obtain that

$$\forall \mathbf{m} \in \mathcal{R}^*, \quad \forall \mathbf{q} \in \Gamma^*, \quad A_{\mathbf{q}+\mathbf{m}} = U_{\mathbf{m}} A_{\mathbf{q}} U_{\mathbf{m}}^{-1}, \tag{1.58}$$

so that the family $(A_{\mathbf{q}})_{\mathbf{q}\in\mathbb{R}^3}$ is entirely characterized by its values for $\mathbf{q} \in \Gamma^*$. We write

$$\mathcal{Z} A \mathcal{Z}^{-1} = \fint_{\Gamma^*}^{\oplus} A_{\mathbf{q}} \, \mathrm{d}\mathbf{q} \quad \text{(Bloch decomposition of } A\text{)}. \tag{1.59}$$

1.4.2 The linear model on the whole space

Let us apply the Bloch theory to the self-adjoint operator H_{per} (with domain $H^2(\mathbb{R}^3, \mathbb{C})$) defined in (1.51). Since H_{per} commutes with $\mathcal{R}$-translations, it admits a Bloch decomposition of the form (1.59):

$$\mathcal{Z} H_{\mathrm{per}} \mathcal{Z}^{-1} = \fint_{\Gamma^*}^{\oplus} H_{\mathbf{q}} \, \mathrm{d}\mathbf{q},$$

with

$$H_{\mathbf{q}} := \frac{1}{2} \left| -\mathrm{i}\nabla_1 + \mathbf{q} \right|^2 + V_{\mathrm{per}} = \frac{1}{2} \left(-\Delta_1 - 2\mathrm{i}\mathbf{q} \cdot \nabla_1 + |\mathbf{q}|^2 \right) + V_{\mathrm{per}}. \tag{1.60}$$

Here, we denoted by[5] ∇_1 the gradient operator acting on $L^2_{\mathrm{per}}(\Gamma)$ and by Δ_1 the Laplacian operator acting on $L^2_{\mathrm{per}}(\Gamma)$. For each $\mathbf{q} \in \mathbb{R}^3$, the operator $H_{\mathbf{q}}$ with domain $H^2_{\mathrm{per}}(\Gamma)$ is self-adjoint, bounded below and with compact resolvent. We denote by $\lambda_{1,\mathbf{q}} \leq \lambda_{2,\mathbf{q}} \leq \cdots$ its eigenvalues, ranked in increasing order, counting multiplicities, and by $(u_{n,\mathbf{q}})_{n\in\mathbb{N}^*} \in (L^2_{\mathrm{per}}(\Gamma))^{\mathbb{N}^*}$ an orthonormal basis of associated eigenvectors, so that

$$\forall \mathbf{q} \in \mathbb{R}^3, \quad \forall n \in \mathbb{N}^*, \quad H_{\mathbf{q}} u_{n,\mathbf{q}} = \lambda_{n,\mathbf{q}} u_{n,\mathbf{q}}. \tag{1.61}$$

From (5.22), we obtain that

$$\forall \mathbf{q} \in \mathbb{R}^3, \quad \forall n \in \mathbb{N}^*, \quad \forall \mathbf{m} \in \mathcal{R}^*, \quad \lambda_{n,\mathbf{q}+\mathbf{m}} = \lambda_{n,\mathbf{q}} \quad \text{and} \quad u_{n,\mathbf{q}+\mathbf{m}} = U_{\mathbf{m}}^{-1} u_{n,\mathbf{q}}.$$

The map $\mathbf{q} \mapsto H_{\mathbf{q}}$ is an holomorphic family of type (A) (see [Kat12, Chapter VII]). In particular, the maps $\mathbf{q} \mapsto \lambda_{n,\mathbf{q}}$ are Lipschitz (hence continuous). As a result, from [RS78, Chapter XIII], we deduce that the spectrum of H_{per} can be recovered from the spectra of $(H_{\mathbf{q}})_{\mathbf{q}\in\Gamma^*}$, with

$$\sigma\left(H_{\mathrm{per}}\right) = \bigcup_{\mathbf{q}\in\Gamma^*} \sigma\left(H_{\mathbf{q}}\right) = \bigcup_{n=1}^{\infty} \left[\Sigma_n^-, \Sigma_n^+\right] \quad \text{with} \quad \left[\Sigma_n^-, \Sigma_n^+\right] = \left\{\lambda_{n,\mathbf{q}}, \ \mathbf{q} \in \Gamma^*\right\}.$$

The spectrum of H is therefore composed of bands. The map $\mathbf{q} \mapsto \{\lambda_{1,\mathbf{q}}, \lambda_{2,\mathbf{q}}, \cdots\}$ is called the *band diagram* (see Figure (1.8)). We define the *integrated density of state* per unit cell by

$$I : \mathbb{R} \ni \varepsilon \mapsto I(\varepsilon) := \sum_{n=1}^{\infty} \fint_{\Gamma^*} \mathbb{1}(\lambda_{n,\mathbf{q}} \leq \varepsilon) \, \mathrm{d}\mathbf{q}. \tag{1.62}$$

It is a continuous non-decreasing function satisfying $I(-\infty) = 0$ and $I(+\infty) = +\infty$. Let N be the number of electrons per unit cell in the system under consideration. We write $I^{-1}(\{N\}) = [\varepsilon_-, \varepsilon_+]$. Any number ε inside this interval is an admissible Fermi level, or Fermi energy of the system. When $\varepsilon_- = \varepsilon_+$, this number ε_F is unique, and the system is a metal. Otherwise, the system is an insulator or a semiconductor, depending on the magnitude of the

[5] If $f \in L^2_{\mathrm{per}}(\Gamma)$ has a Fourier decomposition of the form $f(\mathbf{r}) = \sum_{\mathbf{k}\in\mathcal{R}^*} c_{\mathbf{k}}(f) \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}$, then

$$c_{\mathbf{k}}\left(-\Delta_1 f\right) = |\mathbf{k}|^2 \, c_{\mathbf{k}}(f) \quad \text{and} \quad c_{\mathbf{k}}\left(\mathbf{q} \cdot (-\mathrm{i}\nabla_1) f\right) = (\mathbf{q} \cdot \mathbf{k}) \, c_{\mathbf{k}}(f).$$

gap $g := \varepsilon_+ - \varepsilon_- > 0$, and we set $\varepsilon_F := (\varepsilon_- + \varepsilon_+)/2$. By introducing the *integrated density of energy* per unit cell

$$E : \mathbb{R} \ni \varepsilon \mapsto E(\varepsilon) := \sum_{n=1}^{\infty} \fint_{\Gamma^*} \lambda_{n,\mathbf{q}} \mathbb{1}(\lambda_{n,\mathbf{q}} \leq \varepsilon) \, \mathrm{d}\mathbf{q}, \tag{1.63}$$

the energy per unit cell of the system is $E(\varepsilon_F)$.

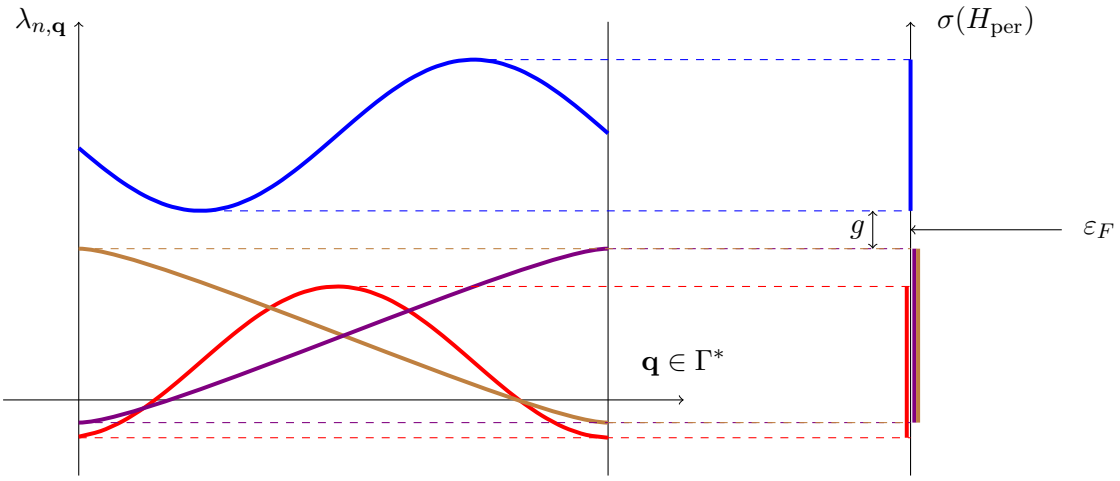

Figure 1.8 – Band diagrams of H_{per}. Here, H_{per} represents an insulator.

The $L^2(\mathbb{R}^3)$-orthogonal projector on the occupied states γ is defined with the spectral theorem by $\gamma := \mathbb{1}(H_{\mathrm{per}} \leq \varepsilon_F)$. If the system is an insulator or a semiconductor, then we can rewrite γ using the Cauchy residual formula as

$$\gamma = \frac{1}{2\mathrm{i}\pi} \oint_{\mathscr{C}} \frac{\mathrm{d}z}{z - H_{\mathrm{per}}}.$$

Here, $\mathscr{C}$ is a positively oriented simple closed loop in the complex plane, schematized in Figure 1.9.

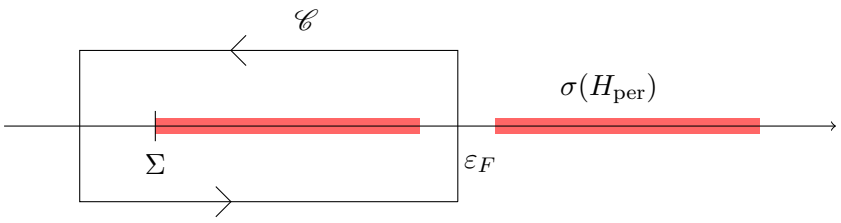

Figure 1.9 – The loop $\mathscr{C}$.

Since γ commutes with $\mathcal{R}$-translations, it admits a Bloch decomposition of the form (1.59) with

$$\mathcal{Z}\gamma\mathcal{Z}^{-1} = \fint_{\Gamma^*}^{\oplus} \gamma_{\mathbf{q}} \, \mathrm{d}\mathbf{q}, \quad \text{with} \quad \gamma_{\mathbf{q}} := \frac{1}{2\mathrm{i}\pi} \oint_{\mathscr{C}} \frac{\mathrm{d}z}{z - H_{\mathbf{q}}}. \tag{1.64}$$

For all $\mathbf{q} \in \Gamma^*$, the operator $\gamma_{\mathbf{q}}$ is trace-class. Let $\rho_{\gamma_{\mathbf{q}}}$ be the $\mathcal{R}$-periodic density of $\gamma_{\mathbf{q}}$. The density of the operator γ is the $\mathcal{R}$-periodic function defined by

$$\rho_\gamma := \fint_{\Gamma^*} \rho_{\gamma_{\mathbf{q}}} \, \mathrm{d}\mathbf{q}. \tag{1.65}$$

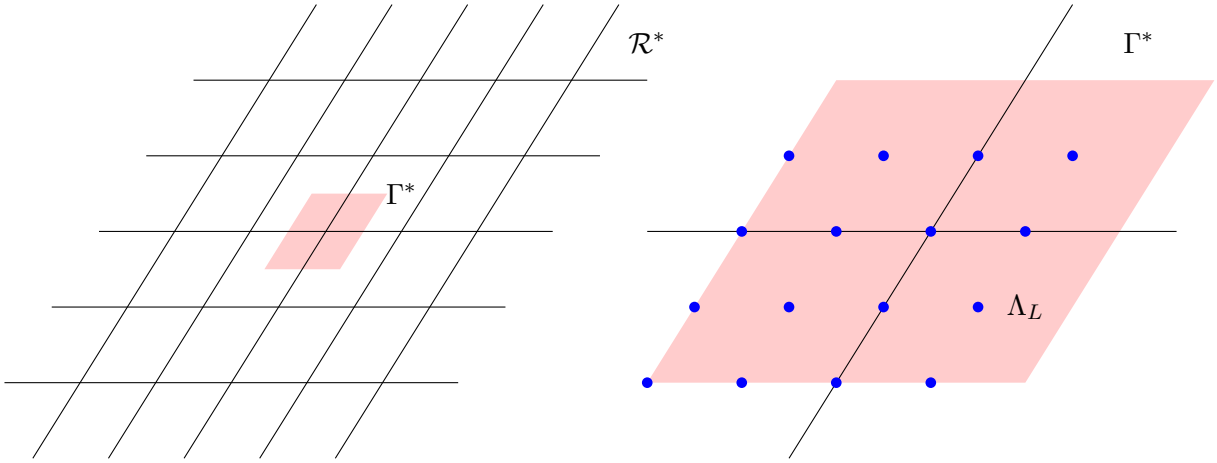

Figure 1.10 – (left) The lattice $\mathcal{R}^*$ and the reciprocal unit cell Γ^* (in red). (right) The discretization Λ_L (in blue) of Γ^* (in red). Here, $L = 4$.

Finally, the energy per unit cell of the system defined in (1.63) is also

$$E_{\mathrm{per}} := E(\varepsilon_F) = \fint_{\Gamma^*} \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma)} \left(H_{\mathbf{q}}\gamma_{\mathbf{q}}\right). \tag{1.66}$$

1.4.3 The linear model on supercells

In practice, the calculation of the Fermi energy and of the total energy would necessitate the calculation of $\lambda_{n,\mathbf{q}}$ for all $\mathbf{q} \in \Gamma^*$ (see (1.62) and (1.63)). This is of course not possible numerically. The reciprocal unit cell Γ^* needs to be discretized. Since the work of Monkhorst and Pack [MP76], it has been observed that very good results were obtained when considering uniform discretizations, at least for insulators and semiconductors. As will be make clear below, this is equivalent to performing a supercell calculation.

We are interested in studying the operator H_L defined in (1.52). The operator H_L is a bounded-below self-adjoint operator with compact resolvent, so that we could directly study the full operator H_L. However, it is possible to further simplify the problem by considering a Bloch-like transform, that we call the *supercell Bloch transform*.

For $L \in N^*$, we introduce the regular sampling of the reciprocal unit cell, $\Lambda_L := \left(L^{-1}\mathcal{R}^*\right) \cap \Gamma^*$, *i.e.*

$$\Lambda_L := \left\{ \frac{2k_1}{L}\mathbf{a}_1^* + \frac{2k_2}{L}\mathbf{a}_2^* + \frac{2k_3}{L}\mathbf{a}_3^*,\ (k_1,k_2,k_3) \in \left\{ \frac{-L+\eta}{2}, \frac{-L+\eta}{2}+1, \cdots, \frac{L+\eta}{2}-1 \right\}^3 \right\}, \tag{1.67}$$

with $\eta = 1$ if L is odd, and $\eta = 0$ if L is even, so that there are exactly L^3 points in Λ_L (see Figure 1.10). Likewise, we define $\mathcal{R}_L := \mathcal{R} \cap \Gamma_L$.

For $w \in C^\infty_{\mathrm{per}}(\Gamma_L)$, we define the supercell Bloch transform of w by

$$\forall \mathbf{Q} \in \Lambda_L, \quad \left(\mathcal{Z}_L w\right)(\mathbf{Q}, \mathbf{r}) := w_{\mathbf{Q}}(\mathbf{r}) := \sum_{\mathbf{R} \in \mathcal{R}_L} \mathrm{e}^{-\mathrm{i}\mathbf{Q}\cdot(\mathbf{r}+\mathbf{R})} w(\mathbf{r}+\mathbf{R}).$$

The operator $\mathcal{Z}_L$ enjoys properties similar to the ones of the operator $\mathcal{Z}$ defined in (1.55). For instance,

$$\forall w \in C^\infty_{\mathrm{per}}(\Gamma_L), \quad \int_{\Gamma_L} |w|^2 = \frac{1}{L^3} \sum_{\mathbf{Q} \in \Lambda_L} \int_{\Gamma} \left|\left(\mathcal{Z}_L w\right)(\mathbf{Q}, \mathbf{r})\right|^2 \mathrm{d}\mathbf{r},$$

so that the operator $\mathcal{Z}_L$ can be extended to an unitary operator from $L^2_{\rm per}(\Gamma_L)$ to $\ell^2\left(\Lambda_L, L^2_{\rm per}(\Gamma)\right)$, where $\ell^2\left(\Lambda_L, L^2_{\rm per}(\Gamma)\right)$ is endowed with the normalized inner product

$$\langle f(\mathbf{Q},\mathbf{r}), g(\mathbf{Q},\mathbf{r})\rangle_{\ell^2(\Lambda_L, L^2_{\rm per}(\Gamma))} := \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L}\int_\Gamma \overline{f}(\mathbf{Q},\mathbf{r})g(\mathbf{Q},\mathbf{r})\,\mathrm{d}\mathbf{r}.$$

The inverse of $\mathcal{Z}_L$ is

$$\begin{array}{rccl} \mathcal{Z}_L^{-1}: & \ell^2(\Lambda_L, L^2_{\rm per}(\Gamma)) & \to & L^2_{\rm per}(\Gamma_L) \\ & w_{\mathbf{Q}}(\mathbf{x}) & \mapsto & (\mathcal{Z}_L^{-1}w)(\mathbf{x}) := \dfrac{1}{L^3}\displaystyle\sum_{\mathbf{Q}\in\Lambda_L} \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{x}} w_{\mathbf{Q}}(\mathbf{x}). \end{array}$$

An easy calculation shows that $\mathcal{Z}_L H_L \mathcal{Z}_L^{-1}$ is block diagonal. We write, by analogy with (1.59),

$$\mathcal{Z}_L H_L \mathcal{Z}_L^{-1} := \frac{1}{L^3}\bigoplus_{\mathbf{Q}\in\Lambda_L} H_{\mathbf{Q}} \quad \text{(supercell Bloch decomposition of } H_L\text{)},$$

where the operators $H_{\mathbf{Q}}$, acting on $L^2_{\rm per}(\Gamma)$, are exactly the ones defined in (1.60). This shows the relationship between the uniform sampling and the supercell calculation. We deduce that, if the crystal is an insulator or a semiconductor,

- the Fermi level of the supercell model can be chosen equal to the one of the periodic model ε_F ;
- the $L^2_{\rm per}(\Gamma)$-orthogonal projection initially defined by $\gamma_L := \mathbb{1}(H_L \le \varepsilon_F^L)$ is also

$$\gamma_L = \frac{1}{L^3}\bigoplus_{\mathbf{Q}\in\Lambda_L}\gamma_{\mathbf{Q}},$$

  where $\gamma_{\mathbf{Q}}$ were introduced in (1.64). It is a trace-class operator, and its density is

$$\rho_{\gamma_L} = \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L}\rho_{\gamma_{\mathbf{Q}}}\ ; \tag{1.68}$$

- the energy per unit cell of the supercell model is

$$E_L := \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L}\mathrm{Tr}_{L^2_{\rm per}(\Gamma)}\left(H_{\mathbf{Q}}\gamma_{\mathbf{Q}}\right). \tag{1.69}$$

1.4.4 Exponential rate of convergence of supercell models

The error on the energy per unit volume $E_{\rm per} - E_L$, where $E_{\rm per}$ and E_L were respectively defined in (1.66) and (1.69), is of the form

$$|E_{\rm per} - E_L| = \left| \fint_{\Gamma^*} f(\mathbf{q})\,\mathrm{d}\mathbf{q} - \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L} f(\mathbf{Q}) \right|, \quad \text{where} \quad f(\mathbf{q}) := \mathrm{Tr}_{L^2_{\rm per}(\Gamma)}\left(H_{\mathbf{q}}\gamma_{\mathbf{q}}\right). \tag{1.70}$$

This is the difference between an integral and a corresponding Riemann sum. From this observation, we were able with Salma Lahbabi to prove the following result (see Chapter 5).

Theorem 1.14 (DG, Salma Lahbabi)**.** *Assume $V_{\rm per} \in L^\infty$. There exist constants $C \in \mathbb{R}^+$ and $\alpha > 0$, that depend on the lattice $\mathcal{R}$, $\|V_{\rm per}\|_{L^\infty}$, g and ε_F only, such that*

$$\forall L \in \mathbb{N}^*, \quad |E_{\rm per} - E_L| \le C\mathrm{e}^{-\alpha L} \quad \textit{(convergence of the ground state energy per unit volume)}$$

and

$$\forall L \in \mathbb{N}^*, \quad \|\rho_\gamma - \rho_{\gamma_L}\|_{L^\infty} \le C\mathrm{e}^{-\alpha L} \quad \textit{(convergence of the ground state density).}$$

The idea of the proof is to show that the integrand f in (1.70) is an $\mathcal{R}^*$-periodic function which admits an analytical continuation on a complex strip of the form $\mathbb{R}^3 + \mathrm{i}[A, A]^3$ for some $A > 0$, and use the theory of convergence for Riemann sums. The same type of arguments were used to prove the exponential decay of Wannier functions for insulators [DC64a, DC64b, Koh59, BPC+07, Pan07].

The reduced Hartree-Fock model

The reduced Hartree-Fock (rHF) model for perfect crystals, or periodic rHF, has been rigorously derived from the rHF model for finite molecular systems by means of the classical thermodynamic limit by Catto, Le Bris and Lions [CLL01]. In [CDL08], Cancès, Deleurence and Lewin proved that the same periodic rHF model is also the supercell thermodynamic limit of the supercell rHF model.

The rHF model is a nonlinear model in which the external potential is solution of a self-consistent equation (both for the supercell model $V_{\mathrm{per},L}$ and for the periodic model V_{per}). We refer to Chapter 5 or to [Del08] for a complete description of these models.

Together with Salma Lahbabi, we proved a result similar to (1.14) in the rHF case (see Chapter 5). We proved that, if the system is an insulator or a semiconductor, then

- the supercell rHF energy per unit cell converges exponentially fast towards the periodic rHF energy per unit cell ;
- the supercell rHF ground state density converges exponentially fast towards the periodic rHF ground state density, in the $L^\infty_{\mathrm{per}}(\Gamma)$ norm.

The theoretical exponential convergence rates are confirmed by numerical simulations in Chapter 5.

1.4.5 Reduced basis methods for Brillouin-zone integration

As mentioned before, a numerical calculation needs the discretization of the reciprocal unit cell. The theory described in the previous section shows that, at least for insulators, the values obtained on a regular coarse grid gives good results (this is due to the exponential rate of convergence proved in Theorem 1.14). For metallic systems, a slower rate of convergence is expected and a much finer sampling is needed to calculate for instance the integrated density of states I defined in (1.62) (from which we obtain the Fermi level). As a consequence, the calculation of the eigenmodes of the operator $H_{\mathbf{q}}$ at all the points $\mathbf{q}$ of the grid is numerically much more expensive than in the insulating case. Together with Eric Cancès, Virginie Ehrlacher and Damiano Lombardi, we proposed a *reduced basis* method to speed up traditional calculations (see Chapter 6). Our approach consists in creating reduced bases that are $\mathbf{q}$-point dependent (hence differs from the method described in [Pau07]).

The basic idea of the proposed numerical scheme is to extract local small reduced bases from calculations on a coarse uniform grid of size $L_1 \times L_1 \times L_1$ of Γ^* for some value $L_1 \in \mathbb{N}^*$. These are used to compute the eigenmodes of $H_{\mathbf{q}}$ for $\mathbf{q}$ on a fine uniform grid of size $L_2 \times L_2 \times L_2$, with $L_2 \gg L_1$. The resulting method is very easy to implement, and already provides very satisfactory results. It is then possible to further improve the accuracy of the approximate eigenmodes at a low extra computational time, using a perturbation-based post-processing method similar to the one introduced in [CDM+14].

The full algorithms and the corresponding numerical results are analysed in Chapter 6.

Part I

Spin Density Functional Theory

CHAPTER 2

THE N-REPRESENTABILITY PROBLEMS

We expose in this chapter the arguments given in [Gon13] and in [Gon15b].

Abstract. This chapter is concerned with the pure-state N-representability problem for systems under a magnetic field. Necessary and sufficient conditions are given for a spin-density 2×2 matrix R to be representable by a Slater determinant. We also provide sufficient conditions on the paramagnetic current $\mathbf{j}$ for the pair $(R,\mathbf{j})$ to be Slater-representable in the case where the number of electrons N is greater than 12. The case $N<12$ is left open.

2.1 The N-representability problem in SDFT

The density functional theory (DFT), first developed by Hohenberg and Kohn [HK64], then further developed and formalized mathematically by Levy [Lev79], Valone [Val80] and Lieb [Lie83], states that the ground state energy and density of a non-magnetic electronic system can be obtained by minimizing some functional of the density only, over the set of all admissible densities. Characterizing this set is called the *N-representability problem*. More precisely, as the so-called constrained search method leading to DFT can be performed either with N-electron wave functions [Lev79, Lie83], or with N-body density matrices [Val80, Lie83], the N-representability problems can be recast in the pure-state setting resp. in the mixed-state setting as follows: *What is the set of electronic densities that come from an admissible N-electron wave function*, resp. *an admissible N-body density matrix?* This question was answered by Gilbert [Gil75], Harriman [Har81] and Lieb [Lie83] (see (2.6) below).

In order to deal with spin magnetic effects, it is necessary to resort to spin-polarized density functional theory (SDFT) where the objects of interest are the spin-polarized densities $\rho^{\alpha\beta}$ with $\alpha,\beta\in\{\uparrow,\downarrow\}$. This theory was first developed by von Barth and Hedin [vBH72] in a very general setting, but most applications use a restricted version of it, where local magnetization is constrained along a fixed direction (collinear spin-polarized DFT). While this simplified version is able to account for many magnetic effects, it misses some important physical behaviors (frustrated solids like γ-Fe or spin dynamics for instance). Actually, the first calculations for non-collinear spin-polarized DFT have been performed by Sandratskii and Guletskii [SG86] and Kübler *et al.* [KHSW88b, KHSW88a] (see [BSFS13] or [SDAD+07] for some recent works), but no rigorous mathematical background has yet been developed in this case. We emphasize that SDFT deals with spin effects, but not with orbital magnetic effects. If the latter are not negligible, we should use another variant of DFT, namely current -spin- density functional theory (C-S-DFT). This will be the topic of Section 2.2.

In this section, we are interested in the N-representability problem for the so-called spin-density 2×2 matrix (from which we recover the spin-polarized densities). The question was addressed but left open in the pioneering work by von Barth and Hedin [vBH72]. We provide in this section a complete characterization of the set of admissible spin-polarized densities used to perform self-consistent minimizations.

2.1.1 Setting the stage: the spin-density 2×2 matrix

Recall that the set of admissible antisymmetric wave functions is

$$\mathcal{W}_N^{\text{pure}} := \left\{ \Psi \in \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}^2),\ \|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1,\ \|\nabla \Psi\|_{L^2(\mathbb{R}^{3N})} < \infty \right\},$$

where $L^2(\mathbb{R}^3, \mathbb{C}^2)$ is the one-electron state-space

$$L^2(\mathbb{R}^3, \mathbb{C}^2) \equiv \left\{ \Phi = (\phi^\uparrow, \phi^\downarrow)^T,\ \|\Phi\|_{L^2}^2 := \int_{\mathbb{R}^3} |\phi^\uparrow|^2 + |\phi^\downarrow|^2 < \infty \right\}.$$

A special case of wave functions is given by Slater determinants: let $\Phi_1, \Phi_2, \ldots, \Phi_N$ be a set of orthonormal functions in $L^2(\mathbb{R}^3, \mathbb{C}^2)$, the Slater determinant generated by $(\Phi_1, \ldots, \Phi_N)$ is (we denote by $\mathbf{x}_k := (\mathbf{r}_k, s_k)$ the k-th spatial-spin component)

$$\mathscr{S}\left[\Phi_1, \ldots, \Phi_N\right](\mathbf{x}_1, \ldots, \mathbf{x}_N) := \frac{1}{\sqrt{N!}} \det\left(\Phi_i(\mathbf{x}_j)\right)_{1 \le i,j \le N}.$$

The subset of $\mathcal{W}_N^{\text{pure}}$ consisting of all finite energy Slater determinants is denoted by $\mathcal{W}_N^{\text{Slater}}$. It holds that $\mathcal{W}_1^{\text{Slater}} = \mathcal{W}_1^{\text{pure}}$ and $\mathcal{W}_N^{\text{Slater}} \subsetneq \mathcal{W}_N^{\text{pure}}$ for $N \ge 2$.

For a wave-function $\Psi \in \mathcal{W}_N^{\text{pure}}$, we define the corresponding N-body density matrix $\Gamma_\Psi := |\Psi\rangle\langle\Psi|$, which corresponds to the projection on $\{\mathbb{C}\Psi\}$ in $\bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}^2)$. The set of pure-state and Slater-state N-body density matrices are respectively

$$G_N^{\text{pure}} := \left\{\Gamma_\Psi,\ \Psi \in \mathcal{W}_N^{\text{pure}}\right\} \quad \text{and} \quad G_N^{\text{Slater}} := \left\{\Gamma_\Psi,\ \Psi \in \mathcal{W}_N^{\text{Slater}}\right\}. \tag{2.1}$$

It holds that $G_1^{\text{Slater}} = G_1^{\text{pure}}$ and that $G_N^{\text{Slater}} \subsetneq G_N^{\text{pure}}$ for $N \ge 2$. The set of mixed-state N-body density matrices G_N^{mixed} is defined as the convex hull of G_N^{pure}:

$$G_N^{\text{mixed}} = \left\{ \sum_{k=1}^\infty n_k |\Psi_k\rangle\langle\Psi_k|,\ 0 \le n_k \le 1,\ \sum_{k=1}^\infty n_k = 1,\ \Psi_k \in \mathcal{W}_N^{\text{pure}} \right\}. \tag{2.2}$$

It is also the convex hull of G_N^{Slater}.

In SDFT, we are interested in the spin-density 2×2 matrix. For $\Gamma \in G_N^{\text{mixed}}$, the associated spin-density 2×2 matrix is the 2×2 hermitian function-valued matrix

$$R_\Gamma(\mathbf{r}) := \begin{pmatrix} \rho_\Gamma^{\uparrow\uparrow} & \rho_\Gamma^{\uparrow\downarrow} \\ \rho_\Gamma^{\downarrow\uparrow} & \rho_\Gamma^{\downarrow\downarrow} \end{pmatrix}(\mathbf{r}),$$

where, for $\alpha, \beta \in \{\uparrow, \downarrow\}^2$,

$$\rho_\Gamma^{\alpha\beta}(\mathbf{r}) := N \sum_{\vec{s} \in \{\uparrow,\downarrow\}^{(N-1)}} \int_{\mathbb{R}^{3(N-1)}} \Gamma(\mathbf{r}, \alpha, \vec{\mathbf{z}}, \vec{s}; \mathbf{r}, \beta, \vec{\mathbf{z}}, \vec{s})\ \mathrm{d}\vec{\mathbf{z}}. \tag{2.3}$$

Here, we denoted by $\Gamma(\mathbf{r}_1, s_1, \ldots; \mathbf{r}'_1, s'_1, \ldots)$ the Schwartz kernel of the operator $\Gamma \in G_N^{\text{mixed}}$. In the case where Γ comes from a Slater determinant $\mathscr{S}[\Phi_1, \ldots, \Phi_N]$, we get

$$R_\Gamma(\mathbf{r}) = \sum_{k=1}^{N} \begin{pmatrix} |\phi_k^\uparrow|^2 & \phi_k^\uparrow \overline{\phi_k^\downarrow} \\ \overline{\phi_k^\uparrow} \phi_k^\downarrow & |\phi_k^\downarrow|^2 \end{pmatrix} (\mathbf{r}). \tag{2.4}$$

The Slater-state, pure-state and mixed-state sets of spin-density 2×2 matrices are respectively defined by

$$\mathcal{J}_N^{\text{Slater}} := \left\{ R_\Gamma,\ \Gamma \in G_N^{\text{Slater}} \right\}, \quad \mathcal{J}_N^{\text{pure}} := \left\{ R_\Gamma,\ \Gamma \in G_N^{\text{pure}} \right\} \quad \text{and} \quad \mathcal{J}_N^{\text{mixed}} := \left\{ R_\Gamma,\ \Gamma \in G_N^{\text{mixed}} \right\}.$$

Since the map $\Gamma \mapsto R_\Gamma$ is linear, it holds that $\mathcal{J}_N^{\text{Slater}} \subset \mathcal{J}_N^{\text{pure}} \subset \mathcal{J}_N^{\text{mixed}}$, that $\mathcal{J}_N^{\text{mixed}}$ is convex, and that $\mathcal{J}_N^{\text{mixed}}$ is the convex hull of both $\mathcal{J}_N^{\text{Slater}}$ and $\mathcal{J}_N^{\text{pure}}$. With this notation, the N-representability problem is

$$\boxed{N\textbf{-representability problem}:\ \text{Characterize the sets } \mathcal{J}_N^{\text{Slater}},\ \mathcal{J}_N^{\text{pure}} \text{ and } \mathcal{J}_N^{\text{mixed}}.} \tag{2.5}$$

2.1.2 Pure-state and mixed-state representable spin-density 2×2 matrices

Before answering problem (2.5), let us address some remarks. In the physics community, the spin density 2×2 matrix R_Γ is usually replaced by the pair $(\rho_\Gamma, \mathbf{m}_\Gamma)$, where, $\rho_\Gamma = \rho_\Gamma^{\uparrow\uparrow} + \rho_\Gamma^{\downarrow\downarrow}$ denotes the total electronic density, and $\mathbf{m}_\Gamma = \text{tr}_{\mathbb{C}^2}[\sigma R_\Gamma]$ the spin angular momentum density. Here,

$$\sigma := (\sigma_x, \sigma_y, \sigma_z) := \left(\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right)$$

contains the Pauli-matrices. The pair $(\rho_\Gamma, \mathbf{m}_\Gamma)$ contains the same information as R_Γ, hence the N-representability problem for the matrix R is the same as the one for the pair $(\rho, \mathbf{m})$. However, as will become clear, it is more natural mathematically speaking to work with R_Γ.

In the spin-unpolarized case, which amounts to setting $\rho_\Gamma^{\uparrow\downarrow} = \rho_\Gamma^{\downarrow\uparrow} = 0$ and $\rho_\Gamma^{\uparrow\uparrow} = \rho_\Gamma^{\downarrow\downarrow}$ (see Chapter 3, Section 3.2), it is sufficient to characterize $\mathcal{I}_N^X = \{\rho_\Gamma,\ \Gamma \in G_N^X\}$, where X represents either the set of Slater, pure of mixed states. This problem was first considered by Gilbert [Gil75] and completely solved by Harriman [Har81]. They proved that $\mathcal{I}_N^{\text{Slater}} = \mathcal{I}_N^{\text{pure}} = \mathcal{I}_N^{\text{mixed}} := \mathcal{I}_N$ with

$$\mathcal{I}_N = \left\{ \rho \in L^1(\mathbb{R}^3),\ \rho \geq 0,\ \int_{\mathbb{R}^3} \rho = N,\ \sqrt{\rho} \in H^1(\mathbb{R}^3) \right\}. \tag{2.6}$$

A rigorous mathematical construction of DFT was then developed by Lieb in [Lie83].

In the spin-polarized setting, unlike the previous case, we have to distinguish pure-state representability from mixed-state representability, as is illustrated by the following example. Let $N = 1$ and $\Phi = (\phi^\uparrow, \phi^\downarrow) \in \mathcal{W}_1^{\text{pure}}$. For $\Gamma = |\Phi\rangle\langle\Phi|$, it holds, according to (2.4), $\rho_\Gamma^{\alpha\beta}(\mathbf{r}) = \phi^\alpha(\mathbf{r})\overline{\phi^\beta}(\mathbf{r})$, so that the determinant of R_Γ is null. Therefore, $\mathcal{J}_1^{\text{pure}}$ only contains fields of at most rank-1 matrices, whereas, as will be proved latter, $\mathcal{J}_1^{\text{mixed}}$ contains full-rank matrices.

We now state the main theorem of this section. We first recall that for a Hermitian matrix R satisfying $R \geq 0$, $\sqrt{R}$ is a well-defined Hermitian matrix. We also recall the definition of the Lebesgue spaces $L^p(\mathbb{R}^d) := \{f, \int_{\mathbb{R}^d} f^p < \infty\}$ and of the Sobolev spaces $W^{1,p}(\mathbb{R}^d) := \{f \in L^p(\mathbb{R}^d), \nabla f \in L^p(\mathbb{R}^d)\}$. We introduce

$$\mathcal{C}_N := \left\{ R \in \mathcal{M}_{2\times 2}(L^1(\mathbb{R}^3, \mathbb{C})),\ R^* = R,\ R \geq 0,\ \int_{\mathbb{R}^3} \text{tr}_{\mathbb{C}^2}[R] = N,\ \sqrt{R} \in \mathcal{M}_{2\times 2}(H^1(\mathbb{R}^3, \mathbb{C})) \right\}, \tag{2.7}$$

and $\mathcal{C}_N^0 := \{R \in \mathcal{C}_N,\ \det R \equiv 0\}$. The characterization of $\mathcal{C}_N$ is given by the following lemma (see Section 2.1.3 for the proof).

Lemma 2.1. *A function-valued matrix* $R = \begin{pmatrix} \rho^\uparrow & \sigma \\ \overline{\sigma} & \rho^\downarrow \end{pmatrix}$ *is in* $\mathcal{C}_N$ *iff its coefficients satisfy*

$$\begin{cases} \rho^{\uparrow/\downarrow} \geq 0, \quad \rho^\uparrow \rho^\downarrow - |\sigma|^2 \geq 0, \quad \displaystyle\int_{\mathbb{R}^3} \rho^\uparrow + \int_{\mathbb{R}^3} \rho^\downarrow = N, \\ \sqrt{\rho^{\uparrow/\downarrow}} \in H^1(\mathbb{R}^3), \quad \sigma, \sqrt{\det(R)} \in W^{1,3/2}(\mathbb{R}^3), \\ |\nabla \sigma|^2 \rho^{-1} \in L^1(\mathbb{R}^3), \\ \left|\nabla \sqrt{\det(R)}\right|^2 \rho^{-1} \in L^1(\mathbb{R}^3). \end{cases} \tag{2.8}$$

The complete answer for N-representability in SDFT is given by the following theorem (see Section 2.1.3 for the proof).

Theorem 2.2.
Case $N = 1$***:*** *It holds that*

$$\mathcal{J}_1^{\text{Slater}} = \mathcal{J}_1^{\text{pure}} = \mathcal{C}_1^0 \quad \textit{and} \quad \mathcal{J}_1^{\text{mixed}} = \mathcal{C}_1.$$

Case $N \geq 2$***:*** *For all* $N \geq 2$*, it holds that*

$$\mathcal{J}_N^{\text{Slater}} = \mathcal{J}_N^{\text{pure}} = \mathcal{J}_N^{\text{mixed}} = \mathcal{C}_N.$$

The first line of (2.8) states that R must be a positive Hermitian matrix and that the number of electrons is N. The other three lines are regularity conditions that ensure the finiteness of the kinetic energy. Comparing (2.6) and (2.7), we see that the above theorem is a natural and nice extension of the classical N-representability result (2.6).

An interesting consequence of our result is that it is possible to control the eigenvalues of R. Most applications of SDFT use exchange-correlation functionals of the form $E_{\text{xc}}(\rho^+, \rho^-)$, where ρ^+ and ρ^- are the eigenvalues of R (see Chapter 3, Equation (3.7) for examples and discussion), so that the knowledge of the regularities of ρ^+ and ρ^- is desirable for the study of these applications.

Corollary 2.3.
If R *is mixed-state representable, then its two eigenvalues* ρ^+ *and* ρ^- *satisfy* $\sqrt{\rho^\pm} \in H^1(\mathbb{R}^3)$.

Let $R \in \mathcal{J}_N^{\text{pure}}$ be represented by a wave-function Ψ_R. One can ask oneself whether there is a way to control the kinetic energy of Ψ_R (which we know is finite by definition of R) with respect to, say, $\left\|\nabla\sqrt{R}\right\|_{L^2}$? In the spin-unpolarized setting, there is such a control: it is possible to represent $\rho \in \mathcal{I}_N$, where $\mathcal{I}_N$ where defined in (2.6), by a wave-function Ψ_ρ such that $\|\nabla\Psi_\rho\|_{L^2(\mathbb{R}^3)} \leq C_N \|\nabla\sqrt{\rho}\|_{L^2}^6$, where $C_N \in \mathbb{R}^+$ is a constant independent of ρ. Unfortunately, we were not able to prove such a control. This is due to the use of the Lazarev-Lieb orthonormalization process [LL13] (see also Lemma 2.5) in the proof. This process is a powerful tool for representability, but looses control on the kinetic energy [Rut13].

We now prove Lemma 2.1, Theorem 2.2 and Corollary 2.3.

2.1.3 Proofs of the SDFT results

Proof of Lemma 2.1

Proof. If R satisfies (2.8), then $R \in \mathcal{C}_N$.
Let R be a matrix satisfying (2.8), so that R is a positive hermitian matrix. The only non-trivial point to check is that $\sqrt{R} \in \mathcal{M}_{2\times 2}(H^1(\mathbb{R}^3, \mathbb{C}))$. Writing $\sqrt{R} := \begin{pmatrix} r^\uparrow & s \\ \overline{s} & r^\downarrow \end{pmatrix}$, the equality $R = \sqrt{R}\sqrt{R}$ is equivalent to

$$\left\{ \begin{array}{rcl} |r^\uparrow|^2 + |s|^2 & = & \rho^\uparrow, \\ |r^\downarrow|^2 + |s|^2 & = & \rho^\downarrow, \\ s(r^\uparrow + r^\downarrow) & = & \sigma. \end{array} \right. \tag{2.9}$$

Together with the relation $\det(\sqrt{R}) = r^\uparrow r^\downarrow - |s|^2 = \sqrt{\det}$, where we denoted by $\det := \det(R)$, this leads to

$$r^\uparrow = \frac{\rho^\uparrow + \sqrt{\det}}{\left(\rho + 2\sqrt{\det}\right)^{1/2}}, \quad r^\downarrow = \frac{\rho^\downarrow + \sqrt{\det}}{\left(\rho + 2\sqrt{\det}\right)^{1/2}}, \quad \text{and} \quad s = \frac{\sigma}{\left(\rho + 2\sqrt{\det}\right)^{1/2}}.$$

Let us show for instance that $r^\uparrow \in H^1(\mathbb{R}^3)$, the other cases being similar. Using the inequalities $(a+b)^2 \leq 2(a^2+b^2)$, $\rho \geq \rho^\uparrow$ and $\det \geq 0$, we obtain

$$\left|r^\uparrow\right|^2 \leq \frac{\left(\rho^\uparrow + \sqrt{\det}\right)^2}{\rho + 2\sqrt{\det}} \leq \frac{2\left|\rho^\uparrow\right|^2 + 2\det}{\rho + 2\sqrt{\det}} \leq 2\rho + \sqrt{\det},$$

and the right-hand side is integrable, thanks to (2.8). On the other hand, the gradient of $r^\uparrow$ is

$$\nabla r^\uparrow = \frac{\nabla\rho^\uparrow + \nabla\sqrt{\det}}{\left(\rho + 2\sqrt{\det}\right)^{1/2}} - \frac{1}{2}\frac{\left(\nabla\rho + 2\nabla\sqrt{\det}\right)\left(\rho^\uparrow + \sqrt{\det}\right)}{\left(\rho + 2\sqrt{\det}\right)^{3/2}},$$

so that, using the same type of inequalities,

$$\begin{aligned} \left|\nabla r^\uparrow\right|^2 &\leq 2\frac{(\nabla\rho^\uparrow + \nabla\sqrt{\det})^2}{\rho + 2\sqrt{\det}} + \frac{(\rho + \sqrt{\det})^2(\nabla\rho + 2\nabla\sqrt{\det})^2}{(\rho + 2\sqrt{\det})^3} \\ &\leq 4\left(\frac{|\nabla\rho^\uparrow|^2}{\rho^\uparrow} + \frac{|\nabla\sqrt{\det}|^2}{\rho} + \frac{|\nabla\rho|^2}{\rho} + \frac{|\nabla\sqrt{\det}|^2}{\rho}\right). \end{aligned}$$

Every term of the right-hand side is in $L^1(\mathbb{R}^3)$ according to (2.8). We deduce that $r^\uparrow \in H^1(\mathbb{R}^3, \mathbb{C})$, and consequently, $\sqrt{R} \in \mathcal{M}_{2\times 2}(H^1(\mathbb{R}^3, \mathbb{C}))$. In conclusion, $R \in \mathcal{C}_N$.

If $R \in \mathcal{C}_N$, then R satisfies (2.8).
Reciprocally, using (2.9), it is not difficult to prove that R satisfies all conditions in (2.8). Let us prove for instance that $\left|\nabla\sqrt{\det}\right| \rho^{-1}$. From $\sqrt{\det} = r^\uparrow r^\downarrow - |s|^2$, we get

$$\nabla\sqrt{\det} = \left(\nabla r^\uparrow\right) r^\downarrow + r^\uparrow\left(\nabla r^\downarrow\right) - 2\mathrm{Re}\left(\overline{s}\nabla s\right).$$

Together with the inequality $(a+b+c)^2 \leq 3(a^2+b^2+c^2)$, we deduce

$$\frac{\left|\nabla\sqrt{\det}\right|^2}{\rho} = 3\frac{\left|\nabla r^\uparrow\right|^2\left|r^\downarrow\right|^2}{\rho} + 3\frac{\left|\nabla r^\downarrow\right|^2\left|r^\uparrow\right|^2}{\rho} + 6\frac{|\nabla s|^2|s|^2}{\rho} \leq 3\left|\nabla r^\uparrow\right|^2 + 3\left|\nabla r^\downarrow\right|^2 + 6|\nabla s|^2,$$

and the right-hand side is in $L^1(\mathbb{R}^3)$ since $R \in \mathcal{C}_N$. The result follows. □

Proof of Theorem 2.2

Proof. We break the proof in many parts.

Step 1: $\mathcal{J}_N^{\rm mixed} \subset \mathcal{C}_N$.

For a mixed state $\Gamma \in G_N^{\rm mixed}$, we define the *one-body spin-density matrix*

$$\gamma_\Gamma(\mathbf{r},\mathbf{r}') = \begin{pmatrix} \gamma_\Gamma^{\uparrow\uparrow} & \gamma_\Gamma^{\uparrow\downarrow} \\ \gamma_\Gamma^{\downarrow\uparrow} & \gamma_\Gamma^{\downarrow\downarrow} \end{pmatrix}(\mathbf{r},\mathbf{r}'), \tag{2.10}$$

where

$$\gamma_\Gamma^{\alpha\beta}(\mathbf{r},\mathbf{r}') := N \sum_{\mathbf{s}\in\{\uparrow,\downarrow\}^{N-1}} \int_{\mathbb{R}^{3(N-1)}} \Gamma(\mathbf{r},\alpha,\mathbf{z},\mathbf{s};\mathbf{r}',\beta,\mathbf{z},\mathbf{s})\, \mathrm{d}\mathbf{z}. \tag{2.11}$$

It holds that $R_\Gamma(\mathbf{r}) = \gamma_\Gamma(\mathbf{r},\mathbf{r}')$. We denote by $R_\gamma := R_\Gamma$ in the sequel. The one-body spin-density matrix is a very useful quantity in quantum chemistry, and is completely understood mathematically. Coleman [Col63] proved that any such γ can be written as

$$\gamma^{\alpha\beta}(\mathbf{r},\mathbf{r}') = \sum_{k=1}^\infty n_k \phi_k^\alpha(\mathbf{r})\overline{\phi_k^\beta(\mathbf{r}')},\ 0 \le n_k \le 1,\ \sum_{k=1}^\infty n_k = N,$$
$$\langle \Phi_k | \Phi_l \rangle = \delta_{kl},\ \mathrm{Tr}(-\Delta\gamma) := \sum_{k=1}^\infty n_k \|\nabla\Phi_k\|^2 < \infty.$$

Let $R \in \mathcal{J}_N^{\rm mixed}$. To prove $R \in \mathcal{C}_N$, it is enough to prove that R satisfies the conditions (2.8), thanks to Lemma 2.1. By definition, there exists γ satisfying the above conditions such that $R = R_\gamma$, so that

$$R = \sum_{k=1}^\infty n_k \begin{pmatrix} \left|\phi_k^\uparrow\right|^2 & \phi_k^\uparrow\overline{\phi_k^\downarrow} \\ \phi_k^\downarrow\overline{\phi_k^\uparrow} & \left|\phi_k^\downarrow\right|^2 \end{pmatrix}.$$

Under this form, the first line of (2.8) is obvious. Also, since all elements of R are of the form $\sum n_k \phi_k^\alpha(\mathbf{r})\overline{\phi_k^\beta}(\mathbf{r})$ with $\sum n_k \|\nabla\phi_k^\sigma\|^2 < \infty$, we easily deduce from the Sobolev embedding that $R \in W^{1,3/2}(\mathbb{R}^3)$. Moreover, using the Cauchy-Schwarz inequality, it follows, for $\alpha \in \{\uparrow,\downarrow\}$,

$$|\nabla\rho^\alpha|^2 = 4\left(\sum_{k=1}^\infty n_k \mathrm{Re}\left(\phi_k^\alpha \overline{\nabla\phi_k^\alpha}\right)\right)^2 \le 4\left(\sum_{k=1}^\infty n_k|\phi_k^\alpha|^2\right)\left(\sum_{k=1}^\infty n_k|\nabla\phi_k^\alpha|^2\right),$$

so that $|\nabla\sqrt{\rho^\alpha}|^2 \le 4\sum n_k|\nabla\phi_k^\alpha|^2$ (we recall that for $f \ge 0$, it holds $|\nabla f|^2 = 4f|\nabla\sqrt{f}|^2$). Integrating this relation gives $\|\nabla\sqrt{\rho^\alpha}\|_{L^2}^2 \le \mathrm{Tr}(-\Delta\gamma^{\alpha\alpha}) < \infty$. Likewise,

$$|\nabla\sigma|^2 = \left|\sum_{k=1}^\infty n_k\left(\nabla\phi_k^\uparrow\overline{\phi_k^\downarrow} + \phi_k^\uparrow\overline{\nabla\phi_k^\downarrow}\right)\right|^2 \le \left|\sum_{k=1}^\infty n_k\left(|\phi_k^\uparrow|^2+|\phi_k^\downarrow|^2\right)^{1/2}\left(|\nabla\phi_k^\uparrow|^2+|\nabla\phi_k^\downarrow|^2\right)^{1/2}\right|^2$$
$$\le \rho\left(\sum_{k=1}^\infty n_k\left(|\nabla\phi_k^\uparrow|^2+|\nabla\phi_k^\downarrow|^2\right)\right),$$

so that $|\nabla\sigma|^2\rho^{-1} \le \sum n_k(|\nabla\phi_k^\uparrow|^2+|\nabla\phi_k^\downarrow|^2)$. Integrating this relation gives the inequality $\||\nabla\sigma|^2\rho^{-1}\|_{L^1} \le \mathrm{Tr}(-\Delta\gamma) < \infty$. Finally, let us evaluate $\det(R)$. From $\det(R) = \rho^\uparrow\rho^\downarrow - |\sigma|^2$,

we get

$$\begin{aligned}\det(R) &= \sum_{k,l=1}^{\infty} n_k n_l \left(\left|\phi_k^\uparrow\right|^2 \left|\phi_l^\downarrow\right|^2 - \phi_k^\uparrow \overline{\phi_k^\downarrow} \phi_l^\downarrow \overline{\phi_l^\uparrow} \right) \\ &= \sum_{1\le k<l<\infty} n_k n_l \left(\left|\phi_k^\uparrow\right|^2 \left|\phi_l^\downarrow\right|^2 + \left|\phi_l^\uparrow\right|^2 \left|\phi_k^\downarrow\right|^2 - \phi_k^\uparrow \overline{\phi_k^\downarrow} \phi_l^\downarrow \overline{\phi_l^\uparrow} - \phi_l^\uparrow \overline{\phi_l^\downarrow} \phi_k^\downarrow \overline{\phi_k^\uparrow} \right) \\ &= \sum_{1\le k<l<\infty} n_k n_l \left| \phi_k^\uparrow \phi_l^\downarrow - \phi_k^\downarrow \phi_l^\uparrow \right|^2 = \frac{1}{2} \sum_{k,l=1}^{\infty} n_k n_l \left| \phi_k^\uparrow \phi_l^\downarrow - \phi_k^\downarrow \phi_l^\uparrow \right|^2 .\end{aligned}$$

Using similar arguments as before, we obtain that $\sqrt{\det} \in W^{1,3/2}(\mathbb{R}^3)$ and that

$$|\nabla \det(R)|^2 \le 8 \det(R) \rho \sum_{k=1}^{\infty} n_k \left(|\nabla \phi_k^\uparrow|^2 + |\nabla \phi_k^\downarrow|^2 \right).$$

Integrating this inequality leads to $\left\| |\nabla \sqrt{\det(R)}|^2 \rho^{-1} \right\|_{L^1} \le 2\mathrm{Tr}(-\Delta\gamma) < \infty$. Therefore, any $R \in \mathcal{J}_N^{\mathrm{mixed}}$ satisfies (2.8), hence is in $\mathcal{C}_N$.

Step 2: Case $N = 1$: $\mathcal{J}_1^{\mathrm{Slater}} = \mathcal{J}_1^{\mathrm{pure}} = \mathcal{C}_1^0$.
The fact that $\mathcal{J}_1^{\mathrm{Slater}} = \mathcal{J}_1^{\mathrm{pure}}$ simply comes from the fact that $G_1^{\mathrm{Slater}} = G_1^{\mathrm{pure}}$. To prove $\mathcal{J}_1^{\mathrm{Slater}} \subset \mathcal{C}_1^0$, we let $R \in \mathcal{J}_1^{\mathrm{Slater}}$ be represented by $\Phi = (\phi^\uparrow, \phi^\downarrow)^T \in H^1(\mathbb{R}^3, \mathbb{C}^2)$, so that

$$R = \begin{pmatrix} |\phi^\uparrow|^2 & \phi^\uparrow \overline{\phi^\downarrow} \\ \phi^\downarrow \overline{\phi^\uparrow} & |\phi^\downarrow|^2 \end{pmatrix}.$$

Since $R \in \mathcal{J}_1^{\mathrm{Slater}} \subset \mathcal{J}_1^{\mathrm{mixed}} \subset \mathcal{C}_N$ according to Step 1, and since $\det(R) \equiv 0$, we deduce that $R \in \mathcal{C}_N^0$.

We now prove that $\mathcal{C}_1^0 \subset \mathcal{J}_1^{\mathrm{Slater}}$. Let $R = \begin{pmatrix} \rho^\uparrow & \sigma \\ \overline{\sigma} & \rho^\downarrow \end{pmatrix} \in \mathcal{C}_1^0$. From $\det R \equiv 0$ and Lemma 2.1, we get

$$\begin{cases} \rho^{\uparrow/\downarrow} \ge 0, \quad \rho^\uparrow \rho^\downarrow = |\sigma|^2, \quad \displaystyle\int_{\mathbb{R}^3} \rho^\uparrow + \int_{\mathbb{R}^3} \rho^\downarrow = 1, \\ \sqrt{\rho^{\uparrow/\downarrow}} \in H^1(\mathbb{R}^3), \quad \sigma \in W^{1,3/2}(\mathbb{R}^3), \\ |\nabla\sigma|^2 \rho^{-1} \in L^1(\mathbb{R}^3). \end{cases} \tag{2.12}$$

There are two natural choices that we would like to make for a representing orbital, namely

$$\Phi_1 = \left(\sqrt{\rho^\uparrow}, \quad \frac{\overline{\sigma}}{\sqrt{\rho^\uparrow}} \right)^T \quad \text{and} \quad \Phi_2 = \left(\frac{\sigma}{\sqrt{\rho^\downarrow}}, \quad \sqrt{\rho^\downarrow} \right)^T. \tag{2.13}$$

Unfortunately, it is not guaranteed that these orbitals are indeed in $H^1(\mathbb{R}^3, \mathbb{C}^2)$. It is the case only if $|\nabla\sigma|^2/\rho^\downarrow$ is in $L^1(\mathbb{R}^3)$ for Φ_1, and if $|\nabla\sigma|^2/\rho^\uparrow$ is in $L^1(\mathbb{R}^3)$ for Φ_2. Due to (2.12), we only know that $|\nabla\sigma|^2/\rho \in L^1(\mathbb{R}^3)$. The idea is therefore to interpolate between these two orbitals, taking Φ_1 in regions where $\rho^\uparrow \gg \rho^\downarrow$, and Φ_2 in regions where $\rho^\downarrow \gg \rho^\uparrow$. This is done via the following process.

Let $\chi \in C^\infty(\mathbb{R})$ be a non-decreasing function such that $0 \le \chi \le 1$, $\chi(x) = 0$ if $x \le 1/2$ and $\chi(x) = 1$ if $x \ge 1$. We write $\sigma = \alpha + \mathrm{i}\beta$ where α is the real-part of σ, and β is its imaginary part. We introduce

$$\begin{aligned} \lambda_1 &:= \frac{\sqrt{\alpha^2 + \chi^2(\rho^\uparrow/\rho^\downarrow)\beta^2}}{\sqrt{\rho^\downarrow}}, & \mu_1 &:= \sqrt{1 - \chi^2(\rho^\uparrow/\rho^\downarrow)} \frac{\beta}{\sqrt{\rho^\downarrow}}, \\ \lambda_2 &:= \frac{\alpha\lambda_1 + \beta\mu_1}{\rho^\uparrow}, & \mu_2 &:= \frac{\beta\lambda_1 - \alpha\mu_1}{\rho^\uparrow}, \end{aligned}$$

and we set

$$\phi^\uparrow := \lambda_1 + \mathrm{i}\mu_1 \quad \text{and} \quad \phi^\downarrow := \lambda_2 + \mathrm{i}\mu_2.$$

Let us prove that $\Phi := (\phi^\uparrow, \phi^\downarrow)$ represents R and that $\Phi \in \mathcal{W}_1^{\mathrm{Slater}}$. First, an easy calculation shows that

$$\begin{aligned}
|\phi^\uparrow|^2 = \lambda_1^2 + \mu_1^2 &= \frac{\alpha^2 + \chi^2\beta^2 + (1-\chi^2)\beta^2}{\rho^\downarrow} = \frac{|\sigma|^2}{\rho^\downarrow} = \rho^\uparrow, \\
|\phi^\downarrow|^2 &= \frac{(\alpha^2+\beta^2)(\lambda_1^2+\mu_1^2)}{(\rho^\uparrow)^2} = \frac{|\sigma|^2}{\rho^\uparrow} = \rho^\downarrow, \\
\mathrm{Re}\left(\phi^\uparrow\overline{\phi^\downarrow}\right) &= \lambda_1\lambda_2 - \mu_1\mu_2 = \frac{\alpha(\lambda_1^2+\mu_1^2)}{\rho^\uparrow} = \alpha, \\
\mathrm{Im}\left(\phi^\uparrow\overline{\phi^\downarrow}\right) &= \lambda_1\mu_2 + \lambda_2\mu_1 = \frac{\beta(\lambda_1^2+\mu_1^2)}{\sqrt{\rho^\uparrow}} = \beta,
\end{aligned}$$

so that $\Phi \in L^2(\mathbb{R}^3, \mathbb{C}^2)$ with $\|\Phi\| = 1$, and Φ represents R. To prove that $\Phi \in \mathcal{W}_1^{\mathrm{Slater}}$, we need to check that $\lambda_1, \lambda_2, \mu_1$ and μ_2 are in $H^1(\mathbb{R}^3)$. For λ_1, we choose another non-increasing function $\xi \in C^\infty(\mathbb{R})$ such that $0 \le \xi \le 1$, $\xi(x) = 0$ for $x \le 1$, and $\xi(x) = 1$ for $x \ge 2$. Note that $(1-\chi)\xi \equiv 0$. It holds that

$$\nabla\lambda_1 = (1 - \xi^2(\rho^\uparrow/\rho^\downarrow))\nabla\lambda_1 + \xi^2(\rho^\uparrow/\rho^\downarrow)\nabla\lambda_1. \tag{2.14}$$

The second term in the right-hand side of (2.14) is non-null only if $\rho^\uparrow \ge \rho^\downarrow$, so that on this part, it holds $\chi(\rho^\uparrow/\rho^\downarrow) = 1$. In particular, from the equality $\rho^\uparrow\rho^\downarrow = |\sigma|^2$, we get

$$\xi^2(\rho^\uparrow/\rho^\downarrow)\lambda_1 = \xi^2(\rho^\uparrow/\rho^\downarrow)\frac{|\sigma|}{\sqrt{\rho^\downarrow}} = \xi^2(\rho^\uparrow/\rho^\downarrow)\sqrt{\rho^\uparrow},$$

and similarly,

$$\xi^2(\rho^\uparrow/\rho^\downarrow)\nabla\lambda_1 = \xi^2(\rho^\uparrow/\rho^\downarrow)\nabla\sqrt{\rho^\uparrow},$$

which is in $L^2(\mathbb{R}^3)$ according to (2.12). On the other hand, the first term in the right-hand side of (2.14) is non-null only if $\rho^\uparrow \le 2\rho^\downarrow$, so that $(1/3)\rho \le \rho^\downarrow$ on this part. In particular, from the following pointwise estimate

$$|\nabla\sqrt{f+g}| = \frac{|\nabla f + \nabla g|}{2\sqrt{f+g}} \le \frac{|\nabla f|}{2\sqrt{f+g}} + \frac{|\nabla g|}{2\sqrt{f+g}} \le \frac{|\nabla f|}{2\sqrt{f}} + \frac{|\nabla g|}{2\sqrt{g}} = |\nabla\sqrt{f}| + |\nabla\sqrt{g}|, \tag{2.15}$$

which is valid almost everywhere whenever $f, g \ge 0$, the inequality $(a+b)^2 \le 2(a^2+b^2)$, and the fact that $\alpha^2 + \chi^2\beta^2 \le |\sigma|^2$, we get (we write χ for $\chi(\rho^\uparrow/\rho^\downarrow)$)

$$\begin{aligned}
|\nabla\lambda_1|^2 &= \left|\frac{\sqrt{\rho^\downarrow}\nabla\sqrt{\alpha^2+\chi^2\beta^2} - \sqrt{\alpha^2+\chi^2\beta^2}\nabla\sqrt{\rho^\downarrow}}{\rho^\downarrow}\right|^2 \\
&\le 2\left(\frac{|\nabla\sqrt{\alpha^2+\chi^2\beta^2}|^2}{\rho^\downarrow} + \frac{(\alpha^2+\chi^2\beta^2)}{(\rho^\downarrow)^2}|\nabla\sqrt{\rho^\downarrow}|^2\right) \\
&\le 2\left(\frac{|\nabla\alpha|^2}{\rho^\downarrow} + \frac{2\left|\nabla\chi\frac{\rho^\downarrow\nabla\rho^\uparrow - \rho^\uparrow\nabla\rho^\downarrow}{(\rho^\downarrow)^2}\right|^2\beta^2}{\rho^\downarrow} + \frac{2\chi^2|\nabla\beta|^2}{\rho^\downarrow} + \frac{2|\sigma|^2}{(\rho^\downarrow)^2}|\nabla\sqrt{\rho^\downarrow}|^2\right).
\end{aligned}$$

We finally use the inequality $(\rho^\downarrow)^{-1} \le (3/\rho)$, and the inequality $|\sigma|^2/(\rho^\downarrow)^2 = \rho^\uparrow/\rho^\downarrow \le 2$ and get

$$|\nabla\lambda_1|^2 \le C\left(\frac{|\nabla\alpha|^2}{\rho} + \|\nabla\chi\|_{L^\infty}^2\left(\frac{|\nabla\rho^\uparrow|^2}{\rho^\uparrow} + \frac{|\nabla\rho^\downarrow|^2}{\rho^\downarrow}\right) + \frac{|\nabla\beta|^2}{\rho} + |\nabla\sqrt{\rho^\downarrow}|^2\right).$$

The right-hand side is in $L^1(\mathbb{R}^3)$ according to (2.12). Hence, $(1-\xi^2(\rho^\uparrow/\rho^\downarrow))\,|\nabla\lambda_1| \in L^2(\mathbb{R}^3)$, and finally $\lambda_1 \in H^1(\mathbb{R}^3)$.
The other cases are treated similarly, observing that,

- whenever $\rho^\uparrow \geq \rho^\downarrow$, then $\chi = 1$, and $\Phi = \Phi_1$ where Φ_1 was defined in (2.13). We then control $(\rho^\uparrow)^{-1}$ with the inequality $(\rho^\uparrow)^{-1} \leq 2\rho^{-1}$;
- whenever $\rho^\uparrow \leq \rho^\downarrow/2$, then $\chi = 0$, $\Phi = \Phi_2$. We control $(\rho^\downarrow)^{-1}$ with the inequality $(\rho^\downarrow)^{-1} \leq \frac{3}{2}\rho^{-1}$;
- whenever $\rho^\downarrow/2 \leq \rho^\uparrow \leq \rho^\downarrow$, then both $(\rho^\uparrow)^{-1}$ and $(\rho^\downarrow)^{-1}$ are controlled via $(\rho^\uparrow)^{-1} \leq 3\rho^{-1}$ and $(\rho^\downarrow)^{-1} \leq 2\rho^{-1}$.

The result follows.

Step 3: Case $N \geq 2$: $\mathcal{J}_N^{\text{Slater}} = \mathcal{J}_N^{\text{pure}} = \mathcal{J}_N^{\text{mixed}} = \mathcal{C}_N$.
Since $\mathcal{J}_N^{\text{Slater}} \subset \mathcal{J}_N^{\text{pure}} \subset \mathcal{J}_N^{\text{mixed}} = \mathcal{C}_N$, according to Step 1, it is enough to prove that $\mathcal{C}_N \subset \mathcal{J}_N^{\text{Slater}}$. We start with a key lemma.

Lemma 2.4. *For all $M, N \in \mathbb{N}^2$, it holds that $\mathcal{J}_{N+M}^{\text{Slater}} = \mathcal{J}_N^{\text{Slater}} + \mathcal{J}_M^{\text{Slater}}$.*

Proof of Lemma 2.4. The case $\mathcal{J}_{N+M}^{\text{Slater}} \subset \mathcal{J}_N^{\text{Slater}} + \mathcal{J}_M^{\text{Slater}}$ is trivial: if $R \in \mathcal{J}_{N+M}^{\text{Slater}}$ is represented by the Slater determinant $\mathscr{S}[\Phi_1, \dots \Phi_{N+M}]$, then, by denoting by R_1 (resp. R_2) the spin-density 2×2 matrix associated to the Slater determinant $\mathscr{S}[\Phi_1, \dots, \Phi_N]$ (resp. $\mathscr{S}[\Phi_{N+1}, \dots, \Phi_{N+M}]$), it holds $R = R_1 + R_2$ (see Equation (2.4) for instance), with $R_1 \in \mathcal{J}_N^{\text{Slater}}$ and $R_2 \in \mathcal{J}_M^{\text{Slater}}$.

The converse is more involving, and requires an orthogonalization step. Let $R_1 \in \mathcal{J}_N^{\text{Slater}}$ be represented by the Slater determinant $\mathscr{S}[\Phi_1, \dots, \Phi_N]$, and $R_2 \in \mathcal{J}_M^{\text{Slater}}$ be represented by the Slater determinant $\mathscr{S}[\widetilde{\Phi}_1, \dots, \widetilde{\Phi}_M]$. We cannot directly consider the Slater determinant $\mathscr{S}[\Phi_1, \dots, \Phi_N, \widetilde{\Phi}_1, \dots, \widetilde{\Phi}_M]$, for $(\Phi_1, \dots, \Phi_N)$ is not orthogonal to $(\widetilde{\Phi}_1, \dots, \widetilde{\Phi}_M)$.

We use the following lemma, which is a smooth version of the Hobby-Rice theorem [HR65] (see also [Pin76]), and that was proved by Lazarev and Lieb in [LL13] (see also [LS13]).

Lemma 2.5 (Lazarev, Lieb)**.** *For all $N \in \mathbb{N}^*$, and for all $(f_1, \dots, f_N) \in L^1(\mathbb{R}^3, \mathbb{C})$, there exists a function $u \in C^\infty(\mathbb{R}^3)$, with bounded derivatives, such that*

$$\forall 1 \leq k \leq N, \quad \int_{\mathbb{R}^3} f_k \mathrm{e}^{\mathrm{i}u} = 0.$$

Moreover, u can be chosen to vary in the r_1 direction only.

We now modify the phases of $\widetilde{\Phi_1}, \dots, \widetilde{\Phi_M}$ as follows. First, we choose $\widetilde{u_1}$ as in Lemma 2.5 such that,

$$\forall 1 \leq k \leq N, \quad \int_{\mathbb{R}^3} \left(\overline{\phi_k^\uparrow}\widetilde{\phi_1^\uparrow} + \overline{\phi_k^\downarrow}\widetilde{\phi_1^\downarrow} \right) \mathrm{e}^{\mathrm{i}\widetilde{u_1}} = 0,$$

and we set $\Phi_{N+1} = \widetilde{\Phi_1}\mathrm{e}^{\mathrm{i}\widetilde{u_1}}$. Note that, by construction, Φ_{N+1} is normalized, in $H^1(\mathbb{R}^3, \mathbb{C}^2)$, and orthogonal to $(\Phi_1, \dots, \Phi_N)$. We then construct $\widetilde{u_2}$ as in Lemma 2.5 such that

$$\forall 1 \leq k \leq N+1, \quad \int_{\mathbb{R}^3} \left(\overline{\phi_k^\uparrow}\widetilde{\phi_2^\uparrow} + \overline{\phi_k^\downarrow}\widetilde{\phi_2^\downarrow} \right) \mathrm{e}^{\mathrm{i}\widetilde{u_2}} = 0,$$

and we set $\Phi_{N+2} = \widetilde{\Phi_2}\mathrm{e}^{\mathrm{i}\widetilde{u_2}}$. We continue this process for $3 \leq k \leq M$ and construct $\Phi_{N+k} = \widetilde{\Phi_k}\mathrm{e}^{\mathrm{i}\widetilde{u_k}}$. We thus obtain an orthonormal family $(\Phi_1, \dots, \Phi_{N+M})$. Since the spin-density 2×2

matrix of the Slater determinant $\mathscr{S}[\widetilde{\Phi_1},\dots,\widetilde{\Phi_M}]$ is the same as the one of $\mathscr{S}[\Phi_{N+1},\dots,\Phi_{N+M}]$ (the phases cancel out), we obtain that $R = R_1 + R_2$, where R is the spin-density 2×2 matrix represented by $\mathscr{S}[\Phi_1,\dots,\Phi_{N+M}]$. The result follows.

□

We now prove that $\mathcal{C}_N \subset \mathcal{J}_N^{\text{Slater}}$ for $N \geq 2$. We start with the case $N = 2$.

Case $N = 2$.
Let $R = \begin{pmatrix} \rho^\uparrow & \sigma \\ \overline{\sigma} & \rho^\downarrow \end{pmatrix} \in \mathcal{C}_2$. We write $\sqrt{R} = \begin{pmatrix} r^\uparrow & s \\ \overline{s} & r^\downarrow \end{pmatrix}$, with $r^\uparrow, r^\downarrow \in H^1(\mathbb{R}^3,\mathbb{R})$ and s in $H^1(\mathbb{R}^3,\mathbb{C})$. Let

$$R^\uparrow := \begin{pmatrix} |r^\uparrow|^2 & sr^\uparrow \\ \overline{s}r^\uparrow & |s|^2 \end{pmatrix} \quad \text{and} \quad R^\downarrow := \begin{pmatrix} |s|^2 & sr^\downarrow \\ \overline{s}r^\downarrow & |r^\downarrow|^2 \end{pmatrix}. \tag{2.16}$$

It is easy to check that $R = R^\uparrow + R^\downarrow$, that $R^{\uparrow/\downarrow}$ are hermitian, of null determinant, and that $\sqrt{R^{\uparrow/\downarrow}} \in \mathcal{M}_{2\times 2}\left(H^1(\mathbb{R}^3,\mathbb{C})\right)$. However, it may hold that $\int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}[R^\uparrow] \notin \mathbb{N}^*$, so that $R^\uparrow$ is not in $\mathcal{C}_M^0$ for some $M \in \mathbb{N}^*$.

The cases $R^\uparrow = 0$ or $R^\downarrow = 0$ are trivial. Let us suppose that $m^\alpha := \int_{\mathbb{R}^3} \rho_{R^\alpha} \neq 0$ for $\alpha \in \{\uparrow,\downarrow\}$. In this case, the matrices $\widetilde{R^\alpha} = (m^\alpha)^{-1} R^\alpha$ are in $\mathcal{C}_1^0$, hence are representable by a single orbital according to Step 2. Let $\widetilde{\Phi} = \left(\widetilde{\phi_1^\uparrow}, \widetilde{\phi_1^\downarrow}\right)^T \in H^1(\mathbb{R}^3,\mathbb{C}^2)$ and $\widetilde{\Phi}_2 = \left(\widetilde{\phi_2^\uparrow}, \widetilde{\phi_2^\downarrow}\right)^T \in H^1(\mathbb{R}^3,\mathbb{C}^2)$ be normalized orbitals that represent respectively $\widetilde{R^\uparrow}$ and $\widetilde{R^\downarrow}$. It holds

$$\widetilde{\Phi}_1\widetilde{\Phi}_1^* = \widetilde{R^\uparrow} = (m^\uparrow)^{-1}R^\uparrow \quad \text{and} \quad \widetilde{\Phi}_2\widetilde{\Phi}_2^* = \widetilde{R^\downarrow} = (m^\downarrow)^{-1}R^\downarrow.$$

From the Lazarev-Lieb orthogonalization process (see Lemma 2.5), there exists a function $u \in C^\infty(\mathbb{R})$ with bounded derivatives such that

$$\langle \widetilde{\Phi}_1 | \widetilde{\Phi}_2 \mathrm{e}^{\mathrm{i}u} \rangle = \int_{\mathbb{R}^3} \left(\overline{\widetilde{\phi_1^\uparrow}}\widetilde{\phi_2^\uparrow} + \overline{\widetilde{\phi_1^\downarrow}}\widetilde{\phi_2^\downarrow} \right) \mathrm{e}^{\mathrm{i}u} = 0. \tag{2.17}$$

Once this function is chosen, there exists a function $v \in C^\infty(\mathbb{R})$ with bounded derivatives such that

$$\langle \widetilde{\Phi}_1 | \widetilde{\Phi}_1 \mathrm{e}^{\mathrm{i}v} \rangle = \langle \widetilde{\Phi}_1 | \widetilde{\Phi}_2 \mathrm{e}^{\mathrm{i}(u+v)} \rangle = \langle \widetilde{\Phi}_2 \mathrm{e}^{\mathrm{i}u} | \widetilde{\Phi}_1 \mathrm{e}^{\mathrm{i}v} \rangle = \langle \widetilde{\Phi}_2 | \widetilde{\Phi}_2 \mathrm{e}^{\mathrm{i}v} \rangle = 0. \tag{2.18}$$

We finally set

$$\Phi_1 := \frac{1}{\sqrt{2}} \left(\sqrt{m^\uparrow}\widetilde{\Phi}_1 + \sqrt{m^\downarrow}\widetilde{\Phi}_2 \mathrm{e}^{\mathrm{i}u} \right) \quad \text{and} \quad \Phi_2 := \frac{1}{\sqrt{2}} \left(\sqrt{m^\uparrow}\widetilde{\Phi}_1 - \sqrt{m^\downarrow}\widetilde{\Phi}_2 \mathrm{e}^{\mathrm{i}u} \right) \mathrm{e}^{\mathrm{i}v}.$$

From (2.17), we deduce $\|\Phi_1\|^2 = \|\Phi_2\|^2 = 1$, so that both Φ_1 and Φ_2 are normalized. Also, from (2.18), we get $\langle \Phi_1 | \Phi_2 \rangle = 0$, hence $\{\Phi_1, \Phi_2\}$ is orthonormal. As $\widetilde{\Phi}_1$ and $\widetilde{\Phi}_2$ are in $H^1(\mathbb{R}^3,\mathbb{C}^2)$, and u and v have bounded derivatives, Φ_1 and Φ_2 are in $H^1(\mathbb{R}^3,\mathbb{C}^2)$. Finally, it holds that

$$\begin{aligned} \Phi_1\Phi_1^* + \Phi_2\Phi_2^* = \frac{1}{2} \Big(& m^\uparrow \widetilde{\Phi}_1\widetilde{\Phi}_1^* + m^\downarrow \widetilde{\Phi}_2\widetilde{\Phi}_2^* + 2\sqrt{m^\uparrow m^\downarrow}\mathrm{Re}\left(\widetilde{\Phi}_1\widetilde{\Phi}_2^* \mathrm{e}^{-\mathrm{i}u}\right) \\ & + m^\uparrow \widetilde{\Phi}_1\widetilde{\Phi}_1^* + m^\downarrow \widetilde{\Phi}_2\widetilde{\Phi}_2^* - 2\sqrt{m^\uparrow m^\downarrow}\mathrm{Re}\left(\widetilde{\Phi}_1\widetilde{\Phi}_2^* \mathrm{e}^{-\mathrm{i}u}\right) \Big) \\ = {} & m^\uparrow \widetilde{\Phi}_1\widetilde{\Phi}_1^* + m^\downarrow \widetilde{\Phi}_2\widetilde{\Phi}_2^* = R. \end{aligned}$$

We deduce that the Slater determinant $\mathscr{S}[\Phi_1,\Phi_2]$ represents R, so that $R \in \mathcal{J}_2^{\text{Slater}}$. Altogether, $\mathcal{C}_2 \subset \mathcal{J}_2^{\text{Slater}}$, and therefore $\mathcal{C}_2 = \mathcal{J}_2^{\text{Slater}}$.

Case $N > 2$.
We proceed by induction. Let $R \in \mathcal{C}_{N+1}$ with $N \geq 2$, and suppose $\mathcal{C}_N = \mathcal{J}_N^{\text{Slater}}$. We use the decomposition (2.16) and write $R = R^\uparrow + R^\downarrow$, where $R^{\uparrow/\downarrow}$ are two null-determinant hermitian matrices. For $\alpha \in \{\uparrow, \downarrow\}$, we denote by $m^\alpha := \int_{\mathbb{R}^3} \rho_{R^\alpha}$. Since $m^\uparrow + m^\downarrow = N + 1 \geq 3$, at least $m^\uparrow$ or $m^\downarrow$ is greater than 1. Let us suppose without loss of generality that $m^\uparrow \geq 1$. We write $R = R_1 + R_2$ with

$$R_1 := (m^\uparrow)^{-1} R^\uparrow \quad \text{and} \quad R_2 := \left(\left(1 - (m^\uparrow)^{-1} \right) R^\uparrow + m^\downarrow R^\downarrow \right).$$

It holds that $R_1 \in \mathcal{C}_1^0 = \mathcal{J}_1^{\text{Slater}}$ and $R_2 \in \mathcal{C}_N = \mathcal{J}_N^{\text{Slater}}$ (by induction). Together with Lemma 2.4, we deduce that $R \in \mathcal{J}_{N+1}^{\text{Slater}}$. The proof is complete. □

Proof of Corollary 2.3

Proof. Let $R \in \mathcal{J}_N^{\text{mixed}} = \mathcal{C}_N$, and let $\sqrt{R} = \begin{pmatrix} r^\uparrow & s \\ \overline{s} & r^\downarrow \end{pmatrix}$. The eigenvalues of R are denoted by $0 \leq \rho^- \leq \rho^+$, so that $\sqrt{\rho^\pm}$ are the eigenvalues of $\sqrt{R}$. In particular,

$$\sqrt{\rho^\pm} = \frac{1}{2} \left(r^\uparrow + r^\downarrow \pm \sqrt{\Delta} \right) \quad \text{with} \quad \Delta = (r^\uparrow - r^\downarrow)^2 + 4|s|^2.$$

According to Theorem 2.2, $r^\uparrow$, $r^\downarrow$ and s are in $H^1(\mathbb{R}^3)$. Hence, Δ is the sum of two quantities whose square roots are in $H^1(\mathbb{R}^3)$, so that $\sqrt{\Delta} \in H^1(\mathbb{R}^3)$ by convexity of $\|\sqrt{\cdot}\|_{L^2}^2$.The result follows. □

2.2 Representability in CSDFT

We now get interested in current-spin-density function theory (CSDFT). For a system subjected to a magnetic field, the energy of the ground state can be obtained by a minimization over the set of admissible pairs $(R, \mathbf{j})$, where R is the spin-density 2×2 matrix introduced in Section 2.1.1, and $\mathbf{j}$ is the paramagnetic current [VR88]. This has lead to several density-based theories, that come from several different approximations. In spin-density functional theory (SDFT), one is only interested in spin effects, hence the paramagnetic term is neglected. In parallel, in current-density functional theory (CDFT), one is only interested in magnetic orbital effects, and spin effects are neglected [Vig87]. In this case, the CDFT energy functional of the system only depends on ρ and $\mathbf{j}$, and we need a characterization of the set of pure-state and mixed-state N-representable pairs $(\rho, \mathbf{j})$. Such a characterization was given recently by Hellgren, Kvaal and Helgaker in the mixed-state setting [TKH14], and by Lieb and Schrader in the pure-state setting, when the number of electrons is greater than 4 [LS13].

In this section, we give some answers to the N-representability problems in the current-spin-density functional theory (CSDFT): *What is the set of pairs* $(R, \mathbf{j})$ *that come from an admissible* N*-electron wave-function*, resp. *an admissible* N*-body density matrix?* (pure-state resp. mixed-state representability). We will answer the question in the mixed-state setting for all $N \in \mathbb{N}^*$, and in the pure-state setting when $N \geq 12$ by combining the results of the previous section and the results in [LS13]. The proof relies on the Lazarev-Lieb orthogonalization process. In particular, our method does not give an upper-bound for the kinetic energy of the wave-function in terms of the previous quantities (we refer to [LL13, Rut13] for more details). We leave open the case $N < 12$ for pure-state CSDFT representability.

2.2.1 Representable spin-density 2×2 matrix with paramagnetic current

We will use the same notation as in the previous section. In addition to the spin-density 2×2 matrix, we need to define the paramagnetic current $\mathbf{j}$. For a N-body density matrix $\Gamma \in G_N^{\text{mixed}}$, the associated paramagnetic current is $\mathbf{j}_\Gamma = \mathbf{j}_\Gamma^\uparrow + \mathbf{j}_\Gamma^\downarrow$ where

$$\mathbf{j}_\Gamma^\alpha = \mathrm{Im}\left(N \sum_{\vec{s} \in \{\uparrow,\downarrow\}^{N-1}} \int_{\mathbb{R}^{3(N-1)}} \nabla_{\mathbf{r}'} \Gamma(\mathbf{r}, \alpha, \vec{\mathbf{z}}, \vec{s}; \mathbf{r}', \alpha, \vec{\mathbf{z}}, \vec{s}) \Big|_{\mathbf{r}'=\mathbf{r}} \mathrm{d}\vec{\mathbf{z}} \right).$$

In the case where Γ comes from a Slater determinant $\mathscr{S}[\Phi_1, \dots, \Phi_N]$, we get

$$\mathbf{j}_\Gamma = \sum_{k=1}^{N} \mathrm{Im}\left(\overline{\phi_k^\uparrow} \nabla \phi_k^\uparrow + \overline{\phi_k^\downarrow} \nabla \phi_k^\downarrow \right). \tag{2.19}$$

While only the total paramagnetic current $\mathbf{j}$ appears in C(S)DFT, the pair $(\mathbf{j}^\uparrow, \mathbf{j}^\downarrow)$ is sometimes used to design accurate current-density functionals (see [VR88] for instance). In this thesis, we only focus on the representability of $\mathbf{j}$, and not on the pair $(\mathbf{j}^\uparrow, \mathbf{j}^\downarrow)$.

Let us recall some classical necessary conditions for a pair $(R, \mathbf{j})$ to be N-representable (we refer to [TKH14, LS13] for the proofs). In the sequel, we will denote by $\rho^\uparrow := \rho^{\uparrow\uparrow}$, $\rho^\downarrow := \rho^{\downarrow\downarrow}$ and $\sigma := \rho^{\uparrow\downarrow}$ the elements of a matrix R, so that $R = \begin{pmatrix} \rho^\uparrow & \sigma \\ \overline{\sigma} & \rho^\downarrow \end{pmatrix}$, and by $\rho = \rho^\uparrow + \rho^\downarrow$ the associated total electronic density. Recall that the set $\mathcal{C}_N$ was defined in (2.7).

Lemma 2.6. *If a pair* $(R, \mathbf{j})$ *is representable by a mixed-state* N*-body density matrix, then*

$$\begin{cases} R \in \mathcal{C}_N \\ |\mathbf{j}|^2 \rho^{-1} \in L^1(\mathbb{R}^3). \end{cases} \tag{2.20}$$

From the second condition of (2.20), it must hold that the support of $\mathbf{j}$ is contained in the support of ρ. The vector $\mathbf{v} := \rho^{-1}\mathbf{j}$ is called the *velocity field*, and $\mathbf{w} := \mathbf{curl}(\mathbf{v})$ is the *vorticity*.

Let us first consider the pure-state setting. In the spin-unpolarized setting, for $N = 1$, a pair $(\rho, \mathbf{j})$ representable by a single orbital ϕ generally satisfies the curl-free condition $\mathbf{curl}(\rho^{-1}\mathbf{j}) = \mathbf{0}$ (this is the case for instance when ϕ is of the form $\phi = |\phi|e^{-iu}$, where the phase u is in $C^1(\mathbb{R}^3)$, see [LS13, TKH14]). This is no longer the case when spin is considered, as is shown is the following Lemma (see Section 2.2.2 for the proof).

Lemma 2.7 (CSDFT, case $N = 1$)**.** *Let $\Phi = (\phi^\uparrow, \phi^\downarrow)^T \in \mathcal{W}_1^{\text{Slater}}$ be such that both $\phi^\uparrow$ and $\phi^\downarrow$ have phases in $C^1(\mathbb{R})$. Then, the associated pair $(R, \mathbf{j})$ satisfies $R \in \mathcal{C}_1^0$, $|\mathbf{j}|^2\rho^{-1} \in L^1(\mathbb{R}^3)$, and the two curl-free conditions*

$$\boldsymbol{curl}\left(\frac{\mathbf{j}}{\rho} - \frac{\mathrm{Im}\,(\overline{\sigma}\nabla\sigma)}{\rho\rho^\downarrow}\right) = \mathbf{0}, \quad \boldsymbol{curl}\left(\frac{\mathbf{j}}{\rho} + \frac{\mathrm{Im}\,(\overline{\sigma}\nabla\sigma)}{\rho\rho^\uparrow}\right) = \mathbf{0}. \tag{2.21}$$

Remark 2.8. *If we write $\sigma = |\sigma|e^{i\tau}$, then, $|\sigma|^2 = \rho^\uparrow\rho^\downarrow$, and*

$$\mathrm{Im}\,(\overline{\sigma}\nabla\sigma) = |\sigma|^2\nabla\tau = \rho^\uparrow\rho^\downarrow\nabla\tau. \tag{2.22}$$

In particular, it holds that

$$\boldsymbol{curl}\left(\frac{\mathrm{Im}\,(\overline{\sigma}\nabla\sigma)}{\rho\rho^\downarrow} + \frac{\mathrm{Im}\,(\overline{\sigma}\nabla\sigma)}{\rho\rho^\uparrow}\right) = \boldsymbol{curl}\,(\nabla\tau) = \mathbf{0},$$

so that one of the equalities in (2.21) implies the other one.

Remark 2.9. *We recover the traditional result in the collinear spin setting, where $\sigma \equiv 0$.*

In the case $N > 1$, things are very different. In [LS13], the authors proved the following theorem for $N \geq 4$.

Theorem 2.10 (Lieb, Schrader)**.**
A sufficient set of conditions for a pair $(\rho, \mathbf{j})$ to be pure-state N-representable is

- *$\rho \in \mathcal{I}_N$ with $N \geq 4$ and $\mathbf{j}$ satisfies $|\mathbf{j}|^2\rho^{-1} \in L^1(\mathbb{R}^3)$.*
- *there exists $\delta > 0$ such that*

$$\sup_{\mathbf{r}\in\mathbb{R}^3} f(\mathbf{r})^{(1+\delta)/2}\big(|\mathbf{w}(\mathbf{r})| + |\nabla\mathbf{w}(\mathbf{r})|\big) < \infty \tag{2.23}$$

where

$$f(\mathbf{r}) := (1 + (r_1)^2)(1 + (r_2)^2)(1 + (r_3)^2). \tag{2.24}$$

By adapting their proof to our case, we are able to ensure representability of a pair $(R, \mathbf{j})$ by a Slater determinant for $N \geq 12$ under the same mild condition (see Section 2.2.2 for the proof).

Theorem 2.11 (CSDFT, case $N \geq 12$)**.**
A sufficient set of conditions for a pair $(R, \mathbf{j})$ to be representable by a Slater determinant is

- *$R \in \mathcal{C}_N$ with $N \geq 12$ and $\mathbf{j}$ satisfies $|\mathbf{j}|^2\rho^{-1} \in L^1(\mathbb{R}^3)$*
- *there exists $\delta > 0$ such that,*

$$\sup_{\mathbf{r}\in\mathbb{R}^3} f(\mathbf{r})^{(1+\delta)/2}\big(|\mathbf{w}(\mathbf{r})| + |\nabla\mathbf{w}(\mathbf{r})|\big) < \infty, \tag{2.25}$$

where f is the function defined in (2.24).

Remark 2.12. *The condition (2.25) has of course the same origin as the condition (2.23). In [LS13], the authors conjectured that this condition "can be considerably loosened".*

Let us turn to the mixed-state case. If $(R, \mathbf{j})$ is representable by a Slater determinant $\mathscr{S}[\Phi_1, \dots, \Phi_N]$, then, for all $k \in \mathbb{N}^*$, the pair $(k/N)(R, \mathbf{j})$ is mixed-state representable, where N is the number of orbitals (simply take the uniform convex combination of the pairs represented by $\mathscr{S}[\Phi_1]$, $\mathscr{S}[\Phi_2]$, etc.). In particular, from Theorem 2.11, we deduce the following corollary.

Corollary 2.13 (CSDFT, case mixed-state)**.**
A sufficient set of conditions for a pair $(R, \mathbf{j})$ to be mixed-state representable is $R \in \mathcal{C}_N$ for some $N \in \mathbb{N}^*$, $\mathbf{j}$ satisfies $|\mathbf{j}|^2\rho^{-1} \in L^1(\mathbb{R}^3)$, and (2.25) holds for some $\delta > 0$.

In [TKH14], the authors provide different sufficient conditions than (2.25) for a pair $(\rho, \mathbf{j})$ to be mixed-state representable. They proved that if

$$(1 + |\cdot|^2)\rho \left|\nabla(\rho^{-1}\mathbf{j})\right|^2 \in L^1(\mathbb{R}^3),$$

then the pair $(\rho, \mathbf{j})$ is mixed-state representable. Their proof can be straightforwardly adapted for the representability of the pair $(R, \mathbf{j})$, so that similar results hold.

We now prove Lemma 2.7 and Theorem 2.11.

2.2.2 Proofs of the CSDFT results

Proof of Lemma 2.7

Proof. Let $\Phi = (\phi^\uparrow, \phi^\downarrow) \in H^1(\mathbb{R}^3, \mathbb{C}^2)$ having phases in $C^1(\mathbb{R})$, and let $(R, \mathbf{j})$ be the associated spin-density 2×2 matrix and paramagnetic current. It holds that

$$R = \begin{pmatrix} \rho^\uparrow & \sigma \\ \overline{\sigma} & \rho^\downarrow \end{pmatrix} := \begin{pmatrix} |\phi^\uparrow|^2 & \phi^\uparrow\overline{\phi^\downarrow} \\ \phi^\downarrow\overline{\phi^\uparrow} & |\phi^\downarrow|^2 \end{pmatrix}.$$

For $\alpha \in \{\uparrow, \downarrow\}$, we let τ^α be the phase of ϕ^α, so that $\phi^\alpha = \sqrt{\rho^\alpha}e^{i\tau^\alpha}$. Setting $\tau = \tau^\uparrow - \tau^\downarrow$, we obtain $\sigma = |\sigma|e^{i\tau} = \sqrt{\rho^\uparrow\rho^\downarrow}e^{i\tau}$. On the other hand, the paramagnetic current is, according to (2.19),

$$\mathbf{j} = \rho^\uparrow\nabla\tau^\uparrow + \rho^\downarrow\nabla\tau^\downarrow = \rho\nabla\tau^\downarrow + \rho^\uparrow\nabla\tau = \rho\nabla\tau^\uparrow - \rho^\downarrow\nabla\tau.$$

In particular, using (2.22),

$$\frac{\mathbf{j}}{\rho} - \frac{\mathrm{Im}\,(\overline{\sigma}\nabla\sigma)}{\rho\rho^\downarrow} = \frac{\mathbf{j} - \rho^\uparrow\nabla\tau}{\rho} = \nabla\tau^\downarrow \quad \text{and} \quad \frac{\mathbf{j}}{\rho} + \frac{\mathrm{Im}\,(\overline{\sigma}\nabla\sigma)}{\rho\rho^\uparrow} = \nabla\tau^\uparrow.$$

are curl-free. □

Proof of Theorem 2.11

Proof. We break the proof in several steps.

Step 1: Any $R \in \mathcal{C}_N$ can be written as $R = R_1 + R_2 + R_3$ with $R_k \in \mathcal{C}^0_{N_k}$, $N_k \geq 4$.

Let $R = \begin{pmatrix} \rho^\uparrow & \sigma \\ \overline{\sigma} & \rho^\downarrow \end{pmatrix} \in \mathcal{C}_N$, with $N \geq 12$. Then, $\sqrt{R} = \begin{pmatrix} r^\uparrow & s \\ \overline{s} & r^\downarrow \end{pmatrix}$, with $r^\uparrow, r^\downarrow \in H^1(\mathbb{R}^3, \mathbb{R})$ and s in $H^1(\mathbb{R}^3, \mathbb{C})$. We write $R = R^\uparrow + R^\downarrow$ where $R^{\uparrow/\downarrow}$ were defined in (2.16). As in the proof of Theorem 2.2 for the case $N = 2$, $R^{\uparrow/\downarrow}$ are hermitian, of null determinant, and $\sqrt{R^{\uparrow/\downarrow}} \in \mathcal{M}_{2\times 2}\left(H^1(\mathbb{R}^3, \mathbb{C})\right)$. However, it may hold that $\int \mathrm{tr}_{\mathbb{C}^2}[R^\uparrow] \notin \mathbb{N}^*$, so that $R^\uparrow$ is not

in $\mathcal{C}^0_M$ for some $M \in \mathbb{N}^*$. In order to handle this difficulty, we will distribute the mass of $R^\uparrow$ and $R^\downarrow$ into three spin-density 2×2 matrices.

More specifically, let us suppose without loss of generality that $\int \mathrm{tr}_{\mathbb{C}^2}[R^\uparrow] \geq \int \mathrm{tr}_{\mathbb{C}^2}[R^\downarrow]$. We set

$$\begin{aligned} R_1 &= (1-\xi_1)R^\uparrow + \xi_2 R^\downarrow, \\ R_2 &= \xi_1(1-\xi_3)R^\uparrow, \\ R_3 &= (1-\xi_2)R^\downarrow + \xi_3 R^\uparrow, \end{aligned} \tag{2.26}$$

where ξ_1, ξ_2, ξ_3 are suitable non-decreasing functions in $C^\infty(\mathbb{R}^3)$, that depends only on r_1, and such that, for $1 \leq k \leq 3$, it holds $0 \leq \xi_k \leq 1$. We will choose them of the form $\xi_k(\mathbf{r}) = 0$ for $r_1 < \alpha_k$ and $\xi_k(\mathbf{r}) = 1$ for $r_1 \geq \beta_k > \alpha_k$, and such that

$$(1-\xi_1)\xi_2 = (1-\xi_2)\xi_3 = (1-\xi_1)\xi_3 = 0. \tag{2.27}$$

These functions are tuned so that $\int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}(R_k) \in \mathbb{N}^*$ and $\int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}(R_k) \geq 4$ for all $1 \leq k \leq 3$ (see Figure 2.1 for a canonical example of such a triplet (ξ_1, ξ_2, ξ_3)). In Figure 2.1, we clearly see how the non-overlapping condition (2.27) guarantees the null-determinant condition everywhere. Note that such a spatial decomposition could not have been performed with only two spin-density 2×2 matrices. Although it is not difficult to convince oneself that such functions ξ_k exist, we provide a full proof of this fact in Section 2.2.3.

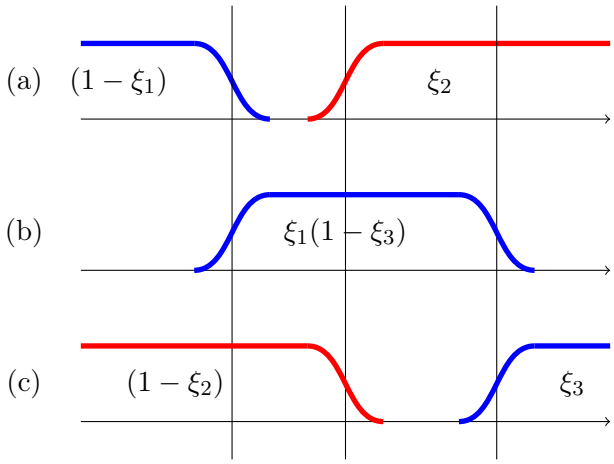

Figure 2.1 – Weights of the matrices $R^\uparrow$ (blue) and $R^\downarrow$ (red) in (a) $R_1 = (1-\xi_1)R^\uparrow + \xi_2 R^\downarrow$, (b) $R_2 = \xi_1(1-\xi_3)R^\uparrow$ and (c) $R_3 = (1-\xi_2)R^\uparrow + \xi_3 R^\downarrow$.

From (2.27), it holds that, for all $1 \leq k \leq 3$, $R_k \in \mathcal{C}^0_{N_K}$, and that $R_1 + R_2 + R_3 = R^\uparrow + R^\downarrow = R$. In order to simplify the notation, we introduce the total densities of $R^\uparrow$ and $R^\downarrow$:

$$f^\uparrow := |r^\uparrow|^2 + |s|^2 \quad \text{and} \quad f^\downarrow := |r^\downarrow|^2 + |s|^2.$$

Recall that $\rho = f^\uparrow + f^\downarrow$. We decompose $\mathbf{j}$ in a similar fashion. We write $\mathbf{j} = \mathbf{j}_1 + \mathbf{j}_2 + \mathbf{j}_3$ with

$$\begin{aligned} \mathbf{j}_1 &:= (1-\xi_1)\left(\frac{f^\uparrow}{\rho}\mathbf{j} - \mathrm{Im}\,(\overline{s}\nabla s)\right) + \xi_2\left(\frac{f^\downarrow}{\rho}\mathbf{j} + \mathrm{Im}\,(\overline{s}\nabla s)\right), \\ \mathbf{j}_2 &:= \xi_1(1-\xi_3)\left(\frac{f^\uparrow}{\rho}\mathbf{j} - \mathrm{Im}\,(\overline{s}\nabla s)\right), \\ \mathbf{j}_3 &:= (1-\xi_2)\left(\frac{f^\downarrow}{\rho}\mathbf{j} + \mathrm{Im}\,(\overline{s}\nabla s)\right) + \xi_3\left(\frac{f^\uparrow}{\rho}\mathbf{j} - \mathrm{Im}\,(\overline{s}\nabla s)\right). \end{aligned} \tag{2.28}$$

Step 2: The pair $(R_1, \mathbf{j}_1)$ is representable by a Slater determinant.
Following [LS13], we introduce

$$\xi(x) = \frac{1}{m}\int_{-\infty}^{x} \frac{1}{(1+y^2)^{(1+\delta)/2}}\mathrm{d}y,$$

where δ is the one in (2.25), and m is a constant chosen such that $\xi(\infty) = 1$. We then introduce

$$\begin{aligned}
\eta_{1,1}(\mathbf{r}) &= \frac{2}{N_1}\xi(\mathbf{r}+\alpha),\\
\eta_{1,2}(\mathbf{r}) &= \frac{2}{N_1-1}\xi(x_1+\beta)(1-\eta_1(\mathbf{r})),\\
\eta_{1,3}(\mathbf{r}) &= \frac{2}{N_1-2}\xi(x_2+\gamma)(1-\eta_1(\mathbf{r})-\eta_2(\mathbf{r})),\\
\eta_{1,k}(\mathbf{r}) &= \frac{1}{N_1-3}(1-\eta_1(\mathbf{r})-\eta_2(\mathbf{r})-\eta_3(\mathbf{r})) \quad \text{for} \quad 4\leq k\leq N_1,
\end{aligned} \tag{2.29}$$

where α, β, γ are tuned so that, if $\rho_1 := \mathrm{tr}_{\mathbb{C}^2} R_1$ denotes the total density of R_1,

$$\forall 1\leq k\leq N_1, \quad \int_{\mathbb{R}^3} \eta_{1,k}\rho_1 = 1. \tag{2.30}$$

It can be checked (see [LS13]) that $\eta_{1,k}\geq 0$ and that $\sum_{k=1}^{N_1}\eta_{1,k} = 1$. We seek orbitals of the form

$$\Phi_{1,k} := \sqrt{\eta_{1,k}}\left(\sqrt{(1-\xi_1)}\begin{pmatrix} r^{\uparrow}\\ \overline{s}\end{pmatrix} + \sqrt{\xi_2}\begin{pmatrix} s\\ r^{\downarrow}\end{pmatrix}\right)\mathrm{e}^{\mathrm{i}u_{1,k}},\ 1\leq k\leq N_1,$$

where the phases $u_{1,k}$ are chosen carefully later. From (2.27), we recall that $(1-\xi_1)\xi_2 = 0$, so that, by construction, $\Phi_{1,k}$ is normalized, and

$$\Phi_{1,k}\Phi_{1,k}^* = \eta_{1,k}R_1.$$

Let us suppose for now that the phases $u_{1,k}$ are chosen so that the orbitals are orthogonal. This will indeed be achieved thanks to the Lazarev-Lieb orthogonalization process (see Lemma 2.5). Then, $\Psi_1 := \mathscr{S}[\Phi_{1,1},\dots,\Phi_{1,N}]$ represents the spin-density 2×2 matrix R_1. According to (2.19), the paramagnetic current of Ψ is (we recall that $r^{\uparrow}$ and $r^{\downarrow}$ are real-valued, and we write $s = |s|\mathrm{e}^{\mathrm{i}\tau}$ for simplicity)

$$\begin{aligned}
\mathbf{j}_\Psi &= \sum_{k=1}^{N_1}\eta_{1,k}(1-\xi_1)\left(|r^{\uparrow}|^2\nabla u_{1,k} + |s|^2\nabla(-\tau+u_{1,k})\right) + \eta_{1,k}\xi_2\left(|s|^2\nabla(\tau+u_{1,k}) + |r^{\downarrow}|^2\nabla u_{1,k}\right)\\
&= \left((1-\xi_1)f^{\uparrow}+\xi_2 f^{\downarrow}\right)\left(\sum_{k=1}^{N_1}\eta_{1,k}\nabla u_{1,k}\right) + (\xi_2-(1-\xi_1))\,|s|^2\nabla\tau.
\end{aligned}$$

Since $|s|^2\nabla\tau = \mathrm{Im}\,(\overline{s}\nabla s)$, this current is equal to the target current $\mathbf{j}_1$ defined in (2.28) if and only if

$$\rho_1\frac{\mathbf{j}}{\rho} = \rho_1\sum_{k=1}^{N_1}\eta_k\nabla u_{1,k}. \tag{2.31}$$

In [LS13], Lieb and Schrader provided an explicit solution $(u_{1,1},\dots,u_{1,N_1})$ of this system when[1] $N_1\geq 4$. We do not repeat the proof, but emphasize on the fact that since condition (2.25) holds true, the phases $u_{1,k}$ can be chosen to have bounded derivatives, so that

[1] In the same article, the authors recall (see [TME09] for instance) that (2.31) may not have solutions when $N_1 = 2$. The case $N_1 = 3$ is still open. Of course, would someone find an explicit solution for $N_1 = 3$, the condition $N\geq 12$ in Theorem 2.11 could be replaced by the weaker condition $N\geq 9$.

the functions $\Phi_{1,k}$ are in $H^1(\mathbb{R}^3,\mathbb{C}^2)$. Also, as their proof relies on the Lazarev-Lieb orthogonalization process, it is possible to choose the phases $u_{1,k}$ so that the functions $\Phi_{1,k}$ are orthogonal, and orthogonal to a finite-dimensional subspace of $L^2(\mathbb{R}^3,\mathbb{C}^2)$.

We proved that the pair $(R_1,\mathbf{j}_1)$ is representable by the Slater determinant $\mathscr{S}[\Phi_{1,1},\dots,\Phi_{1,N_1}]$.

Step 3: Representability of $(R_2,\mathbf{j}_2)$ and $(R_3,\mathbf{j}_3)$, and finally of $(R,\mathbf{j})$.
In order to represent the pair $(R_2,\mathbf{j}_2)$, we first construct the functions $\eta_{2,k}$ for $1\le k\le N_2$ of the form (2.29) so that (2.30) holds for $\rho_2 := \mathrm{tr}_{\mathbb{C}^2}R_2$. We then seek orbitals of the form

$$\Phi_{2,k} := \sqrt{\eta_{2,k}\xi_1(1-\xi_3)}\begin{pmatrix} r^\uparrow \\ \overline{s}\end{pmatrix}\mathrm{e}^{\mathrm{i}u_{2,k}},\quad \text{for}\quad 1\le k\le N_2.$$

Reasoning as above, the Slater determinant of these orbitals represents the pair $(R_2,\mathbf{j}_2)$ if and only if

$$\rho_2\frac{\mathbf{j}_2}{\rho} = \rho_2\sum_{k=1}^{N_2}\eta_{2,k}\nabla u_{2,k}.$$

Again, since $N_2\ge 4$, this equation admits a solution $(u_{2,1},\dots,u_{2,N_2})$. Moreover, it is possible to choose the phases $u_{2,k}$ so that the functions $\Phi_{2,k}$ are orthogonal to the previously constructed $\Phi_{1,k}$.

We repeat again this argument for the pair $(R_3,\mathbf{j}_3)$. Once the new set of functions $\eta_{3,k}$ is constructed, we seek orbitals of the form

$$\Phi_{3,k} := \sqrt{\eta_{3,k}}\left(\sqrt{(1-\xi_2)}\begin{pmatrix} s \\ r^\downarrow\end{pmatrix} + \sqrt{\xi_3}\begin{pmatrix} r^\uparrow \\ \overline{s}\end{pmatrix}\right)\mathrm{e}^{\mathrm{i}u_{3,k}}$$

and construct the phases so that the functions $\Phi_{3,k}$ are orthogonal to the functions $\Phi_{1,k}$ and $\Phi_{2,k}$.

Altogether, the pair $(R,\mathbf{j})$ is represented by the (finite energy) Slater determinant

$$\mathscr{S}[\Phi_{1,1},\dots,\Phi_{1,N_1},\Phi_{2,1},\dots,\Phi_{2,N_2},\Phi_{3,1},\dots,\Phi_{3,N_3}],$$

which concludes the proof. □

2.2.3 Construction of the functions ξ_1, ξ_2 and ξ_3

We explain in this section how to construct three functions $\xi_1,\xi_2,\xi_3\in C^\infty(\mathbb{R})$ like in Figure 2.1. In order to simplify the notation, we introduce

$$f(r) := \iint_{\mathbb{R}\times\mathbb{R}}\mathrm{tr}_{\mathbb{C}^2}(R^\downarrow)(r,r_2,r_3)\,\mathrm{d}r_2\mathrm{d}r_3,\quad\text{and}\quad g(r) := \iint_{\mathbb{R}\times\mathbb{R}}\mathrm{tr}_{\mathbb{C}^2}(R^\uparrow)(r,y,z)\,\mathrm{d}r_2\mathrm{d}r_3,$$

where $R^\uparrow,R^\downarrow$ were defined in (2.16). We denote by

$$F(\alpha) := \int_{-\infty}^{\alpha} f(x)\mathrm{d}x\quad\text{and}\quad G(\alpha) := \int_{-\infty}^{\alpha} g(x)\mathrm{d}x,$$

and we set $\mathcal{F} := F(\infty) = \int_{\mathbb{R}} f$ and $\mathcal{G} := G(\infty) = \int_{\mathbb{R}} g$. Note that F and G are continuous non-decreasing functions going from 0 to $\mathcal{F}$ (respectively $\mathcal{G}$), and that it holds $\mathcal{F}+\mathcal{G}=N$. Let us suppose without loss of generality that $\mathcal{F}\le\mathcal{G}$, so that $0\le\mathcal{F}\le N/2\le\mathcal{G}\le N$. If $\mathcal{F}=0$, then $R^\downarrow=0$ and we can choose $R_1=R_2=(4/N)R^\uparrow\in\mathcal{C}_4^0$ and $R_3=(N-8)/NR^\uparrow\in\mathcal{C}_{N-8}^0$. Since $N\ge 12$, it holds $N-8\ge 4$, so that this gives the desired decomposition. We now

consider the case $\mathcal{F} \neq 0$.

In order to keep the notation simple, we will only study the case $\mathcal{F} < 8$ (the case $\mathcal{F} > 8$ is similar by replacing the integer 4 by a greater integer M such that $\mathcal{F} < 2M < N - 4$ in the sequel). We seek for α such that

$$\begin{cases} \displaystyle\int_{-\infty}^{\alpha} f(x)\mathrm{d}x < 4 \quad \text{and} \quad \int_{-\infty}^{\alpha} f(x) + \int_{\alpha}^{\infty} g(x) > 4, \\ \displaystyle\int_{\alpha}^{\infty} f(x)\mathrm{d}x < 4 \quad \text{and} \quad \int_{-\infty}^{\alpha} g(x)\mathrm{d}x + \int_{\alpha}^{\infty} f(x)\mathrm{d}x > 4, \end{cases}$$

or equivalently

$$\mathcal{F} - 4 < F(\alpha) < 4, \quad \text{and} \quad F(\alpha) + 4 - \mathcal{F} < G(\alpha) < F(\alpha) + \mathcal{G} - 4. \tag{2.32}$$

Let $\alpha_{(\mathcal{F}-4)}$ be such that $F(\alpha_{(\mathcal{F}-4)}) = \mathcal{F} - 4$ (with $\alpha_{(\mathcal{F}-4)} = -\infty$ if $\mathcal{F} \leq 4$), and $\alpha_{(4)}$ be such that $F(\alpha_{(4)}) = 4$ (with $\alpha_{(4)} = +\infty$ if $\mathcal{F} \leq 4$). As F is continuous non-decreasing, the first equation of (2.32) is satisfied whenever $\alpha_{(\mathcal{F}-4)} < \alpha < \alpha_{(4)}$.

The function $[\alpha_{(\mathcal{F}-4)}, \alpha_4] \ni \alpha \mapsto m(\alpha) := F(\alpha) + 4 - \mathcal{F}$ goes continuously and non-decreasingly from 0 to $8 - \mathcal{F}$, and the function $[\alpha_{(\mathcal{F}-4)}, \alpha_4] \ni \alpha \mapsto M(\alpha) := F(\alpha) + \mathcal{G} - 4$ goes continuously and non-decreasingly from $N - 8$ to $\mathcal{G}$ between $\alpha_{(\mathcal{F}-4)}$ and $\alpha_{(4)}$. In particular, since $G(\alpha)$ goes continuously and non-decreasingly from 0 to $\mathcal{G}$, only three cases may happen:

Case 1: There exists $\alpha_0 \in (\alpha_{(\mathcal{F}-4)}, \alpha_{(4)})$ such that $m(\alpha_0) < G(\alpha_0) < M(\alpha_0)$.
In this case, (2.32) holds for $\alpha = \alpha_0$. By continuity, there exists $\varepsilon > 0$ such that

$$F(\alpha + \varepsilon) < 4, \quad F(\alpha) + \mathcal{G} - G(\alpha + \varepsilon) > 4, \quad \text{and} \quad G(\alpha) + \mathcal{F} - F(\alpha + \varepsilon) > 4.$$

Let $\xi_2 \in C^\infty(\mathbb{R})$ be a non-decreasing function such that $\xi_2(x) = 0$ for $x < \alpha$ and $\xi_2(x) = 1$ for $x > \alpha + \varepsilon$. Then, as $0 \leq \xi_2 \leq 1$, it holds that:

$$\int_{\mathbb{R}} (1 - \xi_2) f \leq F(\alpha + \varepsilon) < 4 \quad \text{and} \quad \int_{\mathbb{R}} (1 - \xi_2) f + \int_{\alpha+\varepsilon}^{\infty} g \geq F(\alpha) + \mathcal{G} - G(\alpha + \varepsilon) > 4.$$

We deduce that there exists an non-decreasing function $\xi_3 \in C^\infty(\mathbb{R})$ such that $\xi_3(x) = 0$ for $x < \alpha + \varepsilon$, and such that

$$\int_{\mathbb{R}} (1 - \xi_2) f + \xi_3 g = 4.$$

Note that $(1 - \xi_2)\xi_3 = 0$. On the other hand, from

$$\int_{\mathbb{R}} \xi_2 f \leq \mathcal{F} - F(\alpha) < 4 \quad \text{and} \quad \int_{\mathbb{R}} \xi_2 f + \int_{-\infty}^{\alpha} g \geq \mathcal{F} - F(\alpha + \varepsilon) + G(\alpha) > 4,$$

we deduce that there exists an non-decreasing function $\xi_1 \in C^\infty(\mathbb{R})$ such that $\xi_1(x) = 1$ for $x > \alpha$,

$$\int_{\mathbb{R}} (1 - \xi_1) g + \xi_2 f = 4.$$

and $(1 - \xi_1)\xi_2 = (1 - \xi_1)\xi_3 = 0$. Finally, we set

$$R_1 = (1 - \xi_1)R^{\uparrow} + \xi_2 R^{\downarrow}, \quad R_2 = \xi_1(1 - \xi_3)R^{\uparrow}, \quad \text{and} \quad R_3 = (1 - \xi_2)R^{\downarrow} + \xi_3 R^{\uparrow}.$$

By construction, $R = R^{\uparrow} + R^{\downarrow} = R_1 + R_2 + R_3$, $R_1 \in \mathcal{C}_4^0$ and $R_3 \in \mathcal{C}_4^0$. We deduce that $R_4 \in \mathcal{C}_{N-8}^0$, where $N - 8 \geq 4$. This leads to the desire decomposition.

Case 2: For all $\alpha \in (\alpha_{(\mathcal{F}-4)}, \alpha_{(4)})$, it holds $G(\alpha) < m(\alpha)$.
This may only happen if $m(\alpha_{(4)}) > 0$, or $\mathcal{F} < 4$, so that $\mathcal{G} > N - 4 \geq 8$. It holds $G(\alpha_{(\mathcal{F}-4)}) = 0$, so that $g(r)$ is null for $r < \alpha_{(\mathcal{F}-4)}$. Let α_0 be such that $\alpha_{(\mathcal{F}-4)} < \alpha_0 < \alpha_{(4)}$. As

$$\int_{\mathbb{R}} f = \mathcal{F} > 4 \quad \text{and} \quad \int_{\alpha_0}^{\infty} f = \mathcal{F} - F(\alpha_0) < 4,$$

there exists a non-decreasing function $\xi_1 \in C^\infty(\mathbb{R})$ satisfying $\xi_1(x) = 1$ for $x \geq \alpha_0$ and such that

$$\int_{\mathbb{R}} \xi_1 f = 4.$$

Now, since $G(\alpha_{(4)}) < m(\alpha_{(4)}) = 8 - \mathcal{F}$, it holds that

$$\int_{\mathbb{R}} (1-\xi_1) f \leq F(\alpha_{(4)}) = 4 \quad \text{and} \quad \int_R (1-\xi_1) f + \int_{\alpha_0}^{\infty} g \geq F(\alpha_{(\mathcal{F}-4)}) + \mathcal{G} - G(\alpha_{(4)}) > 4.$$

There exists a non-decreasing function $\xi_2 \in C^\infty(\mathbb{R})$ satisfying $\xi_2(x) = 0$ for $x \leq \alpha_0$ and such that

$$\int_{\mathbb{R}} (1-\xi_1) f + \xi_2 g = 4.$$

Note that $(1 - \xi_1)\xi_2 = 0$. Finally, we set

$$R_1 = \xi_1 R^{\downarrow}, \quad R_2 = (1-\xi_2) R^{\uparrow}, \quad \text{and} \quad R_3 = \xi_2 R^{\uparrow} + (1-\xi_1) R^{\downarrow}.$$

By construction, it holds that $R = R_1 + R_2 + R_3$, and that $R_1 \in \mathcal{C}_4^0$ and $R_3 \in \mathcal{C}_4^0$. We deduce $R_2 \in \mathcal{C}_{N-8}^0$, and the result follows.

Case 3: For all $\alpha \in (\alpha_{(\mathcal{F}-4)}, \alpha_{(4)})$, it holds $\mathcal{G}(\alpha) > M(\alpha)$.
This case is similar to the previous one.

CHAPTER 3

EXISTENCE OF MINIMIZERS FOR KOHN-SHAM WITHIN THE LOCAL SPIN DENSITY APPROXIMATION

We expose in this chapter the results given in [Gon15a].

Abstract. The purpose of this chapter is to extend the work by Anantharaman and Cancès [AC09], and prove the existence of minimizers for the spin-polarized Kohn-Sham model in the presence of a magnetic field within the local spin density approximation. We show that for any magnetic field that vanishes at infinity, the existence of minimizers is ensured for neutral or positively charged systems. The proof relies on classical concentration-compactness techniques.

3.1 Introduction

The density functional theory (DFT) introduced in 1964 by Hohenberg and Kohn [HK64] is a very popular tool in modern quantum chemistry. This theory transforms the high-dimensional Schrödinger problem into a low-dimensional one, hence computationally solvable. The price to pay is the introduction of the so-called exchange-correlation (xc) energy term, which is unknown. Throughout the literature, several different approximations of this energy can be found. The first successful one, and still broadly used nowadays, was proposed by Kohn and Sham [KS65], and is called the local density approximation (LDA). The mathematical properties resulting of the Kohn-Sham LDA are still not fully understood. Proving the existence of minimizers is made difficult by the non-convexity of the problem due to the LDA term. Using concentration-compactness techniques introduced by Lions [Lio84], it has been possible to prove the existence of minimizers in several cases. Le Bris [LB93] proved that for a neutral or positively charged system, the Kohn-Sham problem with LDA exchange-correlation energy admits a minimizer. A similar result was proved by Anantharaman and Cancès [AC09] for the so-called extended-Kohn-Sham model with LDA exchange-correlation energy.

In this chapter, we extend the result by Anantharaman and Cancès to spin-polarized systems, the electrons of the molecular system into consideration being subjected to the electric potential V created by the nuclei, and to an arbitrary external magnetic field $\mathbf{B}$ that vanishes at infinity. In order to take into account spin effects, we have to resort to spin density functional theory (SDFT). In this theory, all magnetic contributions coming from orbital magnetism (paramagnetic current, spin-orbit coupling,...) are neglected. Historically, while Kohn and Sham briefly discussed the inclusion of spin effects in their model, the general theory was pioneered by von Barth and Hedin [vBH72] and is known as the local spin density

approximation (LSDA). These authors proposed the following ansatz to transform a spin-unpolarized exchange-correlation energy to a spin-polarized version of it:

$$E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho^+,\rho^-) := \frac{1}{2}\left[E_{\mathrm{xc}}^{\mathrm{LDA}}(2\rho^+) + E_{\mathrm{xc}}^{\mathrm{LDA}}(2\rho^-)\right],$$

where $E_{\mathrm{xc}}^{\mathrm{LDA}}$ is the spinless exchange-correlation energy, and $\rho^{+/-}$ are the eigenvalues of the spin-density 2×2 matrix (see Chapter 2, Section 2.1.1). There are two other major differences between spin-polarized and spin-unpolarized models. First, the ground state of spin-unpolarized models is given by a minimization problem onto the set of electronic densities, while in spin-polarized models, it is given by a minimization problem onto the set of spin-density 2×2 matrices, which are hermitian matrices. Second, the magnetic field adds a Zeeman-type term $-\mu\int \mathbf{B}\cdot\mathbf{m}$ to the energy functional, where $\mathbf{m}$ is the spin angular momentum density.

Due to all those additional difficulties with respect to the spin-unpolarized case, the fully polarized SDFT has not been very popular until recently. Chemists generally prefer its collinear version (collinear-SDFT), where all the spins are constrained to be orientated along a fixed direction on the whole space. This allows one to work with two scalar fields (one for spin-up, and one for spin-down), instead of fields of hermitian matrices. While this simplification provides very good results, it misses some physical properties (spin dynamics [SDAD+07], frustrated solids [BSFS13], and so on). The implementation of the unconstrained (fully polarizable) model appeared with the work of Sandratskii and Guletskii [SG86], and Kübler *et al.* [KHSW88a, KHSW88b], and this model is becoming a standard tool nowadays. To the best of our knowledge, no rigorous proof of the existence of solutions has yet been provided for this case.

Our result is that, under the same hypotheses as in [AC09], plus some mild conditions on $\mathbf{B}$, the existence of minimizers is still ensured for neutral or positively charged systems. Whereas the main tools of the proof are similar to those used in [AC09], namely concentration-compactness techniques, some adaptations are necessary, in particular to handle the Zeeman term. The structure of this chapter is as follows. We first recall how to derive the LSDA models, and formulate the main theorem. Then, we break the proof of the theorem into several lemmas, that we prove at the end.

3.2 Derivation of the local spin density approximation models

We recall how extended Kohn-Sham models are derived in the spin setting. We start from the Schrödinger-Pauli Hamiltonian for N-electrons in the Born-Oppenheimer approximation. In atomic units, this operator reads

$$H_N^{\text{full-SP}}(V,\mathbf{A}) = \sum_{i=1}^N \frac{1}{2}\left(-\mathrm{i}\nabla_i + \mathbf{A}(\mathbf{r}_i)\right)^2 \mathbb{I}_2 + \sum_{i=1}^N V(\mathbf{r}_i)\mathbb{I}_2 - \mu\sum_{i=1}^N \mathbf{B}(\mathbf{r}_i)\cdot\sigma_i + \sum_{1\le i<j\le N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\mathbb{I}_2,$$

where $\mathbb{I}_2$ is the 2×2 identity matrix,

$$V(\mathbf{r}) = -\sum_{k=1}^M \frac{z_k}{|\mathbf{r}-\mathbf{R}_k|} \tag{3.1}$$

is the electric potential generated by the M nuclei, $\mathbf{A}$ is the external magnetic vector potential, and $\mathbf{B} := \nabla\times\mathbf{A}$ is the external magnetic field. We denote by $\mathbf{r}_i$ (resp. $\mathbf{R}_k$) the positions of the electrons (resp. nuclei). The charge of the k-th nucleus is $z_k\in\mathbb{N}^*$ and $Z := \sum_{k=1}^M z_k$ is

the total nuclear charge. We can assume without loss of generality that $\mathbf{R}_1 = \mathbf{0}$. The constant μ is the Bohr magneton. Its value is $1/2$ in atomic units, but we prefer to keep the notation μ in the rest of the chapter. The term σ_i appearing in the Hamiltonian contains the Pauli matrices acting on the i-th spin variable:

$$\sigma_i := (\sigma_{xi}, \sigma_{yi}, \sigma_{zi}) = \left(\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_i, \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}_i, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_i \right).$$

Although the magnetic field $\mathbf{B}$ and magnetic vector potential $\mathbf{A}$ are linked by the relation $\mathbf{B} = \nabla \times \mathbf{A}$, it is often preferable to consider them as two independent fields. Indeed, $\mathbf{B}$ acts on the spin of the electrons, while $\mathbf{A}$ acts on the spatial component of the orbitals. For instance, would we be interested only in studying orbital effects (*e.g.* paramagnetic currents), we would neglect the spin effects. We would then take $\mathbf{B} = \mathbf{0}$ and $\mathbf{A} \neq \mathbf{0}$. Such an approximation leads to the so-called current-density functional theory [VR88]. In this chapter, we are interested in spin effects. We therefore set $\mathbf{A} = \mathbf{0}$, which amounts to neglecting the paramagnetic currents, while keeping $\mathbf{B} \neq \mathbf{0}$. This approximation is commonly used to study phenomena such as spin dynamics [SDAD+07] or frustrated solids [BSFS13]. With this approximation, our Hamiltonian for N electrons reads

$$H_N^{\mathrm{SP}}(V, \mathbf{B}) = \left(\sum_{i=1}^N -\frac{1}{2}\Delta_i + \sum_{i=1}^N V(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \mathbb{I}_2 - \mu \sum_{i=1}^N \mathbf{B}(\mathbf{r}_i) \cdot \sigma_i.$$

This Hamiltonian acts on the fermionic Hilbert space

$$\begin{aligned} \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}^2) := \Big\{ & \Psi(\mathbf{r}_1, s_1, \cdots, \mathbf{r}_N, s_N), \ \mathbf{r}_i \in \mathbb{R}^3, s_i \in \{\uparrow, \downarrow\}, \\ & \sum_{s_1, \cdots s_N \in \{\uparrow,\downarrow\}^N} \int_{\mathbb{R}^{3N}} |\Psi(\mathbf{r}_1, s_1, \cdots)|^2 \mathrm{d}\mathbf{r}_1 \cdots \mathrm{d}\mathbf{r}_N < \infty, \\ & \forall p \in S_N, \quad \Psi(\mathbf{r}_{p(1)}, s_{p(1)}, \cdots) = \epsilon(p) \Psi(\mathbf{r}_1, s_1, \cdots) \Big\}. \end{aligned}$$

Here, S_N denotes the set of all permutations of $[\![1, \ldots, N]\!]$, and $\epsilon(p)$ is the parity of the permutation p. The space $\bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}^2)$ is endowed with the inner product

$$\langle \Psi_1 | \Psi_2 \rangle = \sum_{(s_1, \cdots s_N) \in \{\uparrow,\downarrow\}^N} \int_{\mathbb{R}^{3N}} \overline{\Psi_1(\mathbf{r}_1, s_1, \cdots)} \Psi_2(\mathbf{r}_1, s_1, \cdots) \mathrm{d}\mathbf{r}_1 \cdots \mathrm{d}\mathbf{r}_N.$$

The ground state energy of the system is obtained by solving the minimization problem

$$E(V, \mathbf{B}) := \inf \left\{ \mathrm{Tr}\left(H_N^{\mathrm{SP}} \Gamma\right), \ \Gamma \in G_N^{\mathrm{pure}} \right\} = \inf \left\{ \mathrm{Tr}\left(H_N^{\mathrm{SP}} \Gamma\right), \ \Gamma \in G_N^{\mathrm{mixed}} \right\}$$

where G_N^{pure} resp. G_N^{mixed} is the set of spin-polarized pure-state (resp. mixed-state) N-body density matrices defined in (2.1) resp. (2.2). We study the extended-Kohn-Sham model based on mixed-state N-body density matrices, for this problem has better properties mathematically speaking, and allows one to handle more general physical situations as, for instance, positive temperatures. For $\Gamma \in G_N^{\mathrm{mixed}}$, direct calculations lead to

$$\mathrm{Tr}\left(H_N^{\mathrm{SP}}(V, \mathbf{B}) \Gamma\right) = \mathrm{Tr}\left(H_N^{\mathrm{SP}}(0, \mathbf{0}) \Gamma\right) + \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2} \left[\begin{pmatrix} V - \mu B_z & -\mu B_x + \mathrm{i}\mu B_y \\ -\mu B_x - \mathrm{i}\mu B_y & V + \mu B_z \end{pmatrix} \begin{pmatrix} \rho_\Gamma^{\uparrow\uparrow} & \rho_\Gamma^{\uparrow\downarrow} \\ \rho_\Gamma^{\downarrow\uparrow} & \rho_\Gamma^{\downarrow\downarrow} \end{pmatrix} \right], \tag{3.2}$$

where, for $\alpha, \beta \in \{\uparrow, \downarrow\}^2$, $\rho_\Gamma^{\alpha\beta}$ was defined in (2.3). In the following, we write

$$U := \begin{pmatrix} V - \mu B_z & -\mu B_x + \mathrm{i}\mu B_y \\ -\mu B_x - \mathrm{i}\mu B_y & V + \mu B_z \end{pmatrix} \quad \text{and} \quad R_\Gamma := \begin{pmatrix} \rho_\Gamma^{\uparrow\uparrow} & \rho_\Gamma^{\uparrow\downarrow} \\ \rho_\Gamma^{\downarrow\uparrow} & \rho_\Gamma^{\downarrow\downarrow} \end{pmatrix}.$$

We recognize in R_Γ the spin-polarized density 2×2 matrix introduced in Chapter 2, Section 2.1. When $\mathbf{B} = \mathbf{0}$, one recovers the usual potential energy density $V\rho_\Gamma$ appearing in spin-unpolarized DFT. Introducing the spin angular momentum density $\mathbf{m}_\Gamma = \mathrm{tr}_{\mathbb{C}^2}[\sigma \cdot R_\Gamma]$, and the total electronic density $\rho_\Gamma = \rho_\Gamma^{\uparrow\uparrow} + \rho_\Gamma^{\downarrow\downarrow}$, it holds

$$\mathrm{tr}_{\mathbb{C}^2}[UR_\Gamma] = V\rho_\Gamma - \mu\mathbf{B} \cdot \mathbf{m}_\Gamma. \tag{3.3}$$

We now apply the constrained search method introduced and studied by Levy [Lev79], Valone [Val80] and Lieb [Lie83], and write the minimization problem (3.2) in terms of R_Γ:

$$E(V, \mathbf{B}) = \inf\left\{F(R) + \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}[UR]\,,\ R \in \mathcal{J}_N^{\mathrm{mixed}}\right\}, \tag{3.4}$$

with

$$F(R) := \inf\left\{\mathrm{Tr}\left[H(0,\mathbf{0})\Gamma\right],\ \Gamma \in G_N^{\mathrm{mixed}},\ R_\Gamma = R\right\}.$$

The set $\mathcal{J}_N^{\mathrm{mixed}}$ is the set of mixed state N-representable spin-density 2×2 matrices, that we characterized in Theorem 2.2. The functional F cannot be straightforwardly evaluated. In order to make this problem practical, we approximate F. It is standard since the work of Kohn and Sham [KS65] to approximate this functional by studying a system of non-interacting electrons. For this purpose, we recall that, for a mixed state $\Gamma \in G_N^{\mathrm{mixed}}$, the spin-polarized one-body density matrix $\gamma_\Gamma(\mathbf{r}, \mathbf{r}')$ was defined in (2.10)-(2.11). The set of mixed-state 1-body density matrices is

$$\mathcal{P}_N := \{\gamma_\Gamma,\ \Gamma \in G_N^{\mathrm{mixed}}\},$$

and, identifying the kernel $\gamma(\mathbf{r}, \mathbf{r}')$ with the corresponding operator of $\mathcal{S}(L^2(\mathbb{R}^3, \mathbb{C}^2))$, the space of self-adjoint operators on $L^2(\mathbb{R}^3, \mathbb{C}^2)$, Coleman [Col63] proved that

$$\mathcal{P}_N = \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3, \mathbb{C}^2)),\ 0 \le \gamma \le 1,\ \mathrm{Tr}(\gamma) = N,\ \mathrm{Tr}(-\Delta\gamma) < \infty\right\}.$$

Physically speaking, this is the set of one-body density matrices of systems with N electrons ($\mathrm{Tr}(\gamma) = N$), satisfying the Pauli principle ($0 \le \gamma \le 1$), and with finite kinetic energy ($\mathrm{Tr}(-\Delta\gamma) < \infty$). In a similar way, we can define, for $\lambda > 0$,

$$\mathcal{P}_\lambda := \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3, \mathbb{C}^2)),\ 0 \le \gamma \le 1,\ \mathrm{Tr}(\gamma) = \lambda,\ \mathrm{Tr}(-\Delta\gamma) < \infty\right\}. \tag{3.5}$$

A more practical and equivalent formulation of the Coleman result is that, using the spectral theory for compact self-adjoint operators, we can write the components $\gamma^{\alpha\beta}$ of any $\gamma \in \mathcal{P}_\lambda$ in the form

$$\gamma^{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \sum_{k=1}^{\infty} n_k \phi_k^\alpha(\mathbf{r})\overline{\phi_k^\beta(\mathbf{r}')},\ 0 \le n_k \le 1,\ \sum_{k=1}^{\infty} n_k = \lambda,\ \Phi_k = \begin{pmatrix}\phi_k^\uparrow \\ \phi_k^\downarrow\end{pmatrix} \in L^2(\mathbb{R}^3, \mathbb{C}^2),$$
$$\langle\Phi_k|\Phi_l\rangle = \delta_{kl}, \quad \mathrm{Tr}(-\Delta\gamma) := \sum_{k=1}^{\infty} n_k \|\nabla\Phi_k\|_{L^2}^2 = \mathrm{Tr}(-\Delta\gamma^{\uparrow\uparrow}) + \mathrm{Tr}(-\Delta\gamma^{\downarrow\downarrow}) < \infty. \tag{3.6}$$

Notice that $\gamma_\Gamma(\mathbf{r}, \mathbf{r}) = R_\Gamma(\mathbf{r})$, so that we will write $R_\gamma(\mathbf{r}) := \gamma(\mathbf{r}, \mathbf{r})$ for $\gamma \in \mathcal{P}_N$. We finally introduce

$$\mathcal{J}_\lambda^{\mathrm{mixed}} := \left\{R \in \mathcal{M}_{2\times 2}(L^1(\mathbb{R}^3)),\ \exists\gamma \in \mathcal{P}_\lambda,\ R = R_\gamma\right\}.$$

The extended version of the Kohn-Sham approach consists in splitting the unknown functional $F(R)$ into three parts:

$$F(R) = T_{\mathrm{KS}}(R) + J(\rho_R) + E_{\mathrm{xc}}(R).$$

The first term $T_{\rm KS}$ represents the kinetic energy of a non-interacting electronic system. It reads, in the one-body formalism,

$$\forall R \in \mathcal{J}_\lambda^{\rm mixed}, \quad T_{\rm KS}(R) := \inf \left\{ \frac{1}{2}{\rm Tr}\left(-\Delta\gamma\right),\ \gamma \in \mathcal{P}_\lambda,\ R_\gamma = R \right\}.$$

The second term is the Hartree term, defined by

$$J(\rho) := \frac{1}{2} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} {\rm d}\mathbf{r}\ {\rm d}\mathbf{r}'.$$

Finally, the last term is the exchange-correlation functional defined by

$$\forall R \in \mathcal{J}_N^{\rm mixed}, \qquad E_{\rm xc}(R) := F(R) - T_{\rm KS}(R) - J(\rho_R).$$

Notice that since F is a non-explicit functional, $E_{\rm xc}$ is also a non-explicit functional. It is however possible to construct explicit approximations of $E_{\rm xc}$ giving rise to accurate predictions of the ground state energies of most molecular systems [ED11]. The case $E_{\rm xc} = 0$ corresponds to the reduced Hartree-Fock model [Sol91].

The local-spin density approximation introduced by von Barth and Hedin [vBH72] consists in writing

$$E_{\rm xc}(R) \approx E_{\rm xc}^{\rm LSDA}(\rho^+,\rho^-) := \frac{1}{2}\left[E_{\rm xc}^{\rm LDA}(2\rho^+) + E_{\rm xc}^{\rm LDA}(2\rho^-)\right] \tag{3.7}$$

where $\rho^{+/-}$ are the two eigenvalues of the spin-density 2×2 matrix R, and $E_{\rm xc}^{\rm LDA}$ is the standard exchange-correlation functional in the spin-unpolarized case, that we can write under the form [KS65]

$$E_{\rm xc}^{\rm LDA}(\rho) = \int_{\mathbb{R}^3} g(\rho(\mathbf{r}))\,{\rm d}\mathbf{r}. \tag{3.8}$$

The fact that $E_{\rm xc}^{\rm LSDA}$ only depends on R via its eigenvalues comes from the locality of the functional. Indeed, this energy functional must be invariant with respect to local spin rotations. Since R is hermitian at each point, we can always diagonalize R locally, so that a local energy functional can only depend on the two eigenvalues of R.

In this chapter, we deal with exchange-correlation functionals of the form (3.7)-(3.8). For all $\overline{\rho} \in \mathbb{R}^+$, the real value $g(\overline{\rho})$ is an approximation of the exchange-correlation energy density of the uniform electron gas with density $\overline{\rho}$. Several functions g are available (VWS [VWN80], PZ81 [PZ81], CP [CP82], PW92 [PW92], ...), which all satisfy the same asymptotic conditions for low and high densities. Their mathematical properties are similar to the ones of the $X\alpha$-functional introduced by Slater [Sla51]

$$E_{\rm xc}^{{\rm LDA},X\alpha}(\rho) = -C_X \int_{\mathbb{R}^3} \rho^{4/3}(\mathbf{r}){\rm d}\mathbf{r}.$$

Altogether, by recasting problem (3.4) in terms of the one-body density matrices, we end up with a variational problem of the form

$$I_\lambda := \inf\left\{\mathcal{E}(\gamma),\ \gamma \in \mathcal{P}_\lambda\right\}, \tag{3.9}$$

where

$$\mathcal{E}(\gamma) = \frac{1}{2}{\rm Tr}\left(-\Delta\gamma^{\uparrow\uparrow}\right) + \frac{1}{2}{\rm Tr}\left(-\Delta\gamma^{\downarrow\downarrow}\right) + J(\rho_\gamma) + \int_{\mathbb{R}^3} {\rm tr}_{\mathbb{C}^2}\left[UR_\gamma\right]{\rm d}\mathbf{r} + E_{\rm xc}^{\rm LSDA}(\rho_\gamma^+,\rho_\gamma^-)$$

and where $\mathcal{P}_\lambda$ has been defined in (3.5). The physical situation corresponds to $\lambda = N \in \mathbb{N}$, but as usual in variational problems set on the whole space, it is useful to relax the constraint

$\mathrm{Tr}(\gamma) = N$ to allow the particles to escape to infinity.

We can recover some other common models by further constraining the minimization set. For instance, the collinear-SDFT consists in minimizing the functional $\mathcal{E}$ onto the set

$$\mathcal{P}_\lambda^{\text{collinear}} := \left\{\gamma \in \mathcal{P}_\lambda,\ \gamma^{\uparrow\downarrow} = \gamma^{\downarrow\uparrow} = 0\right\}.$$

In this case, the matrices γ and R are both diagonal. In particular, the two eigenvalues of R are $\{\rho^+, \rho^-\} = \{\rho^{\uparrow\uparrow}, \rho^{\downarrow\downarrow}\}$. In this model, it holds that

$$\int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}[UR] = \int_{\mathbb{R}^3} V(\rho^{\uparrow\uparrow} + \rho^{\downarrow\downarrow}) - \mu \int_{\mathbb{R}^3} B_z(\rho^{\uparrow\uparrow} - \rho^{\downarrow\downarrow}) = \int_{\mathbb{R}^3} V\rho - \mu \int_{\mathbb{R}^3} B_z\rho\ \zeta.$$

where

$$\zeta := \frac{\rho^{\uparrow\uparrow} - \rho^{\downarrow\downarrow}}{\rho^{\uparrow\uparrow} + \rho^{\downarrow\downarrow}} \in [-1, 1]$$

is the relative spin-polarization. This model is simpler than the noncollinear spin-polarized model, as we are not dealing with fields of matrices, but with two scalar fields. Physically, it corresponds to constraining the spin along a fixed direction on the whole space. This method provides results in good agreement with experiments whenever the energy accounting for the noncollinearity of the spins is negligible.

Then, the spin-unpolarized case consists in minimizing the functional $\mathcal{E}$ onto the set

$$\mathcal{P}_\lambda^{\text{unpolarized}} := \left\{\gamma \in \mathcal{P}_\lambda,\ \gamma^{\uparrow\downarrow} = \gamma^{\downarrow\uparrow} = 0,\ \gamma^{\uparrow\uparrow} = \gamma^{\downarrow\downarrow}\right\}.$$

Equivalently, it corresponds to the collinear case with $\zeta \equiv 0$. It then holds that

$$\int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}[UR] = \int_{\mathbb{R}^3} V\rho,$$

so that the model is independent of the magnetic field $\mathbf{B}$, and can be used whenever spin effects are negligible. We refer to [AC09] for a mathematical introduction of this model.

3.3 An existence result for the Kohn-Sham LSDA model

The main result of this section is the following

Theorem 3.1. *Under the following assumptions*

1/ the function g in (3.8) is of class $C^1(\mathbb{R}^+)$ and satisfies:

$$\begin{cases} g(0) = 0 \\ g' \leq 0 \\ \exists\ 0 < \beta^- \leq \beta^+ < \dfrac{2}{3}, \quad \sup\limits_{\rho\in\mathbb{R}^+} \dfrac{|g'(\rho)|}{\rho^{\beta^-} + \rho^{\beta^+}} < \infty \\ \exists\ 1 \leq \alpha < \dfrac{3}{2}, \quad \limsup\limits_{\rho\to 0^+} \dfrac{g(\rho)}{\rho^\alpha} < 0, \end{cases} \tag{3.10}$$

2/ all entries of U are in $L^{\frac{3}{2}+\epsilon}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ and vanish at infinity, and $V := \mathrm{tr}_{\mathbb{C}^2}(U)$ has the form (3.1),

the problem I_λ defined in (3.9) has a minimizer whenever $\lambda \leq Z$.

Remark 3.2. *The assumptions (3.10) are the same as in [AC09], and are satisfied for all common functionals. Theorem 3.1 extends [AC09, Theorem 1] to the case when the system is spin-polarized by an external magnetic field* $\mathbf{B}$*. While the strategy of proof, based on concentration-compactness arguments, is similar to that in [AC09], an additional technical tool is needed to handle the Zeeman term. This tool seems to be new to the best of our knowledge. We called it the flip transformation (see Equation (3.11) below).*

Remark 3.3. *This result does not make any assumption on the strength of the magnetic field* $\mathbf{B}$ *other than that it vanishes at infinity. If* $\mathbf{B}$ *becomes infinite at infinity, it is easy to see that the energy is not bounded below: we can orientate the spins of all electrons along the magnetic field and push them to infinity, so that the energy can be arbitrarily negative.*

3.3.1 Strategy of the proof of Theorem 3.1

We use the concentration-compactness method introduced in [Lio84]. We introduce the problem at infinity

$$I_\lambda^\infty = \inf\left\{\mathcal{E}^\infty(\gamma),\ \gamma \in \mathcal{P}_\lambda\right\},$$

where

$$\mathcal{E}^\infty(\gamma) := \frac{1}{2}\mathrm{Tr}\left(-\Delta\gamma^{\uparrow\uparrow}\right) + \frac{1}{2}\mathrm{Tr}\left(-\Delta\gamma^{\downarrow\downarrow}\right) + J(\rho_\gamma) + E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho^+,\rho^-).$$

We need several lemmas, the proofs of which are postponed until the following section for the sake of clarity. We begin with some functional inequalities (see Section 3.4.1 for the proof).

Lemma 3.4. *There exists a constant* C *such that for all* $\lambda > 0$ *and all* $\gamma \in \mathcal{P}_\lambda$*, it holds*

$$\|\nabla R_\gamma\|_{L^{3/2}} \le C\mathrm{Tr}(-\Delta\gamma) \quad \text{and} \quad \|\nabla\rho_\gamma^{+/-}\|_{L^{3/2}} \le C\mathrm{Tr}(-\Delta\gamma).$$

In particular, for all $1 \le p \le 3$*, there exists* C_p *such that, for all* $\lambda > 0$ *and all* $\gamma \in \mathcal{P}_\lambda$*,*

$$\|R_\gamma\|_{L^p} \le C_p\lambda^{\frac{3-p}{2p}}\mathrm{Tr}(-\Delta\gamma)^{\frac{3(p-1)}{2p}},$$

and similarly for $\rho_\gamma^{+/-}$*.*

We easily deduce from the above lemma that the energies I_λ and I_λ^∞ are bounded below.

Lemma 3.5. *For all* $\lambda > 0$*, we have* $I_\lambda > -\infty$ *and* $I_\lambda^\infty > -\infty$*. Moreover, all minimizing sequences* (γ_n) *for* I_λ *or* I_λ^∞ *are bounded in the Banach space* $\mathcal{B}$*, where*

$$\mathcal{B} := \{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3,\mathbb{C}^2)),\ \|\gamma\|_{\mathcal{B}} := \mathrm{Tr}(|\gamma|) + \mathrm{Tr}(||\nabla|\gamma|\nabla||) < \infty\}.$$

The proof of Lemma 3.5 is given in Section 3.4.2. In the following, we consider sequences $(\gamma_n)_{n\in\mathbb{N}^*} \in \mathcal{B}$, and we will write $R_n := R_{\gamma_n}$ and $\rho_n := \rho_{\gamma_n}$. The proof of the following lemma is given in Section 3.4.3.

Lemma 3.6. *Let* $(\gamma_n)_{n\in\mathbb{N}^*}$ *be a bounded sequence of* $\mathcal{B}$*. Then, there exists* $\gamma_0 \in \mathcal{B}$*, such that, up to a subsequence,* $(\gamma_n)_{n\in\mathbb{N}^*}$ *converges to* γ_0 *for the weak-* topology of* $\mathcal{B}$*, all components of* R_n *converge to their respective components in* R_0 *strongly in* $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ *for* $1 \le p < 3$*, weakly in* $L^p(\mathbb{R}^3)$ *for* $1 \le p \le 3$*, and almost everywhere. The eigenvalues of* R_n *converge to the eigenvalues of* R_0 *strongly in* $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ *for* $1 \le p < 3$*, weakly in* $L^p(\mathbb{R}^3)$ *for* $1 \le p \le 3$ *and almost everywhere.*

Moreover, if $\gamma_n \in \mathcal{P}_\lambda$ *for all* n*, and* $\gamma_0 \in \mathcal{P}_\lambda$*, the convergences hold strongly in* $L^p(\mathbb{R}^3)$ *for* $1 \le p < 3$*, and* $\mathcal{E}(\gamma_0) \le \liminf \mathcal{E}(\gamma_n)$*.*

It follows from Lemma 3.5 and Lemma 3.6 that one can extract from any minimizing sequence $(\gamma_n)_{n\in\mathbb{N}^*}$ of (3.9) a minimizing sequence, still denoted by $(\gamma_n)_{n\in\mathbb{N}}$, converging to some γ_0 for the weak-$*$ topology of $\mathcal{B}$. In particular, $0 \le \gamma_0 \le 1$ and $\mathrm{Tr}(-\Delta\gamma_0) < \infty$. To prove that γ_0 is indeed a minimizer of (3.9), it remains to prove that $\mathrm{Tr}(\gamma_0) = \lambda$. Let $\alpha = \mathrm{Tr}(\gamma_0)$. It is easy to get $\alpha \le \lambda$. If $\alpha < \lambda$, then we have loss of compactness (some electrons leak away). Therefore, to prove that $\alpha = \lambda$ (at least when $\lambda \le Z$), we need to control the behavior at infinity of the minimizers, which is not as simple as in [AC09] because of the Zeeman term $-\mu\int \mathbf{B}\cdot\mathbf{m}$. In order to control this term, we introduce the following flip transformation:

$$\begin{aligned} &\text{For } \Phi = \begin{pmatrix}\phi^\uparrow\\ \phi^\downarrow\end{pmatrix}, \text{ we define } \widetilde{\Phi} := \begin{pmatrix}\overline{\phi^\downarrow}\\ -\overline{\phi^\uparrow}\end{pmatrix},\\ &\text{For } \gamma = \sum n_k|\Phi_k\rangle\langle\Phi_k|, \text{ we define } \widetilde{\gamma} := \sum n_k|\widetilde{\Phi}_k\rangle\langle\widetilde{\Phi}_k| \end{aligned} \qquad \text{(flip transformation).} \tag{3.11}$$

Note that if

$$\gamma = \begin{pmatrix}\gamma^{\uparrow\uparrow} & \gamma^{\uparrow\downarrow}\\ \gamma^{\downarrow\uparrow} & \gamma^{\downarrow\downarrow}\end{pmatrix} \quad \text{and} \quad R_\gamma = \begin{pmatrix}R^{\uparrow\uparrow} & R^{\uparrow\downarrow}\\ R^{\downarrow\uparrow} & R^{\downarrow\downarrow}\end{pmatrix},$$

then

$$\widetilde{\gamma}(\mathbf{x},\mathbf{y}) = \begin{pmatrix}\gamma^{\downarrow\downarrow} & -\gamma^{\uparrow\downarrow}\\ -\gamma^{\downarrow\uparrow} & \gamma^{\uparrow\uparrow}\end{pmatrix}(\mathbf{y},\mathbf{x}) \quad \text{and} \quad R_{\widetilde{\gamma}} = \begin{pmatrix}R^{\downarrow\downarrow} & -R^{\uparrow\downarrow}\\ -R^{\downarrow\uparrow} & R^{\uparrow\uparrow}\end{pmatrix},$$

from which we deduce the following lemma, whose proof is straightforward.

Lemma 3.7. *If $\gamma \in \mathcal{P}_\lambda$, then $\widetilde{\gamma} \in \mathcal{P}_\lambda$. Moreover, it holds that $\mathrm{Tr}(-\Delta\widetilde{\gamma}_n) = \mathrm{Tr}(-\Delta\gamma_n)$, $\widetilde{\rho} = \rho$, and $\widetilde{\mathbf{m}} = -\mathbf{m}$, where ρ and $\mathbf{m}$ have been defined in (3.3). In particular, it holds that*

$$\mathrm{tr}_{\mathbb{C}^2}[UR] + \mathrm{tr}_{\mathbb{C}^2}\left[U\widetilde{R}\right] = 2\int_{\mathbb{R}^3} V\rho. \tag{3.12}$$

In other words, this transformation flips the spin-up and spin-down channels. Lemma 3.7 allows to cancel the Zeeman term, and is an essential tool throughout the proof. The following lemma is proved in Section 3.4.4.

Lemma 3.8.

(i) For all $\lambda > 0$, it holds $-\infty < I_\lambda < I_\lambda^\infty < 0$.

(ii) For all $0 < \mu < \lambda$, it holds $I_\lambda \le I_\mu + I_{\lambda-\mu}^\infty$.

(iii) The functions $\lambda \mapsto I_\lambda$ and $\lambda \mapsto I_\lambda^\infty$ are non increasing.

We then have the important result (see Section 3.4.5 for the proof).

Lemma 3.9. *Let $\lambda > 0$ and $(\gamma_n)_{n\in\mathbb{N}^*} \in \mathcal{P}_\lambda$ be any minimizing sequence of I_λ that converges to some γ_0 for the weak-$*$ topology of $\mathcal{B}$. Let $\alpha := \mathrm{Tr}(\gamma_0)$. Then*

(i) $\alpha \le \lambda$.

(ii) $\alpha \ne 0$.

(iii) If $0 < \alpha < \lambda$, then γ_0 is a minimizer for the problem I_α, there exists $\beta > 0$ with $\alpha+\beta \le \lambda$ such that I_β^∞ has also a minimizer, and $I_\lambda = I_\alpha + I_\beta^\infty + I_{\lambda-\alpha-\beta}^\infty$.

According to Lemma 3.9, if $\alpha < \lambda$, then γ_0 is a minimizer for I_α. In this case, it satisfies the Euler-Lagrange equation

$$\gamma_0 = \mathbb{1}_{(-\infty,\varepsilon_F)}(H_{\gamma_0}) + \delta \quad \text{with} \quad 0 \le \delta \subset \mathrm{Ker}(H_{\gamma_0} - \varepsilon_F)$$

for some $\varepsilon_F < 0$ called the Fermi energy, and with H_{γ_0} defined in (3.24) below. Here, $\mathbb{1}_{(-\infty,\varepsilon_F)}$ is the characteristic function of the interval $(-\infty,\varepsilon_F)$, and the spectral projection $\mathbb{1}_{(-\infty,\varepsilon_F)}(H_{\gamma_0})$ is defined by the functional calculus. We then use the very general result, whose proof is given in Section 3.4.6.

Lemma 3.10. *It holds $\sigma_{ess}(H_{\gamma_0}) = [0,+\infty[$. Moreover, if $0 < \lambda < Z$, then H_{γ_0} has infinitely many negative eigenvalues, and every eigenvector corresponding to such an eigenvalue is exponentially decreasing.*

From Lemma 3.10, we deduce the concentration-compactness result (see Section 3.4.7 for the proof).

Lemma 3.11. *Let $\alpha > 0$ and $\beta > 0$ be such that $\alpha + \beta \leq Z$. Suppose that I_α and I_β^∞ admit minimizers. Then*

$$I_{\alpha+\beta} < I_\alpha + I_\beta^\infty \quad (< I_\alpha).$$

The end of the proof of Theorem 3.1 goes as follows. Let us assume that $\lambda \leq Z$, and $\alpha < \lambda$. Then, according to the third point of Lemma 3.9, γ_0 is a minimizer for I_α, and there exists $\beta > 0$ such that $\alpha + \beta \leq \lambda \leq Z$ so that I_β^∞ has also a minimizer, and it holds $I_\lambda = I_\alpha + I_\beta^\infty + I_{\lambda-\alpha-\beta}^\infty$. Moreover, Lemma 3.11 holds, and $I_{\alpha+\beta} < I_\alpha + I_\beta^\infty$. Finally, we get

$$I_\lambda = I_\alpha + I_\beta^\infty + I_{\lambda-\alpha-\beta}^\infty > I_{\alpha+\beta} + I_{\lambda-\alpha-\beta}^\infty,$$

which contradicts the second point of Lemma 3.8. Therefore, it holds $\alpha = \lambda$, and, according to Lemma 3.6, γ_0 is a minimizer for I_λ, which concludes the proof.

3.4 Proofs of the sub-lemmas of Theorem 3.1

3.4.1 Proof of Lemma 3.4

Let $\lambda > 0$ and $\gamma \in \mathcal{P}_\lambda$. We use the representation (3.6) of γ, and write

$$\gamma^{\alpha\beta}(\mathbf{r},\mathbf{r}') = \sum_{k=1}^\infty n_k \phi_k^\alpha(\mathbf{r})\overline{\phi_k^\beta(\mathbf{r}')},\ 0 \leq n_k \leq 1,\ \sum_{k=1}^\infty n_k = \lambda,$$
$$\Phi_k = \begin{pmatrix} \phi_k^\uparrow \\ \phi_k^\downarrow \end{pmatrix} \in L^2(\mathbb{R}^3,\mathbb{C}^2),\ \langle \Phi_k | \Phi_l \rangle = \delta_{kl},\ \mathrm{Tr}(-\Delta\gamma) := \sum_{k=1}^\infty n_k \|\nabla\Phi_k\|_{L^2}^2 < \infty.$$

In particular, $\rho^{\alpha\beta}(\mathbf{r}) = \sum n_k \phi_k^\alpha(\mathbf{r})\overline{\phi_k^\beta(\mathbf{r})}$. Differentiating this expression and using the Cauchy-Schwarz inequality lead to

$$\begin{aligned}
|\nabla\rho^{\alpha\beta}|^2 &= \left| \sum_{k=1}^\infty n_k \left(\nabla\phi_k^\alpha(\mathbf{r})\overline{\phi_k^\beta(\mathbf{r})} + \phi_k^\alpha(\mathbf{r})\nabla\overline{\phi_k^\beta(\mathbf{r})} \right) \right|^2 \\
&\leq \left| \sum_{k=1}^\infty n_k \left(|\nabla\phi_k^\alpha|^2 + |\nabla\phi_k^\beta|^2 \right)^{1/2} \left(|\phi_k^\alpha|^2 + |\phi_k^\beta|^2 \right)^{1/2} \right|^2 \\
&\leq \left[\sum_{k=1}^\infty n_k \left(|\nabla\phi_k^\alpha|^2 + |\nabla\phi_k^\beta|^2 \right) \right] \left[\sum_{k=1}^\infty n_k \left(|\phi_k^\alpha|^2 + |\phi_k^\beta|^2 \right) \right].
\end{aligned}$$

We let $\tau^\alpha := \sum_{k=1}^\infty n_k |\nabla\phi_k^\alpha|^2$, so that $\tau^\alpha \in L^1(\mathbb{R}^3)$ and $\int_{\mathbb{R}^3} \tau^\alpha = \mathrm{Tr}(-\Delta\gamma^{\alpha\alpha})$. The previous inequality leads to the pointwise estimate

$$|\nabla\rho^{\alpha\beta}| \leq \left(\tau^\alpha + \tau^\beta \right)^{1/2} \left(\rho^{\alpha\alpha} + \rho^{\beta\beta} \right)^{1/2}. \tag{3.13}$$

In particular, if $\alpha = \beta$, we recover the Hoffman-Ostenhof inequality [HOHO77]

$$\|\nabla\sqrt{\rho^{\alpha\alpha}}\|_{L^2}^2 \leq \mathrm{Tr}(-\Delta\gamma^{\alpha\alpha}).$$

Together with the homogeneous Sobolev embedding $H^1(\mathbb{R}^3) \hookrightarrow L^6(\mathbb{R}^3)$, we deduce

$$\|\rho^{\alpha\alpha}\|_{L^3} \leq C\ \mathrm{Tr}(-\Delta\gamma^{\alpha\alpha}).$$

Then, using the fact that $\left(\tau^\alpha + \tau^\beta\right)^{1/2} \in L^2(\mathbb{R}^3)$ and $\left(\rho^{\alpha\alpha} + \rho^{\beta\beta}\right)^{1/2} \in L^6(\mathbb{R}^3)$ and the Hölder inequality, it follows from (3.13) that

$$\|\nabla\rho^{\alpha\beta}\|_{L^{3/2}} \leq \|(\tau^\alpha + \tau^\beta)^{1/2}\|_{L^2}\ \|(\rho^{\alpha\alpha} + \rho^{\beta\beta})^{1/2}\|_{L^6} \leq 4C\ \mathrm{Tr}(-\Delta\gamma). \tag{3.14}$$

For $\rho^{+/-}$, we use the exact expression of the eigenvalues of a 2×2 hermitian matrix:

$$\rho^{+/-} = \frac{1}{2}\left(\rho \pm \sqrt{\rho^2 - 4\det(R)}\right) = \frac{1}{2}\left(\rho \pm \sqrt{(\rho^{\uparrow\uparrow} - \rho^{\downarrow\downarrow})^2 + 4|\rho^{\uparrow\downarrow}|^2}\right). \tag{3.15}$$

If f and g are non negative, then, according to (2.15), we have the pointwise estimate

$$|\nabla\sqrt{f+g}| = |\nabla\sqrt{f}| + |\nabla\sqrt{g}|.$$

We differentiate (3.15) to get

$$\begin{aligned}|\nabla\rho^{+/-}| &\leq \frac{1}{2}|\nabla\rho| + \frac{1}{2}\left|\nabla\sqrt{(\rho^{\uparrow\uparrow} - \rho^{\downarrow\downarrow})^2 + 4|\rho^{\uparrow\downarrow}|^2}\right| \\ &\leq \frac{1}{2}|\nabla\rho^{\uparrow\uparrow}| + \frac{1}{2}|\nabla\rho^{\downarrow\downarrow}| + \frac{1}{2}\left(|\nabla\rho^{\uparrow\uparrow}| + |\nabla\rho^{\downarrow\downarrow}| + 2\big|\nabla|\rho^{\uparrow\downarrow}|\big|\right).\end{aligned}$$

All the terms on the right-hand side are in $L^{3/2}(\mathbb{R}^3)$ and of norms bounded by $C\mathrm{Tr}(-\Delta\gamma)$, hence the same holds for $\nabla\rho^{+/-}$.

Moreover, γ is in $\mathcal{P}_\lambda$, so that $\mathrm{Tr}(\gamma) = \int_{\mathbb{R}^3}\rho = \lambda$. From the inequality $2|ab| \leq |a|^2 + |b|^2$, we get that

$$|\rho^{\alpha\beta}| = \left|\sum_{k=1}^\infty n_k\phi_k^\alpha(\mathbf{r})\overline{\phi_k^\beta(\mathbf{r})}\right| \leq \sum_{k=1}^\infty \frac{n_k}{2}\left(|\phi_k^\alpha|^2 + |\phi_k^\beta|^2\right) \leq \sum_{k=1}^\infty n_k\left(|\phi_k^\uparrow|^2 + |\phi_k^\downarrow|^2\right) = \rho. \tag{3.16}$$

Integrating on $\mathbb{R}^3$ leads to $\|\rho^{\alpha\beta}\|_{L^1} \leq \lambda$. From the positiveness of R_γ, it also holds that $0 \leq \rho^{+/-} \leq \rho$ so that $\|\rho^{+/-}\|_{L^1} \leq \lambda$. We conclude from (3.14), the homogeneous Sobolev embedding $W^{1,3/2}(\mathbb{R}^3) \hookrightarrow L^3(\mathbb{R}^3)$, and the Hölder inequality with $1 \leq p \leq 3$, that

$$\|\rho^{\alpha\beta}\|_{L^p} \leq C_p\lambda^{\frac{3-p}{2p}}\mathrm{Tr}(-\Delta\gamma)^{\frac{3(p-1)}{2p}},$$

and similarly for $\rho^{+/-}$.

3.4.2 Proof of Lemma 3.5

We prove that $I_\lambda > -\infty$. The proof is similar for I_λ^∞. Let $\lambda > 0$, and $\gamma \in \mathcal{P}_\lambda$. Under conditions (3.10), a straightforward calculation shows that

$$\begin{aligned}\left|E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho^+,\rho^-)\right| &\leq C\left(\int_{\mathbb{R}^3}(\rho^+)^{p^-} + \int_{\mathbb{R}^3}(\rho^+)^{p^+}\right) + C\left(\int_{\mathbb{R}^3}(\rho^-)^{p^-} + \int_{\mathbb{R}^3}(\rho^-)^{p^+}\right) \\ &\leq 2C\left(\int_{\mathbb{R}^3}\rho^{p^+} + \int_{\mathbb{R}^3}\rho^{p^-}\right),\end{aligned}$$

where $p^{+/-} := 1 + \beta^{+/-} < 5/3$. We used the fact that R_γ is a positive hermitian matrix, so that $0 \le \rho^{+/-} \le \rho$. Therefore, since $J(\rho) \ge 0$, we have the estimate

$$\mathcal{E}(\gamma) \ge \frac{1}{2}\mathrm{Tr}(-\Delta\gamma) - C_1\|U\|_{L^{\frac{3}{2}+\epsilon}+L^\infty}\|R\|_{L^1\cap L^{3-\epsilon'}} - C_2\left(\|\rho\|_{L^{p^+}}^{p^+} + \|\rho\|_{L^{p^-}}^{p^-}\right),$$

where $\epsilon' = 4\epsilon/(1+2\epsilon) > 0$ is chosen such that $L^{3-\epsilon'}$ is the dual space of $L^{\frac{3}{2}+\epsilon}$. With Lemma 3.4, it follows

$$\mathcal{E}(\gamma) \ge \frac{1}{2}\mathrm{Tr}(-\Delta\gamma) - C_1'\|U\|_{L^{\frac{3}{2}+\epsilon}+L^\infty}\left(1 + \mathrm{Tr}(-\Delta\gamma)^{\alpha_1}\right) - C_2\left(\mathrm{Tr}(-\Delta\gamma)^{\alpha_2} + \mathrm{Tr}(-\Delta\gamma)^{\alpha_3}\right)$$

with $0 \le \alpha_1, \alpha_2, \alpha_3 < 1$. The function $Y \mapsto \frac{1}{2}Y - C_1''(1+Y^{\alpha_1}) - C_2Y^{\alpha_2} - C_2Y^{\alpha_3}$ goes to $+\infty$ when Y goes to $+\infty$ for $0 \le \alpha_1, \alpha_2, \alpha_3 < 1$. Hence, $\mathcal{E}(\gamma) \ge -C$ for all $\gamma \in \mathcal{P}_\lambda$. It also follows from the above inequality that if $(\gamma_n)_{n\in\mathbb{N}^*}$ is a minimizing sequence for I_λ, then $(\mathrm{Tr}(-\Delta\gamma_n))_{n\in\mathbb{N}^*}$ is uniformly bounded. In particular, $(\gamma_n)_{n\in\mathbb{N}^*}$ is a bounded sequence of $\mathcal{B}$.

3.4.3 Proof of Lemma 3.6

Let $(\gamma_n)_{n\in\mathbb{N}^*}$ be a bounded sequence in $\mathcal{B}$. According to Lemma 3.4, the sequences $\left(\rho_n^{\alpha\beta}\right)_{n\in\mathbb{N}^*}$ for $\alpha, \beta \in \{\uparrow,\downarrow\}^2$ and $\left(\rho_n^{+/-}\right)_{n\in\mathbb{N}^*}$ are bounded in $W^{1,3/2}(\mathbb{R}^3)$. In virtue of the Banach-Alaoglu theorem, up to a subsequence, the sequence $(\gamma_n)_{n\in\mathbb{N}^*}$ converges to some $\gamma_0 \in \mathcal{B}$ for the weak-$*$ topology of $\mathcal{B}$, and $\left(\rho_n^{\alpha\beta}\right)_{n\in\mathbb{N}^*}$ and $\left(\rho_n^{+/-}\right)_{n\in\mathbb{N}^*}$ converge for the weak topology of $W^{1,3/2}(\mathbb{R}^3)$. To identify the limits, we recall that, for any compact operator K on $L^2(\mathbb{R}^3,\mathbb{C}^2)$,

$$\mathrm{Tr}(\gamma_n K) \xrightarrow[n\to\infty]{} \mathrm{Tr}(\gamma_0 K) \quad \text{and} \quad \mathrm{Tr}(|\nabla|\gamma_n|\nabla|K) \xrightarrow[n\to\infty]{} \mathrm{Tr}(|\nabla|\gamma_0|\nabla|K). \tag{3.17}$$

Choose $W \in C_c^\infty(\mathbb{R}^3,\mathbb{R})$. The operator $(1+|\nabla|)^{-1}W(1+|\nabla|)^{-1}$ is compact and in the Schatten class $\mathfrak{S}_p(L^2(\mathbb{R}^3,\mathbb{C}))$ for $p > \frac{3}{2}$ according to the Kato-Seiler-Simon inequality [Sim05]. Taking successively in (3.17)

$$K = \begin{pmatrix} W & 0 \\ 0 & 0 \end{pmatrix}, \quad K = \begin{pmatrix} 0 & 0 \\ 0 & W \end{pmatrix}, \quad K = \begin{pmatrix} 0 & W \\ W & 0 \end{pmatrix} \quad \text{and} \quad K = \begin{pmatrix} 0 & \mathrm{i}W \\ -\mathrm{i}W & 0 \end{pmatrix},$$

we obtain that, for the first choice of K,

$$\begin{aligned}\int_{\mathbb{R}^3} \rho_n^{\uparrow\uparrow}W = \mathrm{Tr}(\gamma_n W) &= \mathrm{Tr}\left((1+|\nabla|)\gamma_n(1+|\nabla|)\cdot(1+|\nabla|)^{-1}W(1+|\nabla|)^{-1}\right) \\ &\xrightarrow[n\to\infty]{} \mathrm{Tr}\left((1+|\nabla|)\gamma_0(1+|\nabla|)\cdot(1+|\nabla|)^{-1}W(1+|\nabla|)^{-1}\right) = \int_{\mathbb{R}^3}\rho_0^{\uparrow\uparrow}W\end{aligned} \tag{3.18}$$

and similarly for $\rho_0^{\downarrow\downarrow}$, $\mathrm{Re}\,(\rho_0^{\uparrow\downarrow})$ and $\mathrm{Im}\,(\rho_0^{\uparrow\downarrow})$. We deduce that $\left(\rho_n^{\alpha\beta}\right)_{n\in\mathbb{N}^*}$ converges to $\rho_0^{\alpha\beta}$ in $\mathcal{D}'(\mathbb{R}^3,\mathbb{C})$ for all $\alpha,\beta \in \{\uparrow,\downarrow\}^2$. Identifying the limits, the convergences hold also weakly in $W^{1,3/2}(\mathbb{R}^3)$, strongly in $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ for $1 \le p < 3$, and almost everywhere, in virtue of the Sobolev embedding theorem. From (3.15) and the pointwise convergence of $\left(\rho_n^{\alpha\beta}\right)_{n\in\mathbb{N}^*}$ to $\rho_0^{\alpha\beta}$, we also deduce that $(\rho_n^{+/-})_{n\in\mathbb{N}^*}$ pointwise converges to $\rho_0^{+/-}$. Again, by identifying the limits, the convergence also holds weakly in $W^{1,3/2}(\mathbb{R}^3)$ and strongly in $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ for $1 \le p < 3$.

Then, let $\chi \in C_c^\infty(\mathbb{R})$ be a cut-off function such that $\chi(x) = 1$ if $|x| < 1$ and $\chi(x) = 0$ if $x \ge 2$. We take $W_A = \chi(x/A)$ in (3.18), and let A go to infinity to obtain that

$$\rho_0^{\uparrow\uparrow} \in L^1(\mathbb{R}^3) \quad \text{and} \quad \int_{\mathbb{R}^3}\rho_0^{\uparrow\uparrow} \le \liminf_{n\to\infty}\int_{\mathbb{R}^3}\rho_n^{\uparrow\uparrow}, \tag{3.19}$$

and similarly for $\rho_0^{\downarrow\downarrow}$. Now, if $\gamma_n \in \mathcal{P}_\lambda$ and $\gamma_0 \in \mathcal{P}_\lambda$, we get

$$\lambda = \int_{\mathbb{R}^3} \rho_0 = \int_{\mathbb{R}^3} \rho_0^{\uparrow\uparrow} + \rho_0^{\downarrow\downarrow} \leq \int_{\mathbb{R}^3} \rho_n^{\uparrow\uparrow} + \rho_n^{\downarrow\downarrow} = \lambda,$$

and the inequality (3.19) is an equality. Therefore, $(\rho_n)_{n\in\mathbb{N}^*}$ converges to ρ_0 strongly in $L^1(\mathbb{R}^3)$. We deduce from (3.16) and $0 \leq \rho_n^{+/-} \leq \rho_n$ that $\rho_n^{\uparrow\downarrow}$ and $\rho_n^{+/-}$ are bounded in $L^1(\mathbb{R}^3)$. A classical application of the dominated convergence theorem then leads to the fact that $\left(\rho_n^{\alpha\beta}\right)_{n\in\mathbb{N}^*}$ converges to $\rho_0^{\alpha\beta}$ strongly in $L^1(\mathbb{R}^3)$ for $\alpha, \beta \in \{\uparrow, \downarrow\}^2$, and that $\left(\rho_n^{+/-}\right)_{n\in\mathbb{N}^*}$ converges strongly to $\rho_0^{+/-}$ in $L^1(\mathbb{R}^3)$. Finally, the strong convergence still holds in $L^p(\mathbb{R}^3)$ for $1 \leq p < 3$ according to the Hölder inequality.

The proof for the energy is similar to the one in [AC09, Lemma 3]. We do not repeat it here, but notice that the strong convergence of $\left(\rho_n^{+/-}\right)_{n\in\mathbb{N}^*}$ to $\rho_0^{+/-}$ in $L^p(\mathbb{R}^3)$ for $1 \leq p < 3$ is needed for the convergence of the exchange-correlation functional.

3.4.4 Proof of Lemma 3.8

(ii) Let us first prove that for $0 < \mu < \lambda$, it holds that $I_\lambda \leq I_\mu + I^\infty_{\lambda-\mu}$. Let $\epsilon > 0$, $\gamma \in \mathcal{P}_\mu$ and $\gamma' \in \mathcal{P}_{\lambda-\mu}$ be such that $I_\mu \leq \mathcal{E}(\gamma) \leq I_\mu + \epsilon$ and $I^\infty_{\lambda-\mu} \leq \mathcal{E}^\infty(\gamma') \leq I^\infty_{\lambda-\mu} + \epsilon$. By density of finite-rank one-body density matrices in $\mathcal{B}$, and density of $C^\infty_c(\mathbb{R}^3, \mathbb{C}^2)$ in $H^1(\mathbb{R}^3, \mathbb{C}^2)$, we can assume that γ and γ' are both of the form

$$\gamma^{(\prime)} = \sum_{i=1}^{M} n_k^{(\prime)} |\Phi_k^{(\prime)}\rangle\langle\Phi_k^{(\prime)}| \quad \text{with} \quad \Phi_k^{(\prime)} \in C^\infty_c(\mathbb{R}^3, \mathbb{C}^2).$$

We consider $\gamma_n := \gamma + \tau_{n\mathbf{e}}\gamma'\tau_{-n\mathbf{e}}$ and $\gamma_n^\sharp := \gamma + \tau_{n\mathbf{e}}\widetilde{\gamma}'\tau_{-n\mathbf{e}}$ where $\tau_{\mathbf{x}} f(\mathbf{r}) = f(\mathbf{r}-\mathbf{x})$, and $\mathbf{e}$ is a non-null vector. We recall that $\widetilde{\gamma}'$ is the flipped transformation of γ', as introduced in (3.11). For n_0 large enough, and for $n \geq n_0$, the supports of the Φ_k's and of the $\tau_{n\mathbf{e}}\Phi'_k$'s are disjoint, so that γ_n and $\gamma_n^\sharp$ are in $\mathcal{P}_\lambda$ for all $n \geq n_0$. Also, for n large enough, $J(\rho_n) \leq J(\rho) + J(\rho') + \epsilon$. Altogether, we get, for n large enough,

$$\begin{aligned}\mathcal{E}(\gamma_n) + \mathcal{E}(\gamma_n^\sharp) &= 2\mathcal{E}(\gamma) + 2\mathcal{E}^\infty(\gamma') + 2\int V\rho'(\cdot - n\mathbf{e}) + 2\varepsilon \leq 2\mathcal{E}(\gamma) + 2\mathcal{E}^\infty(\gamma') + 2\epsilon \\ &\leq 2I_\mu + 2I^\infty_{\lambda-\mu} + 6\epsilon.\end{aligned}$$

Hence, either $\mathcal{E}(\gamma_n)$ or $\mathcal{E}(\gamma_n^\sharp)$ is smaller than $I_\mu + I^\infty_{\lambda-\mu} + 3\epsilon$, so that $I_\lambda \leq I_\mu + I^\infty_{\lambda-\mu}$. Similar arguments show that $I^\infty_\lambda \leq I^\infty_\mu + I^\infty_{\lambda-\mu}$.

(i) We first prove that there exists λ_0 small enough such that for all $0 < \lambda \leq \lambda_0$, it holds $I^\infty_\lambda < 0$. We use a scaling argument. Let $\phi \in C^\infty_c(\mathbb{R}^3, \mathbb{C})$ be such that $\|\phi\|_{L^2} = 1$, and let $\phi_\sigma = \sigma^{3/2}\phi(\sigma\cdot)$ for $\sigma > 0$. Note that $\|\phi_\sigma\|_{L^2} = 1$. For $\lambda \leq 1$, we introduce

$$\gamma_{\lambda\sigma}(\mathbf{r}, \mathbf{r}') = \lambda \begin{pmatrix} \phi_\sigma(\mathbf{r})\overline{\phi_\sigma}(\mathbf{r}') & 0 \\ 0 & 0 \end{pmatrix},$$

so that $\gamma_{\lambda\sigma} \in \mathcal{P}_\lambda$ for all $0 < \lambda \leq 1$ and $\sigma > 0$. Using (3.10), there exists $1 \leq \alpha < 3/2$ such that $E_{\mathrm{xc}}^{\mathrm{LSDA}}(\lambda|\phi_\sigma|^2, 0) \leq -C\lambda^\alpha\sigma^{3(\alpha-1)}\|\phi\|^{2\alpha}_{L^{2\alpha}}$. Direct calculations lead to

$$\begin{aligned}\mathcal{E}^\infty(\gamma_{\lambda\sigma}) &= \frac{\lambda\sigma^2}{2}\int_{\mathbb{R}^3} |\nabla\phi|^2 + \lambda^2\sigma J(|\phi|^2) + \int_{\mathbb{R}^3} E_{\mathrm{xc}}^{\mathrm{LSDA}}(|\phi_{\lambda\sigma}|^2, 0) \\ &\leq \frac{\lambda\sigma^2}{2}\int_{\mathbb{R}^3} |\nabla\phi|^2 + \lambda^2\sigma J(|\phi|^2) - C\lambda^\alpha\sigma^{3(\alpha-1)}\|\phi\|^{2\alpha}_{L^{2\alpha}}.\end{aligned}$$

It is easy to check that under the condition $\alpha < 3/2$, there exists $\lambda_0 > 0$ such that for all $0 < \lambda \leq \lambda_0$, there exists σ such that $\mathcal{E}(\gamma_{\lambda\sigma}) < 0$. In particular, $I_\lambda^\infty \leq \mathcal{E}^\infty(\gamma_{\lambda\sigma}) < 0$. Together with *(ii)*, we deduce that, for all $\lambda > 0$, $I_\lambda^\infty < 0$ and $I_\lambda < 0$.

We now prove that $I_\lambda < I_\lambda^\infty$, for all $\lambda > 0$. Let $(\gamma_n)_{n\in\mathbb{N}^*}$ be a minimizing sequence for I_λ^∞. We first suppose that

$$\forall A > 0, \quad \lim_{n\to\infty} \sup_{\mathbf{r}\in\mathbb{R}^3} \int_{\mathbf{r}+B_A} \rho_n = 0,$$

where B_A is the ball of radius A centered at the origin. Since $(\rho_n)_{n\in\mathbb{N}^*}$ is bounded in $W^{1,3/2}$ according to Lemma 3.5 and 3.6, we deduce from [Lio84, Lemma I.1] that $(\rho_n)_{n\in\mathbb{N}}$ converges to 0 strongly in $L^p(\mathbb{R}^3)$ for $1 < p < 3$. Also, because of (3.16), the components of R_n and its eigenvalues converge to 0 strongly in $L^p(\mathbb{R}^3)$ for $1 < p < 3$. Similarly to [AC09], we deduce that

$$I_\lambda^\infty = \liminf_{n\to\infty} \mathcal{E}^\infty(\gamma_n) = \liminf_{n\to\infty} \left\{ \frac{1}{2}\mathrm{Tr}(-\Delta\gamma_n) + J(\rho_n) + E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_n^+, \rho_n^-) \right\} = \liminf_{n\to\infty} \frac{1}{2}\mathrm{Tr}(-\Delta\gamma_n) \geq 0$$

which contradicts the first point. Therefore

$$\exists A, \eta > 0, \quad \forall n \in \mathbb{N}, \quad \exists \mathbf{r}_n \in \mathbb{R}^3, \quad \int_{\mathbf{r}_n+B_A} \rho_n \geq \eta. \tag{3.20}$$

Up to translations of the γ_n's, we can assume without loss of generality that $\mathbf{r}_n = \mathbf{0}$.

We now introduce $\widetilde{\gamma}_n$, the flipped version of γ_n introduced in (3.11). Using (3.12) and the fact that $V(\mathbf{r}) \leq -\dfrac{z_1}{\mathbf{r}}$, we get

$$\begin{aligned}
\mathcal{E}(\gamma_n) + \mathcal{E}(\widetilde{\gamma}_n) &= \mathrm{Tr}(-\Delta\gamma_n) + 2J(\rho_n) + 2E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_n^+, \rho_n^-) + 2\int_{\mathbb{R}^3} V\rho_n \\
&= 2\mathcal{E}^\infty(\gamma_n) + 2\int_{\mathbb{R}^3} V\rho_n \leq 2\mathcal{E}^\infty(\gamma_n) - 2\int_{B_R} \frac{z_1}{|\mathbf{r}|}\rho_n \leq 2\mathcal{E}^\infty(\gamma_n) - 2\frac{z_1}{R}\eta.
\end{aligned}$$

Hence, either $\mathcal{E}(\gamma_n)$ or $\mathcal{E}(\widetilde{\gamma}_n)$ is smaller than $\mathcal{E}^\infty(\gamma_n) - z_1 R^{-1}\eta$. Therefore, $I_\lambda \leq I_\lambda^\infty - z_1 R^{-1}\eta < I_\lambda^\infty$.

(iii) The fact that $\lambda \mapsto I_\lambda$ and $\lambda \mapsto I_\lambda^\infty$ are non increasing can be read from the other statements.

3.4.5 Proof of Lemma 3.9

Let $\lambda > 0$, and let $(\gamma_n)_{n\in\mathbb{N}^*} \in \mathcal{P}_\lambda$ be a minimizing sequence for I_λ. According to Lemma 3.5, up to a subsequence, we can assume that $(\gamma_n)_{n\in\mathbb{N}^*}$ converges to some $\gamma_0 \in \mathcal{B}$ for the weak-$*$ topology of $\mathcal{B}$.

(i) The fact that $\alpha \leq \lambda$ can be directly deduced from (3.19).

(ii) Suppose that $\alpha = 0$, so that $\gamma = 0$. Then, we have $I_\lambda = \liminf \mathcal{E}(\gamma_n) = \mathcal{E}(\gamma_0) = 0$ (we used the continuity of $\mathcal{E}$, which can be proved similarly to [AC09]). This contradicts the first point of Lemma 3.8. Hence, $\alpha \neq 0$.

(iii) Suppose that $0 < \alpha < \lambda$. Following [AC09, FLSS07], we let $\chi, \xi \in C_c^\infty(\mathbb{R}^3, \mathbb{R}^+)$ be radial functions such that $\chi^2 + \xi^2 = 1$, with $\chi(\mathbf{0}) = 1$, $\chi < 1$ on $\mathbb{R}^3 \setminus \{\mathbf{0}\}$, $\chi(\mathbf{r}) = 0$ for $|\mathbf{r}| > 1$, $\|\nabla\chi\|_{L^\infty} \leq 2$ and $\|\nabla\xi\|_{L^\infty} \leq 2$. We introduce $\chi_A(\mathbf{r}) := \chi(\mathbf{r}/A)$ and $\xi_A(\mathbf{r}) := \xi(\mathbf{r}/A)$ and

finally $\gamma_{n,A} := \chi_A \gamma_n \chi_A$. With those notations, $A \mapsto \mathrm{Tr}(\gamma_{n,A})$ is a continuous and increasing function from 0 to λ. Therefore, there exists A_n such that γ_{n,A_n} is in $\mathcal{P}_\alpha$.

The sequence $(A_n)_{n\in\mathbb{N}^*}$ goes to infinity. Otherwise, we would have for A large enough and according to (3.19),

$$\int_{\mathbb{R}^3} \rho_0 \chi_A^2 = \lim_{n\to\infty} \int_{\mathbb{R}^3} \rho_n \chi_A^2 \ \geq \lim_{n\to\infty} \int_{\mathbb{R}^3} \rho_n \chi_{A_n}^2 \ = \alpha = \int_{\mathbb{R}^3} \rho_0,$$

which is impossible, since $|\chi_A^2| < 1$ on $\mathbb{R}^3$.

We introduce $\gamma_{1,n} := \chi_{A_n} \gamma_n \chi_{A_n}$ and $\gamma_{2,n} := \xi_{A_n} \gamma_n \xi_{A_n}$. Note that $\gamma_{1,n} \in \mathcal{P}_\alpha$ and $\gamma_{2,n} \in \mathcal{P}_{\lambda-\alpha}$, and that $\rho_n = \rho_{1,n} + \rho_{2,n}$. From the decomposition (3.6) of γ_n, we can write $\gamma_n = \sum_{k=1}^{\infty} n_{k,n} |\Phi_{k,n}\rangle\langle\Phi_{k,n}|$, with $0 \leq n_{k,n} \leq 1$. We deduce that

$$\mathrm{Tr}\big(\big||\nabla|\gamma_{1,n}|\nabla|\big|\big) + \mathrm{Tr}\big(\big||\nabla|\gamma_{2,n}|\nabla|\big|\big) \leq \mathrm{Tr}\big(\big||\nabla|\gamma_n|\nabla|\big|\big) + 8\frac{\lambda}{A_n^2}.$$

Hence, $(\gamma_{1,n})_{n\in\mathbb{N}^*}$ and $(\gamma_{2,n})_{n\in\mathbb{N}^*}$ are bounded in $\mathcal{B}$. Also, direct calculations lead to

$$\mathrm{Tr}(-\Delta\gamma_{1,n}) + \mathrm{Tr}(-\Delta\gamma_{2,n}) \leq \mathrm{Tr}(-\Delta\gamma_n) + 8\frac{\lambda}{A_n^2}. \tag{3.21}$$

According to Lemma 3.5, up to a subsequence, $(\gamma_{1,n})_{n\in\mathbb{N}^*}$ converges for the weak-$*$ topology of $\mathcal{B}$. In this case, for $\Phi = (\phi^\uparrow, \phi^\downarrow) \in C_c^\infty(\mathbb{R}^3, \mathbb{C}^2)$, it holds that

$$\mathrm{Tr}(\gamma_{1,n}|\Phi\rangle\langle\Phi|) = \int_{\mathbb{R}^3} \rho_{1,n}^{\uparrow\uparrow} |\phi^\uparrow|^2 + \int_{\mathbb{R}^3} \rho_{1,n}^{\downarrow\downarrow} |\phi^\downarrow|^2 = \int_{\mathbb{R}^3} \chi_{A_n}^2 \rho_n^{\uparrow\uparrow} |\phi^\uparrow|^2 + \int_{\mathbb{R}^3} \chi_{A_n}^2 \rho_n^{\downarrow\downarrow} |\phi^\downarrow|^2.$$

For n large enough, the support of Φ is inside the support of χ_{A_n}, and

$$\mathrm{Tr}(\gamma_{1,n}|\Phi\rangle\langle\Phi|) = \mathrm{Tr}(\gamma_n|\chi_{A_n}\Phi\rangle\langle\Phi\chi_{A_n}|) \xrightarrow[n\to\infty]{} \mathrm{Tr}(\gamma|\Phi\rangle\langle\Phi|).$$

We deduce that $(\gamma_{1,n})_{n\in\mathbb{N}^*}$ converges to γ_0 for the weak-$*$ topology of $\mathcal{B}$. Finally, since $\gamma_{1,n} \in \mathcal{P}_\alpha$ and $\gamma_0 \in \mathcal{P}_\alpha$, $(\rho_{1,n})_{n\in\mathbb{N}^*}$ converges strongly to ρ_0 in $L^p(\mathbb{R}^3)$ for $1 \leq p < 3$, and $\mathcal{E}(\gamma_0) \leq \liminf \mathcal{E}(\gamma_{1,n})$ according to Lemma 3.6.

Let us look more closely to $\gamma_{2,n}$. Since $(\rho_{1,n})_{n\in\mathbb{N}^*}$ converges to ρ_0 strongly in $L^p(\mathbb{R}^3)$ and $(\rho_n)_{n\in\mathbb{N}^*}$ converges to ρ_0 strongly in $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ for $1 \leq p < 3$, we obtain that $\rho_{2,n} = \rho_n - \rho_{1,n}$ (and thus all the components of $R_{2,n}$ and its eigenvalues) converges strongly to 0 in $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ for $1 \leq p < 3$. Also, it holds that $\rho_{1,n}^{+/-} + \rho_{2,n}^{+/-} = \rho_n^{+/-}$. Using (3.21) and the fact that $\iint \rho_{1,n}(\mathbf{r})\rho_{2,n}(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-1}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' \geq 0$, we obtain

$$\begin{aligned}
\mathcal{E}(\gamma_n) &= \frac{1}{2}\mathrm{Tr}(-\Delta\gamma_n) + J(\rho_n) + \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}\left[UR_n\right] + E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_n^+, \rho_n^-) \\
&\geq \frac{1}{2}\mathrm{Tr}(-\Delta\gamma_{1,n}) + \frac{1}{2}\mathrm{Tr}(-\Delta\gamma_{2,n}) - 4\frac{\lambda}{A_n^2} + J(\rho_{1,n}) + J(\rho_{2,n}) + \\
&+ \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}\left[UR_{1,n}\right] + \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}\left[UR_{2,n}\right] + E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_{1,n}^+ + \rho_{2,n}^+, \rho_{1,n}^- + \rho_{2,n}^-) \\
&\geq \mathcal{E}(\gamma_{1,n}) + \mathcal{E}^\infty(\gamma_{2,n}) - 4\frac{\lambda}{A_n^2} + \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}\left[UR_{2,n}\right] + \\
&\quad + E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_{1,n}^+ + \rho_{2,n}^+, \rho_{1,n}^- + \rho_{2,n}^-) - E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_{1,n}^+, \rho_{1,n}^-) - E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_{2,n}^+, \rho_{2,n}^-).
\end{aligned}$$

We first consider the term $\int \mathrm{tr}_{\mathbb{C}^2}[UR_{2,n}]$. We have for $A \geq 0$, (we use, for a matrix M, the notation $|M|$ for the sum of the absolute values of the entries of M)

$$\begin{aligned}\left|\int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}[UR_{2,n}]\right| &= \left|\int_{B_A} \mathrm{tr}_{\mathbb{C}^2}[UR_{2,n}]\right| + \left|\int_{(B_A)^c} \mathrm{tr}_{\mathbb{C}^2}[UR_{2,n}]\right| \\ &\leq \|U\|_{L^{\frac{3}{2}+\epsilon}+L^\infty(B_A)} \|R_{2,n}\|_{L^1\cap L^{3-\epsilon'}(B_A)} + \sup_{\mathbf{r}\in(B_A)^c}|U(\mathbf{r})| \int_{(B_A)^c}|R_{2,n}| \\ &\leq \|U\|_{L^{\frac{3}{2}+\epsilon}+L^\infty(\mathbb{R}^3)} \|R_{2,n}\|_{L^1\cap L^{3-\epsilon'}(B_A)} + \sup_{\mathbf{r}\in(B_A)^c}|U(\mathbf{r})| \int_{\mathbb{R}^3}|R_{2,n}|,\end{aligned}$$

where $\epsilon' = 4\epsilon/(1+2\epsilon) > 0$ is chosen such that $L^{3-\epsilon'}$ is the dual space of $L^{\frac{3}{2}+\epsilon}$. Using inequality (3.16), and the fact that $\int \rho_{2,n}^{\alpha\beta} \leq \lambda$, we get an inequality of the form

$$\left|\int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2}[UR_{2,n}]\right| \leq C_1 \|R_{2,n}\|_{L^1\cap L^{3-\epsilon'}(B_A)} + C_2 \sup_{\mathbf{r}\in(B_A)^c}|U(\mathbf{r})|$$

with C_1 and C_2 independent of A and n. Since all entries of U are vanishing at infinity, we can first choose A large enough to control the second term, and then use the convergence of $(R_{2,n})_{n\in\mathbb{N}^*}$ to 0 strongly in $L^p(B_A)$ for $1 \leq p < 3$, to establish the convergence of the right-hand-side to 0.
For the last term, using (3.10), it holds (we write $g_2(\rho) = g(2\rho)$)

$$\begin{aligned}&E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_{1,n}^+ + \rho_{2,n}^+, \rho_{1,n}^- + \rho_{2,n}^-) - E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_{1,n}^+, \rho_{1,n}^-) - E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_{2,n}^+, \rho_{2,n}^-) = \\ &\quad \frac{1}{2}\left[\int_{\mathbb{R}^3}\Big(g_2(\rho_{1,n}^+ + \rho_{2,n}^+) - g_2(\rho_{1,n}^+) - g_2(\rho_{2,n}^+)\Big) + \int_{\mathbb{R}^3} g_2(\rho_{1,n}^- + \rho_{2,n}^-) - g_2(\rho_{1,n}^-) - g_2(\rho_{2,n}^-)\right].\end{aligned} \tag{3.22}$$

Then, we get (dropping the super-script $+/-$ for the sake of clarity)

$$\begin{aligned}&\left|\int_{\mathbb{R}^3} g_2(\rho_{1,n}+\rho_{2,n}) - g_2(\rho_{1,n}) - g_2(\rho_{2,n})\right| \\ &\quad\leq \int_{B_A} |g_2(\rho_{1,n}+\rho_{2,n}) - g_2(\rho_{1,n})| + \int_{B_A} |g_2(\rho_{2,n})| + \\ &\quad + \int_{(B_A)^c} |g_2(\rho_{1,n}+\rho_{2,n}) - g_2(\rho_{2,n})| + \int_{(B_A)^c} |g_2(\rho_{2,n})| \\ &\quad\leq C\left(\int_{B_A} \rho_{2,n}\left(\rho_n^{p^+} + \rho_n^{p^-}\right) + \int_{B_A}\left((\rho_{2,n})^{p^-} + (\rho_{2,n})^{p^+}\right)\right) \\ &\quad + C\left(\int_{(B_A)^c} \rho_{1,n}\left(\rho_n^{p^+} + \rho_n^{p^-}\right) + \int_{(B_A)^c}\left((\rho_{1,n})^{p^-} + (\rho_{1,n})^{p^+}\right)\right).\end{aligned}$$

We recall that $p^{+/-} = 1 + \beta^{+/-} < 5/3$. Since $(\rho_{1,n})_{n\in\mathbb{N}^*}$ and $(\rho_n)_{n\in\mathbb{N}^*}$ are bounded in $L^p(\mathbb{R}^3)$ for $1 \leq p < 3$, and since $(\rho_{2,n})_{n\in\mathbb{N}^*}$ converges to 0 in $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ for $1 \leq p < 3$, we deduce that (3.22) goes to 0 when n goes to infinity (first take A large enough, then n large enough, as before).
Altogether, for $\epsilon > 0$, for n large enough,

$$\mathcal{E}(\gamma_n) \geq \mathcal{E}(\gamma_{1,n}) + \mathcal{E}^\infty(\gamma_{2,n}) - 3\epsilon \geq I_\alpha + I^\infty_{\lambda-\alpha} - 3\epsilon.$$

Therefore, $\mathcal{E}(\gamma_n) \geq I_\alpha + I^\infty_{\lambda-\alpha}$, and $I_\lambda \geq I_\alpha + I^\infty_{\lambda-\alpha}$. The second point of Lemma 3.8 states that $I_\lambda \leq I_\alpha + I^\infty_{\lambda-\alpha}$. Hence $I_\lambda = I_\alpha + I^\infty_{\lambda-\alpha}$, and $(\gamma_{2,n})_{n\in\mathbb{N}^*}$ is a minimizing sequence for $I^\infty_{\lambda-\alpha}$.

As in the proof of Lemma 3.8, it holds (3.20):

$$\exists A, \eta > 0, \quad \forall n \in \mathbb{N}, \quad \exists \mathbf{r}_n \in \mathbb{R}^3, \quad \int_{\mathbf{r}_n + B_A} \rho_{2,n} \geq \eta.$$

We let $\gamma'_{2,n} = \tau_{\mathbf{r}_n}\gamma_{2,n}\tau_{-\mathbf{r}_n}$. Then, $(\gamma_{2,n})$ is bounded for the weak-$*$ topology of $\mathcal{B}$, and converges, up to a subsequence, to some γ'_0 satisfying $\mathrm{Tr}(\gamma'_0) \geq \eta$. Let $\beta := \mathrm{Tr}(\gamma'_0)$. We can repeat the same arguments as before and truncate $\gamma'_{2,n}$ to ensure that $\mathrm{Tr}(\chi_{A_n}\gamma_{2,n}\chi_{A_n}) = \beta$. We deduce as before that γ'_0 is a minimizer for I^∞_β, and that $I_\lambda = I_\alpha + I^\infty_\beta + I^\infty_{\lambda-\alpha-\beta}$.

3.4.6 Proof of Lemma 3.10

Let us first derive the expression of H_{γ_0}. Suppose that $\gamma_0 \in \mathcal{P}_\lambda$ is a minimizer for I_λ. Then for $\gamma \in \mathcal{P}_\lambda$ and $0 \leq t \leq 1$, it holds $\mathcal{E}(t\gamma + (1-t)\gamma_0) \geq \mathcal{E}(\gamma_0)$. In particular, one must have

$$\frac{\partial \mathcal{E}(t\gamma + (1-t)\gamma_0)}{\partial t}\Big|_{t=0} \geq 0. \tag{3.23}$$

To perform the calculations, we use the explicit formula (3.15) for $\rho^{+/-}$, and get

$$\frac{\partial \left(t\rho + (1-t)\rho_0\right)^{+/-}}{\partial t}\Big|_{t=0} = \\ \frac{1}{2}\mathrm{tr}_{\mathbb{C}^2}\left(\left[\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \pm \frac{1}{\sqrt{(\rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow})^2 + 4|\rho_0^{\uparrow\downarrow}|^2}}\begin{pmatrix}\rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow} & 2\rho_0^{\uparrow\downarrow}\\ 2\rho_0^{\downarrow\uparrow} & \rho_0^{\downarrow\downarrow} - \rho_0^{\uparrow\uparrow}\end{pmatrix}\right](R - R_0)\right).$$

Similarly to [AC09, CDL08], we conclude that

$$\frac{\partial \mathcal{E}(t\gamma + (1-t)\gamma_0)}{\partial t}\Big|_{t=0} = \mathrm{Tr}\left(H_{\gamma_0}(\gamma - \gamma_0)\right)$$

with

$$\begin{aligned} H_{\gamma_0} = &\left(-\frac{1}{2}\Delta + \rho_0 * |\cdot|^{-1}\right)\mathbb{I}_2 + U \\ &+ \frac{g'(\rho_0^+)}{2}\left[\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} + \frac{1}{\sqrt{(\rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow})^2 + 4|\rho_0^{\uparrow\downarrow}|^2}}\begin{pmatrix}\rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow} & 2\rho_0^{\uparrow\downarrow}\\ 2\rho_0^{\downarrow\uparrow} & \rho_0^{\downarrow\downarrow} - \rho_0^{\uparrow\uparrow}\end{pmatrix}\right] \\ &+ \frac{g'(\rho_0^-)}{2}\left[\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} - \frac{1}{\sqrt{(\rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow})^2 + 4|\rho_0^{\uparrow\downarrow}|^2}}\begin{pmatrix}\rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow} & 2\rho_0^{\uparrow\downarrow}\\ 2\rho_0^{\downarrow\uparrow} & \rho_0^{\downarrow\downarrow} - \rho_0^{\uparrow\uparrow}\end{pmatrix}\right]. \end{aligned} \tag{3.24}$$

Using (3.23), we deduce that $\gamma_0 \in \mathrm{arginf}\{\mathrm{Tr}(H_{\gamma_0}\gamma),\ \gamma \in \mathcal{P}_\lambda\}$. Finally,

$$\gamma_0 = \mathbb{1}_{(-\infty,\varepsilon_F)}(H_{\gamma_0}) + \delta \quad \text{with} \quad \delta \subset \mathrm{Ker}(H_{\gamma_0} - \varepsilon_F),$$

where ε_F is the Fermi energy, determined by the condition $\mathrm{Tr}(\gamma_0) = \lambda$.

Let us first calculate the essential spectrum of H_{γ_0}. We recall that $H_0 = -\frac{1}{2}\Delta\mathbb{I}_2$ has domain $H^2(\mathbb{R}^3, \mathbb{C}^2)$ and that if $u \in H^2(\mathbb{R}^3, \mathbb{C})$, then u vanishes at infinity. We also recall that for all $V \in L^{3/2}(\mathbb{R}^3, \mathbb{C}^2) + L^\infty_\epsilon(\mathbb{R}^3, \mathbb{C}^2)$ (that is V is of the form $V = V_{3/2} + V_\infty$ with $V_{3/2} \in L^{3/2}(\mathbb{R}^3, \mathbb{C}^2)$, $V_\infty \in L^\infty(\mathbb{R}^3)$ and $\|V_\infty\|_{L^\infty}$ arbitrary small), V is a compact perturbation of H_0. In our case, we can easily check that $\widehat{\rho_0 * |\cdot|^{-1}} = \widehat{\rho_0}|\cdot|^{-2} \in L^1(\mathbb{R}^3)$, so that $\rho_0 * |\cdot|^{-1}$ vanishes at infinity. Altogether,

- $\rho_0 * |\cdot|^{-1} \in L^{3/2}(\mathbb{R}^3) + L^\infty_\epsilon(\mathbb{R}^3)$;
- $U \in L^{3/2}(\mathbb{R}^3, \mathbb{C}^2) + L^\infty(\mathbb{R}^3, \mathbb{C}^2)$ and all entries of U vanish at infinity ;
- $|g'(\rho_0^{+/-})| \leq C(\rho_0^{\beta^-} + \rho_0^{\beta^+})$ hence $g'(\rho_0^{+/-}) \in L^{3/2}(\mathbb{R}^3, \mathbb{C}^2)$.

Therefore, according to the Weyl's theorem, the domain of H_{γ_0} is $H^2(\mathbb{R}^3,\mathbb{C}^2)$, and its essential spectrum is $\sigma_{\rm ess}(H_{\gamma_0})=\sigma_{\rm ess}(H_0)=[0,+\infty[$.

Let us now prove that H_{γ_0} has infinitely many negative eigenvalues whenever $\lambda<Z$. First notice that the matrix

$$\frac{1}{\sqrt{(\rho_0^{\uparrow\uparrow}-\rho_0^{\downarrow\downarrow})^2+4|\rho_0^{\uparrow\downarrow}|^2}}\begin{pmatrix}\rho_0^{\uparrow\uparrow}-\rho_0^{\downarrow\downarrow} & 2\rho_0^{\uparrow\downarrow}\\ 2\rho_0^{\downarrow\uparrow} & \rho_0^{\downarrow\downarrow}-\rho_0^{\uparrow\uparrow}\end{pmatrix}$$

has two eigenvalues, respectively -1 and 1, so that the matrices appearing into the two pairs of brackets in (3.24) have 0 and 2 as eigenvalues, and therefore are hermitian positive. Also, recall that under the conditions (3.10) on g, it holds $g'\le 0$. Altogether, for $\psi\in C_c^\infty(\mathbb{R}^3,\mathbb{C})$, $\Psi=(\psi,\psi)^T\in C_c^\infty(\mathbb{R}^3,\mathbb{C}^2)$, and $\widetilde{\Psi}$ defined as in (3.11), it holds that

$$\begin{aligned}\langle\Psi|H_{\gamma_0}|\Psi\rangle+\langle\widetilde{\Psi}|H_{\gamma_0}|\widetilde{\Psi}\rangle &\le \left\langle\Psi\right|\left(\left(-\frac{1}{2}\Delta+\rho_0*|\cdot|^{-1}\right)\mathbb{I}_2+U\right)\left|\Psi\right\rangle\\ &\quad+\left\langle\widetilde{\Psi}\right|\left(\left(-\frac{1}{2}\Delta+\rho_0*|\cdot|^{-1}\right)\mathbb{I}_2+U\right)\left|\widetilde{\Psi}\right\rangle\\ &\le 4\left\langle\psi\right|-\frac{1}{2}\Delta+\rho_0*|\cdot|^{-1}+V\left|\psi\right\rangle=\langle\psi|H_1|\psi\rangle_1\end{aligned}$$

where $H_1:=-\frac{1}{2}\Delta+\rho_0*|\cdot|^{-1}+V$ acts on $L^2(\mathbb{R}^3,\mathbb{C})$, and V is defined in (3.1). We used the subscript 1 to emphasize that $\langle\cdot|\cdot\rangle_1$ is the scalar product on $L^2(\mathbb{R}^3,\mathbb{C})$, whereas $\langle\cdot|\cdot\rangle$ is the one on $L^2(\mathbb{R}^3,\mathbb{C}^2)$. In virtue of [Lio87, Lemma 2.1], the operator H_1 has infinitely many negative eigenvalues of finite multiplicity whenever $\lambda<Z$. So has H_{γ_0} by the min-max principle. Eventually, $\varepsilon_F<0$, and

$$\gamma_0=\sum_{i=1}^{N_1}|\Phi_i\rangle\langle\Phi_i|+\sum_{i=N_1+1}^{N_2}n_i|\Phi_i\rangle\langle\Phi_i|\quad\text{with}\quad\langle\Phi_i|\Phi_j\rangle=\delta_{ij}\quad\text{and}\quad H_{\gamma_0}\Phi_i=\varepsilon_i\Phi_i.$$

It holds $\varepsilon_i<\varepsilon_F$ if $i\le N_1$, and $\varepsilon_i=\varepsilon_F$ if $N_1+1\le i\le N_2$. In the following, we set $n_i:=1$ for $i\le N_1$.

Finally, we prove that all eigenvectors associated with negative eigenvalues are exponentially decreasing. Any function u satisfying $H_{\gamma_0}u=\lambda u$ is in $H^2(\mathbb{R}^3,\mathbb{C}^2)$, and each component of u vanishes at infinity. As a byproduct, we obtain that $\rho_0=\sum_{i=1}^{N_2}n_i|\Phi_i|^2$ also vanishes at infinity. Finally, all the components of

$$\begin{aligned}U_{\gamma_0}:=&\rho_0*|\cdot|^{-1}\mathbb{I}_2+U+\\ &+\sum_{\delta=+/-}\frac{g'(\rho_0^\delta)}{2}\left[\begin{pmatrix}1&0\\0&1\end{pmatrix}+(-1)^\delta\frac{1}{\sqrt{(\rho_0^{\uparrow\uparrow}-\rho_0^{\downarrow\downarrow})^2+4|\rho_0^{\uparrow\downarrow}|^2}}\begin{pmatrix}\rho_0^{\uparrow\uparrow}-\rho_0^{\downarrow\downarrow} & 2\rho_0^{\uparrow\downarrow}\\ 2\rho_0^{\downarrow\uparrow} & \rho_0^{\downarrow\downarrow}-\rho_0^{\uparrow\uparrow}\end{pmatrix}\right]\end{aligned}$$

vanish at infinity. Recall that $H_{\gamma_0}\Phi_i=-\frac{1}{2}\Delta\Phi_i+U_\gamma\Phi_i=\varepsilon_i\Phi_i$. Multiplying this equation by Φ_i and adding all the terms with prefactors n_i, it holds that

$$\sum_{i=1}^{N_2}n_i\Phi_i^T\left(-\frac{1}{2}\Delta\right)\Phi_i+\sum_{i=1}^{N_2}n_i\Phi_i^TU_\gamma\Phi_i=\sum_{i=1}^{N_2}\varepsilon_in_i|\Phi_i|^2.\tag{3.25}$$

From the relation $\rho_0=\sum_{i=1}^{N_2}n_i|\Phi_i|^2$, we get

$$\Delta\rho_0=\sum_{i=1}^{N_2}2n_i\left(\Phi_i^T(\Delta\Phi_i)+|\nabla\Phi_i|^2\right)$$

and (3.25) becomes

$$-\frac{\Delta}{4}\rho_0 + \underbrace{\sum_{i=1}^{N_2} \frac{n_i}{2}|\nabla\Phi_i|^2}_{\geq 0} + \sum_{i=1}^{N_2} n_i \Phi_i^T U_\gamma \Phi_i + \underbrace{\sum_{i=1}^{N_2} (\varepsilon_F - \varepsilon_i) n_i |\Phi_i|^2}_{\geq 0} - \varepsilon_F \rho_0 = 0.$$

Let A be large enough such that, for all $\mathbf{r} \in \mathbb{R}^3$ with $|\mathbf{r}| \geq A$, the eigenvalues of the matrix $U_\gamma(\mathbf{r})$ are between $\frac{\varepsilon_F}{2\lambda}$ and $-\frac{\varepsilon_F}{2\lambda}$ (recall that $\varepsilon_F < 0$). In particular, for $|\mathbf{r}| \geq A$, $|\Phi_i^T(\mathbf{r}) U_\gamma(\mathbf{r}) \Phi_i(\mathbf{r})| \leq -\frac{\varepsilon_F}{2\lambda}|\Phi_i|^2$, and, on $(B_A)^c$,

$$-\frac{\Delta}{4}\rho_0 + \frac{\varepsilon_F \lambda}{2\lambda}\rho_0 - \varepsilon_F \rho_0 \leq 0 \quad \text{or} \quad -\frac{\Delta}{2}\rho_0 - \varepsilon_F \rho_0 \leq 0.$$

We easily deduce that ρ_0 decreases exponentially. Hence, the same holds true for all the Φ_i's with $1 \leq i \leq N_2$. A similar proof can be used for the remaining negative eigenvalues.

3.4.7 Proof of Lemma 3.11

Let $\gamma_0 \in \mathcal{P}_\alpha$ be a minimizer for I_α, and $\gamma_0' \in \mathcal{P}_\beta$ be a minimizer for I_β^∞. According to the proof of Lemma 3.10, since $\alpha < \lambda$, then γ_0 is of form

$$\gamma_0 = \sum_{i=1}^{N_2} n_i |\Phi_i\rangle\langle\Phi_i| \quad \text{with} \quad H_{\gamma_0}\Phi_i = \varepsilon_i \Phi_i \quad \text{and} \quad \varepsilon_i \leq \varepsilon_F < 0.$$

We can derive a similar expression for γ_0':

$$\gamma_0' = \sum_{i=1}^{\infty} n_i' |\Phi_i'\rangle\langle\Phi_i'| \quad \text{with} \quad H_{\gamma_0'}^\infty \Phi_i' = \varepsilon_i \Phi_i' \quad \text{and} \quad \varepsilon_i' \leq \varepsilon_F' \leq 0, \tag{3.26}$$

where $H_{\gamma_0'}^\infty$ has a similar expression as $H_{\gamma_0'}$ in (3.24), without the U term. Note that in (3.26), we do not know whether $\varepsilon_F' < 0$ or $\varepsilon_F' = 0$.

First assume that $\varepsilon_F' < 0$, so that Φ_i and Φ_i' are exponentially decreasing, and the sum in (3.26) is finite. We introduce

$$\gamma_n := \min\{1, \|\gamma_0 + \tau_n \gamma_0' \tau_{-n}\|^{-1}\} \left(\gamma_0 + \tau_n \gamma_0' \tau_{-n}\right)$$

and

$$\gamma_n^\sharp := \min\{1, \|\gamma_0 + \tau_n \widetilde{\gamma}_0' \tau_{-n}\|^{-1}\} \left(\gamma_0 + \tau_n \widetilde{\gamma}_0' \tau_{-n}\right),$$

where $\widetilde{\gamma}_0'$ is the flipped transformation of γ_0', as defined in (3.11). Note that $\mathrm{Tr}(\gamma_n) \leq \alpha + \beta$ and $\mathrm{Tr}(\gamma_n^\sharp) \leq \alpha + \beta$, so that $I_{\alpha+\beta} \leq \mathcal{E}(\gamma_n)$ and $I_{\alpha+\beta} \leq \mathcal{E}(\widetilde{\gamma})$ according to the third assertion of Lemma 3.8. A straightforward calculation leads to

$$\begin{aligned}\mathcal{E}(\gamma_n) + \mathcal{E}(\gamma_n^\sharp) &= 2\mathcal{E}(\gamma_0) + 2\mathcal{E}^\infty(\widetilde{\gamma}_0) - \frac{\beta(Z-\alpha)}{n} + O(\mathrm{e}^{-\delta n}) \\ &= 2I_\alpha + 2I_\beta^\infty - \frac{\beta(Z-\alpha)}{n} + O(\mathrm{e}^{-\delta n}).\end{aligned}$$

For n large enough, $-\beta(Z-\alpha)n^{-1} + O(\mathrm{e}^{-\delta n})$ becomes negative. Hence, either $\mathcal{E}(\gamma_n)$ or $\mathcal{E}(\gamma_n^\sharp)$ is strictly less than $I_\alpha + I_\beta^\infty$. Therefore, $I_{\alpha+\beta} < I_\alpha + I_\beta^\infty$.

Let us now assume that $\varepsilon'_F = 0$. Then, there exists $\Psi \in H^2(\mathbb{R}^3, \mathbb{C}^2)$ such that $\|\Psi\|_{L^2} = 1$, $H^\infty_{\gamma'_0}\Psi = 0$ and $\gamma'_0\Psi = \mu\Psi$ with $\mu > 0$. For $0 < \eta < \mu$, we introduce $\gamma_\eta = \gamma_0 + \eta|\Phi_{N_2+1}\rangle\langle\Phi_{N_2+1}|$ and $\gamma'_\eta = \gamma'_0 - \eta|\Psi\rangle\langle\Psi|$, so that $\gamma_\eta \in \mathcal{P}_{\alpha+\eta}$ and $\gamma'_\eta \in \mathcal{P}_{\beta-\eta}$. Moreover,

$$\mathcal{E}(\gamma_\eta) = \mathcal{E}(\gamma_0) + 2\eta\varepsilon_{N_2+1} + o(\eta) = I_\alpha + 2\eta\varepsilon_{N_2+1} + o(\eta)$$

and

$$\mathcal{E}^\infty(\gamma'_\eta) = \mathcal{E}^\infty(\gamma'_0) + o(\eta) = I^\infty_\beta + o(\eta).$$

Using the facts that $\gamma_0 + \eta|\Phi_{N_2+1}\rangle\langle\Phi_{N_2+1}| \in \mathcal{P}_{\alpha+\eta}$ and $\gamma'_0 - \eta|\Psi\rangle\langle\Psi| \in \mathcal{P}_{\beta-\eta}$, it holds that

$$I_{\alpha+\beta} \leq I_{\alpha+\eta} + I^\infty_{\beta-\eta} \leq \mathcal{E}(\gamma_\eta) + \mathcal{E}^\infty(\gamma'_\eta) \leq I_\alpha + I^\infty_\beta + 2\eta\varepsilon_{N_2+1} + o(\eta).$$

Since $\varepsilon_{N_2+1} < 0$, for η small enough, the left hand side is strictly less that $I_\alpha + I^\infty_\beta$, which concludes the proof.

Part II

The GW method for finite systems

CHAPTER 4

THE GW METHOD FOR FINITE SYSTEMS

We expose in this chapter the theory and results given in [CGS15]. This work was done in collaboration with Eric Cancès and Gabriel Stoltz.

Abstract. We analyze the GW method for finite electronic systems in this chapter. In a first step, we provide a mathematical framework for the usual one-body operators that appear naturally in many-body perturbation theory. We then discuss the GW equations which construct an approximation of the one-body Green's function, and give a rigorous mathematical formulation of these equations. Finally, we study the well-posedness of the GW^0 equations, proving the existence of a unique solution to these equations in a perturbative regime.

4.1 Introduction

Computational quantum chemistry is nowadays a standard tool to numerically determine the properties of molecules. The Density Functional Theory (DFT) first developed by Hohenberg and Kohn [HK64] and by Kohn and Sham [KS65], is a very powerful method to obtain ground state properties of molecular systems. However, it does not allow one to compute optical properties and electronic excited energies. In order to calculate such quantities, several approaches have been considered in the last decades [ORR02]. Among them are the time-dependent DFT (TDDFT) [MUN+06, MMN+12], wave-function methods [HJO14] such as Coupled-Cluster, full-CI and Green's function methods. In this chapter, we study the GW method, which is based on Hedin's equations for the one-body Green's function [Hed65]. The formal derivation of the latter equations relies on many-body perturbation techniques. While the GW method has been proven very successful in practice to predict electronic-excited energies, no rigorous mathematical framework has yet been developed to understand its mathematical properties. The aim of this work is to present such a framework.

In non-relativistic first-principle molecular simulation, the electrons of a molecular system are described by an N-body Hamiltonian operator H_N, which is a bounded below self-adjoint operator on the fermionic space $\bigwedge^N L^2(\mathbb{R}^3)$ (see Equation (4.30) below). Whenever $N \leq Z$, where Z is the total nuclear charge of the molecular system, H_N has an infinity of discrete eigenvalues $E_N^0 \leq E_N^1 \leq E_N^2 \leq \cdots$ below the bottom of the essential spectrum, where E_N^0 is its ground state energy. The quantities we would like to evaluate are the *electronic-excitation energies*

$$E_N^0 - E_{N+1}^k \quad \text{(gain of an electron)}, \quad \text{and} \quad E_N^0 - E_{N-1}^k \quad \text{(loss of an electron)}.$$

These energy differences are not to be confused with the optical-excitation energies, which are energy differences of the form $E_N^k - E_N^0$, between two states with the same number of electrons. More generally, it is interesting to compute the particle electronic-excitation set $S_{\mathrm{p}} := \sigma\left(H_{N+1} - E_N^0\right)$ and the hole electronic-excitation set $S_{\mathrm{h}} := \sigma\left(E_N^0 - H_{N-1}\right)$. As will be made clear in Section 4.3.2, these sets are closely linked to the one-body Green's function: the time-Fourier transform of the Green's function becomes singular on these sets. In order to study the electronic-excitation sets, we therefore study the one-body Green's function. Also, the one-body Green's function is a fundamental object which contains a lot of useful information, and allows one to easily compute the ground state electronic density, the ground state one-body density matrix, and even the ground state energy thanks to the Galitskii-Migdal formula [GM58].

Calculating the one-body Green's function is however a difficult task. In his pioneering work in 1965, Hedin proved that the Green's function satisfies a set of (self-consistent) equations, now called the Hedin's equations [Hed65]. These equations link many operator-valued distributions, namely the reducible and irreducible polarizability operators, the dynamically screened interaction operator, the self-energy operator, the vertex operator, and of course the one-body Green's function. The state-of-the-art method to compute the one-body Green's function consists in solving Hedin's equations.

Immediately, two difficulties arise. The first one is related to the lack of regularity of the Green's function (we expect its time-Fourier transform $\widehat{G}$ to be singular on the electronic-excitation sets). One way to get around this problem is to consider the analytical extension of $\widehat{G}$ into the complex plane, which we denote by $\widetilde{G}$. This is possible whenever the following classical stability condition holds true[1]:

Stability assumption: It holds that $2E_N^0 < E_{N+1}^0 + E_{N-1}^0$.

The physical relevance of this inequality is discussed for instance in [Far99, Section 4.2]. It allows one to define the chemical potential μ, chosen such that

$$E_N^0 - E_{N-1}^0 < \mu < E_{N+1}^0 - E_N^0.$$

Instead of studying the Green's function $G(\tau)$ in the time domain, or its Fourier transform $\widehat{G}(\omega)$ in the frequency domain, we rather study its analytical continuation $\widetilde{G}$ on the imaginary axis $\mu + \mathrm{i}\mathbb{R}$. The function $\omega \mapsto \widetilde{G}(\mu + \mathrm{i}\omega)$ enjoys very nice properties, both in terms of regularity and integrability, which makes it a privileged tool for numerical calculations.

The second difficulty comes from the fact that Hedin's equations cannot be exactly solved and, even more importantly, that the mathematical definition of some terms in these equations are unclear. It however opens the way to some approximate resolutions. The most widely used approximation nowadays is the so-called GW-approximation, also introduced by Hedin [Hed65]. These equations are traditionally set on the time-axis, or on the energy-axis [RJT10, KFSP10]. However, as previously mentioned, the various operators under consideration are singular on these axes, which makes the traditional GW equations cumbersome to implement numerically, and difficult to analyze mathematically. In order to manipulate better-behaved equations, it is more convenient to replace every operator-valued distribution involved in the GW equations by its analytic continuation on an appropriate imaginary axis, thanks to the "contour deformation" technique introduced in [RGN95, RSW+99]. The resulting GW equations, which give an approximation of the map $\omega \mapsto \widetilde{G}(\mu + \mathrm{i}\omega)$, turn out to give simulation

[1] The question "Is the stability condition always true for Coulomb systems" is still an open problem [BDS14, Part VII].

results in very good agreement with experimental data [SDvL06, SDvL09, CRR+12, CRR+13].

From the GW equations set on the imaginary axis, several further approximation may be performed. The GW equations are solved self-consistently, and the Green's function is updated at each iteration until convergence. When only one iteration is performed, we obtain the one-shot GW approximation, also called the G_0W^0 approximation of the Green's function. For molecules, self-consistent GW approaches give results of similar quality as G_0W^0, sometimes almost identical [SDvL09, KFSP10], sometimes slightly worse [RJT10], sometimes slightly better [CRR+12, CRR+13]. When several iterations are performed, while keeping the screening operator W fixed, equal to a reference screening operator W^0, we obtain the GW^0 approximation of the Green's function [SDvL09, vBH96]. Since the update of the screening operator W in a self-consistent GW scheme seems difficult to analyze mathematically, we prefer to study in this chapter the equations resulting from the GW^0 approximation.

The purpose of this work is threefold. First, we clarify the mathematical definitions and properties of the usual one-body operators involved in many-body perturbation theory. Then, we embed the GW^0 equations in a mathematical framework. Finally, we prove that, in a perturbative regime, the GW^0 equations admit a unique solution close to a reference Green's function.

From a physical viewpoint, the analysis we perform in this work is more relevant for atoms and molecules. Indeed, as discussed in [BG14, Section 4.1] for instance, fully self-consistent GW approaches are questionable for solid-state systems, for which quasiparticle methods are preferred [AG98, AJW00].

This chapter is organized as follows. In Section 4.2, we provide the mathematical tools that will be used throughout the chapter. We recall the Titchmarsh's theorem, and introduce the kernel-product of two operators, which can be seen as an infinite dimensional version of the Hadamard product for matrices. We also explain the underlying structure that makes the "contour deformation" possible. In Section 4.3, we recall the standard definitions of the usual one-body operators that appear in many-body perturbation theory. A consistent functional setting is given for each of these operators, and their basic properties are recalled and proved. Section 4.4 is concerned with the GW approximation. We explain why some of the GW equations are not well-understood mathematically, and prove that the GW^0 equations are well-posed in a perturbative regime. Most of the proofs are postponed until Section 4.6.

4.2 Setting the stage

4.2.1 Some notation

The GW method is based on time-dependent perturbation theory and therefore involves space-time operators. Following the common notation in physics, we denote by t the time coordinate, by $\mathbf{r}$ the space coordinates, and by $\mathbf{x}$ or $\mathbf{r}t$ the space-time coordinates. The functional spaces considered in this work are by default composed of complex-valued functions, unless we explicitly mention that the functions are real-valued.

Most of the space-time operators appearing in the GW formalism are time-translation invariant. A time-translation invariant operator $\mathcal{C}$ can be characterized by the family of operators $(C(\tau))_{\tau\in\mathbb{R}}$ such that, formally, the kernel of $\mathcal{C}$ is of the form

$$\mathcal{C}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = C(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2),$$

where $C(\mathbf{r}, \mathbf{r}', \tau)$ is the kernel of the operator $C(\tau)$. For clarity, we will systematically use the letter τ to denote a time variable which is in fact a time difference.

Let $\mathcal{H}$ be a separable complex Hilbert space, whose associated scalar product is simply denoted by $\langle \cdot, \cdot \rangle$ and the associated norm $\| \cdot \|$. We denote by $\mathcal{B}(\mathcal{H})$ the space of bounded linear operators on $\mathcal{H}$, by $\mathcal{S}(\mathcal{H})$ the space of bounded self-adjoint operators on $\mathcal{H}$, by $\mathfrak{S}_p(\mathcal{H})$ $(1 \leq p < \infty)$ the Schatten class

$$\mathfrak{S}_p(\mathcal{H}) = \left\{ A \in \mathcal{B}(\mathcal{H}) \;\middle|\; \|A\|_{\mathfrak{S}_p(\mathcal{H})} := \mathrm{Tr}(|A|^p)^{1/p} < \infty \right\},$$

and by A^* the adjoint of a linear operator A on $\mathcal{H}$ with dense domain. The real and imaginary parts of an operator $A \in \mathcal{B}(\mathcal{H})$ are defined as

$$\mathrm{Re}\, A = \frac{A + A^*}{2}, \quad \mathrm{Im}\, A = \frac{A - A^*}{2\mathrm{i}}.$$

Note that, when A is closed (which implies $A^{**} = A$), the operators $\mathrm{Re}\, A$ and $\mathrm{Im}\, A$ are self-adjoint. For $f, g \in \mathcal{H}$ and given operators A, B on $\mathcal{H}$, we will often use the notation

$$\langle f|A|g\rangle_{\mathcal{H}} := \langle f, Ag\rangle_{\mathcal{H}}, \qquad \langle f|AB|g\rangle_{\mathcal{H}} := \langle f, ABg\rangle_{\mathcal{H}},$$

even in cases when the operators are not self-adjoint. Operators are always understood to act on the function on the right in this notation.

We will sometimes need to manipulate the adjoints of operators between two different Hilbert spaces $\mathcal{H}_a$ and $\mathcal{H}_b$. The adjoint of a bounded operator $A \in \mathcal{B}(\mathcal{H}_a, \mathcal{H}_b)$ is the bounded operator $A^* \in \mathcal{B}(\mathcal{H}_b, \mathcal{H}_a)$ defined by

$$\forall (x, y) \in \mathcal{H}_a \times \mathcal{H}_b, \qquad (A^* y, x)_{\mathcal{H}_a} = (y, Ax)_{\mathcal{H}_b}.$$

Let E be a Banach space. We denote by $\mathscr{S}'(\mathbb{R}, E)$ the space of E-valued tempered-distributions on $\mathbb{R}$, *i.e.* the set of continuous linear maps from the Schwartz's functional space $\mathscr{S}(\mathbb{R})$ into E. Recall that, by definition, a family $(T_\eta)_{\eta>0}$ of elements of $\mathscr{S}'(\mathbb{R}, E)$ converges in $\mathscr{S}'(\mathbb{R}, E)$ to some $T \in \mathscr{S}'(\mathbb{R}, E)$ when η goes to 0 if

$$\forall \phi \in \mathscr{S}(\mathbb{R}), \qquad \left\| \langle T_\eta, \phi \rangle_{\mathscr{S}', \mathscr{S}} - \langle T, \phi \rangle_{\mathscr{S}', \mathscr{S}} \right\|_E \underset{\eta \to 0^+}{\longrightarrow} 0.$$

Let $f \in L^1(\mathbb{R}, E)$ be a time-dependent E-valued integrable function. The time-Fourier transform of f is defined, using the standard convention in physics, as

$$\forall \omega \in \mathbb{R}, \quad \widehat{f}(\omega) := (\mathcal{F}_T f)(\omega) := \int_{\mathbb{R}} f(\tau) \mathrm{e}^{\mathrm{i}\omega\tau} \, \mathrm{d}\tau. \tag{4.1}$$

For the sake of clarity, we will sometimes denote by $\mathbb{R}_t$ or $\mathbb{R}_\tau$ the time-domain, by $\mathbb{R}_\omega$ the frequency-domain, by $\mathscr{S}'(\mathbb{R}_\tau, E)$ (resp. $\mathscr{S}'(\mathbb{R}_\omega, E)$) the space of time-dependent (resp. frequency-dependent) E-valued distributions, etc. We will also denote with a hat the functions defined on the frequency domain. Using this notation, $\mathcal{F}_T$ can be extended to a bicontinuous isomorphism from $\mathscr{S}'(\mathbb{R}_\tau, E)$ into $\mathscr{S}'(\mathbb{R}_\omega, E)$. When $\widehat{f} \in L^1(\mathbb{R}_\omega, E)$, we have

$$\forall \tau \in \mathbb{R}, \quad \left(\mathcal{F}_T^{-1} \widehat{f} \right)(\tau) = \frac{1}{2\pi} \int_{\mathbb{R}} \widehat{f}(\omega) \mathrm{e}^{-\mathrm{i}\omega\tau} \, \mathrm{d}\omega.$$

The Dirac distribution at $a \in \mathbb{R}^d$ is denoted by δ_a, and the Heaviside function on $\mathbb{R}$ by Θ:

$$\Theta(\tau) = 1 \text{ for } \tau > 0, \qquad \Theta(\tau) = 0 \text{ for } \tau < 0, \qquad \Theta(0) = 1/2. \tag{4.2}$$

Recall that the time-Fourier transform of Θ is, in the tempered distributional sense,

$$\widehat{\Theta}(\omega) = \pi \delta_0(\omega) + \mathrm{i}\, \mathrm{p.v.} \left(\frac{1}{\omega} \right), \tag{4.3}$$

where p.v. is the Cauchy principal value. We will also make use of the notation τ^+ for a number strictly above τ, but infinitesimally close to τ, and of the convention

$$\Theta(\tau) \delta_0(\tau^+) := \delta_0(\tau), \quad \Theta(-\tau) \delta_0(\tau^+) := 0.$$

4.2.2 Hilbert transform of functions and distributions

The Hilbert transform, which amounts to a convolution by $\pi^{-1}\text{p.v.}(\frac{1}{\cdot})$, plays a crucial role in the GW formalism. We first recall some well-known results on the standard Hilbert transform on $L^p(\mathbb{R}_\omega)$, and extend the results to the Sobolev spaces $H^s(\mathbb{R}_\omega)$ for $s \in \mathbb{R}$. Usually, the name "Hilbert transform" is only used on functional spaces $E \subset L^1_{\text{loc}}(\mathbb{R}_\omega)$ such that, for any function $\widehat{f} \in E$, the limit

$$\left[\widehat{f} * \text{p.v.}\left(\frac{1}{\cdot}\right)\right](\omega) = \text{p.v.}\int_{-\infty}^{+\infty} \frac{\widehat{f}(\omega')}{\omega - \omega'}\,\mathrm{d}\omega' := \lim_{\eta \to 0^+} \int_{\mathbb{R}\setminus[\omega-\eta,\omega+\eta]} \frac{\widehat{f}(\omega')}{\omega - \omega'}\,\mathrm{d}\omega'$$

exists for almost all $\omega \in \mathbb{R}_\omega$. However, in the sequel, we will also use the name "Hilbert transform" in functional spaces where the above integral representation is not always valid (for instance when $\widehat{f}$ is not a locally integrable function). Note that we define the Hilbert transform on Fourier transforms of functions (*i.e.* on functions on the frequency domain) since this is the typical setting in the GW formalism.

Hilbert transform in L^p spaces

We first begin with the following classical definition (see for instance [Gra04, Section 4.1]).

Definition 4.1 (Hilbert transform on $\mathscr{S}(\mathbb{R}_\omega)$)**.** *The Hilbert transform of a function $\widehat{\phi} \in \mathscr{S}(\mathbb{R}_\omega)$ is defined by*

$$\mathfrak{H}\widehat{\phi} := \frac{1}{\pi}\text{p.v.}\left(\frac{1}{\cdot}\right) * \widehat{\phi}, \tag{4.4}$$

or equivalently by

$$\mathfrak{H}\widehat{\phi} := \left(\mathcal{F}_T(-\mathrm{i}\,\mathrm{sgn}(\cdot))\,\mathcal{F}_T^{-1}\right)\widehat{\phi}, \tag{4.5}$$

where $\text{p.v.}\left(\frac{1}{\cdot}\right)$ *is the Cauchy principal value of the function $\omega \mapsto \frac{1}{\omega}$, $*$ the convolution product, $\mathcal{F}_T$ the Fourier transform defined in (4.1) and $-\mathrm{i}\,\mathrm{sgn}(\cdot)$ the multiplication operator by the L^∞ function $t \mapsto -\mathrm{i}\,\mathrm{sgn}(t)$ (where $\mathrm{sgn}(t) = \Theta(t) - \Theta(-t)$ is the sign function).*

The Hilbert transform can be extended by continuity to a large class of tempered distributions. We refer to [Gra04, Rie28] for a proof of the following theorem.

Theorem 4.2. *For all $\widehat{f} \in L^p(\mathbb{R}_\omega)$ with $1 < p < \infty$, the Hilbert transform*

$$\mathfrak{H}\widehat{f}(\omega) = \text{p.v.}\int_{-\infty}^{\infty} \frac{\widehat{f}(\omega')}{\omega - \omega'}\,\mathrm{d}\omega'$$

is well-defined for almost all $\omega \in \mathbb{R}$. It holds $\mathfrak{H} \in \mathcal{B}(L^p(\mathbb{R}_\omega))$ with

$$\|\mathfrak{H}\|_{\mathcal{B}(L^p(\mathbb{R}_\omega))} = \begin{cases} \tan(\pi/(2p)) & \text{if } 1 < p \leq 2, \\ \operatorname{cotan}(\pi/(2p)) & \text{if } 2 \leq p < \infty. \end{cases}$$

Moreover, the Hilbert transform commutes with the translations and the positive dilations, and anticommutes with the reflexions. Finally, it is a unitary operator on $L^2(\mathbb{R}_\omega)$.

Hilbert transform in Sobolev spaces

Recall that for any $s \in \mathbb{R}$, the Sobolev space $H^s(\mathbb{R}_\omega)$ is the Hilbert space defined as

$$H^s(\mathbb{R}_\omega) := \left\{\widehat{f} \in \mathscr{S}'(\mathbb{R}_\omega)) \;\middle|\; (1 + |\cdot|^2)^{s/2}\mathcal{F}_T^{-1}\widehat{f} \in L^2(\mathbb{R}_\tau)\right\},$$

and endowed with the scalar product

$$\left\langle \widehat{f}, \widehat{g} \right\rangle_{H^s} = 2\pi \int_{-\infty}^{+\infty} (1+\tau^2)^s \overline{(\mathcal{F}_T^{-1}\widehat{f})(\tau)}\,(\mathcal{F}_T^{-1}\widehat{g})(\tau)\,\mathrm{d}\tau,$$

and that $H^{-s}(\mathbb{R}_\omega)$ can be identified with the dual of $H^s(\mathbb{R}_\omega)$ when the space $L^2(\mathbb{R}_\omega) = H^0(\mathbb{R}_\omega)$ is used as a pivoting space. One of the reasons to introduce these spaces is that the image of $L^\infty(\mathbb{R}_\tau)$ by the Fourier transform $\mathcal{F}_T$ is contained in the Sobolev spaces of indices strictly lower than $-1/2$.

Lemma 4.3 (Fourier transform in $L^\infty(\mathbb{R}_\tau)$)**.** *Let $s > 1/2$. Then $\mathcal{F}_T\left(L^\infty(\mathbb{R}_\tau)\right) \subset H^{-s}(\mathbb{R}_\omega)$ and*

$$\|\mathcal{F}_T\|_{\mathcal{B}(L^\infty, H^{-s})} = C_s \quad \text{with} \quad C_s = \left(2\pi \int_{\mathbb{R}} \frac{\mathrm{d}\tau}{(1+\tau^2)^s}\right)^{1/2}. \tag{4.6}$$

For completeness, we recall the proof of Lemma 4.3 in Section 4.6.1.

Since the Hilbert transform in $\mathscr{S}(\mathbb{R}_\omega)$ amounts to a multiplication by the bounded function $-\mathrm{i}\,\mathrm{sgn}(\cdot)$ in the time domain (see (4.5)), it can be directly extended to the Sobolev spaces $H^s(\mathbb{R}_\omega)$.

Lemma 4.4. *For any $s \in \mathbb{R}$, the Hilbert transform $\mathfrak{H}$ is a unitary operator on the Sobolev spaces $H^s(\mathbb{R}_\omega)$ satisfying $\mathfrak{H}^{-1} = -\mathfrak{H}$ (and therefore $\mathfrak{H}^2 = -\mathrm{Id}$).*

Remark 4.5 (Hilbert transform of distributions)**.** *Extending the Hilbert transform to Sobolev spaces is straightforward using (4.5). Extensions of the Hilbert transform to other subspaces of $\mathscr{D}'(\mathbb{R}_\omega)$, such as the $\mathscr{D}'_{L^p}(\mathbb{R}_\omega)$ spaces defined in [Sch66, Section VI.8], can be obtained from (4.4).*

Hilbert transforms of operator-valued distributions

We now need to properly define the Hilbert transform of operator-valued distributions on the frequency domain, as such objects naturally appear in the GW formalism. We first introduce, for $s \in \mathbb{R}$, the Banach space

$$H^s(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H})) := \left\{ \widehat{A} \in \mathscr{S}'(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H})) \;\middle|\; (1+|\cdot|^2)^{s/2} \mathcal{F}_T^{-1} \widehat{A} \in L^2(\mathbb{R}_\tau, \mathcal{B}(\mathcal{H})) \right\},$$

endowed with the norm

$$\left\| \widehat{A} \right\|_{H^s(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))} = \sqrt{2\pi} \left(\int_{-\infty}^{+\infty} (1+\tau^2)^s \left\| \left(\mathcal{F}_T^{-1} \widehat{A} \right)(\tau) \right\|_{\mathcal{B}(\mathcal{H})}^2 \mathrm{d}\tau \right)^{1/2}.$$

The following definition makes sense in view of Lemma 4.4.

Definition 4.6 (Hilbert transforms of frequency-dependent operators)**.** *Let $\mathcal{H}$ be a Hilbert space, and consider $s \in \mathbb{R}$ and $\widehat{A} \in H^s(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$. The Hilbert transform of $\widehat{A}$ is the element of $H^s(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$, denoted by $\mathfrak{H}(\widehat{A})$, and defined by*

$$\forall (f,g) \in \mathcal{H} \times \mathcal{H}, \qquad \left\langle f \left| \mathfrak{H}(\widehat{A}) \right| g \right\rangle = \mathfrak{H}\left(\left\langle f \left| \widehat{A} \right| g \right\rangle \right). \tag{4.7}$$

In particular, it is possible to define the Hilbert transform of the Fourier transform of a uniformly bounded field of time-dependent operators, using the following result, which is a straightforward extension of Lemma 4.3.

Lemma 4.7. *Let $\mathcal{H}$ be a Hilbert space, and let $s > 1/2$. Then for all $A \in L^\infty(\mathbb{R}_\tau, \mathcal{B}(\mathcal{H}))$, we have $\widehat{A} \in H^{-s}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$, with*

$$\left\| \widehat{A} \right\|_{H^{-s}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))} = \left(2\pi \int_{\mathbb{R}} \left(1+\tau^2\right)^{-s} \|A(\tau)\|_{\mathcal{B}(\mathcal{H})}^2 \, \mathrm{d}\tau \right)^{1/2} \leq C_s \, \|A\|_{L^\infty(\mathbb{R}_\tau, \mathcal{B}(\mathcal{H}))},$$

where C_s is defined in (4.6).

Let $\mathscr{B}(\mathbb{R})$ be the set of Borel subsets of $\mathbb{R}$, $b \in \mathscr{B}(\mathbb{R})$ a Borelian set, and H a self-adjoint operator on a Hilbert space $\mathcal{H}$. We denote by $P_b^H := \mathbb{1}_b(H)$ the spectral projection on b of H (here, $\mathbb{1}_b$ is the characteristic function of the set b, and $\mathbb{1}_b(H) \in \mathcal{B}(\mathcal{H})$ is defined by the spectral theorem for self-adjoint operators; see for instance [RS78, Theorem VII.2]).

Definition 4.8 (Principal value of the resolvent of a self-adjoint operator)**.** *Let H be a self-adjoint operator on a Hilbert space $\mathcal{H}$. We define the $\mathcal{B}(\mathcal{H})$-valued distribution* $\mathrm{p.v.}\left(\frac{1}{\cdot - H}\right)$ *on the frequency domain $\mathbb{R}_\omega$ by*

$$\forall (f,g) \in \mathcal{H} \times \mathcal{H}, \qquad \left\langle f \left| \mathrm{p.v.}\left(\frac{1}{\cdot - H}\right) \right| g \right\rangle := \pi\, \mathfrak{H}(\mu_{f,g}^H),$$

where $\mu_{f,g}^H$ is the finite complex Borel measure on $\mathbb{R}_\omega$ defined by

$$\forall b \in \mathscr{B}(\mathbb{R}_\omega), \qquad \mu_{f,g}^H(b) = \langle f | P_b^H | g \rangle.$$

As any complex-valued bounded Borel measure on $\mathbb{R}_\omega$ is an element of $H^{-s}(\mathbb{R}_\omega)$ for any $s > 1/2$ (this is a consequence of the continuous embedding $H^s(\mathbb{R}_\omega) \hookrightarrow C^0(\mathbb{R}_\omega) \cap L^\infty(\mathbb{R})$ for $s > 1/2$), it follows from Definitions 4.6 and 4.8 that

$$\mathrm{p.v.}\left(\frac{1}{\cdot - H}\right) = \pi\, \mathfrak{H}(P^H) \quad \text{in } H^{-s}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H})), \quad s > 1/2,$$

which is the operator analog of the well-known formula

$$\mathrm{p.v.}\left(\frac{1}{\cdot}\right) = \pi\, \mathfrak{H}(\delta_0) \quad \text{in } H^{-s}(\mathbb{R}_\omega), \quad s > 1/2, \tag{4.8}$$

which is itself a simple reformulation of the equality

$$\mathcal{F}_T^{-1}\left[\mathrm{p.v.}\left(\frac{1}{\cdot}\right)\right] = -\frac{\mathrm{i}}{2}\,\mathrm{sgn}(\cdot) \quad \text{in } L^\infty(\mathbb{R}_\tau).$$

4.2.3 Causal and anti-causal operators

The GW formalism makes use of families of time-dependent operators $(T_\mathrm{c}(\tau))_{\tau\in\mathbb{R}}$ and $(T_\mathrm{a}(\tau))_{\tau\in\mathbb{R}}$ of the form

$$T_\mathrm{c}(\tau) = \Theta(\tau) A_\mathrm{c}(\tau) \quad \text{and} \quad T_\mathrm{a}(\tau) = \Theta(-\tau) A_\mathrm{a}(\tau),$$

where $\Theta : \mathbb{R} \to \mathbb{R}$ is the Heaviside function (4.2), and A_c and A_a belong to $L^\infty(\mathbb{R}, \mathcal{B}(\mathcal{H}))$ for a given Hilbert space $\mathcal{H}$. The family of operators $(T_\mathrm{c}(\tau))_{\tau\in\mathbb{R}}$ is called a *causal operator*, as $T_\mathrm{c}(\tau) = 0$ for all $\tau < 0$. Likewise, the family of operators $(T_\mathrm{a}(\tau))_{\tau\in\mathbb{R}}$ is called an *anti-causal operator*, as $T_\mathrm{a}(\tau) = 0$ for all $\tau > 0$. We recall in this section the basic properties of causal and anti-causal operators.

Causal operators

Causal functions have very nice properties, because their Fourier transforms have analytic extensions in the upper half-plane

$$\mathbb{U} := \{ z \in \mathbb{C} \,|\, \mathrm{Im}\, z > 0 \}\,.$$

This comes from the fact that, if $f \in L^1(\mathbb{R}_\tau) + L^\infty(\mathbb{R}_\tau)$ is such that $f(\tau) = 0$ for $\tau < 0$, the Laplace transform $\widetilde{f}$ of f, defined on $\mathbb{U}$ by[2]

$$\forall z \in \mathbb{U}, \qquad \widetilde{f}(z) := \int_{\mathbb{R}} f(\tau) \mathrm{e}^{\mathrm{i}z\tau} \, \mathrm{d}\tau = \int_0^{+\infty} f(\tau) \mathrm{e}^{\mathrm{i}z\tau} \, \mathrm{d}\tau, \tag{4.9}$$

is a natural analytic lifting onto $\mathbb{U}$ of the time-Fourier transform $\widehat{f}$ of f defined on $\mathbb{R}_\omega = \partial\mathbb{U}$. Note that the Laplace transform can be extended to appropriate classes of tempered distributions, see [Sch66, Chapter VIII].

Let us first recall the Titchmarsh's theorem [Tit48] (see for instance [Nus72, Section 1.6]).

Theorem 4.9 (Titchmarsh's theorem in L^2 [Tit48])**.** *Let $f \in L^2(\mathbb{R}_\tau)$ and $\widehat{f} \in L^2(\mathbb{R}_\omega)$ be its time-Fourier transform. The following assertions are equivalent:*

(i) f is causal (i.e. $f(\tau) = 0$ for almost all $\tau < 0$);

(ii) there exists an analytic function F in the upper half-plane $\mathbb{U}$ satisfying

$$\sup_{\eta>0} \left(\int_{-\infty}^{+\infty} |F(\omega + \mathrm{i}\eta)|^2 \, \mathrm{d}\omega \right) < \infty$$

and such that, $F(\cdot + \mathrm{i}\eta) \to \widehat{f}$ strongly in $L^2(\mathbb{R}_\omega)$, as $\eta \to 0^+$;

(iii) $\mathrm{Re}\,\widehat{f}$ and $\mathrm{Im}\,\widehat{f}$ satisfy the first Plemelj formula

$$\mathrm{Re}\,\widehat{f} = -\mathfrak{H}\left(\mathrm{Im}\,\widehat{f}\right) \quad \text{in } L^2(\mathbb{R}_\omega); \tag{4.10}$$

(iv) $\mathrm{Re}\,\widehat{f}$ and $\mathrm{Im}\,\widehat{f}$ satisfy the second Plemelj formula

$$\mathrm{Im}\,\widehat{f} = \mathfrak{H}\left(\mathrm{Re}\,\widehat{f}\right) \quad \text{in } L^2(\mathbb{R}_\omega). \tag{4.11}$$

If these four assertions are satisfied, then the function F in (ii) is unique, and coincides with the Laplace transform $\widetilde{f}$ of f.

We refer to [Tit48] for a proof of this theorem. Formulae (4.10)-(4.11) are sometimes referred to as the Kramers-Krönig formulae or the dispersion relations in the physics literature. Titchmarsh's theorem implies in particular that square integrable causal functions, which can be very easily characterized in the time domain (they vanish for negative times), can also be easily characterized in the frequency domain (the imaginary parts of their Fourier transforms are the Hilbert transforms of their real parts).

We emphasize that the above version of Titchmarsh's theorem is only valid in L^2, while the GW setting mostly involves L^∞ causal functions (see Section 4.3.2 for instance). Weaker versions of Titchmarsh's theorem are available for wider classes of tempered distributions (see [Nus72] and references therein), but the L^∞ setting turns out to be sufficient for our purposes and has the advantage of allowing short, self-contained proofs of all statements. Note that the assertions are no longer equivalent.

[2] The Laplace transform is usually defined as

$$F(p) = \int_0^{\infty} f(\tau) \mathrm{e}^{-p\tau} \mathrm{d}\tau.$$

Our definition, which is better adapted to the GW framework, simply amounts to rotating the axis, or, in other words, to setting $z = \mathrm{i}p$.

Theorem 4.10 (Titchmarsh's theorem in $L^\infty(\mathbb{R})$)**.** *Let $g \in L^\infty(\mathbb{R}_\tau)$ be a causal function (i.e. $g(\tau) = 0$ for $\tau < 0$) and let $\widehat{g} \in H^{-s}(\mathbb{R}_\omega)$ for all $s > 1/2$ be its time-Fourier transform, and $\widetilde{g}$ be its Laplace transform defined on $\mathbb{U}$. Then,*

(i) $\widetilde{g}$ is analytic on $\mathbb{U}$;

(ii) the function $\eta \mapsto \widetilde{g}(\cdot + \mathrm{i}\eta)$ is continuous from $(0, +\infty)$ to $H^s(\mathbb{R}_\omega)$ for all $s \in \mathbb{R}$, and is uniformly continuous from $[0, +\infty)$ to $H^{-s}(\mathbb{R}_\omega)$ for all $s > 1/2$. Moreover, $\widetilde{g}(\cdot + \mathrm{i}\eta) \to \widehat{g}$ strongly in $H^{-s}(\mathbb{R}_\omega)$ for all $s > 1/2$, as $\eta \to 0^+$;

(iii) for all $z \in \mathbb{U}$,

$$\widetilde{g}(z) = \frac{1}{2\mathrm{i}\pi} \left\langle \widehat{g}, (\cdot - z)^{-1} \right\rangle_{H^{-1}, H^1}. \tag{4.12}$$

(iv) $\operatorname{Re}\widehat{g}$ and $\operatorname{Im}\widehat{g}$ satisfy the Plemelj formulae:

$$\operatorname{Re}\widehat{g} = -\mathfrak{H}(\operatorname{Im}\widehat{g}) \quad \text{and} \quad \operatorname{Im}\widehat{g} = \mathfrak{H}(\operatorname{Re}\widehat{g}) \quad \text{in } H^{-1}(\mathbb{R}_\omega). \tag{4.13}$$

The proof of Theorem 4.10, which is a simplified version of the proof of the more general result given by [Tay58, Lemma 1] (see also [Nus72, Section 1.7]), is given in Section 4.6.2. For simplicity, we stated (4.12) and (4.13) in H^{-s} for the value $s = 1$, but similar results hold for any value $s > 1/2$.

Let us now extend these results to operator-valued functions. We recall that a map $\widetilde{A}(z)$ from an open set $U \subset \mathbb{C}$ to a Banach space E is said to be strongly analytic on U if $U \ni z \mapsto \widetilde{A}(z) \in E$ is $\mathbb{C}$-differentiable on U, *i.e.* $\mathrm{d}\widetilde{A}(z)/\mathrm{d}z \in E$ for all $z \in U$.

Definition 4.11 (bounded causal operator)**.** *Let $\mathcal{H}$ be a Hilbert space and $T_\mathrm{c} \in L^\infty(\mathbb{R}_\tau, \mathcal{B}(\mathcal{H}))$. We say that T_c is a bounded causal operator on $\mathcal{H}$ if $T_\mathrm{c}(\tau) = 0$ for almost all $\tau < 0$.*

Lemma 4.3 and Theorem 4.10 can be straightforwardly extended to operator-valued maps (see Section 4.6.3 for the proof).

Proposition 4.12. *Let $\mathcal{H}$ be a Hilbert space and $T_\mathrm{c} \in L^\infty(\mathbb{R}_\tau, \mathcal{B}(\mathcal{H}))$ a bounded causal operator on $\mathcal{H}$. Then its time-Fourier transform $\widehat{T}_\mathrm{c}$ belongs to $H^{-s}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$ for any $s > 1/2$, and its Laplace transform*

$$\widetilde{T}_\mathrm{c}(z) := \int_{\mathbb{R}} T_\mathrm{c}(\tau)\, \mathrm{e}^{\mathrm{i}z\tau}\, \mathrm{d}\tau = \int_0^{+\infty} T_\mathrm{c}(\tau)\, \mathrm{e}^{\mathrm{i}z\tau}\, \mathrm{d}\tau$$

is well defined on the upper-half plane $\mathbb{U}$. Moreover,

(i) $\widetilde{T}_\mathrm{c}$ is a strongly analytic function from $\mathbb{U}$ to $\mathcal{B}(\mathcal{H})$;

(ii) the function $\eta \mapsto \widetilde{T}_\mathrm{c}(\cdot + \mathrm{i}\eta)$ is continuous from $(0, +\infty)$ to $H^s(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$ for all $s \in \mathbb{R}$, and uniformly continuous from $[0, +\infty)$ to $H^{-s}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$ for $s > 1/2$. Moreover, for any $s > 1/2$, $\widetilde{T}_\mathrm{c}(\cdot + \mathrm{i}\eta) \to \widehat{T}_\mathrm{c}$ strongly in $H^{-s}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$ as $\eta \to 0^+$;

(iii) for all $z \in \mathbb{U}$, it holds

$$\widetilde{T}_\mathrm{c}(z) = \frac{1}{2\mathrm{i}\pi} \left\langle \widehat{T}_\mathrm{c}, (\cdot - z)^{-1} \right\rangle_{H^{-1}, H^1};$$

(iv) the operators $\operatorname{Re}\widehat{T}_\mathrm{c}$ and $\operatorname{Im}\widehat{T}_\mathrm{c}$ satisfy the Plemelj formulae:

$$\operatorname{Re}\widehat{T}_\mathrm{c} = -\mathfrak{H}\left(\operatorname{Im}\widehat{T}_\mathrm{c}\right) \quad \text{and} \quad \operatorname{Im}\widehat{T}_\mathrm{c} = \mathfrak{H}\left(\operatorname{Re}\widehat{T}_\mathrm{c}\right) \quad \text{in } H^{-1}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H})). \tag{4.14}$$

Besides the general case covered by Proposition 4.12, the particular case of causal time-propagators is often encountered. Explicit formulae can be provided for the Laplace and Fourier transforms in this case, as made precise in the following result (see Section 4.6.4 for the proof).

Proposition 4.13 (Analytic extension of causal time propagators)**.** *Let H be a self-adjoint operator on a Hilbert space $\mathcal{H}$ and $A_{\mathrm{c}}(\tau) := -\mathrm{i}\Theta(\tau)\mathrm{e}^{-\mathrm{i}\tau H}$. The Laplace transform $(\widetilde{A}_{\mathrm{c}}(z))_{z\in\mathbb{U}}$ coincides with the resolvent of H in $\mathbb{U}$:*

$$\widetilde{A}_{\mathrm{c}}(z) = (z - H)^{-1}.$$

Moreover, $\widetilde{A}_{\mathrm{c}}(\cdot + \mathrm{i}\eta)$ converge to $\widehat{A}_{\mathrm{c}}$ in $H^{-1}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$ as $\eta \to 0^+$, and

$$\mathrm{Re}\,\widehat{A}_{\mathrm{c}} = \mathrm{p.v.}\left(\frac{1}{\cdot - H}\right) \quad \text{and} \quad \mathrm{Im}\,\widehat{A}_{\mathrm{c}} = -\pi P^H \quad \text{in } H^{-1}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H})).$$

Let us conclude this section with a useful result (see Section 4.6.5 for the proof).

Lemma 4.14. *Let $T_{\mathrm{c}} \in L^\infty(\mathbb{R}_\tau, \mathcal{B}(\mathcal{H}))$ be a bounded causal operator such that it holds $\mathrm{Supp}(\mathrm{Im}\,\widehat{T}_{\mathrm{c}}) \subset [\omega_0, \infty)$ for some $\omega_0 \in \mathbb{R}$. Then $\mathrm{Im}\,\widehat{T}_{\mathrm{c}} \geq 0$ on $\mathbb{R}_\omega$ if and only if $\mathrm{Re}\,\widehat{T}_{\mathrm{c}} \geq 0$ on $(-\infty, \omega_0]$.*

Anti-causal operators

Definition 4.15 (bounded anti-causal operator)**.** *Let $\mathcal{H}$ be a Hilbert space and $T_{\mathrm{a}} \in L^\infty(\mathbb{R}_\tau, \mathcal{B}(\mathcal{H}))$. We say that T_{a} is a bounded anti-causal operator if $T_{\mathrm{a}}(\tau) = 0$ for almost all $\tau > 0$.*

All the results for causal operators stated in the previous section can be straightforwardly transposed to anti-causal operators, by remarking that if $(T_{\mathrm{a}}(\tau))_{\tau\in\mathbb{R}}$ is an anti-causal operator, then $(T_{\mathrm{a}}(-\tau))_{t\in\mathbb{R}}$ is a causal operator. We will use in particular the following results, which are the counterparts of Proposition 4.12, Proposition 4.13 and Lemma 4.14.

Proposition 4.16. *Let $\mathcal{H}$ be a Hilbert space and $T_{\mathrm{a}} \in L^\infty(\mathbb{R}_\tau, \mathcal{B}(\mathcal{H}))$ a bounded anti-causal operator on $\mathcal{H}$. Then its time-Fourier transform $\widehat{T_{\mathrm{a}}}$ belongs to $H^{-s}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$ for any $s > 1/2$, and its Laplace transform $\widetilde{T_{\mathrm{a}}}$ is well defined on the lower half-plane*

$$\mathbb{L} = \{z \in \mathbb{C} \mid \mathrm{Im}\,(z) < 0\}.$$

Moreover,

(i) $\widetilde{T}_{\mathrm{a}}$ is a strongly analytic function from $\mathbb{L}$ to $\mathcal{B}(\mathcal{H})$;

(ii) the function $\eta \mapsto \widetilde{T}_{\mathrm{a}}(\cdot - \mathrm{i}\eta)$ is continuous from $(0, +\infty)$ to $H^s(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$ for all $s \in \mathbb{R}$, and uniformly continuous from $[0, +\infty)$ to $H^{-s}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$ for $s > 1/2$. Moreover, for any $s > 1/2$, $\widetilde{T}_{\mathrm{a}}(\cdot - \mathrm{i}\eta) \to \widehat{T}_{\mathrm{a}}$ strongly in $H^{-s}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$ as $\eta \to 0^+$;

(iii) for all $z \in \mathbb{L}$, it holds

$$\widetilde{T_{\mathrm{a}}}(z) = -\frac{1}{2\mathrm{i}\pi}\left\langle \widehat{T_{\mathrm{a}}}, (\cdot - z)^{-1} \right\rangle_{H^{-1}, H^1};$$

(iv) the operators $\mathrm{Re}\,\widehat{T_{\mathrm{a}}}$ and $\mathrm{Im}\,\widehat{T_{\mathrm{a}}}$ satisfy the Plemelj formulae:

$$\mathrm{Re}\,\widehat{T_{\mathrm{a}}} = \mathfrak{H}\left(\mathrm{Im}\,\widehat{T_{\mathrm{a}}}\right) \quad \text{and} \quad \mathrm{Im}\,\widehat{T_{\mathrm{a}}} = -\mathfrak{H}\left(\mathrm{Re}\,\widehat{T_{\mathrm{a}}}\right) \quad \text{in } H^{-1}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H})). \tag{4.15}$$

Note that the signs in the Plemelj formulae are different for causal and anti-causal operators (compare (4.14) and (4.15)). Also, the Laplace transform is defined in the lower-half plane $\mathbb{L}$ for anti-causal operators, while it is defined in the upper-half plane $\mathbb{U}$ for causal operators. The counterpart of Proposition 4.13 is the following proposition.

Proposition 4.17 (Analytic extension of anti-causal time propagators)**.** *Let H be a self-adjoint operator on a Hilbert space $\mathcal{H}$ and $A_{\rm a}(\tau) := \mathrm{i}\Theta(-\tau)\mathrm{e}^{\mathrm{i}\tau H}$. The Laplace transform $(\widetilde{A}_{\rm a}(z))_{z\in\mathbb{L}}$ is*

$$\widetilde{A}_{\rm a}(z) = (z+H)^{-1}.$$

Moreover, $\widetilde{A}_{\rm a}(\cdot - \mathrm{i}\eta)$ converge to $\widehat{A}_{\rm a}$ in $H^{-1}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$ as $\eta \to 0^+$, and

$$\mathrm{Re}\,\widehat{A}_{\rm a} = \mathrm{p.v.}\left(\frac{1}{\cdot + H}\right) \quad \text{and} \quad \mathrm{Im}\,\widehat{A}_{\rm a} = \pi P^{-H} \quad \text{in } H^{-1}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H})).$$

Finally, a result similar to Lemma 4.14 can also be stated.

Lemma 4.18. *Let $T_{\rm a} \in L^\infty(\mathbb{R}_\tau, \mathcal{B}(\mathcal{H}))$ be a bounded anti-causal operator such that it holds $\mathrm{Supp}(\mathrm{Im}\,\widehat{T_{\rm a}}) \subset (-\infty, \omega_0]$ for some $\omega_0 \in \mathbb{R}_\omega$. Then, $\mathrm{Im}\,\widehat{T_{\rm a}} \geq 0$ if and only if $\mathrm{Re}\,\widehat{T_{\rm a}}(\omega) \geq 0$ on $[\omega_0, +\infty)$.*

4.2.4 Operators defined by kernel products

Two of the fundamental equations in the GW method (see Sections 4.4.2 and 4.4.3) are of the form

$$\mathcal{C}(\mathbf{x}_1, \mathbf{x}_2) = \mathrm{i}\mathcal{A}(\mathbf{x}_1, \mathbf{x}_2)\mathcal{B}(\mathbf{x}_2, \mathbf{x}_1), \tag{4.16}$$

where $\mathcal{A}(\mathbf{x}, \mathbf{x}')$ and $\mathcal{B}(\mathbf{x}, \mathbf{x}')$ are the kernels of space-time operators invariant by time translations. As the product of the kernels of two operators is not, in general, the kernel of a well-defined operator, we have to clarify the meaning of (4.16). We first treat the case of time-independent operators in Section 4.2.4, and consider time-dependent operators and their Laplace transforms in a second step (see Section 4.2.4).

Definition of the kernel product

We first consider the special case when the operators in (4.16) are time-independent. Our aim is to give a meaning to equalities such as

$$C(\mathbf{r}_1, \mathbf{r}_2) := A(\mathbf{r}_1, \mathbf{r}_2)B(\mathbf{r}_2, \mathbf{r}_1), \tag{4.17}$$

where $A(\mathbf{r}, \mathbf{r}')$ and $B(\mathbf{r}, \mathbf{r}')$ are the kernels of two integral operators A and B on $L^2(\mathbb{R}^3)$. For this purpose, we replace (4.17) by the formally equivalent definition

$$\begin{aligned} \forall (f,g) \in L^2(\mathbb{R}^3) \times L^2(\mathbb{R}^3), \qquad \langle f|C|g\rangle &:= \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \overline{f}(\mathbf{r}_1)C(\mathbf{r}_1,\mathbf{r}_2)g(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 \\ &= \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} A(\mathbf{r}_1,\mathbf{r}_2)g(\mathbf{r}_2)B(\mathbf{r}_2,\mathbf{r}_1)\overline{f}(\mathbf{r}_1)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 \\ &= \mathrm{Tr}_{L^2(\mathbb{R}^3)}\left(AgB\overline{f}\right), \end{aligned} \tag{4.18}$$

where the last line involves the operators A and B themselves, and not their kernels ($\overline{f}$ and g are there seen as multiplication operators by the functions $\overline{f}$ and g respectively).

The formal equalities leading to (4.18) suggest to define the kernel product of two operators A and B (defined on dense subspaces of $L^2(\mathbb{R}^3)$), as the operator on $L^2(\mathbb{R}^3)$ with domain $D \subset L^2(\mathbb{R}^3)$, denoted by $A \odot B$ and characterized by

$$\forall (f,g) \in L^2(\mathbb{R}^3) \times D, \qquad \langle f|(A\odot B)|g\rangle := \mathrm{Tr}_{L^2(\mathbb{R}^3)}\left(AgB\overline{f}\right). \tag{4.19}$$

In particular, the product $A \odot B$ is a well-defined bounded operator on $L^2(\mathbb{R}^3)$ as soon as $AgB\overline{f}$ is trace-class for all $(f,g) \in L^2(\mathbb{R}^3) \times L^2(\mathbb{R}^3)$ and $(f,g) \mapsto \mathrm{Tr}_{L^2(\mathbb{R}^3)}(AgB\overline{f})$ is a continuous sesquilinear form on $L^2(\mathbb{R}^3) \times L^2(\mathbb{R}^3)$. It follows from the above considerations that if A and B are operators with well-behaved (for instance smooth and compactly supported) kernels $A(\mathbf{r}_1, \mathbf{r}_2)$ and $B(\mathbf{r}_1, \mathbf{r}_2)$, then $A \odot B$ is a bounded integral operator with kernel $(A \odot B)(\mathbf{r}_1, \mathbf{r}_2) = A(\mathbf{r}_1, \mathbf{r}_2)B(\mathbf{r}_2, \mathbf{r}_1)$.

Remark 4.19. *It is also possible to rely on the formal equality*

$$\forall (f,g) \in L^2(\mathbb{R}^3) \times L^2(\mathbb{R}^3), \quad \langle f|C|g\rangle = \mathrm{Tr}_{L^2(\mathbb{R}^3)}\left(\overline{f}AgB\right),$$

and define another kernel product $\widetilde{\odot}$ *by*

$$\forall (f,g) \in L^2(\mathbb{R}^3) \times D, \qquad \left\langle f \left| A \,\widetilde{\odot}\, B \right| g \right\rangle := \mathrm{Tr}_{L^2(\mathbb{R}^3)}\left(\overline{f}AgB\right).$$

It may hold that $A \odot B$ *is a well-defined bounded operator, while* $A \,\widetilde{\odot}\, B$ *is an unbounded operator.*[3] *In the sequel, we will mostly state the results for the* $\odot$ *kernel product.*

Remark 4.20. *The product* $A \odot B$ *can be seen as an infinite-dimensional extension of the Hadamard product* $\mathbf{A} \circ \mathbf{B}^T$ *defined for two matrices* $\mathbf{A} \in \mathbb{C}^{m \times n}$ *and* $\mathbf{B} \in \mathbb{C}^{n \times m}$ *by*

$$\forall 1 \leq i \leq m, \quad \forall 1 \leq j \leq n, \quad \left(\mathbf{A} \circ \mathbf{B}^T\right)_{ij} = \mathbf{A}_{ij}\left(\mathbf{B}^T\right)_{ij} = \mathbf{A}_{ij}\mathbf{B}_{ji}.$$

Let us specify possible sufficient conditions for the operator $A \odot B$ to be well-defined. The typical situation we will encounter in the GW setting (see Sections 4.4.2 and 4.4.3) is the case when $A \in \mathcal{B}(L^2(\mathbb{R}^3))$, while B is an operator on $L^2(\mathbb{R}^3)$ satisfying

$$\forall f, g \in L^2(\mathbb{R}^3), \quad \mathrm{Tr}\left(\left|gB\overline{f}\right|\right) \leq C_B \|f\|_{L^2}\|g\|_{L^2}. \tag{4.20}$$

In this case, the operator $A \odot B$ defined in (4.19) is a well-defined bounded linear operator on $L^2(\mathbb{R}^3)$, and

$$\|A \odot B\|_{\mathcal{B}(L^2(\mathbb{R}^3))} \leq C_B \|A\|_{\mathcal{B}(L^2(\mathbb{R}^3))}.$$

The operators B arising in the GW formalism are usually of the form $B = B_1^* B_2 B_1$, where B_1 is an operator from $L^2(\mathbb{R}^3)$ to some Hilbert space $\mathcal{H}$, and $B_2 \in \mathcal{B}(\mathcal{H})$. In fact, assume that the operator B_1 is such that $B_1 f \in \mathfrak{S}_2(L^2(\mathbb{R}^3), \mathcal{H})$ for any $f \in L^2(\mathbb{R}^3)$, with

$$\|B_1 f\|_{\mathfrak{S}_2(L^2(\mathbb{R}^3),\mathcal{H})} \leq K\|f\|_{L^2}, \tag{4.21}$$

for a constant $K \in \mathbb{R}^+$ independent of f. In the left-hand side of (4.21), f denotes the multiplication operator by the function f. In this case, (4.20) holds with

$$C_B = K^2 \|B_2\|_{\mathcal{B}(\mathcal{H})}.$$

Let us conclude by giving a simple example when (4.21) is satisfied, in the situation when $\mathcal{H} = L^2(\mathbb{R}^3)$.

[3] As an example of such a situation, take $\phi \in L^2(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$, $\psi \in L^2(\mathbb{R}^3) \setminus L^\infty(\mathbb{R}^3)$, and set $A = |\psi\rangle\langle\phi|$ and $B = |\phi\rangle\langle\phi|$. Then, for all $f, g \in L^2(\mathbb{R}^3)$, the operator $AgB\overline{f} = |\psi\rangle\langle\phi|g|\phi\rangle\langle\phi f|$ is a well-defined rank-1 bounded operator since $\phi f \in L^2(\mathbb{R}^3)$, hence is trace class. Moreover,

$$\mathrm{Tr}_{L^2(\mathbb{R}^3)}\left(AgB\overline{f}\right) \leq \left(\|\phi\|_{L^\infty}^2 \|\phi\|_{L^2}\|\psi\|_{L^2}\right)\|f\|_{L^2}\|g\|_{L^2},$$

so that $A \odot B$ is a well-defined bounded operator on $L^2(\mathbb{R}^3)$. On the other hand, it formally holds $\overline{f}AgB = |f\psi\rangle\langle\phi|g|\phi\rangle\langle\phi|$. If f is such that $f\psi \notin L^2(\mathbb{R}^3)$, then this operator is not bounded.
We are grateful to Yanqi Qiu for pointing out this counter-example to our attention.

Lemma 4.21. *Let B_1 be a linear operator with integral kernel $B_1(\mathbf{r},\mathbf{r}') \in L^2_{\mathrm{loc}}(\mathbb{R}^3\times\mathbb{R}^3)$, such that $\mathbf{r}\mapsto \|B_1(\mathbf{r},\cdot)\|_{L^\infty}\in L^2(\mathbb{R}^3)$. Then $B_1\in\mathcal{B}(L^1(\mathbb{R}^3),L^2(\mathbb{R}^3))$, so that B_1 defines an operator on $L^2(\mathbb{R}^3)$ with domain $L^1(\mathbb{R}^3)\cap L^2(\mathbb{R}^3)$. Moreover, for any $f\in L^2(\mathbb{R}^3)$, the operator $B_1 f$ is Hilbert-Schmidt on $L^2(\mathbb{R}^3)$, with*

$$\|B_1 f\|_{\mathfrak{S}_2(L^2(\mathbb{R}^3))} \le \left(\int_{\mathbb{R}^3} \|B_1(\mathbf{r},\cdot)\|^2_{L^\infty(\mathbb{R}^3)}\,\mathrm{d}\mathbf{r}\right)^{1/2} \|f\|_{L^2(\mathbb{R}^3)}.$$

The proof of this result can be read in Section 4.6.6. In the GW setting, a technical result similar to Lemma 4.21 is provided by Lemma 4.77.

Properties of the kernel product

Lemma 4.22. *Consider two bounded operators $A,B\in\mathcal{B}(L^2(\mathbb{R}^3))$ such that $A,B\ge 0$ and (4.20) holds. Then, $A\odot B$ is a bounded, positive operator on $L^2(\mathbb{R}^3)$.*

The proof of this result is very simple: it relies on the observation that, for any $f\in L^2(\mathbb{R}^3)$,

$$\langle f\,|A\odot B|\,f\rangle = \mathrm{Tr}_{L^2(\mathbb{R}^3)}\left(Af\overline{Bf}\right) = \mathrm{Tr}_{L^2(\mathbb{R}^3)}\left(A^{1/2}f\overline{Bf}A^{1/2}\right)\ge 0,$$

since $f\overline{Bf}$ is a positive, trace class operator and $A^{1/2}\ge 0$ is a bounded operator.

Lemma 4.23. *Consider two bounded operators $A,B\in\mathcal{B}(L^2(\mathbb{R}^3))$ such that (4.20) holds. Then, $A\odot B$ is a bounded operator with adjoint $(A\odot B)^* = A^*\odot B^*$.*

The proof of this result is also elementary: for any $f,g\in L^2(\mathbb{R}^3)$,

$$\begin{aligned}\left\langle f\right|(A\odot B)\left|g\right\rangle &= \mathrm{Tr}_{L^2(\mathbb{R}^3)}\left(Ag\overline{Bf}\right) = \overline{\mathrm{Tr}_{L^2(\mathbb{R}^3)}\left(\left(Ag\overline{Bf}\right)^*\right)} = \overline{\mathrm{Tr}_{L^2(\mathbb{R}^3)}\left(fB^*\overline{g}A^*\right)}\\ &= \overline{\mathrm{Tr}_{L^2(\mathbb{R}^3)}\left(A^*fB^*\overline{g}\right)} = \overline{\langle g,(A^*\odot B^*)f\rangle} = \langle (A^*\odot B^*)f,g\rangle\,.\end{aligned}$$

In particular, $A\odot B$ is self-adjoint whenever A and B are self-adjoint.

Laplace transforms of kernel products

We finally combine the results on causal operators with those on the kernel product $\odot$ defined in Section 4.2.4 in order to give a meaning to (4.16). Note first that the space-time operator with kernel $\mathcal{C}(\mathbf{x},\mathbf{x}')$ is also time-translation invariant and that the family of operators $(A(\tau))_{\tau\in\mathbb{R}}$, $(B(\tau))_{\tau\in\mathbb{R}}$ and $(C(\tau))_{\tau\in\mathbb{R}}$ such that, formally, $\mathcal{A}(\mathbf{x}_1,\mathbf{x}_2)=A(\mathbf{r}_1,\mathbf{r}_2,t_1-t_2)$, $\mathcal{B}(\mathbf{x}_1,\mathbf{x}_2)=B(\mathbf{r}_1,\mathbf{r}_2,t_1-t_2)$, and $\mathcal{C}(\mathbf{x}_1,\mathbf{x}_2)=C(\mathbf{r}_1,\mathbf{r}_2,t_1-t_2)$, are related by

$$C(\tau) = \mathrm{i}A(\tau)\odot B(-\tau). \tag{4.22}$$

We assume here that A and B are such that (4.22) is well-defined. When all the operator-valued functions have sufficient regularity in time, their Fourier transforms decay sufficiently fast at infinity and it is possible to Fourier transform (4.22). This is however not the typical case in the GW setting since we work with causal and anti-causal operators, whose Fourier transforms are in $H^{-s}(\mathbb{R}_\omega)$ for some $s>1/2$.

We therefore rather consider Laplace transforms. More precisely, for two fields of uniformly bounded operators $(A(\tau))_{\tau\in\mathbb{R}}$ and $(B(\tau))_{\tau\in\mathbb{R}}$, and provided $C(\tau):=\mathrm{i}A(\tau)\odot B(-\tau)$ is well defined, we can decompose A, B and C as the sums of their causal and anti-causal parts as

$$A(\tau)=A^+(\tau)+A^-(\tau)\quad\text{with}\quad A^+(\tau):=\Theta(\tau)A(\tau)\quad\text{and}\quad A^-(\tau):=\Theta(-\tau)A(\tau),$$

and similarly for B and C. Then,

$$C^+(\tau)=\mathrm{i}A^+(\tau)\odot B^-(-\tau)\quad\text{and}\quad C^-(\tau)=\mathrm{i}A^-(\tau)\odot B^+(-\tau). \tag{4.23}$$

We next consider $\omega > 0$ and $0 < \eta < \omega$. From the equality

$$C^+(\tau)\,\mathrm{e}^{-\omega\tau} = \mathrm{i}\left[A^+(\tau)\,\mathrm{e}^{-(\omega-\eta)\tau}\right] \odot \left[B^-(-\tau)\,\mathrm{e}^{-\eta\tau}\right],$$

we deduce, by Fourier transform, that

$$\widetilde{C^+}(\nu + \mathrm{i}\omega) = \frac{\mathrm{i}}{2\pi}\int_{-\infty}^{+\infty} \widetilde{A^+}\big(\nu - \omega' + \mathrm{i}(\omega-\eta)\big) \odot \widetilde{B^-}(-\omega' - \mathrm{i}\eta)\,\mathrm{d}\omega'. \tag{4.24}$$

The convolution on the right-hand side is well defined in view of Propositions 4.12 and 4.16. It however becomes ill-defined as $\omega, \eta \to 0$. In the case when the causal and anti-causal operators A^+ and B^- under consideration are time-propagators, it is possible to remove this singularity by rewriting the convolution on appropriately shifted imaginary axes.

Theorem 4.24. *Consider three Hilbert spaces $\mathcal{H}, \mathcal{H}_a, \mathcal{H}_b$, and assume that*

$$\begin{aligned} A^+(\tau) &= -\mathrm{i}\Theta(\tau)A_1^*\mathrm{e}^{-\mathrm{i}\tau A_2}A_1, \qquad & A^-(\tau) &= \mathrm{i}\Theta(-\tau)A_1^*\mathrm{e}^{\mathrm{i}\tau A_2}A_1, \\ B^+(\tau) &= -\mathrm{i}\Theta(\tau)B_1^*\mathrm{e}^{-\mathrm{i}\tau B_2}B_1, \qquad & B^-(\tau) &= \mathrm{i}\Theta(-\tau)B_1^*\mathrm{e}^{\mathrm{i}\tau B_2}B_1, \end{aligned}$$

where $A_1 \in \mathcal{B}(\mathcal{H}, \mathcal{H}_a)$, $B_1 \in \mathcal{B}(\mathcal{H}, \mathcal{H}_b)$ and A_2, B_2 are possibly unbounded, self-adjoint operators on $\mathcal{H}_a$ and $\mathcal{H}_b$ respectively, for which there exist real numbers a, b such that $A_2 \geq a$ and $B_2 \geq b$. We assume in addition that, for any $f \in \mathcal{H}$, $B_1 f \in \mathfrak{S}_2(\mathcal{H}, \mathcal{H}_b)$ with $\|B_1 f\|_{\mathfrak{S}_2(\mathcal{H},\mathcal{H}_b)} \leq K\|f\|_{\mathcal{H}}$, for a constant $K \in \mathbb{R}^+$ independent of f. Then, the operators C, C^+ and C^- in (4.22)-(4.23) are well-defined, the Laplace transforms of C^+ and C^- admit analytical continuations on $\mathbb{U} \cup \mathbb{L} \cup (-\infty, a+b)$ and $\mathbb{U} \cup \mathbb{L} \cup (-(a+b), \infty)$ respectively, and it holds for any $\nu < a + b$ and $\nu' \in (-b, a - \nu)$,

$$\forall \omega \in \mathbb{R}, \qquad \widetilde{C^+}(\nu + \mathrm{i}\omega) = -\frac{1}{2\pi}\int_{-\infty}^{+\infty} \widetilde{A^+}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) \odot \widetilde{B^-}(\nu' + \mathrm{i}\omega')\,\mathrm{d}\omega', \tag{4.25}$$

while, for any $\nu > -(a+b)$ and $\nu' \in (-a - \nu, b)$,

$$\forall \omega \in \mathbb{R}, \qquad \widetilde{C^-}(\nu + \mathrm{i}\omega) = -\frac{1}{2\pi}\int_{-\infty}^{+\infty} \widetilde{A^-}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) \odot \widetilde{B^+}(\nu' + \mathrm{i}\omega')\,\mathrm{d}\omega'. \tag{4.26}$$

Finally, the following equality holds provided $b > 0$ and $a + b > 0$: for any $\nu \in (-(a+b), a+b)$ and $\nu' \in (-b, b)$,

$$\forall \omega \in \mathbb{R}, \qquad \widetilde{C}(\nu + \mathrm{i}\omega) = -\frac{1}{2\pi}\int_{-\infty}^{+\infty} \widetilde{A}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) \odot \widetilde{B}(\nu' + \mathrm{i}\omega')\,\mathrm{d}\omega'. \tag{4.27}$$

The proof of Theorem 4.24 can be read in Section 4.6.7. The choices of ν, ν' ensure that the function $\omega' \mapsto \widetilde{A^+}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big)$ is in $L^p(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$ for any $p > 1$, while, for any $f, g \in \mathcal{H}$, the function $\omega' \mapsto g\widetilde{B^-}(\nu' + \mathrm{i}\omega')\overline{f}$ is in $L^p(\mathbb{R}_\omega, \mathfrak{S}_1(\mathcal{H}))$ for any $p > 1$. Therefore, in view of (4.25), the function $\omega \mapsto \widetilde{C^+}(\nu + \mathrm{i}\omega)$ is in $L^p(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$ for any $p > 1$. Similar results hold for $\omega \mapsto \widetilde{C^-}(\nu + \mathrm{i}\omega)$ and $\omega \mapsto \widetilde{C}(\nu + \mathrm{i}\omega)$.

Let us conclude this section by deducing interesting properties from the analytic continuation results given by Theorem 4.24 (see Section 4.6.8 for the proof).

Corollary 4.25. *Assume that the conditions of Theorem 4.24 hold. Then,*

$$\begin{aligned} \mathrm{Supp}\left(\mathrm{Im}\,\widehat{C^+}\right) &\subset [a+b, +\infty), \qquad & \mathrm{Im}\,\widehat{C^+} &\geq 0, \\ \mathrm{Supp}\left(\mathrm{Im}\,\widehat{C^-}\right) &\subset (-\infty, -(a+b)], \qquad & \mathrm{Im}\,\widehat{C^-} &\geq 0, \end{aligned} \tag{4.28}$$

so that

$$\mathrm{Supp}\left(\mathrm{Im}\,\widehat{C}\right) \subset \mathbb{R}\backslash\left(-(a+b), a+b\right), \qquad \mathrm{Im}\,\widehat{C} \geq 0.$$

Moreover,

$$\begin{aligned} \widehat{C^+} &= \mathrm{Re}\,\widehat{C^+} \geq 0 \quad \textit{on} \quad \big(-\infty, a+b\big), \\ \widehat{C^-} &= \mathrm{Re}\,\widehat{C^-} \geq 0 \quad \textit{on} \quad \big(-(a+b), +\infty\big). \end{aligned} \tag{4.29}$$

In particular, $\widehat{C} = \mathrm{Re}\,\widehat{C} \geq 0$ *on* $\big(-(a+b), a+b\big)$.

4.2.5 Second quantization formalism

We recall here the definitions of the main mathematical objects used in the second quantization formalism, which are used to define – at least formally – the kernels of the operators arising in the GW method. More details about the second quantization formalism can be found *e.g.* in [DG97].

We consider a system of N electrons in Coulomb interaction subjected to a time-independent real-valued external potential $v_{\mathrm{ext}} \in L^2(\mathbb{R}^3, \mathbb{R}) + L^\infty(\mathbb{R}^3, \mathbb{R})$. In order to study the response of the system when electrons are added or removed, we embed this N-body problem in a more general framework where the number of electrons is not prescribed. We denote by $\mathcal{H}_1 = L^2(\mathbb{R}^3, \mathbb{C})$ the one-electron state space (the spin variable is omitted for simplicity), by $\mathcal{H}_N = \bigwedge^N \mathcal{H}_1$ the N-electron state space, and by $\mathbb{F} = \oplus_{N=0}^{+\infty} \mathcal{H}_N$ the Fock space, with the convention that $\mathcal{H}_0 = \mathbb{C}$. The Hamiltonian of the N-particle system reads

$$H_N = -\frac{1}{2}\sum_{i=1}^N \Delta_{\mathbf{r}_i} + \sum_{i=1}^N v_{\mathrm{ext}}(\mathbf{r}_i) + \sum_{1\leq i<j\leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{4.30}$$

and the corresponding Hamiltonian acting on the Fock space is denoted by $\mathbb{H}$, so that $H_N = \mathbb{H}|_{\mathcal{H}_N}$.

For $f \in \mathcal{H}_1$, the creation and annihilation operators $a^\dagger(f)$ and $a(f)$ are the bounded operators on the Fock space $\mathbb{F}$ defined by

$$\forall N \in \mathbb{N}, \quad a^\dagger(f)|_{\mathcal{H}_N} \in \mathcal{B}(\mathcal{H}_N, \mathcal{H}_{N+1}), \qquad a(f)|_{\mathcal{H}_{N+1}} \in \mathcal{B}(\mathcal{H}_{N+1}, \mathcal{H}_N),$$

and for all $\Phi_N \in \mathcal{H}_N$,

$$\begin{aligned} [a^\dagger(f)\Phi_N](\mathbf{r}_1, \dots \mathbf{r}_{N+1}) &:= \frac{1}{\sqrt{N+1}} \sum_{j=1}^{N+1} (-1)^{j+1} f(\mathbf{r}_j)\Phi_N(\mathbf{r}_1, \dots, \mathbf{r}_{j-1}, \mathbf{r}_{j+1}, \dots, \mathbf{r}_{N+1}), \\ [a(f)\Phi_N](\mathbf{r}_1, \dots \mathbf{r}_{N-1}) &:= \sqrt{N} \int_{\mathbb{R}^3} \overline{f}(\mathbf{r})\Phi_N(\mathbf{r}, \mathbf{r}_1, \dots, \mathbf{r}_{N-1})\,\mathrm{d}\mathbf{r}. \end{aligned} \tag{4.31}$$

The creation and annihilation operators satisfy $a^\dagger(f) = a(f)^*$ and the anticommutation relations

$$\forall (f,g) \in \mathcal{H}_1 \times \mathcal{H}_1, \quad [a(f), a(g)]_+ = 0, \quad [a^\dagger(f), a^\dagger(g)]_+ = 0, \quad [a(f), a^\dagger(g)]_+ = \langle f|g\rangle \mathbb{1}_{\mathbb{F}}, \tag{4.32}$$

where $[A, B]_+ = AB + BA$ is the anti-commutator of the operators A and B, and where $\mathbb{1}_{\mathbb{F}}$ is the identity operator on $\mathbb{F}$. In particular,

$$a^\dagger(f)a(f) + a(f)a^\dagger(f) = \|f\|^2_{\mathcal{H}_1}\, \mathbb{1}_{\mathbb{F}}.$$

The mappings $\mathcal{H}_1 \ni f \mapsto a^\dagger(f) \in \mathcal{B}(\mathbb{F})$ and $\mathcal{H}_1 \ni f \mapsto a(f) \in \mathcal{B}(\mathbb{F})$ are respectively linear and antilinear.

In most physics articles and textbooks, the GW formalism is presented in terms of the quantum field operators in the position representation $\Psi(\mathbf{r})$ and $\Psi^\dagger(\mathbf{r})$. We recall that, formally,

$$\forall \mathbf{r} \in \mathbb{R}^3,\ \Psi^\dagger(\mathbf{r}) = \sum_{i=1}^{\infty} \overline{\phi_i(\mathbf{r})} a^\dagger(\phi_i), \qquad \Psi(\mathbf{r}) = \sum_{i=1}^{\infty} \phi_i(\mathbf{r}) a(\phi_i),$$

where $\{\phi_i\}_{i\in\mathbb{N}}$ is any orthonormal basis of $\mathcal{H}_1$. Note that for any $f \in \mathcal{H}_1$,

$$\int_{\mathbb{R}^3} \Psi^\dagger(\mathbf{r}) f(\mathbf{r}) \mathrm{d}\mathbf{r} = a^\dagger(f) \quad \text{and} \quad \int_{\mathbb{R}^3} \Psi(\mathbf{r}) f(\mathbf{r}) \mathrm{d}\mathbf{r} = a(\overline{f}).$$

In the second-quantization formalism, $\mathbb{H}$ reads,

$$\mathbb{H} = \int_{\mathbb{R}^3} \Psi^\dagger(\mathbf{r}) \left(-\frac{1}{2}\Delta_{\mathbf{r}} + v_{\mathrm{ext}}(\mathbf{r}) \right) \Psi(\mathbf{r})\, \mathrm{d}\mathbf{r} + \frac{1}{2} \int_{(\mathbb{R}^3)^2} \Psi^\dagger(\mathbf{r}) \Psi^\dagger(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1} \Psi(\mathbf{r}') \Psi(\mathbf{r})\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'.$$

Finally, we introduce the Heisenberg representation of the annihilation and creation field operators $\Psi_{\mathrm{H}}(\mathbf{r}t)$ and $\Psi^\dagger_{\mathrm{H}}(\mathbf{r}t)$, formally defined by

$$\Psi^\dagger_{\mathrm{H}}(\mathbf{r}t) = \mathrm{e}^{\mathrm{i}t\mathbb{H}} \Psi^\dagger(\mathbf{r}) \mathrm{e}^{-\mathrm{i}t\mathbb{H}} \quad \text{and} \quad \Psi_{\mathrm{H}}(\mathbf{r}t) = \mathrm{e}^{\mathrm{i}t\mathbb{H}} \Psi(\mathbf{r}) \mathrm{e}^{-\mathrm{i}t\mathbb{H}}.$$

Note that, still formally, $\Psi_{\mathrm{H}}(\mathbf{r}t)^* = \Psi^\dagger_{\mathrm{H}}(\mathbf{r}t)$, and

$$\Psi^\dagger_{\mathrm{H}}(\mathbf{r}t)\big|_{\mathcal{H}_N} = \mathrm{e}^{\mathrm{i}tH_{N+1}} \Psi^\dagger(\mathbf{r})\, \mathrm{e}^{-\mathrm{i}tH_N}, \qquad \Psi_{\mathrm{H}}(\mathbf{r}t)\big|_{\mathcal{H}_{N+1}} = \mathrm{e}^{\mathrm{i}tH_N} \Psi(\mathbf{r})\, \mathrm{e}^{-\mathrm{i}tH_{N+1}}. \tag{4.33}$$

4.3 Operators arising in the GW method for finite systems

This section aims at providing rigorous mathematical definitions of the operators arising in the GW method. For each one of them, we first recall the formal definition given in the physics literature, using the second quantization formalism. We then explain how to recast this formal definition into a (formally equivalent) satisfactory mathematical definition involving only well-defined operators on the k-particle spaces $\mathcal{H}_k$, with $k = 1, N-1, N, N+1$, the Coulomb space $\mathcal{C}$ (defined in Section 4.3.3), and its dual $\mathcal{C}'$. We finally establish some mathematical properties of the operator under consideration, using our definition as a starting point. Unless otherwise specified, scalar products and norms are by default considered on $\mathcal{H}_1 = L^2(\mathbb{R}^3, \mathbb{C})$.

We first need to make some assumptions on the physical system under consideration (see Section 4.3.1). We can then define the one-body Green's functions in Section 4.3.2. Linear response operators are considered in Section 4.3.3, which culminates with the definition of the dynamically screened interaction operator W. We finally introduce the self-energy operator in Section 4.3.4.

4.3.1 Assumptions on the reference N-electron system

Recall that the reference system with N electrons is described by the Hamiltonian H_N on $\mathcal{H}_N$ defined by (4.30). Our first assumption concerns the ground state energy E_N^0 of the reference system described by H_N:

Hyp. 1: The ground state energy E_N^0 is a simple discrete eigenvalue of H_N.

In this case, the normalized ground state wave-function Ψ_N^0 of the reference system is unique up to a global phase. We also define the energy of the first excited state:

$$E_N^1 = \min\left(\sigma(H_N) \backslash \{E_N^0\} \right).$$

Together with Ψ_N^0, we introduce the ground state one-body reduced density-matrix

$$\gamma_N^0(\mathbf{r},\mathbf{r}') := N\int_{(\mathbb{R}^3)^{N-1}} \Psi_N^0(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_N)\overline{\Psi_N^0(\mathbf{r}',\mathbf{r}_2,\cdots,\mathbf{r}_N)}\,\mathrm{d}\mathbf{r}_2\cdots\mathrm{d}\mathbf{r}_N, \tag{4.34}$$

the ground state density

$$\rho_N^0(\mathbf{r}) := \gamma_N^0(\mathbf{r},\mathbf{r}) = N\int_{(\mathbb{R}^3)^{N-1}} |\Psi_N^0(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_N)|^2\,\mathrm{d}\mathbf{r}_2\cdots\mathrm{d}\mathbf{r}_N,$$

and the ground state two-body density

$$\rho_{N,2}^0(\mathbf{r},\mathbf{r}') := \frac{N(N-1)}{2}\int_{(\mathbb{R}^3)^{N-2}} |\Psi_N^0(\mathbf{r},\mathbf{r}',\mathbf{r}_3,\cdots,\mathbf{r}_N)|^2\,\mathrm{d}\mathbf{r}_3\cdots\mathrm{d}\mathbf{r}_N \tag{4.35}$$

of the reference N-electron system.

We recall in the following proposition some important properties on Ψ_N^0, γ_N^0, ρ_N^0 and $\rho_{N,2}^0$ (most of the assertions below are well known; we provide elements of proof in Section 4.6.9 for the less standard statements). Note that both $\gamma_N^0(\mathbf{r},\mathbf{r}')$ and $\rho_{N,2}^0(\mathbf{r},\mathbf{r}')$ can be seen as the kernels of bounded operators on $\mathcal{H}_1 = L^2(\mathbb{R}^3)$ that we also denote by γ_N^0 and $\rho_{N,2}^0$.

Proposition 4.26 (Properties of the ground state)**.** *Assume that v_{ext} is of the form*

$$v_{\mathrm{ext}}(\mathbf{r}) = -\sum_{k=1}^{M}\frac{z_k}{|\mathbf{r}-\mathbf{R}_k|},$$

with $z_k \in \mathbb{N}^*$ and $\mathbf{R}_k \in \mathbb{R}^3$ for all $1 \le k \le M$, and that **Hyp. 1** *is satisfied. Then,*

(1) the ground state wave-function Ψ_N^0 can be chosen real-valued and $\Psi_N^0 \in H^2(\mathbb{R}^{3N})$;

(2) the ground state density ρ_N^0 is in $L^1(\mathbb{R}^3,\mathbb{R}) \cap L^\infty(\mathbb{R}^3,\mathbb{R})$ and $\nabla\sqrt{\rho_N^0} \in \left(L^2(\mathbb{R}^3,\mathbb{R})\right)^3$. Moreover, ρ_N^0 is continuous and everywhere positive on $\mathbb{R}^3$;

(3) the ground state one-body reduced density operator γ_N^0 is in

$$\mathcal{K}_N := \left\{\gamma_N \in \mathcal{S}(\mathcal{H}_1)\;\middle|\; 0 \le \gamma_N \le 1,\ \mathrm{Tr}_{\mathcal{H}_1}(\gamma_N) = N,\ \mathrm{Tr}_{\mathcal{H}_1}(|\nabla|\gamma_N|\nabla|) < \infty\right\},$$

and satisfies

$$\forall (f,g) \in \mathcal{H}_1\times\mathcal{H}_1, \qquad \langle f|\gamma_N^0|g\rangle = \langle\Psi_N^0|a^\dagger(g)a(f)|\Psi_N^0\rangle_{\mathcal{H}_N}; \tag{4.36}$$

(4) the kernel $\gamma_N^0(\mathbf{r},\mathbf{r}')$ satisfies the pointwise estimate $|\gamma_N^0(\mathbf{r},\mathbf{r}')|^2 \le \rho_N^0(\mathbf{r})\rho_N^0(\mathbf{r}')$;

(5) the operator $\rho_{N,2}^0$ belongs to $\mathcal{S}(\mathcal{H}_1)$, and $\|\rho_{N,2}^0\|_{\mathcal{B}(\mathcal{H}_1)} \le \dfrac{N-1}{2}\|\rho_N^0\|_{L^\infty}$.

Much finer regularity results on Ψ_N^0 are available [FHOHOØS02, FHOHOØS05, Yse10], but are not needed for our purpose. Similar results hold true if v_{ext} is replaced by a potential generated by smeared nuclei or pseudo-potentials.

Our second assumption is concerned with the (discrete) convexity of $N \mapsto E_N^0$. We assume that $N \ge 1$, and that (with the convention $E_0^0 = 0$ in the case $N = 1$)

$$\boxed{\textbf{Hyp. 2: } E_N^0 - E_{N-1}^0 < E_{N+1}^0 - E_N^0.}$$

In this case, any real number μ such that $E_N^0 - E_{N-1}^0 < \mu < E_{N+1}^0 - E_N^0$ is an admissible chemical potential (Fermi level) of the electrons for the ground state of the reference system. The physical relevance of this assumption is discussed for instance in [Far99, Section 4.2].

4.3.2 Green's functions

We begin our journey in the GW formalism with Green's functions. The GW method has been designed from the equation of motion for the time-ordered one-body Green's function G [Hed65], which is the concatenation of two meaningful physical objects: the particle Green's function G_{p} and the hole Green's function G_{h}.

The particle Green's function G_{p}

Rigorous definition of the particle Green's function. The particle (or forward, or retarded) Green's function is formally defined by (see for instance [FW03, Section 7])

$$\mathcal{G}_{\mathrm{p}}(\mathbf{r}t,\mathbf{r}'t') := -\mathrm{i}\Theta(t-t')\ \langle\Psi_N^0|\Psi_{\mathrm{H}}(\mathbf{r}t)\Psi_{\mathrm{H}}^\dagger(\mathbf{r}'t')|\Psi_N^0\rangle, \tag{4.37}$$

where Θ is the Heaviside function (4.2), and $\Psi_{\mathrm{H}}(\mathbf{r}t)$ and $\Psi_{\mathrm{H}}^\dagger(\mathbf{r}t)$ are the Heisenberg representations of the annihilation and creation field operators introduced in Section 4.2.5. As $\Psi_N^0 \in \mathcal{H}_N$, we can replace $\Psi(\mathbf{r}t)$ and $\Psi^\dagger(\mathbf{r}t)$ by their expressions (4.33):

$$\begin{aligned}\mathcal{G}_{\mathrm{p}}(\mathbf{r}t,\mathbf{r}'t') &= -\mathrm{i}\Theta(t-t')\ \langle\Psi_N^0|\mathrm{e}^{\mathrm{i}tH_N}\Psi(\mathbf{r})\mathrm{e}^{-\mathrm{i}(t-t')H_{N+1}}\Psi^\dagger(\mathbf{r}')\mathrm{e}^{-\mathrm{i}t'H_N}|\Psi_N^0\rangle \\ &= -\mathrm{i}\Theta(t-t')\ \langle\Psi_N^0|\Psi(\mathbf{r})\mathrm{e}^{-\mathrm{i}(t-t')(H_{N+1}-E_N^0)}\Psi^\dagger(\mathbf{r}')|\Psi_N^0\rangle.\end{aligned}$$

As $\mathcal{G}_{\mathrm{p}}$ only depends on the time difference $t-t'$, it is sufficient to study the function $G_{\mathrm{p}}(\mathbf{r},\mathbf{r}',\tau) := \mathcal{G}_{\mathrm{p}}(\mathbf{r}\tau,\mathbf{r}'0)$. We then notice that, for all $f \in \mathcal{H}_1$,

$$\int_{\mathbb{R}^3} \Psi^\dagger(\mathbf{r}')|\Psi_N^0\rangle f(\mathbf{r}')\,\mathrm{d}\mathbf{r}' = a^\dagger(f)|\Psi_N^0\rangle.$$

Introducing

$$\begin{array}{rccc} A_+^* : & \mathcal{H}_1 & \to & \mathcal{H}_{N+1} \\ & f & \mapsto & a^\dagger(f)|\Psi_N^0\rangle \end{array}$$

and $A_+ = (A_+^*)^*$, we observe that $G_{\mathrm{p}}(\mathbf{r},\mathbf{r}',\tau)$ is formally the kernel of the following one-body operator.

Definition 4.27 (Particle Green's function)**.** *The particle Green's function is defined as*

$$\boxed{G_{\mathrm{p}}(\tau) := -\mathrm{i}\Theta(\tau)\ A_+\mathrm{e}^{-\mathrm{i}\tau(H_{N+1}-E_N^0)}A_+^*.} \tag{4.38}$$

First properties of the particle Green's function. The study of G_{p} can be decomposed into the study of the operators A_+ and $\mathrm{e}^{-\mathrm{i}\tau(H_{N+1}-E_N^0)}$. The latter is clearly bounded on $\mathcal{H}_{N+1}$. As for the operator A_+^*, we deduce from (4.32) and (4.36) that

$$\langle a^\dagger(f)\Psi_N^0|a^\dagger(g)\Psi_N^0\rangle = \langle\Psi_N^0|a(f)a^\dagger(g)|\Psi_N^0\rangle = \langle f|g\rangle - \langle\Psi_N^0|a^\dagger(g)a(f)|\Psi_N^0\rangle = \langle f|1-\gamma_N^0|g\rangle,$$

or equivalently,

$$A_+A_+^* = \mathbb{1}_{\mathcal{H}_1} - \gamma_N^0. \tag{4.39}$$

Hence, A_+^* is a bounded operator from $\mathcal{H}_1$ to $\mathcal{H}_{N+1}$, and A_+ is a bounded operator from $\mathcal{H}_{N+1}$ to $\mathcal{H}_1$. In fact, since

$$\|A_+^*f\|_{\mathcal{H}_{N+1}}^2 = \langle f|(\mathbb{1}_{\mathcal{H}_1}-\gamma_N^0)|f\rangle = \left\|(\mathbb{1}_{\mathcal{H}_1}-\gamma_N^0)f\right\|_{\mathcal{H}_1}^2,$$

it holds $\|A_+^*\|_{\mathcal{B}(\mathcal{H}_1,\mathcal{H}_{N+1})} = 1$. The following properties are obtained as a direct corollary of Proposition 4.13.

Proposition 4.28 (Properties of the particle Green's function)**.** *The family* $(G_{\rm p}(\tau))_{\tau\in\mathbb{R}}$ *defines a bounded causal operator on* $\mathcal{H}_1$*. The real and imaginary parts of its time-Fourier transform are in* $H^{-s}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ *for all* $s > 1/2$*, and are given by*

$$\mathrm{Re}\,\widehat{G_{\rm p}} = A_+ \mathrm{p.v.}\left(\frac{1}{\cdot - (H_{N+1} - E_N^0)}\right) A_+^* \quad \textit{and} \quad \mathrm{Im}\,\widehat{G_{\rm p}} = -\pi A_+ P^{H_{N+1}-E_N^0} A_+^*. \tag{4.40}$$

The analytic operator-valued function $\widetilde{G}_{\rm p}$ *defined in the upper half-plane by*

$$\forall z \in \mathbb{U}, \quad \widetilde{G_{\rm p}}(z) := A_+ \frac{1}{z - (H_{N+1} - E_N^0)} A_+^* \tag{4.41}$$

is the Laplace transform of $G_{\rm p}$ *and satisfies*

$$\widehat{G_{\rm p}} = \lim_{\eta\to 0^+} \widetilde{G_{\rm p}}(. + \mathrm{i}\eta) \quad \textit{in } H^{-s}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)) \quad \textit{for all} \quad s > 1/2.$$

The imaginary part of $\widehat{G_{\rm p}}$ is related to the so-called spectral function $\mathcal{A}_{\rm p}$ (see Section 4.3.2).

Analytic continuation to the complex plane. Let us introduce the particle optical excitation set

$$S_{\rm p} := \sigma(H_{N+1} - E_N^0). \tag{4.42}$$

We recall that the operator $H_{N+1} - E_N^0$ with domain $\mathcal{H}_{N+1} \cap H^2(\mathbb{R}^{3(N+1)})$ is self-adjoint on $\mathcal{H}_{N+1}$. Its essential spectrum is of the form $\sigma_{\rm ess}(H_{N+1} - E_N^0) = [\Sigma_{N+1}, \infty)$, and there are possibly infinitely many eigenvalues below Σ_{N+1} that can only accumulate at Σ_{N+1}. According to the HVZ theorem [Hun66, vW64, Zhi60], $\Sigma_{N+1} = E_N^0 - E_N^0 = 0$. In particular, $S_{\rm p}$ is the union of a discrete negative part, and the half-line $[0, +\infty)$.

We next infer from (4.41) that $\widetilde{G_{\rm p}}(z)$ can be extended to an analytic function from $\mathbb{C} \setminus S_{\rm p}$ to $\mathcal{B}(\mathcal{H}_1)$. This is of particular interest for the following reason. The operator-valued distribution $\widehat{G_{\rm p}}(\omega)$ is highly peaked and irregular (for instance, its imaginary part is a sum of Dirac measures on the discrete part of $S_{\rm p}$). Instead of studying $\widehat{G_{\rm p}}(\omega)$ on the real axis, we will study its analytic continuation $\widetilde{G_{\rm p}}(z)$ (defined *a priori* only in the upper-half plane, but actually on $\mathbb{C}\setminus S_{\rm p}$) *on the imaginary axis* $\mu + \mathrm{i}\mathbb{R}$, where $\mu < E_{N+1}^0 - E_N^0 \le 0$ is an admissible chemical potential (see **Hyp. 2**). The set $S_{\rm p}$ can be recovered from $\omega \mapsto \widetilde{G_{\rm p}}(\mu + \mathrm{i}\omega)$ by locating the singularities of $\widehat{G_{\rm p}}$, obtained from $\widetilde{G_{\rm p}}$ either by analytic continuation, or by fitting some parameters [RGN95]. We will not address this interesting numerical reconstruction problem.

The following lemma makes precise the behavior of the Green's function on the vertical axis $\mu + \mathrm{i}\mathbb{R}$. It is a direct consequence of the representation (4.41).

Lemma 4.29. *Consider* $\mu < E_{N+1}^0 - E_N^0$*. Then the function* $\omega \mapsto \widetilde{G_{\rm p}}(\mu + \mathrm{i}\omega)$ *is real analytic from* $\mathbb{R}_\omega$ *to* $\mathcal{B}(\mathcal{H}_1)$ *and is in* $L^p(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ *for all* $p > 1$*. Moreover, for all* $\omega \in \mathbb{R}$*,*

$$\mathrm{Re}\,\widetilde{G_{\rm p}}(\mu + \mathrm{i}\omega) = -A_+ \frac{H_{N+1} - E_N^0 - \mu}{\omega^2 + (H_{N+1} - E_N^0 - \mu)^2} A_+^*$$

is a negative, bounded, self-adjoint operator on $\mathcal{H}_1$ *which enjoys the following symmetry property:*

$$\forall \omega \in \mathbb{R}_\omega, \quad \mathrm{Re}\,\widetilde{G_{\rm p}}(\mu + \mathrm{i}\omega) = \mathrm{Re}\,\widetilde{G_{\rm p}}(\mu - \mathrm{i}\omega).$$

For any $f \in \mathcal{H}_1$*, the function* $\omega \mapsto \langle f | \mathrm{Re}\,\widetilde{G_{\rm p}}(\mu + \mathrm{i}\omega) | f\rangle$ *is non-positive, in* $L^1(\mathbb{R}_\omega)$*, and*

$$\int_{-\infty}^{+\infty} \left\langle f \left| \mathrm{Re}\,\widetilde{G_{\rm p}}(\mu + \mathrm{i}\omega) \right| f \right\rangle \mathrm{d}\omega = -\pi \langle f | (\mathbb{1}_{\mathcal{H}_1} - \gamma_N^0) | f\rangle. \tag{4.43}$$

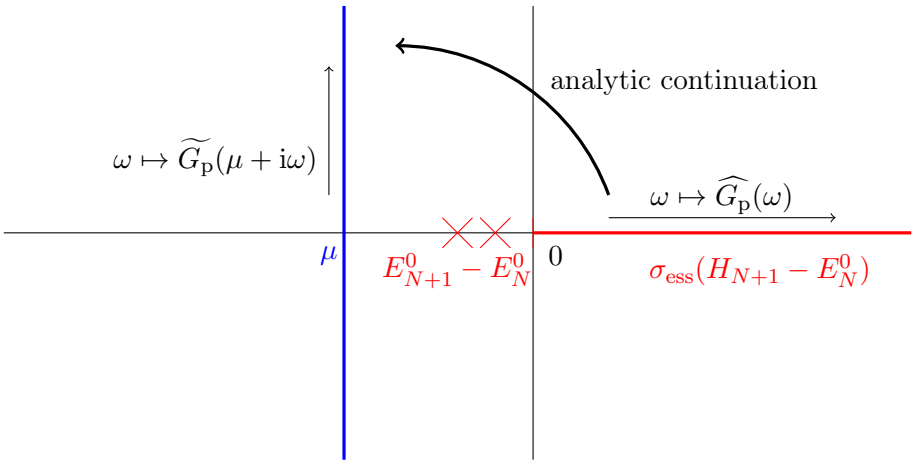

Figure 4.1 – Illustration of the analytic continuation: from $\omega \mapsto \widehat{G_{\rm p}}(\omega)$ to $\omega \mapsto \widetilde{G_{\rm p}}(\mu + {\rm i}\omega)$.

The last assertion comes from the spectral theorem, (4.39), and the equality

$$\forall E > 0, \qquad \int_{-\infty}^{+\infty} \frac{E}{\omega^2 + E^2} \, {\rm d}\omega = \pi.$$

Remark 4.30. *Unfortunately, although* $\operatorname{Re} \widetilde{G_{\rm p}}(\mu + {\rm i}\cdot)$ *has a sign and (4.43) is satisfied for all* $f \in \mathcal{H}_1$*, the function* $\omega \mapsto \left\| \operatorname{Re} \widetilde{G_{\rm p}}(\mu + {\rm i}\cdot) \right\|_{\mathcal{B}(\mathcal{H}_1)}$ *does not belong to* $L^1(\mathbb{R}_\omega)$*. This is essentially due to the fact that*

$$\sup_{E \geq 0} \left(\frac{E}{\omega^2 + E^2} \right) = \frac{1}{2\omega} \notin L^1(\mathbb{R}_\omega).$$

Note that the imaginary part of $\widetilde{G_{\rm p}}(\mu + {\rm i}\omega)$,

$$\operatorname{Im} \widetilde{G_{\rm p}}(\mu + {\rm i}\omega) = -A_+ \frac{\omega}{\omega^2 + (H_{N+1} - E^0_N - \mu)^2} A_+^*,$$

has no definite sign on $\mathbb{R}_\omega$, and that, for a generic $f \in \mathcal{H}_1$, the function $\omega \mapsto \left\langle f \left| \operatorname{Im} \widetilde{G_{\rm p}}(\mu + {\rm i}\omega) \right| f \right\rangle$ does not belong to $L^1(\mathbb{R}_\omega)$. It will therefore be more convenient in general to work with the real part of $\widetilde{G_{\rm p}}({\rm i}\omega)$ only, especially since the imaginary part can be recovered from the real part (see Lemma 4.31 below). Indeed, the operator-valued functions $\widetilde{g_{{\rm p},\eta}} : \omega \mapsto \widetilde{G_{\rm p}}(\mu - \eta + {\rm i}\omega)$ are in $L^2(\mathbb{R}, \mathcal{B}(\mathcal{H}_1))$ for any $\eta > 0$, and converge to $\widetilde{g_{\rm p}} : \omega \mapsto \widetilde{G_{\rm p}}(\mu + {\rm i}\omega)$ in $L^2(\mathbb{R}, \mathcal{B}(\mathcal{H}_1))$ as $\eta \to 0^+$. We can therefore apply Titchmarsh's theorem (see Theorem 4.9), which gives the following result.

Lemma 4.31. *Let* $\mu < E^0_{N+1} - E^0_N$*. The function* $\widehat{g_{\rm p}}(\omega) := \widetilde{G_{\rm p}}(\mu + {\rm i}\omega)$ *is the Fourier transform of the causal function*

$$g_{\rm p}(\tau) = -\Theta(\tau) A_+ {\rm e}^{-\tau(H_{N+1} - E^0_N - \mu)} A_+^*, \tag{4.44}$$

which belongs to $L^2(\mathbb{R}_\tau, \mathcal{S}(\mathcal{H}_1))$*. In particular, the Plemelj formulae hold true:*

$$\operatorname{Re} \widehat{g_{\rm p}} = -\mathfrak{H}\left(\operatorname{Im} \widehat{g_{\rm p}}\right) \quad \text{and} \quad \operatorname{Im} \widehat{g_{\rm p}} = \mathfrak{H}\left(\operatorname{Re} \widehat{g_{\rm p}}\right) \quad \text{in } L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)).$$

Moreover, the function $\tau \mapsto \|g_{\rm p}(\tau)\|_{\mathcal{B}(\mathcal{H}_1)}$ *is exponentially decreasing as* $|\tau| \to +\infty$*.*

Remark 4.32. *The exponential decay of* $g_{\rm p}$ *is consistent with the analyticity of its Fourier transform. This property is of interest when calculating numerically convolutions on the imaginary axis* $\mu + {\rm i}\mathbb{R}$*, since convolutions can be replaced, up to a Fourier transform, with point-wise multiplications of causal functions which are exponentially decreasing. This approach was advocated in [RSW+99], and is now routinely used in GW computations.*

The hole (backward) Green's function $G_{\rm h}$

Definition and first properties of the hole Green's function. Together with the particle Green's function, we introduce the hole (or backward, or advanced) Green's function, formally defined within the second quantization formalism by

$$\mathcal{G}_{\rm h}(\mathbf{r}t,\mathbf{r}'t') := \mathrm{i}\Theta(t'-t)\ \langle\Psi_N^0|\Psi_{\rm H}^\dagger(\mathbf{r}'t')\Psi_{\rm H}(\mathbf{r}t)|\Psi_N^0\rangle.$$

Observing that

$$\int_{\mathbb{R}^3}\Psi(\mathbf{r})|\Psi_N^0\rangle f(\mathbf{r})\,d\mathbf{r} = a(\overline{f})|\Psi_N^0\rangle,$$

we introduce

$$\begin{array}{rccc} A_-: & \mathcal{H}_1 & \to & \mathcal{H}_{N-1} \\ & f & \mapsto & a(\overline{f})|\Psi_N^0\rangle. \end{array}$$

Similarly as before, we note that $\mathcal{G}_{\rm h}(\mathbf{r}t,\mathbf{r}'t')$ only depends on the time difference $t-t'$. Introducing $G_{\rm h}(\mathbf{r},\mathbf{r}',\tau) := \mathcal{G}_{\rm h}(\mathbf{r}\tau,\mathbf{r}'0)$, we see that $G_{\rm h}(\mathbf{r},\mathbf{r}',\tau)$ is formally the kernel of the following one-body operator.

Definition 4.33. *The hole Green's function is defined as*

$$\boxed{G_{\rm h}(\tau) := \mathrm{i}\Theta(-\tau)A_-^*\mathrm{e}^{\mathrm{i}\tau(H_{N-1}-E_N^0)}A_-.} \tag{4.45}$$

Similarly as in (4.39), it holds that

$$A_-^*A_- = \gamma_N^0.$$

Hence, A_- is a bounded operator from $\mathcal{H}_1$ to $\mathcal{H}_{N-1}$, A_-^* is a bounded operator from $\mathcal{H}_{N-1}$ to $\mathcal{H}_1$, and it holds $\|A_-\|_{\mathcal{B}(\mathcal{H}_1,\mathcal{H}_N)} = \|A_-^*\|_{\mathcal{B}(\mathcal{H}_{N-1},\mathcal{H}_1)} \le 1$. The properties of the hole Green's function are quite similar to the properties of the particle Green's function (compare with Proposition 4.28).

Proposition 4.34 (Properties of the hole Green's function)**.** *The family $(G_{\rm h}(\tau))_{\tau\in\mathbb{R}}$ defines a bounded anti-causal operator on $\mathcal{H}_1$. The real and imaginary parts of its time-Fourier transform are in $H^{-s}(\mathbb{R}_\omega,\mathcal{B}(\mathcal{H}_1))$ for all $s>1/2$, and are given by*

$$\mathrm{Re}\,\widehat{G_{\rm h}} = A_-^*\,\mathrm{p.v.}\left(\frac{1}{\cdot-(E_N^0-H_{N-1})}\right)A_- \quad \textit{and} \quad \mathrm{Im}\,\widehat{G_{\rm h}} = \pi A_-^*P^{E_N^0-H_{N-1}}A_-. \tag{4.46}$$

The analytic operator-valued function $\widetilde{G_{\rm h}}$ defined in the lower half-plane by

$$\forall z\in\mathbb{L},\qquad \widetilde{G_{\rm h}}(z) := A_-^*\frac{1}{z-(E_N^0-H_{N-1})}A_- \tag{4.47}$$

is the Laplace transform of $G_{\rm h}$ and satisfies

$$\widehat{G_{\rm h}} = \lim_{\eta\to0^+}\widetilde{G_{\rm h}}(.-\mathrm{i}\eta) \quad \textit{in } H^{-s}(\mathbb{R}_\omega,\mathcal{B}(\mathcal{H})) \quad \textit{for all} \quad s>1/2.$$

Analytic continuation into the complex plane. The hole optical excitation set is defined as

$$S_{\rm h} := \sigma(E_N^0-H_{N-1}). \tag{4.48}$$

It is clear from (4.47) that the operator-valued function $\widetilde{G_{\rm h}}$ can be analytically continued to $\mathbb{C}\setminus S_{\rm h}$. Instead of studying the highly irregular distribution $\omega\mapsto\widehat{G_{\rm h}}(\omega)$, it is more convenient to study its analytical continuation $\widetilde{G_{\rm h}}$ on the imaginary axis $\mu+\mathrm{i}\mathbb{R}$, with $\mu > E_N^0-E_{N-1}^0$.

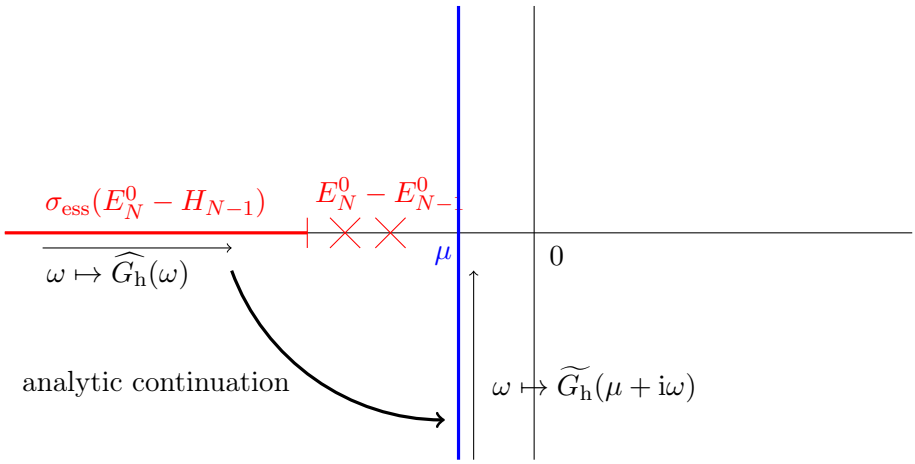

Figure 4.2 – Illustration of the analytic continuation: from $\omega \mapsto \widehat{G_{\rm h}}(\omega)$ to $\omega \mapsto \widetilde{G_{\rm h}}(\mu + {\rm i}\omega)$.

We can state a result similar to Lemma 4.29.

Lemma 4.35. *Consider $\mu > E_N^0 - E_{N-1}^0$. Then the function $\omega \mapsto \widetilde{G_{\rm h}}(\mu + {\rm i}\omega)$ is real analytic from $\mathbb{R}_\omega$ to $\mathcal{B}(\mathcal{H}_1)$ and is in $L^p(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$, for all $p > 1$. Moreover, for all $\omega \in \mathbb{R}$,*

$$\operatorname{Re} \widetilde{G_{\rm h}}(\mu + {\rm i}\omega) = A_-^* \frac{H_{N-1} + \mu - E_N^0}{\omega^2 + (E_N^0 - H_{N-1} - \mu)^2} A_-$$

is a positive, bounded, self-adjoint operator, which enjoys the following symmetry property:

$$\forall \omega \in \mathbb{R}_\omega, \quad \operatorname{Re} \widetilde{G_{\rm h}}(\mu + {\rm i}\omega) = \operatorname{Re} \widetilde{G_{\rm h}}(\mu - {\rm i}\omega).$$

For any $f \in \mathcal{H}_1$, the function $\omega \mapsto \left\langle f \left| \left| \operatorname{Re} \widetilde{G_{\rm h}}(\mu + {\rm i}\omega) \right| f \right. \right\rangle$ is non-negative, in $L^1(\mathbb{R}_\omega)$, and

$$\int_{-\infty}^{+\infty} \left\langle f \left| \operatorname{Re} \widetilde{G_{\rm h}}(\mu + {\rm i}\omega) \right| f \right\rangle \, {\rm d}\omega = \pi \langle f | \gamma_N^0 | f \rangle.$$

The Galitskii-Migdal formula. The hole Green's function is of particular interest, as it contains useful information on the N-body ground state. For instance, from the identity $A_-^* A_- = \gamma_N^0$, we directly obtain $G_{\rm h}(0^-) = {\rm i}\gamma_N^0$, so that the expectation value in the ground state of any one-body operator $\sum_{i=1}^N C_{\mathbf{r}_i}$ (for $C \in \mathcal{B}(\mathcal{H}_1)$) can be evaluated via

$$\left\langle \Psi_N^0 \left| \sum_{i=1}^N C_{\mathbf{r}_i} \right| \Psi_N^0 \right\rangle = \operatorname{Tr}_{\mathcal{H}_1} \left(C \gamma_N^0 \right) = -{\rm i} \operatorname{Tr}_{\mathcal{H}_1} (C G_{\rm h}(0^-)).$$

This calculation is valid only for one-body operators. It is not possible to obtain the expectation value in the ground state of a generic two-body operator from the one-body Green's function. This is however the case for the ground state energy (the expectation value of the two-body Hamiltonian H_N in the ground state), as was first shown by Galiskii and Migdal [GM58]. Alternative formulae for the ground state energy are provided by the Luttinger-Ward formula [LW60] and the Klein's formula [Kle61].

Theorem 4.36 (Galitskii-Migdal formula)**.** *For all $N \geq 2$, the ground state energy can be recovered as*

$$E_N^0 = \frac{1}{2} \operatorname{Tr}_{\mathcal{H}_1} \left(-A_-^* \left(H_{N-1} - E_N^0 \right) A_- + \left(-\frac{1}{2}\Delta + v_{\rm ext} \right) A_-^* A_- \right) \tag{4.49}$$

$$= \frac{1}{2} \operatorname{Tr}_{\mathcal{H}_1} \left[\left(\frac{d}{d\tau} - {\rm i} \left(-\frac{1}{2}\Delta + v_{\rm ext} \right) \right) G_{\rm h}(\tau) \Big|_{\tau = 0^-} \right]. \tag{4.50}$$

The proof of this theorem can be read in Section 4.6.10. Formula (4.50) is one way to obtain the right-hand side of (4.49), and is the one found in the original article [GM58]. There are however other ways to obtain (4.49) from the hole Green's function, without the use of derivative (which are cumbersome to evaluate numerically). One can for instance use the following equality, that we do not prove for the sake of brevity,

$$\mathrm{Tr}_{\mathcal{H}_1}\Big(A_-^*\left(H_{N-1}+\mu-E_N^0\right)A_-\Big)=\lim_{\omega\to\infty}\omega^2\mathrm{Tr}_{\mathcal{H}_1}\left(\mathrm{Re}\,\widetilde{G_{\mathrm{h}}}(\mu+\mathrm{i}\omega)\right).$$

The time-ordered Green's function G

It is often claimed in the physics literature that the main object of interest is neither the particle nor the hole Green's function, but the function

$$\mathcal{G}(\mathbf{r}t,\mathbf{r}'t')=\mathcal{G}_{\mathrm{p}}(\mathbf{r}t,\mathbf{r}'t')+\mathcal{G}_{\mathrm{h}}(\mathbf{r}t,\mathbf{r}'t'),$$

called the time-ordered Green's function, which can be seen as a convenient way to concatenate the information contained in the particle and hole Green's functions. Obviously, the time-ordered Green's function only depends on the time difference $\tau=t-t'$. In view of (4.38) and (4.45), our definition of the time-ordered Green's function therefore is the following.

Definition 4.37 (Green's function)**.** *The (time-ordered) Green's function is the family of bounded operators $(G(\tau))_{\tau\in\mathbb{R}}$ defined as $G(\tau)=G_{\mathrm{p}}(\tau)+G_{\mathrm{h}}(\tau)$, or equivalently,*

$$\boxed{G(\tau)=-\mathrm{i}\Theta(\tau)\,A_+\mathrm{e}^{-\mathrm{i}\tau(H_{N+1}-E_N^0)}A_+^*+\mathrm{i}\Theta(-\tau)\,A_-^*\mathrm{e}^{\mathrm{i}\tau(H_{N-1}-E_N^0)}A_-.}$$

The following results straightforwardly follow from Propositions 4.28 and 4.34, as well as Lemmas 4.29 and 4.35. We recall that μ is a chemical potential of the electrons for the ground state Ψ_N^0 of the reference system, and that $E_N^0-E_{N-1}^0<\mu<E_{N+1}^0-E_N^0$. In the following, we introduce some $C^\infty(\mathbb{R}_\omega)$ cut-off functions $\phi_\pm$ satisfying $0\le\phi_\pm\le1$, $\phi_++\phi_-=1$, $\mathrm{Supp}(\phi_+)\subset(E_N^0-E_{N-1}^0,+\infty)$ and $\mathrm{Supp}(\phi_-)\subset(-\infty,E_{N+1}^0-E_N^0)$ (see Figure 4.3). These cut-off functions allow us to write properties of the Green's function in the time representation without specifying whether τ is positive or negative.

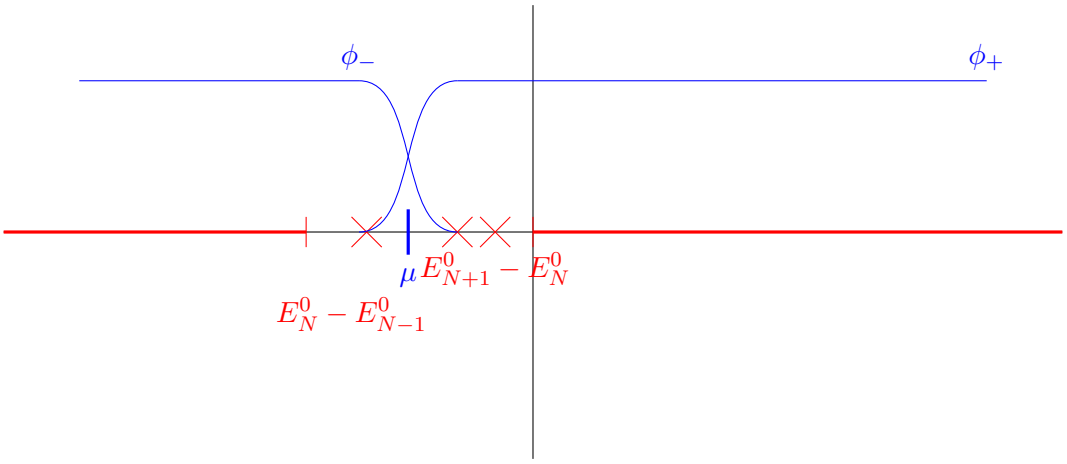

Figure 4.3 – The cut-off functions $\phi_\pm$.

Proposition 4.38 (Properties of the Green's function)**.** *The Fourier transform $\widehat{G}=\widehat{G_{\mathrm{p}}}+\widehat{G_{\mathrm{h}}}$ is in $H^{-s}(\mathbb{R}_\omega,\mathcal{B}(\mathcal{H}_1))$ for any $s>1/2$. The operator-valued analytic function $\widetilde{G}$ defined on the physical Riemann sheet $\mathbb{C}\setminus(S_{\mathrm{p}}\cup S_{\mathrm{h}})$ by*

$$\forall z\in\mathbb{C}\setminus(S_{\mathrm{p}}\cup S_{\mathrm{h}}),\qquad\widetilde{G}(z):=A_+\frac{1}{z-(H_{N+1}-E_N^0)}A_+^*+A_-^*\frac{1}{z-(E_N^0-H_{N-1})}A_-\quad(4.51)$$

is such that

$$\lim_{\eta\to 0+} \phi_\pm \widetilde{G}(\cdot \pm \mathrm{i}\eta) = \phi_\pm \widehat{G} \quad \text{in } H^{-s}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)) \quad \text{for all } s > 1/2.$$

The function $\omega \mapsto \widetilde{G}(\mu + \mathrm{i}\omega)$ *is real analytic from* $\mathbb{R}_\omega$ *to* $\mathcal{B}(\mathcal{H}_1)$*, and is in* $L^p(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ *for all* $p > 1$*. Moreover, it satisfies the symmetry property*

$$\forall \omega \in \mathbb{R}_\omega, \quad \mathrm{Re}\, \widetilde{G}(\mu + \mathrm{i}\omega) = \mathrm{Re}\, \widetilde{G}(\mu - \mathrm{i}\omega).$$

For any $f \in \mathcal{H}_1$*, the function* $\omega \mapsto \langle f | \mathrm{Re}\, \widetilde{G}(\mu + \mathrm{i}\omega) | f \rangle$ *is in* $L^1(\mathbb{R}_\omega)$*, and*

$$\int_{-\infty}^{+\infty} \left\langle f \left| \mathrm{Re}\, \widetilde{G}(\mu + \mathrm{i}\omega) \right| f \right\rangle \mathrm{d}\omega = -\pi \langle f | (\mathbb{1}_{\mathcal{H}_1} - 2\gamma_N^0) | f \rangle.$$

The spectral functions $\mathcal{A}_\mathrm{p}$, $\mathcal{A}_\mathrm{h}$ and $\mathcal{A}$

Spectral functions are essential tools to study many-body effects since they are concentrated on (subsets of) the particle and hole excitation sets.

Definition 4.39 (Spectral functions)**.** *The* particle spectral function *is the operator-valued Borel measure on* $\mathbb{R}_\omega$ *defined by*

$$\forall b \in \mathscr{B}(\mathbb{R}_\omega), \qquad \mathcal{A}_\mathrm{p}(b) = -\frac{1}{\pi} \mathrm{Im}\, \widehat{G_\mathrm{p}}(b) = A_+ P_b^{H_{N+1} - E_N^0} A_+^*. \tag{4.52}$$

The hole spectral function *is similarly defined:*

$$\forall b \in \mathscr{B}(\mathbb{R}_\omega), \qquad \mathcal{A}_\mathrm{h}(b) = \frac{1}{\pi} \mathrm{Im}\, \widehat{G_\mathrm{h}}(b) = A_-^* P_b^{E_N^0 - H_{N-1}} A_-.$$

The time-ordered spectral function *is then obtained as* $\mathcal{A} = \mathcal{A}_\mathrm{p} + \mathcal{A}_\mathrm{h}$.

With those definitions, the following lemma is straightforward, and is usually referred to as the sum-rule for spectral functions (see for instance [Far99, Section 4.5]).

Proposition 4.40. *The spectral functions* $\mathcal{A}_\mathrm{p}$*,* $\mathcal{A}_\mathrm{h}$ *and* $\mathcal{A}$ *are* $\mathcal{S}(\mathcal{H}_1)$*-valued Borel measures on* $\mathbb{R}_\omega$*, with supports contained in* S_p*,* S_h *and* $S_\mathrm{p} \cup S_\mathrm{h}$ *respectively. For all* $b \in \mathscr{B}(\mathbb{R}_\omega)$*,* $\mathcal{A}_\mathrm{p}(b)$*,* $\mathcal{A}_\mathrm{h}(b)$ *and* $\mathcal{A}(b)$ *are bounded positive self-adjoint operators on* $\mathcal{H}_1$ *with norms lower or equal to* 1*. Moreover,* $0 \leq \mathcal{A}_\mathrm{p}(b_1) \leq \mathcal{A}_\mathrm{p}(b_2)$ *as self-adjoint operators when* $b_1 \subset b_2$ *(and similar inequalities for* $\mathcal{A}_\mathrm{h}$ *and* $\mathcal{A}$*), and it holds*

$$\mathcal{A}_\mathrm{p}(\mathbb{R}_\omega) = \mathbb{1}_{\mathcal{H}_1} - \gamma_N^0, \qquad \mathcal{A}_\mathrm{h}(\mathbb{R}_\omega) = \gamma_N^0, \qquad \mathcal{A}(\mathbb{R}_\omega) = \mathbb{1}_{\mathcal{H}_1}.$$

Finally, the Plemelj formulae (4.14) allow us to recover the real part of the Green's functions from the spectral functions: $\mathrm{Re}\, \widehat{G_\mathrm{p}} = \pi \mathfrak{H}(\mathcal{A}_\mathrm{p})$ and $\mathrm{Re}\, \widehat{G_\mathrm{h}} = \pi \mathfrak{H}(\mathcal{A}_\mathrm{h})$. It therefore holds $\mathrm{Re}\, \widehat{G} = \pi \mathfrak{H} \mathcal{A}$.

4.3.3 Linear response operators

We study in this section the reducible polarizability operator χ, which can be defined from the so-called charge-fluctuation operator introduced in Section 4.3.3. We give a precise mathematical meaning to χ in Section 4.3.3, and prove Johnson's sum-rule [Joh74] for χ in Section 4.3.3. We finally define the dynamically screened Coulomb interaction operator (see Section 4.3.3).

The charge-fluctuation operator ρ_{H}

The charge-fluctuation operator is defined, within the second quantization formalism, by (see [Far99, Equation (97)])

$$\rho_{\mathrm{H}}(\mathbf{r}t) := \Psi_{\mathrm{H}}^{\dagger}(\mathbf{r}t)\Psi_{\mathrm{H}}(\mathbf{r}t) - \rho_N^0(\mathbf{r}),$$

so that the action of this operator on the N-body ground state is

$$\begin{aligned}\rho_{\mathrm{H}}(\mathbf{r}t)|\Psi_N^0\rangle &= \left(\mathrm{e}^{\mathrm{i}t(H_N - E_N^0)}\right)\Psi^{\dagger}(\mathbf{r})\Psi(\mathbf{r})|\Psi_N^0\rangle - \rho_N^0(\mathbf{r})|\Psi_N^0\rangle \\ &= \left(\mathrm{e}^{\mathrm{i}t(H_N - E_N^0)}\right)\left(\Psi^{\dagger}(\mathbf{r})\Psi(\mathbf{r}) - \rho_N^0(\mathbf{r})\right)|\Psi_N^0\rangle.\end{aligned} \tag{4.53}$$

In order to define more rigorously ρ_{H}, we need to introduce functional spaces of charge densities (the Coulomb space) and electrostatic potentials. The complex-valued Coulomb space

$$\mathcal{C} := \left\{ f \in \mathscr{S}'(\mathbb{R}^3, \mathbb{C}) \;\middle|\; \widehat{f} \in L^1_{\mathrm{loc}}(\mathbb{R}^3, \mathbb{C}),\ |\cdot|^{-1}\widehat{f}(\cdot) \in L^2(\mathbb{R}^3, \mathbb{C}) \right\}, \tag{4.54}$$

is endowed with the inner product

$$\langle f_1 | f_2 \rangle_{\mathcal{C}} = 4\pi \int_{\mathbb{R}^3} \frac{\overline{\widehat{f}_1(\mathbf{k})}\widehat{f}_2(\mathbf{k})}{|\mathbf{k}|^2}\,\mathrm{d}\mathbf{k},$$

where the normalization condition for the space-Fourier transform is chosen such that its restriction to $L^2(\mathbb{R}^3, \mathbb{C})$ is a unitary operator. The space $\mathcal{C}$ is a Hilbert space, and it holds $L^{6/5}(\mathbb{R}^3, \mathbb{C}) \hookrightarrow \mathcal{C}$ thanks to the Hardy-Littlewood-Sobolev inequality (upon rewriting the products in Fourier space as convolutions). The dual of $\mathcal{C}$ (taking $L^2(\mathbb{R}^3, \mathbb{C})$ as a pivoting space) is

$$\mathcal{C}' := \left\{ v \in L^6(\mathbb{R}^3, \mathbb{C}) \;\middle|\; \nabla v \in \left(L^2(\mathbb{R}^3, \mathbb{C})\right)^3 \right\}, \tag{4.55}$$

endowed with the inner product

$$\langle V_1 | V_2 \rangle_{\mathcal{C}'} := \frac{1}{4\pi}\int_{\mathbb{R}^3} \overline{\nabla V_1} \cdot \nabla V_2 = \frac{1}{4\pi}\int_{\mathbb{R}^3} |\mathbf{k}|^2 \overline{\widehat{V}_1(\mathbf{k})}\,\widehat{V}_2(\mathbf{k})\,\mathrm{d}\mathbf{k}.$$

We also introduce the Coulomb operator v_c, defined as the multiplication operator by $4\pi|\mathbf{k}|^{-2}$ in the Fourier representation, and its square root $v_c^{1/2}$, defined as the multiplication operator by $(4\pi)^{1/2}|\mathbf{k}|^{-1}$ in the Fourier representation. The following result, whose proof is a straightforward consequence of the above definitions, will be repeatedly used throughout this chapter.

Lemma 4.41. *The operator v_c defines a unitary operator from $\mathcal{C}$ to $\mathcal{C}'$. The operator $v_c^{1/2}$ defines a unitary operator from $\mathcal{C}$ to $\mathcal{H}_1$, as well as a unitary operator from $\mathcal{H}_1$ to $\mathcal{C}'$.*

It follows that the adjoint of the unitary operator $v_c : \mathcal{C} \to \mathcal{C}'$ is the unitary operator $v_c^* = v_c^{-1} : \mathcal{C}' \to \mathcal{C}$.

We are now able to reformulate the charge-fluctuation operator in the ground state as a well defined bounded operator. For $v \in C_c^{\infty}(\mathbb{R}^3, \mathbb{C})$, it formally holds

$$\left(\int_{\mathbb{R}^3}\left(\Psi^{\dagger}(\mathbf{r})\Psi(\mathbf{r}) - \rho_N^0(\mathbf{r})\right)|\Psi_N^0\rangle\, v(\mathbf{r})\mathrm{d}\mathbf{r}\right)(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \left[\left(\sum_{i=1}^N v(\mathbf{r}_i)\right) - \int_{\mathbb{R}^3} v\rho_N^0\right]\Psi_N^0(\mathbf{r}_1, \ldots \mathbf{r}_N).$$

In order to rewrite more rigorously this equality, we introduce the operator

$$\begin{aligned} B : \quad \mathcal{C}' &\to \mathcal{H}_N \\ v &\mapsto \left[\left(\sum_{i=1}^N v(\mathbf{r}_i)\right) - \langle v, \rho_N^0\rangle_{\mathcal{C}',\mathcal{C}}\right]|\Psi_N^0\rangle, \end{aligned} \tag{4.56}$$

which is well defined since $\rho_N^0 \in L^{6/5}(\mathbb{R}^3,\mathbb{R})$ by Proposition 4.26. In fact, as made clear in Lemma 4.42 below, B is bounded. In view of (4.53), we can finally define the application to Ψ_N^0 of the charge-fluctuation operator $\rho_{\rm H}(t)$ as follows:

$$\rho_{\rm H}(t)|\Psi_N^0\rangle = \mathrm{e}^{\mathrm{i}t(H_N-E_N^0)}B. \tag{4.57}$$

Let us conclude this section by giving some properties of the operators introduced above (see Section 4.6.11 for the proof).

Lemma 4.42. *The operator B defined by (4.56) is a bounded operator from $\mathcal{C}'$ to $\mathcal{H}_N$. Its adjoint B^* is a bounded operator from $\mathcal{H}_N$ to $\mathcal{C}'$ which satisfies $B^*|\Psi_N^0\rangle = 0$. As a consequence, $\rho_{\rm H}|\Psi_N^0\rangle \in L^\infty(\mathbb{R}_t,\mathcal{B}(\mathcal{C}',\mathcal{H}_N))$, and $\big(\rho_{\rm H}|\Psi_N^0\rangle\big)^* \in L^\infty(\mathbb{R}_t,\mathcal{B}(\mathcal{H}_N,\mathcal{C}'))$.*

The (symmetrized) reducible polarizability operator χ

Definition of the reducible polarizability operator. The reducible polarizability operator $\chi(t,t')$ is the operator giving the response of the density of the system to perturbations of the external potential. It is formally defined by its kernel (see [Far99, Equation (96)])

$$\chi(\mathbf{r}t,\mathbf{r}'t') := -\mathrm{i}\left\langle \Psi_N^0\right| \mathcal{T}\left\{\rho_{\rm H}(\mathbf{r}t)\rho_{\rm H}(\mathbf{r}'t')\right\}\left|\Psi_N^0\right\rangle_{\mathcal{H}_N}. \tag{4.58}$$

In the above equation, $\rho_{\rm H}$ is the charge-fluctuation operator whose action on Ψ_N^0 is defined by (4.57), and $\mathcal{T}$ stands for the bosonic time-ordering operator:

$$\mathcal{T}\left\{A_1(t)A_2(t')\right\} = \begin{cases} A_1(t)A_2(t') & \text{if } t'<t,\\ A_2(t')A_1(t) & \text{if } t'>t.\end{cases}$$

In view of (4.57), the definition (4.58) of the kernel is formally equivalent to the following identity, stated for $t'<t$ (a similar equality being true for $t'>t$):

$$\begin{aligned}\int_{\mathbb{R}^3}\overline{f}\,(\chi(t,t')g) &= -\mathrm{i}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\overline{f}(\mathbf{r})\left\langle\Psi_N^0\right|\rho_{\rm H}(\mathbf{r}t)\rho_{\rm H}(\mathbf{r}'t')\left|\Psi_N^0\right\rangle_{\mathcal{H}_N} g(\mathbf{r}')\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\\ &= -\mathrm{i}\left\langle\int_{\mathbb{R}^3} f(\mathbf{r})\rho_{\rm H}(\mathbf{r}t)\Psi_N^0\,\mathrm{d}\mathbf{r}\,\middle|\,\int_{\mathbb{R}^3} g(\mathbf{r}')\rho_{\rm H}(\mathbf{r}'t')\Psi_N^0\,\mathrm{d}\mathbf{r}'\right\rangle_{\mathcal{H}_N}\\ &= -\mathrm{i}\left\langle \mathrm{e}^{\mathrm{i}t(H_N-E_N^0)}Bf\,\middle|\,\mathrm{e}^{\mathrm{i}t'(H_N-E_N^0)}Bg\right\rangle_{\mathcal{H}_N}\\ &= -\mathrm{i}\left\langle f\,\middle|\,B^*\mathrm{e}^{-\mathrm{i}(t-t')(H_N-E_N^0)}Bg\right\rangle_{\mathcal{C}'}.\end{aligned}$$

In order to interpret χ as giving the variation of the ground state density (an element of $\mathcal{C}$) generated by a variation of the external potential (an element of $\mathcal{C}'$), we rewrite the scalar product in $\mathcal{C}'$ as a duality braket between $\mathcal{C}'$ and $\mathcal{C}$:

$$\langle f_1\,|f_2\rangle_{\mathcal{C}'} = \langle\overline{f_1}, v_c^{-1}f_2\rangle_{\mathcal{C}',\mathcal{C}}. \tag{4.59}$$

This motivates defining $\chi(t,t')$ as the bounded operator from $\mathcal{C}'$ to $\mathcal{C}$ given by

$$\chi(t,t') = -\mathrm{i}v_c^{-1}B^*\mathrm{e}^{-\mathrm{i}|t-t'|(H_N-E_N^0)}B.$$

In particular, $\chi(t,t')$ only depends on the time difference $t-t'$, and we write in the sequel $\chi(\tau) := \chi(\tau,0)$:

$$\boxed{\chi(\tau) = -\mathrm{i}v_c^{-1}B^*\mathrm{e}^{-\mathrm{i}|\tau|(H_N-E_N^0)}B.} \tag{4.60}$$

It turns out to be useful to symmetrize the action of the polarizability operator using appropriate Coulomb operators. We recall that it holds $Bv_c^{1/2} \in \mathcal{B}(\mathcal{H}_1,\mathcal{H}_N)$ while $(Bv_c^{1/2})^* = v_c^{-1/2}B^* \in \mathcal{B}(\mathcal{H}_N,\mathcal{H}_1)$.

Definition 4.43. *The symmetrized reducible polarizability operator* $\chi_{\rm sym} \in L^\infty(\mathbb{R}_\tau, \mathcal{B}(\mathcal{H}_1))$ *is defined by* $\chi_{\rm sym}(\tau) = v_c^{1/2}\chi(\tau)v_c^{1/2}$, *or equivalently,*

$$\boxed{\chi_{\rm sym}(\tau) = -\mathrm{i}v_c^{-1/2}B^*\mathrm{e}^{-\mathrm{i}|\tau|(H_N-E_N^0)}Bv_c^{1/2}.}$$

It is convenient to decompose the symmetrized reducible polarizability operator into two parts, namely its causal part and its anti-causal part:

$$\chi_{\rm sym}(\tau) = \chi^+_{\rm sym}(\tau) + \chi^-_{\rm sym}(\tau) \quad \text{with} \quad \chi^\pm_{\rm sym}(\tau) = \Theta(\pm\tau)\left(-\mathrm{i}v_c^{-1/2}B^*\mathrm{e}^{-\mathrm{i}|\tau|(H_N-E_N^0)}Bv_c^{1/2}\right). \tag{4.61}$$

In the above expression, the Hamiltonian H_N can be replaced by

$$H_N^\sharp := H_N\big|_{\{\Psi_N^0\}^\perp}.$$

This is a consequence of Lemma 4.42 which shows that $\mathrm{Ran}\,(B) \subset \{\Psi_N^0\}^\perp$. Note that $H_N^\sharp - E_N^0 \geq E_N^1 - E_N^0$.

Properties of the symmetrized reducible polarizability operator. As rigorously stated below, the symmetrized polarizability operator has singularities at the energy differences corresponding to excitation energies for a system with a fixed number N of electrons, called neutral excitations in [Far99, Section 8]. We therefore introduce the neutral excitation set

$$S_0^+ := \sigma(H_N - E_N^0) \setminus \{0\} = \sigma\left(H_N^\sharp - E_N^0\right),$$

its reflection $S_0^- := -S_0^+$ and $S_0 := S_0^+ \cup S_0^-$. Note that $S_0^+ \subset [E_N^1 - E_N^0, +\infty)$ so that $S_0^- \cap S_0^+ = \emptyset$.

As for Proposition 4.38, it turns out to be convenient to introduce appopriate cut-off functions. Consider $\phi_\pm^1$ such that ϕ_-^1 and ϕ_+^1 are in $C^\infty(\mathbb{R}_\omega)$ and satisfy $0 \leq \phi_\pm^1 \leq 1$, $\phi_+^1 + \phi_-^1 = 1$, $\mathrm{Supp}(\phi_+^1) \subset (-(E_N^1 - E_N^0), +\infty)$ and $\mathrm{Supp}(\phi_-^1) \subset (-\infty, E_N^1 - E_N^0)$ (see Figure 4.4).

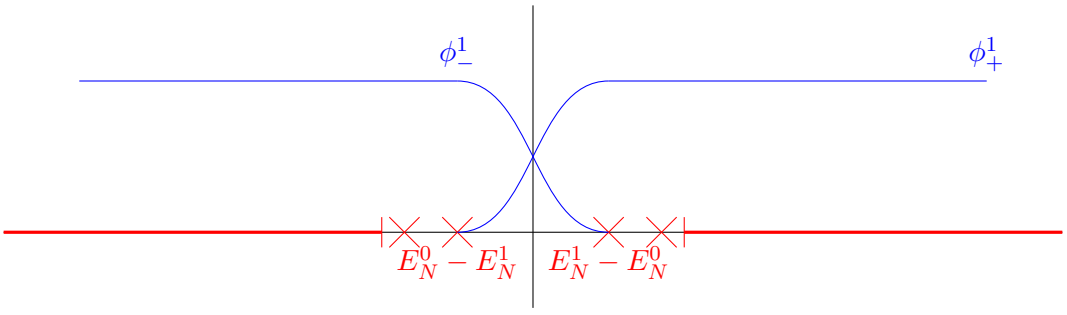

Figure 4.4 – The cut-off functions $\phi_\pm^1$.

Proposition 4.44. *The symmetrized reducible polarizability operator* $\chi_{\rm sym}$ *satisfies the following properties:*

(1) $(\chi^+_{\rm sym}(\tau))_{\tau\in\mathbb{R}}$ *is a bounded causal operator on* $\mathcal{H}_1$ *while* $(\chi^-_{\rm sym}(\tau))_{\tau\in\mathbb{R}}$ *is a bounded anti-causal operator on* $\mathcal{H}_1$. *They satisfy the following symmetry properties:*

$$\forall \tau \in \mathbb{R}, \quad \chi_{\rm sym}(-\tau) = \chi_{\rm sym}(\tau) \quad \textit{and} \quad \chi^+_{\rm sym}(\tau) = \chi^-_{\rm sym}(-\tau); \tag{4.62}$$

(2) the real and imaginary parts of the time-Fourier transforms of $\chi^+_{\rm sym}, \chi^-_{\rm sym}$ *are respectively given by*

$$\widehat{\mathrm{Re}\,\chi^{\pm}_{\rm sym}} = \pm v_c^{-1/2} B^* \mathrm{p.v.} \left(\frac{1}{\cdot \mp (H_N^\sharp - E_N^0)} \right) B v_c^{1/2},$$

and

$$\widehat{\mathrm{Im}\,\chi^{\pm}_{\rm sym}} = -\pi v_c^{-1/2} B^* P^{\pm(H_N^\sharp - E_N^0)} B v_c^{1/2}.$$

In particular, $\mathrm{Supp}\left(\widehat{\mathrm{Im}\,\chi^{\pm}_{\rm sym}}\right) \subset S_0^\pm$ *and* $\mathrm{Supp}\left(\widehat{\mathrm{Im}\,\chi_{\rm sym}}\right) \subset S_0$*;*

(3) consider the $\mathcal{B}(\mathcal{H}_1)$*-valued analytic functions* $\widetilde{\chi^+_{\rm sym}}$, $\widetilde{\chi^-_{\rm sym}}$ *and* $\widetilde{\chi_{\rm sym}}$ *respectively defined by*

$$\forall z \in \mathbb{C} \setminus S_0^\pm, \qquad \widetilde{\chi^{\pm}_{\rm sym}}(z) := \pm v_c^{-1/2} B^* \frac{1}{z \mp (H_N^\sharp - E_N^0)} B v_c^{1/2},$$

and

$$\forall z \in \mathbb{C} \setminus S_0, \qquad \widetilde{\chi_{\rm sym}}(z) := \widetilde{\chi^+_{\rm sym}}(z) + \widetilde{\chi^-_{\rm sym}}(z) = -v_c^{-1/2} B^* \frac{2(H_N^\sharp - E_N^0)}{(H_N^\sharp - E_N^0)^2 - z^2} B v_c^{1/2}. \tag{4.63}$$

It holds

$$\forall z \in \mathbb{C} \setminus S_0^+, \qquad \widetilde{\chi^+_{\rm sym}}(z) = \widetilde{\chi^-_{\rm sym}}(-z) = \left(\widetilde{\chi^+_{\rm sym}}(\overline{z})\right)^*$$

and

$$\forall z \in \mathbb{C} \setminus S_0, \quad \widetilde{\chi_{\rm sym}}(z) = \widetilde{\chi_{\rm sym}}(-z) = \left(\widetilde{\chi_{\rm sym}}(\overline{z})\right)^*.$$

The functions $\widetilde{\chi^+_{\rm sym}}|_{\mathbb{U}}$ *and* $\widetilde{\chi^-_{\rm sym}}|_{\mathbb{L}}$ *are respectively the Laplace transforms of* $\chi^+_{\rm sym}$ *and* $\chi^-_{\rm sym}$*, and the following convergences hold in* $H^{-s}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ *for all* $s > 1/2$*:*

$$\lim_{\eta \to 0^+} \widetilde{\chi^{\pm}_{\rm sym}}(\cdot \pm \mathrm{i}\eta) = \widehat{\chi^{\pm}_{\rm sym}}, \qquad \lim_{\eta \to 0^+} \phi^1_\pm \widetilde{\chi_{\rm sym}}(\cdot \pm \mathrm{i}\eta) = \phi^1_\pm \widehat{\chi_{\rm sym}};$$

(4) for all $\omega \in \left(-(E_N^1 - E_N^0), E_N^1 - E_N^0\right)$, $\widetilde{\chi_{\rm sym}}(\omega) = \widehat{\chi_{\rm sym}}(\omega)$ *is a negative bounded self-adjoint operator on* $\mathcal{H}_1$*;*

(5) for all $\omega \in \mathbb{R}$, $\widetilde{\chi_{\rm sym}}(\mathrm{i}\omega)$ *is a negative bounded self-adjoint operator on* $\mathcal{H}_1$*.*

We omit the proof of Proposition 4.44 since the first three assertions are similar to those of Lemma 4.38, while the last two ones are direct consequences of (4.63).

On the integrability of $\widetilde{\chi_{\rm sym}}(\mathrm{i}\omega)$**.** As for the Green's function, $\omega \mapsto \widehat{\chi_{\rm sym}}(\omega)$ is difficult to study on the real-axis, and it is more convenient to study its analytical continuation $\widetilde{\chi_{\rm sym}}$ on the imaginary axis $\mathrm{i}\mathbb{R}$. This is possible thanks to the existence of the gap $(-(E_N^1 - E_N^0), E_N^1 - E_N^0)$ around 0. The representation provided in Proposition 4.44 allows one to directly deduce the integrability properties of the functions $\omega \mapsto \widetilde{\chi_{\rm sym}}(\mathrm{i}\omega)$ (as in Lemma 4.29).

Corollary 4.45. *The functions* $\omega \mapsto \widetilde{\chi^{\pm}_{\rm sym}}(\mathrm{i}\omega)$ *are real-analytic from* $\mathbb{R}_\omega$ *to* $\mathcal{S}(\mathcal{H}_1)$*, and are in* $L^p(\mathbb{R}_\omega, \mathcal{S}(\mathcal{H}_1))$ *for all* $p > 1$*. For any* $f \in \mathcal{H}_1$*, the function* $\omega \mapsto \langle f | \widetilde{\chi_{\rm sym}}(\mathrm{i}\omega) | f \rangle$ *is non-positive and in* $L^1(\mathbb{R}_\omega)$*, and it holds*

$$\int_{-\infty}^{+\infty} \langle f | \widetilde{\chi_{\rm sym}}(\mathrm{i}\omega) | f \rangle \mathrm{d}\omega = -2\pi \left\| B v_c^{1/2} f \right\|_{\mathcal{H}_N}^2. \tag{4.64}$$

The sum-rule for the reducible polarizability operator χ

The behavior of the reducible polarizability operator in the high imaginary-frequency regime is well understood. This asymptotic behavior is given by the so-called Johnson's sum-rule [Joh74] or f-sum rule, the latter terminology being motivated in [Far99, Section 8.8] by the fact that it can formally be seen as some equality involving the first moment of $\mathrm{Im}\widehat{\chi_{\mathrm{sym}}}$. Knowing the large-$\omega$ behavior of $\widetilde{\chi_{\mathrm{sym}}}$ is important to design appropriate approximate operators, used in plasmon-pole models to avoid the numerical inversion of the dielectric operator (which is computationally expensive).

The fifth point of Proposition 4.44 implies that for all $\omega \in \mathbb{R}_\omega$, the operator

$$-\widetilde{\chi}(\mathrm{i}\omega) := -v_c^{-1/2}\widetilde{\chi_{\mathrm{sym}}}(\mathrm{i}\omega)v_c^{-1/2}$$

defines a symmetric, continuous, non-negative sesquilinear form on $\mathcal{C}'$:

$$\forall (f,g) \in \mathcal{C}' \times \mathcal{C}', \qquad \langle \overline{f}, -\widetilde{\chi}(\mathrm{i}\omega)g\rangle_{\mathcal{C}',\mathcal{C}} = \left\langle Bf \middle| \frac{2(H_N^\sharp - E_N^0)}{(H_N^\sharp - E_N^0)^2 + \omega^2} \middle| Bg \right\rangle_{\mathcal{H}_N},$$

so that, formally,

$$\lim_{\omega\to\pm\infty} \langle \overline{f}, -\omega^2\widetilde{\chi}(\mathrm{i}\omega)g\rangle_{\mathcal{C}',\mathcal{C}} = 2\langle Bf|H_N^\sharp - E_N^0|Bg\rangle_{\mathcal{H}_N} = 2\left\langle \overline{f}, v_c^{-1}B^*\left(H_N^\sharp - E_N^0\right)Bg\right\rangle_{\mathcal{C}',\mathcal{C}}.$$

The following theorem, whose proof is postponed until Section 4.6.12, confirms that this limit exists and allows one to identify it.

Theorem 4.46 (Johnson's sum rule)**.** *The operator $2v_c^{-1}B^*(H_N^\sharp - E_N^0)B$ is bounded from $\mathcal{C}'$ to $\mathcal{C}$, and $2v_c^{-1}B^*(H_N^\sharp - E_N^0)B = -\mathrm{div}\left(\rho_N^0\nabla\cdot\right)$. Moreover, the following weak convergence holds:*

$$\forall (f,g) \in \mathcal{C}' \times \mathcal{C}', \qquad \lim_{\omega\to\pm\infty} \left\langle \overline{f}, -\omega^2\widetilde{\chi}(\mathrm{i}\omega)g\right\rangle_{\mathcal{C}',\mathcal{C}} = \left\langle \overline{f}, -\mathrm{div}\left(\rho_N^0\nabla g\right)\right\rangle_{\mathcal{C}',\mathcal{C}} = \int_{\mathbb{R}^3} \rho_N^0 \overline{\nabla f}\cdot\nabla g.$$

For all $g \in \mathcal{C}'$ such that $\Delta g \in L^2(\mathbb{R}^3)$, the following strong convergence holds:

$$\lim_{\omega\to\pm\infty} \omega^2\widetilde{\chi}(\mathrm{i}\omega)g = \mathrm{div}\left(\rho_N^0\nabla g\right) \quad \text{in } \mathcal{C}.$$

The dynamically screened interaction operator W

As the name indicates, the two key operators in the GW method are on the one hand, the time-ordered Green's function G, and on the other hand, the so-called *dynamically screened interaction* operator W. The latter operator is defined as

$$\boxed{W(\tau) = v_c\delta_0(\tau) + v_c^{1/2}\chi_{\mathrm{sym}}(\tau)v_c^{1/2},} \tag{4.65}$$

where v_c is the Coulomb operator introduced in Lemma 4.41. It is convenient to split W into a local-in-time exchange contribution $v_c\delta_0(\tau)$ (although this is not obvious at this stage, (4.98) below shows that $v_c\delta_0(\tau)$ can be interpreted as an exchange term), and a nonlocal-in-time correlation contribution:

$$W(\tau) = v_c\delta_0(\tau) + W_{\mathrm{c}}(\tau) \quad \text{with} \quad W_{\mathrm{c}}(\tau) := v_c\chi(\tau)v_c = v_c^{1/2}\chi_{\mathrm{sym}}(\tau)v_c^{1/2}. \tag{4.66}$$

The properties of the operator $W_c(\tau) \in \mathcal{B}(\mathcal{C},\mathcal{C}')$ therefore readily follow from the properties of the operators $v_c^{1/2}$ and $\chi_{\mathrm{sym}}(\tau)$ established in Lemma 4.41 and Proposition 4.44.

4.3.4 The self-energy operator Σ

We give in this section the definition of the self-energy operator Σ using the Dyson equation (see (4.72) below). Let us emphasize that, while the Dyson equation provides a definition of Σ in terms of Green's functions, numerical methods work the other way round: an approximation of the Green's function G is obtained from the Dyson equation (4.72), using an approximation of the self-energy operator Σ. This approach is made precise in Section 4.4.

The non-interacting Hamiltonian H_0 and associated Green's function G_0

The self-energy operator is defined as the difference between the inverse of the exact Green's function G and the inverse of some reference Green's function G_0. The reference Green's function is the resolvent of a mean-field non-interacting Hamiltonian. There are several possible choices for this operator, discussed in Remark 4.49 below. In order to remain as general as possible, we introduce a one-body operator h_1 acting on $\mathcal{H}_1$, with domain $H^2(\mathbb{R}^3)$, real-valued (in the sense that $h\psi$ is real-valued whenever ψ is real-valued), and such that $\sigma_{\rm ess}(h_1) = [0, \infty)$. The corresponding effective non-interacting N-body Hamiltonian is defined on $\mathcal{H}_N$ by

$$H_{0,N} = \sum_{i=1}^{N} h_1(\mathbf{r}_i).$$

We define

$$\varepsilon_k := \inf_{V_k \subset \mathcal{V}_k} \sup_{v \in V_k \setminus \{0\}} \frac{\langle v|h_1|v\rangle}{\langle v|v\rangle},$$

where $\mathcal{V}_k$ is the set of the subspaces of $H^1(\mathbb{R}^3)$ of dimension k. Recall that $\varepsilon_k \leq 0$ and that if $\varepsilon_k < 0$, then h_1 has at least k negative eigenvalues (counting multiplicities) and ε_k is the $k^{\rm th}$ smallest eigenvalue of h_1 (still counting multiplicities). We make the following assumption in the sequel.

Hyp. 3: The one-body Hamiltonian h_1 has at least N negative eigenvalues, and $\varepsilon_N < \varepsilon_{N+1}$.

This assumption implies that there is a gap between the $N^{\rm th}$ eigenvalue and the $(N+1)^{\rm st}$ eigenvalue (or the bottom of the essential spectrum if h_1 has only N non-positive eigenvalues).

Let us denote by $(\phi_1, \cdots, \phi_N)$ an orthonormal family of eigenvectors of h_1 associated with the eigenvalues $\varepsilon_1, \cdots, \varepsilon_N$. Without loss of generality, we can assume that the ϕ_k's are real-valued. The ground state energy of $H_{0,N}$ is $E^0_{0,N} = \varepsilon_1 + \ldots + \varepsilon_N$. The condition $\varepsilon_N < \varepsilon_{N+1}$ ensures that $E^0_{0,N}$ is a non-degenerate eigenvalue of $H_{0,N}$ and that the normalized ground state $\Phi^0_N = \phi_1 \wedge \cdots \wedge \phi_N$ of $H_{0,N}$ is unique up to a global phase. We introduce the one-body mean-field density matrix

$$\gamma^0_{0,N}(\mathbf{r}, \mathbf{r}') := \sum_{k=1}^{N} \phi_k(\mathbf{r})\phi_k(\mathbf{r}'). \tag{4.67}$$

This function can be seen as the kernel of the spectral projector $\mathbb{1}_{(-\infty,\mu_0)}(h_1)$, where μ_0 is any real number in the range $(\varepsilon_N, \varepsilon_{N+1})$ (it is an admissible Fermi level for the ground state of the non-interacting effective Hamiltonian $H_{0,N}$). The density of the non-interacting system is denoted by $\rho^0_{0,N}$. Results similar to the ones stated in Proposition 4.26 for $\rho^0_{0,N}$, $\gamma^0_{0,N}$, ... hold true. Finally, similarly as in Section 4.3.2, we introduce

$$A^*_{0,+}(f) = a^\dagger(f)|\Phi^0_N\rangle \quad \text{and} \quad A_{0,-}(f) = a(\overline{f})|\Phi^0_N\rangle.$$

Definition 4.47 (Reference non-interacting Green's functions)**.** *The reference particle, hole and time-ordered non-interacting Green's functions are respectively defined as*

$$G_{0,\rm p}(\tau) = -\mathrm{i}\Theta(\tau)A_{0,+}\mathrm{e}^{-\mathrm{i}\tau(H_{0,N+1}-E^0_{0,N})}A^*_{0,+}, \qquad G_{0,\rm h}(\tau) = \mathrm{i}\Theta(-\tau)A^*_{0,-}\mathrm{e}^{\mathrm{i}\tau(H_{0,N-1}-E^0_{0,N})}A_{0,-},$$

and $G_0(\tau) = G_{0,\rm p}(\tau) + G_{0,\rm h}(\tau)$.

Results similar to Propositions 4.28, 4.34 and 4.38 hold for these operators, but we do not write them explicitly for the sake of brevity. However, it should be noted that, in the non-interacting case, the Green's functions have simple explicit expressions in terms of h_1 (see Section 4.6.13 for the proof).

Proposition 4.48. *It holds*

$$\boxed{G_{0,\mathrm{p}}(\tau) = -\mathrm{i}\Theta(\tau)\left(\mathbb{1}_{\mathcal{H}_1} - \gamma^0_{0,N}\right)\mathrm{e}^{-\mathrm{i}\tau h_1}} \quad \text{and} \quad \boxed{G_{0,\mathrm{h}}(\tau) = \mathrm{i}\Theta(-\tau)\gamma^0_{0,N}\mathrm{e}^{-\mathrm{i}\tau h_1}.}$$

In particular, for any $z \in \mathbb{C} \setminus \sigma(h_1)$,

$$\widetilde{G_{0,\mathrm{p}}}(z) = \left(\mathbb{1}_{\mathcal{H}_1} - \gamma^0_{0,N}\right)(z - h_1)^{-1} \quad \text{and} \quad \widetilde{G_{0,\mathrm{h}}}(z) = \gamma^0_{0,N}(z - h_1)^{-1}. \tag{4.68}$$

Hence,

$$\widetilde{G_0}(z) = (z - h_1)^{-1} \tag{4.69}$$

is the resolvent of the one-body operator h_1.

Remark 4.49 (On the choice of G_0)**.** *There are several possible choices for the one-body operator h_1, although this choice is not really properly discussed in the literature to our knowledge. The first option, which is used in the original derivation of the GW method [Hed65], consists in choosing*

$$h_1 = -\frac{1}{2}\Delta + v_{\mathrm{ext}} + \rho^0_N * |\cdot|^{-1}, \tag{4.70}$$

where ρ^0_N is the exact ground state density. Another option (see for instance [Far99, page 112]) is to consider a one-body operator whose associated ground state density is (as close as possible to) the exact ground state density ρ^0_N. The motivation is that, in this case, the self-energy should be smaller. The Kohn-Sham [KS65] model formally satisfies this requirement. The associated one-body operator reads

$$h_1 = -\frac{1}{2}\Delta + v_{\mathrm{ext}} + \rho^0_N * |\cdot|^{-1} + v_{\mathrm{xc}}\left[\rho^0_N\right], \tag{4.71}$$

where v_{xc} is the (exact) exchange-correlation potential. In practice, approximations of ρ^0_N and $v_{\mathrm{xc}}\left[\rho^0_N\right]$ are computed by means of a Kohn-Sham LDA or GGA calculation [KS65, PBE96]. This is believed to provide a sufficiently accurate approximation of the exact ground state density which does not spoil the results subsequently obtained by GW calculations.

The dynamical Hamiltonian $\widetilde{H}(z)$

In view of (4.69), it is natural to introduce the inverse of the time-ordered Green's function, which will correspond to some dynamical one-body Hamiltonian. More precisely, we would like to define, at least for each $z \in \mathbb{C} \setminus \mathbb{R}$, a one-body operator $\widetilde{H}(z)$ such that

$$\widetilde{G}(z) := \left(z - \widetilde{H}(z)\right)^{-1}, \quad \text{or equivalently,} \quad \widetilde{H}(z) = z - \left(\widetilde{G}(z)\right)^{-1}.$$

The following proposition, proved in Section 4.6.14, shows that such a definition makes sense.

Proposition 4.50. *Let $z \in \mathbb{C} \setminus \mathbb{R}$. The operator $\widetilde{G}(z)$ is an invertible operator from $\mathcal{H}_1$ onto some vector subspace $\widetilde{D}(z)$ of $\mathcal{H}_1$. Moreover, $\widetilde{D}(z)$ is dense in $\mathcal{H}_1$, $\widetilde{D}(z) \subset H^2(\mathbb{R}^3)$, and $\widetilde{H}(z)$ is a well-defined closed operator with domain $\widetilde{D}(z)$.*

Remark 4.51. *We do not know whether the equality $\widetilde{D}(z) = H^2(\mathbb{R}^3)$ is true, nor do we know whether $\widetilde{D}(z_1) = \widetilde{D}(z_2)$ for $z_1 \neq z_2$.*

Definition of the self-energy operator Σ from the Dyson equation

We are now able to define the exact self-energy operator $\widetilde{\Sigma}$ via the Dyson equation. Note that we do not define the self-energy in the time domain, but consider only $\widetilde{\Sigma}(z)$ (as in [Far99, Section 5.1]).

Definition 4.52 (Self-energy)**.** *The self-energy operator is defined as*

$$\boxed{\forall z \in \mathbb{C} \setminus \mathbb{R}, \qquad \widetilde{\Sigma}(z) := \widetilde{G_0}(z)^{-1} - \widetilde{G}(z)^{-1} = (z - h_1) - \left(z - \widetilde{H}(z)\right) = \widetilde{H}(z) - h_1,} \tag{4.72}$$

where h_1 is the one-body mean-field Hamiltonian introduced in Section 4.3.4.

The operator $\widetilde{\Sigma}(z)$ is the difference between the one-body dynamical Hamiltonian and the reference one-body mean-field Hamiltonian h_1. With this writing, $\widetilde{\Sigma}(z)$ can be seen as the correction term to be added to the reference one-body Hamiltonian in order to obtain the dynamical mean-field one-body Hamiltonian:

$$\widetilde{H}(z) = h_1 + \widetilde{\Sigma}(z).$$

4.4 The GW approximation for finite systems

4.4.1 G_0W^0, self-consistent GW^0, self-consistent GW, and all that

The GW equations

We now turn to the GW approximation for finite systems. The purpose of the GW approximation is to estimate the time-ordered Green's function G via the Dyson formula (4.72). Instead of using (4.72) to define the self-energy $\widetilde{\Sigma}(z)$, we use this equation *with some approximation* $\widetilde{\Sigma}^{\mathrm{GW}}(z)$ *of* $\widetilde{\Sigma}(z)$ to obtain an approximation $\widetilde{G}^{\mathrm{GW}}(z)$ of the time-ordered Green's function via

$$\left(\widetilde{G}^{\mathrm{GW}}\right)^{-1}(z) = z - \left(h_1 + \widetilde{\Sigma}^{\mathrm{GW}}(z)\right). \tag{4.73}$$

Using the Dyson equation to *define* the time-ordered Green's function is only possible if an alternative expression of the self-energy operator is available. Such an expression was formally obtained by Hedin in 1965 (see [Hed65]). The GW approximation consists in replacing the so-called vertex function in Hedin's equations by a tensor product of Dirac masses.

The original GW equations were derived on the time domain and on the frequency domain. However, as noticed several times in Section 4.3, the operators involved in the GW equations are not smooth on these axes. It turns out that it is formally possible to recast the equations on some imaginary axis using Theorem 4.24. This approach, first introduced by Rojas, Godby and Needs [RGN95] (see also [RSW+99]), is now known under the name of the "analytic continuation method". For reasons that we will explain throughout this section, these equations are recast as follows within our mathematical framework.

Definition 4.53 (GW equations on the imaginary axis of the frequency domain)**.**
Find $\widetilde{G^{\mathrm{GW}}}(\mu+\mathrm{i}\cdot) \in L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}))$ *solution to the system*

$$\widetilde{P^{\mathrm{GW}}_{\mathrm{sym}}}(\mathrm{i}\omega) = \frac{1}{2\pi} v_c^{1/2} \left(\int_{-\infty}^{\infty} \widetilde{G^{\mathrm{GW}}}\big(\mu + \mathrm{i}(\omega+\omega')\big) \odot \widetilde{G^{\mathrm{GW}}}(\mu+\mathrm{i}\omega')\,\mathrm{d}\omega' \right) v_c^{1/2}, \tag{4.74a}$$

$$\widetilde{\chi^{\mathrm{GW}}_{\mathrm{sym}}}(\mathrm{i}\omega) = \Big(\mathbb{1}_{\mathcal{H}} - \widetilde{P^{\mathrm{GW}}_{\mathrm{sym}}}(\mathrm{i}\omega)\Big)^{-1} - \mathbb{1}_{\mathcal{H}_1}, \tag{4.74b}$$

$$\widetilde{W_c^{\mathrm{GW}}}(\mathrm{i}\omega) = v_c^{1/2} \widetilde{\chi^{\mathrm{GW}}_{\mathrm{sym}}}(\mathrm{i}\omega) v_c^{1/2}, \tag{4.74c}$$

$$\widetilde{\Sigma^{\mathrm{GW}}}(\mu+\mathrm{i}\omega) = K_x - \frac{1}{2\pi} \int_{-\infty}^{\infty} \widetilde{G^{\mathrm{GW}}}\big(\mu+\mathrm{i}(\omega-\omega')\big) \odot \widetilde{W_c^{\mathrm{GW}}}(\mathrm{i}\omega')\,\mathrm{d}\omega', \tag{4.74d}$$

$$\widetilde{G^{\mathrm{GW}}}(\mu+\mathrm{i}\omega) = \Big[\mu + \mathrm{i}\omega - \Big(h_1 + \widetilde{\Sigma^{\mathrm{GW}}}(\mu+\mathrm{i}\omega)\Big)\Big]^{-1}, \tag{4.74e}$$

where h_1 *is the one-body operator defined in (4.70) and where* K_x *is the integral operator on* $\mathcal{H}_1$ *with kernel*

$$K_x(\mathbf{r},\mathbf{r}') := -\frac{\gamma^0_{0,N}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|},$$

where $\gamma^0_{0,N}$ *was defined in (4.67).*

Remark 4.54. *In the* GW *equations (4.74), the chemical potential* μ *is supposed to be known a priori.*

The GW equations (4.74) would be the natural equations to work with from a mathematical viewpoint (they are formally equivalent to the original Hedin's GW equations). However, we were not able to study (4.74) for reasons detailed in Remark 4.55 below.

As one can directly see, the equations involve quite a large number of operators, which all have a physical significance. The operator $\widetilde{P^{\mathrm{GW}}_{\mathrm{sym}}}$ is the GW approximation of the symmetric irreducible polarizability operator, the operator $\widetilde{\chi^{\mathrm{GW}}_{\mathrm{sym}}}$ is the GW approximation of the symmetric reducible polarizability operator, the operator $\widetilde{W^{\mathrm{GW}}}$ is the GW approximation of the dynamically screened Coulomb interaction operator, and finally $\widetilde{\Sigma^{\mathrm{GW}}}$ is the GW approximation of the self-energy operator. We recognize in Equation (4.74e) the Dyson equation. The name "GW" comes from Equation (4.74d).

Different levels of GW approximation

As mentioned below (see Remark 4.55), we were not able to study the full self-consistent problem (4.74). We will therefore restrict ourselves to the so-called $\mathrm{G_0W^0}$ and $\mathrm{GW^0}$ approximations. We explain in this section how these different models are obtained.

(i) In the fully self-consistent GW (sc-GW) approximation, we assume that the full problem (4.74) is well-posed, so that there exists a (unique) solution $\widetilde{G^{\mathrm{GW}}}$. It is then solved self-consistently: the idea is to start from some trial Green's function, and keep updating it with (4.74) until convergence. This method is for instance used in [CRR+12, CRR+13, KFSP10, RJT10, SDvL06]. It was implemented only quite recently due to its high numerical cost (one needs to perform the inversion in (4.74b) at each iteration).

(ii) In the so-called self-consistent $\mathrm{GW^0}$ approximation, or simply $\mathrm{GW^0}$ approximation, only the Green's function (and not the screened Coulomb operator) is updated in (4.74d) (see for instance [SDvL09, vBH96]). This partial update not only speeds up the calculation (the inversion in (4.74b) is only performed once), but is sometimes in better agreement with experimental results than the sc-GW approximation. This is the model that we study in

Section 4.4.3.

(iii) Finally, most works simply consider the G_0W^0 approximation, where only one iteration of the sc-GW (or equivalently one iteration of GW^0) is performed. This model is very popular due to its relatively low computational cost, and provides already very satisfactory results (see for instance [BAO11]).

Let us also emphasize that it is unclear that a solution of the fully self-consistent GW model is a better approximation in any sense to the exact Green's function than a non self-consistent approximation such as the one obtained by the G_0W^0 approximation. This is discussed in [Far99, Section 9.8], where the author also comments on the possibilities to update the effective one-body operator $h_1 + K_x$ along the iterations.

Remark 4.55. *We do not know how to give a proper mathematical meaning to Equation (4.74a). More specifically, one would like to define, for a reasonable choice of Green's function* $\widetilde{G^{\mathrm{app}}}$*, the operator*

$$\forall \omega \in \mathbb{R}_\omega, \quad \widetilde{P_{\mathrm{sym}}}[G^{\mathrm{app}}](\mathrm{i}\omega) := \frac{1}{2\pi} v_c^{1/2} \left(\int_{-\infty}^{\infty} \widetilde{G^{\mathrm{app}}}\big(\mu + \mathrm{i}(\omega+\omega')\big) \odot \widetilde{G^{\mathrm{app}}}(\mu + \mathrm{i}\omega')\, \mathrm{d}\omega' \right) v_c^{1/2},$$

and we would like this operator to be a self-adjoint bounded negative operator on $\mathcal{H}_1$*. It is the case for instance when* $\widetilde{G^{\mathrm{app}}}$ *is the non-interacting Hamiltonian* $\widetilde{G_0}$ *defined in (4.69) (see Proposition 4.59 and Remark 4.64), or when* $\widetilde{G^{\mathrm{app}}}$ *is the exact Green's function defined in (4.51) (this fact can be proved by adapting the arguments given in Section 4.4.2). We were not able to obtain this result for a generic class of approximate Green's functions* $\widetilde{G^{\mathrm{app}}}$*, say* $\widetilde{G^{\mathrm{app}}}$ *of the form (4.74e) with* $\widetilde{\Sigma^{\mathrm{GW}}}(\mu + \mathrm{i}\omega)$ *in a small ball of* $L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$*.*

For this reason, we will not study the self-consistent GW equation (4.74).

4.4.2 The operator $\widetilde{W^0}$ and the random phase approximation

The remainder of this section is devoted to the study of the GW^0 approximation (which includes the G_0W^0 approximation), which amounts to study the two equations (4.74d)-(4.74e) with a specific fixed choice of the screening operator W^0. This approximation bypasses the difficulties mentioned in Remark 4.55. In order to present and study the GW^0 approximation, one must first define the operator W^0.

The RPA irreducible polarizability operator $\widetilde{P^0}$

The GW approximation of the *irreducible polarizability operator* P is formally defined as

$$P^{\mathrm{GW}}(\mathbf{r}, \mathbf{r}', \tau) = -\mathrm{i}G(\mathbf{r}, \mathbf{r}', \tau)G(\mathbf{r}', \mathbf{r}, -\tau). \tag{4.75}$$

When the Green's function G is the non-interacting one G_0 defined in (4.47), this corresponds to the so-called random phase approximation of the reducible polarizability operator (compare for instance (4.83) with the expression in [CS12]) defined by

$$P^0(\mathbf{r}, \mathbf{r}', \tau) := -\mathrm{i}G_0(\mathbf{r}, \mathbf{r}', \tau)G_0(\mathbf{r}', \mathbf{r}, -\tau).$$

This operator is expected to have properties similar to the operator χ defined in Section 4.3.3. In particular, $P^0(\tau)$ is expected to be a bounded operator from $\mathcal{C}'$ to $\mathcal{C}$. It is therefore more convenient to work with its symmetrized counterpart $P^0_{\mathrm{sym}}(\tau) := v_c^{1/2} P^0(\tau) v_c^{1/2}$, which is expected to be a bounded operator on $\mathcal{H}_1$. We decompose P^0_{sym} as $P^0_{\mathrm{sym}} = P^{0,+}_{\mathrm{sym}} + P^{0,-}_{\mathrm{sym}}$ where,

using the kernel-product $\odot$ defined in Section 4.2.4, and the explicit expressions of $G_{0,\mathrm{p}}$ and $G_{0,\mathrm{h}}$ given in Proposition 4.48,

$$P^{0,+}_{\mathrm{sym}}(\tau) = -\mathrm{i}\Theta(\tau) v_c^{1/2} G_{0,\mathrm{p}}(\tau) \odot G_{0,\mathrm{h}}(-\tau) v_c^{1/2} \tag{4.76}$$

$$= -\mathrm{i}\Theta(\tau) v_c^{1/2} \left(\left(\mathbb{1}_{\mathcal{H}_1} - \gamma^0_{0,N} \right) \mathrm{e}^{-\mathrm{i}\tau h_1} \odot \gamma^0_{0,N} \mathrm{e}^{\mathrm{i}\tau h_1} \right) v_c^{1/2} \tag{4.77}$$

and

$$P^{0,-}_{\mathrm{sym}}(\tau) = -\mathrm{i}\Theta(-\tau) v_c^{1/2} G_{0,\mathrm{h}}(\tau) \odot G_{0,\mathrm{p}}(-\tau) v_c^{1/2}$$

$$= -\mathrm{i}\Theta(-\tau) v_c^{1/2} \left(\gamma^0_{0,N} \mathrm{e}^{-\mathrm{i}\tau h_1} \odot \left(\mathbb{1}_{\mathcal{H}_1} - \gamma^0_{0,N} \right) \mathrm{e}^{\mathrm{i}\tau h_1} \right) v_c^{1/2}.$$

Actually, with this definition, we were not able to give a meaning to $P^{0,-}_{\mathrm{sym}}$ (it may not be a bounded operator on $\mathcal{H}_1$). We therefore prefer to use the modified kernel-product $\widetilde{\odot}$ defined in Remark 4.19. Our correct mathematical definition for $P^{0,-}_{\mathrm{sym}}$ then is

$$P^{0,-}_{\mathrm{sym}}(\tau) = -\mathrm{i}\Theta(-\tau) v_c^{1/2} G_{0,\mathrm{h}}(\tau) \,\widetilde{\odot}\, G_{0,\mathrm{p}}(-\tau) v_c^{1/2} \tag{4.78}$$

$$= -\mathrm{i}\Theta(-\tau) v_c^{1/2} \left(\gamma^0_{0,N} \mathrm{e}^{-\mathrm{i}\tau h_1} \,\widetilde{\odot}\, \left(\mathbb{1}_{\mathcal{H}_1} - \gamma^0_{0,N} \right) \mathrm{e}^{\mathrm{i}\tau h_1} \right) v_c^{1/2}. \tag{4.79}$$

As will be shown in Lemma 4.56, this amounts to defining $P^{0,-}(\tau) = P^{0,+}(-\tau)$. We recall that $\gamma^0_{0,N}$ is the orthogonal projector on the vector space spanned by the eigenvectors of h_1 associated with the lowest N eigenvalues (see (4.67)), so that

$$\gamma^0_{0,N} = \sum_{k=1}^{N} |\phi_k\rangle\langle\phi_k|, \tag{4.80}$$

where $h_1\phi_k = \varepsilon_k\phi_k$, and the eigenfunctions ϕ_k are real-valued and orthonormal. The following result shows that our definitions make sense, and gives explicit formulae for $P^{0,+}$ (see Section 4.6.15 for the proof).

Lemma 4.56. *The family* $\left(P^{0,+}_{\mathrm{sym}}(\tau)\right)_{\tau\in\mathbb{R}_\tau}$ *defined by (4.76) is a bounded causal operator on* $\mathcal{H}_1$*, while* $\left(P^{0,-}_{\mathrm{sym}}(\tau)\right)_{\tau\in\mathbb{R}_\tau}$ *defined by (4.78) is a bounded anti-causal operator on* $\mathcal{H}_1$*. It holds* $P^{0,-}_{\mathrm{sym}}(\tau) = P^{0,+}_{\mathrm{sym}}(-\tau)$ *and*

$$P^{0,+}_{\mathrm{sym}}(\tau) = -\mathrm{i}\Theta(\tau) \sum_{k=1}^{N} v_c^{1/2}\phi_k \left(\mathbb{1}_{\mathcal{H}_1} - \gamma^0_{0,N} \right) \mathrm{e}^{-\mathrm{i}\tau(h_1-\varepsilon_k)} \left(\mathbb{1}_{\mathcal{H}_1} - \gamma^0_{0,N} \right) \phi_k v_c^{1/2}. \tag{4.81}$$

Remark 4.57. *For* $1 \le k \le N$*, the notation* ϕ_k *in (4.81) refers to the multiplication operator by the function* ϕ_k*. It is a bounded operator from* $\mathcal{C}'$ *to* $\mathcal{H}_1$*, and from* $\mathcal{H}_1$ *to* $\mathcal{C}$ *(see the proof of Lemma 4.56). The operator* $\phi_k v_c^{1/2}$ *is bounded on* $\mathcal{H}_1$*, and one can check that its adjoint on* $\mathcal{H}_1$ *is* $(\phi_k v_c^{1/2})^* := v_c^{1/2}\phi_k$*.*

The properties of the Laplace and Fourier transforms of $P^{0,+}_{\mathrm{sym}}$ are easily deduced from (4.81) using Proposition 4.13 and Lemma 4.14.

Proposition 4.58. *The function* $z \mapsto \widetilde{P^{0,+}_{\mathrm{sym}}}(z)$ *is analytic on the upper half-plane* $\mathbb{U}$*, and can be analytically continued to the lower half-plane* $\mathbb{L}$ *through the semi-real line* $(-\infty, \varepsilon_{N+1} - \varepsilon_N)$*. For all* $z \in \mathbb{C} \setminus [\varepsilon_{N+1} - \varepsilon_N, \infty)$*,*

$$\widetilde{P^{0,+}_{\mathrm{sym}}}(z) = \sum_{k=1}^{N} v_c^{1/2}\phi_k \left(\frac{\mathbb{1}_{\mathcal{H}_1} - \gamma^0_{0,N}}{z - h_1 + \varepsilon_k} \right) \phi_k v_c^{1/2}. \tag{4.82}$$

Moreover $\widetilde{P^{0,+}_{\rm sym}}(\cdot+\mathrm{i}\eta)$ *converges to* $\widehat{P^{0,+}_{\rm sym}}$ *in* $H^{-1}(\mathbb{R}_\omega,\mathcal{B}(\mathcal{H}_1))$ *as* $\eta\to 0^+$, *with*

$$\operatorname{Re}\widehat{P^{0,+}_{\rm sym}} = \text{p.v.}\left(\sum_{k=1}^N v_c^{1/2}\phi_k\left(\frac{\mathbb{1}_{\mathcal{H}_1}-\gamma^0_{0,N}}{\cdot-h_1+\varepsilon_k}\right)\phi_k v_c^{1/2}\right)$$

and

$$\operatorname{Im}\widehat{P^{0,+}_{\rm sym}} = -\pi\left(\sum_{k=1}^N v_c^{1/2}\phi_k\left(\mathbb{1}_{\mathcal{H}_1}-\gamma^0_{0,N}\right)P^{h_1-\varepsilon_k}\phi_k v_c^{1/2}\right).$$

It also holds

$$\forall z\in\mathbb{C}\setminus[\varepsilon_{N+1}-\varepsilon_N,\infty),\quad \widetilde{P^{0,-}_{\rm sym}}(z)=\widetilde{P^{0,+}_{\rm sym}}(-z),$$

so that, for $z\in\mathbb{U}\cup\mathbb{L}\cup(-(\varepsilon_{N+1}-\varepsilon_N),\varepsilon_{N+1}-\varepsilon_N)$,

$$\widetilde{P^0_{\rm sym}}(z) = -2\sum_{k=1}^N v_c^{1/2}\phi_k(\mathbb{1}_{\mathcal{H}_1}-\gamma^0_{0,N})\left(\frac{h_1-\varepsilon_k}{(h_1-\varepsilon_k)^2-z^2}\right)(\mathbb{1}_{\mathcal{H}_1}-\gamma^0_{0,N})\phi_k v_c^{1/2}. \tag{4.83}$$

The properties of $\widehat{P^{0,+}_{\rm sym}}$ and of $\widehat{P^{0,-}_{\rm sym}}$ can be directly read off from the previous expressions. For instance, we see that $\operatorname{Im}\widehat{P^{0,+}_{\rm sym}}$ and $\operatorname{Im}\widehat{P^{0,-}_{\rm sym}}$ are negative operator-valued measures, with support in $(\varepsilon_{N+1}-\varepsilon_N,\infty)$ and $(-\infty,-(\varepsilon_{N+1}-\varepsilon_N))$ respectively. For ω in the real gap $(-(\varepsilon_{N+1}-\varepsilon_N),\varepsilon_{N+1}-\varepsilon_N)$, we see that $\widehat{P^{0,\pm}_{\rm sym}}(\omega)=\operatorname{Re}\widehat{P^{0,\pm}_{\rm sym}}(\omega)$ is a negative bounded self-adjoint on $\mathcal{H}_1$.

For our purpose, we only need to know the behavior of $\widetilde{P^0_{\rm sym}}$ on the imaginary axis $\mathrm{i}\mathbb{R}_\omega$. We summarize the corresponding most important results in the following proposition (see Section 4.6.16 for the proof).

Proposition 4.59. *It holds*

$$\forall\omega\in\mathbb{R}_\omega,\quad \widetilde{P^0_{\rm sym}}(\mathrm{i}\omega) = -2\sum_{k=1}^N v_c^{1/2}\phi_k\left(\mathbb{1}_{\mathcal{H}_1}-\gamma^0_{0,N}\right)\left(\frac{h_1-\varepsilon_k}{\omega^2+(h_1-\varepsilon_k)^2}\right)\left(\mathbb{1}_{\mathcal{H}_1}-\gamma^0_{0,N}\right)\phi_k v_c^{1/2}. \tag{4.84}$$

In particular, for all $\omega\in\mathbb{R}_\omega$, *the operator* $\widetilde{P^0_{\rm sym}}(\mathrm{i}\omega)$ *is a negative, self-adjoint bounded operator on* $\mathcal{H}_1$ *satisfying* $\widetilde{P^0_{\rm sym}}(-\mathrm{i}\omega)=\widetilde{P^0_{\rm sym}}(\mathrm{i}\omega)$. *In addition, the function* $\omega\mapsto\widetilde{P^0_{\rm sym}}(\mathrm{i}\omega)$ *is analytic from* $\mathbb{R}_\omega$ *to* $\mathcal{S}(\mathcal{H}_1)$, *and is in* $L^p(\mathbb{R}_\omega,\mathcal{S}(\mathcal{H}_1))$ *for all* $p>1$. *For any* $f\in\mathcal{H}_1$, *the function* $\omega\mapsto\left\langle f\middle|\widetilde{P^0_{\rm sym}}(\mathrm{i}\omega)\middle|f\right\rangle$ *is non-positive, in* $L^1(\mathbb{R}_\omega)$, *and*

$$\begin{aligned}\int_{-\infty}^{+\infty}\left\langle f\middle|\widetilde{P^0_{\rm sym}}(\mathrm{i}\omega)\middle|f\right\rangle\mathrm{d}\omega &= -2\pi\left\langle f\middle|v_c^{1/2}\left(\left(\mathbb{1}_{\mathcal{H}_1}-\gamma^0_{0,N}\right)\odot\gamma^0_{0,N}\right)v_c^{1/2}\middle|f\right\rangle\\ &= -2\pi\left\langle f\middle|\sum_{k=1}^N v_c^{1/2}\phi_k\left(\mathbb{1}_{\mathcal{H}_1}-\gamma^0_{0,N}\right)\phi_k v_c^{1/2}\middle|f\right\rangle.\end{aligned} \tag{4.85}$$

Finally, there exists a constant $C\in\mathbb{R}^+$ *such that*

$$\forall\omega\in\mathbb{R}_\omega,\quad 0\le-\widetilde{P^0_{\rm sym}}(\mathrm{i}\omega)\le\frac{C}{(\omega^2+1)^{1/2}}\left(v_c^{1/2}\rho^0_{0,N}v_c^{1/2}\right), \tag{4.86}$$

where $\rho^0_{0,N}$ *is the multiplication operator by the (real-valued) function* $\rho^0_{0,N}$, *the latter operator being bounded from* $\mathcal{C}'$ *to* $\mathcal{C}$.

The sum-rule for the operator $\widetilde{P^0}$. We end this section with the sum-rule for the operator $\widetilde{P^0} = v_c^{-1/2}\widetilde{P^0_{\rm sym}}v_c^{-1/2}$, which goes from $\mathcal{C}'$ to $\mathcal{C}$. We postpone the proof until Section 4.6.17.

Theorem 4.60. *The operator $2\sum_{k=1}^N \phi_k(\mathbb{1}_{\mathcal{H}_1} - \gamma^0_{0,N})(h_1 - \varepsilon_k)\phi_k$ is bounded from $\mathcal{C}'$ to $\mathcal{C}$, and it holds*

$$2\sum_{k=1}^N \phi_k(\mathbb{1}_{\mathcal{H}_1} - \gamma^0_{0,N})(h_1 - \varepsilon_k)\phi_k = \operatorname{div}(\rho^0_{0,N}\nabla\cdot).$$

Moreover, the following weak-convergence holds:

$$\forall (f,g) \in \mathcal{C}' \times \mathcal{C}', \quad \lim_{\omega\to\pm\infty} \left\langle \overline{f}, -\omega^2\widetilde{P^0}(\mathrm{i}\omega)g \right\rangle_{\mathcal{C}',\mathcal{C}} = \left\langle \overline{f}, -\operatorname{div}\left(\rho^0_{0,N}\nabla g\right)\right\rangle_{\mathcal{C}',\mathcal{C}} = \int_{\mathbb{R}^3} \rho^0_{0,N}\overline{\nabla f}\cdot\nabla g.$$

Finally, for all $g \in \mathcal{C}'$ such that $\Delta g \in L^2(\mathbb{R}^3)$, the following strong convergence holds:

$$\lim_{\omega\to\pm\infty} \omega^2\widetilde{P^0}(\mathrm{i}\omega)g = \operatorname{div}\left(\rho^0_{0,N}\nabla g\right) \quad \text{in } \mathcal{C}.$$

This sum-rule automatically leads to a sum-rule for the reducible polarizability operator in the random phase approximation χ^0 (see Theorem 4.67).

The analytical continuation method

In this section, we explain why (4.74a) can be thought of as a natural reformulation of the usual physical definition (4.75), and why problems arise with Definition (4.74a) (see Problem 4.55). This section also serves as a guideline to understand why (4.74d) is a natural reformulation of the usual physical definition of $\Sigma^{\rm GW}$ (see (4.97) below). In the previous section, we gave the properties of $\widetilde{P^0}$ using the explicit expression of P^0 given in (4.81). While this approach simplifies the proofs, it somehow hides some structural properties that we highlight in this section.

Recall that $P^0_{\rm sym} = P^{0,+}_{\rm sym} + P^{0,-}_{\rm sym}$ with

$$P^{0,+}_{\rm sym}(\tau) = -\mathrm{i}\Theta(\tau)v_c^{1/2}G_{0,\rm p}(\tau) \odot G_{0,\rm h}(-\tau)v_c^{1/2}$$

and

$$P^{0,-}_{\rm sym}(\tau) = -\mathrm{i}\Theta(-\tau)v_c^{1/2}G_{0,\rm h}(\tau) \mathbin{\widetilde{\odot}} G_{0,\rm p}(-\tau)v_c^{1/2},$$

where

$$G_{0,\rm p}(\tau) = -\mathrm{i}\Theta(\tau)A_{0,+}\mathrm{e}^{-\mathrm{i}\tau(H_{0,N+1}-E^0_{0,N})}A^*_{0,+}, \qquad G_{0,\rm h}(\tau) = \mathrm{i}\Theta(-\tau)A^*_{0,-}\mathrm{e}^{\mathrm{i}\tau(H_{0,N-1}-E^0_{0,N})}A_{0,-}.$$

The idea is to use the results of Theorem 4.24. We first consider $P^{0,+}_{\rm sym}$, and prove that the hypotheses of Theorem 4.24 are satisfied. This is given by the following lemma.

Lemma 4.61. *There exists a constant $C \in \mathbb{R}^+$ such that, for any $f \in \mathcal{H}_1$, it holds $A_{0,-}\left(v_c^{1/2}f\right) \in \mathfrak{S}_2(\mathcal{H}_1)$ with*

$$\left\|A_{0,-}\left(v_c^{1/2}f\right)\right\|_{\mathfrak{S}_2(\mathcal{H}_1)} \le C\|f\|_{\mathcal{H}_1}.$$

Moreover, $H_{0,N+1} - E^0_{0,N} \ge \varepsilon_{N+1}$ and $H_{0,N-1} - E^0_{0,N} \ge -\varepsilon_N$.

Proof. The first point comes from the fact that $A^*_{0,-}A_{0,-} = \gamma^0_{0,N}$ and that $v_c^{1/2}f \in \mathcal{C}' \hookrightarrow L^6$ whenever $f \in \mathcal{H}_1$, together with Lemma 4.77. □

In particular, the hypotheses of Theorem 4.24 are satisfied, and we deduce that for any $\nu' > \varepsilon_N$ and $\nu + \nu' < \varepsilon_{N+1}$,

$$\forall \omega \in \mathbb{R}, \quad \widetilde{P^{0,+}_{\mathrm{sym}}}(\nu + \mathrm{i}\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} v_c^{1/2} \left(\widetilde{G_{0,\mathrm{p}}}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) \odot \widetilde{G_{0,\mathrm{h}}}(\nu' + \mathrm{i}\omega') \right) v_c^{1/2} \mathrm{d}\omega'. \tag{4.87}$$

We treat $\widetilde{P^{0,-}_{\mathrm{sym}}}$ is a similar way, and find that for any $\nu' < \varepsilon_{N+1}$ and $\nu + \nu' > \varepsilon_N$,

$$\forall \omega \in \mathbb{R}, \quad \widetilde{P^{0,-}_{\mathrm{sym}}}(\nu + \mathrm{i}\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} v_c^{1/2} \left(\widetilde{G_{0,\mathrm{h}}}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) \mathbin{\widetilde{\odot}} \widetilde{G_{0,\mathrm{p}}}(\nu' + \mathrm{i}\omega') \right) v_c^{1/2} \mathrm{d}\omega'. \tag{4.88}$$

Actually, the kernel-product $\widetilde{\odot}$ in the latter expression can be transformed into the kernel-product $\odot$, thanks to the following lemma, whose proof is given in Section 4.6.18.

Lemma 4.62. *For any $\nu' < \varepsilon_{N+1}$, any $\nu + \nu' > \varepsilon_N$ and any $\omega, \omega' \in \mathbb{R}_\omega$,*

$$\widetilde{G_{0,\mathrm{h}}}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) \mathbin{\widetilde{\odot}} \widetilde{G_{0,\mathrm{p}}}(\nu' + \mathrm{i}\omega') = \widetilde{G_{0,\mathrm{h}}}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) \odot \widetilde{G_{0,\mathrm{p}}}(\nu' + \mathrm{i}\omega'),$$

as bounded operators from $\mathcal{C}'$ to $\mathcal{C}$.

We can perform the same type of calculation for $G_{\mathrm{h}} \odot G_{\mathrm{h}}$. Following the proof of Theorem 4.24, we deduce from $G_{\mathrm{h}}(\tau) \odot G_{\mathrm{h}}(-\tau) = 0$ that, for any $\nu' > \varepsilon_N$ and $\nu + \nu' > \varepsilon_N$,

$$\forall \omega \in \mathbb{R}_\omega, \quad \frac{1}{2\pi} \int_{-\infty}^{+\infty} v_c^{1/2} \left(\widetilde{G_{0,\mathrm{h}}}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) \odot \widetilde{G_{0,\mathrm{h}}}(\nu' + \mathrm{i}\omega') \right) v_c^{1/2} \mathrm{d}\omega' = 0. \tag{4.89}$$

Similarly, from $G_{\mathrm{p}}(\tau) \odot G_{\mathrm{p}}(-\tau) = 0$, we deduce that, *at least formally*, for any $\nu' < \varepsilon_{N+1}$, and any $\nu + \nu' < \varepsilon_{N+1}$,

$$\forall \omega \in \mathbb{R}_\omega, \quad \frac{1}{2\pi} \int_{-\infty}^{+\infty} v_c^{1/2} \left(\widetilde{G_{0,\mathrm{p}}}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) \odot \widetilde{G_{0,\mathrm{p}}}(\nu' + \mathrm{i}\omega') \right) v_c^{1/2} \mathrm{d}\omega' = 0. \tag{4.90}$$

Remark 4.63. *The last equality is formal, in the sense that the integrand $\widetilde{G_{0,\mathrm{p}}} \odot \widetilde{G_{0,\mathrm{p}}}$ is actually not well-defined: it does not define a bounded operator from $\mathcal{C}'$ to $\mathcal{C}$. However, we can proceed as follows. For $\omega \in \mathbb{R}_\omega$, let $\widetilde{P^{+,+}_\sharp}(\mathrm{i}\omega)$ be the operator defined on the core $\mathcal{H}_1 \cap \mathcal{C}$ by*

$$\forall f, g \in \mathcal{H}_1 \cap \mathcal{C}, \quad \left\langle f \middle| \widetilde{P^{+,+}_\sharp}(\mathrm{i}\omega) \middle| g \right\rangle := \frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{Tr}_{\mathcal{H}_1} \left[\widetilde{G_{0,\mathrm{p}}}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) \left(v_c^{1/2} g \right) \widetilde{G_{0,\mathrm{p}}}(\nu' + \mathrm{i}\omega') \left(v_c^{1/2} \overline{f} \right) \right] \mathrm{d}\omega'.$$

Noticing that $v_c^{1/2}\overline{f}$ and $v_c^{1/2} g$ are in $\mathcal{H}_1$ since $f, g \in \mathcal{C}$, and reasoning as in the proof of Lemma 4.62, we can prove that the operator in the trace is indeed trace-class, with

$$\left| \mathrm{Tr}_{\mathcal{H}_1} \left[\widetilde{G_{0,\mathrm{p}}}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) \left(v_c^{1/2} g \right) \widetilde{G_{0,\mathrm{p}}}(\nu' + \mathrm{i}\omega') \left(v_c^{1/2} \overline{f} \right) \right] \right| \leq p_\omega(\omega') \|f\|_{\mathcal{C}} \|g\|_{\mathcal{C}},$$

where p_ω is an integrable function independent of f and g. Moreover, following the proof of Theorem 4.24, we can prove that, as expected,

$$\forall f, g \in \mathcal{H}_1 \cap \mathcal{C}, \quad \left\langle f \middle| \widetilde{P^{+,+}_\sharp}(\mathrm{i}\omega) \middle| g \right\rangle = 0.$$

The unique continuation on $\mathcal{H}_1$ of $\widetilde{P^{+,+}_\sharp}(\mathrm{i}\omega)$ therefore is the null operator. It is unclear to us how to extend a similar reasoning for a generic class of approximated Green's function $\widetilde{G^{\mathrm{app}}}$.

By gathering (4.87), (4.88), (4.89) and (4.90), we find that, for any $\nu' \in (\varepsilon_N, \varepsilon_{N+1})$ and $\nu + \nu' \in (\varepsilon_N, \varepsilon_{N+1})$,

$$\forall \omega \in \mathbb{R}_\omega, \quad \widetilde{P^0_{\mathrm{sym}}}(\nu + \mathrm{i}\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} v_c^{1/2} \left(\widetilde{G_0}\big(\nu + \nu' + \mathrm{i}(\omega' + \omega)\big) \odot \widetilde{G_0}(\nu' + \mathrm{i}\omega') \right) v_c^{1/2} \mathrm{d}\omega'.$$

In particular, this equality holds for the particular choice $\nu' = \mu_0$ and $\nu = 0$.

Remark 4.64. *To summarize the work performed in this section, we transformed the equation*

$$P^0(\mathbf{r}, \mathbf{r}', \tau) := -\mathrm{i} G_0(\mathbf{r}, \mathbf{r}', \tau) G_0(\mathbf{r}', \mathbf{r}, -\tau) \tag{4.91}$$

into: for any $\nu' \in (\varepsilon_N, \varepsilon_{N+1})$ and $\nu \in (\varepsilon_N - \nu', \varepsilon_{N+1} - \nu')$

$$\widetilde{P^0}(\nu + \mathrm{i}\cdot) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \left(\widetilde{G_0}\big(\nu + \nu' + \mathrm{i}(\omega' + \cdot)\big) \odot \widetilde{G_0}(\nu' + \mathrm{i}\omega') \right) \mathrm{d}\omega'. \tag{4.92}$$

Note that the manipulations performed in this section to transform (4.91) into (4.92) are possible since the two operators involved in the kernel-product (here, both are equal to $\widetilde{G^0}(z)$) are analytic on some common domain $\mathbb{U} \cup \mathbb{L} \cup (a, b)$ with $a < b$ (the presence of a gap is important to deform the contour as in Theorem 4.24).

The RPA reducible polarizability operator χ^0

In order to calculate the GW approximation of the self-energy, one needs the reducible polarizability operator χ, defined in Section 4.3.3. Unfortunatly, the expression of χ is not accessible in practice. One needs to approximate this operator. The GW approximation, which amounts to approximating the so-called *vertex function*, provides a natural approximation χ^{GW} of χ: in Equation (4.74b), χ^{GW} is defined from G^{GW} (see also [Far99, Equation (103)] or [Hed65, Equations (A.20) and (A.28)]). However, in view of Remark 4.55, the definition of χ^{GW} is not well-understood mathematically. In the GW^0 framework, we use the RPA reducible polarizability operator χ^0, which is itself defined in terms of the RPA irreducible polarizability P^0. The GW^0 approximation of the (symmetrized) reducible polarizability operator is usually defined in the frequency domain as

$$\widehat{\chi^0_{\mathrm{sym}}}(\omega) := \left(\mathbb{1}_{\mathcal{H}_1} - \widehat{P^0_{\mathrm{sym}}}(\omega) \right)^{-1} - \mathbb{1}_{\mathcal{H}_1}.$$

The formal analytic continuation of the above definitions is (see [Far99, Equation (139)])

$$\widetilde{\chi^0_{\mathrm{sym}}}(z) := \left(\mathbb{1}_{\mathcal{H}_1} - \widetilde{P^0_{\mathrm{sym}}}(z) \right)^{-1} - \mathbb{1}_{\mathcal{H}_1}. \tag{4.93}$$

Note that we use the "tilde" notation in $\widetilde{\chi^0_{\mathrm{sym}}}$, although it is unclear that this operator-valued function is indeed the Laplace transform of some operator-valued function in the time domain. Also, it is *a priori* unclear whether the operators $\mathbb{1}_{\mathcal{H}_1} - \widehat{P^{\mathrm{GW}}_{\mathrm{sym}}}(\omega)$ or $\mathbb{1}_{\mathcal{H}_1} - \widetilde{P^{\mathrm{GW}}_{\mathrm{sym}}}(z)$ are invertible. This is however the case for appropriate values of z, as shown by the following lemma.

Lemma 4.65. *For $z \in (-(\varepsilon_{N+1} - \varepsilon_N), \varepsilon_{N+1} - \varepsilon_N)$ and $z \in \mathrm{i}\mathbb{R}$, the operator $\mathbb{1}_{\mathcal{H}_1} - \widetilde{P^0_{\mathrm{sym}}}(z)$ is invertible.*

This result is a direct consequence of the explicit formula (4.83) for $\widetilde{P^0}$, which ensures that $\widetilde{P^0_{\mathrm{sym}}}(z)$ is a bounded self-adjoint negative operator for the values of z under consideration. Let us deduce some extra properties of $\widetilde{\chi^0}$.

Lemma 4.66. *For any $\omega \in \mathbb{R}$, the operator $\widetilde{\chi^0_{\rm sym}}(\mathrm{i}\omega)$ is a bounded, negative, self-adjoint operator on $\mathcal{H}_1$, satisfying $\widetilde{\chi^0_{\rm sym}}(-\mathrm{i}\omega) = \widetilde{\chi^0_{\rm sym}}(\mathrm{i}\omega)$, and such that*

$$\widetilde{P^0_{\rm sym}}(\mathrm{i}\omega) \leq \widetilde{\chi^0_{\rm sym}}(\mathrm{i}\omega) \leq 0. \tag{4.94}$$

The function $\omega \mapsto \widetilde{\chi^0_{\rm sym}}(\mathrm{i}\omega)$ is analytic from $\mathbb{R}_\omega$ to $\mathcal{S}(\mathcal{H}_1)$ and is in $L^p(\mathbb{R}_\omega, \mathcal{S}(\mathcal{H}_1))$ for all $p > 1$. Finally, there exists a constant $C \in \mathbb{R}^+$ such that

$$0 \leq -\widetilde{\chi^0_{\rm sym}}(\mathrm{i}\omega) \leq \frac{C}{(\omega^2+1)^{1/2}} \left(v_c^{1/2} \rho^0_{0,N} v_c^{1/2} \right). \tag{4.95}$$

This result is deduced from the definition (4.93), the inequality $x \leq (1-x)^{-1} - 1 \leq 0$ for $x \leq 0$, and Proposition 4.59.

Sum-rule for $\widetilde{\chi^0}$. From the sum-rule stated in Theorem 4.60, we readily deduce the sum-rule for $\widetilde{\chi^0} := v_c^{-1/2} \widetilde{\chi^0_{\rm sym}} v_c^{-1/2}$, which is a bounded operator from $\mathcal{C}'$ to $\mathcal{C}$. Indeed, from the equality $(1-x)^{-1} - 1 = x + x^2(1-x)^{-1}$, we obtain

$$\forall \omega \in \mathbb{R}_\omega, \quad \widetilde{\chi^0_{\rm sym}}(\mathrm{i}\omega) = \widetilde{P^0_{\rm sym}}(\mathrm{i}\omega) + \left(\widetilde{P^0_{\rm sym}}(\mathrm{i}\omega) \right)^2 \left(\mathbb{1}_{\mathcal{H}_1} - \widetilde{P^0_{\rm sym}}(\mathrm{i}\omega) \right)^{-1}.$$

In particular,

$$\forall \omega \in \mathbb{R}_\omega, \quad \omega^2 \widetilde{\chi^0}(\mathrm{i}\omega) = \omega^2 \widetilde{P^0}(\mathrm{i}\omega) + \frac{1}{\omega^2} \left(\omega^2 \widetilde{P^0}(\mathrm{i}\omega) \right) \left(v_c^{1/2} \left(\mathbb{1}_{\mathcal{H}_1} - \widetilde{P^0_{\rm sym}}(\mathrm{i}\omega) \right)^{-1} v_c^{1/2} \right) \left(\omega^2 \widetilde{P^0}(\mathrm{i}\omega) \right).$$

This shows that the asymptotic behavior of $\widetilde{\chi^0}(\mathrm{i}\omega)$ is, at dominant order, the same as for $\widetilde{P^0}(\mathrm{i}\omega)$. Taking the limit $\omega \to \pm\infty$ leads to a theorem similar to Theorem 4.60, whose proof is skipped here for the sake of brevity.

Theorem 4.67. *The following weak-convergence holds:*

$$\forall (f,g) \in \mathcal{C}' \times \mathcal{C}', \quad \lim_{\omega \to \pm\infty} \left\langle \overline{f}, -\omega^2 \widetilde{\chi^0}(\mathrm{i}\omega) g \right\rangle_{\mathcal{C}',\mathcal{C}} = \left\langle \overline{f}, -\mathrm{div}\, \left(\rho^0_{0,N} \nabla g \right) \right\rangle_{\mathcal{C}',\mathcal{C}} = \int_{\mathbb{R}^3} \rho^0_{0,N} \overline{\nabla f} \cdot \nabla g.$$

For all $g \in \mathcal{C}'$ such that $\Delta g \in L^2(\mathbb{R}^3)$, the following strong convergence holds:

$$\lim_{\omega \to \pm\infty} \omega^2 \widetilde{\chi^0}(\mathrm{i}\omega) g = \mathrm{div}\, \left(\rho^0_{0,N} \nabla g \right) \quad \text{in } \mathcal{C}.$$

By comparing Theorems 4.67 and 4.46, we see why using (4.71) instead of (4.70) for the definition of h_1 may lead to better approximations, since $\rho^0_{0,N} = \rho^0_N$ in this case, so that the GW approximation $\chi^{\rm GW}$ of χ becomes exact in the high imaginary frequency domain.

Theorem 4.67 is useful for the design of the so-called *Plasmon-Pole models* (PPM) [HL86, vdLH88, GN89, EF93]. Since the definition (4.93) requires the computation of a resolvent, the calculation of $\widetilde{\chi^0}(z)$ is numerically very expensive in practice. Some authors suggested to approximate $\widetilde{\chi^0}$ by an operator $\widetilde{\chi^{\rm PPM}}$ which is computationally less expensive. In practice, $\widetilde{\chi^{\rm PPM}}$ has a prescribed functional form, with adjustable parameters. Different approaches are taken in order to tune these parameters, and the previous sum-rule provides a standard way to fit some of them. This is done for instance in the PPM by Hybersten and Louie [HL86] and in the PPM by Engel and Farid [EF93]. In the later article, the authors extensively comment on the fact that this sum-rule is an important requirement to be satisfied for a PPM.

The RPA dynamically screened operator W^0

From the approximation χ^0 of χ, we directly deduce the approximation W^0 of W. Following the path taken in Section 4.3.3, we define

$$\widetilde{W^0}(z) := v_c + \widetilde{W_c^0}(z) \quad \text{with} \quad \widetilde{W_c^0}(z) := v_c^{1/2}\widetilde{\chi^0_{\mathrm{sym}}}(z)v_c^{1/2}. \tag{4.96}$$

This operator, when well-defined (say on the gap $(-(\varepsilon_{N+1}-\varepsilon_N), \varepsilon_{N+1}-\varepsilon_N)$ or on the imaginary axis $\mathrm{i}\mathbb{R}$) is a bounded operator from $\mathcal{C}$ to $\mathcal{C}'$. The properties of $\widetilde{W^0}$ are directly deduced from the ones of $\widetilde{\chi^0_{\mathrm{sym}}}$, so we do not repeat them here for brevity.

4.4.3 A mathematical study of the GW^0 approximation

The $\mathrm{G_0W^0}$ approximation of the self-energy

In this section, we study the $\mathrm{G_0W^0}$ approximation as a preliminary step to the study of the self-consistent GW^0 approximation. This will help us understand some technical points to address in the analysis of the GW^0 method.

The $\mathrm{G_0W^0}$ approximation of the self-energy operator is formally defined as

$$\Sigma^{00}(\mathbf{r},\mathbf{r}',\tau) := \mathrm{i}G_0(\mathbf{r},\mathbf{r}',\tau)W^0(\mathbf{r},\mathbf{r}',-\tau^+). \tag{4.97}$$

Here, G_0 represents the Green's function of the non-interacting system introduced in Definition 4.47, and W^0 is the random phase approximation of the dynamically screened operator defined in Section 4.4.2. Already one difficulty arises: in Section 4.4.2, we only defined the function $\widetilde{W^0}(z)$ on the complex frequency domain, but we did not define some operator-valued function on the time-domain. In this section, we assume that the function $\widetilde{W^0}(z)$ is indeed the Laplace transform of some operator $W^0(\tau)$. This will allow us to transform (4.97) into a formally equivalent definition that only involves $\widetilde{W^0}$. The resulting definition will be our starting point for the GW^0 approximation.

With the kernel-product defined in Section 4.2.4, the definition (4.97) can be recast as

$$\Sigma^{00}(\tau) = \mathrm{i}G_0(\tau^-) \odot W^0(-\tau).$$

In view of the decomposition provided in (4.96), it is natural to split Σ^{00} into an exchange part Σ_x^{00} and a correlation part Σ_c^{00} (the terminology is motivated below):

$$\Sigma^{00} = \Sigma_x^{00} + \Sigma_c^{00} \quad \text{with} \quad \Sigma_x^{00}(\tau) = \mathrm{i}G_{0,\mathrm{h}}(0^-) \odot v_c\delta_0(\tau) \quad \text{and} \quad \Sigma_c^{00}(\tau) = \mathrm{i}G_0(\tau) \odot W_c(-\tau).$$

Let us first consider the exchange part. As $\mathrm{i}G_{0,\mathrm{h}}(0^-) = -\gamma^0_{0,N}$, we obtain

$$\Sigma_x^{00}(\tau) = K_x\delta_0(\tau), \tag{4.98}$$

where K_x is the integral operator on $\mathcal{H}_1$ with kernel

$$K_x(\mathbf{r},\mathbf{r}') := -\frac{\gamma^0_{0,N}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{4.99}$$

We recover the usual Fock exchange operator associated with $\gamma^0_{0,N}$, which justifies the terminology "exchange part" for Σ_x^{00}. Let us now consider the correlation part. Observing that

- $\widetilde{G_0}$ is analytic on $\mathbb{U}\cup\mathbb{L}\cup(\varepsilon_N,\varepsilon_{N+1})$ (hence has a gap around μ_0);

- $\widetilde{W^0}$ is analytic on $\mathbb{U} \cup \mathbb{L} \cup (-(\varepsilon_{N+1} - \varepsilon_N), \varepsilon_{N+1} - \varepsilon_N)$ (hence has a gap around 0),

we can use the same ideas as in Section 4.4.2. *By analogy* with Remark 4.64, we recast the physical definition of $\widetilde{\Sigma^{00}}$ in (4.97) in a *formally equivalent* definition in the complex frequency plane. This reformulation was first given by Rojas, Godby and Needs [RGN95] (see also [RSW+99]), and is now known as the "contour deformation" technique.

Definition 4.68 (G_0W^0 approximation of the self-energy)**.** *The exchange part of the self-energy in the G_0W^0 approximation is defined in the complex frequency domain by*

$$\forall z \in \mathbb{C}, \qquad \widetilde{\Sigma_x^{00}}(z) = K_x,$$

while the correlation part is defined, for $\nu' \in (-(\varepsilon_{N+1}-\varepsilon_N), \varepsilon_{N+1}-\varepsilon_N)$ and $\nu+\nu' \in (\varepsilon_N, \varepsilon_{N+1})$ by

$$\forall \omega \in \mathbb{R}_\omega, \quad \widetilde{\Sigma_c^{00}}(\nu + \mathrm{i}\omega) = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} \widetilde{G_0}\left(\nu + \nu' + \mathrm{i}(\omega + \omega')\right) \odot \widetilde{W_c^0}(\nu' + \mathrm{i}\omega')\, \mathrm{d}\omega.$$

The fact that the above quantity is independent of the choice of ν' comes from the analyticity of the integrand on the region of interest. In practice, we will focus on the case $\nu' = 0$ and $\nu = \mu_0$, and therefore consider the function $\mathbb{R}_\omega \ni \omega \mapsto \widetilde{\Sigma_0^{00}}(\mu_0 + \mathrm{i}\omega)$ defined by

$$\forall \omega \in \mathbb{R}_\omega, \quad \widetilde{\Sigma_c^{00}}(\mu_0 + \mathrm{i}\omega) = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} \widetilde{G_0}\left(\mu_0 + \mathrm{i}(\omega + \omega')\right) \odot \widetilde{W_c^0}(\mathrm{i}\omega')\, \mathrm{d}\omega. \tag{4.100}$$

The next proposition shows that the above definition makes sense.

Proposition 4.69. *The operator K_x arising in the exchange part Σ_c^{00} of the self-energy is a negative Hilbert-Schmidt operator on $\mathcal{H}_1$. Furthermore, for any $\omega \in \mathbb{R}_\omega$, the operator $\widetilde{\Sigma_c^{00}}(\mu_0 + \mathrm{i}\omega)$ is a bounded operator on $\mathcal{H}_1$, and satisfies $\widetilde{\Sigma_c^{00}}(\mu_0 - \mathrm{i}\omega) = \widetilde{\Sigma_c^{00}}(\mu_0 + \mathrm{i}\omega)^*$. The function $\omega \mapsto \widetilde{\Sigma_c^{00}}(\mu_0+\mathrm{i}\omega)$ is analytic from $\mathbb{R}_\omega$ to $\mathcal{B}(\mathcal{H}_1)$ and is in $L^p(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ for all $p > 1$.*

The first statements of Proposition 4.69 can be seen as a special case of Proposition 4.73, while the symmetry property for the adjoint and the L^p integrability follow from the properties of $\widetilde{G^0}$ and $\widetilde{W_c^0}$.

Well-posedness of the GW^0 approximation in the perturbative regime.

We finally study the GW^0 approximation. Following our definition (4.100) of the G_0W^0 approximation of the self-energy, we recast the GW^0 equation as follows.

Definition 4.70 (The GW^0 problem on the imaginary axis in the frequency domain)**.** *Find $G^{GW^0} \in L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ solution to the system*

$$(\mathrm{GW}^0) \quad \begin{cases} \widetilde{\Sigma^{\mathrm{GW}^0}}(\mu_0 + \mathrm{i}\omega) = K_x - \dfrac{1}{2\pi} \displaystyle\int_{-\infty}^{+\infty} \widetilde{G^{\mathrm{GW}^0}}\left(\mu_0 + \mathrm{i}(\omega + \omega')\right) \odot \widetilde{W_c^0}(\mathrm{i}\omega')\, \mathrm{d}\omega', \\ \widetilde{G^{\mathrm{GW}^0}}(\mu_0 + \mathrm{i}\omega) = \left[\mu_0 + \mathrm{i}\omega - \left(h_1 + \widetilde{\Sigma^{\mathrm{GW}^0}}(\mu_0 + \mathrm{i}\omega)\right)\right]^{-1}, \end{cases}$$

where h_1 is the one-body mean-field Hamiltonian defined in (4.70) and K_x is the exchange operator defined by (4.67)-(4.99).

Remark 4.71. *We are looking for a solution in $L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$. Note that the true Green's function $\widetilde{G}(\mu + \mathrm{i}\cdot)$ is in $L^p(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ for all $p > 1$ (in particular for $p = \infty$). We chose to work with $L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)$ for simplicity, but it is possible to work with other spaces $L^p(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ with $p > 1$.*

Since this problem seems quite difficult to study mathematically, we will only study it in a perturbative regime. More specifically, seeing Σ^{GW} as a correction term (see the discussion after Definition 4.52), we propose to study the following problem.

Definition 4.72 (The GW^0_λ problem on the imaginary axis on the frequency domain)**.** *Find $G^{\mathrm{GW}^0_\lambda} \in L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ solution to the system*

$$(\mathrm{GW}^0_\lambda) \quad \begin{cases} \widetilde{\Sigma^{\mathrm{GW}^0_\lambda}}(\mu_0 + \mathrm{i}\omega) = K_x - \dfrac{1}{2\pi}\displaystyle\int_{-\infty}^{+\infty} \widetilde{G^{\mathrm{GW}^0_\lambda}}\big(\mu_0 + \mathrm{i}(\omega+\omega')\big) \odot \widetilde{W^0_c}(\mathrm{i}\omega')\,\mathrm{d}\omega' \\ \widetilde{G^{\mathrm{GW}^0_\lambda}}(\mu_0 + \mathrm{i}\omega) = \left[\mu_0 + \mathrm{i}\omega - \left(h_1 + \lambda\widetilde{\Sigma^{\mathrm{GW}^0_\lambda}}(\mu_0 + \mathrm{i}\omega)\right)\right]^{-1}. \end{cases} \tag{4.101}$$

According to (4.69), the unique solution for $\lambda = 0$ is the Green's function for the non interacting system $\widetilde{G^{\mathrm{GW}^0_{\lambda=0}}} = \widetilde{G_0}$. This fact will allow us to treat the equation perturbatively. The exact GW^0 equations correspond to the case $\lambda = 1$. Of course, several other choices of perturbation can be used. For instance, we can put the parameter λ in front of the correlation part of the self-energy only. This amounts to considering the Hartree-Fock Hamiltonian as the reference Hamiltonian (instead of the Hartree Hamiltonian). The theory that we develop here can be straightforwardly generalized to such other cases.

It is convenient for the mathematical analysis to introduce the functionals $\mathfrak{s}$ and $\mathfrak{g}$ respectively defined as

$$\begin{aligned} \mathfrak{s}: \quad L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)) &\to L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)) \\ \widetilde{G^{\mathrm{app}}}(\mu_0 + \mathrm{i}\cdot) &\mapsto \mathfrak{s}\left[\widetilde{G^{\mathrm{app}}}\right](\mu_0 + \mathrm{i}\cdot) := K_x - \frac{1}{2\pi}\int_{-\infty}^{+\infty} \widetilde{G^{\mathrm{app}}}(\mu_0 + \mathrm{i}(\cdot+\omega')) \odot \widetilde{W^0_c}(\mathrm{i}\omega')\,\mathrm{d}\omega', \end{aligned}$$

and

$$\begin{aligned} \mathfrak{g}_\lambda: \quad L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)) &\to L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)) \\ \widetilde{\Sigma^{\mathrm{app}}}(\mu_0 + \mathrm{i}\cdot) &\mapsto \mathfrak{g}\left[\widetilde{\Sigma^{\mathrm{app}}}\right](\mu_0 + \mathrm{i}\cdot) := \left[\mu_0 + \mathrm{i}\cdot - \left(h_1 + \lambda\widetilde{\Sigma^{\mathrm{app}}}(\mu_0 + \mathrm{i}\cdot)\right)\right]^{-1}. \end{aligned}$$

With this notation, $\widetilde{G^{\mathrm{GW}^0_\lambda}}$ is a solution of the GW^0_λ equations (4.101) if and only if it is a fixed-point of $\mathfrak{g}_\lambda \circ \mathfrak{s}$. The fact that these maps are indeed well-defined is proved in the following proposition (see Section 4.6.19 for the proof).

Proposition 4.73. *The operator $\mathfrak{s}$ is a bounded linear operator from $L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ to $L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$. On the other hand, for all $M > 0$, there exists $\lambda_M > 0$ and $C_M \in \mathbb{R}^+$ such that for all $0 \le \lambda < \lambda_M$, and all $\widetilde{\Sigma^{\mathrm{app}}}$ such that $\left\|\widetilde{\Sigma^{\mathrm{app}}}(\mu_0 + \mathrm{i}\cdot)\right\|_{L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} \le M$, the function $\mathfrak{g}_\lambda[\Sigma^{\mathrm{app}}](\mu_0 + \mathrm{i}\cdot)$ is well-defined as an element of $L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)) \cap L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$, with*

$$\left\|\mathfrak{g}_\lambda\left[\widetilde{\Sigma^{\mathrm{app}}}\right](\mu_0 + \mathrm{i}\cdot)\right\|_{L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} + \left\|\mathfrak{g}_\lambda\left[\widetilde{\Sigma^{\mathrm{app}}}\right](\mu_0 + \mathrm{i}\cdot)\right\|_{L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} \le C_M.$$

Moreover, for all $\widetilde{\Sigma^{\mathrm{app}}_1}, \widetilde{\Sigma^{\mathrm{app}}_2} \in L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ such that $\left\|\widetilde{\Sigma^{\mathrm{app}}_j}(\mu_0 + \mathrm{i}\cdot)\right\|_{L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} \le M$ for $1 \le j \le 2$,

$$\mathfrak{g}_\lambda\left[\widetilde{\Sigma^{\mathrm{app}}_1}\right] - \mathfrak{g}_\lambda\left[\widetilde{\Sigma^{\mathrm{app}}_2}\right] = \lambda\mathfrak{g}_\lambda\left[\widetilde{\Sigma^{\mathrm{app}}_1}\right]\left(\widetilde{\Sigma^{\mathrm{app}}_2} - \widetilde{\Sigma^{\mathrm{app}}_1}\right)\mathfrak{g}_\lambda\left[\widetilde{\Sigma^{\mathrm{app}}_2}\right]. \tag{4.102}$$

To prove the existence of a fixed-point for $\mathfrak{g}_\lambda \circ \mathfrak{s}$, we rely on Picard's fixed-point theorem. Since the solution of the $\mathrm{GW}^0_{\lambda=0}$ equations (4.101) for $\lambda = 0$ is $\widetilde{G_0}$, we are lead to introduce, for $r > 0$, the (closed) ball

$$\mathfrak{B}\left(\widetilde{G_0}, r\right) = \left\{ \widetilde{G^{\mathrm{app}}}(\mu_0 + \mathrm{i}\cdot) \in L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)) \,,\ \left\| \widetilde{G^{\mathrm{app}}}(\mu_0 + \mathrm{i}\cdot) - \widetilde{G_0}(\mu_0 + \mathrm{i}\cdot) \right\|_{L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} \leq r \right\}.$$

The existence of a fixed-point is given by the following theorem (see Section 4.6.20 for the proof).

Theorem 4.74. *There exists $\lambda_* > 0$ and $r > 0$ such that, for all $0 \leq \lambda \leq \lambda_*$, there exists a unique element $\widetilde{G^{\mathrm{GW}^0_\lambda}} \in \mathfrak{B}\left(\widetilde{G_0}, r\right)$ solution to the GW^0_λ equations (4.101), or equivalently to the fixed point equation*

$$\widetilde{G^{\mathrm{GW}^0_\lambda}} = \mathfrak{g}_\lambda \circ \mathfrak{s}\left(\widetilde{G^{\mathrm{GW}^0_\lambda}}\right).$$

In addition, for all $\omega \in \mathbb{R}_\omega$, $\widetilde{G^{\mathrm{GW}^0_\lambda}}(\mu_0 + \mathrm{i}\omega)$ is an invertible operator, and

$$\left\| \left(\widetilde{G^{\mathrm{GW}^0_\lambda}}(\mu_0 + \mathrm{i}\cdot)\right)^{-1} - \left(\widetilde{G_0}(\mu_0 + \mathrm{i}\cdot)\right)^{-1} \right\|_{L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} < \infty. \tag{4.103}$$

Finally, the iterative sequence $(\mathfrak{g}_\lambda \circ \mathfrak{s})^k \left[\widetilde{G_0}\right]$ converges to $\widetilde{G^{\mathrm{GW}^0_\lambda}}$, and there exists $0 \leq \alpha < 1$ and $C \in \mathbb{R}^+$ such that

$$\left\| \left(\widetilde{G^{\mathrm{GW}^0_\lambda}} - (\mathfrak{g}_\lambda \circ \mathfrak{s})^k \left[\widetilde{G_0}\right] \right)(\mu_0 + \mathrm{i}\cdot) \right\|_{L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} \leq C\alpha^k.$$

Remark 4.75. *It is not difficult to deduce from (4.103) that the function $\omega \mapsto \widetilde{G^{\mathrm{GW}^0_\lambda}}(\mu + \mathrm{i}\omega)$ is actually in $L^p(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$, for all $p > 1$.*

4.5 Conclusion

In this chapter, we formalized with full mathematical rigor the GW theory for finite molecular systems derived by Hedin in his seminal work published in 1965 [Hed65]. In Section 4.3, we provided a mathematical definition of some one-body operators arriving in many-body perturbation theory for electronic systems, namely the one-body Green's function G, the spectral function $\mathcal{A}$, the reducible polarizability operator χ, the dynamically screened interaction operator W, and the self-energy operator Σ.

In Section 4.4, we worked out a mathematically consistent formulation of the GW^0 approximation of the GW equations, and we proved that the GW^0 model has a solution in a perturbation regime. As a by-product, we also showed that the widely used $\mathrm{G_0W^0}$ approximation of the self-energy makes perfect mathematical sense.

4.6 Proofs

4.6.1 Proof of Lemma 4.3

Let $s > 1/2$. For $f \in L^\infty(\mathbb{R}_\tau)$ and $\widehat{\varphi} \in \mathscr{S}(\mathbb{R}_\omega)$,

$$\begin{aligned}\left|\langle \mathcal{F}_T f, \widehat{\varphi}\rangle_{\mathscr{S}',\mathscr{S}}\right| = \left|\langle f, \mathcal{F}_T\widehat{\varphi}\rangle_{\mathscr{S}',\mathscr{S}}\right| &= 2\pi\left|\int_{\mathbb{R}} f(-\tau)(\mathcal{F}_T^{-1}\widehat{\varphi})(\tau)\,\mathrm{d}\tau\right| \\ &= 2\pi\left|\int_{\mathbb{R}} \frac{f(-\tau)}{(1+\tau^2)^{s/2}}\,(1+\tau^2)^{s/2}(\mathcal{F}_T^{-1}\widehat{\varphi})(\tau)\,\mathrm{d}\tau\right| \le C_s\,\|f\|_{L^\infty}\|\widehat{\varphi}\|_{H^s},\end{aligned}$$

where we have used the Cauchy-Schwarz inequality in the last step. By density, $\mathcal{F}_T f$ can be extended to a linear form on $H^s(\mathbb{R})$. The equality case $\|\mathcal{F}_T f\|_{H^{-s}} = C_s\|f\|_{L^\infty}$ is obtained for constant functions.

4.6.2 Proof of Theorem 4.10

Proof of (i). The analyticity of $\widetilde{g}$ directly follows from the results of [Sch66, Chapter VIII].

Proof of (ii). Let $s > 1/2$, and consider $\varphi \in \mathscr{S}(\mathbb{R})$. Relying on the fact that $\widetilde{g}(\cdot + \mathrm{i}\eta)$ can be seen as the Fourier transform of $\tau \mapsto g(\tau)\mathrm{e}^{-\eta\tau}$, we obtain

$$\begin{aligned}\langle \widetilde{g}(\cdot+\mathrm{i}\eta),\varphi\rangle_{H^{-s},H^s} - \langle \widehat{g},\varphi\rangle_{H^{-s},H^s} &= \left\langle g\,\mathrm{e}^{-\eta\tau},\widehat{\varphi}\right\rangle_{\mathscr{S}',\mathscr{S}} - \langle g,\widehat{\varphi}\rangle_{\mathscr{S}',\mathscr{S}} \\ &= \int_0^\infty \left(\frac{g(\tau)}{(1+\tau^2)^{s/2}}\right)(1+\tau^2)^{s/2}\widehat{\varphi}(\tau)\left(\mathrm{e}^{-\eta\tau}-1\right)\mathrm{d}\tau,\end{aligned} \tag{4.104}$$

where the integral makes sense since $\tau \mapsto g(\tau)(1+\tau^2)^{-s/2}$ and $\tau \mapsto (1+\tau^2)^{s/2}\widehat{\varphi}(\tau)$ are in $L^2(\mathbb{R})$. It is then possible to extend the above formula to any $\varphi \in H^s(\mathbb{R})$. Moreover, by the Cauchy-Schwarz inequality,

$$\left|\langle \widetilde{g}(\cdot+\mathrm{i}\eta),\varphi\rangle_{H^{-s},H^s} - \langle \widehat{g},\varphi\rangle_{H^{-s},H^s}\right| \le I_{\eta,s}\|\varphi\|_{H^s}\|g\|_{L^\infty},$$

where

$$I_{\eta,s} = \left(2\pi\int_0^{+\infty}\frac{(1-\mathrm{e}^{-\eta\tau})^2}{(1+\tau^2)^s}\,\mathrm{d}\tau\right)^{1/2} < \infty.$$

Therefore, $\|\widetilde{g}(\cdot+\mathrm{i}\eta) - \widehat{g}\|_{H^{-s}} \le \|g\|_{L^\infty} I_{\eta,s}$. By dominated convergence, $I_{\eta,s} \to 0$ as $\eta \to 0^+$, which allows us to conclude to the strong convergence of $\widetilde{g}(\cdot+\mathrm{i}\eta)$ to $\widehat{g}$ in $H^{-s}(\mathbb{R}_\omega)$.

A similar computation shows that, for $0 < \eta_1 \le \eta_2$ and $s \in \mathbb{R}$,

$$\|\widetilde{g}(\cdot+\mathrm{i}\eta_1) - \widetilde{g}(\cdot+\mathrm{i}\eta_2)\|_{H^s} \le \|g\|_{L^\infty}\left(2\pi\int_0^{+\infty}\mathrm{e}^{-2\eta_1\tau}\left(1-\mathrm{e}^{-(\eta_2-\eta_1)\tau}\right)^2(1+\tau^2)^s\,\mathrm{d}\tau\right)^{1/2},$$

where we crucially use that $\eta_1 > 0$ to ensure the convergence of the time integral for $s > -1/2$. The right-hand side goes to 0 as η_2 goes to η_1 by dominated convergence. This allows one to conclude to the continuity of $\eta \mapsto \widetilde{g}(\cdot+\mathrm{i}\eta)$ from $(0,+\infty)$ to $H^s(\mathbb{R})$. When $s < -1/2$, it is possible to pass to the limit $\eta_1 \to 0$ and obtain the uniform continuity from $[0,+\infty)$ to $H^s(\mathbb{R})$.

Proof of (iii). We follow the approach used in [Tay58] for instance. Fix $z_0 \in \mathbb{U}$, and consider, for $R > 0$ and $0 < \alpha \le \mathrm{Im}\,(z_0)/2$, the oriented contour $\mathscr{C}$ in the complex plane composed of the semi-circle $\mathrm{i}\alpha + R\mathrm{e}^{\mathrm{i}\theta}$ for $0 \le \theta \le \pi$ and the line $\mathrm{i}\alpha + \omega$ for $-R \le \omega \le R$. The value R is taken sufficiently large for z_0 to be inside the domain encircled by the contour (see Figure 4.5).

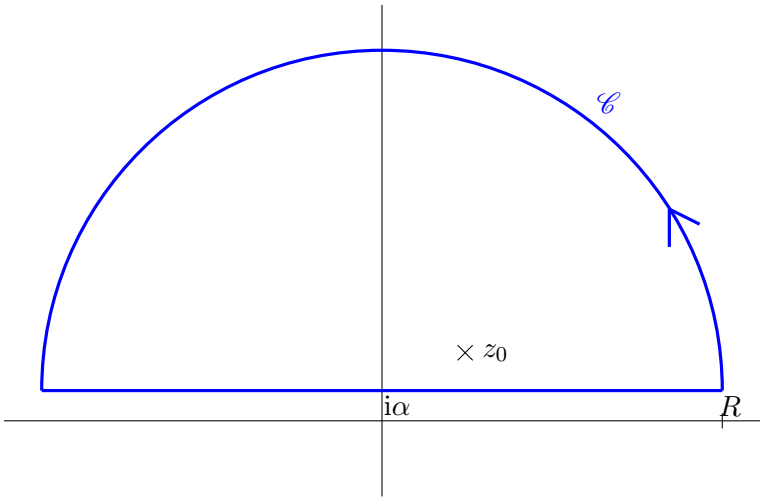

Figure 4.5 – The contour $\mathscr{C}$ used in the proof of (iii).

By Cauchy's residue theorem,

$$\widetilde{g}(z_0) = \frac{1}{2\mathrm{i}\pi} \oint_{\mathscr{C}} \frac{\widetilde{g}(z)}{z - z_0}\,\mathrm{d}z = \frac{1}{2\mathrm{i}\pi} \int_{-R}^{R} \frac{\widetilde{g}(\omega + \mathrm{i}\alpha)}{\omega + \mathrm{i}\alpha - z_0}\,\mathrm{d}\omega + \frac{1}{2\pi} \int_0^{\pi} \widetilde{g}(\mathrm{i}\alpha + R\mathrm{e}^{\mathrm{i}\theta}) \frac{R\mathrm{e}^{\mathrm{i}\theta}}{R\mathrm{e}^{\mathrm{i}\theta} + \mathrm{i}\alpha - z_0}\,\mathrm{d}\theta. \tag{4.105}$$

Now, for $z \in \mathbb{U}$,

$$|\widetilde{g}(z)| \leq \frac{\|g\|_{L^\infty}}{\mathrm{Im}\,(z)},$$

so that

$$\left| \int_0^{\pi} \widetilde{g}(\mathrm{i}\alpha + R\mathrm{e}^{\mathrm{i}\theta}) \frac{R\mathrm{e}^{\mathrm{i}\theta}}{R\mathrm{e}^{\mathrm{i}\theta} + \mathrm{i}\alpha - z_0}\,\mathrm{d}\theta \right| \leq \|g\|_{L^\infty} \int_0^{\pi} \frac{R}{|\alpha + R\sin\theta|\,|R\mathrm{e}^{\mathrm{i}\theta} + \mathrm{i}\alpha - z_0|}\,\mathrm{d}\theta,$$

which, by dominated convergence, converges to 0 as $R \to +\infty$ when α is fixed. On the other hand, $\widetilde{g}(\cdot + \mathrm{i}\alpha)$ belongs to $L^2(\mathbb{R}_\omega)$, while $(\cdot + \mathrm{i}\alpha - z_0)^{-1}$ is in $H^1(\mathbb{R}_\omega)$, since $\mathrm{i}\alpha - z_0$ has a non-zero imaginary part. Therefore, the limit $R \to +\infty$ can be taken in the first integral on the right-hand side of (4.105), which leads to

$$\widetilde{g}(z_0) = \frac{1}{2\mathrm{i}\pi} \int_{-\infty}^{+\infty} \frac{\widetilde{g}(\omega + \mathrm{i}\alpha)}{\omega + \mathrm{i}\alpha - z_0}\,\mathrm{d}\omega = \frac{1}{2\mathrm{i}\pi} \left\langle \widetilde{g}(\cdot + \mathrm{i}\alpha), (\cdot + \mathrm{i}\alpha - z_0)^{-1} \right\rangle_{H^{-1},H^1}.$$

The conclusion now follows from the strong convergences of $(\cdot + \mathrm{i}\alpha - z_0)^{-1}$ to $(\cdot - z_0)^{-1}$ in $H^1(\mathbb{R}_\omega)$ and of $\widetilde{g}(\cdot + \mathrm{i}\alpha)$ to $\widehat{g}$ in $H^{-1}(\mathbb{R}_\omega)$ as $\alpha \to 0$.

Proof of (iv). Let φ be a real-valued function in $\mathscr{S}(\mathbb{R}_\omega)$. From (4.12), we get

$$\int_{\mathbb{R}} \widetilde{g}(\omega + \mathrm{i}\eta)\varphi(\omega)\,\mathrm{d}\omega = \frac{1}{2\mathrm{i}\pi} \int_{\mathbb{R}} \left\langle \widehat{g}, (\cdot - \omega - \mathrm{i}\eta)^{-1} \right\rangle_{H^{-1},H^1} \varphi(\omega)\,\mathrm{d}\omega.$$

Taking the real parts of both sides, we obtain

$$\begin{aligned} &\int_{\mathbb{R}} \mathrm{Re}\,\left(\widetilde{g}(\omega + \mathrm{i}\eta)\right) \varphi(\omega)\,\mathrm{d}\omega \\ &\quad = \frac{1}{2\pi} \int_{\mathbb{R}} \left(\left\langle \mathrm{Im}\,\widehat{g}, \frac{\cdot - \omega}{(\cdot - \omega)^2 + \eta^2} \right\rangle_{H^{-1},H^1} + \left\langle \mathrm{Re}\,\widehat{g}, \frac{\eta}{(\cdot - \omega)^2 + \eta^2} \right\rangle_{H^{-1},H^1} \right) \varphi(\omega)\,\mathrm{d}\omega. \end{aligned} \tag{4.106}$$

Consider now $\phi \in C^\infty(\mathbb{R}^2)$, with support contained in $[-R, R] \times \mathbb{R}$ for some finite $R > 0$. Then, Fubini's theorem for distributions (see [Sch66, Chapter IV, Theorem IV]) asserts that, for a given distribution $T \in \mathscr{S}'(\mathbb{R})$ and $\varphi \in \mathscr{S}(\mathbb{R})$,

$$\int_{\mathbb{R}} \langle T, \phi(\cdot, \omega) \rangle_{\mathscr{S}', \mathscr{S}} \, \varphi(\omega) \, \mathrm{d}\omega = \left\langle T, \int_{\mathbb{R}} \phi(\cdot, \omega) \varphi(\omega) \, \mathrm{d}\omega \right\rangle_{\mathscr{S}', \mathscr{S}}.$$

When $T \in H^{-1}(\mathbb{R})$, the above linear form can be extended to functions in $H^1(\mathbb{R})$. Therefore, (4.106) can be rewritten as

$$\begin{aligned} \int_{\mathbb{R}} \mathrm{Re}\, \left(\widetilde{g}(\omega + \mathrm{i}\eta)\right) \varphi(\omega) \, \mathrm{d}\omega = & \left\langle \mathrm{Im}\, \widehat{g}, \frac{1}{2\pi} \int_{\mathbb{R}} \frac{\cdot - \omega}{(\cdot - \omega)^2 + \eta^2} \varphi(\omega) \, \mathrm{d}\omega \right\rangle_{H^{-1}, H^1} \\ & + \left\langle \mathrm{Re}\, \widehat{g}, \frac{1}{2\pi} \int_{\mathbb{R}} \frac{\eta}{(\cdot - \omega)^2 + \eta^2} \varphi(\omega) \, \mathrm{d}\omega \right\rangle_{H^{-1}, H^1}. \end{aligned} \tag{4.107}$$

In view of the following strong convergences in $H^1(\mathbb{R})$,

$$\frac{1}{2\pi} \int_{\mathbb{R}} \frac{\xi - \omega}{(\xi - \omega)^2 + \eta^2} \, \varphi(\omega) \, \mathrm{d}\omega \xrightarrow[\eta \to 0]{} \frac{1}{2} (\mathfrak{H}\varphi)(\xi), \qquad \frac{1}{2\pi} \int_{\mathbb{R}} \frac{\eta}{(\xi - \omega)^2 + \eta^2} \, \varphi(\omega) \, \mathrm{d}\omega \xrightarrow[\eta \to 0]{} \frac{1}{2} \varphi(\xi),$$

the equality (4.107) leads, in the limit $\eta \to 0^+$, to

$$\langle \mathrm{Re}\, \widehat{g}, \varphi \rangle_{H^{-1}, H^1} = \frac{1}{2} \langle \mathrm{Im}\, \widehat{g}, \mathfrak{H}(\varphi) \rangle_{H^{-1}, H^1} + \frac{1}{2} \langle \mathrm{Re}\, \widehat{g}, \varphi \rangle_{H^{-1}, H^1}.$$

The first equality in the statement of item (iv) is finally obtained with the following lemma (recall that, according to Lemma 4.4, $H^s(\mathbb{R})$ is stable by the Hilbert transform). The second equality follows by applying $\mathfrak{H}$ to both sides and remembering that $\mathfrak{H}^2 = -\mathrm{Id}$.

Lemma 4.76. *Let $s \geq 0$. For any $T \in H^{-s}(\mathbb{R})$ and $\varphi \in H^s(\mathbb{R})$,*

$$\langle \mathfrak{H}(T), \varphi \rangle_{H^{-s}, H^s} = - \langle T, \mathfrak{H}(\varphi) \rangle_{H^{-s}, H^s}.$$

Proof. Consider first the case when $T, \varphi \in \mathscr{S}(\mathbb{R})$. Then, using Plancherel's formula, the duality product can be rewritten using a L^2-scalar product

$$\begin{aligned} \langle \mathfrak{H}T, \varphi \rangle_{\mathscr{S}', \mathscr{S}} = (\overline{\mathfrak{H}T}, \phi)_{L^2} = 2\pi \left(\overline{\mathcal{F}^{-1}(\mathfrak{H}T)}, \mathcal{F}^{-1}\varphi \right)_{L^2} = 2\pi \left(-\mathrm{i}\, \mathrm{sgn}(\cdot) \mathcal{F}^{-1}\overline{T}, \mathcal{F}^{-1}\varphi \right)_{L^2} \\ = 2\pi \left(\mathcal{F}^{-1}\overline{T}, \mathrm{i}\, \mathrm{sgn}(\cdot) \mathcal{F}^{-1}\varphi \right)_{L^2} = - \left(\overline{T}, \mathfrak{H}\varphi \right)_{L^2} = -\langle T, \mathfrak{H}\varphi \rangle_{\mathscr{S}', \mathscr{S}}. \end{aligned}$$

The conclusion is obtained by a density argument. □

4.6.3 Proof of Proposition 4.12

The proof presented in Section 4.6.2 can be followed *mutatis mutandis* upon introducing, for given elements $f, g \in \mathcal{H}$, the bounded causal function

$$a_{f,g}(\tau) = \langle f \, | T_{\mathrm{c}}(\tau) | \, g \rangle,$$

and noting that $\|a_{f,g}\|_{L^\infty} \leq \|T_{\mathrm{c}}\|_{L^\infty(\mathcal{B}(\mathcal{H}))} \|f\| \|g\|$.

The only additional technical point is the strong analyticity property, which is however easily obtained from the following bound: for $z = \omega + \mathrm{i}\eta \in \mathbb{U}$,

$$\begin{aligned} \left\| \frac{\mathrm{d}\widetilde{T}_{\mathrm{c}}(z)}{\mathrm{d}z} \right\|_{\mathcal{B}(\mathcal{H})} &= \left\| \int_0^\infty T_{\mathrm{c}}(\tau)(\mathrm{i}\tau) \mathrm{e}^{-\eta\tau} \mathrm{e}^{\mathrm{i}\omega\tau} \, \mathrm{d}\tau \right\|_{\mathcal{B}(\mathcal{H})} \\ &\leq \|T_{\mathrm{c}}\|_{L^\infty(\mathbb{R}_\tau, \mathcal{B}(\mathcal{H}))} \int_0^\infty \tau \mathrm{e}^{-\eta\tau} \, \mathrm{d}\tau = \frac{\|T_{\mathrm{c}}\|_{L^\infty(\mathbb{R}_\tau, \mathcal{B}(\mathcal{H}))}}{\eta^2} < +\infty. \end{aligned}$$

4.6.4 Proof of Proposition 4.13

For $z \in \mathbb{U}$, we have

$$\widetilde{A}_{\mathrm{c}}(z) = \int_{\mathbb{R}} A_{\mathrm{c}}(\tau)\, \mathrm{e}^{\mathrm{i}z\tau}\, \mathrm{d}\tau = -\mathrm{i} \int_0^{+\infty} \mathrm{e}^{-\mathrm{i}\tau H} \mathrm{e}^{\mathrm{i}z\tau}\, \mathrm{d}\tau.$$

A simple computation shows that

$$\widetilde{A}_{\mathrm{c}}(\omega + \mathrm{i}\eta) = -\mathrm{i} \int_0^{+\infty} \int_{\mathbb{R}} \mathrm{e}^{\mathrm{i}\tau(\omega+\mathrm{i}\eta-\lambda)}\, \mathrm{d}P_\lambda^H\, \mathrm{d}\tau = \int_{\mathbb{R}} \frac{1}{\omega + \mathrm{i}\eta - \lambda}\, \mathrm{d}P_\lambda^H = (\omega + \mathrm{i}\eta - H)^{-1}.$$

The series of equalities can be made rigorous by testing them against functions $f, g \in \mathcal{H}$, and using Fubini's theorem to justify the exchange in the order of integration.

The strong convergence of $\widetilde{A}_{\mathrm{c}}(\cdot + \mathrm{i}\eta)$ to $\widehat{A}_{\mathrm{c}}$ in $H^1(\mathbb{R}_\tau, \mathcal{B}(\mathcal{H}))$ is ensured by Proposition 4.12. The Fourier transform can therefore be deduced from this limiting procedure. We consider the limit of $\operatorname{Im} \widetilde{A}_{\mathrm{c}}(\cdot + \mathrm{i}\eta)$, the real part of $\widetilde{A}_{\mathrm{c}}(\cdot + \mathrm{i}\eta)$ being obtained from (4.14) and Definition 4.8.

Let $f \in \mathcal{H}$ and $\varphi \in \mathscr{S}(\mathbb{R}_\omega)$. Then, using Fubini's theorem,

$$\left\langle \left\langle f \left| \operatorname{Im} \widetilde{A}_{\mathrm{c}}(\cdot + \mathrm{i}\eta) \right| f \right\rangle, \varphi \right\rangle_{\mathscr{S}',\mathscr{S}} = -\int_{\mathbb{R}} \int_{\mathbb{R}} \frac{\eta}{(\omega-\lambda)^2 + \eta^2}\, \varphi(\omega)\, \mu_f^H(\mathrm{d}\lambda)\, \mathrm{d}\omega = -\int_{\mathbb{R}} t_\eta(\lambda)\, \mu_f^H(\mathrm{d}\lambda), \tag{4.108}$$

where the measure μ_f^H is defined by $\mu_f^H(b) = \langle f \left| P_b^H \right| f \rangle$ for any $b \in \mathscr{B}(\mathbb{R})$, and

$$t_\eta(\lambda) = \int_{\mathbb{R}} \frac{\eta}{(\omega-\lambda)^2 + \eta^2}\, \varphi(\omega)\, \mathrm{d}\omega = \int_{\mathbb{R}} \frac{1}{\xi^2 + 1}\, \varphi(\lambda + \eta\xi)\, \mathrm{d}\xi.$$

Note that

$$|t_\eta(\lambda) - \pi\varphi(\lambda)| \le \int_{\mathbb{R}} \frac{1}{\xi^2+1} |\varphi(\lambda + \eta\xi) - \varphi(\lambda)|\, \mathrm{d}\xi \le \sqrt{\eta} \|\varphi'\|_{L^2} \int_{\mathbb{R}} \frac{\sqrt{\xi}}{1+\xi^2}\, \mathrm{d}\xi,$$

where the last bound is obtained by rewriting $\varphi(\lambda + \eta\xi) - \varphi(\lambda)$ as the integral of its derivative and using a Cauchy-Schwarz inequality. This also shows that t_η is uniformly bounded as $\eta \to 0^+$. Since the measure μ_f^H is finite, (4.108) leads by dominated convergence to

$$\left\langle \left\langle f \left| \operatorname{Im} \widetilde{A}_{\mathrm{c}}(\cdot + \mathrm{i}\eta) \right| f \right\rangle, \varphi \right\rangle_{\mathscr{S}',\mathscr{S}} \xrightarrow[\eta\to 0]{} -\pi \int_{\mathbb{R}} \varphi(\lambda)\, \mu_f^H(\mathrm{d}\lambda),$$

which shows that $\operatorname{Im} \widehat{A}_{\mathrm{c}} = -\pi P^H$.

4.6.5 Proof of Lemma 4.14

Let us first assume that $\operatorname{Im} \widehat{T}_{\mathrm{c}} \ge 0$. The aim is to prove that $\operatorname{Re} \widehat{T}_{\mathrm{c}} \ge 0$ on $(-\infty, \omega_0]$. Consider to this end $\varphi \in \mathscr{S}(\mathbb{R})$ with $\operatorname{Supp}(\varphi) \subset (-\infty, \omega_0]$ and $\varphi \ge 0$. Then, for any $\omega \ge \omega_0$ and $\omega' \le 0$, it holds $\varphi(\omega - \omega') = 0$, so that

$$\forall \omega \ge \omega_0, \qquad (\mathfrak{H}\varphi)(\omega) = \lim_{\varepsilon \to 0^+} \int_{\mathbb{R}\setminus[-\varepsilon,\varepsilon]} \frac{\varphi(\omega - \omega')}{\omega'}\, \mathrm{d}\omega' = \lim_{\varepsilon \to 0^+} \int_{\varepsilon}^{+\infty} \frac{\varphi(\omega - \omega')}{\omega'}\, \mathrm{d}\omega' \ge 0. \tag{4.109}$$

Let $f \in \mathcal{H}$. In view of (4.14) and Lemma 4.76,

$$\begin{aligned} \left\langle \left\langle f \left| \operatorname{Re} \widehat{T}_{\mathrm{c}} \right| f \right\rangle, \varphi \right\rangle_{H^{-1},H^1} &= -\left\langle \left\langle f \left| \mathfrak{H}\left(\operatorname{Im} \widehat{T}_{\mathrm{c}} \right) \right| f \right\rangle, \varphi \right\rangle_{H^{-1},H^1} = -\left\langle \mathfrak{H}\left(\left\langle f \left| \operatorname{Im} \widehat{T}_{\mathrm{c}} \right| f \right\rangle \right), \varphi \right\rangle_{H^{-1},H^1} \\ &= \left\langle \left\langle f \left| \operatorname{Im} \widehat{T}_{\mathrm{c}} \right| f \right\rangle, \mathfrak{H}\varphi \right\rangle_{H^{-1},H^1}. \end{aligned}$$

The latter quantity is non-negative since $\operatorname{Im}\widehat{T}_{\mathrm{c}} \geq 0$ and $\mathfrak{H}\varphi \geq 0$ on $\operatorname{Supp}(\operatorname{Im}\widehat{T}_{\mathrm{c}}) \subset [\omega_0, +\infty)$ (by (4.109)).

Let us now assume that $\operatorname{Re}\widehat{T}_{\mathrm{c}} \geq 0$ on $(-\infty, \omega_0]$. The aim is to prove that $\operatorname{Im}\widehat{T}_{\mathrm{c}} \geq 0$ on the support of this distribution, which is included in $[\omega_0, +\infty)$. Consider therefore $\varphi \in \mathscr{S}(\mathbb{R})$ with $\operatorname{Supp}(\varphi) \subset [\omega_0, +\infty)$ and $\varphi \geq 0$. Note that

$$\forall \omega \leq \omega_0, \qquad (\mathfrak{H}\varphi)(\omega) = \lim_{\varepsilon \to 0^-} \int_{-\infty}^{\varepsilon} \frac{\varphi(\omega - \omega')}{\omega'} \, \mathrm{d}\omega' \leq 0,$$

and, for any $f \in \mathcal{H}$,

$$\left\langle \left\langle f \left| \operatorname{Im}\widehat{T}_{\mathrm{c}} \right| f \right\rangle, \varphi \right\rangle_{H^{-1}, H^1} = - \left\langle \left\langle f \left| \operatorname{Re}\widehat{T}_{\mathrm{c}} \right| f \right\rangle, \mathfrak{H}\varphi \right\rangle_{H^{-1}, H^1} \geq 0.$$

This gives the desired conclusion.

4.6.6 Proof of Lemma 4.21

The fact that $B_1 \in \mathcal{B}(L^1(\mathbb{R}^2), L^2(\mathbb{R}^3))$ is a simple consequence of the following inequality: for $\varphi \in L^1(\mathbb{R}^3)$, it holds, for almost all $\mathbf{r} \in \mathbb{R}^3$,

$$|B_1\varphi(\mathbf{r})| = \left| \int_{\mathbb{R}^3} B_1(\mathbf{r}, \mathbf{r}')\varphi(\mathbf{r}') \mathrm{d}\mathbf{r}' \right| \leq \|B_1(\mathbf{r}, \cdot)\|_{L^\infty(\mathbb{R}^3)} \, \|\varphi\|_{L^1(\mathbb{R}^3)}.$$

This shows that $B_1\varphi \in L^2(\mathbb{R}^3)$ with

$$\|B_1\varphi\|_{L^2(\mathbb{R}^3)} \leq \left(\int_{\mathbb{R}^3} \|B_1(\mathbf{r}, \cdot)\|^2_{L^\infty(\mathbb{R}^3)} \, \mathrm{d}\mathbf{r} \right)^{1/2} \|\varphi\|_{L^1(\mathbb{R}^3)}.$$

Now, for $f \in L^2(\mathbb{R}^3)$, it is easy to see that $B_1 f$ is an integral operator with kernel $B_1(\mathbf{r}, \mathbf{r}')f(\mathbf{r}')$. In addition,

$$\begin{aligned} \|B_1 f\|^2_{\mathfrak{S}_2(L^2(\mathbb{R}^3))} &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left| B_1(\mathbf{r}, \mathbf{r}')f(\mathbf{r}') \right|^2 \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}' \leq \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \|B_1(\mathbf{r}, \cdot)\|^2_{L^\infty(\mathbb{R}^3)} |f(\mathbf{r}')|^2 \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}' \\ &= \left(\int_{\mathbb{R}^3} \|B_1(\mathbf{r}, \cdot)\|^2_{L^2(\mathbb{R}^3)} \mathrm{d}\mathbf{r} \right) \|f\|^2_{L^2(\mathbb{R}^3)}. \end{aligned}$$

This gives the claimed result.

4.6.7 Proof of Theorem 4.24

Fix $0 < \eta < \omega$ and $f, g \in \mathcal{H}$. We start from (4.24), which we rewrite as

$$\widetilde{C^+}(\nu + \mathrm{i}\omega) = \frac{\mathrm{i}}{2\pi} \int_{-\infty}^{+\infty} \widetilde{A^+}\big(\nu + \nu' - \omega' + \mathrm{i}(\omega - \eta)\big) \odot \widetilde{B^-}(\nu' - \omega' - \mathrm{i}\eta) \, \mathrm{d}\omega'. \tag{4.110}$$

By Proposition 4.13 and Proposition 4.17,

$$\widetilde{A^+}(z) = A_1^*(z - A_2)^{-1}A_1, \qquad \widetilde{B^-}(z) = B_1^*(z + B_2)^{-1}B_1. \tag{4.111}$$

The poles of $z \mapsto \widetilde{A^+}\big(\nu + \nu' + \mathrm{i}(\omega - \eta) - z\big)$ are located on the half-line $\mathrm{i}(\omega - \eta) + (-\infty, \nu + \nu' - a)$, while those of $z \mapsto \widetilde{B^-}(\nu' - \mathrm{i}\eta - z)$ are located on the half-line $-\mathrm{i}\eta + (b + \nu', +\infty)$. For any closed contour not enclosing any point of those two half-lines, the integral of

$$z \mapsto \widetilde{A^+}\big(\nu + \nu' + \mathrm{i}(\omega - \eta) - z\big) \odot \widetilde{B^-}(\nu' - \mathrm{i}\eta - z)$$

on this contour vanishes. Let us choose the contour $\mathscr{C}_L$ plotted in Figure 4.6 and evaluate the contributions of the left-hand side of

$$\oint_{\mathscr{C}_L} \mathrm{Tr}_{\mathcal{H}} \left[\widetilde{A^+}\big(\nu+\nu'+\mathrm{i}(\omega-\eta)-z\big) g \widetilde{B^-}(\nu'-\mathrm{i}\eta-z)\overline{f} \right] \mathrm{d}z = 0, \tag{4.112}$$

on the various segments. Recall that we choose $\nu < a+b$ and $\nu' \in (-b, a-\nu)$, so that $\nu+\nu'-a<0<\nu'+b$. Let us also emphasize that the operators appearing in the integrand do not have singularities.

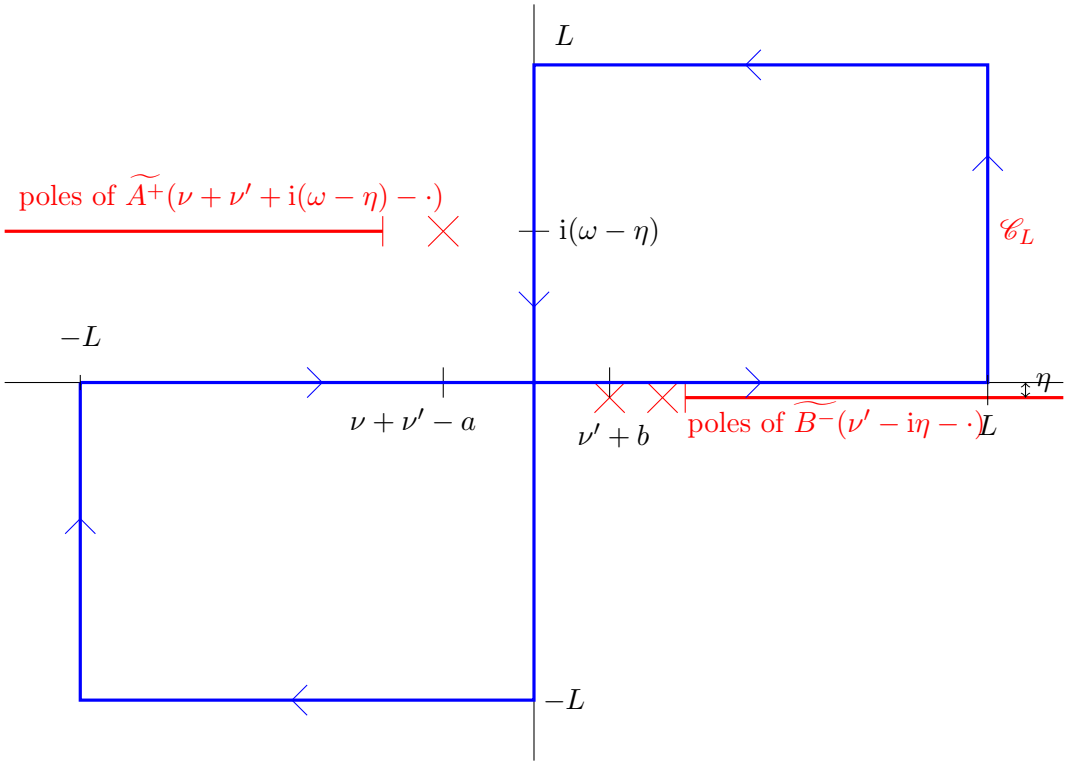

Figure 4.6 – Contour $\mathscr{C}_L$ used to compute the integral (4.112), with $\eta > 0$ small compared to ω. Note that the condition $\nu+\nu'-a<0<\nu'+b$ ensures that the central vertical part of the contour does not intersect the poles of the functions in the integrand.

Let us first consider the part of the integral corresponding to the right side of the contour. Using (4.111), we obtain that for all $\omega' \in [0, L]$,

$$\begin{aligned}
&\left| \int_0^L \mathrm{Tr}_{\mathcal{H}} \left[\widetilde{A^+}\big(\nu+\nu'-L+\mathrm{i}(\omega-\eta-\omega')\big) g \widetilde{B^-}\big(\nu'-L-\mathrm{i}(\omega'+\eta)\big)\overline{f} \right] \mathrm{d}\omega' \right| \\
&\leq \int_0^L \left| \mathrm{Tr}_{\mathcal{H}} \left[A_1^* \frac{1}{\nu+\nu'-L+\mathrm{i}(\omega-\eta-\omega')-A_2} A_1 g B_1^* \frac{1}{\nu'-L-\mathrm{i}(\omega'+\eta)+B_2} B_1 \overline{f} \right] \right| \mathrm{d}\omega' \\
&\leq \big\| B_1 \overline{f} \big\|_{\mathfrak{S}_2(\mathcal{H},\mathcal{H}_b)} \big\| B_1 \overline{g} \big\|_{\mathfrak{S}_2(\mathcal{H},\mathcal{H}_b)} \|A_1\|^2_{\mathcal{B}(\mathcal{H},\mathcal{H}_a)} \\
&\qquad \times \int_0^L \left\| \frac{1}{\nu+\nu'-L+\mathrm{i}(\omega-\eta-\omega')-A_2} \right\|_{\mathcal{B}(\mathcal{H}_a)} \left\| \frac{1}{\nu'-L-\mathrm{i}(\omega'+\eta)+B_2} \right\|_{\mathcal{B}(\mathcal{H}_b)} \mathrm{d}\omega' \\
&\leq C\|f\|_{\mathcal{H}}\|g\|_{\mathcal{H}} \frac{1}{L} \int_0^L \frac{\mathrm{d}\omega'}{\omega'+\eta} = C\|f\|_{\mathcal{H}}\|g\|_{\mathcal{H}} \frac{1}{L} \log\left(\frac{L+\eta}{\eta}\right),
\end{aligned}$$

where we have used $A_2 - (\nu+\nu') + L \geq a - (\nu+\nu') + L \geq L$. Similar estimates can be stated for the upper, lower and left parts of the contour. For the upper part for instance, for which

the integration is performed from $z = L + \mathrm{i}L$ to $z = \mathrm{i}L$, we get

$$\begin{aligned}
&\left| \int_L^0 \mathrm{Tr}_{\mathcal{H}} \left[\widetilde{A^+}\big(\nu + \nu' - \omega' + \mathrm{i}(\omega - \eta - L)\big) g \widetilde{B^-}\big(\nu' - \omega' - \mathrm{i}(\eta + L)\big) \overline{f} \right] \mathrm{d}\omega' \right| \\
&\leq C \|f\|_{\mathcal{H}} \|g\|_{\mathcal{H}} \int_0^L \left\| \frac{1}{\nu + \nu' - \omega' + \mathrm{i}(\omega - \eta - L) - A_2} \right\|_{\mathcal{B}(\mathcal{H}_a)} \left\| \frac{1}{\nu' - \omega' + \mathrm{i}(L + \eta) - B_2} \right\|_{\mathcal{B}(\mathcal{H}_b)} \mathrm{d}\omega' \\
&\leq C \|f\|_{\mathcal{H}} \|g\|_{\mathcal{H}} \int_0^L \left(\frac{1}{L + \eta} \right) \frac{1}{\omega' + a - (\nu + \nu')} \mathrm{d}\omega' \\
&= C \|f\|_{\mathcal{H}} \|g\|_{\mathcal{H}} \frac{\log\big(L + a - (\nu + \nu')\big) - \log\big(a - (\nu + \nu')\big)}{L + \eta},
\end{aligned}$$

where we recall that $a - (\nu + \nu') > 0$. We then take the limit $L \to +\infty$, so that the contributions to the integral which are not on the imaginary axis or on the real axis vanish. We deduce that

$$\begin{aligned}
&\int_{-\infty}^{\infty} \mathrm{Tr}_{\mathcal{H}} \left[\widetilde{A^+}\big(\nu + \nu' - \omega' + \mathrm{i}(\omega - \eta)\big) g \widetilde{B^-}(\nu' - \omega' - \mathrm{i}\eta) \overline{f} \right] \mathrm{d}\omega' \\
&\qquad = \mathrm{i} \int_{-\infty}^{+\infty} \mathrm{Tr}_{\mathcal{H}} \left[\widetilde{A^+}\big(\nu + \nu' + \mathrm{i}(\omega - \eta + \omega')\big) g \widetilde{B^-}\big(\nu' + \mathrm{i}(\omega' - \eta)\big) \overline{f} \right] \mathrm{d}\omega' \\
&\qquad = \mathrm{i} \int_{-\infty}^{+\infty} \mathrm{Tr}_{\mathcal{H}} \left[\widetilde{A^+}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) g \widetilde{B^-}(\nu' + \mathrm{i}\omega') \overline{f} \right] \mathrm{d}\omega'.
\end{aligned}$$

In view of (4.110), we finally obtain that

$$\widetilde{C^+}(\nu + \mathrm{i}\omega) = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} \widetilde{A^+}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) \odot \widetilde{B^-}(\nu' + \mathrm{i}\omega') \, \mathrm{d}\omega'. \tag{4.113}$$

We next note that our choices for ν, ν' ensure that the expressions on both sides are analytic for all $\omega > 0$, and can be extended analytically to all $\omega \in \mathbb{R}$. Therefore, the above equality also holds true for $\omega \leq 0$.

In a similar fashion, we prove that, for all $\omega \in \mathbb{R}$,

$$\widetilde{C^-}(\nu + \mathrm{i}\omega) = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} \widetilde{A^-}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) \odot \widetilde{B^+}(\nu' + \mathrm{i}\omega') \mathrm{d}\omega'.$$

This equality is established as for (4.113) by considering $\widetilde{C^-}(\nu - \mathrm{i}\omega)$ for $\omega > 0$ and evaluating the various parts of the left-hand side of

$$\oint_{\mathscr{C}_L} \mathrm{Tr}_{\mathcal{H}} \left[\widetilde{A^-}\big(\nu + \nu' - \mathrm{i}(\omega - \eta) - z\big) g \widetilde{B^+}(\nu' + \mathrm{i}\eta - z) \overline{f} \right] \mathrm{d}z = 0.$$

The poles of the integrand are on the half-lines

$$-\mathrm{i}(\omega - \eta) + (\nu + \nu' + a, +\infty) \quad \text{and} \quad \mathrm{i}\eta + (-\infty, -b + \nu').$$

The conditions $\nu > -(a + b)$ and $-a - \nu < \nu' < b$ ensure that $-b + \nu' < 0 < \nu + \nu' + a$, so that the integrand has no singularity on the imaginary axis.

Finally, since $A^+(\tau) \odot B^+(-\tau) = A^-(\tau) \odot B^-(-\tau) = 0$ for $\tau \neq 0$, we can concatenate $\widetilde{C^+}(\nu + \mathrm{i}\omega)$ and $\widetilde{C^-}(\nu + \mathrm{i}\omega)$, and obtain

$$\widetilde{C}(\nu + \mathrm{i}\omega) = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} \widetilde{A}\big(\nu + \nu' + \mathrm{i}(\omega + \omega')\big) \odot \widetilde{B}(\nu' + \mathrm{i}\omega') \, \mathrm{d}\omega'.$$

4.6.8 Proof of Corollary 4.25

The proof is based on the representation (4.25) with the choice $\omega = 0$. Consider $\nu < a + b$. It holds

$$\begin{aligned}\widehat{C^+}(\nu) = \widetilde{C^+}(\nu) &= -\frac{1}{2\pi}\int_{-\infty}^{+\infty} \widetilde{A^+}(\nu+\nu'+\mathrm{i}\omega') \odot \widetilde{B^-}(\nu'+\mathrm{i}\omega')\,\mathrm{d}\omega' \\ &= -\frac{1}{2\pi}\int_{-\infty}^{+\infty} \left[A_1^* \frac{\nu+\nu'-A_2-\mathrm{i}\omega'}{(\nu+\nu'-A_2)^2+(\omega')^2} A_1\right] \odot \left[B_1^* \frac{\nu'+B_2-\mathrm{i}\omega'}{(\nu'+B_2)^2+(\omega')^2} B_1\right] \mathrm{d}\omega'.\end{aligned}$$

The odd terms in ω' cancel out by symmetry, so that

$$\begin{aligned}\widehat{C^+}(\nu) = &\frac{1}{2\pi}\int_{-\infty}^{+\infty} \left[A_1^* \frac{A_2-(\nu+\nu')}{(\nu+\nu'-A_2)^2+(\omega')^2} A_1\right] \odot \left[B_1^* \frac{\nu'+B_2}{(\nu'+B_2)^2+(\omega')^2} B_1\right] \mathrm{d}\omega' \\ &+ \frac{1}{2\pi}\int_{-\infty}^{+\infty} \left[A_1^* \frac{\omega'}{(\nu+\nu'-A_2)^2+(\omega')^2} A_1\right] \odot \left[B_1^* \frac{\omega'}{(\nu'+B_2)^2+(\omega')^2} B_1\right] \mathrm{d}\omega'.\end{aligned} \tag{4.114}$$

This shows that this operator is positive and self-adjoint in view of Lemmas 4.22 and 4.23. As a result, $\operatorname{Im}\widehat{C^+}(\nu) = 0$ for $\nu < a+b$. This proves the first assertion in (4.29). Also, we get from (4.114) that $\widehat{C^+}(\nu) = \operatorname{Re}\widehat{C^+} \geq 0$ for $\nu < a+b$. Together with Lemma 4.14, this shows the first assertion of (4.28). The results concerning $\operatorname{Im}\widehat{C^-}$ are proved in a similar way.

4.6.9 Proof of Proposition 4.26

The first assertion follows from the fact that the domain of H_N is $H^2(\mathbb{R}^{3N})$ and from the equalities $H_N \operatorname{Re}(\Psi_N^0) = E_N^0 \operatorname{Re}(\Psi_N^0)$ and $H_N \operatorname{Im}(\Psi_N^0) = E_N^0 \operatorname{Im}(\Psi_N^0)$.

The density ρ_N^0 is bounded since it decreases exponentially fast away from the nuclei and is continuous [FHOHOØS02].

In order to prove (4.36), we rely on (4.31) and (4.34) in order to write (recall that Ψ_N^0 is real valued)

$$\begin{aligned}\left\langle \Psi_N^0 | a^\dagger(g)a(f) | \Psi_N^0 \right\rangle_{\mathcal{H}_N} &= \left\langle a(g)\Psi_N^0 | a(f)\Psi_N^0 \right\rangle_{\mathcal{H}_N} \\ &= N \int_{\mathbb{R}^{3(N-1)}} \left(\int_{\mathbb{R}^3} g(\mathbf{r})\Psi_N^0(\mathbf{r},\vec{\mathbf{z}})\,\mathrm{d}\mathbf{r}\right)\left(\int_{\mathbb{R}^3} \overline{f(\mathbf{r}')}\Psi_N^0(\mathbf{r}',\vec{\mathbf{z}})\,\mathrm{d}\mathbf{r}'\right)\mathrm{d}\vec{\mathbf{z}} \\ &= \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} g(\mathbf{r})\gamma_N^0(\mathbf{r},\mathbf{r}')\overline{f(\mathbf{r}')}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' = \langle f|\gamma_N^0|g\rangle.\end{aligned}$$

To bound the kernel $|\gamma_N^0(\mathbf{r},\mathbf{r}')|^2$, we use the Cauchy-Schwarz inequality and get

$$\begin{aligned}|\gamma_N^0(\mathbf{r},\mathbf{r}')|^2 &= N^2 \left|\int_{(\mathbb{R}^3)^{N-1}} \Psi_N^0(\mathbf{r},\vec{\mathbf{z}})\Psi_N^0(\mathbf{r}',\vec{\mathbf{z}})\,\mathrm{d}\vec{\mathbf{z}}\right|^2 \\ &\leq N^2 \left(\int_{(\mathbb{R}^3)^{N-1}} \left|\Psi_N^0(\mathbf{r},\vec{\mathbf{z}})\right|^2 \mathrm{d}\vec{\mathbf{z}}\right)\left(\int_{(\mathbb{R}^3)^{N-1}} \left|\Psi_N^0(\mathbf{r}',\vec{\mathbf{z}})\right|^2 \mathrm{d}\vec{\mathbf{z}}\right) \leq \rho_N^0(\mathbf{r})\rho_N^0(\mathbf{r}'),\end{aligned}$$

Let us finally recall why $\rho_{N,2}^0$ defines a bounded integral operator. Note first that it

holds $\rho^0_{N,2}(\mathbf{r},\mathbf{r}') \geq 0$. For $f, g \in \mathcal{H}_1$, the Cauchy-Schwarz inequality then leads to

$$\begin{aligned}
\left|\langle f|\rho^0_{N,2}|g\rangle\right| &= \left|\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \overline{f(\mathbf{r})}\rho^0_{N,2}(\mathbf{r},\mathbf{r}')g(\mathbf{r}')\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\right| \\
&\leq \left(\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} |f(\mathbf{r})|^2\rho^0_{N,2}(\mathbf{r},\mathbf{r}')\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\right)^{1/2}\left(\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} |g(\mathbf{r}')|^2\rho^0_{N,2}(\mathbf{r},\mathbf{r}')\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\right)^{1/2} \\
&= \frac{(N-1)}{2}\left(\int_{\mathbb{R}^3} |f|^2\,\rho^0_N\right)^{1/2}\left(\int_{\mathbb{R}^3} |g|^2\,\rho^0_N\right)^{1/2} \\
&\leq \frac{(N-1)}{2}\left\|\rho^0_N\right\|_{L^\infty}\|f\|_{\mathcal{H}_1}\|g\|_{\mathcal{H}_1}.
\end{aligned}$$

This shows that $\rho^0_{N,2}$ defines a bounded operator on $\mathcal{H}_1$, with operator norm lower or equal to $(N-1)\left\|\rho^0_N\right\|_{L^\infty}/2$.

4.6.10 Proof of Theorem 4.36

Since

$$A_-f(\mathbf{r}_1,\ldots,\mathbf{r}_{N-1}) = \sqrt{N}\int_{\mathbb{R}^3} f(\mathbf{r})\Psi^0_N(\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_{N-1})\,\mathrm{d}\mathbf{r},$$

and introducing

$$\Delta_{N-1} = \sum_{i=1}^{N-1}\Delta_{\mathbf{r}_i},$$

it is easily seen that $(1-\Delta_{N-1})A_-$ is an integral operator whose kernel is

$$\left[(1-\Delta_{N-1})\Psi^0_N\right](\mathbf{r}_1,\ldots,\mathbf{r}_{N-1};\mathbf{r}).$$

As $\Psi^0_N \in H^2(\mathbb{R}^{3N})$, it follows that $(1-\Delta_{N-1})A_- \in \mathfrak{S}_2(\mathcal{H}_1,\mathcal{H}_{N-1})$. Therefore, any operator of the form $A_-^*BA_-$, where the operator B on $\mathcal{H}_{N-1}$ is such that

$$(1-\Delta_{N-1})^{-1/2}B(1-\Delta_{N-1})^{-1/2} \in \mathcal{B}(\mathcal{H}_1),$$

is trace-class. In particular, the operator

$$\partial_\tau G_{\mathrm{h}}(\tau)\big|_{\tau=0^-} = -A_-^*(H_{N-1}-E^0_N)A_-,$$

is trace-class.

Let us now compute more explicitly the action of this operator. Let

$$h_1 := -\frac{1}{2}\Delta + v_{\mathrm{ext}}.$$

We use the definition (4.31) of $a(\overline{f})$, and obtain

$$\begin{aligned}
\left(\sum_{i=1}^{N-1} h_1(\mathbf{r}_i)\right)\left[a(\overline{f})\Psi^0_N\right](\mathbf{r}_1,\ldots,\mathbf{r}_{N-1}) &= \sqrt{N}\int_{\mathbb{R}^3} f(\mathbf{r}_N)\left(\sum_{i=1}^{N-1} h_1(\mathbf{r}_i)\right)\Psi^0_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)\,\mathrm{d}\mathbf{r}_N \\
&= \sqrt{N}\int_{\mathbb{R}^3} f(\mathbf{r}_N)\left(H_{0,N}\Psi^0_N\right)(\mathbf{r}_1,\ldots,\mathbf{r}_N)\,\mathrm{d}\mathbf{r}_N \quad (4.115) \\
&\quad - \sqrt{N}\int_{\mathbb{R}^3}(h_1f)(\mathbf{r}_N)\Psi^0_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)\,\mathrm{d}\mathbf{r}_N,
\end{aligned}$$

so that

$$\begin{aligned}
\left(H_{N-1}A_-f\right)(\mathbf{r}_1,\ldots,\mathbf{r}_{N-1}) &= E^0_N\left(A_-f\right)(\mathbf{r}_1,\ldots,\mathbf{r}_{N-1}) - \left(A_-h_1f\right)(\mathbf{r}_1,\ldots,\mathbf{r}_{N-1}) \\
&\quad - \sqrt{N}\sum_{i=1}^{N-1}\int_{\mathbb{R}^3} f(\mathbf{r})\frac{\Psi^0_N(\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_{N-1})}{|\mathbf{r}-\mathbf{r}_i|}\,\mathrm{d}\mathbf{r}.
\end{aligned}$$

Moreover, it is easily seen that, for any $\Phi_{N-1} \in \mathcal{H}_{N-1}$,

$$\left(A_-^* \Phi_{N-1}\right)(\mathbf{r}) = \sqrt{N} \int_{\mathbb{R}^{3(N-1)}} \Psi_N^0(\mathbf{r}, \mathbf{r}_1, \ldots, \mathbf{r}_{N-1}) \Phi_{N-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{N-1}) \, \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_{N-1}.$$

Therefore,

$$\left(A_-^* \left(H_{N-1} - E_N^0\right) A_- f\right)(\mathbf{r}) = -\left(\gamma_N^0 h_1 f\right)(\mathbf{r}) - \int_{\mathbb{R}^3} K_N(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') \, \mathrm{d}\mathbf{r}',$$

with

$$K_N(\mathbf{r}, \mathbf{r}') = N \sum_{i=1}^{N-1} \int_{\mathbb{R}^{3(N-1)}} \frac{\Psi_N^0(\mathbf{r}, \mathbf{r}_1, \ldots, \mathbf{r}_{N-1}) \Psi_N^0(\mathbf{r}', \mathbf{r}_1, \ldots, \mathbf{r}_{N-1})}{|\mathbf{r}' - \mathbf{r}_i|} \, \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_{N-1}.$$

Since we already know that the integral operator K_N on $\mathcal{H}_1$, with kernel $K_N(\mathbf{r}, \mathbf{r}')$ is trace-class, and that Ψ_N^0 is continuous and decays exponentially fast (see *e.g.* [FHOHOØS02]), we have [Sim05, Theorem A.2]

$$\begin{aligned} \mathrm{Tr}_{\mathcal{H}_1}(K_N) = \int_{\mathbb{R}^3} K_N(\mathbf{r}, \mathbf{r}) \, \mathrm{d}\mathbf{r} &= N(N-1) \int_{\mathbb{R}^{3(N-1)}} \frac{\left|\Psi_N^0(\mathbf{r}, \mathbf{r}_1, \ldots, \mathbf{r}_{N-1})\right|^2}{|\mathbf{r} - \mathbf{r}_1|} \, \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_{N-1} \\ &= 2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{N,2}^0(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}', \end{aligned}$$

where we recall that $\rho_{N,2}^0$ is the two-body density matrix defined in (4.35).

Finally,

$$\begin{aligned} \mathrm{Tr}_{\mathcal{H}_1}\left(\partial_\tau G_{\mathrm{h}}(\tau)\big|_{\tau=0^-}\right) &= -\mathrm{Tr}_{\mathcal{H}_1}\left(A_-^*(H_{N-1} - E_N^0)A_-\right) \\ &= \mathrm{Tr}_{\mathcal{H}_1}\left(\gamma_N^0 h_1\right) + 2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{N,2}^0(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}', \end{aligned}$$

which gives the claimed result in view of the following representation of the ground state energy:

$$E_N^0 = \langle \Psi_N^0 | H_N | \Psi_N^0 \rangle = \mathrm{Tr}_{\mathcal{H}_1}\left(h_1 \gamma_N^0\right) + \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{N,2}^0(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}'. \tag{4.116}$$

4.6.11 Proof of Lemma 4.42

Proposition 4.26 shows that $\rho_N^0 \in L^p(\mathbb{R}^3)$ for $1 \leq p \leq +\infty$. This implies that $\left(\sum_{i=1}^N v(\mathbf{r}_i)\right) \Psi_N^0$ belongs to $\mathcal{H}_N$ for $v \in \mathcal{C}'$ since, from the inequality $\left(\sum_{i=1}^N v(\mathbf{r}_i)\right)^2 \leq N \sum_{i=1}^N v(\mathbf{r}_i)^2$ and Hölder's inequality, it holds that

$$\begin{aligned} \int_{\mathbb{R}^{3N}} \left(\sum_{i=1}^N v(\mathbf{r}_i)\right)^2 |\Psi_N^0(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2 \, \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N &\leq N \int_{\mathbb{R}^3} v^2 \rho_N^0 \leq N \|v\|_{L^6}^2 \|\rho_N^0\|_{L^{3/2}} \\ &\leq N C_{\mathcal{C}'} \|v\|_{\mathcal{C}'}^2 \|\rho_N^0\|_{L^{3/2}}, \end{aligned}$$

where we have used the embedding $\mathcal{C}' \hookrightarrow L^6(\mathbb{R}^3)$. Moreover, $\rho_N^0 \in L^{6/5}(\mathbb{R}^3) \hookrightarrow \mathcal{C}$, so that $\left|\langle v, \rho_N^0 \rangle_{\mathcal{C}',\mathcal{C}}\right| \leq \|v\|_{\mathcal{C}'} \|\rho_N^0\|_{\mathcal{C}}$. We therefore deduce that B is a bounded operator from $\mathcal{C}'$ to $\mathcal{H}_N$, whose norm satisfies

$$\|B\|_{\mathcal{B}(\mathcal{C}',\mathcal{H}_N)} \leq \sqrt{N C_{\mathcal{C}'} \|\rho_N^0\|_{L^{3/2}}} + \|\rho_N^0\|_{\mathcal{C}}.$$

We finally have, for $v \in \mathcal{C}'$,

$$\left\langle \Psi_N^0 \left| \sum_{i=1}^N v(\mathbf{r}_i) \right| \Psi_N^0 \right\rangle_{\mathcal{H}_N} = \int_{\mathbb{R}^3} v(\mathbf{r}) \rho_N^0(\mathbf{r}) \, \mathrm{d}\mathbf{r} = \langle v, \rho_N^0 \rangle_{\mathcal{C}',\mathcal{C}}$$

from which we deduce that $\langle \Psi_N^0 | B v \rangle_{\mathcal{H}_N} = 0$. Since v was arbitrary, we conclude that $B^* \Psi_N^0 = 0$.

4.6.12 Proof of Theorem 4.46

Consider $f, g \in C_c^\infty(\mathbb{R}^3, \mathbb{C})$ (that is C^∞ with compact supports). From $(H_N - E_N^0)|\Psi_N^0\rangle = 0$, we obtain

$$\begin{aligned}\langle \overline{f}, v_c^{-1} B^*(H_N - E_N^0)Bg\rangle_{\mathcal{C}',\mathcal{C}} &= \langle f \left| B^*(H_N - E_N^0)B \right| g\rangle_{\mathcal{C}'} = \left\langle Bf \left| H_N - E_N^0 \right| Bg \right\rangle_{\mathcal{H}_N} \\ &= \left\langle \Psi_N^0 \left| \left(\sum_{j=1}^N \overline{f(\mathbf{r}_j)} \right) (H_N - E_N^0) \left(\sum_{i=1}^N g(\mathbf{r}_i) \right) \right| \Psi_N^0 \right\rangle_{\mathcal{H}_N}.\end{aligned}$$

We next observe that

$$\begin{aligned}&(H_N - E_N^0) \left(\sum_{i=1}^N g(\mathbf{r}_i)\Psi_N^0(\mathbf{r}_1, \ldots, \mathbf{r}_N) \right) = \\ &= \left(-\frac{1}{2} \sum_{i=1}^N \Delta g(\mathbf{r}_i) \right) \Psi_N^0(\mathbf{r}_1, \ldots, \mathbf{r}_N) - \sum_{i=1}^N \nabla g(\mathbf{r}_i) \cdot \nabla_{\mathbf{r}_i} \Psi_N^0(\mathbf{r}_1, \ldots, \mathbf{r}_N),\end{aligned}$$

so that, using the fact that Ψ_N^0 is real-valued (see Proposition 4.26),

$$\begin{aligned}&\left\langle f \left| B^*(H_N - E_N^0)B \right| g \right\rangle_{\mathcal{C}'} = \\ &= \sum_{i,j=1}^N \int_{\mathbb{R}^{3N}} \overline{f(\mathbf{r}_j)} \left(-\frac{1}{2}\Delta g(\mathbf{r}_i) \right) |\Psi_N^0(\mathbf{r}_1, \ldots \mathbf{r}_N)|^2 \, \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N \\ &\quad - \sum_{i,j=1}^N \int_{\mathbb{R}^{3N}} \overline{f(\mathbf{r}_j)} \Psi_N^0(\mathbf{r}_1, \ldots, \mathbf{r}_N) \nabla g(\mathbf{r}_i) \cdot \nabla_{\mathbf{r}_i} \Psi_N^0(\mathbf{r}_1, \ldots, \mathbf{r}_N) \, \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N \\ &= \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^{3N}} \overline{\nabla f(\mathbf{r}_j)} \cdot \nabla g(\mathbf{r}_i) |\Psi_N^0(\mathbf{r}_1, \ldots \mathbf{r}_N)|^2 \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N \\ &\quad + \frac{1}{2} \sum_{i,j=1}^N \int_{\mathbb{R}^{3N}} \overline{f(\mathbf{r}_j)} \nabla g(\mathbf{r}_i) \cdot \nabla_{\mathbf{r}_i} \left(\left| \Psi_N^0(\mathbf{r}_1, \ldots, \mathbf{r}_N) \right|^2 \right) \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N \\ &\quad - \sum_{i,j=1}^N \int_{\mathbb{R}^{3N}} \overline{f(\mathbf{r}_j)} \Psi_N^0(\mathbf{r}_1, \ldots, \mathbf{r}_N) \nabla g(\mathbf{r}_i) \cdot \nabla_{\mathbf{r}_i} \Psi_N^0(\mathbf{r}_1, \ldots, \mathbf{r}_N) \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N \\ &= \frac{1}{2} \int_{\mathbb{R}^3} \overline{\nabla f(\mathbf{r})} \cdot \nabla g(\mathbf{r}) \rho_N^0(\mathbf{r}) \mathrm{d}\mathbf{r}.\end{aligned}$$

We deduce that $2v_c^{-1}B^*(H_N - E_N^0)B = 2v_c^{-1}B^*(H_N^\sharp - E_N^0)B = -\mathrm{div}\left(\rho_N^0 \nabla \cdot\right)$ as operators on the core $C_c^\infty(\mathbb{R}^3, \mathbb{C})$. We next observe that $\mathrm{div}\left(\rho_N^0 \nabla \cdot\right)$ can be extended as a bounded operator from $\mathcal{C}'$ to $\mathcal{C}$. Indeed, for $f, g \in C_c^\infty(\mathbb{R}^3, \mathbb{C})$,

$$\left| \langle g, \mathrm{div}\, \left(\rho_N^0 \nabla f\right) \rangle_{\mathcal{C}',\mathcal{C}} \right| \leq \left\| \rho_N^0 \right\|_{L^\infty} \|\nabla f\|_{L^2} \|\nabla g\|_{L^2} = 4\pi \|\rho_N^0\|_{L^\infty} \|f\|_{\mathcal{C}'} \|g\|_{\mathcal{C}'},$$

which shows that

$$\left\| \mathrm{div}\, \left(\rho_N^0 \nabla \cdot\right) \right\|_{\mathcal{B}(\mathcal{C}',\mathcal{C})} \leq 4\pi \left\| \rho_N^0 \right\|_{L^\infty}.$$

Therefore, $2v_c^{-1}B^*(H_N^\sharp - E_N^0)B = -\mathrm{div}\left(\rho_N^0 \nabla \cdot\right)$ as bounded operators from $\mathcal{C}'$ to $\mathcal{C}$.

For the second part of the proof, we first note that it is sufficient to check the convergence in the case when $f = g \in C_c^\infty(\mathbb{R}^3, \mathbb{R})$. It holds:

$$\begin{aligned}&\left\langle \overline{f}, v_c^{-1} B^* \frac{H_N^\sharp - E_N^0}{(H_N^\sharp - E_N^0)^2 + \omega^2} \omega^2 Bf \right\rangle_{\mathcal{C}',\mathcal{C}} - \langle \overline{f}, v_c^{-1} B^*(H_N^\sharp - E_N^0)Bf\rangle_{\mathcal{C}',\mathcal{C}} = \\ &= -\left\langle \overline{f}, v_c^{-1} B^* \left(\frac{(H_N^\sharp - E_N^0)^3}{(H_N^\sharp - E_N^0)^2 + \omega^2} \right) Bf \right\rangle_{\mathcal{C}',\mathcal{C}} = -\int_0^{+\infty} \left(\frac{\lambda^3}{\lambda^2 + \omega^2} \right) \mathrm{d} \left\| P_\lambda^{H_N^\sharp - E_N^0}(Bf) \right\|_{\mathcal{H}_N}^2,\end{aligned}$$

where we used the spectral decomposition of $H_N^\sharp - E_N^0$ in the last equality. The integrand of the last integral converges pointwise to 0 when $|\omega| \to +\infty$. It is also non-negative and uniformly bounded by $\lambda \mathbb{1}_{[0,+\infty)}(\lambda)$, which is integrable since

$$\int_0^{+\infty} \lambda \, \mathrm{d} \left\| P_\lambda^{(H_N^\sharp - E_N^0)}(Bf) \right\|_{\mathcal{H}_N}^2 = \left\langle \overline{f}, v_c^{-1} B^* \left(H_N^\sharp - E_N^0 \right) Bf \right\rangle_{\mathcal{C}',\mathcal{C}} = \frac{1}{2} \int_{\mathbb{R}^3} \rho_N^0 |\nabla f|^2 < \infty.$$

The weak convergence therefore follows from the dominated convergence theorem.

To prove the strong convergence, we use the following rewriting for $g \in \mathcal{C}'$:

$$v_c^{-1} B^* \left(\frac{(H_N^\sharp - E_N^0)^3}{(H_N^\sharp - E_N^0)^2 + \omega^2} \right) Bg = v_c^{-1} B^* A_\omega M g,$$

where

$$A_\omega = \frac{(H_N^\sharp - E_N^0)^2}{(H_N^\sharp - E_N^0)^2 + \omega^2}$$

strongly converge to 0 on $\mathcal{H}_N$, and

$$Mg := (H_N^\sharp - E_N^0) Bg = \sum_{i=1}^N \left(-\frac{1}{2} \Delta g(\mathbf{r}_i) \Psi_N^0 - \nabla g(\mathbf{r}_i) \cdot \nabla_{\mathbf{r}_i} \Psi_N^0 \right).$$

When $g \in \mathcal{C}'$ is such that $\Delta g \in L^2$, it holds that $Mg \in \mathcal{H}_N$ (by a proof similar to the one in Section 4.6.11), which allows us to conclude.

4.6.13 Proof of Proposition 4.48

We first prove (4.68) and (4.69). We start from an expression similar to the one provided by Lemma 4.38:

$$\widetilde{G_0}(z) := A_{0,+} \left(z - (H_{0,N+1} - E_{0,N}^0) \right)^{-1} A_{0,+}^* + A_{0,-}^* \left(z + H_{0,N-1} - E_{0,N}^0 \right)^{-1} A_{0,-}.$$

Then, we notice that, for $f \in \mathcal{H}_1$, it holds

$$\sum_{i=1}^{N+1} h_1(\mathbf{r}_i) \left(A_{0,+}^* f \right) = \sum_{i=1}^{N+1} h_1(\mathbf{r}_i) \left(a^\dagger(f) |\Phi_N^0\rangle \right) = a^\dagger(h_1 f) \, |\Phi_N^0\rangle + a^\dagger(f) \left| \left(\sum_{i=1}^N h_1(\mathbf{r}_i) \right) \Phi_N^0 \right\rangle, \tag{4.117}$$

or, equivalently,

$$H_{0,N+1} A_{0,+}^*(f) = A_{0,+}^* \left(h_1 f \right) + E_{0,N}^0 A_{0,+}^*(f);$$

so that

$$\left(z - (H_{0,N+1} - E_{0,N}^0) \right) A_{0,+}^* = A_{0,+}^* (z - h_1). \tag{4.118}$$

Hence, the particle part of (4.68) is a consequence of the equality $A_{0,+} A_{0,+}^* = \mathbb{1}_{\mathcal{H}} - \gamma_{0,N}^0$ (similarly to (4.39)). To handle the hole part, we use computations similar to (4.115), and find

$$H_{0,N-1} A_{0,-}(f) = E_{0,N}^0 A_{0,-}(f) - A_{0,-} \left(h_1 f \right).$$

We deduce that

$$(z + H_{0,N-1} - E_{0,N}^0) A_{0,-} = A_{0,-}(z - h_1), \tag{4.119}$$

and we conclude using the fact that $A_{0,-}^* A_{0,-} = \gamma_{0,N}^0$. Combining (4.118) and (4.119) leads to $\widetilde{G}_0(z)(z - h_1) = A_{0,-}^* A_{0,-} + A_{0,+} A_{0,+}^* = \mathbb{1}_{\mathcal{H}_1}$. Upon replacing z by $\overline{z}$ and passing to adjoints, it also follows $(z - h_1)\widetilde{G}_0(z) = \mathbb{1}_{\mathcal{H}_1}$. This shows that $\widetilde{G_0}(z) = (z - h_1)^{-1}$.

To prove the first assertion of Proposition 4.48, we notice that the operator-valued functions $\tau \mapsto -\mathrm{i}\Theta(\tau) \left(\mathbb{1}_{\mathcal{H}_1} - \gamma_{0,N}^0 \right) \mathrm{e}^{-\mathrm{i}\tau h_1}$ and $\tau \mapsto G_{0,\mathrm{p}}(\tau)$ have the same Laplace transforms (see Proposition 4.13). We conclude that the two operators coincide since the Laplace transform is one-to-one. The proof for $G_{0,\mathrm{h}}$ is similar.

4.6.14 Proof of Proposition 4.50

Let $z \in \mathbb{C} \setminus \mathbb{R}$. Let us first prove that $\widetilde{G}(z)$ is a one-to-one operator. Let $f \in \mathcal{H}_1$ be such that $\widetilde{G}(z)f = 0$. From

$$\begin{aligned}\operatorname{Im}\left(\left\langle f \left| \widetilde{G}(z) \right| f \right\rangle\right) &= \operatorname{Im}\left(\left\langle A_+^* f \left| \left(z - (H_{N+1} - E_N^0)\right)^{-1} \right| A_+^* f \right\rangle_{\mathcal{H}_{N+1}}\right. \\ &\qquad \left. + \left\langle A_- f \left| \left(z - (E_N^0 - H_{N-1})\right)^{-1} \right| A_- f \right\rangle_{\mathcal{H}_{N-1}}\right) \qquad (4.120)\\ &= -\operatorname{Im}(z) \int_{\mathbb{R}} \left((\operatorname{Re}(z) + E_N^0 - \lambda)^2 + \operatorname{Im}(z)^2\right)^{-1} \mathrm{d} \left\| P_\lambda^{H_{N+1}} \left(A_+^* f\right)\right\|_{\mathcal{H}_{N+1}}^2 \\ &\quad - \operatorname{Im}(z) \int_{\mathbb{R}} \left((\operatorname{Re}(z) - E_N^0 + \lambda)^2 + \operatorname{Im}(z)^2\right)^{-1} \mathrm{d} \left\| P_\lambda^{H_{N-1}} \left(A_- f\right)\right\|_{\mathcal{H}_{N-1}}^2, \qquad (4.121)\end{aligned}$$

we deduce that both terms in the right-hand side must vanish. In particular, since $\operatorname{Im}(z) \neq 0$, it must hold $A_+^* f = A_- f = 0$. In view of the identity $A_-^* A_- + A_+ A_+^* = \mathbb{1}_{\mathcal{H}_1}$, this implies $f = 0$. Hence, $\widetilde{G}(z)$ is one-to-one.

As a consequence, $\widetilde{G}(z)$ is an invertible operator from $\mathcal{H}_1$ to its image $\widetilde{D}(z)$. Since $\left(\widetilde{G}(z)\right)^* = \widetilde{G}(\overline{z})$ is also one-to-one, $\widetilde{D}(z)$ is dense in $\mathcal{H}_1$.

Let us finally prove that $\widetilde{D}(z) \subset H^2(\mathbb{R}^3)$. We use to this end the equality (4.51). Let us consider the first term in this equality. A simple computation shows that,

$$\forall \Phi_{N+1} \in \mathcal{H}_{N+1}, \quad \left(A_+ \Phi_{N+1}\right)(\mathbf{r}) = \sqrt{N+1} \int_{\mathbb{R}^{3N}} \Phi_{N+1}(\mathbf{r}, \vec{\mathbf{z}}) \Psi_N^0(\vec{\mathbf{z}})\, \mathrm{d}\vec{\mathbf{z}},$$

so that A_+ is a bounded operator from $H^2(\mathbb{R}^{3N}) \cap \mathcal{H}_N$ to $H^2(\mathbb{R}^3)$. Since A_+^* is a bounded operator from $\mathcal{H}_1$ to $\mathcal{H}_{N+1}$ and $(z - H_{N+1} + E_N^0)^{-1}$ is a bounded operator from $\mathcal{H}_{N+1}$ to $H^2(\mathbb{R}^{3N}) \cap \mathcal{H}_N$, we deduce that $A_+(z - H_{N+1} + E_N^0)^{-1} A_+^*$ is a bounded operator from $\mathcal{H}_1$ to $H^2(\mathbb{R}^3)$. Similarly, for any $\Phi_{N-1} \in \mathcal{H}_{N-1}$,

$$\left(A_-^* \Phi_{N-1}\right)(\mathbf{r}) = \sqrt{N} \int_{\mathbb{R}^{3(N-1)}} \Phi_{N-1}(\mathbf{r}_2, \ldots, \mathbf{r}_N) \Psi_N^0(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)\, \mathrm{d}\mathbf{r}_2 \ldots \mathrm{d}\mathbf{r}_N,$$

so that A_-^* is a bounded operator from $\mathcal{H}_{N-1}$ to $H^2(\mathbb{R}^3)$. This allows us to prove that $A_-^*(z + H_{N-1} - E_N^0)^{-1} A_-$ is a bounded operator from $\mathcal{H}_1$ to $H^2(\mathbb{R}^3)$. Finally, $\widetilde{G}(z)$ is a bounded operator from $\mathcal{H}_1$ to $H^2(\mathbb{R}^3)$, which proves that $\widetilde{D}(z) \subset H^2(\mathbb{R}^3)$.

4.6.15 Proof of Lemma 4.56

Let us first prove that $\left(P_{\mathrm{sym}}^{0,+}(\tau)\right)_{\tau \in \mathbb{R}}$ defines a bounded causal operator. The proof is similar for $\left(P_{\mathrm{sym}}^{0,-}(\tau)\right)_{\tau \in \mathbb{R}}$. We rely on the following result.

Lemma 4.77. *For all $h \in L^6(\mathbb{R}^3)$, the operator $\gamma_{0,N}^0 h$ is a Hilbert-Schmidt operator on $\mathcal{H}_1$, and there exists $K \in \mathbb{R}^+$ such that*

$$\forall h \in L^6(\mathbb{R}^3), \quad \left\|\gamma_{0,N}^0 h\right\|_{\mathfrak{S}_2(\mathcal{H}_1)} \leq K \|h\|_{L^6}.$$

Proof of Lemma 4.77. Since $\gamma_{0,N}^0$ is a projector, for $h \in L^6(\mathbb{R}^3)$, the operator

$$\overline{h} \gamma_{0,N}^0 \gamma_{0,N}^0 h = \overline{h}(1-\Delta)^{-1/2}(1-\Delta)^{1/2} \gamma_{0,N}^0 (1-\Delta)^{1/2}(1-\Delta)^{-1/2} h$$

is the composition of $(1-\Delta)^{1/2}\gamma^0_{0,N}(1-\Delta)^{1/2} \in \mathfrak{S}_1(\mathcal{H}_1)$ with the two bounded operators $(1-\Delta)^{-1/2}h$ and $\overline{h}(1-\Delta)^{-1/2}$. In fact $(1-\Delta)^{-1/2}h \in \mathfrak{S}_6(\mathcal{H}_1)$ with

$$\left\|(1-\Delta)^{-1/2}h\right\|_{\mathfrak{S}_6(\mathcal{H}_1)} \leq K\|h\|_{L^6}$$

by the Kato-Seiler-Simon inequality [SS75, Sim05]. Therefore, $\gamma^0_{0,N}h \in \mathfrak{S}_2(\mathcal{H}_1)$ with

$$\left\|\gamma^0_{0,N}h\right\|_{\mathfrak{S}_2(\mathcal{H}_1)} \leq K\|h\|_{L^6},$$

which concludes the proof. □

We now proceed to the proof of Lemma 4.56. We first note that, for $f, g \in C^\infty_c(\mathbb{R}^3, \mathbb{C})$, it holds

$$\langle f|v_c^{1/2}g\rangle_{\mathcal{H}_1} = \langle v_c^{-1/2}f|g\rangle_{\mathcal{C}} = \langle v_c^{1/2}\overline{f}, g\rangle_{\mathcal{C}',\mathcal{C}}. \tag{4.122}$$

In particular, for $\tau \in \mathbb{R}^+_\tau$, and for $f, g \in \mathcal{H}_1$, we get

$$\begin{aligned}\langle f|P^{0,+}_{\rm sym}(\tau)g\rangle_{\mathcal{H}_1} &= \left\langle f\middle|v_c^{1/2}P^{0,+}(\tau)v_c^{1/2}g\right\rangle_{\mathcal{H}_1} = -\mathrm{i}\Theta(\tau)\left\langle v_c^{1/2}\overline{f}, G_{0,\rm p}(\tau)\odot G_{0,\rm h}(-\tau)v_c^{1/2}g\right\rangle_{\mathcal{C}',\mathcal{C}} \\ &= -\mathrm{i}\Theta(\tau)\mathrm{Tr}_{\mathcal{H}_1}\left[G_{0,\rm p}(\tau)\left(v_c^{1/2}g\right)G_{0,\rm h}(-\tau)\left(v_c^{1/2}\overline{f}\right)\right].\end{aligned}$$

Let us prove that $G_{0,\rm p}(\tau)\left(v_c^{1/2}g\right)G_{0,\rm h}(-\tau)\left(v_c^{1/2}\overline{f}\right)$ is indeed a trace-class operator. Replacing $G_{0,\rm p}$ and $G_{0,\rm h}$ by their expressions found in Proposition 4.48, and owing to the fact that $\gamma^0_{0,N}$ is a projector commuting with h_1, we obtain

$$\begin{aligned}\left|\langle f|P^{0,+}_{\rm sym}(\tau)|g\rangle\right| &= \left|\mathrm{Tr}_{\mathcal{H}_1}\left((\mathbb{1}_{\mathcal{H}_1}-\gamma^0_{0,N})\mathrm{e}^{-\mathrm{i}\tau h_1}\left(v_c^{1/2}g\right)\gamma^0_{0,N}\mathrm{e}^{\mathrm{i}\tau h_1}\gamma^0_{0,N}\gamma^0_{0,N}\left(v_c^{1/2}\overline{f}\right)\right)\right| \\ &\leq \left\|(\mathbb{1}_{\mathcal{H}_1}-\gamma^0_{0,N})\mathrm{e}^{-\mathrm{i}\tau h_1}\right\|_{\mathcal{B}(\mathcal{H}_1)}\left\|\mathrm{e}^{\mathrm{i}\tau h_1}\right\|_{\mathcal{B}(\mathcal{H}_1)} \\ &\quad\times\left\|\gamma_{0,N}\left(v_c^{1/2}\overline{f}\right)\right\|_{\mathcal{B}(\mathcal{H}_1)}\left\|\gamma_{0,N}\left(v_c^{1/2}g\right)\right\|_{\mathcal{B}(\mathcal{H}_1)}\|\gamma^0_{0,N}\|_{\mathfrak{S}_1(\mathcal{H}_1)}.\end{aligned}$$

According to Lemma 4.41, $v_c^{1/2}\overline{f} \in \mathcal{C}' \hookrightarrow L^6(\mathbb{R}^3)$. Therefore, $\gamma^0_{0,N}\left(v_c^{1/2}f\right) \in \mathfrak{S}_2(\mathcal{H}_1)$ by Lemma 4.77, hence is bounded, with

$$\left\|\gamma^0_{0,N}\left(v_c^{1/2}f\right)\right\|_{\mathcal{B}(\mathcal{H}_1)} \leq \left\|\gamma^0_{0,N}\left(v_c^{1/2}f\right)\right\|_{\mathfrak{S}_2(\mathcal{H}_1)} \leq C\left\|v_c^{1/2}\overline{f}\right\|_{L^6} \leq \widetilde{C}\|f\|_{\mathcal{H}_1}.$$

Similarly, $\left\|\left(v_c^{1/2}g\right)\gamma^0_{0,N}\right\|_{\mathcal{B}(\mathcal{H}_1)} \leq \widetilde{C}\|g\|_{\mathcal{H}_1}$. Altogether, we found a constant $C \in \mathbb{R}^+$ independent of τ such that

$$\forall f, g \in \mathcal{H}_1, \quad \left|\langle f|P^{0,+}_{\rm sym}(\tau)|g\rangle\right| \leq C\|f\|_{\mathcal{H}_1}\|g\|_{\mathcal{H}_1},$$

which proves that $\left(P^{0,+}_{\rm sym}(\tau)\right)_{\tau\in\mathbb{R}}$ is a bounded causal operator on $\mathcal{H}_1$.

Let us now prove that ϕ_k is a bounded operator from $\mathcal{H}_1$ to $\mathcal{C}$. Recall that ϕ_k is real-valued and $\phi_k \in H^2(\mathbb{R}^3) \subset L^2(\mathbb{R}^3, \mathbb{R}) \cap L^\infty(\mathbb{R}^3, \mathbb{R})$ for $1 \leq k \leq N$. For $f \in \mathcal{H}_1$, we obtain

$$\|\phi_k f\|_{\mathcal{C}} \leq C\,\|\phi_k f\|_{L^{6/5}} \leq C\,\|\phi_k\|_{L^3}\,\|f\|_{\mathcal{H}_1},$$

where C is a constant independent of f. The proof that ϕ_k is also a bounded operator from $\mathcal{C}'$ to $\mathcal{H}_1$ is similar, noticing that $\mathcal{C}' \hookrightarrow L^6(\mathbb{R}^3)$. We now use (4.80), and find that, for $f, g \in \mathcal{H}_1$

and for $\tau \in \mathbb{R}_\tau^+$,

$$\begin{aligned}\langle f|P_{\rm sym}^{0,+}(\tau)|g\rangle &= -\mathrm{i}\sum_{k=1}^N \mathrm{Tr}_{\mathcal{H}_1}\left((\mathbb{1}_{\mathcal{H}_1}-\gamma_{0,N}^0)\mathrm{e}^{-\mathrm{i}\tau h_1}\left(v_c^{1/2}g\right)|\phi_k\rangle\mathrm{e}^{\mathrm{i}\tau\varepsilon_k}\langle\phi_k|\left(v_c^{1/2}\overline{f}\right)\right)\\ &= -\mathrm{i}\sum_{k=1}^N \mathrm{Tr}_{\mathcal{H}_1}\left((\mathbb{1}_{\mathcal{H}_1}-\gamma_{0,N}^0)\mathrm{e}^{-\mathrm{i}\tau(h_1-\varepsilon_k)}\left|\left(v_c^{1/2}g\right)\phi_k\right\rangle\left\langle\left(v_c^{1/2}f\right)\phi_k\right|\right)\\ &= -\mathrm{i}\sum_{k=1}^N \left\langle\left(v_c^{1/2}f\right)\phi_k\right|(\mathbb{1}_{\mathcal{H}_1}-\gamma_{0,N}^0)\mathrm{e}^{-\mathrm{i}\tau(h_1-\varepsilon_k)}(\mathbb{1}_{\mathcal{H}_1}-\gamma_{0,N}^0)\left|\left(v_c^{1/2}g\right)\phi_k\right\rangle,\end{aligned} \tag{4.123}$$

which gives (4.81).

We finally prove that $P_{\rm sym}^{0,-}(\tau) = P_{\rm sym}^{0,+}(-\tau)$. Performing similar calculation as for $P_{\rm sym}^{0,+}$, we find that, for $f, g \in \mathcal{H}_1$ and for $\tau < 0$,

$$\begin{aligned}\langle f|P_{\rm sym}^{0,-}(\tau)|g\rangle &= -\mathrm{i}\sum_{k=1}^N \left\langle\left(v_c^{1/2}\overline{g}\right)\phi_k\right|(\mathbb{1}_{\mathcal{H}_1}-\gamma_{0,N}^0)\mathrm{e}^{\mathrm{i}\tau(h_1-\varepsilon_k)}\left|\left(v_c^{1/2}\overline{f}\right)\phi_k\right\rangle\\ &= \langle\overline{g}|P_{\rm sym}^{0,+}(-\tau)|\overline{f}\rangle.\end{aligned}$$

For a bounded operator $A \in \mathcal{B}(\mathcal{H}_1)$ and for $f, g \in \mathcal{H}_1$, it holds $\langle f|Ag\rangle = \overline{\langle Ag|f\rangle} = \langle\overline{g}|\overline{A^*f}\rangle$, so that, since the functions ϕ_k are real-valued for $1 \le k \le N$,

$$\langle f|P_{\rm sym}^{0,-}(\tau)|g\rangle = \left\langle f\middle|\overline{\left(P_{\rm sym}^{0,+}(-\tau)\right)^*\overline{g}}\right\rangle. \tag{4.124}$$

Since h_1 is real-valued, in the sense that $h_1 f$ is real-valued whenever f is real-valued, we easily get that

$$\forall f \in \mathcal{H}_1, \quad \overline{(\mathbb{1}_{\mathcal{H}_1}-\gamma_{0,N}^0)\mathrm{e}^{-\mathrm{i}\tau h_1}f} = (\mathbb{1}_{\mathcal{H}_1}-\gamma_{0,N}^0)\mathrm{e}^{\mathrm{i}\tau h_1}\overline{f},$$

so that,

$$\overline{\left(P_{\rm sym}^{0,+}(-\tau)\right)^*\overline{g}} = P_{\rm sym}^{0,+}(-\tau)g.$$

Together with (4.124), this proves $P^{0,-}(\tau) = P^{0,+}(-\tau)^*$.

4.6.16 Proof of Proposition 4.59

The expression for $\widetilde{P_{\rm sym}^0}$ in (4.84) comes from the expression for $\widetilde{P_{\rm sym}^0}$ in (4.82). Since for $k \le N$, it holds $\varepsilon_k \le \varepsilon_N$, we obtain

$$\forall 1 \le k \le N, \quad (\mathbb{1}_{\mathcal{H}_1}-\gamma_{0,N}^0)(h_1-\varepsilon_k) \ge \varepsilon_{N+1}-\varepsilon_N > 0. \tag{4.125}$$

From (4.84), we deduce that $\widetilde{P_{\rm sym}^0}(\mathrm{i}\omega)$ is a negative bounded operator for all $\omega \in \mathbb{R}_\omega$. The self-adjointness comes from Remark 4.57.

The bound (4.85) is proved similarly as in Lemma 4.29. Let us now prove (4.86). From (4.125), it holds that, for all $1 \le k \le N$,

$$0 \le (\mathbb{1}_{\mathcal{H}_1}-\gamma_{0,N}^0)\frac{h_1-\varepsilon_k}{\omega^2+(h_1-\varepsilon_k)^2} \le \sup_{E\ge\varepsilon_{N+1}-\varepsilon_N}\left(\frac{E}{\omega^2+E^2}\right) = \begin{cases}\dfrac{1}{2\omega} & \text{if} \quad \omega \ge \varepsilon_{N+1}-\varepsilon_N\\ \dfrac{\varepsilon_{N+1}-\varepsilon_N}{\omega^2+(\varepsilon_{N+1}-\varepsilon_N)^2} & \text{otherwise.}\end{cases}$$

In particular, there exists a constant $C \in \mathbb{R}^+$ such that

$$\forall 1 \leq k \leq N, \quad \forall \omega \in \mathbb{R}_\omega, \quad 0 \leq (\mathbb{1}_{\mathcal{H}_1} - \gamma^0_{0,N}) \frac{h_1 - \varepsilon_k}{\omega^2 + (h_1 - \varepsilon_k)^2} \leq \frac{C}{\sqrt{\omega^2 + 1}}.$$

Using the fact that for $1 \leq k \leq N$, ϕ_k is real-valued, with $\sum_{k=1}^N \phi_k^2 = \rho^0_{0,N}$, we obtain

$$\forall \omega \in \mathbb{R}_\omega, \quad 0 \leq -\widetilde{P^0_{\rm sym}}(\mathrm{i}\omega) \leq \frac{2C}{\sqrt{\omega^2+1}} \sum_{k=1}^N v_c^{1/2} \phi_k^2 v_c^{1/2} = \frac{2C}{\sqrt{\omega^2+1}} v_c^{1/2} \rho^0_{0,N} v_c^{1/2},$$

which proves (4.86). The fact that $v_c^{1/2} \rho^0_{0,N} v_c^{1/2}$ is indeed a bounded self-adjoint operator on $\mathcal{H}_1$ comes from the fact that $v_c^{1/2}$ is a bounded operator from $\mathcal{C}$ to $\mathcal{H}_1$ and from $\mathcal{H}_1$ to $\mathcal{C}'$, and that the operator of multiplication by ϕ_k is a bounded operator from $\mathcal{C}'$ to $\mathcal{H}_1$ and from $\mathcal{H}_1$ to $\mathcal{C}$. Together with the fact that the function $\omega \mapsto (\omega^2+1)^{-1/2}$ is in $L^p(\mathbb{R}_\omega)$ for all $p > 1$, this implies that $\widetilde{P^0_{\rm sym}}(\mathrm{i}\cdot) \in L^p(\mathbb{R}_\omega, \mathcal{S}(\mathcal{H}_1))$ for all $p > 1$. The analyticity of this map is straightforward.

4.6.17 Proof of Theorem 4.60

Let us prove the equality $2\sum_{k=1}^N \phi_k (\mathbb{1}_{\mathcal{H}_1} - \gamma^0_{0,N})(h_1 - \varepsilon_k)\phi_k = -\mathrm{div}\left(\rho^0_{0,N} \nabla \cdot\right)$, as operators from $\mathcal{C}'$ to $\mathcal{C}$. We first note that, since $\phi_k \in L^4(\mathbb{R}^3)$ for $1 \leq k \leq N$, it holds $\phi_k \phi_l \in \mathcal{H}_1$ for $1 \leq k, l \leq N$. In particular,

$$\sum_{k=1}^N \phi_k \gamma^0_{0,N} (h_1 - \varepsilon_k)\phi_k = \sum_{k=1}^N \sum_{l=1}^N |\phi_k \phi_l\rangle (\varepsilon_l - \varepsilon_k) \langle \phi_l \phi_k| = 0,$$

so that

$$2\sum_{k=1}^N \phi_k (\mathbb{1}_{\mathcal{H}_1} - \gamma^0_{0,N})(h_1 - \varepsilon_k)\phi_k = 2\sum_{k=1}^N \phi_k (h_1 - \varepsilon_k)\phi_k. \tag{4.126}$$

Consider now $f, g \in C_c^\infty(\mathbb{R}^3, \mathbb{C})$. In view of the equality

$$(h_1 - \varepsilon_k)(\phi_k g) = \phi_k \left(-\frac{1}{2}\Delta g\right) - \nabla \phi_k \cdot \nabla g,$$

it follows that

$$\begin{aligned} 2\left\langle f \middle| \sum_{k=1}^N \phi_k (h_1 - \varepsilon_k)\phi_k \middle| g \right\rangle_{\mathcal{H}_1} &= \left\langle f \middle| \sum_{k=1}^N \phi_k^2 (-\Delta g) \right\rangle_{\mathcal{H}_1} - 2\left\langle f \middle| \sum_{k=1}^N \phi_k \nabla \phi_k \cdot \nabla g \right\rangle_{\mathcal{H}_1} \\ &= \langle f | \rho^0_{0,N}(-\Delta g)\rangle_{\mathcal{H}_1} - \langle f | \nabla \rho^0_{0,N} \cdot \nabla g \rangle_{\mathcal{H}_1} = \int_{\mathbb{R}^3} \rho^0_{0,N} \overline{\nabla f} \cdot \nabla g, \end{aligned}$$

where we used an integration by part to obtain the last equality. Together with (4.126), we obtain that the operators $2\sum_{k=1}^N \phi_k (\mathbb{1}_{\mathcal{H}_1} - \gamma^0_{0,N})(h_1 - \varepsilon_k)\phi_k$ and $-\mathrm{div}\left(\rho^0_{0,N}\nabla\cdot\right)$ are equal on the core $C_c^\infty(\mathbb{R}^3, \mathbb{C})$. The end of the proof is similar to the one of Theorem 4.46.

4.6.18 Proof of Lemma 4.62

It is sufficient to prove that, for any $\nu' < \varepsilon_{N+1}$, $\nu > \varepsilon_N - \nu'$, $\omega, \omega' \in \mathbb{R}_\omega$, and $f, g \in \mathcal{H}_1$, it holds

$$\begin{aligned} &\mathrm{Tr}_{\mathcal{H}_1}\left(\left(v_c^{1/2}\overline{f}\right) \widetilde{G_{0,\mathrm{h}}}(\nu + \nu' + \mathrm{i}(\omega + \omega')) \left(v_c^{1/2} g\right) \widetilde{G_{0,\mathrm{p}}}(\nu' + \mathrm{i}\omega')\right) \\ &\quad = \mathrm{Tr}_{\mathcal{H}_1}\left(\widetilde{G_{0,\mathrm{h}}}(\nu + \nu' + \mathrm{i}(\omega + \omega')) \left(v_c^{1/2} g\right) \widetilde{G_{0,\mathrm{p}}}(\nu' + \mathrm{i}\omega') \left(v_c^{1/2}\overline{f}\right)\right) \end{aligned}$$

We will only consider the case $\nu = 0$, $\nu' = \mu_0$, $\omega = \omega' = 0$ for simplicity, the other cases being similar. We rely on the fact that if $A, B \in \mathcal{B}(\mathcal{H}_1)$ are such that AB and BA are trace-class operators, then $\mathrm{Tr}(AB) = \mathrm{Tr}(BA)$ [Sim05]. In our case, we consider $f, g \in C_c^\infty \subset \mathcal{H}_1$, so that $f_1 := v_c^{1/2} f$ and $g_1 := v_c^{1/2} g$ are in $\mathcal{C}' \cap L^\infty$, and we set $A = \overline{f_1}$ and $B = \widetilde{G_{0,\mathrm{h}}}(\mu_0) g \widetilde{G_{0,\mathrm{p}}}(\mu_0)$. The operators A and B are bounded operators on $\mathcal{H}_1$. Moreover, from Proposition (4.48), we get

$$BA = \widetilde{G_{0,\mathrm{h}}}(\mu_0) g_1 \widetilde{G_{0,\mathrm{p}}}(\mu_0) \overline{f_1} = \gamma_{0,N}^0 \left(\frac{1}{\mu_0 - h_1} g_1 \right) \left(\frac{\mathbb{1}_{\mathcal{H}_1} - \gamma_{0,N}^0}{\mu_0 - h_1} \overline{f_1} \right).$$

It holds $\gamma_{0,N}^0 \in \mathfrak{S}_1(\mathcal{H}_1)$. Also, from the definition of μ_0, it is easy to see that there exists $0 < c \leq C < \infty$ such that

$$c(1 - \Delta) \leq |\mu_0 - h_1| \leq C(1 - \Delta).$$

In particular, the operator $(\mu_0 - h_1)^{-1} g_1 = \left[(\mu_0 - h_1)^{-1} (1 - \Delta) \right] \left[(1 - \Delta)^{-1} g_1 \right]$ is the composition of two bounded operators. Actually, the operator $(1 - \Delta)^{-1} g_1$ is in the Schatten class $\mathfrak{S}_6(\mathcal{H}_1)$, thanks to the Kato-Seiler-Simon inequality [SS75, Sim05], and it holds

$$\left\| (1 - \Delta)^{-1} g_1 \right\|_{\mathcal{B}(\mathcal{H}_1)} \leq \left\| (1 - \Delta)^{-1} g_1 \right\|_{\mathfrak{S}_6(\mathcal{H}_1)} \leq C \|g_1\|_{L^6} \leq C' \|g\|_{\mathcal{H}_1}, \tag{4.127}$$

where $C' \in \mathbb{R}^+$ is a constant independent of g. Similarly, $(\mathbb{1} - \gamma_{0,N})(\mu_0 - h_1)^{-1} \overline{f_1}$ is a bounded operator, satisfying estimates similar to (4.127). Altogether, we deduce that, for all $f, g \in C_c^\infty(\mathbb{R}^3)$,

$$\widetilde{G_{0,\mathrm{h}}}(\mu_0) \left(v_c^{1/2} g \right) \widetilde{G_{0,\mathrm{p}}}(\mu_0) \left(v_c^{1/2} \overline{f} \right) \in \mathfrak{S}_1(\mathcal{H}_1),$$

with

$$\left\| \widetilde{G_{0,\mathrm{h}}}(\mu_0) \left(v_c^{1/2} g \right) \widetilde{G_{0,\mathrm{p}}}(\mu_0) \left(v_c^{1/2} \overline{f} \right) \right\|_{\mathfrak{S}_1(\mathcal{H}_1)} \leq C \|g\|_{\mathcal{H}_1} \|f\|_{\mathcal{H}_1}, \tag{4.128}$$

where $C \in \mathbb{R}^+$ is a constant independent of f and g. The proof that $AB = \widetilde{G_{0,\mathrm{p}}}(\mu_0) g_1 \widetilde{G_{0,\mathrm{h}}}(\mu_0) \overline{f}_1$ is trace-class is similar. As a result, we deduce that for any $f, g \in C_c^\infty$,

$$\mathrm{Tr}_{\mathcal{H}_1} \left(\left(v_c^{1/2} \overline{f} \right) \widetilde{G_{0,\mathrm{h}}}(\mu_0) \left(v_c^{1/2} g \right) \widetilde{G_{0,\mathrm{p}}}(\mu_0) \right) = \mathrm{Tr}_{\mathcal{H}_1} \left(\widetilde{G_{0,\mathrm{h}}}(\mu_0) \left(v_c^{1/2} g \right) \widetilde{G_{0,\mathrm{p}}}(\mu_0) \left(v_c^{1/2} \overline{f} \right) \right).$$

The proof for the general case $f, g \in \mathcal{H}_1$ is deduced by density from the estimate (4.128).

4.6.19 Proof of Proposition 4.73

Let us first prove that $\mathfrak{s}$ is a bounded linear operator. Let $\widetilde{G^{\mathrm{app}}}(\mu_0 + \mathrm{i}\cdot) \in L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$. For $f, g \in \mathcal{H}_1$ and $\omega \in \mathbb{R}_\omega$,

$$\left\langle f \middle| \mathfrak{s} \left[\widetilde{G^{\mathrm{app}}} \right] (\mu + \mathrm{i}\omega) \middle| g \right\rangle = \langle f | K_x | g \rangle - \frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{Tr}_{\mathcal{H}_1} \left(\widetilde{G^{\mathrm{app}}}(\mu_0 + \mathrm{i}(\omega + \omega')) g \widetilde{W_c^0}(\mathrm{i}\omega') \overline{f} \right) \mathrm{d}\omega'.$$

Let us first treat the exchange part K_x, and prove that it is a Hilbert-Schmidt operator. From the definition (4.99), K_x is an integral operator, and, from Proposition 4.26, its kernel satisfies

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left| K_x(\mathbf{r}, \mathbf{r}') \right|^2 \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}' \leq \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{0,N}^0(\mathbf{r}) \rho_{0,N}^0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^2} \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}' < \infty,$$

where the last inequality comes from the fact that $\rho_{0,N}^0 * |\cdot|^{-2} \in L^\infty(\mathbb{R}^3)$ (since it holds $\rho_{0,N}^0 \in L^1(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$, while $|\cdot|^{-2} \in L^1(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$) and $\rho_{0,N}^0 \in L^1(\mathbb{R}^3)$. We conclude that K_x is a Hilbert-Schmidt operator, hence is bounded.

For the correlation part, we use the following lemma.

Lemma 4.78. *For all $f, g \in \mathcal{H}_1$ and all $\omega \in \mathbb{R}_\omega$, the operator $g\widetilde{W_c^0}(\mathrm{i}\omega)\overline{f}$ is trace-class, and*

$$\exists C \in \mathbb{R}^+, \quad \forall f, g \in \mathcal{H}_1, \quad \left\| g\widetilde{W_c^0}(\mathrm{i}\omega)\overline{f} \right\|_{\mathfrak{S}_1(\mathcal{H}_1)} \leq \frac{C}{(\omega^2+1)^{1/2}} \|f\|_{\mathcal{H}_1} \|g\|_{\mathcal{H}_1}. \tag{4.129}$$

Proof of Lemma 4.78. We first prove (4.129) for $f = g \in \mathcal{H}_1$. Let $\psi \in C_c^\infty(\mathbb{R}^3, \mathbb{C})$, we have

$$\left\langle \psi \left| f\widetilde{W_c^0}(\mathrm{i}\omega)\overline{f} \right| \psi \right\rangle = \left\langle \psi \left| \overline{f} v_c^{1/2} \widetilde{\chi_{\mathrm{sym}}^0}(\mathrm{i}\omega) v_c^{1/2} f \right| \psi \right\rangle,$$

and we infer from (4.95) that

$$\forall f \in \mathcal{H}_1, \quad \forall \omega \in \mathbb{R}_\omega, \quad \left\| f\widetilde{W_c^0}(\mathrm{i}\omega)\overline{f} \right\|_{\mathfrak{S}_1(\mathcal{H}_1)} \leq \frac{C}{(\omega^2+1)^{1/2}} \left\| f v_c \rho_{0,N}^0 v_c \overline{f} \right\|_{\mathfrak{S}_1(\mathcal{H}_1)}.$$

Since

$$\left\| f v_c \rho_{0,N}^0 v_c \overline{f} \right\|_{\mathfrak{S}_1(\mathcal{H}_1)} = \left\| \sqrt{\rho_{0,N}^0} v_c \overline{f} \right\|_{\mathfrak{S}_2(\mathcal{H}_1)}^2 = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{0,N}^0(\mathbf{r}) \, |f(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|^2} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}' \leq C \|f\|_{\mathcal{H}_1}^2,$$

where we used again the fact that $\rho_{0,N}^0 * |\cdot|^{-2}$ is bounded, we obtain that (4.129) holds true for $f = g$. For $f \neq g$, we deduce from the fact that $\widetilde{\chi_{\mathrm{sym}}^0}(\mathrm{i}\omega)$ is a bounded self-adjoint negative operator, that

$$\begin{aligned}
\left\| g\widetilde{W_c^0}(\mathrm{i}\omega)\overline{f} \right\|_{\mathfrak{S}_1(\mathcal{H}_1)} &= \left\| g v_c^{1/2} \widetilde{\chi_{\mathrm{sym}}^0}(\mathrm{i}\omega) v_c^{1/2} \overline{f} \right\|_{\mathfrak{S}_1(\mathcal{H}_1)} = \left\| g v_c^{1/2} \sqrt{-\widetilde{\chi_{\mathrm{sym}}^0}(\mathrm{i}\omega)} \sqrt{-\widetilde{\chi_{\mathrm{sym}}^0}(\mathrm{i}\omega)} v_c^{1/2} \overline{f} \right\|_{\mathfrak{S}_1(\mathcal{H}_1)} \\
&\leq \left\| g v_c^{1/2} \sqrt{-\widetilde{\chi_{\mathrm{sym}}^0}(\mathrm{i}\omega)} \right\|_{\mathfrak{S}_2(\mathcal{H}_1)} \left\| \sqrt{-\widetilde{\chi_{\mathrm{sym}}^0}(\mathrm{i}\omega)} v_c^{1/2} \overline{f} \right\|_{\mathfrak{S}_2(\mathcal{H}_1)} \\
&\leq \left\| g v_c^{1/2} \widetilde{\chi_{\mathrm{sym}}^0}(\mathrm{i}\omega) v_c^{1/2} \overline{g} \right\|_{\mathfrak{S}_1(\mathcal{H}_1)}^{1/2} \left\| f v_c^{1/2} \widetilde{\chi_{\mathrm{sym}}^0}(\mathrm{i}\omega) v_c^{1/2} \overline{f} \right\|_{\mathfrak{S}_1(\mathcal{H}_1)}^{1/2} \\
&\leq \frac{C}{(\omega^2+1)^{1/2}} \|f\|_{\mathcal{H}_1} \|g\|_{\mathcal{H}_1}.
\end{aligned}$$

□

We now proceed to the proof of Proposition 4.73. From Lemma 4.78, we get, for $f, g \in \mathcal{H}_1$,

$$\begin{aligned}
\left| \left\langle f \left| \mathfrak{s}_c \left[\widetilde{G^{\mathrm{app}}} \right] (\mu + \mathrm{i}\omega) \right| g \right\rangle \right| &= \frac{1}{2\pi} \left| \int_{-\infty}^{+\infty} \mathrm{Tr}_{\mathcal{H}_1} \left(\widetilde{G^{\mathrm{app}}}\big(\mu_0 + \mathrm{i}(\omega + \omega')\big) g \widetilde{W^0}(\mathrm{i}\omega') \overline{f} \right) \mathrm{d}\omega' \right| \\
&\leq \frac{1}{2\pi} \int_{-\infty}^{+\infty} \left\| \widetilde{G^{\mathrm{app}}}(\mu_0 + \mathrm{i}(\omega + \omega')) \right\|_{\mathcal{B}(\mathcal{H}_1)} \left\| g\widetilde{W^0}(\mathrm{i}\omega')\overline{f} \right\|_{\mathfrak{S}_1(\mathcal{H}_1)} \mathrm{d}\omega' \\
&\leq \int_{-\infty}^{+\infty} \left\| \widetilde{G^{\mathrm{app}}}(\mu_0 + \mathrm{i}(\omega + \omega')) \right\|_{\mathcal{B}(\mathcal{H}_1)} \frac{C}{(\omega'^2+1)^{1/2}} \|f\|_{\mathcal{H}_1} \|g\|_{\mathcal{H}_1} \mathrm{d}\omega' \\
&\leq C' \left\| \widetilde{G^{\mathrm{app}}}(\mu_0 + \mathrm{i}\cdot) \right\|_{L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} \|f\|_{\mathcal{H}_1} \|g\|_{\mathcal{H}_1},
\end{aligned}$$

where we used the Cauchy-Schwarz inequality for the last inequality and the fact that it holds $\omega \mapsto (\omega^2+1)^{-1/2} \in L^2(\mathbb{R}_\omega)$. Here, C' does not depend on $\omega \in \mathbb{R}_\omega$ nor on $f, g \in \mathcal{H}_1$. Altogether, we deduce that $\mathfrak{s}$ is a bounded linear operator from $L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ to $L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$.

We now prove the claimed properties of $\mathfrak{g}_\lambda$. Consider $M > 0$. By definition of μ_0, the real number $d := \max(\varepsilon_{N+1} - \mu_0, \mu_0 - \varepsilon_N)$ is positive, and $|\mu_0 - h_1| \geq d$. Let us

choose $0 < \lambda_M < d/M$. For $0 \leq \lambda \leq \lambda_M$ and $\widetilde{\Sigma^{\rm app}}(\mu_0 + \mathrm{i}\cdot) \in L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ such that $\left\|\widetilde{\Sigma^{\rm app}}(\mu_0 + \mathrm{i}\cdot)\right\|_{L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} \leq M$, it holds for $\omega \in \mathbb{R}_\omega$,

$$\mu_0 + \mathrm{i}\omega - h_1 - \lambda\widetilde{\Sigma^{\rm app}}(\mu_0 + \mathrm{i}\omega) = [\mu_0 + \mathrm{i}\omega - h_1]\left(1 - \lambda\,[\mu_0 + \mathrm{i}\omega - h_1]^{-1}\,\widetilde{\Sigma^{\rm app}}(\mu_0 + \mathrm{i}\omega)\right).$$

Since

$$\left\|\lambda\,[\mu_0 + \mathrm{i}\omega - h_1]^{-1}\,\widetilde{\Sigma^{\rm app}}(\mu_0 + \mathrm{i}\omega)\right\|_{\mathcal{B}(\mathcal{H}_1)} \leq \frac{\lambda}{d}\left\|\widetilde{\Sigma^{\rm app}}(\mu_0 + \mathrm{i}\omega)\right\|_{\mathcal{B}(\mathcal{H}_1)} \leq \frac{\lambda}{d}M \leq \frac{\lambda_M}{d}M < 1,$$

the operator $1 - \lambda\,[\mu_0 + \mathrm{i}\omega - h_1]^{-1}\,\widetilde{\Sigma^{\rm app}}(\mu_0 + \mathrm{i}\omega)$ is invertible, with

$$\left\|\left(1 - \lambda\,[\mu_0 + \mathrm{i}\omega - h_1]^{-1}\,\widetilde{\Sigma^{\rm app}}(\mu_0 + \mathrm{i}\omega)\right)^{-1}\right\|_{\mathcal{B}(\mathcal{H}_1)} \leq \frac{d}{d - \lambda_M M}.$$

Since $\mu_0 + \mathrm{i}\omega - h_1$ is an invertible operator with $\left\|(\mu_0 + \mathrm{i}\omega - h_1)^{-1}\right\|_{\mathcal{B}(\mathcal{H}_1)} \leq (\omega^2 + d^2)^{1/2}$, we obtain that $\mu_0 + \mathrm{i}\omega - h_1 - \lambda\widetilde{\Sigma^{\rm app}}(\mu_0 + \mathrm{i}\omega)$ is invertible, with

$$\left\|\left[\mu_0 + \mathrm{i}\omega - h_1 - \lambda\widetilde{\Sigma^{\rm app}}(\mu_0 + \mathrm{i}\omega)\right]^{-1}\right\|_{\mathcal{B}(\mathcal{H}_1)} \leq \frac{d}{d - \lambda_M M}\left\|(\mu_0 + \mathrm{i}\omega - h_1)^{-1}\right\|_{\mathcal{B}(\mathcal{H}_1)} \leq \frac{K_M}{(\omega^2 + 1)^{1/2}}.$$

We deduce from this inequality that

$$\left\|\mathfrak{g}_\lambda\left(\widetilde{\Sigma^{\rm app}}\right)(\mu_0 + \mathrm{i}\cdot)\right\|_{L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} + \left\|\mathfrak{g}_\lambda\left(\widetilde{\Sigma^{\rm app}}\right)(\mu_0 + \mathrm{i}\cdot)\right\|_{L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} \leq C_M,$$

where the constant $C_M \in \mathbb{R}^+$ does not depend on $\lambda \in [0, \lambda_M]$. This gives the claimed result. Finally, (4.102) is a direct consequence of the resolvent formula.

4.6.20 Proof of Theorem 4.74

Let us denote for simplicity

$$\|\mathfrak{s}\| = \|\mathfrak{s}\|_{\mathcal{B}(L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)), L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)))},$$

and fix $M > \|\mathfrak{s}\|\left\|\widetilde{G^0}(\mu + \mathrm{i}\cdot)\right\|_{L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))}$. Let λ_M and C_M be chosen as in Proposition 4.73 for this choice of $M > 0$, and introduce

$$r = \frac{M}{\|s\|} - \left\|\widetilde{G^0}(\mu + \mathrm{i}\cdot)\right\|_{L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} > 0.$$

For this choice of r, it holds that, for any $\widetilde{G^{\rm app}} \in \mathfrak{B}\left(\widetilde{G_0}, r\right)$,

$$\left\|\mathfrak{s}\left[\widetilde{G^{\rm app}}\right](\mu_0 + \mathrm{i}\cdot)\right\|_{L^\infty(\mathbb{R}_\omega, \mathfrak{B}(\mathcal{H}_1))} \leq M.$$

Therefore, from Proposition 4.73, $\mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G^{\rm app}}\right]$ is well-defined for all $\lambda \in [0, \lambda_M]$.

Let us prove that there exists $\lambda_* > 0$ sufficiently small such that for any $0 \leq \lambda \leq \lambda_*$, $\mathfrak{g}_\lambda \circ \mathfrak{s}$ maps $\mathfrak{B}\left(\widetilde{G^0}, r\right)$ into itself. For $\widetilde{G^{\rm app}} \in \mathfrak{B}\left(\widetilde{G_0}, r\right)$, it holds

$$\begin{aligned}
&\left\|\left(\mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G^{\rm app}}\right] - \widetilde{G_0}\right)(\mu_0 + \mathrm{i}\cdot)\right\|_{L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} \\
&\quad \leq \left\|\left(\mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G^{\rm app}}\right] - \mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G_0}\right]\right)(\mu_0 + \mathrm{i}\cdot)\right\|_{L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} \qquad (4.130) \\
&\qquad + \left\|\left(\mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G_0}\right] - \widetilde{G^0}\right)(\mu_0 + \mathrm{i}\cdot)\right\|_{L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))}. \qquad (4.131)
\end{aligned}$$

To control the first term (4.130), we use the following result.

Lemma 4.79. *The map $\mathfrak{g}_\lambda \circ \mathfrak{s}$ is $(\lambda C_M^2 \|\mathfrak{s}\|)$-Lipschitz on $\mathfrak{B}\left(\widetilde{G_0}, r\right)$.*

Proof of Lemma 4.79. Let $\widetilde{G_1^{\mathrm{app}}}, \widetilde{G_2^{\mathrm{app}}} \in \mathfrak{B}\left(\widetilde{G_0}, r\right)$. From (4.102), we obtain

$$\mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G_1^{\mathrm{app}}}\right] - \mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G_2^{\mathrm{app}}}\right] = \lambda \left(\mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G_1^{\mathrm{app}}}\right]\right)\left(\mathfrak{s}\left[\widetilde{G_2^{\mathrm{app}}}\right] - \mathfrak{s}\left[\widetilde{G_1^{\mathrm{app}}}\right]\right)\left(\mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G_2^{\mathrm{app}}}\right]\right). \tag{4.132}$$

From Proposition 4.73,

$$\left\|\mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G_j^{\mathrm{app}}}\right](\mu_0 + \mathrm{i}\cdot)\right\|_{L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} \leq C_M \quad \text{for} \quad 1 \leq j \leq 2.$$

Moreover,

$$\left\|\left(\mathfrak{s}\left[\widetilde{G_2^{\mathrm{app}}}\right] - \mathfrak{s}\left[\widetilde{G_1^{\mathrm{app}}}\right]\right)(\mu_0 + \mathrm{i}\cdot)\right\|_{L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} \leq \|\mathfrak{s}\| \left\|\left(\widetilde{G_2^{\mathrm{app}}} - \widetilde{G_1^{\mathrm{app}}}\right)(\mu_0 + \mathrm{i}\cdot)\right\|_{L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))}.$$

Plugging these estimates into (4.132), we obtain

$$\begin{aligned}\left\|\left(\mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G_1^{\mathrm{app}}}\right] - \mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G_2^{\mathrm{app}}}\right]\right)(\mu_0 + \mathrm{i}\cdot)\right\|_{L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} \\ \leq \lambda C_M^2 \|\mathfrak{s}\| \left\|\left(\widetilde{G_2^{\mathrm{app}}} - \widetilde{G_1^{\mathrm{app}}}\right)(\mu_0 + \mathrm{i}\cdot)\right\|_{L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))},\end{aligned}$$

which proves that $\mathfrak{g}_\lambda \circ \mathfrak{s}$ is $(\lambda C_M^2 \|\mathfrak{s}\|)$-Lipschitz on $\mathfrak{B}\left(\widetilde{G_0}, r\right)$. □

Let us now control (4.131). By noting that $\mathfrak{g}_{\lambda=0} \circ \mathfrak{s}\left[\widetilde{G_0}\right] = \widetilde{G_0}$, we get from the resolvent formula that

$$\mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G_0}\right] - \widetilde{G_0} = (\mathfrak{g}_\lambda - \mathfrak{g}_0) \circ \mathfrak{s}\left(\widetilde{G_0}\right) = \lambda \left(\mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G_0}\right]\right)\left(\mathfrak{s}\left[\widetilde{G_0}\right]\right)\widetilde{G_0}.$$

Using estimates similar to the ones used in the proof of Lemma 4.79, we deduce that

$$\left\|\left(\mathfrak{g}_\lambda \circ \mathfrak{s}\left[\widetilde{G_0}\right] - \widetilde{G_0}\right)(\mu_0 + \mathrm{i}\cdot)\right\|_{L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))} \leq \lambda C_M^2 \left\|\mathfrak{s}\left[\widetilde{G_0}\right](\mu_0 + \mathrm{i}\cdot)\right\|_{L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))}. \tag{4.133}$$

From Lemma 4.79 and (4.133), we arrive at the conclusion that for all $0 \leq \lambda \leq \lambda_*$, where

$$\lambda_* = \frac{1}{C_M^2\left(\|\mathfrak{s}\| r + \left\|\mathfrak{s}\left[\widetilde{G_0}\right](\mu_0 + \mathrm{i}\cdot)\right\|_{L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))}\right)},$$

it holds $\mathfrak{g}_\lambda \circ \mathfrak{s}\left(\mathfrak{B}\left(\widetilde{G_0}, r\right)\right) \subset \mathfrak{B}\left(\widetilde{G_0}, r\right)$.

Finally, without loss of generality, we can assume that $\lambda_* C_M^2 \|\mathfrak{s}\| < 1$, so that, from Lemma 4.79, we get that for all $0 \leq \lambda \leq \lambda_*$, the map $\mathfrak{g}_\lambda \circ \mathfrak{s}$ is a contraction. The end of the proof follows from Picard's fixed point theorem.

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Part III

Numerical simulation of perfect crystals

CHAPTER 5

CONVERGENCE RATES FOR SUPERCELL MODELS

We expose in this chapter the results given in [GL15]. This work was done in collaboration with Salma Lahbabi.

Abstract. This chapter is concerned with the numerical simulations of perfect crystals. We study the rate of convergence of the reduced Hartree-Fock (rHF) model in a supercell towards the periodic rHF model in the whole space. We prove that, whenever the crystal is an insulator or a semi-conductor, the supercell energy per unit cell converges exponentially fast towards the periodic rHF energy per unit cell, with respect to the size of the supercell.

5.1 Introduction

The numerical simulation of the electronic structure of crystals is a very active research area in solid state physics, materials science and nano-electronics. When the crystal is perfect, a good approximation of its electronic ground state density can be obtained by solving a mean-field nonlinear periodic model set on the whole space. Using the Bloch transform [RS78, Chapter XIII], we can recast such a problem as a continuous family of compact problems indexed by points of the Brillouin zone. In practice, the compact problems are solved on a discretization of this Brillouin zone. There is therefore an inherent error coming from the fact that the Brillouin zone is sampled, and it is not obvious *a priori* whether this error is small, due to the nonlinearity of the problem. It has been observed numerically since the work of Monkhorst and Pack [MP76] that this error is indeed very small when the discretization is uniform, and when the crystal is an insulator or a semiconductor. To our knowledge, no rigorous proof of this fact was ever given. In this chapter, we prove why it is indeed the case in the linear model, and in the reduced Hartree-Fock (rHF) model, which is a Hartree-Fock model where the exchange term is neglected. This model was studied in [CDL08, CLL01].

A crystal is modeled by a periodic nuclear charge distribution $\mu_{\rm per}$. The corresponding rHF energy per unit cell is denoted by $I_{\rm per}^{\mu_{\rm per}}$. When numerical calculations are performed over a regular discretization of the Brillouin-zone, this amounts to calculate the energy on a *supercell*, *i.e.* on a large box containing L times the periodicity of $\mu_{\rm per}$ in each direction (for a total of L^3 unit cells in the supercell), and with periodic boundary conditions. The rHF energy on a supercell of size L is denoted by $I_L^{\mu_{\rm per}}$, so that the corresponding energy per unit cell is $L^{-3} I_L^{\mu_{\rm per}}$.

It was proved in [CDL08] that $L^{-3} I_L^{\mu_{\rm per}}$ converges to $I_{\rm per}^{\mu_{\rm per}}$ as L goes to infinity, when the crystal is an insulator or a semiconductor. However, following the proof in [CDL08], we find

a rate of convergence of order L^{-1}, which is well below what is numerically observed. Our main result is that, if the crystal is an insulator or a semiconductor, then there exist constants $C \in \mathbb{R}^+$ and $\alpha > 0$, such that

$$\forall L \in \mathbb{N}^*, \quad \left|L^{-3} I_L^{\mu_{\rm per}} - I_{\rm per}^{\mu_{\rm per}}\right| \leq C \mathrm{e}^{-\alpha L}. \tag{5.1}$$

We also prove that the supercell electronic density converges exponentially fast to the periodic rHF electronic density, in the $L^\infty(\mathbb{R}^3)$ norm. To prove such rates of convergence, we recast the problem into the difference between an integral and a corresponding Riemann sum, and show that the integrand is both periodic and analytic on a complex strip. Similar tools were used in [DC64a, DC64b, Koh59, BPC+07, Pan07] to prove that the Wannier functions of insulators are exponentially localized.

This chapter is organized as follows. In Section 5.2, we recall how the rHF model is derived, and present the main results. In Section 5.4, we apply the Bloch theory for both periodic models and supercell models. The proofs of the main results are postponed until Section 5.5. Finally, we illustrate our theoretical results with numerical simulations in Section 5.7.

Throughout this chapter, we will give explicit values of the constants appearing in the inequalities. These values are very crude, but allows one to see how these constants depend on the parameters of the electronic problem.

5.2 Presentation of the models

A perfect crystal is a periodic arrangement of atoms. Both the nuclear charge density $\mu_{\rm per}$ and the electronic density are $\mathcal{R}$-periodic functions, where $\mathcal{R}$ is a discrete periodic lattice of $\mathbb{R}^3$. Let Γ be the Wigner-Seitz cell of the lattice, and let Γ^* be the first Brillouin zone. For instance, for $\mathcal{R} = a\mathbb{Z}^3$, $\Gamma = [-a/2, a/2)^3$, $\mathcal{R}^* = (2\pi/a)\mathbb{Z}^3$ and $\Gamma^* = [-\pi/a, \pi/a)^3$. For $\mathbf{R} \in \mathcal{R}$, we let $\tau_{\mathbf{R}}$ be the translation operator on $L^2(\mathbb{R}^3)$ defined by $(\tau_{\mathbf{R}} f)(\mathbf{x}) := f(\mathbf{x} - \mathbf{R})$.

We will assume that the nuclear charge density $\mu_{\rm per}$ is in $L^2_{\rm per}(\Gamma)$ for simplicity, but distributions with singularity points may also be handled [BLL03].

5.2.1 The supercell rHF model

In a supercell model, the system is confined to a box $\Gamma_L := L\Gamma$ with periodic boundary conditions. We denote by $L^2_{\rm per}(\Gamma_L)$ the Hilbert space of locally square integrable functions that are $L\mathcal{R}$-periodic. The Fourier coefficients of a function $f \in L^2_{\rm per}(\Gamma_L)$ are defined by

$$\forall \mathbf{k} \in L^{-1}\mathcal{R}^*, \quad c_{\mathbf{k}}^L(f) = \frac{1}{|\Gamma_L|} \int_{\Gamma_L} f(\mathbf{x}) \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{x}} \mathrm{d}\mathbf{x},$$

so that, for any $f \in L^2_{\rm per}(\Gamma_L)$,

$$f(\mathbf{x}) = \sum_{\mathbf{k} \in L^{-1}\mathcal{R}^*} c_{\mathbf{k}}^L(f) \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}} \quad \text{a.e. and in } L^2_{\rm per}(\Gamma_L).$$

The set of admissible electronic states for the supercell model is

$$\mathcal{P}_L := \left\{ \gamma_L \in \mathcal{S}(L^2_{\rm per}(\Gamma_L)),\ 0 \leq \gamma_L \leq 1,\ \mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}(\gamma_L) + \mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}(-\Delta_L \gamma_L) < \infty \right\},$$

where $\mathcal{S}(\mathcal{H})$ denotes the space of the bounded self-adjoint operators on the Hilbert space $\mathcal{H}$. Here, $\mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}(-\Delta_L \gamma_L)$ is a shorthand notation for

$$\mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}(-\Delta_L \gamma_L) := \sum_{i=1}^{3} \mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}(P_{j,L} \gamma_L P_{j,L}), \tag{5.2}$$

where, for $1 \leq j \leq 3$, $P_{j,L}$ is the self-adjoint operator on $L^2_{\rm per}(\Gamma_L)$ defined by $c^L_{\mathbf{k}}(P_{j,L}f) = k_j c^L_{\mathbf{k}}(f)$ for all $\mathbf{k} = (k_1, k_2, k_3) \in L^{-1}\mathcal{R}^*$. Note that $c^L_{\mathbf{k}}(-\Delta_L f) = |\mathbf{k}|^2 c^L_{\mathbf{k}}(f)$ for all $\mathbf{k} \in L^{-1}\mathcal{R}^*$.

We introduce the $L\mathcal{R}$-periodic Green kernel G_L of the Poisson interaction [LS77], solution of

$$\begin{cases} -\Delta G_L = 4\pi \left(\sum_{\mathbf{k}\in\mathcal{R}} \delta_{\mathbf{k}} - 1 \right) \\ G_L \text{ is } L\mathcal{R}\text{-periodic.} \end{cases}$$

The expression of G_L is given in the Fourier basis by

$$G_L(\mathbf{x}) = c_L + \frac{4\pi}{|\Gamma_L|} \sum_{\mathbf{k}\in L^{-1}\mathcal{R}^*\setminus\{\mathbf{0}\}} \frac{\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}}}{|\mathbf{k}|^2}, \tag{5.3}$$

where $c_L = |\Gamma_L|^{-1} \int_{\Gamma_L} G_L$. The constant c_L can be any fixed constant *a priori*. In one of the first article on the topic [LS77], the authors chose to set $c_L = 0$, but other choices are equally valid (see [CDL08] for instance). This is due to the fact that c_L does not play any role for neutral systems. We choose to set $c_L = 0$ for simplicity. The supercell Coulomb energy is defined by

$$\forall f, g \in L^2_{\rm per}(\Gamma_L), \quad D_L(f,g) := \int_\Gamma (f *_{\Gamma_L} G_L)(\mathbf{x}) g(\mathbf{x}) \mathrm{d}\mathbf{x}, \tag{5.4}$$

where $(f *_{\Gamma_L} G_L)(\mathbf{x}) := \int_\Gamma f(\mathbf{y}) G_L(\mathbf{x}-\mathbf{y}) \mathrm{d}\mathbf{y}$. We recall that the map $\rho \mapsto \rho *_{\Gamma_L} G_L$ is continuous from $L^2_{\rm per}(\Gamma_L)$ to $L^\infty_{\rm per}(\Gamma_L)$.

Any $\gamma_L \in \mathcal{P}_L$ is locally trace-class, and can be associated an $L\mathcal{R}$-periodic density $\rho_{\gamma_L} \in L^2_{\rm per}(\Gamma_L)$. For $\gamma_L \in \mathcal{P}_L$, the supercell reduced Hartree-Fock energy is

$$\mathcal{E}^{\mu_{\rm per}}_L(\gamma_L) := \frac{1}{2} \mathrm{Tr}_{L^2_{\rm per}(\Gamma_L)}(-\Delta_L \gamma_L) + \frac{1}{2} D_L(\rho_{\gamma_L} - \mu_{\rm per}, \rho_{\gamma_L} - \mu_{\rm per}). \tag{5.5}$$

The first term of (5.5) corresponds to the supercell kinetic energy, and the second term represents the supercell Coulomb energy. The ground state energy of the system is given by the minimization problem

$$I^{\mu_{\rm per}}_L = \inf \left\{ \mathcal{E}^{\mu_{\rm per}}_L(\gamma_L),\ \gamma_L \in \mathcal{P}_L,\ \int_{\Gamma_L} \rho_{\gamma_L} = \int_{\Gamma_L} \mu_{\rm per} \right\}. \tag{5.6}$$

Using techniques similar to [CDL08, Theorem 4], the following result holds (we do not prove it, for the arguments are similar to the ones in [CDL08]).

Theorem 5.1 (Existence of a supercell minimizer)**.** *For all $L \in \mathbb{N}^*$, the minimization problem (5.6) admits minimizers. One of these minimizers $\gamma_{L,0}$ satisfies $\tau_{\mathbf{R}}\gamma_{L,0} = \gamma_{L,0}\tau_{\mathbf{R}}$. All minimizers share the same density $\rho_{\gamma_{L,0}}$, which is $\mathcal{R}$-periodic. Finally, $\gamma_{L,0}$ satisfies the self-consistent equation*

$$\begin{cases} \gamma_{L,0} &= \mathbb{1}\left(H_{L,0} < \varepsilon^L_F\right) + \delta \\ H_{L,0} &= -\frac{1}{2}\Delta_L + V_{L,0} \\ V_{L,0} &= \left(\rho_{\gamma_{L,0}} - \mu_{\rm per}\right) *_\Gamma G_1. \end{cases} \tag{5.7}$$

where $H_{L,0}$ acts on $L^2_{\rm per}(\Gamma_L)$ and $0 \leq \delta \leq \mathbb{1}(H_{L,0} = \varepsilon^L_F)$ is a finite rank operator.

Here, ε^L_F is the Fermi level of the supercell model. It is chosen so that the charge constraint in (5.6) is satisfied.

Remark 5.2. *The $L\mathcal{R}$-periodic density of the minimizers $\rho_{\gamma_{L,0}}$ is actually $\mathcal{R}$-periodic. It is unclear that such a property should hold for more complex models (e.g. Kohn-Sham models). This is the reason why we state our results for the rHF model. We believe however that similar results should hold true for more complex systems, provided that the supercell density is $\mathcal{R}$-periodic for each size of the supercell.*

5.2.2 The reduced Hartree-Fock model for perfect crystals

The rHF model for perfect crystals, or periodic rHF, has been rigorously derived from the rHF model for finite molecular systems by means of a thermodynamic limit procedure by Catto, Le Bris and Lions [CLL01]. In [CDL08], Cancès, Deleurence and Lewin proved that the same periodic rHF model is the limit of the rHF supercell model as the size of the supercell goes to infinity.

We introduce the set of admissible density matrices

$$\mathcal{P}_{\rm per} := \left\{\gamma \in \mathcal{S}(L^2_{\rm per}(\Gamma)),\ 0 \le \gamma \le 1,\ \forall \mathbf{R} \in \mathcal{R},\ \tau_{\mathbf{R}}\gamma = \gamma\tau_{\mathbf{R}},\ \underline{\rm Tr}\,(\gamma) + \underline{\rm Tr}\,(-\Delta\gamma) < \infty\right\}, \tag{5.8}$$

where $\underline{\rm Tr}$ denotes the trace per unit volume. For any locally trace class operator A that commutes with $\mathcal{R}$-translations, it reads

$$\underline{\rm Tr}\,(A) := \lim_{L\to\infty} \frac{1}{L^3}{\rm Tr}\,(\mathbb{1}_{L\Gamma}A\mathbb{1}_{L\Gamma}). \tag{5.9}$$

The trace per unit volume $\underline{\rm Tr}$ can also be defined via the Bloch transform (see Equation (5.23) below). Here, $\underline{\rm Tr}\,(-\Delta\gamma)$ is a shorthand notation for

$$\underline{\rm Tr}\,(-\Delta\gamma) := \sum_{j=1}^{3} \underline{\rm Tr}\,(P_j\gamma P_j),$$

where $P_j = -{\rm i}\partial_{x_j}$ is the momentum operator in the $j^{\rm th}$ direction. The Coulomb energy per unit volume is defined by

$$\forall f, g \in L^2_{\rm per}(\Gamma), \quad D_1(f,g) := \int_\Gamma (f *_\Gamma G_1)(\mathbf{x})g(\mathbf{x}){\rm d}\mathbf{x}, \tag{5.10}$$

where G_1 was introduced in (5.3).

Any $\gamma \in \mathcal{P}_{\rm per}$ is locally trace-class, and can be associated an $\mathcal{R}$-periodic density $\rho_\gamma \in L^2_{\rm per}(\Gamma)$. For $\gamma \in \mathcal{P}_{\rm per}$, the reduced Hartree-Fock energy is given by

$$\mathcal{E}^{\mu_{\rm per}}_{\rm per}(\gamma) := \frac{1}{2}\underline{\rm Tr}\,(-\Delta\gamma) + \frac{1}{2}D_1\left(\rho_\gamma - \mu_{\rm per}, \rho_\gamma - \mu_{\rm per}\right). \tag{5.11}$$

The first term of (5.11) corresponds to the kinetic energy per unit volume, and the second term represents the Coulomb energy per unit volume. Finally, the periodic rHF ground state energy is given by the minimization problem

$$I^{\mu_{\rm per}}_{\rm per} := \inf\left\{\mathcal{E}^{\mu_{\rm per}}_{\rm per}(\gamma),\ \gamma \in \mathcal{P}_{\rm per},\ \int_\Gamma \rho_\gamma = \int_\Gamma \mu_{\rm per}\right\}. \tag{5.12}$$

It has been proved in [CDL08] that the minimization problem (5.12) admits a unique minimizer γ_0, which is the solution of the self-consistent equation

$$\left\{\begin{array}{rcl} \gamma_0 &=& \mathbb{1}(H_0 < \varepsilon_F) + \delta \\ H_0 &=& -\frac{1}{2}\Delta + V_0 \\ V_0 &=& (\rho_{\gamma_0} - \mu_{\rm per}) *_\Gamma G_1, \end{array}\right. \tag{5.13}$$

where H_0 acts on $L^2(\mathbb{R}^3)$ and $0 \le \delta \le \mathbb{1}(H_0 = \varepsilon_F)$ is a finite rank operator. Here, the Fermi energy ε_F is the Lagrange multiplier corresponding to the charge constraint $\int_\Gamma \rho_{\gamma_0} = \int_\Gamma \mu_{\rm per}$. We make the following assumption:

(A1) The system is an insulator, in the sense that H_0 has a spectral gap around ε_F.

In particular, $\delta = 0$.

5.3 Main results

Our main results are concerned with the rate of convergence of supercell models towards corresponding periodic models. We first prove the exponential rate of convergence in a linear setting, where the mean-filed potential V is a fixed $\mathcal{R}$-periodic function: $V \in L^\infty_{\rm per}(\Gamma)$. We then extend our result to the nonlinear rHF model, where the external potential is the solution of the self-consistent equation (5.7) or (5.13).

We start with the linear case. The proof of the following proposition is given in Section 5.5.

Proposition 5.3 (Convergence rate of the linear supercell model)**.** *Let $V \in L^\infty_{\rm per}(\Gamma)$ be such that the operator $H = -\frac{1}{2}\Delta + V$ acting on $L^2(\mathbb{R}^3)$ has a gap of size $g > 0$ centered around the Fermi level ε_F. Then, for any $L \in \mathbb{N}^*$, the operator $H^L := -\frac{1}{2}\Delta_L + V$ acting on $L^2_{\rm per}(\Gamma_L)$ has a gap of size at least g around ε_F. Let*

$$\gamma = \mathbb{1}\left(H \leq \varepsilon_F\right) \quad \text{and} \quad \gamma_L = \mathbb{1}\left(H^L \leq \varepsilon_F\right). \tag{5.14}$$

Then, $\gamma \in \mathcal{P}_{\rm per}$ and $\gamma_L \in \mathcal{P}_L$, and there exist constants $C \in \mathbb{R}^+$ and $\alpha > 0$, that depend on the lattice $\mathcal{R}$, $\|V\|_{L^\infty}$, g and ε_F only, such that

$$\forall L \in \mathbb{N}^*, \quad \left|\underline{\rm Tr}\,(\gamma H) - \underline{\rm Tr}_L\left(\gamma_L H^L\right)\right| \leq C{\rm e}^{-\alpha L} \quad \textit{(ground state energy per unit volume)} \tag{5.15}$$

and

$$\forall L \in \mathbb{N}^*, \quad \|\rho_\gamma - \rho_{\gamma_L}\|_{L^\infty} \leq C{\rm e}^{-\alpha L} \quad \textit{(ground state density)}. \tag{5.16}$$

In a second step, we will use the projectors γ and γ_L obtained for well chosen potentials V as candidates for the minimization problems (5.12) and (5.6) respectively. We have the following result (see Section 5.5.5 for the proof).

Corollary 5.4. *With the same notation as in Proposition 5.3, there exist constants $C \in \mathbb{R}^+$ and $\alpha > 0$, that depend on the lattice $\mathcal{R}$, $\|V\|_{L^\infty}$, g and ε_F only, such that*

$$\forall L \in \mathbb{N}^*, \quad \left|\mathcal{E}^{\mu_{\rm per}}_{\rm per}(\gamma) - L^{-3}\mathcal{E}^{\mu_{\rm per}}_L(\gamma_L)\right| \leq C{\rm e}^{-\alpha L}. \tag{5.17}$$

We are now able to state our main result for the rHF model. The proof of the following theorem is given in Section 5.6. In the sequel, we denote by $\mathcal{B}(E)$ the set of bounded operators acting on the Banach space E.

Theorem 5.5 (Convergence rate of the rHF supercell model)**.** *Under hypothesis (**A1**), there exist $C \in \mathbb{R}^+$ and $\alpha > 0$ independent of L such that the following estimates hold true:*

- *convergence of the ground state energy per unit volume:*

$$\forall L \in \mathbb{N}^*, \quad |L^{-3}I^{\mu_{\rm per}}_L - I^{\mu_{\rm per}}_{\rm per}| \leq C{\rm e}^{-\alpha L};$$

- *convergence of the ground state density:*

$$\forall L \in \mathbb{N}^*, \quad \|\rho_{\gamma_{L,0}} - \rho_{\gamma_0}\|_{L^\infty_{\rm per}(\Gamma)} \leq C{\rm e}^{-\alpha L};$$

- *convergence of the mean-field Hamiltonian:*

$$\forall L \in \mathbb{N}^*, \quad \|H_L - H_0\|_{\mathcal{B}(L^2(\mathbb{R}^3))} \leq C{\rm e}^{-\alpha L},$$

where $H_L := -\frac{1}{2}\Delta + \left(\rho_{\gamma_{L,0}} - \mu_{\rm per}\right) *_\Gamma G_1$ and $H := -\frac{1}{2}\Delta + \left(\rho_{\gamma_0} - \mu_{\rm per}\right) *_\Gamma G_1$ are acting on $L^2(\mathbb{R}^3)$.

The fact that the supercell quantities converge to the corresponding quantities of the periodic rHF model was already proved in [CDL08, Theorem 4]. However, following the proof of the latter article, we only find a $O\left(L^{-1}\right)$ convergence rate.

The proof of Proposition 5.3 and Theorem 5.5 rely on Bloch transforms.

5.4 Bloch transform and supercell Bloch transform

5.4.1 Bloch transform from $L^2(\mathbb{R}^3)$ to $L^2_{\rm per}(\Gamma^*, L^2(\Gamma))$

We recall in this section the basic properties of the usual Bloch transform [RS78, Chapter XIII]). Let $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ be a basis of the lattice $\mathcal{R}$, so that $\mathcal{R} = \mathbb{Z}\mathbf{a}_1 + \mathbb{Z}\mathbf{a}_2 + \mathbb{Z}\mathbf{a}_3$. We define the dual lattice $\mathcal{R}^*$ by $\mathcal{R}^* = \mathbb{Z}\mathbf{a}_1^* + \mathbb{Z}\mathbf{a}_2^* + \mathbb{Z}\mathbf{a}_3^*$ where the vectors $\mathbf{a}_i^*$ are such that $\mathbf{a}_i^* \cdot \mathbf{a}_j = 2\pi\delta_{ij}$. The unit cell and the reciprocal unit cell are respectively defined by

$$\Gamma := \left\{\alpha_1\mathbf{a}_1 + \alpha_2\mathbf{a}_2 + \alpha_3\mathbf{a}_3,\ (\alpha_1,\alpha_2,\alpha_3) \in [-1/2,1/2)^3\right\},$$

and

$$\Gamma^* := \left\{\alpha_1\mathbf{a}_1^* + \alpha_2\mathbf{a}_2^* + \alpha_3\mathbf{a}_3^*,\quad (\alpha_1,\alpha_2,\alpha_3) \in [-1/2,1/2)^3\right\}.$$

Note that Γ^* differs from the first Brillouin-zone when the crystal is not cubic. We consider the Hilbert space $L^2(\Gamma^*, L^2_{\rm per}(\Gamma))$, endowed with the normalized inner product

$$\langle f(\mathbf{q},\mathbf{x}), g(\mathbf{q},\mathbf{x})\rangle_{L^2(\Gamma^*,L^2_{\rm per}(\Gamma))} := \fint_{\Gamma^*}\int_{\Gamma} \overline{f}(\mathbf{q},\mathbf{x})g(\mathbf{q},\mathbf{x})\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{q}.$$

The Bloch transform is defined by

$$\begin{array}{rccl} \mathcal{Z}: & L^2(\mathbb{R}^3) & \to & L^2(\Gamma^*, L^2_{\rm per}(\Gamma)) \\ & w & \mapsto & (\mathcal{Z}w)(\mathbf{q},\mathbf{x}) := w_{\mathbf{q}}(\mathbf{x}) := \displaystyle\sum_{\mathbf{R}\in\mathcal{R}} \mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot(\mathbf{x}+\mathbf{R})} w(\mathbf{x}+\mathbf{R}). \end{array} \tag{5.18}$$

Its inverse is given by

$$\begin{array}{rccl} \mathcal{Z}^{-1}: & L^2(\Gamma^*, L^2_{\rm per}(\Gamma)) & \to & L^2(\mathbb{R}^3) \\ & w_{\mathbf{q}}(\mathbf{x}) & \mapsto & (\mathcal{Z}^{-1}w)(\mathbf{x}) := \displaystyle\fint_{\Gamma^*} \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{x}} w_{\mathbf{q}}(\mathbf{x})\,\mathrm{d}\mathbf{q}. \end{array}$$

It holds that $\mathcal{Z}$ is an isometry, namely

$$\|\mathcal{Z}w\|^2_{L^2(\Gamma^*,L^2_{\rm per}(\Gamma))} = \fint_{\Gamma^*}\int_{\Gamma} |(\mathcal{Z}w)(\mathbf{q},\mathbf{x})|^2\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{q} = \|w\|^2_{L^2(\mathbb{R}^3)}.$$

For $\mathbf{m} \in \mathcal{R}^*$, we introduce the unitary operator $U_{\mathbf{m}}$ acting on $L^2_{\rm per}(\Gamma)$ defined by

$$\forall \mathbf{m} \in \mathcal{R}^*,\quad \forall f \in L^2_{\rm per}(\Gamma),\quad (U_{\mathbf{m}} f)(\mathbf{x}) = \mathrm{e}^{-\mathrm{i}\mathbf{m}\cdot\mathbf{x}} f(\mathbf{x}). \tag{5.19}$$

From (5.18), it is natural to consider $\mathcal{Z}w$ as a function of $L^2_{\rm loc}\left(\mathbb{R}^3, L^2_{\rm per}(\Gamma)\right)$ such that

$$\forall w \in L^2(\mathbb{R}^3),\quad \forall \mathbf{m} \in \mathcal{R}^*,\quad \forall \mathbf{q} \in \Gamma^*,\quad (\mathcal{Z}w)(\mathbf{q}+\mathbf{m},\cdot) = w_{\mathbf{q}+\mathbf{m}} = U_{\mathbf{m}} w_{\mathbf{q}} = U_{\mathbf{m}}\left(\mathcal{Z}w(\mathbf{q},\cdot)\right). \tag{5.20}$$

Let A with domain $\mathcal{D}(A)$ be a possibly unbounded operator acting on $L^2_{\rm per}(\Gamma)$. We say that A commutes with $\mathcal{R}$-translations if $\tau_{\mathbf{R}} A = A\tau_{\mathbf{R}}$ for all $\mathbf{R} \in \mathcal{R}$. If A commutes with $\mathcal{R}$-translations, then it admits a Bloch decomposition. The operator $\mathcal{Z}A\mathcal{Z}^{-1}$ is block diagonal, which means that there exists a family of operators $(A_{\mathbf{q}})_{\mathbf{q}\in\Gamma^*}$ acting on $L^2_{\rm per}(\Gamma)$, such that, if $f \in L^2(\mathbb{R}^3)$ and $g \in \mathcal{D}(A)$ are such that $f = Ag$, then, for almost any $\mathbf{q} \in \Gamma^*$, $g_{\mathbf{q}} \in L^2_{\rm per}(\Gamma)$ is in the domain of $A_{\mathbf{q}}$, and

$$f_{\mathbf{q}} = A_{\mathbf{q}} g_{\mathbf{q}}. \tag{5.21}$$

In this case, we write

$$\mathcal{Z}A\mathcal{Z}^{-1} = \fint_{\Gamma^*}^{\oplus} A_{\mathbf{q}}\mathrm{d}\mathbf{q} \quad \text{(Bloch decomposition of } A\text{)}.$$

From (5.20), we extend the definition of $A_{\mathbf{q}}$, initially defined for $\mathbf{q} \in \Gamma^*$, to $\mathbf{q} \in \mathbb{R}^3$, with

$$\forall \mathbf{m} \in \mathcal{R}^*, \quad \forall \mathbf{q} \in \Gamma^*, \quad A_{\mathbf{q}+\mathbf{m}} = U_{\mathbf{m}} A_{\mathbf{q}} U_{\mathbf{m}}^{-1}, \tag{5.22}$$

so that (5.21) holds for almost any $\mathbf{q} \in \mathbb{R}^3$. If A is locally trace-class, then $A_{\mathbf{q}}$ is trace-class on $L^2_{\mathrm{per}}(\Gamma)$ for almost any $\mathbf{q} \in \mathbb{R}^3$. The operator A can be associated a density ρ_A, which is an $\mathcal{R}$-periodic function, given by

$$\rho_A = \fint_{\Gamma^*} \rho_{A_{\mathbf{q}}} \mathrm{d}\mathbf{q},$$

where $\rho_{A_{\mathbf{q}}}$ is the density of the trace-class operator $A_{\mathbf{q}}$. The trace per unit volume of A (defined in (5.9)) is also equal to

$$\underline{\mathrm{Tr}}\,(A) = \fint_{\Gamma^*} \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma)}\,(A_{\mathbf{q}})\,\mathrm{d}\mathbf{q}. \tag{5.23}$$

5.4.2 Bloch transform from $L^2_{\mathrm{per}}(\Gamma_L)$ to $\ell^2(\Lambda_L, L^2_{\mathrm{per}}(\Gamma))$

We present in this section the "supercell" Bloch transform. This transformation goes from $L^2_{\mathrm{per}}(\Gamma_L)$ to $\ell^2(\Lambda_L, L^2_{\mathrm{per}}(\Gamma))$, where $\Lambda_L := \left(L^{-1}\mathcal{R}^*\right) \cap \Gamma^*$, *i.e.*

$$\Lambda_L := \left\{ \frac{2k_1}{L}\mathbf{a}_1^* + \frac{2k_2}{L}\mathbf{a}_2^* + \frac{2k_3}{L}\mathbf{a}_3^*,\ (k_1,k_2,k_3) \in \left\{ \frac{-L+\eta}{2}, \frac{-L+\eta}{2}+1, \cdots, \frac{L+\eta}{2}-1 \right\}^3 \right\}, \tag{5.24}$$

with $\eta = 1$ if L is odd, and $\eta = 0$ if L is even, so that there are exactly L^3 points in Λ_L. Similarly, we define $\mathcal{R}_L := \mathcal{R} \cap \Gamma_L$, which contains L^3 points of the lattice $\mathcal{R}$. The supercell Bloch transform has properties similar to those of the standard Bloch transform, the main difference being that there are only a finite number of fibers. We introduce the Hilbert space $\ell^2(\Lambda_L, L^2_{\mathrm{per}}(\Gamma))$ endowed with the normalized inner product

$$\langle f(\mathbf{Q},\mathbf{x}), g(\mathbf{Q},\mathbf{x})\rangle_{\ell^2(\Lambda_L, L^2_{\mathrm{per}}(\Gamma))} := \frac{1}{L^3} \sum_{\mathbf{Q}\in\Lambda_L} \int_\Gamma \overline{f}(\mathbf{Q},\mathbf{x}) g(\mathbf{Q},\mathbf{x})\,\mathrm{d}\mathbf{x}.$$

The supercell Bloch transform is defined by

$$\begin{array}{rccl} \mathcal{Z}_L: & L^2_{\mathrm{per}}(\Gamma_L) & \to & \ell^2(\Lambda_L, L^2_{\mathrm{per}}(\Gamma)) \\ & w & \mapsto & (\mathcal{Z}_L w)(\mathbf{Q},\mathbf{x}) := w_{\mathbf{Q}}(\mathbf{x}) := \displaystyle\sum_{\mathbf{R}\in\mathcal{R}_L} \mathrm{e}^{-\mathrm{i}\mathbf{Q}\cdot(\mathbf{x}+\mathbf{R})} w(\mathbf{x}+\mathbf{R}). \end{array}$$

Its inverse is given by

$$\begin{array}{rccl} \mathcal{Z}_L^{-1}: & \ell^2(\Lambda_L, L^2_{\mathrm{per}}(\Gamma)) & \to & L^2_{\mathrm{per}}(\Gamma_L) \\ & w_{\mathbf{Q}}(\mathbf{x}) & \mapsto & (\mathcal{Z}_L^{-1} w)(\mathbf{x}) := \dfrac{1}{L^3} \displaystyle\sum_{\mathbf{Q}\in\Lambda_L} \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{x}} w_{\mathbf{Q}}(\mathbf{x}). \end{array}$$

It holds that $\mathcal{Z}_L$ is an isometry, *i.e.*

$$\|w\|^2_{L^2_{\mathrm{per}}(\Gamma_L)} = \frac{1}{L^3} \sum_{\mathbf{Q}\in\Lambda_L} \int_\Gamma \left|\left(\mathcal{Z}_L w\right)(\mathbf{Q},\mathbf{x})\right|^2 \mathrm{d}\mathbf{x}.$$

We can extend $\mathcal{Z}$ to $\ell^\infty\left(L^{-1}\mathcal{R}^*, L^2_{\mathrm{per}}(\Gamma)\right)$ with

$$\forall w \in L^2_{\mathrm{per}}(\Gamma_L), \quad \forall \mathbf{m} \in \mathcal{R}^*, \quad \forall \mathbf{Q} \in \Lambda_L, \quad w_{\mathbf{Q}+\mathbf{m}} = U_{\mathbf{m}} w_{\mathbf{Q}},$$

where the operator $U_{\mathbf{m}}$ was defined in (5.19).

Let A^L with domain $\mathcal{D}\left(A^L\right)$ be an operator acting on $L^2_{\mathrm{per}}(\Gamma_L)$. If A commutes with $\mathcal{R}$-translations, then it admits a supercell Bloch decomposition. The operator $\mathcal{Z}^L A^L \mathcal{Z}^L$ is block diagonal, which means that there exists a family of operators $(A^L_{\mathbf{Q}})_{\mathbf{Q}\in\Lambda_L}$ acting on $L^2_{\mathrm{per}}(\Gamma)$ such that if $f = A^L g$ with $f \in L^2_{\mathrm{per}}(\Gamma_L)$ and $g \in \mathcal{D}(A^L)$, then for all $\mathbf{Q} \in \Lambda_L$,

$$f_{\mathbf{Q}} = A^L_{\mathbf{Q}} g_{\mathbf{Q}}. \tag{5.25}$$

We write

$$\mathcal{Z}_L A^L \mathcal{Z}_L^{-1} := \frac{1}{L^3} \bigoplus_{\mathbf{Q}\in\Lambda_L} A^L_{\mathbf{Q}} \quad \text{(supercell Bloch decomposition of } A^L\text{)}.$$

The spectrum of A^L can be deduced from the spectra of $\left(A^L_{\mathbf{Q}}\right)_{\mathbf{Q}\in\Lambda_L}$ with

$$\sigma\left(A^L\right) = \bigcup_{\mathbf{Q}\in\Lambda_L} \sigma\left(A^L_{\mathbf{Q}}\right). \tag{5.26}$$

Similarly to (5.22), we extend the definition of $A_{\mathbf{Q}}$ to $L^{-1}\mathcal{R}^*$ with

$$\forall \mathbf{m} \in \mathcal{R}^*, \quad \forall \mathbf{Q} \in \Lambda_L, \quad A_{\mathbf{Q}+\mathbf{m}} = U_{\mathbf{m}} A_{\mathbf{Q}} U_{\mathbf{m}}^{-1},$$

so that (5.25) holds for all $\mathbf{Q} \in L^{-1}\mathcal{R}^*$.

Finally, if the operator A^L is trace-class, we define the trace per unit volume by

$$\underline{\mathrm{Tr}}_L(A^L) = \frac{1}{L^3}\mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma_L)}(A^L) = \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L} \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma)}(A^L_{\mathbf{Q}}), \tag{5.27}$$

and the associated density is given by $\rho_{A^L} = \dfrac{1}{L^3}\displaystyle\sum_{\mathbf{Q}\in\Lambda_L} \rho_{A^L_{\mathbf{Q}}}$, where $\rho_{A^L_{\mathbf{Q}}}$ is the density of the trace-class operator $A^L_{\mathbf{Q}}$.

5.5 Proof of Proposition 5.3: the linear case

The proofs of Proposition 5.3 and Theorem 5.5 are based on reformulating the problem using the Bloch transforms. Comparing quantities belonging to the whole space model on the one hand, and to the supercell model on the other hand amounts to comparing integrals with Riemann sums. The exponential convergence then relies on two arguments: quantities of interest are $\mathcal{R}^*$-periodic and have analytic continuations on a complex strip, and the Riemann sums for such functions converge exponentially fast to the corresponding integrals.

We prove in this section the exponential convergence of Proposition 5.3.

5.5.1 Convergence of Riemann sums

We recall the following classical lemma. For $A > 0$, we denote by

$$S_A := \left\{\mathbf{z} \in \mathbb{C}^3,\ |\mathrm{Im}\,(\mathbf{z})|_\infty \le A\right\} = \mathbb{R}^3 + \mathrm{i}\,[-A, A]^3.$$

If E is a Banach space and $d \in \mathbb{N}^*$, an E-valued function $F : \Omega \subset \mathbb{C}^d \to E$ is said to be (strongly) analytic if $(\nabla_{\mathbf{z}} F)(\mathbf{z})$ exists in E^d for all $\mathbf{z} \in \Omega$. In the sequel, we assume without loss of generality that the vectors spanning the lattice $\mathcal{R}^*$ are ordered in such a way that $|\mathbf{a}_1^*| \le |\mathbf{a}_2^*| \le |\mathbf{a}_3^*|$.

Lemma 5.6. *Let $f : \mathbb{R}^3 \to \mathbb{C}$ be an $\mathcal{R}^*$-periodic function that admits an analytic continuation on S_A for some $A > 0$. Then, there exists $C \in \mathbb{R}^+$ and $\alpha > 0$ such that*

$$\forall L \in \mathbb{N}^*, \quad \left| \fint_{\Gamma^*} f(\mathbf{q})\, \mathrm{d}\mathbf{q} - \frac{1}{L^3} \sum_{\mathbf{Q} \in \Lambda_L} f(\mathbf{Q}) \right| \leq C_0 \sup_{\mathbf{z} \in S_A} |f(\mathbf{z})|\, \mathrm{e}^{-\alpha L}.$$

The constants may be chosen equal to

$$\alpha = (2/3)\pi A |\mathbf{a}_3^*|^{-1} \quad \textit{and} \quad C_0 = 2\left(\frac{3 + \mathrm{e}^{-2\alpha}}{(1 - \mathrm{e}^{-\alpha})^3} \right). \tag{5.28}$$

Proof of Lemma 5.6. Let $c_{\mathbf{R}}(f) := \fint_{\Gamma^*} f(\mathbf{q}) \mathrm{e}^{-\mathrm{i}\mathbf{R}\cdot\mathbf{q}}\, \mathrm{d}\mathbf{q}$ be the Fourier coefficients of f, so that

$$f(\mathbf{q}) = \sum_{\mathbf{R} \in \mathcal{R}} c_{\mathbf{R}}(f) \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{R}}.$$

It holds

$$\begin{aligned} \left| \fint_{\Gamma^*} f(\mathbf{q}) \mathrm{d}\mathbf{q} - \frac{1}{L^3} \sum_{\mathbf{Q} \in \Lambda_L} f(\mathbf{Q}) \right| &= \left| c_{\mathbf{0}}(f) - \frac{1}{L^3} \sum_{\mathbf{Q} \in \Lambda_L} \sum_{\mathbf{R} \in \mathcal{R}} c_{\mathbf{R}}(f) \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}} \right| \\ &= \left| \sum_{\mathbf{R} \in \mathcal{R} \setminus \{\mathbf{0}\}} c_{\mathbf{R}}(f) \left(\frac{1}{L^3} \sum_{\mathbf{Q} \in \Lambda_L} \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}} \right) \right|. \end{aligned}$$

By noticing that

$$\sum_{\mathbf{Q} \in \Lambda_L} \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}} = \begin{cases} 0 & \text{if} \quad R \notin L\mathcal{R} \\ L^3 & \text{otherwise} \end{cases},$$

we obtain

$$\left| \fint_{\Gamma^*} f(\mathbf{q}) \mathrm{d}\mathbf{q} - \frac{1}{L^3} \sum_{\mathbf{Q} \in \Lambda_L} f(\mathbf{Q}) \right| = \left| \sum_{\mathbf{R} \in \mathcal{R} \setminus \{\mathbf{0}\}} c_{L\mathbf{R}}(f) \right|. \tag{5.29}$$

If f is analytic on S_A, we deduce from $f(\mathbf{q}) = \sum_{\mathbf{R} \in \mathcal{R}} c_{\mathbf{R}}(f) \mathrm{e}^{\mathrm{i}\mathbf{R}\cdot\mathbf{q}}$ that the analytic continuation of f is given by

$$\forall \mathbf{q} \in \mathbb{R}^3, \quad \forall \mathbf{y} \in [-A, A]^3, \quad f(\mathbf{q} + \mathrm{i}\mathbf{y}) = \sum_{\mathbf{R} \in \mathcal{R}} c_{\mathbf{R}}(f) \mathrm{e}^{\mathrm{i}\mathbf{R}\cdot\mathbf{q}}\, \mathrm{e}^{-\mathbf{R}\cdot\mathbf{y}},$$

so that $\left\{ c_{\mathbf{R}}(f) \mathrm{e}^{-\mathbf{R}\cdot\mathbf{y}} \right\}_{\mathbf{R} \in \mathcal{R}}$ are the Fourier coefficients of the $\mathcal{R}^*$-periodic function $\mathbf{q} \mapsto f(\mathbf{q} + \mathrm{i}\mathbf{y})$. In particular,

$$\forall \mathbf{R} \in \mathcal{R}, \quad \forall \mathbf{y} \in [-A, A]^3, \quad |c_{\mathbf{R}}(f)| \leq \sup_{\mathbf{q} \in \Gamma^*} |f(\mathbf{q} + \mathrm{i}\mathbf{y})|\, \mathrm{e}^{\mathbf{R}\cdot\mathbf{y}}. \tag{5.30}$$

We make the following choice for $\mathbf{y}$. We write $\mathbf{R} = k_1\mathbf{a}_1 + k_2\mathbf{a}_2 + k_3\mathbf{a}_3$ with $k_1, k_2, k_3 \in \mathbb{Z}$, and we let $1 \leq m \leq 3$ be the index such that $|k_m| = |k_j|_\infty$. Choosing $\mathbf{y} = -\mathrm{sgn}(\mathrm{k_m})\mathrm{A}|\mathbf{a}_3^*|^{-1}\mathbf{a}_{\mathrm{m}}^* \in [-\mathrm{A}, \mathrm{A}]^3$, leads to

$$|c_{\mathbf{R}}(f)| \leq \sup_{\mathbf{z} \in S_A} |f(\mathbf{z})|\, \mathrm{e}^{-2\pi A |\mathbf{a}_3^*|^{-1} |k|_\infty} \leq \sup_{\mathbf{z} \in S_A} |f(\mathbf{z})|\, \mathrm{e}^{-\alpha |k_1|_1}$$

where we used the inequality $|\mathbf{k}|_\infty \geq (1/3)|\mathbf{k}|_1$, and we set $\alpha = (2/3)\pi A |\mathbf{a}_3^*|^{-1}$. Note that the Fourier coefficients of f are exponentially decreasing. We conclude with (5.29) and the

inequality

$$\left|\sum_{\mathbf{R}\in\mathcal{R}\setminus\{\mathbf{0}\}} c_{L\mathbf{R}}(f)\right| \leq \sum_{\mathbf{R}\in\mathcal{R}\setminus\{\mathbf{0}\}} |c_{L\mathbf{R}}(f)| \leq \sup_{\mathbf{z}\in S_A} |f(\mathbf{z})| \sum_{\mathbf{k}\in\mathbb{Z}^3\setminus\{\mathbf{0}\}} \mathrm{e}^{-\alpha L|\mathbf{k}|_1}$$
$$\leq \sup_{\mathbf{z}\in S_A} |f(\mathbf{z})| \left[\left(\sum_{k\in\mathbb{Z}} \mathrm{e}^{-\alpha L|k|}\right)^3 - 1\right] = \sup_{\mathbf{z}\in S_A} |f(\mathbf{z})| \left(\frac{2(3+\mathrm{e}^{-2\alpha})}{(1-\mathrm{e}^{-\alpha})^3}\right) \mathrm{e}^{-\alpha L}.$$

□

5.5.2 Analyticity and basic estimates

The exponential rates of convergence observed in (5.15), (5.16) and (5.17) will come from Lemma 5.6 for appropriate choices of functions f. In order to construct such functions, we notice that H and H^L defined in Proposition 5.3 commute with $\mathcal{R}$-translations, thus admit Bloch decompositions. From

$$\forall \mathbf{q}\in\mathbb{R}^3,\ (-\Delta)_{\mathbf{q}} = |-\mathrm{i}\nabla_1 + \mathbf{q}|^2 = \sum_{j=1}^3 (P_{j,1}+q_j)^2 \quad \text{and} \quad \forall \mathbf{Q}\in L^{-1}\mathcal{R}^*,\ (-\Delta_L)_{\mathbf{Q}} = (-\Delta)_{\mathbf{Q}},$$

where ∇_1 denotes the gradient on the space $L^2_{\mathrm{per}}(\Gamma)$, we obtain (recall that Δ_1 was defined in (5.2))

$$\mathcal{Z}H\mathcal{Z}^{-1} = \fint_{\Gamma^*}^{\oplus} H_{\mathbf{q}}\,\mathrm{d}\mathbf{q} \quad \text{with} \quad H_{\mathbf{q}} := \frac{1}{2}|-\mathrm{i}\nabla_1+\mathbf{q}|^2 + V = \frac{1}{2}\left(-\Delta_1 - 2\mathrm{i}\mathbf{q}\cdot\nabla_1 + |\mathbf{q}|^2\right) + V, \tag{5.31}$$

and

$$\mathcal{Z}_L H^L \mathcal{Z}_L^{-1} = \frac{1}{L^3}\bigoplus_{\mathbf{Q}\in\Lambda_L} H_{\mathbf{Q}}.$$

In other words, for all $\mathbf{Q}$ in Λ_L, $\left(H^L\right)_{\mathbf{Q}} = H_{\mathbf{Q}}$. In addition, the spectrum of H can be recovered from the spectra of $(H_{\mathbf{q}})_{\mathbf{q}\in\Gamma^*}$ with [RS78, Chapter XIII]

$$\sigma(H) = \bigcup_{\mathbf{q}\in\Gamma^*} \sigma(H_{\mathbf{q}})$$

Together with (5.26) we deduce that, since H has a gap of size g centered around ε_F, then H^L has a gap of size at least g around ε_F.

In the sequel, we introduce, for $\mathbf{z}\in\mathbb{C}^3$, the operator (we denote by $\mathbf{z}^2 := \sum_{j=1}^3 z_j^2$ for simplicity)

$$H_{\mathbf{z}} := \frac{1}{2}\left(-\Delta_1 - 2\mathrm{i}\mathbf{z}\cdot\nabla_1 + \mathbf{z}^2\right) + V \quad \text{acting on} \quad L^2_{\mathrm{per}}(\Gamma). \tag{5.32}$$

With the terminology of [Kat12, Chapter VII], the map $\mathbf{z}\mapsto H_{\mathbf{z}}$ is an holomorphic family of type (A). Let $\Sigma := \inf\sigma(H)$ be the bottom of the spectrum of H. We consider the positively oriented simple closed loop $\mathscr{C} = \mathscr{C}_1\cup\mathscr{C}_2\cup\mathscr{C}_3\cup\mathscr{C}_4$ in the complex plane, consisting of the following line segments: $\mathscr{C}_1 = [\varepsilon_F - \mathrm{i}, \varepsilon_F + \mathrm{i}]$, $\mathscr{C}_2 = [\varepsilon_F + \mathrm{i}, \Sigma - 1 + \mathrm{i}]$, $\mathscr{C}_3 = [\Sigma - 1 + \mathrm{i}, \Sigma - 1 - \mathrm{i}]$ and $\mathscr{C}_4 = [\Sigma - 1 - \mathrm{i}, \varepsilon_F - \mathrm{i}]$.

The projectors defined in (5.14) can be written, using the Cauchy's residue theorem, as

$$\gamma = \frac{1}{2\mathrm{i}\pi}\oint_{\mathscr{C}} \frac{\mathrm{d}\lambda}{\lambda - H} \quad \text{and} \quad \gamma_L = \frac{1}{2\mathrm{i}\pi}\oint_{\mathscr{C}} \frac{\mathrm{d}\lambda}{\lambda - H^L}.$$

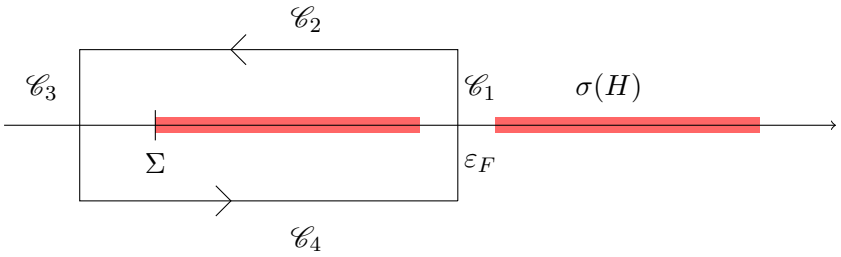

Figure 5.1 – The loop $\mathscr{C}$.

Together with (5.31), it follows that γ and γ_L commutes with $\mathcal{R}$-translations, with

$$\mathcal{Z}\gamma\mathcal{Z}^{-1} = \fint_{\Gamma^*}^{\oplus} \gamma_{\mathbf{q}} \mathrm{d}\mathbf{q} \quad \text{and} \quad \mathcal{Z}_L\gamma_L\mathcal{Z}_L^{-1} = \frac{1}{L^3} \bigoplus_{\mathbf{Q}\in\Lambda_L} \gamma_{\mathbf{Q}}, \tag{5.33}$$

where we set

$$\forall \mathbf{q} \in \mathbb{R}^3, \quad \gamma_{\mathbf{q}} := \frac{1}{2\mathrm{i}\pi} \oint_{\mathscr{C}} \frac{\mathrm{d}\lambda}{\lambda - H_{\mathbf{q}}}. \tag{5.34}$$

For $\mathbf{Q} \in \mathcal{R}^*$, it holds $(\gamma_L)_{\mathbf{Q}} = \gamma_{\mathbf{Q}}$. The analytic continuation of (5.34) is formally

$$\forall \mathbf{z} \in \mathbb{C}^3, \quad \gamma_{\mathbf{z}} := \frac{1}{2\mathrm{i}\pi} \oint_{\mathscr{C}} \frac{\mathrm{d}\lambda}{\lambda - H_{\mathbf{z}}}.$$

The fact that $\lambda - H_{\mathbf{z}}$ is indeed invertible, at least for $\mathbf{z}$ in some S_A for $A > 0$ is proved in the following lemma. For $\mathbf{z} \in \mathbb{C}^3$, and $\lambda \in \mathscr{C}$, we introduce

$$B_1(\lambda, \mathbf{z}) := (1 - \Delta_1)\frac{1}{\lambda - H_{\mathbf{z}}} \quad \text{and} \quad B_2(\lambda, \mathbf{z}) := \frac{1}{\lambda - H_{\mathbf{z}}}(1 - \Delta_1). \tag{5.35}$$

Lemma 5.7. *For all $\mathbf{q} \in \mathbb{R}^3$, and all $\lambda \in \mathscr{C}$, the operator $\lambda - H_{\mathbf{q}}$ is invertible, and there exists a constant $C_1 \in \mathbb{R}^+$ such that,*

$$\forall \mathbf{q} \in \Gamma^*, \quad \forall \lambda \in \mathscr{C}, \quad \|B_1(\lambda, \mathbf{q})\|_{\mathcal{B}(L^2_{\mathrm{per}}(\Gamma))} \leq C_1 \quad \textit{and} \quad \|B_2(\lambda, \mathbf{q})\|_{\mathcal{B}(L^2_{\mathrm{per}}(\Gamma))} \leq C_1. \tag{5.36}$$

Denoting by $|\Gamma^*|_2 := \sup\{|\mathbf{q}|_2,\ \mathbf{q} \in \Gamma^*\}$, we can choose

$$C_1 = 4 + \frac{2 + 4|\Gamma^*|_2^2 + 8\|V\|_{L^\infty} + 8\varepsilon_F}{\min(1, g)}. \tag{5.37}$$

Moreover, there exists $A > 0$ such that, for all $\mathbf{z} \in S_A$ and all $\lambda \in \mathscr{C}$, the operator $\lambda - H_{\mathbf{z}}$ is invertible, and there exists a constant $C_2 \in \mathbb{R}^+$ such that

$$\forall \mathbf{z} \in \Gamma^* + \mathrm{i}\,[-A, A]^3, \quad \forall \lambda \in \mathscr{C}, \quad \|B_1(\lambda, \mathbf{z})\|_{\mathcal{B}(L^2_{\mathrm{per}}(\Gamma))} \leq C_2 \quad \textit{and} \quad \|B_2(\lambda, \mathbf{z})\|_{\mathcal{B}(L^2_{\mathrm{per}}(\Gamma))} \leq C_2. \tag{5.38}$$

We can choose

$$A = \min\left(1,\ \frac{1}{2C_1(1 + |\Gamma^*|_2)}\right) \quad \textit{and} \quad C_2 = 2C_1. \tag{5.39}$$

This lemma was proved in the one-dimensional case by Kohn in [Koh59], and similar results were discussed by Des Cloizeaux in [DC64a, DC64b].

Remark 5.8. *The bounds (5.36) and (5.38) are not uniform for $\mathbf{q} \in \mathbb{R}^3$ (they are only valid for $\mathbf{q} \in \Gamma^*$). This comes from the fact that, for $\mathbf{m} \in \mathcal{R}^*$,*

$$\left\| \frac{1 - \Delta_1}{1 + (-\mathrm{i}\nabla_1 + \mathbf{m})^2} \right\|_{\mathcal{B}(L^2_{\mathrm{per}}(\Gamma))} \geq \left\langle \frac{\mathrm{e}^{-\mathrm{i}\mathbf{m}\cdot\mathbf{x}}}{|\Gamma|^{1/2}} \left| \frac{1 - \Delta_1}{1 + (-\mathrm{i}\nabla_1 + \mathbf{m})^2} \right| \frac{\mathrm{e}^{-\mathrm{i}\mathbf{m}\cdot\mathbf{x}}}{|\Gamma|^{1/2}} \right\rangle = \frac{1 + |\mathbf{m}|^2}{|\Gamma|}.$$

Remark 5.9. *From Lemma 5.7, we deduce that* $(\gamma_{\mathbf{z}})_{\mathbf{z}\in S_A}$ *is an analytic family of bounded operators. Since* $\gamma_{\mathbf{q}}$ *is an orthogonal projector for* $\mathbf{q}\in\mathbb{R}^3$*, i.e.* $\gamma_{\mathbf{q}}=\gamma_{\mathbf{q}}\gamma_{\mathbf{q}}$*, we deduce that* $\gamma_{\mathbf{z}}=\gamma_{\mathbf{z}}\gamma_{\mathbf{z}}$ *for all* $\mathbf{z}\in S_A$*, so that* $\gamma_{\mathbf{z}}$ *is a (not necessarily orthogonal) projector. Also,* $\mathrm{Tr}(\gamma_{\mathbf{z}})$ *is a constant independent of* $\mathbf{z}\in S_A$*.*

Proof of Lemma 5.7. From the inequality $|a|^2\le 2|a+b|^2+2|b|^2$, we get that, for $\mathbf{q}\in\Gamma^*$, it holds $|-\mathrm{i}\nabla_1+\mathbf{q}|^2+|\mathbf{q}|^2\ge-\frac{1}{2}\Delta_1$. We deduce that

$$\forall\mathbf{q}\in\Gamma^*,\quad H_{\mathbf{q}}\ge-\frac{1}{4}\Delta_1-\frac{1}{2}|\Gamma^*|_2^2-\|V\|_{L^\infty}. \tag{5.40}$$

We first consider the part $\mathscr{C}_1$ of the contour $\mathscr{C}$ (see Figure 5.1). It holds

$$\forall\lambda\in\mathscr{C}_1,\quad\forall\mathbf{q}\in\Gamma^*,\quad|H_{\mathbf{q}}-\lambda|^2\ge|\mathrm{Re}\,(H_{\mathbf{q}}-\lambda)|^2=|H_{\mathbf{q}}-\varepsilon_F|^2\,. \tag{5.41}$$

Since $|H_{\mathbf{q}}-\varepsilon_F|\ge g/2$, we get

$$\forall\lambda\in\mathscr{C}_1,\quad\forall\mathbf{q}\in\Gamma^*,\quad|H_{\mathbf{q}}-\lambda|\ge g/2. \tag{5.42}$$

On the other hand, from (5.40) and (5.41), it holds that

$$\forall\lambda\in\mathscr{C}^1,\quad\forall\mathbf{q}\in\Gamma^*,\quad|H_{\mathbf{q}}-\lambda|\ge H_{\mathbf{q}}-\varepsilon_F\ge-\frac{1}{4}\Delta_1-\frac{1}{2}|\Gamma^*|_2^2-\|V\|_{L^\infty}-\varepsilon_F. \tag{5.43}$$

Combining (5.42) and (5.43) leads to

$$\forall M\ge0,\quad\forall\lambda\in\mathscr{C}_1,\quad\forall\mathbf{q}\in\Gamma^*,\quad(M+4)|H_{\mathbf{q}}-\lambda|\ge-\Delta_1+M\frac{g}{2}-2|\Gamma^*|_2^2-4\|V\|_{L^\infty}-4\varepsilon_F.$$

Choosing $M=(2+4|\Gamma^*|_2^2+8\|V\|_{L^\infty}+8\varepsilon_F)/g$ gives

$$\forall\lambda\in\mathscr{C}^1,\quad\mathbf{q}\in\Gamma^*,\quad|H_{\mathbf{q}}-\lambda|\ge\left(4+\frac{2+4|\Gamma^*|_\infty^2+8\|V\|_{L^\infty}+8\varepsilon_F}{g}\right)^{-1}(1-\Delta_1),$$

which proves (5.36) for $\lambda\in\mathscr{C}_1$. The inequalities on the other parts of $\mathscr{C}$ are proved similarly, the inequalities (5.42) and (5.43) being respectively replaced by their equivalent

$$\begin{aligned}\forall\lambda\in\mathscr{C}_2\cup\mathscr{C}_4,\quad&|H_{\mathbf{q}}-\lambda|^2\ge|\mathrm{Im}\,(H_{\mathbf{q}}-\lambda)|^2\ge1\quad\text{and}\quad|H_{\mathbf{q}}-\lambda|\ge H_{\mathbf{q}}-\Sigma-1\ge H_{\mathbf{q}}-\varepsilon_F,\\ \forall\lambda\in\mathscr{C}_3,\quad&|H_{\mathbf{q}}-\lambda|^2\ge|\mathrm{Re}\,(H_{\mathbf{q}}-\lambda)|^2\ge1\quad\text{and}\quad|H_{\mathbf{q}}-\lambda|\ge H_{\mathbf{q}}-\Sigma-1\ge H_{\mathbf{q}}-\varepsilon_F.\end{aligned}$$

This proves (5.36). We now prove (5.38). For $\mathbf{z}=\mathbf{q}+\mathrm{i}\mathbf{y}\in\mathbb{C}^3$ with $\mathbf{q}\in\Gamma^*$ and $\mathbf{y}\in\mathbb{R}^3$, one can rewrite (5.32) as

$$H_{\mathbf{z}}=H_{\mathbf{q}}+\mathbf{y}\cdot\nabla_1+\mathrm{i}\mathbf{q}\cdot\mathbf{y}-\frac{1}{2}|\mathbf{y}|^2=H_{\mathbf{q}}+\mathbf{y}\cdot\left(\nabla_1-\frac{1}{2}\mathbf{y}+\mathrm{i}\mathbf{q}\right).$$

In particular,

$$\begin{aligned}\lambda-H_{\mathbf{z}}&=\lambda-H_{\mathbf{q}}+H_{\mathbf{q}}-H_{\mathbf{z}}=(\lambda-H_{\mathbf{q}})\left(1-(\lambda-H_{\mathbf{q}})^{-1}\left[\mathbf{y}\cdot\left(\nabla_1-\frac{1}{2}\mathbf{y}+\mathrm{i}\mathbf{q}\right)\right]\right)\\&=(\lambda-H_{\mathbf{q}})\left(1-B_2(\lambda,\mathbf{q})\frac{1}{1-\Delta_1}\left[\mathbf{y}\cdot\left(\nabla_1-\frac{1}{2}\mathbf{y}+\mathrm{i}\mathbf{q}\right)\right]\right).\end{aligned} \tag{5.44}$$

For $|\mathbf{y}|_\infty\le1$, we have

$$\left|\frac{1}{1-\Delta_1}\left[\mathbf{y}\cdot\left(\nabla_1-\frac{1}{2}\mathbf{y}+\mathrm{i}\mathbf{q}\right)\right]\right|\le|\mathbf{y}|_\infty\left(\left|\frac{|\nabla_1|}{1-\Delta_1}\right|+\frac{1}{2}|\mathbf{y}|_\infty+|\mathbf{q}|_\infty\right)\le|\mathbf{y}|_\infty(1+|\Gamma^*|_2)\,.$$

Together with (5.36), we obtain that for all $|\mathbf{y}|_\infty \leq A := \min\left(1, (2C_1(1+|\Gamma^*|_2))^{-1}\right)$,

$$\left\| B_2(\lambda, \mathbf{q}) \frac{1}{1-\Delta_1} \left[\mathbf{y} \cdot \left(\nabla_1 - \frac{1}{2}\mathbf{y} + \mathrm{i}\mathbf{q} \right) \right] \right\| \leq \frac{1}{2}.$$

As a result, from (5.44), we get that for all $\mathbf{q} \in \Gamma^*$ and all $\mathbf{y} \in [-A, A]$, the operator $\lambda - H_{\mathbf{z}}$ is invertible, with

$$\left\| \frac{1}{\lambda - H_{\mathbf{z}}}(1-\Delta_1) \right\|_{\mathcal{B}(\mathcal{H}_1)} \leq C_2 := 2C_1 \quad \text{and} \quad \left\| (1-\Delta_1) \frac{1}{\lambda - H_{\mathbf{z}}} \right\|_{\mathcal{B}(\mathcal{H}_1)} \leq C_2.$$

□

For $\mathbf{z} \in S_A$, we introduce the operators $\widetilde{B_1}(\mathbf{z})$ and $\widetilde{B_2}(\mathbf{z})$ respectively defined by

$$\widetilde{B_1}(\mathbf{z}) := (1-\Delta_1)\gamma_{\mathbf{z}} \quad \text{and} \quad \widetilde{B_2}(\mathbf{z}) := \gamma_{\mathbf{z}}(1-\Delta_1). \tag{5.45}$$

In the sequel, for $k \in \mathbb{N}^*$, we denote by $\mathfrak{S}_k(\mathcal{H})$ the k-th Schatten class [Sim05] of the Hilbert space $\mathcal{H}$; $\mathfrak{S}_1(\mathcal{H})$ is the set of trace-class operators, and $\mathfrak{S}_2(\mathcal{H})$ is the set of Hilbert-Schmidt operators. From Lemma 5.7, we obtain the following result.

Lemma 5.10. *There exists a constant $C_3 \in \mathbb{R}^+$ such that*

$$\forall \mathbf{z} \in \Gamma^* + \mathrm{i}[-A, A]^3, \quad \left\| \widetilde{B_1}(\mathbf{z}) \right\|_{\mathcal{B}(L^2_{\mathrm{per}}(\Gamma))} \leq C_3 \quad \textit{and} \quad \left\| \widetilde{B_2}(\mathbf{z}) \right\|_{\mathcal{B}(L^2_{\mathrm{per}}(\Gamma))} \leq C_3.$$

The value of C_3 can be chosen equal to

$$C_3 = \frac{1}{\pi} C_1 \left(3 + \varepsilon_F + \|V\|_{L^\infty}\right).$$

Also, for all $\mathbf{z} \in \Gamma^* + \mathrm{i}[-A, A]^3$, the operator $\gamma_{\mathbf{z}}$ is trace-class, and

$$\|\gamma_{\mathbf{z}}\|_{\mathfrak{S}_1(L^2_{\mathrm{per}}(\Gamma))} \leq C_4 \quad \textit{with} \quad C_4 = C_1^2 \sum_{\mathbf{k} \in \mathcal{R}^*} \left(\frac{1}{1+|\mathbf{k}|^2} \right)^2. \tag{5.46}$$

Proof. The first assertion comes from the fact that

$$\widetilde{B_1}(\mathbf{z}) = \frac{1}{2\mathrm{i}\pi} \oint_{\mathscr{C}} B_1(\lambda, \mathbf{z}) \, \mathrm{d}\lambda,$$

and the fact that $|\mathscr{C}| = 6 + 2(\varepsilon_F - \Sigma)$ (see Figure 5.1). Note that since $|-\mathrm{i}\nabla_1 + \mathbf{q}|^2 \geq 0$, it holds $\Sigma \geq -\|V\|_{L^\infty}$. To get the second assertion, we note that $\gamma_{\mathbf{z}}$ is a projector, so that

$$\gamma_{\mathbf{z}} = \gamma_{\mathbf{z}}\gamma_{\mathbf{z}} = \widetilde{B_2}(\mathbf{z}) \left(\frac{1}{1-\Delta_1} \right)^2 \widetilde{B_1}(\mathbf{z}).$$

The operator $(1-\Delta_1)^{-2}$ being trace-class, with

$$\left\| (1-\Delta)^{-2} \right\|_{\mathfrak{S}_1(L^2_{\mathrm{per}}(\Gamma))} = \sum_{\mathbf{k} \in \mathcal{R}^*} \left(\frac{1}{1+|\mathbf{k}|^2} \right)^2,$$

we obtain (5.46). □

5.5.3 Convergence of the kinetic energy per unit volume

The kinetic energy per unit volume of the states γ and γ_L defined in (5.14) are respectively given by

$$K_{\rm per} := \underline{\rm Tr}\,(-\Delta\gamma) \quad \text{and} \quad K_L := \underline{\rm Tr}_L\,(-\Delta_L\gamma_L)\,.$$

Using the Bloch decomposition of γ and γ_L in (5.33)-(5.34), and the properties (5.23) and (5.27), we obtain that

$$K^{\rm per} = \sum_{j=1}^{3} \fint_{\Gamma^*} K_j(\mathbf{q})\,{\rm d}\mathbf{q} \quad \text{and} \quad K^L = \sum_{j=1}^{3} \frac{1}{L^3} \sum_{\mathbf{Q}\in\Lambda_L} K_j(\mathbf{Q})$$

where, for $1 \le j \le 3$, we introduced the function

$$K_j : \mathbf{q} \in \mathbb{R}^3 \mapsto {\rm Tr}_{L^2_{\rm per}(\Gamma)}\left((P_j+q_j)\,\gamma_{\mathbf{q}}\,(P_j+q_j)\right).$$

Here, we denoted by $P_j := P_{1,j}$ for simplicity. Recall that the operator $P_{1,j}$ was defined in (5.2). The error on the kinetic energy per unit volume $K^{\rm per} - K^L$ is therefore equal to the difference between integrals and corresponding Riemann sums. In the sequel, we introduce, for $1 \le j \le 3$, the function

$$\forall \mathbf{z} \in S_A, \quad K_j(\mathbf{z}) := {\rm Tr}_{L^2_{\rm per}(\Gamma)}\left((P_j+z_j)\,\gamma_{\mathbf{z}}\,(P_j+z_j)\right).$$

Lemma 5.11 (Exponential convergence of the kinetic energy)**.** *For all $1 \le j \le 3$, the function K_j is $\mathcal{R}$-periodic, and admits an analytic continuation on S_A, where $A > 0$ was defined in (5.39). Moreover, it holds*

$$\sup_{\mathbf{z}\in S_A} |K_j(\mathbf{z})| \le C_5 \quad \textit{where} \quad C_5 = \left(|\Gamma^*|_2 + A + \frac{1}{2}\right)^2 C_3^2 C_4. \tag{5.47}$$

As a consequence, from Lemma 5.6, it holds

$$\left|K^{\rm per} - K^L\right| \le C_0 C_5 {\rm e}^{-\alpha L},$$

where $C_0 \in \mathbb{R}^+$ and $\alpha > 0$ were defined in (5.28).

Proof. The $\mathcal{R}$-periodicity comes from the covariant identity (5.22). To prove the analyticity, it is enough to prove that $\partial_{z_k}\left((P_j+z_j)\gamma_{\mathbf{z}}(P_j+z_j)\right)$ is a trace-class operator for all $\mathbf{z} \in \Gamma^* + {\rm i}[-A,A]^3$. We only consider the case $j=1$ and $k=1$, the other cases being similar. We have

$$\partial_{z_1}\left((P_1+z_1)\gamma_{\mathbf{z}}(P_1+z_1)\right) = \gamma_{\mathbf{z}}(P_1+z_1) + (P_1+z_1)(\partial_{z_1}\gamma_{\mathbf{z}})(P_1+z_1) + (P_1+z_1)\gamma_{\mathbf{z}}. \tag{5.48}$$

We first show that $(P_1+z_1)\gamma_{\mathbf{z}}$ is a bounded operator. We have

$$(P_1+z_1)\gamma_{\mathbf{z}} = \frac{(P_1+z_1)}{1-\Delta_1}\widetilde{B_1}(\mathbf{z}),$$

where $\widetilde{B_1}$ was defined in (5.45). From Lemma (5.10) and the fact that $(P_1+z_1)(1-\Delta_1)^{-1}$ is a bounded operator, we deduce that $(P_1+z_1)\gamma_{\mathbf{z}}$ is bounded. The proof is similar for the operator $\gamma_{\mathbf{z}}(P_1+z_1)$. We now turn to the middle term of (5.48). Since $\gamma_{\mathbf{z}}$ is a projector, it holds $\gamma_{\mathbf{z}} = \gamma_{\mathbf{z}}\gamma_{\mathbf{z}}$. We obtain

$$\begin{aligned}(P_1+z_1)(\partial_{z_1}\gamma_{\mathbf{z}})(P_1+z_1) &= (P_1+z_1)\left[\gamma_{\mathbf{z}}(\partial_{z_1}\gamma_{\mathbf{z}}) + (\partial_{z_1}\gamma_{\mathbf{z}})\gamma_{\mathbf{z}}\right](P_1+z_1)\\ &= \left[(P_1+z_1)\gamma_{\mathbf{z}}\right]\gamma_{\mathbf{z}}(\partial_{z_1}\gamma_{\mathbf{z}})(P_1+z_1) + (P_1+z_1)(\partial_{z_1}\gamma_{\mathbf{z}})\gamma_{\mathbf{z}}\left[\gamma_{\mathbf{z}}(P_1+z_1)\right].\end{aligned}$$

We already proved that the operators $(P_1+z_1)\gamma_{\mathbf{z}}$ and $\gamma_{\mathbf{z}}(P_1+z_1)$ were bounded. Also, $\gamma_{\mathbf{z}}$ is a trace-class operator. To prove that $(P_1+z_1)\,(\partial_{z_1})\,\gamma_{\mathbf{z}}(P_1+z_1)$ is trace class, it is therefore sufficient to show that $(P_1+z_1)(\partial_{z_1}\gamma_{\mathbf{z}})$ is bounded. We have

$$\begin{aligned}(P_1+z_1)(\partial_{z_1}\gamma_{\mathbf{z}}) &= \frac{1}{2\mathrm{i}\pi}\oint_{\mathscr{C}}(P_1+z_1)\frac{1}{\lambda-H_{\mathbf{z}}}(P_1+z_1)\frac{1}{\lambda-H_{\mathbf{z}}}\mathrm{d}\lambda\\ &= \frac{1}{2\mathrm{i}\pi}\oint_{\mathscr{C}}\left(\frac{P_1+z_1}{1-\Delta_1}B_1(\lambda,\mathbf{z})\right)^2\mathrm{d}\lambda,\end{aligned}$$

which is a bounded operator. We conclude that $\partial_{z_1}\left((P_1+z_1)\gamma_{\mathbf{z}}(P_1+z_1)\right)$ is a trace-class operator. Finally, for $1\le j\le 3$, K_j is an analytic function on S_A.

To get the bound (5.47), we write that

$$\begin{aligned}K_j(\mathbf{z}) &= \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma)}\left((P_j+z_j)\gamma_{\mathbf{z}}(P_j+z_j)\right) = \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma)}\left((P_j+z_j)\gamma_{\mathbf{z}}\gamma_{\mathbf{z}}\gamma_{\mathbf{z}}(P_j+z_j)\right)\\ &= \mathrm{Tr}_{L^2_{\mathrm{per}}(\Gamma)}\left(\frac{P_j+z_j}{1-\Delta_1}\widetilde{B_1}(\mathbf{z})\gamma_{\mathbf{z}}\widetilde{B_2}(\mathbf{z})\frac{P_j+z_j}{1-\Delta_1}\right).\end{aligned}$$

The bound (5.47) easily follows from Lemma 5.10 and the estimate

$$\forall\mathbf{z}\in\Gamma^*+\mathrm{i}[-A,A]^3,\quad \left\|\frac{P_j+z_j}{1-\Delta_1}\right\|_{\mathcal{B}(L^2_{\mathrm{per}}(\Gamma))}\le|z_j|+\left\|\frac{P_j}{1-\Delta_1}\right\|_{\mathcal{B}(L^2_{\mathrm{per}}(\Gamma))}\le|\Gamma^*|_2+A+\frac{1}{2}.$$

□

5.5.4 Convergence of the ground state density

We now prove (5.16). The densities of γ and γ_L defined in (5.33)-(5.34) are respectively

$$\rho_\gamma := \fint_{\Gamma^*}\rho_{\gamma_{\mathbf{q}}}\,\mathrm{d}\mathbf{q}\quad\text{and}\quad \rho_{\gamma_L} := \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L}\rho_{\gamma_{\mathbf{Q}}}.$$

In particular, if W is a regular $\mathcal{R}$-periodic trial function, it holds that

$$M_W^{\mathrm{per}} := \int_\Gamma\rho_\gamma W = \fint_{\Gamma^*}\mathrm{Tr}_{L^2_{\mathrm{per}}}(\gamma_{\mathbf{q}}W)\,\mathrm{d}\mathbf{q}\quad\text{and}\quad M_W^L := \int_\Gamma\rho_{\gamma_L}W = \frac{1}{L^3}\sum_{\mathbf{Q}\in\Lambda_L}\mathrm{Tr}_{L^2_{\mathrm{per}}}(\gamma_{\mathbf{Q}}W),$$

so that the error $M_W^{\mathrm{per}}-M_W^L$ is again the difference between an integral and a corresponding Riemann sum. We introduce, for $W\in L^1_{\mathrm{per}}(\Gamma)$ the function

$$\forall\mathbf{z}\in S_A,\quad M_W(\mathbf{z}) := \mathrm{Tr}_{L^2_{\mathrm{per}}}(\gamma_{\mathbf{z}}W). \tag{5.49}$$

Lemma 5.12. *For all $W\in L^1_{\mathrm{per}}(\Gamma)$, M_W defined in (5.49) is well-defined $\mathcal{R}^*$-periodic analytic function on S_A, where $A>0$ was defined in (5.39), and it holds that*

$$\sup_{\mathbf{z}\in S_A}|M_W(\mathbf{z})|\le C_6\|W\|_{L^1_{\mathrm{per}}(\Gamma)}\quad\textit{with}\quad C_6=C_3^2\sum_{\mathbf{k}\in\mathcal{R}^*}\left(\frac{1}{1+|\mathbf{k}|^2}\right)^2. \tag{5.50}$$

As a consequence, from Lemma 5.6, it holds that

$$\|\rho_\gamma-\rho_{\gamma_L}\|_{L^\infty(\Gamma)}\le C_0C_6\mathrm{e}^{-\alpha L}, \tag{5.51}$$

where C_0 and α were defined in (5.28).

Proof of lemma 5.12. We first prove that M_W is well defined whenever $W \in L^1_{\rm per}(\Gamma)$. For $W \in L^1_{\rm per}(\Gamma)$, we have

$$\begin{aligned} M_W(\mathbf{z}) &= \mathrm{Tr}_{L^2_{\rm per}(\Gamma)}\left(\gamma_{\mathbf{z}} W\right) = \mathrm{Tr}_{L^2_{\rm per}(\Gamma)}\left(\gamma_{\mathbf{z}} W \gamma_{\mathbf{z}}\right) \\ &= \mathrm{Tr}_{L^2_{\rm per}(\Gamma)}\left(\widetilde{B_2}(\mathbf{z})(1-\Delta_1)^{-1} W (1-\Delta_1)^{-1}\widetilde{B_1}(\mathbf{z})\right). \end{aligned}$$

According to the Kato-Seiler-Simon inequality [Sim05, Theorem 4.1][1], it holds that the operator $(1-\Delta_1)^{-1}\sqrt{|W|}$ is Hilbert-Schmidt (*i.e.* in the Schatten space $\mathfrak{S}_2(L^2_{\rm per}(\Gamma))$), and satisfies

$$\left\|(1-\Delta_1)^{-1}\sqrt{|W|}\right\|_{\mathfrak{S}_2(L^2_{\rm per}(\Gamma))} \leq \left(\sum_{\mathbf{k}\in\mathcal{R}^*}\left(\frac{1}{1+|\mathbf{k}|^2}\right)^2\right)^{1/2} \|W\|^{1/2}_{L^1(\Gamma)}.$$

It follows that $(1-\Delta_1)^{-1}W(1-\Delta_1)^{-1}$ is in $\mathfrak{S}_1(L^2_{\rm per}(\Gamma))$ with

$$\left\|(1-\Delta_1)^{-1}W(1-\Delta_1)^{-1}\right\|_{\mathfrak{S}_1(L^2_{\rm per}(\Gamma))} \leq \left(\sum_{\mathbf{k}\in\mathcal{R}^*}\left(\frac{1}{1+|\mathbf{k}|^2}\right)^2\right)\|W\|_{L^1(\Gamma)}, \tag{5.52}$$

The proof of (5.50) then follows from Lemma 5.10.

Let us now prove that, for $W \in L^1(\Gamma)$, M_W is analytic on S_A. To do so, it is sufficient to show that, for $1 \leq k \leq 3$, $\partial_{z_k}(\gamma_{\mathbf{z}} W \gamma_{\mathbf{z}})$ is a trace class operator. We do the proof for $k=1$. We have

$$\begin{aligned} \partial_{z_1}(\gamma_{\mathbf{z}} W \gamma_{\mathbf{z}}) &= (\partial_{z_1}\gamma_{\mathbf{z}}) W \gamma_{\mathbf{z}} + \gamma_{\mathbf{z}} W (\partial_{z_1}\gamma_{\mathbf{z}}) \\ &= \frac{1}{(2\mathrm{i}\pi)^2}\oint_{\mathscr{C}}\oint_{\mathscr{C}} B_2(\lambda,\mathbf{z})\frac{1}{1-\Delta_1}(P_1+z_1)B_2(\lambda,\mathbf{z})\frac{1}{1-\Delta_1}W\frac{1}{1-\Delta_1}B_1(\lambda',\mathbf{z})\mathrm{d}\lambda\mathrm{d}\lambda' \\ &+ \frac{1}{(2\mathrm{i}\pi)^2}\oint_{\mathscr{C}}\oint_{\mathscr{C}} B_2(\lambda,\mathbf{z})\frac{1}{1-\Delta_1}W\frac{1}{1-\Delta_1}B_1(\lambda',\mathbf{z})(P_1+z_1)\frac{1}{1-\Delta_1}B_1(\lambda',\mathbf{z})\mathrm{d}\lambda\mathrm{d}\lambda'. \end{aligned}$$

We deduce as in the proof of Lemma 5.11 that $\nabla_{\mathbf{z}}(\gamma_{\mathbf{z}} W \gamma_{\mathbf{z}})$ is trace class, which concludes the proof. □

5.5.5 Proof of Proposition 5.3 and Corollary 5.4

We now proceed with the proof of Proposition 5.3. The assertion (5.16) was proved in Lemma 5.12. To get (5.15), we write that

$$\underline{\mathrm{Tr}}\,(\gamma H) = \frac{1}{2}\underline{\mathrm{Tr}}\,(-\Delta\gamma) + \underline{\mathrm{Tr}}\,(V\gamma) \quad \text{and} \quad \underline{\mathrm{Tr}}_L\left(\gamma_L H^L\right) = \frac{1}{2}\underline{\mathrm{Tr}}_L\left(-\Delta_L\gamma\right) + \underline{\mathrm{Tr}}_L\left(V\gamma_L\right),$$

so that

$$\left|\underline{\mathrm{Tr}}\,(\gamma H) - \underline{\mathrm{Tr}}_L\left(\gamma_L H^L\right)\right| \leq \frac{1}{2}\left|\underline{\mathrm{Tr}}\,(-\Delta\gamma) - \underline{\mathrm{Tr}}_L\,(-\Delta_L\gamma)\right| + \|V\|_{L^1_{\rm per}(\Gamma)}\left\|\rho_\gamma - \rho_{\gamma_L}\right\|_{L^\infty_{\rm per}(\Gamma)}.$$

The proof of (5.15) then follows from Lemma 5.11 and (5.51).

We now prove Corollary 5.4. We compare the total energies

$$\begin{aligned} \mathcal{E}^{\mu_{\rm per}}_{\rm per}(\gamma) - \mathcal{E}^{\mu_{\rm per}}_L(\gamma_L) &= \frac{1}{2}\left(\underline{\mathrm{Tr}}\,(-\Delta\gamma) - \underline{\mathrm{Tr}}_L(-\Delta_L\gamma_L)\right) \\ &+ \frac{1}{2}\left(D_1(\rho_\gamma - \mu_{\rm per}, \rho - \mu_{\rm per}) - D_1(\rho_{\gamma_L} - \mu_{\rm per}, \rho_{\gamma_L} - \mu_{\rm per})\right), \end{aligned} \tag{5.53}$$

[1] The proof in [Sim05] is actually stated for operators acting on $L^p(\mathbb{R}^3)$. However, the proof applies straightforwardly to our bounded domain case $L^p_{\rm per}(\Gamma)$.

and notice that

$$|D_1(\rho_\gamma - \mu_{\rm per}, \rho_\gamma - \mu_{\rm per}) - D_1(\rho_{\gamma_L} - \mu_{\rm per}, \rho_{\gamma_L} - \mu_{\rm per})| = |D_1(\rho_\gamma - \rho_{\gamma_L}, \rho_\gamma + \rho_{\gamma_L} - 2\mu_{\rm per})| \tag{5.54}$$

Using for instance the inequality (recall that $|\mathbf{a}_1^*| \leq |\mathbf{a}_2^*| \leq |\mathbf{a}_3^*|$)

$$\begin{aligned} \forall f, g \in L^2_{\rm per}(\Gamma), \quad |D_1(f,g)| &= \left| \sum_{\mathbf{R} \in \mathcal{R}\setminus\{\mathbf{0}\}} \frac{\overline{c_{\mathbf{k}}(f)} c_{\mathbf{k}}(g)}{|\mathbf{k}|^2} \right| \leq \frac{1}{|\mathbf{a}_3^*|^2} \sum_{\mathbf{R} \in \mathcal{R}\setminus\{\mathbf{0}\}} \left| \overline{c_{\mathbf{k}}(f)} c_{\mathbf{k}}(g) \right| \\ &\leq \frac{1}{|\mathbf{a}_3^*|^2 \, |\Gamma|} \|f\|_{L^2_{\rm per}(\Gamma)} \|g\|_{L^2_{\rm per}(\Gamma)}, \end{aligned} \tag{5.55}$$

and combining (5.53), (5.54) and (5.55), we obtain

$$\begin{aligned} \left| \mathcal{E}^{\mu_{\rm per}}_{\rm per}(\gamma) - \mathcal{E}^{\mu_{\rm per}}_L(\gamma_L) \right| \leq \frac{1}{2} \left| \underline{\rm Tr}(-\Delta\gamma) - \underline{\rm Tr}_L(-\Delta_L \gamma_L) \right| \\ + \frac{1}{2|\mathbf{a}_3^*|^2 |\Gamma|} \|\rho_\gamma - \rho_{\gamma_L}\|_{L^2_{\rm per}(\Gamma)} \|\rho_\gamma + \rho_{\gamma_L} - 2\mu_{\rm per}\|_{L^2_{\rm per}(\Gamma)}. \end{aligned}$$

Corollary 5.4 is therefore a consequence of Lemma 5.11, (5.51) and the embedding $L^\infty_{\rm per}(\Gamma) \hookrightarrow L^2_{\rm per}(\Gamma)$.

5.6 Proof for the nonlinear reduced Hartree-Fock case

In this section, we prove the exponential rate of convergence of the supercell model to the periodic model in the nonlinear rHF case (see Theorem 5.5). The proof consists of three steps.

Step 1: *Convergence of the ground-state energy per unit volume*

In the sequel, we denote by $V_0 := (\rho_{\gamma_0} - \mu_{\rm per}) *_\Gamma G_1$ and $V_{L,0} := \left(\rho_{\gamma_{L,0}} - \mu_{\rm per}\right) *_\Gamma G_1$ (see also (5.7) and (5.13)). We recall that

$$\begin{aligned} H_0 &= -\frac{1}{2}\Delta + V_0 \quad \text{and} \quad \gamma_0 = \mathbb{1}(H_0 < \varepsilon_F) \quad \text{act on} \quad L^2(\mathbb{R}^3), \\ H_{L,0} &= -\frac{1}{2}\Delta_L + V_{L,0} \quad \text{and} \quad \gamma_{L,0} = \mathbb{1}(H_{L,0} < \varepsilon_F) \quad \text{act on} \quad L^2_{\rm per}(\Gamma_L). \end{aligned}$$

We denote by $g > 0$ the gap of H_0 around the Fermi level ε_F.

It was proved in [CDL08] that the sequence $(V_{L,0})_{L \in \mathbb{N}^*}$ converges to V_0 in $L^\infty_{\rm per}(\Gamma)$. We will prove later that this convergence is actually exponentially fast. As a result, we deduce that for L large enough, say $L \geq L^{\rm gap}$, the operator $H_{L,0}$ is gapped around ε_F, and one may choose the Fermi level of the supercell ε_F^L defined in (5.7) equal to ε_F. We denote by g_L the size of the gap of $H_{L,0}$ around ε_F. Without loss of generality we may assume that $L^{\rm gap}$ is large enough so that

$$\forall L \geq L^{\rm gap}, \quad g_L \geq \frac{g}{2}.$$

In the last section, we proved that the constants $C \in \mathbb{R}^+$ and $\alpha > 0$ appearing in Proposition 5.3 are functions of the parameters $\mathcal{R}$, $\|V\|_{L^\infty}$, g and ε_F of the problem only. In particular, it is possible to choose $C \in \mathbb{R}^+$ and $\alpha > 0$ such that, for any choice of potentials V among $\left\{V_0, (V_{L,0})_{L \geq L^{\rm gap}}\right\}$, the inequalities (5.15), (5.16) and (5.17) hold true.

We first consider $V = V_0$ in Proposition 5.3. We denote by $\gamma_L \in \mathcal{P}_L$ the one-body density matrix defined in (5.33) for this choice of potential. Together with Corollary 5.4, we get

$$\forall L \in \mathbb{N}^*, \quad L^{-3} I_L^{\mu_{\rm per}} = L^{-3} \mathcal{E}_L^{\mu_{\rm per}}(\gamma_{L,0}) \leq L^{-3} \mathcal{E}_L^{\mu_{\rm per}}(\gamma_L) \leq \mathcal{E}_{\rm per}^{\mu_{\rm per}}(\gamma_0) + C\mathrm{e}^{-\alpha L} = I_{\rm per}^{\mu_{\rm per}} + C\mathrm{e}^{-\alpha L}.$$

On the other hand, choosing $V = V_{L,0}$ with $L \geq L^{\rm gap}$ in Proposition 5.3, and denoting by $\gamma'_L \in \mathcal{P}_{\rm per}$ the one-body density matrix defined in (5.33) for this choice of potential, we get

$$\forall L \geq L^{\rm gap}, \quad I_{\rm per}^{\mu_{\rm per}} = \mathcal{E}_{\rm per}^{\mu_{\rm per}}(\gamma_0) \leq \mathcal{E}_{\rm per}^{\mu_{\rm per}}(\gamma'_L) \leq L^{-3} \mathcal{E}_L^{\mu_{\rm per}}(\gamma_{L,0}) + C\mathrm{e}^{-\alpha L} = L^{-3} I_L^{\mu_{\rm per}} + C\mathrm{e}^{-\alpha L}.$$

Combining both inequalities leads to

$$\forall L \geq L^{\rm gap}, \quad \left| L^{-3} I_L^{\mu_{\rm per}} - I_{\rm per}^{\mu_{\rm per}} \right| \leq C\mathrm{e}^{-\alpha L}. \tag{5.56}$$

This leads to the claimed rate of convergence for the ground-state energy per unit cell.

Step 2: *Convergence of the ground state density*

In order to compare ρ_{γ_0} and $\rho_{\gamma_{L,0}}$, it is useful to introduce the Hamiltonian $H^L := -\frac{1}{2}\Delta_L + V_0$ acting on $L^2_{\rm per}(\Gamma_L)$. We also introduce $\gamma_L := \mathbb{1}(H^L < \varepsilon_F)$. Note that $\gamma_L \in \mathcal{P}_L$ is the operator obtained in (5.33) by taking $V = V_0$ in Proposition 5.3. Therefore, according to this proposition, there exist $C \in \mathbb{R}^+$ and $\alpha > 0$ such that

$$\forall L \in \mathbb{N}^*, \quad \|\rho_{\gamma_0} - \rho_{\gamma_L}\|_{L^\infty(\Gamma)} \leq C\mathrm{e}^{-\alpha L}. \tag{5.57}$$

In order to compare ρ_{γ_L} with $\rho_{\gamma_{L,0}}$, we note that, since $\gamma_{L,0}$ is a minimizer of (5.6), then, using (5.17) and (5.56), we get that, for any $L \in \mathbb{N}^*$,

$$\begin{aligned} 0 \leq L^{-3} \mathcal{E}_L^{\mu_{\rm per}}(\gamma_L) - L^{-3} \mathcal{E}_L^{\mu_{\rm per}}(\gamma_{L,0}) &= \left(L^{-3} \mathcal{E}_L^{\mu_{\rm per}}(\gamma_L) - \mathcal{E}_{\rm per}^{\mu_{\rm per}}(\gamma_0)\right) + \left(\mathcal{E}_{\rm per}^{\mu_{\rm per}}(\gamma_0) - L^{-3} \mathcal{E}_L^{\mu_{\rm per}}(\gamma_{L,0})\right) \\ &\leq 2C\mathrm{e}^{-\alpha L}, \end{aligned}$$

so that

$$\forall L \in \mathbb{N}^*, \quad 0 \leq \mathcal{E}_L^{\mu_{\rm per}}(\gamma_L) - \mathcal{E}_L^{\mu_{\rm per}}(\gamma_{L,0}) \leq L^3 2C\mathrm{e}^{-\alpha L} \leq C'\mathrm{e}^{-\alpha' L}$$

for some constants $C' \in \mathbb{R}^+$ and $\alpha' > 0$ independent of L. This inequality can be recast into

$$\forall L \in \mathbb{N}^*, \quad 0 \leq \underline{\mathrm{Tr}}_L \left((H_{L,0} - \varepsilon_F)(\gamma_L - \gamma_{L,0}) \right) + \frac{1}{2} D_1(\rho_{\gamma_L} - \rho_{\gamma_{L,0}}, \rho_{\gamma_L} - \rho_{\gamma_{L,0}}) \leq C'\mathrm{e}^{-\alpha' L}.$$

Both terms are non-negative, so each one of them is decaying exponentially fast. From the inequality (recall that we assumed $|\mathbf{a}_1^*| \leq |\mathbf{a}_2^*| \leq |\mathbf{a}_3^*|$)

$$\forall f \in L^2_{\rm per}(\Gamma), \quad \|f *_\Gamma G_1\|^2_{L^2_{\rm per}(\Gamma)} = \sum_{\mathbf{R} \in \mathcal{R} \setminus \{\mathbf{0}\}} \frac{|c_{\mathbf{k}}(f)|^2}{|\mathbf{k}|^4} \leq \frac{1}{|\mathbf{a}_3^*|^2} \sum_{\mathbf{R} \in \mathcal{R} \setminus \{\mathbf{0}\}} \frac{|c_{\mathbf{k}}(f)|^2}{|\mathbf{k}|^2} = \frac{1}{|\mathbf{a}_3^*|^2} D_1(f, f),$$

we obtain that

$$\forall L \in \mathbb{N}^*, \quad \|(\rho_{\gamma_L} - \rho_{\gamma_{L,0}}) *_\Gamma G_1\|^2_{L^2_{\rm per}(\Gamma)} \leq \frac{1}{|\mathbf{a}_3^*|^2} D_1(\rho_L - \rho_{\gamma_{L,0}}, \rho_L - \rho_{\gamma_{L,0}}) \leq \frac{2C'}{|\mathbf{a}_3^*|^2} \mathrm{e}^{-\alpha' L}. \tag{5.58}$$

Consider $W \in L^2_{\rm per}(\Gamma)$. It holds that, for any $L \geq L^{\rm gap}$,

$$\begin{aligned} \int_\Gamma (\rho_{\gamma_L} - \rho_{\gamma_{L,0}}) W &= \frac{1}{L^3} \sum_{\mathbf{Q} \in \Lambda_L} \mathrm{Tr}_{L^2_{\rm per}(\Gamma)} \left[\left((\gamma_L)_{\mathbf{Q}} - (\gamma_{L,0})_{\mathbf{Q}} \right) W \right] \\ &= \frac{1}{2\mathrm{i}\pi L^3} \sum_{\mathbf{Q} \in \Lambda_L} \oint_{\mathscr{C}} \mathrm{Tr}_{L^2_{\rm per}(\Gamma)} \left(\frac{1}{\lambda - (H_0)_{\mathbf{Q}}} \left((\rho_{\gamma_{L,0}} - \rho_{\gamma_L}) *_\Gamma G_1 \right) \frac{1}{\lambda - (H_{L,0})_{\mathbf{Q}}} W \right) \mathrm{d}\lambda \qquad (5.59) \\ &= \frac{1}{2\mathrm{i}\pi L^3} \sum_{\mathbf{Q} \in \Lambda_L} \oint_{\mathscr{C}} \mathrm{Tr}_{L^2_{\rm per}(\Gamma)} \left(B_2^{\rm per}(\lambda, \mathbf{Q}) \frac{1}{1 - \Delta_1} \left((\rho_{\gamma_{L,0}} - \rho_{\gamma_L}) *_\Gamma G_1 \right) B_2^L(\lambda, \mathbf{Q}) \frac{1}{1 - \Delta_1} W \right) \mathrm{d}\lambda, \end{aligned}$$

where $B_2^{\rm per}$ is the operator defined in (5.35) for $H = H_0$, and B_2^L is the one for $H = H_{L,0}$. From the expression of the constant C_1 in (5.37), we deduce that there exists a constant $\widetilde{C_1} \in \mathbb{R}^+$ such that, for all $L \geq L^{\rm gap}$,

$$\forall \lambda \in \mathscr{C}, \quad \forall \mathbf{Q} \in \Lambda_L, \quad \|B_2^{\rm per}(\lambda, \mathbf{Q})\|_{\mathcal{B}(L^2_{\rm per}(\Gamma))} \leq \widetilde{C_1} \quad \text{and} \quad \left\|B_2^L(\lambda, \mathbf{Q})\right\|_{\mathcal{B}(L^2_{\rm per}(\Gamma))} \leq \widetilde{C_1}.$$

As a result,

$$\left|\int_\Gamma (\rho_{\gamma_L} - \rho_{\gamma_{L,0}})W\right| \leq \frac{|\mathscr{C}|\,\widetilde{C_1}^2}{2\pi} \left\|\frac{1}{1-\Delta_1}\left((\rho_{\gamma_{L,0}} - \rho_{\gamma_L}) *_\Gamma G_1\right)\right\|_{\mathfrak{S}_2(L^2_{\rm per}(\Gamma))} \left\|\frac{1}{1-\Delta_1}W\right\|_{\mathfrak{S}_2(L^2_{\rm per}(\Gamma))}.$$

We deduce from the Kato-Seiler-Simon inequality [Sim05, Theorem 4.1] and the estimate (5.58) that there exists constant $C \in \mathbb{R}^+$ and $\alpha > 0$ independent of W such that,

$$\left|\int_\Gamma (\rho_{\gamma_L} - \rho_{\gamma_{L,0}})W\right| \leq C\mathrm{e}^{-\alpha L} \|W\|_{L^2_{\rm per}(\Gamma)}.$$

This being true for all $W \in L^2_{\rm per}(\Gamma)$, we obtain

$$\forall L \geq L^{\rm gap}, \quad \left\|\rho_{\gamma_L} - \rho_{\gamma_{L,0}}\right\|_{L^2_{\rm per}(\Gamma)} \leq C\mathrm{e}^{-\alpha L}.$$

This proves the convergence in $L^2_{\rm per}(\Gamma)$. To get the convergence in $L^\infty_{\rm per}(\Gamma)$, we bootstrap the procedure. Since $(\rho_{\gamma_{L,0}} - \rho_{\gamma_L}) \in L^2_{\rm per}(\Gamma)$, then $(\rho_{\gamma_{L,0}} - \rho_{\gamma_L}) *_\Gamma G_1 \in L^\infty_{\rm per}(\Gamma)$ with

$$\forall L \geq L^{\rm gap}, \quad \left\|(\rho_{\gamma_{L,0}} - \rho_{\gamma_L}) *_\Gamma G_1\right\|_{L^\infty_{\rm per}}(\Gamma) \leq C'\mathrm{e}^{-\alpha L}. \tag{5.60}$$

Consider $W \in L^1_{\rm per}(\Gamma)$. Performing similar calculations as in (5.59), we get (with obvious notation)

$$\begin{aligned}
&\int_\Gamma (\rho_{\gamma_L} - \rho_{\gamma_{L,0}})W \\
&\quad = \frac{1}{2\mathrm{i}\pi L^3} \sum_{\mathbf{Q}\in\Lambda_L} \oint_{\mathscr{C}} \mathrm{Tr}_{L^2_{\rm per}(\Gamma)}\left(B_1^{\rm per}(\lambda, \mathbf{Q})\left((\rho_{\gamma_{L,0}} - \rho_{\gamma_L}) *_\Gamma G_1\right) B_2^L(\lambda, \mathbf{Q}) \frac{1}{1-\Delta_1} W \frac{1}{1-\Delta_1}\right) \mathrm{d}\lambda,
\end{aligned}$$

so that

$$\left|\int_\Gamma (\rho_{\gamma_L} - \rho_{\gamma_{L,0}})W\right| \leq \frac{|\mathscr{C}|\,\widetilde{C_1}^2}{2\pi} \left\|(\rho_{\gamma_{L,0}} - \rho_{\gamma_L}) *_\Gamma G_1\right\|_{L^\infty_{\rm per}(\Gamma)} \left\|\frac{1}{1-\Delta_1} W \frac{1}{1-\Delta_1}\right\|_{\mathfrak{S}_1(L^2_{\rm per}(\Gamma))},$$

and we conclude from (5.52) and (5.60) that there exist constants $C \in \mathbb{R}^+$ and $\alpha > 0$ such that

$$\forall L \geq L^{\rm gap}, \quad \left\|\rho_{\gamma_L} - \rho_{\gamma_{L,0}}\right\|_{L^\infty_{\rm per}(\Gamma)} \leq C\mathrm{e}^{-\alpha L}.$$

Together with (5.57), we finally obtain

$$\forall L \geq L^{\rm gap}, \quad \left\|\rho_{\gamma_0} - \rho_{\gamma_{L,0}}\right\|_{L^\infty_{\rm per}(\Gamma)} \leq C\mathrm{e}^{-\alpha L}.$$

Step 3: ***Convergence of the mean-field Hamiltonian***

Finally, since

$$H_L - H_0 = (\rho_{\gamma_{L,0}} - \rho_{\gamma_0}) *_\Gamma G_1,$$

the estimate (5.60) implies the convergence of the operator $H_L - H_0$ to 0 in $\mathcal{B}(L^2(\mathbb{R}^3))$ with an exponential rate of convergence.

Remark 5.13. *The convergence of the operators implies the convergence of the eigenvalues. More specifically, from the min-max principle, we easily deduce that*

$$\sup_{\mathbf{q}\in\Gamma^*}\sup_{n\in\mathbb{N}^*}|\varepsilon_{n,\mathbf{q}}[H_L]-\varepsilon_{n,\mathbf{q}}[H_0]|\leq C\mathrm{e}^{-\alpha L}$$

where $(\varepsilon_{n,\mathbf{q}}[H])_{n\in\mathbb{N}^*}$ *denotes the eigenvalues of the operator* $H_\mathbf{q}$ *ranked in increasing order, counting multiplicities.*

5.7 Numerical simulations

In this final section, we illustrate our theoretical results with numerical simulations. The simulations were performed using a home-made Python code, run on a 32 core Intel Xeon E5-2667.

The linear model (Proposition 5.3)
We consider crystalline silicon in its diamond structure. A qualitatively correct band diagram of this system can be obtained from a linear Hamiltonian of the form $H=-\frac{1}{2}\Delta+V_{\rm per}^{\rm lin}$, where the potential $V_{\rm per}^{\rm lin}$ is the empirical pseudopotential constructed in [CB66]. The lattice vectors are

$$\mathbf{a}_1=\frac{a}{2}(0,1,1)^T,\quad \mathbf{a}_2=\frac{a}{2}(1,0,1)^T\quad\text{and}\quad \mathbf{a}_3=\frac{a}{2}(1,1,0)^T$$

and the reciprocal lattice vectors are

$$\mathbf{a}_1^*=\frac{2\pi}{a}(-1,1,1)^T,\quad \mathbf{a}_2^*=\frac{2\pi}{a}(1,-1,1)^T\quad\text{and}\quad \mathbf{a}_3^*=\frac{2\pi}{a}(1,1,-1)^T,$$

where the lattice constant is [CB66] $a=10.245$ Bohr (that is about $a=5.43$ Å). In the sequel, Γ^* denotes the Brillouin zone of the fcc lattice. The high-symmetry points of Γ^* are

$$\Gamma=\frac{2\pi}{a}(0,0,0)^T,\quad L=\frac{2\pi}{a}(1/2,1/2,1/2)^T,\quad X=\frac{2\pi}{a}(1,0,0)^T,$$
$$W=\frac{2\pi}{a}(1,1/2,0^T),\quad K=\frac{2\pi}{a}(3/4,3/4,0)^T\quad\text{and}\quad U=\frac{2\pi}{a}(1,1/4,1/4)^T.$$

The pseudopotential $V_{\rm per}^{\rm lin}$ is given by the expression [CB66]

$$V_{\rm per}^{\rm lin}(\mathbf{x})=\sum_{\mathbf{k}\in\mathcal{R}^*}V_\mathbf{k}\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}}\quad\text{with}\quad\forall\mathbf{k}\in\mathcal{R}^*,\quad V_\mathbf{k}=S[\mathbf{k}]\cos\left(\frac{a(k_1+k_2+k_3)}{8}\right)\tag{5.61}$$

where

$$S[\mathbf{k}]=\begin{cases}-0.105 & \text{if} \quad |\mathbf{k}|^2=3(2\pi/a)^2\\ 0.02 & \text{if} \quad |\mathbf{k}|^2=8(2\pi/a)^2\\ 0.04 & \text{if} \quad |\mathbf{k}|^2=11(2\pi/a)^2\\ 0 & \text{otherwise.}\end{cases}$$

The band diagram of this system is represented in Figure 6.1 along the path $L\to\Gamma\to X\to W\to\Gamma\to U\to X$.

This system is an insulator when the number of particle (electron pairs) per unit cell is $N=4$, so that the hypotheses of Proposition 5.3 are satisfied. In the sequel, the calculations are performed in the planewave basis

$$X=\left\{e_\mathbf{k},\ \mathbf{k}\in\mathcal{R}^*,\ \frac{|\mathbf{k}|^2}{2}<E_{\text{cut-off}}\right\},\tag{5.62}$$

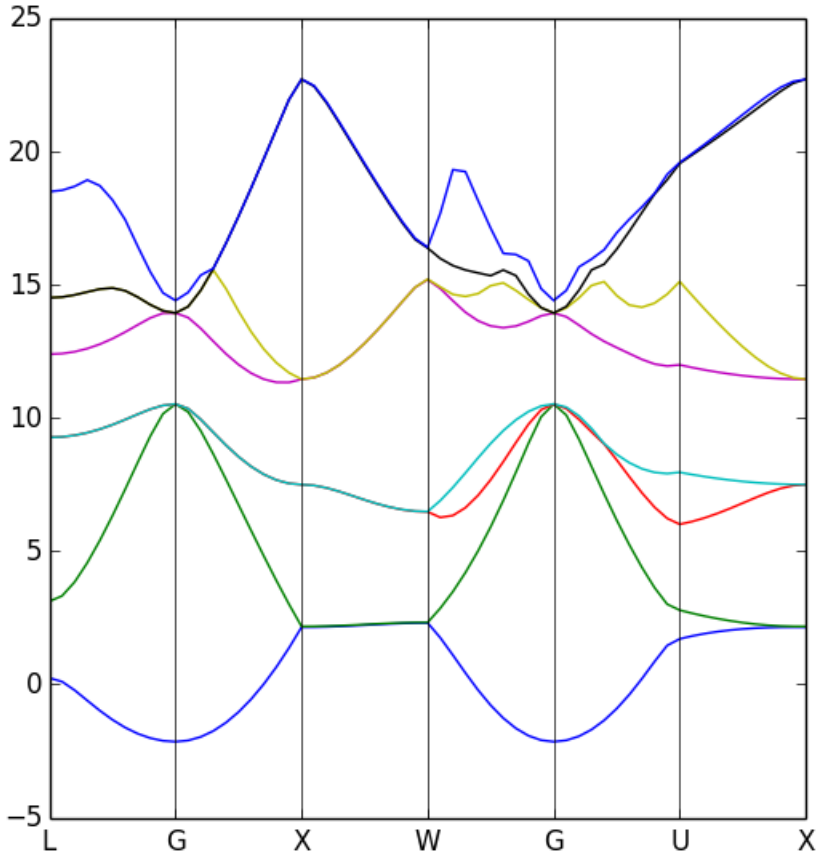

Figure 5.2 – Band diagram (in eV) of crystalline silicon in its diamond structure along the path $L \to \Gamma \to X \to W \to \Gamma \to U \to X$.

where the cut-off energy is $E_{\text{cut-off}} = 736$ eV. The corresponding size of the basis is $|X| = 749$.

In Figure 5.3, we represent the error on the ground state energy per unit cell and the $L^\infty(\mathbb{R}^3)$ error on the ground state density (in log scale) for different sizes of the regular grid. The value of L in (5.24) varies between 4 to 28. The quantities of reference are the ones calculated for the regular grid of size 60. We observe in Figure 5.3 the exponential convergence for both the energy per unit cell and the density as predicted in Proposition 5.3.

The rHF model (Theorem 5.5)

We now consider the rHF model. To our knowledge, no pseudopotential has ever been designed for this model. Since constructing pseudopotentials is a formidable task, we limit ourselves to the following poor man's solution, which does not aim at capturing the physics but only at illustrating numerically our theoretical convergence results. We decompose the potential self-consistent V_0 appearing in (5.13) into

$$V_0 = (\rho_{\gamma_0} - \mu_{\text{per}}) *_\Gamma G_1 = \rho_{\gamma_0} *_\Gamma G_1 - \mu_{\text{per}} *_\Gamma G_1,$$

and we make the approximation $V_0 = V_{\text{per}}^{\text{lin}}$, where $V_{\text{per}}^{\text{lin}}$ is the pseudopotential defined in (5.61). This leads to the rHF pseudopotential of the form

$$V_{\text{per}}^{\text{rHF}} := V_{\text{per}}^{\text{lin}} - \rho_{\gamma_0} *_\Gamma G_1.$$

In practice, we calculate $V_{\text{per}}^{\text{rHF}}$ with the potential ρ_{γ_0} obtained previously for the grid of size 60. The minimization problem (5.6)-(5.7) is solved self-consistently in the basis X defined in (5.62)

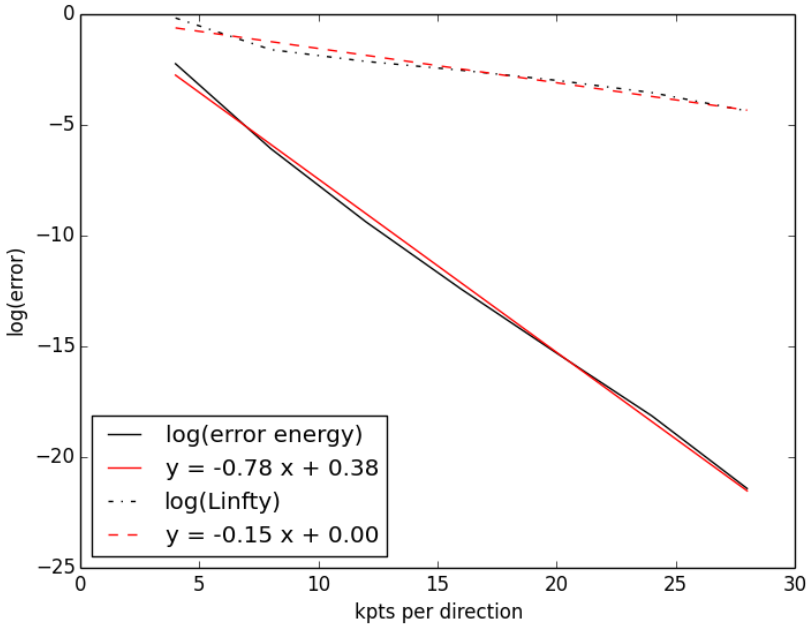

Figure 5.3 – The error on the ground-state energy (in eV) and the L^∞ error on the ground-state density with respect to the size of the regular mesh for the linear model. The logarithm of the errors are represented. The linear regression curves are also displayed.

(we refer to [Can00] for a survey on self-consistent procedures for such problems). We stop the self-consistent procedure when the $L^\infty(\mathbb{R}^3)$ difference between two consecutive densities is less than 10^{-7}. The size of the regular mesh varies between 8 to 36. The quantities of reference are the ones calculated for the regular mesh of size 60. The error on the energy per unit cell and the $L^\infty(\mathbb{R}^3)$ error on the density are displayed in Figure 5.4.

We observe in Figure 5.4 the exponential convergence announced in Theorem 5.5.

Acknowledgements

We are grateful to Gianluca Panati and Domenico Monaco for answering our questions about analyticity.

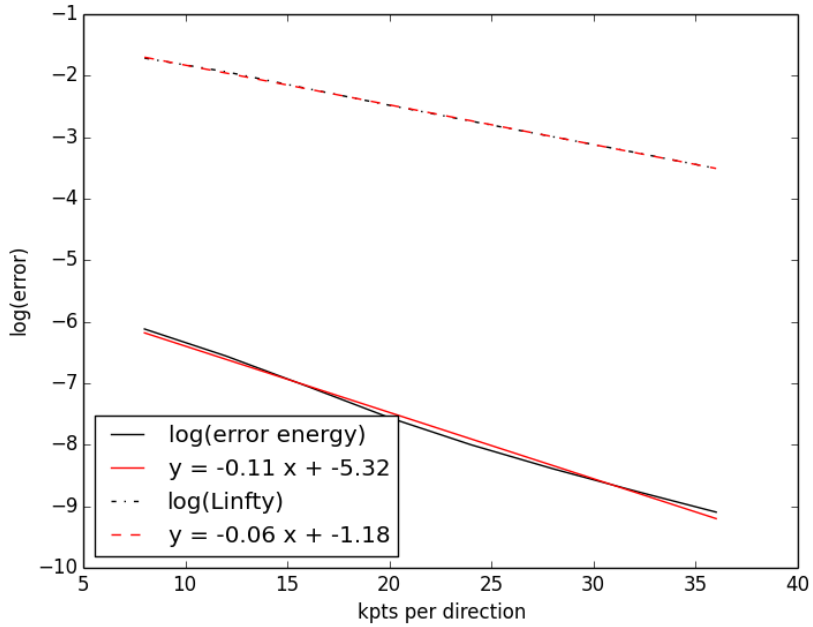

Figure 5.4 – The error in energy (in eV) and the L^∞ error of the density with respect to the size of the regular mesh for the rHF model. The logarithm of the errors are represented. The linear regression curves are also displayed.

CHAPTER 6

REDUCED BASIS METHODS FOR BRILLOUIN-ZONE INTEGRATION

This work was done in collaboration with Eric Cancès, Virginie Ehrlacher and Damiano Lombardi. It is part of a comprehensive numerical analysis article [CEG+15] (in preparation) on quadrature methods for Brillouin-zone integration.

Abstract. We introduce new reduced basis techniques that allow fast and accurate calculations of the Fermi level and the ground state energy per unit cell for empirical effective Hamiltonian models.

6.1 Introduction

The study of the electronic structure of perfect crystals is a central problem in solid-state physics and materials science. Although perfect crystals do not exist in nature, they constitute useful idealized systems to understand many fundamental properties of real crystalline solids (electric conductivity, dielectric permittivity of insulators and semiconductors, photoelectric effect, ...). Besides, the study of perfect crystals is an unavoidable preliminary to the one of real crystals, that are crystals with point and extended defects (vacancies, interstitials, impurities, dislocations, grain boundaries).

A perfect crystal is modeled by a Bravais lattice $\mathcal{R}$ of $\mathbb{R}^3$, and a motif, that is an $\mathcal{R}$-periodic distribution describing the natures and the positions of the atoms, or more specifically of the bare nuclei in all-electron models, and of the ionic cores in empirical models, or in models with pseudopotentials. The Fermi level and the energy per unit cell of a such a crystal can be evaluated from the study of an electronic (empirical or mean-field) Hamiltonian H. Mathematically speaking, H is an unbounded one-body operator acting on $L^2(\mathbb{R}^3)$ that commutes with the translations of the lattice $\mathcal{R}$. Thanks to the Bloch transformation [RS78, Chapter XIII], the study of this Hamiltonian amounts to studying a continuous set of compact resolvent operators $H_{\mathbf{q}}$ indexed by points $\mathbf{q}$ of the Brillouin zone. In particular, one can evaluate the Fermi level and the energy per unit cell by evaluating integrals over the Brillouin zone. The integrands are functions of the eigenvalues (and of the eigenvectors in mean-field models) of the compact resolvent operators $H_{\mathbf{q}}$ (see Section 6.2).

From a numerical point of view, such integrals cannot be computed exactly, and the Brillouin zone needs to be sampled. In [MP76, BJA94] for instance, the authors considered uniform samplings of the Brillouin zone. If L denotes the number of points per direction

of such a sampling, the total number of points is L^3. This number of points to explicitly consider can be reduced using the symmetries of the crystal [MP76]. For insulating systems, the energy per unit cell can be estimated precisely with a coarse grid (small value of L). This is due to the exponential rate of convergence proved in Chapter 5. For metallic systems, a slower rate of convergence is expected and a much finer sampling is needed (large value of L). As a consequence, the calculation of the eigenmodes of the operator $H_{\mathbf{q}}$ at all the points $\mathbf{q}$ of the grid is numerically much more expensive than in the insulating case.

The goal of this chapter is to explain how to use the information on a coarse grid to speed up the calculation on a much finer grid by means of reduced basis techniques. Similar ideas were already considered by Pau in [Pau07]. Our approach, which consists in creating bases that are $\mathbf{q}$-point dependent, allows the identification of the main contribution of the reduced basis error, resulting in much more accurate results at low extra-costs.

The proposed numerical methods are illustrated by the computation of the Fermi level and total energy per unit cell for both insulating and metallic systems.

6.2 Notation and presentation of the model

We consider closed-shell electronic structure models and assume that each spatial electronic state is either empty or doubly occupied (that is filled with two electrons, one with spin up and one with spin down). In both empirical and mean-field electronic structure models of perfect crystals, a key role is played by the electronic (empirical or mean-field) Hamiltonian, which is an unbounded self-adjoint operator H on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$ of the form

$$H = -\frac{1}{2}\Delta + V_{\mathrm{per}}, \tag{6.1}$$

where V_{per} is either a real-valued locally square integrable $\mathcal{R}$-periodic function on $\mathbb{R}^3$, or a bounded self-adjoint operator on $L^2(\mathbb{R}^3)$ commuting with the translations of the lattice $\mathcal{R}$. The latter situation is encountered in particular in Hartree-Fock models and in Kohn-Sham models with pseudopotentials. Since the operator H commutes with $\mathcal{R}$-translations we can consider its Bloch transform [RS78, Chapter XIII]. We denote by Γ the Wigner-Seitz cell of $\mathcal{R}$, by $\mathcal{R}^*$ the reciprocal lattice, by Γ^* the first Brillouin zone, by

$$L^2_{\mathrm{per}}(\Gamma) := \left\{ f \in L^2_{\mathrm{loc}}(\mathbb{R}^3), \quad f \ \mathcal{R}\text{-periodic} \right\}$$

the periodic L^2 space and by

$$\forall s \in \mathbb{R}, \quad H^s_{\mathrm{per}}(\Gamma) := \left\{ f \in H^s_{\mathrm{loc}}(\mathbb{R}^3), \quad f \ \mathcal{R}\text{-periodic} \right\}$$

the periodic Sobolev spaces. It holds that (we denote by $⨍_{\Gamma^*} := |\Gamma^*|^{-1} \int_{\Gamma^*}$)

$$H = ⨍_{\Gamma^*}^{\oplus} H_{\mathbf{q}} \, \mathrm{d}\mathbf{q}, \quad \text{with} \quad H_{\mathbf{q}} := \frac{1}{2}\left|-\mathrm{i}\nabla + \mathbf{q}\right|^2 + V_{\mathrm{per}}, \tag{6.2}$$

where, for all $\mathbf{q} \in \Gamma^*$, the operator $H_{\mathbf{q}}$ with domain $H^2_{\mathrm{per}}(\Gamma)$, is a bounded below self-adjoint compact resolvent operator acting on $L^2_{\mathrm{per}}(\Gamma)$. We denote by $\lambda_{1,\mathbf{q}} \leq \lambda_{2,\mathbf{q}} \leq \cdots$ its eigenvalues, ranked in increasing order, counting multiplicities, and by $(u_{n,\mathbf{q}})_{n\in\mathbb{N}^*} \in (L^2_{\mathrm{per}}(\Gamma))^{\mathbb{N}^*}$ an orthonormal basis of associated eigenvectors.

With this notation, the *integrated density of state* (per unit cell) I and the *integrated density of energy* (per unit cell) E are respectively defined by

$$\forall \varepsilon \in \mathbb{R}, \quad I(\varepsilon) = \sum_{n=1}^{\infty} ⨍_{\Gamma^*} \mathbb{1}_{(-\infty,\varepsilon]}(\lambda_{n,\mathbf{q}}) \, \mathrm{d}\mathbf{q} \tag{6.3}$$

and

$$\forall \varepsilon \in \mathbb{R}, \quad E(\varepsilon) = 2 \sum_{n=1}^{\infty} \fint_{\Gamma^*} \lambda_{n,\mathbf{q}} \mathbb{1}_{(-\infty,\varepsilon]}(\lambda_{n,\mathbf{q}}) \, \mathrm{d}\mathbf{q}, \tag{6.4}$$

where $\mathbb{1}_{(-\infty,\varepsilon]}$ denotes the characteristic function of the interval $(-\infty, \varepsilon]$. The factor 2 in (6.4) accounts for the spin. Note that the sums appearing in (6.3) and in (6.4) are finite for any value of ε, since the sequence $(\lambda_{n,\mathbf{q}})_{n\in\mathbb{N}^*}$ goes to infinity, uniformly in $\mathbf{q} \in \Gamma^*$.

Let N_{pair} be the number of electron pairs in the crystal. As the function I is continuous, non-decreasing, and satisfies

$$I(\varepsilon) = 0 \quad \text{for} \quad \varepsilon < \min(\sigma(H)) = \inf\{\lambda_{1,\mathbf{q}}, \ \mathbf{q} \in \Gamma^*\} \quad \text{and} \quad \lim_{\varepsilon \to +\infty} I(\varepsilon) = +\infty,$$

the set $I^{-1}(\{N\})$ is a non-empty bounded closed interval of $\mathbb{R}$. We write $I^{-1}(\{N\}) = [\varepsilon_-, \varepsilon_+]$. Any number ε inside this interval is an admissible Fermi level of the system. When $\varepsilon_- = \varepsilon_+$, this number ε_F is unique, and the system is a metal. Otherwise, the system is an insulator or a semi-conductor, depending on the magnitude of the (indirect) gap $g := \varepsilon_+ - \varepsilon_-$. The function E has a constant value $E(\varepsilon_F)$ on this interval, called the energy per unit cell, where ε_F is any number in this interval. For our purpose, we can choose for instance $\varepsilon_F = (\varepsilon_- + \varepsilon_+)/2$.

The expressions (6.3) and (6.4) involve integrations over the Brillouin zone Γ^*. In practice, an analytical integration cannot be performed and hence numerical quadrature techniques must be resorted to. Several methods were proposed to sample the Brillouin zone. In [MP76] for instance, Monkhorst and Pack suggested to use a regular grid. Let us consider a basis $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ of the lattice $\mathcal{R}$, so that $\mathcal{R} = \mathbb{Z}\mathbf{a}_1 + \mathbb{Z}\mathbf{a}_2 + \mathbb{Z}\mathbf{a}_3$, and the associated dual basis $(\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*)$ of the reciprocal lattice, so that $\mathcal{R}^* := \mathbb{Z}\mathbf{a}_1^* + \mathbb{Z}\mathbf{a}_2^* + \mathbb{Z}\mathbf{a}_3^*$ and $\mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi\delta_{ij}$. For $L \in \mathbb{N}^*$, the $L \times L \times L$ regular grid is defined by

$$\Lambda_L := \left\{ \frac{2k_1}{L}\mathbf{a}_1^* + \frac{2k_2}{L}\mathbf{a}_2^* + \frac{2k_3}{L}\mathbf{a}_3^*, \ (k_1,k_2,k_3) \in \left\{ \frac{-L+\eta}{2}, \frac{-L+\eta}{2}+1, \cdots, \frac{L+\eta}{2}-1 \right\}^3 \right\}, \tag{6.5}$$

where $\eta = 0$ if L is even, and $\eta = 1$ otherwise. Note that there are exactly L^3 points in Λ_L, and that the point $\mathbf{q} = \mathbf{0}$ lies inside Λ_L for all $L \in \mathbb{N}^*$. This grid can be reduced using the symmetries of the system [MP76].

Finally, the infinite dimensional form domain $H^1_{\text{per}}(\Gamma)$ of $H_{\mathbf{q}}$ is approximated by a finite-dimensional conformal discretization space $X^{\mathcal{N}} \subset H^1_{\text{per}}(\Gamma)$. In this chapter, we mostly study the planewave discretization case, where

$$X^{\mathcal{N}} := \text{Span}\left\{ e_{\mathbf{k}}, \ \mathbf{k} \in \mathcal{R}^*, \ \frac{|\mathbf{k}|^2}{2} \le E_{\text{cut-off}} \right\}. \tag{6.6}$$

Here, $e_{\mathbf{k}}(\mathbf{x}) := |\Gamma|^{-1/2} \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}}$ is the Fourier mode with wave vector $\mathbf{k}$, and $E_{\text{cut-off}}$ is the cut-off energy. Usually in physics, the approximation space $X^{\mathcal{N}}$ is characterized by the value of $E_{\text{cut-off}}$ (in eV) rather than by the value of $\mathcal{N} := \dim(X^{\mathcal{N}})$.

In the sequel, we consider that $\lambda_{n,\mathbf{q}}$ and $u_{n,\mathbf{q}}$ are the reference solutions computed in a fine discretization space $X^{\mathcal{N}}$ ($\mathcal{N} \gg 1$), and we will compare the results obtained with our reduced basis methods to the ones obtained with those reference solutions. The Dirac's bra-ket notation refers to the $L^2_{\text{per}}(\Gamma)$ inner product on $X^{\mathcal{N}}$.

6.3 The simple reduced basis method

The basic idea of the proposed numerical scheme is to extract local reduced bases from calculations on a coarse uniform grid of size $L_1 \times L_1 \times L_1$ of Γ^* for some value $L_1 \in \mathbb{N}^*$. These

are used to compute the eigenmodes of $H_{\mathbf{q}}$ for $\mathbf{q}$ on a fine uniform grid of size $L_2 \times L_2 \times L_2$, with $L_2 \gg L_1$. In order to give rise to fast computations on the fine grid, the size $N \in \mathbb{N}^*$ of the reduced bases must be much smaller than the size of the initial basis: $N \ll \mathcal{N}$.

Let $L_1 \in \mathbb{N}^*$ be the number of points per direction of the coarse grid Λ_{L_1}. A point of the coarse grid will be denoted by $\mathbf{Q}$ (uppercase letter) for the sake of clarity. For $\mathbf{Q} \in \Lambda_{L_1}$ and $N \in \mathbb{N}^*$ we denote by

$$X_{\mathbf{Q}}^N := \mathrm{Span}\left\{\mathrm{u}_{1,\mathbf{Q}}, \ldots, \mathrm{u}_{\mathrm{N},\mathbf{Q}}\right\}$$

the subspace of $X^{\mathcal{N}}$ of dimension N consisting of the eigenvectors associated to the lowest N eigenvalues of the operator $H_{\mathbf{Q}}$. Let $L_2 \in \mathbb{N}^*$ be the number of points per direction of the fine grid Λ_{L_2}. A point of the fine grid will be denoted by $\mathbf{q}$ (lowercase letter). For $\mathbf{q}$ in the fine grid Λ_{L_2}, we denote by $P(\mathbf{q})$ a set of points of the coarse grid that are close to $\mathbf{q}$. One can take for instance

$$P(\mathbf{q}) := \left\{\mathbf{Q} \in \Lambda_{L_1},\ |\mathbf{Q} - \mathbf{q}|_\infty < r\right\},$$

where $|\cdot|_\infty$ denotes the ℓ^∞ norm in the euclidian basis, and where r is a well-chosen positive cut-off radius. In what follows, we take $r = L_1^{-1}$.

The first method, called hereafter *simple reduced basis*, or simple-RB, is straightforward. Let m be a positive integer chosen beforehand so that $\lambda_{m,\mathbf{q}} \geq \varepsilon_F$ for all $\mathbf{q} \in \Gamma^*$. If the system into consideration is an insulator, we take $m = N_{\mathrm{pair}}$. For each point $\mathbf{q} \in \Lambda_{L_2}$ and each $\mathbf{Q} \in P(\mathbf{q})$, we compute the first m eigenmodes of $H_{\mathbf{q}}$ in the basis $X_{\mathbf{Q}}^N$. We obtain a set of eigenvalues $\left(\lambda_{n,\mathbf{q}}^{N,\mathbf{Q}}\right)_{1\leq n\leq m}$, and an orthonormal family of associated eigenvectors $\left(u_{n,\mathbf{q}}^{N,\mathbf{Q}}\right)_{1\leq n\leq m}$, in the sense that

$$\lambda_{1,\mathbf{q}}^{N,\mathbf{Q}} \leq \lambda_{2,\mathbf{q}}^{N,\mathbf{Q}} \leq \ldots \leq \lambda_{m,\mathbf{q}}^{N,\mathbf{Q}}$$

and

$$\forall 1 \leq n \leq m, \quad \forall w \in X_{\mathbf{Q}}^N, \quad \left\langle w \middle| H_{\mathbf{q}} \middle| u_{n,\mathbf{q}}^{N,\mathbf{Q}} \right\rangle = \lambda_{n,\mathbf{q}}^{N,\mathbf{Q}} \left\langle w \middle| u_{n,\mathbf{q}}^{N,\mathbf{Q}} \right\rangle.$$

We then choose $\mathbf{Q}_0 \in P(\mathbf{q})$ such that

$$\sum_{k=1}^{m} \lambda_{n,\mathbf{q}}^{N,\mathbf{Q}_0} = \inf\left\{\sum_{k=1}^{m} \lambda_{n,\mathbf{q}}^{N,\mathbf{Q}},\ \mathbf{Q} \in P(\mathbf{q})\right\}.$$

Another, more expensive, option consists in considering the approximation space spanned by all the eigenvectors $\left(u_{n,\mathbf{q}}^{N,\mathbf{Q}}\right)_{1\leq n\leq m,\, \mathbf{Q}\in P(\mathbf{q})}$ The simple-RB method consists in making the approximation

$$\lambda_{n,\mathbf{q}} \approx \lambda_{n,\mathbf{q}}^{N,\mathbf{Q}_0} \quad \text{and} \quad u_{n,\mathbf{q}} \approx u_{n,\mathbf{q}}^{N,\mathbf{Q}_0}.$$

This method is very easy to implement, and already provides satisfactory results. It is however possible to improve subsequently the results by further analyzing the source of the error coming from the reduced basis approximation.

6.4 Perturbation expansion

We present in this section an approach to improve the accuracy of the approximate eigenmodes obtained by the procedure described in the previous section, using a perturbation-based post-processing method similar to the one introduced in [CDM+14]. We first make the following observation. From the definition of $H_{\mathbf{q}}$ in (6.2), it holds that

$$H_{\mathbf{q}} = \frac{1}{2}\left|-\mathrm{i}\nabla + \mathbf{q}\right|^2 + V_{\mathrm{per}} = -\frac{1}{2}\Delta - \mathrm{i}\mathbf{q}\cdot\nabla + \frac{|\mathbf{q}|^2}{2} + V_{\mathrm{per}} = A_{\mathbf{q}} + \frac{|\mathbf{q}|^2}{2},$$

where

$$A_{\mathbf{q}} := -\frac{1}{2}\Delta - \mathrm{i}\mathbf{q}\cdot\nabla + V_{\mathrm{per}}$$

is a bounded below self-adjoint operator acting $L^2_{\mathrm{per}}(\Gamma)$ with domain $H^2_{\mathrm{per}}(\Gamma)$. The eigenvalues of $A_{\mathbf{q}}$ are

$$\mu_{n,\mathbf{q}} := \lambda_{n,\mathbf{q}} - \frac{|\mathbf{q}|^2}{2},$$

and its eigenvectors are the same as those of $H_{\mathbf{q}}$. It is more convenient to work with the operator $A_{\mathbf{q}}$ than with the operator $H_{\mathbf{q}}$, as the former depends linearly on $\mathbf{q} \in \Gamma^*$.

Let $\mathbf{q} \in \Lambda_{L_2}$ and $\mathbf{Q} \in P(\mathbf{q})$. Our analysis is based on the fact that

$$A_{\mathbf{q}} = A_{\mathbf{Q}} + (\mathbf{q}-\mathbf{Q})\cdot(-\mathrm{i}\nabla) = A^{N,\mathbf{Q}}_{\mathbf{q}} + W^{N,\mathbf{Q}}_{\mathbf{q}} \tag{6.7}$$

where $A^{N,\mathbf{Q}}_{\mathbf{q}}$ and $W^{N,\mathbf{Q}}_{\mathbf{q}}$ are respectively defined by

$$A^{N,\mathbf{Q}}_{\mathbf{q}} = \left(A_{\mathbf{Q}} + \Pi_{X^N_{\mathbf{Q}}}(\mathbf{q}-\mathbf{Q})\cdot(-\mathrm{i}\nabla)\Pi_{X^N_{\mathbf{Q}}}\right)$$

and

$$W^{N,\mathbf{Q}}_{\mathbf{q}} = \left((\mathbf{q}-\mathbf{Q})\cdot(-\mathrm{i}\nabla) - \Pi_{X^N_{\mathbf{Q}}}(\mathbf{q}-\mathbf{Q})\cdot(-\mathrm{i}\nabla)\Pi_{X^N_{\mathbf{Q}}}\right).$$

Here, $\Pi_{X^N_{\mathbf{Q}}}$ denotes the orthogonal projector on $X^N_{\mathbf{Q}}$ (for the $L^2_{\mathrm{per}}(\Gamma)$ inner product). The approximate and exact eigenmodes respectively satisfy

$$A^{N,\mathbf{Q}}_{\mathbf{q}}\, u^{N,\mathbf{Q}}_{n,\mathbf{q}} = \mu^{N,\mathbf{Q}}_{n,\mathbf{q}}\, u^{N,\mathbf{Q}}_{n,\mathbf{q}} \quad \text{and} \quad \left(A^{N,\mathbf{Q}}_{\mathbf{q}} + W^{N,\mathbf{Q}}_{\mathbf{q}}\right) u_{n,\mathbf{q}} = \mu_{n,\mathbf{q}}\, u_{n,\mathbf{q}}.$$

The exact eigenmodes can therefore be considered as perturbations of the approximate eigenmodes. Using first-order perturbation theory, we obtain

$$u_{n,\mathbf{q}} = u^{N,\mathbf{Q}}_{n,\mathbf{q}} + v^{N,\mathbf{Q}}_{n,\mathbf{q}} + r^{N,\mathbf{Q}}_{n,\mathbf{q}}, \tag{6.8}$$

where

$$v^{N,\mathbf{Q}}_{n,\mathbf{q}} := -\frac{\Pi^{\perp}_{X^N_{\mathbf{Q}}}}{A_{\mathbf{Q}} - \mu^{N,\mathbf{Q}}_{n,\mathbf{q}}}\left((\mathbf{q}-\mathbf{Q})\cdot(-\mathrm{i}\nabla u^{N,\mathbf{Q}}_{n,\mathbf{q}})\right), \tag{6.9}$$

and where, for $(\mathbf{q}-\mathbf{Q})$ small enough, the $H^1_{\mathrm{per}}(\Gamma)$-norm of the remainder $r^{N,\mathbf{Q}}_{n,\mathbf{q}}$ is of order $|\mathbf{q}-\mathbf{Q}|^2$. Here, $\Pi^{\perp}_{X^N_{\mathbf{Q}}} := 1 - \Pi_{X^N_{\mathbf{Q}}}$ denotes the orthogonal projector on ${X^N_{\mathbf{Q}}}^{\perp}$.

The approximation (6.8) suggests that the eigenvector $u_{n,\mathbf{q}}$ is better approximated by $u^N_{n,\mathbf{q}} + v^{N,\mathbf{Q}}_{n,\mathbf{q}}$ than by $u^N_{n,\mathbf{q}}$. The idea is then to replace the initial discretization space $X^N_{\mathbf{Q}}$ by

$$\widetilde{X^{M,\mathbf{Q}}_{\mathbf{q}}} := \mathrm{Span}\left\{u^{N,\mathbf{Q}}_{1,\mathbf{q}} + v^{N,\mathbf{Q}}_{1,\mathbf{q}}, \ldots, u^{N,\mathbf{Q}}_{M,\mathbf{q}} + v^{N,\mathbf{Q}}_{M,\mathbf{q}}\right\}, \tag{6.10}$$

and hopefully get better approximations with this new basis set. The method using this correction will be called the *corrected reduced basis*, or corrected-RB, method.

Remark 6.1. *While the initial discretization space $X^M_{\mathbf{Q}}$ was only $\mathbf{Q}$-dependent, the new one is $(\mathbf{Q},\mathbf{q})$-dependent: a new reduced basis is created for each point $\mathbf{q}$ of the fine grid Λ_{L_2}, and each point $\mathbf{Q} \in P(\mathbf{q})$.*

Remark 6.2. *The new discretization space is of dimension $M \leq N$. In general, one needs to take $M < N$. This comes from the fact that the operator $\left(A_{\mathbf{Q}} - \mu^N_{n,\mathbf{q}}\right)\Pi^{\perp}_{X^N_{\mathbf{Q}}}$ appearing in (6.9) needs to be invertible on $(X^N_{\mathbf{Q}})^{\perp}$. A natural way to ensure invertibility is to impose $\mu_{M,\mathbf{Q}} < \mu_{N+1,\mathbf{Q}}$.*

Note that the multiplication of a vector by the operator $(\mathbf{q}-\mathbf{Q})\cdot(-\mathrm{i}\nabla)$ appearing in (6.9) is inexpensive if the initial basis set is the planewave basis $X^{\mathcal{N}}$ defined in (6.6). However, in order to evaluate the new basis, one must also be able to compute the multiplication of a vector by the large matrix $\left(A_{\mathbf{Q}}-\mu_{n,\mathbf{q}}^{N}\right)\Pi_{X_{\mathbf{Q}}^{N}}^{\perp}$ appearing in (6.9). This may be troublesome in practice if $\mathcal{N}$ is too large. The approximation of this operator is discussed in the next section.

6.5 An approximation of the resolvent

We discuss in this section some numerical methods to approximate the inverse of the operator $\left(A_{\mathbf{Q}}-\mu_{n,\mathbf{q}}^{N}\right)\Pi_{X_{\mathbf{Q}}^{N}}^{\perp}$. The first natural way to approximate it is to set

$$\Pi_{X_{\mathbf{Q}}^{N}}^{\perp}\approx\Pi_{X_{\mathbf{Q}}^{N_{\mathrm{med}}}}-\Pi_{X_{\mathbf{Q}}^{N}} \tag{6.11}$$

where $N_{\mathrm{med}}\in\mathbb{N}^{*}$ is chosen such that $N\ll N_{\mathrm{med}}\ll\mathcal{N}$. In this case, only the first N_{med} eigenmodes of $A_{\mathbf{Q}}$ must be computed for all $\mathbf{Q}\in\Lambda_{L_1}$, and it holds

$$\frac{\Pi_{X_{\mathbf{Q}}^{N}}^{\perp}}{A_{\mathbf{Q}}-\mu_{n,\mathbf{q}}^{N,\mathbf{Q}}}\approx\sum_{k=N+1}^{N_{\mathrm{med}}}\frac{|u_{k,\mathbf{Q}}\rangle\langle u_{k,\mathbf{Q}}|}{\mu_{k,\mathbf{Q}}-\mu_{n,\mathbf{q}}^{N}}.$$

However, by making the approximation (6.11), the resulting $v_{n,\mathbf{Q},\mathbf{q}}^{N}$ defined in (6.9) belong to $X_{\mathbf{Q}}^{N_{\mathrm{med}}}$. Since $u_{n,\mathbf{q}}^{N}\in X_{\mathbf{Q}}^{N}\subset X_{\mathbf{Q}}^{N_{\mathrm{med}}}$, we deduce that the space $\widetilde{X_{n,\mathbf{Q},\mathbf{q}}^{M}}$ defined in (6.10) satisfies $\widetilde{X_{n,\mathbf{Q},\mathbf{q}}^{M}}\subset X_{\mathbf{Q}}^{N_{\mathrm{med}}}$. As a consequence, the results obtained with the corrected-RB method together with the approximation (6.11) are less accurate than the simple-RB method with bases of size N_{med}. Another approach is to make the crude approximation

$$\frac{\Pi_{X_{\mathbf{Q}}^{N}}^{\perp}}{A_{\mathbf{Q}}-\mu_{n,\mathbf{q}}^{N,\mathbf{Q}}}\approx\Pi_{X_{\mathbf{Q}}^{N}}^{\perp}\frac{1}{1+\frac{1}{2}\left|-\mathrm{i}\nabla+\mathbf{q}\right|^{2}}\Pi_{X_{\mathbf{Q}}^{N}}^{\perp}. \tag{6.12}$$

Note that it holds

$$\frac{\Pi_{X_{\mathbf{Q}}^{N}}^{\perp}}{A_{\mathbf{Q}}-\mu_{n,\mathbf{q}}^{N,\mathbf{Q}}}-\Pi_{X_{\mathbf{Q}}^{N}}^{\perp}\frac{1}{1+\frac{1}{2}\left|-\mathrm{i}\nabla+\mathbf{q}\right|^{2}}\Pi_{X_{\mathbf{Q}}^{N}}^{\perp}=\frac{\Pi_{X_{\mathbf{Q}}^{N}}^{\perp}}{A_{\mathbf{Q}}-\mu_{n,\mathbf{q}}^{N,\mathbf{Q}}}\left(V_{n,\mathbf{q}}^{N,\mathbf{Q}}\frac{1}{1+\frac{1}{2}\left|-\mathrm{i}\nabla+\mathbf{q}\right|^{2}}\right)\Pi_{X_{\mathbf{Q}}^{N}}^{\perp},$$

where

$$V_{n,\mathbf{q}}^{N,\mathbf{Q}}:=1+\mu_{n,\mathbf{q}}^{N,\mathbf{Q}}+\frac{|\mathbf{q}|^{2}}{2}-V_{\mathrm{per}}$$

is a multiplication operator. In particular, thanks to the Kato-Seiler-Simon inequality [Sim05], the operator $\left(V_{n,\mathbf{q}}^{N,\mathbf{Q}}\frac{1}{1+\frac{1}{2}\left|-\mathrm{i}\nabla+\mathbf{q}\right|^{2}}\right)\Pi_{X_{\mathbf{Q}}^{N}}^{\perp}$ is compact, and, for fixed n, converges to 0 when N goes to infinity. While this argument is not sufficient to mathematically certify the suggested approximation, it hints that it should significantly improve the results of a naive computation. This will be confirmed in the numerical experiments presented in Section 6.6.

The corrected-RB method together with the approximation (6.12) is called the *partially corrected reduced basis*, or partially-corrected-RB, method. In this case, we solve the eigenvalue problem of $H_{\mathbf{q}}$ in the basis

$$\widetilde{X_{\mathbf{q}}^{M,\mathbf{Q}}}:=\mathrm{Span}\left\{u_{1,\mathbf{q}}^{N,\mathbf{Q}}+\widetilde{v_{1,\mathbf{q}}^{N,\mathbf{Q}}},\ldots,u_{M,\mathbf{q}}^{N,\mathbf{Q}}+\widetilde{v_{M,\mathbf{q}}^{N,\mathbf{Q}}}\right\},$$

where we set

$$\widetilde{v_{n,\mathbf{q}}^{N,\mathbf{Q}}}:=-\Pi_{X_{\mathbf{Q}}^{N}}^{\perp}\frac{1}{1+\frac{1}{2}\left|-\mathrm{i}\nabla+\mathbf{q}\right|^{2}}\Pi_{X_{\mathbf{Q}}^{N}}^{\perp}\left((\mathbf{q}-\mathbf{Q})\cdot(-\mathrm{i}\nabla u_{n,\mathbf{q}}^{N,\mathbf{Q}})\right). \tag{6.13}$$

Remark 6.3. *The functions appearing in (6.13) are inexpensive to compute in the plane-wave basis $X^{\mathcal{N}}$ defined in (6.6).*

6.6 Numerical results

We illustrate our method with numerical tests. The simulations were performed using a home-made Python code, run on a 32 core Intel Xeon E5-2667. The purpose of this section is to demonstrate the accuracy of the various reduced basis methods described in the previous sections. We do not report computational times, since our Python code uses very efficient parallel linear algebra packages to diagonalize the matrices, which favors the full-diagonalization approach, while our implementation of the reduced basis method was not optimized. An implementation of our reduced basis method in Abinit [GAA+09] is in progress.

Insulating case

We first consider the insulating case and study the crystalline silicon in its diamond structure. We take the empirical pseudopotential described in [CB66]. The corresponding Bravais lattice is generated by the vectors $\mathbf{a}_1 := (a/2)(0,1,1)^T$, $\mathbf{a}_2 := (a/2)(1,0,1)^T$ and $\mathbf{a}_3 := (a/2)(1,1,0)^T$, where a is the lattice constant of the crystal $a = 10.245$ Bohr (that is $a \approx 5.43$Å). In the sequel, Γ^* denotes the Brillouin zone of the fcc lattice. The high-symmetry points of Γ^* are $\Gamma = (2\pi/a)(0,0,0)^T$, $L = (2\pi/a)(1/2,1/2,1/2)^T$, $X = (2\pi/a)(1,0,0)^T$, $W = (2\pi/a)(1,1/2,0)$, $K = (2\pi/a)(3/4,3/4,0)^T$ and $U = (2\pi/a)(1,1/4,1/4)^T$.
In atomic units, the corresponding linear mean-field Hamiltonian is $H = -\frac{1}{2}\Delta + V_{\rm per}$, where $V_{\rm per}$ is the effective pseudopotential constructed in [CB66] of the form

$$V_{\rm per}(\mathbf{x}) = \sum_{\mathbf{k}\in\mathcal{R}^*} V_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{x}} \quad \text{with} \quad \forall \mathbf{k} \in \mathcal{R}^*, \quad V_{\mathbf{k}} = S[\mathbf{k}] \cos\left(\frac{a(k_1+k_2+k_3)}{8}\right)$$

where

$$S[\mathbf{k}] = \begin{cases} -0.105 & \text{if} \quad |\mathbf{k}|^2 = 3(2\pi/a)^2 \\ 0.02 & \text{if} \quad |\mathbf{k}|^2 = 8(2\pi/a)^2 \\ 0.04 & \text{if} \quad |\mathbf{k}|^2 = 11(2\pi/a)^2 \\ 0 & \text{otherwise.} \end{cases}$$

There are $N_{\rm pair} = 4$ electron-pairs per unit cell. The band diagram of this system is represented in Figure 6.1 along the path $L \to \Gamma \to X \to W \to \Gamma \to U \to X$.

To illustrate our methods in the insulating case, we choose the coarse grid to be $6 \times 6 \times 6$ (that is 10 irreducible $\mathbf{q}$-points) and the fine grid to be $24 \times 24 \times 24$ (that is 240 irreducible $\mathbf{q}$-points). We take $\mathcal{N} = 749$ (which corresponds to a cut-off energy $E_{\text{cut-off}} = 736$ eV), and we vary the size of the reduced basis from 20 to 150. The error on the ground state energy per unit cell is displayed in Figure 6.2 and the error in the $L^\infty(\mathbb{R}^3)$ norm of the electronic density is displayed in Figure 6.3.

We see from Figures 6.2 and 6.3 that our simple-RB method already provides results in good agreement with the full calculation. The corrected-RB method improves the simple-RB method by a factor 10^2 for the energy and a factor 3 to 10 for the density. Finally, the partial-corrected-RB method provides results which are close to the ones obtained with the corrected-RB.

Metallic case

We now consider the metallic case. We study the fcc structure crystalline aluminum with the empirical pseudopotential described in [HA93]. The Bravais lattice is generated by the vectors $\mathbf{a}_1 := (a/2)(0,1,1)^T$, $\mathbf{a}_2 := (a/2)(1,0,1)^T$ and $\mathbf{a}_3 := (a/2)(1,1,0)^T$ with $a = 7.64$ Bohr

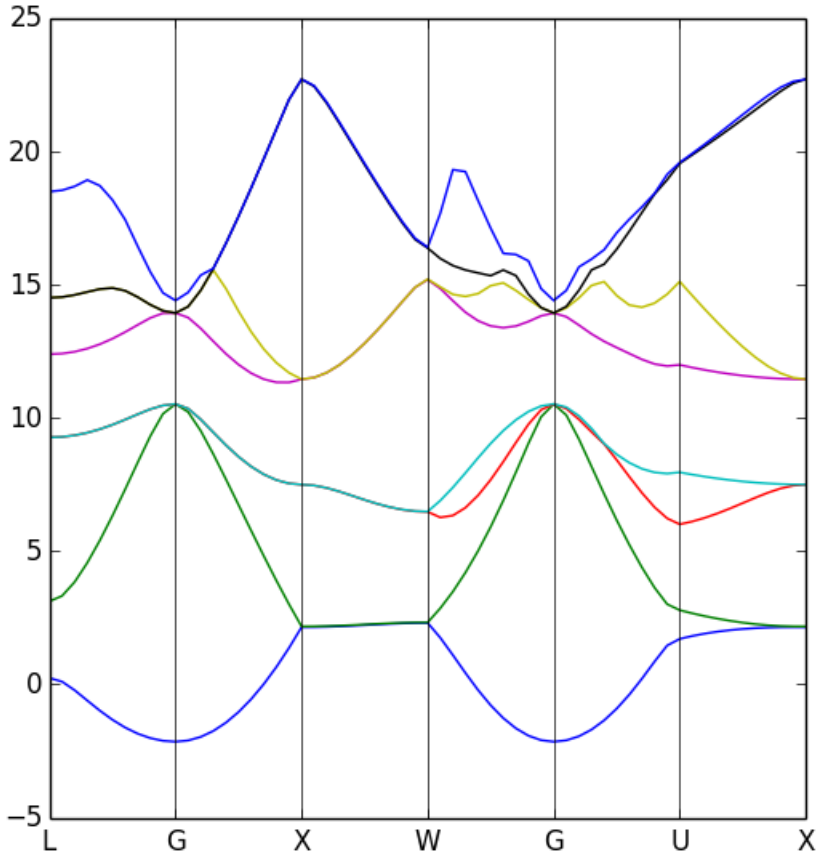

Figure 6.1 – Band diagram (in eV) of crystalline silicon in its diamond structure along the path $L \to \Gamma \to X \to W \to \Gamma \to U \to X$.

(that is $a \approx 4.05$ Å). The mean-field Hamiltonian is $H = -\frac{1}{2}\Delta + V_{\text{per}}$ where the effective pseudopotential V_{per} is of the form [HA93]

$$V_{\text{per}}(\mathbf{x}) = \sum_{\substack{\mathbf{k}\in\mathcal{R}^*,\\ |\mathbf{k}|^2/2\leq E_{\text{cut-off}}}} V_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{x}} \quad \text{with} \quad \forall \mathbf{k} \in \mathcal{R}^*, \quad V_{\mathbf{k}} = \widetilde{V}(|\mathbf{k}|),$$

where, for all $q \in \mathbb{R}^3$,

$$\widetilde{V}(q) = -\beta \cos(q r_c) \frac{\varepsilon(q)}{q^2} \quad \text{with} \quad \varepsilon(q) = 1 + \frac{\Pi(q)}{1 - g(q)\Pi(q)}.$$

The functions Π and g are given by (we denote by $x := q/(2k_f)$)

$$\Pi(q) = \left(\frac{1}{\pi k_f a_0}\right) \frac{1}{x^2} \left(\frac{1}{2} + \frac{(1-x^2)}{4x} \ln\left|\frac{1+x}{1-x}\right|\right) \quad \text{and} \quad g(q) = \left(2 + \frac{1}{\alpha x^2}\right)^{-1}.$$

The values of the constants are, in atomic units, $\beta = 0.338$, $r_c = 1.338$ (which corresponds to $r_c = 0.709$ Å found in [HA93]), $a_0 = 1$ and $k_f = 0.927$. The number of electron pairs is $N_{\text{pair}} = 1.5$. The band diagram of this system is represented in Figure 6.4 along the path $L \to \Gamma \to X \to W \to \Gamma \to U \to X$.

The Fermi level, the total energy per unit cell and the density are calculated with the improved tetrahedron method together with the Blöchl correction [BJA94]. The Fermi level is calculated with a simple dichotomy method with a precision of 10^{-7} eV.

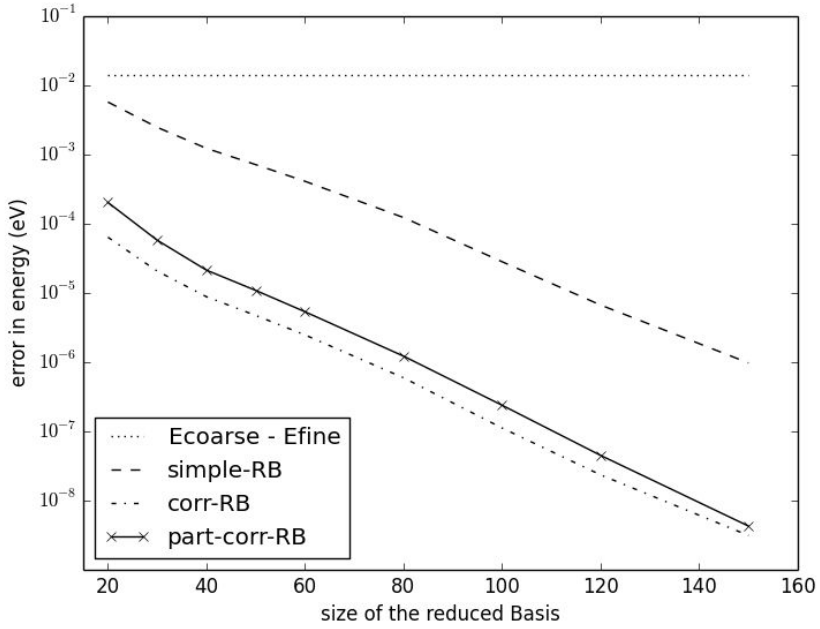

Figure 6.2 – Error on the ground state energy per unit cell (in log scale) with respect to the size of the reduced basis for crystalline silicon. The dotted line represents the error between the energy calculated on the coarse grid and the one calculated on the fine grid.

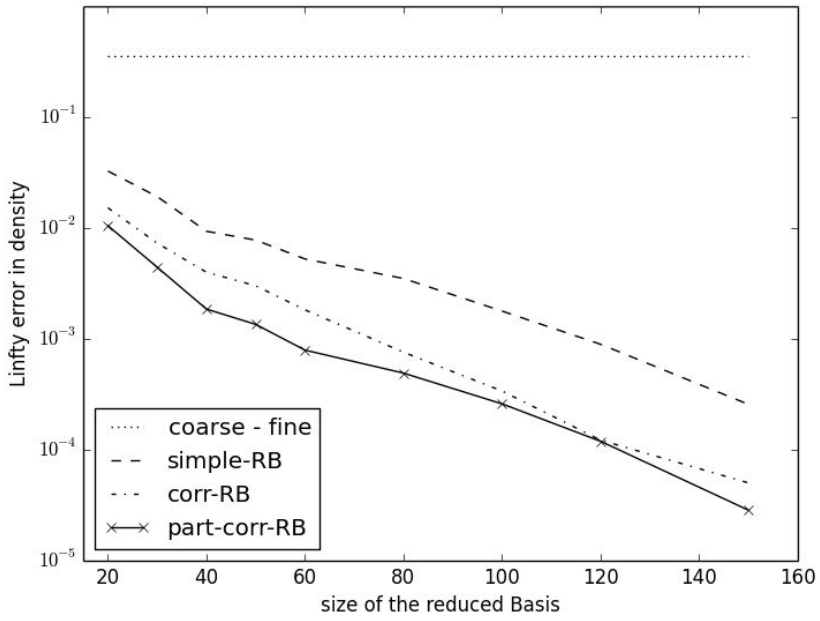

Figure 6.3 – L^∞ error on the ground state electronic density (in log scale) with respect to the size of the reduced basis for crystalline silicon. The dotted line represents the L^∞ error between the electronic density calculated on the coarse grid and the one calculated on the fine grid.

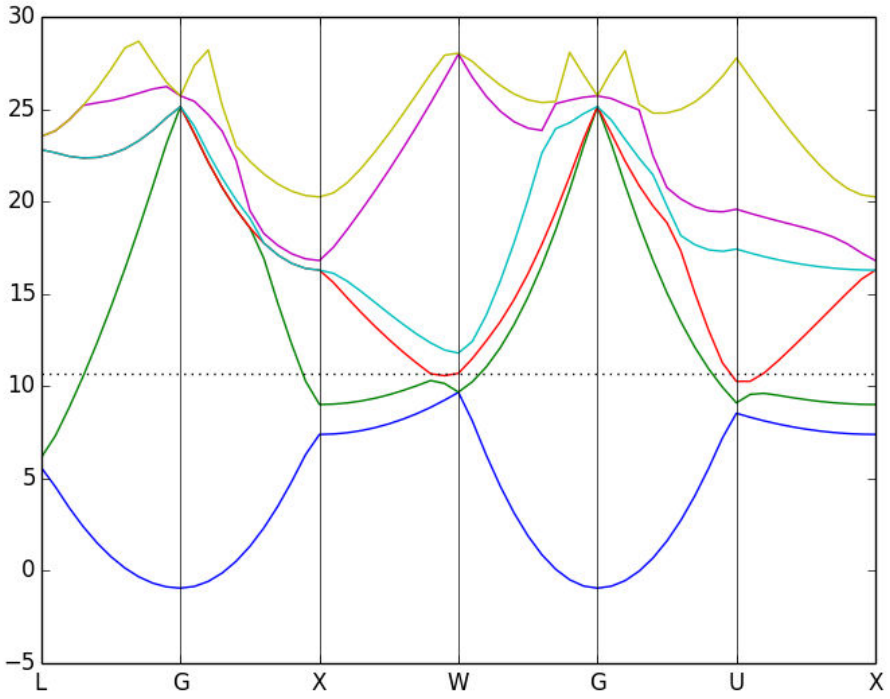

Figure 6.4 – Band diagram of Al in its fcc structure (in eV) along the path $L \to \Gamma \to X \to W \to \Gamma \to U \to X$. The dotted line represents the Fermi level.

The error on the Fermi level and on the total energy per unit cell with respect to the size of the regular grid (the integer L in (6.5)) is displayed in Figure 6.5. The size of the grid varies from 4 to 60. The quantities of reference are the ones calculated at $L = 80$.

In Figure 6.5, we see the slow convergence of these quantities with respect to the size of the grid. To obtain an accuracy of 10^{-2} eV on the energy per unit cell, we need to consider a grid of size at least $30 \times 30 \times 30$. In the sequel, the calculations are performed with the coarse grid $8 \times 8 \times 8$ (that is 20 irreducible $\mathbf{q}$-points) and the fine grid $40 \times 40 \times 40$ (that is 916 irreducible $\mathbf{q}$-points). The error on the ground state energy per unit cell with respect to the size of the reduced basis is displayed in Figure 6.6, the error on the Fermi level is displayed in Figure 6.7 and the L^∞ error for the ground state electronic density is displayed in Figure 6.8.

Whereas the convergence in the insulating case with respect to the size of the reduced basis looks exponentially fast (see Figure 6.2 and Figure 6.3), the convergence in the conducting case looks much slower. However, we see that even a very small reduced basis already recovers the Fermi level and the energy per unit cell with an accuracy of 10^{-3}.

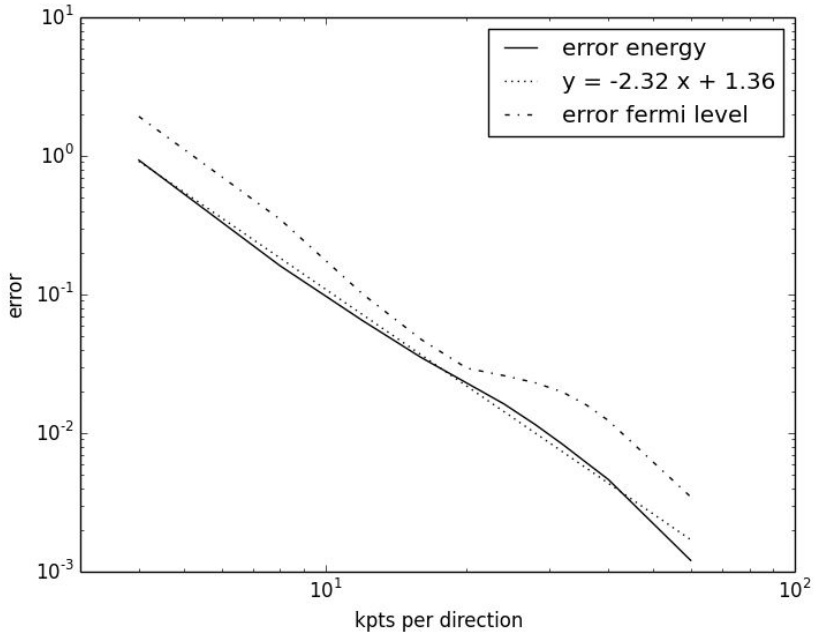

Figure 6.5 – The error on the Fermi level and on the total energy per unit cell (in log scale) with respect to the number of k-pts per direction. The linear regression curve for the energy is also plotted.

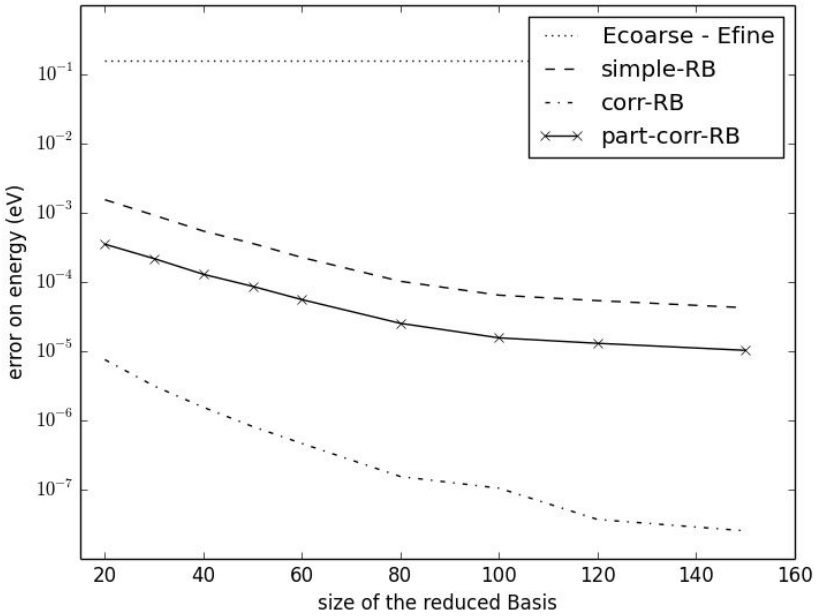

Figure 6.6 – Error on the ground state energy (in log scale) with respect to the size of the reduced basis for crystalline aluminum. The dotted line represents the error between the energy calculated on the coarse grid and the one calculated on the fine grid.

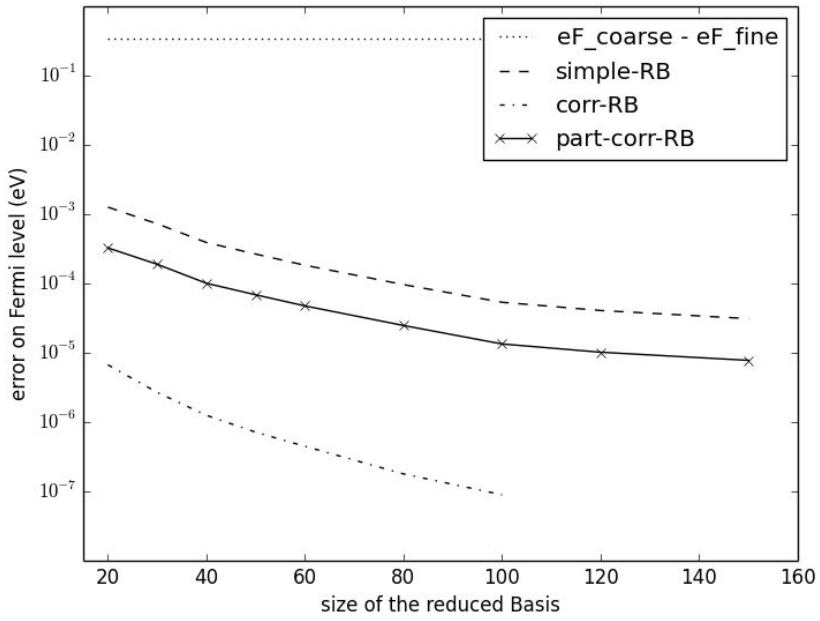

Figure 6.7 – The error of the Fermi level (in log scale) with respect to the size of the reduced basis for crystalline aluminum. The dotted line represents the error between the Fermi level calculated on the coarse grid and the one calculated on the fine grid.

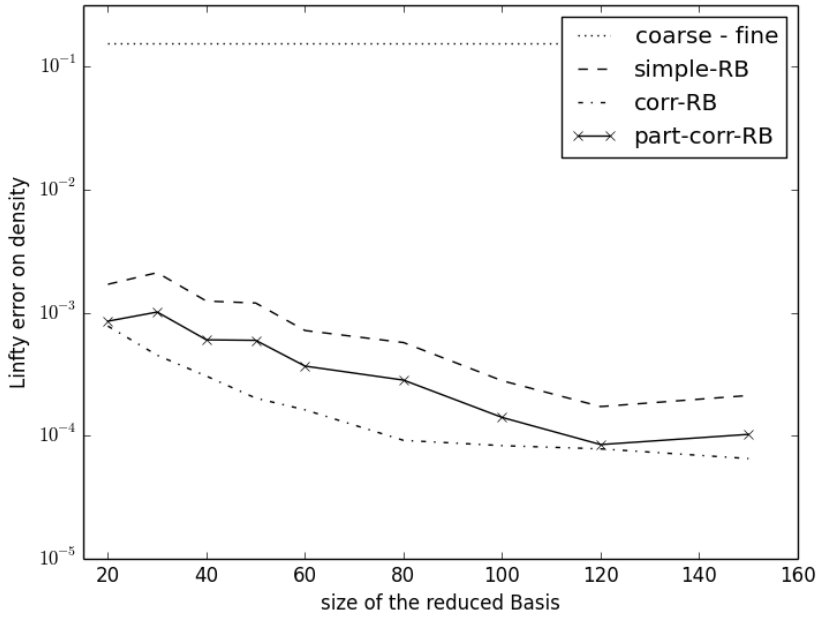

Figure 6.8 – The L^∞ error of the electronic density (in log scale) with respect to the size of the reduced basis aluminum. The dotted line represents the L^∞ error between the electronic density calculated on the coarse grid and the one calculated on the fine grid.

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